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An innovative static mixer photoreactor: Proof of concept

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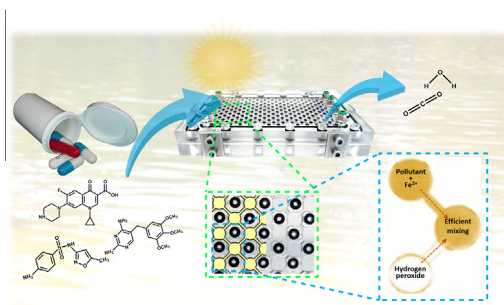
HIGHLIGHTS

- NETmix® reactor can be designed for antibiotic abatement using photo-Fenton process.
- NETmix® improves Fenton's reagents mixture.
- 25% of mineralization is achieved for a residence time of 4′06″.

GRAPHICAL ABSTRACT



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ABSTRACT

An innovative application for the NETmix® reactor is validated in the present work, namely the homogeneous photo-Fenton treatment of natural waters contaminated with organic pollutants using solar light. Three antibiotics presenting high bacterial resistance (ciprofloxacin, sulfamethoxazole and trimethoprim) were selected as model pollutants. The influence of Reynolds number (Re = 38–400) on the pollutants degradation was studied in continuous flow, and the flow rate and pH optimized (i.e., 500 mL min^{-1} and pH of 2.8, respectively). Under recirculation flow, the effect of different operating conditions on the degradation of the mixture of three antibiotics was then studied by changing the hydrogen peroxide (0–2.5 mM) and iron (II) sulfate (0–4 mg Fe L^{-1}) concentrations. Results establish high degradation rates using, 2.5 mM H_2O_2, 2 mg L^{-1} Fe^{2+}, pH of 2.8, 262 W m^{-2} irradiance and Re = 300. Complete conversion of the antibiotics was achieved, demonstrating the potential application of the NETmix® technology as an efficient photoreactor configuration.

1. Introduction

Pharmaceuticals and personal care products (PPCPs), including antibiotics, are widely used and continuously introduced into the environment. Some of them present low biodegradability and appear in natural resources and/or even in drinking water [1]. Cek et al. [2] studied the bacterial resistance to a number of antibiotics used for urinary tract infections (UTIs) – some of the most common human diseases – and they found bacterial resistance rates larger than 30% for most of the studied antibiotics. In fact, bacterial resistance to antibiotics has dramatically increased and public health may regress to stages equivalent to pre-penicillin years in a near future if this scenario is not changed [3–5].

Trimethoprim (TMP) and sulfamethoxazole (SMX) are often used together because the efficacy of the resulting formulation is higher than that of formulations prepared with these components individually [6]. However, the Infectious Diseases Society of America and the European Association of Urology do not recommend the use of TMP and SMX when the bacterial resistance to this mixture of antibiotics is higher than 10–20% [7,8]. In this case, 2nd generation fluoroquinolone and well-established broad spectrum

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Table 1
Overview of NETmix® reactor applications.

Objective	Application	Scale	Refs.
Synthesis of hydroxyapatite (HAp) nanoparticles and HAp composites	Tissue engineering; dentary medicine and medical implants	Industrial	[20,22]
Synthesis of magnetic nanoparticles (MNP)	MRI imaging and drug delivery; waste water treatment using MNP (photo-Fenton like reactions)	Laboratory	[23,24]
Synthesis of metal–organic frameworks (MOF)	Hydrogen and methane storage; catalysis; drug delivery; gas adsorption	Laboratory	[25]
Degradation of antibiotics in aqueous solutions by photo-Fenton process	Waste water treatment	Laboratory	This study

antibiotics (such as ciprofloxacin, CIPRO) can be used for bacterial infections treatment, due to their recognized bactericidal activity against clinically important pathogens [9]. Even so, the bacterial resistance to the antibiotics is still increasing due to their widespread use.

In this context, to find appropriate environmentally friendly technologies for the treatment of waste waters containing antibiotics is a crucial issue since all antibiotics should be definitively removed from industrial effluents as well as from those effluents generated in urban waste water treatment plants (WWTPs).

Advanced oxidation processes (AOPs) are conceptually based on the production of hydroxyl radicals ($HO^{\cdot}$) and known as efficient technologies for the degradation of antibiotics in aqueous media [10–12]. One of these processes, the photo-Fenton process consists in the combination of the classical Fenton reaction (a mixture of hydrogen peroxide and Fe^{2+} at low pH, Eq. (1)), with the possible photo-assisted regeneration of Fe^{3+} into Fe^{2+}, Eq. (2) [13–15]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO^{\cdot} \quad (1)$$

$$Fe^{3+} + H_2O \xrightarrow{h\upsilon} Fe^{2+} + H^+ + HO^{\cdot} \quad (2)$$

An optimized excess of hydrogen peroxide will regenerate Fe^{3+} ions into Fe^{2+} by Eqs. (3) and (4). However, the excess amount of hydrogen peroxide should be optimized to avoid the reactions described in Eqs. (5) and (6) [13].

$$Fe^{3+} + H_2O_2 \rightleftharpoons Fe{-}OOH^{2+} + H^+ \quad (3)$$

$$Fe{-}OOH^{2+} \rightarrow Fe^{2+} + HOO^{\cdot} \quad (4)$$

$$H_2O_2 + HO^{\cdot} \rightarrow HOO^{\cdot} + H_2O \quad (5)$$

$$HOO^{\cdot} + HO^{\cdot} \rightarrow H_2O + O_2 \quad (6)$$

Some studies [16,17] have shown the need of using great amounts of dissolved iron to obtain high pollutant and organic carbon conversions, thus exceeding the permissible limit of 2 mg L^{-1} in waters [18]. Therefore, the reactor configuration is still considered one key parameter to increase the effectiveness of the treatment by increasing heat and mass transfer, by improving reagents mixing and/or exploiting solar energy associated with low-cost and scalable configurations for industrial applications.

The NETmix® reactor is a new type of static mixer that proved its efficiency in increasing process performance and yield in the field of nanoparticles synthesis [19] (Table 1). This patented technology, already applied at industrial scale, improves mixing due to the regular network of interconnected chambers and channels [19–21], as shown in Fig. 1.

The aim of this study is to assess and validate the NETmix® reactor performance for the photo-Fenton treatment of waters contaminated with antibiotics. The efficiency of the NETmix® reflects the ability for enhanced mixture of the Fenton reagents. In addition, its flat configuration increases the surface area for solar irradiation and consequently the mass and heat transfer. The operating conditions are optimized for degradation of the antibiotics CIPRO, SMX and TMP in a mixture (CST), under simulated solar light in aqueous solutions. These particular compounds were chosen for this study since they are three of the most prescribed antibiotics and also because they are commonly found in natural waters and waste waters [26]. High degradation rates of these antibiotics using photo-Fenton treatment were found in previous studies [12,27,28] indicating the effectiveness of this process for the treatment of water streams containing these particular compounds.

2. Experimental

2.1. Materials

Photo-Fenton experiments were performed using iron (II) sulfate heptahydrate, $FeSO_4{\cdot}7H_2O$ (99.5%, Merck), ciprofloxacin, $C_{17}H_{18}FN_3O_3$, (CIPRO, ⩾98%, Fluka), sulfamethoxazole,

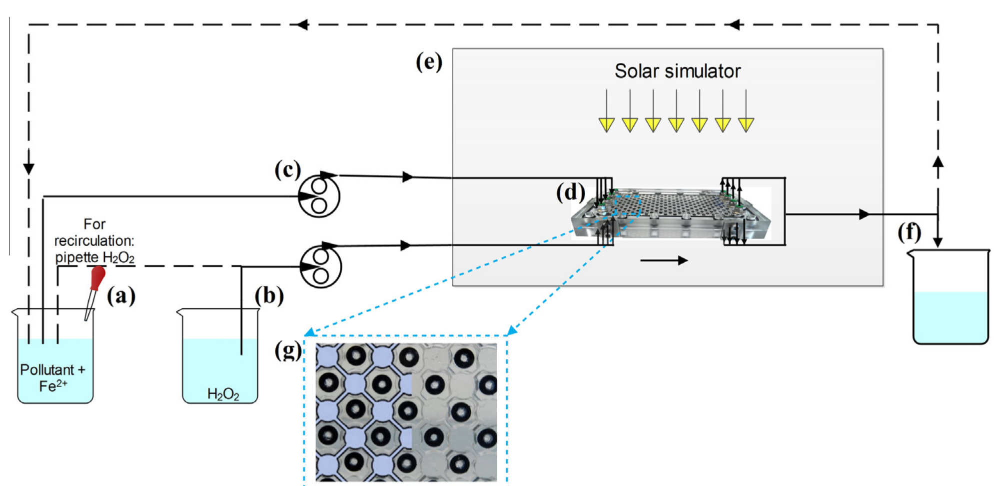

Fig. 1. Scheme of photo-Fenton reaction setup: continuous (solid line) and recirculation (dashed line) mode.