Research Article

Received: 22 March 2019 Revised: 8 May 2019 Accepted article published: 15 May 2019

(wileyonlinelibrary.com) DOI 10.1002/jctb.6080

Screening of heterogeneous catalysts for the activated persulfate oxidation of sulfamethoxazole in aqueous matrices. Does the matrix affect the selection of catalyst?

Rui S Ribeiro,[a,b] Zacharias Frontistis,[c] Dionissios Mantzavinos,[d*]
Adrián M T Silva,[a] Joaquim L Faria[a] and Helder T Gomes[a,b*]

Abstract

BACKGROUND: The contribution of persulfate oxidation to water treatment technologies based on advanced oxidation processes is nowadays widely accepted. However, the importance of the water matrix on the removal of micropollutants has been neglected during early screening of heterogeneous catalysts, which can hinder further developments in the field.

RESULTS: Three magnetic graphitic nanocomposites (MGNCs), obtained by carbon encapsulation of magnetite (Fe_3O_4), nickel ferrite ($NiFe_2O_4$) and cobalt ferrite ($CoFe_2O_4$), were prepared and employed as heterogeneous catalysts in the activation of persulfate for the degradation of antibiotic sulfamethoxazole (SMX). The importance of the water matrix and its constituents on the performance of the MGNC materials was assessed. It was found that their relative performance in terms of oxidation of SMX in pure water decreases in the order: $NiFe_2O_4$/MGNC > Fe_3O_4/MGNC > $CoFe_2O_4$/MGNC. However, the order changed (Fe_3O_4/MGNC > $NiFe_2O_4$/MGNC > $CoFe_2O_4$/MGNC) when drinking water or secondary treated wastewater were employed. The individual effects of the water matrix constituents, such as bicarbonate, chloride, pH, and humic acid, or the use of added radical scavengers, on the catalyst performance were investigated, while the heterogeneous nature of the process was confirmed through leaching tests.

CONCLUSION: A realistic water matrix should be considered throughout all the steps involved in the evaluation of new heterogeneous catalysts for the activated persulfate oxidation of SMX. Otherwise, misleading conclusions may be drawn, limiting potential improvements of this treatment technology.

Keywords: catalytic activity; contaminants of emerging concern; magnetic graphitic nanocomposites; water quality

INTRODUCTION

The inadequacy of conventional water treatments based on biological processes to remove persistent organic contaminants from water matrices has driven the scientific community towards the study of alternative treatment processes and related technologies, such as the so-called Advanced Oxidation Processes (AOPs) and Advanced Oxidation Technologies (AOTs). Different AOPs and AOTs have been studied, including photocatalysis,[1] ozonation,[2] electro-oxidation,[3] cavitation,[4] Fenton process,[5] catalytic wet air oxidation,[6] catalytic wet peroxide oxidation[7] and persulfate oxidation.[8] They were initially regarded as relying on the generation of hydroxyl radicals ($HO^\bullet$), which subsequently act as the active species for the destruction of the organic pollutants present in water.[9] Nowadays, the participation of other reactive oxygen species is also recognized. This is the case of persulfate oxidation, in which highly reactive sulfate radicals ($SO_4^{\bullet-}$) are formed upon activation of the persulfate anion ($S_2O_8^{2-}$).[8] Among the different strategies for persulfate activation (e.g. thermal, alkaline, ultraviolet, ultrasonic, electrochemical and/or adding catalysts),[8,10] the application of transition metals allows obtaining $SO_4^{\bullet-}$ through a reaction mechanism similar to that of the

---

* Correspondence to: D Mantzavinos, Department of Chemical Engineering, University of Patras, 2 Seferi St., GR-30100 Agrinio, Greece, E-mail: mantzavinos@chemeng.upatras.gr; or HT Gomes, Instituto Politécnico de Bragança, Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300–253 Bragança, Portugal. E-mail: htgomes@ipb.pt

a Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials (LSRE-LCM), Faculdade de Engenharia, Universidade do Porto, Porto, Portugal

b Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Bragança, Portugal

c Department of Environmental Engineering, University of Western Macedonia, Kozani, Greece

d Department of Chemical Engineering, University of Patras, Patras, Greece

Fenton process (cf. Eqns (1) and (2)), i.e. via a one-electron transfer mechanism from the ferrous ion (Fe^{2+}) to $S_2O_8^{2-}$.[11] Secondary $HO^\bullet$ radicals are also expected to participate in the activated persulfate treatment, as they can be obtained through the reaction described in Eqn (3).[8,11] In this case, the participation of $HO^\bullet$ radicals becomes increasingly relevant as the solution pH increases.[8,12] In addition, a non-radical mechanism was also reported.[12,13] This alternative reaction pathway is based on the ability of persulfate to act as electron acceptor; it involves electron transfer from the organic pollutant to persulfate, occurring preferably in the presence of an electron transfer mediator (e.g. conductive materials such as carbon nanotubes).[13] A non-radical reaction mechanism involving the formation of singlet oxygen ($^1O_2$) has also been reported.[14]

$$S_2O_8^{2-} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-} + SO_4^{\bullet -} \quad (1)$$

$$Fe^{3+} + S_2O_8^{2-} \rightarrow Fe^{2+} + S_2O_8^{\bullet -} \quad (2)$$

$$SO_4^{\bullet -} + OH^- \rightarrow SO_4^{2-} + HO^\bullet \quad (3)$$

In order to avoid the typical constrains of using homogenous catalysts, our previous studies were focused on the application of magnetic carbon xerogels containing iron and/or cobalt microspheres embedded in its structure to promote persulfate activation.[14,15] In those studies, the ability of the heterogeneous catalysts for activated persulfate oxidation was evaluated using different model systems for contaminants of emerging concern. In both cases, it was found that the efficiency of the treatment decreases when ultrapure water is replaced by environmentally relevant water matrices, such as drinking water and secondary treated wastewater.[14–16] Several examples of similar phenomena were also reported for other heterogeneous AOPs,[17,18] including our previous studies.[19,20] In spite of the recognized impact resulting from the type of water matrix,[21] the performance of new catalytic systems developed for AOPs is still widely evaluated using unrealistic water matrices, mainly laboratory grade water (distilled or ultrapure), containing the model pollutant under consideration.[22,23]

The continuous developments achieved in the field of materials science pose an enormous potential to improve the efficiency of the different AOPs and AOTs. In that sense, the goal of this study is to provide further insights on the importance of the water matrix during the preliminary evaluation of heterogeneous catalysts for activated persulfate oxidation, i.e. during the initial screening of catalysts. Unlike the common practice, in which different catalysts are initially employed in unrealistic water matrices to select the best performing system for additional studies, the performances of three hybrid magnetic graphitic nanocomposites (MGNCs) were compared in this work using drinking water and secondary treated wastewater, in addition to ultrapure water. The MGNC materials prepared in our previous work were employed for that purpose.[24] These materials are core-shell structures composed of a magnetic core and a carbonaceous shell, which were obtained by hierarchical co-assembly of magnetite (Fe_3O_4), nickel ferrite ($NiFe_2O_4$) and cobalt ferrite ($CoFe_2O_4$) nanoparticles, and carbon precursors, followed by thermal annealing.[24] The antibacterial agent sulfamethoxazole (SMX), often found throughout the urban water cycle,[25,26] was selected as a model system of persistent micropollutants. Sodium persulfate (SPS) was used as a source of persulfate radicals.

MATERIALS AND METHODS

Chemicals

SMX (analytical standard), acetonitrile (99.9 wt%), humic acid (technical grade), sodium bicarbonate (99.7 wt%), sodium chloride (99.8 wt%), sodium hydroxide (98 wt%), SPS (99 wt%) and sulfuric acid (95 wt%) were purchased from Sigma-Aldrich (Buchs, Switzerland). *N*,*N*-Diethyl-*p*-phenylenediamine (99 wt%), monosodium phosphate (99 wt%), disodium phosphate (99 wt%) and *tert*-butanol (*t*-BuOH, 99 wt%) were obtained from Fluka, Buchs, Switzerland. Methanol (MeOH, 99.9 wt%) was purchased from Riedel-de-Haën, Seelze, Germany.

All chemicals were used as received, without further purification.

Water matrices

SMX solutions were prepared in: (i) ultrapure water ($pH = 6.5$; 0.056 µS cm^{-1} conductivity); (ii) drinking water ($pH = 7.8$; 357 µS cm^{-1} conductivity; 250 mg L^{-1} bicarbonates; 9.1 mg L^{-1} sulfates; 5.0 mg L^{-1} chlorides) obtained from a bottle of the commercially available brand Zagori®, Greece; (iii) secondary treated wastewater ($pH = 7.9$; 6.2 mg L^{-1} total organic carbon; 1.07 mg L^{-1} total suspended solids; 18.9 mg L^{-1} chemical oxygen demand; 311 µS cm^{-1} conductivity; 30 mg L^{-1} sulfates; 0.44 mg L^{-1} chlorides) collected from the wastewater treatment plant of the University of Patras, Greece; and ultrapure water in the presence of (iv) sodium chloride (5.0 mg L^{-1} chlorides), (v) sodium bicarbonate (250 mg L^{-1} bicarbonates), (vi) humic acid (10 mg L^{-1}) and (vii) MeOH or *t*-BuOH (10 g L^{-1} either) used as radical scavengers.[10]

Synthesis of hybrid magnetic graphitic nanocomposites (MGNCs)

The hybrid MGNCs were prepared as described in our previous work, by hierarchical co-assembly of magnetic nanoparticles and carbon precursors, followed by thermal annealing.[24] Magnetite (Fe_3O_4), nickel ferrite ($NiFe_2O_4$) and cobalt ferrite ($CoFe_2O_4$) were prepared by co-precipitation and then encapsulated within carbonaceous frameworks, producing three different materials. The materials were denoted as X/MGNC, in which X represents the magnetic material. Additional details on the synthesis procedure are provided in our previous publication.[24]

Experimental procedure

Activated persulfate oxidation experiments were performed at room temperature ($T = 25 \pm 1$ °C), in a cylindrical glass reactor (internal diameter = 6 cm; height = 9.5 cm) with magnetic stirring (500 rpm). The reactor was loaded with a SMX solution (75 mL; 500 µg L^{-1}, prepared in the water matrices described in the Water matrices section), the catalyst was loaded (50 mg L^{-1}) and SPS (250 mg L^{-1}) was added. When necessary, the solution pH was adjusted before catalyst addition, by means of sodium hydroxide and sulfuric acid solutions. In all cases, the reaction was allowed to proceed without further pH conditioning, during 2 h.

Pure adsorption experiments were performed in the absence of SPS, while non-catalytic experiments were performed in the absence of catalyst. Leaching tests were performed by removing the catalyst after 30 min of reaction and allowing the reaction to proceed further.

The standard deviation of the SMX determination was never greater than 2.5% in selected experiments performed in duplicate.

Table 1. Properties of the magnetic graphitic nanocomposite (MGNC) materials: specific surface area (S_{BET}), micropore volume (V_{micro}), total pore volume (V_{total}), pH at the point of zero charge (pH_{PZC}), ash content, and crystallographic phases (data collected from Ribeiro *et al.* [24])

	Parameter					
Material	$S_{BET}{}^{a}$ ($m^2\ g^{-1}$)	$V_{micro}{}^{a}$ ($cm^3\ g^{-1}$)	$V_{total}{}^{a}$ ($cm^3\ g^{-1}$)	$pH_{PZC}{}^{b}$	Ashes[c] (wt%)	Crystallographic phases[d]
Fe_3O_4/MGNC	330	0.07	0.31	7.1	27.3	Magnetite, graphite, maghemite, iron and traces of hematite (proto)
$NiFe_2O_4$/MGNC	345	0.10	0.29	8.7	10.4	Nickel ferrite, graphite and nickel
$CoFe_2O_4$/MGNC	330	0.07	0.31	9.0	14.4	Cobalt ferrite, graphite and iron

[a] Determined from nitrogen adsorption–desorption isotherms at −196 °C.
[b] Obtained by pH drift tests.
[c] Determined by thermogravimetric analysis (TGA).
[d] Identified by X-ray diffraction (XRD).

Analytical methods

SMX concentration was determined by high performance liquid chromatography (HPLC), using a previously described method.[19] An excess of MeOH was added to each aliquot withdrawn from the reactor in order to stop the reaction instantaneously. The amount of SPS was determined by a colorimetric method with *N*,*N*-diethyl-*p*-phenylenediamine, adapting the procedure described elsewhere.[27]

RESULTS AND DISCUSSION

Catalyst characterization

Fe_3O_4/MGNC, $NiFe_2O_4$/MGNC and $CoFe_2O_4$/MGNC are core-shell hybrid materials obtained by encapsulation of Fe_3O_4, $NiFe_2O_4$ and $CoFe_2O_4$ nanoparticles within carbon frameworks.[24] The most relevant textural and surface chemistry properties of these materials are summarized in Table 1. A thorough characterization can be found in our previous publication.[24]

Activated persulfate oxidation experiments: the importance of the water matrix

The performance of the MGNC materials for the activated persulfate oxidation of SMX (500 μg L^{-1}) was initially evaluated in ultrapure water. SMX conversions obtained after 2 h of reaction are given in Fig. 1(a). For comparison purposes, SMX removal obtained in pure adsorption runs is also provided. As shown in our previous publication, adsorption of antibiotic substances over graphitic materials is usually a multilayer process involving mainly electronic interactions rather than strong chemical interactions.[28] In this case, a direct comparison between SMX removals obtained by adsorption and persulfate oxidation should not be performed as both SMX and SPS are expected to compete for the same active sites/functional groups during persulfate oxidation experiments.[29] Indeed, it was demonstrated in our previous publication that the amount of SMX (and its oxidation by-products) adsorbed on the catalyst surface after the activated persulfate treatment is negligible when hybrid magnetic carbon nanocomposites are employed.[19] Nevertheless, the higher SMX removal obtained in the presence of SPS, when compared to those obtained only in the presence of the MGNC materials (i.e. by adsorption), confirms that the three MGNC materials are active for persulfate oxidation. The non-catalytic SMX removal obtained under the same conditions, but in the absence of catalyst, is negligible, corresponding to less than 10% of its initial content. It can also be observed that the highest SMX removal is obtained in the presence of $NiFe_2O_4$/MGNC. Therefore, based on the results shown in Fig. 1(a), it is concluded that $NiFe_2O_4$/MGNC is the MGNC material with the best performance for the activated persulfate oxidation of SMX. This is usually a fair assumption. However, it may be an oversimplified conclusion, as ultrapure water is an unrealistic simple water matrix. In order to explore this hypothesis, additional experiments were performed under the same conditions, except that ultrapure water was replaced by drinking water (additional details on this water matrix are given in the Water matrices section). As observed in Fig. 1(b), the non-catalytic SMX removal obtained under these conditions is still negligible (*ca* 5%), actually decreasing when compared to that obtained in ultrapure water. Likewise, the SMX removal obtained in the presence of $NiFe_2O_4$/MGNC and $CoFe_2O_4$/MGNC also decreases. This detrimental effect is particularly relevant in the presence of $CoFe_2O_4$/MGNC, the SMX removal obtained by persulfate activation being actually lower than that obtained by pure adsorption (possibly due to some competition for the active/adsorptive sites at the surface of the catalyst).

The decrease of pollutant removal observed when ultrapure water is replaced by drinking water is usually explained by radical scavenging promoted by inorganic species such as bicarbonates (250 mg L^{-1}) and chlorides (5.0 mg L^{-1}).[15] However, exceptions to this behavior were already reported, as in a recent publication of our group.[16] In the present study, unlike the detrimental effect observed when $NiFe_2O_4$/MGNC and $CoFe_2O_4$/MGNC are employed, the SMX removal obtained by activated persulfate oxidation in the presence of Fe_3O_4/MGNC is unaffected when ultrapure water is replaced by drinking water (cf. Fig. 1(a, b)). Consequently, based on the results given in Fig. 1(b), it is concluded that Fe_3O_4/MGNC is the MGNC material with the best performance for the activated persulfate oxidation of SMX. This is in direct contradiction with the conclusion previously drawn from the analysis of the results given in Fig. 1(a). In order to provide further insights on this subject, experiments with secondary treated wastewater (additional details on this water matrix are given in the Water matrices section) were also performed. As observed in Fig. 1(c), the SMX removal obtained under these conditions is always below 30% of its initial content. If the results given in Fig. 1(a) and Fig. 1(c) are compared, it is observed that the catalytic activity of the MGNC materials significantly decreases when ultrapure water is replaced by secondary treated wastewater. The presence of organic species is expected to hinder the performance of the activated persulfate treatment, mainly due to competition with the target SMX molecules for the oxidizing species.[10] Nevertheless, this negative effect is more pronounced in the case of $CoFe_2O_4$/MGNC and $NiFe_2O_4$/MGNC, turning Fe_3O_4/MGNC the catalyst with the best

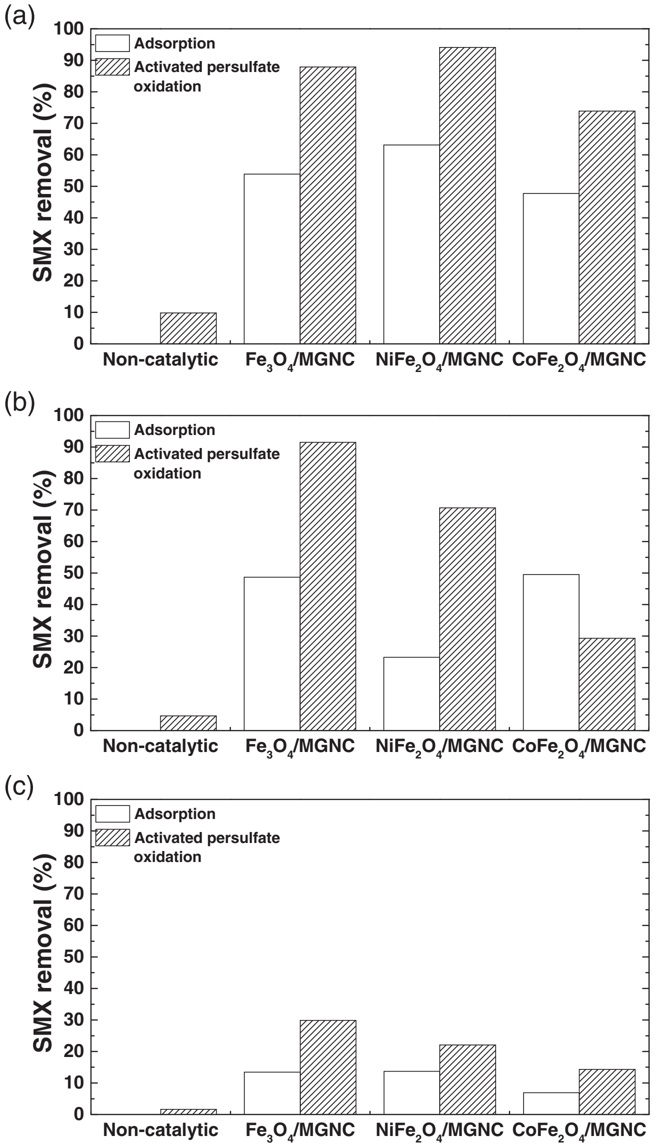

Figure 1. Sulfamethoxazole (SMX) removal in (a) ultrapure water, (b) drinking water and (c) secondary treated wastewater, obtained after 2 h in adsorption and activated persulfate oxidation experiments performed with the magnetic graphitic nanocomposite (MGNC) materials. Non-catalytic removals of SMX (i.e. with sodium persulfate (SPS) but in the absence of catalyst) are also shown. Experiments performed with $[SMX]_0 = 500\ \mu g\ L^{-1}$, $T = 25\ °C$ (room temperature), $[SPS] = 250\ mg\ L^{-1}$, $[adsorbent/catalyst] = 50\ mg\ L^{-1}$ and without pH conditioning ($pH_0 = 5.7$, 7.8 and 8.3, in (a), (b) and (c), respectively).

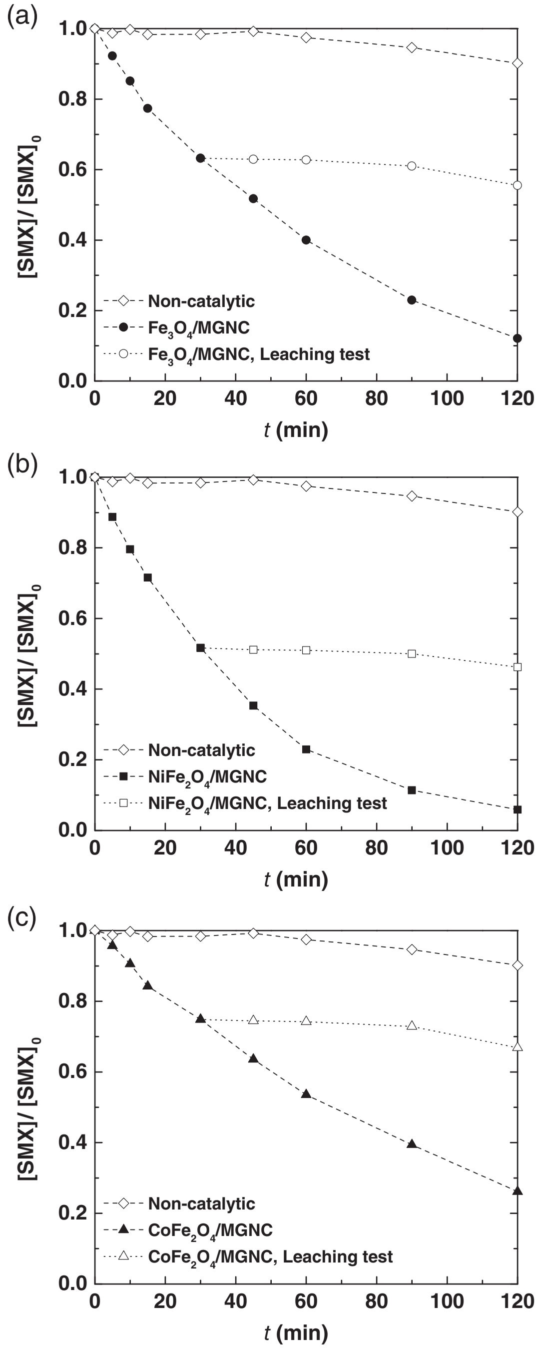

Figure 2. Sulfamethoxazole (SMX) removal as a function of time in activated persulfate oxidation experiments performed in ultrapure water, with (a) Fe_3O_4/MGNC, (b) $NiFe_2O_4$/MGNC and (c) $CoFe_2O_4$/MGNC, as well as SMX removal obtained during the 'leaching tests' performed (i.e. where the corresponding catalyst was removed from the solution after 30 min of reaction). The non-catalytic removal of SMX (i.e. in the absence of catalyst) is also shown. Operating conditions as given in Fig. 1.

performance for the activated persulfate oxidation of SMX in secondary treated wastewater, as in the case of drinking water. The extent upon which water matrix impacts the catalyst performance may be explained by the different reaction mechanisms discussed in the Reaction mechanisms and sites section later.

The performance of the activated persulfate treatment obtained in the presence of the MGNC materials follows the order $NiFe_2O_4$/MGNC > Fe_3O_4/MGNC > $CoFe_2O_4$/MGNC, when SMX solutions are prepared in ultrapure water, while the relative order of catalytic activity changes to Fe_3O_4/MGNC > $NiFe_2O_4$/MGNC > $CoFe_2O_4$/MGNC, when SMX solutions are prepared in realistic water matrices (i.e. drinking water and secondary treated wastewater). These results allow concluding on the critical importance of choosing a realistic water matrix when evaluating heterogeneous catalysts for activated persulfate oxidation of SMX.

Complementary experiments were performed in order to confirm the heterogeneous reaction with MGNC catalysts. For that purpose, the so-called 'leaching tests' were performed as described in the Experimental procedure section. As observed in Fig. 2(a), the reaction solution reveals negligible activity for SMX removal once Fe_3O_4/MGNC is removed after 30 min of reaction.

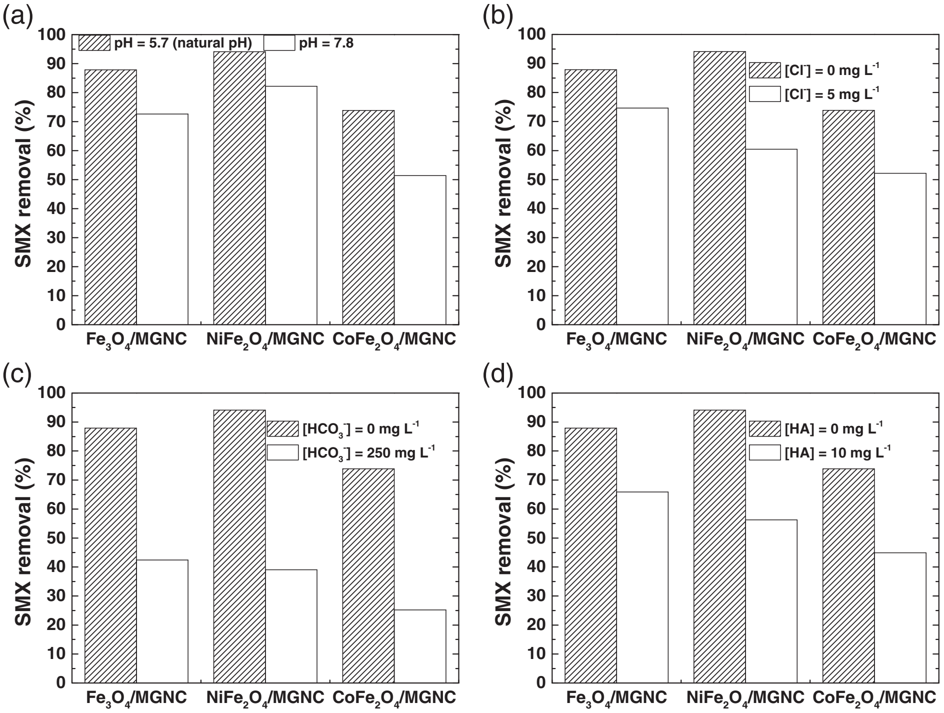

Figure 3. Effect of (a) pH, (b) chlorides, (c) bicarbonates, and (d) humic acid (HA), on the removal of sulfamethoxazole (SMX) obtained after 2 h in activated persulfate oxidation experiments performed in ultrapure water, with the magnetic graphitic nanocomposite (MGNC) materials. Operating conditions as given in Fig. 1.

This result allows concluding that (i) the contribution of metal species, possibly leached from Fe_3O_4/MGNC during the reaction, is negligible when compared to the overall SMX removal obtained in the presence of the heterogeneous catalyst, and/or (ii) the catalyst itself is stable. Similar phenomena are observed for $NiFe_2O_4$/MGNC and $CoFe_2O_4$/MGNC (cf. Fig. 2(b, c), respectively), confirming the heterogeneous nature of persulfate oxidation promoted by the MGNC materials.

Individual effect of typical constituents of environmentally relevant water matrices

The natural pH of SMX solutions prepared in ultrapure water is 5.7. However, the pH of SMX solutions prepared in drinking water and secondary treated wastewater is 7.8 and 8.3, respectively. In order to study the individual effect of pH on the activated persulfate oxidation of SMX performed in the presence of the MGNC materials, three experiments were performed by adjusting the initial pH of SMX solutions prepared in ultrapure water to 7.8. This increase of pH from 5.7 to 7.8 leads to a similar decrease of the SMX removal for all the MGNC materials (cf. Fig. 3(a)). Therefore, the effect of pH does not explain why $NiFe_2O_4$/MGNC performs better than Fe_3O_4/MGNC in ultrapure water, while the latter exhibits the best performance in drinking water. Additional experiments were performed with SMX solutions prepared in ultrapure water, using sodium chloride (5 mg L^{-1} chlorides) and sodium bicarbonate (250 mg L^{-1} bicarbonates) to mimic the presence of some of the typical inorganic constituents of drinking water (cf. Water matrices section). Overall, SMX removal is limited both by the presence of chlorides as of bicarbonates (cf. Fig. 3(b, c), respectively). Nevertheless, in both cases, the detrimental effect seems more pronounced for $NiFe_2O_4$/MGNC and $CoFe_2O_4$/MGNC. Indeed, the performance of Fe_3O_4/MGNC surpasses that of $NiFe_2O_4$/MGNC when chlorides or bicarbonates are added to SMX solutions. These results allow concluding that the performance of the MGNC materials for the activated persulfate oxidation of SMX is affected differently by the presence of chlorides and bicarbonates. Moreover, it is suggested that the presence of inorganic species can be held responsible for the change of the relative order of catalytic activities of the MGNC materials observed when drinking water is employed instead of ultrapure water (as previously discussed).

The effect of dissolved organic matter, typically found in secondary treated waste waters, was also evaluated. For that purpose, humic acid (10 mg L^{-1}) was added to SMX solutions prepared in ultrapure water. As observed in Fig. 3(d), the presence of humic acid limits the SMX removal obtained in the presence of the MGNC materials. However, as previously observed regarding the presence of inorganic species, the negative effect promoted by humic acid is more pronounced when $NiFe_2O_4$/MGNC and $CoFe_2O_4$/MGNC are employed in the activated persulfate oxidation of SMX. It is thus suggested that the presence of organic species accounts for the change of the relative order of catalytic activities of the MGNC materials observed when ultrapure water is replaced by secondary treated wastewater (as previously discussed).

Reaction mechanisms and sites

The heterogeneous activation of persulfate begins upon the reaction described in Eqn (1) regardless of the iron oxide encapsulated within the carbon frameworks of the MGNC materials. Nevertheless, the reaction can then proceed via different pathways (involving secondary HO$^\bullet$ radicals and/or non-radical electron transfer mechanism). An indirect way to assess the contribution of radicals in the activated persulfate process is to perform experiments in the presence of various scavengers. In this case, MeOH and

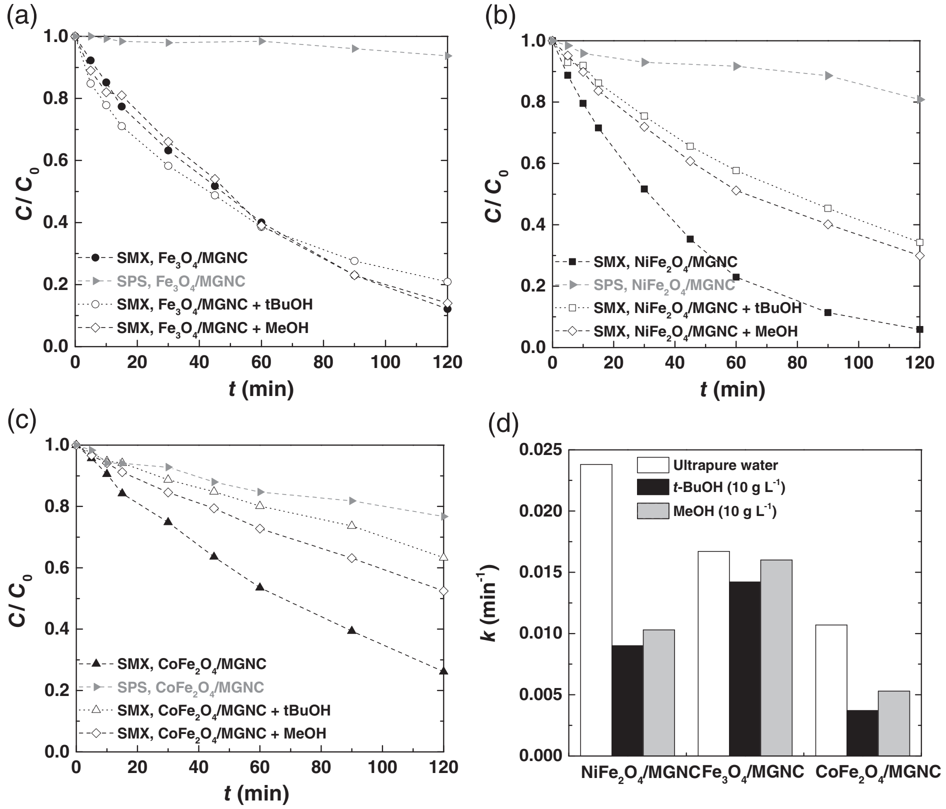

Figure 4. Effect of *tert*-butanol (*t*-BuOH; 10 g L^{-1}) or methanol (MeOH; 10 g L^{-1}) on the removal of sulfamethoxazole (SMX) in activated persulfate oxidation experiments performed in ultrapure water, with (a) Fe_3O_4/MGNC, (b) $NiFe_2O_4$/MGNC and (c) $CoFe_2O_4$/MGNC. The evolution of sodium persulfate (SPS) concentration is also provided in (a)–(c) for the experiments performed in the absence of radical scavengers. (d) Pseudo-first order rate constants for the profiles shown in (a)–(c). Operating conditions as given in Fig. 1.

t-BuOH were selected as typical scavengers of hydroxyl and sulfate radicals,[10] at a concentration which is 20 000 times greater than SMX. As seen in Fig. 4(a–c), the detrimental effect of adding either alcohol on SMX removal is evident for the $NiFe_2O_4$/MGNC and $CoFe_2O_4$/MGNC catalysts, but such effect is insignificant in the case of Fe_3O_4/MGNC.

The comparison of the performances of the three catalysts on a quantitative basis can be made through Fig. 4(d) where the pseudo-first order rate constants are computed from the profiles shown in Fig. 4(a–c). It is clear that different mechanisms are involved in SMX degradation, whose relative contribution depends on the interactions between the chemicals and the catalyst surface. The evolution of SPS concentration during the activated persulfate oxidation experiments performed in the absence of radical scavengers is also given in Fig. 4(a–c). As observed, the conversion of SPS obtained after 2 h under these conditions amounts to *ca* 24% and 20% of its original content when in the presence of $CoFe_2O_4$/MGNC and $NiFe_2O_4$/MGNC, respectively, while it amounts to *ca* 6% only when in the presence of Fe_3O_4/MGNC. The negligible conversion of SPS promoted by Fe_3O_4/MGNC, together with the negligible inhibitory action of the added radical scavengers in comparison with the other catalysts, suggests that a non-radical mechanism is the main reaction pathway for the degradation of SMX when in the presence of Fe_3O_4/MGNC. Although non-radical reactions are not fully understood and their occurrence is case-specific, it has been shown that carbon-based materials can activate persulfate via a non-radical pathway involving the formation of singlet oxygen ($^1O_2$) and/or mediate electron transfer from the organic pollutant (in this case SMX) to persulfate.[13,14,30] The higher overall resistance to radical scavenging of Fe_3O_4/MGNC when the activated persulfate oxidation of SMX is performed in the presence of alcohols and typical organic and inorganic constituents of real waters and wastewaters can thus be held responsible for its superior performance in complex water matrices. On the contrary, the higher conversions of SPS promoted by $CoFe_2O_4$/MGNC and $NiFe_2O_4$/MGNC, together with the higher inhibitory action of the added radical scavengers, suggests that a radical mechanism is the main reaction pathway for the degradation of SMX when in the presence of these catalysts.

Although not all these phenomena can be adequately explained based on the structural and/or surface chemistry properties of the MGNC materials, the observations reported in the present study unequivocally highlight the relevance of conducting future experiments/studies with realistic water matrices.

CONCLUSIONS

There is little doubt that the field of advanced catalytic oxidation processes for environmental applications has gained enormous attention over the past few decades. Research advances include, predominantly, the preparation and characterization of new catalytic materials and, secondarily, the design and testing of water/wastewater treatment technologies. It was not until recently, though, that the quality of the aqueous phase was recognized as a critical parameter affecting treatment performance. In this respect, a growing number of studies are being performed in matrices other than pure water, i.e. in real or synthetic systems.

This is a step in the right direction since the interactions amongst catalysts, oxidants, water constituents and contaminants can be extremely complicated leading to unpredictable effects. This being said, the so-called 'water matrix effect' is usually considered as a later stage operating factor rather than a tool to pre-screen similar but not identical materials (i.e. catalysts, photocatalysts, activators, electrodes in electrochemical processes), from which the best one will be selected for subsequent and more thorough testing.

In this light, this study showcases the critical importance of choosing appropriately a realistic water matrix for the evaluation of heterogeneous catalysts for the activated persulfate oxidation of SMX. Ignoring the nature and impact of the water matrix may result in misleading conclusions, ultimately limiting potential improvements of this treatment technology arising from the application of new materials. For example, SMX removal in the presence of MGNC materials follows the order $NiFe_2O_4$/MGNC > Fe_3O_4/MGNC > $CoFe_2O_4$/MGNC, when ultrapure water is employed as matrix, while the order changes to Fe_3O_4/MGNC > $NiFe_2O_4$/MGNC > $CoFe_2O_4$/MGNC, when drinking water or secondary treated wastewater are considered instead. Although the individual effects of the various water constituents could, to some extent, be predicted and explained, this may not be the case for the overall, net effect, thus making the selection of water matrix an imperative step during catalyst and process screening. This is the case of the present study, in which the application of apparently similar catalysts leads to different reaction mechanisms, such as those involving mainly (i) sulfate and hydroxyl radicals ($NiFe_2O_4$/MGNC and $CoFe_2O_4$/MGNC), or (ii) non-radical reactions (Fe_3O_4/MGNC).

ACKNOWLEDGEMENTS

This work is a result of project 'AIProcMat@N2020 – Advanced Industrial Processes and Materials for a Sustainable Northern Region of Portugal 2020', with the reference NORTE-01-0145-FEDER-000006, supported by Norte Portugal Regional Operational Program (NORTE2020), under the Portugal 2020 Partnership Agreement, through the European Regional Development Fund (ERDF) and of Project POCI-01-0145-FEDER-006984 – Associate Laboratory LSRE-LCM – funded by ERDF through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) – and by national funds through FCT – Fundação para a Ciência e a Tecnologia I.P.

REFERENCES

1 Morales-Torres S, Pastrana-Martínez LM, Figueiredo JL, Faria JL and Silva AMT, Design of graphene-based TiO_2 photocatalysts – a review. *Environ Sci Pollut Res* **19**:3676–3687 (2012).
2 Umar M, Roddick F, Fan L and Aziz HA, Application of ozone for the removal of bisphenol A from water and wastewater – a review. *Chemosphere* **90**:2197–2207 (2013).
3 Särkkä H, Bhatnagar A and Sillanpää M, Recent developments of electro-oxidation in water treatment – a review. *J Electroanal Chem* **754**:46–56 (2015).
4 Eren Z, Ultrasound as a basic and auxiliary process for dye remediation: a review. *J Environ Manage* **104**:127–141 (2012).
5 Nidheesh PV, Gandhimathi R and Ramesh ST, Degradation of dyes from aqueous solution by Fenton processes: a review. *Environ Sci Pollut Res* **20**:2099–2132 (2013).
6 Kim K-H and Ihm S-K, Heterogeneous catalytic wet air oxidation of refractory organic pollutants in industrial wastewaters: a review. *J Hazard Mater* **186**:16–34 (2011).
7 Ribeiro RS, Silva AMT, Figueiredo JL, Faria JL and Gomes HT, Catalytic wet peroxide oxidation: a route towards the application of hybrid magnetic carbon nanocomposites for the degradation of organic pollutants. A review. *Appl Catal B* **187**:428–460 (2016).
8 Matzek LW and Carter KE, Activated persulfate for organic chemical degradation: a review. *Chemosphere* **151**:178–188 (2016).
9 Glaze WH, Kang J-W and Chapin DH, The chemistry of water treatment processes involving ozone, hydrogen peroxide and ultraviolet radiation. *Ozone Sci Eng* **9**:335–352 (1987).
10 Wang J and Wang S, Activation of persulfate (PS) and peroxymonosulfate (PMS) and application for the degradation of emerging contaminants. *Chem Eng J* **334**:1502–1517 (2018).
11 Liu H, Bruton TA, Doyle FM and Sedlak DL, In situ chemical oxidation of contaminated groundwater by persulfate: decomposition by Fe(III)- and Mn(IV)-containing oxides and aquifer materials. *Environ Sci Technol* **48**:10330–10336 (2014).
12 Zhao L, Hou H, Fujii A, Hosomi M and Li F, Degradation of 1,4-dioxane in water with heat- and Fe^{2+}-activated persulfate oxidation. *Environ Sci Pollut Res* **21**:7457–7465 (2014).
13 Yun E-T, Yoo H-Y, Bae H, Kim H-I and Lee J, Exploring the role of persulfate in the activation process: radical precursor versus electron acceptor. *Environ Sci Technol* **51**:10090–10099 (2017).
14 Xiao R, Luo Z, Wei Z, Luo S, Spinney R, Yang W *et al.*, Activation of peroxymonosulfate/persulfate by nanomaterials for sulfate radical-based advanced oxidation technologies. *Curr Opin Chem Eng* **19**:51–58 (2018).
15 Metheniti ME, Frontistis Z, Ribeiro RS, Silva AMT, Faria JL, Gomes HT *et al.*, Degradation of propyl paraben by activated persulfate using iron-containing magnetic carbon xerogels: investigation of water matrix and process synergy effects. *Environ Sci Pollut Res* **25**:34801–34810 (2017).
16 Outsiou A, Frontistis Z, Ribeiro RS, Antonopoulou M, Konstantinou IK, Silva AMT *et al.*, Activation of sodium persulfate by magnetic carbon xerogels (CX/CoFe) for the oxidation of bisphenol A: process variables effects, matrix effects and reaction pathways. *Water Res* **124**:97–107 (2017).
17 Tsydenova O, Batoev V and Batoeva A, Solar-enhanced advanced oxidation processes for water treatment: simultaneous removal of pathogens and chemical pollutants. *Int J Environ Res Public Health* **12**:9542–9561 (2015).
18 Carbonaro S, Sugihara MN and Strathmann TJ, Continuous-flow photocatalytic treatment of pharmaceutical micropollutants: activity, inhibition, and deactivation of TiO_2 photocatalysts in wastewater effluent. *Appl Catal B* **129**:1–12 (2013).
19 Ribeiro RS, Frontistis Z, Mantzavinos D, Venieri D, Antonopoulou M, Konstantinou I *et al.*, Magnetic carbon xerogels for the catalytic wet peroxide oxidation of sulfamethoxazole in environmentally relevant water matrices. *Appl Catal B* **199**:170–186 (2016).
20 Frontistis Z, Kouramanos M, Moraitis S, Chatzisymeon E, Hapeshi E, Fatta-Kassinos D *et al.*, UV and simulated solar photodegradation of 17α-ethynylestradiol in secondary-treated wastewater by hydrogen peroxide or iron addition. *Catal Today* **252**:84–92 (2015).
21 Lado Ribeiro AR, Moreira NFF, Li Puma G and Silva AMT, Impact of water matrix on the removal of micropollutants by advanced oxidation technologies. *Chem Eng J* **363**:155–173 (2019).
22 Neamtu M, Nadejde C, Hodoroaba V-D, Schneider RJ, Verestiuc L and Panne U, Functionalized magnetic nanoparticles: synthesis, characterization, catalytic application and assessment of toxicity. *Sci Rep* **8**:6278 (2018).
23 Jeirani Z and Soltan J, Improved formulation of Fe-MCM-41 for catalytic ozonation of aqueous oxalic acid. *Chem Eng J* **307**:756–765 (2017).
24 Ribeiro RS, Rodrigues RO, Silva AMT, Tavares PB, Carvalho AMC, Figueiredo JL *et al.*, Hybrid magnetic graphitic nanocomposites towards catalytic wet peroxide oxidation of the liquid effluent from a mechanical biological treatment plant for municipal solid waste. *Appl Catal B* **219**:645–657 (2017).
25 Luo Y, Guo W, Ngo HH, Nghiem LD, Hai FI, Zhang J *et al.*, A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment. *Sci Total Environ* **473–474**:619–641 (2014).
26 Benner J, Helbling DE, Kohler H-PE, Wittebol J, Kaiser E, Prasse C *et al.*, Is biological treatment a viable alternative for micropollutant removal in drinking water treatment processes? *Water Res* **47**:5955–5976 (2013).

27 Gokulakrishnan S, Mohammed A and Prakash H, Determination of persulphates using *N*,*N*-diethyl-*p*-phenylenediamine as colorimetric reagent: oxidative coloration and degradation of the reagent without bactericidal effect in water. *Chem Eng J* **286**:223–231 (2016).

28 Álvarez-Torrellas S, Ribeiro RS, Gomes HT, Ovejero G and García JF, Removal of antibiotic compounds by adsorption using glycerol-based carbon materials. *Chem Eng J* **296**:277–288 (2016).

29 Álvarez-Torrellas S, Ribeiro RS, Gomes HT, Sotelo JL and García JF, Synthesis of carbon xerogels and their application in adsorption studies of caffeine and diclofenac as emerging contaminants. *Chem Eng Res Des* **95**:229–238 (2015).

30 Wacławek S, Lutze HV, Grübel K, Padil VVT, Černík M and Dionysiou DD, Chemistry of persulfates in water and wastewater treatment: a review. *Chem Eng J* **330**:44–62 (2017).