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Degradation of bisphenol A in aqueous solution by a novel electro/Fe^{3+}/peroxydisulfate process

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ABSTRACT

The removal of bisphenol A (BPA) by a novel "electro/Fe^{3+}/peroxydisulfate" process is reported in this study. The effects of initial pH, electrolyte concentration, Fe^{3+} concentration, peroxydisulfate (PDS) concentration and current density were investigated. The results indicated that the removal efficiency of BPA declined with the increase of initial pH and electrolyte concentration, but increased with an increase of Fe^{3+} concentration and current density. The BPA degradation efficiency was improved significantly when the PDS concentration was increased from 1 to 10 mM, but further PDS increase had little effect. BPA was almost completely removed after 60 min reaction and a TOC removal efficiency of 94.3% was achieved when the reaction time was extended to 120 min.

1. Introduction

Bisphenol A (BPA: 2,2-bis(4-hydroxyphenyl)propane), a known endocrine disrupter and industrial chemical, is commonly used as an intermediate in the production of polycarbonate plastics and epoxy resins [1]. The final products are used in a large number of food and drink storage containers, polycarbonate bottles, tableware, white dental fillings and sealants [2]. The release of BPA into the aquatic environment can disturb the behavior of living organisms due to its endocrine disrupting effect at low concentration [3–5]. Therefore, the treatment of wastewater contaminated by BPA has aroused great interest.

Due to its biological resistance, BPA is rather recalcitrant to classical wastewater treatments. Thus more powerful treatment methods are required. Among the emerging treatment approaches, advanced oxidation processes (AOPs), which involve the in situ production of nonselective hydroxyl radicals (·OH) [6,7] are effective in eliminating BPA from aqueous media [8,9]. In recent years, sulfate radical-based AOPs have also been shown to be promising techniques for the oxidation of organic pollutants. Sulfate radicals ($SO_4^{\cdot-}$) have a high standard redox potential (E^0 = 2.6 V) [7] and are more selective for oxidation than hydroxyl radicals at acidic pH [10,11]. In addition, sulfate radicals have more opportunities to react with organic pollutants because they have a longer lifetime (30–40 μs) [12] than hydroxyl radicals (20 ns) [13]. These features make sulfate radicals a promising choice for water clean-up applications. Recent studies have shown that sulfate radicals can be generated by activating peroxydisulfate (PDS, $S_2O_8^{2-}$) or peroxymonosulfate (PMS, HSO_5^-) with heat [14–16], UV [12,17–19] or transition metals (Fe^{2+},Co^{2+}, Ag^+) [20–22]. Compared to other transition metals, Fe^{2+} has the advantages of being inexpensive and nontoxic, which has resulted in its widely application as a catalyst to effectively activate PDS [23–25] via Eq. (1).

$$S_2O_8^{2-} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{\cdot-} + SO_4^{2-} \quad (1)$$

However, there are some drawbacks in the $Fe^{2+}/S_2O_8^{2-}$ process. First, Fe^{2+} cannot be regenerated after Eq. (1) occurs, therefore, a high concentration of Fe^{2+} is required and consequently a large amount of iron sludge is generated in the $Fe^{2+}/S_2O_8^{2-}$ process. Second, excessive Fe^{2+} can significantly scavenge $SO_4^{\cdot-}$ and inhibit radical oxidation of target pollutants via Eq. (2) [26,27]. Finally, Fe^{2+} is easily oxidized by air to Fe^{3+} and the ferrous solution should be stored under an acidic condition.

$$Fe^{2+} + SO_4^{\cdot-} \rightarrow Fe^{3+} + SO_4^{2-} \quad (2)$$

In order to solve the first two problems, a novel method named the "electro/Fe^{2+}/peroxydisulfate" process was applied to degrade azo dyes as described in our previous study [7]. The technique combined an electrochemical (EC) process in conjunction with Fe^{2+} activation of peroxydisulfate. The Fe^{2+}, which was scavenged as shown in Eq. (1), could be regenerated by cathodic reduction (Eq. (3)). In addition, sulfate radicals could be produced via an electron transfer reaction (Eq. (4)), as suggested by Wang and Chu [10].

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (3)$$

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$$S_2O_8^{2-} + e^- \rightarrow SO_4^{\cdot-} + SO_4^{2-} \quad (4)$$

When it comes to the last issue, the instability of Fe^{2+} solution, another novel process named the "electro/Fe^{3+}/peroxydisulfate" process has now been investigated and is reported in this current study. Ferrous ions were generated as shown in Eq. (3) and reacted with PDS to produce sulfate radicals. The cathodic reduction reaction enhanced the regeneration of ferrous ions simultaneously. In this study, the performance of the electro/Fe^{3+}/peroxydisulfate process in the degradation of BPA was investigated through examination of different operating conditions such as initial pH, electrolyte concentration, Fe^{3+} concentration, PDS concentration and current density. The mineralization of BPA in terms of TOC removal efficiency was also studied.

2. Materials and methods

2.1. Materials

BPA was obtained from Aladdin Chemistry Co., Ltd. (Shanghai, China) and used without further purification. Sodium peroxydisulfate ($Na_2S_2O_8$, 98%), ferric sulfate ($Fe_2(SO_4)_3$) and anhydrous sodium sulfate (Na_2SO_4, 99%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and were of analytical grade. HPLC grade acetonitrile was also purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

2.2. Apparatus and procedure

Electrolyzes were performed at constant current controlled by a direct current (DC) power supply (Model RYI-3010) from Shenzhen Yizhan Source, Co., Ltd. (China). Batch experiments were conducted in an undivided electrolytic reactor (glass beaker) containing 200 mL of solution. A 5.0 cm × 11.9 cm plate anode (Ti/RuO_2–IrO_2) and a plate cathode (stainless steel) of the same dimensions were arranged parallel to each other at a distance of 4.0 cm. The reactor was immersed in a water bath to keep the temperature constant at 20 °C.

Before each run, a stock solution of BPA was freshly prepared with deionized water and the initial concentration (C_0) was fixed at 0.22 mM. Sodium sulfate was added as a background electrolyte and prior to the electrolysis, and the initial pH (pH_0) of the BPA solutions was measured with a Mettler-Toledo FE20 pH-meter (Mettler-Toledo Instruments Co., Ltd., Shanghai) and adjusted appropriately with sulfuric acid or sodium hydroxide. A magnetic stirrer (model 78-1, Hangzhou Instrument Motors Factory, China) was used to agitate the solution throughout the reaction. When the DC power supply was initiated, the PDS and Fe^{3+} solutions were added to the electrolytic cell. At predetermined time intervals, aliquots (1 mL) of samples were taken and filtered through 0.22 μm membranes (Millipore Co.), then mixed with the same volume of methanol to quench the reaction before analysis.

2.3. Analytical methods

The residual BPA concentration was monitored by high-performance liquid chromatography (HPLC) [28,29]. The HPLC system consisted of a LC-20AB pump, a SPDM20A chromatograph equipped with a C-18 column (Shim-PackVP-ODS-C8, 250 × 4.6 mm, 5 μm) and a SPD-10A UV–visible detector set at the maximum absorption wavelength of BPA (280 nm). An acetonitrile/water (50:50, v/v) mixture was used as the mobile phase at room temperature with a constant flow rate of 1.0 mL/min. The injection volume was 20 μL. The concentration of residual PDS was measured by an iodometric titration method [30].

The UV–visible spectrum from 200 to 800 nm was obtained using a spectrophotometer (Shimadzu, UV-1700). The TOC concentrations of the initial and electrolyzed samples were determined by an Analytikjena multi N/C 3100 analyzer. The carrier gas was oxygen with a flow rate of 150 mL/min. The detector was a non dispersive infrared absorption detector.

3. Results and discussion

3.1. Degradation of BPA under different conditions

To investigate the degradation of BPA under different oxidation conditions, experiments were carried out with PDS alone, Fe^{3+}/PDS, EC alone (anodic oxidation), EC/Fe^{3+}, EC/PDS and EC/Fe^{3+}/PDS, with BPA (0.22 mM), Fe^{3+} (2 mM), PDS (10 mM), Na_2SO_4 (50 mM), a current density (j) of 16.8 mA/cm^2 and an initial pH of 3.0. It can be seen from Fig. 1 that the concentration of BPA barely changed when it was treated by PDS alone due to the limited oxidation power of PDS (E^0 = 2.01 V) [7,22]. The removal of BPA was also negligible in the Fe^{3+}/PDS process which indicated that Fe^{3+} cannot activate PDS to generate sulfate radicals and virtually no removal occurred using EC alone. This can be explained by the fact that hydroxyl radicals (M(·OH)) formed at the anode, Eq. (5), are tightly adsorbed on the anode surface and unable to oxidize BPA in the bulk solution [31–33].

$$M(H_2O) \rightarrow M(\cdot OH) + H^+ + e^- \quad (5)$$

Even though Fe^{3+} could be converted to Fe^{2+} through the cathodic reduction reaction, Eq. (3), the concentration of BPA did not significantly decrease due to the absence of oxidant in EC/Fe^{3+} process. When PDS was added to the electrolytic reactor (EC/PDS process), the degradation efficiency was slightly improved (26.3%) confirming that sulfate radicals could be produced via Eq. (4). The highest removal efficiency (76.5%) was achieved when the electrochemical process was coupled with the Fe^{2+}-activated PDS process (EC/Fe^{3+}/PDS process), in which Fe^{2+} could be regenerated through Eq. (3). The degradation efficiency achieved in the EC/Fe^{3+}/PDS process (76.5%) was much higher than the sum of the degradation efficiencies obtained in the EC (3.5%) and Fe^{3+}/PDS (3.8%) processes, indicating a synergistic effect between the EC and the Fe^{3+}/PDS processes.

3.2. Effect of initial pH

To investigate the pH effect on the degradation of BPA, the initial pH values were adjusted to 3.0, 6.0 and 9.0, and the reaction

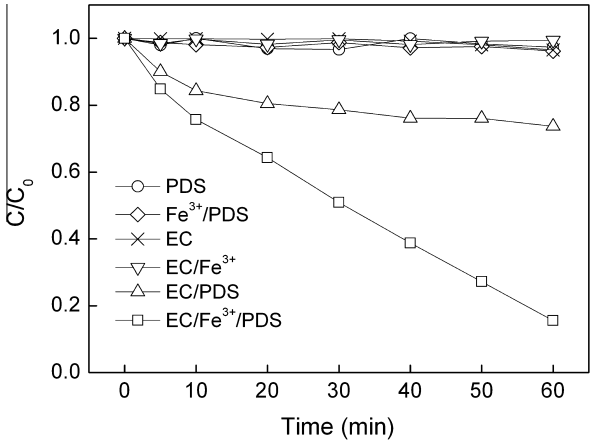

Fig. 1. Degradation of BPA in different systems (BPA = 0.22 mM, Na_2SO_4 = 50 mM, Fe^{3+} = 2 mM, PDS = 10 mM, j = 16.8 mA/cm^2, pH_0 = 3.0).