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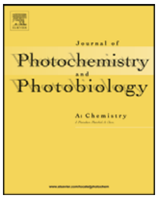

Sequential helio-photo-Fenton and sonication processes for the treatment of bisphenol A

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ABSTRACT

This paper demonstrates the coupling of ultrasound (300 kHz, 80 W) with Fe(II) to degrade the contaminant bisphenol A by a solar photo-assisted process carried out at natural pH ~ 5. An experimental design that allowed runs in batch (ultrasound → Fe^{2+}/UV and Fe^{2+}/UV → ultrasound) or in simultaneous (ultrasound/Fe^{2+}/UV) modes was developed. To gain a better understanding of the phenomena involved in the systems, ultrasound, ultrasound/Fe^{2+}, Fe^{2+}/UV, and Fe^{2+}/UV/H_2O_2 (photo-Fenton) were also performed. After 4 h of treatment, 11%, 29%, and 70% of the initial total organic carbon had been removed by ultrasound, photo-Fenton, and ultrasound/Fe^{2+}/UV, respectively. The synergistic effect can be explained by the complementarity of the two processes: ultrasound more effectively destroys the initial bisphenol A compound, whereas the photo-Fenton system is better able to eliminate the bisphenol A by-products. The influence of the type of saturating gas (oxygen or air) used was also investigated.

1. Introduction

Bisphenol A [2,2-bis(4-hydroxyphenyl)propane; BPA], a chemical compound used widely in industry as a monomer for the production of epoxy resins and polycarbonate, is an endocrine-disrupting compound that is released into the environment from bottles, packaging, landfill leachates, paper, and plastics plants [1–3]. Even at low-dose exposure, BPA induces feminization during the gonadal ontogeny of fishes, reptiles, and birds. Adult exposure to environmental concentrations of BPA is detrimental to spermatogenetic endpoints and stimulates vitellogenin synthesis in model species of fish [4]. Due to its large consumption and adverse health effects on wildlife, BPA is one of the xenobiotic substances that has generated the greatest amount of interest and controversy during the past decade [4].

Advanced oxidation processes (AOPs), which are based on the production and use of the hydroxyl radical, have been tested for the elimination of BPA [5–9]. However, these procedures sometimes result in secondary products that are not eliminated significantly by the same technique or that may be more hazardous than the original compound [9,10].

Ultrasonic treatment as an AOP is considered particularly efficient for the breakdown of volatile and nonpolar compounds. In this process, $^{\bullet}OH$ radicals are generated by acoustic cavitation, which is defined as the cyclic formation, growth, and collapse of microbubbles. The fast collapse of bubbles adiabatically compresses gas and entrapped vapor, which produces small local hot spots [11]. At the final step of the bubble collapse, the temperature inside the residual bubble is thought to be >2000 K. Under these conditions, entrapped molecules of dissolved gases, vaporized water, and solutes can be brought to an excited state and dissociate. As a result, a volatile organic compound will be pyrolysed in the bubble [12,13]. A nonpolar compound with low volatility will be hydroxylated at the bubble-bulk solution interface, and, to a lesser extent, a hydrophilic compound will react with $^{\bullet}OH$ radicals in the bulk solution. During the sonication of water, $^{\bullet}OH$ radicals are generated from water and oxygen dissociation according to the following reactions [13]:

$$H_2O \rightarrow {}^{\bullet}H + {}^{\bullet}OH \tag{1}$$

$$O_2 \rightarrow 2O \tag{2}$$

$$O + H_2O \rightarrow 2{}^{\bullet}OH \tag{3}$$

$${}^{\bullet}H + O_2 \rightarrow {}^{\bullet}OH + O \tag{4}$$

During the ultrasonic treatment a high fraction of $^{\bullet}OH$ radicals that cannot reach the target compound recombine to produce hydrogen peroxide.

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The Fenton reaction is another AOP that has been used with great success to treat a wide variety of contaminants [14,15]. In this homogenous process, $^{\bullet}OH$ radical formation can be outlined as follows:

$$Fe^{2+} + H_2O_2 \rightarrow OH^- + {}^{\bullet}OH + Fe^{3+} \quad (5)$$

The photoassisted Fenton reaction (photo-Fenton) is a strongly enhanced version of the Fenton process. The positive effect of irradiation on the degradation rate is due to the photochemical regeneration of ferrous ions (Fe^{2+}) by the photoreduction of ferric ions (Fe^{3+}), with the production of additional $^{\bullet}OH$ radicals [16]:

$$Fe^{3+} + H_2O \rightarrow + H^+ \, Fe(OH)^{2+} + h\nu \rightarrow + H^+ \, {}^{\bullet}OH + Fe^{2+} \quad (6)$$

The newly generated ferrous ion reacts with H_2O_2 to produce a second $^{\bullet}OH$ radical (Eq. (5)), and the cycle continues. Under these conditions, iron can be considered an actual catalyst. The main advantage of the photo-Fenton process is the light sensitivity up to a wavelength of 600 nm (35% of the solar irradiation). Because photo-Fenton can be carried out with the residual H_2O_2 produced by ultrasonic BPA treatment, a system that employs the two AOPs simultaneously, without H_2O_2 addition, should be a worthwhile endeavor.

In a previous study [17], we found that mineralization of a BPA solution (118 μmol L^{-1}, 300 mL) could be accomplished in a simultaneous ultrasound/Fe^{2+}/UV system. However, because of the experimental conditions (initial acidic pH, UV radiation at 254 nm, and the use of oxygen as the saturating gas), the potential usefulness of this combination could not be established. To explore the practical applicability of this system, the present work investigated BPA treatment via ultrasound and photo-Fenton coupling under conditions encountered in wastewater treatment: natural pH (pH ∼ 5, obtained by bare BPA without the addition of any acid or basic substances) and solar radiation. The experiments were carried out in two separate systems (one irradiated with a Suntest lamp and the other subjected to ultrasound). The use of air or oxygen as the saturating gas was also investigated.

2. Experimental

2.1. Reagents

Bisphenol A (99%) and ammonium heptamolybdate (99.98%) were obtained from Aldrich. Ferrous sulfate (99.5%), potassium iodide (99%), acetic acid, and sulfuric acid were supplied by Fluka. Potassium hydrogen phthalate (99.95%) and hydrogen peroxide (35%) were obtained from Merck. Acetonitrile (99.99%) and methanol (99.9%) were purchased from Fisher Chemicals and Riedel-de-Haen, respectively. All chemicals were used without further purification. During all experiments, oxygen (provided by Carbagas) or air was added to the system. Milli-Q water was used for the preparation of aqueous solutions and as a component of the mobile phase in the HPLC analysis.

2.2. Apparatus

All experiments were carried out with 600 mL of 118 μmol L^{-1} bisphenol A, in one of two separate systems: one irradiated with a Suntest lamp, and the other subjected to ultrasound (Fig. 1).

To maintain a constant temperature (22 ± 2 °C), a cylindrical water-jacketed glass reactor (500-mL capacity) was used as the sonochemical system. Ultrasonic waves (300 kHz and 80 W) were emitted from the bottom of the reactor through a piezoelectric disc (4-cm diameter) fixed on a Pyrex plate (5-cm diameter) [18]. The ultrasonic energy dissipated in the reactor (∼50% of the electrical power used) was estimated by the calorimetric method [19].

The photochemical reactor consisted of three serial Pyrex glass vessels with an illuminated volume of 50 mL. The Pyrex vessels were irradiated from the outside with a Suntest CPS solar lamp system (Atlas GmbH) with an irradiation intensity of 830 W m^{-2}. This lamp has a spectral distribution of ∼0.5% of the emitted photons at wavelengths shorter than 300 nm and of ∼7% at wavelengths between 300 and 400 nm. For wavelengths between 400 and 800 nm, the emission spectrum follows the solar spectrum. A peristaltic pump recirculated the solutions from the sonochemical reactor to the photochemical reactor with a flow rate of 230 mL min^{-1}. The total volume of the system (600 mL) is divided into three parts: 300 mL in the sonochemical vessel, 150 mL in the photochemical reactor, and the remaining 150 mL in the connecting tubes. This configuration allowed combinations of the two processes in simultaneous (ultrasound/Fe^{2+}/light) or batch (ultrasound followed by Fe^{2+}/light or Fe^{2+}/light followed by ultrasound) modes. Moreover, each system (ultrasound, ultrasound/Fe^{2+}, Fe^{2+}/light, and Fe^{2+}/H_2O_2/light) was tested separately. In the Fe^{2+}/H_2O_2/light method, H_2O_2 (35×10^{-3} mol L^{-1}) was delivered continuously (2.7 mL h^{-1}) with a syringe pump. In experiments with Fe^{2+}, 0.0167 g $FeSO_4 \cdot 7H_2O$ (100 μmol L^{-1} Fe^{2+}) was added to the system. Reaction sets were sampled periodically for analyses. The runs were carried out at least by duplicate. The uncertainties were found lower than 2, 5 and 7% for figures reporting H_2O_2, HPLC and DOC evolution, respectively.

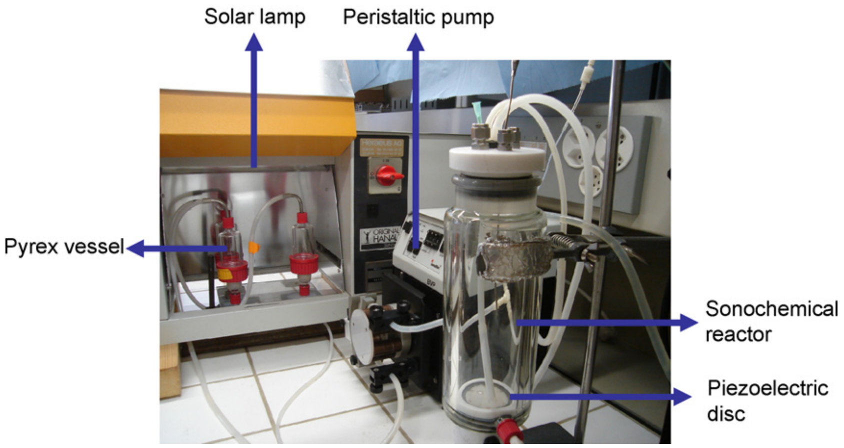

Fig. 1. Sonochemical/photocatalysis reactor used for BPA treatment.