Strategies for reducing cost by using solar photo-Fenton treatment combined with nanofiltration to remove microcontaminants in real municipal effluents: Toxicity and economic assessment

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HIGHLIGHTS

- Treating microcontaminants by solar photo-Fenton combined with nanofiltration.
- Photo-Fenton was operated at circumneutral pH using iron complexing agent.
- 35 microcontaminants were monitored by LC-Qtrap, reaching >90% degradation.
- Degradation did not produced intermediates with any significant effect on toxicity.
- Operating costs were between 0.48 and 1.7 €/m^3.

GRAPHICAL ABSTRACT
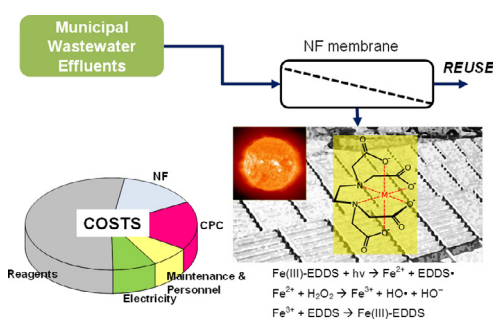
ARTICLE INFO

ABSTRACT

This study shows solar photo-Fenton combined with nanofiltration (NF) to treat microcontaminants (MCs) in actual MWTP effluents. Photo-Fenton was operated at circumneutral pH using (S,S)-Ethylenediamine-N,N′-disuccinic acid trisodium salt (EDDS) as the iron complexing agent (Fe:EDDS in a molar ratio of 1:2) and compared with classical photo-Fenton at pH3. Starting H_2O_2 concentration was 50 mg/L and Fe was 0.1 mM or 0.2 mM. MC degradation was over 90% in all cases and 35 different MCs were monitored by Liquid Chromatography–Mass Spectrometry enabling the two processes to be compared under real conditions. NF pretreatment enabled photocatalysis to be run at lower flow rates and with higher starting concentrations reducing the surface area of solar collectors and reagents needed. Acute and chronic toxicity tests were also carried out before and at the end of each treatment evaluated and it seemed clear that MC degradation did not produce intermediates with any significant effect on toxicity. In addition, a detailed economic assessment was also performed. Operating costs were higher at circumneutral pH (0.76 €/m^3) with EDDS than with classical photo-Fenton at pH3 (0.48 €/m^3).

1. Introduction

The growing demand for water and continual discovery of new potentially harmful contaminants make the need for further research in any area that can contribute to protecting human health and the environment, achieve sustainable water reuse and

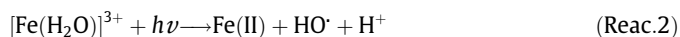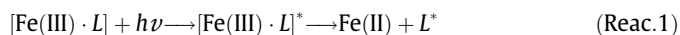∗ Corresponding author at: Plataforma Solar de Almería-CIEMAT, Ctra Senés km 4, 04200 Tabernas (Almería), Spain.
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mitigate the effects of drought and climate change self-evident. But this problem is compounded even more because some biorecalcitrant microcontaminants (detergents, pharmaceuticals, personal care products, flame retardants, antiseptics, industrial additives, steroids, hormones, pesticides, etc.) are not eliminated by conventional biological municipal wastewater treatment plants [1].

Physical treatments, such as membrane nanofiltration (NF) and reverse osmosis have been shown to be promising technologies for removing microcontaminants (MCs) [2]. However, these techniques do not destroy dissolved organic carbon, salts, turbidity or all MCs in the concentrate, which must then be treated. In the past few years, the combination of membrane treatment with Advanced Oxidation Processes (AOPs), mainly ozonation, Fenton, photocatalysis and photo-oxidation, sonolysis and electrochemical processes applied to NF/RO concentrate oxidation, has been studied for tertiary treatment in Municipal Wastewater Treatment Plants (MWTPs) [3]. However, most of these studies have been based on removing DOC. To date, studies on MC elimination from NF/RO concentrates are very limited [4–6]. Recently, Ganiyu et al. 2015 [2] reviewed combination of membrane filtration and AOPs for removal of pharmaceutical residues. This complete review shows the lack of development of inexpensive alternatives to facilitate industrial application. In addition, Ganiyu et al. 2015 underlined the importance of conducting studies to determine the economic and environmental implications of applying these techniques for water/wastewater treatment.

To date, the photo-Fenton process is perhaps one of the AOPs most studied. Today, the trend in photo-Fenton research is to study its effectiveness at neutral or circumneutral pH [7–10] for several reasons: (i) To avoid acidification and neutralization stages, thereby lowering costs without increasing water salinity, (ii) Reduce reagent and iron consumption, and (iii) Avoid addition of hydroxyl radical scavengers such as sulfate or chloride.

It is common knowledge that the optimum pH for solar photo-Fenton is from 2.8 to 3, when iron is soluble and $[Fe(OH)]^{2+}$ is the most photoactive aquo-complex. At pH above 3, Fe(III) precipitates in the form of $Fe(OH)_3$ and the process loses efficiency [11]. On the other hand, Fe(III) can form complexes with other ligands present in natural or wastewater, such as HO^-, H_2O, HO_2^-, Cl^-, $R-COO^-$, $R-OH$, $R-NH_2$, etc., or in fact, any Lewis base able to form complexes with ferric iron, and obtain $HO^\cdot$, or other organic radical, as a product (Reactions (1)–(4)), in a wide pH range ($3 < pH < 9$). In addition, these complexes have different quantum yields, which, depending on the ligands [11], may be even higher than the quantum yields of aquo-complexes.

$$[Fe(III) \cdot L] + h\nu \longrightarrow [Fe(III) \cdot L]^* \longrightarrow Fe(II) + L^* \qquad \text{(Reac.1)}$$

$$[Fe(H_2O)]^{3+} + h\nu \longrightarrow Fe(II) + HO^\cdot + H^+ \qquad \text{(Reac.2)}$$

$$[Fe(HO)]^{2+} + h\nu \longrightarrow Fe(II) + HO^\cdot \qquad \text{(Reac.3)}$$

$$[Fe(OOC-R)]^{2+} + h\nu \longrightarrow Fe(II) + CO_2 + R^\cdot \qquad \text{(Reac.4)}$$

The main purpose of this study was to show a new pilot-plant operating strategy for solar photo-Fenton combined with NF to treat MCs in actual MWTP effluents. This paper mainly focuses on the treatment of concentrate from MWTP effluents obtained by operating NF system in batch mode and not in continuous, as a way for obtaining a realistic concentrate. Photo-Fenton was operated at circumneutral pH using EDDS as the iron complexing agent and compared with classical photo-Fenton at pH3. 35 different MCs were monitored enabling the two processes to be compared under real conditions. Acute and chronic toxicity tests were also carried out before and at the end of each treatment evaluated. In addition, a detailed economic assessment was also performed.

2. Materials and methods

2.1. Reagents and chemicals

All MC standards were analytical grade (>99%) purchased from Sigma-Aldrich (Steinheim, Germany). Samples from experiments were prepared by appropriate dilution of the stock solutions in acetonitrile (ACN)/water, 10:90 (v/v). Fe(II) from $FeSO_4 \cdot 7H_2O$ was used for the solar photo-Fenton experiment at pH3, while Fe(III) from $Fe_2(SO_4)_3 \cdot H_2O$ 75% provided by Sigma Aldrich was used for photo-Fenton at neutral pH. (S,S)-Ethylenediamine-N,N′-disuccinic acid trisodium salt (EDDS) solution in water (35% w/v) was provided by Panreac. Reagent-grade hydrogen peroxide (30% w/v), sulfuric acid (98%) and NaOH (0.1 N) were provided by Sigma-Aldrich. Commercial cartridges packed with Oasis™ HLB (200 mg, 6 cm^3) were purchased from Waters (Mildford, MA, USA).

2.2. Analytical measurements

Dissolved organic carbon (DOC) and total inorganic carbon (TIC) were measured with a Shimadzu TOC-VCSN analyzer (Kyoto, Japan). Anion concentrations were determined with a Metrohm 872 Extension Module 1 and 2 ion chromatograph system configured for gradient analysis. Cation and ammonium concentrations were determined with a Metrohm 850 Professional IC configured for isocratic analysis. Water conductivity was analyzed using a CRISON GLP3u conductivity meter. Turbidity was measured using a Hach 2100 N turbidimeter. Chemical Oxygen Demand was determined with Merck kits in a 10–50 mg/L range using a NOVA-30 Spectroquant photometer. The H_2O_2 concentration was determined by spectrophotometry using titanium (IV) oxysulfate following DIN 38402H15. Total iron concentration (filtered with a 0.45-μm diameter PTFE syringe-driven filter) was measured using the 1,10-phentranoline method following ISO 6332.

The samples were concentrated 100 times by automatic solid phase extraction, using 6-cm^3 OASIS HLB cartridges (Waters) and a vacuum chamber (Supleco Visiprep). Cartridges were conditioned with 5 mL of MeOH and 5 mL of H_2O at pH8, water samples were adjusted to pH8 and extracted at 10 mL/min. The cartridges were washed with 4 mL H_2O (pH 8), dried with N_2, eluted with 2×4 mL Methanol, evaporated to dryness with N_2, and recovered in 1 mL ACN/H_2O (1:9), filtered through a 0.2 mM syringe-driven filter and injected into the Liquid chromatograph.

The analytical method used for the detection and quantification of the target MCs in the MWTP effluent used in this study was carried out in a hybrid quadrupole/linear ion trap mass spectrometer system (5500 QTRAP®, AB Sciex Instruments, Foster City, CA, USA) under Multiple Reaction Monitoring conditions (LC-QTRAP-MS/MS). The instrument was equipped with an electrospray ionization source operating in positive mode. The analytes were separated using an HPLC series 1200 (Agilent Technologies, Wilmington, DE, USA) equipped with a reverse-phase C-18 analytical column (Zorbax eclipse plus SB, Agilent Technologies, 5 μm 150 × 4.6 mm). LC analytical conditions were 10% ACN: 90% MiliQ-Water (0.1% formic acid) at t = 0 min to 100% ACN in t = 40 min and held for 10 min at a flow rate of 400 μL/min. The injection volume was 5 μL.

The mass spectrometer was optimized to identify 75 MCs, which were quantified by matrix matched calibration. Calibration curves included analyte concentrations at 0.01, 0.05, 0.1, 0.5 and 1 μg/L. The MS–MS parameters (declustering potential, collision energy and cell exit potential) were optimized for maximum sensitivity by direct infusion of the standards of each compound into the MS. Two MRM transitions were selected for each compound, one for quantification and the second for confirmation. Tandem