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Bio-based substances from urban waste as auxiliaries for solar photo-Fenton treatment under mild conditions: Optimization of operational variables

J. Gomis[a], L. Carlos[b], A. Bianco Prevot[c], A.C.S.C. Teixeira[d], M. Mora[e], A.M. Amat[a], R. Vicente[a], A. Arques[a,*]

[a] Grupo de Procesos de Oxidación Avanzada, Dpto de Ingeniería Textil y Papelera, Universitat Politècnica de València, Plaza Ferrándiz y Carbonell s/n, Alcoy, Spain
[b] Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), CCT-La Plata-CONICET, Universidad Nacional de La Plata, Diag 113 y 64, La Plata, Argentina
[c] Dipartimento di Chimica, Università di Torino, Via Giuria 7, Torino, Italy
[d] Escola Politécnica da Universidade de São Paulo, Av. Prof. Luciano Gualberto, tr.3, 380 São Paulo, Brazil
[e] Dpto de Matemática Aplicada, Universitat Politècnica de València, Plaza Ferrándiz y Carbonell s/n, Alcoy, Spain

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ABSTRACT

The use of soluble bio-based organic substances (SBO) obtained from urban wastes to expand the pH region where the photo-Fenton process can be applied has been investigated in this study. For this purpose, a mixture of six pollutants, namely acetaminophen, carbamazepine, amoxicillin, acetamiprid, clofibric acid and caffeine, at an initial concentration of 5 mg L^{-1} each, has been employed. Surface response methodology, based on the Doehlert matrix, has shown to be a useful tool to determine the effect of pH (in the range 3–7), concentration of SBO (15–25 mg L^{-1}) and iron (2–6 mg L^{-1}) on the performance of the photodegradation of the studied pollutants, measured by their half-life. Results indicate that, at high SBO concentration, the optimum pH shifts in most cases to a higher value (between 3 and 4) and that a significant loss of efficiency of the process was only observed at pH values above 5. An iron concentration of 4–5 mg L^{-1} and an amount of SBO of 19–22 mg L^{-1} have been determined to be the optimal conditions for the degradation of most of the studied pollutants at pH = 5.

1. Introduction

Wastes have deserved attention from researchers, as they could be a sustainable source of materials with a wide range of potential applications [1]. In particular, soluble bio-based organic substances (SBO) have been isolated from solid organic wastes submitted to aging under aerobic fermentation conditions, following a process that involves extraction of the soluble fraction at basic pH and posterior precipitation at acidic media [2]. SBO are constituted by a mixture of macromolecules, which average molecular weight ranges from 67 to 463 kg mol^{-1}; they consist of long aliphatic chains, aromatic rings and several oxygen and nitrogen-containing functional groups [2]. Hence, these materials show basic structural similarities with some macromolecules found in natural organic matter (NOM), such as humic and fulvic acids, which play an important role in photochemical processes leading to the self-remediation of ecosystems [3]. In this context, determining the potential use of SBO for water detoxification is meaningful, as this may be considered a green process since it valorises solid wastes as sources of photoactive materials with similar properties as less available NOM. Information on this issue is very scarce, and only some recent papers have been published reporting on the ability of these compounds to act as photocatalysts in the degradation of chlorophenols [4,5], sulphonic acids [6], dyes [7,8] or pharmaceuticals [9]. SBOs action can be related to an enhanced photogeneration of reactive species; however, the strong screen effect produced by these coloured materials negatively affects the degradation of pollutants that can undergo direct photolysis. When simulated sunlight was employed as irradiation source, the screen effect becomes predominant, thus making SBOs unattractive as solar photocatalysts [9].

Alternatively, SBOs might also be employed as complexing agents to drive photo-Fenton processes at mild conditions. Photo-Fenton is based on the ability of iron salts to catalyse

* Corresponding author. Tel.: +34 966528417.
E-mail address: aarques@txp.upv.es (A. Arques).

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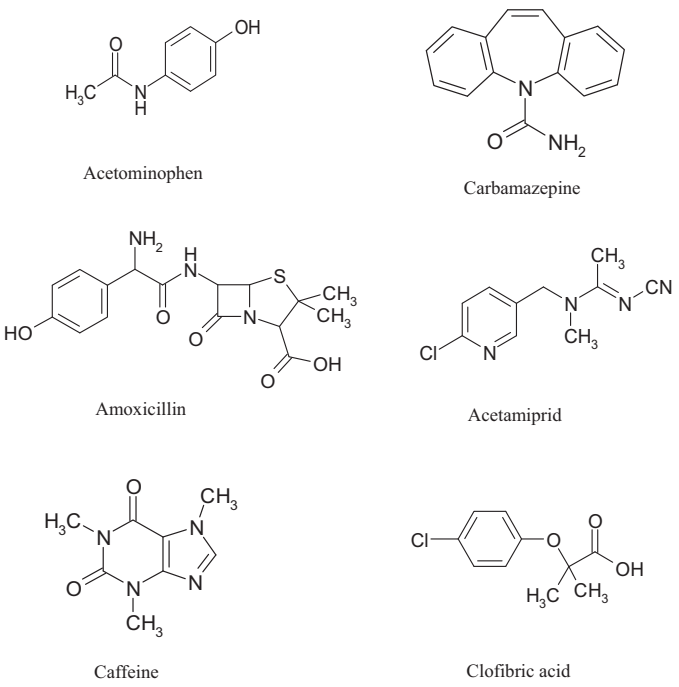

Fig. 1. Chemical structures of EPs used in this study.

decomposition of hydrogen peroxide into highly oxidizing species (mainly hydroxyl radicals, although other species might also contribute) in a process that is accelerated by irradiation [10]. One major drawback of this process is the highly acidic media required to avoid formation of non-active iron oxides or hydroxides. However, some efforts have been recently made for the implementation of photo-Fenton at circumneutral pH. This approach might be especially useful to treat emerging pollutants (EPs) as a certain loss of efficiency in the generation of reactive species might be acceptable in this case, as EPs are commonly found at low concentration, and hence lesser amounts of oxidizing species are necessary [11,12]. This strategy can be improved by using chemical auxiliaries, able to form photoactive complexes, at mild pH, with the iron added [13]. Humic acids are among the materials employed for this purpose, because of their ability for iron complexation [13–16].

Because of their similarity with humic substances, SBOs are also candidates to extend the application of photo-Fenton to pH conditions where iron ions are normally not soluble. Indeed, photo-Fenton process in the presence of SBOs have been recently shown to be able to remove a mixture of EPs at pH = 5.2 [9]. Hence, a logical step beyond is to determine the role of the operational parameters on the efficiency of the process. For this purpose, a response surface methodology based on Doehlert design has been chosen in this work in order to determine the effect of SBOs and iron concentrations at the pH interval between 3, close to the optimal value, and 7. The Doehlert design has been commonly employed as a chemometric tool, enabling to minimize the number of experiments required to obtain the response surface [17,18]. The mixture of EPs employed in previous work [9,16] has been chosen as target solution: acetaminophen, carbamazepine, amoxicillin, acetamiprid, clofibric acid and caffeine (see Fig. 1 for structures).

2. Experimental

2.1. Reagents

Acetaminophen, caffeine, amoxicillin, clofibric acid, carbamazepine and acetamiprid were purchased from Sigma-Aldrich and used as received. Hydrogen peroxide (30% v/v), ferric chloride, sulphuric acid and sodium hydroxide, were obtained from Panreac. Water was Milli-Q grade.

The SBO employed in this work, namely CVT230, was obtained from urban biowastes supplied by ACEA Pinerolese waste treatment plant (Pinerolo, Italy) following a procedure detailed elsewhere [2,19]. Briefly, the starting material was compost from gardening-park trimming residues matured for 230 days: it was digested 4 h at 60 °C at alkaline conditions (pH = 13) and 4 v/w water/solid ratio to favour hydrolysis of organics. Alkaline hydrolyzed solution have been recognized as very similar to the humic matter, in turn characterized by the presence of a dimensionally smaller fraction (fulvic acid) soluble in all the pH range, and of a larger one (humic acid), not soluble below pH 3. Instead of separating the two fractions by means of pH variation, the size difference was exploited. The recovered liquid phase was therefore circulated through a polysulfone ultrafiltration membrane with 5 kD molecular weight cut-off to yield a retentate with 5–10% dry matter content. The membrane retentate was dried at 60 °C to yield the final water soluble bio-based product (SBO). It contained 72.1% (w/w) of volatile solids and the carbon content was 38.3% (see [8] for further details).

2.2. Reactions

Experiments were performed in a 250 mL cylindrical Pyrex vessel irradiated with a solar simulator (Sun 2000, ABET Technologies) equipped with a 550 W Xenon Short Arc Lamp. A pyrex glass filter was used to cut off radiation below 300 nm (which only accounted for a residual fraction of the lamp irradiance). The vessel was loaded with an aqueous solution containing the six EPs at an initial concentration of 5 mg L^{-1} each. SBO concentration was varied in the range 15–25 mg L^{-1}; $FeCl_3$ was added to reach a concentration of iron between 2 and 6 mg L^{-1}. The initial amount of hydrogen peroxide was 2.2 mmol L^{-1} in all cases, which is half the stoichiometric amount required to mineralize the EPs; this concentration was employed in order to obtain a relatively slow kinetics, which allows a better determination and comparison of illumination times required to remove the EPs under the different conditions that have been studied. The pH was adjusted to the desired value (3–7) by dropwise addition of either 0.1 mmol L^{-1} NaOH or 0.1 mmol L^{-1} H_2SO_4. Temperature was kept in the range 30–35 °C throughout the reaction. Samples were periodically taken from the solution, filtered through a polypropylene membrane (0.45 μm) and diluted 1:1 with methanol.

Control experiments showed that direct photolysis of the pollutants was negligible under the employed conditions and irradiation in the presence of H_2O_2 solely resulted in a moderate degradation of amoxicillin (less than 20% after 200 min of irradiation).

2.3. Analysis

The concentration of each EP was determined by UPLC (Perkin Elmer model Flexar UPLC FX-10). A Brownlee Analytical column (DB-C18) was employed as stationary phase. The eluent consisted in a mixture of acetonitrile (A) and a 0.1% formic acid aqueous solution (B); the relative amount of each solvent was changed following a linear gradient, from 3% A to 70% A in 8 min; the flow rate was 0.3 mL min^{-1}. Detection wavelengths were 205 nm (acetaminophen, amoxicillin, caffeine and carbamazepine), 225 nm (clofibric acid) and 245 nm (acetamiprid). Identification and quantification of the EPs were performed by comparison with standards.

2.4. Surface response methodology

In order to gain further insight into the effect of the studied operational variables (pH, SBO and iron concentration), an