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Effective benzalkonium chloride degradation by Fenton oxidation with iron–carbon–bentonite–alginate beads

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ABSTRACT

Novel iron–carbon–bentonite–alginate beads (Fe/C-BABs) were prepared by sol–gel method to trigger advanced Fenton oxidation to realize benzalkonium chloride (BAC) degradation. Degradation results revealed that the optimal conditions of H_2O_2/Fe/C-BABs for BAC degradation were pH 3.0, [BAC] = 50 mg/L, [H_2O_2] = 60 mM, and [Fe/C-BABs] = 50.0 g/L (wet weight). BAC removal efficiency reached 87% within 30 min. Results indicated that BAC degradation was mainly attributed to the heterogeneous rather than the homogeneous reaction. The catalyst showed high-efficiency catalytic performance and ability to control metal-ion leaching to avoid environmental pollution. To expound the pathway of BAC degradation, gas chromatography–mass spectrometry analysis method was used to examine the intermediate products, and a plausible degradation pathway was also proposed. The oxidation of the benzene ring and long-chain alkane into organic acids indicated BAC degradation and nontoxicity of the products.

Keywords: Fe/C-BABs; Benzalkonium chloride; Advanced oxidation; Intermediates

1. Introduction

As a universal type of ionic surfactants, quaternary ammonium compounds (QACs) are widely used in enterprise and industrial production such as scouring agent, emulsifying agent, softener, and disinfectants [1]. QAC abuse causes water pollution, thus creating the potential risk for aquatic organisms [2]. In Austria, the residues of QAC concentrations in industrial wastewater, effluent, surface water, and sludge were detected as 25–300, 0.3–3.6, 22–103 mg/kg (weight/dry-weight), and 0.2–3.0 mg/L, respectively [3,4]. Some studies also showed that the emergence of QACs in the environment can cause bacterial resistance and drug coselection; this condition attracted considerable attention on human health [5]. In addition, benzalkonium chloride (BAC) as a typical QAC, exhibits high toxicity to aquatic organisms at extremely low concentration (5.0 μg/L) on account of the irreversible influence on the microbials' gene [6,7] to the toxic and anti-biodegradable properties. Thus, an effective method should be developed to deal with this kind of pollution.

Investigation results on BAC degradation in some biological treatments showed that conventional water treatment methods are not effective in BAC degradation due to BAC toxicity [8,9]. In general, advanced oxidation processes (AOPs) seem effective in treating such refractory organic wastewaters [10]. As a typical AOPs, using Fe^{2+} and H_2O_2 to produce hydroxyl radicals ($^{\bullet}OH$) with an extremely high oxidation potential of 2.8 V has been verified to be effective in the degradation of organic pollutants [11]. However, the traditional Fenton system can be constrained by the accumulation of ferric oxide sludge, causing the decline of oxidation rates. Homogeneous Fenton catalyzed reactions need up to 60–180 mg/L of Fe ions in solution [12]. This value is far greater than that of the European Union standard that allows only 2.0 mg/L of iron ions released directly into the environment after treatment [13]. An enormous increase in ferrous ions contributes to an increase in the total dissolved

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iron or iron sludge content of the effluent stream and is thus not permitted. To overcome the disadvantages of the homogeneous Fenton or Fenton-like processes uses some attempts have been made to develop the heterogeneous catalysts. Heterogeneous Fenton process using iron-based catalysts such as zero-valent iron, Fe_3O_4, and α-FeOOH to replace the homogeneous Fenton process [14,15]. For example, immobilizing iron ions on the polymer substrates such as a Nafion membrane [16] was used for the degradation of azo dye in water. But, it is known that the Nafion membrane will cost much, which is not suitable for industrialization. Zero-valent iron (Fe^0) is increasingly being used as the catalyst in heterogeneous Fenton process, due to its high reactivity [17,18]. The removal of pollutants in the Fe^0 Fenton system involves two steps [19]: First, Fe^0 can react with H_2O_2 to form Fe^{2+} (Eq. (1)). Afterwards, Fe^{2+} reacted with H_2O_2 to produce $^{\bullet}OH$ (Eq. (2)).

$$Fe^0 + H_2O_2 + H^+ \rightarrow Fe^{2+} + 2H_2O \quad (1)$$

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

Alginate is a natural polysaccharide extracted from brown algae and has many advantages, such as cheap, non-toxic, and can react with metal ions to form stable hybrid composite materials because of the unique gelling properties [20,21]. These properties may allow promising applications in the environmental purification and remedy areas. Recently, iron can be effectively entrapped in a biopolymer matrix, such as alginate [22]. Reportedly, using the complex of Fe ions with alginate as the Fenton catalyst can effectively control the iron leaching. For example, the dissolved iron in the alginate beads based on Fe_3O_4 nanoparticles/Fenton was 0.8 mg/L when the catalyst dosage is 0.8 g/L at pH = 3.0 [22]. Additionally, these samples possessed much lower leaching degree than nano-Fe_3O_4 (approximately 9.8 mg/L) and the value previously reported [23]. These results implied that iron alginate gel beads are used as the effective heterogeneous catalysts to degrade pollutants over a broad pH range.

Thus, iron–carbon–bentonite–alginate beads (Fe/C-BABs) were prepared by sol–gel process to trigger Fenton process to treat BAC in this research. Several important affecting factors, for example, initial pH values, the H_2O_2 concentration, and catalyst dosage, were investigated in this research to achieve the best effect in BAC degradation. Fe/C-BABs are an environment-friendly catalyst that can not only exert high catalytic performance but also effectively control iron ion leaching. The stability of Fe/C-BABs was analyzed by recycling. BAC degradation by Fe/C-BABs was detected by high-performance liquid chromatography (HPLC), and the intermediates were analyzed by gas chromatography–mass spectrometry (GC–MS).

2. Material and methods

2.1. Chemicals

Dodecyl dimethyl benzyl dimethyl dodecyl ammonium chloride (DDBAC) was purchased from Aladdin (China). Sodium alginate, ferrous sulfate ($FeSO_4 \cdot 7H_2O$), and calcium chloride (AR) were obtained from Shanghai (China). Hydrogen peroxide (30%), bentonite, and reduced iron powder (AR) were obtained from Shantou Xi long, Co., Ltd. (China). The 1,10-phenanthroline and hydroxylammonium chloride were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). *tert*-Butyl alcohol (TBA), methanol, and *p*-benzoquinone (BQ) were obtained from Aladdin. The 1 mol/L H_2SO_4 and NaOH were preprepared to adjust pH. All chemicals were used without further purification.

2.2. Preparation and characterization of catalyst

The Fe/C-BABs were synthesized by using sol–gel method. Calcium chloride was used as cross-linking agent to prepare the cross-linking solution [22,24]. The steps are as follows [25]. First, bentonite (2.0 g), carbon powders (0.2 g), and sodium alginate (2.0 g) were dissolved in 100 mL ultrapure water and mechanically stirred for approximately 3 h to let sodium alginate dissolve completely. Iron powder was loaded on alginate by a wet impregnation technique. 2.0 g reduced iron powders was added in this sticky liquid and then added dropwise into the solution of 0.1 mol/L calcium chloride. The beads were formed and immersed in the calcium chloride solution. All beads were washed thrice by distilled water before use. The resultant Fe/C-BAB products can be used in the further experiment.

The total iron content of Fe/C-BABs was analyzed according to the procedure of literature [26]. The 10.0 g (wet weight) sample was dried in vacuum for 24 h at 65°C and then charged in the muffle furnace at 250°C for 2 and held further for 24 h at 550°C. Finally, the sample was cooled to room temperature, and nitric acid was added to dissolve the sample [27]. The moisture content of the beads is approximately 92%, and the iron content in the catalyst is approximately 0.04 g/g.

The physicochemical characterization of the Fe/C-BABs was performed using Fourier transform infrared spectroscopy (FTIR, Thermo Nicolet iS50) at the wavelength range of 4,000–500 cm^{-1}. The surface structure of the beads was analyzed by scanning electron microscopy (SEM, Phenom G2 pure) at an acceleration voltage of 15 kV at room temperature. The crystalline structure of the synthesized catalyst was characterized by X-ray powder diffraction (XRD, Smar/SmartLa) over a 2θ range of 10°–80°.

2.3. Experimental procedure

All the experiments were carried out in a 100 mL beaker at a BAC concentration of 50 mg/L at room temperature (25°C ± 1°C). The reaction was mixed completely using a magnetic stirrer at 200 rpm. To identify the optimal operation conditions, H_2SO_4 and NaOH were used to adjust the initial pH of the solution at four different values (3.0, 5.0, 7.0, and 9.0). The catalyst dosage was controlled at 20, 30, 50, and 70 g/L (wet weight), respectively. Five different concentrations of H_2O_2 were allowed at 0, 20, 40, 60, and 80 mM, respectively. After reaction, the samples were collected and withdrawn in 2 mL centrifuge tubes every 5 min, and 1 mL methanol was added to terminate the radical reactions. Finally, the samples were filtered by using a 0.22 μm filter film before chromatographic analysis. Each experiment was carried out in parallel experiment.

The BAC concentration was analyzed by HPLC (Waters 2695) with a UV detector (262 nm) with the column of Waters XBridge C18 (46 × 250 mm, 3.5 μm). Ammonium acetate (0.385 g) and 1% triethylamine at adjusted pH of 5.0 (using acetic acid) were used as a mobile phase. The ratio of acetonitrile and mobile phase was 72:28 at a flow rate of 1.0 mL/min. For detecting the degradation intermediates, 50 mL samples were extracted by ethyl acetate, and then spin steaming instrument was used to obtain a final volume of 1 mL before analysis. The intermediates of BAC degradation were identified by GC–MS (QP2010 Ultra, Shimadzu, Japan). The total iron and ferrous iron leaching during the reaction were detected by means of 1,10-phenantroline spectrophotometric method at 510 nm by using a UV–Vis spectrophotometer (TU-1900). The solution pH was measured by a sartorius PB-10 pH meter.

To determine the kinetics of BAC degradation, first-order and second-order kinetics were used to fit BAC degradation, respectively (Eqs. (3) and (4)). The apparent rate constant (k) was calculated from transient dynamics of BAC according to the following equation:

First-order kinetics:

$$\ln\left(\frac{C_t}{C_0}\right) = -kt \tag{3}$$

Second-order kinetics:

$$\frac{1}{C_t} = kt + \frac{1}{C_0} \tag{4}$$

where C_t and C_0 are the BAC concentrations at initial and at time (t), and k is the apparent rate constant. The correlation coefficients (R^2) are shown in Table 2. The correlation coefficient for fitting with pseudo-first-order kinetics was high.

3. Results and discussion

3.1. Characterization of Fe/C-BABs

Morphological observation of the surface and internal structure of the dried beads was carried out by SEM and the result was shown in Fig. 1. The pictures revealed that the beads were with rough surface and several spaces inside. This condition might increase the surface area of the catalyst. Some small particles loaded on the catalyst can also be clearly observed and attributed to the iron leaching. The complex structure possibly resulted from the Fe cross-linking between alginate ions during the gelation.

To identify the surface functional groups, synthesized beads were detected by FTIR spectroscopy. The results were shown in Fig. 2, and the absorption band at 3,400 cm^{-1} could be distributive to the stretching vibrations of the –OH group. The weak band at 2,900 cm^{-1} was assigned to the stretch vibration absorption of C–H in alginate [28]. In addition, the absorption band at 1,630 and 1,430 cm^{-1} was assigned to the carboxyl group −COOH of alginate molecule [26,29]. The absorption band at 1,040 cm^{-1} was related to the –C–O extensional vibration of alginate [28]. Finally, the absorption band at 690–700 cm^{-1} in Fe/C-BABs can be accounted for the oscillations of the Fe–OH bond. This finding confirmed the successful and effective incorporation of iron into the alginate. Fig. 3 shows the XRD pattern of Fe/C-BABs, and the typical peak of Fe^0 was located at a 2θ value of 45° (JCPDS06-0696). This observation indicated a stable Fe^0 in Fe/C-BAB catalyst.

3.2. Effect of catalyst dosage

The effect of the catalyst dosage on BAC degradation efficiency was investigated. As shown in Fig. 4, the removal rate of BAC increased from 74% to 87% at an increased dosage of catalyst from 20.0 to 50.0 g/L. This result can be due to the increased number of surface active sites of the catalyst at the catalyst dose ranging from 20.0 to 50.0 g/L. This phenomenon promoted the release of several ferrous ions into the solution and consequently accelerated the H_2O_2 decomposition to produce several $^\bullet$OH (Eqs. (1) and (2)) [30]. However, when the catalyst dosage reached 70.0 g/L, the removal efficiency was reduced because a large amount of the catalyst generated excess Fe^{2+} to quench $^\bullet$OH (Eq. (4)) [31]. The kinetics of BAC degradation was investigated at different catalyst dosages, and the results are shown in Table 2. BAC degradation in the Fe/C-BABs/H_2O_2 system was well fitted by pseudo-first-order kinetics (Eq. (3)). Most importantly, the increase in the amount of catalyst leads to a great amount of metal-ion leaching, which is equivalent to pollution. Therefore, in this study, we chose 50.0 g/L (wet weight) as the best dosage for the catalyst. In this condition, the amount of iron leaching can also be within the standard range.

$$\mathrm{Fe^{2+}} + {}^\bullet\mathrm{OH} \rightarrow \mathrm{Fe^{3+}} + \mathrm{OH^-} \tag{5}$$

3.3. Effect of initial pH

In general, the initial pH plays a vital role in the Fenton process to eliminate pollutants. The effect of initial pH on BAC degradation in Fe/C-BABs/H_2O_2 system was investigated. As shown in Fig. 5(a), with increased pH from 3.0 to 9.0, the degradation efficiency of BAC decreased from 87% to 50%. Obviously, the most appropriate pH was 3.0. Obviously, the fast generation of radicals in the Fenton reaction is under acidic condition (Eqs. (1) and (2)) [32]. The kinetics of BAC degradation was investigated at different initial pH, the results were shown in Table 2. Moreover, Fig. 5(b) showed the concentration of dissolved iron species including total iron and ferrous ions. Both total iron and ferrous ions decreased when the pH range from 3.0 to 9.0. The highest amounts of total iron and ferrous ion leached were 2.65 and 0.615 mg/L at pH 3.0, respectively. The high pH led to the precipitation of Fe^{3+} or Fe^{2+} ions to form oxyhydroxides. Eqs. (6) and (7) demonstrated the processes of Fe^{3+} or Fe^{2+} oxyhydroxide formation [33]. The formed ferric hydroxide complexes adsorbed onto the catalyst surface; this condition inhibited the Fe^{2+} release [34]. Enough ferrous ions could activate H_2O_2 to produce hydroxyl radicals in this case. To determine where the reaction occurred, Fe_2SO_4 was used as the Fe^{2+} source to identify the function of dissolved iron ions. The concentration of leached Fe^{2+} in heterogeneous Fenton was 0.615 mg/L. Therefore, the Fe^{2+} in the homogeneous Fenton reaction was selected at a concentration of 0.615 mg/L. As can be seen in Fig. 6, compared with the heterogeneous Fenton reaction in the same condition, BAC was hardly removed

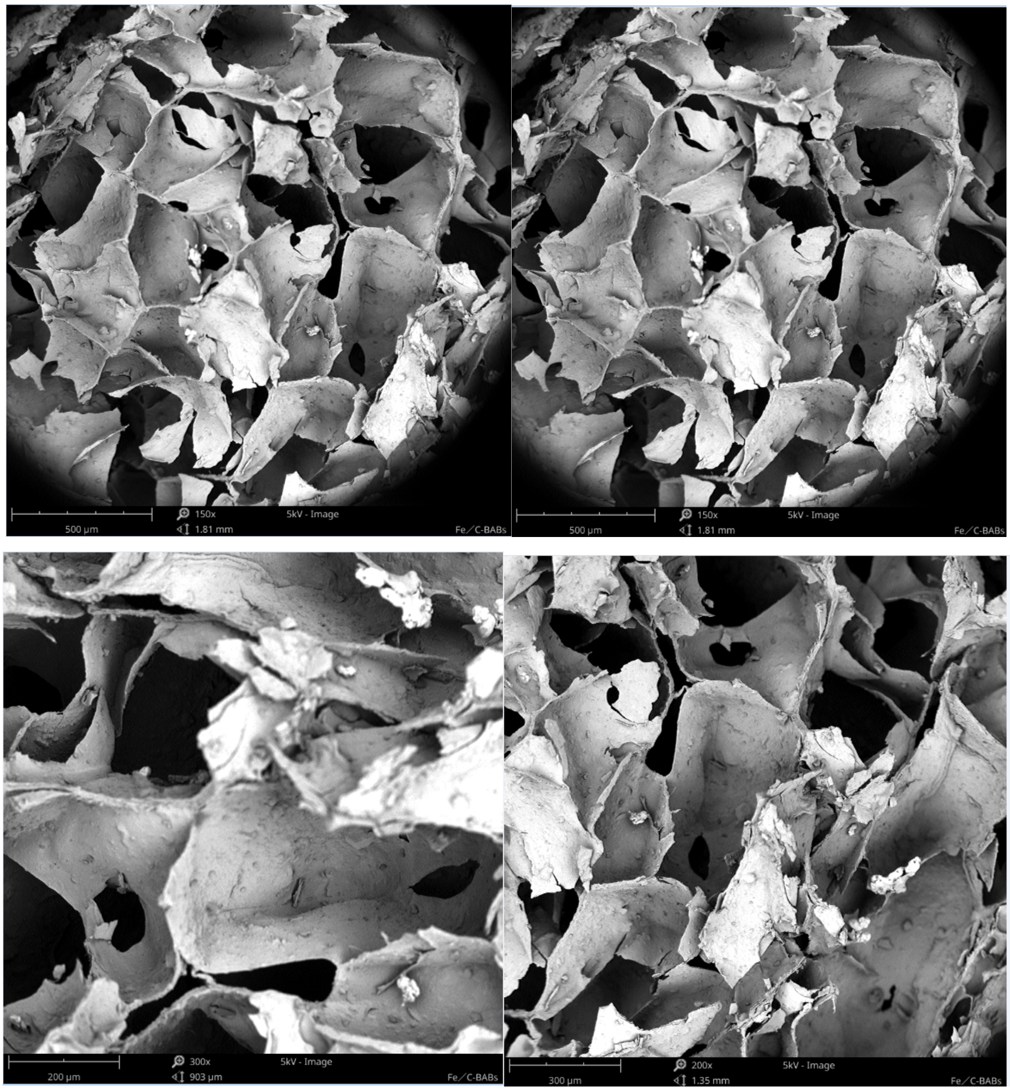


Fig. 1. SEM images of surface of Fe alginate beads.

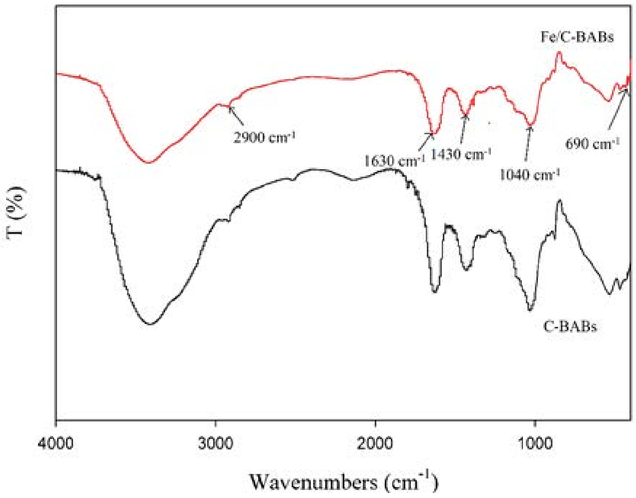


Fig. 2. FTIR spectra of Fe/C-BABs and C-BABs.

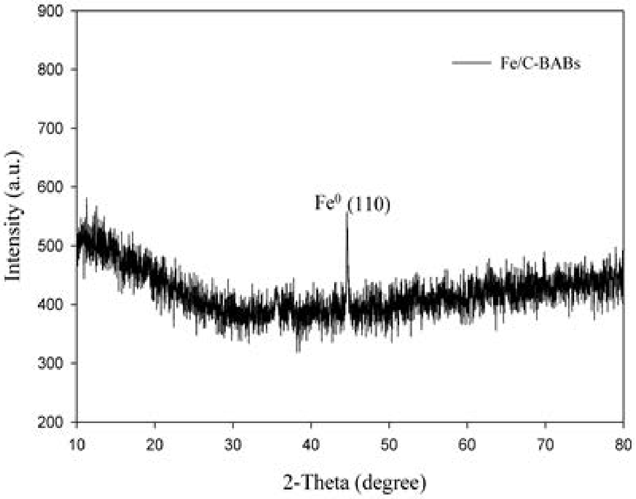


Fig. 3. XRD pattern of Fe/C-BABs.

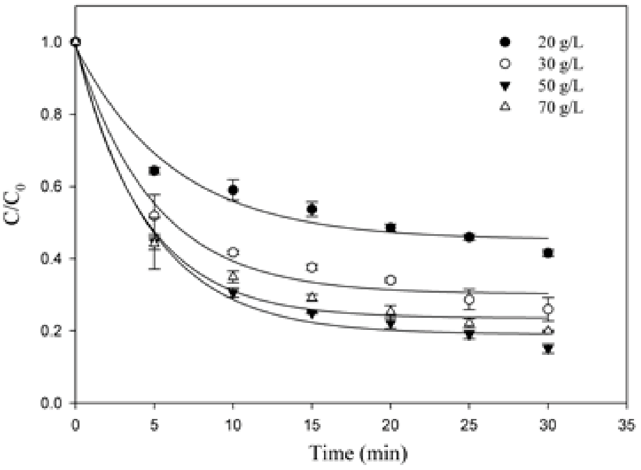


Fig. 4. The effect of catalyst dosages on the degradation of BAC. Conditions: [BAC] = 50 mg/L, [H_2O_2] = 60 mM, initial pH = 3.0, at room temperature.

in the homogeneous Fenton. The concentration of ferrous ions in heterogeneous and homogeneous Fenton reactions is shown in Fig. 6. In homogeneous Fenton reactions, ferrous ion cannot be detected after 20 min of reaction. This phenomenon is similar with the result of the literature [33], indicating that the amount of Fe^{2+} ions in the solution was insufficient to activate H_2O_2 to produce enough free radicals to degrade organic matter. This result also demonstrated that the concentration of metal-ion leaching in the heterogeneous Fenton reaction in this system was very small. The catalyst can effectively control the metal-ion leaching, and the Fe^{2+} on the catalyst surface (≡Fe^{2+}) played the key role in the reaction rather than the dissolved Fe^{2+}. Thus, the hydroxyl radicals might be produced on the surface of the catalyst rather than in the solution (Eq. (8)).

$$Fe^{2+} + H_2O \rightarrow Fe(OH)^{+} + H^{+} \tag{6}$$

$$Fe^{3+} + 2H_2O \rightarrow Fe(OH)_2^{+} + 2H^{+} \tag{7}$$

$$\equiv Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^{-} \tag{8}$$

The ratio of iron leached for Fenton reaction under different systems was summarized in Table 1. The results indicated that this study has a great effect on controlling iron leached. Moreover, the iron leaching ratio was only 0.07%. This value was far less than that of other systems.

3.4. Effect of H_2O_2 concentration

The initial H_2O_2 concentration will affect the generation of hydroxyl radicals. The effect of initial H_2O_2 concentration was investigated at pH = 3.0, and the catalyst dosage was 50.0 g/L. As can be seen in Fig. 7(a), under optimum H_2O_2 concentration of 60 mM, the removal rate reached 87%. When the H_2O_2 concentration increased at 80 mM, the BAC removal efficiency decreased to 75%. This phenomenon was also confirmed by some previous studies considering that the ${}^{\bullet}OH$ radicals can react with extra H_2O_2 (Eq. (9)) to generate $HO_2^{\bullet}/O_2^{-\bullet}$. Those secondary radicals are less reactive than ${}^{\bullet}OH$ [37]. Thus, the excess H_2O_2 would cause the ${}^{\bullet}OH$ scavenging and decrease the degradation efficiency of organic pollutants [38]. The kinetics of BAC degradation investigated at different H_2O_2 concentrations is shown in Table 2. BAC degradation in the Fe/C-BAB/H_2O_2 system is well fitted by pseudo-first-order kinetics (Eq. (3)). To evaluate the H_2O_2 efficiency, 60 mM of H_2O_2 was added to the reaction system in batches (add 15 mM every 5 min). As shown in Fig. 7(b) the reaction rate of the first 10 min has become significantly fast. Then, the reaction rate was not much different than before. This result proved that the previous 60 mM H_2O_2 was excessive, but the efficiency of the entire reaction was feasible in removing BAC. After 30 min reaction, the efficiency of H_2O_2 one-time addition and H_2O_2 gradual addition was 87% and 93%.

$${}^{\bullet}OH + H_2O_2 \rightarrow HO_2^{\bullet} / O_2^{-\bullet} + H_2O \tag{9}$$

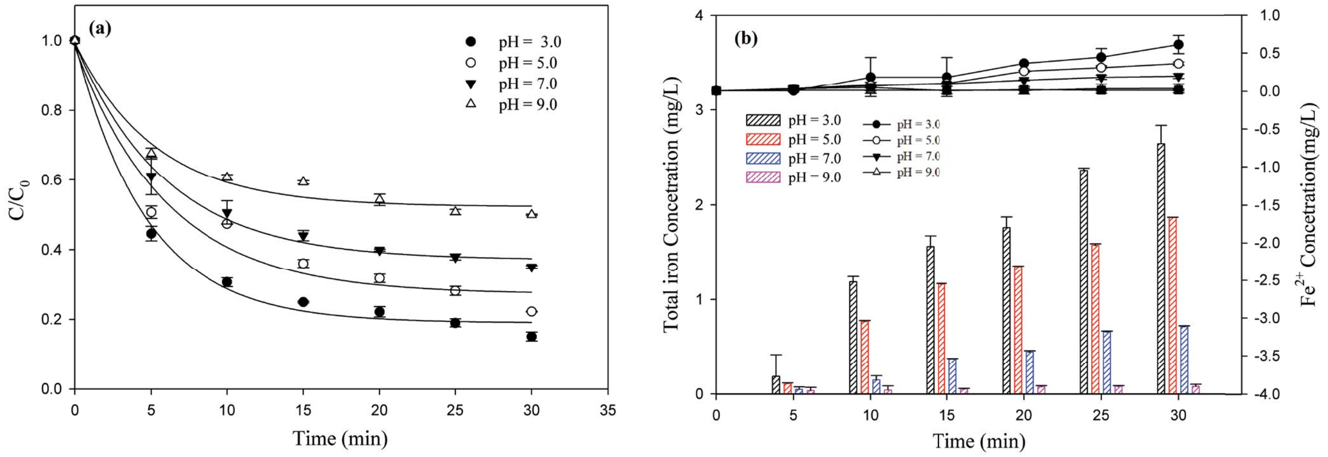


Fig. 5. (a) The effect of initial pH value on the degradation of BAC; (b) the concentration of total iron and ferrous leaching at different initial pH value during the whole reaction. Conditions: [BAC] = 50 mg/L, catalyst = 50 g/L, initial pH = 3.0, at room temperature.

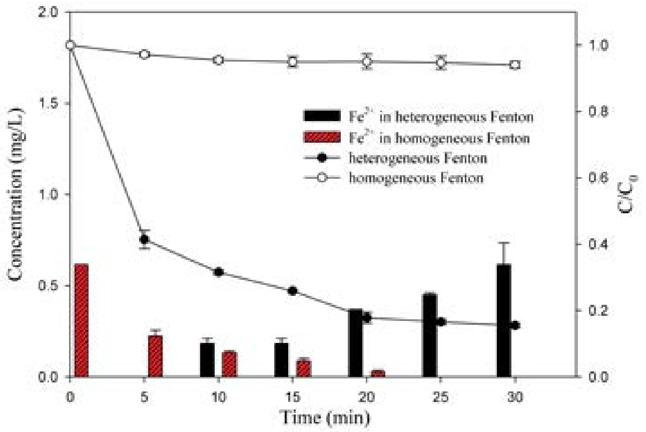


Fig. 6. The degradation efficiency of BAC and the concentration of ferrous ions in homogeneous Fenton and heterogeneous Fenton using Fe/C-BABs. Conditions: [BAC] = 50 mg/L, $[Fe^{2+}]$ = 0.615 mg/L, catalyst = 50 g/L, $[H_2O_2]$ = 60 mM, initial pH = 3.0, at room temperature.

3.5. Reactive species identification for proposed mechanism

For analyzing which are the main reactive species during the BAC degradation in this reaction, methanol, TBA, and BQ were chosen as the scavenger to detect the reactive radicals. As shown in Fig. 8, the Fenton reaction was significantly inhibited when TBA and methanol were added because TBA and methanol can scavenge hydroxyl radicals that affect the BAC degradation efficiency [39]. When adding BQ to scavenge superoxide radical ($^{\bullet}O_2^-$) [40,41], the removal rate decreased only slightly during the entire reaction, indicating that the role of $^{\bullet}O_2^-$ in the reaction system is very small. Therefore, hydroxyl radicals play an important role in the heterogeneous Fenton reaction. We also compared the catalytic performance of BAC degradation between

Table 2
Regression result of the degradation of BAC in different catalyst dosage

H_2O_2 (mM)	C_{cat} (g/L)	pH	k (min^{-1}) × 10^{-2}	$R^2_{(first)}$	$R^2_{(second)}$
60.0	20.0	3.0	1.74	0.995	0.990
60.0	30.0	3.0	2.78	0.983	0.983
60.0	50.0	3.0	4.82	0.991	0.987
60.0	70.0	3.0	3.40	0.988	0.990
60.0	50.0	3.0	4.82	0.991	0.987
60.0	50.0	5.0	3.32	0.990	0.976
60.0	50.0	7.0	2.14	0.988	0.988
60.0	50.0	9.0	1.22	0.988	0.982
20.0	50.0	3.0	1.88	0.998	0.991
40.0	50.0	3.0	3.86	0.987	0.965
60.0	50.0	3.0	4.82	0.991	0.987
80.0	50.0	3.0	2.43	0.997	0.987

Table 1
Comparison of iron leached under the different reaction system

Catalyst dosage (g/L)	Oxidants (mM)	Pollutants (mg/L)	pH	Iron leached (%)	Ref.
RFFe (0.5)	H_2O_2 (13.8)	APAP (50.0)	3.0	3.20	[35]
RFFeC (0.5)	H_2O_2 (13.8)	APAP (50.0)	3.0	5.80	[35]
Fe^{2+} (0.07)	H_2O_2 (30.0)	Phenol (200.0)	3.0	1.72	[36]
Fe_3O_4 (1.0)	H_2O_2 (12.0)	2,4-DCP (100.0)	3.0	1.0	[25]
Fe/C-BABs **(50.0) (wet weight)**	**H_2O_2 (60.0)**	**BAC (50.0)**	**3.0**	**0.07**	**This study**

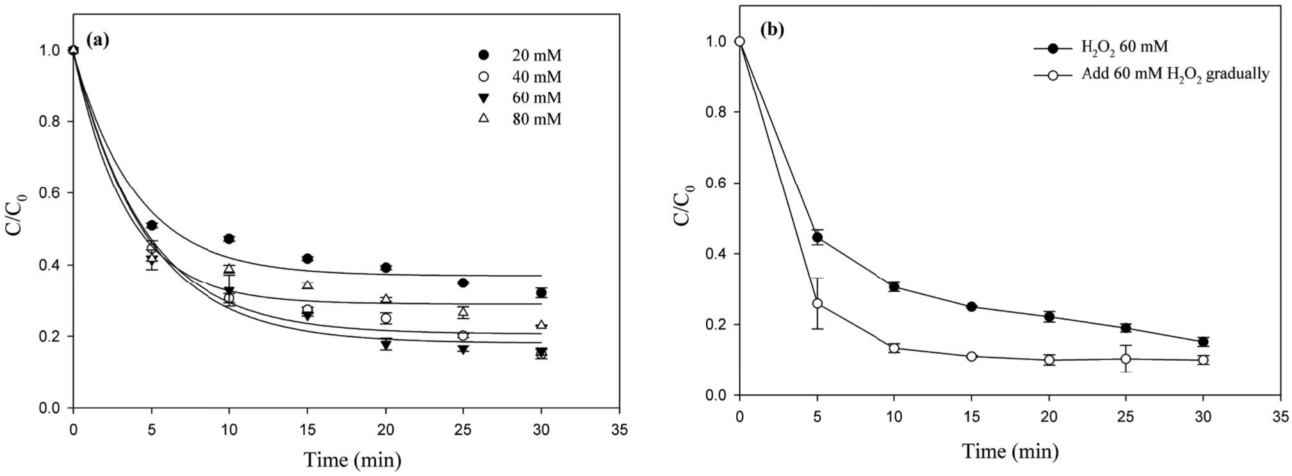


Fig. 7. (a) The effect of varies initial H_2O_2 concentration on the degradation of BAC; (b) the effect of adding H_2O_2 gradually. Conditions: [BAC] = 50 mg/L, catalyst = 50 g/L, initial pH = 3.0, at room temperature.

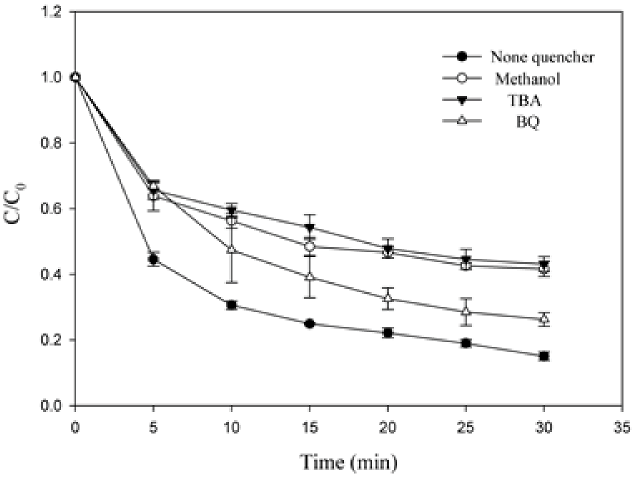


Fig. 8. Degradation of BAC in the Fe/C-BABs/H_2O_2 system with different radical scavengers (0.1 mM). Conditions: [BAC] = 50 mg/L, catalyst = 50 g/L, [H_2O_2] = 60 mM, initial pH = 3.0, at room temperature.

Fe/C-BAB/H_2O_2 system and the previously reported system. As shown in Table 3, Fe/C-BABs prepared in this study can achieve high degradation efficiency in a short time in BAC degradation. Moreover, the catalyst can effectively control metal-ion leaching (Table 1). This condition can reduce environmental pollution.

3.6. The reuse of catalyst

To evaluate catalyst reusability for sustainable operation of Fe/C-BAB/H_2O_2 system, the catalyst was serially reused thrice, and the spherical-shaped catalyst was recovered and washed with deionized water. As shown in Fig. 9(a), the BAC removal efficiency can reach up to 70% after three cycle times. These results simply confirmed the promising feasibility of catalyst reuse. In addition, Fig. 9(b) is the iron leaching of the catalyst after using three times. Obviously, iron leaching is almost stable after three times use. The catalyst also has a very good effect in controlling iron leaching even in multiple uses. Thus, the result indicates that the catalyst has good stability and easy recovery.

3.7. Mechanism analysis

The degradation intermediates of BAC in Fe/C-BAB/H_2O_2 system were determined by GC–MS. Our findings were in accordance with that of Refs. [47–49], and a probable pathway for BAC oxidative destruction is proposed in Fig. 10. First, the benzyl C–N bond was broken down to produce *N*,*N*-dimethylbenzylamine-1-dodecane (retention time (RT) = 11.4 min). Then, dodecane was fractured and can be

Table 3
Comparison between Fe/C-BABs/H_2O_2 system and the previously reported system in the catalytic performance for BAC degradation

No.	System	Method	Pollutants (mg/L)	pH	Removal rate (%)	Ref.
1	TiO_2/UV	Photocatalytic	BAC (70.0)	4.6	73.0 (60 min)	[42]
2	UV/Cl_2	Photocatalytic	BAC (100.0)	7.0	65.0 (12 min)	[43]
3	O_3	Chemical oxidation	BAC (50.0)	11.0	65.7 (30 min)	[44]
4	H_2O_2	Chemical oxidation	BAC (50.0)	11.0	4.5 (30 min)	[44]
5	Fe^{2+}/PS	AOPs	BAC (100.0)	3.0	84.7 (60 min)	[45]
6	Fe^{2+}/H_2O_2	AOPs	BAC (100.0)	3.0	79.0 (60 min)	[46]
7	**Fe/C-BABs/H_2O_2**	**AOPs**	**BAC (50.0)**	**3.0**	**87.0 (30 min)**	**This study**

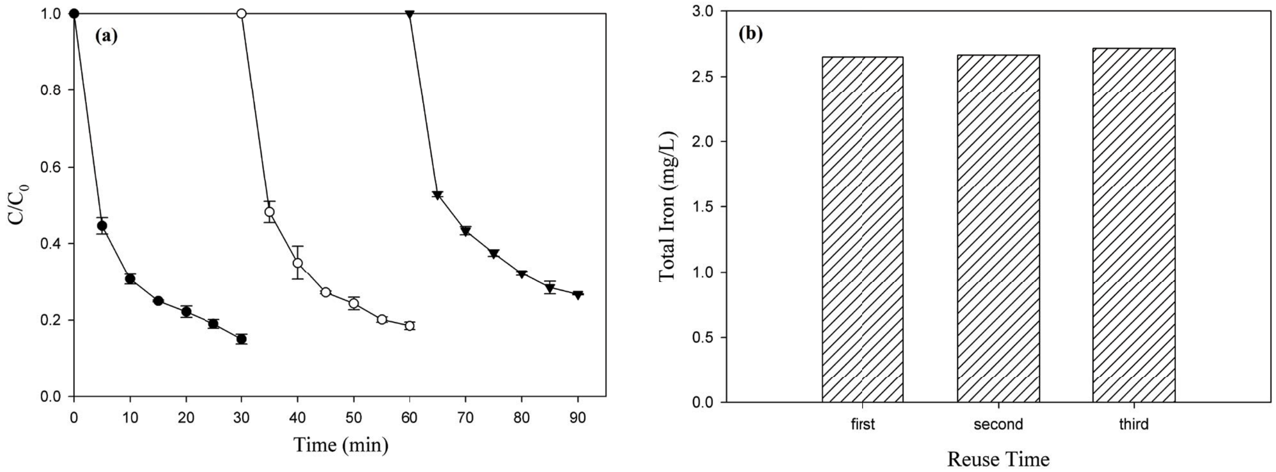


Fig. 9. (a) The reusability of Fe/C-BABs in the Fe/C-BABs/H_2O_2 system. (b)Total iron leaching in solution during three cycle times. Conditions: [BAC] = 50 mg/L, catalyst = 50 g/L, [H_2O_2] = 60 mM, initial pH = 3.0, at room temperature.

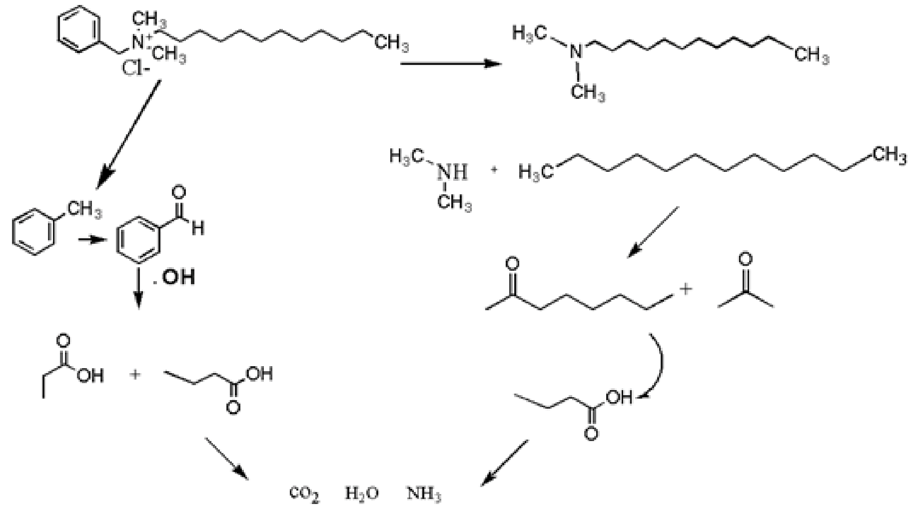
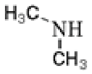
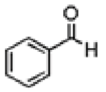
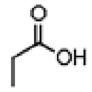
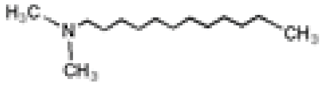


Fig. 10. The proposed degradation pathway of BAC oxidation by Fe/C-BABs H_2O_2 system. Conditions: [BAC] = 50 mg/L, catalyst = 50 g/L, $[H_2O_2]$ = 60 mM, initial pH = 3.0, at room temperature.

Table 4
The possible transformation products of BAC after treated by Fenton system

No.	retention time (RT) (min)	Intermediates	Structure
1	8.4	Dimethylamine	
2	10.8	Benzaldehyde	
3	11.0	Propanoic acid	
4	11.4	*N,N*-Dimethylbenzylamine-1-dodecane	
5	11.8	Dodecane	

oxidized into short chains of organic acids. According to the detected substances, we can speculate that the benzene ring can be considered for oxidation into CO_2 and H_2O because at the end of the reaction, the aromatic compounds are not detected in the solution. Moreover, the possible intermediates of BAC after being treated by Fenton system is shown in Table 4.

4. Conclusion

In this research, a novel Fe/C-BAB has been synthesized and applied successfully for BAC degradation. The results revealed that the catalyst can effectively inhibit excessive iron leaching, and the iron leaching ratio was only 0.07%, which was far less than that of other systems. In Fe/C-BAB/H_2O_2 system, approximately 87% BAC was significantly removed at pH 3.0, [BAC] = 50.0 mg/L, $[H_2O_2]$ = 60 mM, and [Fe/C-BABs] = 50.0 g/L (wet weight). The porous catalyst structure will provide a good catalytic activity for BAC degradation. Through GC–MS analysis, several degradation products could be identified and structurally characterized. Through the analysis results, we can presume that the fission of alkyl C–N was the first step to BAC degradation to produce dodecane trimethylammonium. Further oxidation led to the generation of some short chains of organic acids and other intermediates and then to the final products of CO_2 and H_2O. The result of catalyst recycling showed that the removal rate of BAC can still reach up to 70%, and the iron leached from the catalyst after three times leaching is stable. Therefore, the development and application of catalyst would bring good effect, such as simple synthesis, good structural stability, easy recovery, high catalytic activity, and prevention of environmental pollution.

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