



Homogeneous and heterogeneous photo-Fenton degradation of antibiotics using an innovative static mixer photoreactor



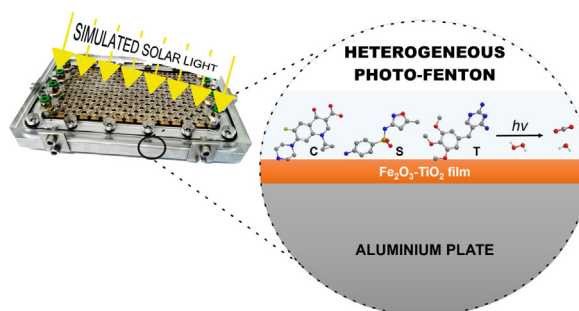
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HIGHLIGHTS

- NETmix[®] is a feasible alternative as photo-Fenton reactor.
- Fe₂O₃-TiO₂ film shows high efficiency for degradation of antibiotics.
- Fe₂O₃-TiO₂ film stabilize with reuse without a significant photo-activity loss.
- Leached Fe adds to the antibiotics' removal by a homogeneous photo-Fenton route.

GRAPHICAL ABSTRACT



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ABSTRACT

The use and disposal of antibiotics results in their release in large quantities to the environment, posing serious threats to human and ecological health. In the present work, two different conceptual photoreactors are tested for the treatment of recalcitrant aqueous solutions containing three common antibiotics (ciprofloxacin, sulfamethoxazole and trimethoprim). In a first stage, NETmix[®], a novel static mixer photoreactor, is compared against the conventional compound parabolic collector (CPC) under homogeneous photo-Fenton treatment conditions. In a second stage, commercial Fe₂O₃, as well as sol-gel synthesized Fe₂O₃, TiO₂ and Fe₂O₃-TiO₂ composites, are used in the form of films for catalyst screening experiments in a heterogeneous photo-Fenton like treatment. The highest efficiency was obtained with the Fe₂O₃-TiO₂ catalytic film, that was then tested in the NETmix[®] photoreactor. A conversion of antibiotics higher than 60% (in terms of carbon content) was achieved in three consecutive utilizations of the same Fe₂O₃-TiO₂ film. The used materials were thoroughly characterized by microscopic and spectroscopic techniques.

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1. Introduction

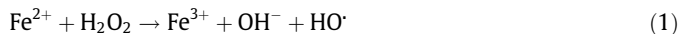
Antibiotics are worldwide manufactured and widely prescribed to treat bacterial infections in human and animal therapy. As result of their generalized use and incomplete treatment of urban and industrial effluents, these drugs are easily found in different types of treated waste waters and can be even transferred to fresh waters

[1,2]. Once a microorganism is able to reproduce in the presence of an antibiotic, it becomes antibiotic resistant. Several studies suggest that the overuse and misuse of antibiotics results in the development of drug-resistant microorganisms [3]. The resistance to antibiotics poses a serious threat to human and ecological health. Thus, the effective treatment of water streams containing this class of pollutants is of crucial importance to public health due to its widespread use, low biodegradability and encoded bacterial resistance [4]. Ciprofloxacin (CIPRO), sulfamethoxazole (SMX) and trimethoprim (TMP) are examples of antibiotics generally found in waste waters, which show bacterial resistance rates larger than

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30% [5]. Concerning ciprofloxacin, for example, there are records of concentrations between 0.7 and 124.5 µg/L in hospital effluent [6].

Advanced oxidation processes (AOPs), characterized by the production of highly reactive hydroxyl radicals (HO·), capable to unselectively degrade organic pollutants into CO₂ and H₂O, have been successfully used for the treatment of antibiotic-contaminated waters [7–9]. Specifically, the photo-Fenton process (homogeneous), which consists in the combination of the classical Fenton reaction (the catalyzed decomposition of hydrogen peroxide, H₂O₂, by ferrous iron, Fe²⁺ to produce HO· at low pH, Eq. (1)) with the photo-assisted regeneration of Fe²⁺ from Fe³⁺, Eq. (2) [10–12], has been shown to be an effective alternative to treat these particular pollutants [13,14].



Despite the effectiveness of the homogeneous photo-Fenton treatment, it presents major limitations, mostly related to the large amounts of dissolved iron needed that have to be removed to comply with the legislated discharge thresholds indicated in the European legislation [15].

Heterogeneous catalysts can overcome the described limitations. Current photo-assisted heterogeneous technologies are mainly based on the use of TiO₂ due to its chemical stability, inexpensiveness and relative low toxicity for humans and environment [16]. However, TiO₂ requires UV light photoactivation, a disadvantage when the applications are focused on solar sunlight, only accounting with 5% of UV irradiation at sea level [17–19]. Heterogeneous photo-Fenton uses iron-based solid catalysts that can enable the sunlight harvesting, such as Fe₂O₃, at the same time avoiding the use of excessive amounts of dissolved iron and permitting the easy separation and recovery of the catalysts from the treated waste waters [20–23]. However, Fe₂O₃ has short carrier diffusion lengths facilitating the electron–hole recombination [24]. To overcome this drawback, mixed oxides (Fe₂O₃–TiO₂) can be employed taking advantage of the main favorable photocatalytic properties of each material [25,26].

Yet, the use of catalyst suspensions for effluent remediation is often inadequate due to particle aggregation, formation of slurries, the unviability of continuous-flow conditions and the inherent costs of catalyst separation [27]. Magnetically recoverable catalysts [28,29], combination with plants [30,31] as well as catalyst immobilization in the form of films, or coatings, on fixed supports, such as glass slides [27,32,33], raschig rings and beads [34–36], stainless steel [37,38] and polymers [39,40] has been used to overcome these limitations.

Reactor engineering is one of the most challenging research areas in what concerns to photo-assisted processes. During the last decades, an enormous effort has been devoted to the development of more energy-efficient and environmental-friendly photoreactors with a high emphasis in solar-assisted technologies.

Compound parabolic collector (CPC) photoreactors have been applied for the treatment of a great variety of contaminated waste waters due to their efficacy to collect sunlight, possibility of using high flow rates and relatively small reactor volumes [41–47]. Recently, seeking for higher efficiencies of real scale waste water decontamination, novel configurations have been proposed such as flat raceway ponds and snake-shaped photoreactors [48–50].

In a previous work, a new easily scalable photo-reactor configuration was proposed and validated for waste water treatment by photo-Fenton process: the NETmix[®] photoreactor [51]. NETmix[®] is a patented technology for enhanced mixing of liquids and/or gases by using a regular network of interconnected chambers and channels with small cross-section area [52,53]. It was shown that

NETmix[®] improved the mixture of Fenton's reagents (H₂O₂ and Fe²⁺ precursor) boosting the performance of the photo-Fenton treatment for waste waters contaminated with antibiotics.

Because CPC and NETmix[®] can operate in similar reactor volumes, at high flow rates, a comparison of performances is required in order to establish the domains of application of each equipment. Due to their tubular configuration, CPC's are difficult to scale up, require a reasonable capital cost and generate a moderate amount of heat during operation [48]. In the present work, we present a comparison between NETmix[®] and CPC performances as solar photoreactors for the homogeneous photo-Fenton treatment of antibiotic-containing waters. The combination of NETmix[®] technology with solar photocatalytic properties of catalyst films using Fe₂O₃–TiO₂ as catalyst is also explored for heterogeneous photo-Fenton treatment of water containing ciprofloxacin, sulfamethoxazole and trimethoprim antibiotics.

2. Experimental

2.1. Materials

Photo-Fenton experiments were performed using iron sulfate heptahydrate (FeSO₄·7H₂O, 99.5%) from Merck, iron oxide (Fe₂O₃, labeled as Fe₂O₃-c, 99%), ciprofloxacin (C₁₇H₁₈FN₃O₃, CIPRO, ≥98%), trimethoprim (C₁₄H₁₈N₄O₃, TMP, ≥98%), hydrogen peroxide (H₂O₂, 30%) from Fluka/Sigma-Aldrich, and sulfamethoxazole (C₁₀H₁₁N₃O₃S, SMX, 99%) from Sigma-Aldrich. Sodium sulfite anhydrous (Na₂SO₃, ≥98%) purchased from Fluka/Sigma-Aldrich was used to stop the reaction when collecting the samples. Sulfuric acid (H₂SO₄, 95–98%) and sodium hydroxide (NaOH, 97%) purchased from Sigma-Aldrich were used for pH adjustment. Acetonitrile (CH₃CN, HPLC grade) from VWR, sodium hydrogen phosphate (NaH₂PO₄, ≥99.0%) from Fluka/Sigma-Aldrich, phosphoric acid (H₃PO₄, 85.4%) from Fisher Scientific, and ultra-pure water (Direct-Q Millipore) were used for high performance liquid chromatography (HPLC). Ammonium acetate (CH₃CO₂NH₄, 99%), acetic acid (CH₃CO₂H, 99.8%) from Fluka/Sigma-Aldrich, ascorbic acid (C₆H₈O₆, 99%) and 1,10-phenantrolin (C₁₂H₈N₂, ≥99%) from Sigma-Aldrich, were used for the spectrophotometric measurement of dissolved iron.

2.2. Catalyst synthesis

A sol-gel technique was used to produce Fe₂O₃, TiO₂ and Fe₂O₃–TiO₂ composites [54]. Briefly, for Fe₂O₃–TiO₂ composite synthesis, a 0.5 M iron (III) chloride hexahydrate (99%, Riedel-de Haën) aqueous solution (10 mL) was stirred for 15 min and after that, 1.44 g of sodium dodecyl sulfate (SDS, ≥99%, Sigma Aldrich) was slowly added and let to stir during 30 min. Then, titanium isopropoxide (97%, Aldrich) was dissolved in 5 mL of isopropyl alcohol (≥99%) from Fluka/Sigma-Aldrich, to achieve a 2 M solution. Finally, the two solutions were mixed and stirred for 3 h and then reserved under freezing conditions (277 K) for 36 h. The Fe₂O₃ and TiO₂ samples were prepared similarly maintaining the above-mentioned experimental conditions but without the addition of one of the metal oxide precursors. The precipitate was filtered and washed several times to remove by-products of the sol-gel technique. The collected materials were calcined under air atmosphere at 773 K during 6 h.

2.3. Catalyst films preparation

The preparation of the catalyst pastes and cleaning of the glass slides are described in a previous work [27]. Concisely, suspensions of catalysts were prepared using 50 mg of catalyst and 1.5 mL of a solution of α-terpineol (90%, Merck), acetone (≥99.5%, Fluka

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