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Sono-photo-Fenton oxidation of bisphenol-A over a $LaFeO_3$ perovskite catalyst

Meral Dükkancı

Ege University, Engineering Faculty, Chemical Engineering Department, 35100, Bornova, Izmir, Turkey

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ABSTRACT

In this study, oxidation of bisphenol-A (IUPAC name – 2,2-(4,4-dihydroxyphenyl, BPA), which is an endocrine disrupting phenolic compound used in the polycarbonate plastic and epoxy resin industry, was investigated using sono-photo-Fenton process under visible light irradiation in the presence of an iron containing perovskite catalyst, $LaFeO_3$. The catalyst prepared by sol–gel method, calcined at 500 °C showed a catalytic activity in BPA oxidation using sono-photo-Fenton process with a degradation degree and a chemical oxygen demand (COD) reduction of 21.8% and 11.2%, respectively. Degradation of BPA was studied by using individual and combined advanced oxidation techniques including sonication, heterogeneous Fenton reaction and photo oxidation over this catalyst to understand the effect of each process on degradation of BPA. It was seen, the role of sonication was very important in hybrid sono-photo-Fenton process due to the pyrolysis and sonoluminescence effects caused by ultrasonic irradiation. The prepared $LaFeO_3$ perovskite catalyst was a good sonocatalyst rather than a photocatalyst. Sonication was not only the effective process to degrade BPA but also it was the cost effective process in terms of energy consumption. The studies show that the energy consumption is lower in the sono-Fenton process than those in the photo-Fenton and sono-photo- Fenton processes.

1. Introduction

Bisphenol A (BPA) is a commercial product and is the primary material for polycarbonate and epoxy resins fabrication. It is an organic synthetic compound with the chemical formula of $C_{15}H_{16}O_2$ belonging to the group of diphenylmethane derivatives and bisphenols, with two hydroxyphenyl groups [1]. BPA is released into the ground water through sewage treatment effluent, landfill leachate, or discharge of effluent from wastewater and washwater of plants which produce material containing BPA. BPA can also be found in food and drinking water, and in living organisms (especially in fatty tissues).

Since it is a synthetic hazardous compound, it affects the endocrine system primarily, plays a role in thyroid hormone dysfunctions, central nervous system function disorder and immune suppression above a certain limit [2–4].

BPA contamination became a real threat for human health even at low dose of 0.05 mg per kg body weight. Research on BPA as environmental contaminant has now major regulatory implications towards ecosystem health [5,6]. Acute toxicity of BPA for aquatic organisms was about 1–10 mg/L in fresh and marine species [1]. Due to the reasons mentioned above BPA must be treated before discharged to environment.

A wide range of studies are reported on BPA removal from aqueous systems through various Advanced Oxidation Processes (AOPs) [7–32] which offer several particular advantages in terms of unselective degradation of BPA into a final mineralized form with the production of a highly oxidative hydroxyl radicals ($OH^{\cdot}$). Among the available AOPs, Fenton reaction is based on the electron transfer between H_2O_2 and a transition metal ion (iron is the most common one) acting as a catalyst. However, homogeneous Fenton reactions have some disadvantages such as, limited pH range for the reaction, production of iron containing sludge and difficulty of regeneration of catalyst. The drawbacks of homogeneous Fenton reactions can be overcome by using heterogeneous catalysts. Photo-Fenton process is a hybrid technique that uses Fenton reagent together with light (in this study visible light, $\lambda > 400$ nm) for the oxidation. Photoreactions often require the use of a photocatalyst. The most known photocatalyst is TiO_2 [33] however it is not a good photocatalyst under the visible light. Nevertheless, perovskite based catalysts show good photocatalytic activity under visible light. Because they have lower band gap than semi-conductor catalysts such as TiO_2. The other AOPs used in this study is sonication which is based on the acoustic cavitation created in the presence of ultrasound. Acoustic cavitation can be defined as the formation, growth and implosive collapse of microbubbles at very small time intervals which release large magnitudes of energy over a small area but at millions of places in the reactor [34]. The collapse of these micro-

E-mail address: meral.dukkanci@ege.edu.tr.

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bubbles induces the phenomenon of sonoluminescence and generates local hot spots with pressures higher than 500 atm and temperatures as high as 5200 K in cavitation bubble and about 1900 K in the interfacial region between the solution and the collapsing bubble. Under such conditions species such as $OH^{\cdot}$, $H^{\cdot}$,$OOH^{\cdot}$, and O are created from H_2O and O_2 dissociation and their associate reactions in the bubble [35–39]. The intensity of cavity implosion, and hence the nature of reaction are controlled by frequency of sonication, acoustic intensity (amount of power dissipated per square cm of the emitter area), bulk temperature, and static pressure [40]. The collapse of cavitation bubbles also initiates physical effects which include the production of shear forces and shock waves [41]. It is known that volatile organic compounds are degraded by pyrolysis inside the cavitation bubble by high temperature or at the bubble liquid interface by oxidation with $OH^{\cdot}$ radicals, whereas nonvolatile compounds are degraded by oxidation with hydroxyl radicals at the bulk liquid. When the photocatalytic reaction accomplished with sonication, oxidation rate increases by the increased generation of $OH^{\cdot}$ radicals and the mass transfer limitations are reduced by the turbulence created by sonication [42]. Also sonication helps in cleaning of the catalyst surface which increases its efficiency.

In this study, sono-photo-Fenton oxidation of BPA was studied over the $LaFeO_3$ perovskite catalyst in the presence of visible light irradiation. Degradation of BPA was investigated by individual and several combinations of AOPs including sonication, Fenton reaction and photo oxidation to understand the effect of each process on oxidation of BPA. A simple energy consumption analysis was done for the processes using sonication and/or light irradiation.

Up to now, no study was reported in the literature for degradation of BPA by sono-photo-Fenton oxidation in the presence of $LaFeO_3$ perovskite catalyst and by the individual and combined advanced oxidation processes of Fenton reaction, photo degradation and sonication. In addition to this, applying energy consumption analysis on the individual and combined processes of sonication and photo oxidation reactions is considered to be a significant contribution to the related literature.

2. Experimental study

Experimental set-up is shown in Fig. 1. A typical experiment was performed with 0.5 dm^3 of 15 ppm of BPA aqueous solution in a cylindrical reactor. In the experiments containing catalyst at an amount of 0.5 g/dm^3, the suspension was left for 30 min in the dark to establish the adsorption-desorption equilibrium of the BPA on the catalyst surface. The amount of the BPA adsorbed by the catalyst was determined by measuring the BPA concentration after 30 min. The experiment in the presence of H_2O_2 was performed with an initial concentration of H_2O_2 of 2.38 mM, under a stirring speed of 500 rpm with an initial BPA pH of around 6.7. Two visible light lamps (high pressure Na lamps, each 150 W of two lamps, Philips) were used as a light source. An ultrasonic probe of 20 kHz with an output power of 40 W (Bandelin HD3200) was used as a source of ultrasound. Each run took 3 h. The reaction temperature was kept constant at 298 ± 2 K by circulating cooling water (PolyScience, MX07R-20-A12E) around the reactor to avoid the significant overheating of the reaction media. The reaction vessel was maintained in a box to prevent photochemical reactions excited by natural light. Samples were periodically drawn from the vessel and reaction was stopped by keeping the samples in iced-bed. Then the samples were centrifuged and filtrated with 0.45 μm PTFE syringe filters. The catalyst free samples were analyzed with a HPLC (Agilent 1200 series) with a ZORBAX Eclipse Plus C18 (4.6 × 150 mm, 5 μm) column. Detection was achieved with an UV detector at 278 nm, with a 20 μL sampling loop. The mobile phase, ultrapure water/acetonitrile (50/50, v/v) was run in an isocratic mode with a flow rate of 0.5 ml/min. The column oven was maintained at 25 °C.

In addition to these measurements, the chemical oxygen demand (COD) removal of the BPA solution was determined by measuring initial COD and final COD (at the end of the run) of the BPA solution with a COD device (Lovibond Checkit Direct). Sono-Fenton, photo-Fenton and sono-photo-Fenton reactions were also performed in pure water in the presence of 0.5 g/dm^3 $LaFeO_3$ perovskite catalyst to investigate the formation of H_2O_2 in each process in order to establish a relationship between the H_2O_2 production and degradation of BPA in related process. The formed H_2O_2 was measured with Lovibond $PC_{CHECKIT}$ H_2O_2 device by using hydrogenperoxide LR Tablets (Lovibond).

3. Results and discussion

3.1. Sono-photo-Fenton oxidation of BPA over perovskite catalysts

In the previous study [43], the degradation of BPA was performed by sono-photo-Fenton oxidation over perovskite catalysts, prepared by sol–gel method, calcined at different temperatures of 500, 700 and 800 °C in order to determine the most effective catalyst. The prepared samples were denoted as $LaFeO_3$-500, $LaFeO_3$-700, and $LaFeO_3$-800, respectively. The sono-photo-Fenton experiments were carried out

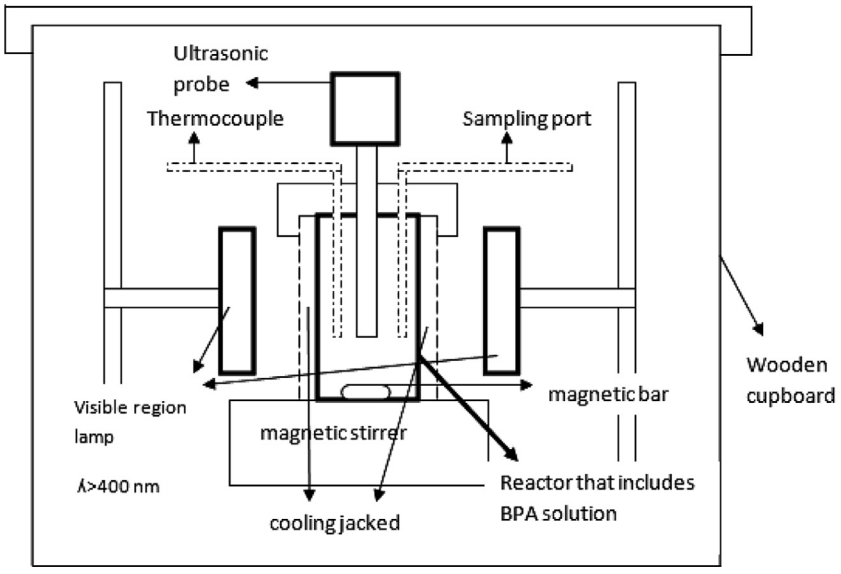

Fig. 1. Experimental set-up used for the oxidation of BPA.