Azo-dye Orange II degradation by Fenton's reaction using Fe/ZSM-5 zeolite as catalyst

FILIPA DUARTE & LUIS M. MADEIRA *

LEPAE, Departamento de Engenharia Química, Faculdade de Engenharia da Universidade do Porto,
Rua Dr. Roberto Frias, 4200-465 Porto, Portugal. mmadeira@fe.up.pt

Abstract

This work deals with the non-biodegradable azo-dye Orange II degradation using the heterogeneous Fenton-like reaction using Fe/ZSM-5 zeolite as catalyst. The influence of some relevant parameters was studied, namely pH and temperature in the ranges 3.0 – 8.5 and 30 – 53 ºC, respectively. Decolorization degree, TOC removal and leaching were evaluated along time in the experiments done. It was found that temperature has a predominant effect in OII concentration and TOC reduction while pH is more important in the metal loss from the support. Degradation increases with temperature and leaching decreases when initial pH value increases. It was possible to decolorized OII under less acidic conditions than those conventionally performed in Fenton's oxidation, compensating this with the increase of temperature (30 to 35 ºC for a pH increase from 3.0 to 5.2), which is a promising approach since textile effluents are characterized by high temperatures and pH values.

Key Words : Orange II, heterogeneous Fenton, leaching, zeolites

1 Introduction

Pollution of water caused by industries is a serious problem all over the world and its elimination is a great challenge. For instance, to destroy synthetic dyes is to some extent difficult because they are usually stable compounds and often non-biodegradable or even toxic, formed by long organic molecules. Advanced chemical oxidation methods can be effective for their degradation as they can result in almost complete mineralization in a non-expensive and easy way. One of the most well-known methods is the oxidation with Fenton's reagent, where hydrogen peroxide reacts with iron in acidic medium, leading to the production of powerful radicals (HO•), which are able to attack the organic compounds [1].

The advantages of the Fenton's process are focused in its simplicity, in the fact of being accomplished under moderate operating conditions (atmospheric pressure and temperatures close to the room one) and in the low investment cost, once it doesn't require specific equipment. On the other hand, Fenton process uses H_2O_2 as oxidant, which self-decomposition leads to non-toxic products (H_2O and O_2).

The Fenton reaction can be carried out in a homogeneous or heterogeneous system. The first process is often not adequate because it leads to a very high metal concentration in solution, ca. 50-80 ppm, while European directives don't allow more than 2 ppm of Fe in discharged water [2]. Thus, the heterogeneous process has been the focus of intensive research, aiming to introduce the catalyst into different supports. In particular, zeolites containing transition metal ions have been shown to be promising solid-phase catalysts in the oxidation of a series of organic pollutants with hydrogen peroxide [3], and several papers have recently reported that heterogeneous zeolite-based Fe catalysts could even provide similar catalytic activities as homogeneous Fe(II) ions [e.g., 4].

In this work, the Fenton's reaction has been carried out using Fe as active phase, supported on a commercial ZSM-5 zeolite. The influence of the main parameters on the azo-dye Orange II degradation has been studied, such as temperature and pH. Temperatures around 30 ºC and pH values close to 3 are known to be the optimum conditions for the Fenton's reaction, even in heterogeneous systems [5]. However, textile effluents are characterized by higher values of pH and temperature [6-7]. Therefore, one of the main objectives of this study is to evaluate the possibility of treating such wastewaters under higher pH values, avoiding acid consumption in the pre-acidification stage and increasing catalyst stability (by decreasing metal leaching). To compensate the increase of pH, temperature was increased too and to evaluate the performances reached, decolourization, degree of mineralization and iron leaching were evaluated.

2 Materials and Methods

In order to determine the catalyst iron content (commercial Alsi-Penta Fe/ZSM-5 zeolite, ref. FE-SH-27, was used), ICP (Inductively Coupled Plasma) analyses were made.

The dye degradation experiments were performed in a slurry batch reactor provided with a magnetic stirrer and operated at atmospheric pressure, using a 0.1 mM Orange II (OII, the model compound) solution, which is in the range of azo dyes' concentrations usually found in industrial waste streams [8]. Temperature was studied in the range 30 ºC – 53 ºC and it was controlled by coupling a thermostatic bath (Huber, Polystat CC1) to the jacketed reactor. Initial pH was varied from 3.0 to 8.5, being adjust with a 0.1 M solution of H_2SO_4 or NaOH.

After stabilization of temperature and pH, the powder catalyst (0.2 g L^{-1}) and H_2O_2 (6 mM, 30 wt.%, Merck) were added, this being considered the initial instant of the reaction (t = 0). The absorbance was continuously read by a Philips PU8625 UV/VIS spectrophotometer at maximum absorbance wavelength of 486 nm (characteristic wavelength of the Orange II molecule and corresponding to a region wherein interference by oxidation products does not exist [9]), what required the use of a flow-through cell and recirculation of the reaction mixture by a peristaltic pump. Temperature, pH and absorbance are registered and recorded along time using the in-house designed LabVIEW 5.0 software interface. Besides, samples were regularly taken for evaluation of both metal leaching, quantified by a UNICAM 939/959 atomic absorption spectrophotometer, and for the evaluation of the degree of mineralization by Total Organic Carbon - TOC analysis in a TOC-500A equipment from Shimadzu. Before that, samples were filtered through Albert FV-C microfibre glass filter paper and sodium sulphite added to instantaneously consumed residual hydrogen peroxide.

Some runs were performed in duplicate and it was possible to conclude that for the same instant, OII concentrations do not differ more than 6%.

3 Results and Discussion

The catalyst was analysed by ICP and the results show 4.8 wt. % of Fe and Si/Al = 10.35.

Adsorption tests were firstly carried out at the different temperatures and pH values tested and the OII elimination was negligible after 9 hours. Besides, OII removal by the action of H_2O_2 alone was also not observed.

Experiments at pH = 5.2 (natural pH of the OII solution) were then carried out at different temperatures, in the range 30-53 ºC. Higher temperatures were not used because this way thermal decomposition of hydrogen peroxide would be favoured. It was observed that the rate of the OII degradation rises with the increase of this parameter, as expected, due to the increase of the kinetic rate constants (Arrhenius dependence). Dye concentration histories are shown in Fig. 1a). TOC values are also in agreement with this trend since the higher mineralization degrees are verified at the higher temperatures (Fig. 1b). In spite of this, high TOC removal is not achieved, which is probably related to peroxide stability, worse at high temperatures. Leaching values are also higher at the highest temperatures (Fig. 1c). At an initial pH value of 5.2 and 53 ºC colour removal is almost complete after 3-4 h, but the mineralization degree is low, even after 24 h of operation (25.6 %). The concentrations of Fe in solution are low (<0.12 mg/L), corresponding to a loss of metal of only 1.20 % (see also Table 1).

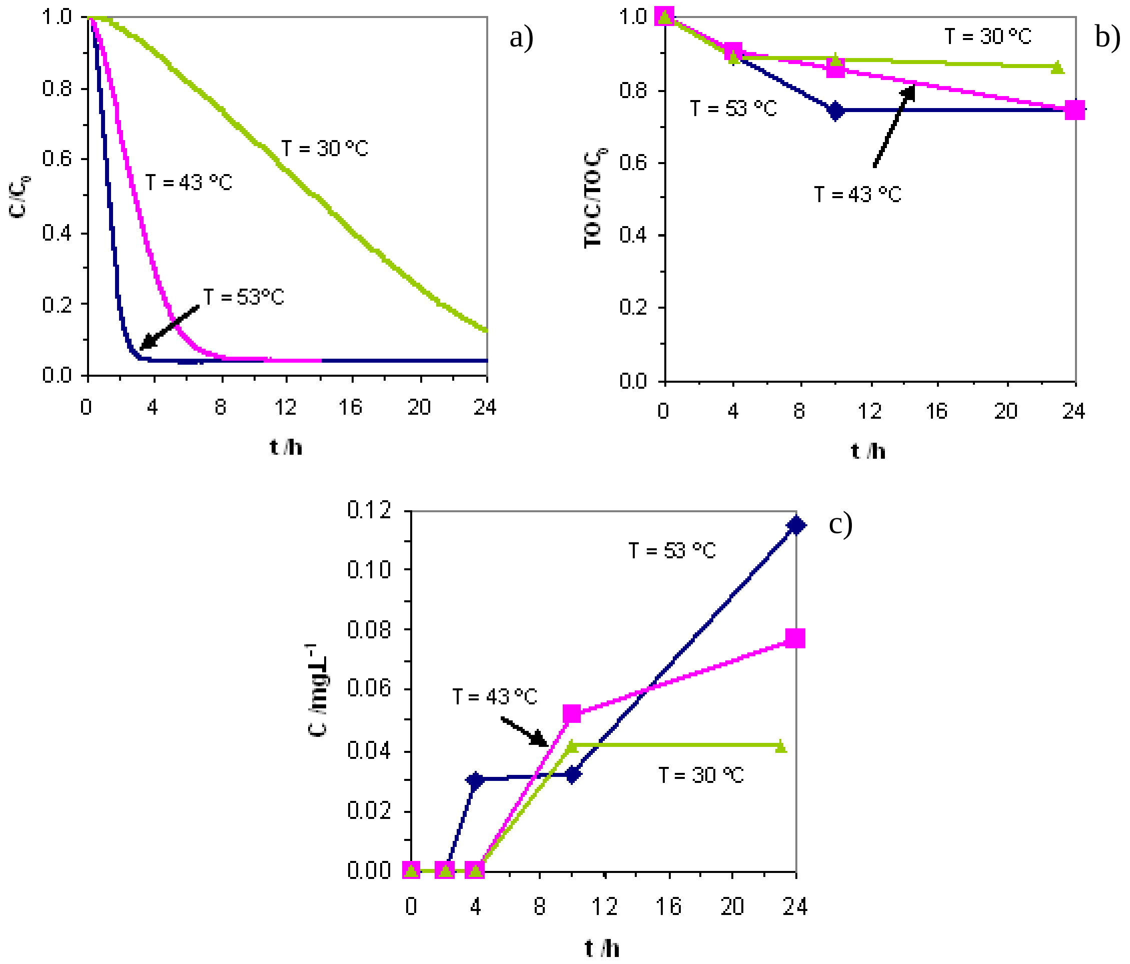

Figure 1. OII degradation at natural pH of the solution (5.2) at different temperatures (a) and the corresponding TOC removal (b) and leaching values (c) (C_{OII} = 0.1 mM, C_{cat} = 200mg.L^{-1}, C_{H2O2} = 6 mM).

To study the effect of pH, experiments at 30 ºC and 53 ºC were carried out at initial pH of 3.0, 5.2 (natural pH of the solution) and 8.5 (see Table 1). The highest pH value leads to a slower OII degradation, as evidenced by the increase in the time required to achieve a dye removal of 50 % ($t_{½}$), particularly at 53 ºC. This trend was already expected since the optimum pH is usually around 3 for the Fenton's reaction, even with heterogeneous systems [5,8,9]. It is worth noting that the effect of pH in OII concentration reduction was not as significant as that of temperature. On the other hand, the increasing pH led to lower leaching values, being now the effect of this parameter (pH) more pronounced than that of temperature. At pH = 8.5, Fe leached out amounts to only 0.23 or 0.66% at 30 and 53 ºC, respectively.

Regarding the pH evolution during each experiment, it is possible to conclude that it decreases after catalyst and peroxide addition, which is probably due to the catalyst itself and the production of H^+ ions in the hydrogen peroxide decomposition [10]. The contribution of oxidation products from OII degradation is here very small hence in absence of the organic compound, the pH decrease was also verified (data not shown).

This pH decrease at the beginning of the experiments brings an importance advantage from the industrial point of view because it allows operating at higher pH values without requiring intensive acidification. Although catalytic performances are not as good as under acid conditions, results obtained allow concluding that at 53 ºC the process runs efficiently at initial pH values up to 5.2. Under such conditions Fe leached out is ≤ 1.20 %, pointing for a good stability of this catalyst. At pH 8.5 the process slows down, and there is no mineralization (cf. Table 1). Operating at temperatures close to 30 ºC, although with the advantage of decreasing Fe leaching, the use of an initial pH ≥ 5.2 would require, for instance, the use of a higher amount of catalyst and/or radiation (photo-Fenton process), otherwise the process runs too slowly.

Table 1. Half-life time values for OII decolorization, TOC conversion and leaching values after 24 hours of reaction at different initial pH values and temperatures.

		Decolorization $t_{½}$ (h)	$X_{TOC,\,24h}$ (%)	$C_{Fe,\,24h}$ ($mg.L^{-1}$) *
pH = 3.0	T = 30 ºC	8.2	17.9	0.126 (1.31 %)
	T = 53 ºC	0.9	30.9	0.161 (1.68 %)
pH = 5.2	T = 30 ºC	13.5	13.6	0.042 (0.44 %)
	T = 53 ºC	1.3	25.6	0.115 (1.20 %)
pH = 8.5	T = 30 ºC	13.9	≈ 0	0.022 (0.23 %)
	T = 53 ºC	7.0	≈ 0	0.063 (0.66 %)

[*] Values between brackets refer to the percentage of Fe lost from the support.

Regarding the leaching phenomenon, the results suggest that oxidation products can promote the metal loss from the support. Figure 2 shows that at pH = 3.0, this loss increases just from the beginning of the reaction, whereas at pH = 8.5, where catalytic activity is lower, it is only verified after a certain time. At T = 30 ºC, where the decolorization is slower, this time-lag is large (10 h – Fig. 2a), decreasing significantly to only ca. 4 h at 53 ºC (Fig. 2b).

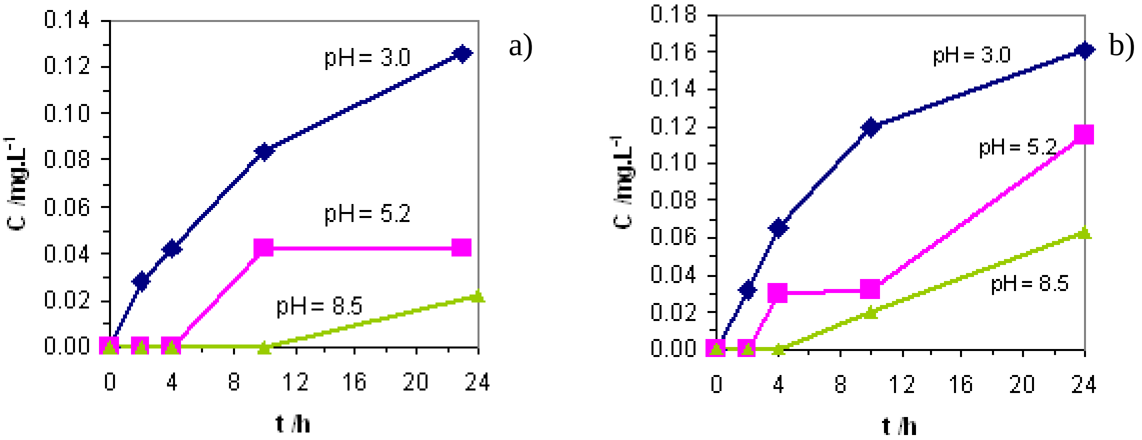

Figure 2. Leaching values for experiments running under different initial pH values at T = 30 ºC (a) and T = 53 ºC (b). (C_{OII} = 0.1 mM, C_{cat} = 200 mg.L^{-1}, C_{H2O2} = 6 mM).

As it was shown, it is possible to remove OII at pH values and temperatures higher than those of reference in Fenton´s process, which is promising since textile effluents use to be characterized by high temperatures and pH values. Thus, experiments were performed in order to observe how the increase of pH can be compensated by the increase of temperature. Figure 3a shows that the increase of the pH from 3.0 to 5.2 can be compensated with an increase in the reaction temperature of only 5 ºC (from 30 ºC to 35 ºC), yielding both experiments similar OII degradation profiles. Besides, at a pH as high as 8.5, a temperature of only 40 ºC is enough to yield even better decolourization performances. On the other hand, less iron was lost from the support under such conditions (Fig. 3b). This issue can be very useful in real practice if one aims mainly decolorization. If further oxidation is aimed, other approaches are required. Actually, to improve the performances, namely the TOC removal, the possibility of using the photo-Fenton process should be envisaged. On the other hand, it may be interesting to divide the addition of peroxide in 2 or 3 times, avoiding its consumption along the reaction in a non-efficient way, particularly at high pH and/or temperatures. These issues will be the aim of future work.

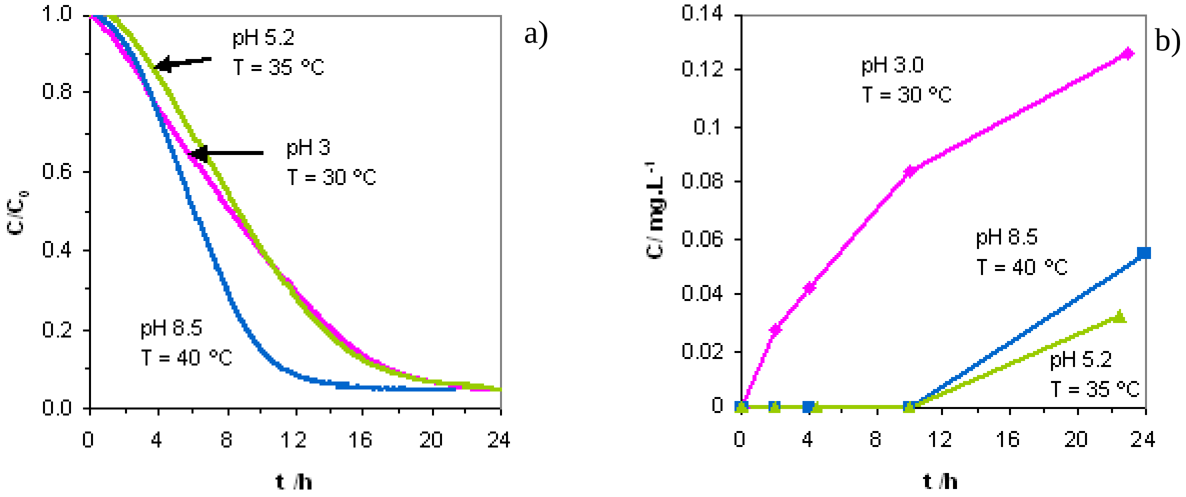

Figure 3: OII degradation profiles at different temperature and pH values (a) and leaching values (b).

4 Conclusions

The azo-dye OII degradation by heterogeneous Fenton’s reagent using Fe/ZSM-5 zeolite as catalyst was studied in terms of decolorization, TOC removal and metal loss by the support (leaching). This process is faster at lower initial pH values and higher temperatures in the ranges studied (3.0-8.5 and 30-53 ºC, respectively). At pH = 5.2, natural pH of the dye solution, total decolorization is almost achieved at the highest temperatures in only 3-4 h, but this is not followed by TOC removal, which was of only 25.6 %. This can be a consequence of the parallel consumption of the peroxide by thermal self- decomposition, which increases with temperature and pH. Actually, at pH = 8.5, TOC removal values were insignificant.

Leaching values were very low in all the experiments, being always much lower than the limit imposed by European directives (2 mg.L^{-1}). This is not only good for environment and human health but also it allows the catalyst reutilization or stability in batch or continuous operation. Iron loss increases with the temperature and decreases with the increasing of pH values. This last parameter has here a predominant role, whereas the temperature has a larger influence in dye degradation. On the other hand, the leaching results suggest that the oxidation products might have an important contribution for this phenomenon.

This work shows that it is possible to work above the reference pH value for the Fenton’s process (3.0), taking advantage of the high temperature of textile effluents. This is a promising approach since one can treat effluents without important acid and energy consumption.

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