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Removal of pharmaceuticals from MWTP effluent by nanofiltration and solar photo-Fenton using two different iron complexes at neutral pH

S. Miralles-Cuevas [a], I. Oller [a], J.A. Sánchez Pérez [b], S. Malato [a,*]

[a] Plataforma Solar de Almería-CIEMAT. Carretera Senés km 4, 04200 Tabernas (Almería), Spain
[b] Departamento de Ingeniería Química de la Universidad de Almería. Carretera Sacramento S/N, 04120 Almería, Spain

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ABSTRACT

In recent years, membrane technologies (nanofiltration (NF)/reverse osmosis (RO)) have received much attention for micropollutant separation from Municipal Wastewater Treatment Plant (MWTP) effluents. Practically all micropollutants are retained in the concentrate stream, which must be treated. Advanced Oxidation Processes (AOPs) have been demonstrated to be a good option for the removal of microcontaminants from water systems. However, these processes are expensive, and therefore, are usually combined with other techniques (such as membrane systems) in an attempt at cost reduction. One of the main costs in solar photo-Fenton comes from reagent consumption, mainly hydrogen peroxide and chemicals for pH adjustment. Thus, in this study, solar photo-Fenton was used to treat a real MWTP effluent with low initial iron (less than 0.2 mM) and hydrogen peroxide (less than 2 mM) concentrations. In order to work at neutral pH, iron complexing agents (EDDS and citrate) were used in the two cases studied: direct treatment of the MWTP effluent and treatment of the concentrate stream generated by NF. The degradation of five pharmaceuticals (carbamazepine, flumequine, ibuprofen, ofloxacin and sulfamethoxazole) spiked in the effluent at low initial concentrations ($\mu g\ L^{-1}$) was monitored as the main variable in the pilot-plant-scale photo-Fenton experiments. In both effluents, pharmaceuticals were efficiently removed (>90%), requiring low accumulated solar energy ($2\ kJ_{UV}\ L^{-1}$, key parameter in scaling up the CPC photoreactor) and low iron and hydrogen peroxide concentrations (reagent costs, 0.1 and 1.5 mM, respectively). NF provided a clean effluent, and the concentrate was positively treated by solar photo-Fenton with no significant differences between the direct MWTP effluent and NF concentrate treatments.

1. Introduction

In recent years, there has been a strong desire to treat microcontaminants found in natural waters, the main source of which is the effluents from municipal wastewater treatment plants (MWTP), where they are not completely removed in biological secondary treatments. An Advanced Oxidation Process (AOP) polishing step could solve the problems that these compounds cause in the aquatic environment and

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* *Corresponding author*. Tel.: +34 95387940; fax: +34 950365015.
E-mail address: sixto.malato@psa.es (S. Malato).

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consequently the human health (Hollender et al., 2009). Fenton and photo-Fenton have been demonstrated to be good options for the removal of micro-contaminants from water systems (Klavarioti et al., 2009; Rivera-Utrilla et al., 2013). However, these treatments normally involve high operating costs, and so AOPs should be optimized to minimize the associated costs, especially when used for tertiary treatment. One of the main costs comes from reagent consumption, mainly hydrogen peroxide and chemicals for pH adjustment (pH should be adjusted to around 2.8 for best photo-Fenton efficiency, and then increased to neutral after photo-Fenton treatment) (Pignatello et al., 2006). Therefore, there is strong interest in working at neutral pH to avoid pH adjustment, especially in large-scale operations (Batista and Nogueira, 2012; Sánchez Pérez et al., 2013). In view of the above, photo-Fenton should be carried out with low iron and hydrogen peroxide concentrations to enhance process competitiveness (Klamerth et al., 2013).

The problems encountered with the lack of efficiency of photo-Fenton at neutral pH could be solved by adding compounds able to form stable complexes with iron. It is known that iron is complexed in water by polycarboxylates and aminopolycarboxylates and that these complexes typically have higher molar absorption coefficients in the near-UV and visible regions than the aquo complexes do (Faust and Hoigne, 1990; Pignatello et al., 2006). Consequently, both effects could substantially improve photo-Fenton economics.

The presence of such complexes can produce hydroxyl radicals by other mechanisms apart from Fenton and photo-Fenton reactions. For instance, previous studies have shown (Stasicka, 2011) that the complexes formed with Fe(III) could produce both Fe(II) and ligand-free radicals by ligand-to-metal charge transfer (LMCT) under irradiation (see Reac. 1). The ligand-free radical is able to react with dissolved oxygen in water to form superoxide radicals ($O_2^{\bullet -}$) (Reac. 2). The $O_2^{\bullet -}$ radical and its conjugated acid form $HO_2^{\bullet}$ (Reac. 3) can participate in further reactions generating H_2O_2 (Reac. 4–7). As a consequence, $HO^{\bullet}$ can be formed by Fenton reaction by oxidizing Fe(II) with H_2O_2 (Reac. 8).

$$\mathrm{Fe(III)} - \mathrm{L} + h\upsilon \rightarrow [\mathrm{Fe(III)} - L]^{*} \rightarrow \mathrm{Fe(II)} + \mathrm{L}^{\cdot} \qquad \text{Reac. 1}$$

$$\mathrm{L}^{\cdot} + \mathrm{O}_2 \rightarrow \mathrm{O}_2^{\cdot -} + \mathrm{L}^{'} \qquad \text{Reac. 2}$$

$$\mathrm{O}_2^{\cdot -} + \mathrm{H}^{+} \leftrightarrow \mathrm{HO}_2^{\cdot}; \quad pK_a = 4.8 \qquad \text{Reac. 3}$$

$$\mathrm{Fe(II)} + \mathrm{O}_2^{\cdot -} + 2\mathrm{H}_2\mathrm{O} \rightarrow \mathrm{Fe(III)} + \mathrm{H}_2\mathrm{O}_2 + 2\mathrm{OH}^{-} \qquad \text{Reac. 4}$$

$$\mathrm{Fe(II)} + \mathrm{HO}_2^{\cdot} + \mathrm{H}_2\mathrm{O} \rightarrow \mathrm{Fe(III)} + \mathrm{H}_2\mathrm{O}_2 + \mathrm{OH}^{-} \qquad \text{Reac. 5}$$

$$\mathrm{O}_2^{\cdot -} + \mathrm{HO}_2^{\cdot} + \mathrm{H}_2\mathrm{O} \rightarrow \mathrm{H}_2\mathrm{O}_2 + \mathrm{O}_2 + \mathrm{OH}^{-} \qquad \text{Reac. 6}$$

$$\mathrm{HO}_2^{\cdot} + \mathrm{HO}_2^{\cdot} \rightarrow \mathrm{H}_2\mathrm{O}_2 + \mathrm{O}_2 \qquad \text{Reac. 7}$$

$$\mathrm{Fe(II)} + \mathrm{H}_2\mathrm{O}_2 \rightarrow \mathrm{Fe(III)} + \mathrm{HO}^{\cdot} + \mathrm{OH}^{-} \qquad \text{Reac. 8}$$

On the other hand, other technologies have also been used successfully to remove pharmaceuticals contained in the MWTP effluents, especially the membrane system and AOP combination (Pérez-Gonzalez et al., 2012). Membrane systems are known to be very efficient in the retention of micro-contaminants due to their physicochemical properties, but a concentrate stream is also generated. Currently, this stream is directly discharged to the sea or to the MWTP without any further treatment. Therefore management and treatment of the concentrate are likely to be key components for reducing the environmental impact of wastewater reclamation (Bagastyo et al., 2011; Benner et al., 2008).

Photochemical and photo-Fenton reactions using iron complexing agents have recently received much attention because they can be carried out at neutral pH. Removal with complexing agents, such as citric acid and ethylenediamine-disuccinic acid (EDDS), of model contaminants at high initial concentrations (mg L^{-1}) and micropollutants in municipal wastewater treatment plant effluents (MWTPs) at low initial concentrations (ng L^{-1}–μg L^{-1}) has been investigated (Silva et al., 2007; Trovó, A.G. et al., 2011; Li et al., 2010; Huang et al., 2012; Klamerth et al., 2013). However, the solar photo-Fenton process with iron complexing agents at neutral pH has not been evaluated for the treatment of membrane concentrates of MWTP effluents.

The main purpose of this work was to compare direct treatment of a real MWTP effluent by solar photo-Fenton at neutral pH with complexing agents (EDDS and citrate) and the same treatment applied to the nanofiltration (NF) concentrate. With this purpose in mind, a real MWTP effluent was spiked with five pharmaceuticals (15 μg L^{-1} each, close to real concentrations) used as model pollutants to evaluate the different oxidation processes.

2. Materials and methods

2.1. *Reagents and chemicals*

All solvents used for liquid chromatography analyses and solid phase-extraction (SPE) were HPLC-grade. The five pharmaceuticals selected for this study, carbamazepine, flumequine, ibuprofen, ofloxacin, and sulfamethoxazole, were all high-purity grade (>99%), and purchased from Sigma–Aldrich. The iron source was $Fe_2(SO_4)_3 \times H_2O$ 75% provided by Sigma Aldrich. The complexing agents used were citric acid anhydrous (>99.5%) and (S,S)-ethylenediamine-N,N'-disuccinic acid trisodium salt (EDDS) solution in water (35%w/v) provided by Fluka and Sigma Aldrich, respectively. Reagent-grade hydrogen peroxide (30% w/v) and sulphuric acid (98%) were from Sigma Aldrich. The real effluents were taken downstream from the secondary biological treatment in the El Ejido MWTP (province of Almería, Spain) and used as received within the next five days. The effluents were pretreated by silex (sand) filters and micro-filtration (E, see Fig. 1) before NF, removing all particles over 5 μm. Characteristics of the pretreated MWTP effluent are shown in Table 1.

2.2. *Analytical determinations*

The concentration profiles of each compound were monitored by UPLC/UV (Agilent Technologies, Series 1200) and a C-18 analytical column (Agilent XDB-C18 1.8 μm, 4.6 × 50 mm). The