CWPO of bisphenol A with iron catalysts supported on microporous carbons from grape seeds activation

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HIGHLIGHTS

- Fe catalyst were prepared on pyrolized and activated grape seeds support.
- Fe-GS-1 catalyst was highly active and stable upon CWPO of BPA.
- Complete removal of BPA and 60% mineralization was reached at 80 °C.
- BPA CWPO enhanced the biodegradability and reduced the toxicity of the effluent.

GRAPHICAL ABSTRACT
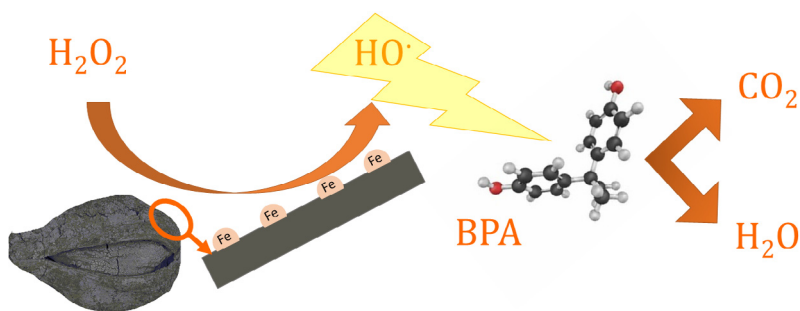
ARTICLE INFO

ABSTRACT

The catalytic wet peroxide oxidation (CWPO) of bisphenol A (BPA) with Fe catalysts supported on activated carbon from grape seeds (GS) has been studied. The GS were pyrolized (N_2, 600 °C, 2 h) and subjected to activation upon partial gasification with air (400 °C, 2 h). Oxidized samples of the char and activated carbon were also obtained upon treatment with HNO_3. The Fe catalysts were prepared by incipient wetness impregnation with ferric nitrate solution. They showed narrow microporosity, with surface area values $\approx$350–500 $m^2 g^{-1}$ and total iron contents between 2.8 and 4.2% wt. The CWPO experiments were carried out at 50–80 °C. The best catalyst allowed complete conversion of BPA (100 mg L^{-1}) and a 60% TOC reduction in 3 h reaction time at 80 °C and the theoretical stoichiometric amount of H_2O_2 (530 mg L^{-1}). The ecotoxicity of the effluent was negligible and the biodegradability was highly improved. In a long-term experiment (100 h), the catalyst suffered a loss of activity upon the early stages on stream ($\approx$15 h), where about 20% of Fe was lost, followed by a highly stable behavior for the rest of the experiment.

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1. Introduction

One of the greatest challenges facing today's society is the correct management of the large amount of wastes produced. Agricultural wastes represent potential resources since they are available at low cost in their occurrence areas. Depending on the starting material, the pyrolysis of these wastes provides chars with certain characteristics of composition, porosity, specific surface area, pore structure and physicochemical properties [1,2]. Different kind of wastes have been studied to obtain char, like apricot and cherry stones [3], olive and grape bagasse [4] or pomegranate seeds [5]. Grape seeds represent up to 15% of the solid wastes from the wine industry [2]. The use of grape seeds for the preparation of adsorbents or catalytic supports appears very interesting owing to their granular morphology and their ready availability from winery works [2,6,7]. Satisfactory results have been obtained when this material has been used as adsorbent for the removal of diuron

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[7] or support of Pd catalyst in the hydrodechlorination of diuron [8] and in nitrate reduction [9].

Advanced oxidation processes (AOPs) have the capability to remove refractory or non-biodegradable pollutants operating at mild conditions [10,11]. Specifically, the potential of catalytic wet peroxide oxidation (CWPO), which implies the generation of HO• radicals from H_2O_2 decomposition has been widely investigated for the abatement of toxic and bio-recalcitrant organic pollutants in water [12–17]. Regarding the operating conditions, CWPO reactions are usually carried out at ambient-like conditions [18–20], but recent studies have reported significant improvement of the degradation and mineralization rates of recalcitrant compounds at temperatures above 50 °C [13,15]. Inchaurrondo et al. [13] achieved 4-fold higher TOC conversion (from 20 to 80%) in the CWPO of phenol by increasing the temperature from 25 to 70 °C. The main drawbacks of CWPO is associated with the high requirements of H_2O_2. For this reason, many works focused on the amount of reactant needed as a main issue [14,15,21]. Traditionally CWPO Fe supported catalysts consist of silica, alumina, pillared clays and carbonaceous materials. The use of carbon materials as supports leads to highly dispersed metal catalysts but they show relatively high iron leaching due to the acidic pH or the low chemical stability of the supports [14,22].

Bisphenol A (2,2-bis(4-hydroxyphenyl)propane, BPA) is an industrial chemical which is extensively consumed for polycarbonates manufacture as well as in the production of epoxy resins. Other applications include the manufacture of flame retardants such as tetrabromobisphenol A [23–25]. The world rate of production of this chemical (BPA) reached about 5.4 million tons in 2015 [26]. BPA is identified as an endocrine disrupting chemical, and it can be found in the water bodies either directly or indirectly via degradation of various BPA containing materials such as plastic bottles, containers, toys, food/soft drink cans, packaged food, etc. [27–29]. Because of its slow biodegradation, BPA concentrations from 100 to 100,000 ng L^{-1} and from 1 to 100 ng L^{-1} have respectively reported in influent and effluent streams from several WWTPs worldwide [30].

Conventional physical–chemical or biological processes are unable to remove BPA from water [31]. Therefore, several AOPs such as CWPO [32–34], Fenton/photo-Fenton oxidation [35–37], sonochemical treatment [38], photochemical/photocatalytic oxidation [39–42], ozonation [43], and hybrid processes [44–48] have been tested.

The aim of this study is to prepare iron catalysts supported on grape seeds-derived carbon materials and to test them in CWPO using BPA as target compound. The fresh and used catalysts have been characterized by several techniques including CO_2 adsorption at 273 K, elemental analysis, ash content, total reflection X-ray fluorescence spectroscopy (TXRF), X-ray photoelectron spectroscopy (XPS) and Scanning Electron Microscopy–Energy Dispersive X-ray spectroscopy (SEM-EDX). The CWPO results have been analyzed in terms of H_2O_2 decomposition, BPA removal and TOC conversion. Additionally, the toxicity and biodegradability of BPA and the CWPO effluent were evaluated. The stability of the most interesting catalyst was also tested in long-term continuous operation (100 h on stream).

2. Material and methods

2.1. Catalysts preparation and characterization

The grape seeds used as precursor were from the red wine variety "Tinta de Toro" harvested in Toro (Zamora, Spain). The sizes of the raw seeds were between 2 and 4 mm. The seeds were washed with distilled water, dried at 105 °C for 24 h and pyrolyzed in a rotatory quartz furnace (CARBOLITE CB HTR 11/150P8) at 600 °C for 2 h [2]. The working temperature was reached at a 10 °C min^{-1} heating rate and N_2 was continuously passed at a 1 NL min^{-1} flow rate. The resulting char is identified as GS-0. It was activated with air (2 NL min^{-1}) for 2 h at 400 °C, reached at 10 °C min^{-1} [6]. This activated carbon was named GS-1. The GS-0 char was also subjected to oxidative treatment with HNO_3 which was carried out boiling 1 g of char in 10 mL of a 6 N HNO_3 solution for 20 min followed by washing with distilled water until neutral pH [49]. This oxidized carbon was identified as GS-2. The HNO_3 oxidation treatment was also applied to the air-activated carbon giving rise to the GS-3 carbon. Iron was incorporated on each carbon support by incipient wetness impregnation with an aqueous solution of Fe (NO_3)$_3$·9H_2O (Panreac, 97%) to obtain catalysts with a 4.0% wt. of Fe. Once impregnated, each catalyst was dried at 60 °C for 12 h and calcined for 4 h at 300 °C, reached at 3 °C min^{-1}. The catalysts, with granular morphology, were identified adding Fe to the name of the support (Fe-GS-1, Fe-GS-2 and Fe-GS-3).

The surface area and total pore volume of the catalysts were determined by CO_2 adsorption at 0 °C in an automated volumetric gas adsorption apparatus (MicromeriticsTristar 3020). Previous to adsorption the samples (0.15 g) were degasified under vacuum at 150 °C for 7 h using a degas system (Micromeritics VacPrep 061). The surface area (S_{DA}) and the micropore volume ($V_{microCO2}$, 0.4–0.9 nm) were calculated using the Dubinin–Astakhov equation. This approach was used because materials with narrow microporosity were expected according to previous works [2,6]. The pH slurry was determined measuring, until constant value, the pH of an aqueous suspension of catalyst (1 g) in distilled water (10 mL). The morphology of the catalyst and its surface composition were analyzed by Scanning Electron Microscopy–Energy Dispersive X-ray spectroscopy (SEM-EDX) with a Hitachi S-3000N apparatus. The samples for SEM observation were metalized with gold using a Sputter Coater SC502. Imaging was performed in the high vacuum mode under an accelerating voltage of 20 kV, using secondary and backscattered electrons. Elemental analyses (C, N, S, and H) were carried out with a LECO CHNS-932 analyzer, while the ash content was determined following the standard ASTM D1506-99 method. The oxygen content was calculated by difference to 100%. Moreover, catalyst surface composition was quantified by X-ray photoelectron spectroscopy (XPS) using a 5700C model Physical Electronics apparatus, with MgKα radiation (1253.6 eV) and energy dispersive X-ray spectroscopy analysis (EDAX). The bulk Fe loading was determined by total reflection X-ray fluorescence spectroscopy (TXRF), using Si-Li detector in a TXRF Extra-II Rich & Seifert spectrometer.

2.2. CWPO experiments

The CWPO runs were carried out in glass-made stirred batch reactors at atmospheric pressure, 600 rpm stirring velocity and temperatures within 50–80 °C for 4 h. Duplicate runs were always made. The starting concentration of BPA (Sigma-Aldrich, >99%) was 100 mg L^{-1}, the H_2O_2 (Panreac, 33%w/v) doses were 265 and 530 mg L^{-1}, which correspond, respectively, to 50 and 100% of the theoretical stoichiometric amount for complete oxidation of BPA to CO_2 and H_2O (mineralization). The catalyst concentration was fixed at 500 mg L^{-1}. The initial pH was adjusted to 3.0 with nitric acid and continuously monitored along the experiment. A set of experiments were carried out to check the H_2O_2 decomposition (50 °C, 530 mg L^{-1} H_2O_2 and 500 mg L^{-1} catalyst), and the adsorption of BPA on the catalysts in absence of H_2O_2 (50 and 80 °C, 100 mg L^{-1} BPA and 500 mg L^{-1} catalyst). Long-term experiments (100 h on stream) were performed in a continuous stirred tank reactor (CSTR) fed with BPA (200 mg L^{-1}) and H_2O_2 (1060 mg L^{-1}) aqueous solutions at 2 ml min^{-1} of each reactant.