Catalysis Today 252 (2015) 177–183

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Determination of photostability, biocompatibility and efficiency as photo-Fenton auxiliaries of three different types of soluble bio-based substances (SBO)

Juan Gomis[a], Mayara G. Gonçalves[b], Rosa F. Vercher[a], Consuelo Sabater[c], María-Angeles Castillo[c], Alessandra Bianco Prevot[d], Ana M. Amat[a], Antonio Arques[a,*]

[a] Grupo de Procesos de Oxidación Avanzada, Universitat Politècnica de València, Plaza Ferrándiz y Carbonell (s/n), E-03801 Alcoy, Spain
[b] U. Tecnológica Federal do Paraná, Rua Deputado Heitor Alencar Furtado, 4900 Curitiba, Brazil
[c] Dpto. Biotecnología, Univ. Politècnica de València, Camino de Vera, s/n., 46022 Valencia, Spain
[d] Università. di Torino, Dipartimento di Chimica, Via Giuria 7, Torino, Italy

ARTICLE INFO

Article history:
Received 12 July 2014
Received in revised form
23 September 2014
Accepted 10 October 2014
Available online 24 November 2014

Keywords:
SBO
Photostability
Photo-Fenton
Biocompatibility

ABSTRACT

The aim of this work is to determine the photostability biocompatibility and efficiency of water soluble bio-based substances (SBO) in photo-oxidative processes for wastewater treatment. Three batches of SBO, isolated from different sources, have been investigated. Differences in the functional groups present in these substances can explain major trends in their physical/chemical properties. Bioassays have proven those materials to be non-toxic but to show poor biodegradability. Their ability to enhance a photo-Fenton process at milder pH (5.2) has been investigated using a mixture of emerging compounds in wastewaters. All the tested SBO were able to remove all pollutants in less than one hour irradiation, and the best results were obtained with those substances showing higher hydrophilic/hydrophobic ratio. Moreover, although SBOs themselves undergo a slight oxidation, no relevant negative effect has been observed for their use in wastewater treatment.

1. Introduction

Generation of increasing amount of wastes from human activities has become a serious environmental concern. Developing technologies and processes able to minimize their production should be a priority; however, this is not always possible and alternative approaches are required to deal with this problem, such valorization through their re-use in other processes. In this context, much effort has been devoted in recent years to obtain valuable products from urban bio-wastes (UBW) (see [1] and references therein cited).

UBW have become a sustainable source of valuable materials, such as water soluble bio-organic substances (SBO). They have been isolated from organic wastes submitted to anaerobic and/or aerobic treatment, yielding biomasses successively hydrolyzed at alkaline pH, the obtained solutions submitted to ultrafiltration, then the retentate is dried and soluble bio-based products obtained as potassium salts [2]. Depending on the origin and treatment of the sourcing UBW, different batches of SBO can be obtained, showing a wide range of chemical composition and properties [3]. In general, SBO are constituted by a mixture of macromolecules which average molecular weight ranges from 67 to 463 kg mol^{-1}. These supramolecular assemblies contain long aliphatic chains, aromatic rings and several functional groups as carboxyl, primary and substituted amine and amide, carbonyl, hydroxyl, phenol, ether or esther. Previous papers studied the potential applications of SBO as surfactants [4], in materials chemistry [5], in soil-washing treatments [6], in agriculture [7] or animal husbandry [8].

SBO chemical composition shows high similarity with that of dissolved organic matter (DOM, e.g. humic or fulvic acids), which is known to generate, upon solar irradiation, highly reactive species able to oxidize pollutants, thus contributing to the abiotic self-remediation of natural ecosystems [9–11]. For this reason, SBO might also be employed in solar photochemical processes for wastewater treatment. Some works have been published reporting on the use of SBO as photosensitizer for the degradation of aromatic sulphonic acids [12], phenols [13] or dyes [14,15]. In addition, SBO might be used to drive a photo-Fenton process under milder conditions. Photo-Fenton is based on the ability of iron salts to decompose hydrogen peroxide into highly reactive species, and

* Corresponding author. Tel.: +34 96652841; fax: +34 966528438.
E-mail address: aarques@txp.upv.es (A. Arques).

http://dx.doi.org/10.1016/j.cattod.2014.10.015
0920-5861/

the process is greatly enhanced upon irradiation [16]. One major drawback is the highly acidic pH which is required to avoid the formation of photochemically inactive iron oxides and hydroxides; in this context the ability of SBO to complex metal cations, such as iron, is useful for the development of photo-Fenton at circumneutral media [17].

However, some important issues still remain unexplored. For instance, SBO could only be employed for wastewater detoxification if they show a good biocompatibility, namely low toxicity and high biodegradability. Furthermore, SBO are mainly formed of organic molecules, and can in turn be attacked by reactive species generated in the photo-oxidative processes, with possible changes in their biological or chemical properties. Any modification in SBO composition might result in different performance of these materials and hence, comparison of different batches of SBO is meaningful. With this background the aim of this paper is to gain further insight into the performance, photo-stability and biocompatibility of three types of SBO obtained from different sources. A battery of bioassays have been employed for toxicity and biodegradability determination; SBO performance before and after irradiation has been tested in the degradation of a mixture of emerging pollutants (EPs), namely acetaminophen, caffeine, amoxicillin, clofibric acid, carbamazepine and acetamiprid. These chemicals have been chosen because they are examples of xenobiotics commonly employed in the literature and they have been previously employed as target pollutants in works involving SBO in the photo-Fenton process [17].

2. Experimental

2.1. Materials

The following types of SBO were employed: (a) FORSUD, isolated from the urban waste organic humid fraction (UWOHF) obtained from separate source collection, mixed with the digestate from an anaerobic reactor fed with UWOHF; (b) CVT230, obtained from home gardening and park trimming residues (GR) piles aerated for 230 days; (c) CVDFT110, isolated from a mixture 35/55/10 (w/w/w) of FORSUD, GR and urban sewage sludge mix, aerated for 110 days. Chemical composition for sourcing bio-wastes (BW) has been reported in detail in the previously published paper [3].

The SBO isolation was performed in a pilot plant at the Studio Chiono & Associati in Rivarolo Canavese, Italy [2]. Briefly, it consisted in an electrically heated and mechanically stirred 500 L reactor, a 102 cm long × 10.1 cm diameter polysulfone ultrafiltration (UF) membrane with 5 kDa molecular weight cut-off, and a forced ventilation drying oven. A stirred stainless steel reactor was loaded with 300 L of aqueous solution of KOH and 75 kg of solid biomass at 65 °C and a pH value of ca. 13. After 4 h, the reactor turned off automatically and the mixture was settled down overnight. The supernatant was pumped to a centrifuge (9000 rpm) to remove the small insoluble fraction (mainly silicoaluminates) that was still present after the treatment. The recovered liquid phase was flown at 40 L/h through an UF membrane operating with tangential flow at 7 bar inlet and 4.5 bar outlet pressure to yield a retentate containing 5–10% of dry matter, which was finally dried at 60 °C. Solid SBO products were obtained in 15–30% w/w yield, relatively to the starting UBW dry matter. The analytical procedures used to measure the elemental composition and functional groups of SBO were ^{13}C NMR, microanalysis and potentiometric titration, and have been described in detail in previous papers [18,19].

Acetaminophen, caffeine, amoxicillin, clofibric acid, carbamazepine and acetamiprid, employed as target pollutants, were purchased from Sigma-Aldrich. Hydrogen peroxide (30% v/v) and ferrous sulphate were supplied by Panreac. Water employed in all the experiments was Milli-Q grade.

The bioluminescent bacteria *Vibrio fischeri* (strain NRRL-B-11177) were purchased by Macherey-Nagel GmbH & Co. (Düren, Germany). *Pseudokirchneriella subcapitata*, and ephippia (dormant eggs) of crustacean *Daphnia magna* were supplied by ECOtest S.L. (Valencia, Spain).

2.2. Reactions

Experiments devoted to check the SBO photo-stability were performed in cylindrical Pyrex vessel (55 mm i.d.). A solar simulator (Sun 2000, ABET Technologies) equipped with a 550 W Xenon Short Arc Lamp was used as irradiation source (see [20] for the spectrum, which closely matches the solar one). For each experiment, the reactor was loaded with 250 mL of solution containing the SBO (100 mg/L). The pH was adjusted to the desired value by adding diluted sulphuric acid. Eventually, the stoichiometric amount of hydrogen peroxide required to oxidize completely each SBO was added, and irradiation was kept until the solution was free of H_2O_2. The amount of H_2O_2 was obtained from the initial chemical oxygen demand (COD) of the SBO, as COD indicates the amount of O_2 required to oxidize completely the sample.

The same experimental device was employed to check the performance of SBO in a mild photo-Fenton process. In this case, the mixture of all six EPs was employed at an initial concentration of each pollutant of 5 mg/L. All three types of SBO (10 mg/L) were used in parallel experiments. The initial concentration of iron(II) was 5 mg/L (added as sulfate salt) and half the stoichiometric amount of hydrogen peroxide to mineralize the pollutants present in the solution was added. The pH was adjusted to 5.2.

2.3. Chemical analysis

The EPs concentration was determined by chromatography (Perkin Elmer model Flexar UPLC FX-10) equipped with a UV–vis detector. A DB-C18 Brownlee Analytical column was used and the eluent was a mixture of acetonitrile (A) and a 0.1% formic acid aqueous solution (B); its composition was changed in a linear gradient, from 3% A to 70% A in 8 min with a flow rate of 0.3 mL/min. Wavelengths employed for detection were: 205 nm (acetaminophen, amoxicillin, caffeine and carbamazepine), 225 nm (clofibric acid) and 245 nm (acetamiprid). Samples were filtered through polypropylene filters (VWR, 0.45 μm) before analysis.

Dissolved organic carbon (DOC) was determined with a Shimadzu model TOC-V CSH apparatus. Chemical oxygen demand (COD) was determined according to the dichromate method [21]: sample digestions were performed at 148 °C in a Thermoreaktor TR300 (Merck) and a Spectroquant NOVA 60 (Merck) was used for the photometric determination. The surface tension of samples was determined by a Krüss K-9 tensiometer.

2.4. Bioassays

In order to check the biodegradability of all three substances, biological oxygen demand (BOD_5) assays were carried out according to the standard manometric method (OECD 301 B, CO_2 evolution test), using an OxiTop© (WTW) to seal the bottle and determine the pressure inside [21]. The BOD_5 values were determined for SBO concentrations of 100 mg/L and 1000 mg/L.

Toxicity assays based on *V. fischeri* bacteria were performed based on ISO 11348-3:2007 standardized test; algae growth inhibition assay was performed according to an adaptation of ISO 8692:2004 test, using the chlorophyceae algae *P. subcapitata*; bioassays based on the inhibition of the mobility of *D. magna* were performed according to the standard ISO 6341:199632 procedure. A detailed description of the experimental procedure followed in