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Antibiotics abatement in synthetic and real aqueous matrices by H_2O_2/natural magnetite

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ABSTRACT

The removal of micropollutants in wastewater treatment plants (WTTPs) is a challenging issue which requires the development of effective but also green and low-cost strategies. In this work, we explore the capability of naturally-occurring magnetite combined with H_2O_2 for the degradation of the highly persistent antibiotic sulfamethoxazole (SMX). A complete operating condition study has been performed to evaluate the effect of initial pH (3–7), temperature (15–50 °C), magnetite concentration (0.5–2 g L^{-1}) and H_2O_2 dose (12.5–100 mg L^{-1}), using an initial SMX amount of 5 mg L^{-1}. Remarkably, complete removal of the target pollutant and the aromatic intermediates was achieved operating under ambient-like conditions (25 °C) and circumneutral pH (pH_0 = 5) using the stoichiometric dose of H_2O_2 (25 mg L^{-1}) and a catalyst load of 1 g L^{-1}. The mineralization yield was above 50%, being the final oxidation products short-chain organic acids. The oxidation pathway of SMX was accordingly proposed. The stability of magnetite was confirmed upon three sequential runs, where a similar catalytic activity and negligible iron leaching (< 0.15% wt) were observed. As a proof of concept, the performance of the catalytic system was also evaluated in different real aqueous matrices, such as WWTP effluent, surface water and hospital wastewater. Although the catalyst did not show any sign of deactivation, partial inhibition of the oxidation reaction was observed due to scavenging effects.

1. Introduction

Over the past few years, the occurrence of pharmaceuticals in the aquatic ecosystems is considered to be an emerging environmental problem [1]. These micropollutants are becoming ubiquitous in the environment due to their extensive use and poor removal by the conventional biological wastewater treatment plants (WWTPs) [2–4]. Furthermore, their concentration is expected to increase in future years due to the continually ageing population and improving quality of life, which implies a higher consumption of pharmaceuticals [5]. Drugs are designed to have a physiological effect on humans and animals in trace concentrations, thus their continuous input constitute a potential risk for aquatic and terrestrial organisms. The presence of antibiotics is of special concern since, apart from their negative effect on important ecosystem bacteria (through death or inhibition), they accelerate widespread bacterial resistance to these compounds [6]. Among them, sulfamethoxazole (SMX) is one of the most frequently reported antibiotic compounds in wastewater, surface water, ground water and even drinking water, which evidences its high persistence and the correlation of its presence in different aquatic systems [3].

Municipal WWTPs are generally not prepared to deal with complex pharmaceuticals, as their main aim is removing easily or moderately biodegradable organic matter and microorganisms. Therefore, although the degradation of pharmaceuticals depends on a number of factors, such as their physicochemical properties and WWTP operational conditions, most of them are not effectively removed upon the treatment [2–4]. For instance, the average removal efficiency of SMX at WWTPs has been estimated around 60% [3]. On the other hand, the efficiency of conventional physicochemical treatments *viz.* coagulation-flocculation and adsorption is strongly limited by the properties and concentrations of the micropollutant. Suarez et al. [7] studied the treatment of hospital wastewater by coagulation-flocculation and flotation, focusing on the abatement of pharmaceuticals. Maximum removal of 46% was achieved for diclofenac whereas SMX was not affected by the treatment due to its strong hydrophilic character. In the same line, Kovalova et al. [8] obtained fairly low removal efficiencies (62% at the most) for SMX adsorption onto activated carbon in the post-treatment of hospital wastewater, whereas lipophilic and neutral compounds like diclofenac and carbamazepine were completely eliminated.

Advanced Oxidation Processes (AOPs) are being regarded as the most promising alternative for pharmaceuticals degradation. Their advantages against conventional technologies can be summarized in the

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simplicity of the equipment, the operation at mild conditions and the ability to treat a wide range of non-biodegradable pollutants. Among AOPs, photocatalysis and ozonation have received major attention for micropollutants abatement but their implementation at WWTPs is restricted by the high energy requirements [9–11]. In this sense, Fenton oxidation is usually identified as the most viable AOP for micropollutants degradation [12], not only from the economic point of view, but also for its green character as the reagents are safe to handle and non-threating to the environment. This process has been successfully tested in the treatment of a number of pharmaceuticals [13–16]. Nevertheless, the homogeneous Fenton process is limited by the unavoidable loss of catalyst, the need to deal with the iron sludge generated after the treatment and the operation at acidic pH (~3.0). In this sense, the use of solid iron catalysts in the so-called Catalytic Wet Peroxide Oxidation (CWPO) process has proved to overcome those limitations [1,17–20]. The use of iron minerals as catalysts is especially interesting given their environmentally-friendly character, high availability and low cost. In our recent contribution, the successful application of several iron minerals upon CWPO of industrial wastewaters containing phenolic compounds was demonstrated but it implied operating under relatively severe conditions (70 °C, pH 3) [21]. In particular, magnetite-based catalysts have been recently investigated for the removal of several micropollutants like paracetamol [22] and norfloxacin [23]. Nevertheless, H_2O_2 doses above the stoichiometric amount, high catalyst loads (up to 6 g L^{-1}), acidic pH values (2.6–3.5) and temperatures well above the ambient (40–60 °C) were required to achieve the complete degradation of the pollutants.

The removal of micropollutants at WWTPs requires the development of effective but also green and low-cost strategies. In particular, the catalytic system should allow operating under ambient temperature and circumneutral pH while implying the consumption of low H_2O_2 doses and reasonable catalyst loads. Following this goal, in this work the capability of naturally-occurring magnetite combined with H_2O_2 for the degradation of the highly persistent antibiotic SMX has been explored. A complete operating condition study has been performed to evaluate the effect of initial pH, temperature, magnetite concentration and H_2O_2 dose. Particular attention has been paid to the intermediates generated along the process, and the oxidation pathway of SMX has been accordingly proposed. The stability of magnetite has been also addressed by its sequential use in three consecutive runs. As a proof of concept, the performance of the catalytic system has been also evaluated in different real aqueous matrices, such as WWTP effluent, surface water and real hospital wastewater.

2. Materials and methods

2.1. Chemicals

Sulfamethoxazole (SMX), hydrogen peroxide solution (30% wt.), nitric acid (65%) and acetic acid (> 99%) acid were supplied by Sigma-Aldrich. Sodium hydroxide (> 98%) was purchased from Panreac and titanium oxysulfate (> 99%) and acetonitrile (99.8%) from Fluka and Scharlau, respectively. All these chemicals were used without further purification. Unless otherwise indicated, deionized water was the matrix used to perform the experiments.

2.2. Magnetite characterization

Magnetite (Ref. 50121500) was provided by Marphil S.L. (Spain). The composition of magnetite was determined by total reflection X-ray fluorescence (TXRF) using a TXRF spectrometer 8030 c. Its crystallinity was analyzed by X-ray diffraction by a Siemens model D-5000 diffractometer with Cu kα radiation. The textural properties were characterized from nitrogen adsorption-desorption isotherms at −196 °C using a Micromeritics Tristar 3020 apparatus. Magnetic measurements were performed with a Quantum Design MPMS XL-5 superconducting quantum interference device (SQUID). The magnetic moment (M) was measured as function of the applied field (H) at room temperature.

The point of zero charge (pH_{PZC}) of the mineral was determined following a method described elsewhere [24]. Briefly, eleven solutions with varying initial pH values were prepared using different volumes of 0.1 M NaOH/HCl solutions and KCl (1 M) as electrolyte. 10 mL of each solution was contacted with 0.1 g of magnetite and the suspension was left under stirring for 24 h and the equilibrium pH was measured. The pH_{PZC} value of the mineral was determined intercepting the obtained final pH *versus* initial pH curve with the straight line corresponding to final pH = initial pH.

2.3. Typical reaction procedure

Oxidation runs were carried out at ambient pressure within the range of 15–50 °C in a glass batch reactor (500 mL), equipped with a stirrer (700 rpm) and temperature control. The initial concentration of SMX was fixed at 5 mg L^{-1}. The effect of the main operating conditions *viz.* H_2O_2 dose (50–400% the stoichiometric amount for SMX mineralization), magnetite concentration (0.5–2 g L^{-1}) and initial pH (3–7) was investigated. With the aim of describing the route of SMX oxidation, an additional experiment was carried out using a low H_2O_2 dose (20% of the stoichiometric amount), which facilitates the identification of the intermediates formed at the early stages of the reaction [25].

The catalytic activity of magnetite in CWPO was also investigated in different real aqueous matrices where SMX usually appears: WWTP effluent, hospital wastewater and surface water. All the experiments were carried out in triplicate being the standard deviation lower than 5% in all cases.

2.4. Analytical methods

Liquid samples were periodically taken from the reactor during the oxidation reaction and immediately analyzed. The catalyst was previously separated by filtration using a PTFE filter (pore size 0.45 μm). SMX and the aromatic reaction intermediates were analyzed by high performance liquid chromatography, HPLC-UV (Varian, Mod. ProStar) using an Eclipse Plus C18 column (15 cm length, 4.6 mm diameter) (Agilent) as stationary phase. The analyses were carried out at 270 nm using a 25/75% (v/v) mixture of acetonitrile and acetic acid aqueous solution (75 mM) as the mobile phase.

The effluents from the experiments under substoichiometric conditions were analyzed by HPLC–MS with the aforementioned column and analytical method for the tentative identification of the reaction by-products. All MS data acquisition and processing were carried out using the software package LC/MSD ChemStation.

Total organic carbon (TOC) was measured with a TOC analyzer (Shimadzu TOC V_{SCH}). Short-chain organic acids were quantified by means of ionic chromatography with chemical suppression (Metrohm 790 IC) using a conductivity detector. A 3.2 mM Na_2CO_3 aqueous solution was used as mobile phase and a Metrosep A sup 5–250 column (25 cm length, 4 mm internal diameter) as stationary phase. H_2O_2 and leached iron were analyzed by colorimetric titration with a UV 2100 Shimadzu UV–vis spectrophotometer using the titanium sulfate [26] and the o-phenantroline [27] methods, respectively.

3. Results and discussion

3.1. Magnetite characterization

The measured concentration of iron (73% wt) was close to the theoretical one for pure Fe_3O_4. Accordingly, the XRD pattern mostly corresponded to the standard card of pure magnetite (see Fig. S1 of the Supplementary material for details), and the material showed strong magnetic properties (M_S = 77.9 emu g^{-1}). On the other hand, the surface area value (7.5 m^2 g^{-1}) was consistent with this kind of