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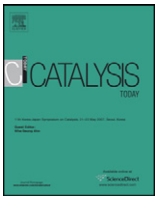

Modified photo-Fenton for degradation of emerging contaminants in municipal wastewater effluents

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ABSTRACT

As normal municipal wastewater treatment plants (MWTP) are not able to entirely degrade xenobiotic substances, this study focuses on modified solar photo-Fenton treatment ($5\,\mathrm{mg\,L^{-1}}$ Fe, initial pH ≈ 7) of a municipal wastewater treatment plant (MWTP) effluent. However, effluents do not contain compounds which could form photoactive Fe^{3+} complexes. The use of ferrioxalate, humic substances (HA) and mixing the MWTP effluent with small amounts of influent could be justified to form photoactive Fe^{3+} complexes. All experiments were done in MWTP effluent spiked (5 or 100 μg/L) with 15 emerging contaminants (ECs) using a pilot compound parabolic collector (CPC) solar plant designed for solar photocatalytic applications. Dissolved organic carbon and UPLC–UV (with prior solid phase extraction) were applied for evaluating the results. The oxalate-enhanced process provided satisfactory EC degradation results but low residual pH of the treated water. HA ($10\,\mathrm{mg\,L^{-1}}$) enhanced the process, balancing degradation time and residual pH. Mixing of MWTP influent and effluent delivered rather disappointing results, as EC degradation was unsuccessful in all cases tested.

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1. Introduction

Growing use of xenobiotic substances like pharmaceuticals, synthetic fragrances, pesticides, drugs and other contaminants is leading to increasing concentrations of these substances in waste water [1–4]. As normal municipal wastewater treatment plants (MWTP) are not able to entirely degrade these contaminants, present in $\mu\mathrm{g}$-$\mathrm{ng\,L^{-1}}$ concentration levels, they end up in the aquatic environment and may cause ecological problems, such as feminization of higher organisms, microbiological resistance and accumulation of these substances in soil, plants and animals [5–7]. It is therefore important to degrade these emerging contaminants (ECs) prior to their release into the environment, and even more so if the water is reused for irrigation. If treated water is reused for irrigating crops, golf courses, public gardens and so forth, they not only have to be disinfected (free of pathogens), but entirely free of these ECs as well.

Among the advanced treatment technologies for degrading ECs in waste water, advanced oxidation processes (AOPs) present a particularly attractive option, as they produce OH radicals, which are capable of oxidizing almost any organic molecule, yielding short-chain organic acids, inorganic ions and CO_2 as final products. The usual drawback of AOPs are their high electricity demand for devices such as UV lamps and ozonators, and large amounts of oxidants and catalysts, as well as low pH operating conditions (for Fenton and photo-Fenton) [8,9], which is why commercial applications are still scarce. Processes like photo-Fenton can be made feasible for commercial applications by using solar energy, and optimizing the pH and amounts of iron and oxidant [10].

This study focuses on modified solar photo-Fenton treatment ($5\,\mathrm{mg\,L^{-1}}$ Fe, initial pH ≈ 7, $50\,\mathrm{mg\,L^{-1}}$ initial H_2O_2) of an MWTP effluent in which the pH is far from the optimum of 2.8 for photo-Fenton treatment [11,12]. At this pH, there is still no precipitation and the dominant iron species in solution is $[Fe(OH)]^{2+}$, the most photoactive ferric iron–water complex (Eqs. (2) and (3)). A pH far from 2.8 is detrimental to the process, as the concentration of $[Fe(OH)]^{2+}$ is low, thereby justifying the use of oxalic acid, humic acid or a mixture of secondary MWTP effluents with influent wastewater, which could compensate for the disadvantage of the lack of $[Fe(OH)]^{2+}$ by forming ferric iron complexes ($Fe^{3+}L$) from other compounds (Eq. (1)). This study focuses in all these matters. However, effluents from MWTPs do not contain compounds, such as oxalic acid, lactic acid, quinolinic acid, fusaric acid or pinolenic acid, to name only a few [11] which could form photoactive $Fe^{3+}L$, as they are usually highly biodegradable.

$$[Fe^{3+}L] + h\nu \rightarrow [Fe^{3+}L]^{*} \rightarrow Fe^{2+} + L^{\bullet} \qquad (1)$$

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$$[Fe(H_2O)]^{3+} + h\nu \rightarrow Fe^{2+} + OH^{\bullet} + H^{+} \quad (2)$$

$$[Fe(OH)]^{2+} + h\nu \rightarrow Fe^{2+} + OH^{\bullet} \quad (3)$$

The use of ferrioxalate has certain advantages: it is a photosensitive complex, which allows the solar spectrum up to 450 nm to be used, thus improving solar photo-Fenton oxidation efficiency, and complexation of iron with oxalate widens the pH operating range to near neutrality. Apart from that, its chemistry provides additional sources of oxidant H_2O_2 and catalyst Fe^{2+} for the Fenton reaction, thus yielding more OH radicals according to the following reactions (Eqs. (4)–(9)) [13,14]:

$$[Fe(C_2O_4)_3]^{3-} + h\nu \rightarrow Fe^{2+} + 2C_2O_4{}^{2-} + C_2O_4{}^{\bullet -} \quad (4)$$

$$C_2O_4{}^{\bullet -} + [Fe(C_2O_4)_3]^{3-} \rightarrow Fe^{2+} + 3C_2O_4{}^{2-} + 2CO_2 \quad (5)$$

$$C_2O_4{}^{\bullet -} + O_2 \rightarrow 2CO_2 + O_2{}^{-} \quad (6)$$

$$O_2{}^{-} + H^{+} \rightarrow HO_2{}^{\bullet} \quad (7)$$

$$2HO_2{}^{\bullet} \rightarrow H_2O_2 + O_2 \quad (8)$$

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + HO^{\bullet} + OH^{-} \quad (9)$$

Humic substances (HS) are naturally occurring organic substances resulting from microbiological and chemical transformation of organic debris. Although there are differences in HS from different sources, some general properties are similar. They are the largest fraction of dissolved organic matter in natural water and are categorized as humic acid (HA), fulvic acid and humin (according to their solubility). They strongly absorb sunlight and generate exited triplet states ($^3HS^*$), various reactive oxygen species, hydroxyl radicals, singlet oxygen ($^1O_2$) and hydrogen peroxide, and may therefore photoinduce the transformation of non-absorbing organic chemicals. They behave like colloids and have absorptive qualities. They contain carboxylic acids, phenolic, alcoholic quinine, and amino and amido groups which enable them to support ion exchange and redox processes, and to form complexes. They contain also large numbers of stable free radicals which can react with various substances [15–18].

Finally, as a way to avoid adding other chemicals to the treatment, mixing the MWTP effluent with small amounts of influent wastewater could be justified, as influent wastewater could contain substances that form photoactive ferric iron complexes ($Fe^{3+}L$), which, as mentioned above, are very unusual in effluents because, as they are so biodegradable, they are eliminated during the MWTP treatment.

2. Materials and methods

2.1. Reagents

All reagents used for chromatographic analyses, acetonitrile, methanol and ultrapure water (Milli-Q) were HPLC grade. Analytical standards for chromatography analyses were purchased from Sigma–Aldrich. The 15 compounds selected were: acetaminophen, antipyrine, atrazine, caffeine, carbamazepine, diclofenac, flumequine, hydroxybiphenyl, ibuprofen, isoproturon, ketorolac, ofloxacin, progesterone, sulfamethoxazole and triclosan. Photo-Fenton experiments were performed using iron sulfate ($FeSO_4 \cdot 7H_2O$), reagent grade hydrogen peroxide (30%, w/v), sulfuric acid (98%) for carbonate stripping, oxalic acid ($C_2H_2O_4 \cdot 2H_2O$) and HA, all provided by Panreac. The filters used were Millipore Millex syringe driven 0.2 μm (pore size) nylon membrane filters.

2.1.1. MWTP effluent and influent

All experiments were done in MWTP effluent spiked with ECs. The treated waste water was taken downstream of the MWTP secondary biological treatment in El Ejido (province of Almería, Spain) and used as received within the next 3 days. Initial COD (chemical oxygen demand), DOC (dissolved organic carbon) and TIC (total inorganic carbon) were between: 26 and 63, 10 and 24 and 91 and 120 mg L^{-1} respectively. The main characteristics of the MWTP influent were COD between 250 and 300, DOC between 97 and 120 and TIC 95 and 120 mg L^{-1}.

2.2. Solar photo-Fenton pilot plant

Photo-Fenton experiments were performed at the Plataforma Solar de Almería in a pilot compound parabolic collector (CPC) solar plant designed for solar photocatalytic applications [19]. This batch reactor is composed of two 11 L modules (CPC) with 12 pyrex glass tubes (30 mm O.D.) operated in series mounted on a fixed platform tilted 37° (local latitude). The water flows (20 L min^{-1}) directly from one module to the other and finally to a 10 L tank. From the tank it is pumped again to the solar collectors. The piping and valves (3 L) between the reactor and the tank are black HDPE, which is highly resistant to chemicals, weatherproof and opaque, preventing any photochemical effect from outside the collectors. The total illuminated area is 3 m^2, the total volume (two modules + tank + piping and valves) is 35 L (V_T) and the irradiated volume is 22 L (V_i). Solar ultraviolet radiation (UV) was measured by a global UV radiometer (Kipp & Zonen, model CUV 3) mounted on a platform tilted 37° (the same as the CPCs) and connected to a computer for continuous recording (data every 1 s). The temperature inside the reactor was continuously recorded by a temperature probe (Crioterm PT-100 3H) inserted in the piping. With Eq. (10), combination of the data from several days of experiments and their comparison with other photocatalytic experiments is possible,

$$t_{30\,W,n} = t_{30\,W,n-1} + \Delta t_n \frac{UV}{30}\frac{V_i}{V_T}; \quad \Delta t_n = t_n - t_{n-1}; \quad t_0 = 0\,(n = 1) \quad (10)$$

where t_n is the experimental time for each sample, UV is the average solar ultraviolet radiation ($\lambda < 400$ nm) measured between t_{n-1} and t_n, and $t_{30\,W}$ is a “normalized illumination time”. In this case, time refers to a constant solar UV power of 30 Wm^{-2} (typical solar UV power on a perfectly sunny day around noon).

2.3. Experimental setup

The MWTP effluent was stripped of carbonates with H_2SO_4 (98%), as it is a well known fact that $CO_3{}^{2-}$ and $HCO_3{}^{-}$ are efficient radical scavengers [20–22], and spiked with 15 ECs at 100 μg L^{-1} each, selected from those often found in MWTP effluents [23]. Although the concentration of 100 μg L^{-1} for each compound is quite high compared to the real concentration of these ECs in the μg L^{-1} range [1,4], it is still low enough to simulate real conditions and compare the different approaches. In any case, the approach considered most suitable was tested under realistic conditions, spiking MWTP effluent with 5 μg L^{-1} of each EC. Samples were concentrated 50 times for analysis by SPE, as mentioned below.

Between 0.4 and 0.5 g of acid per liter effluent water was used to lower the TIC below 1 mg L^{-1}. After the stripping of CO_2, 1.4 mL of a solution containing the 15 compounds (2.5 g L^{-1} of each compound in MeOH, DOC from methanol was 12 mg L^{-1} or 0.6 mg L^{-1} for 100 μg L^{-1} and 5 μg L^{-1} experiments, respectively) was added directly into the reactor containing the effluent water. After homogenization, three different approaches were used:

(a) Adding peroxide, then after homogenization, 5 mg L^{-1} Fe and 35 mg L^{-1} oxalic acid which ads up to a molar ratio of 1:3.6 (ratio derived from Eq. (4)). Some excess oxalic acid was added, as it is consumed throughout the process.

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