

## Degradation of bisphenol A in water by the heterogeneous photo-Fenton

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Bisphenol A (BPA) is a kind of a controversial endocrine disruptor, and is ubiquitous in environment. The degradation of BPA with the heterogeneous photo-Fenton system was demonstrated in this study. The Fe-Y molecular sieve catalyst was prepared with the ion exchange method, and it was characterized by X-ray radiation diffraction (XRD). The effects of pH, initial concentration of H<sub>2</sub>O<sub>2</sub>, initial BPA concentration, and irradiation intensity on the degradation of BPA were investigated. The service life and iron solubility of catalyst were also tested. XRD test shows that the major phase of the Fe-Y catalyst was Fe<sub>2</sub>O<sub>3</sub>. The method of heterogeneous photo-Fenton with Fe-Y catalyst was superior to photolysis, photo-oxidation with only hydrogen, heterogeneous Fenton, and homogeneous photo-Fenton approaches. pH value had no obvious effects on BPA degradation over the range of 2.2–7.2. The initial concentration of H<sub>2</sub>O<sub>2</sub> had an optimal value of  $20 \times 10^{-4}$  mol/L. The decrease in initial concentration of BPA was favourable for degradation. The intensity of ultraviolet irradiation has no obvious effect on the BPA removal. The stability tests indicated that the Fe-Y catalyst can be reused and iron solubility concentration ranged from NA to 0.0062 mg/L. Based on the results, the heterogeneous photo-Fenton treatment is the available method for the degradation of BPA.

**Keywords:** photo-Fenton; heterogeneous; BPA; degradation; Fe-Y

### 1. Introduction

Bisphenol A (BPA) is a kind of endocrine disrupter chemicals, used in the manufacture of plastic articles and polycarbonate.[1] These products are applied to many food and drinking storage containers. It has been reported that more than 200,000 tonnes of BPA was produced per year in Japan. The wild use of BPA caused the release of it into the nature environment. Kolpin et al. [2] reported that the high level concentration of 12.0 µg/L for BPA was detected in rivers. In Japan, up to 10 mg/L of BPA was reported in the leachates from waste landfill sites.[3] In addition to the existence of BPA in the surface water, a dozen of studies also found that BPA existed in the human body using different analytical techniques. BPA concentration in the breast milk ranged from ND to 7.3 µg/L.[4] In total,  $1.49 \pm 0.11$  µg/L of BPA was detected in the normal male serum,[5] 2.24 µg/L in the normal maternal serum,[6] and 0.26 µg/L in the normal foetal amniotic fluid.[6] The environmental and body distribution of BPA promoted the toxicity test, and estimated the effect of BPA on the human body and animal. After several experiments, researchers have found that BPA at very low concentration were detrimental to the development of the reproductive organs,[7] such as the formation of additional female organs, enlargement

of accessory sex glands and a stimulation of egg and egg mass production.[8] The wild lives, which were exposed to low concentration of BPA, may develop the symptom of puberty earlier.[9] Given the adverse effect of BPA on the human body, it was necessary to find an efficient approach to degrade BPA.

Various technologies have been attempted to decomposed BPA in recent years, involving adsorption,[10–13] solvent extraction,[14] biodegradation technology,[15] and photo degradation technology.[16] One of the promising methods is the photocatalytic approach due to its high mineralization efficiency, low toxigenicity, and relative rapid degradation time.[17] Fenton technology is a well-known process and has been reported as an effective alternative for the treatment of the industrial wastewater.[18] Hydroxyl radical, generated by the Fenton reagents, was a very strong and non-specific oxidant. However, its overall efficiency was limited with some significant disadvantages, such as tight range of pH, iron ions deactivated, and iron hydroxide sludge generated.[19] One of the most practical ways to overcome these limitations is to use Fenton heterogeneous catalysts and introduce ultraviolet (UV) irradiation. The porous-activated carbon,[20–23] zeolites,[24–26] resin,[27] clays,[28,29] and mesoporous silica [30–33]

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were used as supporters more often. However, these researchers indicated that there were still some drawbacks, such as low iron loading (only 0.1–5%), pH range extending not obvious, week stability, iron leached phenomenon, and so on. Hence, it is necessary to make attempts to find the supporter and a new preparation method of catalyst, which can work in the broad pH range, possess low leachability, and can be reused as well.

In the article, Na-Y zeolites-type molecular sieve was chosen as a catalyst supporter, Na-Y molecular sieve is a usual catalyst supporter for heterogeneous Fenton. It has an open porous structure capable of accommodating a wide variety of exchangeable cations, including iron. Its internal and external surface areas may extend to hundreds of square per gram, and its cation exchange capacities are up to several mill equivalents per kilogram.[34] As reported, it can form the Fe-Y catalyst thorough cation exchange with iron and provide similar catalytic activities as homogeneous Fe(II) ions.[35] However, their catalytic activity and stability depend much on synthesis methods in addition to their composition and framework structure. Moreover, leakage of iron ions from the supporter would result in secondary contamination.[36] So it would be interesting to study the preparation method of the Fe-Y catalyst and the Fenton performance of the catalyst.

To the best of our knowledge, the degradation of BPA with the heterogeneous photo-Fenton system has been only investigated up to a limited extent. In this study, the preparation method of the Fe-Y catalyst was illustrated, its loading capacity was determined, and characterized by X-ray radiation diffraction (XRD). The effects of pH, initial concentration of H<sub>2</sub>O<sub>2</sub>, initial BPA concentration, and irradiation intensity on the degradation ratios were investigated. The leachability and the reuse of the catalyst were also examined.

## 2. Experimental

### 2.1. Reagents

Analytical-grade BPA, hydrogen peroxide solution (30% w/w), and FeSO<sub>4</sub>·7H<sub>2</sub>O were purchased from Damao reagent factory, Tianjin, China, and the Na-Y molecular sieve was purchased from Tianyi inorganic chemical factory, Nanjing, China. All the other chemicals used were of analytical grade and used without further purification. All solutions were prepared with deionized water.

### 2.2. Preparation of Fe-Y molecular sieve catalyst

The catalysts (Fe-Y) were prepared starting from commercially available Na-Y molecular sieve. Prior to ferric ion exchanged experiments, FeSO<sub>4</sub> solution (250 mL of 3.00 g/L) was nitrogen-blown for 15 min to remove the dissolved oxygen, and then 2.00 g Na-Y molecular sieve was kept in the above solution (pH = 4) for 12 h at 80°C. After

filtration, the sample was thoroughly rinsed with distilled water and dried at 60°C for 12 h in the oven.

### 2.3. Photo-Fenton degradation of BPA

Photo-Fenton degradation was conducted in a quartz reactor of 200 mL capacity. The reaction mixture, consisting of 150 mL of BPA solution and the precise amount of Fenton reagent, was continuously stirred with a magnetic bar. The pH of the sample solution was adjusted with HCl (0.01 mol/L) and/or NaOH (0.01 mol/L) solution. The reaction solution was kept at 25 ± 2°C by a circulating water jacket, and was conducted in the black-box to keep away from any other light irradiation. Prior to irradiation, the suspension was magnetically stirred in the dark for 30 min to get an adsorption/desorption equilibrium status. BPA solution concentration dropped from an initial concentration of 20.000 to 19.204 mg/L and kept at 19.204 mg/L after adsorption of 30 min. As the adsorption capacity was low, it can be ignored. The sample solution was irradiated with five pieces of low-voltage mercury lamps (8 W, Philips Co.).

### 2.4. Analyses

The iron ions concentration in the solution was measured with atomic absorption spectrometry (PE-AA800). Prior to the measurement, a calibration curve was obtained by using the standard iron ion solution in 0.1 mol/L HNO<sub>3</sub> solution with known concentrations.

The crystalline structure of Fe-Y was analysed by an Empyrean diffractometer, using CuK $\alpha$  radiation and a graphite secondary beam monochromator at 40 kV and 30 mA with filtered CuK $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ).

After irradiation of BPA, the sample solution was filtered through a membrane filter (0.45  $\mu\text{m}$ ) in order to remove a precipitation. The concentration of BPA was determined with a high performance liquid chromatography (Model 1220, Agilent.) equipped with a UV detector (217 nm). A separation column used was an Agilent Poroshell 120 EC-C18 Threaded Column (4.6 × 100 mm, particle size 2.7  $\mu\text{m}$ ). The mobile phase A was a mixture of water/acetonitrile/tetrahydrofuran (44:8:8, v:v:v), and the mobile phase B was methanol with the volume ratio of 60:40 for A:B. The flow rate was 1.0 mL/min, and the retention time was 5.3 min.

The intensity of the irradiation was measured by a UV radiometer (UV-B, Photoelectric Instrument Factory of Beijing Normal University). The wavebands range from 230 to 300 nm, and the central wavelength was 254 nm.

## 3. Results and discussion

### 3.1. Characterization of Fe-Y molecular sieve catalyst

The results of ion exchange rate of ferric ion on Na-Y molecular sieve are shown in Figure 1(a). In the 250 mL

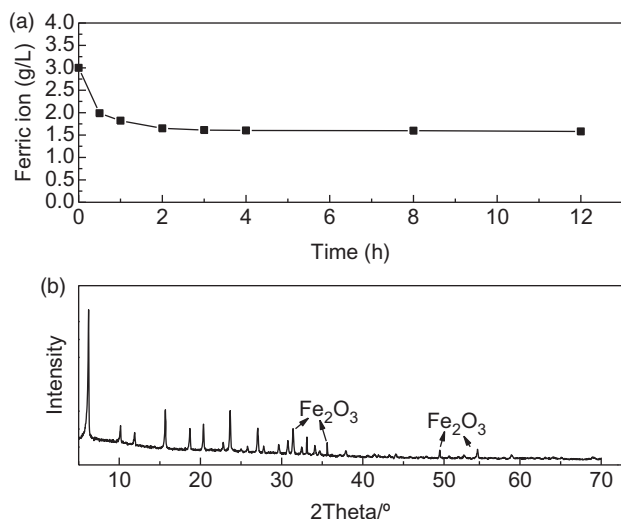


Figure 1. (a) Variation of ferric ion concentration left in the FeSO<sub>4</sub> solution in the preparation processes of the Fe-Y molecular sieve catalyst and (b) XRD for the Fe-Y molecular sieve catalyst.

of 3.00 g/L FeSO<sub>4</sub> solution and 2.00 g Na-Y molecular sieve system, ferric ion concentration in solution reduced sharply after shaking for 1 h. The exchange adsorption processes basically reached a dynamic equilibrium after 2 h ion exchange process, ferric ion concentration in the solution changed little and stabilized about 1.58 g/L. So the ferric ion inside the molecular was saturated about 0.177 g (Fe)/1 g (molecular sieve). However, as the molecular sieve particles inside has a porous structure, sufficient exchange time is favourable for the ferric ion to evenly distribute within the molecular sieve pore and become more stable. Therefore, in this batch of experiments, the exchange time was extended to 12 h.

Figure 1(b) showed the XRD spectra for Fe-Y. The diffractogram showed that Fe-Y revealed a typical Faujasite structure (joint committee powder diffraction standard (JCPDS) No. 45-0128). It was suggested that impregnation of Na-Y with ferric ion did not change the d-spacing on the lattice structure of Na-Y to any significant degree, as similar peaks with those for typical Faujasite were obtained, and the impregnation with ferric ion was effective only on the surface of the molecular sieve and not on the crystal of the molecular sieve.[20] Four peaks of ferrous species were detected at 2θ values of 33.09°, 35.58°, 49.43°, and 54.10°, which implied that ferrous species were oxidized to form Hematite Fe<sub>2</sub>O<sub>3</sub> (JCPDS No. 33-0664).

### 3.2. Comparison of five different degradation approaches for BPA removal

Figure 2 shows five kinds of processes for degradation of BPA. The degradation ratio of BPA was 22% by heterogeneous Fenton reagents, and only 3.6% by photolysis, 9.4% by photo-oxidation with only hydrogen. It was interesting

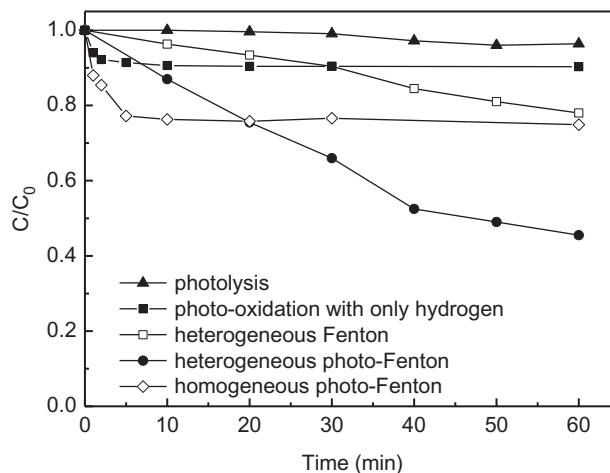
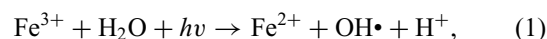


Figure 2. Degradation of BPA by photolysis, photo-oxidation with only hydrogen, heterogeneous Fenton, heterogeneous photo-Fenton, and homogeneous photo-Fenton approaches.

to find that the synergistic technology of the heterogeneous photo-Fenton system was more favourable for the degradation of BPA, and more than 50% of BPA was decomposed after 60 min irradiation at pH 4.3. These results can be explained by the fact that the presence of UV radiation increased the amount of the hydroxyl radical produced by the photoreduction reaction of Fe(III) (Reaction (1)) [37–39] and the decomposition of hydrogen peroxide (Reaction(2)).[28,40]



In the homogeneous photo-Fenton experiment, ferric species were used instead of FeSO<sub>4</sub> with the same Fe content, and other conditions were the same with heterogeneous photo-Fenton. From the curve of homogeneous photo-Fenton experiment, the degradation ratio of BPA reached 22.8% just in 5 min, but kept this ratio in the rest time of 30 min. It can be explained that the homogeneous photo-Fenton had a quick reaction rate in the initial stage, but no sustained capacity for BPA degradation.

Compared with the homogeneous Fenton, the aqueous solution would not become turbid in the heterogeneous photo-Fenton reaction, but the turbid phenomenon occurred in the homogeneous photo-Fenton reaction. This phenomenon was caused by the chemical coagulation functions of homogeneous Fenton. The concentration of iron species after the heterogeneous photo-Fenton reaction ranged from NA to 0.006 mg/L. It indicated that the Fe-Y catalyst prepared had good mechanical stability during the reactions, and there was little leaching of ferric species from the catalyst to the aqueous solution. Given the higher degradation ratio and the resistance leachability of the heterogeneous photo-Fenton system, it was adopted in the following experiments.

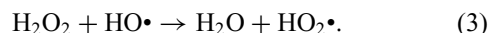
### 3.3. Effect of pH

The effect of pH on the degradation of BPA by using the photo catalysis process was investigated over the pH range of 2.2–7.2 (Figure 3(a)). The degradation percentage of BPA increased with pH increasing up to 4.3, and then decreased after reaching the maximum at pH 4.3. However, pH has no obvious effect on the degradation ratio of BPA, and the removal rate of BPA was within 45.5–56.0% in the broad pH from 2.2 to 7.2. This result was different from that in the homogeneous Fenton system. In homogeneous Fenton reaction, less photoactive materials  $\text{Fe}^{3+}(\text{H}_2\text{O})_6$  would be generated at lower pH and  $\text{Fe}(\text{OH})_3$  at higher pH, [18,28] and the optimal pH in the homogeneous Fenton reaction was around 3. [41] However, the Fe-Y molecular sieve can be effective in the broad pH from 2.2 to 7.2 in this study. This was because the ferric ions were immobilized inside the molecular sieve and the formation of less photoactive materials was avoided.

### 3.4. Effect of initial $\text{H}_2\text{O}_2$ concentration

The effect of  $\text{H}_2\text{O}_2$  dosage on the degradation of BPA was investigated by varying initial concentration of  $\text{H}_2\text{O}_2$  from  $1 \times 10^{-4}$  to  $40 \times 10^{-4}$  mol/L and the result is presented in

Figure 3(b). The degradation rate of BPA increased as  $\text{H}_2\text{O}_2$  concentration was increased. This can be explained that the more produced OH radicals in the high  $\text{H}_2\text{O}_2$  concentration led to the high decomposition rate. When the concentration of  $\text{H}_2\text{O}_2$  was  $20 \times 10^{-4}$  mol/L, almost all the BPA can be degraded within 60 min. With continued increase in  $\text{H}_2\text{O}_2$  concentration from  $20 \times 10^{-4}$  to  $40 \times 10^{-4}$  mol/L, the BPA decomposition ratio decreased from 92.0% to 65.0% within 60 min. The extra  $\text{H}_2\text{O}_2$  can scavenge OH radicals and produce the less reactive species such as  $\text{HO}_2$  (3). [42,43]



Such a reaction reduces the probability of attack of organic molecules by hydroxyl radicals, and causes the degradation rate to drop. So, in order to get an optimal removal ratio of BPA, it was necessary to add an optimal  $\text{H}_2\text{O}_2$  dosage, and the optimal  $\text{H}_2\text{O}_2$  dosage was  $20 \times 10^{-4}$  mol/L in this experiment.

The photo-Fenton reaction of BPA under different initial  $\text{H}_2\text{O}_2$  concentrations was estimated to follow a pseudo first-order kinetic law, according to the following equation:

$$\frac{dC_{\text{subs}}}{dt} = -k_{\text{obs}}C_{\text{subs}}, \quad (4)$$

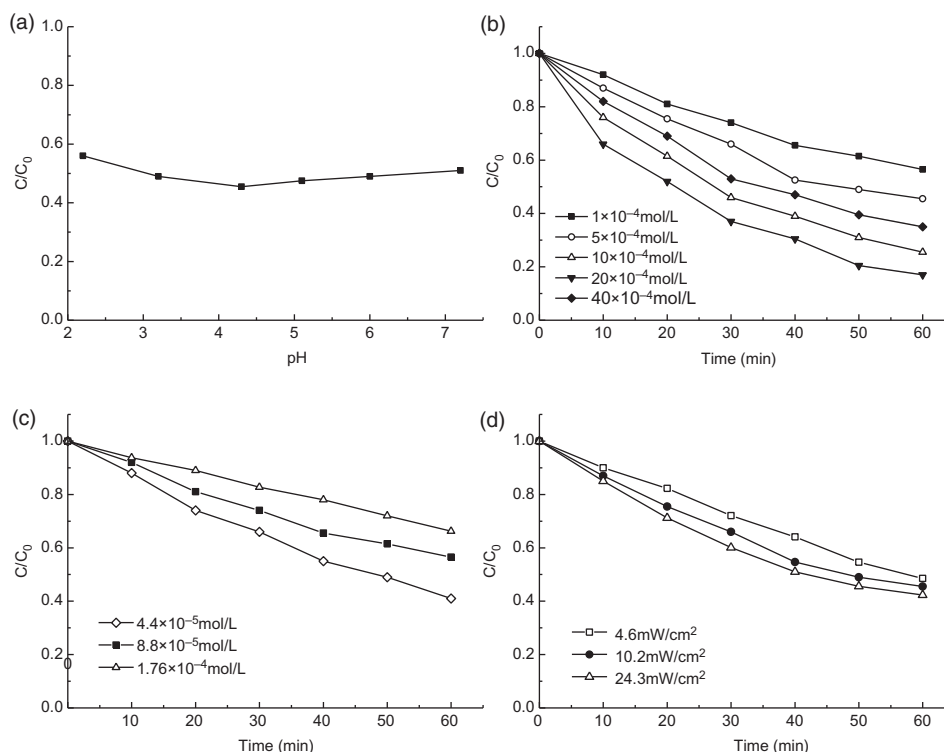


Figure 3. (a) Effect of pH on the degradation of BPA (reaction condition:  $[\text{BPA}] = 8.8 \times 10^{-5}$  mol/L,  $[\text{H}_2\text{O}_2] = 5 \times 10^{-4}$  mol/L,  $[\text{Fe-Y}] = 0.1$  g/L, irradiation intensity =  $4.6 \text{ mW/cm}^2$ , irradiation time = 60 min); (b) effect of initial concentration of  $\text{H}_2\text{O}_2$  on the degradation of BPA (reaction condition:  $[\text{BPA}] = 8.8 \times 10^{-5}$  mol/L,  $[\text{Fe-Y}] = 0.1$  g/L, pH = 4.3, irradiation intensity =  $4.6 \text{ mW/cm}^2$ , irradiation time = 60 min); (c) effect of initial concentration of BPA on the degradation of BPA (reaction condition:  $[\text{H}_2\text{O}_2] = 5 \times 10^{-4}$  mol/L,  $[\text{Fe-Y}] = 0.1$  g/L, pH = 4.3, irradiation intensity =  $4.6 \text{ mW/cm}^2$ , irradiation time = 60 min); and (d) effect of irradiation intensity on the degradation of BPA (reaction condition:  $[\text{BPA}] = 8.8 \times 10^{-5}$  mol/L,  $[\text{H}_2\text{O}_2] = 5 \times 10^{-4}$  mol/L,  $[\text{Fe-Y}] = 0.1$  g/L, pH = 4.3, irradiation time = 60 min).

Table 1. Pseudo first-order constant ( $k$ ), correlation coefficient ( $R^2$ ), half-lives ( $t_{1/2}$ ), and 90% degradation ( $t_{90\%}$ ) times for treatment of BPA of five different  $H_2O_2$  initial concentrations.

$C_0$ (mol/L)	Fe-Y (g/L)	$H_2O_2$ (mol/L)	$k$ ( $\text{min}^{-1}$ )	$R^2$	$t_{1/2}$ (min)	$t_{90\%}$ (min)
$8.8 \times 10^{-5}$	0.1	$1 \times 10^{-4}$	0.0098	0.994	70.72	234.90
$8.8 \times 10^{-5}$	0.1	$5 \times 10^{-4}$	0.0141	0.982	49.16	163.26
$8.8 \times 10^{-5}$	0.1	$10 \times 10^{-4}$	0.0235	0.994	29.49	97.96
$8.8 \times 10^{-5}$	0.1	$20 \times 10^{-4}$	0.0405	0.989	17.11	56.84
$8.8 \times 10^{-5}$	0.1	$40 \times 10^{-4}$	0.0185	0.989	37.46	124.43

Table 2. Pseudo first-order constant ( $k$ ), correlation coefficient ( $R^2$ ), half-lives ( $t_{1/2}$ ), and 90% degradation ( $t_{90\%}$ ) times for treatment of BPA of three different BPA initial concentrations.

$C_0$ (mol/L)	Fe-Y (g/L)	$H_2O_2$ (mol/L)	$k$ ( $\text{min}^{-1}$ )	$R^2$	$t_{1/2}$ (min)	$t_{90\%}$ (min)
$4.4 \times 10^{-5}$	0.1	$5 \times 10^{-4}$	0.0146	0.9935	47.47	157.67
$8.8 \times 10^{-5}$	0.1	$5 \times 10^{-4}$	0.0098	0.9973	70.72	234.90
$1.76 \times 10^{-4}$	0.1	$5 \times 10^{-4}$	0.0066	0.9938	105.12	348.79

Table 3. Pseudo first-order constant ( $k$ ), correlation coefficient ( $R^2$ ), half-lives ( $t_{1/2}$ ), and 90% degradation ( $t_{90\%}$ ) times for treatment of BPA of three different irradiation intensity.

$C_0$ (mol/L)	Fe-Y (g/L)	$H_2O_2$ (mol/L)	Irradiation intensity ( $\text{mW}/\text{cm}^2$ )	$k$ ( $\text{min}^{-1}$ )	$R^2$	$t_{1/2}$ (min)	$t_{90\%}$ (min)
$8.8 \times 10^{-5}$	0.1	$5 \times 10^{-4}$	4.6	0.0117	0.9913	59.24	196.75
$8.8 \times 10^{-5}$	0.1	$5 \times 10^{-4}$	10.2	0.0139	0.991	49.86	165.61
$8.8 \times 10^{-5}$	0.1	$5 \times 10^{-4}$	24.3	0.0156	0.983	44.43	147.56

where,  $C_{\text{subs}}$  is BPA concentration and  $k_{\text{obs}}$  is the pseudo first-order rate constant. In order to confirm the speculation,  $\ln(C/C_0)$  was plotted as a function of the reaction time. The calculated results indicated that the first-order model gives a better fit (data not shown). Therefore, the primary photo-degradation of BPA followed the pseudo first-order kinetics. The substrate half-lives, 90% conversion times, and pseudo first-order rate constant for the degradation of BPA calculated from the equation are summarized in Table 1.

### 3.5. Effect of initial BPA concentration

The influence of various initial BPA concentration on the degradation process was investigated (Figure 3(c)). The results showed that the BPA removal was 59% when initial concentration was  $4.4 \times 10^{-5}$  mol/L, higher than 43.5% for initial concentration  $8.8 \times 10^{-5}$  mol/L and 33.75% for  $1.76 \times 10^{-4}$  mol/L. In the heterogeneous Fenton process, the reaction occurred on the surface of Fe-Y, where the adsorbed BPA molecules were decomposed by  $\text{OH}\cdot$  radicals generated at the active sites. Thus, when the BPA concentration was higher, the number of active sites available was covered by the BPA molecules due to their competitive adsorption on the catalytic surface. In addition, the intermediate products of BPA might also compete for the limited adsorption sites with BPA molecules, which blocked their interactions with ferric active sites. The dynamic parameters of this group experiments are summarized in Table 2.

### 3.6. Effect of irradiation intensity

Figure 3(d) showed the effect of UV irradiation intensity on the degradation of BPA and the dynamic parameters are summarized in Table 3. When the UV irradiation intensity was 4.6, 10.2, and  $24.3 \text{ mW}/\text{cm}^2$ , the pseudo first-order kinetic constants  $k$  were 0.0117, 0.0139, and  $0.0156 \text{ min}^{-1}$ , respectively, indicating that the irradiation intensity has no appreciable effect on the degradation of BPA. So, there is no need to select the light source with very high intensity from an economic perspective.

### 3.7. Stability tests

For the heterogeneous catalysis, stability was an important index for the catalyst. In order to test the stability, it took four times to degrade BPA with the same batch Fe-Y, and the results are shown in Figure 4. In the first three tests, the degradation ratios were 54.5%, 55.1%, and 51.8%, respectively. In the fourth time, the degradation ratio was 45.2%; just reduced 9.3% compared with the maximum. Therefore, it was indicated that the Fe-Y prepared had good stability and was well reusable.

### 3.8. Comparison of $TiO_2$ and Fe-Y for BPA degradation

The results of this study were compared with the results obtained by using  $TiO_2$ . Ohko et al. [44] reported that when



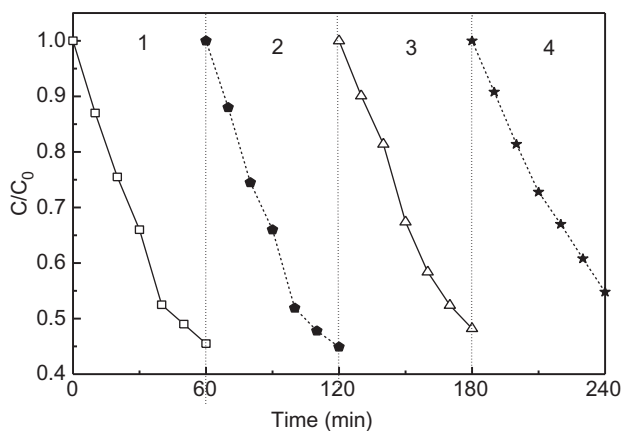


Figure 4. Stability tests for Fe-Y with the same condition.

the initial BPA concentration was 40 mg/L (double times than that of the present study), it took 15 h to degrade BPA for the TiO<sub>2</sub>-photocatalysed reaction with 1 g/L TiO<sub>2</sub> and an energy consumption of 10 mW/cm<sup>2</sup>. Watanabe et al. [45] performed the degradation of BPA (20 mg/L) in the presence of TiO<sub>2</sub> (2 g/L) with an irradiation intensity of 2.5 mW/cm<sup>2</sup>. It took 2 h for BPA complete degradation under the conditions. In this article, it just took 1 h to reach a 92.0% removal of BPA in the situation of 0.1 g/L Fe-Y, 20 × 10<sup>-4</sup> mol/L H<sub>2</sub>O<sub>2</sub>, and irradiation intensity of 4.6 mW/cm<sup>2</sup>. Therefore, the Fe-Y catalyst can be considered for the degradation of BPA in terms of time and cost for degradation.

#### 4. Conclusions

This study applied the heterogeneous photo-Fenton method to degrade BPA solution and evaluated the effects of pH, initial H<sub>2</sub>O<sub>2</sub> concentration, initial BPA concentration, and irradiation intensity on the degradation of BPA. The Fe-Y molecular sieve catalyst was fabricated with the ion exchange method, and the loading capacity was 0.177 g (Fe)/1 g (molecular sieve). The existence form of iron in the Fe-Y was Fe<sub>2</sub>O<sub>3</sub> according to the analysis by XRD. The Fe-Y catalyst showed high catalytic ability in the Photo-Fenton system, and iron ion possessing the low leachability ranged from NA to 0.006 mg/L. Over the range of 2.2–7.2, the pH value had no obvious effect on BPA degradation. The initial concentration of H<sub>2</sub>O<sub>2</sub> had an optimal value of 20 × 10<sup>-4</sup> mol/L; if over this value, H<sub>2</sub>O<sub>2</sub> would give a negative effect. Photo-Fenton on degradation of BPA was superior to traditional Fenton; however, photo-Fenton was not distinctly enhanced by increasing the intensity of UV irradiation. Stability tests indicated that when the Fe-Y catalyst was reused for the fourth time, the degradation ratio was reduced by 9.3%. Based on the results, the heterogeneous photo-Fenton treatment was the available method for the degradation of BPA.

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