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Solar photo-Fenton at mild conditions to treat a mixture of six emerging pollutants

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HIGHLIGHTS

- Solar photo-Fenton has been able to remove a mixture of six emerging pollutants.
- The reaction was performed at acidic and circumneutral media.
- Reaction rate was highly influenced by the sample matrix.
- Intermediates were detected and related with changes in toxicity.

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ABSTRACT

The applicability of photo-Fenton to degrade a mixture of emerging pollutants (EPs) namely amoxycillin, acetaminophen, acetemiprid, caffeine, clofibric acid and carbamazepine has been studied at different scenarios. At high concentrations, acidic photo-Fenton was able to achieve a fast removal of the EPs. Although, complete mineralization was not reached, the toxicity of the solution was decreased according to the respiration of activated sludge and luminescence of *Vibrio fischeri* assays, although according to this last assay a transitory enhancement of the toxicity was found, attributable to the formation of toxic by-products such as phenols, chlorophenols and chlorinated pyrydines. Experiments carried out with 5 mg/l of each EP showed that at neutral media the process was two orders of magnitude less efficient than at acidic pH, although it was still able to remove the EPs. The aqueous matrix has a remarkable effect on the process as the presence of humic acids increased the reaction rate and inorganic salts played an inhibitory role. Finally, experiments performed with 10 μg/l of each EP showed that under those experimental conditions nearly complete removal of the EPs was reached with neutral photo-Fenton after 120 min of irradiation; in this case, humic substances played a disfavorable role.

1. Introduction

In recent years, an important number of synthetic compounds have been found in surface waters at trace amounts, as a consequence of human activity. They are commonly referred to as emerging pollutants (EPs), because they have been recently detected and hence their potential effects on humans and natural ecosystems have not yet been elucidated [1]. Among the substances that can be considered within this group are perfluorinated compounds, pharmaceuticals, hormones, endocrine disruptors, sunscreens, algal toxins, dioxane or nanomaterials [2,3].

Emerging pollutants have been found in the effluent of wastewater treatment plants, which constitutes a major limitation for their potential reuse. Hence, development of new strategies to deal with this concern are needed. In particular, coagulation–floculation, adsorption onto activated carbon, biological processes or nanofiltration have been employed, as recently reviewed [4,5]. Oxidative processes are promising methods to deal with this environmental concern [6]: electrochemical methods have been demonstrated to be efficient to remove pharmaceuticals and personal care products, as reviewed by Brillas et al. [7] and, on the other hand, photochemical methods employing sunlight as irradiation source might also be of special interest because of the enhanced sustainability they involve [8]. In this context, the Fenton reagent could be useful. It consists in a mixture of iron salts and hydrogen peroxide at acidic pH; under these conditions, iron catalyzes decomposition of hydrogen peroxide into highly oxidizing species, such as hydroxyl radicals. Although this process occurs in the dark, it is greatly enhanced upon UV–vis irradiation ($\lambda < 500$ nm) and hence, sunlight can be used as irradiation source [9].

There is some information on the treatment of emerging pollutants by the photo-Fenton process [10]; however, the use of highly acidic pH might be an important drawback for the real applicability of this method. Processes based in the Fenton reagent, including

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photo-Fenton, are less efficient at circumneutral media than at the optimum acidic pH because of the low solubility of iron at neutral media, but also to a modified mechanism which favors formation of highly oxidized iron species (e.g. ferryl ions) instead of the more reactive hydroxyl radical [11–14]. However this process might be a useful alternative to remove chemicals at µg or ng L^{-1}, as it is the case of EPs in effluent of wastewater treatment plants. In fact, some recent work has been devoted to explore the applicability of this methodology for this purpose [15,16].

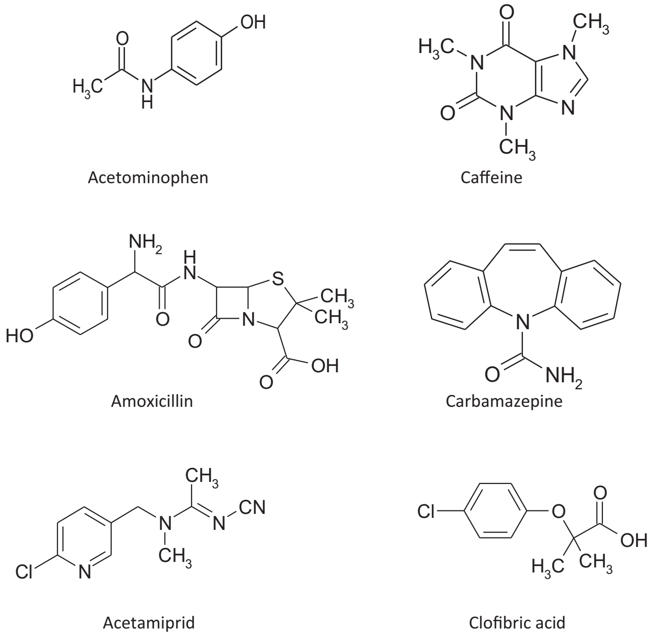
However, further research on this topic is meaningful. As EPs show diverse chemical structures, their behavior vs. photo-Fenton might be different. In addition, primary removal of the pollutant might not represent detoxification of the effluent and a careful identification of major intermediates and assessment of the toxicity of treated solutions is required. Finally, the presence of natural organic matter (e.g. humic acids) can play an important role in the process that deserves to be investigated.

With this background, the aim of this work is to gain further insight into the use of circumneutral photo-Fenton as a tertiary process to remove EPs at the effluent of a wastewater treatment plant. Experiments have been performed with a mixture of six EPs, namely amoxycillin (antibiotic), acetaminophen (analgesic), acetemiprid (insecticide), caffeine (stimulating agent), clofibric acid (metabolite of clofibrate, also employed as herbicide) and carbamazepine (psychiatric drug); chemical structures can be found at Scheme 1. Preliminary experiments have been performed at high initial concentrations of the EPs in order to allow a reliable monitoring of the process, then concentrations have been decreased down to 10 µg/l to better reproduce EPs in the effluents of wastewater treatment plants. Changes in the toxicity, major by products formed in the process and the role of humic acids have been studied.

2. Experimental

2.1. Reagents

Acetaminophen, caffeine, amoxicillin, clofibric acid, carbamazepine, acetamiprid and humic acid sodium salt (AHA) were purchased from Sigma–Aldrich. Hydrogen peroxide (30% v/v) and ferrous sulfate, used in the photo-Fenton reactions, were obtained from Panreac.



Acetominophen

Caffeine

Amoxicillin

Carbamazepine

Acetamiprid

Clofibric acid

Scheme 1. Chemicalstructures of EPs employed in this work.

Water employed in most reactions was Milli-Q grade. In other experiments, EPs were spiked in samples taken from the effluent of the secondary settling tank of a wastewater treatment plant, which consisted in a physical–chemical primary treatment followed by an aerobic activated sludge biological reactor. The main parameters of these samples were systematically inside the following ranges: pH, 7.5; conductivity, 2.4–2.8 ms/cm; dissolved organic carbon (DOC), 15–50 mg/l; inorganic carbon, IC, 70–90 mg/l (which results in a HCO_3^- concentration of ca. 350–450 mg/l) and chemical oxygen demand (COD) 60–120 mg/l.

2.2. Photo-Fenton experiments

Photo-Fenton processes were carried out with the mixture of six EPs; the initial concentration of each EP was between 10 µg/l and 50 mg/l. The amount of iron was 5 mg/l, added as iron(II) sulfate. The stoichiometric amount of hydrogen peroxide required to mineralize all the organics was added at the beginning of the experiment. The reaction was carried out at the optimal pH value (2.8), and at pH = 7; sulfuric acid or sodium hydroxide were employed to adjust the pH. Eventually, humic acids (10 mg/l) were added to the reaction mixture.

Samples were irradiated with a solar simulator (Oriel Instruments, Model 81160 equipped with a 300 W xenon lamp) in cylindrical open glass vessels. Magnetic stirring was kept all along the reaction time and water was periodically added in order to compensate for the evaporation loss. Temperature was ca. 30 °C throughout the experiment. Before analysis all samples were filtered through polypropylene (0.45 µm) and, eventually, preconcentrated following the procedure described below, or neutralized when submitted to bioassays. Those samples used for biological analysis or for COD measurements were free of hydrogen peroxide.

2.3. Analysis

The concentration of each EP was determined by UHPLC (Perkin Elmer model Flexar UPLC FX-10) equipped with a Brownlee Analytical column (DB-C18). A mixture of acetonitrile (A) and a 0.1% formic acid aqueous solution (B) was used as eluent. The relative amount of each solvent was changed in a linear gradient, from 3% A to 70% A in 8 min; the flow rate was 0.3 ml/min. Retention times were 1.7 for acetaminophen 2.1 for amoxicillin, 3.3 for caffeine, 4.9 for acetamiprid, 5.6 for carbamazepine and 6.2 for clofibric acid. The wavelengths used for the EPs quantitations were: 205 nm (acetaminophen, amoxicillin, caffeine and carbamazepine), 225 nm (clofibric acid) and 245 nm (acetamiprid). For the experiments containing 10 µg/l of each EP, the samples were preconcentrated by solid phase extraction (SPE); briefly, 250 ml of sample were flown through a LiChrolut EN 200 mg (Merck) cartridge; then EPs were recovered with 3 ml of methanol.

Eventually, the reaction products were analyzed by GC–MS; a gas chromatograph GCMS-QP2010S (Shimadzu) equipped with a quadrupole mass analyzer was employed. 10 µl of sample obtained after SPE concentration (see above) were injected; the temperature of the injector was 250 °C and the split ratio was 1:30. A Meta X5 Teknokroma column was used and helium was employed as carrier gas, with a flow rate of 35 cm/s. The column temperature was kept at 60 °C for 3 min, then it was increased with a 8 °C/min rate from 60 °C to 280 °C and finally it was kept at 280 °C for 3 min.

DOC was determined with a Shimadzu model TOC-V CSH apparatus. COD was determined photometrically according to the dichromate method [17]; digestions were performed at 148 °C in a Thermoreaktor TR300 (Merck) and a Spectroquant NOVA 60