

Magnetite-decorated catalytic membrane reactor for the continuous-flow CWPO of micropollutants

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Abstract. This work aims at developing a contactor type Catalytic Membrane Reactor (CMR) for its application in the continuous removal of micropollutants by Catalytic Wet Peroxide Oxidation (CWPO). For such goal, a porous alumina membrane tube was homogeneously decorated with magnetite nanoparticles following an optimized method (ion-adsorption, microwave drying, calcination and reduction). In this interfacial system, the water effluent and the H₂O₂ solution are separated by the catalytic porous membrane, where a controlled reaction zone is formed. The Fe/CMR (0.5% wt.) developed was applied for the treatment of a representative micropollutants mixture (sulfamethoxazole (SMX), metronidazole (MNZ) and carbamazepine (CBZ)) under ambient conditions and slightly acidic pH (pH₀ = 5). The initial concentration of each compound was established at 100 µg L⁻¹. Despite the relatively low micropollutants conversion achieved (22.1%, 27.8% and 32.2% for MNZ, SMX and CBZ, respectively), the catalytic system showed a high stability in long-term application (100 h). Further research is currently on the way with the aim of increasing the iron load in the surface of the membrane in order to improve the catalytic performance of the system.

Keywords: structured catalyst; catalytic membrane reactor; continuous water treatment; micropollutants; magnetite.

1. Introduction

The wide occurrence of micropollutants in the aquatic environment represents an issue of increasing concern. In particular, pharmaceutical compounds, characterized by a remarkably low biodegradability, have caused important negative effects in the aquatic ecosystems (Serrano *et al.*, 2018). These micropollutants are usually present in urban wastewaters because of their high consumption by the general society. Unfortunately, they cannot be completely removed in conventional wastewater treatment plants (WWTPs), as conventional treatments are mainly focused on the removal of organic matter, suspended solids, and nutrients (Khetan *et al.*, 2007; Cjamgotra *et al.*, 2019). Although these emerging pollutants are not regulated yet, it is expected that this situation will change in the next few

years. In fact, the European Union is already analysing the occurrence and risk of a wide range of micropollutants in its water basins, including diverse pharmaceuticals (e.g., sulfamethoxazole), with the aim of defining new environmental quality norms (Decision 2020/1161).

Advanced Oxidation Processes (AOPs) are regarded as promising technologies for the elimination of micropollutants. These processes are based on the generation of hydroxyl radicals, extraordinarily reactive species which allow the removal of a wide range of persistent pollutants (Kanakaraju *et al.*, 2018; Oturan *et al.*, 2014).

Among AOPs, Fenton process appears as one of the most cost-effective (Neyens *et al.*, 2012). The Fenton process is based on a redox cycle in which hydrogen peroxide is decomposed by the action of a catalyst, usually iron, to give rise to the generation of hydroxyl radicals (HO·) (Fig. 1).

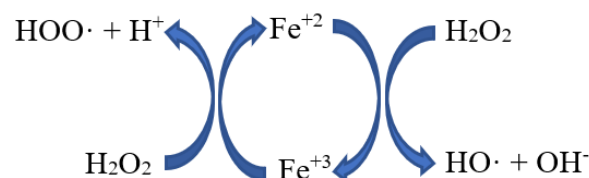


Figure 1. Redox cycle in Fenton process.

The heterogeneous version of the conventional Fenton process, the so called Catalytic Wet Peroxide Oxidation (CWPO), is particularly attractive as it allows to operate under a wide range of pH, and also facilitates the recovery and reusability of the catalyst (Munoz *et al.*, 2013). The use of magnetite (Fe₃O₄) as active phase in this system has attracted wide attention as it contains both iron species (Fe(II) and Fe(III)) in its structure, which dramatically increases the rate of the process (Munoz *et al.*, 2015).

Although CWPO has proved to be highly effective for the removal of micropollutants in batch reactor, scarce studies can be found for its implementation in continuous flow process (Serrano *et al.*, 2019). The main problems associated to this continuous operation mode is the difficulty to retain the powdered catalysts, and the high-pressure drops derived from their use in a fixed-bed

reactor. In this context, the use of structured catalysts represents a promising alternative. In our recent contribution, catalytic foams based on magnetite nanoparticles supported on inert materials like alumina, zirconia and silicon carbide were developed (Nieto-Sandoval *et al.*, 2021). They proved to be highly effective for the removal of micropollutants. Fe/Al₂O₃ foams showed an outstanding stability in long-term application (200 h).

In this work, a contactor-type magnetite-based catalytic membrane reactor (CMR) has been developed with the aim of improving the efficiency of the previous catalytic foams by controlling the dosage of H₂O₂ along the treatment. A porous Al₂O₃ membrane tube was used as catalytic support for such goal. The catalytic system was tested in the continuous-flow CWPO of a representative micropollutants mixture (sulfamethoxazole (SMX),

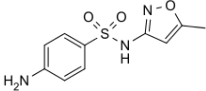
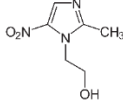
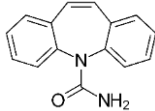
metronidazole (MNZ) and carbamazepine (CBZ)) at a relevant concentration of 100 µg L⁻¹.

2. Material and methods

2.1. Materials

The three pharmaceuticals (SMX (analytical standard), MNZ (analytical standard), and CBZ (≥99%)), hydrogen peroxide solution (33% wt.), nitric acid (65%) and hydroxylamine (≥99%) were provided by Sigma-Aldrich. Iron (III) nitrate nonahydrate (98%) and acetic acid (99.5%) were supplied by Panreac. Acetonitrile (99.9%) and 1,10-phenantroline (≥99%) were obtained from Scharlau and Fulka, respectively. All reagents were used without further purification. Deionized water was used to carry out all the experiments. The main properties of the pharmaceuticals tested are summarized in Table 1.

Table 1. Main properties of the pharmaceutical compounds tested and theoretical stoichiometric dose for their complete oxidation.

Pharmaceutical	Structural formula	Molecular weight (g mol ⁻¹)	pKa ^a	log K _{ow} ^b	Reaction	H ₂ O ₂ (mg L ⁻¹) ^c
Sulfamethoxazole (SMX)		253.3	5.7	0.89	$C_{10}H_{11}N_3O_3S + 33 H_2O_2 \rightarrow 10 CO_2 + 35 H_2O + 3 HNO_3 + H_2SO_4$	0.44
Metronidazole (MNZ)		171.2	2.38	-0.1	$C_6H_9N_3O_3 + 21 H_2O_2 \rightarrow 6 CO_2 + 24 H_2O + 3 HNO_3$	0.42
Carbamazepine (CBZ)		236.3	13.9	2.5	$C_{15}H_{12}N_2O + 40 H_2O_2 \rightarrow 15 CO_2 + 45 H_2O + 2 HNO_3$	0.58

^a M. Patel *et al.*, 2019.

^b M. Loke *et al.*, 2002; M. Williams *et al.*, 2009.

^c Theoretical stoichiometric concentration of H₂O₂ referred to an initial target pollutant of 100 µg L⁻¹.

2.2. Fe₃O₄/CMR preparation

Commercial cylindrical α-Al₂O₃ membranes were used as support material (atech innovations GmbH) to prepare the CMR. The pieces presented an inner and outer diameter of 6 mm and 10 mm, respectively, with 12 cm of length and a mean pore diameter of 0.2 µm.

Magnetite nanoparticles were *in-situ* developed by following a preparation method which consisted of ion adsorption followed by thermal treatments. Briefly, the membrane was immersed in 90 mL of Fe(NO₃)₃·9H₂O in ethanol (3.02 g_{Fe} g⁻¹_{support}). To avoid iron penetration into

the pore structure of the membrane, it was capped at one end, and a continuous N₂ flow was passed through the pores from its core during the ion-adsorption stage.

Five immersion cycles of 30 min each were performed, followed by microwave drying at 600 W for 10 min. The membrane was rotated every 10 seconds to ensure a homogeneously dispersion of iron.

Then, the obtained material was dried for 24 h at 60°C. Subsequently, it was thermally treated by calcination at 600°C in air atmosphere for 3 h, followed by reduction in H₂ (100 NmL min⁻¹) at 350°C for 4 h (Fig. 2).



Figure 2. Images of the membrane after different stages of the optimized catalyst preparation procedure (A: impregnation, B: calcination, C: reduction).

2.3. Experimental procedure

The continuous-flow CWPO reactions were carried out in a double jacketed glass reactor (3 cm inner diameter) continuously fed in up-flow mode with a water stream containing a mixture of pharmaceuticals (MNZ, SMX, CBZ). In this system the hydrogen peroxide solution was fed from the core of the membrane, creating a controlled reaction zone in its external surface, where magnetite nanoparticles were present. The stoichiometric dose of hydrogen peroxide for the complete removal of the micropollutants was used. The experiments were performed under ambient conditions (25°C, 1 atm) at slightly acidic pH using HNO₃ (pH₀ = 5), and with a total volumetric flow rate of 0.4 mL min⁻¹.

Liquid samples were periodically taken from the reactor outlet. The pharmaceuticals were quantified by HPLC-UV (Shimadzu, Prominence-I model, LC-2030C LT) using an Eclipse Plus C18 column (15 cm length, 4.6 mm diameter) (Agilent) as stationary phase. A gradient method of 0.8 mL min⁻¹ acetonitrile and acetic acid aqueous solution (75 mM) was used, depending on the pharmaceutical (10/90%, 27/75% and 55/45% (v/v) for MNZ, SMX and CBZ, respectively). In addition, dissolved iron concentration was quantified by colorimetry with a UV 2100 Shimadzu UV-VIS spectrophotometer using the *o*-phenantroline method (Sandell *et al.*, 1959).

3. Results and discussion

3.1. Catalytic activity and stability

The developed Fe₃O₄/CMR catalytic system showed an iron content of 0.5% wt. According to SEM images, magnetite nanoparticles were homogeneously distributed on the surface of the membrane.

Figure 3 shows the results obtained in the continuous-flow CWPO of the pharmaceuticals mixture. As can be seen, the catalytic system was active in the oxidation process, but relatively low conversion values of the micropollutants were achieved: 22.1%, 27.8% and 32.2% for MNZ, SMX, CBZ, respectively. Consistent with our previous work (Nieto-Sandoval *et al.*, 2021), the pharmaceuticals reactivity towards CWPO decreased in the following order: CBZ>SMX>MNZ.

Despite the relatively low activity of the catalytic system, which was mainly attributed to the low iron content immobilized, it showed an extremely good performance in terms of stability. As observed in Figure 3, pharmaceutical conversion remained almost unchanged during the 100 h continuous flow experiment. Moreover, iron leaching along the treatment was relatively low, being stabilized at 1.4 mg L⁻¹ over time, below the maximum limit allowed in the EU (2 mg L⁻¹ (Hartmann *et al.*, 2010)) (Fig. 4).

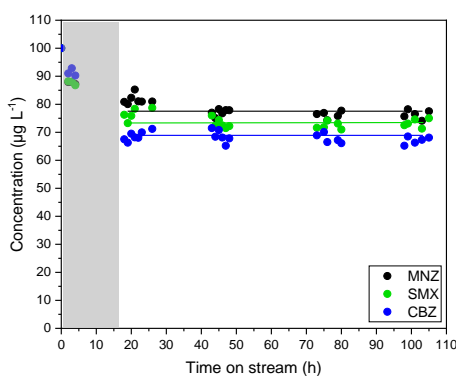


Figure 3. Evolution of the pharmaceuticals upon CWPO with Fe/CMR (the shaded part corresponds to the non-steady state). [Pharmaceuticals]₀ = 100 µg L⁻¹; [H₂O₂] = 1.44 mg L⁻¹; Flow rate = 0.4 mL min⁻¹; 25°C; pH₀ = 5.

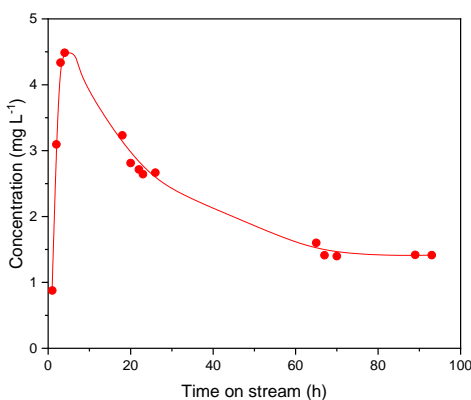


Figure 4. Evolution of dissolved iron upon CWPO with the Fe/CMR. [Pharmaceuticals]₀ = 100 µg L⁻¹; [H₂O₂] = 1.44 mg L⁻¹; Flow rate = 0.4 mL min⁻¹; 25°C; pH₀ = 5.

4. Conclusions

A magnetite-decorated catalytic membrane reactor has been developed and successfully tested in the continuous-flow CWPO of a representative group of micropollutants. Despite its relatively low activity, it exhibited an outstanding stability in long-term application. Further research is currently being developed in order to increase the load of magnetite at the membrane surface and thus, to dramatically enhance its activity. For such goal, the porosity of the membrane as well as the possibility of combining several tubes within the same reactor are being evaluated.

Acknowledgments

This research has been supported by the Spanish AEI through the project PID2019-105079RB-100 and by the CM through the project P2018/EMT-4341. Munoz and J. Nieto-Sandoval thank the Spanish AEI for the Ramón y Cajal postdoctoral contract (RYC-2016-20648) and the FPI predoctoral grant (BES-2017-081346), respectively.

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