

Textile Dyeing Wastewater Treatment by Single and Integrated Processes of Coagulation, Chemical Oxidation and Biological Degradation

Carmen Susana de Deus Rodrigues

Dissertation presented for the Ph.D. Degree in Environmental Engineering at the Faculty of Engineering, University of Porto, Portugal

Supervisors **Rui Alfredo da Rocha Boaventura**

Luís Miguel Palma Madeira

Laboratory of Separation and Reaction Engineering/Associated Laboratory LSRE/LCM

Laboratory for Process, Environmental and Energy Engineering (LEPAE)

Chemical Engineering Department

Faculty of Engineering, University of Porto



Porto, September 2013

Acknowledgments

To my supervisors, Doctor Rui Boaventura and Prof. Miguel Madeira, in part responsible for my interest in scientific research, I want to thank the opportunity to perform this work, as well as all the support, motivation, understanding and tremendous willingness over the years that we worked together. Also thanks for all suggestions, criticisms, compliments and encouragement to do more and better.

I'm also grateful to all organizations and people without which this work would not have been possible:

Fundação para a Ciência e a Tecnologia (FCT) for the PhD scholarship (SFRH/BD/46704/2008).

Faculty of Engineering, University of Porto (FEUP) and, particularly, the Laboratory of Separation and Reaction Engineering – LSRE, the Laboratory for Process, Environmental and Energy Engineering – LEPAE, and the Department of Chemical Engineering, for making available the resources and facilities to carry out this work.

Erfoc - Acabamentos Têxteis S.A., namely Mr. Armando Amaro and Mr. Virgílio Guimarães, and DyStar (Porto), namely Mrs. Goretti Quinaz, for gently supplying the chemicals and dyes and the information required for effluents simulation.

Textil Luís Simões, that provided a real effluent sample used in this study. Particularly I want to thank Mrs. Susana Costa for kindly receiving me, and for all the information and valuable assistance in collecting the effluent sample.

Quimitécnica, namely Mr. Luís Quelhas, and Rivaz Química, for supplying the flocculants, as well as the prices of the chemicals used in this work.

Mr. Cláudio Costa from Tratave and Mrs. Carla Azevedo from Rabada WWTP, for providing the biomass used in the degradation tests and in the acclimatization of the biological reactor.

Prof. Fernando Pereira from the Laboratory of Catalysis and Materials (LCM) at FEUP for the help in establishing contact with the textile industry, as well as, in the last phase of the work, for the access to the Laboratory of Environmental Sciences.

Professor Joaquim Faria and Doctor Claudia Silva from LCM at FEUP for kindly providing the actinometry data and supplying the mercury lamp TQ 150 for photo-Fenton experiments.

Luís Carlos and Nuno Guereiro from the Department of Chemical Engineering at FEUP for the promptness in solving some problems concerning the experimental setup of the Sequencing Batch Reactor (SBR) and the pilot plant of Fenton process.

Doctor Salomé Soares from LCM, Mrs. Dionísia Portela from Centro Tecnológico das Indústrias Têxtil e do Vestuário de Portugal (CITEVE) and Mrs. Patrícia Alves for providing scientific literature, encouragement, sharing of knowledge, but rather by the friendship demonstrated since the 1st year of the graduation in Chemical Engineering.

Doctor Nídia Caetano, Doctor Olga Freitas and Doctor Sónia Figueiredo from the Chemical Engineering Department, School of Engineering, Polytechnic Institute of Porto, for the friendship, encouragement and knowledge sharing.

Liliana Pereira, Sílvia Faia, Paula Pinheiro, Maria do Céu, Serafim Pereira, not only for providing the best working conditions at the Laboratory of Environmental Sciences, but also for the friendship, the precious help and the useful advices.

I am also grateful to all people (so many that I cannot nominate all of them...) that I met at LSRE during this period of my life for the help, companionship and all the words of encouragement. Thanks to Filipa Duarte and Cátia Feliz from LEPAE for the very special friendship, companionship, help, conversations and confidences, and for all good time we spent together.

Finally my eternal gratitude to my parents, my husband, my daughter, my brother, my sister, my sister in law and my niece, for the love, the unconditional support, the optimistic view of life and for making me a better person.

Preface

This PhD thesis was carried out at the Laboratory of Separation and Reaction Engineering, Associated Laboratory LSRE/LCM, and at the Laboratory for Process, Environmental and Energy Engineering (LEPAE) of the Department of Chemical Engineering, at the Faculty of Engineering – University of Porto.

The thesis is structured into five parts divided in chapters with the following content:

Part I – The background and motivation of this study are described in chapter 1, and the work to be performed in order to achieve the objectives is also referred to. A brief characterization of the textile sector in Portugal and the treatment technologies for this type of wastewater are also presented. Chapter 2 presents the state of the art of textile wastewater treatment by chemical coagulation/flocculation, advanced chemical oxidation with Fenton's reagent, photo-Fenton process and biological oxidation in sequencing batch reactors (SBR).

Part II consists in one chapter (chapter 3) concerning the preparation of synthetic wastewaters and their characterization as well as the characterization of the textile industrial wastewater. The materials and methods used and the experimental procedures are also described.

Part III is divided in 7 chapters presenting the experimental results obtained in the treatment of synthetic dyeing wastewaters either by single or combined processes.

Part IV (Chapter 11) regards the treatment of a real cotton dyeing effluent by an integrated process of coagulation/flocculation plus Fenton's oxidation, Fenton's reagent alone and a combination of Fenton's oxidation, coagulation/flocculation and biological degradation in SBR.

Part V points out the main conclusions from this study and some suggestions for future work.

The parts III and IV correspond to chapters 4 to 11, which are based on 8 scientific papers, 3 of which already published/accepted in scientific journals, 3 under review and 2 submitted.

Abstract

Coagulation/flocculation using ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) as coagulant was studied in this work for the removal of organic compounds and color from simulated cotton, acrylic and polyester dyeing wastewaters. The effect of the coagulant dose, temperature, pH, stirring speed and stirring time on the removal of dissolved organic carbon (DOC) and color was assessed for each effluent. Then the effect of the stirring speed, stirring time and flocculant (Magnafloc 155 or Superfloc C-573) dose on flocculation was also evaluated at the optimal conditions previously determined in the coagulation stage. The obtained results allowed concluding that the optimal operating conditions vary with the effluent and that the overall process (coagulation/flocculation) is very efficient as regards color removal (91.4% for cotton, 93.8% for acrylic effluents; polyester effluent is practically colorless). However, the DOC removal is not very significant (33.3%, 45.4% and 28.3% for polyester, cotton and acrylic dyeing effluents, respectively). On the other hand, one can take advantage of the remaining dissolved iron content for further integrating this treatment with an iron catalyzed Fenton process, thus reducing the consumption of chemicals in the overall treatment; such reduction depends on the effluent nature, but the use of this previous treatment stage facilitates the chemical oxidation in the subsequent one. A similar coagulation/flocculation treatability study was conducted using ferric sulphate ($\text{Fe}_2(\text{SO}_4)_3$) as coagulant. The influence of pH and Fe^{3+} concentration in both color and DOC removal from the same effluents was assessed in the coagulation stage. The effect of the type and flocculant dose was also evaluated at the better operating conditions found in the coagulation step. Once again the optimum pH and the better coagulant and flocculant doses were found to depend on the effluent under study. Maximum DOC removals of 40.2, 43.0 and 16.5% were found for polyester, cotton and acrylic dyeing wastewaters, respectively. The color removal for the acrylic dyeing effluent (44.7%) was slightly higher than for the cotton one (33.2%); both were however much smaller as compared to the use of ferrous salt.

Other treatment approaches were applied to the same effluents. The Fenton's reagent was applied to the acrylic effluent previously treated by coagulation/flocculation (Approach 1) for organic matter and color removal, while improving the biodegradability. The initial iron load varied from the residual soluble iron resulting from coagulation/flocculation (275 mg Fe/L) up to 400 mg/L, by adding ferrous sulfate. The combination of the two treatments led to overall removals of 99.8, 84.2 and 78.6% for color, DOC and chemical

oxygen demand (COD), respectively, and to a final effluent that meets the legislated discharge limits. The Fenton process was also directly applied to the same effluent (Approach 2). Under the optimal conditions, the color removal (99.5%) was similar to that obtained in the combined process, but DOC and COD removals were lower (66.5 and 65.1%, respectively). An improvement of the wastewater biodegradability was observed, both in terms of the specific oxygen uptake rate and biochemical oxygen demand:chemical oxygen demand (BOD₅:COD) ratio. The effluent toxicity (inhibition of *V. Fischeri*) also decreased. The use of Fenton's reagent followed by coagulation/flocculation (Approach 3) at the optimal conditions led to the higher color and organic matter removals for this effluent (99,7, 75,8 e 80,1% for color, COD and DOC, respectively). However, the Approach 1 permits to reach a treated effluent meeting the discharge standards at the smallest operating cost (~7 €/m³).

Regarding the cotton effluent, the operating cost is also higher in Approach 2 and Approach 3 due to the required dose of hydrogen peroxide. The application of the Fenton's process before coagulation/flocculation provided an effluent that meets the discharge limits, with global organic matter removals of 55.6% for COD, 42.7% for BOD₅ and 70.4% for DOC, and almost complete color reduction (99.6%). However, the combination of coagulation/flocculation with Fenton's oxidation (Approach 1) also exhibits high overall efficiencies (61.7%, 25.8% and 71.2% for COD, BOD₅ and DOC removal, respectively, and almost complete decolorization) with lower costs associated with chemicals consumption (0.83 €/m³).

The same treatment approaches were also applied to the simulated polyester dyeing effluent. The effect of Fe²⁺ dose, initial H₂O₂ concentration and temperature on organic matter by Fenton's oxidation was evaluated in Approaches 1 and 2, while in Approach 3 only the influence of pH and flocculant dose was assessed in the coagulation/flocculation process. A slight increase in the specific oxygen uptake rate (SOUR) of the effluent was observed in Approaches 1 and 2 (from 27.0 to 28.5-30.0 mgO₂/(g_{VSS} h)) and the inhibition to *Vibrio Fischeri* was eliminated after Fenton's oxidation. In all cases, an effluent that complies with discharge standards was obtained; however, Approach 3 leads to smaller operating costs with chemicals. The use of dissolved iron resulting from Fenton's oxidation as coagulant in the second stage is thus an efficient and economically attractive strategy for treating this effluent.

The simulated effluents were also subjected to the photo-Fenton process, aiming at reducing the consumption of chemicals, as compared to the dark Fenton process, while simultaneously minimizing the energy costs by using solar radiation. The reduction of the hydrogen peroxide dose is limited by the need of achieving treated effluents complying with discharge limits. The costs associated with the use of artificial radiation in the photo-Fenton process (17.4, 9.6 and 2.9 €/m³ for acrylic, cotton and polyester effluents, respectively) are still too high. The use of (simulated) solar light allows obtaining high removals of color (>98-99%) and significant COD (30.1-72.0%) and DOC (46.2-71.5%) abatements at an operating cost reduced by a factor of ca. 3. Treated effluents by the solar photo-Fenton process also meet the discharge standards.

As the acrylic dyeing effluent is practically non biodegradable, only the biological treatability of polyester and cotton dyeing effluents was evaluated. The biodegradability after Fenton's oxidation was also assessed for all effluents. Raw and chemically oxidized (pre-treated) wastewaters were fed to a Sequencing Batch Reactor (SBR) during 10 cycles (i.e., up to pseudo steady-state conditions). In the integrated chemical-biological process optimum doses of Fe(II) and H₂O₂ (for biodegradability enhancement and maximization of color and DOC removals) were determined for Fenton's oxidation, with the simultaneous objective of minimizing the operating costs. The integration of Fenton's oxidation with a downstream SBR provides much better removals of organic matter (87.7 – 98.2% for COD, 83.2 – 94.5% for BOD₅ and 91.2 – 98.4% for DOC, depending on the particular textile effluent) and color (>98.5%) than the biological or chemical treatment alone. Besides, such integrated treatment allows to meet the discharge limits with a reduction of the operating costs, in the range 24-44 % comparatively to Fenton's oxidation alone.

This study also focused on the treatability evaluation of industrial dyeing wastewaters; due to time limitations only one cotton dyeing wastewater was used. Four treatment approaches, including single and integrated processes, were studied, namely: coagulation/flocculation per se and its combination with Fenton oxidation (Approach 1), Fenton's process alone (Approach 2) and its integration with either coagulation/flocculation (Approach 3) or biological oxidation in SBR (Approach 4). Biological degradation of the raw wastewater in SBR was not tested because the ratio BOD₅:COD and the value of SOUR are very small, which indicates low biodegradability. All the considered approaches provided a wastewater that meets the discharge limits, however Approaches 1 and 3 led to smaller operating costs (0.83 and 0.87 €/m³,

respectively) with global removal efficiencies for these two strategies of 62.6-70.8% for COD, 64.4-66.1% for DOC and ~48% for BOD₅, along with almost complete color removal (96.6-99.5%) and toxicity reduction (0.0% inhibition of *Vibrio fischeri* in the effluent resulting from Approach 1).

Resumo

O processo de coagulação/floculação usando sulfato ferroso ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) como coagulante foi estudado neste trabalho com o objetivo de remover compostos orgânicos e cor de efluentes sintéticos de tingimento de algodão e de fibras acrílicas e de poliéster. O efeito da dose de coagulante, temperatura, pH, velocidade de agitação e tempo de agitação na remoção de carbono orgânico dissolvido (COD) e cor foi avaliado para cada efluente. Em seguida, avaliou-se, na etapa de floculação, o efeito da velocidade e tempo de agitação, e dose de floculante (Magnafloc 155 ou Superfloc C-573) após os efluentes terem sido tratados nas condições ótimas de coagulação, previamente determinadas. Os resultados obtidos permitiram concluir que as condições de funcionamento ótimas variam de acordo com o efluente, e que o processo global (coagulação/floculação) é muito eficiente no que respeita à remoção de cor (91,4% para o algodão, 93,8% para o acrílico; o efluente de poliéster é praticamente incolor). No entanto, a remoção de COD não é muito significativa (33,3%, 45,4% e 28,3% para os efluentes de tingimento de poliéster, algodão e acrílico, respectivamente). Por outro lado, o teor de ferro dissolvido remanescente pode ser aproveitado para a integração deste tratamento com um processo catalisado por Fe^{2+} (processo Fenton), reduzindo assim o consumo de produtos químicos no tratamento global; tal redução depende no entanto do efluente usado, mas o uso desta etapa prévia facilita a oxidação química como etapa secundária. Realizou-se um estudo similar de avaliação da tratabilidade por coagulação/floculação usando sulfato férrico ($\text{Fe}_2(\text{SO}_4)_3$) como coagulante. A influência do pH e da concentração de Fe^{3+} na remoção de cor e de COD dos mesmos efluentes foi estudada na fase de coagulação. O mesmo aconteceu relativamente ao efeito do tipo e dose de floculante aplicado após a coagulação, realizada nas melhores condições de operação. Mais uma vez, o pH ótimo, os melhores coagulantes e floculantes e respetivas doses dependem do efluente. Obtiveram-se remoções máximas de COD de 40,2, 43,0 e 16,5% para os efluentes de tingimento de poliéster, algodão e acrílico, respectivamente. A remoção de cor para o tingimento efluente acrílico (44,7%) foi ligeiramente superior à obtida para o efluente do tingimento de algodão (33,2%), mas foram ambas muito menores comparativamente com a utilização do sal ferroso.

Os mesmos efluentes foram objeto de outras abordagens de tratamento. O reagente de Fenton foi aplicado ao efluente acrílico previamente tratado por coagulação/floculação (Abordagem 1) para remoção de matéria orgânica e cor, e para aumentar a

biodegradabilidade. A concentração inicial de ferro foi variada entre a concentração residual resultante do processo de coagulação/floculação (275 mg Fe/L) e 400 mg/L, através da adição de sulfato ferroso. A combinação dos dois tratamentos levou a remoções globais de 99,8, 84,2 e 78,6% para a cor, COD e carência química de oxigênio (CQO), respectivamente, e a um efluente final que cumpre os limites de descarga fixados na legislação. O processo Fenton foi também aplicado diretamente ao mesmo efluente (Abordagem 2). Sob as condições ótimas, a remoção de cor alcançada (99,5%) foi semelhante à obtida no processo combinado, mas as remoções de COD e CQO foram inferiores (66,5 e 65,1%, respectivamente). Observou-se um aumento da biodegradabilidade da água residual, tanto em termos da velocidade específica de consumo de oxigênio como da razão carência biológica de oxigênio: carência química de oxigênio (CBO₅:CQO). A toxicidade do efluente (inibição de *V. Fischeri*) também diminuiu. A utilização do reagente de Fenton, seguido de coagulação/floculação nas condições ótimas (Abordagem 3), levou às maiores remoções de cor e de matéria orgânica para este efluente (99,7, 75,8 e 80,1% para a cor, CQO e o COD, respectivamente). Contudo a Abordagem 1 permite obter um efluente tratado que cumpre as normas de descarga ao mais baixo custo operacional (~ 7 €/m³).

Quanto ao efluente de algodão, o custo de operação foi superior nas Abordagens 2 e 3, devido à dose de peróxido de hidrogênio necessária. A aplicação do processo de Fenton antes da coagulação/floculação proporcionou um efluente que cumpre os limites de descarga, com remoções globais de matéria orgânica de 55,6% para CQO, 42,7% para CBO₅ e 70,4% para COD e uma quase completa redução de cor (99,6%). No entanto, a combinação de coagulação/floculação com a oxidação Fenton (Abordagem 1) também conduziu a elevadas eficiências globais (remoções de 61,7%, 25,8% e 71,2% para CQO, CBO₅ e COD, respectivamente, e descoloração quase completa), com menores custos associados ao consumo de produtos químicos (0,83 €/m³).

As mesmas abordagens de tratamento também foram aplicadas ao efluente sintético de tingimento de poliéster. Avaliou-se o efeito da dose de Fe²⁺, da concentração inicial de H₂O₂ e da temperatura na remoção da matéria orgânica por oxidação Fenton nas Abordagens 1 e 2, enquanto que na Abordagem 3 apenas foi avaliada a influência do pH e dose de floculante no processo de coagulação/floculação. Observou-se um ligeiro aumento da velocidade específica de consumo de oxigênio (SOUR) do efluente nas Abordagens 1 e 2 (de 27,0 para 28,5-30,0 mg O₂/(g_{SSV}.h)) e a inibição da *Vibrio Fischeri* foi eliminada após oxidação com processo Fenton. Em todos os casos foi obtido um

efluente que cumpre as normas de descarga, no entanto com a Abordagem 3 são menores os custos operacionais relativos ao consumo de produtos químicos. A utilização de ferro dissolvido, resultante da oxidação Fenton, como coagulante na segunda fase é assim uma estratégia eficaz e economicamente atraente para o tratamento destes efluentes.

Os efluentes sintéticos foram também submetidas ao processo foto-Fenton, a fim de se reduzir o consumo de produtos químicos comparativamente ao processo Fenton, ao mesmo tempo que se minimizam os custos de energia, usando a radiação solar. A redução da dose de peróxido de hidrogénio está no entanto limitada pela necessidade da obtenção de efluentes que cumpram os limites de descarga. Os custos associados com o uso de radiação artificial no processo foto-Fenton (17,4, 9,6 e 2,9 €/m³ para os efluentes de acrílico, algodão e poliéster, respectivamente) são demasiado elevados. O uso de radiação solar (simulada) permite a obtenção de elevadas remoções de cor (> 98-99%) e reduções significativas de CQO (30,1-72,0%) e de COD (46,2-71,5%), a um custo operacional reduzido por um fator de cerca de 3. Os efluentes tratados pelo processo foto-Fenton solar também cumprem as normas de descarga.

Como o efluente de tingimento de fibras acrílicas é praticamente não biodegradável, apenas foi avaliada a utilização do tratamento biológico nos efluentes de tingimento de poliéster e algodão. A oxidação biológica após oxidação Fenton foi também aplicada a todos os efluentes. Os efluentes tal e qual e pré-tratados por oxidação química foram alimentados a um Reator Descontínuo Sequencial (SBR), durante 10 ciclos (ou seja, até se atingirem as condições de estado pseudo-estacionário). Nos processos integrados químico-biológico, foram determinadas as doses ótimas de Fe (II) e de H₂O₂ para a oxidação Fenton (em termos de aumento da biodegradabilidade e maximização da remoção de cor e COD) com o objectivo simultâneo de minimizar os custos de operação. A integração de oxidação Fenton com SBR a jusante proporciona melhores remoções de matéria orgânica (87,7-98,2% para CQO, 83,2-94,5% para CBO₅ e 91,2-98,4% para COD, dependendo do efluente têxtil) e de cor (> 98,5 %) do que o tratamento químico ou biológico isolado. Além disso, o tratamento integrado permite cumprir os limites de descarga com uma redução dos custos operacionais, na gama de 24-44% comparativamente com a oxidação Fenton isoladamente.

Este estudo também se concentrou na avaliação da tratabilidade de um efluente industrial de tingimento, mas devido a limitações de tempo foi apenas utilizado um efluente de

tingimento de algodão. Foram estudadas quatro abordagens de tratamento, incluindo processos individuais e integrados, nomeadamente: coagulação/floculação apenas e a sua combinação com oxidação Fenton (Abordagem 1), processo Fenton apenas (Abordagem 2) e a sua integração quer com a coagulação/floculação (Abordagem 3) quer com a oxidação biológica em SBR (Abordagem 4). A degradação biológica em SBR do próprio efluente industrial não foi testada porque a razão $CBO_5:CQO$ e o valor de $SOUR$ são muito pequenos, o que indica baixa biodegradabilidade. Todas as abordagens consideradas permitiram obter um efluente que cumpre os limites de descarga, porém as Abordagens 1 e 3 levaram a custos operacionais menores (0,83 e 0,87 €/m³, respectivamente), com eficiências globais de remoção de 62,6-70,8% para CQO, 64,4-66,1 % para COD e ~ 48% para CBO_5 , juntamente com uma remoção quase completa de cor (96,6-99,5%) e redução de toxicidade (0,0% de inibição de *Vibrio fischeri* no efluente resultante da Abordagem 1).

Contents

List of Figures	xix
List of Tables	xxv

Part I – Introduction and State of Art

1 Thesis Framework	5
1.1 Introduction	5
1.2 Outline and Motivation	5
1.3 The Textile Industry	6
1.3.1 Economic Perspective and Textile Industry Distribution.....	6
1.3.2 Industrial Process	8
1.3.3 Textile Wastewaters and Environmental Problems.....	12
1.4 References	15
2 State of the Art	19
2.1 Introduction	21
2.2 Coagulation/Flocculation	21
2.2.1 Textile Wastewater Treatment by Coagulation/Flocculation	23
2.2.2 Textile Wastewater Treatment by Coagulation/Flocculation Combined with Other Processes	27
2.3 Fenton’s Oxidation	29
2.3.1 Textile Wastewater Treatment by Homogeneous Fenton’s Oxidation	31
2.3.2 Textile Wastewater Treatment by Integration of Homogeneous Fenton’s Oxidation with Sequencing Batch Reactor	34
2.4 Photo-Fenton Process	36
2.4.1 Textile Wastewater Treatment by Homogeneous Photo-Fenton Process	39
2.4.2 Combination of Photo-Fenton with Other Processes for Treating Textile Wastewaters	42
2.5 Biological Treatment in Sequencing Batch Reactor	44
2.5.1 Textile Wastewater Treatment by Biological Oxidation using SBR.....	45
2.5.2 Textile Wastewater Treatment by Combination of SBR and Other Techniques ..	48
2.6 References	51

Part II – Experimental Section

3 Materials and Methods	65
3.1 Introduction	65

3.2	Textile Dyeing Wastewaters	65
3.2.1	Simulated Textile Dyeing Wastewaters.....	65
3.2.1.1	Dyes.....	65
3.2.1.2	Auxiliary Chemicals.....	66
3.2.1.3	Preparation of the Simulated Textile Dyeing Effluents.....	69
3.2.2	Real Cotton Dyeing Wastewater	75
3.3	Analytical Methods	77
3.3.1	Alkalinity	77
3.3.2	Biodegradability	77
3.3.3	Biochemical Oxygen Demand	77
3.3.4	Chemical Oxygen Demand	78
3.3.5	Chlorides, Dissolved Phosphorus, Nitrates and Sulfates.....	78
3.3.6	Color	78
3.3.7	Conductivity	79
3.3.8	Dissolved Iron.....	79
3.3.9	Dissolved Oxygen Carbon.....	79
3.3.10	Hydrogen Peroxide.....	79
3.3.11	Inhibition of <i>Vibrio Fischeri</i>	79
3.3.12	pH	80
3.3.13	Total Nitrogen	80
3.3.14	Total Phosphorus	80
3.3.15	Total Suspended Solids and Volatile Suspended Solids	80
3.3.16	HPLC Analyses	81
3.3.17	Zahn-Wellens Test	81
3.4	Experimental Procedure	82
3.4.1	Coagulation/Flocculation	82
3.4.2	Fenton’s Reaction	83
3.4.3	Photo-Fenton Oxidation.....	84
3.2.1.1	Photo-Fenton with Artificial Radiation.....	85
3.2.1.1	Photo-Fenton using Simulated Solar Radiation.....	87
3.4.4	Biological Oxidation in Sequencing Batch Reactor	87
3.5	References	89

Part III – Simulated Dyeing Wastewaters Treatment

4	Coagulation/Flocculation with Fe²⁺ as Coagulant	95
4.1	Introduction	95
4.2	Materials and Methods	95
4.2.1	Preparation of Simulated Textile Wastewaters	95
4.2.2	Coagulation/Flocculation Experiments	95
4.2.3	Analytical Methods	96

4.3	Results and Discussion	96
4.3.1	Effect of Stirring Speed and Time on the Coagulation Stage.....	97
4.3.2	Effect of the Temperature on the Coagulation Stage.....	97
4.3.3	Effect of the pH on the Coagulation Stage	98
4.3.4	Effect of the Coagulant (Fe^{2+}) Concentration	100
4.3.5	Influence of the Stirring Speed and Time in the Flocculation Stage	102
4.3.6	Influence of the Flocculant Type and Dosage.....	102
4.4	Conclusions	107
4.5	References	107
5	Coagulation/Flocculation with Fe^{3+} as Coagulant	113
5.1	Introduction	113
5.2	Materials and Methods	114
5.2.1	Preparation of Simulated Textile Effluents	114
5.2.2	Coagulation/Flocculation Experiments	114
5.2.3	Analytical Methods	114
5.3	Results and Discussion	115
5.3.1	Influence of pH	115
5.3.2	Influence of the Fe^{3+} Concentration.....	116
5.3.3	Influence of the Flocculant Nature and Dose	118
5.3.4	Overall Process Efficiency.....	123
5.4	Conclusions	126
5.5	References	126
6	Integration of Physical-Chemical and Oxidation Processes for Acrylic Effluent Treatment	131
6.1	Introduction	131
6.2	Materials and Methods	131
6.2.1	Preparation of the Simulated Textile Effluent.....	131
6.2.2	Experimental Procedure	131
6.2.3	Analytical Methods	132
6.3	Results and Discussion	132
6.3.1	Combination of Coagulation/Flocculation plus Fenton's oxidation and Fenton's oxidation alone.....	132
6.3.1.1	Effect of the Ferrous Ion Concentration.....	133
6.3.1.2	Effect of the Hydrogen Peroxide Concentration	135
6.3.1.3	Effect of the Temperature.....	137
6.3.1.4	Influence of pH	140
6.3.1.5	Optimized Treatment of Simulated Dyeing Wastewater	141
6.3.2	Fenton's Reaction Followed by Coagulation/Flocculation	145

6.3.2.1	Effect of the pH	146
6.3.2.2	Effect of Supperfloc C-573 Doses	147
6.3.2.3	Overall Process Efficiency	148
6.4	Conclusions	150
6.5	References	151
7	Integration of Physical-Chemical and Oxidation Processes for Cotton Dyeing Effluent Treatment	157
7.1	Introduction	157
7.2	Materials and Methods	157
7.2.1	Preparation of the Simulated Textile Effluent.....	157
7.2.2	Experimental Procedure	158
7.2.3	Research Strategy.....	158
7.2.4	Analytical Methods	160
7.3	Results and Discussion	160
7.3.1	Combination of Coagulation/Flocculation and Fenton's Reagent (Approach 1) 160	
7.3.1.1	Influence of Ferrous Ion Concentration	161
7.3.1.2	Effect of the Initial Hydrogen Peroxide Concentration	162
7.3.1.3	Effect of the Temperature.....	163
7.3.1.4	Optimized Treatment Performance	165
7.3.2	Fenton Oxidation (Approach 2)	166
7.3.2.1	Influence of Ferrous Ion Concentration	167
7.3.2.2	Effect of the Initial Hydrogen Peroxide Concentration	168
7.3.2.3	Effect of the Temperature.....	170
7.3.2.4	Optimized Treatment of the Simulated Cotton Dyeing Wastewater	172
7.3.3	Fenton's Oxidation Followed by Coagulation/Flocculation (Approach 3).....	173
7.3.3.1	Influence of pH	174
7.3.3.2	Effect of Magnafloc 155 Doses	175
7.3.3.3	Overall Process Efficiency	176
7.3.4	Costs Evaluation.....	178
7.4	Conclusions	180
7.5	References	181
8	Integration of Physical-Chemical and Oxidation Process for Polyester Dyeing Effluent Treatment	185
8.1	Introduction	185
8.2	Materials and Methods	185
8.2.1	Preparation of Synthetic Textile Wastewaters	185
8.2.2	Experimental Procedure	186
8.2.3	Analytical Methods	186
8.3	Results and Discussion	187
8.3.1	Combination of Coagulation/Flocculation and Fenton Reagent (Approach 1)...	187

8.3.1.1	Influence of Ferrous Ion Concentration Added During the Chemical Oxidation Stage	188
8.3.1.2	Effect of the Initial Hydrogen Peroxide Concentration on the Chemical Oxidation Stage.....	189
8.3.1.3	Effect of the Temperature During the Chemical Oxidation Stage	190
8.3.1.4	Optimized Integrated Coagulation/Flocculation plus Fenton's Oxidation	191
8.3.2	Fenton's Oxidation (Approach 2).....	193
8.3.2.1	Influence of Ferrous Ion Concentration	194
8.3.2.2	Effect of the Initial Hydrogen Peroxide Concentration	195
8.3.2.3	Effect of the Temperature.....	197
8.3.2.4	Optimized Treatment by Fenton's Oxidation.....	198
8.3.3	Fenton's Oxidation followed by Coagulation/Flocculation (Approach 3).....	200
8.3.3.1	Influence of pH in the Coagulation Process.....	201
8.3.3.2	Effect of Superfloc C-573 Doses	202
8.3.4	Operating Costs.....	205
8.4	Conclusions	207
8.5	References	208
9	Simulated Dyeing Textile Effluents Treatment by the Photo-Fenton Process	213
9.1	Introduction	213
9.2	Materials and Methods	213
9.2.1	Preparation of Simulated Textile Wastewaters	213
9.2.2	Experimental Procedure.....	213
9.2.3	Analytical Methods	214
9.3	Results and Discussion	214
9.3.1	Photoreactor with Artificial Radiation.....	214
9.3.1.1	Comparison Between Direct Photolysis, UV-visible+H ₂ O ₂ and Photo-Fenton Processes	216
9.3.1.2	Photo-Fenton Process.....	218
9.3.1.2.1	Effect of Hydrogen Peroxide Concentration.....	218
9.3.1.2.2	Effect of Radiation Intensity	222
9.3.1.2.3	Operating Costs	224
9.3.2	Photoreactor with Simulated Solar Radiation.....	227
9.4	Conclusions	232
9.5	References	233
10	Simulated Textile Dyeing Effluents Treatment by SBR alone and Combined with Fenton's Oxidation	237
10.1	Introduction	237
10.2	Materials and Methods	237
10.2.1	Preparation of the Simulated Textile Effluents	237

10.2.2	Experimental Procedure	237
10.2.3	Analytical Methods	238
10.3	Results and Discussion	238
10.3.1	Biological Treatment.....	238
10.3.2	Integration of Fenton's Reagent Followed by Biological Treatment.....	243
10.3.3	Costs Evaluation.....	251
10.4	Conclusions	252
10.5	References	253

Part IV – Real Cotton Dyeing Wastewater

11	Cotton Dyeing Wastewater Treatment	259
11.1	Introduction.....	259
11.2	Operating Costs.....	261
11.3	Materials and Methods	262
11.3.1	Experimental Procedure	262
11.3.2	Analytical Methods	262
11.4	Results and Discussion	263
11.4.1	Textile Dyeing Wastewater.....	263
11.4.2	Coagulation/Flocculation plus Fenton's Reaction (Approach 1)	263
11.4.3	Fenton's Oxidation (Approach 2).....	266
11.4.4	Integration of Fenton's Oxidation and Coagulation/ Flocculation (Approach 3) .	269
11.4.5	Combination of Fenton's Reaction and SBR (Approach 4)	272
11.5	Conclusions	275
11.6	References	276

Part I – Conclusions and Suggestion for Future Work

12	Concluding Remarks and Forthcoming Work.....	283
12.1	Concluding Remarks.....	283
12.1.1	Simulated Textile Dyeing Effluents.....	283
12.1.2	Industrial Cotton Dyeing Wastewater.....	285
12.1.3	Brief Comparison of Processes.....	285
12.2	Forthcoming Work.....	287
Appendix	291
A.1	Supporting Information for Chapter 4	291
A.2	Supporting Information for Chapter 9	293

List of Figures

Part I – Introduction and State of Art

Figure 1.1 – Textile industry geographpic distribution in Portugal	7
Figure 1.2 – Representative flowchart of textile and clothing manufacturing process	9

Part II – Experimental Section

Figure 3.1 – Scheme of polyester fibers dyeing: a) fiber preparation, b) dyeing and c) reduction washing.....	72
Figure 3.2 – Scheme of acrylic fibers dyeing	73
Figure 3.3 – Scheme of cotton fibers dyeing: a) fiber preparation, b) dyeing and c) washing	73
Figure 3.4 – UV/visible spectrum for polyester, acrylic and cotton wastewaters	75
Figure 3.5 – UV/visible spectrum for real cotton dyeing wastewater	76
Figure 3.6 – Diagram of the Jar-test set-up	82
Figure 3.7 – Diagram of Fenton’s oxidation set-up	83
Figure 3.8 – Diagram of the photo-Fenton set-up with mercury lamp TQ 150	84
Figure 3.9 - Variation of the radiation intensity with the Solophenyl Green BLE 155% concentration circulating in the photo-reactor jacket	86
Figure 3.10 – Diagram of the sun-test set-up	87
Figure 3.11 – Diagram of the SBR set-up	88

Part III – Simulated Dyeing Wastewaters Treatment

Figure 4.1 – Variation of DOC (a) and color (b) removals with temperature in the coagulation stage for the different simulated effluents ($v_{\text{coagulation}}=150$ rpm, $t_{\text{coagulation}}=3$ min, $[\text{Fe}^{2+}]=200$ mg/L and $\text{pH}=8.3$).	98
Figure 4.2 – Influence of pH on DOC (a) and color (b) removals by coagulation applied to the different simulated effluents ($v_{\text{coagulation}}=150$ rpm, $t_{\text{coagulation}}=3$ min, $[\text{Fe}^{2+}]=200$ mg/L and $T=T_{\text{ambient}}=22-23$ °C)	99
Figure 4.3 – Variation of DOC (a) and color (b) removals with the concentration of coagulant (Fe^{2+}) for the different simulated effluents ($v_{\text{coagulation}}=150$ rpm, $t_{\text{coagulation}}=3$ min, $T=T_{\text{ambient}}=23-25$ °C and $\text{pH}_{\text{polyester}}=8.3$, $\text{pH}_{\text{cotton}}=9.4$ and $\text{pH}_{\text{acrylic}}=7.2$)	100
Figure 4.4 - Variation of DOC (a) and color (b) removals with the dose of flocculant (Magnafloc 155) for the different simulated effluents ($v_{\text{coagulation}}=150$ rpm, $t_{\text{coagulation}}=3$ min, $T=T_{\text{ambient}}=23-25$ °C, $\text{pH}_{\text{polyester}}=8.3$, $\text{pH}_{\text{cotton}}=9.4$, $\text{pH}_{\text{acrylic}}=7.2$, $[\text{Fe}^{2+}]_{\text{polyester}}=[\text{Fe}^{2+}]_{\text{cotton}}=200$ mg/L, $[\text{Fe}^{2+}]_{\text{acrylic}}=3000$ mg/L, $v_{\text{flocculation}}=20$ rpm and $t_{\text{flocculation}}=15$ min)	101

Figure 4.5 - Variation of DOC (a) and color (b) removals with the dose of flocculant (Superfloc C-573) for the different simulated effluents ($v_{\text{coagulation}}=150$ rpm, $t_{\text{coagulation}}=3$ min, $T=T_{\text{ambient}}=23-25$ °C, $\text{pH}_{\text{polyester}}=8.3$, $\text{pH}_{\text{cotton}}=9.4$, $\text{pH}_{\text{acrylic}}=7.2$, $[\text{Fe}^{2+}]_{\text{polyester}}=[\text{Fe}^{2+}]_{\text{cotton}}=200$ mg/L, $[\text{Fe}^{2+}]_{\text{acrylic}}=3000$ mg/L, $v_{\text{flocculation}}=20$ rpm and $t_{\text{flocculation}}=15$ min)	104
Figure 5.1 – Influence of pH in DOC (a) and color (b) removal from the different effluents ($v_{\text{coagulation}} = 150$ rpm, $t_{\text{coagulation}} = 3$ min, $[\text{Fe}^{3+}]_{\text{polyester}} = [\text{Fe}^{3+}]_{\text{cotton}} = 200$ mg/L, $[\text{Fe}^{3+}]_{\text{acrylic}} = 500$ mg/L and $T=T_{\text{ambient}} = 22-23$ °C)	116
Figure 5.2 – Effect of Fe^{3+} concentration on DOC (a) and color (b) removal from the different effluents ($v_{\text{coagulation}} = 150$ rpm, $t_{\text{coagulation}} = 3$ min, $T=T_{\text{ambient}} = 23-25$ °C and $\text{pH}_{\text{polyester}} = 9.4$, $\text{pH}_{\text{cotton}} = 5.0$ and $\text{pH}_{\text{acrylic}} = 8.3$)	117
Figure 5.3 – Effect of Magnafloc155 concentration on DOC (a) and color (b) removal from the different effluents ($v_{\text{coagulation}} = 150$ rpm, $t_{\text{coagulation}} = 3$ min, $T=T_{\text{ambient}} = 23-26$ °C, $\text{pH}_{\text{polyester}} = 9.4$, $\text{pH}_{\text{cotton}} = 5.0$, $\text{pH}_{\text{acrylic}} = 8.3$, $[\text{Fe}^{3+}]_{\text{polyester}} = 500$ mg/L, $[\text{Fe}^{3+}]_{\text{cotton}} = 200$ mg/L, $[\text{Fe}^{3+}]_{\text{acrylic}} = 1000$ mg/L, $v_{\text{flocculation}} = 20$ rpm and $t_{\text{flocculation}} = 15$ min)	119
Figure 5.4 – Effect of Superfloc C-573 concentration on DOC (a) and color (b) removal from the different effluents ($v_{\text{coagulation}} = 150$ rpm, $t_{\text{coagulation}} = 3$ min, $T = T_{\text{ambien t}} = 23-26$ °C, $\text{pH}_{\text{polyester}} = 9.4$, $\text{pH}_{\text{cotton}} = 5.0$, $\text{pH}_{\text{acrylic}} = 8.3$, $[\text{Fe}^{3+}]_{\text{polyester}} = 500$ mg/L, $[\text{Fe}^{3+}]_{\text{cotton}} = 200$ mg/L, $[\text{Fe}^{3+}]_{\text{acrylic}} = 1000$ mg/L, $v_{\text{flocculation}} = 20$ rpm and $t_{\text{flocculation}} = 15$ min)	120
Figure 6.1 - Variation of DOC removal and k' with the total iron concentration, in the first (a) and c), respectively) and second experiment (b) and (d), respectively) (initial $\text{pH}=3.5$, $T=30$ °C, initial $[\text{H}_2\text{O}_2]=5$ g/L)	134
Figure 6.2 - Influence of the H_2O_2 concentration on DOC removal and k' in the first (a) and c), respectively) and second experiment (b) and d), respectively) (initial $\text{pH}=3.5$, $T=30$ °C, initial $[\text{Fe}]=350$ mg/L)	136
Figure 6.3 - Effect of temperature on DOC removal and k' in the first (a) and c), respectively) and second experiment (b) and d), respectively) (initial $\text{pH}=3.5$, $[\text{Fe}]=350$ mg/L, $[\text{H}_2\text{O}_2]_1^{\text{st exp}}=3.5$ g/L, $[\text{H}_2\text{O}_2]_2^{\text{nd exp}}=20$ g/L)	139
Figure 6.4 - Effect of temperature on the residual hydrogen peroxide concentration in the first (a) and second experiment (b) (initial $\text{pH}=3.5$, $[\text{Fe}]=350$ mg/L, $[\text{H}_2\text{O}_2]_1^{\text{st exp}}=3.5$ g/L, $[\text{H}_2\text{O}_2]_2^{\text{nd exp}}=20$ g/L)	140
Figure 6.5 - Variation of DOC removal (a) and k' (b) with the initial pH in the first experiment ($T=50$ °C, $[\text{Fe}]=350$ mg/L and $[\text{H}_2\text{O}_2]=3.5$ g/L)	140
Figure 6.6 - Evolution of the inhibition of <i>Vibro fischeri</i> of samples taken along 60 min of Fenton's reaction for contact times of 5, 15 and 30 min in the first (a) and second experiment (b) ($\text{pH}= 3.5$, $T=50$ °C, $[\text{Fe}]=350$ mg/L and $[\text{H}_2\text{O}_2]_1^{\text{st exp}}=3.5$ g/L, $[\text{H}_2\text{O}_2]_2^{\text{nd exp}}=20$ g/L)	143
Figure 6.7 - Time evolution of HPLC chromatogram in the first (a) and second experiment (b) ($\text{pH}= 3.5$, $T=50$ °C, $[\text{Fe}]=350$ mg/L and $[\text{H}_2\text{O}_2]_1^{\text{st exp}}=3.5$ g/L, $[\text{H}_2\text{O}_2]_2^{\text{nd exp}}=20$ g/L)	143
Figure 6.8 – Variation of DOC (a) and color (b) removals with pH in the coagulation stage for different doses of hydrogen peroxide applied in the previous Fenton's process - runs #1, #2 and #3 ($v_{\text{coagulation}}=150$ rpm, $t_{\text{coagulation}}=3$ min, $[\text{Fe dissolved}]_{\text{run \#1}} = 75.5$ mg/L, $[\text{Fe dissolved}]_{\text{run \#2}}=118.1$ mg/L, $[\text{Fe dissolved}]_{\text{run \#3}}=275$ mg/L and $T = T_{\text{ambient}} = 22-24$ °C)	146
Figure 6.9 – Variation of DOC (a) and color (b) removals with flocculant concentration in the flocculation step for different hydrogen peroxide doses applied in the previous Fenton's process - runs #1, #2 and #3 ($v_{\text{coagulation}}=150$ rpm, $t_{\text{coagulation}}=3$ min, $[\text{Fe dissolved}]_{\text{run \#1}} =75.5$ mg/L, $[\text{Fe}$	

dissolved] _{run #2} =118.1 mg/L, [Fe dissolved] _{run #3} =275 mg/L and T =T _{ambient} = 22-24 °C, v _{flocculation} =20 rpm, t _{flocculation} =15 min)	147
Figure 7.1 - Schematic diagram of process configurations adopted	159
Figure 7.2 – Variation of dissolved organic carbon (a) and color (b) removal along time with the iron dose during the Fenton reaction after the coagulation/flocculation stage – Approach 1 (initial pH=3.5, T=30 °C, [H ₂ O ₂] _o =500 mg/L)	161
Figure 7.3 – Variation of dissolved organic carbon (a) and color (b) removal along time with the concentration of H ₂ O ₂ added during the Fenton’s reaction after the coagulation/flocculation stage – Approach 1 (initial pH=3.5, T=30 °C, [Fe]=100 mg/L)	163
Figure 7.4 – Variation of dissolved organic carbon (a) and color (b) removal along time with the temperature during the Fenton reaction after the coagulation/flocculation stage – Approach 1 (initial pH=3.5, [Fe]=100 mg/L and [H ₂ O ₂] _o =500 mg/L)	165
Figure 7.5 – Variation of dissolved organic carbon (a), color (b) removal and specific oxygen uptake rate (c) along time with the initial concentration of Fe ²⁺ during the Fenton reaction – Approach 2 (initial pH=3.5, T=30 °C, [H ₂ O ₂] _o =5 g/L)	168
Figure 7.6 – Variation of dissolved organic carbon (a), color (b) removal and specific oxygen uptake rate (c) along time with the initial concentration of H ₂ O ₂ ⁺ during the Fenton reaction – Approach 2 (initial pH=3.5, T=30 °C, [Fe ²⁺] _o =300 mg/L)	169
Figure 7.7 – Variation of dissolved organic carbon (a), color (b) removal and specific oxygen uptake rate (c) along time with the temperature during the Fenton reaction – Approach 2 (initial pH=3.5, [Fe ²⁺] _o =300 mg/L and [H ₂ O ₂] _o =10 g/L)	171
Figure 7.8 – Variation of DOC (a) and color (b) removals with pH during the coagulation stage – Approach 3 – for different doses of hydrogen peroxide employed in the previous Fenton’s process in runs #1, #2 and #3 (v _{coagulation} =150 rpm, t _{coagulation} =3 min, [Fe dissolved] _{run #1} =52.1 mg/L, [Fe dissolved] _{run #2} =85.6 mg/L, [Fe dissolved] _{run #3} =167 mg/L and T =T _{ambient} =23-25 °C)	173
Figure 7.9 – Variation of DOC (a) and color (b) removals with the flocculant concentration during the flocculation step – Approach 3 – for the different doses of hydrogen peroxide employed in the previous Fenton’s process in runs #1, #2 and #3 (v _{coagulation} =150 rpm, t _{coagulation} =3 min, T=T _{ambient} =23-25 °C, pH=5.0, [Fe dissolved] _{run #1} =52.1 mg/L, [Fe dissolved] _{run #2} =85.6 mg/L, [Fe dissolved] _{run #3} =167 mg/L, v _{flocculation} =20 rpm and t _{flocculation} =15 min)	175
Figure 7.10 – Effect of Fe and H ₂ O ₂ doses in the total operating cost of wastewater treatment by coagulation/flocculation plus Fenton processes – Approach 1 (a), Fenton’s reagent – Approach 2 (b) and influence of Magnafloc 155 and H ₂ O ₂ concentration in the total treatment costs by Fenton’s process followed by coagulation/flocculation – Approach 3 (c)	179
Figure 8.1 – Variation of DOC removal (a) and percentage of H ₂ O ₂ consumption (b) along time, with the iron dose added during the 2 nd stage – Fenton oxidation in Approach 1 (initial pH=3.5, T=30 °C, initial [H ₂ O ₂]= 500 mg/L)	188
Figure 8.2 – Effect of H ₂ O ₂ dose in DOC removal (a) and percentage of H ₂ O ₂ consumption (b) along time during the 2 nd stage i.e. Fenton oxidation in Approach 1 (initial pH=3.5, T=30 °C, [Fe]=200 mg/L)	190
Figure 8.3 – Variation of DOC removal (a) and percentage of H ₂ O ₂ consumption (b) along time with the reaction temperature during the 2 nd stage – Fenton oxidation in Approach 1 (initial pH=3.5, [Fe]=200 mg/L and initial [H ₂ O ₂]=1000 mg/L)	191

Figure 8.4 – Evolution of the inhibition of <i>V. fischeri</i> at 5, 15 and 30 minutes of contact (a) and HPLC chromatograms (b) of samples taken along time during the 2 nd stage – Fenton oxidation in Approach 1 (initial pH=3.5, T=50 °C, initial [Fe]=200 mg/L and initial [H ₂ O ₂]=1000 mg/L)	192
Figure 8.5 – Variation of DOC removal (a), percentage of H ₂ O ₂ consumption (b) and k'(c) along time with the initial Fe ²⁺ dose during Fenton's reaction in Approach 2 (initial pH=3.5, T=30 °C, initial [H ₂ O ₂]= 5.0 g/L)	193
Figure 8.6 – Variation of DOC removal (a), percentage of H ₂ O ₂ consumption (b) and k'(c) along time with the initial H ₂ O ₂ dose during Fenton's reaction in Approach 2 (initial pH=3.5, T=30 °C, initial [Fe ²⁺]=350 mg/L)	196
Figure 8.7 – Variation of DOC removal (a), percentage of H ₂ O ₂ consumption (b) and k'(c) along time with the reaction temperature during Fenton's reaction in Approach 2 (initial pH=3.5, initial [Fe ²⁺]=350 mg/L and initial [H ₂ O ₂]=2.5 g/L)	198
Figure 8.8 – Evolution of <i>V. fischeri</i> inhibition after 5, 15 and 30 minutes of contact (a) and HPLC chromatograms (b) of samples taken along time during Fenton's oxidation in Approach 2 (initial pH=3.5, T=50 °C, initial [Fe ²⁺]=350 mg/L and initial [H ₂ O ₂]=2.5 g/L)	199
Figure 8.9 – Variation of DOC removal with pH during the coagulation stage – Approach 3 – for the different doses of hydrogen peroxide employed in the previous Fenton's process in runs #1, #2 and #3 (v _{coagulation} =150 rpm, t _{coagulation} =3 min, [Fe] _{dissolved run #1} = 64.8mg/L, [Fe] _{dissolved run #2} =88.5 mg/L, [Fe] _{dissolved run #3} =222 mg/L and T =T _{ambient} =22-24 °C)	201
Figure 8.10 – Variation of DOC removal with the flocculant concentration during the flocculation step – Approach 3 – for the different doses of hydrogen peroxide employed in runs #1, #2 and #3 of the previous Fenton's process (v _{coagulation} =150 rpm, t _{coagulation} =3 min, T=T _{ambient} =22-24 °C, pH=5.0, [Fe] _{dissolved run #1} = 64.8mg/L, [Fe] _{dissolved run #2} =88.5 mg/L, [Fe] _{dissolved run #3} =222 mg/L, v _{flocculation} =20 rpm and t _{flocculation} =15 min)	203
Figure 8.11 – Effect of Fe and H ₂ O ₂ doses on the operating cost of wastewater treatment by: coagulation/flocculation plus Fenton processes – Approach 1 (a) or Fenton's reagent – Approach 2 (b), and influence of [Superfloc C-573] and [H ₂ O ₂] on the operating cost of Fenton's process followed by coagulation/flocculation – Approach 3 (c)	206
Figure 9.1 – Evolution of DOC and color removal for acrylic (a), cotton (b) and polyester (c) wastewater during 120 minutes of direct photolysis, H ₂ O ₂ -assisted photolysis ([H ₂ O ₂] _{acrylic} =20 g/L, [H ₂ O ₂] _{cotton} =10 g/L and [H ₂ O ₂] _{polyester} =2.5 g/L) or photo-Fenton ([H ₂ O ₂] _{acrylic} =20 g/L, [H ₂ O ₂] _{cotton} =10 g/L and [H ₂ O ₂] _{polyester} =2.5 g/L, [Fe ²⁺] _{cotton} =300 mg/L, [Fe ²⁺] _{acrylic} =[Fe ²⁺] _{polyester} =350 mg/L). In all cases radiation intensity = 500 W/m ² , pH=3.5, T=50°C	216
Figure 9.2 – Effect of H ₂ O ₂ dose on DOC and color removal in the photo-Fenton process for acrylic (a), cotton (b) and polyester (c) wastewaters (radiation intensity = 500 W/m ² , T=50 °C, pH=3.5, Fe ²⁺ :H ₂ O ₂ acrylic =1:57, Fe ²⁺ :H ₂ O ₂ cotton =1:33, Fe ²⁺ :H ₂ O ₂ polyester =1:7 – wt. ratios)	219
Figure 9.3 – Effect of radiation intensity on DOC and color removal of the acrylic effluent during the photo-Fenton process for different dosages of hydrogen peroxide: 6.5 g/L (a), 10.0 g/L (b) or 20.0 g/L (c) (T=50 °C, Fe ²⁺ :H ₂ O ₂ =1:57 and pH=3.5)	223
Figure 9.4 – Effect of hydrogen peroxide doses and radiation intensity on the total operating cost associated with the photo-Fenton process with TQ 150 lamp for treating acrylic (a), cotton (b) and polyester (c) wastewaters	226

Figure 9.5 – Effect of H ₂ O ₂ dose on DOC and color removal with simulated solar radiation at intensity of 253 W/m ² for acrylic (a), cotton (b) and polyester (c) wastewaters (T=50 °C, Fe ²⁺ :H ₂ O ₂ _{acrylic} =1:57, Fe ²⁺ :H ₂ O ₂ _{cotton} =1:33 Fe ²⁺ :H ₂ O ₂ _{polyester} =1:7, pH=3.5)	228
Figure 9.6 – Effect of H ₂ O ₂ and Fe ²⁺ doses on the total operating cost associated with the photo-Fenton with simulated solar radiation for treating acrylic (a), cotton (b) and polyester (c) wastewaters	231
Figure 10.1 – Evolution of percentage of COD degradation along time in Zahn-Wellens test for acrylic wastewater	233
Figure 10.2 - Variation of COD (a), BOD ₅ (b), DOC (c), total nitrogen (d) and color (e) removals along 10 cycles of SBR operation for polyester and cotton wastewaters	240
Figure 10.3 - Variation of COD (a), BOD ₅ (b), DOC (c), total nitrogen (d) and color (e) removals during 10 cycles of SBR operation for acrylic effluent, previously treated by Fenton's oxidation. Runs#1 to #3 represent experiments with decreasing doses of chemicals in the Fenton's stage	248
Figure 10.4 - Variation of COD (a), BOD ₅ (b), DOC (c), total nitrogen (d) and color (e) removals during 10 cycles of SBR operation for synthetic cotton dyeing effluent, previously treated by Fenton's reaction. Runs#1 to #3 represent experiments with decreasing doses of chemicals in the Fenton's stage	249
Figure 10.5 - Evolution of COD (a), BOD ₅ (b), DOC (c) and total nitrogen (d) removals during 10 cycles of SBR operation for polyester dyeing wastewater, previously treated by Fenton's reaction. Runs#1 to #3 represent experiments with decreasing doses of chemicals in the Fenton's stage	250
Figure 10.6 - Total operating costs for biological, Fenton alone and integrated treatment of acrylic, cotton and polyester dyeing wastewaters	252

Part IV – Real Cotton Dyeing Wastewater

Figure 11.1 - Schematic diagram of all process configurations adopted	260
Figure 11.2 - Effect of H ₂ O ₂ concentration on COD, BOD ₅ , DOC and color removals during Fenton's oxidation (Approach 2) (initial pH=3.5, T=50 °C, t = 60 min and [Fe ²⁺]= 300 mg/L)	266
Figure 11.3 - Effect of Fe ²⁺ concentration on COD, BOD ₅ , DOC and color removals during Fenton's oxidation (Approach 2) (initial pH=3.5, T=50 °C, t = 60 min and [H ₂ O ₂]= 1.25 g/L)	268
Figure 11.4 - Variation of COD (a), DOC (b), BOD ₅ (c), color (d) total nitrogen (e) and total phosphorus (f) removals along 10 cycles of SBR operation, after treatment by Fenton's oxidation. Runs #3 to #1 refer to Fenton's stage with progressively decreasing doses of chemicals	273
Figure 11.5 - Operating costs of Fenton alone and Fenton plus SBR for treatment of a real cotton dyeing wastewater	275

Appendix

Figure A.1 – Influence of the stirring rate on the coagulation stage for DOC (a) and color (b) removal from polyester and cotton simulated effluents (t _{coagulation} =3 min, T=T _{ambient} =23-25 °C, [Fe ²⁺]=200 mg/L and pH=8.3)	291
---	-----

Figure A.2 – Effect of the coagulation time on DOC (a) and color (b) removal from polyester and cotton simulated effluents ($v_{\text{coagulation}}=150$ rpm, $T=T_{\text{ambient}}=22-24$ °C, $[\text{Fe}^{2+}]=200$ mg/L and $\text{pH}=8.3$)	291
Figure A.3 - Variation of DOC (a) and color (b) removal with the stirring speed in the flocculation stage for polyester and cotton simulated effluents ($v_{\text{coagulation}}=150$ rpm, $t_{\text{coagulation}}=3$ min, $T=T_{\text{ambient}}=22-28$ °C, $\text{pH}_{\text{polyester}}=8.3$, $\text{pH}_{\text{cotton}}=9.4$, $[\text{Fe}^{2+}]_{\text{polyester}}=[\text{Fe}^{2+}]_{\text{cotton}}=200$ mg/L, $t_{\text{flocculation}}=15$ min and $[\text{Magnafloc 155}]=2.5$ mg/L)	292
Figure A.4 – Influence of the flocculation time on DOC (a) and color (b) removal from polyester and cotton simulated effluents ($v_{\text{coagulation}}=150$ rpm, $t_{\text{coagulation}}=3$ min, $T=T_{\text{ambient}}=22-28$ °C, $\text{pH}_{\text{polyester}}=8.3$, $\text{pH}_{\text{cotton}}=9.4$, $[\text{Fe}^{2+}]_{\text{polyester}}=[\text{Fe}^{2+}]_{\text{cotton}}=200$ mg/L, $v_{\text{flocculation}}=20$ rpm and $[\text{Magnafloc 155}]=2.5$ mg/L)	292
Figure A.5 – Effect of radiation intensity on DOC and color removal from the cotton effluent during the photo-Fenton process with artificial radiation for 3.75 g/L (a), 5 g/L (b) and 10 g/L (c) of hydrogen peroxide ($T=50$ °C, $\text{Fe}^{2+}:\text{H}_2\text{O}_2=1:33$ and $\text{pH}=3.5$)	293
Figure A.6 – Effect of the radiation intensity on DOC removal from the polyester effluent during the photo-Fenton process for 0.938 g/L (a), 1.25 g/L (b) and 2.5 g/L (c) of hydrogen peroxide ($T=50$ °C, $\text{Fe}^{2+}:\text{H}_2\text{O}_2=1:7$ and $\text{pH}=3.5$)	294
Figure A.7 – Effect of H_2O_2 dose on DOC and color removal from the acrylic (a), cotton (b) and polyester (c) effluents using photo-Fenton's oxidation with simulated sunlight (radiation intensity = 500 W/m ² , $T=50$ °C, $\text{Fe}^{2+}:\text{H}_2\text{O}_2_{\text{acrylic}}=1:57$, $\text{Fe}^{2+}:\text{H}_2\text{O}_2_{\text{cotton}}=1:33$, $\text{Fe}^{2+}:\text{H}_2\text{O}_2_{\text{polyester}}=1:7$, $\text{pH}=3.5$)	295

List of Tables

Part I – Introduction and State of Art

Table 1.1 – Principal auxiliaries' products and corresponding functions	10
Table 1.2 – Suitability of each dye for different fibers types	11
Table 1.3 – Estimative rejection degree for different dye/fiber combination	11
Table 1.4 – Type characterization of wastewaters generated in textile industries	13
Table 1.5 – Maximum allowable values for textile sector, excluding the wool subsector	15
Table 2.1 – Research works on the application of coagulation/flocculation for treating dye solutions and textile effluents	23
Table 2.2 – Studies on the integration of coagulation/flocculation with other processes for treating dye solutions and textile effluents	28
Table 2.3 – Studies on the treatment of dye solutions and textile effluents by Fenton's reaction ..	32
Table 2.4 – Studies on the integration Fenton's reaction with SBR	36
Table 2.5 – Studies on the treatability of dye solutions and textile effluents by photo-Fenton's oxidation.....	40
Table 2.6 – Studies on the treatability of dye solutions and textile effluents by SBR	46
Table 2.7 – Studies on the integration of SBR with other processes for treating dye solutions and textile effluents	49

Part II – Experimental Section

Table 3.1- Characteristics of the dyes present in each simulated effluent	67
Table 3.2 - General characteristics of the auxiliary products used for dyeing polyester, acrylic and cotton fibers	68
Table 3.3 - Estimated concentration of each component in the polyester, acrylic or cotton simulated effluents	70
Table 3.4 - Characteristics of the synthetic textile effluents	74
Table 3.5 - Characteristics of the real cotton dyeing wastewater	76

Part III – Simulated Dyeing Wastewaters Treatment

Table 4.1 – Optimal conditions for coagulation/flocculation and DOC and color removal efficiencies for each synthetic effluent	106
Table 5.1 – Optimum conditions for the coagulation/flocculation process and performances achieved (DOC and color removal) for each effluent when using Fe ³⁺ as coagulant	121

Table 5.2 – Optimum conditions for the coagulation/flocculation process and performances achieved (DOC and color removal) for each effluent when using Fe ²⁺ as coagulant (chapter 4) .	122
Table 5.3 - Optimum conditions for the coagulation/flocculation of textile dyeing wastewaters using Fe ²⁺ (chapter 4) and Fe ³⁺ (this chapter) at ambient temperature (26-28 °C)	124
Table 5.4 - Characterization of the wastewaters after treatment by coagulation/flocculation using Fe ²⁺ or Fe ³⁺ , as described in Table 5.3, and efficiencies attained	125
Table 6.1. Characteristics of the synthetic acrylic wastewater, after coagulation/flocculation and after Fenton oxidation (percent removal efficiencies within brackets) and global removal for the combined process	144
Table 6.2 - Characteristics of the synthetic acrylic dyeing wastewater after Fenton oxidation and coagulation/flocculation (percent removal efficiencies within brackets) and global removal for the combined process; runs #1 to #3 correspond to different dosages of hydrogen peroxide in the Fenton's stage	149
Table 7.1 - Characteristics of the synthetic cotton dyeing wastewater after coagulation/flocculation and after Fenton oxidation (percent removal efficiencies within brackets) and global removal for the combined process (Approach 1)	166
Table 7.2 - Characteristics of the synthetic cotton dyeing wastewater after Fenton oxidation and respective removal efficiencies (Approach 2)	173
Table 7.3 - Characteristics of the synthetic cotton dyeing wastewater after Fenton oxidation and coagulation/flocculation – Approach 3 (percent removal efficiencies within brackets) and global removal for the combined process; runs #1 to #3 correspond to different dosages of hydrogen peroxide in the Fenton's stage	177
Table 8.1 - Characteristics of the synthetic wastewater after coagulation/flocculation and after coagulation/flocculation followed by Fenton oxidation (percent removal efficiencies for each stage are indicated within brackets), and global removal for the combined process (Approach 1). Maximum allowable values for legislated parameters are also shown	193
Table 8.2 - Characteristics of the synthetic polyester dyeing wastewater after Fenton's oxidation and respective removals (Approach 2). Maximum allowable values for legislated parameters are also shown	200
Table 8.3 - Characteristics of the synthetic wastewater after Fenton's oxidation and coagulation/flocculation – Approach 3 (percent removal efficiencies within brackets) and global removal for the combined process; runs #1 to #3 correspond to different dosages of hydrogen peroxide in the Fenton's stage. Maximum allowable values for legislated parameters are also shown	204
Table 9.1 – Values of COD, BOD ₅ and visible color (1:40 dilution) after 60 minutes of oxidation for different doses of H ₂ O ₂ and radiation intensity using the TQ150 lamp (in bold: conditions that allow meeting the discharge limits at the minimum cost)	221
Table 9.2 – Values of COD, BOD ₅ and visible color (1:40 dilution) after 60 minutes of oxidation for different doses of H ₂ O ₂ and radiation intensities using simulated solar irradiation (in bold: conditions that allow meeting the discharge limits at the minimum cost)	229
Table 10.1 – Characteristics of the simulated dyeing raw wastewaters and after SBR treatment and respective removal efficiencies	242

Table 10.2 – Characteristics of the synthetic acrylic dyeing wastewaters after Fenton reaction and SBR and respective removal efficiencies (within brackets) and global removals. Runs#1 to #3 represent experiments with decreasing doses of chemicals in the Fenton’s stage 244

Table 10.3 – Characteristics of the synthetic cotton dyeing wastewater after Fenton reaction and SBR and respective removal efficiencies (within brackets) and global removals. Runs#1 to #3 represent experiments with decreasing doses of chemicals in the Fenton’s stage 245

Table 10.4 – Characteristics of the synthetic polyester dyeing wastewaters after Fenton reaction and SBR and respective removal efficiencies (within brackets), and global removals. Runs#1 to #3 represent experiments with decreasing doses of chemicals in the Fenton’s stage 246

Part IV – Real Cotton Dyeing Wastewater

Table 11.1 - Characteristics of the industrial cotton dyeing wastewater, after coagulation/flocculation and after coagulation/flocculation plus Fenton’s oxidation (Approach 1), and global removals for the combined processes (percent removal efficiencies are given within brackets for each isolated process) 265

Table 11.2 - Characteristics of the cotton dyeing wastewater after Fenton’s oxidation and respective removal efficiencies (Approach 2) 268

Table 11.3 - Characteristics of the cotton dyeing wastewater after Fenton’s oxidation and coagulation/flocculation (Approach 3) and global removal for the combined process (runs #1 to #3 correspond to different dosages of hydrogen peroxide in the Fenton’s stage; percent removal efficiencies are given within brackets for each isolated process) 271

Table 11.4 – Characteristics of the cotton dyeing wastewater after Fenton’s reaction and SBR (Approach 4) and average (last four cycles for SBR) and global removals (respective removal efficiencies are given within brackets for each processes) 274

Part V – Conclusions and Suggestion for Future Work

Table 12.1 – Treatment approaches tested, analysis of compliance with maximum allowable values and operating costs for each simulated effluent and real wastewater tested. In bold are highlighted the cheapest strategies for each effluent that comply with legal limits for discharge 286

NOMENCLATURE

List of symbols

Roman Letters

Symbol	Designation	Unity
A	Peak Amplitude	[mAU]
Abs	Absorbance	[a.u.]/[abs.units]
BOD ₅	Biochemical Oxygen Demand after 5 days	[mg O ₂ /L]
BOD ₇	Biochemical Oxygen Demand after 7 days	[mg O ₂ /L]
BOD ₅ :N:P	Biochemical Oxygen Demand:Nitrogen:Phosphorus ratio	[w:w:w]
COD	Chemical Oxygen Demand	[mg O ₂ /L]
[<i>i</i>]	Concentration of compound/species <i>i</i>	[M] [mg/L]
DOC	Dissolved Organic Carbon	[mg C/L]
D _t	Biodegradation	[%]
Fe ²⁺ :H ₂ O ₂	Ferrous Ion:Hydrogen Peroxide Ratio	[w:w]
HRT	Hydraulic Retention Time	[days]
I	Radiation Intensity	[W/m ²]
[<i>I</i>] ₀	Initial Concentration of compound/species <i>i</i>	[mM]
COD ₀	Initial Chemical Oxygen Demand	[mg O ₂ /L]
K	Kinetic constant	[min ⁻¹] [s ⁻¹] [L mg ⁻¹ min ⁻¹]
k _{COD in anaerobic reaction}	Kinetic Constant for COD Degradation in anaerobic reaction	[h ⁻¹]
k _{color in anaerobic reaction}	Kinetic Constant for Color Degradation in anaerobic reaction	[h ⁻¹]
k _{H₂O₂}	Kinetic Constant for H ₂ O ₂ Consumption	[ppm/min]

KTN	Kjeldhal Total Nitrogen	[mg/L]
P	Power	[W]
SRT	Sludge Retention Time	[day]
SOUR or k'	Specific Oxygen Uptake Rate	[mg O ₂ /(g _{VSS} ·h)]
$V_{\text{coagulation}}$	Stirring Speed in Coagulation Step	[rpm]
$V_{\text{flocculation}}$	Stirring Speed in Flocculation Step	[rpm]
T	Temperature	[°C]
T_{amb}	Ambient Temperature	[°C]
T	Time	[min]
t_{feed}	Time of Feeding	[days]
$t_{\text{coagulation}}$	Time of Coagulation Stage	[min]
$t_{\text{flocculation}}$	Time of Flocculation Stage	[min]
t_{reaction}	Time of reaction	[min]
TDS	Total Dissolved Solids	[mg/L]
TOC	Total Organic Carbon	[mg C/L]
TS	Total Solids	[mg/L]
TSS	Total Suspended Solids	[mg/L]
G	Velocity gradient	[s ⁻¹]
VSS	Volatil Suspended Solids	[mg/L]
		[mg MLSS/L]

Greek Letters

Symbol	Designation	Unity
λ	Wavelength	[nm]
λ_{max}	Wavelength for Maximum Absorbance Value	[nm]

Abbreviations

Abbreviation	Designation
AA – SBR	Aerobic - Anaerobic Sequential Batch Reactor
AOP	Advanced Oxidation Process
E.L.V.	Emission Limit Value
FCS	Ferric Chloride Sludge
GAC	Granular Activated Carbon
HPLC	High Performance Liquid Chromatography
R	Organic compound
M.A.V.	Maximum Allowable Value
MLSS	Mixed Liquor Suspended Solids
PDMDAAC	Polidimetildialilamonium Chloride
PAC	Polyaluminum Chloride
PFC	Polyferric Chloride
PAS	Polyalumimium Sulfate
SBR	Sequential Batch Reactor
UV	Ultra-violet
hv	Radiation
<i>V. fischeri</i>	<i>Vibrio fischeri</i>
WWTP	Wastewater Treatment Plant

Part I

Introduction and State of Art



Chapter 1

Thesis Framework

1 Thesis Framework

1.1 Introduction

This chapter presents the outline and motivation of the thesis, a brief overview of the textile industry in Portugal, a short description of the industrial process, the characterization of the textile wastewaters generated and the identification of the major environmental impacts associated with the discharge of textile effluents.

1.2 Outline and Motivation

Environmental protection and correction of environmental dysfunctions are key issues for effectively improving the quality of life and sustainable development. The water is used for very diverse purposes, which include domestic and public supply, irrigation, transport, industrial processes, recreation and other human activities. These activities generate heavily contaminated wastewaters, that if discharged without any treatment can cause strong negative impacts on the receiving bodies.

The textile industry is known as one of the most polluting industrial sectors [Vandevivere et al., 1998], given the large amounts of wastewater rejected, the composition of the effluents and the fact that dyes are the most notorious pollutants, and often toxic [Figueiredo, 2002].

The adoption of legislation that addresses the need to control the contamination by reducing the pollutants discharged (2000/60/EC Directive) and the imposition of emission limit values (E.L.V.) by Decree - Law No. 236/98 of 1 August and maximum allowable values (M.A.V.) for the discharge of textile effluents (Ordinance No. 423/97 of 25 June) makes the study of new treatment processes a need increasingly urgent. Moreover, the possibility of reusing the treated effluent in industrial processes must necessarily be exploited, since it allows the minimization of water consumption as well as the elimination of pollutants discharge [Silva, 2003].

For the treatment of textile effluents, chemical, biological or a combination of both processes are generally envisaged. The biological treatment by activated sludge is efficient in removing the biodegradable organic matter, but often ineffective in removing

the color from wastewaters, since this is only removed by flocculation and adsorption of the dyes to flocs of microorganisms [Halliday and Beszedits, 1986]. Chemical coagulation/flocculation is also not fully effective in removing certain dyes [Rodrigues, 2007].

As a contribution to overcome this problem it was decided to study the combination of coagulation/flocculation, chemical oxidation by Fenton's reagent – both in darkness and under artificial or solar (simulated) radiation (photo-Fenton oxidation) – and an aerobic biological process (SBR - sequential batch reactor) to improve decolorization and organic matter removal.

Research was focused on three simulated effluents (resulting from the dyeing of acrylic, cotton and polyester fibers) and the treatability of each effluent was assessed by the individual processes mentioned above and their integration in order to obtain a treated effluent complying with the discharge limits imposed by Ordinance No. 423/97 of 25 June at the lowest operation cost. Taking into account the results obtained when treating a simulated cotton dyeing wastewater, a combination of coagulation/flocculation and Fenton's oxidation, Fenton's oxidation alone and an integrated process consisting in Fenton's oxidation plus coagulation/flocculation or biological oxidation in SBR, were applied to a real cotton dyeing wastewater having also in mind the need to meet the discharge limits at the lowest operating costs.

1.3 The Textile Industry

1.3.1 Economic Perspective and Textile Industry Distribution in Portugal

The European textile and clothing industry, which represents approximately 7% of employment and 4% of total manufacturing output in the E.U. [Commission of the European Communities, 2003], is in a difficult economic situation due to the high competition from Asian countries like China, India and Pakistan and the abolition of import quotas by January 1st 2005. In fact, there was a decline in the production (8.7%) and in the employment (8.4%) in 2001 and 2002 [Commission of the European Communities, 2003]. In 2003 the decrease was 4.4% and 7.1% for production and employment, respectively [Commission of the European Communities, 2004].

In Portugal, the textile and clothing industry has a large representation in the industrial structure with a prominent role in terms of employment and weight in the national economy [Vasconcelos, 2006]. According to the Textile and Clothing Association [ATP, 2013], in 2011 there were, in Portugal, about 7000 companies laboring in all textile and clothing sub-sectors, which accounted for 10% of Portuguese exports, 19% of employment in manufacturing industry, 8% of turnover and 8% of production. National strengths lie in geographical and cultural proximity to the European market, tradition and accumulated "know-how", moderate wage costs as regards the European levels, growing international recognition of the products, progressive development of a culture of quality and rapid response [Vasconcelos, 2006].

The textile sector in Portugal also felt pressure from the Asian market and the abolition of import quotas led to a considerable decrease of total exports since 2007 [ATP, 2013].

The textile industries in Portugal are located mainly in three regions: North, Centre and Tagus Valley, and there has been in recent years an increase in the relative weight of the North and Centre, to the detriment of Lisbon, as can be seen in Figure 1.1 [Vasconcelos, 2006].

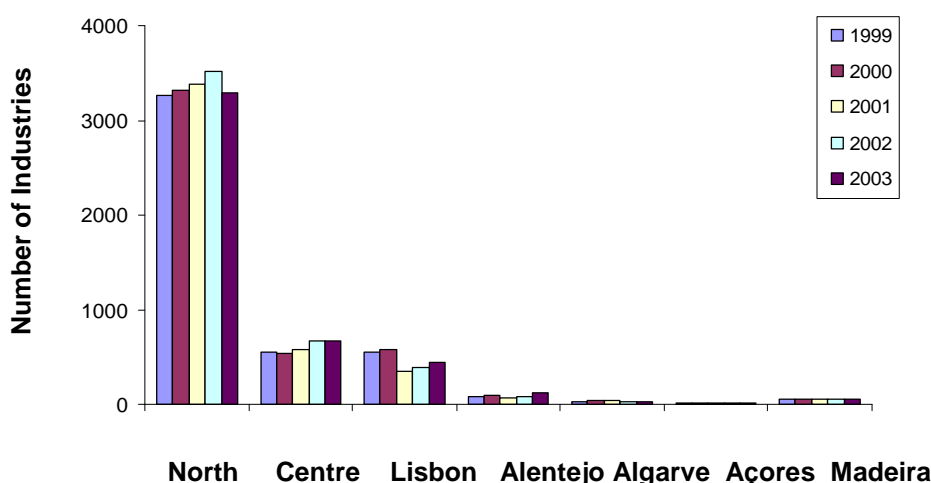


Figure 1.1 – Textil industry geographic distribution in Portugal (adapted from Vasconcelos, 2006).

In Portugal, there are two major concentrations of the textile industry. The first one, concerning the subsectors of cotton and synthetic fibers, is found in the northern region,

with 70% of the companies and 78% of the employment in this sector, which represents 28.4% of the number of companies and 38.9% of employment in manufacturing [AMAVE and S.I.D.V.A., 2002; cited by Silva, 2003]. The second one is located in Beira interior region and covers the wool sector. This dynamic historical location is mainly due to the tangible factors of production, such as the cost of skilled labor and raw materials that eventually become a competitive advantage for companies in the sector [Vasconcelos, 2006].

1.3.2 Industrial Process

The textile industry uses fibers as raw material which can be natural (e.g. cotton, wool, silk and linen) or synthetic (as is the case of polyester and polyamide), or made from regenerated cellulose such as rayon and acetate [Figueiredo et al., 2000]. It is estimated that companies in this sector use 80.9, 59.4 and 26.7% of man-made fibers, cotton and wool, respectively [Figueiredo et al., 2000].

The supply chain of the textile and clothing industry is comprised of several interrelated stages. They give rise to a fairly linear chain, as illustrated in Figure 1.2. The process begins with the wiring, passes through the intermediate stages of weaving and finishing, appearing as the last link in the chain (closest to the consumer), the garment industry and garment [Vasconcelos, 2006].

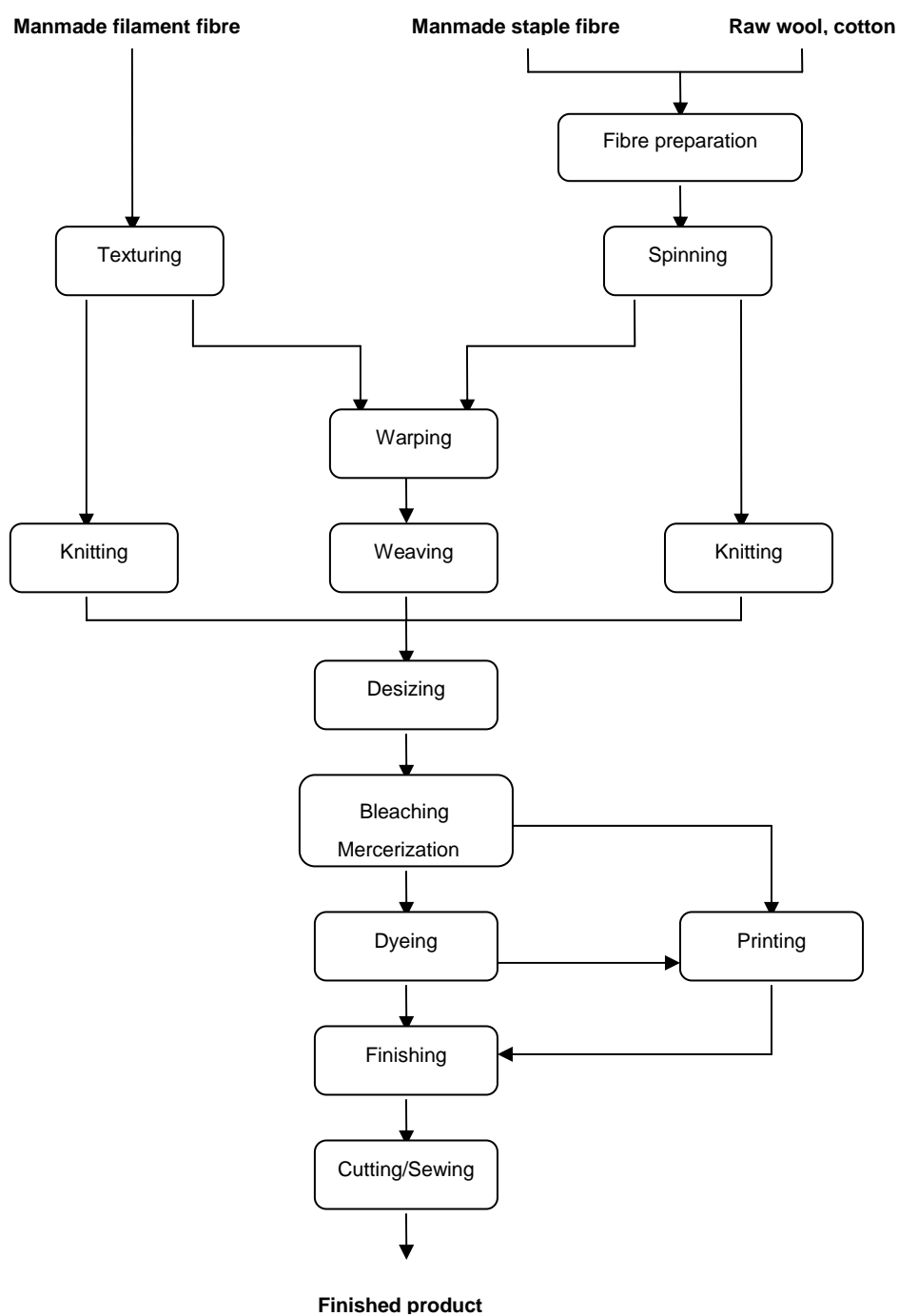


Figure 1.2 – Representative flowchart of textile and clothing manufacturing process (adapted from U.S. EPA, 1997; Bisschops and Spanjers, 2003).

The textile manufacturing process, in addition to the fibers, uses various auxiliaries with different functions. Table 1.1 shows the main products used, as well as their function.

Table 1.1 – Principal auxiliaries in textile industry and corresponding functions (adapted from Faria, 2008).

Auxiliary products	Function
Sizing agents	Improve the mechanical resistance of the fibers
Bleaching agents	Remove the natural color of the fibers
Surfactants	Decrease the surface tension of the fibers when contact with water
Softeners	Softening the fibers
Sequestrants	Form complexes with metallic ions to prevent their interference in the process
Salts (NaCl, Na ₂ SO ₄)	Neutralization of charges (electrolyte)
NaOH	Purification and mercerization of cotton; pH adjustment in dyebaths
Acids and alkalis	pH adjustment

In the dyeing step (cf. Figure 1.2) various dyes are applied. They include one or more chromophor groups which give the color property, and have a chemical structure and characteristics suitable to transport and bind the molecule to the textile fiber.

The dyes can be classified according to their chemical structure (in different chemical classes) or according to their properties and applications. However, it is common to simultaneously use the terminology considered by the two classification systems, such as the Color Index, widely accepted for assigning one color, and the generic name (according to the characteristics of application) followed by a number of formation (based on the chemical structure). As regards the classification by the chemical structure, the dyes can be of different types: azo, azoic, nitro, nitroso, stilbene, diphenylmethane, triarylmethane, xanthene, acridine, quinoline, methane, triazole, indamines, azine, sulphur, lactone, anthraquinone, indigoid and phthalocyanine [Abrahart, 1977; Morais, 1996]. As regards the application properties they are divided into direct, acid, mordant, metallized, reactive, cationic, vat, sulfur, azo and disperse [Abrahart, 1977; Waters, 1979]. The first six types of dyes are soluble in water and the others are insoluble.

Generally, the degree of fixation of dyes in fibers depends upon the combination dye type/fiber. Table 1.2 shows the suitability of each dye to the fibers. Table 1.3 presents an estimate of the degree of rejection of the dyes.

Table 1.2 – Suitability of each dye for different fiber types (adapted from Araújo e Castro, 1984).

Dye	Fiber					
	Proteic (wool and silk)	Cellulosic (cotton, viscose and modal)	Acetate and triacetate	Polyamide	Polyester	Acrylic
Acid	V.A.			V.A.		
Azoic		V.A.	A.	A.	A.	A.
Basic						*
Vat	A.	V.A.				
Direct	A.	V.A.		A.		
Disperse			V.A.	V.A.	V.A.	V.A.
Metallized	V.A.			V.A.		
Mordant	V.A.				A.	
Reactive	V.A.	V.A.		A.		
Sulfur		V.A.				

A.- appropriate; V.A. - very appropriate

Table 1.3 – Estimated rejection degree for different dye/fiber combinations (adapted from Easton, 1995).

Dye	Fiber	Rejection degree (%)
Acid	Polyamide	5-20
Cationic	Acrylic	0-5
Direct	Celulosic	5-30
Disperse	Polyester	0-10
Metallized	Wool	2-10
Reactive		10-50
Sulfur	Celulosic	10-40
Vat		5-20

The problem of incomplete fixation of the dyes to fibers is particularly important in the case of dyeing cellulosic fibers with reactive dyes because these dyes have a low degree of fixation and are used worldwide. This is also the case of other pairs of dyes/fiber types, as shown in Table 1.3. Thus, studies have been developed [Taylor et al. 2001; Mokhtari et

al., 2005] to improve the efficiency of dyeing, particularly the development of dyes with more than one reactive group, such as bi-functional dyes for which the rejection rate is lower.

1.3.3 Textile Wastewaters and Environmental Problems

In the textile industry many chemicals are used in the wet phases that generate organic loaded wastewater. Due to the variety of fibers, dyes and chemicals used in the finishing processes, effluents of great complexity and chemical diversity are produced.

The composition of wastewaters from the textile and dyeing processes shows a high variation from day to day or hour to hour, depending on the dye type and concentration of auxiliaries added [Kim et al., 2004].

The textile effluents are generally characterized by high pH, alkalinity and temperature, containing a high concentration of organic compounds, non-biodegradable matter, toxic substances, detergents, fats and oils, sulfides and suspended and dissolved solids [Gao et al., 2007]. The effluents from the dyeing and finishing processes present elevated temperature, elevated pH, strong coloration, medium chemical oxygen demand (COD), low biodegradability, and high amounts of suspended solids [Kim et al., 2004; Joo et al., 2007]. The values of these parameters usually vary from factory to factory. Table 1.4 shows some characterization values of textile effluents, in terms of COD, biological oxygen demand (BOD₅), total suspended solids (TSS), total solids (TS) total dissolved solids (TDS), chlorides (Cl⁻), oil, sulfites (SO₃²⁻), Kjeldhal total nitrogen (KTN), nitrates (NO₃⁻), ammonia (NH₃), dissolved phosphorus (PO₄²⁻), color, pH and temperature (T), as reported in the literature.

Table 1.4 – Characterization of wastewaters generated in textile industries.

COD (mgO ₂ /L)	BOD ₅ (mgO ₂ /L)	pH	T (°C)	TSS (mg/L)	TS (mg/L)	TDS (mg/L)	Oil (mg/L)	Cl ⁻ (mg/L)	SO ₃ ²⁻ (mg/L)	KTN (mg/L)	NO ₃ ⁻ (mg/L)	NH ₃ (mg/L)	PO ₄ ²⁻ (mg/L)	Color (Pt-Co scale)	References
460-1500		9-10			91-250										[Hi and Peng, 1994]
680	200	10.1		55											[Silva, 1999]
786	378	10.1												1716	[Andrade, 2003]
150-12000	80-6000	7-9		15-8000		2900-3100		1000-1600		70-80				50-2500	[Al-Kadasi et al., 2004]
2570-3012	1645-1974	9.8-11.1	39-48	254-367		1056-1254	19-37		14-29		12-17	11-15	16-28	156-213	[Rofail et al., 2005]
649	237	10		151											[Roriz et al., 2007]

The uncontrolled discharge without any prior treatment of such heavily contaminated effluents (cf. Table 1.4) generates negative impacts on the environment, namely:

- pH increase of the receiving waters, causing damage to fauna and flora;
- Presence of high levels of dissolved solids can generate increased salinity and turbidity associated with the proliferation of microorganisms or eutrophization of the water resources;
- Possible occurrence of low dissolved oxygen concentration in water due to its consumption by aerobic microorganisms that oxidize the biodegradable organic matter present in the effluent, then causing the death of aquatic organisms; the organic matter may also be degraded anaerobically, yielding toxic and unpleasant odorous compounds (such as hydrogen sulfide);
- One of the most important adverse effects resulting from the discharge of textile wastewater comes from non-fixed dyes to the fiber. Because dyes present a great chemical and photolytic stability [Silva, 2003] and are visible at low concentrations (1 mg/L) [O'Neill et al., 1999], they prevent the use of water for certain uses, particularly for producing drinking water and for recreational purposes [Rodrigues, 2007 and Santos, 2009]; moreover, when ingested they pose risks associated with chronic biotransformations, as specific enzymes can produce carcinogenic and mutagenic compounds (aromatic amines such as, toluidines, active radicals, etc.), which may cause dermatitis when in contact with the skin [Silva, 2003].
- Another negative impact of dyes is associated with a decrease in sunlight penetration, affecting photosynthesis and plant growth [Rodrigues, 2007; Santos, 2009], and with disturbances in the solubility of gases causing damage to the aquatic fauna [Silva, 2003].

The competent authorities have been developing legislation that limits the concentration of these pollutants in effluents discharged, to minimize environmental impacts. For the textile sector, excluding the wool subsector, the Portuguese Legislation (Ordinance No. 423/97 of 25 June) imposes maximum allowable values (M.A.V.) for pH, COD, BOD₅ and visible color after dilution 1:40 (Table 1.5).

Table 1.5 – Maximum allowable values for the textile sector, excluding the wool subsector.

Parameter	Maximum Allowable Values
pH	5.5 – 9.0
BOD ₅	100 mgO ₂ /L
COD	250 mgO ₂ /L
Color	not visible after dilution 1:40

The values of pH, COD, BOD₅ and color typically do not comply with the values established by law, so it is necessary to treat the textile effluents before discharge. Various studies concerning the treatment of these effluents, namely, by physical processes (coagulation/flocculation, adsorption and membrane separation), advanced chemical oxidation, biological oxidation and chemical reduction, are reported in the literature [Lourenço et al., 2001; Figueiredo, 2002; Walker et al., 2002; Malik et al., 2003; Fersi et al., 2005; Ramirez et al., 2005; Joo et al., 2007; Rodrigues, 2007].

In this thesis, coagulation/flocculation, Fenton and photo-Fenton oxidation, and biological processes were selected to treat textile dyeing wastewaters. The next chapter presents a description of these technologies and the reasons for their choice.

1.4 References

- Abrahart, E.N. (1977). *Dyes and Their Intermediates*. 2nd Edition, Edward Arnold Ltd, London.
- Al-Kadasi, A.; Idris, A.; Saed, K.; Guan, C.T. (2004). Treatment of textile wastewater by advanced oxidation process – a review. *International Journal*, 6 (3), 222-230.
- AMAVE – Associação de Municípios do Vale do AVE, S.I.D.V.A. – Sistema Integrado de Despoluição do Vale do Ave (2002).
- Andrade, F. (2003). Remoção de cor de efluentes têxteis com tratamento de lodos ativados e um polieletrólito orgânico. Dissertação de Mestrado em Engenharia Ambiental, Departamento de Engenharia Sanitária, Universidade Federal de Santa Catarina, Florianópolis. (access: <http://www.tede.ufsc.br/teses/PGEA0163.pdf>).
- Araújo, M. e Castro, E. M. (1984). *Manual de Engenharia Têxtil*, volume II. Lisboa: Fundação Calouste Gulbenkian.
- ATP (2013). Associação Têxtil e Vestuário de Portugal. <http://www.atp.pt/gca/index.php?id=18>. (last access 23/03/2013).

Chapter 1 - Introduction

Bisschops, I.; Spanjers, H. (2003). Literature Review on Textile Wastewater Characterisation. *Environmental Technology*, 24, 1399-1411.

Commission of the European Communities (2003). O futuro do sector dos têxteis e do Vestuário na União Europeia alargada. Communication from the Council Commission, the European Parliament, the European Economic and Social Committee and the Committee of the Regions, Brussels.

Commission of the European Communities (2004). O sector dos têxteis e do Vestuário após 2005 – Recomendações do Grupo de Alto Nível para os Têxteis e o Vestuário. Communication from the Council Commission, the European Parliament, the European Economic and Social Committee and the Committee of the Regions, Brussels.

2000/60/CE Directive of European Parliament Council, 23 October 2000, establishing a framework for Community action in the field of water policy.

Easton, J. R. (1995). The dye maker's view. In *Colour in Dyehouse Effluent*, P. Cooper (Ed.). Oxford, The Society of dyers and Colourists, The Alden Press, 9-21.

Faria, P.C.C. (2008). Catalytic Ozonation of Effluents from the Textile Industry. PhD thesis, University of Porto – Faculty of Engineering.

Fersi, C.; Gzara, L.; Dhahbi, M. (2005). Treatment of textile effluents by membrane technologies. *Desalination*, 185 (1-3), 399-409.

Figueiredo, J.M.; Rodrigues, F.; Correia, A.; Barros, M. (2000). *Guia Técnico do Sector Têxtil*. Lisbon.

Figueiredo, S. A. R. C. (2002). Remoção de corantes têxteis em solução aquosa usando materiais naturais contendo quitina. PhD thesis, University of Porto – Faculty of Engineering.

Gao, B.-Y.; Wang, Y.; Yue, Q.-Y.; Wei, J.-C.; Li, Q. (2007). Color removal from simulated dye water and actual textile wastewater using a composite coagulant prepared by polyferric chloride and polydimethyldiallylammonium chloride. *Separation and Purification Technology*, 54, 157-163.

Halliday, P.J.; Beszedits, S. (1986). Color Removal from Textile Mill Wastewater. *Canadian Textile Journal*, April, 78-84.

Hi, S.H.; Peng, C.F. (1994). Treatment of textile wastewater by electrochemical method, *Water Research* 28 (2), 277–282.

Joo, D.J.; Shin, W.S.; Choi, J.-H.; Choi, S. J.; Kim, M.-C.; Han, M.H.; Ha, T. W.; Kim, Y.-H. (2007). Decolorization of reactive dyes using inorganic coagulants and synthetic polymer. *Dyes and Pigments*, 73, 59-64.

Kim, T.-H.; Park, C.; Yang, J.; Kim, S. (2004) Comparison of disperse and reactive dye removals by chemical coagulation and Fenton oxidation. *Journal of Hazardous Materials*, B 112, 95-103.

Lourenço, N.D.; Novais, J.M.; Pinheiro, H.M. (2001). Effect of some operational parameters on textile dye biodegradation in a sequential batch reactor. *Journal of Biotechnology*, 89, 163-174.

Malik, P.K.; Saha, S.K. (2003). Oxidation of direct dyes with hydrogen peroxide using ferrous ion catalyst. *Separation and Purification Technology*, 31, 241-250.

- Mokhtari, J., Phillips, D. A. S., Taylor, J. A. (2005). Synthesis and evaluation of a series of trisazo heterobi-functional reactive dyes for cotton. *Dyes and Pigments*, 64 (2), 163-170.
- Morais, L.C.P. (1996). Tratamento de Efluentes Têxteis Simulados Usando Técnicas de Adsorção. Master dissertation in environmental engineering, University of Porto – Faculty of Engineering.
- O'Neill, C., Hawkes, F. R., Hawkes, D. L., Lourenco, N. D., Pinheiro, H. M. e Delee, W. (1999), Colour in textile effluents – sources, measurement, discharge consents and simulation: a review. *Journal of Chemical Technology and Biotechnology*, 74 (11), 1009-1018.
- Ramirez, J.H.; Costa, C.A.; Madeira, L.M. (2005). Experimental design to optimize the degradation of the synthetic dye orange II using Fenton's reagent. *Catalysis Today*, 107-108, 68-76.
- Rodrigues, C.S.D. (2007). Tratamento de Efluentes Têxteis por Processos Combinados de Oxidação Química e Biológica. Master dissertation in environmental engineering, University of Porto – Faculty of Engineering.
- Rofail, M.; Seif, H.; El-Rasoul, F.A.; Moustafa, M. (2005). Chemical-biological treatment of polyester textile wastewater (case study). *Alexandria Engineering Journal*, 44 (5), 773-778.
- Roriz, A.; Machado, I.; Cunha, J. (2007). Tratamento de efluentes têxteis de uma indústria do ramo têxtil. Master dissertation, University of Minho.
- Santos, S.C.R. (2009). Adsorção de corantes têxteis em materiais naturais e residuais de matriz inorgânica. PhD dissertation, University of Porto – Faculty of Engineering.
- Silva, M. (1999). A Indústria Têxtil e o Ambiente – Desafios actuais do Sector. *Revista AEP* 28.
- Silva, C.S.C.G. (2003). Processos Avançados de Oxidação Fotoquímica na Descoloração de Soluções Aquosas Fortemente Coradas. Master dissertation, University of Porto – Faculty of Engineering.
- Taylor, J. A., Pasha, K., Phillips, D. A. S. (2001). The dyeing of cotton with hetero bi-functional reactive dyes containing both a monochlorotriazinyl and a chloroacetyl amino reactive group. *Dyes and Pigments*, 51 (2-3), 145-152.
- U.S. EPA – Environmental Protection Agency (1997). Profile of the Textile Industry. Office of Compliance, Office of Enforcement and Compliance Assurance, Washington, EPA/310-R-97-009.
- Vandevivere, P.C.; Bianchi, R.; Verstraete, W. (1998). Treatment and reuse of wastewater from the textile wet-processing industry: review of emerging technologies. *Journal of Chemical Technology and Biotechnology*, 72, 289-302.
- Vasconcelos, E. (2006), Análise da Indústria Têxtil e do Vestuário. Análise da Indústria Têxtil e do Vestuário. Braga, Portugal, 26 de Outubro de 2006.
- Walker, G.M.; Weatherley, L.R. (2002). Textile Wastewater Treatment Using Granular Activated Carbon Adsorption in Fixed Beds. *Separation Science and Technology*, 35 (9), 1329-1341.
- Waters, B. D. (1979), Treatment of dye waste. *Water Pollution Control*, 78, Waters, B. D. (1979), Treatment of dye waste. *Water Pollution Control*, 78, 12-26.



Chapter 2

State of the Art

2 State of the Art

2.1 Introduction

In the present chapter the processes of coagulation/flocculation, Fenton and photo-Fenton's oxidation and biological degradation in sequencing batch reactor (SBR) are reviewed, particularly their application to textile wastewater treatment.

The selection of these treatment processes took into account the ease of operation, the ability to eliminate pollutants and the operating cost.

2.2 Coagulation/Flocculation

Natural waters and wastewaters contain suspended or colloidal insoluble particles. Colloids are particles with diameter in the range of 0.1-1 μm [Eckenfelder, 2000], usually negatively charged. The surface attracts oppositely charged ions in solution, thereby forming a fixed Stern layer. The remaining ions present in solution form a diffuse layer around the Stern layer. The combination of the two layers is called a double layer [Eckenfelder, 2000].

The colloids are stable owing to repulsive electrostatic forces which prevent their agglomeration or flocculation [Eckenfelder, 2000]. Accordingly, these particles present a very low settling rate and thus cannot be removed by traditional gravitic processes [Eckenfelder, 2000; Samyer et al., 1994]. Colloids also exhibit attractive forces, with smaller amplitude than the repulsive ones (Van der Waals forces), with the ability to aggregate particles that surround themselves enough.

For the occurrence of such particles removal it is necessary to agglomerate them, forming larger particles. Thus, the coagulation/flocculation process is based on the destabilization of colloids and subsequent formation of flocs (that occurs after addition of a polyelectrolyte or an inorganic coagulant - normally aluminium or iron salts) and makes use of a polymer to promote the flocs aggregation, which are further separated by sedimentation [Cánizares et al., 2009].

The coagulation stage is a somewhat complicated process involving a series of physical-chemical interactions: electrostatic attraction, sorption, bridging (related to high molecular weight polymers) and inclusion in metal precipitates [Peavy et al., 1985; Sawyer et al., 1994; Eckenfelder, 2000; Alves, 2007]. Normally the destabilization of the colloids in water and wastewater treatment processes is achieved through mechanisms of charge neutralization and inclusion in metal precipitates. These mechanisms are affected by various parameters such as: type of coagulant, coagulant dose, pH, stirring rate and contact time [Metcalf & Eddy, 2003; Alves, 2007].

To determine the optimum values of the parameters for coagulation it is necessary to perform laboratory experiments, since they depend on the characteristics of the effluent to be treated and the type of coagulant used. However, in the literature can be found typical values for stirring speed around 100 rpm [Satterfield, 2004; Bose, 2010; Poland and Pagano, 2010] and stirring time in the order of 1-3 minutes [Peavy, 1985; Eckenfelder, 2000; Bose, 2010; Poland and Pagano, 2010]. For the treatment of textile effluents, doses of 250-1000 mg/L and pH values from 3 to 11 for $\text{Fe}_2(\text{SO}_4)_3$ and doses of 250-750 mg/L and pH values of 5 to 10 for $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ have been reported [Eckenfelder, 2000].

After stabilization of colloids the aggregation of particles must be promoted to obtain particles with higher diameter, which facilitates their sedimentation (flocculation step). This is achieved through collisions between particles and can be triggered by two mechanisms, perikinetic or orthokinetic flocculation [Vigneswaran and Visvanathan, 1995; Alves, 2007].

In the flocculation step it is necessary to take into account the type and dose of flocculant, stirring speed and contact time. The optimal values of these variables are also determined by performing laboratory tests and mainly varying the type and dose of flocculant, since they depend on the characteristics of the wastewater, as in the coagulation step [Alves, 2007]. Values of 10 to 45 minutes for the contact time [Peavy et al., 1985; Alves, 2007; Bose, 2010; Poland and Pagano, 2010] and 25 to 35 rpm [Phipps & Bird, 1995; Lafleur, 1997; Eckenfelder, 2000; Bose, 2010; Poland and Pagano, 2010] for the stirring speed, have been reported.

The main advantages of this treatment process are the following ones: low residence/contact time, flexibility and efficiency for most classes of dyes, low capital costs, use of relatively simple equipment and simultaneous removal of other pollutants (for example allows the COD reduction). However, this technique has some disadvantages, such as: use of flocculants to increase the efficiency of the process, considerable volume

of chemical sludge produced, necessity of adding chemicals, relatively high operating costs, and some cationic organic polymers can be toxic to fishes, even at low concentrations [Easton, 1995].

In the literature are reported studies where coagulation/flocculation or a combination of this technique with other process has been applied in the treatment of textile effluents. In the two next sections a brief description of these studies is presented.

2.2.1 Textile Wastewater Treatment by Coagulation/Flocculation

In the last years various works have been reported in the open literature regarding the treatment of dye solutions and simulated or real textile wastewaters by coagulation/flocculation. Table 2.1 summarizes some of those works.

Table 2.1 – Research works on the application of coagulation/flocculation for treating dye solutions and textile effluents.

Dye solution or Effluent type	Optimal Operating Conditions	Efficiencies (%)	Reference
Blue Suncron RD-400 dye	$V_{\text{coagulation}} = 250 \text{ rpm}$ $t_{\text{coagulation}} = 2 \text{ min}$ $V_{\text{flocculation}} = 40 \text{ rpm}$ $t_{\text{flocculation}} = 15 \text{ min}$ $t_{\text{sedimentation}} = 30 \text{ min}$ $\text{pH} = 6$ $[\text{FeCl}_3 \cdot 6\text{H}_2\text{O}] = 0.93 \text{ mM}$	COD = 84 Dye = 98	Kim et al. [2004]
Yellow Suncron 3GE-200 dye	$V_{\text{coagulation}} = 250 \text{ rpm}$ $t_{\text{coagulation}} = 2 \text{ min}$ $V_{\text{flocculation}} = 40 \text{ rpm}$ $t_{\text{flocculation}} = 15 \text{ min}$ $t_{\text{sedimentation}} = 30 \text{ min}$ $\text{pH} = 5$ $[\text{FeCl}_3 \cdot 6\text{H}_2\text{O}] = 0.74 \text{ mM}$	COD = 88 Dye = 100	Kim et al. [2004]
Blue Suncron P-3R dye	$V_{\text{coagulation}} = 250 \text{ rpm}$ $t_{\text{coagulation}} = 2 \text{ min}$ $V_{\text{flocculation}} = 40 \text{ rpm}$ $t_{\text{flocculation}} = 15 \text{ min}$ $t_{\text{sedimentation}} = 30 \text{ min}$ $\text{pH} = 7$ $[\text{FeCl}_3 \cdot 6\text{H}_2\text{O}] = 2.78 \text{ mM}$	COD = 25 Dye = 61	Kim et al. [2004]

Chapter 2 - State of the Art

Table 2.1 – Research works on the application of coagulation/flocculation for treating dye solutions and textile effluents (cont.).

Dye solution or Effluent type	Optimal Operating Conditions	Efficiencies (%)	Reference
Yellow Suncron E4R-H dye	$V_{\text{coagulation}} = 250 \text{ rpm}$ $t_{\text{coagulation}} = 2 \text{ min}$ $V_{\text{flocculation}} = 40 \text{ rpm}$ $t_{\text{flocculation}} = 15 \text{ min}$ $t_{\text{sedimentation}} = 30 \text{ min}$ $\text{pH} = 6$ $[\text{FeCl}_3 \cdot 6\text{H}_2\text{O}] = 1.85 \text{ mM}$	COD = 67 Dye = 71	Kim et al. [2004]
Mixture of cotton and polyester dyeing effluents (in ratio 64%:36%, respectively)	$[\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}] = 40 \text{ mg/L}$ $[\text{Colfloc Ciba RD}] = 3 \text{ mL/L}$ $[\text{Antifoaming}] = 0.4 \text{ mL/L}$	TOC = 75 COD = 76 BOD ₇ = 28 Dye = 99	Golob et al. [2005]
Remazol Black B dye Procion Blue HB dye Cibacron Brilliant Yellow 3G-P	$V_{\text{coagulation}} = 200 \text{ rpm}$ $t_{\text{coagulation}} = 1 \text{ min}$ $V_{\text{flocculation}} = 50 \text{ rpm}$ $t_{\text{flocculation}} = 10 \text{ min}$ $t_{\text{sedimentation}} = 30 \text{ min}$ $\text{pH} = 5$ $[\text{Alum}] = 400 \text{ mg/L}$ $[\text{Flocculant}] = 0.15 \text{ g/L}$	Dye = 100	Joo et al. [2007]
Procion Red MX-5B	$V_{\text{coagulation}} = 200 \text{ rpm}$ $t_{\text{coagulation}} = 1 \text{ min}$ $V_{\text{flocculation}} = 50 \text{ rpm}$ $t_{\text{flocculation}} = 10 \text{ min}$ $t_{\text{sedimentation}} = 30 \text{ min}$ $\text{pH} = 5$ $[\text{Alum}] = 400 \text{ mg/L}$ $[\text{Flocculant}] = 0.25 \text{ g/L}$	Dye = 100	Joo et al. [2007]
Real effluent	$V_{\text{coagulation}} = 200 \text{ rpm}$ $t_{\text{coagulation}} = 1 \text{ min}$ $V_{\text{flocculation}} = 50 \text{ rpm}$ $t_{\text{flocculation}} = 10 \text{ min}$ $t_{\text{sedimentation}} = 30 \text{ min}$ $\text{pH} = 5$ $[\text{Alum}] = 5 \text{ g/L}$ $[\text{Flocculant}] = 0.5 \text{ g/L}$	COD = 40 Dye = 62 Turbidity = 90	Joo et al. [2007]

Table 2.1 – Research works on the application of coagulation/flocculation for treating dye solutions and textile effluents (cont.).

Dye solution or Effluent type	Optimal Operating Conditions	Efficiencies (%)	Reference
Reactive Red - K-2BP dye			
Reactive Yellow - K-4G dye			
Reactive Blue - K-GL dye	[MgCl ₂] = 400 mg/L pH = 12	Dye > 90	Gao et al. [2007 a]
Reactive Purple - K-3R dye	(pH adjusted with Ca(OH) ₂)		
Dispersant Dark Red - PR dye			
Disperse Yellow - SE-6GFL dye			
Disperse Blue HGL dye	[PFC/PDMDAAC] = 30 mg/L pH = 6	Dye = 96	Gao et al. [2007 b]
Reactive Blue STE dye	[PFC/PDMDAAC] = 60 mg/L pH = 7.5	Dye = 99	Gao et al. [2007 b]
Real effluent	[PFC/PDMDAAC] = 150 mg/L	Dye = 99	Gao et al. [2007 b]
Disperse Blue 79 dye	SIWW dose (containing 1787 mg/L FeCl ₃) = 1 mL pH = 4.25 [dye] = 150 mg/L	Color = 99 COD = 94	Anouzla et al. [2009]
Acid Red 119 dye	pH = 3.5 [Ferric chloride sludge] = 236.68 mg/L [dye] = 65.91 mg/L	Dye = ~97	Modhaddam et al. [2010]
Acid Black 210 dye	[dye] = 4 g/L pH = 5 [Al ³⁺] = 0.003 M [ACCEPTA 2058] = 3.5 mg/L t _{sedimentation} = 60 min	Dye > 90	Zahrim et al. [2010]
Blue Bezaktiv S-GLD 150 dye	V _{coagulation} = 180 rpm t _{coagulation} = 3 min V _{flocculation} = 30 rpm t _{flocculation} = 15 min t _{sedimentation} = 15 min pH = 8.47 [PAS] = 1.805 g/L [CHT-Flocculant CV] = 3.76 mg/L	Color > 94	Khouni et al. [2011 a]

Chapter 2 - State of the Art

Table 2.1 – Research works on the application of coagulation/flocculation for treating dye solutions and textile effluents (cont.).

Dye solution or Effluent type	Optimal Operating Conditions	Efficiencies (%)	Reference
Simulated effluent containing Blue Bezaktiv S-GLD 150	$V_{\text{coagulation}} = 180 \text{ rpm}$ $t_{\text{coagulation}} = 3 \text{ min}$ $V_{\text{flocculation}} = 30 \text{ rpm}$ $t_{\text{flocculation}} = 15 \text{ min}$ $t_{\text{sedimentation}} = 15 \text{ min}$ $\text{pH} = 8.2$ $[\text{PAS}] = 1.842 \text{ g/L}$ $[\text{CHT-Flocculant CV}] = 3.82 \text{ mg/L}$	Color = 96	Khouni et al.[2011 a)]
Black Novacron R dye	$V_{\text{coagulation}} = 180 \text{ rpm}$ $t_{\text{coagulation}} = 3 \text{ min}$ $V_{\text{flocculation}} = 30 \text{ rpm}$ $t_{\text{flocculation}} = 15 \text{ min}$ $t_{\text{sedimentation}} = 15 \text{ min}$ $\text{pH} = 8.31$ $[\text{PAS}] = 1.804 \text{ g/L}$ $[\text{CHT-Flocculant CV}] = 3.85 \text{ mg/L}$	Color = 94 at 530 nm Color = 90 at 400 nm	Khouni et al.[2011 a)]
Synthetic wastewater containing Black Novacron R dye	$V_{\text{coagulation}} = 180 \text{ rpm}$ $t_{\text{coagulation}} = 3 \text{ min}$ $V_{\text{flocculation}} = 30 \text{ rpm}$ $t_{\text{flocculation}} = 15 \text{ min}$ $t_{\text{sedimentation}} = 15 \text{ min}$ $\text{pH} = 8.55$ $[\text{PAS}] = 1.925 \text{ g/L}$ $[\text{CHT-Flocculant CV}] = 3.69 \text{ mg/L}$	Color = 94 at 530 nm Color = 90 at 400 nm	Khouni et al.[2011 a)]
Disperse Red dye	$V = 60 \text{ rpm}$ $t = 30 \text{ min}$ $t_{\text{sedimentation}} = 30 - 40 \text{ min}$ $\text{pH} = 6.4$ $[\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}] = 40 \text{ mg/L}$ $[\text{dye}] = 60-230 \text{ g/L}$	Color = 90	Merzouk et al. [2011]

Further works have been reported in recent years. For instance, Moghaddam et al. [2011] compared the performance of polyaluminium chloride (PAC) and polyaluminium chloride sludge (PACs) as coagulants for Acid Red 119 dye removal. The coagulation/flocculation tests procedure involved 2 min of rapid mixing (100 rpm), followed by slow mixing (40 rpm) for 30 minutes and 30 minutes of clarification. The effect of pH (3-12), PAC dose (15-

120 mg/L) and PACs dose (0.5-9 g/L) on the dye removal (80 mg/L solution) were evaluated through a parametric study. The results indicated better performance at pH in acid zone for both coagulants, for doses of 70 mg/L and 5.4 g /L of PAC and PACs, respectively. Afterwards, the influence of pH (2.31 to 5.68), dose of coagulant (0.57 to 5.4 g/L for PACs and 16.36 to 83.63 mg/L for PAC) and dye concentration (65.91 to 234.08 mg/L) on color removal was analysed. The authors found, after application of statistical multivariate tools that: i) as concerns PACs, pH, coagulant dose and dose of dye concentration presented statistical significance, as well as the square of pH, dosage of coagulant and the interactions between pH and dose of coagulant and coagulant doses and dye cocentrations; ii) as regards PAC, pH, coagulant dose and its square, dye concentration and the interaction of dye and coagulant concentrations showed statistical significance. Dye removal was maximized for pH=3.42, [coagulant]= 4.55 g/L and [dye]= 140 mg/L for PACs (94.1% color removal) and pH=3.8, [coagulant]= 57 mg/L and [dye]=140 mg/L for PAC (95.25% color removal).

Very recently, Wu et al. [2012] performed coagulation/flocculation tests to remove Yellow Disperse dye (RGFL) in solution. Coagulation was carried out at 200 rpm (velocity gradient - G - equal to 51.6 s^{-1}), using aluminum sulfate as coagulant, and flocculation was performed at 40 rpm ($G=11.8 \text{ s}^{-1}$) adding sodium alginate as coagulant aid. Sedimentation of the flocs lasted 30 minutes. The effect of pH (6-8), the aluminum sulfate dose (4.0-6.5 mg/L) and the amount of sodium alginate (0-2.0 mg) on color removal was assessed. Maximum removal (86%) was achieved at pH 8, $[\text{Al}_2(\text{SO}_4)_3] = 6.5 \text{ mg/L}$ and 1.0 mg of sodium alginate. The efficiencies of color and COD removal from a real dyeing wastewater containing two reactive yellow dyes were also compared using aluminum sulfate alone and combined with sodium alginate. In these experiments the dose of alumni sulfate were varied in the range 15 to 65 mg/L. The color and COD removals were higher (93.5 and 80.1%, respectively) when using 65 mg/L of aluminum sulfate and 1 mg of sodium alginate.

2.2.2 Textile Wastewater Treatment by Coagulation/Flocculation Combined with Other Processes

Studies on the application of Coagulation/Flocculation combined with other processes were also found in the literature. Table 2.2 summarizes some of these studies, including

the best operating conditions and efficiencies achieved in the coagulation/flocculation step.

Table 2.2 – Studies on the integration of coagulation/flocculation with other processes for treating dye solutions and textile effluents.

Dye solution or Effluent type	Optimal Operating Conditions in Coagulation/flocculation	Other Processes	Efficiencies (%)	Reference
Real effluent	[DK-FER 20] = 200 mg/L pH = 8.5 [Anionic flocculant] = 1 mg/L	Membrane separation	COD = 50 Substantial reduction of turbidity	Bes-Piá et al. [2002]
Jean-Wash effluent	pH = 9 [Polymeric ferrous sulfate] = 150 mg/L	Anaerobic process and Fenton's reagent	COD = 70 Color = 50	Wang et al. [2008]
Real effluent	[Al ₂ (SO ₄) ₃] = 100 mg/L pH = 5 [Flocculant] = 4 mg/L	Membrane separation or Adsorption on activated carbon	Low residual turbidity	Harrelkas et al. [2009]
Black 5 dye	[Aluminum chloride] = 200 mg/L pH = 6 [Na ₂ CO ₃] = 110 mg/L	Adsorption on activated carbon	color = 97	Furlan et al. [2007]
Orange 16 dye	[Aluminum chloride] = 250 mg/L pH = 6 [Na ₂ CO ₃] = 140 mg/L	Adsorption on activated carbon	color = 78	Furlan et al. [2007]

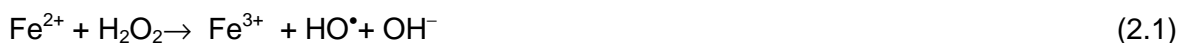
Additionally, El-Gohary and Tawfik [2009] evaluated the decolorization and reduction of COD of an effluent containing disperse and reactive dyes, by coagulation/flocculation coupled with a biological process. In the coagulation/flocculation step, the authors obtained maximum color (100%) and COD (50%) removals using CaO as coagulant (600 mg/L) and pH 11.7. The effluent from coagulation/flocculation was then subjected to biological oxidation (SBR). After acclimatation of the microorganisms in the SBR by gradually replacing the sewage by pre-treated wastewater, and operating at an hydraulic retention time (HRT) of 5 days, removals of 68.2, 76.3, 61.4 and 75.4% were achieved for

COD, BOD₅, TSS and oils and grease, respectively. The overall efficiencies of the two treatments were 86.9, 92.6, 93.8 and 92.2% for COD, BOD₅, TSS and oils and grease, respectively.

Quite recently, Al-Ani and Li [2012] studied the application of electro-coagulation with iron scrap particles followed by coagulation/flocculation using Al(OH)₃-polyacrylamide polymer in the degradation of reactive blue 19. The pre-treatment removed only 26% of COD and 45% of color. Coagulation/flocculation led to maximum COD (69%) and color (95%) removals using 700 mg/L of coagulant and 60 minutes of clarification. The influence of pH, in the range 4 to 9, was then quantified and higher removals (90% for color and 82% for COD) were obtained for pH 5-6.

2.3 Fenton's Oxidation

By the end of the 19th century, H.J.H. Fenton reported the strong tartaric acid oxidation by hydrogen peroxide in the presence of soluble iron [Fenton, 1894]. Later, Haber Weiss [1934] found that hydroxyl radicals (with high oxidation potential – 2.8 V against 1.0 V for chlorine [Bigda, 1995]) were responsible for the oxidation. It has been proposed that Fe²⁺/Fe³⁺ is the catalyst involved in the decomposition of the hydrogen peroxide, yielding hydroxyl radicals (HO[•]) responsible for the oxidation of a wide variety of organic substrates. Thus, the Fenton's reaction is based on the formation of hydroxyl radicals resulting from the catalytic decomposition of hydrogen peroxide in the presence of the Fe²⁺ catalyst (Fenton's process – Equation 2.1). The organic compounds are oxidized according to Equation 2.2 [Walling, 1975; Kuo, 1992].



The intermediates oxidation can ultimately proceed up to mineralization (i.e., suffer further oxidation up to CO₂). However, in the Fenton process many other reactions simultaneously take place [Walling, 1975], being of relevance the ones associated with the scavenging of the radicals in the presence of excess of either oxidant (Equation 2.3) or ferrous iron (Equation 2.4) and that for catalyst regeneration (Equation 2.5):



The Fenton process efficiency is influenced by several variables, including pH, temperature, concentration of ferrous ion and hydrogen peroxide. The pH is a crucial parameter in the Fenton process. The decrease in reaction efficiency at pH above 4 is associated with the formation of complexes of Fe^{2+} [Benitez et al., 2001], precipitation of $\text{Fe}(\text{OH})_3$, which inhibits the regeneration of Fe^{2+} (Equation 2.5), and also with the decomposition of hydrogen peroxide in water and oxygen [Szpyrkowicz et al., 2001]. At pH below 2, the generation of hydroxyl radicals decreases, and is almost totally suppressed at pH 1. For so low pH values the hydrogen peroxide forms H_3O_2^+ , reducing the reactivity with Fe^{2+} [Schirman and Delavarenne, 1979, cited in Morais, 2005]. On the other hand, the concentration of Fe^{3+} , responsible for the continued oxidation (Equation 2.5) is small [Pignatello, 1992] as the ferric iron is in the form of $\text{Fe}(\text{OH})_2^+$ and $\text{Fe}(\text{OH})^{2+}$. Various authors indicated optimal values for this parameter in the range 2-5 [Sims, 1983; Rivas et al., 2001; Zhu et al., 2001], or more specifically pH around 3 [Neyens and Baeyens, 2003], regardless the characteristics of the effluent to treat [Morais, 2005].

The reaction rate increases with increasing temperature, since it increases the kinetic constants according to the Arrhenius law, and particularly between 5 and 30-40 °C [Flaherty and Huang, 1992]. However, the extent of reaction decreases for temperatures above 40-50 °C because occurs the thermal decomposition of hydrogen peroxide into water and oxygen. In the literature there are several works reporting optimal operating temperatures between 20 and 50 °C [Gulkaya et al., 2006; Tekin et al., 2006; Sun et al., 2007].

The Fenton's reaction also depends on the ferrous ion dose, the minimum required for the reaction to proceed at reasonable rate being between around 3 to 15 mg/L [Morais, 2005]. However, the substrate removal increases with the catalyst concentration up to a point beyond which the reaction of excess of ferrous ion with the hydroxyl radical occurs (Equation 2.4) [Walling, 1975] – the so-called scavenging effect. The required catalyst dose depends on the type of effluent to be treated; however Morais [2005] indicates values of 1:10 to 1:50 for the Fe^{2+} :substrate ratio (w:w).

Finally, the efficiency of Fenton's oxidation increases with the hydrogen peroxide concentration but when this reagent is in excess, it reacts with the radicals (Equation 2.3 [Waling, 1975]). The required dose of H_2O_2 to be used depends on the amount of organic compounds, but it is necessary to add an excess over the stoichiometric amount to compensate the quantity of hydrogen peroxide which decomposes into water and oxygen and also the one consumed in parallel / undesired reactions [Southworth and Voelker, 2003].

This homogeneous process has several advantages such as high efficiency, simple applicability, operation at room temperature and atmospheric pressure, and non-selectivity, i.e. ability to oxidize various pollutants at the same time. However, the main disadvantage is the generation of ferric iron sludge which requires separation and disposal and/or reuse [Hsueh et al., 2005].

2.3.1 Textile Wastewater Treatment by Homogeneous Fenton's Oxidation

The Fenton process has been widely applied in the treatment of textile effluents. Recent studies are summarized below.

Malik and Saha [2003] studied the degradation of two direct dyes (Blue 2B – B54 and Red 12B - R31) by the Fenton process. A parametric study was performed to evaluate the effect of various parameters. The maximum dye removal (97%) was achieved for $pH=3$, $[H_2O_2]=1.47$ and 2.94 mM for B54 and R31, respectively, $[Fe^{2+}]=8.93 \times 10^{-2}$ mM, $T=40$ °C and $t=30$ minutes. The authors also assessed the effect of the presence of chlorides and sulfates in the removal efficiency and found that up to 600 mg/L the sulfate ion had no effect on the removal of the two dyes, but the chloride ion negatively affected the dyes removal, because this anion "scavenges" the hydroxyl radical.

Other authors [Swaminathan et al., 2003] evaluated the effect of process variables on the decolorization and degradation of two commercial azo dyes (Red M5B and Blue MR) and H-acid dye, by the Fenton's reaction. For the Red M5B dye the maximum color (~100%) and DOC (78%) removals were achieved by using 10 mg/L of Fe^{2+} , 400 mg/L of H_2O_2 , $pH=3$ and 120 minutes of reaction time. For the Blue MR dye high color and COD removals were obtained (99% for COD and ~100% for color) in the following conditions:

20 mg/L, 500 mg/L, 3 and 20 minutes for Fe^{2+} dose, H_2O_2 concentration, pH and reaction time, respectively. Finally 99% of COD and ~100% of color removals were achieved for the H-acid dye by using 25 mg Fe^{2+} /L, 500 mg H_2O_2 /L, pH=3 and t=120 minutes. Decolorization followed 1st order kinetics and the computed rate constant was greater for H-acid dye ($k = 0.0106 \text{ min}^{-1}$) followed by red M5B dye ($k = 0.0413 \text{ min}^{-1}$) and finally blue MR ($k = 0.0727 \text{ min}^{-1}$). The sulfate concentration in H-acid and Blue MR solutions and the concentration of chlorides and sulfates in Red M5B solutions increased with reaction time allowing the authors to conclude that these anions are replaced in the structure of the dyes when the HO^\bullet species breaks the molecular bonds.

Many more studies are reported in the literature. Table 2.3 presents the optimal operating conditions used in these studies and the maximum removals achieved.

Table 2.3 – Studies on the treatment of dye solutions and textile effluents by Fenton's reaction.

Dye solution or Effluent type	Optimal Operating Conditions	Efficiencies (%)	Comments	Reference
Real effluent of acetate and polyester dyeing	pH = 5 [FeSO_4] = 500 mg/L [H_2O_2] = 300 mg/L	Color = 94 COD = 96		Azbar et al. [2004]
Reactive Black 5 dye solution	pH = 3 T = 40 °C [dye] = 100 mg/L [FeSO_4] = 100 mg/L [H_2O_2] = 400 mg/L	Color = 99 COD = 71		Meriç et al. [2004]
Reactive Black 5 dye solution	pH = 3 T = 40 °C [dye] = 200 mg/L [FeSO_4] = 225 mg/L [H_2O_2] = 1000 mg/L	Color = 99 COD = 84		Meriç et al. [2004]
Reactive Orange 4 dye solution	pH = 5 [Fe^{2+}] = 0.075 mM [H_2O_2] = 15 mM	Dye = 97		Muriganandham and Swaminathan, [2004]
Blue Suncron RD-400 dye solution	[Fe^{2+}] = 0.38 mM [H_2O_2] = 2.48 mM	COD = 60 Dye = 90		Kim et al. [2004]
Yellow Suncron 3GE-200 dye solution	[Fe^{2+}] = 0.41 mM [H_2O_2] = 1.91 mM	COD = 48 Dye = 90		Kim et al. [2004]
Blue Suncron P-3R dye solution	[Fe^{2+}] = 1.61 mM [H_2O_2] = 4.41 mM	COD = 80 Dye = 90		Kim et al. [2004]
Yellow Suncron E4R-H dye solution	[Fe^{2+}] = 0.23 mM [H_2O_2] = 1.15 mM	COD = 70 Dye = 90		Kim et al. [2004]

Table 2.3 – Studies on the treatment of dye solutions and textile effluents by Fenton's reaction.
(cont.)

Dye solution or Effluent type	Optimal Operating Conditions	Efficiencies (%)	Comments	Reference
Orange II dye	pH = 3 T = 29 °C t = 120 min [H ₂ O ₂] = 10 mM Fe ²⁺ :H ₂ O ₂ ratio (w/w) = 0.08	Color = 100		Ramirez et al. [2005]
Orange II dye	pH = 3 T = 50 °C t = 120 min [H ₂ O ₂] = 13.8 mM Fe ²⁺ :H ₂ O ₂ ratio (w/w) = 0.05	TOC = 71		Ramirez et al. [2005]
Reactive Black 5	pH = 5 t = 120 min [dye] ₀ = 1.0x10 ⁻⁴ M [Fe ²⁺] = 1.5x10 ⁻⁴ M [H ₂ O ₂] ₀ = 7.3x10 ⁻⁴ M	Color = 98 TOC = 22		Lucas and Peres [2006]
Synthetic Dyeing effluent containing acid dyes	pH = 3 t = 30 min [Fe ²⁺] = 10 mM [H ₂ O ₂] = 30 mM	Color = 92 COD = 24	Low toxicity to bacteria from activated sludge	Alaton and Teksoy [2007]
Remazol Turquoise Blue G-133 dye solution	pH = 3 t = 45 min [Fe ²⁺] = 25 mg/L [H ₂ O ₂] = 50 mg/L	Color = 99	k = 0,0102 L mg ⁻¹ min ⁻¹	Bali and Karagozoglu [2007]
Acid Yellow 23 dye solution	pH = 3 [Fe ²⁺] = 0.1 mmol [H ₂ O ₂] = 500 mg/L	Color ~ 100		Modirshahla et al. [2007]
Real effluent from polyethylene fibers processing	pH = 3 t = 24 h [Fe ²⁺] = 40 mg/L [H ₂ O ₂] = 30 mg/L	Color = 72 COD = 45 BOD ₅ = 60 TOC = 40	BOD ₅ :COD ≤ 0.15 (after treatment)	Papadopoulos et al. [2007]
Amido Black 10B dye solution	pH = 3.5 [dye] ₀ = 50 mg/L [Fe ²⁺] ₀ = 0.025 mM [H ₂ O ₂] ₀ = 0.50 mM	Dye = 99		Sun et al. [2007]

Table 2.3 – Studies on the treatment of dye solutions and textile effluents by Fenton’s reaction. (cont.)

Dye solution or Effluent type	Optimal Operating Conditions	Efficiencies (%)	Comments	Reference
Procion Red H-EXL gran dye solution	pH = 3.5 t = 120 min [dye] = 100 mg/L T = 73.6 °C [Fe ²⁺] = 0.12 mM [H ₂ O ₂] = 2.9 mM	Color = ~100 TOC = 58		Rodrigues [2007]
Wastewater from acrylic fiber manufacturing	pH = 3 t = 2 h [Fe ²⁺] = 300 mg/L [H ₂ O ₂] = 500 mg/L	COD = 66	BOD ₅ :COD = 0.5 (after treatment)	Li et al. [2012]
Real textile effluent	pH = 6.6 T = 35 °C [FeSO ₄] = 0.75 g/L [H ₂ O ₂] = 15 g/L	Color = 98 COD = 39	BOD ₅ :COD = 0.45 (after treatment)	Wu and Wang [2012]
Real dry-spun acrylic fiber effluent	pH = 3 T = 30 °C t = 120 min [Fe ²⁺] = 20 mM [H ₂ O ₂] = 90 mM	COD = 47 TOC = 35	BOD ₅ :COD = 0.69 (after treatment)	Wei et al. [2013]
Real dry-spun acrylic fiber effluent	pH = 3 T = 50 °C t = 120 min [Fe ²⁺] = 20 mM [H ₂ O ₂] = 90 mM		k = 0.265 min ⁻¹	Wei et al. [2013]

2.3.2 Textile Wastewater Treatment by Integration of Homogeneous Fenton’s Oxidation with Sequencing Batch Reactor

Treatability studies of textile effluents by Fenton’s oxidation combined with sequencing batch reactor (SBR) are succinctly described in this section.

Fongsatitkul et al. [2004] evaluated the integration of Fenton’s reagent with biological oxidation in SBR for treating wastewater generated in the textile industry. Experimental conditions were pH 3, T = 28-30 °C, reaction time about 30 minutes and total dose of reagents between 25 mg/L and 300 mg/L (FeSO₄.7H₂O and H₂O₂ - 1:1 molar ratio).

Maximum color and COD removals (~ 70% and ~ 30%, respectively) were achieved for reagent doses of 75 mg/L. To increase the efficiency of organic matter removal, the authors tested the combination Fenton's oxidation plus SBR. The biological treatment was performed at pH 7, the operating cycle of SBR was 24 hours, distributed as follows: 4 hours feeding, 2 hours anoxic, 4 hours aerobic, 7 hours anoxic, 4 hours aerobic, 1.5 hours sedimentation, 0.5 hours draw and 1 hour sludge removal. The global efficiency was given by: 90% COD removal, ~ 80% maximum color removal, 81 phosphorus removal and 92% KTN removal. Afterwards the treatability of the effluent by the combination of SBR with chemical oxidation was also investigated. The SBR was operated under the same conditions described above and was fed for 50 days. The biological process was able to remove ~ 80% COD, ~50% color, ~ 82% KTN and ~ 58% total phosphorus. Then the biologically treated effluent was subjected to chemical oxidation, after adjusting the pH to 3. The dose of reagent varied in the range 25-200 mg/L. Removals increased with the dose of reagent, reaching 27 and 60% for COD and color, respectively, using 200 mg/L of reagent. The combination SBR plus Fenton's oxidation led to overall efficiencies of 87% for COD, 68% for color, 91% for KTN and 80% for total phosphorus. The first combination of processes (Fenton's oxidation followed by SBR) yielded better results, because the pre-treatment increased the biodegradability of the effluent to be subjected to biological treatment.

More recently Lodha and Chaudhari [2007] evaluated the treatability of azo dyes (Reactive Black 5 dye - RB5 - Reactive Blue 13 - RB13 - and Acid Orange 7 - AO7) solutions. The Fenton process was optimized by varying the pH (2-7), $[H_2O_2]$ (between 25 and 150 mg/L) and $[Fe^{2+}]$ (from 5 to 50 mg/L) and setting the reaction time within 30 minutes. The conditions that maximized color (>97% for all dyes tested) and COD (63, 89 and 68% for RB5, RB13 and AO7, respectively) removals were pH = 3, $[Fe^{2+}]$ = 15 mg/L and $[H_2O_2]$ = 50 mg/L. For the biological treatment, the biomass was previously acclimatized. Thus, for a period of 20 days, the SBR was fed with 0.5 L of a solution containing 0.4 g of dextrose, alternating the next day with 0.5 L of pretreated effluent. The solids content in the SBR was maintained in 3000 mg MLSS/L. The SBR reached steady state after 40 days (20 days of acclimatization and 20 fed with pre-oxidized effluent), achieving COD removals of 82, 89 and 84% for RB5, RB13 and AO7 dyes, respectively. An integrated process (chemical oxidation with Fenton's reagent followed by biological oxidation) was also performed yielding total decolorization (> 99% for all dyes) and higher COD removals (93, 99 and 95% for RB5, RB13 and AO7, respectively).

More studies can be found in the literature regarding the treatment of textile effluents or dye solutions by the combination of Fenton's reaction with SBR. Table 2.4 briefly presents the best operating conditions for both processes and the overall efficiencies achieved.

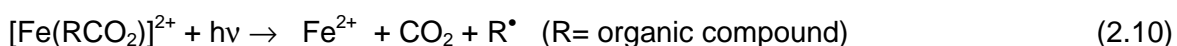
Table 2.4 – Studies on the integration Fenton's reaction with SBR.

Dye solution or Effluent type	Operatory Conditions in Fenton	Operatory Conditions in SBR	Overall Efficiencies (%)	Comments	Reference
Reactive Black 5 solution	pH = 3 T = 25-30 °C [Fe ²⁺] = 1.05 mM [H ₂ O ₂] = 72 mM	t _{feed} = 20 days HRT = 96 h SRT = 45 days	COD = 82	The SBR was previously acclimated by feeding dextrose solution	Tanatak and Chaudhari [2007]
Reactive Blue 13 solution	pH = 3 T = 25-30 °C [Fe ²⁺] = 1.05 mM [H ₂ O ₂] = 72 mM	t _{feed} = 20 days HRT = 96 h SRT = 45 days	COD = 86	The SBR was previously acclimated by feeding dextrose solution	Tanatak and Chaudhari [2007]
Acid Orange 7 solution	pH = 3 T = 25-30 °C [Fe ²⁺] = 1.05 mM [H ₂ O ₂] = 72 mM	t _{feed} = 20 days HRT = 96 h SRT = 45 days	COD = 78	The SBR was previously acclimated by feeding dextrose solution	Tanatak and Chaudhari [2007]
Synthetic cotton deying effluent	pH = 3.5 T = 73.6 °C [Fe ²⁺] = 11 mM [H ₂ O ₂] = 305 mM	1.1 h feed 6 h reaction 3.5 h sedimentation 0.9 h supernatant discharge [O ₂] ~3 mg/L pH ~7 T ~25 °C [VSS] ~5 g/L	BOD ₅ = 96 COD = 90 Color = 97		Rodrigues [2007]

2.4 Photo-Fenton Process

The photo-Fenton process is based on principles that are common to the dark Fenton one, namely the generation of extremely reactive hydroxyl radicals (that will unselectively

attack the organic compounds) by breaking hydrogen peroxide molecules, in acidic medium, making use of a catalyst like ferrous ion (Equation 2.6) [Walling, 1975], but with simultaneous use of ultra-violet/visible radiation. Thus, the photo-Fenton process is faster and enables reducing the consumption of chemicals as the hydroxyl radicals generation occurs by three different mechanisms: i) the decomposition of hydrogen peroxide by the Fe^{2+} catalyst (Equation 2.6); ii) the incidence of ultraviolet radiation, with $\lambda < 360\text{-}365$ nm, decomposes the hydrogen peroxide into hydroxyl radicals (Equation 2.7) [Galvez and Rodriguez, 2003]; and iii) by using radiation with wavelengths in the range $290 < \lambda < 410$ nm [Sun and Pignatello, 1993], there is the additional production of HO^\bullet radicals upon Fe^{2+} regeneration either by Equation 2.8 or by photolysis of iron (III) hydroxides (Equation 2.9); finally, Equation 2.10 still refers to Fe^{2+} regeneration by photolysis of complexes formed between the organic compounds or their intermediates with Fe^{3+} [Galvez and Rodriguez, 2003; Morais, 2005; Huang et al., 2008]. The regeneration of Fe^{2+} species by several reactions is another reason for the faster rate of the photo-Fenton process as compared to the dark one, where catalyst regeneration is commonly rate-limiting.



The $\text{Fe}(\text{OH})^{2+}$ complex is predominant under acidic conditions (pH in the range 2-3 [Torrades et al., 2004]), and plays an important role in the photo-Fenton process since it is the compound with greater ability to generate hydroxyl radicals by absorbing UV/visible radiation. The photolysis of hydrogen peroxide (Equation 2.7), which has low absorptivity ($19.6 \text{ M}^{-1} \text{ cm}^{-1}$ at 254 nm [Engwall et al., 1998]), has a limited contribution towards the formation of radicals when iron complexes are present in solution.

The photo-Fenton process is influenced by many variables, such as pH, hydrogen peroxide concentration, ferrous ion concentration and radiation intensity (and nature). At $\text{pH} > 6$ the Fe^{3+} forms insoluble oxides [Pérez et al., 2002]. In very acidic pH values the complex $\text{Fe}(\text{OH})^{2+}$ is present in a reduced amount, and the two more photo reactive

compounds ($\text{Fe}(\text{OH})(\text{H}_2\text{O})_5^{2+}$ and $\text{Fe}(\text{OH})_2(\text{H}_2\text{O})_4^+$) are present in smaller quantities to generate the radicals and regenerate the catalyst [Morais, 2005; Nogueira, 2007], however the $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ species is present in greater amount but it has lower absorptivity, which limits the absorption of radiation [Nogueira et al., 2007]. Moreover, $\text{pH} < 2.5$ allows to occur the scavenging reaction between the hydroxyl radical and H^+ (Equation 2.11) [Nogueira et al., 2007]:



For these reasons, optimum pH values in the range 2-3 have been pointed out [Pignatello, 1992; Kim, 1997; Wu et al., 1999; Elmolla and Chaudhuri, 2009]. Actually, in this range increased amounts of photo reactive species (Fe^{3+} and $\text{Fe}(\text{OH})^{2+}$) are present in solution. For removal of dyes some authors have suggested pH values of 3-5 [Kang et al., 2000; Liu et al., 2007; Modirshahla et al., 2007].

The amount of catalyst to be used must be determined and optimized, since it depends on the nature of the effluent to be treated. Nonetheless, it is not advisable to use an excess of Fe^{2+} because this generates turbidity which hinders the absorption of the radiation and, on the other hand, as in dark Fenton, occurs the scavenging reaction of hydroxyl radicals with the excess Fe^{2+} (Equation 2.4).

The pollutant removal is related to the amount of hydrogen peroxide, thus it is necessary to determine the optimum dose of reagent considering that: i) when its concentration is low the oxidation degree is low and there is the possible formation of undesirable intermediate compounds, ii) its excess reacts with hydroxyl radicals generating HO_2^\bullet radicals with lower oxidative potential and iii) an excess is required to compensate the decomposition into water and oxygen and other parallel /undesirable reactions.

The radiation intensity or photonic flux is related to the lamp power i.e. the capacity to emit photons. In general, an increase in the radiation intensity leads to an increase in the reaction rate, hence an increased degradation of organic compounds.

According to Malato et al. [2002], the advantages of the photo-Fenton process, compared to other photochemical techniques, are the operation at UV or near UV wavelengths (300-400 nm), the sensitivity to light up to wavelengths ≤ 600 nm, which makes possible the use of solar radiation, the light penetration is deeper and the contact between pollutant and oxidizing agent is intimate, because of the homogenous phase. The major disadvantages

of this process are associated with the use of low pH (<4) to obtain the maximum efficiency and the generation of chemical sludge containing iron.

2.4.1 Textile Wastewater Treatment by Homogeneous Photo-Fenton Process

A lot of studies can be found in the literature using the photo-Fenton process for dyes removal in aqueous solution, as well as in the treatment of effluents from the textile industry. A brief description of some of these studies is presented below.

Kang et al. [2000] evaluated the removal of color from a synthetic textile dyeing effluent (containing 100 mg/L of polyvinyl alcohol – PVA – and 100 mg/L of Reactive R94H dye) by the photo-Fenton process. Under optimal conditions (pH = 4, [H₂O₂] = 100 mg/L, [Fe²⁺] = 20 mg/L, lamp power = 64 W and t = 30 min) the authors obtained 95% color removal. Subsequently, the effect of the PVA concentration was evaluated by varying its concentration (COD between 200 to 620 mg/L) and it was found that the increase of COD showed no effect on color removal. Comparing photo-Fenton at pH of 4 and 7 with Fenton at pH 4 and photolysis at pH 4, it was observed that photo-Fenton process at pH 4 led to a higher removal (93%) for a reaction time of 30 min, followed by photolysis (82% color removal in the same period), then photo-Fenton at pH 7 (73% color removal) and finally dark Fenton at pH 4 (64% color removal).

Pérez et al. [2002] studied the treatability of a real textile effluent by the photo-Fenton process. The authors started the study by evaluating the effect of Fe²⁺, H₂O₂ and combination of the two reagents. Varying the temperature (25-70 °C) higher removals of TOC were achieved at 70 °C. The effect of ferrous ion (up to 400 mg/L) and hydrogen peroxide (up to 10 g/L), setting the pH at 3 and temperature at 40 °C, was also analyzed. Maximum TOC removal (70% after 2 hours of reaction) was achieved when using 100 mg/L of Fe²⁺ and H₂O₂ between 2.5 and 5 g/L. At these operating conditions, the effect of the type of radiation (light from luminescent black lamp of 6 W, sunlight and xenon lamp of 250 W) was assessed. For the first 60 min of reaction TOC removal was high when using xenon and solar radiation, but for t>60 min the luminescent black lamp showed better removal efficiency. The authors state that an intense irradiation favors the exhaustion of

H₂O₂, in case of the xenon lamp. Additionally, it was difficult to maintain the temperature constant in runs using solar radiation.

Other authors conducted a parametric study to evaluate the effect of ferric ion and hydrogen peroxide doses (≤ 1.8 mM and ≤ 600 mM, respectively) and temperature (30-60 °C) on organic matter removal (DOC) by the photo-Fenton process applied to a real textile effluent [Rodriguez et al., 2002]. Maximum DOC removal (65%) was achieved when using 1.43 mM of [Fe³⁺], 441.2 mM of [H₂O₂] and T=60 °C. The biodegradability of the effluent after photo-Fenton treatment was also estimated and only 50% of DOC reduction was found after 28 days (Zahn-Wellens test) which indicates that the treated effluent is not biodegradable [Rodriguez et al., 2002].

Table 2.5 presents the optimal operating conditions and the removals achieved in other studies regarding the treatment of dye solutions or textile effluents by the photo-Fenton process.

Table 2.5 – Studies on the treatability of dye solutions and textile effluents by photo-Fenton's oxidation.

Dye solution or Effluent type	Optimal Operating Conditions	Efficiencies (%)	Comments	Reference
Real effluent	pH = 3 T = 60 °C [Fe ³⁺] = 1.43 mM [H ₂ O ₂] = 441.2 mM	DOC = 65	Effluent not biodegradable (50% DOC reduction after 28 days in Zahn-Wellens test)	Rodriguez et al. [2002]
Reactive Orange 4 dye solution	pH = 3 t = 40 min P = 32 W [dye] = 5x10 ⁻⁴ mol/L [Fe ²⁺] = 2.8 mg/L [H ₂ O ₂] = 340 mg/L	Color = 90		Muruganadham and Swaminathan [2004]
Procion Red H-E7B dye solution	pH = 3 T = 40 °C t = 120 min [Fe ²⁺] = 10 mg/L [H ₂ O ₂] = 100 mg/L Simulated sun light	TOC = ~100 Color = 81	BOD ₅ :COD = 0.3	Torrades et al. [2004]

Table 2.5 – Studies on the treatability of dye solutions and textile effluents by photo-Fenton's oxidation (cont.).

Dye solution or Effluent type	Operatory Conditions	Efficiencies (%)	Comments	Reference
Cibracon Red FN-R dye solution	pH = 3 T = 40 °C t = 120 min [Fe ²⁺] = 10 mg/L [H ₂ O ₂] = 100 mg/L	TOC = ~100 Color = 75	BOD ₅ :COD = 0.2 Simulated sun light	Torrades et al. [2004]
Mixture of Cibacron Yellow FN-2R, Cibracon Red FN-R and Cibracon Navy NF-B	pH = 3 T = 40 °C t = 120 min [Fe ²⁺] = 10 mg/L [H ₂ O ₂] = 100 mg/L	TOC = ~100 Color = ~100	Simulated sun light	Torrades et al. [2004]
Reactive Black 5 dye solution	pH = 3 t = 7.5 min [Fe ²⁺] = 1.5x10 ⁻⁴ mol/L [H ₂ O ₂] = 7.3x10 ⁻⁴ mol/L [Dye] = 5x10 ⁻⁵	Dye = 98		Lucas and Peres [2006]
Acid Yellow 23 dye solution	pH = 3 I = 30.3 W/m ² [Fe ²⁺] = 5.6 mg/L [H ₂ O ₂] = 700 mg/L [Dye] = 40 mg/L	Color = 95	The presence of 250 mg/L NaCl caused the decay in dye removal only about 2%	Modrishahla et al. [2007]
Direct Red 28 dye solution	[Fe ²⁺] = 71 mg/L [H ₂ O ₂] = 715 mg/L [Dye] = 250 mg/L	Color = 100		Ay et al. [2009]
Direct Red 28 dye solution	[Fe ²⁺] = 97 mg/L [H ₂ O ₂] = 1550 mg/L [Dye] = 250 mg/L	TOC = 98		Ay et al. [2009]
Reactive Yellow 86 dye solution	pH = 3 T = 60 °C I = 2.0 mW/cm ² [Fe ²⁺] = 5x10 ⁻⁴ M [H ₂ O ₂] = 0.5 M	Color = ~100		Katsumata et al. [2010]
Reactive Blue 19 solution	pH = 3 [Fe ²⁺] = 32 mg/L [H ₂ O ₂] = 150 mg/L	Color = 100 COD = 96		Guimarães et al. [2012]
Azure-B dye solution	pH = 2.2 I = 75.5 mW/cm ² [Fe ³⁺] = 6.7x10 ⁻⁴ M [H ₂ O ₂] = 1.5 mL [dye] = 1.0 x10 ⁻⁴ M		k = 3.0x10 ⁻³ s ⁻¹ (dye degradation)	Vaishnave et al. [2012]

Other authors [Arslan-Alaton et al., 2009] used an experimental design approach to determine the optimum values of the process variables ($[\text{Fe}^{3+}]$, varied between 0.5 and 4.5 mM, $[\text{H}_2\text{O}_2]$, in the range 25-65 mM, t_{reaction} up to 60 min and initial COD between 100 and 300 mg/L) and their interactions with statistical significance to maximize color, COD and TOC removals from a solution containing acid blue 193 dye. The authors found that all variables and interactions were statistically significant for all three responses considered, the optimum operating conditions allowing 99, 81 and 60% of color, COD and TOC removals, respectively, were $\text{COD} \leq 200$ mg/L, $[\text{Fe}^{3+}] = 1.5$ mM, $[\text{H}_2\text{O}_2] = 35$ mM and $t_{\text{reaction}} = 45$ min. The study proceeded with the application of the model and the optimal conditions determined for acid blue 193 dye to Reactive Black 39 dye solution ($\text{CQO}_0 = 195$ mg/L) and a real effluent containing the same dye ($\text{CQO} = 165$ mg/L). Color (100%), COD (84%) and TOC (53%) removals from dye solutions were close to those predicted by the model (100% for color, 82% for COD and 61% for TOC). Color removal from the real effluent was equal to that predicted by the model (100%), but COD (69%) and TOC (37%) removals were much lower (84% for COD and 70% for TOC, as predicted by the model).

2.4.2 Combination of Photo-Fenton with Other Processes for Treating Textile Wastewaters

García-Montaño et al. [2006 a)] studied the treatability of a solution containing 250 mg/L of the Cibacron Red FN-R dye by a combination of photo-Fenton process and biological oxidation in SBR. Maximum color (~100%) and COD (49.6%) removal and $\text{BOD}_5:\text{COD}$ ratio (0.36) was achieved for 20 mg Fe^{2+}/L , 250 mg $\text{H}_2\text{O}_2/\text{L}$ and 90 min irradiation time. The study proceeded by integrating the photo-Fenton process with SBR. The authors found that COD removal in SBR increased with the dose of Fe^{2+} and irradiation time used in photo-Fenton process, from 46.6% in run#1 (10 mg/L and 150 min for $[\text{Fe}^{2+}]$ and irradiation time, respectively) to 58.1% and 60.4% in runs #2 (20 mg/L of Fe^{2+} and 60 minutes of irradiation time) and #3 (20 mg/L for $[\text{Fe}^{2+}]$ and 90 min for irradiation time), respectively. They also found that the 3rd experiment with 2 days of HRT allowed obtaining higher overall efficiency (80% COD removal).

The same authors [García-Montaño et al. (2006 b))] investigated the treatment of dye solution containing 250 mg/L of Procion Red H-E7B by integrating photo-Fenton oxidation and biological SBR. In photo-Fenton process the maximum dye (~ 100%) and DOC (39%)

removal and BOD₅:COD ratio (0.35) was achieved for 10 mg Fe²⁺/L, 125 mg H₂O₂/L and 60 min reaction time, when using a 6W Philips black light fluorescent lamp. The combination of photo-Fenton followed by SBR yielded the highest global efficiencies (71% DOC removal and ~100% color removal) when using 10 mg Fe²⁺/L, 125 mg H₂O₂/L and 60 minutes of radiation in photo-Fenton and 15 cycles with 1 day of HRT in SBR.

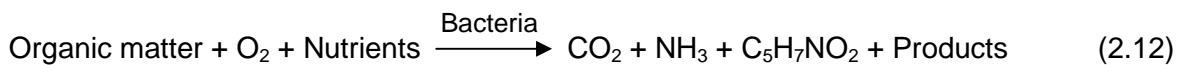
Jonstrup et al. [2011] studied the degradation of Remazol Red RR solution by photo-Fenton process (Approach 1), integration of photo-Fenton with aerobic oxidation (Approach 2) and anaerobic digestion plus photo-Fenton (Approach 3). In Approach 1, the authors found complete decolorization and COD reduction and maximum reduction of Abs_{290nm} (93%), after 15 minutes of radiation exposure, when employing optimal conditions (0.25 mM, 3 mM and 3 for Fe²⁺ doses, H₂O₂ concentration and pH, respectively). In Approach 2, total decolorization and COD reduction (100%) was obtained using 3 mM of H₂O₂ in the photo-Fenton process. In Approach 3, complete decolorization and considerable COD reduction (71%) was achieved in the anaerobic digestion. The combination of anaerobic digestion plus photo-Fenton oxidation allowed to obtain higher COD reduction (94%) when using 2 mM of Fe²⁺ and 1-3 mM of H₂O₂ after 2 h irradiation. Approach 2 provided the better efficiency, possibly because the oxidative process increased the biodegradability of the effluent.

More recently, Tokumura et al. [2013] investigated the decolorization kinetics of Orange II dye solutions by integrating the photo-Fenton process with electrochemical corrosion of iron, which generates electricity and hydrogen simultaneously. In the photo-Fenton process, pH was set at 2.5 and three black light lamps (6 W near UV-A) were used. Pseudo-first-order kinetics for dye degradation ($k=0.349 \text{ min}^{-1}$) and pseudo-zero-order kinetics for hydrogen peroxide consumption ($k_{\text{H}_2\text{O}_2}=9.54 \text{ ppm/min}$) were achieved for [dye]=22 ppm, [Fe²⁺]=11 ppm, [H₂O₂]= 297 ppm and radiation intensity=94.7 W/m². The combination of electrochemical corrosion followed by photo-Fenton performed at the best conditions obtained for each technique permitted to achieve 81% dye mineralization (after 64 min of reaction), generating 3.8 mA of electric current and producing 1.88×10^{-3} mmol/min of hydrogen.

2.5 Biological Treatment in Sequencing Batch Reactor

Wastewater treatment by biological processes is based on the ability of microorganisms (as fungi, protozoa, algae and bacteria) to degrade or accumulate pollutants [Gray, 2004], which are removed by sorption on flocs or biofilms, entrainment in flocs and/or biodegradation. Biological treatment aims to coagulate and remove non settleable colloids, stabilize organic matter and remove nutrients, as nitrogen and phosphorus [Metcalf & Eddy, 2003].

Various configurations can be used in biological treatment, and biomass may be in suspension or attached to an inert support (biofilm reactors). SBR uses chemoheterotrophs microorganisms in suspension that utilize organic matter as source of carbon, for synthesis of new cells, and energy. The bacteria need organic nutrients (purines, pyrimidines, amino acids and vitamins) and inorganic nutrients (phosphorus, nitrogen, sulfur, potassium, magnesium, calcium, iron, sodium, chlorine and little amounts of zinc, manganese, selenium, copper, cobalt, nickel, molybdenum, vanadium and tungsten) [Metcalf & Eddy, 2003]. The production of energy (catabolism) and cellular synthesis (anabolism) are achieved through a series of enzymatic reactions in which the substrate is oxidized and transfers electrons to dissolved oxygen (final acceptor) [Sawyer et al., 1994], which is reduced and binds to one molecule of water [Metcalf & Eddy, 2003]. The mechanism of oxidation of organic matter, reduction of oxygen and production of new cells, salts and other products is briefly described by Equation 2.12 [Metcalf & Eddy, 2003]:



The SBR operates in discontinuous mode with five sequencing stages in each treatment cycle: 1st - feeding the reactor – fill stage, 2nd - degradation of organic matter and growth of biomass, providing oxygen by agitation and aeration – reaction step, 3rd - settle – the sludge is separated from liquid by gravity, 4th - effluent discharge and purge of excess sludge – decant/draw, and 5th - idle, optional step, corresponding to a relatively short waiting time between discharge and feeding the effluent for the following cycle. The steps of each cycle can be defined by partial percentages compared with the total cycle time

(e.g. 25, 35, 20, 15 and 5% to fill, react, settle, draw and idle, respectively) or with the total reactor volume (e.g. 25 to 100, 100, 100, 100 to 35, 35 to 25% in filling, reacting, settling, drawing and idling, respectively) [U.S. EPA, 1986]. Typical values for total duration of cycles are between 4 to 48 h and organic loads in the range 0.03 to 0.6 kg BOD₅/kg/d have been reported to be treated in industrial wastewaters [U.S. EPA, 1999; Gray, 2004].

As in all biological processes, the efficiency of degradation of compounds in a SBR is affected by pH, temperature, amount of biodegradable organic matter, presence of toxic or inhibitory compounds, amounts of nutrients and dissolved oxygen concentration.

The SBR presents some advantages over conventional biological treatment, namely simplicity and flexibility (in terms of sequence and cycle time), low cost, higher resistance to fluctuations in influent feeding, and the fact that equalization, reaction and clarification occur in the same reactor without sludge recirculation [U.S. EPA, 1999; Mahvi, 2008; Suresh et al., 2011]. The principal disadvantages of this reactor are the higher level of maintenance associated with somewhat sophisticated controls, eventual discharge of floating or settled sludge during draw or decantation step, potential plugging of diffusers and potential batch feeding from storage tanks or bioselectors to control bulking [U.S. EPA, 1999; Mahvi, 2008].

The SBR-based technology has been effective in removal of nutrients present in domestic wastewaters [Bernardes and Klapwijk, 1996] and swinery effluents [Kishida et al., 2003; Bortone, 2009], and also pollutants from industrial effluents, namely dairy [Mohseni and Bazari, 2004] and paper mills [Tsang et al., 2007], effluents from piggeries [Su et al., 1997] and landfill leachate [Kulikowsha and Klimiuk, 2004; Morling, 2010]. It has also been used in the treatment of textile effluents or removal of dyes, as described in the next section.

2.5.1 Textile Wastewater Treatment by Biological Oxidation using SBR

In the literature various studies can be found focusing on the use of SBR in the treatment of dye solutions and textile effluents. Some of those studies are briefly presented below.

Fu et al. [2001] investigated the treatment of a synthetic effluent containing Reactive Turquoise Blue (RTB), urea, glucose, KH₂PO₄ and other nutrients by 2 systems AA-SBR

(anaerobic/aerobic SBR). The 1st system operated during 48 h per cycle, comprising several minutes for feeding the wastewater, 20 h-anaerobic reaction, 4h-settle, 20 h-aerobic reaction, 4 h-settle/draw. In the 2nd system the anaerobic and aerobic reaction occurred in separated reactors, and each cycle of 48 h was divided as follows: several minutes for feeding the effluent into the anaerobic reactor, 20 h-anaerobic reaction, 2 h-settle and 2 h to draw the supernatant that fed the aerobic reactor for 2 h, 20 h of reaction and 4 h-settle/draw. The maximum decolorization (80.8% after 36 cycles) was obtained when anaerobic and aerobic reactions occurred separately (2nd system).

Lourenço et al. [2001] also studied the degradation of Remazol Brilliant Violet 5R and Remazol Black B dyes by AA-SBR. For Remazol Brilliant Violet 5R the authors obtained 90% dye removal when operating 24 h per cycle (50 min-fill, 11 h-anaerobic reaction, 10 h-aeration, 60 min-settle, 55 min-draw and 15 min-idle) and 10 days of SRT (sludge retention time), while for Remazol Black B reached 75% of dye removal using 24 h per cycle (53 min-fill, 11 h-anaerobic reaction, 10 h-aeration, 50 min-settle, 65 min-draw and 10 min-idle) and 15 days of SRT.

Table 2.6 presents optimal operating conditions and efficiencies attained in other research works concerning the treatment of dye solutions and textile effluents in SBR.

Table 2.6 – Studies on the treatability of dye solutions and textile effluents by SBR.

Dye solution or Effluent type	Optimal Operating Conditions	Efficiencies (%)	Comments	Reference
Simulated effluent containing Remazol Red RR dye	5 min fill 12 h anaerobic reaction 11 h reaction 30 min settle 10 min draw [Dye] = 60 mg/L [COD] ₀ = 800 mg/L SRT = 15 days	Color = 95 COD = 70	Addition of phosphates, sulfates and glucose to the effluent	Kapdan and Oztuk [2005]
	1 h fill (with aeration) 19 h react 3 h settle 0.5 h draw 0.5 h idle (in anoxic conditions) HRT = 3 days [VSS] = 2000 mg MLSS/L	Color = 99 COD = 97 BOD ₅ = 99 KTN = 93	Addition of urea, glucose, KH ₂ PO ₄ and other nutrients to the effluent	Siriamuntapiboon et al. [2006]

Table 2.6 – Studies on the treatability of dye solutions and textile effluents by SBR (cont.).

Dye or Effluent type	Optimal Operating Conditions	Efficiencies (%)	Comments	Reference
Real wastewater plus 0.89 g/L of glucose	1 h fill (with aeration)	Color = 75	Addition of glucose and nutrients to the wastewater	Siriamuntapiboon et al. [2006]
	19 h react 3 h settle 0.5 h draw	COD = 71 BOD ₅ = 97 KTN = 63		
Synthetic wastewater containing Acid Black 210 dye	0.5 h idle (in anoxic conditions)		Addition of glucose and nutrients to the wastewater	Mohan et al. [2007]
	30 min fill 23 h aeration with recirculation 15 min settle 15 min draw	Color = 100 COD = 92		
Simulated effluent containing Remazol Brilliant Violet 5R dye	3 min fill	Color = 72	Addition of glucose and nutrients to the dye solution	Çinar et al. [2008]
	12 h anaerobic reaction 11.9 h aerobic reaction 3 min draw	COD = 75 Benzene based aromatic amines = 92		
Synthetic wastewater containing Reactive Red 195 dye	[Dye] = 40 mg/L	Color > 90 COD > 90	Addition of nutrients and acetic acid to the wastewater	Farabegoli et al. [2010]
	[COD] ₀ = 800 mg/L SRT = 50 days 24 h per cycle			
Synthetic Wastewater containing Blue Bezaktiv S-GLD 150 dye	15 min fill	Color = 88-97 COD = 95-98	Addition of glucose, (NH ₄) ₂ SO ₄ and KH ₂ PO ₄ to the dye solution	Khouni et al. [2011 b])
	23 h aerobic reaction 30 min settle 15 min draw SRT = 30 days Volumetric dye rate 15 g/(m ³ d)			
Simulated effluent containing Acid Black 10B dye	15 min fill	Color _{after 18 cycles} = 67	Addition of glucose and nutrients to the effluent	Mohan et al. [2012]
	2820 min aeration reaction with recirculation 30 min settle 15 min decant	COD _{after 10 cycles} = 88		

Other authors [Kapdan and Oztekin, 2006] evaluated the effect of the anaerobic stage time (2-19h) and initial COD concentration (400-1800 mg/L) on the performance of a SBR system treating a simulated wastewater containing Remazol Red RR dye, phosphates,

sulfates and glucose. The color removal, in the anaerobic phase, was completed in the first 4-6 h, achieving 90% decolorization. Operating the aerobic phase for 19-20 h, 80% COD removal was achieved, while 50% was reached in the anaerobic stage. The aerobic stage was efficient even when reducing the period of the anaerobic stage (2-4 h).

Finally, Vaigan et al. [2009] evaluated the effect of Brill Blue KN-R dye concentration in the performance of SBR. The reactor operated during 36 cycles (5 for sludge acclimatization and 31 for normal operation) with 24 h per cycle comprising 2 min to fill, 22.5 h for aerated reaction, 1 h settling, 2 min of draw and 25 min for idle. Color removal decreased from 57.0% to 31.0% when the dye concentration increased from 20 to 40 mg/L, however COD removal was practically constant (~97%) for all concentrations.

2.5.2 Textile Wastewater Treatment by Combination of SBR and Other Techniques

In this section are presented some studies concerning the treatability of simulated effluents containing dyes or real textile wastewaters by biological oxidation in SBR integrated with other treatment methods.

Krull and Hempel [2001] evaluated the color and COD removals and toxicity reduction of dye-house liquor by combining SBR with ozonation. After the chemical treatment the effluent was introduced into the SBR and subjected to aerobic degradation. By integrating the two processes the authors obtained 90 and 98% of COD and color removals, respectively, and toxicity was reduced by 99%, as determined by bioluminescence tests.

Other authors [Zuriaga-Agusti et al., 2010] evaluated the treatment of a simulated textile wastewater (containing 20 mg/L of Remazol Yellow RR, Remazol Red RR and Remazol Blue RR, glucose and nutrients) by combining biological oxidation in SBR with nanofiltration. The SBR was operated at 2.5 days of HRT and 20 h per cycle comprising 0.2 h-fill, 9 h-anaerobic react, 8 h-aerobic react, 2 h-settle, 0.3 h-draw and 0.5 h-idle. In the first 55 cycles the SBR was fed with synthetic wastewater and removals of 80 to 90% were achieved for Red and Blue dyes and 70 to 80% for Yellow dye. Afterwards the SBR was fed with three different mixtures: i) 4.0 L of synthetic textile wastewater (STW) and 1.0 L of nanofiltration rejection (NFR), ii) 3.5 L of STW and 1.5 L of NFR and iii) 2.5 L of

both effluents. It was found that higher amounts of NFR in the feed stream caused a more marked decay in the efficiency of dye removal, due to conductivity increase.

Blanco et al. [2012] studied the applicability of Fenton's reaction and combination of SBR with Fenton's reagent for treating a real textile wastewater. In the Fenton process alone, the authors evaluated the effect of H₂O₂ dose (1650-4950 ppm), Fe²⁺ dose (109-540 ppm) and temperature (25-35 °C) and achieved maximum TOC removal (64%) and *Escherichia coli* reduction (>99%) in the following conditions: 25 °C, 3, 1650 mg/L and 216 mg/L for T, pH, [H₂O₂] and [Fe²⁺], respectively. The treatment in SBR alone was carried out after pH adjustment to 6.5-7.5, addition of nutrients, oxygen at 3 mgO₂/L and T=25 °C. 75% TOC removal was reached for HRT=1 day. Finally, using the combination of biological oxidation followed by Fenton process (pH=3, [H₂O₂]=1518 mg/L and [Fe²⁺]=66.5 mg/L) remarkable removal efficiencies of 92 and 99% for TOC and E. coli, respectively, were achieved, showing the interest in integrating both processes.

Additional studies focused on the combination of SBR with adsorption by GAC are reported in the literature and summarized in Table 2.7, where the operating conditions and global removal efficiencies are also presented.

Table 2.7 – Studies on the integration of SBR with other processes for treating dye solutions and textile effluents.

Dye solution or Effluent type	Operating Conditions in SBR	Other Process	Overall Efficiencies (%)	Comments	Reference
Disperse Red 60 dye	1 h fill	Granular Activated Carbon	BOD ₅ = 97 COD = 97 KTN = 90		Siriamunta piboon and Srisornsak [2007]
	19 h reaction				
	3 h settle				
	0.5 h draw				
	0.5 h idle				
	HRT = 3 days [dye] = 80 mg/L				
Real wastewater containing Disperse Red 60 and Disperse Blue 60 dyes	1 h fill	Granular Activated Carbon	Color = 95 BOD ₅ = 94 COD = 94 KTN = 59	Addition of glucose to the wastewater No production of excess sludge	Siriamunta piboon and Srisornsak [2007]
	19 h reaction				
	3 h settle				
	0.5 h draw				
	0.5 h idle				
	SRT = 67 days HRT = 5 days				

Chapter 2 - State of the Art

Table 2.7 – Studies on the integration of SBR with other processes for treating dye solutions and textile effluents (cont.).

Dye solution or Effluent type	Operating Conditions in SBR	Other Process	Overall Efficiencies (%)	Comments	Reference
Direct Red 23 and Direct Blue 201 dyes solutions	1 h fill 19 h reaction 3 h settle 0.5 h draw 0.5 h idle	Granular Activated Carbon	BOD ₅ , COD and KTN in the order 89-99		Sirianuntap boon et al. [2007]
Real wastewater containing Direct Red 23 and Direct Blue 201 dyes	1 h fill 19 h reaction 3 h settle 0.5 h draw 0.5 h idle	Granular Activated Carbon	Color = 76 BOD ₅ = 84 COD = 86 KTN = 68	Addition of glucose to the wastewater No production of excess sludge	Sirianuntap boon et al. [2007]
Simulated effluent containing Direct Blue 201	1 h fill 19 h reaction 3 h settle 0.5 h draw 0.5 h idle HRT = 7.5 days SRT = 22 days [VSS] = 3000 mg MLSS/L	Granular Activated Carbon	BOD ₅ , COD and KTN >93	Addition of urea, glucose and nutrients to the effluent	Sirianuntap boon and Sansak [2007]
Simulated effluent containing Direct Red 23 dye	1 h fill 19 h reaction 3 h settle 0.5 h draw 0.5 h idle HRT = 7.5 days SRT = 22 days [VSS] = 3000 mg MLSS/L	Granular Activated Carbon	BOD ₅ , COD and KTN >93	Addition of urea, glucose and nutrients to the effluent	Sirianuntap boon and Sansak [2007]
Real effluent	1 h fill 19 h reaction 3 h settle 0.5 h draw 0.5 h idle SRT = 28 days	Granular Activated Carbon	BOD ₅ , COD and KTN >93	Addition of glucose to the effluent	Sirianuntap boon and Sansak [2007]
Real effluent	1 h fill 19 h reaction 3 h settle 0.5 h draw 0.5 h idle SRT = 28 days	Granular Activated Carbon	BOD ₅ , COD and KTN >93	Addition of rice wastewater to the effluent	Sirianuntap boon and Sansak [2007]

2.6 References

- Al-Ani, Y.; Li, Y. (2012). Degradation of C.I. Reactive Blue 19 using combined iron scrap process and coagulation/flocculation by a novel Al(OH)₃-polyacrylamide hybrid polymer. *Journal of Taiwan Institute of Chemical Engineers*, 43, 942-947.
- Alaton, I.A. e Teksoy, S. (2007). Acid dyebath effluent pretreatment using Fenton reagent: Process optimization, reaction kinetics and effects on acute toxicity. *Dyes and Pigments*, 73, 31-39.
- Alves C. (2007). "Tratamento de Águas de Abastecimento". 2ª Edição, Publindústria, Porto.
- Anouzla, A.; Abrouki, Y.; Souabi, S.; Safi, M.; Rhabal, H. (2009). Colour and COD removal of disperse dye solution by a novel coagulant: Application of statistical design for the optimization and regression analysis. *Journal of Hazardous Materials*, 166, 1302-1306.
- Arslan-Alaton, I.; Tureli, G.; Olmez-Hanci, T. (2009). Treatment of azo dye production wastewaters using Photo-Fenton-like advanced oxidation processes: Optimization by response surface methodology. *Journal of Photochemistry and Photobiology A: Chemistry*, 202, 142-153.
- Ay, F.; Catakaya, E.C.; Kargi, F. (2009). A statistical experimental design approach for advanced oxidation of Direct Red azo-dye by photo-Fenton treatment. *Journal of Hazardous Materials*, 162, 230-236.
- Azbar, N.; Yonar, T.; Kestioglu, K. (2004). Comparison of Various Advanced Oxidation Processes and Chemical Treatment Methods for COD and Color Removal from a Polyester and Acetate Fiber Dyeing Effluent. *Chemosphere*, 55, 35-43.
- Bali, U.; Karagözoglu B. (2007). Performance comparison of Fenton process, ferric coagulation and H₂O₂/pyridine/Cu (II) system for decolourization of Remazol Turquoise Blue G-133. *Dyes and Pigments*, 74, 73-80.
- Benítez, F.; Acero, J.; Real, F.; Rubio, F.; Leal, A. (2001). The role of hydroxyl radicals for the decomposition of p-hydroxy phenylacetic acid in aqueous solutions. *Water Research*, 35, 1338-1343.
- Bernardes, R.S.; Klapwijk, A. (1996). Biological nutrient removal in a sequencing batch reactor treating domestic wastewaters. *Water Science and Technology*, 42, 321-328.
- Bes-Piá, A.; Mendoza-Roca, J.A.; Alcaina-Miranda, M.I.; Iborra-Clar, A.; Iborra-Clar M.I. (2002). Reuse of wastewater of the textile industry after its treatment with combination of physical-chemical treatment and membrane technologies. *Desalination*, 149, 169-174.
- Bigda, R.J. (1995). Consider Fenton chemistry for wastewater treatment. *Chemical Engineering and Processing*, 91, 62-66.
- Blanco, J.; Torrades, F.; Varga, M. De la, García-Montáño, J. (2012). Fenton and biological-Fenton coupled processes for textile wastewater treatment and reuse. *Desalination*, 286, 34-399.
- Bortone, G. (2009). Integrated anaerobic/aerobic biological treatment for intensive swine production. *Bioresource Technology*, 100, 5424-5430.

Chapter 2 - State of the Art

Bose, P. (2010). *Water and Wastewater Engineering*. Indian Institute of Technology, Kanpur, Indian.

Cañizares, P.; Jiménez, C.; Martínez, F.; Rodrigo, M.A.; Sáez, C.; (2009). The pH as a key parameter in the choice between coagulation and electrocoagulation for the treatment of wastewaters. *Journal of Hazardous Materials*, 163, 158-164.

Çinar, Ö., Yaşar, S.; Kertmen, M.; Demiröz, K.; Yigit, N.Ö., Kitis, MM. (2008). Effect of cycle time on biodegradation of azo dye in sequencing batch reactor. *Process Safety and Environmental Protection*, 86, 455-460.

Easton, J. R. (1995). The dye maker's view. In *Colour in Dyehouse Effluent*, P. Cooper (Ed.). Oxford, The Society of dyers and Colourists, The Alden Press.

Eckenfelder, W.W. Jr. (2000). *Industrial water pollution control*. McGraw-Hill, 3^a Ed., Singapore.

El-Gohary, F., Tawfik, A. (2009). Decolourization and COD reduction of disperse and reactive dyes wastewater using chemical-coagulation followed by sequential batch reactor (SBR) process. *Desalination*, 249, 1159-1164.

Elmolla, E.S.; Chaudhuri, M. (2009). Degradation of the antibiotics amoxicillin, ampicillin and cloxacillin in aqueous solution by the photo-Fenton process. *Journal of Hazardous Materials*, 172, 1476–1481.

Engwall M.A., Pignatello J.J., Grasso D. (1998). Degradation and detoxification of the wood preservatives creosote and pentachlorophenol in water by photo-Fenton reaction. *Water Research*, 33, 1151-1158.

Farabegoli, G.; Chiavola, A.; Rolle, E.; Naso, M. (2010). Decolourization of Reactive Red 195 by a mixed culture in an alternating anaerobic-aerobic Sequencing Batch Reactor. *Biochemical Engineering Journal*, 52, 220-226.

Fenton, H. J. H. (1894). Oxidation of Tartaric Acid in Presence of Iron. *Journal of the Chemical Society*, 65, 899-910.

Flaherty, K.A.; Huang, C.P. (1992). Continuous Flow Applications of Fenton's Reagent for the Treatment of Refractory Wastewater. In: *Proceedings of the Second International Symposium on Chemical Oxidation-Technologies for the Nineties*, Nashville, Tennessee, U.S.A., 58-77.

Fongsatitkul, P.; Elefsiniotis, P.; Yamasmit, A.; Yamasmit, N. (2004). Use of Sequential Batch Reactors and Fenton's Reagent to Treat a Wastewater from a Textile Industry. *Biochemical Engineering Journal*, 21, 213-220.

Fu, L.-y.; Wen, X.-h.; Lu, Q.-l.; Qian, Y. (2001). Treatment of dyeing wastewater in two SBR systems. *Process Biochemistry*, 36, 1111-1118.

Furlan, F.R.; da Silva, L.G. de M.; Morgado, A.F.; de Souza, A.A.U.; de Souza, S.M.A.G.U. (2010). Removal of Reactive dyes from aqueous solutions using combined coagulation/flocculation and adsorption on activated carbon. *Resources, Conservation and Recycling*, 54, 283-290.

Galvez, J.B.; Rodriguez, S.M. (2003). *Solar Detoxification*. United Nations Educational, Scientific and Cultural Organization (UNESCO).

Gao, B.-Y.; Yue, Q.-Y.; Wang, Y.; Zhou, W.-Z. (2007a). Color removal from dye-containing wastewater by magnesium chloride. *Journal Environmental Management*, 82, 167-172.

Gao, B.-Y.; Wang, Y.; Yue, Q.-Y.; Wei, J.-C.; Li, Q. (2007 b). Color removal from simulated dye water and actual textile wastewater using a composite coagulant prepared by polyferric chloride and polydimethyldiallylammonium chloride. *Separation and Purification Technology*, 54, 157-163.

García-Montaña, J., Torrades, F., García-Hortal, J.A., Domènech, X., Peral, J. (2006 a)). Combining photo-Fenton process with aerobic sequencing batch reactor for comercial hetero-bireactive dye removal. *Applied Catalysis B: Environmental*, 67, 86-92.

García-Montaña, J.; Torrades, F.; García-Hortal, J.A.; Domènech; X.; Peral, J. (2006 b)). Degradation of Procion Red H-E7B reactive dye by coupling a photo-fenton system with sequencing batch reactor. *Journal of Hazardous Materials*, B134, 220-229.

Golob, V.; Vinder, A.; Simonic, M. (2005). Efficiency of the coagulation/flocculation method for the treatment of dyebath effluents. *Dyes and Pigments*, 67, 93-97.

Gray, N. F. (2004). *Biology of wastewater treatment*. 2nd edition, Imperial College Press, London.

Guimarães, J.R.; Maniero, M.G.; Araújo, R.N. de (2012). A comparative study on the degradation of RB-19 dye in na aqueous médium by advaced oxidation processes. *Journal of Environmental Management*, 10, 33-39.

Gulkaya, Í.; Surucu, G.A.; Dilek, F.B. (2006). Importance of H₂O₂/Fe²⁺ ratio in Fenton's treatment of a carpet dyeing wastewater. *Journal of Hazardous Materials*, B136, 763-769.

Harrelkas, F.; Azizi, A.; Yaacoubi, A.; Benhammou, A.; Pons, M.N. (2009). Treatment of textile dyes effluents using coagulation-flocculation coupled with membrane processes or adsorption on powdered activated carbon. *Desalination*, 235, 330-339.

Haber, F. and Weiss, J. (1934). The catalytic decomposition of hydrogen peroxide by iron salts. *Proceedings of the Royal Society London*, 147, 332-351.

Hsueh, C.; Huang, Y.; Wang, C.; Cheng, C. (2005). Degradation of azo dyes using low iron concentration of Fenton and Fenton-like system. *Chemosphere*, 58, 1409-1414.

Huang Y.-H., Huang Y.-F., Chang P.-S., Chen C.-Y. (2008). Comparative study of oxidation of dye-Reactive Black B by different advanced oxidation processes: Fenton, electro-Fenton and photo-Fenton. *Journal of Hazardous Materials*, 154, 655-662.

Jonstrup, M.; Punzi, M.; Mattiasson, B. (2011). Comparison of anaerobic pre-treatment and aerobic post-treatment coupled to photo-Fenton oxidation for degradation of azo dyes. *Journal of Photochemistry and Protobiology A: Chemistry*, 224, 55-61.

Joo, D.J.; Shin, W.S.; Choi, J.-H.; Choi, S.J.; Kim M.-C.; Han, M.H.; Ha, T.W.; Kim, Y.-H. (2007). Decolourization of reactive dyes using inorganic coagulants and synthetic polymer. *Dyes and Pigments*, 73, 59-64.

Kang, S.-F.; Liao, C.-H.; Po, S.-T. (2000). Decolourization of textile wastewater by photo-fenton oxidation technology. *Chemosphere*, 41, 1287-1294.

Kapdan, I. K.; Oztekin, R. (2006). The effect of hydraulic residence time and initial COD concentration on color and COD removal performance of the anaerobic-aerobic SBR system. *Journal of Hazardous Materials*, 136 (3), 896-901.

Kapdan, I. K.; Ozturk, R. (2005). Effect of operating parameters on color and COD removal performance of SBR: Sludge age and initial dyestuff concentration. *Journal of Hazardous Materials*, 123 (1-3), 217-222.

Katsumata, H.; Koike, S.; Kaneco, S.; Suzuki, T.; Ohta, K. (2010). Degradation of Reactive Yellow 86 with photo-Fenton process driven by solar light. *Journal of Environmental Sciences*, 22 (9), 1455-1461.

Khouni, I.; Marrot, B.; Moulin, P.; Amar, R.B. (2011 a)). Decolourization of the reconstituted textile effluent by different process treatments: Enzymatic catalysis, coagulation/flocculation and nanofiltration processes. *Desalination*, 268, 27-37.

Khouni I.; Marrot, B.; Amar, R.B. (2011 b)). Treatment of reconstituted textile wastewater containing a reactive dye in an aerobic sequencing batch reactor using a novel bacterial Consortium. *Separation and Purification Technology*. DOI: 10.1016/j.seppur.2011.11.030.

Kim, S.-M.; Geissen, S.-U.; Vogelpohl, A. (1997). Landfill leachate treatment by a photoassisted Fenton reaction. *Water Science and Technology*, 35 (4), 239-248.

Kim, T.-H.; Park, C.; Yang, J.; Kim S. (2004). Comparison of dispersed and reactive dye removals by chemical coagulation and Fenton oxidation. *Journal of Hazardous Materials*, B 112, 95-103.

Kishida, N.; Kim, J.-H.; Chen, M.; Sasaki, H.; Sudo, R. (2003). Effectiveness of oxidation-reduction potential and pH as monitoring and control parameters for nitrogen removal in swine wastewater treatment by sequencing batch reactors. *Journal of Bioscience and Bioengineering*, 96, 285-290.

Krull, R.; Hempel, D.C. (2001). Treatment of dyehouse liquors in a biological sequencing batch reactor with recursive chemical oxidation. *Water Science and Technology*, 44 (5), 85-92.

Kulikowsha, D.; Klimiuk, E. (2004). Removal of organic and nitrogen from municipal landfill leachate in two-stage SBR reactors. *Polish Journal of Environmental Studies*, 13, 389-396.

Kuo, W.G. (1992). Decolorizing Dye Wastewater with Fenton's Reagent. *Water Research*, 26, 881-886.

Lafleur, T. (1997). Jar testing. Rensselaer Polytechnic Institute, Troy, NY, USA.

Li, J.; Luan, Z.; Yu, L.; Ji, Z. (2012). Pretreatment of acrylic fiber manufacturing wastewater by Fenton process. *Desalination*, 284, 62-65.

Liu, R.; Chiu, H.M.; Shiau, C.-H.; Yeh, R.Y.-L.; Hung, Y.-T. (2007). Degradation and sludge production of textile dyes by Fenton and photo-Fenton processes. *Dyes and Pigments*, 73, 1-6.

Lodha, B.; Chaudhari, S. (2007). Optimization of Fenton-Biological treatment scheme for the treatment of aqueous dye solutions. *Journal of Hazardous Materials*, 148, 459-466.

Lourenço, N.D.; Novais, J.M.; Pinheiro, H.M. (2001). Effect of some operational parameters on textile dye biodegradation in sequential batch reactor. *Biotechnology*, 89, 163-174.

- Lucas, M.S.; Peres, J.A. (2006). Decolourization of the azo dye Reactive Black 5 by Fenton and photo-Fenton oxidation. *Dyes and Pigments*, 71, 236-244.
- Mahvi, A.H. (2008). Sequencing batch reactor: A promising technology in wastewater treatment. *Iranian Journal of Environmental Health Science & Engineering*, 5, 79-90.
- Malato, S.; Blanco, J.; Vidal, A.; Richter, C. (2002). Photocatalysis with solar energy at a pilot-plant scale: an overview. *Applied Catalysis B: Environmental*, 37, 1–15.
- Malik, P.K.; Saha, S.K. (2003). Oxidation of direct dyes with hydrogen peroxide using ferrous ion as catalyst. *Separation and Purification Technology*, 31, 241-250.
- Metcalf & Eddy (2003). *Wastewater Engineering: Treatment, Disposal and Reuse*. 4^a Ed. McGraw – Hill, New York.
- Meriç, S.; Kaptan, D.; Ölmez, T (2004). Color and COD removal from wastewater containing Reactive Black 5 using Fenton's oxidation process. *Chemosphere*, 54, 435-441.
- Merzouk, B.; Gourich, B.; Madani, K.; Vial, Ch.; Sekki, A. (2011). Removal of a disperse red dye from synthetic wastewater by chemical coagulation and continuous electrocoagulation. A comparative study. *Desalination*, 272, 246-253.
- Modirshahla, N.; Behnajady, M.A.; Ghanbary, F. (2007). Decolorization and mineralization of C.I. Acid Yellow 23 by Fenton and photo-Fenton processes. *Dyes and Pygments*, 73, 305-310.
- Moghaddam, S.S.; Moghaddam, M.R.A.; Arami, M. (2010). Coagulation/flocculation process for dye removal using sludge from water treatment plant: Optimization through response surface methodology. *Journal of Hazardous Materials*, 175, 651-657.
- Moghaddam, S.S.; Moghaddam, M.R.A.; Arami, M. (2011). Response surface optimization of acid red 119 dye from simulated wastewater using Al based waterworks sludge and polyaluminium chloride as coagulant. *Journal of Environmental Management*, 92, 1284-1291.
- Mohan, S. V., Rao, N. C. e Sarma, P. N. (2007), Simulated acid azo dye (Acid black 210) wastewater treatment by periodic discontinuous batch mode operation under anoxic-aerobic-anoxic microenvironment conditions. *Ecological Engineering*, 31 (4), 242-250.
- Mohan, S.V.; Babu, P.S.; Naresh, K.; Velvizhi, G.; Madamwar, D. (2012). Acid azo dye remediation in anoxic-aerobic-anoxic microenvironment under periodic discontinuous batch operation: Bio-electro kinetics and microbial inventory. *Bioresource Technology*, 119, 362-372.
- Mohseni, B.A.; Bazari, H. (2004). Biological treatment of dairy wastewater by sequencing batch reactor. *Iranian Journal of Environmental Health Science & Engineering*, 1, 65-69.
- Morais, L.C.P. (2005). Avaliação da Tratabilidade de Efluentes da Indústria de Curtumes por Oxidação Química e Biológica. Dissertation of doctor degree in chemical engineering, University of Porto – Faculty of Engineering.
- Morling, S. (2010). Nitrogen removal and heavy metals in leachate treatment using SBR technology. *Journal of Hazardous Materials*, 174, 679-686.

Chapter 2 - State of the Art

Muruganandham, M.; Swaminathan, M. (2004). Decolourisation of Reactive Orange 4 by Fenton and photo-Fenton oxidation technology. *Dyes and Pigments*, 63, 315-321.

Neyens, E.; Baeyens, J. (2003). A review of classic Fenton's peroxidation as an advanced oxidation technique. *Journal of Hazardous Materials*, 98, 33-50.

Nogueira, R.F.P.; Trovól, A.G.; Silval, M.R.A. da; Villal, R.D.; Oliveirall, M.C. de (2007). Fundamentos e aplicações ambientais dos processos fenton e foto-fenton. *Química Nova*, Vol.30, nº2, São Paulo.

Papadopoulos, A.E.; Fatta, D.; Loizidou, M. (2007). Development and optimization of dark Fenton oxidation for the treatment of textile wastewaters with high organic load. *Journal of Hazardous Materials*, 146, 558-563.

Peavy, H.S.; Rowe, D.R.; Tchobanoglous, G. (1985). *Environmental Engineering*. McGraw-Hill, Singapore.

Pérez, M.; Torrades, F.; Doménech, X.; Peral, J. (2002). Fenton and photo-Fenton oxidation of textile effluents. *Water Research*, 36, 2703-2710.

Phipps & Bird (1995). A simplified jar test procedure, 1519 Summit Av., Richmond, Virginia 23230, USA.

Pignatello, J. (1992). Dark and photoassisted Fe³⁺-catalyzed degradation of chlorophenoxy herbicides by hydrogen peroxide. *Environmental Science Technology*, 26, 944-951.

Poland, J.; Pagano T. (2010). Jar testing. Civil Engineering Department, Virginia Polytechnic Institute and State University, USA.

Ramirez, J.H.; Costa, C.A.; Madeira, L.M. (2005). Experimental design to optimization the degradation of the synthetic dye Orange II using Fenton's reagent. *Catalysis Today*, 107-108, 68-76.

Rivas, F. J.; Beltrán, F. J.; Frades, J.; Buxeda, P. (2001). Oxidation of p-hydroxybenzoic acid by Fenton's reagent. *Water Research*, 35 (2), 387-396.

Rodrigues, C.S.D. (2007). Tratamento de Efluentes Têxteis por Processos Combinados de Oxidação Química e Biológica. Dissertation of master degree in environmental engineering, University of Porto – Faculty of Engineering.

Rodriguez, M.; Sarria, V.; Esplugas, S.; Pulgarin, C. (2002). Photo-Fenton treatment of a bio recalcitrant wastewater generated in textile activities: biodegradability of the photo-treated solution. *Journal of Photochemistry and Photobiology A: Chemistry*, 151, 129-135.

Satterfield, Z. (2004). Jar testing. NESC, West Virginia University, USA.

Sauer, T.; Neto, C.; José, H.J.; Moreira, R.F.P.M. (2002). Kinetics of photocatalytic degradation of reactive dyes in TiO₂ slurry reactor. *Journal of Photochemistry and Photobiology A: Chemistry*, 149 (1-3), 147-154.

Sawyer, C.N.; McCarty, P.L.; Parking, G.F. (1994). *Chemistry for Environmental Engineering*. McGraw-Hill, Fourth Edition, New York.

Silva, C.S.C.G. (2003). Processos Avançados de Oxidação Fotoquímica na Descoloração de Soluções Aquosas Fortemente Coradas. Dissertation of master degree in environmental engineering, University of Porto – Faculty of Engineering.

Sims, A. F. E. (1983). Industrial effluent treatment with Hydrogen Peroxide. *Chemistry and Industry*, 555-558.

Sirianuntapiboon, S.; Chairattanawan, K.; Jungphongsukpanich, S. (2006). Some properties of a sequencing batch reactor system for removal of vat dyes. *Bioresource Technology*, 97, 1243-1252.

Sirianuntapiboon, S.; Sadahiro, O.; Salee, P. (2007). Some properties of a granular activated carbon sequencing batch reactor (GAC-SBR) system for treatment of textile wastewater containing direct dyes. *Journal of Environmental Management*, 85 (1), 162-170.

Sirianuntapiboon, S.; Sansak, J. (2008). Treatability studies with granular activated carbon (GAC) and sequencing batch reactor (SBR) system for textile wastewater containing direct dyes. *Journal of Hazardous Materials*, 159, 404-411.

Sirianuntapiboon, S.; Srisornsak, P. (2007). Removal of disperse dyes from textile wastewater using biosludge. *Bioresource Technology*, 98 (5), 1057-1066.

Southworth, B. A.; Voelker, B. M. (2003). Hydroxyl radical production via the Photo-Fenton reaction in the presence of fulvic acid. *Environmental Science and Technology*, 37, 1130-1136.

Su, J.-J.; Kungd, C.-M.; Lina, J.; Liana W.-C.; Wu J.-F. (1997). Utilization of sequencing batch reactor for in situ piggy wastewater treatment. *Journal of Environmental Science and Health, Part A*, 32, 391-405.

Sun, Y.; Pignatello J.J. (1993). Photochemical reactions involved in the total mineralization of 2-4-D by $\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{UV}$. *Environmental Science Technology*, 27, 304-310.

Sun, J.-H.; Sun, S.-P.; Wang, G.-L.; Qiao, L.-P. (2007). Degradation of azo dye amido black 10B in aqueous solution by Fenton oxidation process. *Dyes and Pigments*, 74, 647-652.

Suresh, S.; Tripathi, R.K.; Rana, M.N.G. (2011). Review on treatment of industrial wastewater using sequential batch reactor. *International Journal of Science Technology & Management*, 2, 64-84.

Szpyrkowicz, L.; Juzzolino, C.; Kaul, S. (2001). A comparative study on oxidation of disperse dyes by electrochemical process, ozone, hypochlorite and Fenton reagent. *Water Research*, 35, 2129-2136.

Swaminathan, K.; Sandhya, S.; Sophia, A.C.; Pachhade, K.; Subrahmanyam, Y.V. (2003). Decolourization and degradation of H-acid and other dyes using ferrous-hydrogen peroxide system. *Chemosphere*, 50, 619-625.

Tanatak, N.P.; Chaudhari, S. (2006). Degradation of Azo Dyes by Sequential Fenton's Oxidation and Aerobic Biological Treatment. *Journal of Hazardous Materials*, 136 (3), 698-705.

Tekin, H.; Bilkay, O., Ataberk S.S.; Balta, T.H.; Ceribasi, I.H.; Sanin F.D.; Dilek, F.B.; Yetis, U. (2006). Use of Fenton oxidation to improve the biodegradability of a pharmaceutical wastewater. *Journal Hazardous Materials*, B136, 258-265.

Torrades, F.; García- Montañó, J.; García-Hortal, J.A.; Domènech, X.; Peral, J. (2004). Decolourization and mineralization of commercial reactive dyes under solar light assisted photo-Fenton conditions. *Solar Energy*, 77, 573-581.

Tokumura, M.; Morito, R.; Kawase, Y. (2012). Photo-Fenton process for simultaneous colored wastewater treatment and electricity and hydrogen production. *Chemical Engineering Journal*, 221, 81-89.

Tsang, Y.F.; Hua, F.L.; Chua, H.; Sin, S.N.; Wang, Y.J. (2007). Optimization of biological treatment of paper mill effluent in a sequencing batch reactor. *Bioresource Technology*, 98, 2142-2147.

U.S. EPA (1986). Summary Report: Sequencing Batch Reactors. U.S. Environmental Protection Agency, Center for Environmental Research Information. Cincinnati, OH, Technology Transfer, EPA/625/8-86/011.

U.S. EPA (1999). Wastewater, Technology Fact Sheet: Sequencing Batch Reactors. U.S. Environmental Protection Agency, Office of Water. Washington, D.C., EPA 932-F-99-073.

Vaigan, A.A.; Moghaddam, M.R.A.; Hashemi, H. (2009). Effect of Dye concentration on sequencing batch reactor performance. *Iranian Journal of Environmental Health Science & Engineering*, 6, 11-16.

Vaishnave, P.; Kumar, A.; Ameta, R.; Punjabi, P.B.; Ameta, S.C. (2012). Photo oxidative degradation of azure-B by sono-photo-Fenton and photo-Fenton reagents. *Arabian Journal of Chemistry*, doi: 10.1016/j.arabjc.2010.12.019.

Vigneswaran, S.; Visvanathan, C. (1995). *Water Treatment Process – Simple Options*, CRC Press LLC, Florida.

Walling, C. (1975). Fenton's reagent revisited. *Accounts of Chemical Research*, 8, 125-131.

Wang, X.; Zeng, G.; Zhu, J. (2008). Treatment of jean-wash wastewater by combined coagulation, hydrolysis/acidification and Fenton oxidation. *Journal of Hazardous Materials*, 153, 810-816.

Wei, J.; Song, Y.; Tu, X.; Zhao, L.; Zhi, E. (2013). Pretreatment of dry-spun acrylic fiber manufacturing wastewater by Fenton process: optimization, kinetics and mechanisms. *Chemical Engineering Journal*, 218, 319-326.

Wu, C.; Wang, Y.; Gao, B.; Zhao, Y.; Yue, Q. (2012). Coagulation performance and floc characteristics of aluminum sulfate using sodium alginate as coagulant aid for synthetic dyeing wastewater treatment. *Separation and purification Technology*, 95, 180-187.

Wu, H.; Wang, S. (2012). Impacts of operating parameters on oxidation-reduction potential and pretreatment efficacy in the pretreatment of printing and dyeing wastewater by Fenton process. *Journal of Hazardous Materials*, 243, 86-94.

Wu, K.; Xie, Y.; Zhao, J.; Hidaka, H. (1999) Photo-Fenton degradation of a dye under visiblelight irradiation. *Journal of Molecular Catalysis A: Chemical*, 144, 77-84.

Zahrim, A.Y.; Tizaoui, C.; Hilal, N. (2010). Evaluation of several commercial synthetic polymers as flocculant aids for removal of highly concentrated C.I. Acid Black 210 dye. *Journal of Hazardous Materials*, 182, 624-630.

Zhu,W.; Yang, Z.; Wang, L. (2001). Application of ferrous hydrogen peroxide for treatmentof DSC-acid manufacturing process wastewater. *Water Research*, 35 (8), 2087-2091.

Zuriaga-Agustí, E.; Iborra-Clar, M.I.; Mendoza-Roca, J.A.; Tancredi, M.; Alcaína-Miranda, M.I.; Iborra-Clar, A. (2010). Sequencing batch reactor technology coupled with nanofiltration for textile wastewater reclamation. *Chemical Engineering Journal*, 161, 122-128.



Part II

Experimental Section



Chapter 3

Materials and Methods

3 Materials and Methods

3.1 Introduction

This part of the thesis regards the preparation and characterization of synthetic effluents as well as the characterization of a real cotton dyeing effluent. A brief description of the analytical methods and experimental procedures is also presented.

3.2 Textile Dyeing Wastewaters

3.2.1 Simulated Textile Dyeing Wastewaters

Once the treatability of a given effluent depends on the constituents present therein and their respective concentration, this study started by establishing a contact with the textile dyeing company Erfoc – Acabamentos Têxteis S.A. (located in Famalicão) – so as to collect information regarding the amounts of dyes and auxiliary products used in dyebaths of synthetic (polyester and acrylic) and natural (cotton) fibers and the degree of fixation of each chemical on the fibers. This way one could predict the concentration of each individual chemical in the final (and complex) effluent and prepare the corresponding simulated wastewaters.

3.2.1.1 Dyes

Two disperse (Dianix Blue K-FBL and Dianix Orange K3G), one basic (Astrazon Blue FGGL 03 300%) and two reactive (Procion Yellow H-EXL gran and Procion Deep Red H-EXL gran) dyes were selected for the preparation of the simulated effluents, as they are commonly used for dyeing polyester, acrylic and cotton fibers, respectively.

Table 3.1 shows the structures (available from the manufacturer) of the dyes present in each effluent as well as some other characteristics such as the dye class and the experimentally determined wavelength of maximum absorbance in the visible region. The chemical structure and generic name of the Procion deep red H-EXL gran dye is not

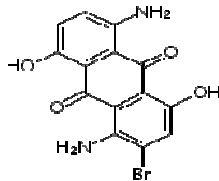
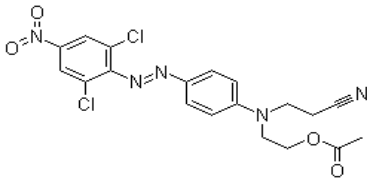
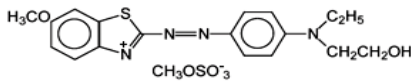
presented as this dye is a mixture of two dyes (reactive yellow 138:1 and another reactive azo dye). These dyes were kindly provided by DyStar-Anilinas Têxteis Unipessoal Lda.

The selection of these dyes also took into account the following aspects: i) the reactive dyes, which are used in large amounts for dyeing fibers in Portugal, deserve special attention because of their low degree of fixation on the fibers, so that considerable quantities are rejected and will be present in the effluent; furthermore, some reactive dyes are not easily removed by conventional processes, such as biological treatment and coagulation/flocculation using inorganic coagulants; ii) the basic dyes exhibit an increase in consumption due to their high tintorial value and increased consumption of acrylic fibers; iii) the consumption of disperse dyes has been rising following the increase in demand for polyester fibers.

3.2.1.2 Auxiliary Chemicals

The dyeing auxiliaries were also supplied by DyStar – Anilinas Têxteis Unip. Lda. Table 3.2 presents the auxiliary products used in the preparation of the dyebaths for each fiber considered and their main characteristics.

Table 3.1- Characteristics of the dyes present in each simulated effluent.

Commercial name	Generic name	Class	Molar mass (g/mol)	Chemical structure	λ_{\max} (nm)
Polyester effluent					
Dianix Blue K-FBL	Disperse Blue 56	Anthraquinone	304.14		600
Dianix Orange K3G	Disperse Orange 30	Azo	450.27		450
Acrylic effluent					
Astrazon Blue FGGL 300% 03	Basic Blue 41	Azo	482.57		610
Cotton effluent					
Procion Yellow H-EXL gran	Reactive Yellow 138:1	Azo	n.a. *	n.a. *	420
Procion Deep Red H-EXL gran	n.a. *	Azo	n.a. *	n.a. *	520

* not available.

Chapter 3 - Materials and Methods

Table 3.2 - General characteristics of the auxiliary products used for dyeing polyester, acrylic and cotton fibers.

Comercial name	Dyeing step	Function	Chemical characteristic
Polyester effluent			
Adranol NL	Fiber preparation	Anti-oil	-
Antibacol R	Fiber preparation/Dyeing	Anti-crease	-
Trisodium phosphate	Fiber preparation	Electrolyte	Salt
Sera Gal PLP	Dyeing	Equalizing/dispersant	Alkyl polyglycol ether solution
Ammonium sulfate	Dyeing	Electrolyte	Salt
Acetic acid	Dyeing	Acid generator	Acid
Sodium hydroxide 32% (w/v)	Washing	Alkaline system	Base
Sodium hydrosulfite	Washing	Reducer system	Reducer
Acrylic effluent			
Sera Con N-VS	Dyeing	Acid generator	Carboxylic acid ester solution
Sera Spere M-IW	Dyeing	Dispersant	Alkyl polyglycol ether solution
Sera Tard A-AS	Dyeing	Retarder	N-alkyl-N, N-dimethylbenzylammonium
Sodium sulfate	Dyeing	Electrolyte	Salt
Sera Lube M-CF	Dyeing	Anti-crease/lubricant	Polymeric amides solution
Cotton effluent			
Mouillant BG/JT	Fiber preparation	Anti-oil	Composition based in aliphatic ethoxylates
Anticassure BG/BD	Fiber preparation	Anti-crease	Acryamide aqueous solution
Sodium hydroxide 50% (w/v)	Fiber preparation	Alkaline system	Base
Hydrogen peroxide 200 vol.	Fiber preparation	Oxidizing the dye	Oxidant reagent
Acetic acid	Fiber preparation	Acid generator	Acid
Zerox	Fiber preparation	Hydrogen peroxide neutralizer	Catalase
Enzyme BG/FB	Fiber preparation	Bleaching	Fungal cellulase
Sequion M150	Dyeing	Water corrector	Composed by phosphanates/carboxylates
Sodium chloride	Dyeing	Electrolyte	Electrolyte
Sodium carbonate	Dyeing	Alkaline system	Base
Sandozin NRW LIQ ALT C	Washing	Detergent	Polyethylene glycol isotridecyl ether

3.2.1.3 Preparation of the Simulated Textile Dyeing Effluents

The effluents were prepared taking into account that for every process there are several stages, namely fiber preparation, dyeing and washing (although the fiber preparation stage is not used in acrylic dyeing). Moreover, it is worth mentioning that in each particular case different volumes of water and chemicals are employed along the process, as shown in Table 3.3, and that the ratio between the amount of fiber to be dyed and the water used in the bath was assumed to be 1:10 (kg:L). Finally, the percentage of these products unfixed in the textile fibers (and therefore released into the water) should be also taken into account. This information was provided by a dye-house (Erfoc-Acabamentos Têxteis S.A. - Famalicão, Portugal) and by DyStar Anilinas Têxteis, Unip Ltd (Portugal), and is summarized in Table 3.3 along with the estimated concentration of each reagent in the simulated effluents (polyester, acrylic and cotton), which was based in the total volume of water employed in all stages. Figures 3.1 to 3.3 show the temperature profiles of the respective dyeing processes and the moment of addition of each component.

Chapter 3 - Materials and Methods

Table 3.3 - Estimated concentration of each component in the polyester, acrylic or cotton simulated effluents.

Chemical	Dyeing stage	Dyeing stage Concentration	Rejection**	Concentration in the final effluent from each step	Concentration in the global effluent
Polyester effluent					
Adranol NL	Fiber preparation	1 g/L	100%	1 g/L	0.33 g/L
Antibacol R	Fiber preparation	1 g/L	100%	1 g/L	0.33 g/L
Trissodic phosphate	Fiber preparation	1 g/L	90%	0.9 g/L	0.30 g/L
Sera Gal PLP	Dyeing	0.5 g/L	100%	0.5 g/L	0.17 g/L
Antibacol R	Dyeing	1 g/L	100%	1 g/L	0.33 g/L
Ammonium sulfate	Dyeing	2 g/L	90%	1.8 g/L	0.60 g/L
Acetic acid	Dyeing	0.5 g/L	100%	0.5 g/L	0.17 g/L
Dianix Blue KFBL	Dyeing	0.71%*	5%	0.036 g/L	0.012 g/L
Dianix Orange K3G	Dyeing	1.2%*	5%	0.06 g/L	0.02 g/L
Sodium hydroxide 32% (w/v)	Washing	3 g/L	100%	3 g/L	1.0 g/L
Sodium hydrosulfite	Washing	3 g/L	90%	2.7 g/L	0.90 g/L
Acrylic effluent					
Sera con N-VS	Dyeing	0.4 mL/L	100%	0.4 mL/L	0.13 mL/L
Sera sparse M-IW	Dyeing	0.5 g/L	100%	0.5 g/L	0.17 g/L
Sera tard A-AS	Dyeing	1 g/L	100%	1 g/L	0.33 g/L
Sodium sulfate	Dyeing	3 g/L	90%	2.7 g/L	0.90 g/L
Sera lube M-CF	Dyeing	2 g/L	100%	2 g/L	0.67 g/L
Astrazon Blue FGGL 300% 03	Dyeing	1.5%*	5%	0.025 g/L	0.008 g/L
Cotton effluent					
Mouillant BG/JT	Fiber preparation	0.7 mL/L	90%	0.21 mL/L	0.09 mL/L
Anticassure BG/BD	Fiber preparation	0.5 mL/L	90%	0.15 mL/L	0.06 mL/L

Table 3.3 - Estimated concentration of each component in the polyester, acrylic or cotton simulated effluents. (cont.)

Chemical	Dyeing stage	Dyeing stage Concentration	Rejection**	Concentration in the final effluent from each step	Concentration in the global effluent
Cotton effluent					
Sodium hydroxide 50% (w/v)	Fiber preparation	4 mL/L	100%	1.3 mL/L	0.57 mL/L
Hydrogen peroxide 200 vol.	Fiber preparation	1.5 mL/L	85%	0.4 mL/L	0.18 mL/L
Acetic acid	Fiber preparation	0.8 mL/L	100%	0.26 mL/L	0.11 mL/L
Zerox	Fiber preparation	0.6 mL/L	90%	0.18 mL/L	0.08 mL/L
Enzyme BG/FB	Fiber preparation	0.4 mL/L	90%	0.12 mL/L	0.05 mL/L
Sequion M150	Dyeing	1 mL/L	100%	1 mL/L	0.14 mL/L
Sodium chloride	Dyeing	9 g/L	90%	8.1 g/L	1.16 g/L
Sodium carbonate	Dyeing	20 g/L	90%	18 g/L	2.6 g/L
Procion Yellow H-EXL gran	Dyeing	0.45%*	10%	0.045 g/L	0.006 g/L
Procion Deep Red H-EXL gran	Dyeing	2.8 %*	10%	0.28 g/L	0.04 g/L
Sandozin NRW LIQ ALT C	Washing	0.9 mL/L	90%	0.27 mL/L	0.12 mL/L

* w dye/w fiber;

** Percentage of dyes and auxiliary products not fixed by the fibers.

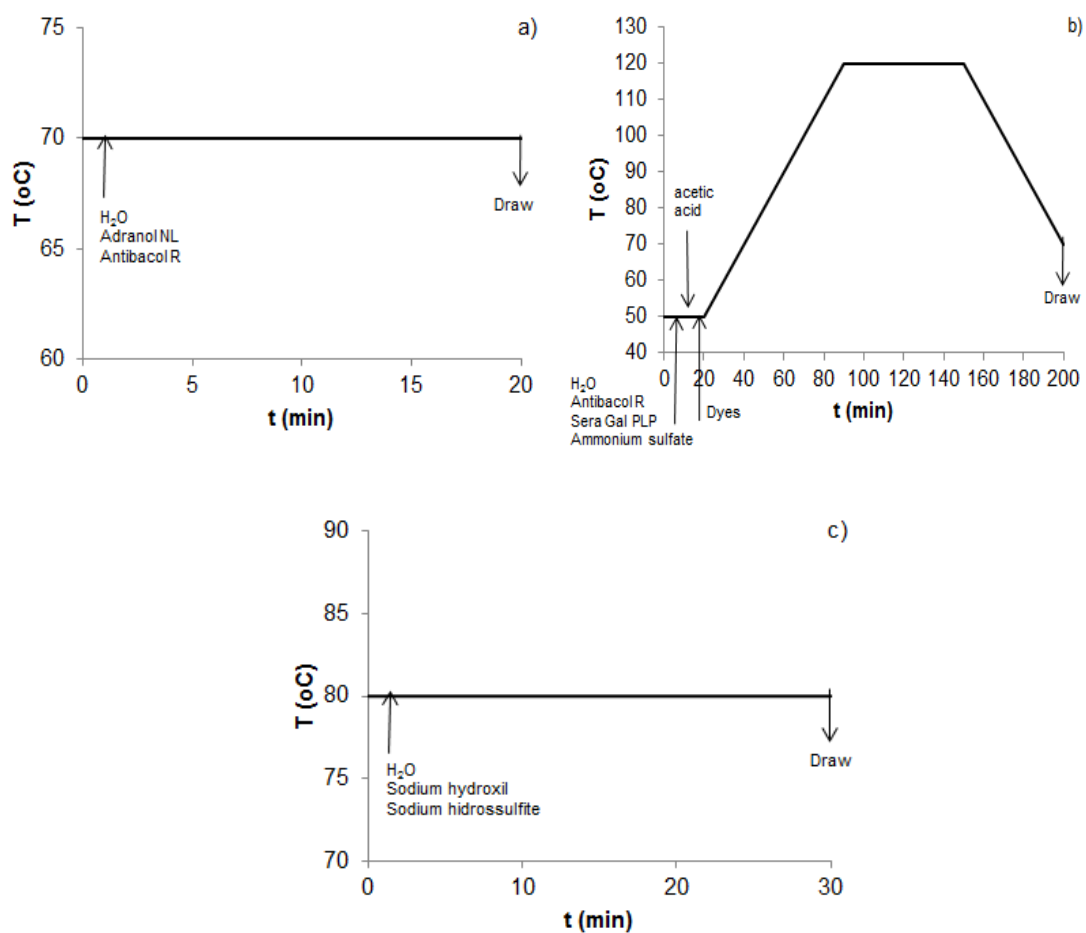


Figure 3.1 – Scheme of polyester fibers dyeing: a) fiber preparation, b) dyeing and c) reduction washing.

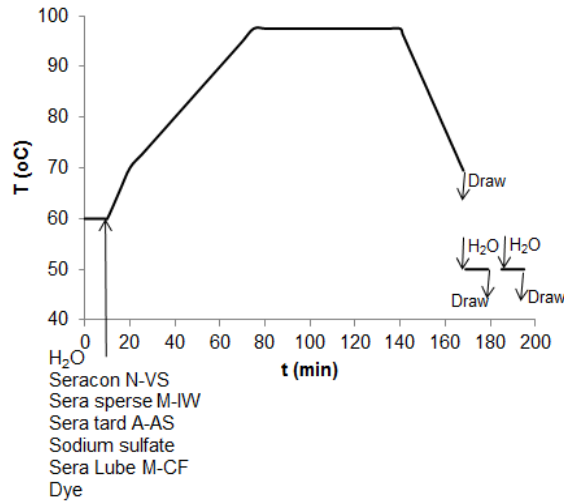


Figure 3.2 – Scheme of acrylic fibers dyeing.

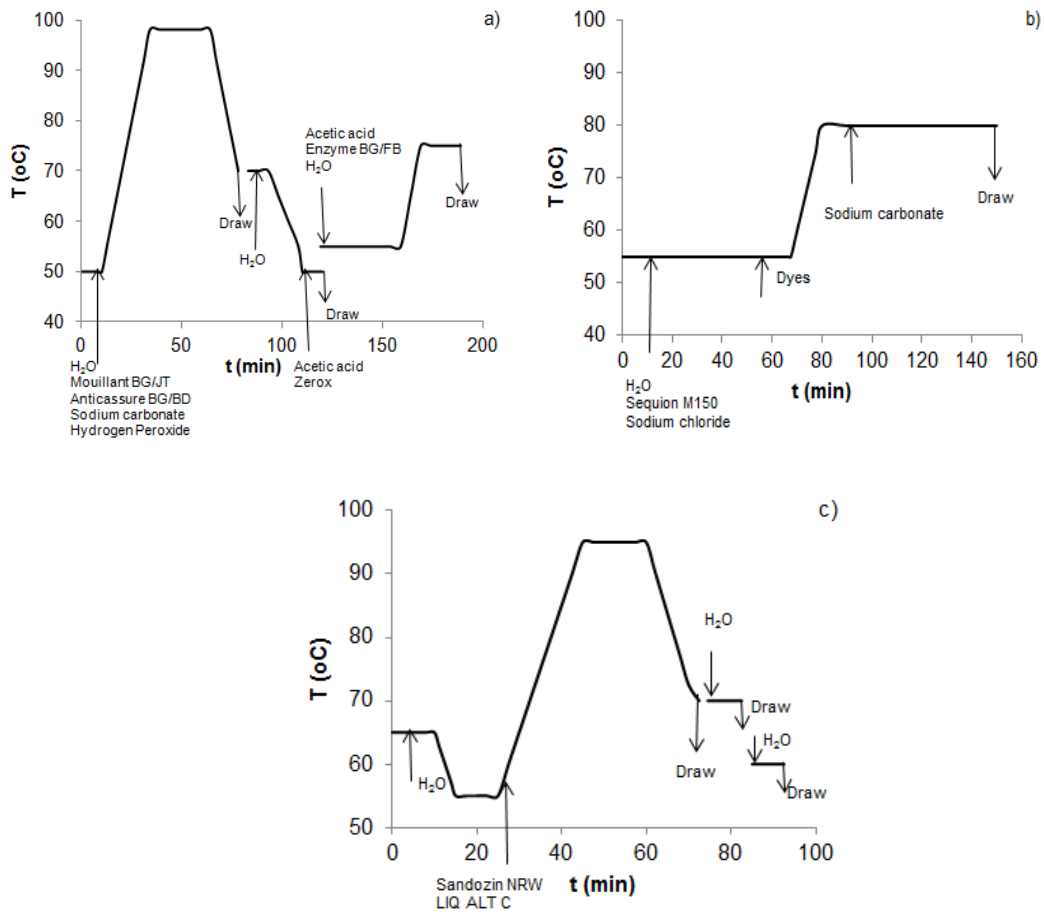


Figure 3.3 – Scheme of cotton fibers dyeing: a) fiber preparation, b) dyeing and c) washing.

The main characteristics of the synthetic effluents are reported in Table 3.4. They are markedly colored, with the exception of the polyester one which exhibits only a very slight yellowish tone, almost imperceptible. Color was measured for the acrylic and cotton effluents at 610 nm and 520 nm, the maximum absorbance wavelengths (λ_{\max}) in the visible range, respectively, as illustrated by the spectrum of each wastewater (cf. Figure 3.4). The polyester and particularly the acrylic effluents present a significant concentration of organic compounds (DOC and COD), and a low biodegradability (BOD₅:COD ratio <0.4) is observed in all effluents. In addition, the acrylic and polyester effluents present high toxicity, as indicated by *Vibrio fischeri* inhibition. The cotton effluent is strongly alkaline and contains a high amount of chlorides.

Table 3.4 - Characteristics of the synthetic textile effluents.

Parameter	Effluent		
	Polyester	Acrylic	Cotton
pH	8.3	6.8	11.4
Conductivity at 20 °C (mS/cm)	2.9	1503.0	23.2
Total suspended solids (mg/L)	21.7	16.0	67.0
Total nitrogen (mg N/L)	15.9	16.4	3.9
Nitrates (mg NO ₃ ⁻ /L)	7.5	15.7	4.25
Total phosphorus (mg P/L)	3.0	0.2	5.9
Dissolved phosphorus (mg P/L)	2.7	< 0.06	0.1
COD – Chemical oxygen demand (mg O ₂ /L)	517.9	828.1	350.0
BOD ₅ – Biochemical oxygen demand (mg O ₂ /L)	130.7	< 1.0	77.5
DOC – Dissolved organic carbon (mg C/L)	143.1	334.1	117.5
Sulfates (mg/L)	885.8	598.0	41.0
Chlorides (mg Cl ⁻ /L)	17.3	44.1	7981.8
Alkalinity (mg CaCO ₃ /L)	774.4	51.8	4425.0
SOUR – Specific oxygen uptake rate (k') (mg O ₂ /(g _{VSS} .h))	27.0	< 0.2	5.6
BOD ₅ :COD ratio	0.26	< 0.0012	0.22
Absorbance at λ_{\max} (a.u.)	---	1.592	0.437
Visible color after dilution 1:40	not visible	visible	Visible
<i>Vibro fischeri</i> Inhibition 5 min (%)	74.5	94.0	0.0
<i>Vibro fischeri</i> Inhibition 15 min (%)	82.5	96.0	0.0
<i>Vibro fischeri</i> Inhibition 30 min (%)	84.5	97.0	0.0

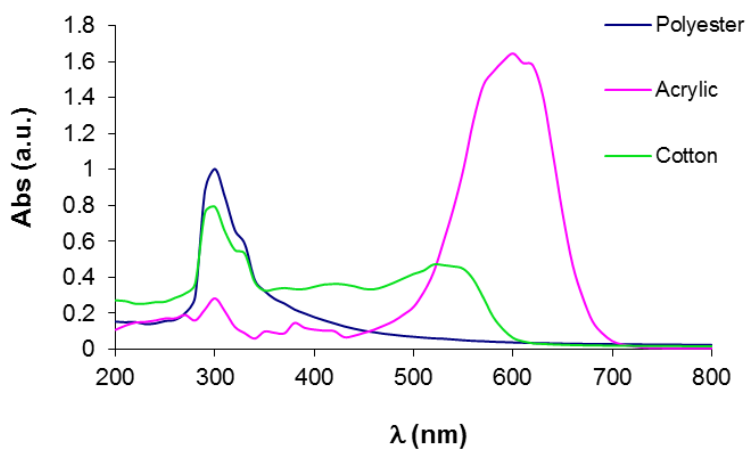


Figure 3.4 – UV/visible spectrum for the simulated polyester, acrylic and cotton wastewaters.

3.2.2 Real Cotton Dyeing Wastewater

The real cotton dyeing wastewater mentioned in chapter 11 was collected from the equalization tank of a dye-house located in Barcelos, Portugal. The respective characterization data are shown in Table 3.5. The effluent presents blue color, resulting from the mixture of diverse reactive dyes, moderate DOC and COD values, high pH, alkalinity, conductivity and total nitrogen, low biodegradability ($BOD_5:COD < 0.4$ and small value of k' - specific oxygen uptake rate) and strong inhibition of *Vibrio fischeri*.

The UV-visible absorbance spectrum of the cotton dyeing wastewater is presented in Figure 3.5. The peak of absorbance in the UV region (at 280 nm) indicates the presence of aromatic compounds and the maximum absorbance peak in the visible region observed at 600 nm is associated with the blue color of the effluent.

Table 3.5 - Characteristics of the real cotton dyeing wastewater.

Parameter	Real wastewater
pH	10.0
T (°C)	35.6
TSS (mg/L)	38.0
Conductivity at 20 °C (mS/cm)	11.5
Total nitrogen (mg N/L)	1064.4
Nitrates (mg NO ₃ ²⁻ /L)	0.008
Total phosphorus (mg P/L)	4.2
Dissolved phosphorus (mg P/L)	0.06
Chemical oxygen demand (mg O ₂ /L)	495.0
Biochemical oxygen demand (mg O ₂ /L)	127.5
Dissolved organic carbon (mg C/L)	174.7
Chlorides (mg Cl ⁻ /L)	1241.5
Sulfates (mg SO ₄ ²⁻ /L)	0.23
Alkalinity (mg CaCO ₃ /L)	456.8
Specific oxygen uptake rate (k') (mg O ₂ /(g _{vss} h))	8.85
BOD ₅ :COD ratio	0.26
Absorbance at 600 nm (abs. units)	1.0251
Visible color after dilution 1:40	Visible
<i>Vibro fischeri</i> Inhibition 5 min (%)	81.1
<i>Vibro fischeri</i> Inhibition 15 min (%)	70.4
<i>Vibro fischeri</i> Inhibition 30 min (%)	70.5

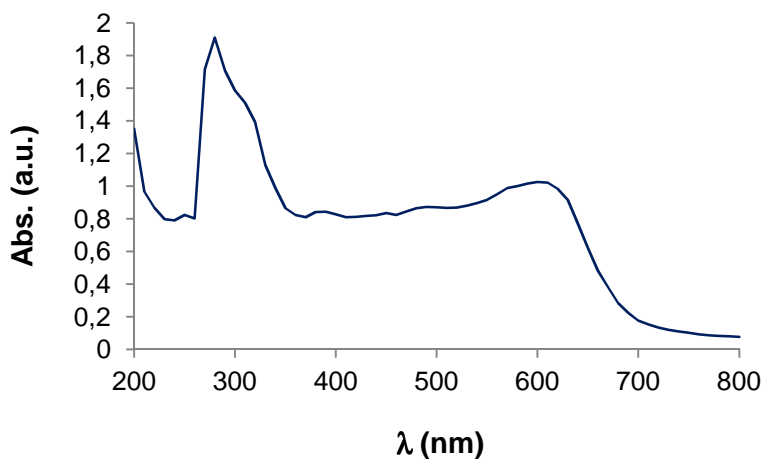


Figure 3.5 – UV-visible spectrum of the real cotton dyeing wastewater.

3.3 Analytical Methods

Along this thesis various analytical determinations were performed. A brief description of the analytical methods used is given below.

3.3.1 Alkalinity

The alkalinity was evaluated by titration with H_2SO_4 at pH 4.5 (Method 2320 D) [APHA, 1998].

3.3.2 Biodegradability

The biodegradability was assessed by respirometry, measuring the oxygen uptake rate (k) at 20 °C. First, the samples were inoculated with biomass from the activated sludge tank of a wastewater treatment plant (WWTP) treating textile effluents (Rabada – Santo Tirso), and the concentration of dissolved oxygen was recorded for thirty minutes (a linear decrease was always observed in this period) using an YSI Model 5300 B biological oxygen monitor. The specific oxygen uptake rate (SOUR or k') was calculated by dividing the decay rate of the dissolved oxygen ($\text{mg O}_2/\text{L}\cdot\text{h}$) by the volatile suspended solids concentration after the addition of the inoculum (625-725 mg VSS/L) [Ramalho, 1977; APHA, 1998].

3.3.3 Biochemical Oxygen Demand

The biochemical oxygen demand (BOD_5) quantifies the biodegradable organic matter. It was determined according to the procedure described in Method 5210 B [APHA, 1998]. This method is based on the difference between the initial and final (after 5 days incubation at 20 °C - oven Memmert, Model 854 Schwabach) dissolved oxygen concentration (assessed with a Crison OXI 45 meter and the electrode WTW CellOx 325). The quantification of BOD_5 of wastewaters usually requires a previous dilution of the sample.

3.3.4 Chemical Oxygen Demand

The determination of the COD was performed according to method 5220 B [APHA, 1998], which quantifies the $K_2Cr_2O_7$ reduction by oxidizable organic and inorganic compounds in an open reflux digester (G.VITTADINI Record/6Test digester), at 150 °C for 2 hours. The remaining dichromate was determined by titration with ammonium iron sulphate. COD was also determined by the closed reflux method (Method 5220 D [APHA, 1998]), at 150 °C (Thermoreactor TR 300 from Merck) for 2 hours, then measuring the absorbance (Spectroquant Nova 60) corresponding to the reduced chromium.

The samples with concentrations of chlorides higher than the maximum permissible by the method (2000 mg/L), such as the simulated cotton effluent, were firstly diluted.

3.3.5 Chlorides, Dissolved Phosphorus, Nitrates and Sulfates

Chlorides, nitrates, dissolved phosphorus and sulfates were measured by ion chromatography (Dionex DX 120) using a Dionex Ionpac AS9-HC 4 mm (10-32) column and sodium carbonate 9 mM as eluent – Method 4110 B [APHA, 1998].

3.3.6 Color

The color of the samples was quantified by measuring the absorbance at the wavelength of maximum absorbance (520, 600 and 610 nm for synthetic cotton, real cotton and synthetic acrylic effluents, respectively), using a molecular absorption spectrophotometer (Pye Unicam, model Helios α). As the absorbance of the wastewaters varies with pH, the pH in the treated effluent was adjusted to the initial value, whenever necessary, before absorbance measurement.

To evaluate de compliance with the discharge limit as defined in Ordinance No. 423/97 of 25 June, the samples were diluted 40 times and visually checked the presence or absence of color.

3.3.7 Conductivity

The conductivity at 20 °C was determined using a conductivity probe (WTW TetraCon 325) and a conductivity meter (WTW LF538) - Method 2510 B [APHA, 1998].

3.3.8 Dissolved Iron

The dissolved iron was determined by the atomic absorption spectrometry-flame method (AAS GBC model 932 AB Plus) - Method 3111 B [APHA, 1998], after filtration of the samples through cellulose nitrate membranes (Albeit) with pore size of 0.45 µm.

3.3.9 Dissolved Oxygen Carbon

The DOC of the samples was obtained, after filtration through nylon filter membranes with pore diameter of 0.45 µm, by catalytic oxidation at 680 °C using a 5000 A - Shimadzu Total Carbon analyzer, followed by quantification of the CO₂ formed by infra-red spectrometry as described in Method 5310 D [APHA, 1998]. DOC was calculated as the difference between the total dissolved carbon (TDC) and the inorganic carbon (IC) in the liquid sample.

3.3.10 Hydrogen Peroxide

The quantification of the hydrogen peroxide was performed as described by Sellers [1980]. The method is based on the measurement of the intensity of the yellow-orange color resulting from the reaction of hydrogen peroxide with titanium oxalate. The samples were previously filtered through nylon filter membranes with pore diameter of 0.45 µm.

3.3.11 Inhibition of *Vibrio Fischeri*

The inhibition test of bacterium *Vibrio fischeri* was performed according to the standard DIN/EN/ISO 11348-3 [International Organization for Standardization, 2005]. The samples

were added to *V. fischeri* culture medium at 15 °C and the bioluminescence was measured after 5, 15 and 30 minutes in a Microtox Model 500 analyzer. The samples were first neutralized to pH ~ 7 with HCl or NaOH 1N.

3.3.12 pH

The pH was measured with a combined electrode (Hanna Instruments HI 1230) connected to a pH-meter (Hanna Instruments HI 8424)- Method 4500 H⁺ B [APHA, 1998].

3.3.13 Total Nitrogen

Total nitrogen was quantified by potassium persulfate digestion (Method 4500 N. C [APHA, 1998]), which converts organic nitrogen, ammonia and nitrite into nitrate, with subsequent determination of nitrate by molecular absorption spectrophotometry after reaction with brucine (Method D992-71 of ASTM [1973]).

3.3.14 Total Phosphorus

The total phosphorus was quantified by measuring the intensity of blue color resulting from the reaction of orthophosphate with ascorbic acid, after acid digestion with ammonium persulfate to convert all phosphorus into orthophosphate (Method 4500 P. E [APHA, 1998]).

3.3.15 Total Suspended Solids and Volatile Suspended Solids

Total suspended solids (TSS) and volatile suspended solids (VSS) were evaluated by gravimetry - Method 2540 B and Method 2540 E [APHA, 1998], respectively.

3.3.16 HPLC Analyses

For the high performance liquid chromatography (HPLC) analyses (in a VWR chromatograph, Elite Lachrom model) of the intermediates formed during oxidation, a Purospher Star RP-18 (5 μm) column was used, at a temperature of 30 $^{\circ}\text{C}$, with a mixture of acetonitrile (A) and water (W) as eluent, flow rate of 1 mL/min in gradient mode (at $t=0$ min, 30% of A and 70% of W, $t=20$ min, 63% of A and 37% of W, $t=22$ min, 63% of A and 37% of W, $t=23$ min, 30% of A and 70% of W and $t=30$ min, 30% of A and 70% of W). The peak amplitude was measured with a diode array detector (DAD) (at 254 nm for acrylic effluent and 200 nm for polyester effluent).

3.3.17 Zahn-Wellens Test

The Zahn–Wellens test was performed according to method 302B of OECD [1992]. A volume of 250 mL of wastewater was added to an open glass vessel, magnetically stirred (Velp Scientifica model Multi15 Stirrer) and kept in the dark inside a thermostatic refrigerator (PSelecta model HOTCOLD - M) at 25 $^{\circ}\text{C}$. Then 0.25 g of activated sludge from the aeration tank of a WWTP treating textile effluents (Rabada, Santo Tirso), previously centrifuged, and mineral nutrients (KH_2PO_4 , K_2HPO_4 , Na_2HPO_4 , NH_4Cl , CaCl_2 , MgSO_4 and FeCl_3) were added to the samples. The control and blank experiments were prepared substituting the effluent by lauryl sulfonate (0.2 g/L) and distilled water, respectively. The percentage of biodegradation (D_t) was determined by Equation 3.1:

$$D_t = \left[1 - \frac{C_t - C_B}{C_A - C_{BA}} \right] * 100 \quad (3.1)$$

where C_A and C_{BA} are the DOC concentrations (mg/L) of the mixture and blank, measured 3 h after the beginning of the experiment, C_t and C_B are the DOC (mg/L) of the mixture and blank, measured at the sampling time t .

3.4 Experimental Procedure

3.4.1 Coagulation/Flocculation

The coagulation/flocculation experiments were carried out in a Jar-test apparatus (Isco) (Figure 3.6). A volume of 300-500 mL of effluent was used and the pH adjusted using NaOH (1 or 10 N) or H₂SO₄ (1 N), depending on the pH required for the coagulation stage and on the effluent natural pH. A high stirring speed (which was varied in the parametric studies in the range 100-200 rpm, corresponding to a velocity gradient, G , between 237 and 669 s⁻¹) was then promoted and the coagulant (FeSO₄·7H₂O – Merck, 99% of purity – or Fe₃(SO₄)₂ – Rieden Häen, 99% of purity) added. Immediately after this, the pH was readjusted (if necessary) and the agitation was prolonged for the intended time ($t_{\text{coagulation}}$). After the coagulation, the flocculant was added just before the beginning of the slow stirring stage (20-50 rpm, corresponding to a velocity gradient between 21 and 84 s⁻¹). This stage proceeded for a given time ($t_{\text{flocculation}} = 15\text{-}45$ minutes) in order to facilitate the flocs aggregation for an easier sedimentation. The experiments were performed at controlled temperature by placing the Jar-test apparatus (VELP P4) inside a thermostated chamber (Velp Scientifica FOC 225E), the addition of the coagulant being done only after temperature stabilization.

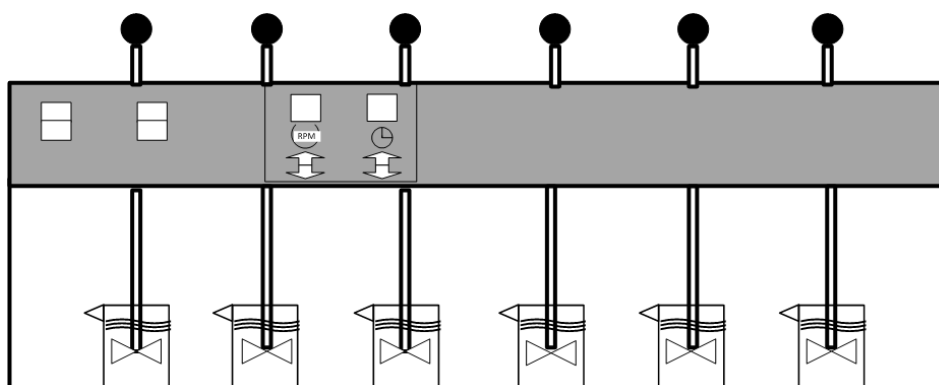


Figure 3.6 – Diagram of the Jar-test set-up.

3.4.2 Fenton's Reaction

Fenton's oxidation was carried out in an 1 L-capacity jacketed batch reactor connected to a thermostatic bath (Grant Y6) for water circulation (Figure 3.7), in order to maintain the temperature inside the reactor at the desired value.

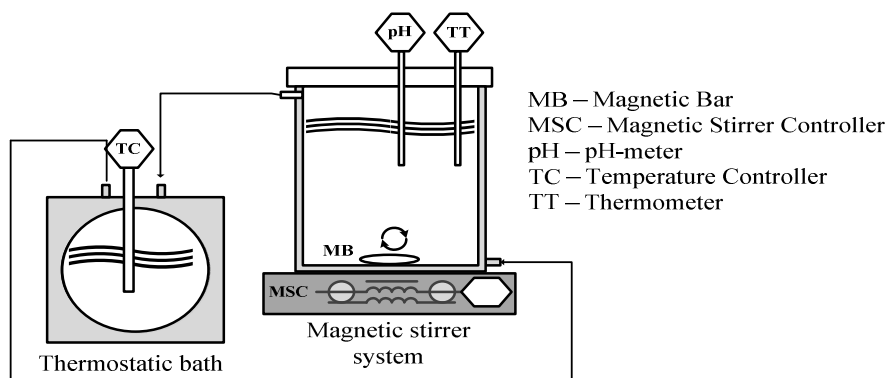


Figure 3.7 – Diagram of the Fenton's oxidation set-up.

In all runs, 500 mL of raw wastewater or pre-treated effluent was loaded into the reactor and after temperature stabilization, the pH was adjusted to a predefined value with 1 N H_2SO_4 or 1 or 10 N NaOH. When required, ferrous sulfate heptahydrate was added and the reaction started with the addition of H_2O_2 , 30% (w/v). All reagents were from Merck, analytical grade.

The oxidation reaction proceeded under constant stirring, using a magnetic bar and a stir plate (Falc). Periodically, samples were taken from the reactor and the reaction stopped in the flasks by the addition of large excess sodium sulfite (that reacts instantaneously with remaining hydrogen peroxide) for measuring the dissolved organic carbon (DOC) as described above. As regards other parameters, namely chemical oxygen demand (COD), biochemical oxygen demand after 5 days (BOD_5), pH, color, specific oxygen uptake rate (SOUR or k') and toxicity (inhibition of *Vibrio fischeri*), the reaction was stopped by eliminating the residual H_2O_2 and by precipitation of the iron catalyst. For that, the pH of the final effluent was raised to 12.3 by addition of 10 N NaOH, the sample was heated at 80 °C for 10 minutes and finally neutralized (to pH ~7.0) with conc. H_2SO_4 . The samples for toxicity assessment were neutralized with HCl 1N, instead of H_2SO_4 , as proposed by

the analytical methodology. In this case sodium sulfite was not used because it leads to deactivation of *V. fischeri* and consequently to a decay in the luminescence.

The supernatant resulting from the Fenton's oxidation was acidified to pH 1 with conc. HNO_3 to ensure that the iron was kept dissolved for the subsequent stage of coagulation/flocculation. The analyses of the effluent were performed immediately.

3.4.3 Photo-Fenton Oxidation

3.4.3.1 Photo-Fenton with Artificial Radiation

The tests took place in a closed cylindrical reactor of 1-liter capacity, which was loaded with 800 ml of effluent to be treated. The reactor was equipped with a UV/visible lamp (150 W high pressure mercury vapor - Heraeus TQ 150, corresponding to 500 W/m^2 - which emits UV/visible radiation at wavelengths from 200 to $\sim 600 \text{ nm}$), located axially inside a dip immersion quartz tube (cf. Figure 3.8). The jacketed quartz tube was connected to a thermostatic bath (GRANT Y6) for temperature control through water recirculation. The reactor was also provided with a magnetic stir plate (Falc).

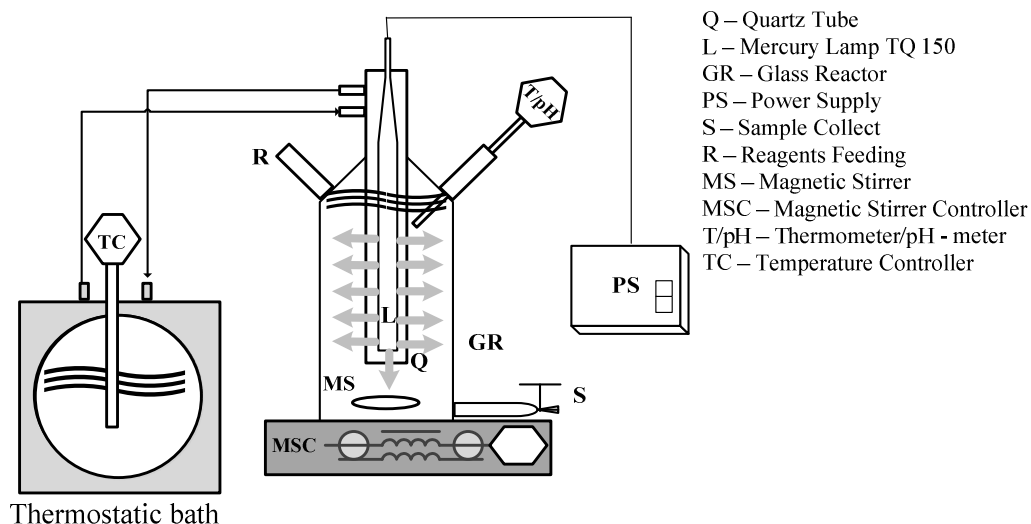


Figure 3.8 – Diagram of the photo-Fenton set-up with mercury lamp TQ 150.

In runs using artificial radiation, the reactor was loaded with 800 ml of effluent to be treated. After the effluent reached the desired temperature, the pH was adjusted to the established value with 1N H₂SO₄. In the case of direct photolysis experiments, the lamp was then connected, and samples collected at pre-established periods to measure the absorbance and dissolved organic carbon (DOC). In runs where one intended to combine UV/Vis radiation with H₂O₂ (30% w/v from Merck), the mercury lamp was switched on at the same time that the reagent (H₂O₂) was added. In this case, before analyzing the samples, the remaining hydrogen peroxide was removed by the addition of large excess of sodium sulfite (six times the stoichiometric value corresponding to the amount of hydrogen peroxide added at the beginning of the test).

In photo-Fenton experiments, the adopted procedure was basically the same, with one intermediate step for adding ferrous sulfate heptahydrate (Merck) before turning on the lamp and adding hydrogen peroxide. Again, hydrogen peroxide was eliminated from the samples taken throughout the reaction by adding sodium sulfite, before DOC and the absorbance measurement. In the samples collected after 60 minutes of reaction for the subsequent determination of COD and BOD₅, the reaction was stopped by raising the pH to 12.3 with the addition of 10 M NaOH (from Merck), heating the samples at 80 °C for 10 minutes and neutralizing with concentrated H₂SO₄ until pH ~ 7.0; this procedure was adopted because sodium sulfite interferes with those analytical determinations.

In photo-Fenton tests the light flux that reached the wastewater was varied by circulating, in the jacket of the quartz tube, a solution of dye Solophenyl Green BLE 155% at different concentrations, as described by Silva and Faria [2009]. These concentrations have been previously determined by potassium ferrioxalate actinometry [Kuhn et al., 2004]. Figure 3.9 shows the variation of the radiation intensity (measured with a Kipp & Zonen B.V., model CUV 5 UV radiometer, and a Delta OHM, model D9221 visible radiometer - placed outside the reactor and at mid-height of the dip immersion quartz tube) that reaches the solution to be treated as a function of the dye concentration in the solution circulating in the jacket.

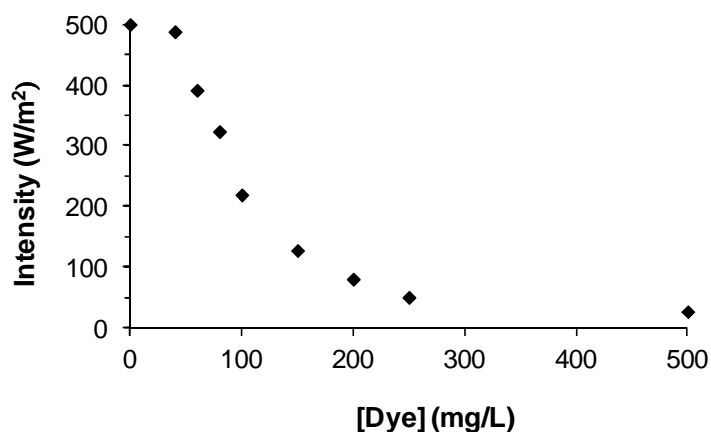


Figure 3.9 - Variation of the radiation intensity with the Solophenyl Green BLE 155% concentration circulating in the photo-reactor jacket.

3.4.3.2 Photo-Fenton using Simulated Solar Radiation

The photoreactor using simulated solar radiation actually comprises two reactors (Figure 3.10): i) an 1-liter capacity closed cylindrical reactor equipped with a jacket for water recirculation from a thermostatic bath (RW-0525G the Lab Companion) for temperature control and ii) a tubular reactor (volume of ~ 0.78 L, 100% volume irradiated) placed inside the Solarbox (ATLAS, model SUNTEST XLS+). The Solarbox has a Xenon lamp of 1700 W that emits radiation at wavelengths from 300 to 800 nm.

In runs with simulated solar radiation the cylindrical reactor was fed with 800 mL of effluent and the pH adjusted to the predefined value with 1 N H₂SO₄. The solution was continuously pumped to the tubular reactor and recirculated back into the cylindrical one (with the aid of a peristaltic pump - Ecoline VC-380 II Ismatec), at a flow rate of 0.65 L/min (~ 0.12 min residence time in the tubular reactor). After reaching the desired temperature, heptahydrated ferrous sulfate (Merck) and hydrogen peroxide (30% w/v – Merck) were added to the cylindrical reactor. Then the lamp was switched on. During the reaction the cylindrical reactor contents were stirred by a magnetic bar and stir plate (Velp Scientifica, model ARE).

Samples were taken at pre-defined times and the reaction was stopped as described in the previous section for dark Fenton experiments. The radiation intensity in the range 300

- 400 nm was measured in the tubular reactor by an UV radiometer (Kipp & Zonen B.V., model CUV 5).

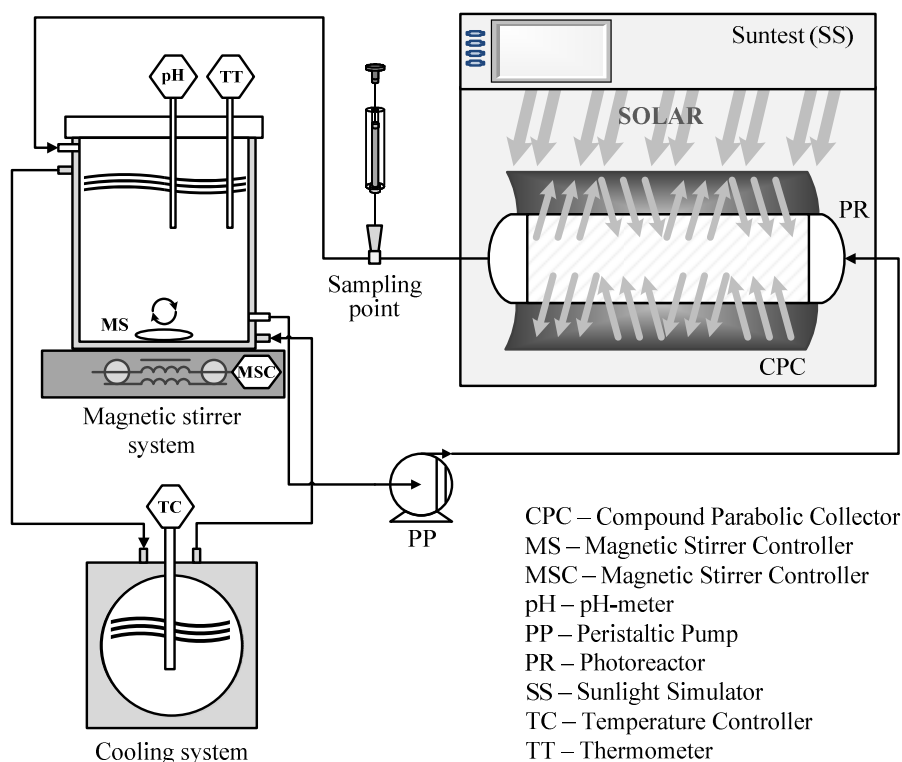


Figure 3.10 – Diagram of the sun-test set-up.

3.4.4 Biological Oxidation in Sequencing Batch Reactor

The SBR is a jacketed cylinder (20 cm internal diameter, 45 cm total height and 30° slope conical bottom; effective working volume = 5.0 L) connected to a thermostatic bath (Isco GTR 90, from Italy). Figure 3.11 shows the installation set-up. The biological reactor was operated at constant temperature (25 °C) during 12 hours per cycle (1 h feeding, 6 h reaction, 4 h sedimentation, 0.8 h discharge and 0.2 h idle), up to 10 cycles (i.e., when the parameters analysed in the treated effluent and described below showed nearly constant values from cycle to cycle – pseudo steady-state conditions). In the first cycle the reactor was fed with 2.5 L of wastewater with pH previously adjusted to ~7.0 using 1M H₂SO₄ and 10 M NaOH, after adding phosphorus (as phosphate buffer) or nitrogen (as urea) whenever necessary to ensure the minimum quantity required for biological treatment

(BOD₅:N:P ratio of 100:5:1). Then 2.5 L of activated sludge (~ 5 g VSS/L) from the aeration tank of the Rabada WWTP (Santo Tirso - Portugal) were added to the reactor, resulting in a final volume of 5.0 L. In subsequent cycles the reactor was fed with 2.5 L of effluent to compensate the amount of treated effluent discharged. During the reaction stage, a mechanical stirrer was employed (stirring rate = 400 rpm) and the dissolved oxygen content was maintained at 3.0±1.3 mg O₂/L by aeration using air diffusers.

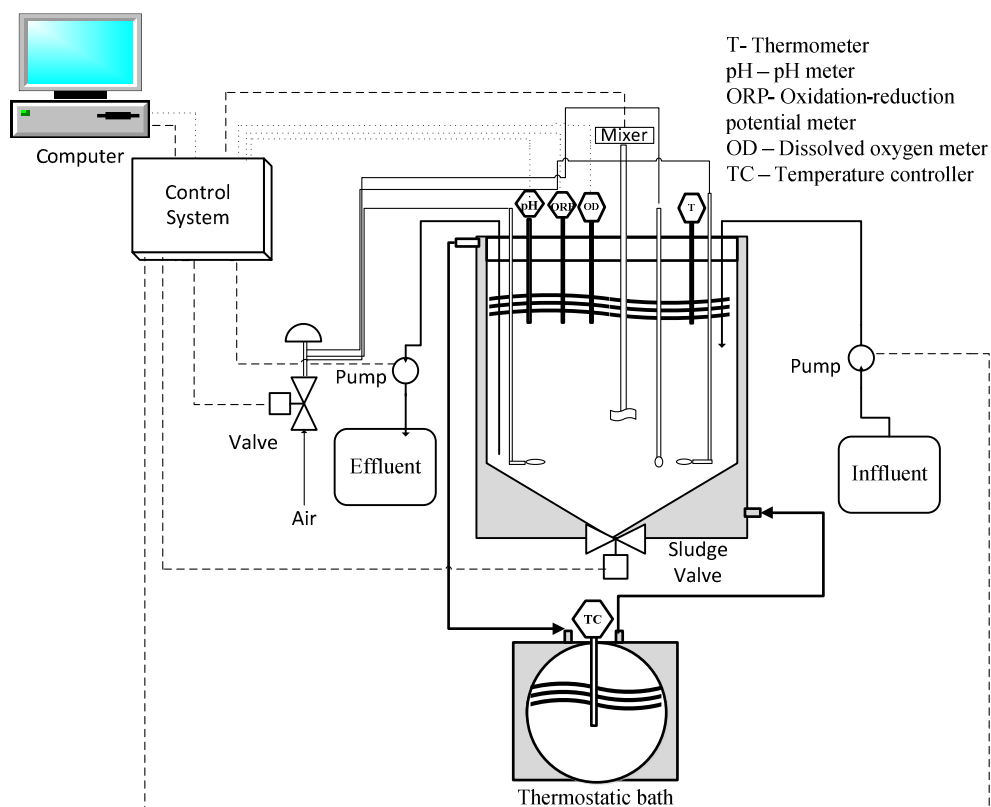


Figure 3.11 – Diagram of the SBR set-up.

The values of temperature, dissolved oxygen and duration of each cycle and each cycle stage were established in accordance with literature [U.S. EPA, 1999; Lourenço et al., 2001; Gray, 2004; García-Montaño et al., 2006; Sirianuntapiboon et al, 2006; Çinar et al., 2008; Rodrigues et al., 2009].

The pH (electrode HI 1332 and pH-meter HI 8720E from Hanna Instruments, Italy), temperature (thermocouple type K) and ORP (electrode HI 3230 and mV-meter HI 8711E from Hanna Instruments, Italy) were continuously monitored (cf. Figure 3.11). At the end of each cycle, the total suspended solids (TSS), biological oxygen demand (BOD₅), chemical oxygen demand (COD), dissolved organic carbon (DOC), absorbance at a predefined wavelength (which depends on the effluent to be treated), total nitrogen and total phosphorus were determined in the effluent discharged, as detailed in the previous sections. The content of volatile suspended solids (VSS) was measured, in some cycles, in samples collected inside the reactor.

The data acquisition and the automatic control of the unit, i.e., operation of the peristaltic pumps (Watson-Marlow 502S, England), Burckert valve (from Germany) and mechanical stirrer (VWR VOS power control, Germany), were achieved by using the software Labview 5.0 (National Instruments), through a home-built interface.

3.5 References

APHA, AWWA, WEF (1998). Standard Methods for the Examination of Water and Wastewater. 20th Ed., American Public Health Association/American Water Works Association/Water Environment Federation, Washington DC, USA.

Annual Book of ASTM Standards (1973). Water; Atmospheric Analysis. Part 23, American Society for Testing and Materials, Philadelphia.

Çinar, Ö., Yaşar, S.; Kertmen, M.; Demiröz, K.; Yigit, N.Ö., Kitis, MM. (2008). Effect of cycle time on biodegradation of azo dye in sequencing batch reactor. *Process Safety and Environmental Protection*, 86, 455-460.

García-Montaño, J.; Torrades, F.; García-Hortal, J.A.; Domènech; X.; Peral, J. (2006). Degradation of Procion Red H-E7B reactive dye by coupling a photo-fenton system with sequencing batch reactor. *Journal of Hazardous Materials*, B134, 220-229.

Gray, N. F. (2004), *Biology of wastewater treatment*, second edition, Imperial College Press, London.

International Organization for Standardization (2005). *Water Quality - Determination of the Inhibitory Effect of Water Samples on the Light Emission of Vibrio Fischeri (luminescent Bacteria Test) - Part 3: Method Using Freeze-dried Bacteria*.

Kuhn, H.J.; Braslavsky, S.E.; Schmidt, R. (2004). *Chemical Actinometry*. *Pure and Applied Chemistry*, 76 (12), 2105-2146.

Chapter 3 - Materials and Methods

Lourenço, N.D.; Novais, J.M.; Pinheiro, H.M. (2001). Effect of some operational parameters on textile dye biodegradation in sequential batch reactor. *Biotechnology*, 89, 163-174.

OECD (1992). Test No. 302B: Inherent Biodegradability: Zahn–Wellens/EMPA Test in: OECD Guidelines for the Testing of Chemicals. OECD Publishing.

Ramalho, R.S. (1977). *Introduction to Wastewater Treatment Processes*. Academic Press, New York, USA.

Rodrigues, C.S.D.; Madeira, L.M.; Boaventura, R.A.R. (2009). Treatment of textile effluent by chemical (Fenton's Reagent) and biological (Sequencing Batch Reactor) oxidation. *Journal of Hazardous Materials*, 172, 1551-1559.

Sellers, R.M. (1980). Spectrophotometric determination of hydrogen peroxide using potassium titanium (IV) oxalate, *Analyst*, 105, 950-954.

Silva, C. G.; Faria, J. L. (2009). Effect of key operational parameters on the photocatalytic oxidation of phenol by nanocrystalline sol–gel TiO₂ under UV irradiation. *Journal of Molecular Catalysis A: Chemical*, 305, 147-154.

Sirianuntapiboon, S.; Chairattanawan, K.; Jungphongsukpanich, S. (2006). Some properties of a sequencing batch reactor system for removal of a vat dyes. *Bioresource Technology*, 97, 1243-1252.

U.S. EPA (1999). *Wastewater, Technology Fact Sheet: Sequencing Batch Reactors*. U.S. Environmental Protection Agency, Office of Water. Washington, D.C., EPA 932-F-99-073.



Part III

Simulated Dyeing Wastewaters Treatment

Chapter 4

Coagulation/Flocculation with Fe^{2+} as Coagulant *

* This Chapter is based on the publication "Rodrigues C.S.D.; Madeira, L.M.; Boaventura, R.A.R. (2013). Treatment of Textile Dye Wastewaters using Ferrous Sulphate in a Chemical Coagulation/Flocculation Process. *Environmental Technology*, 34 (6), 719-729."

4 Coagulation/Flocculation with Fe²⁺ as Coagulant

4.1 Introduction

The present chapter focuses on determining the best operating conditions for the coagulation/flocculation process using iron (II) as coagulant to treat different types of synthetic textile wastewaters simulating cotton, acrylic and polyester dyeing. It is evaluated the effect of stirring speed, contact time, temperature, pH and doses of coagulant (ferrous sulphate) and flocculants (Magnafloc 155 or Superfloc C-573) in color and dissolved organic carbon (DOC) removal from the wastewaters. The selected flocculants are commonly employed in the treatment of textile dyeing wastewaters. However, the use of an iron salt as coagulant is related to the possibility of integrating the coagulation/flocculation process with a subsequent Fenton-like oxidation treatment in which the soluble remaining iron is used as catalyst, thus decreasing the overall consumption of chemicals. The use of the soluble iron resulting from the coagulation/flocculation in the partial mineralization of organic compounds by such oxidation treatment is addressed in chapters 6-8.

4.2 Materials and Methods

4.2.1 Preparation of Simulated Textile Wastewaters

The simulated effluents were prepared as described in section 3.2 of chapter 3 and the main characteristics of the synthetic effluents are reported in Table 3.4 (cf. section 3.2.1).

4.2.2 Coagulation/Flocculation Experiments

The experimental procedure concerning the coagulation/flocculation experiments was described in section 3.4.1 – Materials and Methods.

The effluent pre-treated by coagulation employing the optimal conditions was then subjected to flocculation experiments. Magnafloc, an anionic polyacrylamide (molecular weight around 5×10^6 , density $\sim 750 \text{ kg/m}^3$, incolor solid) and Superfloc C-573, a cationic

polyamine (molecular weight around 10^4 , density 1.14-1.18 kg/m^3 , yellow liquid), were tested as flocculants, since they have been considered as suitable polymers to treat this kind of wastewaters.

The samples of supernatant were collected after 30 minutes of sedimentation and the dissolved organic carbon (DOC) determined immediately (despite DOC values in the supernatant of the same samples analysed after 24 h of sedimentation were identical to those obtained after 30 minutes). The absorbance was, however, read after one day of sedimentation to minimize the number of very small particles of iron hydroxide in suspension. Moreover, the supernatant sample for color measurement was centrifuged (Mini Spin Eppendorf) at 13400 rpm for 2 minutes.

4.2.3 Analytical Methods

The experimental methods used in this study were already mentioned in section 3.3 of Chapter 3.

The parameters were measured in duplicate and the variation coefficients were less than 2% for DOC, < 1% for absorbance, < 9% for BOD_5 and < 3% for the other parameters.

4.3 Results and Discussion

In this chapter are reported experiments carried out to determine the effect of stirring rate and time on the color and DOC removal during the coagulation process. However, these variables were not very effective, as shown below from the results obtained for the polyester and cotton effluents. Further, the effect of other more relevant operating conditions as temperature, pH and ferrous salt concentration on the color and DOC removal efficiency was analyzed for the three effluents.

The same approach was adopted for the flocculation stage after being submitted to coagulation at the optimal conditions. Thus, the influence of stirring speed and time is discussed for two effluents, but other more significant variables (flocculant type and concentration) are analyzed in further detail for all effluents.

4.3.1 Effect of Stirring Speed and Time on the Coagulation Stage

The stirring rate in the coagulation stage should be high and according to previous workers values around 100 rpm were proposed [Satterfield, 2004; Bose, 2010; Poland and Pagano, 2010]. Thus, experiments were performed changing this variable in the range 100 - 200 rpm (G between 237 and 669 s^{-1}) for cotton and polyester effluents. Values from 1 minute to 3 minutes [Eckenfelder, 2000; Bose, 2010; Poland and Pagano, 2010] have been proposed for the duration of this initial stage. To study the effect of this variable, the stirring time ($t_{\text{coagulation}}$) was varied between 1 to 5 minutes. It was found that both variables do not affect the color or the DOC removal for both effluents (cf. Appendix - Figures. A1 and A2). DOC removals were ~27% and ~30% for the polyester and cotton effluents, respectively. Around 74% of color removal was obtained for the cotton effluent whatever the stirring rate and time (the polyester is colorless). These results allow concluding that these variables, stirring rate and time, do not play an important role in the coagulation stage.

4.3.2 Effect of the Temperature on the Coagulation Stage

In this study the effect of temperature in the coagulation process was analyzed; although it has not been commonly investigated in the open literature, Edeline [1992] reported the temperature as being a variable to take into account. Thus, the temperature was varied between 15 and 50 °C while the previous variables were fixed at $v_{\text{coagulation}} = 150$ rpm ($G = 435$ s^{-1}) and $t_{\text{coagulation}} = 3$ min.

Figure 4.1 shows that for the polyester wastewater, the DOC removal is almost independent of temperature, remaining nearly constant (~27%) in the studied range; the same applies with the cotton effluent. In the acrylic wastewater a slight increase is noticed in the temperature range from 15 to 22 °C, then remaining nearly constant. Removal of organic carbon is higher in the cotton and lower in the acrylic compared to the polyester effluent. The effect of temperature on color removal is much more marked, increasing from 11.4% and 4.7% at 15 °C up to ~74% and ~32% at 22 °C for cotton and acrylic wastewaters, respectively, but performance is no further improved at 50 °C (Figure 4.1 b). Thus, subsequent runs were performed at room temperature. The increased performance with temperature may be a consequence of the improved kinetics as occurs in most

chemical reactions (Arrhenius dependency). The effect of temperature on coagulation has been analyzed by Duan and Gregory [2003], indicating that at lower temperatures the coagulation with hydrolyzing metals is less efficient. Temperature effects may be due to physical or chemical factors, where physically the temperature affects the viscosity and consequently the transport or collision rates. On the other hand, the chemical influence is on the level of hydrolysis reactions, precipitation and solubility of the metal hydroxide.

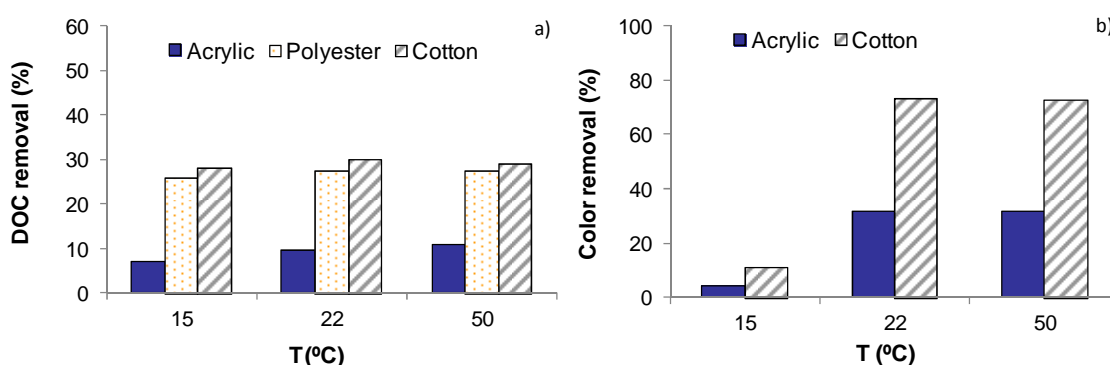


Figure 4.1 – Variation of DOC (a) and color (b) removals with temperature in the coagulation stage for the different simulated effluents ($v_{\text{coagulation}}=150$ rpm, $t_{\text{coagulation}}=3$ min, $[Fe^{2+}]=200$ mg/L and $pH=8.3$).

4.3.3 Effect of the pH on the Coagulation Stage

One of the most important variables in the coagulation process using inorganic salts is the pH. This occurs because the coagulant (iron salt in this case) is converted into different ionic species as the pH value changes thus, influencing the coagulation. In alkaline pH, depending on the redox potential, some iron (II) precipitates as a hydroxide (green rust) capable of absorbing anions because of the presence of positive electrical charges on its surface. However, for $pH < 10$ the predominant iron species are Fe^{2+} (practically the only species for $pH < 7$) and $Fe(OH)^+$. In this work, the pH was changed in the range from 3.5 to 10.4 but in the acrylic effluent experiments a pH above 8.3 was not used because a change of the blue color to light grey was observed.

Figure 4.2 shows that there are optimum pH values for the DOC and color removal which changes from one effluent to another. In general, the optimum pH value is the same for

either DOC or color removal for each wastewater used. It can be summarized that for the polyester effluent there is no DOC removal at all at pH 3.5 or 5, but an optimum exists at pH 8.3 (27.6% removal). For the cotton effluent, a pH of ca. 9.4 led to the greatest DOC and color removals (40.3% and 90.1%, respectively). As for the acrylic effluent, the DOC removal at a pH of 3.5 and 5 was low and the higher removals were observed at a pH of 7.2 (~10% for DOC and 55.3% for color). It is worth mentioning that the optimal pH follow the order of the effluent's natural pH values; acrylic < polyester < cotton (cf. Table 3.4 in section 3.2.1.3).

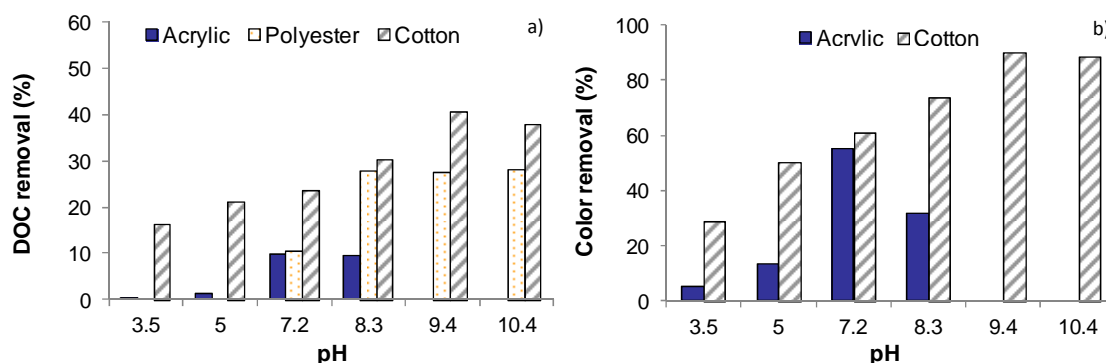


Figure 4.2 – Influence of pH on DOC (a) and color (b) removals by coagulation applied to the different simulated effluents ($v_{\text{coagulation}}=150$ rpm, $t_{\text{coagulation}}=3$ min, $[\text{Fe}^{2+}]=200$ mg/L and $T=T_{\text{ambient}}=22-23$ °C).

The optimum pH values obtained, which will be adopted in the subsequent runs, are close to the values commonly appointed in others studies with the same coagulant for textile effluents, but the optimum pH depends strongly on the nature of the wastewater to be treated. For example, pH values of 5.0 and 6.0 have been reported for white and red wine effluents, respectively [Braz et al., 2010], 7.4 for mechanical pulping effluent coagulation [Stephenson and Duff, 1996], around 8.0 for dairy wastewater [Kushwaha et al., 2010] and cosmetic manufacturing wastewater [Perdigón-Melón et al., 2010], 8.5 for purified terephthalic acid wastewater [Verma et al., 2010] and 9.4 for effluent from personnel care products manufacturing [El-Gohary et al., 2010]. Other authors fixed the pH at 9.0 [Golob et al., 2005] or 9.5 [Selcuk, 2005] for dye containing wastewaters.

4.3.4 Effect of the Coagulant (Fe^{2+}) Concentration

The dose of coagulant necessary for the treatment of effluents by coagulation, and particularly those from textile industries, depends on the characteristics of the wastewaters [Eckenfelder, 2000]. Therefore, it is necessary to evaluate the effect of the coagulant dose (Fe^{2+}), which was herein changed in the range of 15 to 1000 mg/L for polyester and cotton effluents and from 200 to 4000 mg/L for acrylic ones. These ranges were enough to find optimum doses, and the others variables that influence the process were fixed at the optimum values obtained before.

The results of DOC removal (Figure 4.3 a) permitted concluding that for cotton wastewaters, the optimum Fe^{2+} dose is 200 mg/L and higher doses are also not required for reducing the color of such effluents (Figure 4.3 b). For the acrylic, the optimum is shifted towards a much higher coagulant dose; 3000 mg/L for DOC removal while for the color removal it increased up to 500 mg/L and then remained almost unchanged. The higher concentration of Fe^{2+} required is probably a consequence of the higher load of organic matter in this effluent (Table 3.4 in section 3.2.1.3). For the polyester, Figure 4.3 a shows that the DOC removal increases with the Fe^{2+} concentration up to a dosage of 200 mg/L, and that for higher doses the efficiency remains nearly constant. The optimum dose of Fe^{2+} in this case is quite similar to that observed with the cotton effluent, which might be related to the similar organic carbon content of both wastewaters (Table 3.4 of section 3.2.1.3). In the selected conditions, around 90% of color removal was reached for cotton and 65.8% for acrylic, while efficiencies of 40.3%, 17.7% and 27.6% were obtained for DOC removal in cotton, acrylic and polyester effluents, respectively. Other studies report the occurrence of an optimal in coagulant dose for treat wastewaters by chemical coagulation/flocculation [Amokrane et al., 1997 Tatsi et al., 2003].

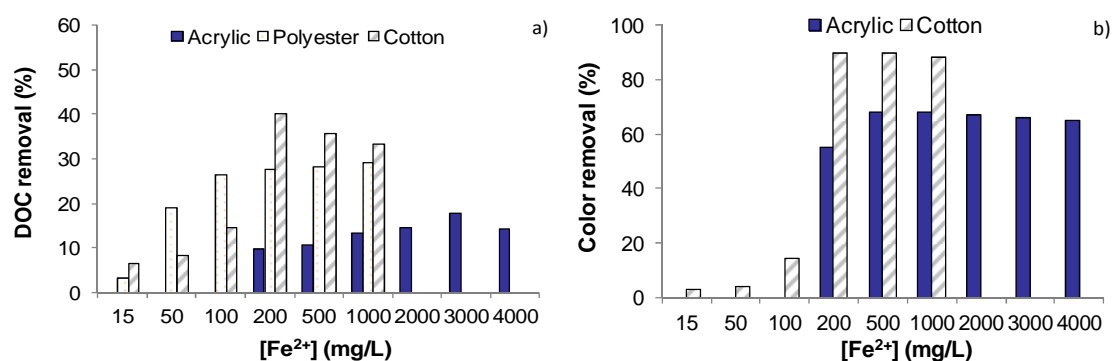


Figure 4.3 – Variation of DOC (a) and color (b) removals with the concentration of coagulant (Fe^{2+}) for the different simulated effluents ($v_{coagulation}=150$ rpm, $t_{coagulation}=3$ min, $T=T_{ambient}=23-25$ °C and $pH_{polyester}=8.3$, $pH_{cotton}=9.4$ and $pH_{acrylic}=7.2$).

Georgious et al. [2003] achieved the best results for color and COD elimination from cotton dyeing wastewater using a combination of lime (800 mg/L) and $FeSO_4 \cdot 7H_2O$ (1000 mg/L). On the other hand, Golob et al. [2005] achieved almost full decolourization of dyebath effluents (cotton/polyamide blends) using 20 mg/L of $FeSO_4 \cdot 7H_2O$ but TOC was only reduced by 25%. In spite of using a ferric salt, Joo et al. [2007] concluded that 3000 mg/L was the required dose for maximizing the color removal and 4000 mg/L for maximizing the COD removal of a reactive dye synthetic wastewater. These and other published data show that the coagulant dose is highly variable, depending on the wastewater characteristics, dye concentration and overall organic content, in agreement with our findings. Additionally, it must be emphasized that excess of coagulant can promote the undesirable stabilization of colloids, which has been observed in different studies [Aziz et al., 2007; Liang et al., 2009].

In the present study, for the acrylic dyeing wastewater, a dose around 500 mg/L should be adequate to maximize the color removal but it was increased to maximize DOC removal (in spite of not exceeding 17.7% without flocculant addition). Of course, for practical purposes other criteria should be also taken into account, namely the extra cost of the coagulant dose, and balanced with the benefit in terms of process performance.

4.3.5 Influence of the Stirring Speed and Time in the Flocculation Stage

Usually the stirring speed in the flocculation stage varies in the range 25-35 rpm [Bose, 2010; Poland and Pagano, 2010] and lasts between 12 and 35 min [Phipps & Bird, 1995; Lafleur, 1997; Eckenfelder, 2000; Bose, 2010; Poland and Pagano, 2010]. For evaluating the effect of stirring speed on the flocculation, this parameter ($v_{\text{flocculation}}$) was varied in the range 20-50 rpm, i.e., G between 21 and 84 s^{-1} (at a fixed time of 15 min and a Magnafloc 155 concentration of 2.5 mg/L). Then, further experiments were performed while changing the flocculation time from 15 to 45 min. With these experiments it was concluded that $v_{\text{flocculation}}$ and $t_{\text{flocculation}}$ do not have any appreciable influence on either color or DOC removal (cf. Figures A.3 and A.4 in Appendix). Therefore, in subsequent experiments these variables were fixed at 20 rpm ($G = 39 s^{-1}$) and 15 min, respectively.

4.3.6 Influence of the Flocculant Type and Dosage

Small dosages of a polyelectrolyte (0.5-3 mg/L and 1-5 mg/L) permit the formation of large flocks and accelerate sedimentation [Grau, 1991; Poland and Pagano, 2010]. Two series of experiments were then performed for each synthetic effluent using two flocculants: Magnafloc 155 (dose in the range 0.25 - 5 mg/L) and Superfloc C-573 (from 0.25 to 5 mg/L for cotton and polyester effluents and from 0.1 to 5 mg/L for the acrylic one) in order to study the influence of the flocculant type and dosage on the flocculation stage.

Figure 4.4 shows that the optimum doses of Magnafloc 155 are as follows: ca. 1 mg/L for polyester and 0.5 mg/L for both cotton and acrylic effluents. The overall DOC removals using the optimum doses were 33.3, 45.4 and 21.4% for polyester, cotton and acrylic effluents, respectively, while color removals were of 91.4% and 78.9%, respectively for cotton and acrylic effluents.

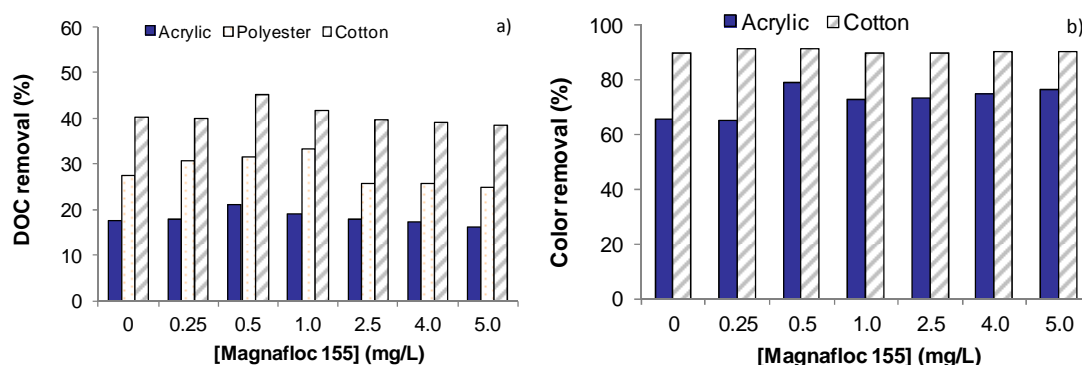


Figure 4.4 - Variation of DOC (a) and color (b) removals with the dose of flocculant (Magnafloc 155) for the different simulated effluents ($v_{\text{coagulation}}=150$ rpm, $t_{\text{coagulation}}=3$ min, $T=T_{\text{ambient}}=23-25$ °C, $\text{pH}_{\text{polyester}}=8.3$, $\text{pH}_{\text{cotton}}=9.4$, $\text{pH}_{\text{acrylic}}=7.2$, $[\text{Fe}^{2+}]_{\text{polyester}}=[\text{Fe}^{2+}]_{\text{cotton}}=200$ mg/L, $[\text{Fe}^{2+}]_{\text{acrylic}}=3000$ mg/L, $V_{\text{flocculation}}=20$ rpm and $t_{\text{flocculation}}=15$ min).

Doses of Superfloc C-573 for maximum DOC removals were 0.5 mg/L for cotton and polyester effluents and 0.25 mg/L for the acrylic one, these doses leading to DOC removals of 43.2%, 32.0%, and 28.3%, respectively (Figure 4.5 a). Moreover, Figure 4.5 b shows that color removal in cotton wastewater (~90%) is almost independent of the flocculant dose, but for the acrylic effluent the best overall efficiency for color reduction (93.8%) was obtained using a Superfloc dose of 0.25 mg/L. Similar doses were determined by other authors for dyes containing wastewaters, although different flocculants were used [Bes-Piá et al., 2002; Joo et al., 2007; El-Gohary and Tawfik, 2009].

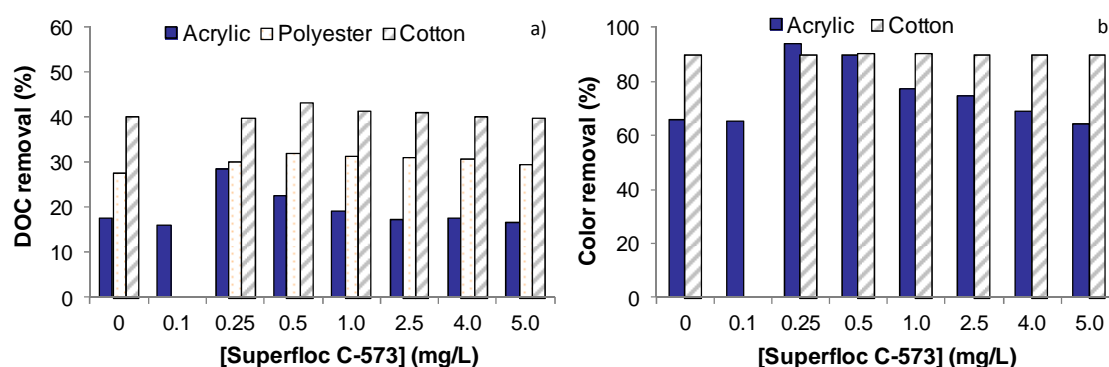


Figure 4.5 - Variation of DOC (a) and color (b) removals with the dose of flocculant (Superfloc C-573) for the different simulated effluents ($v_{\text{coagulation}}=150$ rpm, $t_{\text{coagulation}}=3$ min, $T=T_{\text{ambient}}=23-25$ °C, $pH_{\text{polyester}}=8.3$, $pH_{\text{cotton}}=9.4$, $pH_{\text{acrylic}}=7.2$, $[Fe^{2+}]_{\text{polyester}}=[Fe^{2+}]_{\text{cotton}}=200$ mg/L, $[Fe^{2+}]_{\text{acrylic}}=3000$ mg/L, $V_{\text{flocculation}}=20$ rpm and $t_{\text{flocculation}}=15$ min).

Comparing the optimum operating conditions in each stage of the coagulation/flocculation process (Table 4.1), it can be observed that optimal pH values fall in the alkaline range for all the effluents and the optimum coagulant dose for the polyester and cotton effluents is very similar (200 mg/L), which is much below the dose required for the acrylic effluent (3000 mg/L). This is a consequence of the differences in the organic content of the wastewaters; 143.1 and 117.5 mg C/L for the first two versus 334.1 mg C/L for the latter, but the presence of other chemicals also affects the process. Apparently, the acrylic effluent requires smaller doses of flocculant although differences are not significant. On the other hand, slightly smaller doses of Superfloc C-573 (cationic polyamine) are required as compared with Magnafloc 155 (anionic polyacrylamide). However, performances were not significantly enhanced by the flocculant addition, except for the acrylic effluent where the Superfloc C-573 provides better efficiencies for both color and DOC removal. In general, DOC and color removal efficiencies follow the order cotton > polyester > acrylic effluents, indicating that the organic carbon content of the effluents might negatively affect the process efficiency (Table 3.4 of section 3.2.1.3 and Table 4.1).

Operating at the optimal conditions the concentration of dissolved iron remaining in solution that can be used as catalyst in the subsequent Fenton process is 0.29, 8.7 and 275 mg/L for cotton, polyester and acrylic wastewaters, respectively.

After the coagulation/flocculation process, the biodegradability of the acrylic and polyester effluents, expressed as SOUR, remained approximately constant, respectively, <0.2 and $\sim 27.0 \text{ mgO}_2/(\text{g}_{\text{VSS}}\cdot\text{h})$. For the cotton wastewater, SOUR increased slightly, from 5.6 to $8.0 \text{ mgO}_2/(\text{g}_{\text{VSS}}\cdot\text{h})$.

Table 4.1 – Optimal conditions for coagulation/flocculation and DOC and color removal efficiencies for each synthetic effluent.

	Variables	Polyester		Cotton			Acrylic		
		Optimal conditions	DOC removal (%)	Optimal conditions	DOC removal (%)	Color removal (%)	Optimal conditions	DOC removal (%)	Color removal (%)
Coagulation	v _{coagulation} (rpm)	150		150			150		
	t _{coagulation} (min)	3		3			3		
	T (°C)	22	27.6	22	40.3	90.1	22	17.7	65.8
	pH	8.3		9.4			7.2		
	[Fe ²⁺] (mg/L)	200		200			3000		
Flocculation	v _{flocculation} (rpm)	20		20			20		
	t _{flocculation} (min)	15	33.3	15	45.4	91.4	15	21.4	78.9
	[Magnafloc 155] (mg/L)	1.0		0.5			0.5		
	v _{flocculation} (rpm)	20		20			20		
	t _{flocculation} (min)	15	32.0	15	43.2	90.4	15	28.3	93.8
	[Superfloc C-573] (mg/L)	0.5		0.5			0.25		

4.4 Conclusions

A coagulation/flocculation process has been applied to synthetic textile effluents with the purpose of removing color and organic compounds while minimizing the chemicals consumption. The optimum operating conditions obtained for color removal were the same as the optimum conditions maximizing the DOC removal, whatever the nature of the wastewater. However, those conditions changed from effluent to another indicating the importance of the organic content and the characteristics of the wastewater to be treated.

The process efficiency in terms of DOC removal was almost not affected by the temperature in the coagulation stage, but color removal was significantly improved particularly in the range 15-22 °C for the cotton effluent, which increased from ~11% to ~74%. For temperatures above 22 °C, the color removal is nearly constant.

The optimum pH for coagulation was clearly dependent on the nature of the effluent, being 8.3 for polyester, 9.4 for cotton and 7.2 for acrylic wastewaters. The order of the optimum pH is the same as the natural pH of the effluents; acrylic < polyester < cotton.

The optimal doses of coagulant were 200 mg/L of Fe²⁺ for cotton and polyester wastewaters and 3000 mg/L for acrylic wastewater, which is due to the higher organic load of the latter effluent. Comparatively, the combination of Fe²⁺/Magnafloc 155 (for cotton and polyester effluents) presents slightly better results as compared to Fe²⁺/Superfloc C-573 although the latter requires smaller doses. For the acrylic effluent, Superfloc C-573 provided better removal efficiencies. At the optimal conditions it was possible to reach overall DOC removals of 33.3, 45.4 and 28.3% for polyester, cotton and acrylic effluents, respectively, and color removals of 91.4% for cotton and 93.8% for acrylic effluents were attained.

4.5 References

- Amokrane, A.; Comel, C.; Veron, J. (1997). Landfill Leachates Pretreatment by Coagulation-Flocculation. *Water Research*, 31, pp.2775-2782.
- Aziz, H.A.; Alias, S.; Adlan, M.N.; Faridah; Assari, A.H.; Zahari, M.S. (2007). Colour removal from landfill leachate by coagulation and flocculation processes. *Bioresource Technology*, 98, 218-220.

Bes-Piá, A.; Mendoza-Roca, J.A.; Alcaina-Miranda, M.I.; Iborra-Clar, A.; Iborra-Clar, M.I. (2002). Reuse of wastewater of the textile industry after its treatment with combination of physical-chemical treatment and membrane technologies. *Desalination*, 149, 169-174.

Bose, P. (2010). *Water and Wastewater Engineering*. Indian Institute of Technology, Kanpur, Indian.

Braz, R.; Pirra, A.; Lucas, A.S.; Peres, J.A. (2010). Combination of long term aerated storage and chemical coagulation/flocculation to winery wastewater treatment. *Desalination*, 263, 226-232.

Duan, J.; Gregory, J. (2003). Coagulation by hydrolysing metals salts. *Advances in Colloid and Interface Science*, 100-102, 475-502.

Eckenfelder, Jr. W.W. (2000). *Industrial Water Pollution Control*, 3rd ed., McGraw-Hill International Editions, Singapore.

Edeline, F. (1992). *L'épuration physico-chimique des eaux – théorie & technologie*, 2e édition, Editions CEBEDOC.

El-Gohary, F.; Tawfik, A. (2009). Decolourization and COD reduction of disperse and reactive dyes wastewater using chemical-coagulation followed by sequential batch reactor (SBR) process. *Desalination*, 249, 1159-1164.

El-Gohary, F.; Tawfik, A.; Mahmoud, U. (2010). Comparative study between chemical coagulation/precipitation (C/P) versus coagulation/dissolved air flotation (C/DAF) for pre-treatment of personal care products (PCPs) wastewater. *Desalination* 252, 106-112.

Grau, P. (1991). *Textile Industry Wastewaters Treatment*. *Water Science and Technology*, 24, 97-103.

Georgious, D.; Aivazidis, A.; Hatiras, J.; Gimouhopoulos, K. (2003). Treatment of cotton textile wastewater using lime and ferrous sulfate. *Water Research*, 37, 2248–2250.

Golob, V.; Vinder, A.; Simonic, M. (2005). Efficiency of the coagulation/flocculation method for the treatment of dyebath effluents. *Dyes and Pigments*, 67, 93-97.

Joo, D.J., Shin, W.S.; Choi, J.-H.; Choi, S. J., Kim, M.-C.; Han; Had, T. W.; Kim, Y.-H. (2007). Decolourization of reactive dyes using inorganic coagulants and synthetic polymer. *Dyes and Pigments*, 73, 59-64.

Kushwaha, J.P.; Srivastava, V.C.; Mall, I.D. (2010). Treatment of dairy wastewater by inorganic coagulants: Parametric and disposal studies. *Water Reseach*, 44, 5867-5874.

Lafleur; T. (1997). Jar testing. Rensselaer Polytechnic Institute, Troy, NY, USA.

Liang, Z.; Wang, Y.; Zhou, Y.; Liu, H.; Wu, Z. (2009). Hydrolysis and coagulation behavior of polyferric sulfate and ferric sulfate. *Water Science and Technology*, 59, 1129-1135.

Perdigón-Melón; J.A.; Carbajo, J.B.; Petre, A.L.; Rosal, R.; García-Calvo, E. (2010). Coagulation-Fenton coupled treatment for ecotoxicity reduction in highly polluted industrial wastewater. *Journal of Hazardous Materials*, 181,127-132.

Phipps & Bird (995). A simplified jar test procedure, 1519 Summit Av., Richmond, Virginia 23230, USA.

Poland, J.; Pagano, T. (2010). Jar testing. Civil Engineering Department, Virginia Polytechnic Institute and State University, USA.

Rodrigues, C.S.D.; Boaventura, R.A.R.; Madeira, L.M. (2012). Application of Fenton's reagent for acrylic dyeing wastewater decolourization, organic matter reduction and biodegradability improvement. *Journal of Advanced Oxidation Technologies*, 15, 78-88.

Satterfield, Z. (2004). Jar testing. NESC, West Virginia University, USA.

Selcuk, H. (2005). Decolourization and detoxification of textile wastewater by ozonation and coagulation processes. *Dyes and Pigments*, 64, 217-222.

Stephenson R.J.; Duff, S.J.B. (1996). Coagulation and precipitation of a mechanical pulping effluent – I. Removal of carbon, colour and turbidity. *Water Research*, 30, 781-792.

Tatsi, A.A.; Zouboulis, A.I.; Matis, K.A.; Samaras, P. (2003). Coagulation-Flocculation Pretreatment of Sanitary Landfill Leachates. *Chemosphere*, 53, 737-744.

Verma, S.; Prasad, B.; Mishra, I.M. (2010). Pretreatment of petrochemical wastewater by coagulation and flocculation and the sludge characteristics. *Journal of Hazardous Materials*, 178, 1055-1064.

Chapter 5

Coagulation/Flocculation with Fe^{3+} as Coagulant *

* This Chapter is based on the publication "Rodrigues C.S.D.; Madeira, L.M.; Boaventura, R.A.R. Synthetic Textile Wastewaters Treatment Using Ferric Salt as Coagulant". Submitted to Environmental Engineering and Management Journal.

5 Coagulation/Flocculation with Fe^{3+} as Coagulant

5.1 Introduction

The combination of coagulation/flocculation and Fenton oxidation processes has been already applied to wastewaters from the textile industry [Kang et al., 2002; Wang et al., 2008] and other effluents [Martins et al., 2005]. However, when using iron salts as coagulants, the residual soluble iron contributes to a reduction in the operating costs associated with Fenton's oxidation, often used downstream from coagulation/flocculation, wherein the residual iron is used as catalyst.

The purpose of this chapter is to assess the applicability of ferric sulphate as coagulant in combination with an anionic (Magnafloc 155) or cationic (Superfloc C-573) flocculant for the removal of organic matter and color from polyester, cotton and acrylic dyeing synthetic wastewaters. In spite of the recommendations of the manufacturers (Allied Colloids and American Cyanamid Co., respectively), Magnafloc 155 and Superfloc C-573 have not been used so far for textile dyeing wastewater treatment. Optimized conditions for key variables as pH, Fe^{3+} and flocculant doses were also determined. This work is the continuation of a previous one (chapter 4) where ferrous sulphate was used as coagulant and therefore it allows comparing the performances of Fe(II) and Fe(III) salts for each synthetic effluent, thus aiming to infer if the same salt could be beneficially used in all cases or not. The main objective of both studies was to take advantage of the dissolved iron present in the effluent resulting from the coagulation process in a downstream iron-catalysed oxidation – the well-known Fenton's advanced oxidation process, addressed in subsequent chapters. This additional treatment, alone or supplemented by a biological process, is justified by the limited capability of coagulation/flocculation for producing per se an effluent that meets the discharge limits (for pH, COD, BOD_5 and color) imposed by the Portuguese legislation (Ordinance No. 423 of June 25, 1997, for discharge of textile wastewaters).

5.2 Materials and Methods

5.2.1 Preparation of Simulated Textile Effluents

The simulated effluents used in the work reported in this chapter were prepared as described in section 3.2.1 of chapter 3.

5.2.2 Coagulation/Flocculation Experiments

Iron sulfate ($\text{Fe}_2(\text{SO}_4)_3$; CAS: 10028-22-5) used as coagulant was supplied by Quimitécnica S.A. (Portugal) as a brown solution with $\text{pH} = 2.0 \pm 0.5$ and specific gravity = 1.56 ± 0.2 at 20°C . The working solution was prepared by diluting the commercial product with distilled water to obtain a solution with $50 \text{ g Fe}^{3+}/\text{L}$.

Magnafloc 155 is an anionic polyacrylamide (molecular weight around 5×10^6 , density $\sim 750 \text{ kg/m}^3$, whitish-yellow solid) from Allied Colloids (England) and Superfloc C-573 is a cationic polyamine (molecular weight around 10^4 , density $1.14\text{-}1.18 \text{ kg/m}^3$, yellow liquid) from American Cyanamid Co (USA), both used as flocculants in this work.

The optimum pH as well as the optimal coagulant and flocculant doses were determined from experiments performed in a Jar-test apparatus according to the description given in section 3.4.1.

For either DOC or color analyses the supernatant was previously centrifuged (Mini Spin Eppendorf, Germany) at 13400 rpm for 2 minutes.

5.2.3 Analytical Methods

The analytical procedures were performed as described in section 3.3 of chapter 3.

5.3 Results and Discussion

In a previous work (chapter 4) it was found that some operating conditions, namely the stirring speed and stirring time during the coagulation stage, have almost no effect on either color or DOC reduction from synthetic textile dyeing effluents. So, those parameters were kept constant at 150 rpm and 3 min, respectively, while determining the effect of both pH and Fe^{3+} concentration on color and organic matter removal in the coagulation stage. The responses selected in this parametric study were color and DOC reduction because they are faster to assess; besides, they are closely related to legislated parameters (pH, COD, BOD_5 and color), which are nevertheless assessed after optimizing process conditions to see if the final effluent meets legislated standards.

5.3.1 Influence of pH

As found previously with a Fe^{2+} salt (chapter 4), the pH is one of the most important factors to take into account in the coagulation process. In this work, where a Fe^{3+} salt was used as coagulant, the pH was varied from 3.5 to 10.4 for polyester and cotton effluents. For the acrylic effluent no results are presented for $\text{pH} > 8.3$ because it was observed a change in the colour of the effluent (from blue to light grey).

The obtained results concerning the effect of the pH are shown in Figure 5.1. They allow concluding that there are optimal pH values for DOC removal (Figure 5.1 a): 9.4 for the polyester effluent (33.4% of DOC reduction) and 5.0 for the cotton effluent (38.7% of DOC reduction). For the acrylic effluent the removal increased with the pH, but at pH 8.3 only a reduction of 13.6% in DOC was obtained. Regarding color removal (Figure 5.1 b), the optimum occurred at $\text{pH} = 5.0$ (32.0% of color reduction) for the cotton effluent and increased with pH, in the range studied, for the acrylic effluent, with maximum color removal of 41.2% at $\text{pH} = 8.3$.

At the optimum conditions, and for the cotton effluent, the coagulation occurs most probably by charge neutralization and inclusion in an amorphous hydroxide precipitate (sweep flocculation), because at pH 5.0 the species present in solution are Fe^{3+} ions and hydrolysable species ($\text{Fe}(\text{OH})^{2+}$ and $\text{Fe}(\text{OH})_3$) [Duan and Gregory, 2003]. For the acrylic and polyester effluents, with optimum coagulation pH in the alkaline zone, $\text{Fe}(\text{OH})_3$ and $\text{Fe}(\text{OH})_4^-$ are the main species present in solution (Duan and Gregory, 2003), and one can

consider that the coagulation principally occurs by incorporation in iron hydroxide precipitates.

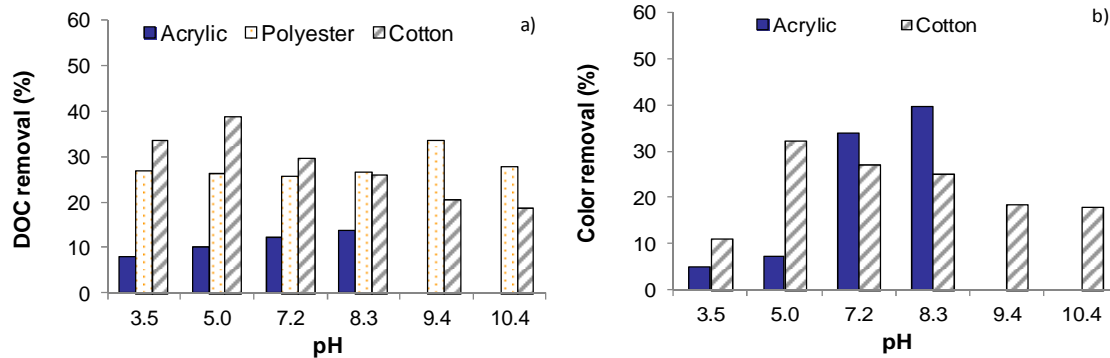


Figure 5.1 – Influence of pH in DOC (a) and color (b) removal from the different effluents ($v_{\text{coagulation}} = 150$ rpm, $t_{\text{coagulation}} = 3$ min, $[\text{Fe}^{3+}]_{\text{polyester}} = [\text{Fe}^{3+}]_{\text{cotton}} = 200$ mg/L, $[\text{Fe}^{3+}]_{\text{acrylic}} = 500$ mg/L and $T = T_{\text{ambient}} = 22\text{-}23$ °C).

The optimum pH values obtained for the cotton and polyester effluents are within the ranges indicated by Edeline (1992) when using $\text{Fe}_2(\text{SO}_4)_3$ as coagulant: 3.5-7 and > 9. The best pH for the acrylic effluent was not determined due to the color change for pH > 8.3, as above mentioned. The optimum pH for the cotton effluent (5.0) is also close to that obtained in other studies with the same coagulant, even applied to different wastewaters. For instance, Joo et al. (2007) pointed out an optimum pH between 4 to 7 for the treatment of textile effluents, while Aziz et al. (2007) and Liang et al. (2009) obtained the maximum efficiency at pH 4 in the treatment of landfill leachate and molasses wastewaters.

5.3.2 Influence of the Fe^{3+} Concentration

The effect of the coagulant dose was assessed by varying the dosage in the range 15 - 1000 mg/L for polyester and cotton effluents and 200 - 4000 mg/L for the acrylic one. The other variables of the process were fixed at the optimal values determined before, namely the pH.

The results obtained (Figure 5.2) show a Fe^{3+} optimum dose of 500 mg/L for the polyester wastewater, leading to 35.1% DOC removal. For the cotton effluent both the color and DOC removals increase with $[\text{Fe}^{3+}]$ up to 200 mg/L, decreasing for higher concentrations. Maximum removals of 38.7 and 32.0% were achieved for DOC and color, respectively. An optimal concentration of 1000 mg/L was found for the acrylic effluent, yielding 44.7% decolorization and a DOC reduction of only 16.5%. The existence of optimum Fe^{3+} doses has been also reported in other studies [Kim et al., 2004; Joo et al., 2007; Anouzla et al., 2009] and has been attributed to the fact that when the coagulant dosage is in excess, the restabilization of colloids can occur [Aziz et al., 2007].

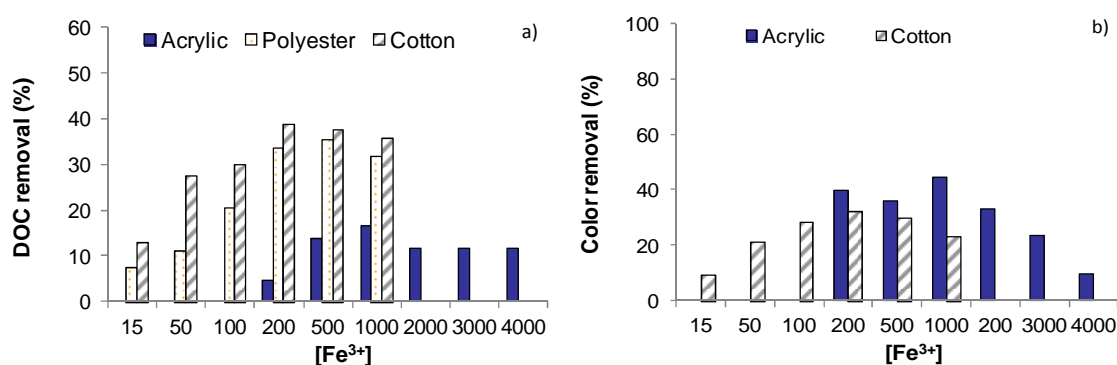


Figure 5.2 – Effect of Fe^{3+} concentration on DOC (a) and color (b) removal from the different effluents ($v_{\text{coagulation}} = 150$ rpm, $t_{\text{coagulation}} = 3$ min, $T = T_{\text{ambient}} = 23\text{-}25$ °C and $\text{pH}_{\text{polyester}} = 9.4$, $\text{pH}_{\text{cotton}} = 5.0$ and $\text{pH}_{\text{acrylic}} = 8.3$).

In a previous work using a Fe^{2+} salt as coagulant (chapter 4) it was observed that for each textile dyeing effluent the highest reductions both in color and DOC were in general obtained for the same pH and coagulant dose. A similar result was obtained in this study using Fe^{3+} . The dose of coagulant necessary for the coagulation process is related to the organic load of the effluent. For the acrylic effluent, with higher organic load (cf. Table 3.4, section 3.2.1.3), a higher dosage of ferric salt is needed. However, the coagulant dose also depends on the global wastewater characteristics, as reported by other authors. For instance, Liang et al. (2009) reported an optimum dose of 3 g/L of ferric sulfate for the treatment of a molasses effluent with a COD of 975 ± 25 mg O_2/L while Joo et al. (2007)

obtained the optimum at 4 g/L of ferric salt for the treatment of a textile effluent with a much higher COD load (2968 mg O_2 /L).

5.3.3 Influence of the Flocculant Nature and Dose

Some operating conditions, namely the stirring speed and stirring time during the flocculation stage, have almost no effect in either color or DOC reduction for the tested effluents (chapter 4). So, after the coagulation stage, the influence of the nature and concentration of flocculant on color and DOC removal was evaluated, in the flocculation stage, but speed and stirring time were kept constant at 20 rpm and 15 min, respectively. The flocculants (Magnafloc 155 and Superfloc C-573) were employed in concentrations varying between 0.25 to 5 mg/L. The flocculation study was performed using effluents pre-treated by coagulation at the best operating conditions previously determined (cf. Table 5.1).

Figure 5.3 presents the results obtained using Magnafloc 155. As regards the polyester effluent it can be seen that the DOC removal slightly increases with the flocculant concentration up to 2.5 mg/L (39.9% of DOC removal), but higher doses do not improve the process performance. There is also a very slight increase in DOC reduction for the cotton dyeing wastewater when Magnafloc 155 dose is increased from 0.25 to 0.5 mg/L (41.2%), but then remains nearly constant or is somewhat smaller. Color reduction is nearly independent of the flocculant dose (in the range studied) for this effluent (average reduction ~32.5%). DOC and color removal for the acrylic effluent are low compared to those obtained during the coagulation step, which could be due to the existence of an interaction of the flocculant with the flocs formed during the coagulation and, consequently, the organic compounds and dye are redissolved. It is noteworthy that these runs were repeated several times and the same effect on DOC and color removal was always observed.

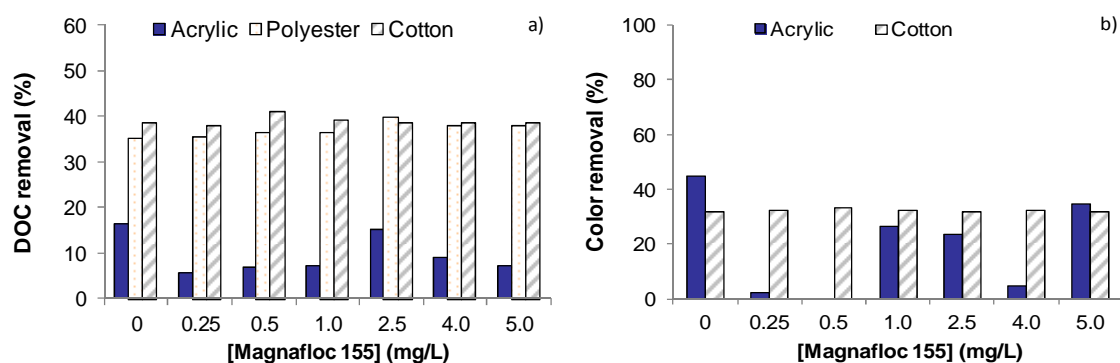


Figure 5.3 – Effect of Magnafloc155 concentration on DOC (a) and color (b) removal from the different effluents ($v_{\text{coagulation}} = 150$ rpm, $t_{\text{coagulation}} = 3$ min, $T = T_{\text{ambient}} = 23\text{-}26$ °C, $\text{pH}_{\text{polyester}} = 9.4$, $\text{pH}_{\text{cotton}} = 5.0$, $\text{pH}_{\text{acrylic}} = 8.3$, $[\text{Fe}^{3+}]_{\text{polyester}} = 500$ mg/L, $[\text{Fe}^{3+}]_{\text{cotton}} = 200$ mg/L, $[\text{Fe}^{3+}]_{\text{acrylic}} = 1000$ mg/L, $v_{\text{flocculation}} = 20$ rpm and $t_{\text{flocculation}} = 15$ min).

In experiments with Superfloc C-573 (Figure 5.4), the reduction of the DOC (and also color) removal is again observed, as compared to the coagulation step, for the acrylic effluent. DOC removal slightly increases up to 1 mg/L (40.2%) for the polyester dyeing effluent and remains constant for higher doses. A very small increase occurs at 0.5 mg/L (maximum DOC removal of 43.0%) for the cotton effluent. Color removal is again constant in the dose range studied (average ~32.5%).

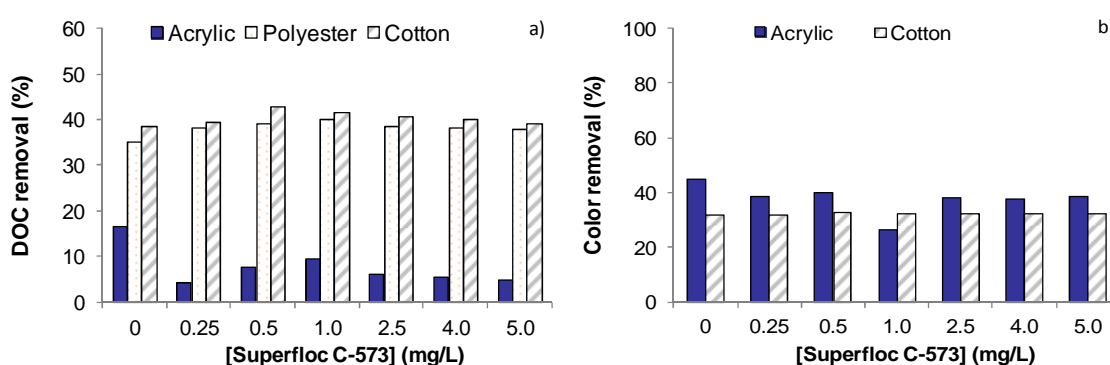


Figure 5.4 – Effect of Superfloc C-573 concentration on DOC (a) and color (b) removal from the different effluents ($v_{\text{coagulation}} = 150$ rpm, $t_{\text{coagulation}} = 3$ min, $T = T_{\text{ambient}} = 23\text{-}26$ °C, $\text{pH}_{\text{polyester}} = 9.4$, $\text{pH}_{\text{cotton}} = 5.0$, $\text{pH}_{\text{acrylic}} = 8.3$, $[\text{Fe}^{3+}]_{\text{polyester}} = 500$ mg/L, $[\text{Fe}^{3+}]_{\text{cotton}} = 200$ mg/L, $[\text{Fe}^{3+}]_{\text{acrylic}} = 1000$ mg/L, $v_{\text{flocculation}} = 20$ rpm and $t_{\text{flocculation}} = 15$ min).

The optimal flocculants' doses obtained after coagulation using Fe^{3+} (Table 5.1) are similar to those observed when using Fe^{2+} (Table 5.2) for the same effluents (chapter 4), and to those reported in other studies employing different flocculants [Bes-Piá et al., 2002; Joo et al., 2007; El-Gohary and Tawfik, 2009].

Table 5.1 – Optimum conditions for the coagulation/flocculation process and performances achieved (DOC and color removal) for each effluent when using Fe³⁺ as coagulant.

Variables		Polyester		Cotton			Acrylic		
		Optimum conditions	DOC removal (%)	Optimum conditions	DOC removal (%)	Color removal (%)	Optimum conditions	DOC removal (%)	Color removal (%)
Coagulation	pH	9.4	33.4	5.0	38.7	32.0	8.3	13.6	41.2
	[Fe ³⁺] (mg/L)	500	35.1	200			1000	16.5	44.7
Flocculation	[Magnafloc 155] (mg/L)	2.5	39.9	0.5	41.2	33.2	---	---	---
	[Superfloc C-573] (mg/L)	1.0	40.2	0.5	43.0	33.2	---	---	---

Chapter 5 - Coagulation/Flocculation with Fe³⁺ as Coagulant

Table 5.2 – Optimum conditions for the coagulation/flocculation process and performances achieved (DOC and color removal) for each effluent when using Fe²⁺ as coagulant (chapter 4).

Variables		Polyester		Cotton			Acrylic		
		Optimum conditions	DOC removal (%)	Optimum conditions	DOC removal (%)	Color removal (%)	Optimum conditions	DOC removal (%)	Color removal (%)
Coagulation	pH	8.3		9.4			7.2	10.5	68.2
	[Fe ³⁺] (mg/L)	200	27.6	200	40.2	90.1	3000	17.7	65.8
Flocculation	[Magnafloc 155] (mg/L)	1.0	33.3	0.5	45.4	91.4	0.5	21.4	78.9
	[Superfloc C-573] (mg/L)	0.5	32.0	0.5	43.2	90.4	0.25	28.3	93.8

The global process (coagulation/flocculation) efficiency is only slightly better than for the coagulation process alone. This is explained by the fact that the flocculation stage has as main result the agglomeration of flocs to facilitate their sedimentation. In the case of the acrylic effluent the flocculation stage inclusively leads to a worse performance, for the reasons above mentioned.

5.3.4 Overall Process Efficiency

The optimal operating conditions for coagulation (with an iron III salt) and coagulation/flocculation applied to each effluent are presented in Table 5.1. In general, it can be observed that optimal pH values are in the alkaline range for polyester and acrylic wastewaters and in the acid zone for the cotton one; the optimum coagulant dose is lower for the cotton effluent (200 mg/L) and higher for the acrylic (1000 mg/L) one, which is partly related to the organic content of the wastewater, i.e., more Fe^{3+} is required when the effluent organic load (assessed in terms of either COD or DOC) increases (Table 3.4 of section 3.2.1.3); color and DOC removal efficiencies are similar for the two flocculants; in general, higher percentages of DOC removal are obtained for the cotton and polyester wastewaters, comparing with the acrylic one. However, greater color removals are reached for this effluent (as compared to the cotton one).

Comparing the results obtained with Fe^{3+} (this chapter) and Fe^{2+} (chapter 4), presented in Tables 5.1 and 5.2, respectively, it can be observed that the optimum pH is similar for the polyester and acrylic effluents (for the cotton effluent, the optimum pH was 5.0 for Fe^{3+} and 9.4 for Fe^{2+}); the optimum doses of coagulant are of the same order of magnitude, except for the polyester effluent (where Fe^{3+} is a better coagulant); the overall DOC removals are slightly higher when using Fe^{2+} , except for the polyester, but decolorization is strongly improved; for the acrylic effluent, the addition of flocculants improved the removal efficiencies by Fe^{2+} but showed a detrimental effect on the coagulation by Fe^{3+} .

For each effluent, the coagulation/flocculation process was then carried out under the optimal conditions obtained using either Fe^{2+} (chapter 4) or Fe^{3+} (this chapter) as coagulant, combined with either Magnafloc 155 or Superfloc C-573 as flocculant. In all cases, the best conditions for DOC removal are the same that maximize decolorization. The initial and final effluents were characterized in terms of DOC, COD, BOD_5 , color,

phosphate, nitrate, total nitrogen, chloride, etc. and the removal efficiencies were calculated, along with measurement of the biodegradability. The operating conditions that maximize DOC and color removal for each effluent are presented in Table 5.3. It can be observed that Fe²⁺ salt provides better efficiencies for cotton and acrylic wastewaters, while Fe³⁺ is recommended for the polyester one. The optimal doses of coagulant are also quite different and much higher for the more organic loaded acrylic effluent.

Table 5.3 - Optimum conditions for the coagulation/flocculation of textile dyeing wastewaters using Fe²⁺ (chapter 4) and Fe³⁺ (this chapter) at ambient temperature (26-28 °C).

Variable	Effluent		
	Polyester	Cotton	Acrylic
Coagulant	Fe ³⁺	Fe ²⁺	Fe ²⁺
Coagulant dose (mg/L)	500	200	3000
Flocculant	Superfloc C-573	Magnafloc 155	Superfloc C-573
Flocculant dose (mg/L)	1	0.5	0.25
pH	9.4	9.4	7.2

Other variables: $v_{\text{coagulation}} = 150$ rpm, $t_{\text{coagulation}} = 3$ min, $v_{\text{flocculation}} = 20$ rpm and $t_{\text{flocculation}} = 15$ min, as reported in chapter 4.

The characteristics of the simulated effluents (Table 3.4) and after the coagulation/flocculation process carried out in the optimum conditions are presented in Tables 5.3 and 5.4, respectively. It can be seen that the removals of nitrate, phosphate (except for the cotton dyeing effluent) and chloride are low ($\leq 17\%$); the decrease of the organic matter content (expressed as DOC, COD and BOD₅) is not too significant, being worse for the acrylic effluent and better for the polyester one; the increase of the biodegradability (as inferred from the BOD₅:COD ratio, which is always smaller than 0.4, and from the specific oxygen uptake rate, k') is not significant (except k' for the polyester wastewater) and thus the effluents can still be considered as non (or low) biodegradable after treatment. This points out for the interest of using an integrated treatment process, for instance coagulation/flocculation followed by chemical oxidation, before a biological process. This will be the aim of subsequent work, using either simulated or real wastewaters, as detailed in further chapters. The coagulation/flocculation process is however quite efficient in terms of color removal, as decolorization of 92.2% for the cotton effluent and 97.0% for the acrylic one were obtained.

Table 5.4 - Characterization of the wastewaters after treatment by coagulation/flocculation using Fe²⁺ or Fe³⁺, as described in Table 5.3, and efficiencies attained.

Parameter	Polyester		Cotton		Acrylic	
	After Treatment	Removal (%)	After Treatment	Removal (%)	After Treatment	Removal (%)
Total nitrogen (mgN/L)	14.2	10.4	3.8	2.6	15.3	7.0
Nitrate (mg NO ₃ ²⁻ /L)	6.7	10.1	4.22	0.0	13.0	17.2
Total phosphours (mg P/L)	2.3	22.0	4.5	24.3	0.1	50.0
Phosphate (mg P/L)	2.4	9.4	< 0.06	100.0	< 0.06	0.0
Chemical oxygen demand (mg O ₂ /L)	276.2	46.7	261.9	25.2	741.7	10.4
Biochemical oxygen demand (mg O ₂ /L)	89.7	31.3	74.1	4.3	< 1.0	---
Dissolved organic carbon (mg C/L)	78.9	44.8	68.2	41.9	240.1	28.1
Chloride (mg Cl ⁻ /L)	15.3	11.3	8030	0.0.	45.0	0.0
Specific oxygen uptake rate (k') (mg O ₂ /mg v _{SS} . h)	28.5	---	8.0	---	<0.2	---
BOD ₅ :COD ratio	0.32	---	0.28	---	<0.0013	---
Absorbance at λ _{max}	---	---	0.034*	92.2	0.047**	97.0
Dissolved iron (mg/L)	8.7	---	0.29	---	275	---
<i>Vibro fischeri</i> Inhibition 5 min (%)	43.0	---	0.0	---	94.0	---
<i>Vibro fischeri</i> Inhibition 15 min (%)	62.0	---	0.0	---	95.0	---
<i>Vibro fischeri</i> Inhibition 30 min (%)	67.0	---	0.0	---	96.0	---

(*) at 520 nm; (**) at 610 nm

5.4 Conclusions

Coagulation/flocculation using ferric sulphate as coagulant proved to be an efficient process for organic matter removal and particularly for decolorization of polyester, cotton and acrylic dyeing effluents. It was found that:

- Color and DOC reduction is maximized at the same pH, although different for the three effluents (9.4 for polyester, 5.0 for cotton and 8.3 for acrylic);
- The optimum dose of coagulant increases with the organic content of the effluent (200 mg/L for cotton, 500 mg/L for polyester and 1000 mg/L for acrylic);
- The type and dose of the flocculant (Magnafloc 155 or Superfloc C-573) has a minor effect on DOC and color reduction of all effluents.

Comparing the results obtained using ferric and ferrous sulphate one can conclude that the best combinations coagulant/flocculant and respective doses depend on the effluent: Fe^{3+} /Superfloc C-573 for polyester, Fe^{2+} /Magnafloc 155 for cotton and Fe^{2+} /Superfloc C-573 for acrylic. Using these combinations and the optimal conditions experimentally determined, color removal was quite high (>90%), but the process was not so efficient as regards organic matter removal. The effluents treated by coagulation/flocculation are apparently non-biodegradable, so a further stage (e.g. chemical oxidation) might be recommendable before a biological treatment.

5.5 References

Anouzla, A.; Abrouki, Y.; Souabi, S.; Safi, M.; Rhal, H.; (2009). Colour and COD removal of disperse dye solution by a novel coagulant: Application of statistical design for the optimization and regression analysis. *Journal of Hazardous Materials*, 166, 1302-1306.

Aziz, H.A.; Alias, S.; Adlan, M.N.; Faridah; Assar, A.H.; Zahari, M.S. (2007). Colour removal from landfill leachate by coagulation and flocculation processes. *Bioresources Technology*, 98, 218-220.

Bes-Piá, A.; Mendoza-Roca, J.A.; Alcaina-Miranda, M.I.; Iborra-Clar, A.; Iborra-Clar, M.I. (2002). Reuse of wastewater of the textile industry after its treatment with combination of physical-chemical treatment and membrane technologies. *Desalination*, 149, 169-174.

Duan, J.; Gregory, J. (2003). Coagulation by hydrolysing metals salts. *Advanced in Colloid and Interface Science*, 100-102, 475-502.

Edeline, F. (1992). L'épuration physico-chimique des eaux – théorie & technologie, 2e édition, Editions CEBEDOC.

El-Gohary, F.; Tawfik, A. (2009). Decolourization and COD reduction of disperse and reactive dyes wastewater using chemical-coagulation followed by sequential batch reactor (SBR) process. *Desalination*, 249, 1159-1164.

Joo, D.J.; Shin, W.S.; Choi, J.-H.; Choi, S. J.; Kim, M.-C.; Han, M.H.; Ha, T. W.; Kim, Y.-H. (2007). Decolourization of reactive dyes using inorganic coagulants and synthetic polymer. *Dyes and Pigments*, 73, 59-64.

Kang, S.-F.; Liao, C.-H.; Chen, M.-C. (2002). Pre-oxidation and coagulation of textile wastewater by the Fenton process. *Chemosphere*, 46, 923–928.

Kim, T.-H.; Park, C.; Yang, J.; Kim, S. (2004). Comparison of disperse and reactive dye removals by chemical coagulation and Fenton oxidation. *Journal of Hazardous Materials*, B112, 95-103.

Liang, Z.; Wang, Y.; Zhou, Y.; Liu, H.; Wu, Z. (2009). Hydrolysis and coagulation behavior of polyferric sulfate and ferric sulfate. *Water Science and Technology*, 1129-1135.

Martins, A.F.; Vasconcelos, T.G.; Wilde, M.L. (2005). Influence of variables of the combined coagulation-Fenton-sedimentation process in the treatment of trifluraline effluent. *Journal of Hazardous Materials*, B127, 111–119.

Wang, X.; Zeng, G.; Zhu, J. (2008). Treatment of jean-wash wastewater by combined coagulation, hydrolysis/acidification and Fenton oxidation. *Journal of Hazardous Materials*, 153, 810-816.

Chapter 6

Integration of Physical-Chemical and Oxidation Processes for Acrylic Effluent Treatment *

* This Chapter is based upon the publication "Rodrigues C.S.D.; Boaventura, R.A.R.; Madeira, L.M. (2012). Application of Fenton's Reagent for Acrylic Dyeing Wastewater Decolorization, Organic Matter Reduction and Biodegradability Improvement. *Journal of Advanced Oxidation Technologies*, 15 (1),78-88."

6 Integration of Physical-Chemical and Oxidation Processes for Acrylic Effluent Treatment

6.1 Introduction

A treatability study of a simulated acrylic dyeing effluent previously treated by chemical coagulation/flocculation, using the Fenton's reagent, was the main purpose of this chapter. In practice one aims to evaluate the possibility of implementing an integrated process, making use of the dissolved iron remaining after coagulation as catalyst in the oxidation stage, an issue rarely addressed in the literature [Peres et al., 2004; Xing and Sun, 2009; Perdigon-Melon et al., 2010]. The effect of the key operating variables in the Fenton process (Fe(II) concentration, H₂O₂ dose, temperature and pH) on dissolved organic carbon (DOC) and color removal and on the increase of the effluent biodegradability was studied; the decrease of the wastewater toxicity was also assessed. Additionally, the Fenton process directly applied to the synthetic wastewater was also optimized with the purpose of submitting the treated effluent to a subsequent process, if the chemical oxidation stage is not completely effective per se. For any strategy, the final effluent must accomplish the maximum allowable limits imposed by legislation for discharges into the aquatic environment.

6.2 Materials and Methods

6.2.1 Preparation of the Simulated Textile Effluent

The acrylic dyeing effluent was simulated according to the information reported in chapter 3, section 3.2.1.

6.2.2 Experimental Procedure

The chemical coagulation/flocculation and Fenton's reaction studies were performed in batch mode, as described in sections 3.4.1 and 3.4.2, respectively.

In the combination of coagulation/flocculation plus Fenton's oxidation, the first process was carried out at the best conditions achieved in the studies already presented in chapters 4 and 5. These conditions were as follows: stirring rate of 150 or 20 rpm and contact time of 3 or 15 minutes, respectively, for the coagulation and flocculation stages, temperature = 21-23 °C, pH = 7.2, $[\text{Fe}^{2+}] = 3000 \text{ mg/L}$ and $[\text{Superfloc C-573}] = 0.25 \text{ mg/L}$. The liquid phase from coagulation/flocculation was collected after 30 min of sedimentation and acidified with HNO_3 (68%, from Merck) to pH 1 to keep the iron dissolved (so that it could be used as a catalyst in Fenton's reaction).

When the coagulation/flocculation was performed after the Fenton's oxidation, the operating conditions were similar except for the following issues: i) no additional coagulant was added, just because only the dissolved iron resulting from the Fenton's process was employed, and ii) the supernatant was not acidified. The collected samples were centrifuged at 13400 rpm during 2 minutes (Mini Spin Eppendorf) and some parameters measured for process optimization.

6.2.3 Analytical Methods

The analytical determinations were performed according to the methods described in section 3.3 of chapter 3 – Materials and Methods.

All analyses were performed in duplicate, with the exception of the absorbance measurement at 610 nm. The coefficients of variation were less than 2% for DOC, 4% for COD, 10% for BOD_5 , 13% for k' , 9% for *V. fischeri* percent inhibition and below 5% for the remaining parameters.

6.3 Results and Discussion

6.3.1 Combination of Coagulation/Flocculation plus Fenton's oxidation and Fenton's oxidation alone

Table 5.4 shows that the coagulation/flocculation process for the acrylic effluent (operated in the optimum conditions defined in chapters 4 and 5) does not allow complying with the

maximum admissible discharge value for COD (250 mg/L), thus a supplementary treatment is required. However, the BOD₅/COD ratio of the resulting effluent is too low for a biological treatment, and the toxicity (as inferred from *V. fischeri* inhibition) is high. Therefore, coupling this treatment with an AOP like the Fenton's reagent seems to be attractive, which could be, if necessary, complemented by a biological process.

Decolorization and organic matter removal were assessed using two different approaches: i) applying the Fenton's reagent to the effluent resulting from the preliminary coagulation/flocculation step (thus making use of the remaining dissolved iron employed as coagulant) and ii) applying directly the same oxidative process to the raw synthetic wastewater. The last approach aimed evaluating if the AOP was effective per se for treating the dyeing wastewater, thus complying with legislated maximum allowable values.

In the oxidation by Fenton' reagent the effect of key process variables, such as the amount of ferrous ion added to the effluent resulting from coagulation/flocculation (1st experiment) or ferrous ion added to the raw synthetic wastewater (2nd experiment), hydrogen peroxide concentration, temperature and pH (only in the 1st experiment for the reasons mentioned below) was evaluated in terms of mineralization and biodegradability; such parametric study is described below, in the following sections.

6.3.1.1 Effect of the Ferrous Ion Concentration

The catalyst concentration is a parameter to be taken into consideration in the Fenton's process, as it influences the process reaction rate while without its presence the reaction does not start [Walling, 1975]. So, the effect of the total iron concentration in the range 275-400 mg/L (which corresponds to the addition of 0.0 to 125 mg/L of Fe²⁺ to the amount of iron in solution resulting from the coagulation/flocculation stage) was studied, keeping the pH at 3.5, the temperature at 30 °C and the initial concentration of H₂O₂ at 5 g/L.

Figure 6.1 a shows that, in the first experiment (coagulation/flocculation followed by Fenton oxidation), DOC removal takes place mostly in the first 30 minutes of reaction. Moreover, DOC removal increases with the iron dose up to 350 mg/L and then decreases. Maximum removal efficiency was 54.0% after 30 min of reaction and only slightly improved (up to 55.1%) after 120 min. In the second experiment (Fenton oxidation applied directly to the raw wastewater) the DOC decay was also rapid (but mainly occurred in the

first 60 min) and a maximum was achieved for Fe = 350 mg/L, yielding DOC removals of 46.3 and 53.4% after 30 and 120 min of reaction, respectively (Figure 6.1 b).

In the 1st experiment, the biodegradability, expressed in terms of the specific oxygen uptake rate, k' , as defined in section 3.3 of chapter 3, increases up to 30 min (Figure 6.1 c), then decreases, but a marked recovery is observed for Fe doses of 275 and 300 mg/L and reaction times higher than 60 min. For higher Fe doses, only a slight improvement is observed after 90 min, but k' values are clearly higher. A possible explanation for this behavior is related with the presence of smaller amounts of biodegradable intermediates when lower Fe doses are used, in conformity with the lower DOC removals shown in Figure 6.1 a). On the other hand, it can be anticipated the formation of more recalcitrant compounds at the earlier stages of the reaction (responsible for the lowest k' values), which are further converted into more biodegradable compounds as reaction proceeds. Maximum biodegradability, corresponding to k' around 8 mg O₂/(g_{VSS}.h), was reached after 30 min reaction when using 350 mg Fe/L. As regards the Fenton oxidation alone (2nd experiment), biodegradability tends to increase up to ca. 60 min reaction time and then remains nearly constant, although the pattern depends on the catalyst dose (Figure 6.1 d). Again, an inversion of the initial k' increase was noticed. Depending on the experimental conditions, this phenomenon can be observed sooner or later; in this case, when higher catalyst doses were employed, this phenomenon was observed sooner because the reaction is faster. Biodegradability also increases with the Fe concentration up to 350 mg/L and the best result ($k' \approx 10$ mg O₂/(g_{VSS}.h)) is reached after 60 min reaction.

The existence of an optimal dose of Fe in all plots of Figure 6.1 is explained by the reaction of excess of iron ions with the hydroxyl radical (Equation 2.4), thereby decreasing the concentration of radicals available and limiting the oxidation of the organic compounds. This has been reported by several researchers whom studied the removal of color and organic matter by this process [Azbar et al., 2004; Tekin et al., 2006; Bautista et al., 2007; Lodha and Chaudhari et al., 2007; Martins et al., 2010].

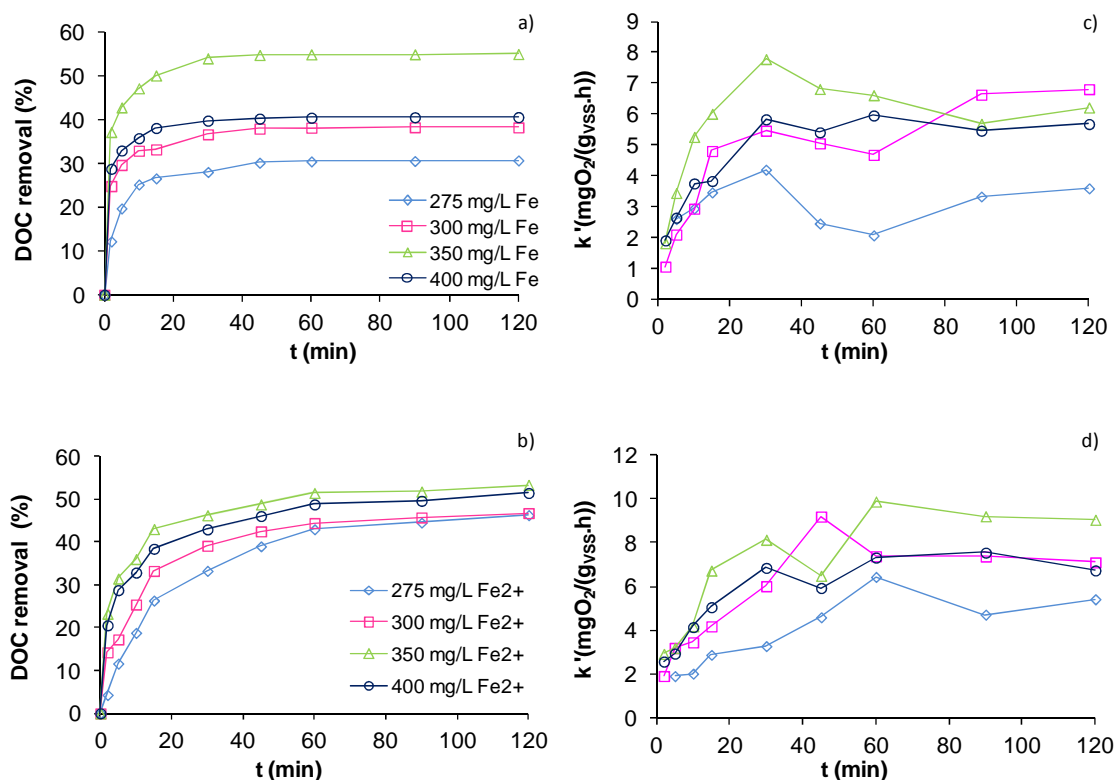


Figure 6.1 - Variation of DOC removal and k' with the total iron concentration, in the first (a) and c), respectively) and second experiment (b) and d), respectively) (initial pH=3.5, T=30 °C, initial $[H_2O_2]=5$ g/L).

The dose of 350 mg/L of iron (75 mg/L added to 275 mg/L resulting from the coagulation/flocculation stage) is consistent with that obtained in other studies of effluent's treatability with Fenton's reagent. For instance, Rodrigues et al. [2009 a]) found an optimal Fe^{2+} dose in the range 325-616 mg/L to remove TOC and color and increase the biodegradability of a synthetic wastewater from cotton dyeing with an organic load of 428 mg O₂/L and 161 mg C/L, expressed as COD and TOC, respectively.

6.3.1.2 Effect of the Initial Hydrogen Peroxide Concentration

As the concentration of hydrogen peroxide influences the efficiency of the oxidation process, after some preliminary runs different doses were selected (1.75, 2.5, 3.5 and 5 g/L in the first experiment and 5, 10, 20 and 30 g/L in the second one) for determining the

best operating conditions, maintaining constant the pH (3.5), the temperature (30 °C) and the initial total Fe concentration (350 mg/L).

The results of DOC removal obtained during the 120 minutes of oxidation are presented in Figures 6.2 a and 6.2 b and show that: i) in the first experiment, the removal mainly occurs in the first 30 minutes of reaction and the influence of H₂O₂ concentration is notorious, leading to ~ 66% DOC removal for [H₂O₂] = 3.5 g/L and t ~ 30 min, without any further increase for longer times, and ii) in the second experiment, most DOC is also removed in the first 30 minutes but continues to slightly increase till 60-90 min, in some cases till the end of the experiment. In this case the DOC removal increases with the H₂O₂ concentration up to 20 g/L and decreases for a higher dose. For [H₂O₂]=20 mg/L, DOC removals are 54.6 and 64.5%, respectively, after 30 and 120 minutes of reaction.

As concerns the evolution of the specific oxygen uptake rate (k'), maximum values are found at t=60 min (Figures 6.2 c and 6.2 d), after a more or less marked decay at t=45 min. As stated before, the reduction of k' may be related to the formation of less biodegradable organic intermediates during the oxidative process.

The H₂O₂ concentration influences therefore the biodegradability of the reaction products, as can be seen in Figures 6.2 c and 6.2 d. Maximum specific oxygen uptake rates, observed after 60 min of reaction, are 18.0 mgO₂/(g_{VSS}.h) in the first experiment, for [H₂O₂]=3.5 g/L, and 14.7 mgO₂/(g_{SSV}.h), in the second one, for [H₂O₂]=20 g/L.

It is noteworthy that in both experiments, the oxidant dose that maximizes the DOC removal is the same that provides a maximum increase in k' (3.5 g/L and 20 g/L, for the 1st and 2nd runs, respectively). This means that, again, higher oxidation degrees lead in general to higher increases in the biodegradability. The existence of an optimum peroxide concentration, also reported in similar studies [Ramirez et al., 2005; Tantak and Chaudhari, 2006; Sun et al., 2007; Rodrigues et al., 2009 b)], is justified by the fact that parallel reactions between H₂O₂ in excess and the hydroxyl radical can occur, generating HO₂^{*} species (Equation 2.3), with a lower oxidation potential [Ramirez et al., 2005].

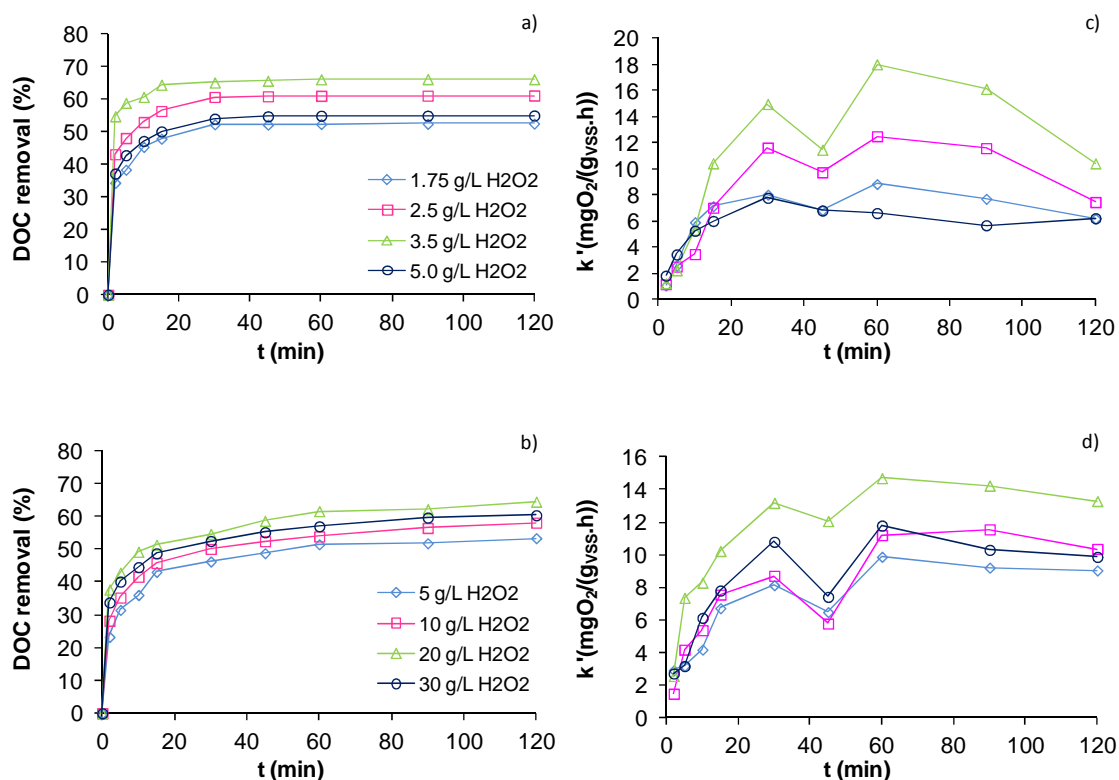


Figure 6.2 - Influence of the H₂O₂ concentration on DOC removal and k' in the first (a) and c), respectively) and second experiment (b) and d), respectively) (initial pH=3.5, T=30 °C, initial [Fe]=350 mg/L).

Rodrigues et al. [2009 a]) found an optimal H₂O₂ dose of 5 g/L for maximizing the biodegradability increase of a simulated dyeing cotton wastewater (COD = 428 mg O₂/L and TOC = 161 mg C/L). Li et al. [2009] obtained optimal doses of 30 g/L and 22.5 g/L for the oxidation of synthetic (COD=3242 mgO₂/L) and industrial (COD=3418 mg/L) triazophos pesticide-containing wastewaters, respectively.

6.3.1.3 Effect of the Temperature

The temperature, on the one hand, generally has a positive effect on the reaction rate of the Fenton process [Flaherty and Huang, 1992], according to the Arrhenius law, but, on the other hand, breaks down hydrogen peroxide into water and oxygen for values above 40-50 °C ($2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$). To assess the influence of the temperature on the acrylic wastewater treatment, four runs were carried out, in which this parameter varied in the

range 10-70 °C. The pH and [Fe] were fixed in 3.5 and 350 mg/L, respectively, and [H₂O₂] in 3.5 g/L (first experiment) and 20 g/L (second experiment). During the 120 minutes of reaction, the DOC removal and the specific oxygen uptake rate (k') of the wastewater were assessed, and the results are shown in Figures 6.3 a to 6.3 d.

In the first experiment (Fenton's process applied to the effluent resulting from the coagulation/flocculation stage), the removal of DOC by complete oxidation of organics is slow at 10 °C and a maximum value of ~31% was achieved after 90 minutes of reaction (Figure 6.3 a). In the second experiment (Fenton's process applied directly to the synthetic wastewater) the removal rate is higher but only ~40% removal was reached after 120 minutes of reaction (Figure 6.3 b). For higher temperatures, the DOC removal is improved and mainly occurs in the first 30 minutes of reaction. Significant DOC removals were reached at 50 °C after 30 minutes of reaction (~78% and ~68.2% in the first and second experiments, respectively).

In the first experiment (Figure 6.3 c), there is only a small increase of biodegradability (k') at 10 °C, but it clearly improves at higher temperatures. Maximum values of the specific oxygen uptake rate were obtained at 30 °C (18.0 mgO₂/(g_{VSS}.h) after 60 min of reaction), although values are similar to those at higher temperatures. Once again, a marked decrease is observed for a reaction time of 45 min, and for reaction times above 60 min for a very low temperature of 10 °C. This fact is probably due to the generation of less biodegradable intermediates, as mentioned before, which are produced later when the temperature is decreased, because the reaction slows down. In the second experiment the biodegradability increase at 10 °C is also negligible but it is apparent at higher temperatures. Although the variations with temperature are again small, the maximum value of k' occurred at 50 °C (17.9 mgO₂/(g_{VSS}.h) after 60 min of reaction).

The worse performances obtained in general at high temperatures (50-70 °C) are probably related to the thermal decomposition of H₂O₂, as pointed out above. The optimal values of temperature achieved in this work are in agreement with other studies that suggest similar values [Meriç et al., 2004; Gulkaya et al., 2006; Ramirez et al., 2007; Sun et al., 2008; Li et al., 2009; Fu et al., 2009; Rodrigues et al., 2009 b); Wu et al., 2011].

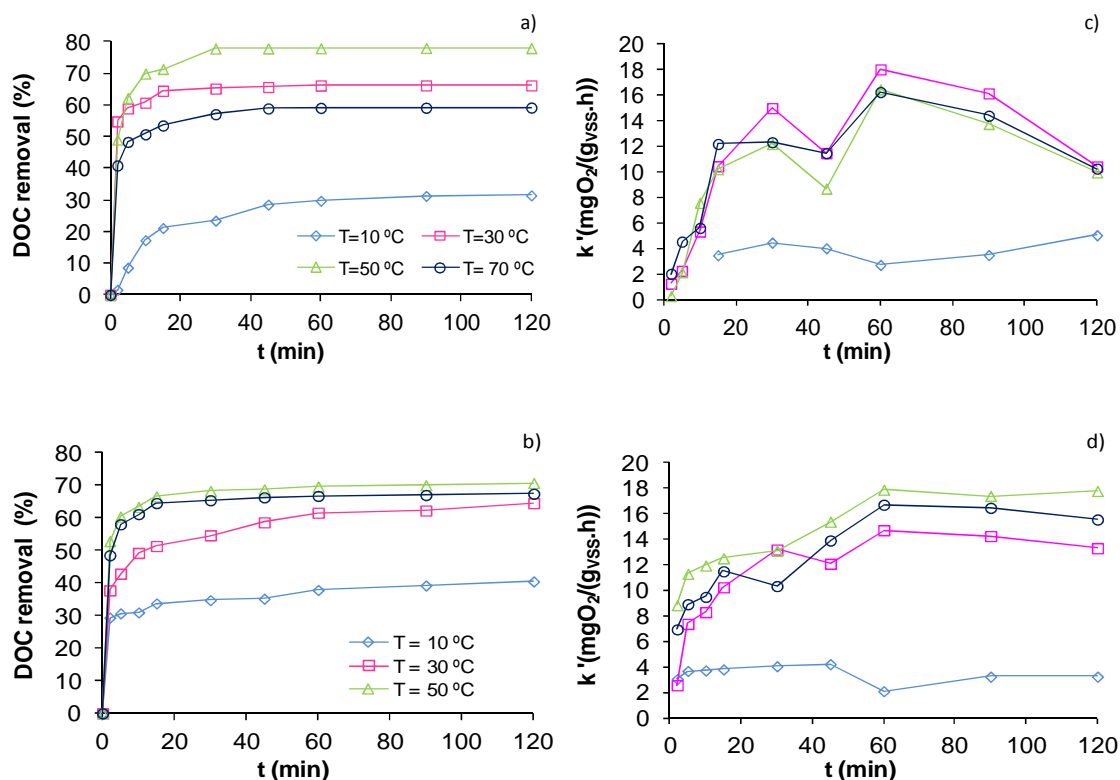


Figure 6.3 - Effect of temperature on DOC removal and k' in the first (a) and c), respectively) and second experiment (b) and d), respectively) (initial pH=3.5, [Fe]=350 mg/L, [H₂O₂]_{1st exp}=3.5 g/L, [H₂O₂]_{2nd exp}=20 g/L).

To check the effect of temperature in the hydrogen peroxide stability, its concentration was measured in both experiments. As shown in Figures 6.4 a and 6.4 b, H₂O₂ concentration decreases in the batch reactor along time, being this decrease particularly noteworthy for higher temperatures. In fact, at 50 and 70 °C the residual peroxide concentration becomes negligible or even null in short reaction times. The concentration histories match clearly the DOC data. As shown, the oxidant consumption occurs mainly in the first ca. 30 min, then proceeding more slowly.

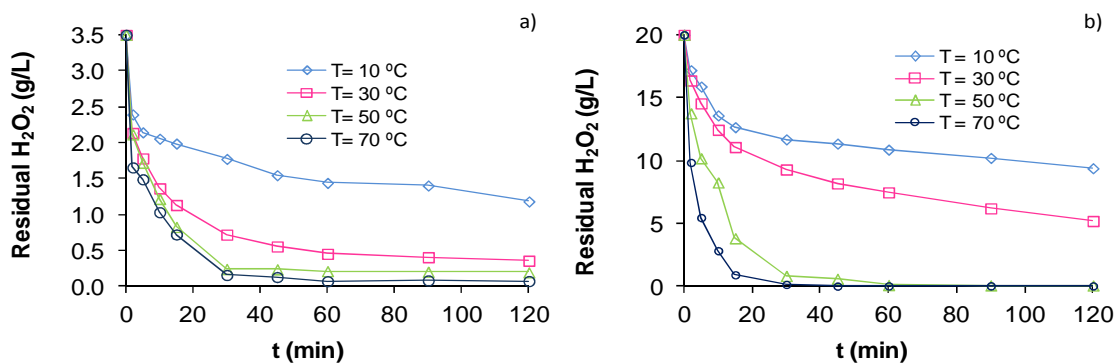


Figure 6.4 - Effect of temperature on the residual hydrogen peroxide concentration in the first (a) and second experiment (b) (initial pH=3.5, [Fe]=350 mg/L, $[H_2O_2]_1^{st} \text{ exp}=3.5 \text{ g/L}$, $[H_2O_2]_2^{nd} \text{ exp}=20 \text{ g/L}$).

6.3.1.4 Influence of pH

The effect of pH on DOC removal and biodegradability improvement during Fenton's oxidation in the effluent resulting from the combined process (coagulation/flocculation + Fenton oxidation) was assessed by performing several experiments varying the initial pH in the range 2-4. The initial iron and hydrogen peroxide concentrations were set at 350 mg/L and 3.5 g/L, respectively, and temperature was controlled at 50 °C. Figures 6.5 a and 6.5 b show the temporal evolution of DOC removal and biodegradability, expressed as k' .

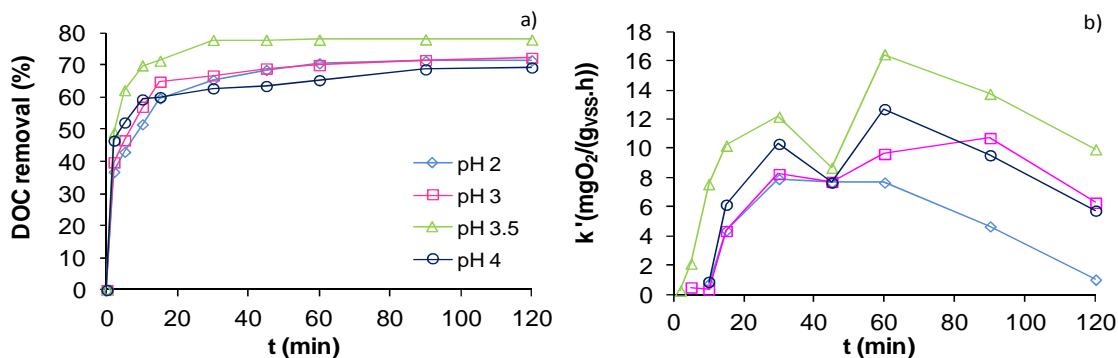


Figure 6.5 - Variation of DOC removal (a) and k' (b) with the initial pH in the first experiment ($T=50 \text{ }^\circ\text{C}$, $[\text{Fe}]=350 \text{ mg/L}$ and $[\text{H}_2\text{O}_2]=3.5 \text{ g/L}$).

The DOC removal occurs again within the first 30 minutes of reaction, remaining almost constant for higher reaction times. Maximum removal (78%) occurred at pH= 3.5, after 30 minutes. Biodegradability generally increases up to 60 minutes of reaction, showing low values, as reported in previous figures, at t=45 min, and then decreases (Figure 6.5 b). Maximum value of k' ($16.5 \text{ mgO}_2/(\text{g}_{\text{VSS}}\cdot\text{h})$) was obtained at pH 3.5, after 60 minutes of reaction.

The optimum pH value of 3.5 was the same whatever the response considered, i.e. the mineralization degree or the biodegradability increase, which are probably related, as discussed previously. The optimum pH value is similar to that found in several other studies dealing with oxidation by the Fenton's process [Meriç et al., 2004; Heredia et al., 2005; Gulkaya et al., 2006; Tekin et al., 2006; Ramirez et al., 2008; Sun et al., 2007; Rodrigues et al., 2009 b)]. The explanation for the occurrence of such an optimum is, in short, related to the decrease of dissolved Fe^{2+} in solution at higher pHs (along with the decreased stability of hydrogen peroxide), while at lower pHs the reaction rate slows down. These issues are well documented in the literature [Szpyrkowicz et al., 2001; Benitez et al., 2001; Lucas and Peres, 2006], and for that reason pH effect was not tested for the 2nd experiment.

6.3.1.5 Optimized Treatment of Simulated Acrylic Dyeing Wastewater

After evaluating the effect of each operating variable on the Fenton process, two new experiments were carried out: in the first experiment, the effluent pre-treated by coagulation/flocculation was submitted to Fenton oxidation at the operating conditions that maximize DOC removal ($[\text{Fe}] = 350 \text{ mg/L}$, $[\text{H}_2\text{O}_2] = 3.5 \text{ g/L}$, $T=50 \text{ }^\circ\text{C}$ and $\text{pH}=3.5$); in the second one, the Fenton's reagent was directly applied to the synthetic wastewater, using the operating conditions that maximize the DOC removal/biodegradability increase, which are the same ($[\text{Fe}^{2+}] = 350 \text{ mg/L}$, $[\text{H}_2\text{O}_2] = 20 \text{ g/L}$, $T=50 \text{ }^\circ\text{C}$ and $\text{pH}=3.5$).

Along 60 minutes of reaction, samples were taken to follow up the toxicity (*Vibrio fischeri* percent inhibition) and HPLC chromatograms (Figures 6.6 and 6.7, respectively). In the first experiment, the *Vibrio fischeri* inhibition decreases along the reaction time, except for t= 45 min (Figure 6.6 a), probably due to the formation of more toxic intermediate compounds, which is also confirmed by the fact that for t=45 min the main peak of the chromatogram shifts to the right and is higher than for t =30 min (Figure 6.7 a). The

Fenton process reduces the toxicity of the effluent (pre-treated wastewater by coagulation/flocculation) from ~ 94-96 to ~ 24-35% after 60 min of reaction, the values depending on the contact time of the sample with the bacteria, which are higher for longer contact times, as could be expected (Figure 6.6 a).

In the second experiment, the toxicity decreased from the initial value of 94-97% to ca. 29% after 60 min of reaction (Figure 6.6 b). The reduction in toxicity for $t \geq 30$ min is small, which is confirmed by the time evolution of the chromatograms (Figure 6.7 b). Obviously, the huge complexity of the raw wastewater and final effluent do not allow an easy identification of the species present therein.

The treated effluent, after 60 minutes of reaction, was chemically analyzed and the results of pH, DOC, BOD₅, COD, visible color after 1:40 dilution and absorbance at 610 nm are presented in Table 6.1. In what concerns color removal, efficiency by chemical coagulation/flocculation was higher than 97% but it increased to 99.8% when coupling the Fenton's oxidation process (Table 6.1). When applying the Fenton's reagent directly to the raw wastewater, the color removal efficiency was similar (99.5%). It is noteworthy that, in all experiments, the entire UV-Visible spectrum was monitored, and as mentioned no other peaks were observed in the visible region, apart from that characteristic of the dye. It was also noticed that efficiencies were similar for the wide range of conditions adopted, and color was always removed in a very short reaction time (typically in less than 2 min – data not shown).

The organic matter removal in the first experiment mainly results from the Fenton process (76.1 and 78.1% for COD and DOC, respectively) as compared with coagulation/flocculation (10.4% for COD and 28.1% for DOC). The combination of both processes allows overall removals of 78.6, 84.2 and 99.8% for COD, DOC and color, respectively. The wastewater treated by the combination of coagulation/flocculation and Fenton's reagent shows values below the maximum allowable limits, and so can be discharged into water bodies or disposed on land. Nevertheless, large quantities of ferrous ion (3075 mg/L; 3000 mg/L in the coagulation and 75 mg/L in the Fenton's process) are consumed in this treatment and consequently great amounts of chemical sludge can be produced.

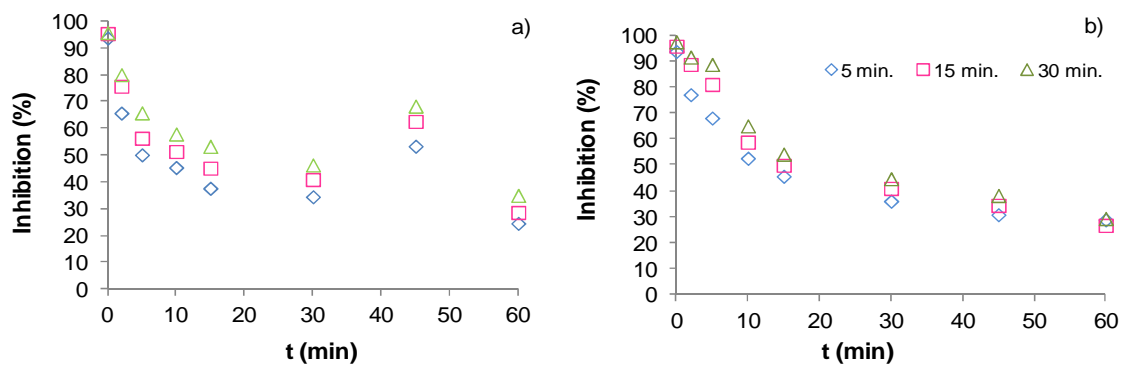


Figure 6.6 - Evolution of the inhibition of *Vibrio fischeri* of samples taken along 60 min of Fenton's reaction for contact times of 5, 15 and 30 min in the first (a) and second experiment (b) (pH= 3.5, T=50 °C, [Fe]=350 mg/L and $[H_2O_2]_1^{st\ exp}=3.5\ g/L$, $[H_2O_2]_2^{nd\ exp}=20\ g/L$).

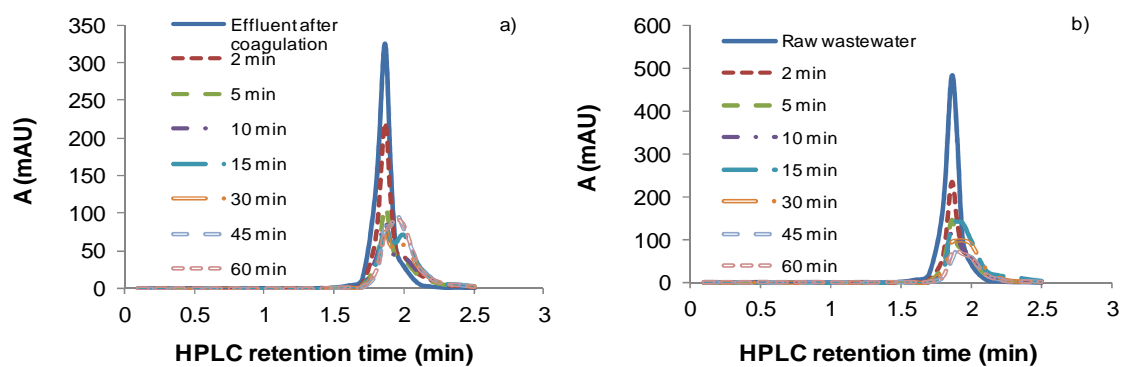


Figure 6.7 - Time evolution of HPLC chromatogram in the first (a) and second experiment (b) (pH= 3.5, T=50 °C, [Fe]=350 mg/L and $[H_2O_2]_1^{st\ exp}=3.5\ g/L$, $[H_2O_2]_2^{nd\ exp}=20\ g/L$).

Chapter 6 - Integration of Physical-Chemical and Oxidation Processes for Acrylic Effluent Treatment

Table 6.1. Characteristics of the synthetic acrylic wastewater, after coagulation/flocculation and after Fenton oxidation (percent removal efficiencies within brackets) and global removal for the combined process.

Parameter	1 st experiment			2 nd experiment	
	Coagulation & flocculation	Fenton	Global removal (%)	Fenton	Maximum Allowable Value****
pH	7.2	7.15	---	7.10	5.5-9.0
Total nitrogen (mg N/L)	15.3 (6.7)	n.d.	n.d.	16.0 (2.4)	
Nitrates (mg NO ₃ ²⁻ /L)	13.0 (17.2)	n.d.	n.d.	13.1 (16.5)	
Total phosphorus (mg P/L)	0.1 (50.0)	n.d.	n.d.	0.2 (0.0)	
Dissolved phosphorus (mg P/L)	< 0.06	n.d.	n.d.	< 0.06	
Chemical oxygen demand (mg O ₂ /L)	741.7 (10.4)	177.2 (76.1)	78.6	289.0 (65.1)	250
Biochemical oxygen demand (mg O ₂ /L)	< 1.0	24.1	---	116.5	100
Dissolved organic carbon (mg C/L)	240.1 (28.1)	52.7 (78.1)	84.2	112.0 (66.5)	
Chlorides (mg Cl ⁻ /L)	45.0 (0.0)	n.d.	n.d.	40.9 (7.3)	
Specific oxygen uptake rate (k') (mg O ₂ /(g _{VSS} .h))	<0.2	16.5	---	17.9	
BOD ₅ :COD ratio	<0.0013	0.14	---	0.40	
Absorbance at λ _{max} (abs. units)	0.047 (97.0*)	0.0055 (91.1**)	99.8	0.0079 (99.5***)	
Visible color after dilution 1:40	not visible	not visible	---	not visible	not visible
<i>Vibro fischeri</i> Inhibition 5 min (%)	94.0	24.0	---	29.0	
<i>Vibro fischeri</i> Inhibition 15 min (%)	95.0	29.0	--	27.0	
<i>Vibro fischeri</i> Inhibition 30 min (%)	96.0	35.0	---	29.0	

n.d. – not determined.

* calculated from the absorbance of raw wastewater at pH 7.2 (1.5502 abs. units).

** calculated from the absorbance after coagulation/flocculation at pH 3.5 (0.0615 abs. units).

*** calculated from the absorbance of raw wastewater at pH 3.5 (1.624 abs. units).

**** Portuguese legislation for discharge of textile wastewaters (Ordinance No. 423/97 of 25 June)

The removal efficiencies in the second experiment (Fenton process alone) were 65.1% for COD, 66.5% for DOC and 99.5% for color, but the values of COD and BOD₅ do not accomplish the maximum allowable discharge limits, although are only slightly above (cf. Table 6.1). So, a subsequent treatment (coagulation/flocculation or biological oxidation) is required, which will be the aim of a subsequent chapter (no 10). The biodegradability of the synthetic effluent increased using both treatment processes, from an initial value of $k' < 0.2 \text{ mg O}_2/(\text{g}_{\text{VSS}} \text{ h})$ up to 16.5 and 17.9 $\text{mg O}_2/(\text{g}_{\text{VSS}} \text{ h})$ for the effluent treated by the combined process and by Fenton oxidation alone, respectively. The ratio BOD₅:COD also indicates an increase of the biodegradability, which is higher (0.40) for the effluent resulting from the Fenton's oxidation directly applied to the raw wastewater, with a value that recommends a subsequent biological treatment with the objective of improving organic compounds removal. In the integrated process, lower amounts of chemicals should therefore be applied in the Fenton's stage, taking advantage of the cheaper biological unit.

The removals of color and organic compounds obtained in the two runs are similar, but given the costs associated with the reagents consumption (based on the industrial cost of each reagent), it was found that the combined process has a lower cost ($\sim 7 \text{ €/m}^3$) than the Fenton alone ($\sim 18.1 \text{ €/m}^3$). Given this fact and the additional advantage that an effluent that can be discharged (in accordance with national legislation) was reached with the combined process of coagulation/flocculation + Fenton, it seems that this is potentially more promising, although requiring a higher investment, but this investment is recovered in the medium time because the operating cost is lower.

6.3.2 Fenton's Reaction Followed by Coagulation/Flocculation

The application of the Fenton process alone does not permit to achieve an effluent that meets the discharge limits (cf. Table 6.1). So, coagulation/flocculation was applied after oxidation aiming at reducing the organic matter concentration. A parametric study was carried out to evaluate the effect of pH and flocculant dose on DOC and color removal. The influence of the coagulant dose was not assessed because only the dissolved iron from the Fenton reaction was employed, thus minimizing the treatment costs.

In the Fenton's step different conditions were tested: one experiment was performed in the conditions that maximized DOC removal and biodegradability, as determined in the 2nd

experiment above mentioned (run #3); in the other experiments the doses of H_2O_2 and Fe^{2+} were reduced to 1/2 and 1/4, respectively, with the objective of lowering the operating costs (runs #2 and #1, respectively). The residual iron concentration used in the coagulation/flocculation stage was 75.5, 118.1 and 275 mg/L in run#1, run#2 and run#3, respectively.

6.3.2.1 Effect of the pH

In order to evaluate the influence of pH on the coagulation/flocculation step, five experiments were carried out in which this parameter was varied between 3.5 and 9.4. Figure 6.8 a and b show the results of DOC and color removal, respectively, for different hydrogen peroxide doses previously employed in Fenton's oxidation. It can be seen that, in all cases, DOC removals increased when the pH varied from 3.5 to 8.3 (for instance, in run #1, for a hydrogen peroxide dose of 5.0 g/L in the Fenton's stage, the DOC removal increased from 33.8 to 39.0% and, from 48.8 to 60.7% in run #3, where 20 g/L of hydrogen peroxide were used in the oxidation stage). Color removal was found to be independent of pH and doses of chemicals used in Fenton's reaction, achieving 99.5% in all experiments.

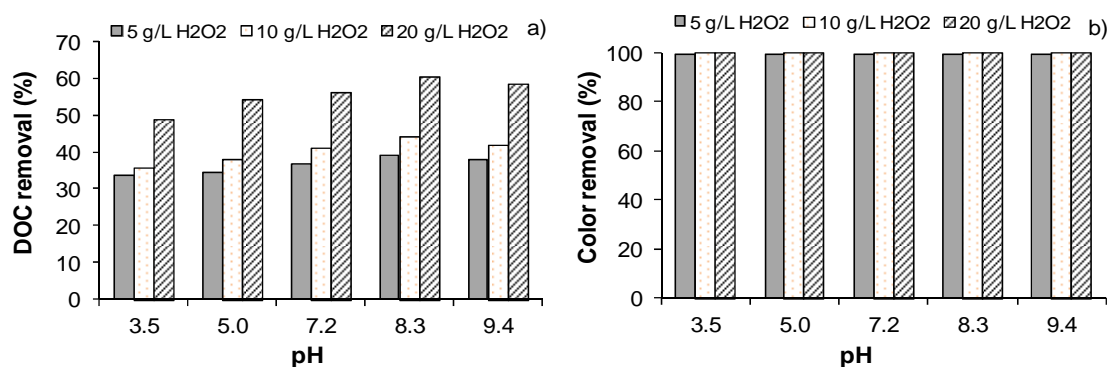


Figure 6.8 – Variation of DOC (a) and color (b) removals with pH in the coagulation stage for different doses of hydrogen peroxide applied in the previous Fenton's process - runs #1, #2 and #3 ($v_{\text{coagulation}}=150$ rpm, $t_{\text{coagulation}}=3$ min, $[Fe \text{ dissolved}]_{\text{run \#1}} = 75.5$ mg/L, $[Fe \text{ dissolved}]_{\text{run \#2}}=118.1$ mg/L, $[Fe \text{ dissolved}]_{\text{run \#3}}=275$ mg/L and $T = T_{\text{ambient}}= 22-24$ °C).

The optimal pH is in the alkaline zone (8.3) and coagulation probably occurs by inclusion of colloids into iron hydroxide, because at this pH the species that are present in solution are $\text{Fe}(\text{OH}_4)^-$ and $\text{Fe}(\text{OH})_3$ [Duan and Gregory, 2003].

6.3.2.2 Effect of Superfloc C-573 Doses

The selection of Superfloc C-573 (cationic polymer) as flocculant took into account the results obtained in preliminary studies (chapters 4 and 5). It was evaluated the effect of flocculant dose (in the range 0.1 to 5 mg/L) on DOC and color removal. Figure 6.9 a and b present the results obtained. It can be observed that DOC removal only slightly increases with the flocculant dose but color removal strongly improved with flocculant addition up to concentrations around 2.5 mg/L.

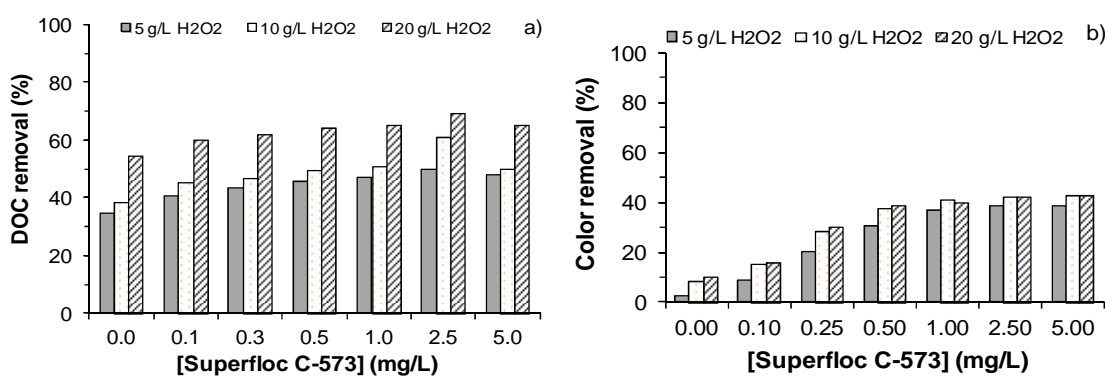


Figure 6.9 – Variation of DOC (a) and color (b) removals with flocculant concentration in the flocculation step for different hydrogen peroxide doses applied in the previous Fenton's process - runs #1, #2 and #3 ($v_{\text{coagulation}}=150$ rpm, $t_{\text{coagulation}}=3$ min, $[\text{Fe dissolved}]_{\text{run \#1}}=75.5$ mg/L, $[\text{Fe dissolved}]_{\text{run \#2}}=118.1$ mg/L, $[\text{Fe dissolved}]_{\text{run \#3}}=275$ mg/L and $T = T_{\text{ambient}}= 22-24$ °C, $v_{\text{flocculation}}=20$ rpm, $t_{\text{flocculation}}=15$ min).

Figure 6.9 a and b also shows maximum removals of 49.7, 60.9 and 69.2% for DOC and 38.8, 41.6 and 42.0% for color in run #1, run #2 and run #3, respectively (i.e., when increasing doses of hydrogen peroxide were employed in the previous Fenton's process). Thus, the optimum flocculant dose considered for subsequent experiments was 2.5 mg/L, a value that is similar to those reported in literature, even with other flocculants [Bes-Piá, 2002; Joo et al., 2007; El-Gohary and Tawfik, 2009].

6.3.2.3 Overall Process Efficiency

After optimizing the coagulation/flocculation stage downstream the Fenton's oxidation process (also carried out under optimized conditions, but using different hydrogen peroxide doses – runs #1 to #3) the overall efficiency of the integrated treatment was assessed.

Table 6.2 presents the characteristics of the effluent after treatment, for runs #1 to #3, the removal efficiencies obtained in each treatment stage and the global efficiency of the integrated process. The results obtained permit concluding that, in all runs, DOC removals were higher in coagulation/flocculation than in Fenton's oxidation, but as regards COD and color removals it was observed the opposite, possibly due to the fact that some organic compounds and dyes are completely mineralized in the oxidative process. Runs #2 and #3, where higher doses of chemicals were employed in Fenton's stage, led to final COD and BOD₅ values in the treated effluent below the maximum legislated limits. In run#3 the global efficiencies achieved with the combination of the two treatment techniques were 85.5, 15.6, 88.9 and 99.8% for COD, BOD₅, DOC and color, respectively. However, taking into account the costs associated with the reagents consumption, the conditions of run #2 are the best choice because they correspond to smaller costs (9.1 €/m³) compared to run #3 (18.1 €/m³).

Table 6.2 - Characteristics of the synthetic acrylic dyeing wastewater after Fenton oxidation and coagulation/flocculation (percent removal efficiencies within brackets) and global removal for the combined process; runs #1 to #3 correspond to different dosages of hydrogen peroxide in the Fenton's stage.

Parameter	Run #1			Run #2			Run #3			Maximum Allowable Value***
	Fenton's oxidation	Coagulation & flocculation	Global removal (%)	Fenton's oxidation	Coagulation & flocculation	Global removal (%)	Fenton's oxidation	Coagulation & flocculation	Global removal (%)	
pH	-	8.31	-	-	8.30	-	-	8.32	-	5.5-9.0
Chemical oxygen demand (mg O ₂ /L)	425.4 (48.6)	298.3 (29.9)	64.0	371.6 (55.1)	200.5 (46.1)	75.8	303.6 (63.3)	120.5 (60.3)	85.5	250
Biochemical oxygen demand (mg O ₂ /L)	28.7 (0.0)	24.0 (16.4)	16.4	49.5 (0.0)	41.4 (16.3)	16.3	106.0 (0.0)	89.5 (15.6)	15.6	100
Dissolved organic carbon (mg C/L)	206.5 (38.2)	103.9 (49.7)	68.9	170.2 (49.1)	66.5 (60.9)	80.1	120.0 (64.1)	37.0 (69.2)	88.9	
BOD ₅ :COD ratio	0.07	0.08	-	0.13	0.21	-	0.35	0.74	-	
Absorbance at λ_{max} (abs. units)	0.009 (99.5*)	0.0052 (42.2**)	99.7	0.0089 (99.7*)	0.0053 (41.0**)	99.7	0.0089 (99.5*)	0.0031 (65.2**)	99.8	
Visible color after dilution 1:40	not visible	not visible	-	not visible	not visible	-	not visible	not visible	-	not visible

* calculated from the absorbance of wastewater at pH 3.5 (1.6399 abs. units).

** calculated from the absorbance after Fenton at pH 8.3 (0.009 abs. units for run #1, #2 and #3).

*** Portuguese legislation for discharge of textile wastewaters (Ordinance No. 423/97 of 25 June).

6.4 Conclusions

The combined treatment of a synthetic acrylic dyeing effluent by coagulation/flocculation and Fenton's reagent showed that: i) Fe and H₂O₂ doses of 350 mg/l and 3.5 g/L, respectively, maximize DOC removal and biodegradability increase in the Fenton's stage; ii) DOC removal is better at 50 °C, although biodegradability only increased up to 30 °C; iii) optimum pH for Fenton oxidation is 3.5; iv) overall efficiencies of 99.8, 84.2 and 78.6% were obtained for color, DOC and COD, respectively; v) biodegradability was improved (the specific oxygen uptake rate increased from <0.2 to 16.5 mg O₂/(g_{SSV}·h) and BOD₅:COD ratio from <0.0013 to 0.14); and vi) inhibition of *Vibrio fischeri* was reduced (from ~ 94-97 to ~ 24-35% after 60 min of reaction). The integrated process provided an effluent that meets maximum allowable discharge values, but high doses of iron are consumed in the overall process (3075 mg/L).

Fenton oxidation applied directly to the dyeing wastewater provided also very high color removal (99.5%) and considerable DOC (66.5%) and COD (65.1%) abatements using 350 mg/L of Fe²⁺, 20 g/L of H₂O₂ and operating at pH 3.5 and 50 °C, but COD and BOD₅ levels are still slightly higher than the discharge values. An additional treatment step is necessary, which could be biological oxidation, since Fenton's pre-oxidation improved considerably the biodegradability of the effluent (BOD₅:COD ratio raised from <0.0013 to 0.40); chemical coagulation/flocculation could be also considered, taking advantage of the dissolved iron. In any case, reduction of chemicals should be envisaged, particularly hydrogen peroxide.

It was in general observed the existence of a relationship between mineralization and increase of biodegradability, as inferred from the DOC and specific oxygen uptake rate (k') histories. In most experiments, optimum conditions for DOC removal are the same as for k' increase, meaning that higher oxidation degrees lead to the decrease of toxic substances in the wastewater/formation of more biodegradable species. This was also corroborated by the evolution of the inhibition of *Vibro fischeri* in independent experiments. However, along oxidation different intermediates are formed, and therefore biodegradability (or toxicity) does not monotonically increases (or decreases) along time.

The combination of Fenton's oxidation plus coagulation/flocculation, using optimized conditions for both techniques, provided a final effluent that can be discharged into water

bodies, leading to global removals of 85.5, 15.6, 88.9 and 99.8% for COD, BOD₅, DOC and color, respectively. However, the associated costs (~18 €/m³) can decrease to ~9 €/m³ by reducing the H₂O₂ dose to 1/2 of the optimum one, the effluent still complying with the discharge limits.

When applying coagulation/flocculation followed by Fenton's reaction slightly smaller costs regarding reagents consumption (~7 €/m³) were reached.

6.5 References

Azbar, N.; Yonar, T.; Kestioglu, K. (2004). Comparison of Various Advanced Oxidation Processes and Chemical Treatment Methods for COD and Color Removal from a Polyester and Acetate Fiber Dyeing Effluent. *Chemosphere*, 55, 35-43.

Bautista, P.; Mohedano, A.F.; Gilarranz, M.A.; Casas, J.A.; Rodriguez, J.J (2007). Application of Fenton oxidation to domestic wastewaters treatment. *Journal of Hazardous Materials*, 143, 128-134.

Benítez, F.; Acero, J.; Real, F.; Rubio, F.; Leal, A. (2001). The role of hydroxyl radicals for the decomposition of p-hydroxy phenylacetic acid in aqueous solutions. *Water Research*, 35, 1338-1343.

Bes-Piá, A.; Mendoza-Roca, J.A.; Alcaina-Miranda, M.I.; Iborra-Clar, A.; Iborra-Clar M.I. (2002). Reuse of wastewater of the textile industry after its treatment with combination of physical-chemical treatment and membrane technologies. *Desalination*, 149, 169-174.

El-Gohary, F., Tawfik, A. (2009). Decolourization and COD reduction of disperse and reactive dyes wastewater using chemical-coagulation followed by sequential batch reactor (SBR) process. *Desalination*, 249, 1159-1164.

Flaherty, K.A.; Huang, C.P. (1992). Continuous Flow Applications of Fenton's Reagent for the Treatment of Refractory Wastewater. In: *Proceedings of the Second International Symposium on Chemical Oxidation-Technologies for the Nineties*, Nashville, Tennessee, U.S.A., 58-77.

Fu, F.; Wang, Q.; Tang, B. (2009). Fenton and Fenton-like reaction followed by hydroxide precipitation in the removal of Ni(II) from NiEDTA wastewater: A comparative study. *Chemical Engineering Journal*, 155, 769-774.

Gulkaya, Í.; Surucu, G.A.; Dilek, F.B. (2006). Importance of H₂O₂/Fe²⁺ ratio in Fenton's treatment of a carpet dyeing wastewater. *Journal of Hazardous Materials*, B136, 763-769.

Heredia, A.B. de; Torregrosa, J.; Dominguez, J.R.; Partido, E. (2005). Physico-chemical treatment for the depuration of wine distillery wastewaters (vinasses). *Water Science and Technology*, 51 (1), 159-166.

Chapter 6 - Integration of Physical-Chemical and Oxidation Processes for Acrylic Effluent Treatment

Joo, D.J.; Shin, W.S.; Choi, J.-H.; Choi, S. J.; Kim, M.-C.; Han, M.H.; Ha, T. W.; Kim, Y.-H. (2007). Decolourization of reactive dyes using inorganic coagulants and synthetic polymer. *Dyes and Pigments*, 73, 59-64.

Li, R.; Yang C.; Chen, H.; Zeng, G.; Yu, G.; Guo, J. (2009). Removal of triazophos pesticide from wastewater with Fenton reagent. *Journal of Hazardous Materials*, 167, 1028-1032.

Lodha, B.; Chaudhari, S. (2007). Optimization of Fenton-Biological treatment scheme for the treatment of aqueous dye solutions. *Journal of Hazardous Materials*, 148, 459-466.

Lucas, M.S.; Peres, J.A. (2006). Decolourization of the azo dye Reactive Black 5 by Fenton and photo-Fenton oxidation. *Dyes and Pigments*, 71, 236-244.

Martins, R.C.; Rossi, A.F.; Quinta-Ferreira, R.M. (2010). Fenton's oxidation process for phenolic wastewater remediation and biodegradability enhancement. *Journal of Hazardous Materials*, 180, 716-721.

Meriç, S.; Kaptan, D.; Ölmez, T (2004). Color and COD removal from wastewater containing Reactive Black 5 using Fenton's oxidation process. *Chemosphere*, 54, 435-441.

Perdigon-Melon, J.A.; Carbajo, J.B.; Petre, A.L.; Rosal, R.; Garcia-Calvo, E. (2010). Coagulation - Fenton coupled treatment for ecotoxicity reduction in highly polluted industrial wastewater. *Journal of Hazardous Materials*, 181, 127-132.

Peres, J. A.; Heredia, J.B. de; Domínguez, J.R. (2004). Integrated Fenton's reagent - coagulation/flocculation process for the treatment of cork processing wastewaters. *Journal of Hazardous Materials*, 107 (3), 115-121.

Ramirez, J.H.; Costa, C.A.; Madeira, L.M. (2005). Experimental design to optimization the degradation of the synthetic dye Orange II using Fenton's reagent. *Catalysis Today*, 107-108, 68-76.

Ramirez, J.H.; Lampinen, M.; Vicente, M.A.; Costa, C.A.; Madeira, L.M. (2008). Experimental design to optimize the oxidation of Orange II dye solution using a clay-based Fenton-like catalyst. *Industrial & Engineering Chemistry Research*, 47 (2), 284-294.

Rodrigues, C.S.D.; Madeira, L.M.; Boaventura, R.A.R. (2009 a)). Optimization of the azo dye Procion Red H-EXL degradation by Fenton's reagent using experimental design. *Journal of Hazardous Materials*, 164, 987-994.

Rodrigues, C.S.D.; Madeira, L.M.; Boaventura, R.A.R. (2009 b)). Treatment of textile effluent by chemical (Fenton's Reagent) and biological (Sequencing Batch Reactor) oxidation. *Journal of Hazardous Materials*, 172, 1551-1559.

Szpyrkowicz, L; Juzzolino, C; Kaul, S. (2001). A comparative study on oxidation of disperse dyes by electrochemical process, ozone, hypochlorite and Fenton reagent. *Water Research*, 35, 2129-2136.

Sun, J.-H.; Sun, S.-P.; Wang, G.-L.; Qiao, L.-P. (2007). Degradation of azo dye amido black 10B in aqueous solution by Fenton oxidation process. *Dyes and Pigments*, 74, 647-652.

Tantak, N.P.; Chaudhari, S. (2006). Degradation of azo dyes by sequential Fenton's oxidation and aerobic biological treatment. *Journal of Hazardous Materials*, B136, 698-705.

Tekin, H.; Bilkay, O., Ataberk S.S.; Balta, T.H.; Ceribasi, I.H.; Sanin F.D.; Dilek, F.B.; Yetis, U. (2006). Use of Fenton oxidation to improve the biodegradability of a pharmaceutical wastewater. *Journal Hazardous Materials*, B136, 258-265.

Wu, Y.; Zhou, S.; Ye, X.; Zhao, R.; Chen, D. (2011). Oxidation and coagulation removal of humic acid using Fenton process. *Colloids and Surface A: Physicichemical and Engineering Aspects*, 379,151-156.

Xing, Z.-P.; Sun, D.-Z. (2009). Treatment of antibiotic fermentation wastewater by combined polyferric sulfate coagulation, Fenton and sedimentation process. *Journal of Hazardous Materials*, 168, 1264-126.

Chapter 7

Integration of Physical-Chemical and Oxidation Processes for Cotton Dyeing Effluent Treatment *

* This Chapter is based on the publication "Rodrigues C.S.D.; Boaventura, R.A.R.; Madeira, L.M. A New Strategy for Treating a Cotton Dyeing Wastewater - Integration of Physical-Chemical and Advanced Oxidation Processes". Submitted to International Journal of Environment and Waste Management.

7 Integration of Physical-Chemical and Oxidation Processes for Cotton Dyeing Effluent Treatment

7.1 Introduction

This chapter regards the evaluation of the treatability of a simulated cotton dyeing effluent by combining coagulation/flocculation and Fenton's oxidation processes to reduce the disadvantages of each treatment when used alone. Besides, by using an iron salt as coagulant in the first stage, the amount of catalyst added in the chemical oxidation step is reduced, thus decreasing the overall treatment cost. The same also applies if coagulation is preceded by Fenton's oxidation. A synthetic wastewater with a composition similar to that of a real effluent was used, for minimizing the experimental problems that result from the seasonal variations in real effluents from this type of industries. The main objective was therefore to find the best treatment approach and adjust the operating conditions in order to obtain an effluent that can be discharged into water bodies, i.e., an effluent that accomplishes the maximum allowable limits imposed by legislation for discharge, while simultaneously reducing the operating costs. An economic analysis was thus accomplished, taking into account the operating costs associated to the consumption of chemicals in each stage. The approaches herein considered are only scarcely addressed in the scientific literature, are almost always focused in processes efficiencies only and, up to the author knowledge, were never integrated with costs assessment. In fact, different combinations of these types of treatments allow reaching very good performances, which makes the operating costs associated with each process or strategy a key factor to be considered.

7.2 Materials and Methods

7.2.1 Preparation of the Simulated Textile Effluent

The cotton dyeing effluent was simulated according to the information reported in chapter 3, section 3.2.1.

7.2.2 Experimental Procedure

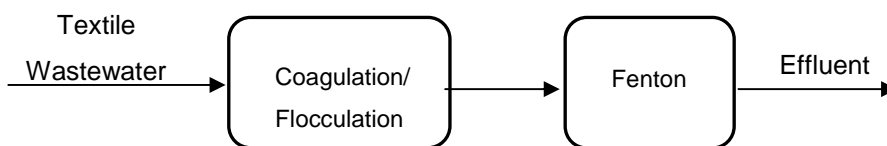
The coagulation/flocculation and Fenton's oxidation experiments were performed as described, respectively, in sections 3.4.1 and 3.4.2 of chapter 3.

In the coagulation/flocculation process, after 30 min of sedimentation, the supernatant was collected and acidified to pH 1 with HNO₃ (68%, from Merck) to keep the iron dissolved (so that it could be used as catalyst in Fenton's reaction). In the integration of Fenton's reaction with coagulation/flocculation the supernatant from the Fenton's process was previously centrifuged at 13400 rpm for 2 min (Mini Spin Eppendorf), and then acidified with HNO₃ (68%, from Merck) to pH 1 to keep the iron dissolved for the coagulation/flocculation stage and simultaneously slow down or inhibit the Fenton's reaction.

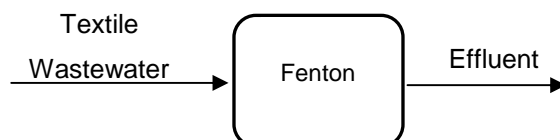
All coagulation/flocculation experiments were conducted at room temperature (21-23 °C).

7.2.3 Research Strategy

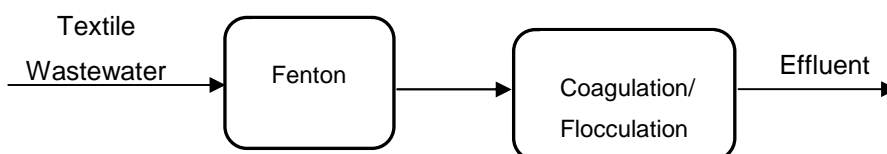
The methodology adopted involved three different approaches depending on the type and sequence of the treatment processes applied (see Figure 7.1). Because the pre-treatment of the raw wastewater by coagulation/flocculation did not allow obtaining an effluent that can be discharged into water bodies (the value of COD was slightly above the maximum allowable discharge limit – cf. Table 5.4 of chapter 5), it was necessary to use a further treatment. However, the BOD₅/COD ratio of the resulting effluent is too low (0.28 – Table 5.4 of chapter 5) for considering a biological treatment. So, integration of coagulation/flocculation with chemical oxidation by Fenton's reagent was attempted (Approach 1 – Figure 7.1). In the chemical oxidation stage performed, a parametric study was carried out where it was individually varied the dose of Fe²⁺ added, the initial concentration of hydrogen peroxide and the temperature, to better understand the effect of each variable in color and DOC removal. Then, an experiment was carried out to assess if the final effluent had characteristics that allowed discharging it into the environment, and the operating costs assessed.



Approach 1: Integration of coagulation/flocculation followed by Fenton's reaction



Approach 2: Fenton's oxidation alone



Approach 3: Combination of Fenton's oxidation followed by coagulation/flocculation

Figure 7.1 - Schematic diagram of process configurations adopted.

In Approach 2 Fenton's oxidation was directly applied to the effluent. The objective was to assess if the chemical oxidation per se would be able to produce an effluent meeting legal standards. This treatment will be analyzed in section 7.3.2 and, again, and a parametric study was implemented to better comprehend the effect of each variable (Fe^{2+} concentration, initial H_2O_2 concentration and temperature) in the process efficiency.

In Approach 3, the Fenton's reagent (under the previously determined optimum conditions of Approach 2) was followed by coagulation/flocculation (because it was concluded that chemical oxidation alone is not effective enough). For the coagulation stage it was also analyzed the effect of the most relevant conditions (pH and flocculant dose), using as coagulant the dissolved iron resulting from Fenton's oxidation. Because for this strategy the costs revealed to be quite high, further runs were carried out in which the dose of chemicals (H_2O_2 and Fe^{2+}) was progressively reduced in the Fenton's stage: first by 1/2, and subsequently to 1/4; as detailed below, no further runs were done because the effluent was no longer meeting legislation standards.

7.2.4 Analytical Methods

The analytical determinations of the various parameters were performed as described in section 3.3 of the Experimental Section (chapter 3).

All analytical determination were performed in duplicate, with exception of absorbance at 520 nm, and the coefficients of variation were less than to 2% for DOC, 17% for BOD₅, 6% for COD and k', 3% for inhibition of *V. fisheri* and 5% for the other parameters.

7.3 Results and Discussion

The more relevant characteristics of the synthetic cotton dyeing wastewater used in this study are reported in Table 3.4 of chapter 3. It is a colored effluent presenting high values of pH and chlorides, moderate concentration of organic matter (DOC and COD) and low biodegradability (BOD₅:COD ratio <0.4) but is not toxic for *Vibrio fischeri*.

7.3.1 Combination of Coagulation/Flocculation and Fenton's Reagent (Approach 1)

Section 7.2.3 presents a brief explanation about: i) the need of a subsequent process after the coagulation/flocculation stage and ii) the reasons for choosing the Fenton's reagent. So, a detailed parametric study was carried out, analyzing the effect of the most important variables in the Fenton's process, aiming choosing the best ones that lead to higher color and DOC removals. Among the variables studied, the concentration of catalyst (ferrous iron salt) was considered, in addition to the dose resulting from the coagulation stage (0.29 mg Fe/L); the effect of the initial concentration of hydrogen peroxide and temperature on color and DOC removal was also analyzed. In the following subsections are presented the results obtained for each variable studied during the Fenton's stage.

7.3.1.1 Influence of Ferrous Ion Concentration

To study the effect of the iron dose in color and DOC removal, the following range was considered: from 0.29 up to 200 mg/L; higher doses did not lead to improved performances, as shown below. The H_2O_2 concentration and temperature were fixed at 500 mg/L and 30 °C, respectively.

In general, and as can be seen in Figure 7.2 a-b, color removal is very rapid in the first 15 minutes, remaining practically constant for longer reaction times. DOC removal is also fast in the first 15 minutes of reaction, then slows down till 60 minutes of reaction, and presents a negligible increase for $t > 60$ minutes.

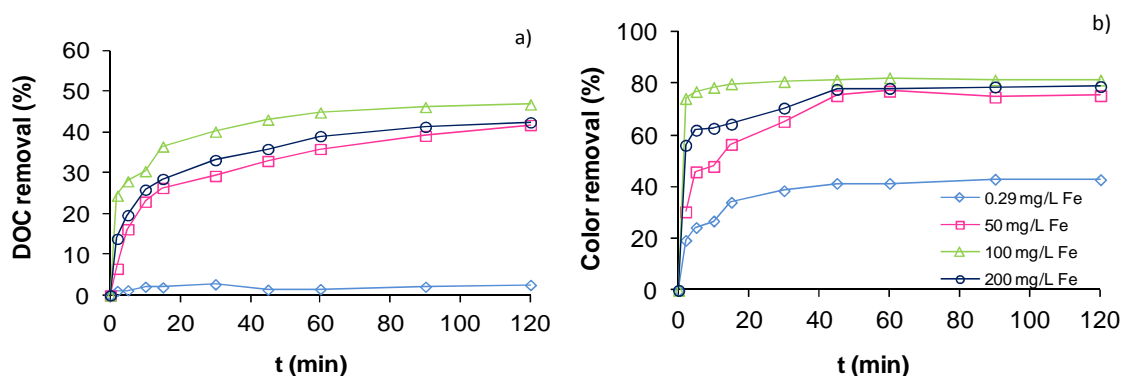


Figure 7.2 – Variation of dissolved organic carbon (a) and color (b) removal along time with the iron dose during the Fenton reaction after the coagulation/flocculation stage – Approach 1 (initial pH=3.5, T=30 °C, $[\text{H}_2\text{O}_2]_0=500$ mg/L).

The two responses considered (color and dissolved organic carbon removal) increased with the iron dose up to 100 mg/L, and the reaction rate is also higher. However, if the amount of iron is increased up to 200 mg/L, both the rate of reaction and process performance are detrimentally affected, either in terms of color or DOC removal. The existence of an optimum iron dose is also reported in others works that evaluated either dyes or organic compounds removal [Malik and Saha, 2003; Meriç et al., 2004; Sun et al., 2007; Rodrigues et al., 2009 a)] and is explained by the scavenging reaction of the hydroxyl radicals by excess of iron ions (Equation 2.4 of chapter 2), thereby decreasing the concentration of radicals available and limiting the oxidation of the organic

compounds. With 100 mg/L of Fe added it was obtained ~81% of color removal (as long as $t > 15$ minutes), and 46.8% for DOC reduction after 120 min of reaction. It is noteworthy that if no iron was added in the Fenton's process, making use of the dissolved iron proceeding from the coagulation/flocculation stage, it is possible to degrade the dyes, but at a slow rate. However, mineralization was insignificant. This evidences the need of adding further iron in the Fenton's step.

The optimum iron dose found is similar to that reported in other studies. For instance, Kim et al. [2004] obtained the optimum concentration of ferrous ion of 90.2 mg/L for removing the Reactive Dye Blue 49 and also for COD abatement (initial COD=300 mg/L and $[\text{dye}]_0=500$ mg/L).

7.3.1.2 Effect of the Initial Hydrogen Peroxide Concentration

The reaction of hydrogen peroxide with Fe^{2+} in acidic conditions generates hydroxyl radicals (Equation 2.1 of chapter 2), and thus the H_2O_2 concentration influences the decomposition of the dyes and organic matter by Fenton's oxidation. In this study the dose of oxidant was varied between 250 and 750 mg/L (this range was established taking into account the organic load, in terms of COD present in solution after the coagulation/flocculation step). The other parameters were kept constant at 30 °C for temperature and 100 mg/L for the amount of iron.

In Figure 7.3 a are shown the results of DOC removal. It can be see that most of the organic carbon is removed in the first 30-40 minutes, but continues to slightly increase till 60 or 120 min. The DOC removal increases with the H_2O_2 concentration up to 500 mg/L, and slightly decreases for a higher dose. For this optimum dose the DOC removals are 40.1 and 46.8%, respectively, after 30 and 120 minutes of reaction. The results of color removal during 120 minutes of reaction are presented in Figure 7.3 b, showing again that its removal occurs, preferentially, in the first 5-15 minutes of reaction (depending on the initial concentration of hydrogen peroxide). It is notorious the influence of the hydrogen peroxide dose in this period, leading to ~80% of color removal for $[\text{H}_2\text{O}_2] = 500$ mg/L and $t \sim 15$ min, without any significant increase for longer reaction times. The same optimum dose of peroxide was observed in the color removal (Figure 7.3 b).

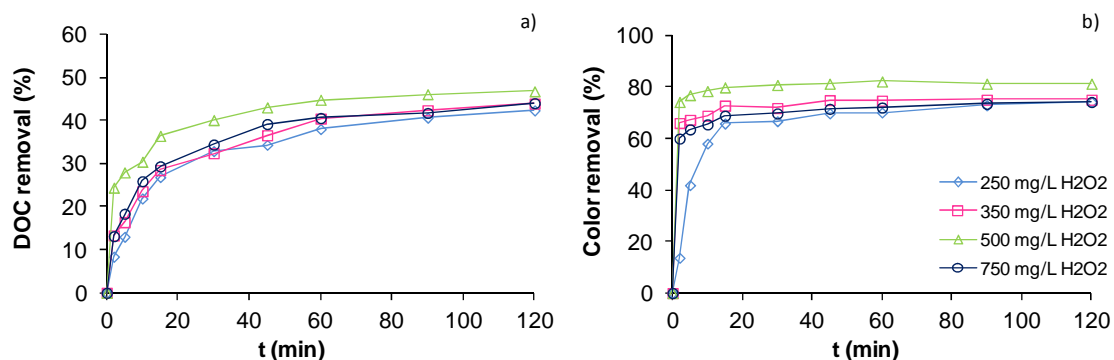


Figure 7.3 – Variation of dissolved organic carbon (a) and color (b) removal along time with the concentration of H_2O_2 added during the Fenton's reaction after the coagulation/flocculation stage – Approach 1 (initial pH=3.5, T=30 °C, [Fe]=100 mg/L).

The existence of an optimum H_2O_2 concentration was also observed by other authors [Azbar et al., 2004; Ramirez et al., 2005; Alaton and Teksoy, 2007; Rodrigues et al., 2009 a)] and is explained by the fact that a parallel reaction between H_2O_2 , in excess, with the hydroxyl radicals occurs, generating HO_2^\bullet species with a lower oxidation potential (Equation 2.3 of chapter 2).

In the literature there are various studies dealing with the treatment of dye-containing solutions or effluents through Fenton's oxidation where optimum H_2O_2 concentration, similar to that obtained in this study, have been reported. In particular, Swaminathan et al. [2003] studied the degradation of three different dye solutions with 250 mg/L of Red M5B (initial COD=142 mg/L), of an H-acid (initial COD=215 mg/L) and of Blue MR (initial COD=180 mg/L) and obtained the optimum dose of hydrogen peroxide in the range of 400-500 mg/L. Meriç et al. [2004] obtained 98% color removal and 76% of COD reduction in a solution with 100 mg/L of RB5 dye (initial COD=75 mg/L) when using 500 mg/L of H_2O_2 (optimum dose) through the Fenton's process. Later on, Meriç et al. (2005) tested the treatment of a synthetic dyeing wastewater (BOD=150 mg/L, COD=560 mg/L) and found an optimum hydrogen peroxide concentration of 800 mg/L.

7.3.1.3 Effect of the Temperature

The temperature is a key variable that has to be taken into account because has an important influence in the efficiency and rate of the Fenton's reactions. In order to

Chapter 7 - Integration of Physical-Chemical and Oxidation Processes for Cotton Dyeing Effluent Treatment

determine the effect of this parameter in color and COD removal, a series of experiments were conducted by varying the reaction temperature between 10 and 70 °C while fixing the other variables in the optimum values determined before.

Figure 7.4 a-b presents the results obtained and show that temperature exerts a strong effect in the mineralization of the organic compounds and color removal. These removals are accelerated when the temperature increased up to 50 °C, but at 70 °C the color removal was not improved, and the DOC removal inclusively slightly decreased as compared to performances reached at 50 °C.

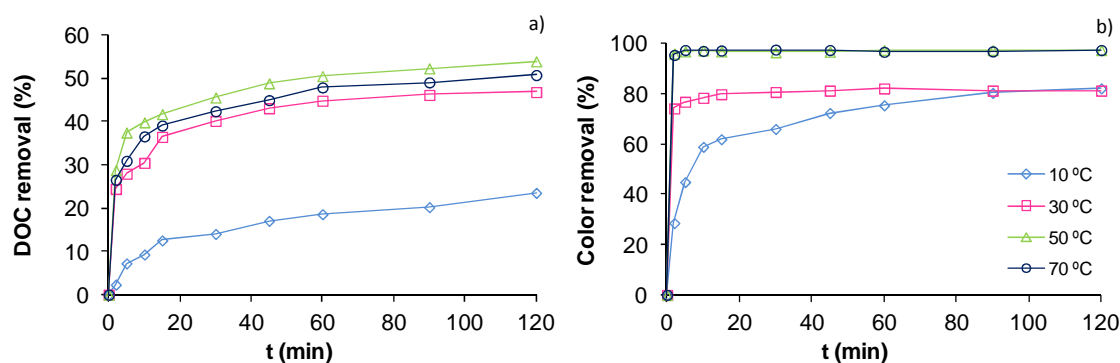


Figure 7.4 – Variation of dissolved organic carbon removal (a) and color (b) along time with the temperature during the Fenton reaction after the coagulation/flocculation stage – Approach 1 (initial pH=3.5, [Fe]=100 mg/L and [H₂O₂]₀=500 mg/L).

At the optimum temperature of 50 °C, a very high color removal was obtained in only 2 minutes of reaction (95.9%), which was nearly the same as that reached after 120 minutes of reaction (97.3%). For mineralization, after 30 min a value of 45.5% was achieved, but it continued to increase slowly (50.4% and 53.8% for 60 and 120 min of reaction, respectively). This optimum value for temperature was also reported in other studies that evaluated the removal of total organic carbon and dyes [Ramirez et al., 2005; Gulkaya et al., 2006; Sun et al., 2007; Rodrigues et al., 2009 a)].

The reason for obtaining an optimum temperature has been attributed to the fact that, on one hand, the rate of reaction and inherently the performance increases, because the kinetic constants also increase with the temperature (Arrhenius law), but on the other

hand, for higher temperatures ($T > 40-50$ °C) the hydrogen peroxide decomposes into oxygen and water [Ramirez et al., 2008].

7.3.1.4 Optimized Treatment Performance

After having carrying out the parametric study, which allowed to establish the optimal conditions for the Fenton process ($[Fe] = 100$ mg/L, $[H_2O_2] = 500$ mg/L and $T = 50$ °C), an additional run was performed using these operating conditions for 60 minutes of reaction only (because for longer reaction times oxidation performance is almost not improved, as shown in the previous Figures). Under such optimized conditions, the inhibitory effect of the effluent on *Vibrio fischeri* was analyzed. It was observed that the inhibition remained at 0%, meaning that the organic intermediates generated in the Fenton's process show no toxicity to these bacteria.

The treated effluent, after 60 minutes of reaction, was analyzed and the results (upon neutralization) of DOC, BOD₅, COD, visible color after 1:40 dilution and absorbance at 520 nm are presented in Table 7.1. The organic matter removal reached in the Fenton process (48.8% for COD, 22.5% for BOD₅ and 50.4% for DOC) was higher than in the coagulation/flocculation stage (25.2% for COD, 4.3% for BOD₅ and 41.9% for DOC); the overall removal efficiencies obtained with the combination of these two treatments were 61.7, 25.8, 71.2 and 99.8% for COD, BOD₅, DOC and color, respectively. The wastewater biodegradability, as inferred from the BOD₅/COD ratio, increased slightly with the coagulation/flocculation process, from 0.22 to 0.28. A more significant increase was observed with the chemical oxidation, the final effluent being biodegradable (BOD₅/COD=0.43). However, it is important to highlight that the wastewater, after being submitted to the combined treatment of coagulation/flocculation and Fenton's oxidation (Approach 1), can be discharged into water bodies because it exhibits values below the maximum allowable limits (according to Portuguese legislation for the textile sector – cf. Table 7.1). Such limits are not reached by the coagulation/flocculation process alone.

Chapter 7 - Integration of Physical-Chemical and Oxidation Processes for Cotton Dyeing Effluent Treatment

Table 7.1 - Characteristics of the synthetic cotton dyeing wastewater after coagulation/flocculation and after Fenton oxidation (percent removal efficiencies within brackets) and global removal for the combined process (Approach 1).

Parameter	Coagulation & flocculation	Fenton	Global removal (%)	Maximum Allowable Limit***
pH	9.4	7.05	-	5.5-9.0
Total nitrogen (mg N/L)	3.8 (2.6)	n.d.	-	
Nitrates (mg NO ₃ ²⁻ /L)	4.22 (0.0)	n.d.	-	
Total phosphorus (mg P/L)	4.5 (24.3)	n.d.	-	
Dissolved phosphate (mg P/L)	< 0.06 (100)	n.d.	-	
Chemical oxygen demand (mg O ₂ /L)	261.9 (25.2)	134.0 (48.8)	61.7	250
Biochemical oxygen demand (mg O ₂ /L)	74.1 (4.3)	57.4 (22.5)	25.8	100
Dissolved organic carbon (mg C/L)	68.2 (41.9)	33.9 (50.4)	71.2	
Chlorides (mg Cl ⁻ /L)	8030 (0.0)	n.d.	-	
BOD ₅ :COD ratio	0.28	0.43	-	
Absorbance at λ _{max} (abs. units)	0.034 (92.2*)	0.0015 (97.3**)	99.8	
Visible color after dilution 1:40	not visible	not visible	-	not visible

n.d. – not determined.

* calculated from the absorbance of wastewater at pH 9.4 (0.3875 abs. units).

** calculated from the absorbance after coagulation/flocculation at pH 3.5 (0.0564 abs. units).

*** Portuguese legislation for discharge of textile wastewaters (Ordinance No. 423/97 of 25 June).

7.3.2 Fenton Oxidation (Approach 2)

In Approach 2 it was evaluated the treatability of the synthetic cotton dyeing wastewater by Fenton's oxidation *per se*. A parametric study was performed, being evaluated the influence of initial ferrous salt and hydrogen peroxide concentrations and temperature in color and DOC removal. The effects in the effluent biodegradability (assessed by measuring k' – specific oxygen uptake rate) were also determined, aiming assessing the possibility of integrating subsequently a biological treatment.

7.3.2.1 Influence of Ferrous Ion Concentration

For evaluating the effect of the catalyst dose four runs were carried out wherein this parameter was varied between 100 and 350 mg/L. The other variables were fixed at 5 g/L for H₂O₂, 3.5 for pH and 30 °C for temperature.

The organic carbon removal (see Figure 7.5 a) occurs more rapidly in the first 20-30 minutes of reaction, and after this time the rate of mineralization slows down, whatever the load of catalyst employed. The mineralization at the end of the experiments increased from 30.7 to 41.4% when the dose of ferrous ion increased from 100 to 300 mg/L, but further increasing the dose of catalyst do not result in any improvement in DOC removal.

In Figure 7.5 b are shown the results obtained for color removal. It can be concluded that: i) for 100 and 275 mg/L of Fe²⁺ color abatement proceeded at a slower rate as compared to the other runs, where higher concentrations of catalyst were employed; ii) for the first two concentrations the color removal reaches its maximum (and then remains nearly constant) within 10-15 minutes of reaction while for 300 and 350 mg/L of Fe²⁺ only 5 minutes were required to reach that point; iii) for 300-350 mg/L of Fe²⁺ a color removal of ~90% was reached.

The biodegradability, expressed in terms of the specific oxygen uptake rate - k' , decreased after 2 minutes of reaction as compared to the raw wastewater, but tended to increase up to 60 min of reaction (Figure 7.5 c); afterwards an inversion of the k' value was noticed. A possible explanation for the k' profiles is related to the formation of more recalcitrant compounds at the earlier stages of the reaction (responsible for the lowest k' values), which are further converted into more biodegradable compounds as reaction proceeds. These intermediates in turn revert into less biodegradable substances for very long reaction times. A similar pattern was also observed in a previous work, with a similar effluent (c.f. results in chapter 6). The maximum biodegradability, corresponding to k' of 10.8 mg O₂/(g_{VSS}.h), was achieved after 60 minutes of reaction and when using 300 mg/L of ferrous ion.

Chapter 7 - Integration of Physical-Chemical and Oxidation Processes for Cotton Dyeing Effluent Treatment

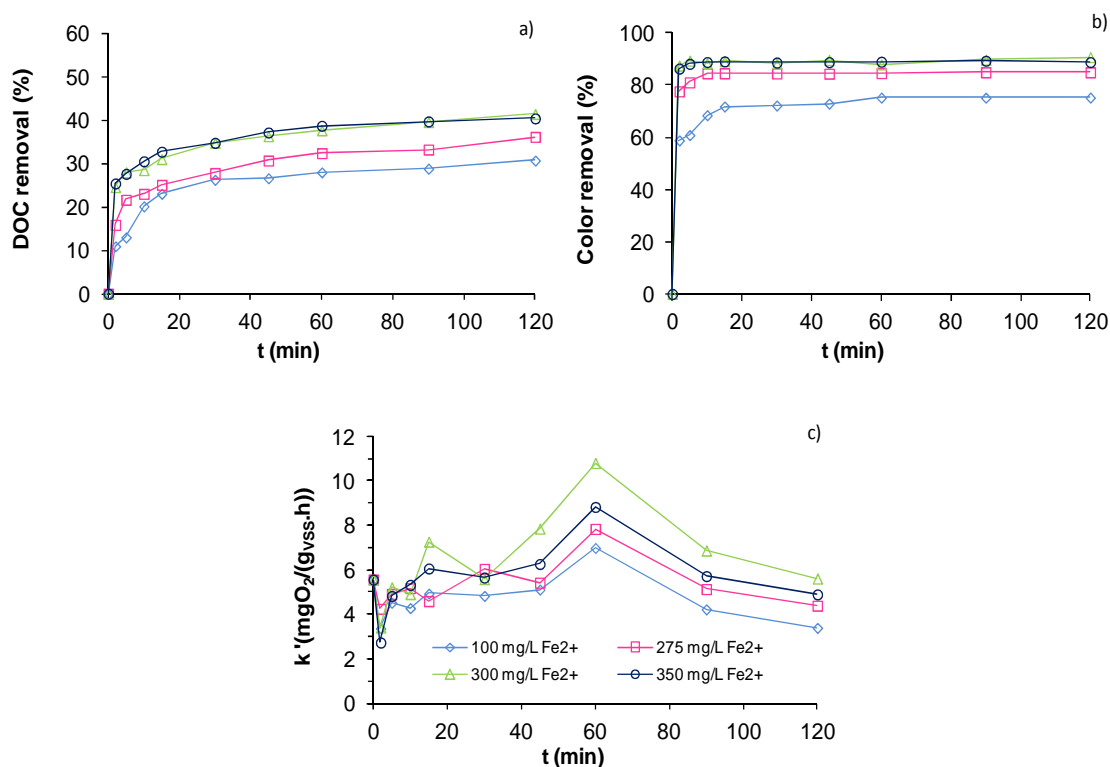


Figure 7.5 – Variation of dissolved organic carbon (a), color (b) removal and specific oxygen uptake rate (c) along time with the initial concentration of Fe²⁺ during the Fenton reaction – Approach 2 (initial pH=3.5, T=30 °C, [H₂O₂]₀=5 g/L).

Again, as in section 7.3.1.1, it was observed an optimum dose of catalyst (which is the same in the different responses considered), what can be attributed to the scavenging reaction between excess of ferrous ion with the hydroxyl radicals.

The optimum dose of ferrous iron achieved is similar to that obtained in other studies. For example, Rodrigues et al. [2009 b]) obtained an optimum concentration of ferrous ion for maximizing the color and DOC removal of 404 mg/L and 325 mg/L, respectively, when treating a simulated cotton dyeing effluent, prepared in different conditions (initial DOC=161.4 mg/L).

7.3.2.2 Effect of the Initial Hydrogen Peroxide Concentration

For selecting the optimum hydrogen peroxide concentration to treat a cotton dyeing wastewater by Fenton oxidation, which is quite important when assessing the costs of this process, four experiments were carried out wherein this variable was varied in the range 2.5-20 g/L (while fixing the ferrous ion concentration in the optimum value determined before – 300 mg/L – and the temperature in 30 °C). The high concentrations of H₂O₂ employed are justified by the oxidation of the high amount of chloride present in the effluent (around 8 g/L), which is used as electrolyte (9 g/L) in the cotton dyeing bath. The chlorides act as scavengers of the hydroxyl radicals, thus requiring the use of high oxidant doses.

The DOC removal (Figure 7.6 a) does not proceed so quickly, as in the previous experiments. The mineralization degree increased with the hydrogen peroxide concentration, in the range tested. However, we will consider 10 g/L as the more suitable dose of hydrogen peroxide because when doubling it (till 20 g/L), increase in DOC removal is almost negligible. For a concentration of 10 g/L the DOC reduction was 36.2% at 15 minutes and 44.2% at 120 minutes of reaction.

Figure 7.6 b shows the variation of the color removal with the initial H₂O₂ dose; it can be seen that, in general, color was quickly removed (in only 2-5 minutes of reaction) whatever the oxidant concentration, and that removals of ~ 90% were reached.

The effluent biodegradability (assessed through k') along reaction time for different H₂O₂ concentrations is presented in Figure 7.6 c. Although there are slight oscillation in k' at the earlier stages of reaction, a maximum was obtained again at t= 60 min. As stated before, the reduction of k' for longer reaction times may be related to the formation of less biodegradable organics during the oxidative process. The H₂O₂ concentration influences the biodegradability of the final effluent, a maximum value of k' of 14.1 mg O₂/(g_{VSS}.h) being obtained when using an oxidant dose of 10 g/L, after 60 minutes of reaction.

Chapter 7 - Integration of Physical-Chemical and Oxidation Processes for Cotton Dyeing Effluent Treatment

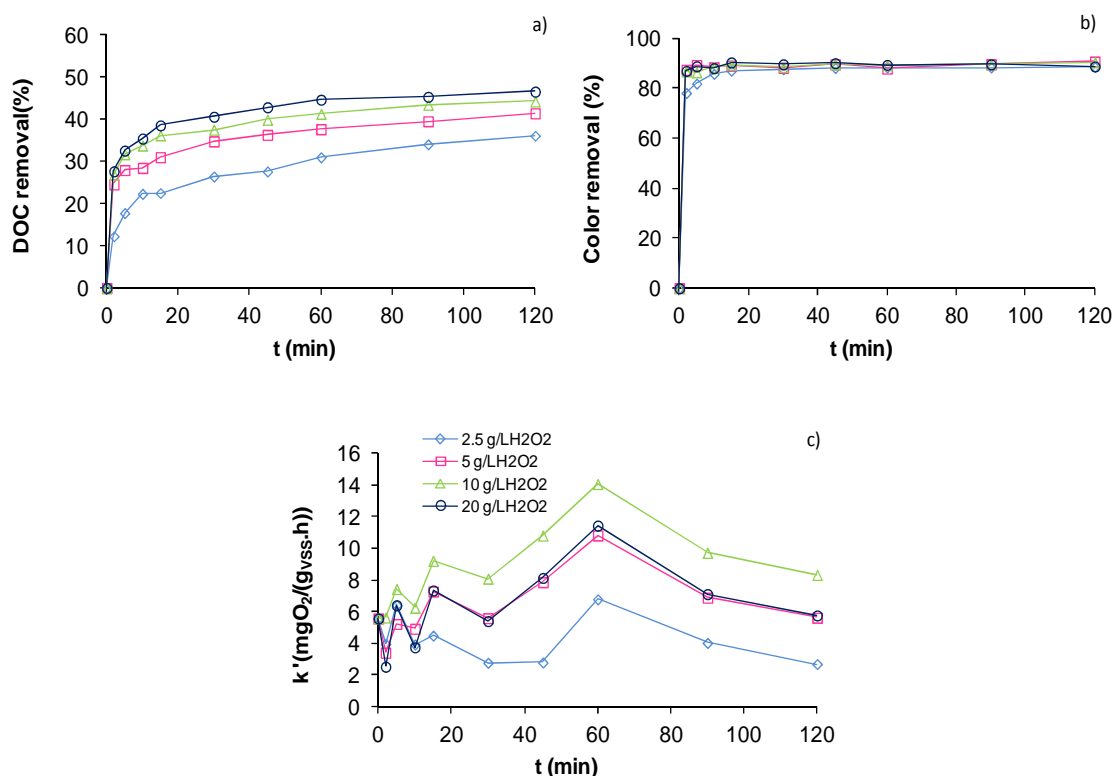


Figure 7.6 – Variation of dissolved organic carbon (a), color (b) removal and specific oxygen uptake rate (c) along time with the initial concentration of H₂O₂⁺ during the Fenton reaction – Approach 2 (initial pH=3.5, T=30 °C, [Fe²⁺]₀=300 mg/L).

The optimum dose of oxidant obtained was similar to that achieved in other works reported in literature. Namely, Rodrigues et al. [2009 b)] found an optimal H₂O₂ dose of 5 g/L for maximizing the biodegradability increase of a simulated dyeing cotton wastewater (COD = 428 mg O₂/L and TOC = 161 mg C/L).

7.3.2.3 Effect of the Temperature

DOC removal histories (Figure 7.7 a) are similar to those reported previously, the temperature exhibiting in this case a more notorious effect. Best results were obtained in the run at 50 °C (42.8% of mineralization after 15 min, which increased up to 52.2% after 120 min of reaction). In Figure 7.7 b is presented the variation of the color removal with temperature, along the reaction time. Again, color removal was very fast (only ca. 2 min were required to reach levels of ~90% that were maintained constant for longer times).

In what concerns biodegradability (k' – cf. Figure 7.7 c, it is noteworthy that it remained constant at $T=10$ °C, but clearly improves for higher temperatures. Higher values of k' were obtained at 50 °C, with the maximum being again observed after 60 min of reaction ($15.5 \text{ mgO}_2/(\text{g}_{\text{VSS}}\cdot\text{h})$).

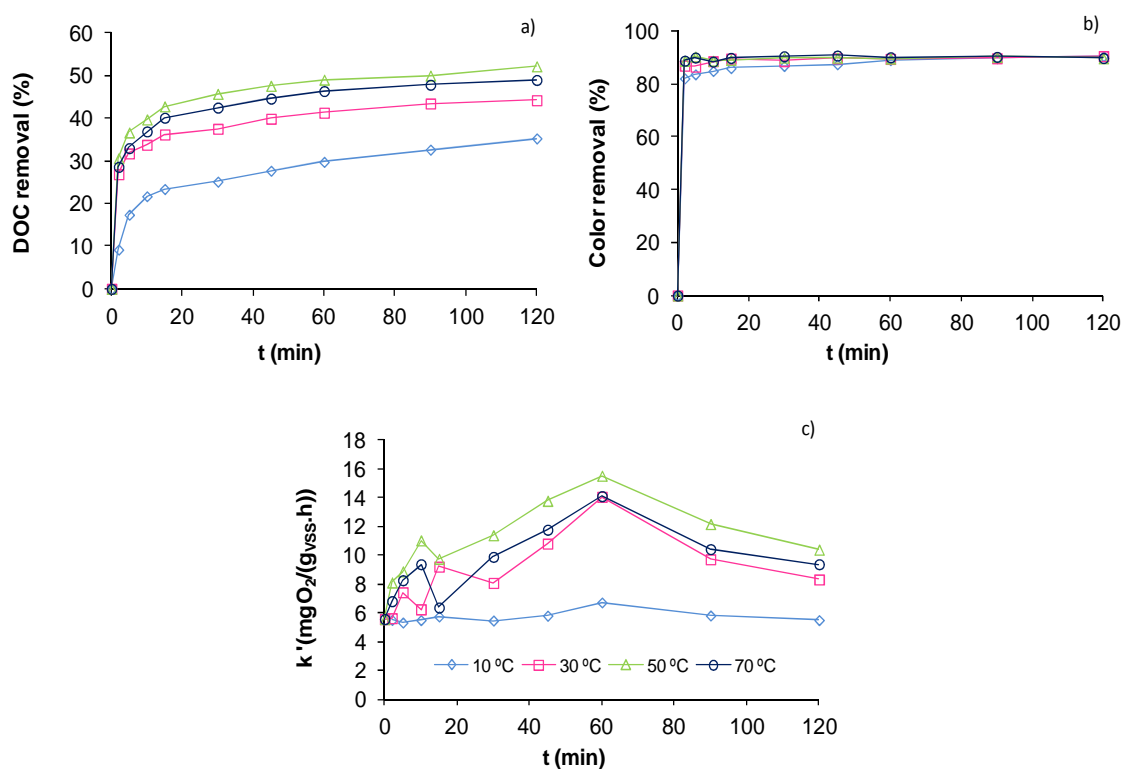


Figure 7.7 – Variation of dissolved organic carbon (a), color (b) removal and specific oxygen uptake rate (c) along time with the temperature during the Fenton reaction – Approach 2 (initial pH=3.5, $[\text{Fe}^{2+}]_0=300 \text{ mg/L}$ and $[\text{H}_2\text{O}_2]_0=10 \text{ g/L}$).

The higher performances obtained at 50 °C can be due to the thermal decomposition of hydrogen peroxide in water and oxygen at higher temperatures. The optimum value achieved was equal to that obtained when applying the Fenton process to the pre-treated effluent (Approach 1) and similar to that reported in other works [Ramirez et al., 2005; Gulkaya et al., 2006; Sun et al., 2007; Rodrigues et al., 2009 a)].

7.3.2.4 Optimized Treatment of the Simulated Cotton Dyeing Wastewater

After evaluating the influence of each variable on the efficiency of the Fenton's process, a further run was carried out under the more suitable conditions previously identified (those maximizing color and DOC removal, and also biodegradability): $[\text{Fe}^{2+}] = 300 \text{ mg/L}$, $[\text{H}_2\text{O}_2] = 10 \text{ g/L}$ and $T = 50 \text{ }^\circ\text{C}$. The run lasted only 60 minutes (time after which it was obtained the maximum biodegradability - k' value); besides, after such time no further improvement was observed in color reduction, and DOC removal only slightly increased. Samples were collected and taken to follow up the toxicity (inhibition of *Vibrio fischeri*). At all times of reaction and contact with bacterium the effluent exhibited no toxic behavior (data not shown), i.e. the percentage of inhibition was 0.0% (value equal to that obtained for the simulated effluent – Table 3.4).

The treated effluent was analyzed in terms of several legislated parameters and the results are shown in Table 7.2. With the Fenton's process alone a high color removal (89.9%) was obtained but the organic matter removal was inferior (25.1% for COD and 48.8% for DOC). Besides, it allowed to make the effluent more biodegradable because i) the BOD_5 value increased, ii) the $\text{BOD}_5:\text{COD}$ ratio was increased (from 0.22 to 0.52) and iii) k' was also considerably increased from 0.7 to $15.5 \text{ mg O}_2/(\text{g}_{\text{VSS}} \text{ h})$.

However, the effluent obtained upon treatment by the Fenton's reaction alone is not suitable to be discharged because the values of COD and BOD were slightly higher than the maximum allowable discharge limits (Table 7.2). So, it is necessary to apply a subsequently treatment that can be: i) coagulation/flocculation, for instance using as coagulant the quantity of dissolved iron resulting from the Fenton's process – study presented in section 7.3.3 – or ii) biological oxidation (since the effluent can be considered as biodegradable after the Fenton's process); this later topic will be the aim of subsequent work (chapter 10).

Table 7.2 - Characteristics of the synthetic cotton dyeing wastewater after Fenton oxidation and respective removal efficiencies (Approach 2).

Parameter	Fenton	Removal (%)	Maximum Allowable Limit**
pH	6.99	-	5.5-9.0
Chemical oxygen demand (mg O ₂ /L)	262.1	25.1	250
Biochemical oxygen demand (mg O ₂ /L)	135.7	0.0	100
Dissolved organic carbon (mg C/L)	60.2	48.8	
Chlorides (mg Cl ⁻ /L)	8017	-	
Specific oxygen uptake rate (k') (mg O ₂ /(g _{VSS} h))	15.51	-	
BOD ₅ :COD ratio	0.52	-	
Absorbance at λ _{max} (abs. units)	0.0331	89.9*	
Visible color after dilution 1:40	not visible	-	not visible

* calculated from the absorbance at pH 3.5 (0.3267 abs. units).

** Portuguese legislation for discharge of textile wastewaters (Ordinance No. 423/97 of 25 June).

7.3.3 Fenton's Oxidation Followed by Coagulation/Flocculation (Approach 3)

To increase the removal of organic compounds and aiming obtaining a wastewater with characteristics that would allow its discharge or disposal in the environment, the coagulation/flocculation technique was applied to the effluent previously treated by the Fenton process. So, in the following sections are presented the results of the parametric study, in which it was evaluated the effect of pH and dose of flocculant in the removal of DOC and color. The effect of coagulant was not evaluated, because it was only employed the dissolved iron resulting from Fenton's oxidation (to reduce costs).

As above mentioned, different conditions were attempted in the Fenton's stage: one experiment was performed in conditions that maximized DOC removal and biodegradability increase, as determined in Approach 2 (run #3); in the other runs the doses of H₂O₂ and Fe²⁺ were reduced for 1/2 and 1/4, respectively, with the objective of reducing the operating costs (runs #2 and #1, respectively). In the coagulation/flocculation stage the coagulant used is the dissolved iron resulting from the previous oxidation (52.1, 85.6 and 167 mg/L of Fe in run #1, run #2 and run #3, respectively).

7.3.3.1 Influence of pH

In order to evaluate the influence of pH in the coagulation/flocculation step, six experiments were carried out in which this parameter was varied between 3.5 and 10.4. Figure 7.8 a and b show the results of DOC and color removal obtained, respectively, for different hydrogen peroxide doses previously employed in Fenton's oxidation. It can be seen that, in all cases, the performances slightly increased when the pH was varied from 3.5 to 5.0 (for instance, in run #1, for a hydrogen peroxide dose of 2.5 g/L in the Fenton's stage, the DOC and color removal increased from 20.5 to 21.2% and from 77.7 to 83.7%, respectively, while in run #3, where the highest dose of oxidant was employed in the oxidation stage, performances raised from 30.9 to 42.3% and from 93.3 to 94.7%, respectively for DOC and color). At pH above 5 there is a slight decrease in the removal performances, becoming more pronounced for increased pH values.

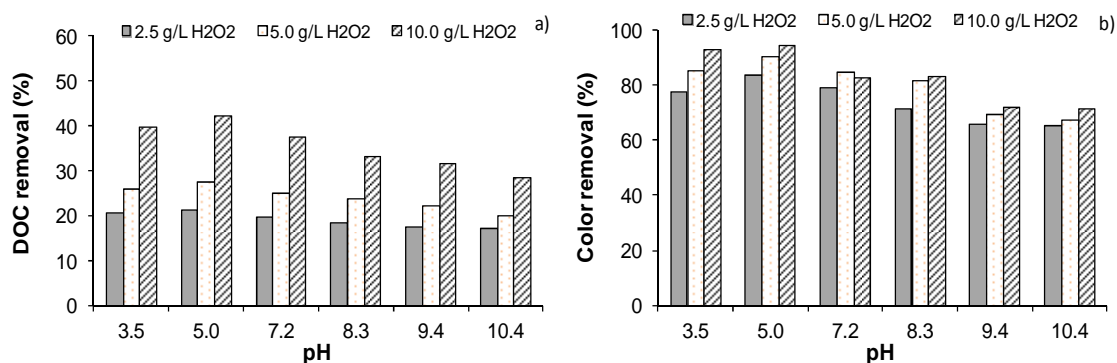


Figure 7.8 – Variation of DOC (a) and color (b) removals with pH during the coagulation stage – Approach 3 – for different doses of hydrogen peroxide employed in the previous Fenton's process in runs #1, #2 and #3 ($v_{\text{coagulation}}=150$ rpm, $t_{\text{coagulation}}=3$ min, $[\text{Fe}_{\text{dissolved}}]_{\text{run \#1}}=52.1$ mg/L, $[\text{Fe}_{\text{dissolved}}]_{\text{run \#2}}=85.6$ mg/L, $[\text{Fe}_{\text{dissolved}}]_{\text{run \#3}}=167$ mg/L and $T = T_{\text{ambient}}=23-25$ °C).

In accordance with Duan and Gregory [2003], in the optimum range obtained (pH= 5) the coagulation probably occurs by charge neutralization and inclusion in a precipitate, because at this pH value the species that are present in solution are Fe^{3+} ions and some hydrolysable species ($\text{Fe}(\text{OH})^{2+}$ and $\text{Fe}(\text{OH})_3$).

The optimal pH found is in the acidic zone, which is in accordance with literature reports when ferric sulfate is used as coagulant (from 3.5 to 7.0) [Edeline, 1992]. Besides, the value herein determined is equal to the optimum pH value obtained in a preliminary work where ferric sulfate was employed as coagulant (cf. chapter 5), and also within the range found by Joo et al. [2007] that obtained an pH optimum between 4 to 7 for treating a textile wastewater. Additionally, Aziz et al. [2007] and Liang et al. [2009] obtained the maximum removal at pH 4 when treating a landfill leachate and molasses effluents, respectively. So, in subsequent runs the optimum pH value of 5.0 was used.

7.3.3.2 Effect of Magnafloc 155 Doses

The selection of Magnafloc 155 (anionic polymer) as flocculant takes into account the results obtained in preliminary studies with the raw wastewater (cf. chapters 4 and 5). It was thus evaluated the effect of flocculant dose in both color and DOC removal, varying the concentration of Magnafloc 155 in the range 0.25 to 5 mg/L. Figure 7.9 a and b present the results obtained, where it can be seen that both responses only slightly increased when the flocculant was used vs. simple coagulation (null concentration of Magnafloc). The very small increment in efficiency is justified by the fact that the removal of dyes and organic compounds occur, in general, in the coagulation step. The flocculation stage has the objective to aggregate the flocs, yielding larger particles that are more prone to suffer sedimentation.

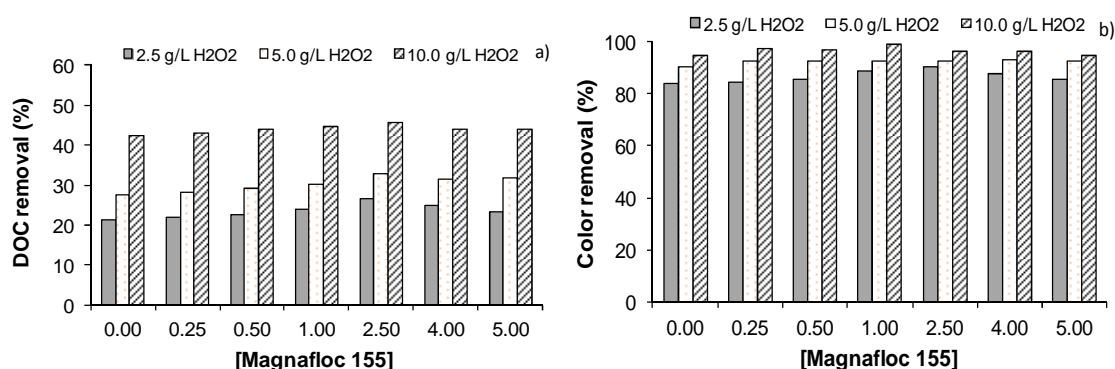


Figure 7.9 – Variation of DOC (a) and color (b) removals with the flocculant concentration during the flocculation step – Approach 3 – for the different doses of hydrogen peroxide employed in the previous Fenton's process in runs #1, #2 and #3 ($v_{\text{coagulation}}=150$ rpm, $t_{\text{coagulation}}=3$ min, $T=T_{\text{ambient}}=23-25$ °C, pH=5.0, $[\text{Fe}_{\text{dissolved}}]_{\text{run \#1}}=52.1$ mg/L, $[\text{Fe}_{\text{dissolved}}]_{\text{run \#2}}=85.6$ mg/L, $[\text{Fe}_{\text{dissolved}}]_{\text{run \#3}}=167$ mg/L, $v_{\text{flocculation}}=20$ rpm and $t_{\text{flocculation}}=15$ min).

Figure 7.9 a also shows that the DOC removal increased with the dose of flocculant up to 2.5 mg/L, and for this optimum dose performances reached are 26.6, 32.9 and 45.7% for run #1, run #2 and run #3, respectively (i.e., when different doses of hydrogen peroxide were employed in the previous Fenton's process). In what concerns decolorization (Figure 7.9 b), results are not too different when the dose of Maganafloc is changed, being however apparent that the optimum dose is in the range 1.0-2.5 mg/L. Thus, the optimum dose considered for subsequent experiments was 2.5 mg/L, a value that is similar to those reported in literature, even with other flocculants [Bes-Piá, 2002; Joo et al., 2007; El-Gohary and Tawfik, 2009].

7.3.3.3 Overall Process Efficiency

After determining the operating conditions that maximize color and DOC removal in the coagulation/flocculation stage, further tests were carried out using the effluent previously treated by the Fenton's process (but with different hydrogen peroxide doses – runs #1 to #3) to assess the overall efficiency of the integrated treatment. The first experiment was performed in conditions that maximized DOC removal and biodegradability increase (run #3); in the other runs the doses of H_2O_2 and Fe^{2+} were reduced for 1/2 and 1/4, respectively, with the objective of reducing the operating costs (runs #2 and #1, respectively).

Table 7.3 presents, for the three experiments, the results of the characterization of the effluent resulting from Fenton's oxidation and from coagulation/flocculation, and the removal efficiencies obtained for each treatment technique; the global efficiency of the overall treatment is also reported. The results obtained allow concluding that, in all runs, higher organic matter removals were reached in the coagulation/flocculation step than in Fenton's oxidation. Decolorization performances were similar in both processes. It is also noteworthy that values below the maximum legislated limit values of COD and BOD_5 were only reached in runs #2 and #3, where higher H_2O_2 doses were employed. In run #3, where higher removal efficiencies were attained, the global efficiencies obtained with the combination of the two treatment techniques were 55.6, 42.7, 70.4 and 99.6% for COD, BOD_5 , DOC and color, respectively.

Table 7.3 - Characteristics of the synthetic cotton dyeing wastewater after Fenton oxidation and coagulation/flocculation – Approach 3 (percent removal efficiencies within brackets) and global removal for the combined process; runs #1 to #3 correspond to different dosages of hydrogen peroxide in the Fenton's stage.

Parameter	Run #1			Run #2			Run #3			Maximum Allowable Value***
	Fenton's oxidation	Coagulation & flocculation	Global removal (%)	Fenton's oxidation	Coagulation & flocculation	Global removal (%)	Fenton's oxidation	Coagulation & flocculation	Global removal (%)	
pH	-	7.14	-	-	7.10	-	-	7.25	-	5.5-9.0
Chemical oxygen demand (mg O ₂ /L)	324.2 (7.4)	261.8 (19.2)	25.2	286.8 (18.1)	187.0 (34.8)	46.6	266.6 (23.8)	155.3 (41.7)	55.6	250
Biochemical oxygen demand (mg O ₂ /L)	89.2 (0.0)	70.7 (20.7)	20.7	113.2 (0.0)	76.0 (32.9)	32.9	135.4 (0.0)	77.6 (42.7)	42.7	100
Dissolved organic carbon (mg C/L)	103.9 (11.6)	76.8 (26.1)	34.6	96.2 (18.1)	64.45 (33.0)	45.1	65.4 (44.4)	34.8 (46.7)	70.4	
BOD ₅ :COD ratio	0.28	0.27	-	0.39	0.41	-	0.51	0.50	-	
Absorbance at λ _{max} (abs. units)	0.0256 (92.2*)	0.00195 (89.5**)	99.2	0.0235 (92.8*)	0.0013 (92.7**)	99.5	0.0340 (89.6*)	0.0005 (95.9**)	99.6	
Visible color after dilution 1:40	not visible	not visible	-	not visible	not visible	-	not visible	not visible	-	not visible

* calculated from the absorbance of wastewater at pH 3.5 (0.3267 abs. units).

** calculated from the absorbance after Fenton at pH 5.0 (0.0190, 0.0177 and 0.0123 abs. units for run #1, #2 and #3, respectively).

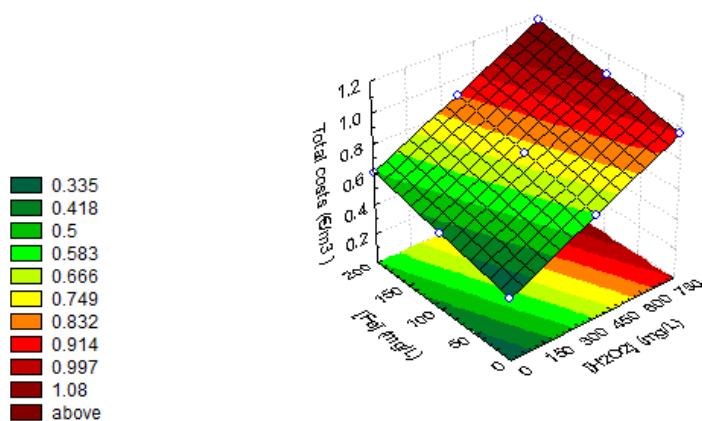
*** Portuguese legislation for discharge of textile wastewaters (Ordinance No. 423/97 of 25 June).

7.3.4 Costs Evaluation

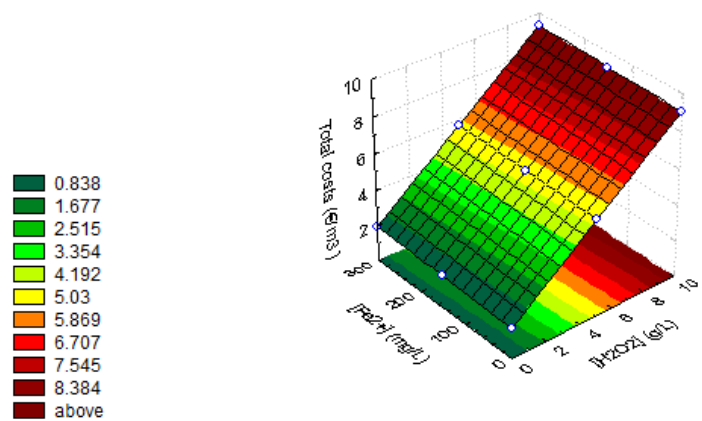
The overall costs of the treatment process are represented by the sum of the capital, operating and maintenance costs. For a full-scale system these costs depend on the flow rate of the effluent, the nature of wastewater, as well as the configuration of the reactors. In this study, we considered only the costs with the chemicals, i.e., the costs of reagents obtained from Quimitécnica S.A. and Rivaz Química S.A. the average values considered were as follows: H_2O_2 (49.5% w/v, density at 25 °C = 1.2 g/cm³ - 365 €/ton; $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (93 % of purity) – 233.7 €/ton and Magnafloc 155 – 3850 €/ton). The prices of acid (H_2SO_4) and base (NaOH) were not considered, because the quantities consumed are insignificant.

Figure 7.10 shows the influence of the reagents doses in the total cost of the reagents used in the processes, for the different strategies mentioned above. In Figure 7.10 a and b are shown the effects of the Fe^{2+} and H_2O_2 doses during the Fenton's stage when the effluent was previously treated by coagulation/flocculation (Figure 7.10 a) or when directly applied to the raw wastewater (Figure 7.10 b). It turns out, as expected, that the cost increases with increasing concentrations of either chemical; however, this increase is far more pronounced for the hydrogen peroxide dose than for the ferrous salt one. So, it is concluded that hydrogen peroxide is the chemical that has a greater contribution to the total cost of operation, particularly in the latter case (Figure 7.10 b). Besides, it is noteworthy that in Approach 1 (coagulation/flocculation + Fenton's oxidation) the costs are below 1.2 €/m³, while in Approach 2 (Fenton's process alone) they are considerably higher as a consequence of requiring much higher consumption of those chemicals. The use of coagulation/flocculation upstream from Fenton's oxidation revealed therefore to be a very promising strategy to considerably decrease the operating costs. In the optimal conditions of operation, as determined in previous sections, the cost to perform the treatment by coagulation/flocculation followed by Fenton's oxidation is 0.83 €/m³ while it amounts to 9.2 €/m³ when the Fenton's process is applied per se. Besides, only the first strategy allowed reaching global efficiencies that would permit to meet the discharge limits.

a)



b)



c)

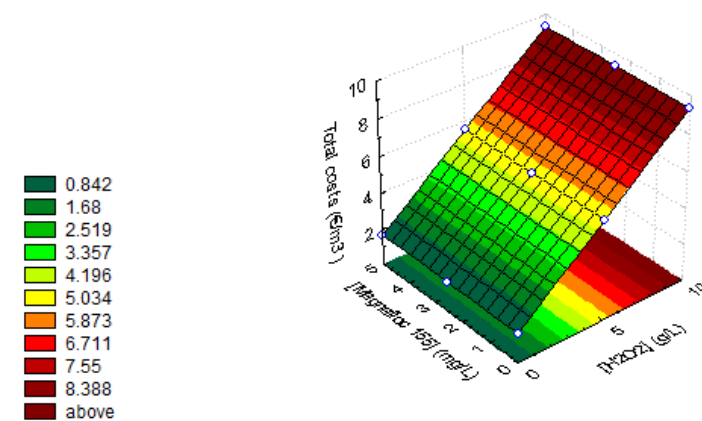


Figure 7.10 – Effect of Fe and H₂O₂ doses on the total cost of the reagents used in wastewater treatment by coagulation/flocculation plus Fenton processes – Approach 1 (a), Fenton’s reagent – Approach 2 (b) and influence of Magnafloc 155 and H₂O₂ concentration in the total treatment costs by Fenton’s process followed by coagulation/flocculation – Approach 3 (c).

Figure 7.10 c shows the influence of the hydrogen peroxide and the Magnafloc 155 cost upon combination of Fenton's process with coagulation/flocculation. It appears that overall cost increases with increasing concentrations of either reagent; however, this increase is clearly more pronounced for the hydrogen peroxide dose than for the Magnafloc 155 one. In fact, the flocculant contribution to the overall cost is almost negligible, because the doses used for the treatment are small (one should remark that the cost of this reagent is very high). Thus, the total cost of the treatment by Fenton's reagent followed by coagulation/flocculation (Approach 3) is almost entirely due to the consumption of hydrogen peroxide (and iron) in the Fenton reaction (that amounts to ca. 2.3, 4.6 and 9.2 €/m³ in runs #1, #2 and #3, respectively). Run #2 seems therefore to be the best choice for this strategy, because the effluent produced complies the discharge limits (cf. Table 7.3) and allows reducing the overall cost, as compared to run #3 (which was carried out in the optimum conditions determined in the parametric study). Even so, the cost is much higher than in Approach 1.

7.4 Conclusions

The present study demonstrated the applicability of integrating coagulation/flocculation and Fenton's process in the treatment of a synthetic cotton dyeing wastewater. It was found that:

- The coagulation/flocculation *per se* did not allowed to obtain an effluent that meets discharge limits;
- The application of the combined treatment (coagulation/flocculation followed by Fenton's reagent) under optimized conditions allows to achieve high efficiencies of color (99.8%) and organic matter removal (61.7% for COD, 71.2% for DOC, and 25.8% for BOD₅). This combination allowed to obtain an effluent that can be discharged into the environment;
- The application of the Fenton's process *per se* in oxidation of the raw wastewater allows obtaining high color removal (89.9%), with considerable efficiencies in reduction of organic compounds (25.1% for COD and 48.8% for DOC), yielding a non-toxic effluent (0.0% for inhibition of *Vibrio fischeri*) and significant improvement of the effluent biodegradability (both *k'* and BOD₅:COD increased). However, the wastewater resulting from this treatment cannot be

discharged, according to Portuguese legislation; the treatment could, nonetheless, be complemented by a biological process.

- The integration of Fenton's process followed by coagulation/flocculation in optimized conditions of both processes provided an effluent that can be discharged into the environment, with global organic matter removals of 55.6% for COD, 42.7% for BOD₅ and 70.4% for DOC, and almost complete color reduction (99.6%); the costs can however be decreased by reducing the H₂O₂ dose, the effluent still complying with the discharge limits.
- The treatment of the dyeing wastewater by coagulation/flocculation followed by Fenton's reagent allowed obtaining an effluent that meets the discharge limits with the smaller costs concerning reagents consumption (0.83 €/m³). So, the use of coagulation/flocculation before chemical oxidation revealed to be a very promising strategy to considerably decrease the operating costs.

7.5 References

Alaton, I.A.; Teksoy, S. (2007). Acid dyebath effluent pretreatment using Fenton's reagent: Process optimization, reaction kinetics and effects on acute toxicity. *Dyes and Pigments*, 73, 31-39.

Azbar, N.; Yonar, T.; Kestioglu, K. (2004). Comparison of various advanced oxidation processes and chemical treatment methods for COD and color removal from a polyester and acetate fiber dyeing effluent. *Chemosphere*, 55, 35-43.

Aziz, H.A.; Alias, S.; Adlan, M.N.; Faridah; Assari, A.H.; Zahari, M.S. (2007). Colour removal from landfill leachate by coagulation and flocculation processes. *Bioresource Technology*, 98, 218-220.

Bes-Piá, A.; Mendoza-Roca, J.A.; Alcaina-Miranda, M.I.; Iborra-Clar, A.; Iborra-Clar, M.I. (2002). Reuse of wastewater of the textile industry after its treatment with combination of physical-chemical treatment and membrane technologies. *Desalination*, 149, 169-174.

Duan, J.; Gregory, J. (2003). Coagulation by hydrolysing metals salts. *Advances in Colloid and Interface Science*, 100-102, 475-502.

Edeline, F. (1992). *L'épuration physico-chimique des eaux – théorie & technologie*, 2e édition, Editions CEBEDOC.

El-Gohary, F.; Tawfik, A. (2009). Decolorization and COD reduction of disperse and reactive dyes wastewater using chemical-coagulation followed by sequential batch reactor (SBR) process. *Desalination*, 249, 1159-1164.

Gulkaya, I.; Surucu, G.A.; Dilek, F.B. (2006). Importance of H₂O₂/Fe²⁺ ratio in Fenton's treatment of a carpet dyeing wastewater. *Journal of Hazardous Materials*, 136, 763-769.

Chapter 7 - Integration of Physical-Chemical and Oxidation Processes for Cotton Dyeing Effluent Treatment

Joo, D.J.; Shin, W.S.; Choi, J.-H.; Choi, S.J.; Kim, M.-C.; Han, M.H.; Ha, T.W.; Kim, Y.-H. (2007). Decolorization of reactive dyes using inorganic coagulants and synthetic polymer. *Dyes and Pigments*, 73, 59-64.

Kim, T.-H.; Park, C.; Yang, J.; Kim, S. (2004). Comparison of disperse and reactive dye removals by chemical coagulation and Fenton oxidation. *Journal of Hazardous Materials*, 112, 95-103.

Liang, Z.; Wang, Y.; Zhou, Y.; Liu, H.; Wu, Z. (2009). Hydrolysis and coagulation behavior of polyferric sulfate and ferric sulfate. *Water Science Technology*, 59, 1129-1135.

Malik, P.K.; Saha, K. (2003). Oxidation of direct dyes with hydrogen peroxide using ferrous ion as catalyst. *Separation and Purification Technology*, 31, 241-250.

Meriç, S.; Kaptan, D.; Ölmez, T. (2004). Color and COD removal from wastewater containing reactive black 5 using Fenton's oxidation process. *Chemosphere*, 54, 435-441.

Meriç, S.; Selçuk, H.; Belgiorno, V. (2005). Acute toxicity removal in textile finishing wastewater by Fenton's oxidation, ozone and coagulation-flocculation processes. *Water Research*, 39 (6), 1147-1153.

Ramirez, J.H.; Costa, C.A.; Madeira, L.M. (2005). Experimental design to optimize the degradation of the synthetic dye Orange II using Fenton's reagent. *Catalysis Today*, 107-108, 68-76.

Ramirez, J.H.; Lampinen, M.; Vicente, M.A.; Costa, C.A.; Madeira, L.M. (2008). Experimental design to optimize the oxidation of Orange II dye solution using a clay-based Fenton-like catalyst. *Industrial & Engineering Chemistry Research*, 47, 284-294.

Rodrigues, C.S.D.; Madeira, L.M.; Boaventura, R.A.R. (2009 a)). Optimization of the azo dye Procion Red H-EXL degradation by Fenton's reagent using experimental design. *Journal of Hazardous Materials*, 164, 987-994.

Rodrigues, C.S.D.; Madeira, L.M.; Boaventura, R.A.R. (2009 b)). Treatment of textile effluent by chemical (Fenton's Reagent) and biological (Sequencing Batch Reactor) oxidation. *Journal of Hazardous Materials*, 172, 1551-1559.

Swaminathan, K.; Sandhya, S.; Sophia, C.A.; Pachhade, K.; Subrahmanyam, Y.V. (2003). Decolorization and degradation of H-acid and others dyes using ferrous-hydrogen peroxide system. *Chemosphere*, 50, 619-625.

Sun, J.-H.; Sun, S.-P.; Wang, G.-L.; Qiao, L.-P. (2007). Degradation of azo dye Amido black 10B in aqueous solution by Fenton oxidation process. *Dyes and Pigments*, 74, 647-652.

Chapter 8

Integration of Physical-Chemical and Oxidation Processes for Polyester Dyeing Effluent Treatment *

This Chapter is based on the publication "Rodrigues C.S.D.; Boaventura, R.A.R.; Madeira, L.M. Technical and Economic Feasibility of Polyester Dyeing Wastewater Treatment by Coagulation/Flocculation and Fenton's Oxidation". Submitted to Environmental Technology.

8 Integration of Physical-Chemical and Oxidation Process for Polyester Dyeing Effluent Treatment

8.1 Introduction

For minimizing some disadvantages of each individual process [Flaherty and Huang, 1992; Rodrigues et al., 2009 a)], the treatability of polyester dyeing effluents by the combination of coagulation/flocculation and Fenton treatment techniques is reported in this chapter, in particular, when one of the treatments per se is not enough efficient to meet discharge limits. Besides using the residual iron from coagulation/flocculation as catalyst in Fenton's oxidation, which has been rarely addressed in the literature [Peres et al., 2004; Xing et al., 2009; Perdigon-Melon et al., 2010], the residual catalyst from the Fenton process was also used as the only coagulant in the subsequent coagulation step, which is an innovative approach.

The aim of this study was therefore to find the best integration strategy of the two techniques and optimize the respective operating conditions for obtaining an effluent that meets the discharge standards at minimum operating costs associated with chemicals consumption. In the scientific literature just a few works focused on obtaining the maximum removal efficiency employing different integration strategies of these types of treatment. Moreover, in practical applications it is mandatory to take into account the treatment costs and this has been often ignored; this is also an innovative aspect of this work.

8.2 Materials and Methods

8.2.1 Preparation of Synthetic Textile Wastewaters

The polyester dyeing effluent was simulated according to the information reported in chapter 3, section 3.2.1.

8.2.2 Experimental Procedure

The coagulation/flocculation and Fenton's oxidation experiments were performed as described in sections 3.4.1 and 3.4.2.

In the runs combining coagulation/flocculation with Fenton's reaction, the supernatant from coagulation/flocculation was collected after 30 minutes of sedimentation and acidified with HNO₃ 68% (Merck) to pH ≈1 to keep the remaining iron dissolved for further use as catalyst in the Fenton's reaction. When treating the effluent by Fenton's oxidation followed by coagulation/Flocculation, the effluent from the first treatment was acidified with HNO₃ 68% (Merck) to pH ≈1 to keep the iron dissolved for the coagulation/flocculation stage and simultaneously slow down or inhibit the Fenton's reaction.

When the coagulation/flocculation was performed after the Fenton's oxidation, the collected samples were centrifuged at 13400 rpm during 2 minutes (Mini Spin Eppendorf) and some parameters measured for process optimization. The pH for Fenton's oxidation was adjusted to 3.5, as it has been proposed for treating textile effluents [Tekin et al., 2006; Sun et al., 2007; Rodrigues et al., 2009 a)].

All runs of coagulation/flocculation process were carried out at room temperature (22-24 °C).

8.2.3 Analytical Methods

The analytical determinations were performed as described in section 3.3 of the Experimental Section (chapter 3).

All analytical determinations were performed in duplicate and the coefficients of variation were less than 2% for DOC, 14% for BOD₅, 8% for COD, 10% for k', 3% for inhibition of *V. fischeri* and 7% for the other parameters.

8.3 Results and Discussion

The more relevant characteristics of the effluent under study are reported in Table 3.4. Several parameters such as BOD₅, DOC, k', N, P and ecotoxicity were analyzed to decide on the possibility of directly applying a biological treatment to this kind of effluent, which would be cheaper than the chemical processes. Considering the low values of BOD₅/COD (<0.4), k', nitrogen and phosphorus concentrations, and the high toxicity to *V. fischeri*, that possibility was excluded. The same evaluation was made after the coagulation/flocculation process and the conclusion was the same. The effluent does not comply with limits for BOD₅ and COD, as established in the Portuguese legislation (Ordinance No. 423/97 of 25 June, for discharge of textile wastewaters). So, different approaches have been attempted, as described below.

8.3.1 Combination of Coagulation/Flocculation and Fenton Reagent (Approach 1)

After treating the effluent by coagulation/flocculation under the better operating conditions found previously (pH=9.4, [Fe³⁺]=500 mg/L, $v_{\text{coagulation}} = 150$ rpm, $t_{\text{coagulation}} = 3$ min, $T = T_{\text{amb}} = 23\text{-}25$ °C, $v_{\text{flocculation}} = 20$ rpm, $t_{\text{flocculation}} = 15$ min, [Superfloc C-573] = 1 mg/L) (see chapter 4), an additional treatment must be implemented because COD is still above the discharge limit (cf. Table 5.4). Considering the biodegradability and toxicity values, the subsequent treatment cannot be biological. Alternatively, Fenton's reagent using part of the dissolved iron coming from chemical coagulation/flocculation stage (8.7 mg Fe/L) as catalyst was employed. Although the amount of residual iron is low, for an acrylic dyeing effluent this methodology was found to be very promising because only 75 mg/L of Fe²⁺ was added to the soluble iron resulting from the coagulation/flocculation (275 mg/L) (results in chapter 6).

A parametric study was then carried out aiming at finding the best amount of Fe²⁺ salt to be added, the dose of H₂O₂ required and the operating temperature that maximized the DOC removal.

8.3.1.1 Influence of Ferrous Ion Concentration Added During the Chemical Oxidation Stage

To evaluate the influence of Fe concentration in DOC removal, five experiments were performed by changing the supplemental dose of Fe^{2+} , in the range 8.7-250 mg/L and maintaining initial $[\text{H}_2\text{O}_2] = 500 \text{ mg/L}$ and $T = 30 \text{ }^\circ\text{C}$.

Figure 8.1 a presents the DOC removal along time for different runs. It is very fast in the first 15 minutes of reaction (time after which most of the hydrogen peroxide has been consumed – cf. Figure 8.1 b), but then it slows down till 60 minutes of reaction, and presents a negligible increase in the range 60-120 minutes. A very similar pattern was observed for the consumption of H_2O_2 (Figure 8.1 b). On the other hand, DOC removal increased with the iron dose up to 200 mg/L, leading to a removal of ~45% with a H_2O_2 consumption of 96%. The efficiency of the process declined for a Fe dose of 250 mg/L (~41% of DOC removal) and also decreased the H_2O_2 consumption (90-91%).

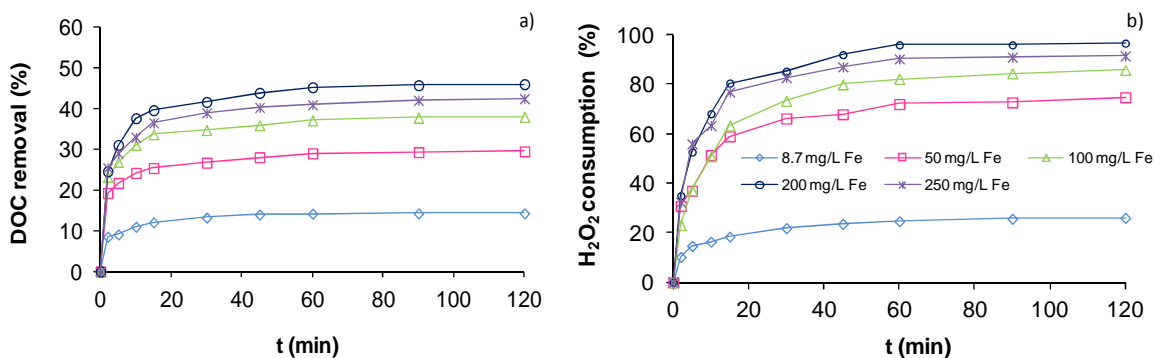


Figure 8.1 – Variation of DOC removal (a) and percentage of H_2O_2 consumption (b) along time, with the iron dose during the 2nd stage – Fenton oxidation in Approach 1 (initial $\text{pH}=3.5$, $T=30 \text{ }^\circ\text{C}$, initial $[\text{H}_2\text{O}_2]= 500 \text{ mg/L}$).

In the literature concerning either dyes or organic matter removal by Fenton's oxidation optimum doses of ferrous ion are often reported [Azbar et al., 2004; Gulkaya et al., 2006; Alaton and Teksoy, 2007; Rodrigues et al., 2009 a)], which is explained by the detrimental

effect of excessive catalyst dosages leading to competitive reactions ($\text{Fe}^{2+} + \text{HO}^\cdot \rightarrow \text{Fe}^{3+} + \text{HO}^-$) that reduce the amount of available radicals.

The optimal dose of Fe (200 mg/L) required for Fenton's oxidation of the polyester dyeing pre-treated effluent is between those obtained for cotton (100 mg/L) (chapter 7) and acrylic (350 mg/L) (chapter 6) dyeing effluents, both pre-treated by coagulation/flocculation. Azbar et al. [2004] achieved 96% and 94% of COD and color removal, respectively, using an optimum concentration of Fe^{2+} =184 mg/L for treating a mixture of polyester and acetate dyeing effluents (COD=930 mg/L and BOD₅=375) and Blanco et al. [2012] found 64% TOC removal when treating a textile wastewater by Fenton's oxidation, using 216 mg/L of Fe^{2+} .

8.3.1.2 Effect of the Initial Hydrogen Peroxide Concentration on the Chemical Oxidation Stage

The hydrogen peroxide dose has a significant impact on the operating costs of wastewater treatment by the Fenton process. On the other hand, when using an excess of H_2O_2 the parallel and undesirable HO^\cdot scavenging reaction may occur (Equation 2.3 of chapter 2) [Ramirez et al., 2005]. Therefore, it is necessary to optimize this parameter to increase the process efficiency and reduce operating costs. The minimum tested dose of hydrogen peroxide is around the stoichiometric theoretical value (587 mg/L), and was further increased to compensate side reactions.

For H_2O_2 in the range 500-1500 mg/L, Figures 8.2 a and 8.2 b evidence that the DOC was mostly removed in the first 30-40 minutes of reaction, leading to a higher consumption of H_2O_2 . For reaction times between 30 and 60 min only a slight increase in the DOC removal and H_2O_2 consumption was observed. For $t > 60$ minutes a plateau was reached in both cases. The DOC removal increases with the H_2O_2 concentration up to 1000 mg/L, and decreases for higher doses.

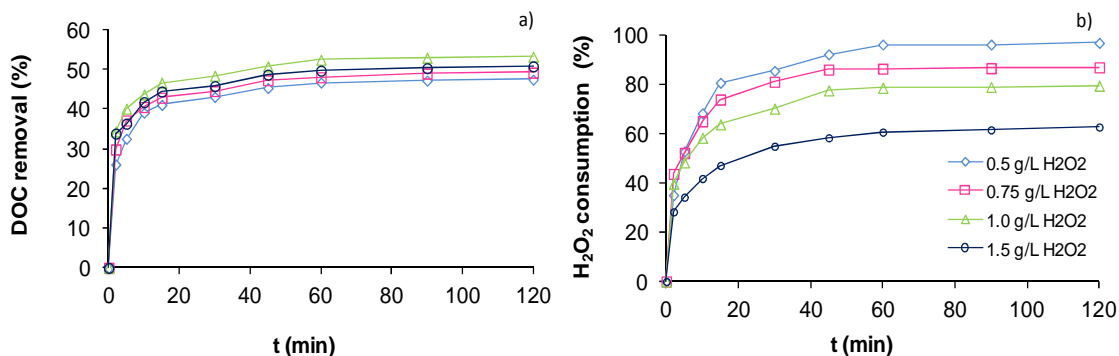


Figure 8.2 – Effect of H₂O₂ dose in DOC removal (a) and percentage of H₂O₂ consumption (b) along time during the 2nd stage i.e. Fenton oxidation in Approach 1 (initial pH=3.5, T=30 °C, [Fe]=200 mg/L).

The existence of an optimal H₂O₂ dose was also observed by others authors [Swaminathan et al., 2003; Papadopoulos et al., 2007; Rodrigues et al., 2009 a)], which is usually attributed to the fact that reaction between H₂O₂ with HO[•] occurs when there is an excess of oxidant. For the optimum H₂O₂ dose (1000 mg/L) the DOC removal is ~53% after 60 minutes of reaction. This value is close to those obtained by other authors, namely, Blanco et al. [2012] achieved an optimum H₂O₂ dose of 1650 mg/L for treating a textile wastewater and Wu and Wang [2012] an optimum of 1500 mg/L to treat a mixture of printing and dyeing wastewaters.

8.3.1.3 Effect of the Temperature During the Chemical Oxidation Stage

The influence of temperature on the mineralization of the dyeing polyester effluent was assessed by a series of experiments varying this parameter in the range 10-70 °C. This range takes into account that textile dyeing processes are carried out at elevated temperatures (50-70 °C or even higher), but on the other hand the effluent is often sent to an open air equalization tank for homogenization. In this case the effluent temperature can strongly decrease when the ambient temperature is low, depending on the region and the time of the year. Other variables were fixed at the optimum values determined before ([Fe] =200 mg/L, [H₂O₂]= 1000 mg/L) and pH was set 3.5

Results of DOC removal and percentage of H_2O_2 consumed are shown in Figures 8.3 a and b, respectively. Organics oxidation rises considerably when T increases from 10 to 30 °C. A similar effect is noticed in the peroxide consumption. DOC removal still slightly increases with the temperature up to 50 °C, but at 70 °C a negative effect was observed. The consumption of H_2O_2 increases with temperature, but beyond 40-50 °C there is no production of radicals, rather occurs its thermal decomposition into oxygen and water [Ramirez et al., 2008] and the fast hydroxyl radicals “scavenging” reactions take place. This explains the results shown in Figure 8.3 a, where maximum mineralization is reached at 50 °C.

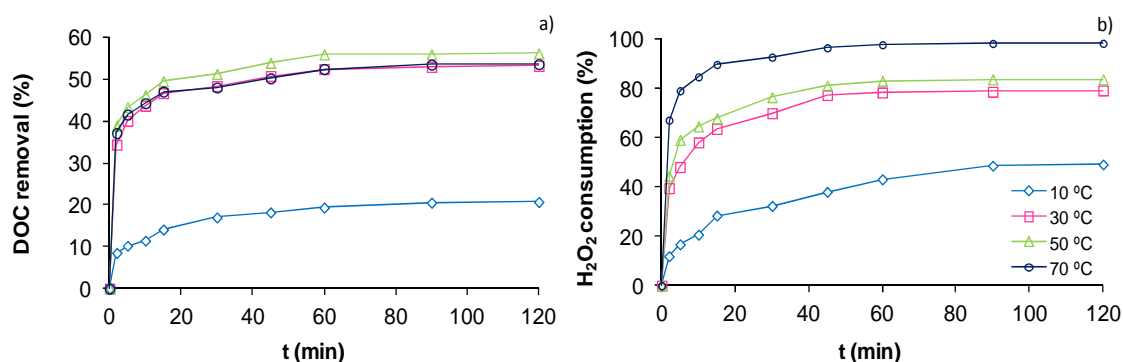


Figure 8.3 – Variation of DOC removal (a) and percentage of H_2O_2 consumption (b) along time with the reaction temperature during the 2nd stage – Fenton oxidation in Approach 1 (initial pH=3.5, $[\text{Fe}] = 200 \text{ mg/L}$ and initial $[\text{H}_2\text{O}_2] = 1000 \text{ mg/L}$).

At this temperature 56% of DOC removal was achieved after 60 min. An optimum value was also reported in chapters 6 and 7 and in other Fenton's oxidation studies of textile effluents [Ramirez et al., 2005; Gulkaya et al., 2006; Alaton and Teksoy, 2007; Rodrigues et al., 2009 a); Rodrigues et al., 2009 b)].

8.3.1.4 Optimized Integrated Coagulation/Flocculation plus Fenton's Oxidation

After determining the conditions that maximize DOC removal by the Fenton's process (pH=3.5, T=50 °C, [Fe]=200 mg/L and [H₂O₂]=1000 mg/L), an additional experiment was performed in those conditions, using the effluent pre-treated by coagulation/flocculation.

Samples were taken during 60 minutes of reaction for measuring the toxicity (*V. fischeri* inhibition - see Figure 8.4 a and registering HPLC chromatograms (Figure 8.4 b). After 30 minutes the effluent does not present any negative effect on *V. fischeri*; a similar behavior was observed for acrylic dyeing wastewater (cf. chapter 6). The changes in the HPLC chromatograms (Figure 8.4 b) prove the formation and disappearance of intermediates responsible for the above-described change in effluent's toxicity.

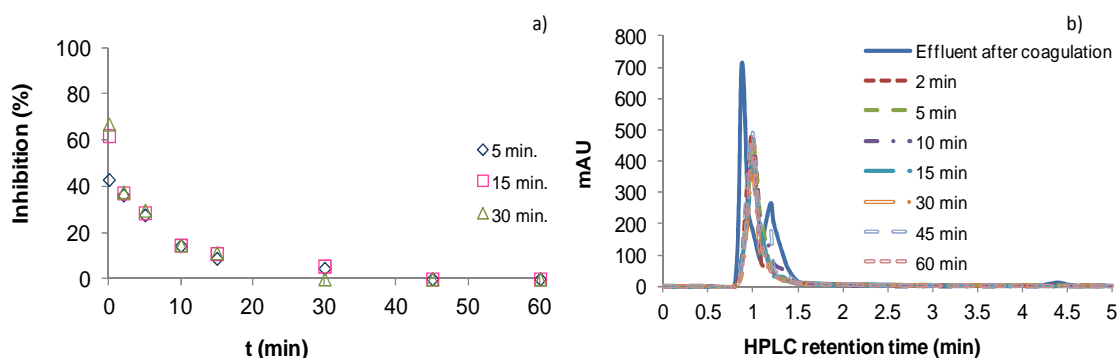


Figure 8.4 – Evolution of the inhibition of *V. fischeri* at 5, 15 and 30 minutes of contact (a) and HPLC chromatograms (b) of samples taken along time during the 2nd stage – Fenton oxidation in Approach 1 (initial pH=3.5, T=50 °C, initial [Fe]=200 mg/L and initial [H₂O₂]=1000 mg/L).

Table 8.1 presents the results of pH, COD, BOD₅, DOC, and visible color (after 1:40 dilution) for the treated effluent. The organic matter removal in the Fenton's process (61.0% for COD, 44.5% for BOD₅ and 56.0% for DOC) was higher than in the previous coagulation/flocculation stage. The overall efficiencies of the combined treatment were 79.2%, 61.9% and 75.7% for COD, BOD₅ and DOC, respectively. The characteristics of the final effluent comply with the discharge standards (cf. Table 8.1).

Table 8.1 - Characteristics of the synthetic wastewater after coagulation/flocculation and after coagulation/flocculation followed by Fenton oxidation (percent removal efficiencies for each stage are indicated within brackets), and global removal for the combined process (Approach 1). Maximum allowable values for legislated parameters are also shown.

Parameter	Coagulation & flocculation	Fenton	Global removal (%)	Maximum Allowable Value*
pH	7.3	7.02	-	5.5-9.0
Total nitrogen (mg N/L)	14.2 (10.4)	n.d.	-	
Nitrates (mg NO ₃ ²⁻ /L)	6.7 (10.1)	n.d.	-	
Total phosphorus (mg P/L)	2.3 (22.0)	n.d.	-	
Dissolved phosphorus (mg P/L)	2.4 (9.4)	n.d.	-	
Chemical oxygen demand (mg O ₂ /L)	276.2 (46.7)	108.1 (61.0%)	79.2	250
Biochemical oxygen demand (mg O ₂ /L)	89.7 (31.3)	49.7 (44.5%)	61.9	100
Dissolved organic carbon (mg C/L)	78.9 (44.8)	34.7 (56.0%)	75.7	
Chlorides (mg Cl ⁻ /L)	15.3 (11.3)	n.d.	-	
Specific oxygen uptake rate (k') (mg O ₂ /(g _{VSS} h))	28.5	n.d.	-	
BOD ₅ :COD ratio	0.32	0.46		
Visible color after dilution 1:40	not visible	not visible	-	not visible
<i>Vibro fischeri</i> Inhibition 5 min (%)	43.0	0.0	-	
<i>Vibro fischeri</i> Inhibition 15 min (%)	62.0	0.0	-	
<i>Vibro fischeri</i> Inhibition 30 min (%)	67.0	0.0	-	

n.d. – not determined.

* Portuguese legislation for discharge of textile wastewaters (Ordinance No. 423/97 of 25 June).

8.3.2 Fenton's Oxidation (Approach 2)

The treatability study of the polyester dyeing effluent also included the application of the Fenton's reagent alone. A parametric study was performed to evaluate the effect of ferrous ion, initial H₂O₂ concentration and temperature on DOC removal and biodegradability.

8.3.2.1 Influence of Ferrous Ion Concentration

The effect of Fe^{2+} dose in the range 275-400 mg/L was evaluated, maintaining $[\text{H}_2\text{O}_2] = 5$ g/L and $T = 30$ °C. DOC removal occurs rapidly in first 15-20 minutes (Figure 8.5 a) and at the same time there is a faster H_2O_2 consumption (Figure 8.5 b). Then the increase of DOC removal and H_2O_2 consumption proceeded at a slower rate until ca. 60 min, and afterwards remained nearly constant.

DOC removal raises with Fe^{2+} concentration up to 350 mg/L but greater doses do not result in increased mineralization. For that dose ~43% of DOC removal was achieved at the end of the reaction.

The biodegradability (k') decreased after 2 minutes of reaction (as compared to raw synthetic wastewater), but it tends afterwards to remain nearly constant whatever the load of catalyst (Figure 8.5 c).

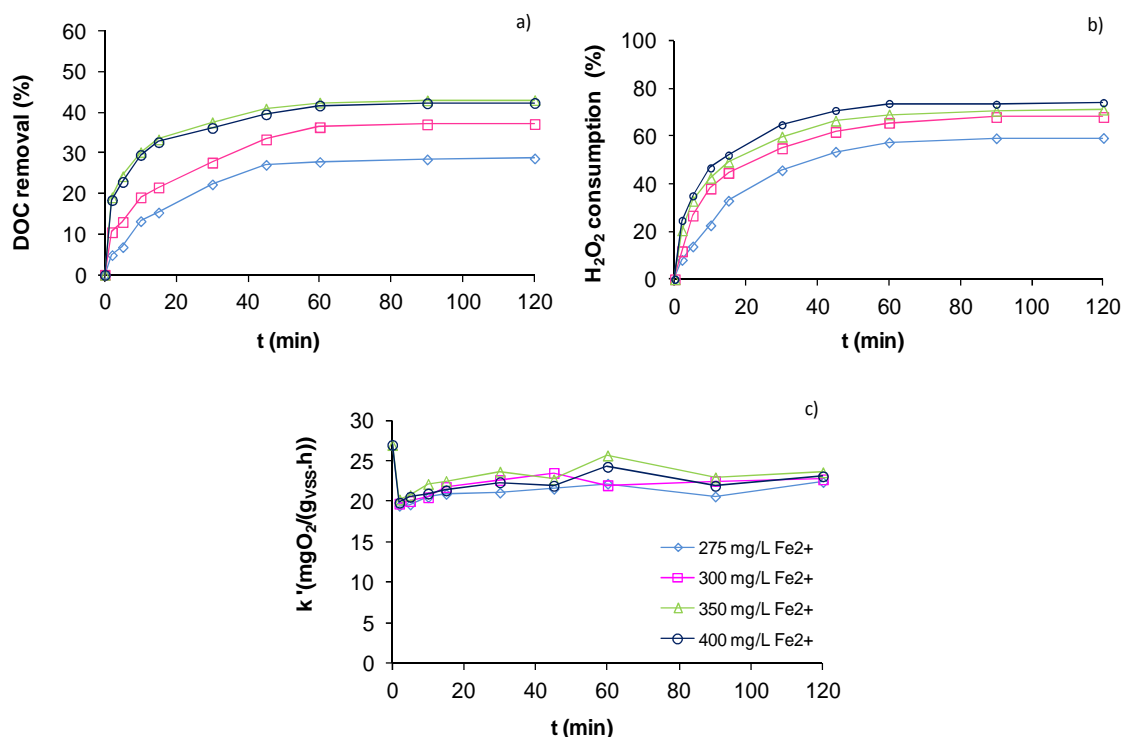


Figure 8.5 – Variation of DOC removal (a), percentage of H_2O_2 consumption (b) and k' (c) along time with the initial Fe^{2+} dose during Fenton's reaction in Approach 2 (initial pH=3.5, $T=30$ °C, initial $[\text{H}_2\text{O}_2]= 5.0$ g/L).

The optimum dose of ferrous iron (350 mg/L) is within the range obtained by Rodrigues et al. [2009 b)] for maximizing color and DOC removals and biodegradability of a cotton dyeing effluent.

8.3.2.2 Effect of the Initial Hydrogen Peroxide Concentration

To minimize the operating costs of the Fenton's process, H_2O_2 concentration must be optimized. Four runs were performed varying this parameter between 1 and 10 g/L (this range was established considering its relation with COD of the raw effluent), at $\text{pH} = 3.5$, $T = 30\text{ }^\circ\text{C}$ and $[\text{Fe}^{2+}] = 350\text{ mg/L}$.

Figure 8.6 a shows the variation of DOC removal with initial $[\text{H}_2\text{O}_2]$; once again, the removal is much faster in the first 15-20 min, when a faster consumption of hydrogen peroxide is also observed. However, DOC removal and H_2O_2 consumption continue to increase till 60 min of reaction.

The DOC removal increased with H_2O_2 concentration up to 2.5 g/L and decreased for higher doses. The optimum reagent dose is justified by the occurrence of parallel reactions between excess of H_2O_2 and the hydroxyl radical (scavenging effect), generating lower oxidation potential radicals like HO_2^\bullet . For $[\text{H}_2\text{O}_2] = 2.5\text{ g/L}$ the DOC removal was ~47% at the end of the run.

The percentage of oxidant consumed is maximal for initial doses of 1.0-2.5 g/L (Figure 8.6 b); above this value hydrogen peroxide is not effectively consumed to generate hydroxyl radicals and part remains in solution.

The effect of initial $[\text{H}_2\text{O}_2]$ in the biodegradability (k') is shown in Figure 8.6 c. There is a decrease in k' upon 2 minutes of reaction in all runs as compared to raw wastewater. However, as the oxidation proceeds, k' increases up to 60 min and then remains nearly constant.

Chapter 8 - Integration of Physical-Chemical and Oxidation Processes for Polyester Dyeing Effluent Treatment

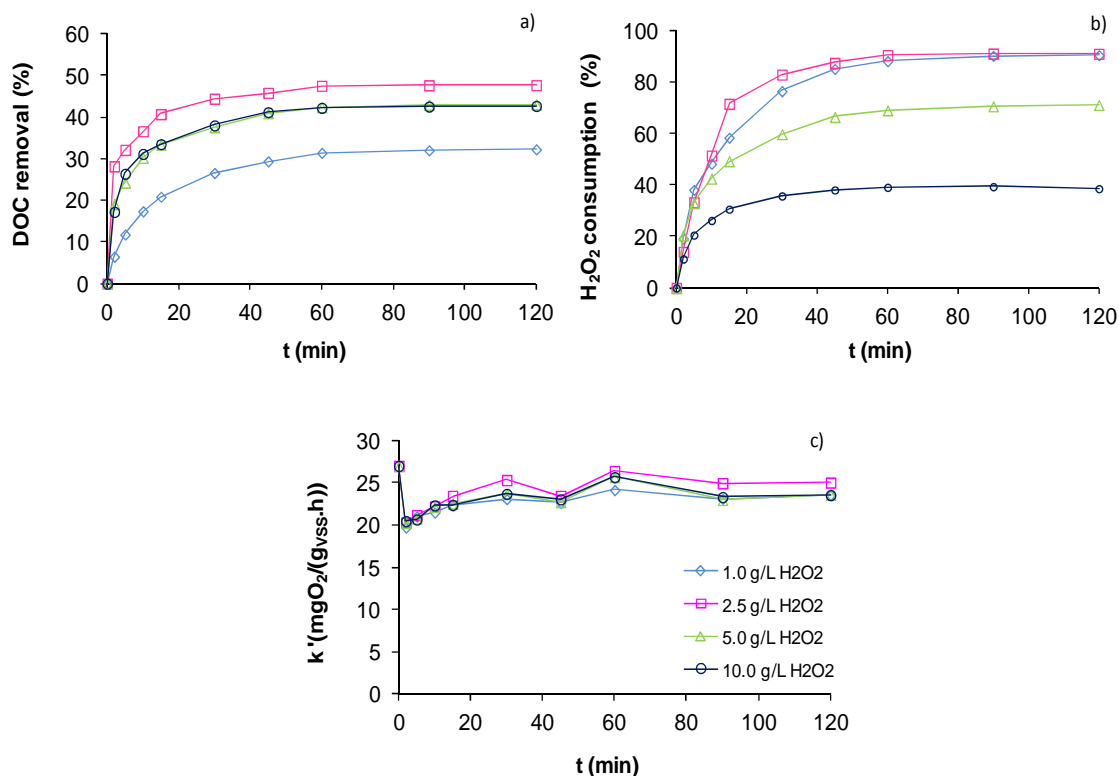


Figure 8.6 – Variation of DOC removal (a), percentage of H₂O₂ consumption (b) and k'(c) along time with the initial H₂O₂ dose during Fenton's reaction in Approach 2 (initial pH=3.5, T=30 °C, initial [Fe²⁺]=350 mg/L).

The optimal oxidant dose (2.5 g/L) is very different from that required for treating cotton and acrylic dyeing effluents (20 g/L for acrylic and 10 g/L for cotton, as shown in chapters 6 and 7, respectively), which is related to the organic load (DOC) of each effluent (350, 500 and 828.1 mg/L for cotton, polyester and acrylic, respectively) but also to the nature of the organics in each one and to other compounds that impair the organics oxidation (for example chlorides). Tantak and Chaudhari [2006] obtained the maximum reduction of organic matter for Reactive Black 5, Reactive Blue 13 and Acid Orange 7 solutions using 2.45 g/L of hydrogen peroxide, Shrivastava and Rao [2011] achieved maximum dyes and COD removals by using 2.1 g/L of hydrogen peroxide in the Fenton's oxidation of a simulated effluent containing Reactive Blue 4 and Reactive Orange 16. Other authors [Wei et al., 2013] found 3.06 g/L as the better dose of H₂O₂ for treating dry-spun acrylic fiber effluent and in this thesis it was found (cf. results presented in chapter 6) a value of

3.5 g/L for the oxidation of acrylic dyeing effluent previously treated by coagulation/flocculation (DOC=334.1 mg/L, COD=828.1 mg/L and BOD₅<1.0 mg/L).

8.3.2.3 Effect of the Temperature

To determine the effect of temperature on DOC removal and biodegradability, various experiments were conducted by varying this parameter from 10 °C to 70 °C (Figures. 8.7 a, b and c). As above-mentioned, this range was selected taking into account the ambient temperature in Portugal, that can be ~10 °C or even lower in some times of the year, and the temperature of the wastewater at the outlet of the drainage system (usually in the range 50-70 °C or even higher). It can be seen that: i) DOC reduction is low at 10 °C (21.9% after 120 min), and a small percentage of H₂O₂ was consumed; ii) the mineralization improved at higher temperatures, mostly in the first 45 min, and the H₂O₂ consumption also increased; iii) the maximum DOC removal was reached at 50 °C (56.3% after 45 min), but the H₂O₂ consumption increased until 70 °C, due to the thermal decomposition of H₂O₂ into water and oxygen at T > 50 °C, as mentioned previously, and by the increased kinetics of “scavenging” reactions.

It was again observed a small decrease of the biodegradability (inferred from k' – see Figure 8.7 c for short reaction times, in all runs, but then it increases, in some cases with slight oscillations. In the runs at 50 and 70 °C, k' increases up to 60 min, and then remains nearly constant. The decrease of biodegradability can probably be associated to the generation of less biodegradable intermediates. Maximum k' values were obtained at 50 °C (30.0 mgO₂/(g_{VSS}.h)) after 60 min of reaction), the same temperature that led to maximum mineralization.

The optimum value of temperature was the same found in the pre-treatment of either acrylic (results in chapter 6) or cotton dyeing wastewaters (results in chapter 7), dye solutions and textile dyeing wastewaters [Ramirez et al., 2005; Gulkaya et al., 2006; Alaton and Teksoy, 2007; Rodrigues et al., 2009 a); Rodrigues et al., 2009 b)] by the Fenton's process.

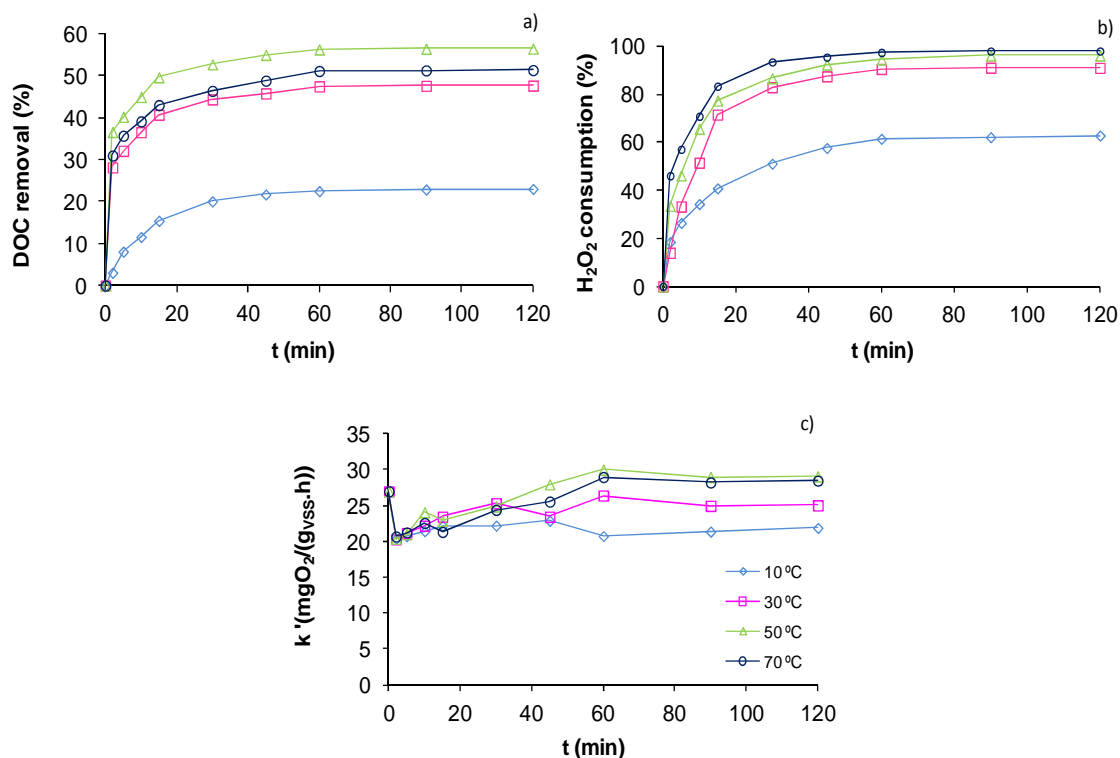


Figure 8.7 – Variation of DOC removal (a), percentage of H₂O₂ consumption (b) and k' (c) along time with the reaction temperature during Fenton's reaction in Approach 2 (initial pH=3.5, initial [Fe²⁺]=350 mg/L and initial [H₂O₂]=2.5 g/L).

8.3.2.4 Optimized Treatment by Fenton's Oxidation

A Fenton's oxidation run was carried out under the conditions that maximize DOC removal and biodegradability ([Fe²⁺]= 350 mg/L, [H₂O₂]= 2.5 g/L, T=50 °C at pH 3.5).

Along 60 minutes (corresponding to the maximum biodegradability – as inferred from k'), samples were collected to follow up the toxicity (inhibition of *V. fischeri*) and HPLC chromatograms (Figures 8.8 a and b, respectively). *V. fischeri* toxicity decreases up to 30-45 minutes for all contact times (5, 15 or 30 min) and then the inhibition percentage is null, indicating that the effluent is no longer toxic. HPLC chromatograms confirm the formation and disappearance of intermediates responsible for the decreased effluent's toxicity.

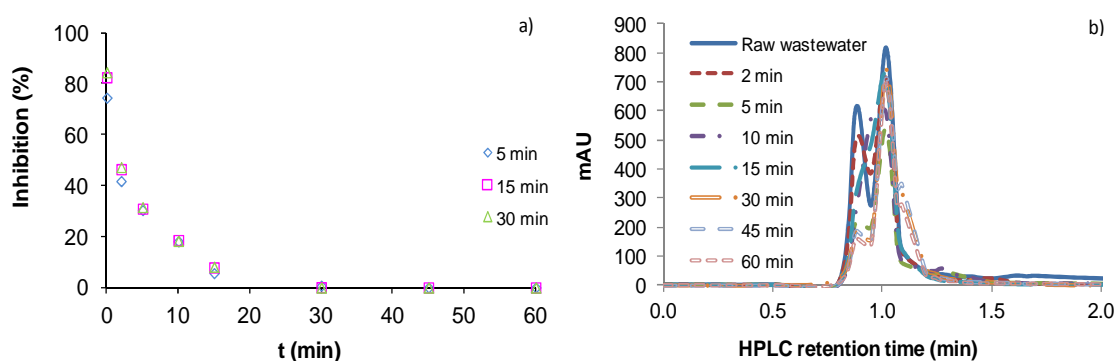


Figure 8.8 – Evolution of *V. fischeri* inhibition after 5, 15 and 30 minutes of contact (a) and HPLC chromatograms (b) of samples taken along time during Fenton's oxidation in Approach 2 (initial pH=3.5, T=50 °C, initial $[\text{Fe}^{2+}]$ =350 mg/L and initial $[\text{H}_2\text{O}_2]$ =2.5 g/L).

The treated effluent was analyzed after 60 minutes of reaction (Table 8.2). A considerable organic matter removal was obtained (57.3% for COD, 55.7% for DOC and 52.0% for BOD_5) and the effluent is not toxic (0.0% of *Vibrio fischeri* inhibition); the ratio of BOD_5 :COD slightly increased from 0.26 to 0.28 and k' from 27.0 to 30.0 $\text{mg O}_2/(\text{g}_{\text{VSS}} \text{h})$. The effluent meets the discharge limits. However, as the value of COD is very close to the maximum allowable value (Table 8.2), a subsequent treatment such as coagulation/flocculation, using the dissolved iron from the Fenton's process as coagulant, might be recommended.

Chapter 8 - Integration of Physical-Chemical and Oxidation Processes for Polyester Dyeing Effluent Treatment

Table 8.2 - Characteristics of the synthetic polyester dyeing wastewater after Fenton's oxidation and respective removals (Approach 2). Maximum allowable values for legislated parameters are also shown.

Parameter	Fenton	Removal (%)	Maximum Allowable Value*
pH	7.05	-	5.5-9.0
Total nitrogen (mg N/L)	15.1	5.0	
Total phosphorus (mg P/L)	2.8	6.7	
Chemical oxygen demand (mg O ₂ /L)	221.1	57.3	250
Biochemical oxygen demand (mg O ₂ /L)	62.8	52.0	100
Dissolved organic carbon (mg C/L)	63.4	55.7	
Specific oxygen uptake rate (k') (mg O ₂ /(g _{VSS} h))	30.0	-	
BOD ₅ :COD ratio	0.28	-	
Visible color after dilution 1:40	not visible	-	not visible
<i>Vibro fischeri</i> Inhibition 5 min (%)	0.0	-	
<i>Vibro fischeri</i> Inhibition 15 min (%)	0.0	-	
<i>Vibro fischeri</i> Inhibition 30 min (%)	0.0	-	

* Portuguese legislation for discharge of textile wastewaters (Ordinance No. 423/97 of 25 June).

8.3.3 Fenton's Oxidation followed by Coagulation/Flocculation (Approach 3)

To increase the removal of organics and aiming at obtaining an effluent with COD values much lower than maximum allowable values, the effluent from the Fenton's process was treated by coagulation/flocculation. The results from the parametric study of the 2nd process stage, in which the effect of pH and dose of flocculant on DOC removal was evaluated, are presented in this section. The Fenton's stage included three experiments: run #3 corresponding to the conditions that maximized DOC removal and biodegradability; runs #2 and #1 where the H₂O₂ and Fe²⁺ doses were reduced to 1/2 and 1/4, respectively. The main goal behind this strategy was to reduce the operating costs associated with chemicals consumption. In the coagulation/flocculation stage the coagulant used was the dissolved iron resulting from the previous oxidation step (64.8, 88.5 and 222 mg/L of Fe in run#1, run#2 and run#3, respectively).

8.3.3.1 Influence of pH in the Coagulation Process

The influence of pH was assessed by carrying out six runs in which this parameter varied between 3.5 and 10.4, using as coagulant the residual dissolved iron from the previous Fenton's reaction.

Figure 8.9 shows the results of DOC removal for different pH levels. The performances slightly improved when the pH was varied from 3.5 to 5.0 and worsened for higher pHs (for instance, in run #1, for a hydrogen peroxide dose of 0.625 g/L in the Fenton's stage, the DOC removal increased from 35.8% to 38.5%, while in run #3, where the highest dose of oxidant was employed in the chemical oxidation stage, the removal raised from 41.6% to 55.0%).

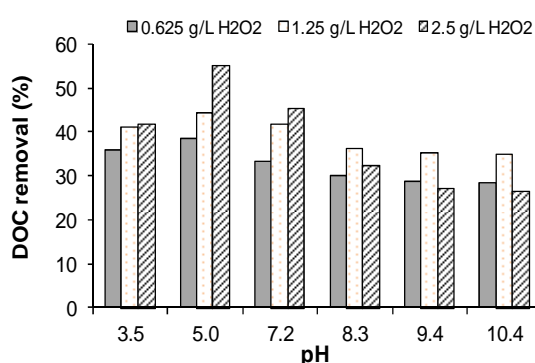


Figure 8.9 – Variation of DOC removal with pH during the coagulation stage – Approach 3 – for the different doses of hydrogen peroxide employed in the previous Fenton's process in runs #1, #2 and #3 ($v_{\text{coagulation}}=150$ rpm, $t_{\text{coagulation}}=3$ min, $[\text{Fe}]_{\text{dissolved run \#1}} = 64.8\text{mg/L}$, $[\text{Fe}]_{\text{dissolved run \#2}}=88.5$ mg/L, $[\text{Fe}]_{\text{dissolved run \#3}}=222$ mg/L and $T = T_{\text{ambient}}=22\text{-}24$ °C).

According to Duan and Gregory [2003], the coagulation most probable mechanism in the optimum range obtained (pH= 5) is charge neutralization and precipitate inclusion, because at this pH the species present in solution are Fe^{3+} , $\text{Fe}(\text{OH})^{2+}$ and $\text{Fe}(\text{OH})_3$.

The optimal pH found is in the acidic zone, which is in accordance with literature reporting the use of ferric sulfate as coagulant (from 3.5 to 7.0) [Edeline, 1992], as the dissolved iron resulting from the chemical oxidation is mainly in the Fe^{3+} form. Besides, the value is similar to that determined in other works using ferric sulfate as coagulant. In particular,

Joo et al. [2007] obtained an optimum pH between 4 and 7 for treating a textile wastewater. Aziz et al. [2007] and Liang et al. [2009] achieved the maximum removal at pH=4 for a landfill leachate and a molasses effluent treatment, respectively.

8.3.3.2 Effect of Superfloc C-573 Doses

The selection of Superfloc C-573 (cationic polymer) as flocculant takes into account the results obtained in preliminary studies using synthetic textile wastewaters (see chapters 4 and 5). Indeed, this flocculant shows better performance when using ferric ion salt as coagulant.

The effect of the flocculant dose, in the range 0.1 to 5 mg/L, on DOC removal was evaluated. The results obtained (cf. Figure 8.10) show a small increment in efficiency when the flocculant was used (0 vs. 0.1 mg/L dose), because the removal of organic compounds mainly occurs in the coagulation step. In all experiments (i.e., whatever the dose of chemicals in the oxidation stage) the DOC removal slightly increased with the flocculant dose up to 0.5 mg/L, and for this optimum dose the performances reached were 42.0, 51.1 and 60.5% for run #1, run #2 and run #3, respectively. The optimum dose obtained is equal to that found when treating simulated cotton dyeing wastewater by coagulation/flocculation using ferric sulphate as coagulant (chapter 5). Besides, it is similar to those reported in literature, even with other flocculants [El-Gohary and Tawfik, 2009; Liang et al., 2009; Zahrim et al., 2010].

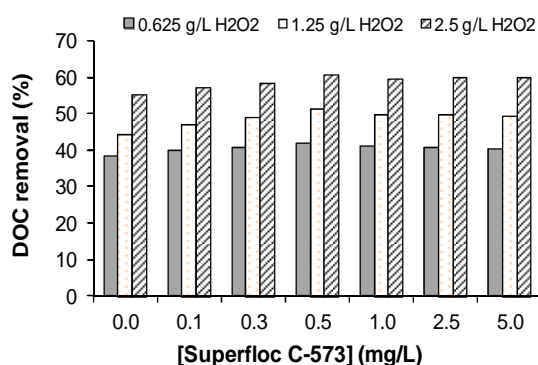


Figure 8.10 – Variation of DOC removal with the flocculant concentration during the flocculation step – Approach 3 – for the different doses of hydrogen peroxide employed in runs #1, #2 and #3 of the previous Fenton's process ($v_{\text{coagulation}}=150$ rpm, $t_{\text{coagulation}}=3$ min, $T=T_{\text{ambient}}=22-24$ °C, pH=5.0, $[\text{Fe}]_{\text{dissolved run \#1}} = 64.8\text{mg/L}$, $[\text{Fe}]_{\text{dissolved run \#2}}=88.5$ mg/L, $[\text{Fe}]_{\text{dissolved run \#3}}=222$ mg/L, $v_{\text{flocculation}}=20$ rpm and $t_{\text{flocculation}}=15$ min).

8.3.3.3 Optimized Integrated Fenton's Oxidation Plus Coagulation / Flocculation Treatment

After determining the operating conditions that maximize DOC removal in the coagulation/flocculation stage, three runs were carried out, as previously described – treating the effluent by the Fenton's process using different hydrogen peroxide doses (0.625, 1.25 and 2.5 g/L – runs #1 to #3), and subsequently submitting it to coagulation/flocculation under the better conditions determined before. Table 8.3 presents the results of the effluent characterization after each stage, together with the respective removal efficiencies and the overall treatment efficiency. The results indicate that the removal of organic compounds is higher in the coagulation/flocculation stage if low doses of chemicals are employed in the Fenton's process (run #1); for higher doses, the performances are similar in each stage. It is also noteworthy that values below the maximum COD and BOD₅ discharge limits were reached in all runs. In run#3, where higher removal efficiencies were attained, the global efficiencies were 78.9, 73.3 and 82.9% for COD, BOD₅ and DOC, respectively.

Chapter 8 - Integration of Physical-Chemical and Oxidation Processes for Polyester Dyeing Effluent Treatment

Table 8.3 - Characteristics of the synthetic wastewater after Fenton's oxidation and coagulation/flocculation – Approach 3 (percent removal efficiencies within brackets) and global removal for the combined process; runs #1 to #3 correspond to different dosages of hydrogen peroxide in the Fenton's stage. Maximum allowable values for legislated parameters are also shown.

Parameter	Run #1			Run #2			Run #3			Maximum Allowable Value*
	Fenton	Coagulation & flocculation	Global removal (%)	Fenton	Coagulation & flocculation	Global removal (%)	Fenton	Coagulation & flocculation	Global removal (%)	
pH	1.21	7.10	-	1.22	7.09	-	1.10	7.15	-	5.5-9.0
Chemical oxygen demand (mg O ₂ /L)	403.4 (19.3)	207.8 (48.5)	58.4	301.5 (39.7)	186.3 (38.2)	62.7	230.4 (53.9)	105.4 (54.3)	78.9	250
Biochemical oxygen demand (mg O ₂ /L)	105.1 (24.8)	60.7 (42.2)	56.6	85.5 (38.8)	56.9 (33.5)	59.3	67.0 (52.1)	37.3 (44.3)	73.3	100
Dissolved organic carbon (mg C/L)	115.9 (24.1)	67.3 (41.9)	56.0	83.1 (45.6)	40.6 (51.1)	73.4	65.7 (57.0)	26.1 (60.3)	82.9	
BOD ₅ :COD ratio	0.26	0.29	-	0.28	0.31	-	0.29	0.35	-	
Visible color after dilution 1:40	not visible	not visible	-	not visible	not visible	-	not visible	not visible	-	not visible

* Portuguese legislation for discharge of textile wastewaters (Ordinance No. 423/97 of 25 June)

8.3.4 Operating Costs

The selection of the best treatment process, besides considering efficiency and ability to comply with legislation, should also take into account the treatment costs. Thus, an economic analysis was made, focused in the total costs of reagents given by Quimitécnica S.A.: H₂O₂ (49.5% (w/v), density at 25 °C = 1.2 g cm⁻³) – 365 €/ton; FeSO₄·7H₂O (93 wt.% of purity) – 233.7 €/ton; Fe₂(SO₄)₃ (solution with 44% (w/w)) – 240 €/ton; and Superfloc C-573 – 2500 €/ton. The costs of acids and base were not considered as they are almost negligible compared to the other chemicals.

Figure 8.11 shows the influence of the reagents doses on the treatment cost, for the different strategies mentioned above. In particular, are shown the effects of the Fe²⁺ and H₂O₂ doses during the Fenton's stage when the effluent was previously treated by coagulation/flocculation (Figure 8.11 a, Approach 1), including in the costs those of the coagulant and flocculant, or when directly applied to the raw wastewater - Approach 2 - (Figure 8.11 b). It turns out, as expected, that the cost increases with increasing concentrations of either reagent but the major contribution comes from the hydrogen peroxide, being far most notorious in Approach 2.

When treating the synthetic wastewater by combining coagulation/flocculation and Fenton's oxidation at the better conditions, the operating costs amount 3.1 €/m³, slightly above the costs of applying directly the Fenton's reagent to the raw simulated wastewater (2.7 €/m³). Besides, the two strategies allowed reaching global efficiencies that would permit to meet the discharge limits, but in Approach 2 (Fenton's reagent alone) the final COD value (221.1 mg O₂/L) is close to the legislated one (250 mg O₂/L).

Chapter 8 - Integration of Physical-Chemical and Oxidation Processes for Polyester Dyeing Effluent Treatment

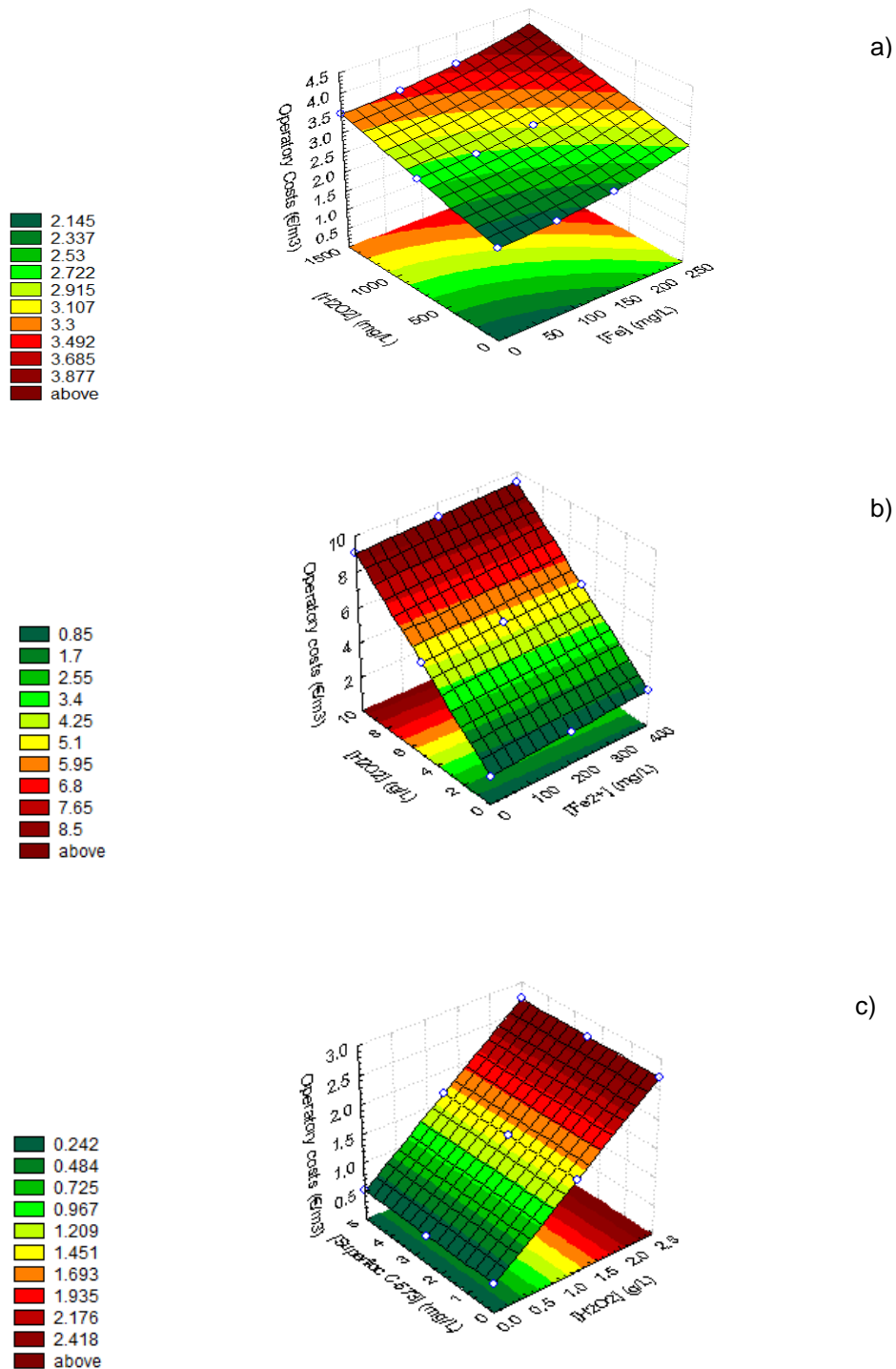


Figure 8.11 – Effect of Fe and H₂O₂ doses on the cost of the reagents used in wastewater treatment by: coagulation/flocculation plus Fenton processes – Approach 1 (a) or Fenton’s reagent – Approach 2 (b), and influence of [Superfloc C-573] and [H₂O₂] on the operating cost of Fenton’s process followed by coagulation/flocculation – Approach 3 (c).

Figure 8.11 c shows the influence of Superfloc C-573 and hydrogen peroxide costs upon the integration of chemical oxidation followed by coagulation/flocculation process. The operatory costs increased with the doses of reagents, however, this increase is more notorious for hydrogen peroxide than Superfloc C-573. In fact, the effect of flocculant in the global cost is almost negligible because the doses used are small. Thus, the total cost of the treatment according to Approach 3 is almost entirely due to the consumption of reagents in oxidation (that amounts to ca. 0.7, 1.3 and 2.7 €/m³ in runs #1, #2 and #3, respectively). The three experiments allowed obtaining an effluent that can be discharged, but given the low differences of the operating costs of runs #1 and #2 and the COD value obtained in run #1, which is close to the maximum allowable value, the conditions of run #2 for treating the simulated wastewater by Fenton's oxidation plus coagulation/flocculation are recommended. In this case, it was possible to reduce the cost from 3.1-2.7 €/m³ in previous Approaches to only 1.3 €/m³ due to the better integration strategy of the treatment stages.

8.4 Conclusions

The integration of coagulation/flocculation and Fenton's process (using the dissolved iron resulting from the coagulation stage as part of the catalyst in the second one) leads to high organic matter removals (79.2% for COD, 61.9% for BOD₅ and 75.7% for DOC) and generates a nontoxic effluent meeting the discharge limits at an operating cost of around 3.1 €/m³;

The Fenton's oxidation per se allows obtaining slightly smaller removal efficiencies (57.3% for COD, 52.0% for BOD₅ and 55.7% for DOC), yielding also a nontoxic effluent and a small improvement of the biodegradability. The treated effluent meets the discharge limits although the COD value is near the maximum allowable value. The estimated costs associated to chemicals consumption in this process are 2.7 €/m³;

The combination of Fenton's process plus coagulation/flocculation in optimized conditions provided an effluent that meets the discharge limits, with high global organic matter removals (78.9% for COD, 73.3% for BOD₅ and 82.9% for DOC). Considerable organic matter removals (62.7% for COD, 59.3% for BOD₅ and 73.4% for DOC) are also reached

when reducing H_2O_2 dose to one-half (run #2), the effluent still complying with the maximum legislated values at a much smaller operating cost (1.3 €/m³).

The operating costs regarding the reagents consumption can be further decreased (0.7 €/m³) using a smaller dose of H_2O_2 (run #1), but in this case the final COD value is close to the discharge limit. However we propose not to reduce further the amount of reagents used in the Fenton reaction to ensure that the final COD values do not exceed 250 mg/L (legal limit) even when the COD of the raw wastewater slightly increases due to daily or seasonal variations.

The use of the dissolved iron resulting from the Fenton's process as coagulant in the subsequent treatment step revealed to be an innovative and promising strategy to considerably decrease operating costs.

8.5 References

Alaton, I.A.; Teksoy, S. (2007). Acid dyebath effluent pretreatment using Fenton's reagent: Process optimization, reaction kinetics and effects on acute toxicity. *Dyes and Pigments*, 73, 31-39.

Azbar, N.; Yonar, T.; Kestioglu, K. (2004). Comparison of various advanced oxidation processes and chemical treatment methods for COD and color removal from a polyester and acetate fiber dyeing effluent. *Chemosphere*, 55, 35-43.

Aziz, H.A. ; Alias, S. ; Adlan, M.N. ; Faridah ; Assari, A.H.; Zahari, M.S. (2007). Colour removal from landfill leachate by coagulation and flocculation processes. *Bioresource Technology*, 98, 218-220.

Blanco, J.; Torrades, F.; Varga, M. de la; García-Montaña, J. (2012). Fenton and biological-Fenton coupled processes for textile wastewater treatment and reuse. *Desalination*, 286, 34-399.

Duan, J.; Gregory, J. (2003). Coagulation by hydrolysing metals salts. *Advances in Colloid and Interface Science*, 100-102, 475-502.

Edeline, F. (1992). *L'épuration physico-chimique des eaux – théorie & technologie*, 2e édition, Editions CEBEDOC.

El-Gohary, F.; Tawfik, A. (2009). Decolorization and COD reduction of disperse and reactive dyes wastewater using chemical-coagulation followed by sequential batch reactor (SBR) process. *Desalination*, 249, 1159-1164.

Gulkaya, Í.; Surucu, G.A.; Dilek, F.B. (2006). Importance of $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio in Fenton's treatment of a carpet dyeing wastewater. *Journal of Hazardous Materials*, B136, 763-769.

- Joo, D.J.; Shin, W.S.; Choi, J.-H.; Choi, S.J.; Kim, M.-C.; Han, M.H.; Ha, T.W.; Kim, Y.-H. (2007). Decolorization of reactive dyes using inorganic coagulants and synthetic polymer. *Dyes and Pigments*, 73, 59-64.
- Liang, Z.; Wang, Y.; Zhou, Y.; Liu, H.; Wu, Z. (2009). Hydrolysis and coagulation behavior of polyferric sulfate and ferric sulfate. *Water Science and Technology*, 1129-1135.
- Papadopoulos, A.E.; Fatta, D.; Loizidou, M. (2007). Development and optimization of dark Fenton oxidation for the treatment of textile wastewaters with high organic load. *Journal of Hazardous Materials*, 146, 558-563.
- Perdigon-Melon, J.A.; Carbajo, J.B.; Petre, A.L.; Rosal, R.; Garcia-Calvo, E. (2010). Coagulation-Fenton coupled treatment for ecotoxicity reduction in highly polluted industrial wastewater. *Journal of Hazardous Materials*, 181, 127-132.
- Peres, J.A.; Heredia, J.B.; Domínguez, J.R. (2004). Integrated Fenton's reagent – coagulation/flocculation process for the treatment of cork processing wastewater. *Journal of Hazardous Materials*, 107 (3), 115-121.
- Ramirez, J.H.; Costa, C.A.; Madeira, L.M. (2005). Experimental design to optimize the degradation of the synthetic dye Orange II using Fenton's reagent. *Catalysis Today*, 107-108, 68-76.
- Ramirez, J.H.; Costa, C.A.; Madeira, L.M. (2008). Experimental design to optimize the oxidation of Orange II dye solution using a clay-based Fenton-like catalyst. *Industrial Engineering Chemical Research*, 47, 284-294.
- Rodrigues, C.S.D.; Madeira, L.M.; Boaventura, R.A.R. (2009 a)). Optimization of the azo dye Procion Red H-EXL degradation by Fenton's reagent using experimental design. *Journal of Hazardous Materials*, 164, 987-994.
- Rodrigues, C.S.D.; Madeira, L.M.; Boaventura, R.A.R. (2009 b)). Treatment of textile effluent by chemical (Fenton's Reagent) and biological (Sequencing Batch Reactor) oxidation. *Journal of Hazardous Materials*, 172, 1551-1559.
- Shrivastava, S.; Rao, S. N. (2011). Pickling Waste as an Inexpensive Iron Source for Fenton Oxidation of Synthetic Dye Bath Waste. *Clean – Soil, Air, Water*, 39 (11), 996–1000.
- Swaminathan, K.; Sandhya, S.; Sophia, A.C.; Pachhade, K.; Subrahmanyam, Y.V. (2003). Decolorization and degradation of H-acid and other dyes using ferrous-hydrogen peroxide system. *Chemosphere*, 50, 619-625.
- Sun, J.-H.; Sun, S.-P.; Wang, G.-L.; Qiao, L.-P. (2007). Degradation of azo dye amido black 10B in aqueous solution by Fenton oxidation process. *Dyes and Pigments*, 74, 647-652.
- Tantak, N.P. ; Chaudhari, S. (2006). Degradation of azo dyes by sequential Fenton's oxidation and aerobic biological treatment. *Journal of Hazardous Materials*, B136, 698-705.
- Tekin, H.; Bilkay, O., Ataberk S.S.; Balta, T.H.; Ceribasi, I.H.; Sanin F.D.; Dilek, F.B.; Yetis, U. (2006). Use of Fenton oxidation to improve the biodegradability of a pharmaceutical wastewater. *Journal Hazardous Materials*, B136, 258-265.

Chapter 8 - Integration of Physical-Chemical and Oxidation Processes for Polyester Dyeing Effluent Treatment

Wei, J.; Song, Y.; Tu, X.; Zhao, L.; Zhi, E. (2013). Pretreatment of dry-spun acrylic fiber manufacturing wastewater by Fenton process: optimization, kinetics and mechanisms. *Chemical Engineering Journal*, 218, 319-326.

Wu, H.; Wang, S. (2012). Impacts of operating parameters on oxidation-reduction potential and pretreatment efficacy in the pretreatment of printing and dyeing wastewater by Fenton process. *Journal of Hazardous Materials*, 243, 86-94.

Xing, Z.-P.; Sun, D.-Z. (2009). Treatment of antibiotic fermentation wastewater by combined polyferric sulfate coagulation, Fenton and sedimentation process. *Journal of Hazardous Materials*, 168, 1264-1268.

Zahrim, A.Y.; Tizaoui, C.; Hilal, N. (2010). Evaluation of several commercial synthetic polymers as flocculant aids for removal of highly concentrated C.I. Acid Black 210 dye. *Journal of Hazardous Materials*, 182, 624-630.

Chapter 9

Simulated Dyeing Textile Effluents Treatment by the Photo-Fenton Process*

* This Chapter is based on the publication "Rodrigues C.S.D.; Madeira, L.M.; Boaventura, R.A.R. (2013). Optimization and Economic Analysis of Textile Wastewater Treatment by Photo-Fenton under Artificial and Simulated Solar Radiation". Industrial & Engineering Chemistry Research. DOI: 10.1021/ie401301h.

9 Simulated Dyeing Textile Effluents Treatment by the Photo-Fenton Process

9.1 Introduction

In this work, a treatability study of acrylic, cotton and polyester simulated effluents (which are typical of textile dyeing industry) is done, making use of photo-Fenton technology with artificial and sunlight radiation. The main purpose of this work is to evaluate the possibility of reducing the chemicals consumption associated to the dark Fenton reaction and also energy, while obtaining final effluents that accomplish the maximum allowable limits imposed by legislation for discharge into the aquatic environment. So, an economical analysis is carried out, with the goal of reducing, as much as possible, operation costs of treatment. Such analysis is crucial for implementation of these promising technologies in industrial environments, and maximizing process performance while reducing cost is mandatory although, up to the authors knowledge has not been reported before.

9.2 Materials and Methods

9.2.1 Preparation of Simulated Textile Wastewaters

The simulated dyeing textile effluents were prepared in accordance with the information given in section 3.2 of chapter 3.

9.2.2 Experimental Procedure

In the photo-Fenton's oxidation two different types of radiation (artificial and simulated solar) were used. The experiments were performed as described in sections 3.4.3.1 and 3.4.3.2 of chapter 3. The temperature and pH were set at 50 °C and 3.5, respectively. These values took into account the optimum conditions obtained in dark Fenton process (chapters 6 to 8) and are similar to those reported in the literature by several authors, for decolorization of textile effluents by this process [Rodriguez et al., 2002; Pérez et al., 2002; Muruganandham and Swaminathan, 2004; Torrades et al. 2004; Lucas and Peres, 2006; Riga et al., 2007; Devi et al., 2009].

9.2.3 Analytical Methods

The analytical methods used for the determination of the various parameters are described in chapter 3 (section 3.3).

All determinations were performed in duplicate and the coefficients of variation were less than 2% for DOC, 12 % for BOD₅, 5% for COD and 2% for the absorbance.

9.3 Results and Discussion

In this study, synthetic acrylic, polyester and cotton textile dyeing wastewaters were used. In Table 3.4 (chapter 3) are reported the more relevant characteristics of each one, being of relevance the fact that cotton and acrylic wastewaters are colored. Besides, the polyester and particularly the acrylic present reasonable concentration of organic compounds (DOC and COD), and a low biodegradability (BOD₅:COD ratio <0.4) is observed in all cases. In addition, the acrylic and polyester effluents present high toxicity values for *Vibrio fischeri*. Because none of the effluents comply with legislated standards, particularly in what concerns COD, they have to be treated before discharge or disposal. Once the biological process cannot be used (due to low biodegradability/high toxicity values), chemical oxidation by photo-Fenton was attempted, making use of two different types of radiation (artificial and simulated solar). Results obtained are described along the following sections.

9.3.1 Photoreactor with Artificial Radiation

9.3.1.1 Comparison Between Direct Photolysis, UV-visible+H₂O₂ and Photo-Fenton Processes

The study started with the use of a high pressure mercury lamp (TQ 150) for comparing the performances of i) direct photolysis, ii) combination of UV-visible radiation + hydrogen peroxide (concentration of H₂O₂ used was the optimum one found in dark Fenton – 2.5 g/L, 10 g/L and 20 g/L for polyester, cotton and acrylic, respectively, as shown in chapters 6, 7 and 8) and iii) photo-Fenton process (with optimal conditions determined in dark

Fenton – 300 mg/L of Fe^{2+} in cotton and 350 mg/L of Fe^{2+} for acrylic and polyester, with the same doses of H_2O_2 described above). Performances were assessed in terms of the removal of DOC and color. In all experiments the maximum intensity of light – 500 W/m^2 - (corresponding to 150 W lamp power) was used. Figure 9.1 presents the results obtained. It can be seen that, for the acrylic dyeing wastewater (Figure 9.1 a), the direct photolysis provides a low color and DOC removal (~ 14% and ~ 39% after 15 minutes of reaction, respectively). With the addition of hydrogen peroxide (UV/vis+ H_2O_2) it is achieved an increase in the removal performance; for DOC it is about 55% after 15 minutes and then remains nearly constant while color elimination reaches the plateau after 60 minutes with about 99.6%. However, the photo-Fenton process is the one that provides the best efficiencies, in very short reaction times (~ 1-2 minutes), due to the presence of the catalyst; removals reached are > 86% and 99% for DOC and color, respectively. The removal of DOC is much greater than the one achieved in the Fenton's process (66.5%), although complete color removal was achieved in both oxidation processes (cf. results in chapter 6).

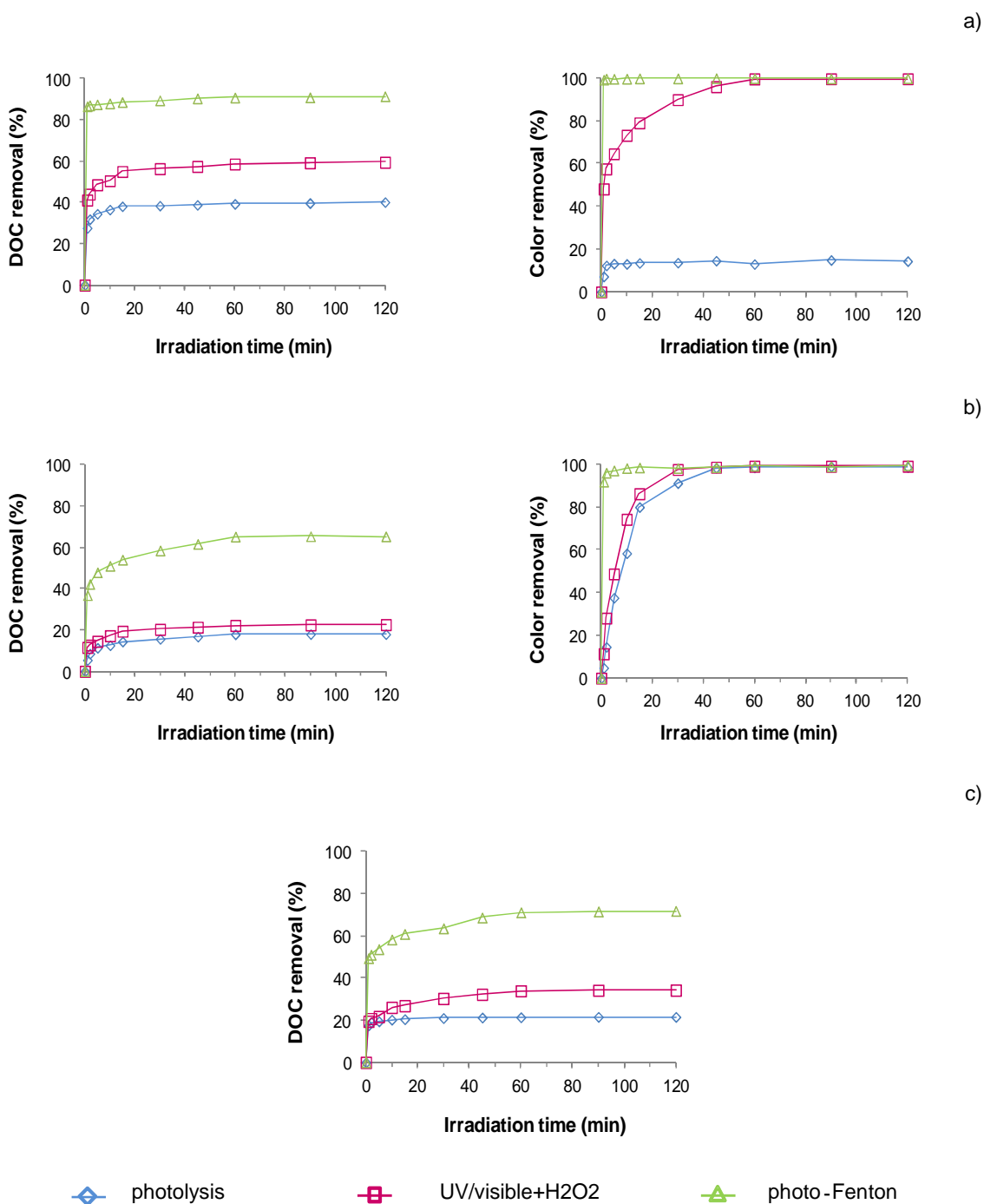


Figure 9.1 – Evolution of DOC and color removal for acrylic (a), cotton (b) and polyester (c) wastewater during 120 minutes of direct photolysis, H₂O₂-assisted photolysis ([H₂O₂]_{acrylic}=20 g/L, [H₂O₂]_{cotton}=10 g/L and [H₂O₂]_{polyester}=2.5 g/L) or photo-Fenton ([H₂O₂]_{acrylic}=20 g/L, [H₂O₂]_{cotton}=10 g/L and [H₂O₂]_{polyester}=2.5 g/L, [Fe²⁺]_{cotton}=300 mg/L, [Fe²⁺]_{acrylic}=[Fe²⁺]_{polyester}=350 mg/L). In all cases radiation intensity = 500 W/m², pH=3.5, T=50°C.

In what concerns the cotton effluent treatment, Figure 9.1 b shows that, in all runs, the DOC removal increases more rapidly in first 15 minutes, which is followed by a slower increase until reaction times of 60 minutes, after which removals are no longer improved. For this reaction time the mineralization achieved was 17.9%, 22.1% and 65.1% in photolysis, UV+visible/H₂O₂ and photo-Fenton, respectively. In what concerns decolorization, it was found that for the cotton effluent photolysis and UV-visible+H₂O₂ provide similar efficiencies, the removal increasing with reaction time up to 45 minutes where a level of ~98% was reached. Again, the photo-Fenton provided a very fast decolorization, and in the first 2-5 minutes it was reached ~98% of color removal. Better performances were again reached in the presence of light (i.e. photo-Fenton reaction) when compared with the dark Fenton, where DOC removal obtained was 49% and decolorization ~90% (cf. results in chapter 7).

The results of DOC reduction in the polyester effluent are also shown in Figure 9.1 c. Again it increases more rapidly in first 15 minutes, and then slows down until reaction times of ca. 60 minutes, remaining constant for longer times. For this time the mineralization achieved was 21.4%, 33.9% and 71.0% for photolysis, UV/visible radiation+H₂O₂ and photo-Fenton, respectively. The corresponding value obtained previously through dark Fenton was 56.0% (cf. results in chapter 8).

For all wastewaters the performances achieved in the photo-Fenton process are always higher than for the other oxidation processes employed, as also observed in studies reported in the literature with dyes or textile wastewaters [Muruganandham and Swaminathan, 2004; Riga et al., 2007].

It is worth mentioning that, with the photo-Fenton process, mineralization degrees reached for all the dyeing effluents are remarkable, in the range 65-86%, with almost complete color removal. The different performances reached are not only a consequence of the different doses of chemicals employed (more oxidant was required for the effluent with more organic load – acrylic, where 86% of DOC reduction was reached), but also of their different compositions, due to their complex nature (the polyester wastewater required less H₂O₂, but smaller mineralization was reached in the cotton one), which can be due to decreased kinetics because the organic load is smaller and/or to the hydroxyl radicals scavenging reactions due to the presence of very high chloride content – Table 3.4.

9.3.1.2 Photo-Fenton Process

9.3.1.2.1 Effect of Hydrogen Peroxide Concentration

As the photo-Fenton process showed very good and the better efficiencies, further tests were carried out where the dose of hydrogen peroxide was decreased aiming decreasing treatment costs (although final effluents should still meet the discharge limits); iron concentration was also decreased, by keeping constant the Fe^{2+} : H_2O_2 weight ratios at the optimum values previously found in dark (chapters 6, 7 and 8): 1:57, 1:33 and 1:7 for acrylic, cotton and polyester, respectively.

The performances results obtained along the irradiation time are presented in Figure 9.2. For the acrylic effluent (Figure 9.2 a) it can be observed that DOC removal rate (and final mineralization performance) increase with the dose of oxidant; for a dose of 20 g/L removals reached are higher than 85%. Color removal is however nearly equal at all doses of reagent used, requiring a very short irradiation time (~ 5-10 minutes) to obtain complete decolorization of the effluent.

For the cotton wastewater, the conclusions are similar (removal increases with increasing dose of the reagent), although mineralizations reached are smaller; 40.8% for a dose of 2.5 g/L and 64.8% for 10 g/L, at the end of the run (Figure 9.2 b). The discoloration is again very quick and almost complete. In addition, for all hydrogen peroxide concentrations tested, DOC removal occurs more rapidly in the first 20-30 minutes, then slows down till ca. 60 minutes and after this period there is no further organics mineralization up to CO_2 .

For the polyester wastewater, the patterns of DOC are quite similar to those observed for the other effluents, particularly for the cotton one, although smaller doses of peroxide are employed but still providing better performances (71.0% mineralization was reached for a dose of 2.5 g/L, after 60 minutes of irradiation) – Figure 9.2 c.

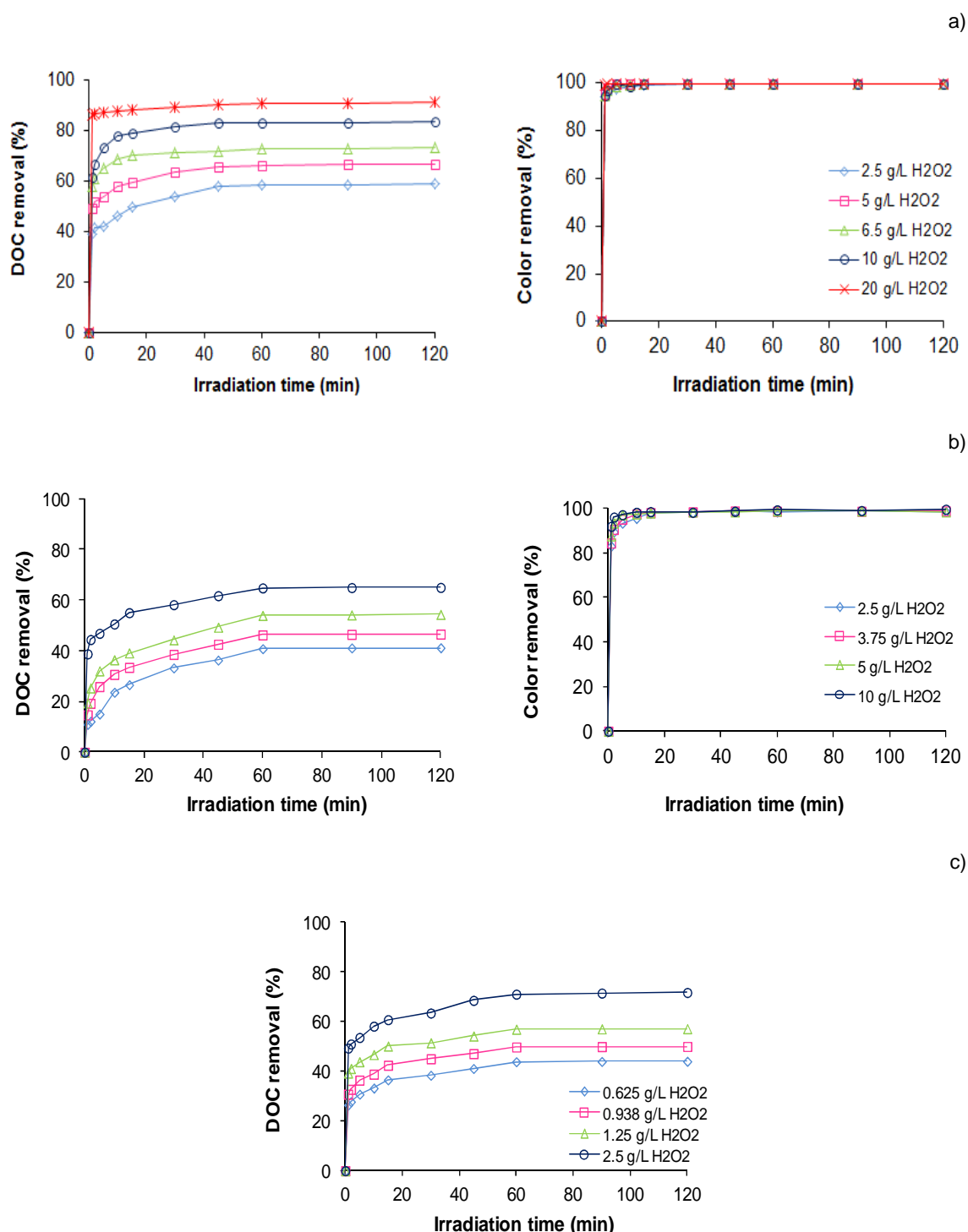


Figure 9.2 – Effect of H_2O_2 dose on DOC and color removal in the photo-Fenton process for acrylic (a), cotton (b) and polyester (c) wastewaters (radiation intensity = 500 W/m^2 , $T=50 \text{ }^\circ\text{C}$, $\text{pH}=3.5$, $\text{Fe}^{2+}:\text{H}_2\text{O}_2_{\text{acrylic}}=1:57$, $\text{Fe}^{2+}:\text{H}_2\text{O}_2_{\text{cotton}}=1:33$, $\text{Fe}^{2+}:\text{H}_2\text{O}_2_{\text{polyester}}=1:7$ – wt. ratios).

Chapter 9 - Simulated Dyeing Textile Effluents Treatment by the Photo-Fenton Process

In order to assess the minimum doses of reagents that would allow obtaining an effluent that still meets the legislated values for discharge or landfill disposal, the legislated parameters (COD, BOD₅ and visible color after dilution by a factor of 40) were assessed in each case after 60 minutes of reaction time (longer oxidation times did not prove to improve oxidation performances – cf. Figures 9.1 and 9.2). Values obtained are shown in Table 9.1, although the reader should at this stage focus only in the runs with radiation intensity of 500 W/m² (corresponding to P = 150 W). It is worth noting that all tests showed no visible color and that BOD₅ values were always lower than the maximum allowable value (100 mgO₂/L – cf. Table 9.1); however, COD values are in some circumstances above the legislated value of 250 mgO₂/L. This occurs for the runs with 2.5 and 5 g/L for the acrylic effluent, 2.5 g/L for the cotton, and 0.625 g/L of H₂O₂ for the polyester. Consequently, it is possible to define the “minimum” dose of hydrogen peroxide, i.e. the “minimum” amount of hydrogen peroxide required to achieve an effluent ready for discharge, of 6.5, 3.75 and 0.938 g/L (Table 9.1) and of ferrous iron of 113.8, 112.5 and 131.2 mg/L for acrylic, cotton and polyesters effluents, respectively. The values of [Fe²⁺] were obtained from the optimum values of Fe²⁺:H₂O₂ weight ratios reported above and that were kept constant (cf. beginning of this section).

It is finally worth mentioning that the high amounts of hydrogen peroxide needed to treat the effluents are related to undesirable side reactions that occur between the hydroxyl radicals and anions present in the effluent, such as sulfates for polyester and acrylic, chlorides and carbonates for cotton and carbonates for polyester effluents. These amounts of chemicals are similar to those obtained in other studies reported in literature, either regarding the treatment of dye solutions [Ay et al., 2009] or synthetic and real textile wastewaters [Pérez et al., 2002; Rodriguez et al., 2002; Arsalan-Alaton et al., 2009; Módenes et al., 2012] by the photo-Fenton process.

Table 9.1 – Values of COD, BOD₅ and visible color (1:40 dilution) after 60 minutes of oxidation for different doses of H₂O₂ and radiation intensity using the TQ150 lamp (in bold: conditions that allow meeting the discharge limits at the minimum cost).

[H ₂ O ₂] (g/L)	Radiation intensity (W/m ²)	COD (mgO ₂ /L)	BOD ₅ (mgO ₂ /L)	Visible color after dilution 1:40	Total Costs (€/m ³)
Acrylic					
2.5	500	342.3	25.3	not visible	21.0
5.0	500	271.4	27.2	not visible	23.3
6.5	253	311.1	25.8	not visible	15.5
	500	227.2	33.3	not visible	24.7
10.0	7	300.7	24.1	not visible	9.4
	107	278.7	39.7	not visible	13.2
	220	246.9	42.6	not visible	17.4
	253	237.2	44.0	not visible	18.7
	500	139.4	39.8	not visible	27.9
20.0	7	222.5	25.9	not visible	18.6
	107	205.4	31.8	not visible	22.3
	253	149.1	41.4	not visible	27.8
	500	90.5	55.3	not visible	37.0
Cotton					
2.5	500	271.6	77.4	not visible	2.6
3.75	253	284.0	74.5	not visible	13.0
	500	235.7	78.5	not visible	22.2
5.0	7	284.0	65.0	not visible	4.9
	107	271.6	68.7	not visible	8.7
	220	223.3	73.4	not visible	12.9
	253	210.0	76.4	not visible	14.2
	500	185.2	81.3	not visible	23.4
10.0	7	234.6	76.5	not visible	9.6
	107	210.0	78.5	not visible	13.3
	253	160.5	80.2	not visible	18.8
	500	135.8	85.5	not visible	28.1
Polyester					
0.625	500	264.1	74.9	not visible	19.4
0.938	253	267.3	77.8	not visible	10.5
	500	225.2	65.7	not visible	19.8
1.25	7	251.2	85.1	not visible	1.6
	107	241.4	67.5	not visible	5.3
	220	230.2	66.6	not visible	9.6
	253	221.7	73.8	not visible	10.8
	500	202.9	61.1	not visible	20.1
2.5	7	219.2	62.3	not visible	2.9
	107	199.5	59.4	not visible	6.7
	253	179.8	57.2	not visible	12.2
	500	154.0	56.2	not visible	21.4

9.3.1.2.2 Effect of Radiation Intensity

In order to minimize the energy costs of the photo-Fenton process, it was decided to analyze the effect of the radiation intensity (between 7 and 500 W/m² – corresponding to lamp powers between 2.1 to 150 W) with the doses of reagents tested previously that allowed complying with discharge standards. For example, and according with the data of Table 9.1, for the acrylic effluent the light radiation could be less than 500 W/m² for H₂O₂ doses in the range 6.5-20.0 g/L but not for [H₂O₂] = 2.5-5.0 g/L because in the latter conditions COD of the effluent was above the legislated standard of 250 mgO₂/L.

Figure 9.3 shows the removal of DOC and color for the different radiation intensity tested in the assays with 6.5, 10 and 20 g/L of H₂O₂ for the effluent resulting from dyeing of acrylic fibers. It can be seen that in all tests the color removal is very fast, requiring only 1-5 minutes of radiation to reach nearly complete decolorization, and is almost independent of the radiation flux reaching the solution. Regarding the removal of DOC, it can be seen that, in general, and whatever the radiation flux and peroxide dose, it is very fast in the first 15 minutes, then slightly decreases till 60 minutes of reaction, after which DOC remains approximately constant. However, the removal of organic compounds increases with increasing radiation intensity for all hydrogen peroxide concentrations, in agreement with other studies [Kang et al., 2000; Muruganandhan and Swaninathan, 2004; Modirshahla et al., 2007]. For the maximum radiation used of 500 W/m² 73, 83 and 96.7% of DOC removal was reached for H₂O₂ doses of 6.5, 10 and 20 g/L, respectively.

Similar experiments were performed for the other effluents, and the conclusions reached are quite similar, of course with different performances. Results obtained are shown in Figures A.5 and A.6 of the Appendix for the cotton and polyester wastewaters, respectively.

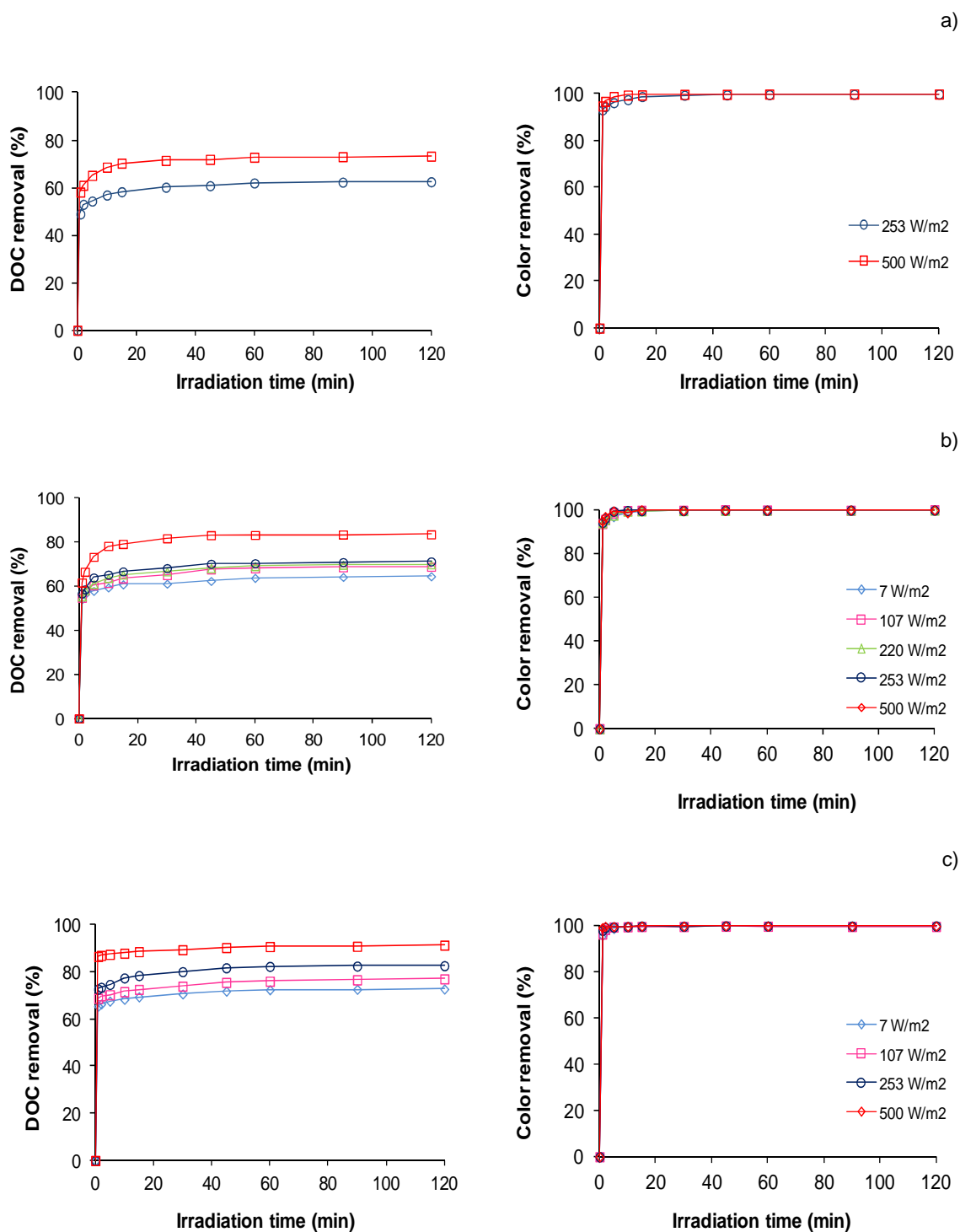


Figure 9.3 – Effect of radiation intensity on DOC and color removal of the acrylic effluent during the photo-Fenton process for different dosages of hydrogen peroxide: 6.5 g/L (a), 10.0 g/L (b) or 20.0 g/L (c) ($T=50\text{ }^{\circ}\text{C}$, $\text{Fe}^{2+}:\text{H}_2\text{O}_2=1:57$ and $\text{pH}=3.5$).

Again, in all assays performed in this section the final effluent was characterized in terms of legislated parameters. As illustrated in Table 9.1, in all tests the color was not visible in the effluents after the required dilution. Besides, for every effluent and oxidant dose, it is noticed that the lower the radiation intensity, the lower are the performances reached in terms of COD removal, so that final values of this parameter after 60 min of irradiation are higher; for BOD₅ this not always observed (the small variations observed in this parameter are associated with uncertainties in its determination), but the values reached are always below the legislated standard of 100 mgO₂/L. This means that for each dose of hydrogen peroxide, for a given type of effluent, there is a radiation intensity threshold below which effluent's characteristics do not comply with legislated standards. For instance, and taking into the account the values tested, for the acrylic one these values are 500 W/m² for [H₂O₂] = 6.5 g/L, 220 W/m² for [H₂O₂] = 10.0 g/L and 7 W/m² for [H₂O₂] = 20.0 g/L. Of course, the higher the oxidant concentration, the lower is the radiation intensity required to reach COD values below 250 mgO₂/L. The question remaining is which set of values is more advantageous for industrial implementation; the answer can be given by comparing associated costs, as detailed in the following section.

9.3.1.3 Operating Costs

The overall costs of the treatment process are represented by the sum of the capital, operating and maintenance costs. For a full-scale system these costs depend on the flow rate of the effluent, the nature of wastewater, as well as the configuration of the reactors, among other issues. In this study we considered only the costs with the chemicals, i.e., the costs of reagents, and the costs of energy. The first were obtained from Quimitécnica S.A., the average values considered being as follows: H₂O₂ (49.5% w/v, density at 25 °C = 1.2 g/cm³) - 365 €/ton; FeSO₄·7H₂O (93 % of purity) – 233.7 €/ton, while the latter is about 0.10 €/(kWh). The prices of acid (H₂SO₄) and base (NaOH) were not considered, because the quantities consumed are insignificant.

The operating cost was calculated by the sum of costs of hydrogen peroxide, ferrous sulfate and energy consumption, as shown by Equation 9.1. The partial costs were calculated according to Equations. 9.2 - 9.4.

$$\text{Operating Cost} = \text{Cost}_{\text{H}_2\text{O}_2} + \text{Cost}_{\text{Fe}^{2+}} + \text{Cost}_{\text{energy}} \quad (9.1)$$

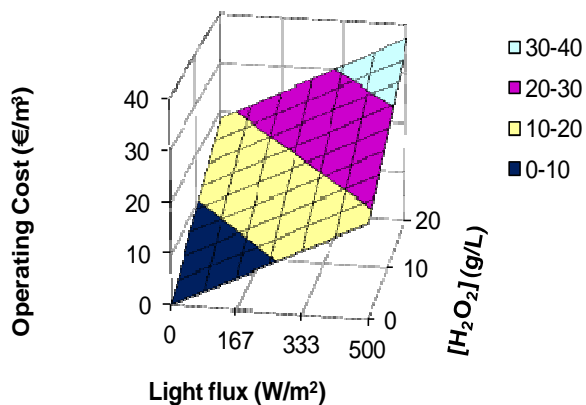
$$\text{Cost}_{\text{H}_2\text{O}_2} = \frac{\text{Price H}_2\text{O}_2 \left(\frac{\text{€}}{\text{ton}} \right) [\text{H}_2\text{O}_2] * 10^{-3} \left(\frac{\text{ton}}{\text{m}^3} \right) * \rho_{\text{H}_2\text{O}_2} \left(\frac{\text{kg}}{\text{L}} \right)}{\frac{\% \text{H}_2\text{O}_2}{100} \left(\frac{\text{kg}}{\text{L}} \right)} \quad (9.2)$$

$$\text{Cost}_{\text{Fe}^{2+}} = \frac{\text{Price FeSO}_4 \cdot 7\text{H}_2\text{O} \left(\frac{\text{€}}{\text{ton}} \right) [\text{Fe}^{2+}] * 10^{-6} \left(\frac{\text{ton}}{\text{m}^3} \right) * \frac{\text{MM}_{\text{FeSO}_4 \cdot 7\text{H}_2\text{O}}}{\text{MM}_{\text{Fe}^{2+}}}}{\frac{\% \text{ of purity}}{100}} \quad (9.3)$$

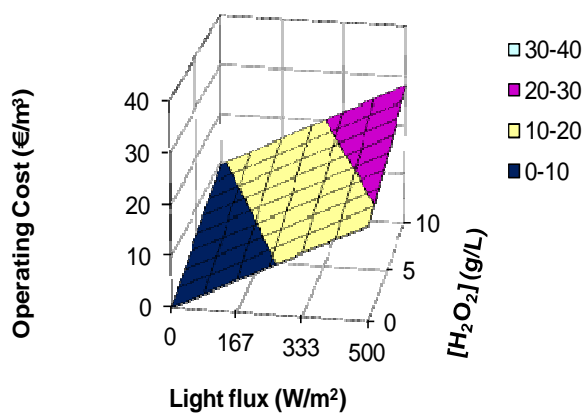
$$\text{Cost}_{\text{energy}} = \frac{\text{Power of lamp} * 10^{-3} \text{ (kW)} * \text{Price energy} \left(\frac{\text{€}}{\text{kWh}} \right) * \text{time}_{\text{reaction}} \text{ (h)}}{\text{Volume}_{\text{treated effluent}} \text{ (m}^3\text{)}} \quad (9.4)$$

Figure 9.4 shows the effect of hydrogen peroxide dose and the radiation intensity in the total operating costs for treating the acrylic (a), cotton (b) and polyester (c) effluents; in each case, the $\text{H}_2\text{O}_2:\text{Fe}^{2+}$ ratio was kept constant, so that changing the oxidant dose implies also a change in the catalyst concentration. As expected, the cost increases with increasing doses of chemicals and power applied. The overall cost is higher for the treatment of acrylic effluent, followed by cotton and the polyester, which is related to the amount of hydrogen peroxide used (the acrylic requires a higher concentration of this reagent and the polyester a lower dose). For this reason, the weight of the chemicals in the overall cost also varies from effluent to effluent, being very relevant in the acrylic one, while in the polyester the radiation intensity is preponderant.

a)



b)



c)

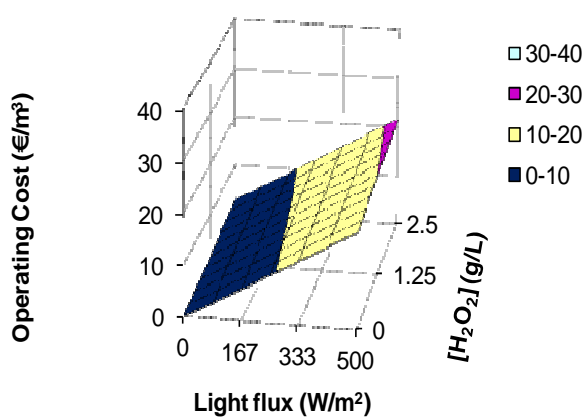


Figure 9.4 – Effect of hydrogen peroxide doses and radiation intensity on the total operating cost associated with the photo-Fenton process with TQ 150 lamp for treating acrylic (a), cotton (b) and polyester (c) wastewaters.

The main purpose of this analysis was to find which set of conditions described in the previous section and that allow reaching a final effluent complying with legislated standards provide a smaller cost. Values obtained for such costs are included in Table 9.1. It can be seen that the conditions providing smaller costs for each effluent but still complying with legislation are the following: i) acrylic – $[H_2O_2] = 10.0$ g/L, intensity = 220 W/m², cost = 17.4 €/m³; ii) cotton – $[H_2O_2] = 10.0$ g/L, intensity = 7 W/m², cost = 9.6 €/m³; iii) polyester – $[H_2O_2] = 2.5$ g/L, intensity = 7 W/m², cost = 2.9 €/m³. For all effluents, but particularly for the acrylic and cotton ones, the treatment costs are quite high. Therefore, with the purpose of minimizing the costs, namely in terms of energy, the work proceeded by testing the photo-Fenton process with simulated solar radiation (for which energy costs are null).

9.3.2 Photoreactor with Simulated Solar Radiation

Tests were carried out as when using lamp TQ 150 with the purpose of not exceeding the maximum allowable values for the treated effluents, with the exception that with the Solarbox it was not possible to decrease the radiation intensity below 253 W/m² (lamp power = 76 W). On the other hand, values above 500 W/m² (lamp power = 150 W) were also not tested. First, to compare with data obtained with TQ lamp, but also to keep at reasonable levels the power corresponding to the radiation intensity close to real conditions (150 W correspond to ~ 60 W/m² at wavelengths in the range 300 - 400 nm, which is only slightly above the typical maximum radiation intensity in the north of Portugal – 50 W/m²).

9.3.2.1 Effect of Hydrogen Peroxide Concentration

Results of color and DOC removals obtained for runs with the Solarbox employing a radiation intensity of 253 W/m² at different dosages of oxidant are shown in Figure 9.5. For both the acrylic and cotton dyeing wastewaters the color removal is very rapid (only 1 - 2 minutes are required for complete decolorization at all doses tested). However, for DOC removal it is necessary more time, and again after ~ 60 minutes the maximum performance is reached, which is not further improved. Better performances are reached

Chapter 9 - Simulated Dyeing Textile Effluents Treatment by the Photo-Fenton Process

for higher H₂O₂ doses: 82.4% for 20 g/L of H₂O₂ in the acrylic; 54.6% for 10 g/L in the cotton, and 66.3% for 2.5 g/L for the polyester.

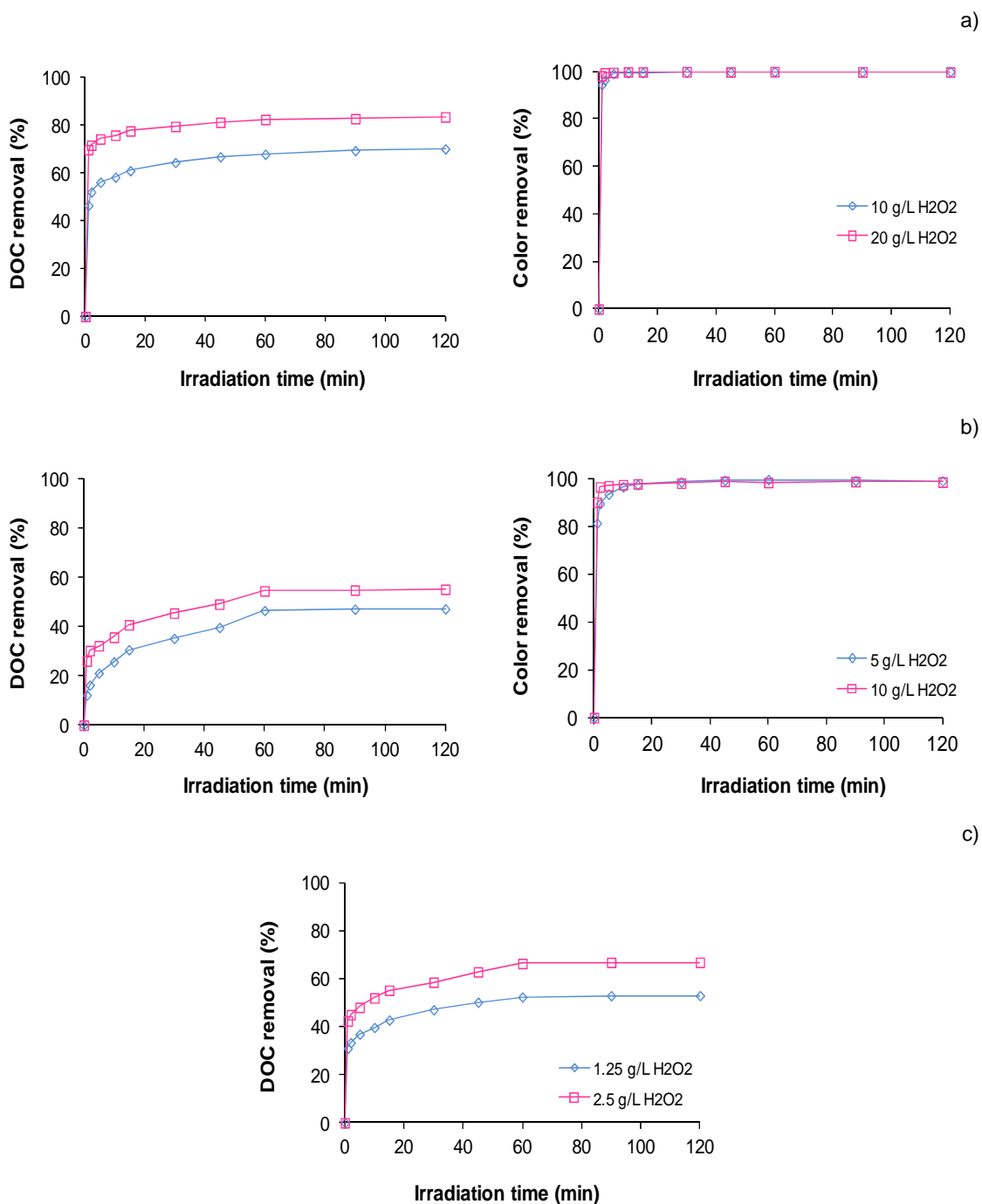


Figure 9.5 – Effect of H₂O₂ dose on DOC and color removal with simulated solar radiation at intensity of 253 W/m² for acrylic (a), cotton (b) and polyester (c) wastewaters (T=50 °C, Fe²⁺:H₂O₂ acrylic =1:57, Fe²⁺:H₂O₂ cotton =1:33 Fe²⁺:H₂O₂ polyester =1:7, pH=3.5).

Again, the final COD, BOD₅ and visible color (after dilution of 1:40) after 60 minutes of reaction were measured for each effluent (see Table 9.2). It is worth noting that in all tests with radiation intensity of 253 W/m² the effluents does not exhibit visible color, and the values of the other two parameters are smaller than the maximum allowable values. So, it is possible to decrease the oxidant dose in each case, possibly requiring however a higher radiation intensity. This does not imply however higher costs, once we are now using solar radiation (although simulated).

Table 9.2 – Values of COD, BOD₅ and visible color (1:40 dilution) after 60 minutes of oxidation for different doses of H₂O₂ and radiation intensities using simulated solar irradiation (in bold: conditions that allow meeting the discharge limits at the minimum cost).

[H ₂ O ₂] (g/L)	Radiation intensity (W/m ²)	COD (mgO ₂ /L)	BOD ₅ (mgO ₂ /L)	Visible color after dilution 1:40	Total Costs (€/m ³)
Acrylic					
6.5	500	232.1	32.4	not visible	5.8
10.0	253	242.0	44.6	not visible	9.2
	500	143.2	33.1	not visible	9.2
20.0	253	150.6	40.8	not visible	18.3
	500	101.2	55.8	not visible	
Cotton					
3.75	500	244.5	76.3	not visible	3.5
5.0	253	207.8	75.0	not visible	4.7
	500	183.4	80.9	not visible	4.7
10.0	253	158.9	79.3	not visible	9.3
	500	134.5	83.5	not visible	9.3
Polyester					
0.938	150	231.0	66.4	not visible	1.0
1.25	76	221.1	74.3	not visible	1.3
	150	206.4	61.4	not visible	1.3
2.5	76	179.4	60.8	not visible	2.7
	150	167.1	57.6	not visible	2.7

The trends reached with the maximum solar radiation intensity of 500 W/m^2 for different hydrogen peroxide doses are nearly the same as before (cf. Figure A.7 in Appendix): color removal is very quick, requiring only 1 to 5 minutes of exposure to radiation to reach values $> 99\%$; removal of DOC is again very fast mainly in the first 15 minutes, and nearly stabilizes after 60 minutes of irradiation; higher performances are reached for increased amount of reagents used. Mineralization achieved was 91.7% for the acrylic effluent using 20 g/L of H_2O_2 ; $\sim 64\%$ for the cotton one with $10 \text{ g H}_2\text{O}_2/\text{L}$ and 71.2% at a dose of $2.5 \text{ g H}_2\text{O}_2/\text{L}$ for the polyester one. As expected, DOC removals are higher at 500 W/m^2 vs. 253 W/m^2 , for the same doses of reagents.

For all effluents and after exposure to irradiation during 60 minutes, the remaining loads of COD, BOD_5 and visible color visible are shown in Table 9.2. Again, in all tests the effluents are colorless, and the values of the other two parameters are still smaller than the legislated standards ($100 \text{ mgO}_2/\text{L}$ for BOD_5 and $250 \text{ mgO}_2/\text{L}$ for COD).

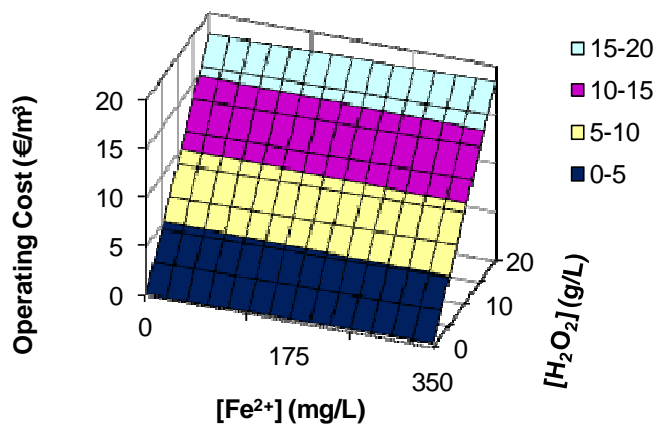
Finally, it is worth mentioning that performances reached (in terms of COD, BOD_5 , DOC and color removal) in the all tests performed with the simulated solar radiation are very close to those obtained with the TQ150 lamp (of course data must be compared for identical conditions, i.e., doses of chemicals and radiation intensity, for every effluent).

9.3.2.2 Operating Costs

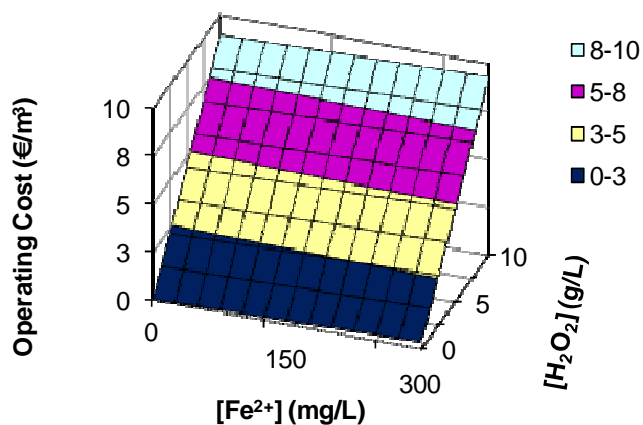
In the treatment of the wastewaters by photo-Fenton oxidation with simulated solar radiation, as stated earlier, for the calculation of the total cost of operation only the consumption of reagents was taken into account (Equations. 9.2 and 9.3), while the energy costs (Equation 9.4) were assumed to be null.

Figure 9.6 shows the effect of hydrogen peroxide and ferrous ion concentrations in the wastewaters treatment cost. Both reactants increase total costs, however this is far more influenced by the H_2O_2 dose. Obviously, for the acrylic higher costs are reached, while the smaller are for the polyester, because of the different ranges of hydrogen peroxide concentrations employed. It is also noteworthy that the costs are much smaller than in the photo-Fenton using the TQ 150 lamp (Figure 9.5), where energy costs were also taken into account.

a)



b)



c)

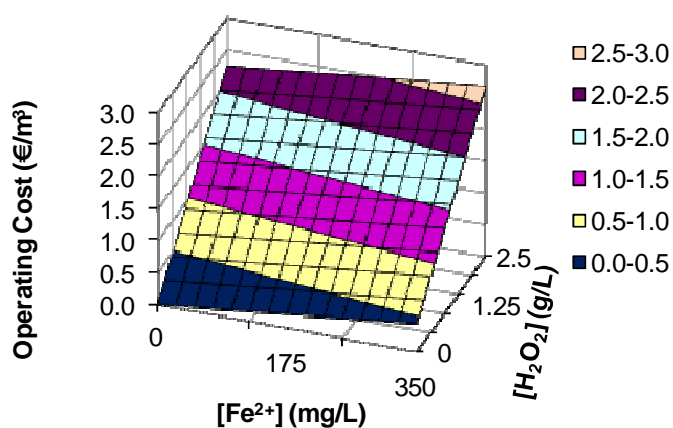


Figure 9.6 – Effect of H₂O₂ and Fe²⁺ doses on the total operating cost associated with the photo-Fenton with simulated solar radiation for treating acrylic (a), cotton (b) and polyester (c) wastewaters.

For the runs described above and reported in Table 9.2, the associated costs were then assessed and included in such a table. As mentioned, all the conditions allowed obtaining an effluent that can be discharged into the environment. Because reduced doses of reagents provided smaller costs, the conditions selected for each effluent are now as follows: i) acrylic – $[\text{H}_2\text{O}_2] = 6.5 \text{ g/L}$, radiation intensity = 500 W/m^2 , cost = 5.8 €/m^3 ; ii) cotton – $[\text{H}_2\text{O}_2] = 3.75 \text{ g/L}$, radiation intensity = 500 W/m^2 , cost = 3.5 €/m^3 ; iii) polyester – $[\text{H}_2\text{O}_2] = 0.938 \text{ g/L}$, radiation intensity = 500 W/m^2 , cost = 1.0 €/m^3 . Consequently, the use of solar radiation allowed decreasing considerably the treatment cost, as compared with the photo-Fenton process under artificial radiation (with lamp TQ 150 – see Table 9.1).

The required doses of H_2O_2 are smaller than when treating the effluents by artificial radiation; however, they are still high, which is justified by the “scavenging” of the hydroxyl radicals by the anions present in wastewaters, as above reported.

9.4 Conclusions

The color and organic compounds removal from acrylic, cotton and polyester dyeing wastewaters was investigated by the photo-Fenton process with artificial radiation and simulated sunlight. It was found that:

- The photo-Fenton process with artificial radiation permits reaching high efficiencies in decolorization and considerable organic compounds removals and to obtain wastewaters with characteristics that can be discharged into bodies of water; however, the operating costs were high (17.4 , 9.6 and 2.9 €/m^3 for acrylic, cotton and polyester effluents, respectively, which is related with the organic load and composition of each one);
- Wastewaters treatment by photo-Fenton assisted by simulated sunlight also allows meeting the discharge limits imposed by the Portuguese legislation, with identical performances as the artificial radiation. However, because in this case energy cost is null, working under high radiation fluxes allows using less amounts of reagents and consequently reduce the costs. Total costs decrease to 5.8 , 3.5 and 1.0 €/m^3 for acrylic, cotton and polyester effluents, respectively (reduction by a factor of ca. 3 in all cases);
- The solar photo-Fenton process under optimized conditions ($[\text{H}_2\text{O}_2] = 6.5 \text{ g/L}$, $[\text{Fe}^{2+}] = 113.8 \text{ mg/L}$ and radiation intensity = 500 W/m^2 for acrylic; $[\text{H}_2\text{O}_2] = 3.75$

g/L, $[\text{Fe}^{2+}] = 112.5 \text{ mg/L}$ and radiation intensity $= 500 \text{ W/m}^2$ for cotton; and $[\text{H}_2\text{O}_2] = 0.938 \text{ g/L}$, $[\text{Fe}^{2+}] = 131.2 \text{ mg/L}$, and radiation intensity $= 500 \text{ W/m}^2$ for polyester) provided always high color removals ($>98-99\%$), considerable COD reductions (72.0, 30.1 and 55.4% for acrylic, cotton and polyester, respectively) and also significant mineralization degrees (71.5, 46.2 and 49.6% for acrylic, cotton and polyester, respectively).

9.5 References

- Arslan-Alaton, I.; Tureli, G.; Olmez-Hanci, T. (2009). Treatment of azo dye production wastewaters using Photo-Fenton-like advanced oxidation process: Optimization by response surface methodology. *Journal of Photochemistry and Photobiology A: Chemistry*, 202, 142-153.
- Ay, F.; Catalkaya, E.C.; Kargi, F. (2009). A statistical experiment design approach for advanced oxidation of Direct Red azo-dye by photo-Fenton treatment. *Journal of Hazardous Materials*. 162, 230-236.
- Devi, L.G.; Kumar, S.G.; Reddy, K.M.; Munikrisnappa, C. (2009). Photo degradation of Methyl Orange an azo dye by advanced Fenton Process using zero valent metallic iron: Influence of various reaction parameters and its degradation mechanism. *Journal of Hazardous Materials*, 164, 459-467.
- Kang, S.-F.; Liao, C.-H.; Po, S.-T. (2000). Decolorization of textile wastewater by photo-Fenton oxidation technology. *Chemosphere*, 41, 1287-1294.
- Lucas, M.S.; Peres, J.A. (2006). Decolourization of the azo dye Reactive Black 5 by Fenton and photo-Fenton oxidation. *Dyes and Pigments*, 71, 236-244.
- Módenes, A.N.; Espinoza-Quiñones, F.R.; Manenti, D.R.; Borba, F.H.; Palácio, S.M.; Colombo A. (2012). Performance evaluation of a photo-Fenton process applied to pollutant removal from textile effluents in a batch system. *Journal of Environmental Management*, 104, 1-8.
- Modirshahla, N.; Behnajady, M.A.; Ghanbary, F. (2007). Decolorization and mineralization of C.I. Acid Yellow 23 by Fenton and photo-Fenton processes. *Dyes and Pigments*, 73, 305-310.
- Muruganandham, M.; Swaminathan, M. (2004). Decolourisation of Reactive Orange 4 by Fenton and photo-Fenton oxidation technology. *Dyes and Pigments*, 63, 315-321.
- Pérez, M.; Torrades, F.; Domènech, X.; Peral J. (2002). Fenton and photo-Fenton oxidation of textile effluents. *Water Research*, 36, 2703-2710.
- Riga, A.; Soutsas, K.; Ntampeglitis, K.; Karayannis, V.; Papapolymerou, G. (2007). Effect of system parameters and of inorganic salts on the decolorization and degradation of Procion H-exl dyes. Comparison of $\text{H}_2\text{O}_2/\text{UV}$, Fenton, UV/Fenton , TiO_2/UV and $\text{TiO}_2/\text{UV}/\text{H}_2\text{O}_2$ processes. *Desalination*, 211, 72-86.

Chapter 9 - Simulated Dyeing Textile Effluents Treatment by the Photo-Fenton Process

Rodriguez, M.; Sarria, V., Esplugas, S; Pulgarin, C. (2002). Photo-Fenton treatment of a biorecalcitrant wastewater generated in textile activities: biodegradability of the photo-treated solution. *Journal of Photochemistry and Photobiology A: Chemistry*, 151, 129-135.

Torrades, F.; García-Montaña, J.; García-Hortal, J.A.; Domènech, X.; Peral, J. (2004). Decolourization and mineralization of commercial reactive dyes under solar light assisted photo-Fenton conditions. *Solar Energy*, 77, 573-581.

Chapter 10

Simulated Textile Dyeing Effluents Treatment by SBR alone and Combined with Fenton's Oxidation*

* This Chapter is based on the publication "Rodrigues C.S.D.; Madeira, L.M.; Boaventura, R.A.R. Textile Dyeing Wastewater Treatment by Integration of Advanced Oxidation and Biological Processes - Performance Analysis with Costs Reduction". Submitted.

10 Simulated Textile Dyeing Effluents Treatment by SBR alone and Combined with Fenton's Oxidation

10.1 Introduction

In this work, a treatability study of simulated acrylic, cotton and polyester dyeing effluents (representing typical dyeing industrial wastewaters) was done, either using an SBR or an integrated process combining the Fenton's reaction with an SBR process. The main purpose of this research was to evaluate the possibility of reducing the chemicals consumption in the Fenton's reaction to make the pre-treated effluents able to be fed to a subsequent biological treatment, while obtaining final effluents that accomplish the maximum allowable limits imposed by legislation for discharge into the aquatic environment, at a lower operating cost. So, an economic analysis was also performed, since it is very important to maximize wastewater treatment efficiency while reducing running costs. Up to the author's knowledge, none scientific report in this area has addressed a similar approach, i.e., maximizing treatment efficiency while simultaneously minimizing operating costs.

10.2 Materials and Methods

10.2.1 Preparation of the Simulated Textile Effluents

The simulated textile dyeing effluents were prepared according to the information given in section 3.2 of chapter 3.

10.2.2 Experimental Procedure

The Fenton's reaction experiments were carried out in accordance with the procedure described in section 3.4.2 of chapter 3. The SBR experiments were performed as detailed in section 3.4.4.

10.2.3 Analytical Methods

The analytical methods used for the determination of the various parameters are described in section 3.3 of chapter 3.

All determinations were performed in duplicate and the coefficients of variation were less than to 2% for DOC, 8% for BOD₅, 4% for COD and SOUR, 3% for inhibition of *V. fisheri* and 5% for the other parameters.

10.3 Results and Discussion

The more relevant characteristics of the synthetic acrylic, cotton and polyester dyeing wastewaters used in this study are reported in Table 3.4. Cotton and acrylic wastewaters are colored even at 1:40 dilution but polyester effluent is practically colorless. The organic load (expressed as COD or DOC) is moderate for all wastewaters but the biodegradability is low as indicated by the BOD₅:COD ratio and the values of SOUR; actually, the acrylic wastewater can be classified as non biodegradable and the other wastewaters can be considered as only slightly biodegradable. Acrylic and polyester effluents strongly inhibit *V. fisheri* activity, which proves their toxicity. Taking into account the low biodegradability and the high toxicity (except for the cotton wastewater), a biological treatment of these wastewaters does not probably allow meeting the discharge limits, as established by the Portuguese legislation (cf. Table 3.4). Even so, the feasibility of using a biological process (SBR) alone or downstream from a chemical oxidation process (Fenton's reaction) to achieve the discharge limits was investigated in this study.

The results obtained when applying this strategy for treating the three different kinds of textile dyeing wastewaters are shown in the next sections.

10.3.1 Biological Treatment

The biological degradation was only applied to raw polyester and cotton effluents because the acrylic one presents very low biodegradability (BOD₅/COD ratio <0.0012 and SOUR

<0.2 – Table 3.4), also confirmed by the Zahn Wellens test (see Figure 10.1), which indicated that the degradation obtained after 28 days does not exceed 15%.

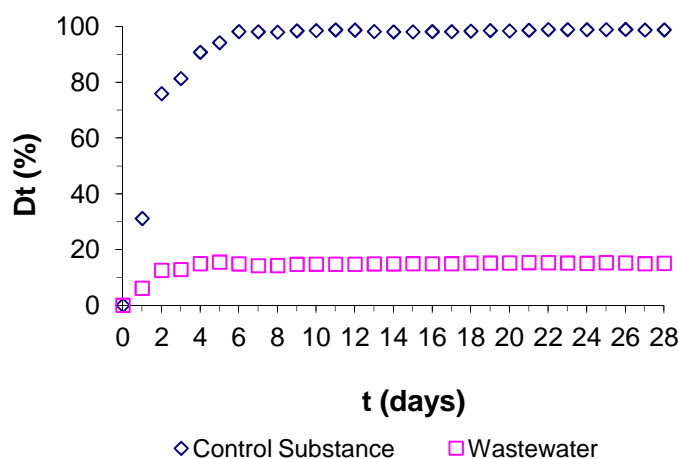


Figure 10.1 – Evolution of percentage of COD degradation along time in Zahn-Wellens test for acrylic wastewater.

Figure 10.2 shows the COD, BOD₅, DOC, total nitrogen and color removals obtained in 10 successive cycles of SBR treatment of polyester and cotton effluents; no further cycles were applied because nearly steady-state conditions were reached in all cases, i.e., stable performances in consecutive cycles. The polyester effluent exhibits a considerable increase of COD, BOD₅, DOC and total nitrogen removal during the first 5 cycles that continue to increase, albeit more slowly, up to the 7th cycle, and then remain almost constant with average values of 24.2, 39.4, 39.7 and 16.4% for COD, BOD₅, DOC and nitrogen, respectively. For the cotton effluent the removals also increase during the first 5 cycles and then the removal rate decreases or maintains constant leading to average final values of 19.9, 19.6, 19.9 and 20.5% for COD, BOD₅, DOC and nitrogen, respectively. The low efficiencies achieved can be explained by the presence in the effluents of a significant proportion of refractory or only slightly biodegradable compounds, as could be inferred from the low BOD₅/COD ratios and SOUR values, particularly for the cotton one (cf. Table 3.4). As regards color removal, in the cotton wastewater the values of absorbance at 520 nm decreased in the first 4 cycles and kept constant in the subsequently cycles, achieving an average value of 50.6% of decolorization. The removal may be the result of some biological degradation of the textile dyes present in the effluent

Chapter 10 - Simulated Textile Dyeing Effluents Treatment by SBR alone and Combined with Fenton's Oxidation

but the adsorption onto the biomass flocs probably also contributes for color elimination [Waters, 1995]. The color removal obtained for cotton wastewater is similar to that reported by Vaigan et al. [2009]. These authors achieved color removals of 31-57% when treating 20 to 40 mg/L of reactive Blue B-16, respectively, in an SBR.

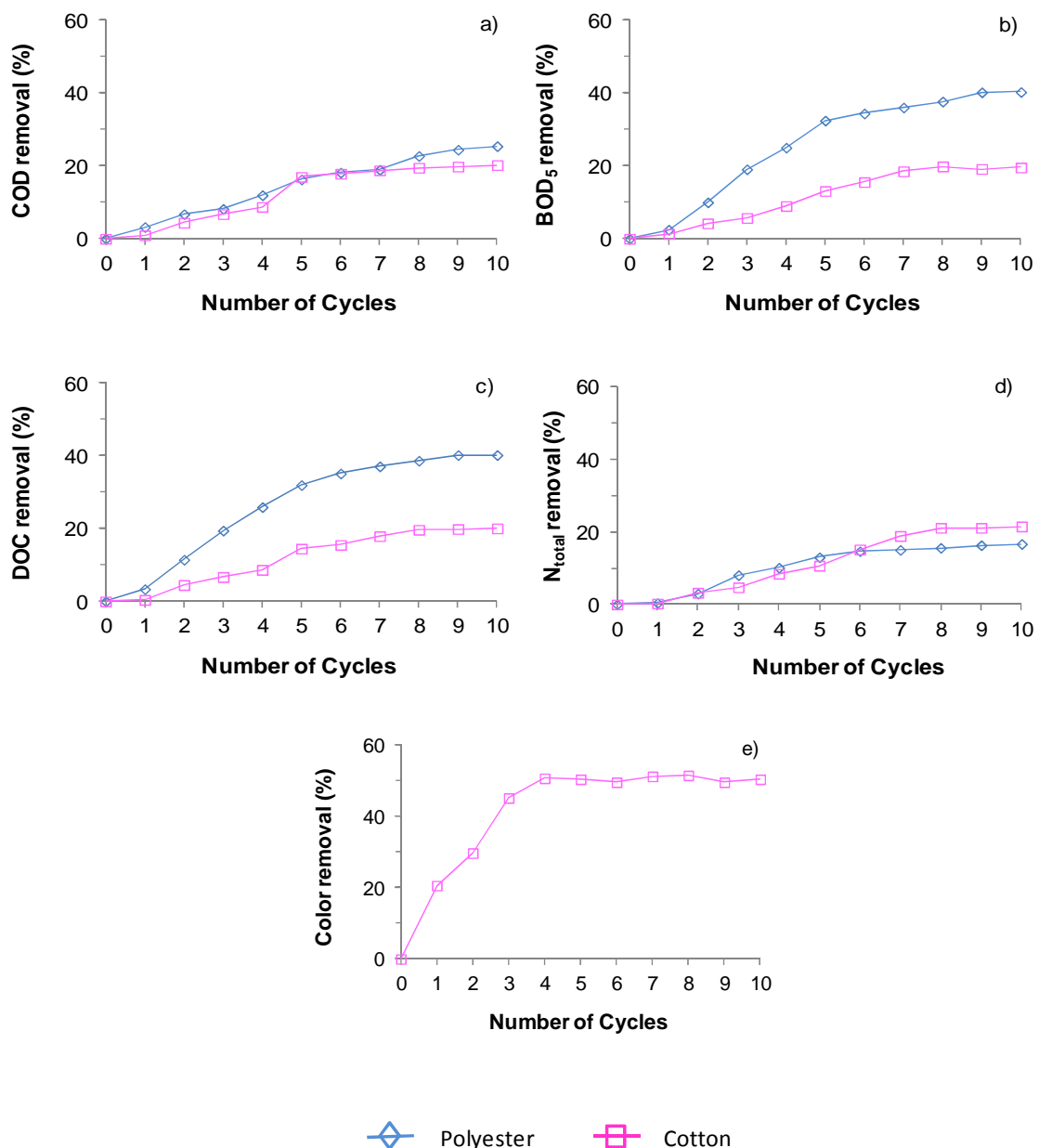


Figure 10.2 - Variation of COD (a), BOD₅ (b), DOC (c), total nitrogen (d) and color (e) removals along 10 cycles of SBR operation for polyester and cotton wastewaters.

With regard to other monitored parameters, whose values are not presented in Figure 10.2, it was noted that during all SBR cycles the concentrations in the treated effluents were in the range 2.4 - 2.9 mg P/L, 22 – 29 mg TSS/L and 2530-2970 mg VSS/L for the polyester effluent and 5.7 - 5.9 mg P/L, 27 - 32 mg TSS/L and 2350-2680 mg VSS/L for the cotton one.

The pseudo-steady state was reached after ca. 7 cycles for both cotton and polyester effluents. Table 10.1 presents the average values of different parameters after reaching the pseudo-steady state. It can be concluded that the effluents resulting from biological treatment do not meet the discharge limits, since the values of COD (392.4 and 280.4 mg/L for polyester and cotton, respectively) are above 250 mg/L and the color of the cotton effluent is visible after 1:40 dilution. So, a pre-treatment or subsequent treatment is required. We choose to apply the chemical oxidation by Fenton's reagent as pre-treatment to enhance the biodegradability and remove color and, then, subject the wastewater to biological treatment. The results obtained from the combined process are presented in the following section.

Chapter 10 - Simulated Textile Dyeing Effluents Treatment by SBR alone and Combined with Fenton's Oxidation

Table 10.1 – Characteristics of the simulated dyeing raw wastewaters and after SBR treatment and respective removal efficiencies.

Parameter	Acrylic	Polyester			Cotton			Maximum Allowable Value*
	Raw Wastewater	Raw Wastewater	After SBR	Removal (%)	Raw Wastewater	After SBR	Removal (%)	
pH	6.8	8.3	7.10	---	11.4	7.15	---	5.5-9.0
Conductivity at 20 °C (mS/cm)	1503.0	2.9	n.d.	---	23.2	n.d.	---	
Total suspended solids (mg/L)	16.0	21.7	25.1		67.0	28.3		
Total nitrogen (mg N/L)	16.4	15.9	13.3	16.4	3.9	3.1	20.5	
Nitrates (mg NO ₃ ⁻ /L)	15.7	7.5	n.d.	---	4.25	n.d.	---	
Total phosphorus (mg P/L)	0.2	3.0	2.4	20.0	5.9	5.7	3.4	
Dissolved phosphorus (mg P/L)	< 0.06	2.7	n.d.	---	0.1	n.d.	---	
COD – Chemical oxygen demand (mg O ₂ /L)	828.1	517.9	392.4	24.2	350.0	280.4	19.9	250
BOD ₅ – Biochemical oxygen demand (mg O ₂ /L)	< 1.0	130.7	79.1	39.4	77.5	62.3	19.6	100
DOC – Dissolved organic carbon (mg C/L)	334.1	143.1	86.3	39.7	117.5	94.1	19.9	
Sulfates (mg/L)	598.0	885.8	n.d.	---	41.0	n.d.	---	
Chlorides (mg Cl ⁻ /L)	44.1	17.3	n.d.	---	7981.8	n.d.	---	
Alkalinity (mg CaCO ₃ /L)	51.8	774.4	n.d.	---	4425.0	n.d.	---	
SOUR – Specific oxygen uptake rate (mg O ₂ /(g _{VSS} .h))	< 0.2	27.0	n.d.	---	5.6	n.d.	---	
BOD ₅ :COD ratio	< 0.0012	0.26	0.20	---	0.22	0.22	---	
Maximum absorbance wavelength, λ _{max} (nm)	610	---	n.d.	---	520	n.d.		
Absorbance at λ _{max} (a.u.)	1.592	---	n.d.	---	0.437	0.179	50.6**	
Visible color after dilution 1:40	Visible	not visible	not visible	---	Visible	visible	---	not visible
<i>Vibrio fischeri</i> Inhibition 5 min (%)	94.0	74.5	n.d.	---	0.0	n.d.	---	
<i>Vibrio fischeri</i> Inhibition 15 min (%)	96.0	82.5	n.d.	---	0.0	n.d.	---	
<i>Vibrio fischeri</i> Inhibition 30 min (%)	97.0	84.5	n.d.	---	0.0	n.d.	---	

n.d. – not determined

* Portuguese legislation for discharge of textile wastewaters (Ordinance No. 423/97 of 25 June).

** calculated from the absorbance of raw wastewater at pH 7.0 (0.3617 abs. units)

10.3.2 Integration of Fenton's Reagent Followed by Biological Treatment

As the oxidation process allows increasing the biodegradability of the acrylic and cotton effluents while reducing the toxicity of the acrylic and polyester effluents, as shown below (cf. Tables 10.2-10.4), the combination of Fenton reaction with the biological oxidation in SBR was studied. Aiming reducing the doses of chemicals, and inherently the operating costs (described in the following section), three experiments were performed, i.e., the preliminary Fenton reaction stage was performed with different doses of reagents. The 1st run was performed at the best conditions for maximizing color and DOC removals and improving biodegradability already determined in previous studies (chapters 6-8): $[\text{H}_2\text{O}_2]=20$ g/L and $[\text{Fe}^{2+}]=350$ mg/L for acrylic, $[\text{H}_2\text{O}_2]=10$ g/L and $[\text{Fe}^{2+}]=300$ mg/L for cotton and $[\text{H}_2\text{O}_2]=2.5$ g/L and $[\text{Fe}^{2+}]=350$ mg/L for polyester wastewaters, all at pH 3.5 and 50 °C. In runs #2 and #3 the doses of hydrogen peroxide and ferrous iron were reduced to 3/4 and 1/2 for acrylic and 1/2 and 1/4 for polyester and cotton effluents, respectively, with the aim of decreasing the treatment cost (associated with the consumption of chemicals in the Fenton's process) while obtaining a final effluent that should meet the discharge limits imposed by the national legislation for the textile industry. Results obtained during Fenton's oxidation have been reported previously (in the works mentioned above) and only overall performances reached are described herein – run #1 in Tables 10.2, 10.3 and 10.4 for the acrylic, cotton and polyester effluents, respectively.

Chapter 10 - Simulated Textile Dyeing Effluents Treatment by SBR alone and Combined with Fenton's Oxidation

Table 10.2 – Characteristics of the synthetic acrylic dyeing wastewaters after Fenton reaction and SBR and respective removal efficiencies (within brackets) and global removals. Runs#1 to #3 represent experiments with decreasing doses of chemicals in the Fenton's stage.

Parameter	Run #1 – Optimal dose of chemicals			Run #2 – 0.75 of optimal dose of chemicals			Run #3 – 0.5 of optimal dose of chemicals			Maximum Allowable Value*
	Fenton (removal (%))	SBR (removal (%))	Global Removal (%)	Fenton (removal (%))	SBR (removal (%))	Global Removal (%)	Fenton (removal (%))	SBR (removal (%))	Global Removal (%)	
pH	7.10	7.15	---	7.06	7.09	---	7.01	6.98	---	5.5-9.0
Total nitrogen (mg N/L)	16.0 (2.4)	8.8 (45.0)	46.3	16.1 (2.4)	9.3 (41.9)	43.3	16.3 (2.4)	12.4 (22.5)	24.4	
Total phosphorus (mg P/L)	0.2 (0.0)	0.61 (47.9**)	47.9	0.2 (0.0)	0.20 (74.7**)	74.7	0.2 (0.0)	0.16 (68.0**)	68.0	
COD (mg O ₂ /L)	289.0 (65.1)	14.6 (94.9)	98.2	294.5 (64.4)	104.3 (64.6)	87.4	349.7 (57.7)	273.7 (21.8)	66.9	250
BOD ₅ (mg O ₂ /L)	116.5	6.4 (94.5)	94.5	78.8	12.0 (84.8)	84.8	46.8	14.5 (69.0)	69.0	100
DOC (mg C/L)	112.0 (66.5)	5.4 (95.2)	98.4	124.7 (62.7)	34.5 (72.3)	89.7	132.3 (60.4)	109.3 (17.4)	67.3	
SOUR – Specific oxygen uptake rate (mg O ₂ /(g _{VSS} .h))	17.9	n.d.	---	10.2	n.d.	---	2.7	n.d.	---	
BOD ₅ :COD ratio	0.40	0.46	---	0.27	0.12	---	0.13	0.05	---	
Absorbance at λ _{max} (a.u.)	0.0079 (99.5****)	0.0025 (68.4****)	99.8	0.0080 (99.5****)	0.0025 (68.8****)	99.8	0.0089 (99.4****)	0.0025(71.9***)	99.8	
Visible color after dilution 1:40	not visible	not visible	---	not visible	not visible	---	not visible	not visible	---	not visible
<i>Vibrio fischeri</i> Inhibition 5 min (%)	29	n.d.	---	38	n.d.	---	77	n.d.	---	
<i>Vibrio fischeri</i> Inhibition 15 min (%)	27	n.d.	---	41	n.d.	---	81	n.d.	---	
<i>Vibrio fischeri</i> Inhibition 30 min (%)	29	n.d.	---	41	n.d.	---	82	n.d.	---	

n.d. – not determined.

* Portuguese legislation for discharge of textile wastewaters (Ordinance No. 423/97 of 25 June).

** calculated from total phosphorus in effluent after Fenton reaction after adding phosphate buffer (1.17, 0.79, 0.5 mg P/L in run #1, #2, #3, respectively).

*** calculated from the absorbance at 610 nm of raw wastewater at pH 3.5 (1.624 abs. units).

**** calculated from the absorbance at 610 nm of wastewater after Fenton at pH 7.0 (0.0079, 0.0080 and 0.0089 abs. units in run #1, #2 and #3, respectively).

Table 10.3 – Characteristics of the synthetic cotton dyeing wastewater after Fenton reaction and SBR and respective removal efficiencies (within brackets) and global removals. Runs#1 to #3 represent experiments with decreasing doses of chemicals in the Fenton's stage.

Parameter	Run #1– Optimal dose of chemicals			Run #2 – 0.5 of optimal dose of chemicals			Run #3 – 0.25 of optimal dose of chemicals			Maximum Allowable Value*
	Fenton (removal (%))	SBR (removal (%))	Global Removal (%)	Fenton (removal (%))	SBR (removal (%))	Global Removal (%)	Fenton (removal (%))	SBR (removal (%))	Global Removal (%)	
pH	6.99	7.05	---	7.04	7.10	---	7.09	7.03	---	5.5-9.0
Total nitrogen (mg N/L)	3.9 (0.0)	1.2 (82.4)	82.4	3.9 (0.0)	2.1 (62.5)	62.5	3.8 (2.6)	3.7 (15.9)	18.1	
Total phosphorus (mg P/L)	5.9 (0.0)	4.8 (18.6)	18.6	5.9 (0.0)	5.2 (11.9)	11.9	5.8 (1.7)	5.6 (3.4)	5.1	
COD (mg O ₂ /L)	262.1 (25.1)	43.2 (83.5)	87.7	281.9 (19.5)	113.2 (59.8)	67.7	318.6 (9.0)	261.8 (17.8)	25.2	250
BOD ₅ (mg O ₂ /L)	135.7 (0.0)	22.8 (83.2)	83.2	112.9 (0.0)	45.1 (60.1)	60.1	88.0 (0.0)	72.3 (17.8)	17.8	100
DOC (mg C/L)	60.2 (48.8)	9.95 (83.5)	91.5	94.1 (19.9)	37.6 (60.0)	68.0	100.3 (14.6)	82.0 (18.2)	30.2	
SOUR – Specific oxygen uptake rate (mg O ₂ /(g _{VSS} .h))	15.51	n.d.	---	8.11	n.d.	---	2.54	n.d.	---	
BOD ₅ :COD ratio	0.52	0.53	---	0.40	0.40	---	0.33	0.28	---	
Absorbance at λ _{max} (a.u.)	0.0331 (89.9***)	0.0037 (86.6****)	98.6	0.0310 (90.5***)	0.0053 (81.9****)	98.3	0.0349 (89.3***)	0.0126 (65.8****)	96.3	
Visible color after dilution 1:40	not visible	not visible	---	not visible	not visible	---	not visible	not visible	---	not visible
<i>Vibrio fischeri</i> Inhibition 5 min (%)	0.0	n.d.	---	0.0	n.d.	---	0.0	n.d.	---	
<i>Vibrio fischeri</i> Inhibition 15 min (%)	0.0	n.d.	---	0.0	n.d.	---	0.0	n.d.	---	
<i>Vibrio fischeri</i> Inhibition 30 min (%)	0.0	n.d.	---	0.0	n.d.	---	0.0	n.d.	---	

n.d. – not determined.

* Portuguese legislation for discharge of textile wastewaters (Ordinance No. 423/97 of 25 June).

** calculated from total phosphorus in effluent after Fenton reaction after adding urea (6.8, 5.6, 4.4 mg N/L in run #1, #2, #3, respectively).

*** calculated from the absorbance at 520 nm of raw wastewater at pH 3.5 (0.3615 abs. units).

**** calculated from the absorbance at 520 nm of wastewater after Fenton at pH 7.0 (0.0276, 0.0293 and 0.0368 abs. units in run #1, #2 and #3, respectively).

Chapter 10 - Simulated Textile Dyeing Effluents Treatment by SBR alone and Combined with Fenton's Oxidation

Table 10.4 – Characteristics of the synthetic polyester dyeing wastewaters after Fenton reaction and SBR and respective removal efficiencies (within brackets), and global removals. Runs#1 to #3 represent experiments with decreasing doses of chemicals in the Fenton's stage.

Parameter	Run #1 – Optimal dose of chemicals			Run #2 – 0.5 of optimal dose of chemicals			Run #3– 0.25 of optimal dose of chemicals			Maximum Allowable Value*
	Fenton (removal (%))	SBR (removal (%))	Global Removal (%)	Fenton (removal (%))	SBR (removal (%))	Global Removal (%)	Fenton (removal (%))	SBR (removal (%))	Global Removal (%)	
pH	7.05	7.10	---	7.11	7.08	---	7.15	7.10	---	5.5-9.0
Total nitrogen (mg N/L)	15.1 (5.0)	12.3 (18.5)	22.6	15.3 (3.8)	12.4 (19.0)	22.0	15.9 (0.0)	13.3 (16.4)	16.4	
Total phosphorus (mg P/L)	2.8 (6.7)	2.2 (20.0)	25.3	2.9 (3.3)	2.2 (22.8)	25.3	3.0 (0.0)	2.4 (20.3)	20.3	
COD (mg O ₂ /L)	221.1 (57.3)	44.4 (79.9)	91.4	291.7 (43.7)	104.3 (64.2)	79.9	389.7 (24.7)	267.7 (31.3)	48.3	250
BOD ₅ (mg O ₂ /L)	62.8 (52.0)	11.4 (81.8)	91.3	80.2 (38.6)	29.4 (63.4)	77.5	103.8 (20.6)	54.3 (47.7)	58.5	100
DOC (mg C/L)	63.4 (55.7)	12.6 (80.1)	91.2	80.6 (43.7)	27.7 (65.6)	80.6	106.9 (25.3)	58.1 (45.7)	59.4	
SOUR – Specific oxygen uptake rate (mg O ₂ /(g _{VSS} .h))	30.0	n.d.	---	29.0	n.d.	---	28.1	n.d.	---	
BOD ₅ :COD ratio	0.28	0.26	---	0.28	0.28	---	0.27	0.20	---	
Visible color after dilution 1:40	not visible	not visible	---	not visible	not visible	---	not visible	not visible	---	not visible
<i>Vibrio fischeri</i> Inhibition 5 min (%)	0.0	n.d.	---	10.4	n.d.	---	43.3	n.d.	---	
<i>Vibrio fischeri</i> Inhibition 15 min (%)	0.0	n.d.	---	15.0	n.d.	---	55.8	n.d.	---	
<i>Vibrio fischeri</i> Inhibition 30 min (%)	0.0	n.d.	---	17.6	n.d.	---	59.4	n.d.	---	

n.d. – not determined.

* Portuguese legislation for discharge of textile wastewaters (Ordinance No. 423/97 of 25 June).

Regarding the results obtained in the SBR, Figure 10.3 shows the removal performances achieved, in terms of COD, BOD₅, DOC, total nitrogen and color, for the acrylic wastewater. It can be observed that removals increased during the first 4 cycles, although the improvement is more notorious in the 1st and 2nd runs; therefore, we can say that the pseudo-steady state was reached at end of 4-5 cycles. After reaching the pseudo-steady state, the average removals achieved in the SBR for the parameters analyzed are higher in run #1 (94.9, 94.5, 95.2, 45.0 and 68.4% for COD, BOD₅, DOC, total nitrogen and color, respectively), followed by run #2 (64.6, 84.8, 72.3, 41.9 and 68.8% for COD, BOD₅, DOC, total nitrogen and color, respectively) and then by run #3 (21.8, 69.0, 17.4, 22.5 and 71.9% for COD, BOD₅, DOC, total nitrogen and color, respectively). The reason is that from run #1 to run #3 less chemicals were used in the Fenton's stage, so that the effluent fed to the SBR is less biodegradable (cf. Table 10.2). In runs #1 and #2 it was possible to reach, after the integrated treatment, an effluent that is ready for discharge into water bodies – see Table 10.2. On the other hand, although in run #3 less chemicals were employed in the Fenton's stage as compared to run #2, it was not possible to fulfill the limits imposed by the national legislation for the discharge of textile effluents, namely in terms of COD (cf. Table 10.2).

The removals obtained during 10 cycles of SBR for the cotton effluent previously treated by Fenton's oxidation are shown in Figure 10.3. During the first 6 cycles an increase was observed for all runs, and then the removals remain nearly constant, which means that the pseudo-steady state was reached. In runs #1 and #2 the average values of COD, BOD₅ and visible color (after dilution of 1:40) at the outlet of the SBR, during the last 4 cycles of operation, are smaller than the maximum allowable discharge values (see Table 10.3). This is however not the case of run #3, in which very low doses of chemicals were used in the Fenton's oxidation (25% of those employed in run #1); thus, final effluent shows COD values not complying with the legislated standard.

Chapter 10 - Simulated Textile Dyeing Effluents Treatment by SBR alone and Combined with Fenton's Oxidation

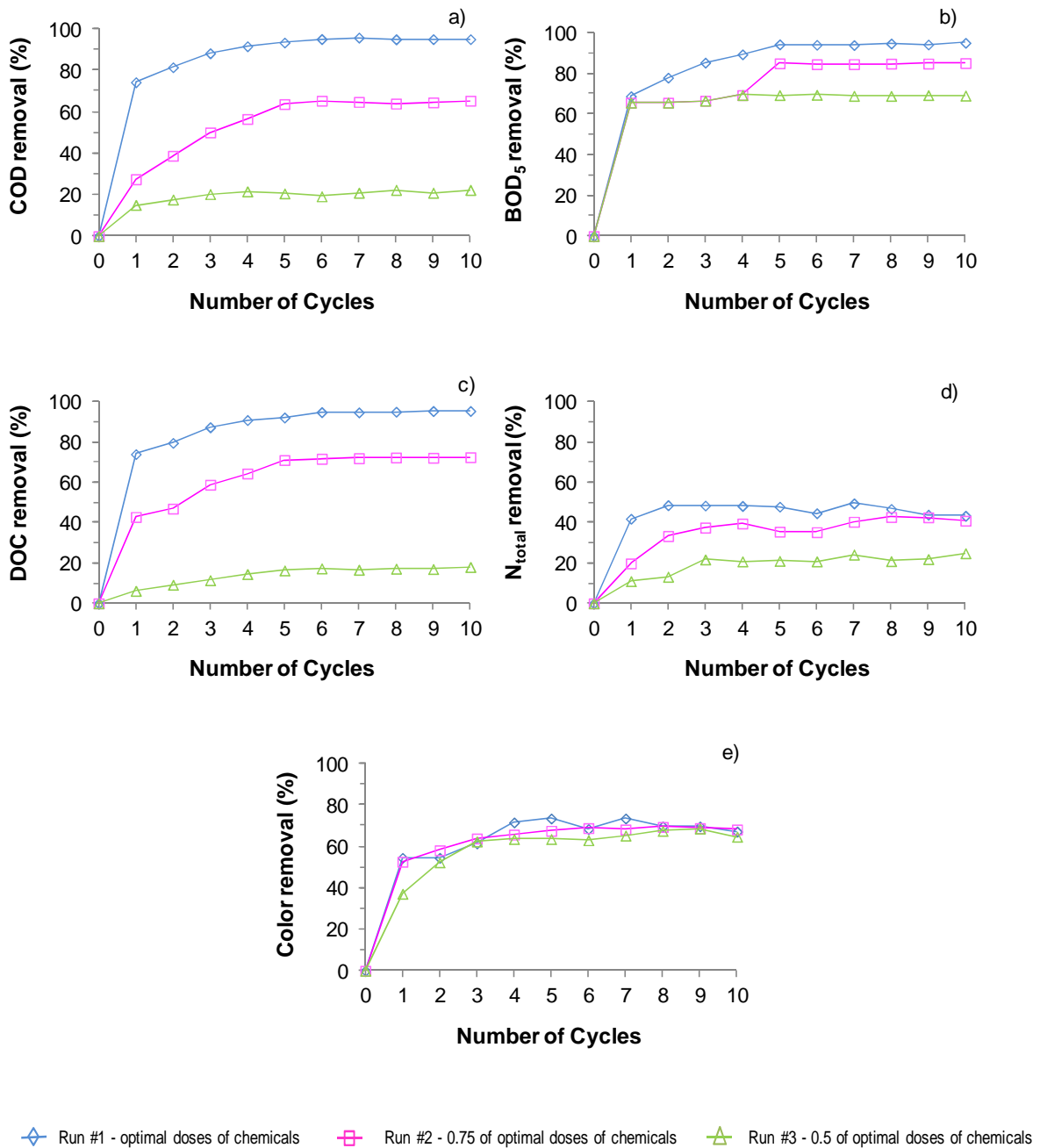


Figure 10.3 - Variation of COD (a), BOD₅ (b), DOC (c), total nitrogen (d) and color (e) removals during 10 cycles of SBR operation for acrylic effluent, previously treated by Fenton's oxidation. Runs #1 to #3 represent experiments with decreasing doses of chemicals in the Fenton's stage.

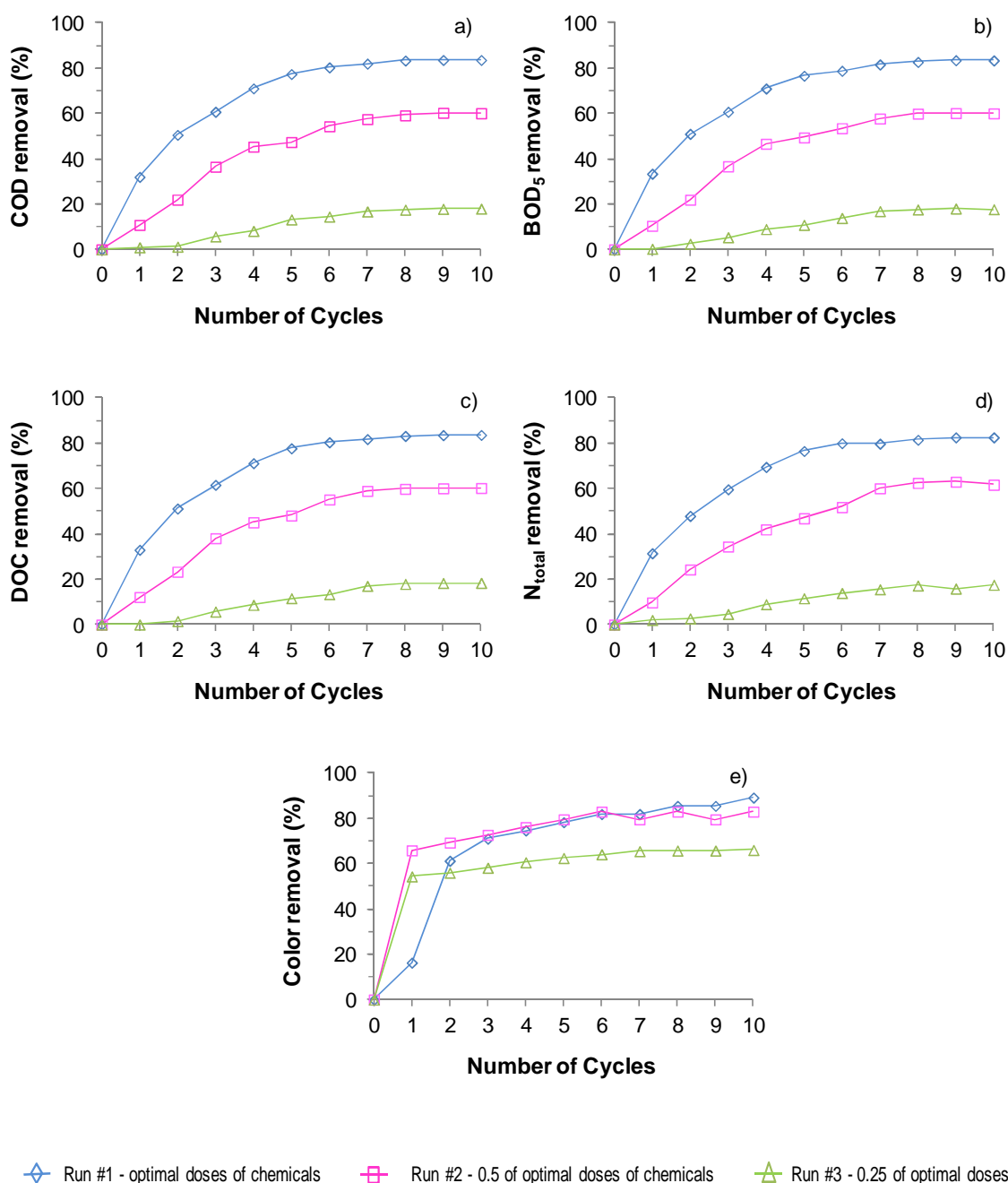


Figure 10.4 - Variation of COD (a), BOD₅ (b), DOC (c), total nitrogen (d) and color (e) removals during 10 cycles of SBR operation for synthetic cotton dyeing effluent, previously treated by Fenton's reaction. Runs#1 to #3 represent experiments with decreasing doses of chemicals in the Fenton's stage.

As far as concerns the polyester dyeing wastewater biological treatment, 6-7 cycles are needed for reaching the pseudo-steady state (cf. Figure 10.5), after Fenton's oxidation.

Chapter 10 - Simulated Textile Dyeing Effluents Treatment by SBR alone and Combined with Fenton's Oxidation

The average removal values achieved after 7 cycles are higher in the 1st run (79.9, 81.8, 80.1 and 18.5% for COD, BOD₅, DOC and total nitrogen, respectively), followed by the 2nd one (64.2, 63.4, 65.6 and 19.0% for COD, BOD₅, DOC and total nitrogen, respectively) and then by 3rd one (31.3, 47.7, 45.7 and 16.4% for COD, BOD₅, DOC and total nitrogen, respectively); this is the order of decreased doses of chemicals in the previous chemical oxidation process. Again, the wastewater resulting from the SBR operating in the conditions used in runs #1 and #2 can be discharged into water bodies, because the values of the legislated parameters are smaller than the discharge limits for the textile industry (see Table 10.4).

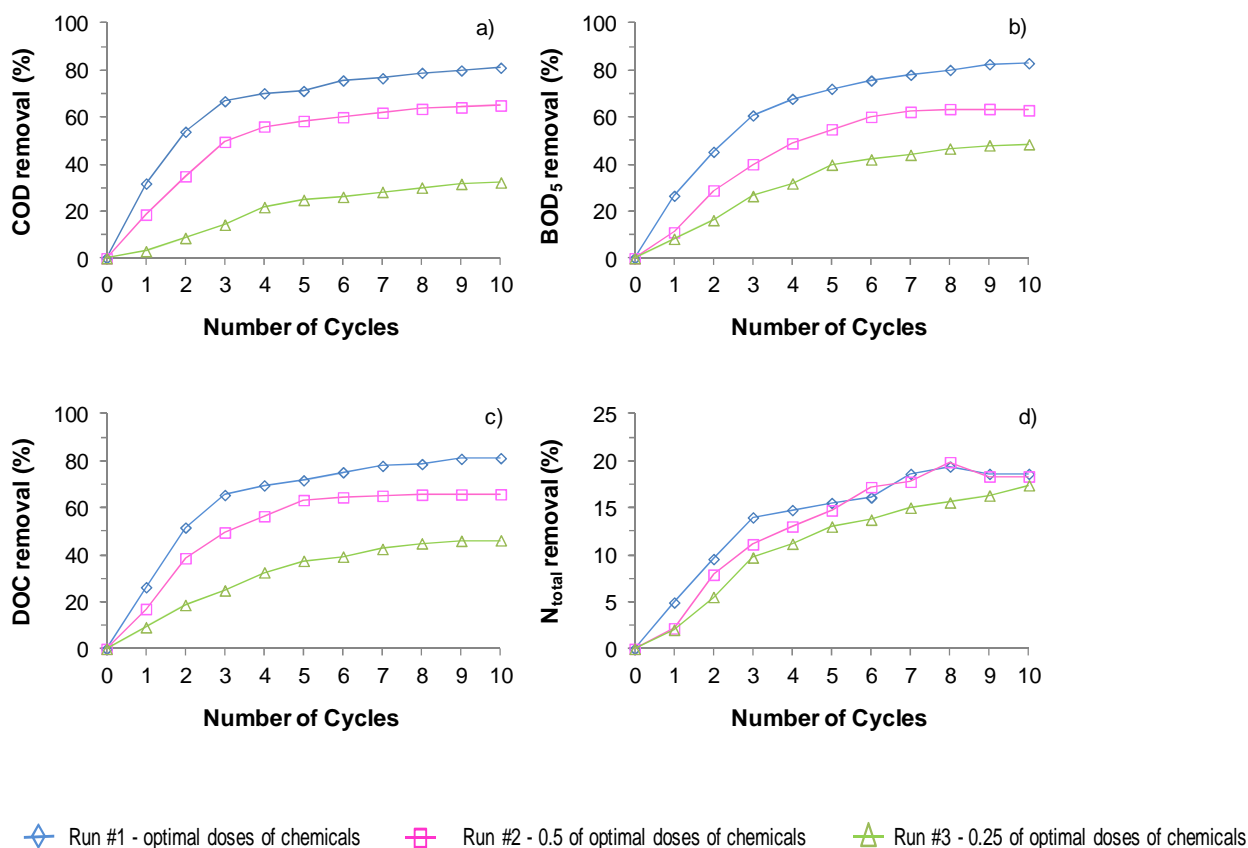


Figure 10.5 - Evolution of COD (a), BOD₅ (b), DOC (c) and total nitrogen (d) removals during 10 cycles of SBR operation for polyester dyeing wastewater, previously treated by Fenton's reaction. Runs #1 to #3 represent experiments with decreasing doses of chemicals in the Fenton's stage.

The high overall COD and color removal efficiencies obtained in run#1, for the three effluents, are very similar to those reported by Tantak and Chaudhari [2006] (> 95% for color vs. > 98% in our work, and in the range 77.8-85.6% for COD vs. 87.7-98.2% in our work); such authors treated by Fenton's oxidation and SBR aqueous solutions of textile dyes (Reactive Black 5, Reactive Blue 13 and Acid Orange 7).

10.3.3 Costs Evaluation

In this study, we considered only the costs with the chemicals, i.e., the costs of reagents obtained from Quimitecnica S.A. (Portugal), used in the Fenton's stage, and the energy consumed in agitation (power required = 0.61 W) and air insufflated (power = 4.5 W) in the SBR stage. The average values considered were as follows: H₂O₂ (49.5% w/v, density at 25 °C = 1.2 g/cm³ - 365 €/ton; FeSO₄·7H₂O (93 % of purity) – 233.7 €/ton, energy - 0.10 €/(kW h)). The prices of acid (H₂SO₄) and base (NaOH) were not considered, because the quantities consumed are insignificant.

Figure 10.6 shows the total operating cost of the Fenton's oxidation alone, biological treatment and the combination of both techniques, considering the conditions of runs #1, #2 and #3 mentioned above. The inclusion of a pre-treatment (Fenton's reaction) led to a significant increase in the operating costs (1.9 – 3.9 and 3.5-10.4 €/m³ in the combination Fenton+SBR for polyester and cotton, respectively, compared with 1.2 €/m³ in SBR alone). However, the biological treatment directly applied to the effluents does not allow meeting the discharge limits. As could be expected, in the integrated process (chemical and biological oxidation), the costs raised when increasing the doses of the reagents used in the Fenton stage (higher in run #1, for all effluents).

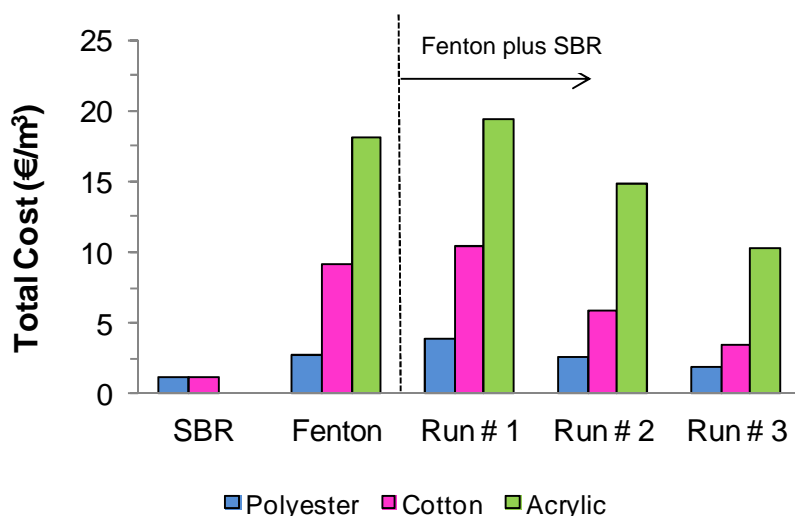


Figure 10.6 - Total operating costs for biological, Fenton alone and integrated treatment of acrylic, cotton and polyester dyeing wastewaters.

Since the objective of this study was to obtain an effluent complying with the discharge limits after treatment (runs #1 and #2 for the acrylic, cotton and polyester effluents) at the lowest treatment cost, the selected operating conditions were those of run# 2 for acrylic (total cost of 14.8 €/m³), cotton (5.8 €/m³) and polyester (2.6 €/m³) wastewaters, using an integrated process of Fenton' oxidation and SBR. The operating costs are associated with the consumption of hydrogen peroxide and iron in the oxidative process, which follows the order: acrylic > cotton > polyester. The hydrogen peroxide consumption is associated with the larger amount of organic matter (acrylic has higher values of COD and DOC), but also with the high content of chlorides (~ 9 g/L in the cotton effluent).

The total costs of the integrated process (run# 2) are smaller than those corresponding to the Fenton's reaction alone (18.1, 9.2 and 2.7 €/m³ for acrylic, cotton and polyester effluents, respectively), which, even so, did not allowed per se obtaining effluents respecting legislated standards.

10.4 Conclusions

The treatability of synthetic acrylic, cotton and polyester dyeing wastewaters by SBR and an integrated process consisting of Fenton's reaction and SBR was investigated. It was found that the biological degradation in SBR per se did not allow obtaining effluents complying with the discharge limits, the same applying for the chemical oxidation stage

when used alone. Fenton's oxidation improved the biodegradability of all dyeing wastewaters while reducing their toxicity, which allows its integration with a biological treatment. The application of Fenton's process in optimized conditions followed by biological oxidation (SBR) provided effluents that comply with discharge limits, with global organic matter removals of 98.2, 87.7 and 91.4% for COD, 94.5, 83.2 and 91.3% for BOD₅ and 98.4, 91.5 and 91.2% for DOC, for acrylic, cotton and polyester wastewaters, respectively, and almost complete color reduction (>98.5%). Under such conditions total operating costs are significant: 19.4 €/m³ for acrylic, 10.4 €/m³ for cotton and 3.9 €/m³ for polyester. However, the operating costs might be decreased by reducing the H₂O₂ and Fe²⁺ doses without compromising compliance with discharge limits. The use of the lowest doses of reagents that allowed meeting the discharge limits led to operating costs of 14.8, 5.8 and 2.6 €/m³ for acrylic, cotton and polyester effluents, respectively. These costs represent a reduction of 24-42% as regards the application of Fenton's oxidation alone.

10.5 References

- Tantak, N.P.; Chaudhari, S. (2006). Degradation of azo dyes by sequential Fenton's oxidation and aerobic biological treatment. *Journal of Hazardous Materials*, B 136, 698-750.
- Vaigan, A.A.; Moghaddam, R.A.; Hashemi, H. (2009). Effect of Dye concentration on sequencing batch reactor performance. *Iranian Journal of Environmental Health Science & Engineering*, 6, 11-16.
- Waters, B.D. (1995). The regulator's view. In *Colour in Dyehouse effluent*, P. Cooper (Ed.). Oxford, The Society of Dyers and Colourists, The Alden Press.



Part IV

Real Cotton Dyeing Wastewater

Chapter 11

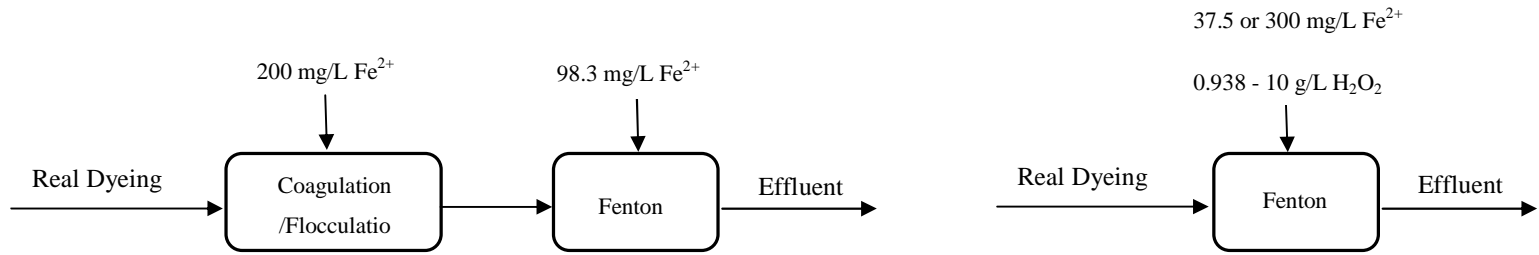
Cotton Dyeing Wastewater Treatment *

* This Chapter is based on the publication "Rodrigues C.S.D.; Madeira, L.M.; Boaventura, R.A.R. Decontamination of an industrial cotton dyeing wastewater by chemical and biological processes". Submitted to Industrial & Engineering Chemistry Research.

11 Cotton Dyeing Wastewater Treatment

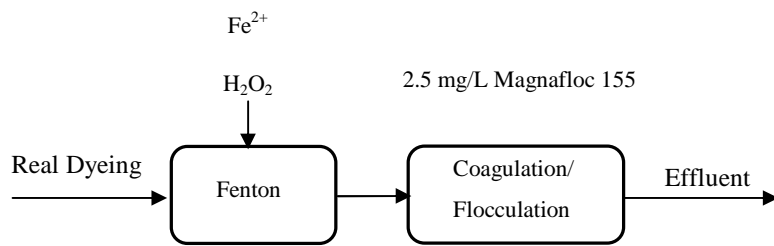
11.1 Introduction

This work aimed at evaluating four approaches for treating a real cotton dyeing wastewater (see Figure 11.1). In Approach 1 coagulation/flocculation was combined with Fenton's reaction (as coagulation/flocculation per se is not effective to comply with legislated discharge standards for textile wastewater under study, as detailed below). In Approach 2 only Fenton's oxidation was applied and in Approaches 3 and 4 the wastewater was pre-treated by Fenton's oxidation and then treated by coagulation/flocculation and a biological process (SBR), respectively. In all situations it was intended to obtain the lowest operating cost and an effluent that meets the discharge limits imposed by the national legislation for textile effluents. Therefore, to reduce costs, part of the catalyst used in the Fenton's reaction of Approach 1 was the residual dissolved iron resulting from coagulation/flocculation (this methodology has been already applied to industrial wastewaters other than textile dyeing ones) [Peres et al., 2004; Xing and Sun, 2009; Perdigon-Melon et al., 2010]. In the same way, in Approach 3 the coagulant used was the residual iron resulting from the Fenton's reaction; however, in this case the final effluent clearly complied with legislated standards, and so the Fenton's stage was also performed with doses of chemicals reduced to 3/4 and 1/2 of the optimum value found in Approach 2 (this methodology has not yet been described in the literature). In Approach 4 the doses of reagents used in the Fenton's oxidation were also reduced, as described above, and the resulting effluent was subjected to a biological process. It has been reported in literature [Oller et al., 2011] the need of using oxidative processes as a pre-treatment step of industrial textile wastewaters with the aim of generating a biodegradable effluent without extensive testing the behavior of the biological process. Recent works already integrated both processes, particularly combining Fenton's oxidation and biological degradation in SBR [Rodrigues et al., 2009 a); Blanco et al., 2012; Elmolla and Chaudhuri, 2012; Sanchis et al., 2013; Wu et al., 2013]. The ultimate choice of the technology to adopt should take also into account economic indicators, and so a cost analysis was performed for each treatment strategy, as detailed in the next section.

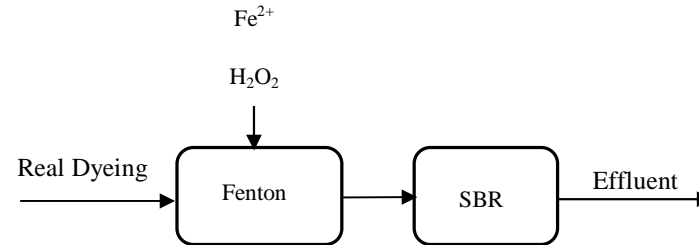


Approach 1: Coagulation/flocculation followed by Fenton's reaction alone

Approach 2: Fenton's oxidation alone



Approach 3: Fenton's oxidation followed by coagulation/flocculation plus SBR



Approach 4: Integration of Fenton's oxidation plus SBR

Approaches 3 and 4

- Run #1: 18.8 mg/L Fe²⁺ and 0.625 mg/L H₂O₂ in Fenton's oxidation
- Run #2: 28.2 mg/L Fe²⁺ and 0.938 mg/L H₂O₂ in Fenton's oxidation
- Run #3: 37.5 mg/L Fe²⁺ and 1.25 mg/L H₂O₂ in Fenton's oxidation

Figure 11.1 - Schematic diagram of all process configurations adopted.

11.2 Operating Costs

To select the better integration of stages for wastewater treatment, but ensuring that the generated effluent meets the discharge standards, the operating costs associated to the consumption of chemicals and energy were also assessed. For the latter it was considered the energy consumed in agitation (power required = 0.61 W) and air insufflated (power = 4.5 W) in the SBR stage. The costs of acids and base were not considered as they are almost negligible compared to the other chemicals.

In the economic analysis the costs of reagents were those given by Quimitécnica S.A. and Rivaz Química S.A.: H_2O_2 (49.5% (w/v), density at 25 °C = 1.2 g/cm³) – 365 €/ton; $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (93 wt.% of purity) – 233.7 €/ton; and Magnafloc 155 – 3850 €/ton. For energy it was considered the average value of 0.10 €/(kW h)).

The operating cost for the coagulation/flocculation step is the sum of costs of Fe^{2+} (Equation 11.1) and Magnafloc 155 (Equation 11.2), while for Fenton's reaction is the sum of costs of Fe^{2+} (Equation 11.1) and H_2O_2 (Equation 11.3) consumption; finally, for SBR is the cost of energy (Equation 11.4) only.

$$\text{Cost}_{\text{Fe}^{2+}} = \frac{\text{Price}_{\text{FeSO}_4 \cdot 7\text{H}_2\text{O}} \left(\frac{\text{€}}{\text{ton}} \right) * \left[\text{Fe}^{2+} \right] * 10^{-6} \left(\frac{\text{ton}}{\text{m}^3} \right) * \frac{\text{MM}_{\text{FeSO}_4 \cdot 7\text{H}_2\text{O}}}{\text{MM}_{\text{Fe}^{2+}}}}{\frac{\% \text{ of purity}}{100}} \quad (11.1)$$

$$\text{Cost}_{\text{Magnafloc 155}} = \text{Price}_{\text{Magnafloc 155}} \left(\frac{\text{€}}{\text{ton}} \right) * \left[\text{Magnafloc 155} \right] * 10^{-6} \left(\frac{\text{ton}}{\text{m}^3} \right) \quad (11.2)$$

$$\text{Cost}_{\text{H}_2\text{O}_2} = \frac{\text{Price}_{\text{H}_2\text{O}_2} \left(\frac{\text{€}}{\text{ton}} \right) * \left[\text{H}_2\text{O}_2 \right] * 10^{-3} \left(\frac{\text{ton}}{\text{m}^3} \right) * \rho_{\text{H}_2\text{O}_2} \left(\frac{\text{kg}}{\text{L}} \right)}{\frac{\% \text{H}_2\text{O}_2}{100} \text{ (kg/L)}} \quad (11.3)$$

$$\text{Cost}_{\text{energy}} = \frac{(\text{Power}_{\text{air insufflated}} + \text{Power required agitation}) * 10^{-3} \text{ (kW)} * \text{Price}_{\text{energy}} \text{ (kW h)} * \text{time}_{\text{aeration}} \text{ (h)}}{\text{Volume}_{\text{treated effluent}} \text{ (m}^3\text{)}} \quad (11.4)$$

In the previous Equations, $[i]$ represents the concentration of species i (in g/L for H_2O_2 and mg/L for Fe^{2+} and Magnafloc 155), MM_i stands for molar mass (in g/mol) and the power required for agitation is expressed in W .

The total operating costs for the integrated processes are calculated by the sum of costs associated with each process involved.

11.3 Materials and Methods

11.3.1 Experimental Procedure

The coagulation/flocculation, Fenton's reaction and SBR experiments were performed as detailed in sections 3.4.1, 3.4.2 and 3.4.4, respectively.

The supernatant resulting from coagulation/flocculation was collected and acidified with HNO_3 (68%, from Merck, Germany) to $pH < 4$ to keep the iron dissolved (to be later used as catalyst in the Fenton's reaction), when treating the effluent by the combination of coagulation/flocculation plus Fenton's reaction.

When applying Fenton's oxidation followed by coagulation/flocculation, the effluent from the oxidation stage was acidified to $pH \approx 1$ to keep the iron dissolved for the coagulation/flocculation study, while simultaneously slowing down or inhibiting the Fenton's reaction. The analyses of the effluent were performed immediately.

All coagulation/flocculation experiments were conducted at room temperature (22-24 °C). All operating conditions were set taking into account previous results achieved with a similar simulated effluent (chapter 7).

11.3.2 Analytical Methods

All analytical parameters were determined as described in section 3.3 of chapter 3.

The analytical determinations were performed in duplicate, and the coefficients of variation were less than 2% for DOC, 6% for BOD_5 , 4% for COD and k' , and 5% for the other parameters.

11.4 Results and Discussion

11.4.1 Textile Deying Wastewater

The industrial cotton deying wastewater was provided by Têxtil Luis Simões S.A. and its main characteristics are reported in Table 3.5 (section 3.2.2).

11.4.2 Coagulation/Flocculation plus Fenton's Reaction (Approach 1)

This study started with the application of coagulation/flocculation to the raw wastewater, using ferrous sulfate and Maganafloc 155 as coagulant and flocculant, respectively. The operating conditions used were the optimal ones determined in a prior study on the treatment of a synthetic cotton wastewater (chapter 4): $V_{\text{coagulation}}=150$ rpm, $t_{\text{coagulation}}=3$ min, $[\text{Fe}^{2+}]=200$ mg/L, $\text{pH}=9.4$, $V_{\text{flocculation}}=20$ rpm, $t_{\text{flocculation}}=15$ min, $[\text{Maganafloc 155}]=0.5$ mg/L. The characteristics of the wastewater after treatment are presented in Table 11.1. One can conclude that coagulation/flocculation is very efficient as regards color removal (95.1% - percent removal efficiencies are within brackets in the table), leads to a considerable removal of organic matter (36.9% and 39.4% respectively for COD and DOC) and phosphorus (47.2%), but it is quite inefficient concerning the removal of BOD_5 (17.2%) and nitrogen (1.9%). Moreover, the values of COD and BOD_5 in the final effluent are above the discharge standards imposed by the Portuguese legislation, which makes necessary an additional treatment.

So, for increasing the efficiency of organic matter removal, the effluent from the coagulation/flocculation stage was subjected to Fenton's oxidation, applying the operating conditions already optimized when treating a synthetic effluent by the same integrated process (chapter 7): $T=50$ °C, $\text{pH}=3.5$, $t=60$ min, $[\text{H}_2\text{O}_2]=500$ mg/L and $[\text{Fe}^{2+}]_{\text{added}}=98.3$ mg/L (total iron concentration = 100 mg/L, taking into account that 1.7 mg Fe/L remained from the coagulation/flocculation step). Results included in Table 11.1 point out that Fenton's oxidation applied to the pre-treated effluent allowed obtaining COD, BOD_5 and DOC removals of 53.7, 36.7 and 44.1%, respectively, color reduction of 89.3% and smaller decreases in total phosphorus and total nitrogen concentrations (29.7 and 2.7%, respectively).

The global efficiencies for the combined process (coagulation/flocculation plus Fenton's reaction) are significant for color (99.5%), COD (70.8%), DOC (66.1%) and total phosphorous (62.9%), moderate for BOD₅ (47.6%) and low for total nitrogen (4.5%). Except for BOD₅ the efficiencies reached are similar to those obtained when treating a synthetic cotton dyeing effluent by the same integrated process (61.7, 25.8, 71.2 and 99.8% for COD, BOD₅, DOC and color, respectively) (chapter 7). Moreover, the resulting effluent meets the discharge standards (Table 11.1), and this is reached at a low operating cost as regards the amounts of chemicals employed in coagulation/flocculation and Fenton's steps (0.83 €/m³), calculated as described in section 11.2. Fenton's oxidation contributes to the overall cost by about 70%. This puts into evidence the importance of the integrated treatment strategy adopted. A cheaper process (coagulation/flocculation) used as pre-treatment permits reducing the amounts of chemicals required by Fenton's oxidation, thus lowering the global operating cost.

Table 11.1 - Characteristics of the industrial cotton dyeing wastewater, after coagulation/flocculation and after coagulation/flocculation plus Fenton's oxidation (Approach 1), and global removals for the combined processes (percent removal efficiencies are given within brackets for each isolated process).

Parameter	Raw wastewater	Coagulation & flocculation	Fenton	Global removal (%)	Discharge limits***
pH	10.0	1.2 ^{a)}	7.10 ^{b)}	---	5.5-9.0
T (°C)	35.6	n.d.	n.d.	---	
TSS (mg/L)	38.0	n.d.	n.d.	---	
Conductivity a 20 °C (mS/cm)	11.5	n.d.	n.d.	---	
Total nitrogen (mg N/L)	1064.4	1043.6 (1.9)	1015.6 (2.7)	4.5	
Nitrates (mg NO ₃ ²⁻ /L)	0.008	n.d.	n.d.	---	
Total phosphorous (mg P/L)	4.2	2.2 (47.2)	1.5 (29.7)	62.9	
Dissolved phosphorous (mg P/L)	0.06	n.d.	n.d.	---	
Chemical oxygen demand (mg O ₂ /L)	495.0	312.5 (36.9)	144.6 (53.7)	70.8	250
Biochemical oxygen demand (mg O ₂ /L)	127.5	105.6 (17.2)	66.9 (36.7)	47.6	100
Dissolved organic carbon (mg C/L)	174.7	105.8 (39.4)	59.1 (44.1)	66.1	
Chlorides (mg Cl ⁻ /L)	1241.5	n.d.	n.d.	---	
Sulfates (mg SO ₄ ²⁻ /L)	0.23	n.d.	n.d.	---	
Alkalinity (mg CaCO ₃ /L)	456.8	n.d.	n.d.	---	
Specific oxygen uptake rate (k') (mg O ₂ /(g _{vss} h))	8.85	9.9	11.3	---	
BOD ₅ :COD ratio	0.26	0.34	0.46	---	
Absorbance at 600 nm (abs. units)	1.0251	0.0382 (95.1*)	0.0028 (89.3**)	99.5	
Visible color after dilution 1:40	Visible	not visible	not visible	---	not visible
<i>Vibro fischeri</i> Inhibition 5 min (%)	81.1	47.8	0.0	---	
<i>Vibro fischeri</i> Inhibition 15 min (%)	70.4	50.6	0.0	---	
<i>Vibro fischeri</i> Inhibition 30 min (%)	70.5	51.7	0.0	---	

n.d. – not determined

* calculated from the absorbance of real wastewater at pH 9.4 (0.7865 abs. units).

** calculated from the absorbance after coagulation/flocculation at pH 3.5 (0.0261 abs. units).

*** Ordinance No. 423/97 of 25 June.

a) After acidification

b) After neutralization

11.4.3 Fenton's Oxidation (Approach 2)

The study proceeded by applying the Fenton's oxidation directly to the raw effluent having in mind the possibility of meeting the discharge standards by this chemical process alone.

The effect of the hydrogen peroxide dose was first assessed, starting with the optimal dose found in the treatment of synthetic cotton dyeing effluent by the same process (10 g/L) - chapter 7 - and then gradually decreasing the dose down to 0.938 g/L, to reduce the costs associated with chemicals consumption. Reducing the oxidant consumption, while complying legislated limits, is of paramount importance because it represents the main contribution to the operating costs. The other variables were fixed according to the previous work using simulated wastewater(chapter 7): pH = 3.5, T = 50 °C, t = 60 min and $[\text{Fe}^{2+}] = 300 \text{ mg/L}$.

BOD₅, COD, DOC, and color removals (see Figure 11.2) increased from 29.4, 46.5, 46.3 and 94.6 % to 38.9, 62.4, 63.2, and 97.8%, respectively, when raising the hydrogen peroxide dose from 0.938 to 1.25 g/L, but further increases of the hydrogen peroxide dose did not result in any efficiency improvement. The optimal dose found is much below that obtained in the previous study conducted with a synthetic dyeing cotton wastewater (10 g/L) (chapter 7); this is due to the fact that the chloride concentration in the real effluent (~ 1.2 g/L) is much lower than in the synthetic effluent (~ 8.0 g/L), thus decreasing considerably the effect of hydroxyl radical scavenging by this anion.

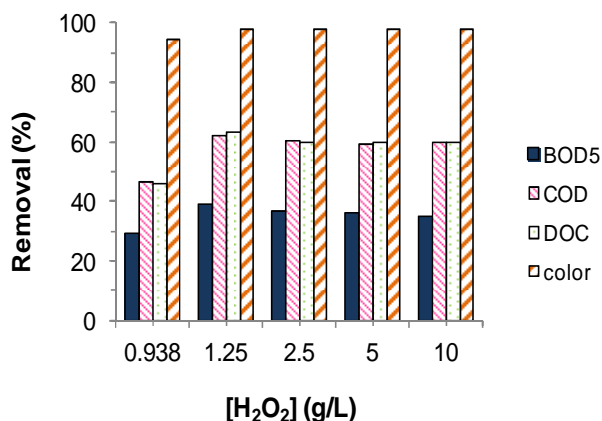


Figure 11.2 - Effect of H₂O₂ concentration on COD, BOD₅, DOC and color removals during Fenton's oxidation (Approach 2) (initial pH=3.5, T=50 °C, t = 60 min and $[\text{Fe}^{2+}] = 300 \text{ mg/L}$).

The existence of an optimum H_2O_2 concentration was also observed by other authors [Azbar et al., 2004; Ramirez et al., 2005; Alaton and Teksoy, 2007; Rodrigues et al., 2009 b); Li et al., 2012; Wu and Wang, 2012] and is explained by the fact that a parallel reaction between H_2O_2 , in excess, with the hydroxyl radicals occurs, generating HO_2^\bullet species with a lower oxidation potential (Equation 2.3 of chapter 2). The optimum value achieved (1.25 g/L) is close to those obtained by other authors, namely, Meriç et al. [2005] reached an optimum H_2O_2 dose of 1.0 g/L for treating a Reactive Black 5 dye solution, Blanco et al. [2012] found 1.65 g/L as the optimum dose for treating a real textile effluent and Wu and Wang [2012] achieved 1.5 g/L when treating a mixture of printing and dyeing wastewaters by Fenton's reaction.

To reduce the operating costs associated with the catalyst use, the Fe^{2+} dose was set at 37.5 mg/L (corresponding to a $\text{Fe}^{2+}:\text{H}_2\text{O}_2$ ratio of 1:33.3 (w/w) – optimum value reached when treating a synthetic cotton wastewater by Fenton's oxidation) – chapter 7, maintaining the other variables (3.5, 50 °C, 60 min and 1.25 g/L for pH, temperature, reaction time and H_2O_2 concentration, respectively). Figure 11.3 shows the results obtained for DOC, COD, BOD_5 and color removals and it can be seen that only a small decrease occurred (33.6 % for BOD_5 , 53.0% for COD, 52.8% for DOC and 94.3% for color) in comparison with that corresponding to the Fe^{2+} concentration previously employed (about one order of magnitude higher – 300 mg/L). It is worthy remarking that this much smaller iron dose still allows obtaining an effluent that meets the legislated discharge limits (see Table 11.2), although the COD value (232.8 mg/L) is not very far from the legislated limit (250 mg/L). Daily or seasonal variations in the wastewater composition can cause that limit to be exceeded and so additional subsequent treatments could be required to increase the overall efficiency, as described below.

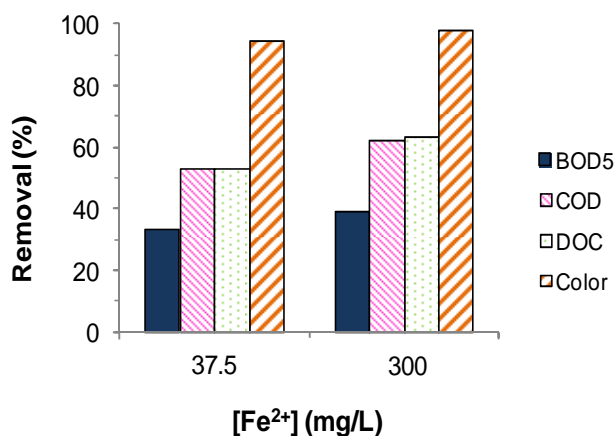


Figure 11.3 - Effect of Fe²⁺ concentration on COD, BOD₅, DOC and color removals during Fenton's oxidation (Approach 2) (initial pH=3.5, T=50 °C, t = 60 min and [H₂O₂] = 1.25 g/L).

Table 11.2 - Characteristics of the cotton dyeing wastewater after Fenton's oxidation and respective removal efficiencies (Approach 2).

Parameter	Fenton's oxidation	Removal (%)	Discharge Limit**
pH	7.9	-	5.5-9.0
Total nitrogen (mg N/L)	1021.8	4.0	
Total phosphorus (mg P/L)	4.15	1.2	
Chemical oxygen demand (mg O ₂ /L)	232.8	53.0	250
Biochemical oxygen demand (mg O ₂ /L)	84.6	33.6	100
Dissolved organic carbon (mg C/L)	82.5	57.8	
Specific oxygen uptake rate (k') (mg O ₂ /(g _{VSS} h))	9.5	-	
BOD ₅ :COD ratio	0.36	-	
Absorbance at λ _{max} (abs. units)	0.0386	94.3*	
Visible color after dilution 1:40	not visible	-	not visible
<i>Vibro fischeri</i> Inhibition 5 min (%)	0.0	-	
<i>Vibro fischeri</i> Inhibition 15 min (%)	0.0	-	
<i>Vibro fischeri</i> Inhibition 30 min (%)	0.0	-	

* calculated from the absorbance at pH 3.5 (0.6805 abs. units).

** Portuguese legislation for discharge of textile wastewaters (Ordinance No. 423/97 of 25 June 25).

The selected dose of ferrous ion (37.5 mg/L) is similar to that reached by other authors to treat dye-containing solutions, as well as synthetic and real wastewaters. Ramirez et al. [2005] obtained an optimum amount of catalyst of 27.2 mg/L for 99.7% color removal and 23.5 mg/L for 70.7% TOC reduction from an orange II dye solution. Bali and Karagözoglu [2007] reached 25 mg/L of Fe^{2+} as the dose that maximized the color removal (96.2%) of a synthetic textile effluent containing polyvinyl and Remazol Turquoise Blue G-133. Finally, Papadopoulos et al. [2007] needed to add 40 mg/L of Fe^{2+} to treat a real effluent from polyethylene fibers processing.

The operating cost associated with chemicals when applying the optimal doses achieved in treatment of simulated cotton dyeing wastewater (300 mg Fe^{2+} /L and 10 g H_2O_2 /L) is 9.2 €/m³. However, this cost is reduced to 1.2 €/m³ when using, in Fenton's oxidation of the real wastewater, the selected doses of 37.5 mg Fe^{2+} /L and of 1.25 g H_2O_2 /L; such reduced cost is ascribed to the much lower concentration of chlorides in the real wastewater.

11.4.4 Integration of Fenton's Oxidation and Coagulation/ Flocculation (Approach 3)

Coagulation/flocculation was applied to the effluent previously treated by the Fenton process to further increase the organic matter reduction. However, several strategies were considered aiming reducing costs. In this perspective, different conditions were tested in the Fenton's stage: one run was performed in conditions considered as the optimal ones – 1.25 g/L of H_2O_2 and 37.5 mg/l of Fe^{2+} (run #3); in the other runs the doses of H_2O_2 and Fe^{2+} were reduced to 3/4 and 1/2, respectively (see Figure 11.1), with the objective of decreasing the operating costs (runs #2 and #1, respectively). In the coagulation/flocculation stage the coagulant used was the dissolved iron resulting from Fenton's oxidation (13.3, 23.1 and 32.7 mg/L of Fe in run#1, run#2 and run#3, respectively), for minimizing costs. The other variables correspond to the optimal conditions obtained when treating the simulated cotton dyeing effluent by Fenton's reagent plus coagulation/flocculation (chapter 7): $V_{\text{coagulation}}=150$ rpm, $t_{\text{coagulation}}=3$ min, pH=5, $V_{\text{flocculation}}=20$ rpm, $t_{\text{flocculation}}=15$ min, [Magnafloc 155] = 2.5 mg/L.

Table 11.3 presents the results obtained after Fenton's oxidation and after coagulation/flocculation, as well as the global removal efficiencies for each strategy (runs

#1 to #3). The COD, DOC and color removals reached in Fenton's reaction are in all strategies higher than in the coagulation/flocculation stage, but BOD₅ shows an opposite behavior. As expected, much better treatment efficiencies are reached in run #3, where doses of chemicals in the Fenton's stage are higher (69.2, 60.4, 72.4, and 96.6% for COD, BOD₅, DOC and color, respectively).

Final COD values below the discharge standards were only reached in runs#2 and #3, where greater H₂O₂ (and Fe²⁺) doses were used. However, despite the slightly lower organic matter removal efficiency, the chemical dosages used in run #2 were selected because they originate smaller operating costs (0.87 €/m³), comparatively to run #3 (1.2 €/m³), which is associated with the lower H₂O₂ and Fe²⁺ concentration employed, without compromising compliance with the legislated discharge standards.

The use of dissolved iron resulting from Fenton process as coagulant in the subsequently stage of coagulation/flocculation represents an economic advantage, since the operating cost is reduced by 27.5% comparatively to Fenton's oxidation alone.

Table 11.3 - Characteristics of the cotton dyeing wastewater after Fenton's oxidation and coagulation/flocculation (Approach 3) and global removal for the combined process (runs #1 to #3 correspond to different dosages of hydrogen peroxide in the Fenton's stage; percent removal efficiencies are given within brackets for each isolated process).

Parameter	Run #1 – 0.625 g H ₂ O ₂ /L			Run #2 – 0.938 g H ₂ O ₂ /L			Run #3 – 1.25 g H ₂ O ₂ /L			Discharge limit***
	Fenton's oxidation	Coagulation & flocculation	Global removal (%)	Fenton's oxidation	Coagulation & flocculation	Global removal (%)	Fenton's oxidation	Coagulation & flocculation	Global removal (%)	
pH	1.20	7.0	-	1.25	7.02	-	1.10	7.03	-	5.5-9.0
Chemical oxygen demand (mg O ₂ /L)	347.5 (29.8)	270.0 (22.3)	45.5	292.5 (40.9)	185.0 (36.8)	62.6	260.0 (47.5)	152.5 (41.3)	69.2	250
Biochemical oxygen demand (mg O ₂ /L)	116.3 (8.8)	91.8 (21.1)	28.0	106.4 (16.5)	66.9 (37.1)	47.5	85.3 (33.1)	50.5 (40.8)	60.4	100
Dissolved organic carbon (mg C/L)	124.9 (28.5)	94.9 (24.0)	45.7	98.4 (43.7)	62.2 (36.8)	64.4	82.4 (52.8)	48.3 (41.4)	72.4	-
BOD ₅ :COD ratio	0.33	0.34	-	0.36	0.36	-	0.33	0.33	-	-
Absorbance at λ _{max} (abs. units)	0.0407 (94.0*)	0.0234 (43.2**)	96.6	0.0392 (94.2*)	0.0230 (41.6**)	96.6	0.0387 (94.3*)	0.0233 (40.4**)	96.6	-
Visible color after dilution 1:40	not visible	not visible	-	not visible	not visible	-	not visible	not visible	-	not visible

* calculated from the absorbance of wastewater at pH 3.5 (0.6805 abs. units).

** calculated from the absorbance after Fenton at pH 5.0 (0.0412, 0.0394 and 0.0391 abs. units for run #1, #2 and #3, respectively).

*** Portuguese legislation for discharge of textile wastewaters (Ordinance No. 423/97 of 25 June).

11.4.5 Combination of Fenton's Reaction and SBR (Approach 4)

As the biodegradability of the raw wastewater (in terms of BOD₅:COD ratio and k') slightly increased after Fenton's oxidation (from 0.26 and 8.85 mg O₂/(g_{vss} h) to 0.36 and 9.5 mg O₂/(g_{vss} h), respectively), and there was also a reduction in *Vibro fischeri* inhibition, as shown in Tables 11.1 and 11.2, the alternative integrated process consisting of Fenton's reaction followed by SBR was studied.

Three experiments were performed using different doses of chemicals in Fenton's oxidation stage. One experiment (run #3) was performed under the optimal conditions determined in Approach 2 (37.5 mg/L Fe²⁺ and 1.25 g/L H₂O₂); in the other runs the doses of H₂O₂ and Fe²⁺ were reduced to 3/4 and 1/2, respectively, with the objective of reducing the operating costs (runs #2 and #1, respectively) (see Figure 11.1).

Figure 11.4 shows the COD, DOC, BOD₅, color, total nitrogen and total phosphorus removals during 10 cycles of SBR operation for the 3 runs; one can conclude that the removals for all parameters analyzed remained practically constant after 6 cycles in all runs/strategies tested, which means that a pseudo-steady state was reached. The efficiencies increased with the doses of chemicals used in the Fenton's reaction (run #3 > run #2 > run #1), simultaneously with a significant decay of toxicity and a slight increase of biodegradability (see also Table 11.4). Particularly the inhibition of *Vibrio fischeri* decreased from 44.5-49.2% in run # 1 to 0.0 (non-inhibition) in run # 3. The average removals achieved in the last 4 cycles are presented in Table 11.4. BOD₅ removal was greater in SBR probably due to the breakdown of the more recalcitrant compounds by chemical oxidation. As regards decolorization, about 94% of the absorbance of raw wastewater was removed by the Fenton's reaction and only 38-40% of the residual absorbance was removed in the SBR.

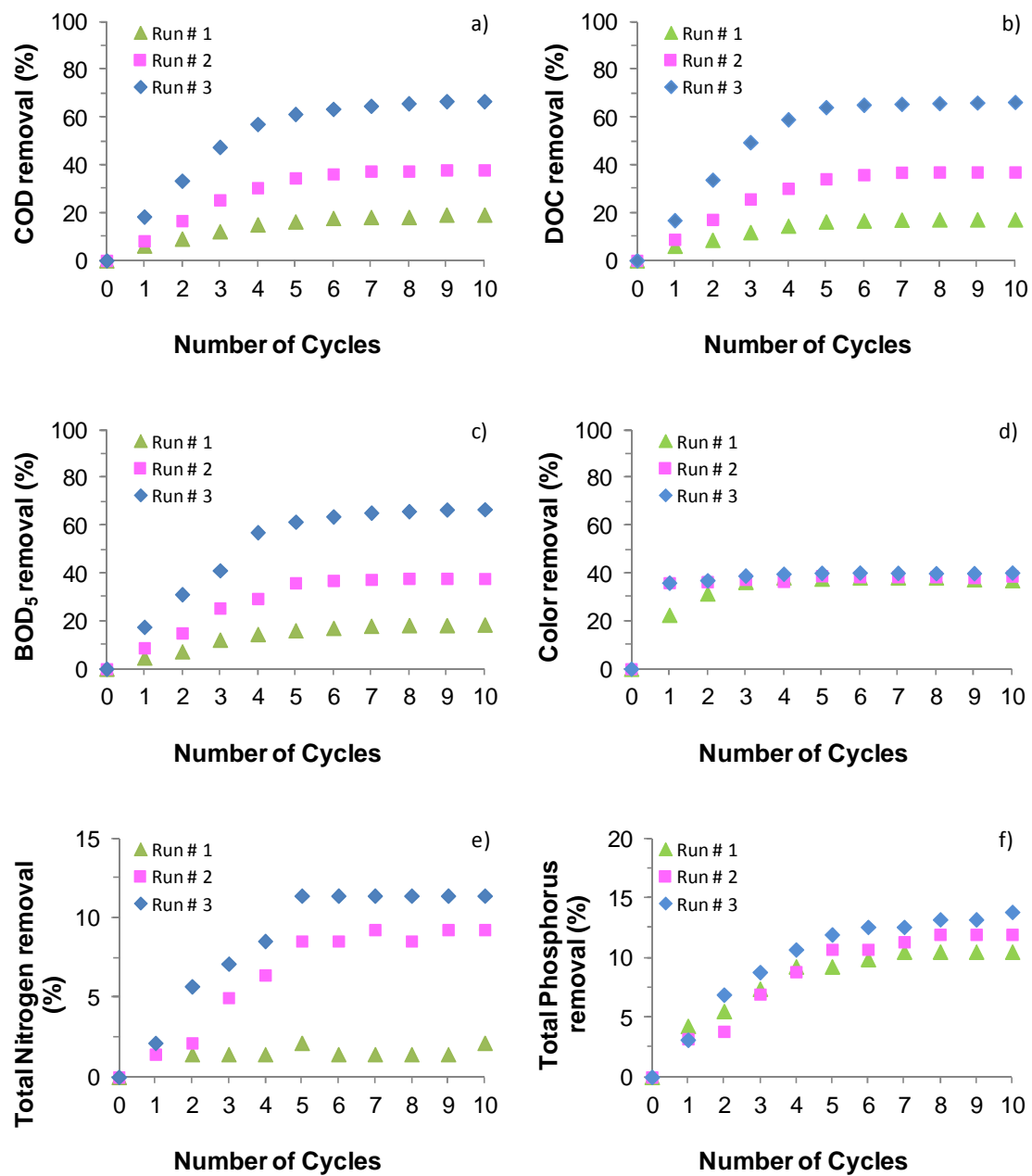


Figure 11.4 - Variation of COD (a), DOC (b), BOD₅ (c), color (d) total nitrogen (e) and total phosphorus (f) removals along 10 cycles of SBR operation, after treatment by Fenton's oxidation. Runs #3 to #1 refer to Fenton's stage with progressively decreasing doses of chemicals.

Chapter 11 – Cotton Dyeing Wastewater Treatment

Table 11.4 – Characteristics of the cotton dyeing wastewater after Fenton’s reaction and SBR (Approach 4) and average (last four cycles for SBR) and global removals (respective removal efficiencies are given within brackets for each processes).

Parameter	Run #1 – 0.625 g H ₂ O ₂ /L			Run #2 – 0.938 g H ₂ O ₂ /L			Run #3 – 1.25 g H ₂ O ₂ /L			Discharge limit***
	Fenton	SBR	Global Removal (%)	Fenton	SBR	Global Removal (%)	Fenton	SBR	Global Removal (%)	
pH	7.12	7.17	---	7.05	7.15	---	7.09	7.17	---	5.5-9.0
Total nitrogen (mg N/L)	1021.8 (4.0)	1005.4 (1.6)	5.5	1021.8 (4.0)	929.1 (9.1)	12.7	1021.8 (4.0)	905.5 (11.4)	14.9	
Total phosphorus (mg P/L)	4.2 (1.2)	3.8 (8.4)	9.5	4.2 (1.7)	3.7 (10.4)	11.9	4.2 (1.2)	3.6 (13.3)	14.3	
COD (mg O ₂ /L)	346.5 (30.0)	281.8 (18.7)	43.1	294.1 (40.6)	183.3 (37.7)	63.0	232.8 (53.0)	79.2 (66.0)	84.0	250
BOD ₅ (mg O ₂ /L)	114.2 (10.4)	93.4 (18.2)	26.7	103.4 (18.9)	64.4 (37.7)	49.5	84.7 (32.6)	28.6 (66.2)	77.6	100
DOC (mg C/L)	124.7 (28.5)	103.3 (17.2)	40.8	98.0 (43.8)	61.7 (37.0)	64.6	82.5 (52.7)	28.1 (65.9)	83.9	
SOUR – Specific oxygen uptake rate (k') (mg O ₂ /(g _{VSS} .h))	8.9	n.d.	---	9.1	n.d.	---	9.5	n.d.	---	
BOD ₅ :COD ratio	0.33	0.33	---	0.35	0.35	---	0.36	0.36	---	
Absorbance at λ _{max} (a.u.)	0.0410 (94.0*)	0.0257 (38.1**)	96.3	0.0393 (94.2*)	0.0240 (39.5**)	96.5	0.0386 (94.3*)	0.0234 (40.0**)	96.6	
Visible color after dilution 1:40	not visible	not visible	---	not visible	not visible	---	not visible	not visible	---	not visible
<i>Vibrio fischeri</i> Inhibition 5 min (%)	44.5	n.d.	---	11.0	n.d.	---	0.0	n.d.	---	
<i>Vibrio fischeri</i> Inhibition 15 min (%)	46.7	n.d.	---	23.1	n.d.	---	0.0	n.d.	---	
<i>Vibrio fischeri</i> Inhibition 30 min (%)	49.2	n.d.	---	26.7	n.d.	---	0.0	n.d.	---	

n.d. – not determined.

* calculated from the absorbance at 520 nm of raw wastewater at pH 3.5 (0.6805 abs. units).

** calculated from the absorbance at 520 nm of wastewater after Fenton at pH 7.0 (0.0415, 0.0397 and 0.0390 abs. units in run #1, #2 and #3, respectively).

*** . Ordinance No. 423/97 of 25 June.

As shown in Figure 11.5, the operating costs associated with the consumption of chemicals and energy increase with the amount of chemicals used in the chemical treatment, i.e, run #3 (2.4 €/m³) > run #2 (2.1 €/m³) > run #1 (1.8 €/m³). However, only runs #2 and #3 allowed obtaining effluents that meet the discharge standards, namely in terms of COD (see Table 4). As the costs are slightly smaller, conditions used in run #2 are proposed for practical applications. The overall efficiencies achieved by the combination of Fenton's oxidation and biological degradation in SBR under such conditions are 63.0, 49.5, 64.6, 12.7, 11.9 and 96.5% for COD, BOD₅, DOC, total nitrogen, total phosphorus and color, respectively. It is noteworthy that such integrated process is more expensive than Fenton's oxidation per se (cf. Figure 11.5), which is due to energy consumption in the SBR, although doses of chemicals were minimized in the chemical oxidation stage.

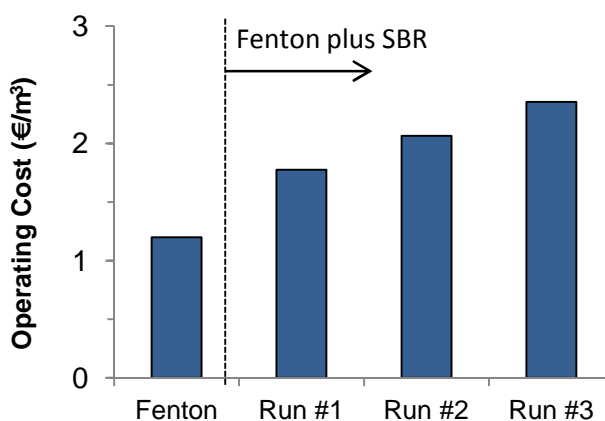


Figure 11.5 - Operating costs of Fenton alone and Fenton plus SBR for treatment of a real cotton dyeing wastewater.

11.5 Conclusions

A combination of coagulation/flocculation and Fenton's oxidation, Fenton's oxidation alone, and integrated processes of Fenton's oxidation with coagulation/flocculation or biological degradation in SBR was applied to a real cotton dyeing wastewater aiming at

organic matter mineralization, color removal and toxicity reduction while obtaining an effluent that meets the legislated discharge limits at the lower operating cost.

All the treatment processes tested allowed obtaining an effluent that comply with the discharge limits, but the cheapest alternatives are the application of coagulation/flocculation followed by Fenton's oxidation or, inversely, the combination of Fenton's oxidation with subsequent coagulation/flocculation process. The operating costs associated to the consumption of chemicals are 0.83 and 0.87 €/m³, respectively. This is in part explained by initially using a cheaper treatment that permits a reduction of the amounts of chemicals employed in the second process, then decreasing the total costs (Approach 1) and by taking advantage of dissolved iron resulting from Fenton's reaction, as coagulant in the coagulation/flocculation step (Approach 3). Global removal efficiencies of 99.5, 70.8, 66.1, 47.6% and 96.6, 62.6, 64.4 and 47.5 % were obtained for color, COD, DOC and BOD₅, respectively, in the first and second integrated treatment processes (Approaches 1 and 3).

11.6 References

Alaton, I.A.; Teksoy, S. (2007). Acid Dyebath Effluent Pretreatment Using Fenton's Reagent: Process Optimization, Reaction Kinetics and Effects on Acute Toxicity. *Dyes Pigments*, 73, 31-39.

Azbar, N.; Yonar, T.; Kestioglu, K. (2004). Comparison of various advanced oxidation processes and chemical treatment methods for COD and color removal from a polyester and acetate fiber dyeing effluent. *Chemosphere*, 55, 35-43.

Bali, U.; Karagözoglu, B. (2007). Performance comparison of Fenton process, ferric coagulation and H₂O₂/pyridine/Cu (II) system for decolourization os Remazol Turquoise Blue G-133. *Dyes Pigments*, 74, 73-80.

Blanco, J.; Torrades, F.; Varga, M. de la; García-Montaña, J. (2012). Fenton and biological-Fenton coupled processes for textile wastewater treatment and reuse. *Desalination*, 286, 394-399.

Elmolla, E.S.; Chaudhuri, M. (2012). The feasibility of using combined Fenton-SBR for antibiotic wastewater treatment. *Desalination*, 285, 14-21.

Li, J.; Luan, Z.; Yu, L.; Ji, Z. (2012). Pretreatment of acrylic fiber manufacturing wastewater by the Fenton process. *Desalination*, 284, 62-65.

Meriç, S.; Selçuk, H.; Belgiorno, V. (2005). Acute toxicity removal in textile finishing wastewater by Fenton's oxidation, ozone and coagulation-flocculation processes. *Water Research*, 39 (6), 1147-1153.

- Oller, I.; Malato, S.; Sánchez-Pérez, J.A. (2011). Combination of advanced oxidation process and biological treatments for wastewater decontamination – A review. *Science of the Total Environment*, 409, 4141-4156.
- Papadopoulos, A.E.; Fatta, D.; Loizidou, M. (2007). Development and optimization of dark Fenton oxidation for treatment of textile wastewaters with high organic load. *Journal of Hazardous Material*, 146, 558-563.
- Perdigon-Melon, J.A.; Carbajo, J.B.; Petre, A.L.; Rosal, R.; Garcia-Calvo, E. (2010). Coagulation-Fenton coupled treatment for ecotoxicity reduction in highly polluted industrial wastewater. *Journal of Hazardous Materials*, 181, 127-132.
- Peres, J.A.; Heredia, J.B. de; Domínguez, J.R. (2004). Integrated Fenton's reagent – coagulation/flocculation process for the treatment of cork processing wastewaters. *Journal of Hazardous Materials*, 107 (3), 15-121.
- Ramirez, J.H.; Costa, C.A.; Madeira, L.M. (2005). Experimental design to optimize the degradation of the synthetic dye orange II using Fenton's reagent. *Catalysis Today*, 107-108, 68-76.
- Rodrigues, C.S.D.; Madeira, L.M.; Boaventura, R.A.R. (2009 a)). Treatment of textile effluent by chemical (Fenton's Reagent) and biological (Sequencing batch reactor) oxidation. *Journal of Hazardous Materials*, 172, 1551-1559.
- Rodrigues, C.S.D.; Madeira, L.M.; Boaventura, R.A.R. (2009 b)). Optimization of the azo dye Procion Red H-EXL degradation by Fenton's reagent using experimental design. *Journal of Hazardous Materials*, 164, 987-994.
- Sanchis, S.; Polo, A.M.; Tobaja, M.; Rodriguez, J.J.; Mohedano, A.F. (2013). Degradation of chlorophenoxy herbicides by coupled Fenton and biological oxidation. *Chemosphere*, in press. DOI:10.1016/j.chemosphere.2013.04.097.
- Wu, D.-L.; Wang, W.; Guo, Q.-W.; Shen, Y.-H. (2013). Combined Fenton-SBR process for bamboo industry wastewater treatment. *Chemical Engineering Journal*, 214, 278-284.
- Wu, H.; Wang, S. (2012). Impacts of operating parameters on oxidation-reduction potential and pretreatment efficacy in the pretreatment of printing and dyeing wastewater by Fenton process. *Journal of Hazardous Materials*, 243, 86-94.
- Xing, Z.-P.; Sun, D.-Z. (2009). Treatment of antibiotic fermentation wastewater by combined polyferric sulfate coagulation, Fenton and sedimentation process. *Journal of Hazardous Materials*, 168, 1264-1268.

Part V

Conclusions and Suggestions for Future Work



Chapter 12
Concluding Remarks and Forthcoming Work

12 Concluding Remarks and Forthcoming Work

12.1 Concluding Remarks

To minimize environmental impacts caused by the discharge of textile dyeing effluents various treatment technologies have been studied to achieve a more effective performance in color and organics removal at low operating cost. Therefore, this study aimed to evaluate the possibility of integrating coagulation/flocculation, chemical oxidation (Fenton or photo/Fenton processes) and biological treatment in a sequencing batch reactor (SBR) to treat simulated and real wastewaters in order to obtain a final effluent meeting the discharge standards.

The overall conclusions of this study are presented below.

12.1.1 Simulated Textile Dyeing Effluents

As regards the treatment of simulated dyeing effluents one can conclude that:

- In general, coagulation/flocculation, Fenton's oxidation and biological oxidation alone, even when using optimal conditions for pollutants removal, do not allow to obtain effluents complying with discharge standards. Only the polyester dyeing effluent met the legislated discharge limits when treated by Fenton's reaction but the value of COD (221.1 mg O₂/L) was very close to the maximum allowable value (250 mg/L);
- The integration of coagulation/flocculation with Fenton's oxidation using as catalyst the residual iron from coagulation/flocculation allowed the reduction of the operating costs, most notably in the acrylic dyeing effluent treatment because only 75 mg/L of Fe²⁺ was added to the amount resulting from the coagulation/flocculation (275 mg/L);
- The combination of Fenton's reaction followed by coagulation/flocculation taking advantage from the dissolved iron resulting from Fenton's reaction was shown to be an efficient and economically attractive strategy. Particularly, the operating

costs can be reduced by using only 1/2 of H_2O_2 and Fe^{2+} doses required for the maximization of color and DOC removals and biodegradability improvement by Fenton's oxidation;

- The solar photo-Fenton process alone permits to reduce the treatment costs of the three simulated effluents (by a factor of ≈ 3), compared with dark Fenton's reaction, with the additional advantage of obtaining an effluent with characteristics that meet the legislated discharge standards for textile wastewaters;
- The application of chemical oxidation as pre-treatment increased the biodegradability of the effluents, thus making possible its integration with a biological treatment. The effluents resulting from this integrated process can be discharged into the aquatic environment. Moreover it was possible to reduce the chemicals consumption in the first stage to 3/4 for acrylic dyeing effluent and to 1/2 for cotton and polyester dyeing effluents (compared to the required amounts of H_2O_2 and Fe^{2+} when applying Fenton's reaction alone) and, consequently cut the global operating costs;
- The combination that permits to obtain treated effluents with characteristics meeting the legislated discharge standards at the lowest cost is coagulation/flocculation followed by Fenton's reaction for the cotton simulated dyeing effluent (0.83 €/m³), photo-Fenton with simulated sunlight (1.0 €/m³) or Fenton's oxidation plus coagulation/flocculation (1.3 €/m³) for the polyester effluent and photo-Fenton with simulated solar radiation (5.8 €/m³) for acrylic.
- Operating in the conditions corresponding to the lowest operating costs, high color removals (>98.0% for acrylic and cotton effluents), moderate COD (72.0 and 61.7% for acrylic and cotton effluents, respectively) and DOC (71.5% for acrylic effluent and 71.2% for cotton effluent) removals were achieved; BOD₅ reductions are in general low.
- Regarding the polyester dyeing effluent, the photo-Fenton process allowed reaching removals of 55.4% for COD, 49.6% for DOC and 49.2% for BOD₅, however the removals slightly increased when applying Fenton's oxidation followed by coagulation/flocculation (62.7, 73.4 and 59.3% for COD, DOC and BOD₅, respectively).

12.1.2 Industrial Cotton Dyeing Wastewater

The treatability study of the real cotton dyeing wastewater included various processes such as, the combination of the coagulation/flocculation with Fenton's oxidation, Fenton's oxidation alone and the integration of Fenton's oxidation with coagulation/flocculation and biological treatment in SBR. The experimental results showed that:

- All combined processes, as well as and Fenton's oxidation alone led to a treated effluent that can be discharged into aquatic bodies. However, when applying Fenton's reaction alone the value of COD (232.8 mg O₂/L) is close to the maximum allowable value (250 mg/L);
- The integrated processes of coagulation/flocculation followed by Fenton's oxidation and Fenton's reaction followed by coagulation/flocculation led to the lowest operating costs (0.83 and 0.87 €/m³, respectively). These combinations allowed achieving high removal efficiencies of color (96.6 - 99.5%), COD and DOC (62.6 and 70.8% for COD, 64.4 - 66.1% for DOC) but BOD₅ removals slightly lower (~48%).

12.1.3 Brief Comparison of Processes

Table 12.1 compares the processes applied to the simulated effluents and industrial wastewater, as regards the compliance with legal discharge standards and costs associated with chemicals and energy consumption.

It is worth mentioning that the best treatment approach for cotton dyeing effluent, either simulated or industrial, is a combination of Coagulation/Flocculation plus Fenton's oxidation. Otherwise, for acrylic and polyester dyeing effluents, the photo-Fenton process proved to be the optimal choice.

Chapter 12 - Concluding Remarks and Forthcoming Work

Table 12.1 – Treatment approaches tested, analysis of compliance with maximum allowable values and operating costs for each simulated effluent and real wastewater tested. In bold are highlighted the cheapest strategies for each effluent that comply with legal limits for discharge.

Treatment Approach *	Simulated Effluents						Real Wastewater	
	Acrylic Dyeing		Cotton Dyeing		Polyester Dyeing		Cotton Dyeing	
	Compliance with Discharge Standards **	Operating Cost (€/m ³)	Compliance with Discharge Standards **	Operating Cost (€/m ³)	Compliance with Discharge Standards **	Operating Cost (€/m ³)	Compliance with Discharge Standards **	Operating Cost (€/m ³)
C/F	No	3.7	No	0.25	No	2.0	No	0.25
C/F + FR	Yes	7.0	Yes	0.83	Yes	3.1	Yes	0.83
FR	No	18.1	No	9.2	Yes	2.7	Yes	1.2
FR + C/F	Yes	9.1	Yes	4.6	Yes	1.3	Yes	0.87
PhFR	Yes	5.8	Yes	3.5	Yes	1.0	---	---
SBR	---	---	No	1.2	No	1.2	---	---
FR + SBR	Yes	14.8	Yes	5.8	Yes	2.6	Yes	2.1

* C/F – coagulation/flocculation; FR – Fenton's reaction; PhFR – photo-Fenton's reaction with solar radiation; SBR – sequencing batch reactor.

** According to Portuguese legislation – Ordinance No. 423/97 of 25 June.

12.2 Forthcoming Work

For future work it is suggested to study the possibility of recycling the iron sludge resulting from the Fenton process as catalyst in the same oxidation process or as coagulant, thus decreasing the treatment costs and avoiding the sludge deposition. Such approach could also be tested in reactors operating in continuous rather than discontinuous mode.

When applying the combination of Fenton's oxidation plus coagulation/flocculation or SBR it was possible to reduce the doses of chemicals in the oxidation stage while maintaining the compliance with the discharge limits. Such approach could also be tested in reactors operating in continuous rather than discontinuous mode.

With respect to the biological process it would be interesting to investigate the influence of the duration of each cycle and the duration of each phase of the cycle, as well as the effect of the temperature and other conditions on the efficiency of the biological degradation.

The treatment of industrial textile dyeing wastewaters by the photo-Fenton process using natural sunlight instead of simulated sunlight should be further studied and optimized.

The treatability study of the real cotton (and other) dyeing wastewater could include the optimization of each process or combination of processes, namely by using multivariate statistical tools.

Given the high treatment efficiency resulting from the application of the integrated process of coagulation/flocculation followed by Fenton's reaction and vice versa, and particularly to the real cotton dyeing wastewater, allowing obtaining an effluent that meets the discharge standards at low operating cost, the study should proceed in continuous mode operation for similar and other types of effluents.

Finally, this study could be extended by applying the electro-Fenton or electro-photo-Fenton processes to real textile dyeing effluents.



Appendix
Supporting Information

A.1 Supporting Information for Chapter 4

This appendix shows the experimental results obtained in the evaluation of the effect of the stirring speed and time of coagulation (Figures A.1 and A.2) and flocculation (Figures A.3 and A.4) on the synthetic cotton and polyester wastewaters treatment by coagulation/flocculation using Fe^{2+} as coagulant and Magnafloc 155 as flocculant.

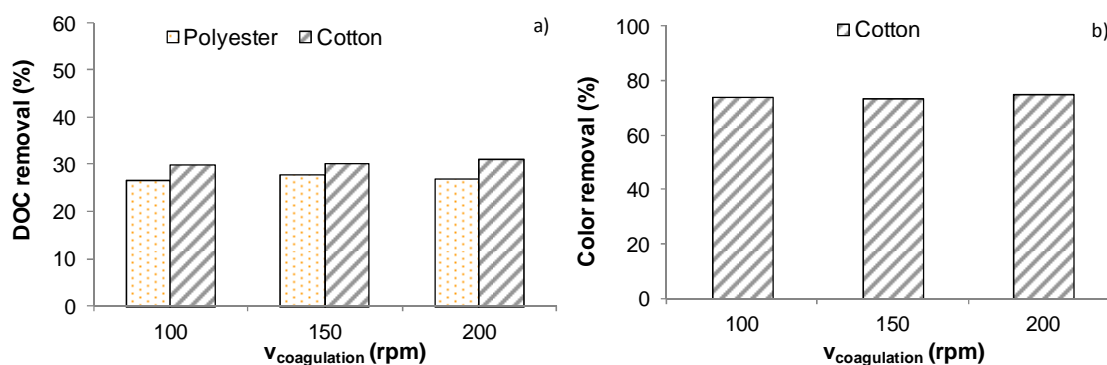


Figure A.1 – Influence of the stirring rate on the coagulation stage for DOC (a) and color (b) removal from polyester and cotton simulated effluents ($t_{\text{coagulation}}=3$ min, $T=T_{\text{ambient}}=23-25$ °C, $[\text{Fe}^{2+}]=200$ mg/L and $\text{pH}=8.3$).

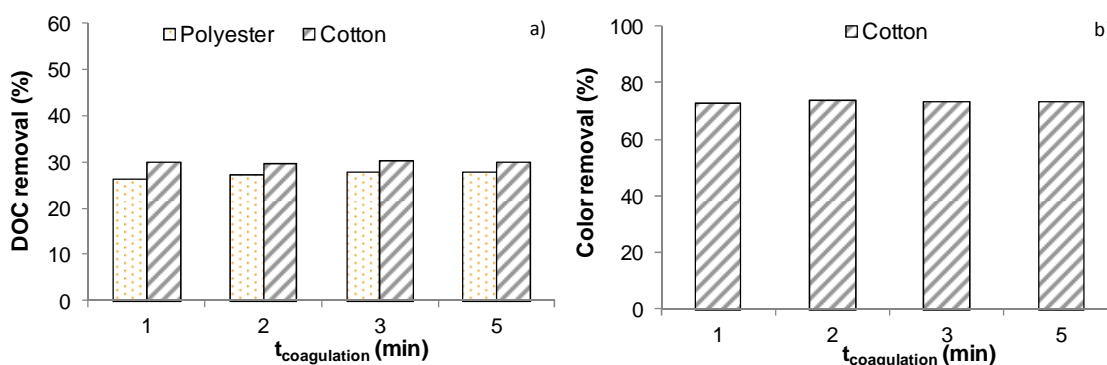


Figure A.2 – Effect of the coagulation time on DOC (a) and color (b) removal from polyester and cotton simulated effluents ($v_{\text{coagulation}}=150$ rpm, $T=T_{\text{ambient}}=22-24$ °C, $[\text{Fe}^{2+}]=200$ mg/L and $\text{pH}=8.3$).

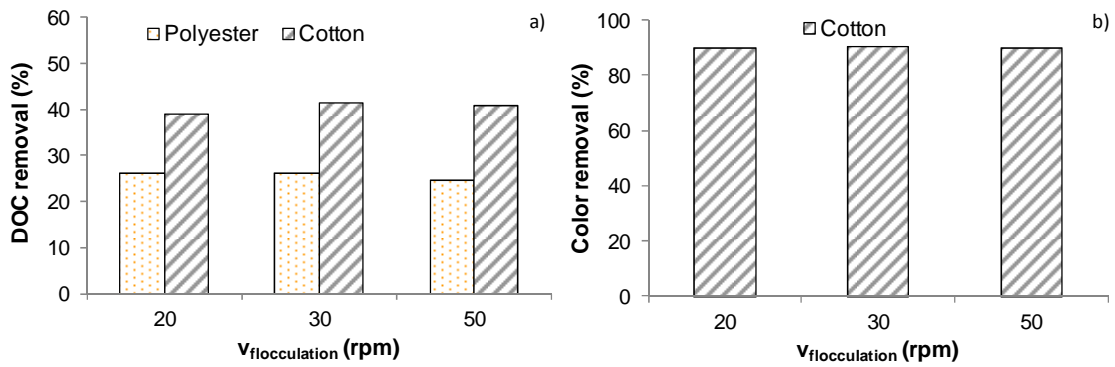


Figure A.3 - Variation of DOC (a) and color (b) removal with the stirring speed in the flocculation stage for polyester and cotton simulated effluents ($v_{\text{coagulation}}=150$ rpm, $t_{\text{coagulation}}=3$ min, $T=T_{\text{ambient}}=22-28$ °C, $\text{pH}_{\text{polyester}}=8.3$, $\text{pH}_{\text{cotton}}=9.4$, $[\text{Fe}^{2+}]_{\text{polyester}}=[\text{Fe}^{2+}]_{\text{cotton}}=200$ mg/L, $t_{\text{flocculation}}=15$ min and $[\text{Magnafloc 155}]=2.5$ mg/L).

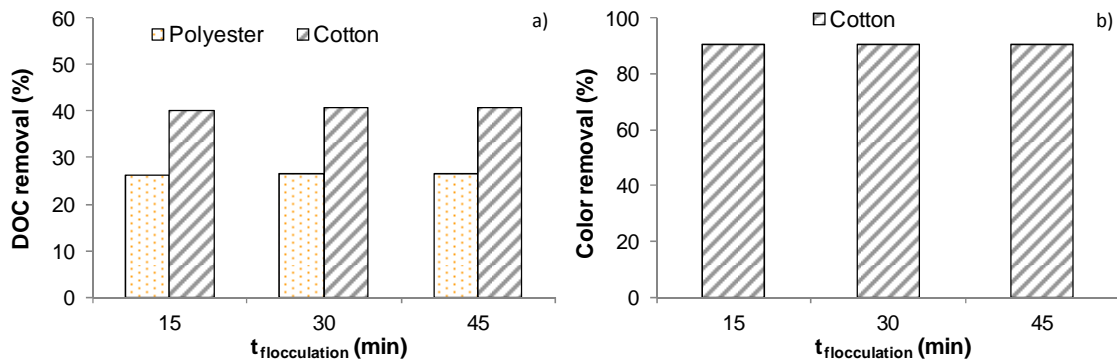


Figure A.4 – Influence of the flocculation time on DOC (a) and color (b) removal from polyester and cotton simulated effluents ($v_{\text{coagulation}}=150$ rpm, $t_{\text{coagulation}}=3$ min, $T=T_{\text{ambient}}=22-28$ °C, $\text{pH}_{\text{polyester}}=8.3$, $\text{pH}_{\text{cotton}}=9.4$, $[\text{Fe}^{2+}]_{\text{polyester}}=[\text{Fe}^{2+}]_{\text{cotton}}=200$ mg/L, $v_{\text{flocculation}}=20$ rpm and $[\text{Magnafloc 155}]=2.5$ mg/L).

A.2 Supporting Information for Chapter 9

Some experimental results obtained in the treatment of the simulated effluents by the photo-Fenton process are presented below.

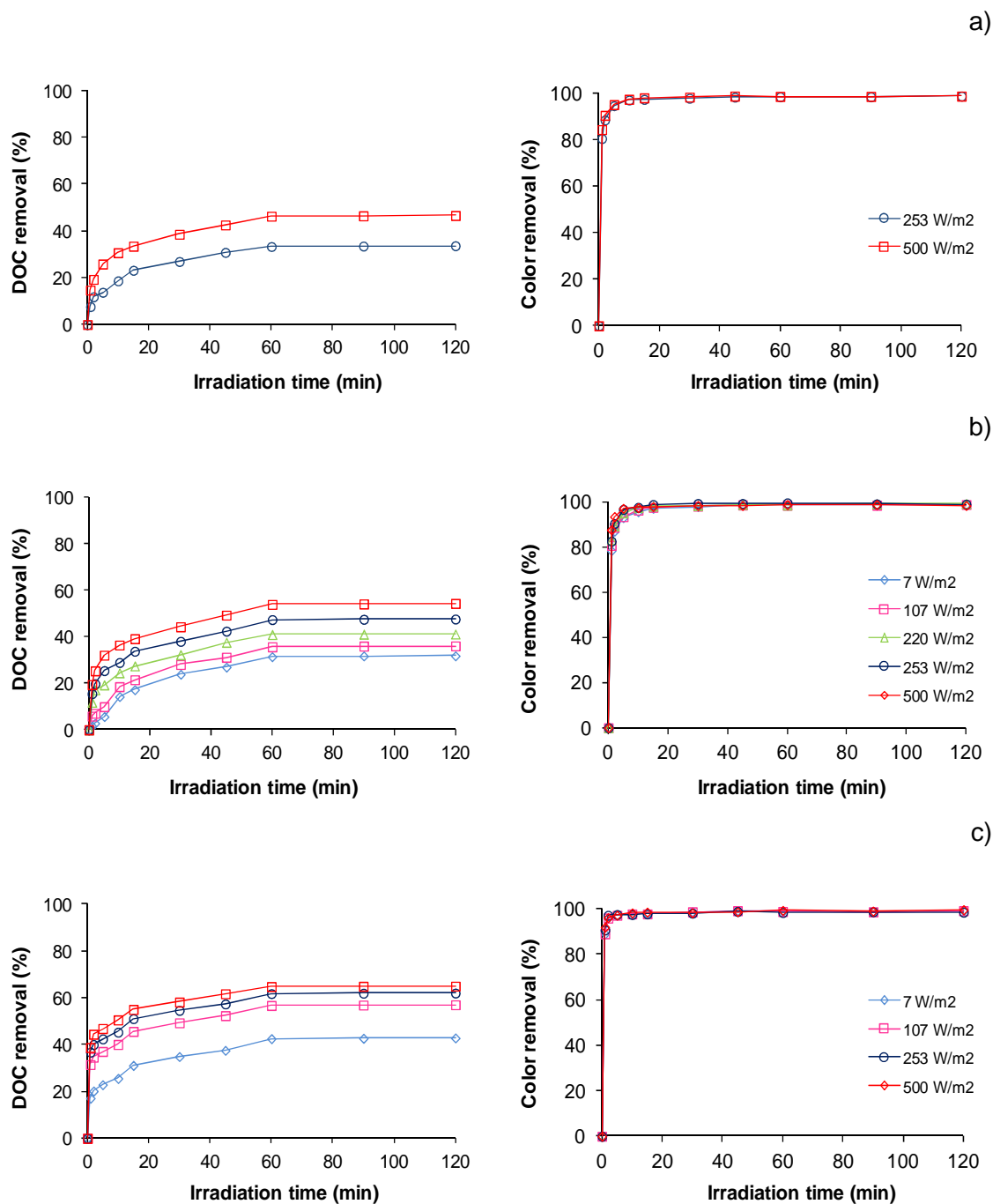
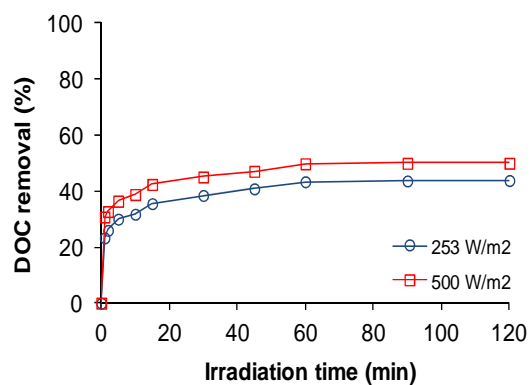
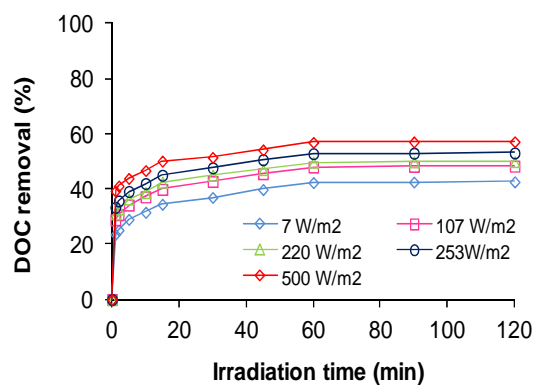


Figure A.5 – Effect of radiation intensity on DOC and color removal from the cotton effluent during the photo-Fenton process with artificial radiation for 3.75 g/L (a), 5 g/L (b) and 10 g/L (c) of hydrogen peroxide ($T=50\text{ }^{\circ}\text{C}$, $\text{Fe}^{2+}:\text{H}_2\text{O}_2=1:33$ and $\text{pH}=3.5$).

a)



b)



c)

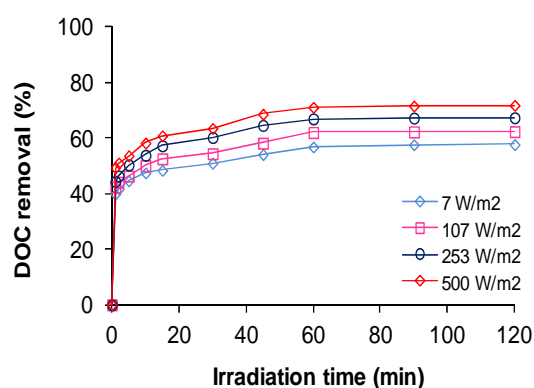


Figure A.6 – Effect of the radiation intensity on DOC removal from the polyester effluent during the photo-Fenton process for 0.938 g/L (a), 1.25 g/L (b) and 2.5 g/L (c) of hydrogen peroxide (T=50 °C, Fe²⁺:H₂O₂=1:7 and pH=3.5).

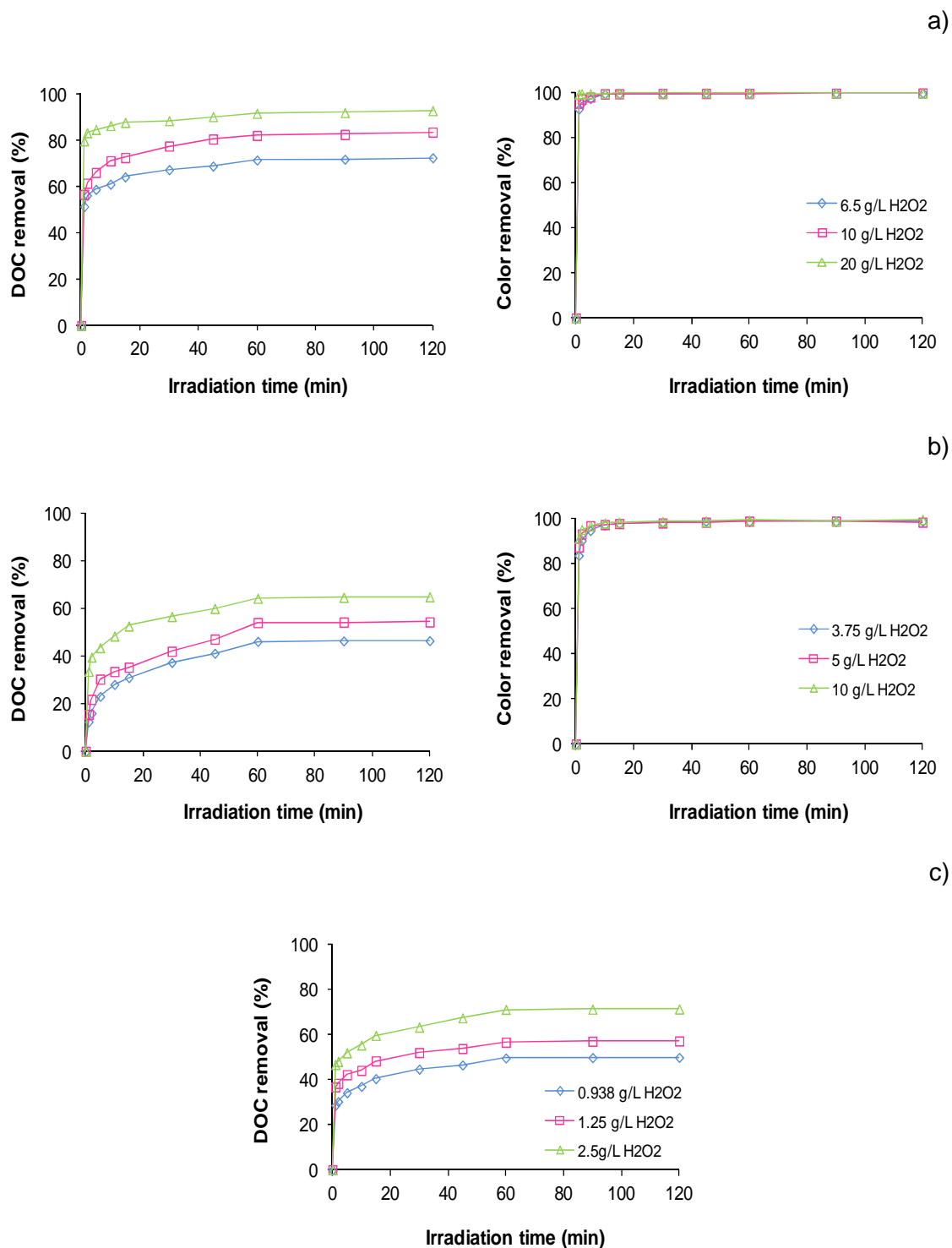


Figure A.7 – Effect of H₂O₂ dose on DOC and color removal from the acrylic (a), cotton (b) and polyester (c) effluents using photo-Fenton's oxidation with simulated sunlight (radiation intensity = 500 W/m², T=50 °C, Fe²⁺:H₂O₂_{acrylic} =1:57, Fe²⁺:H₂O₂_{cotton} =1:33 Fe²⁺:H₂O₂_{polyester} =1:7, pH=3.5).