Bisphenol A degradation by Fenton Advanced Oxidation Process and operation parameters optimization

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Abstract. Bisphenol A (BPA) is a kind of environmental endocrine disrupting substance, which has been used as an organic chemical as unsaturated polyester resin. The degradation of BPA includes biological methods, physical adsorption and chemical oxidation, all which have their own disadvantages. Owing to its strong oxidization capability and stable treatment performance, Fenton process can degrade organic substances at a high reactive rate and stably effective. In this paper, Fenton oxidation method was optimized to remove BPA in water, during which the intermediate products were analysed to examine its degradation path. The optimal conditions of degradation of BPA by Fenton method were a ratio of $C(H_2O_2)/C(Fe^{2+})$ of 10, a pH of 3.5, and the degradation rate increased with the increasing of reaction temperature. It was found that Fenton could break the chemical bond at the junction of BPA and isopropyl group to produce p-diphenol, phenol, isopropyl phenol and other intermediate products.

Keywords: Bisphenol A, Fenton advanced oxidation process, Operation parameters optimization, Intermediates

1 Introduction

Bisphenol A (BPA) is a synthetic chemical that does not exist in nature. As an important industrial chemical such as epoxy resin, it brings convenience to human life [1]. Although BPA is a low toxic chemical, it is an environmental endocrine disruptor of additive type, which has been proved to be xenoestrogen by animal experiments. BPA has serious impact on biological reproduction and immune system [2], which is frequently detected in raw water and drinking water [3-4]. Nowadays, with rapid development of electronic manufacture, a large amount of wastewater containing BPA, which could be characterized as wide range, low concentration, high biological toxicity, and difficult degradation under natural conditions, discharge into the water body, to bring potential

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threat to ecological environment and human health. Many countries prohibit the use of bottles containing BPA [5-6]. China also forbids the disordered use of BPA, and a lot of related research has been carried out [7]. In 2006, Chinese regulation, Standards for drinking water quality stipulates that the upper limit of BPA emission is 10 µg/L.

Many technologies were applied to remove BPA. However, these methods have different defects. For instance, physical adsorption has a disadvantage of equipment manufacturing, microbial degradation may cause secondary pollution [8], oxidation method has a high cost of processing [9]. These defects limit their real application to a certain extent, therefore, it is urgent to develop a cost-effective technology for BPA treatment [10].

Fenton is an advanced oxidation process (AOP) combined divalent iron salt and hydrogen peroxide [11], and from the late 1960s, Fenton reagent began to be used as oxidant to degrade high concentration organic wastewater [12]. Fenton reagent has been widely used in remediation of organic contaminated soil, treatment of wastewater containing alkene, alcohol, and benzene [13-14]. The principle of Fenton reagent is the decomposition of oxidant to form hydroxyl radical, which can oxidize organic pollutants. Hu et al. [15] found that Fenton reagent can degrade BPA in a high rate when the reaction pH was kept at 3.94. Iordache et al. [16] also investigated the degradation of BPA by Fenton reagent, and the results showed that BPA can be almost completely degraded after one hour reaction when the initial mass concentration of BPA was 25 mg/L. Although it has been proved that Fenton reagent can degrade BPA, there are still some deficiencies, such as the removal of BPA needs a good effect when the pH is about 3. On the other hand, $\cdot\text{OH}$ would be quenched quickly once it is generated, resulted to a rather high consumption of H_2O_2 . Compared with other oxidation technologies, Fenton has the characteristics of fast, efficient, mild reaction conditions and strong oxidation; H_2O_2 eventually converted into water. In addition, Fenton also has advantages of simple equipment, low energy consumption and operating cost.

This paper is to study the degradation of BPA by Fenton reagent under different reaction conditions, and the experimental results are analyzed to determine the optimal parameters and operation condition parameters, and also to unveil its degradation path.

2 Materials and Methods

2.1 Reagents and materials

The chemical reagents were not all analytically. Bisphenol A (BPA GR), potassium bisulfate ($\text{KHSO}_5 \cdot 0.5\text{KHSO}_4 \cdot 0.5\text{K}_2\text{SO}_4$ AR), cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ AR) were obtained from Aladdin Reagent Co., Ltd. Sodium hydroxide (NaOH AR), Ferrous sulfate heptahydrate, ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ AR), hydrogen peroxide (30% H_2O_2 AR) were obtained from Tianjin Damao chemical reagent plant. Sodium chloride (NaCl AR) was purchased from Tianjin Baishi Chemical Co., Ltd. Sulfuric acid (H_2SO_4 AR) and sodium sulfite (Na_2SO_3) were purchased from Guoyao Chemical Reagent Co., Ltd. Methanol (CH_3OH HP) and dichloromethane (CH_2Cl_2 HP) were purchased from Duksan company in Germany, respectively. All experiments were carried out using double distilled water.

2.2 Instruments and equipment used in the experiment

In the experiment, Centrifuge 5418 model from Eppendorf was used to separate solid and liquid. Use WATERS Acquity HClass UPLC to detect the concentration of BPA. GC-MS model is 7890a-5975c, Agilent. Other instruments includes, Qingdao Haike DCY-12S

nitrogen blowing concentrator, Shanghai Meixiang CJJ-6 magnetic heating agitator, and Shanghai Leici PHS-3C pH meter.

2.3 Analytical methods

2.3.1 BPA detection indicators

UPLC was used to detect the concentration of BPA. The degradation rate of BPA was taken as an indicator. The pretreatment of the experiment was divided into two steps. In the water distribution part, if the concentration of BPA in water samples was below 1 mg/L, 1.5 mL of the samples were placed in the colorimetric tube, and were mixed with 3.5 mL of the chromatographic pure methanol solution, and then poured into the sample bottles for testing. For the actual wastewater, more than 2 mL of the static BPA sample was centrifuged at a speed of 12000 r/min for 5 min. Afterwards, 1.5 mL supernatant was placed in a colorimetric tube, and was mixed with 3.5 mL of the chromatographic pure methanol solution, and then poured into the sample bottles for testing.

2.3.2 Detection of oxidation intermediates

GC-MS was used to detect the intermediates in the reaction process. About 50 mL water sample after pretreatment was taken, and was adjusted its pH to 2.0 using hydrochloric acid. More than 1 g sodium chloride and 5 mL dichloromethane were added to oscillate extraction for 10 min. After stratified statically, the sample was dehydrated with anhydrous sodium sulfate and transferred to the colorimetric tube. The extraction was repeated twice, the extracting liquid was mixed. A nitrogen concentrator was used to concentrate at 25 °C. After the liquid was dried, 1 mL n-hexane was added, shook appropriately, and poured into the sample to be tested.

3 Results and discussion

3.1 Effect of initial BPA concentration and reaction time

During the degradation of BPA by Fenton reagent, the main factors influencing the degradation of BPA were $C(H_2O_2)/C(Fe^{2+})$, pH and temperature. The importance ranking is $C(H_2O_2)/C(Fe^{2+}) > pH > temperature$ [15] [17]. Through the following single-factor experiments, the factors were investigated and the optimal conditions were determined. During the experiment, the initial concentration of BPA was 1000 $\mu\text{g/L}$, the concentration of Fe^{2+} was 8 $\mu\text{mol/L}$, and the concentration of H_2O_2 was 80 $\mu\text{mol/L}$. The initial pH value of the solution was 3.5, the temperature was 25 ± 1 °C, and the oxidation reaction time was 30 min.

As shown in Figure 1 a) and b), using H_2O_2 only had a poor ability to remove BPA, but when Fe^{2+} and H_2O_2 were added together, the degradation rate of BPA was significantly increased. The degradation rate of BPA also increased with the increase of Fe^{2+} and H_2O_2 concentration. However, with the further increase of Fe^{2+} concentration, the degradation rate of BPA decreased. When the concentration of H_2O_2 was increased to 1000 $\mu\text{mol/L}$, the removal effect of BPA degradation rate did not increase significantly with the increase of H_2O_2 concentration.

This is because H_2O_2 can hardly form hydroxyl radicals ($\bullet\text{OH}$) without Fe^{2+} , and the addition of Fe^{2+} can trigger a chain reaction to produce $\bullet\text{OH}$. With the increase of the initial

concentrations of Fe^{2+} , H_2O_2 and BPA, the generation of $\bullet\text{OH}$ yields, the degradation effect of organic compounds increases, and the removal amount of BPA increases. However, for a certain amount of reactive substances, due to the limited generation rate of $\bullet\text{OH}$, when the concentration of reactive substances increases to a certain extent, even further increasing the concentration would not improve the removal effect of BPA, the removal ability of BPA decreases.

Fig. 1. Effect of different reagent concentration and reaction time in Fenton process: (a) Fe^{2+} concentration, (b) H_2O_2 concentration, (c) BPA initial concentration, (d) reaction time

As shown in Figure 1 c), along with the increase of initial concentration of BPA, it had a relatively increased of removal amount and the reduce of removal rate of BPA. This is because with the increase of initial concentration of BPA, the number of molecules per unit volume BPA also had a increase. In the case of the Fenton reagent concentration was constant, increasing the chance of a collision between them can remove more BPA. but for a certain amount of H_2O_2 , the production rate of $\bullet\text{OH}$ was limited, thus BPA removal ability was limited, so the removal rate of BPA decreased along with the increased of initial concentration of BPA. As shown in Figure 1 d), After a 15 min reaction, the degradation rate of BPA was 77.95%, which had achieve basically stable. Even if the reaction time increased, BPA removal efficiency was not significantly increased. So there have a advise that similar experiments to control the reaction time of 15 min.

The optimal dosage ratio of $C(H_2O_2)/C(Fe^{2+})$ is approximately 10, at which has the best degradation effect of BPA. Therefore, during the following study, the concentration of H_2O_2 was set as 80 $\mu\text{mol/L}$, the concentration of Fe^{2+} as 8 $\mu\text{mol/L}$ in the BPA experiment. The reaction time could be kept as low as 15 min.

3.2 Optimization of operation conditions

In order to study the effect of pH and temperature, the initial concentration of BPA was controlled at 1000 $\mu\text{g/L}$, the concentration of H_2O_2 was controlled at 80 $\mu\text{mol/L}$, and the concentration of Fe^{2+} was controlled at 8 $\mu\text{mol/L}$.

Fig. 2. Effect of different concentration and reaction time in Fenton process: (a) solution initial pH, (b) reaction temperature

As shown in figure 2, the results showed that the pH value had a great influence on the degradation of BPA. When the pH was between 3 and 4, Fenton method had a good degradation effect on BPA. Higher or lower pH would reduce the degradation effect of Fenton® reagent. The classic Fenton process theory believes that higher pH leads to Fe^{2+} being oxidized to iron hydroxide complex, and lower pH prevents Fe^{3+} from being reduced to Fe^{2+} . Temperature can affect the rate of chemical reaction as well. As the temperature increases, the removal effect of BPA increases. Appropriate temperature increases the reactivity, but excessive temperature leads to H_2O_2 breaking down into H_2O and O_2 , weakening the treatment effect of BPA.

3.3 Degradation mechanism of BPA by Fenton oxidation

In this section, GC-MS method was used to qualitatively analyze the BPA products treated by Fenton® reagent. Based on previous study, the possible degradation path of BPA by Fenton process would be inferred [18-19]. The relevant experimental conditions were as follows, the initial concentration of BPA was 1000 $\mu\text{g/L}$, the concentration of H_2O_2 was 80 $\mu\text{mol/L}$, the concentration of Fe^{2+} was 8 $\mu\text{mol/L}$, the initial pH of the solution was 3.5, the temperature was 25 ± 1 °C, and the reaction time was 30 s, 1 min, 3 min, 5 min and 10 min respectively.

3.3.1 Intermediate product

The intermediate products are shown in table 1 below.

Table 1. Intermediates during BPA degradation by Fenton method

NO.	Retention time (min)	Name	Molecular formula	Molecular weight	Molecular structure formula	Detection ion (m/z)
1	5.99	Phenol	C ₆ H ₆ O	94		94(86) 66(47)
2	6.35	1,4-Benzoquinone	C ₆ H ₄ O ₂	108		108(100) 82(61) 54(86) 55(55)
3	6.85	Hydroquinone	C ₆ H ₆ O ₂	110		110(41) 99(56) 65(48) 55(100)
4	9.13	Maleic acid	C ₄ H ₄ O ₄	116		99(39) 72(32) 68(44) 55(100)
5	12.86	4-Isopropenylphenol	C ₉ H ₁₀ O	134		134(100) 119(83) 91(52) 78(19)
6	15.00	4-Isopropylphenol	C ₉ H ₁₂ O	136		136(22) 121(35) 103(100) 91(100)
7	16.60	4-Hydroxyacetophenone	C ₈ H ₈ O ₂	136		136(29) 93(40) 121(100) 65(40)

8 21.70 Bisphenol A $C_{15}H_{16}O_2$ 228

3.3.2 Fenton degradation pathway of BPA

According to the previous study, the degradation path of BPA in solution was speculated, as shown in Fig 3. Fenton process is essentially a process in which H_2O_2 is catalyzed by Fe^{2+} to produce hydroxyl radicals ($\bullet OH$) with strong oxidation, high electronegative or electrophilic (electron affinity is 569.3 kJ) that degrade BPA. $\bullet OH$ reacts with BPA molecules, gradually oxidizing them into small molecules of organic matter until they are thoroughly mineralized into CO_2 and H_2O .

Fig. 3. Degradation path of bisphenol A in water by Fenton method

When BPA in water is oxidized by Fenton method, hydroxyl radicals attack the connection between benzene ring and isopropyl of BPA, breaking it off and forming intermediate products such as p-diphenol, phenol and isopropyl phenol. Under the action of hydrogen peroxide and hydroxyl free radical, the phenol hydroxyl groups in counterpoint is more active, easily oxidized into the two ketone benzene, hydroquinone can also be further oxidation of phenol and benzoquinone, benzoquinone ring fractures, further generates maleic acid, and finally will be mineralized to CO_2 and H_2O . Additionally, isopropyl

phenol can be oxidized to 4-(1-hydroxy-1-methyl-ethyl)-phenol (HMEP), then HMEP is further dehydrated to produce p-isopropyl phenol. P-isopropyl phenol generates hydroxy acetophenone under the oxidation of H_2O_2 , hydroxy acetophenone is further oxidized into maleic acid. Finally, it is thoroughly mineralized.

4 Conclusion

In this paper, the degradation of BPA by Fenton oxidation was studied. Single factor experiments were used to find out the optimal experimental conditions. The degradation mechanism and pathway of BPA under Fenton oxidation were further analyzed. When the ratio of $\text{C}(\text{H}_2\text{O}_2) / \text{C}(\text{Fe}^{2+})$ is 10 (mole ratio) and the initial pH is 3.5 ~ 4.5, Fenton method has a good degradation effect on BPA. The degradation effect of BPA increases with the increase of temperature. When the concentration of the BPA is 1 mg/L, the optimal conditions are as follows, the initial pH is 3.5, the concentration of H_2O_2 is 80 $\mu\text{mol/L}$, and the concentration of Fe^{2+} is 8 $\mu\text{mol/L}$. After 15 min reaction at $25 \pm 1^\circ\text{C}$, the degradation rate of BPA is 77.95%. GC-MS was used to detect the intermediate products in Fenton process. It was found that the degradation of BPA by Fenton method could destroy the molecular structure of BPA, break the chemical bond between benzene ring and isopropyl, and then produce the intermediate products such as p-diphenol, phenol and isopropyl phenol. Under the further action of hydroxyl radical, the final ring opening mineralization was CO_2 and H_2O .

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