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Heterogeneous UV-Fenton catalytic degradation of dyestuff in water with hydroxyl-Fe pillared bentonite

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Abstract

In recent years, much attention has been focused on developing heterogeneous catalyst for Fenton or photo-Fenton process to reuse the catalyst and avoid the possible pollution caused by the metal ions in the solution. Through cation exchange reaction, hydroxyl-Fe pillared bentonite (H-Fe-P-B) was successfully prepared as a solid catalyst for UV-Fenton process. Compared with raw bentonite, the content of iron, interlamellar distance and external surface area of H-Fe-P-B increased remarkably. Heterogeneous UV-Fenton catalytic degradation of azo-dye Acid Light Yellow G (ALYG) was investigated in aqueous using UVA (365 nm) light as irradiation source. The effects of H_2O_2 concentration, catalyst dosage, initial pH and temperature on degradation of ALYG were studied in detail. The results demonstrated that the H-Fe-P-B had high catalytic activity. In optimal operation conditions, more than 98% discoloration and 65% TOC removal of 50 mg/L ALYG could be achieved after 120 min treatment. The iron leaching rates of H-Fe-P-B were all below 0.6% in multiple runs in the degradation of ALYG, which indicated that the heterogeneous catalyst had long-term stability and activity. Another advantage of this catalyst was its strong surface acidity, which made the range of pH for heterogeneous UV-Fenton system extended from 3.0 to 9.0. The results indicated that the H-Fe-P-B was a promising catalyst for heterogeneous UV-Fenton system.

Keywords: UV-Fenton; Azo-dye; Hydroxyl radical; Bentonite; Degradation

1. Introduction

Dye pollutant from the textile industries is a principle source of environmental contamination. The quality and quantity, especially pH value, of dyestuffs wastewater are diverse. In China, the annual production of the dyestuffs wastewater is over 5.5×10^9 m^3 and above 1.6×10^9 m^3 of dye-containing wastewater drains directly into environmental water system [1]. There are over 3000 dyes available on the commercial market and more than half of commercial dyes are azo-dyes. Some of these dyes are toxic in nature and their removal from the industrial effluents is a major environmental problem. Dyestuffs have complex chemical structure, which is hard to degrade by the conventional biological treatment method [2,3]. For example, it was reported that azo-dyes are nonbiodegradable under aerobic conditions and can undergo anaerobic degradation to potentially carcinogenic amines [2–4]. Various chemical and physical methods, such as chemical coagulation and adsorption on activated carbon, are currently used. However, these traditional methods mainly transfer the contaminants from wastewater to solid wastes, which may lead to a new kind of pollution [5,6].

Homogeneous photo-Fenton or photo-Fenton like process, which could generate hydroxyl radical ($^\bullet$OH) and destroy organic pollutants significantly, have been reported for treatment of dye effluents [1,7–9]. In these systems, the catalysts of iron ions are dissolved in water so they are called homogeneous photo-Fenton systems [10]. However, there are two major drawbacks that limit the further application of homogeneous photo-Fenton system in wastewater treatment: (1) the range of pH for Fenton reaction is tight (e.g., pH = 2–4), and the acidification is more costly than the energy and oxidant used in Fenton degradation [11–13]; (2) the catalysts of iron ions cannot be reused and may result in second pollution of water, and removal of them at the end of treatment will increase the cost [10–14].

To overcome these drawbacks, much attention has been focused on development of heterogeneous catalyst for Fenton

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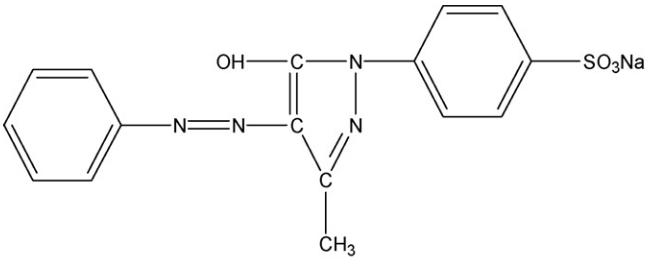


Fig. 1. Structure of Acid Light Yellow G.

or photo-Fenton process in recent years. Selection of catalyst supports is important during the preparation of heterogeneous catalyst. At present, the catalyst supports include organic (such as C-Nafion and resin) and inorganic materials (such as HY zeolite, C fabrics and pillared clays) [10–16]. During these supports, pillared clays may be one of ideal supports because of its unique characteristics, abundance and low cost. Being pillared, the clay's micropore volume and specific surface area could increase remarkably, and the nano-size pillars could provide more special catalytic sites [14,15,17,18]. For example, Feng et al. [14,15] have successfully developed α-Fe_2O_3–bentonite nanocomposite as catalyst for heterogeneous UV-Fenton to discolor and mineralize azo-dye Orange II. In their experiment, the α-Fe_2O_3–bentonite nanocomposite was obtained from the hydroxyl-Fe pillared bentonite by calcinations at 350 °C for 24 h. However, if the pillars are not modified by calcinations, which will increase the cost for catalyst preparation, the pillared clay contained of Fe^{3+} could also show significant catalytic activity for hydrogen peroxide to degrade organic pollutant [18,19]. For example, Catrinescu et al. [18] have successfully developed Fe-exchanged Al-pillared synthetic beidellite for heterogeneous Fenton oxidation of phenolic aqueous wastes. This catalyst had high catalytic activity with low iron leaching rate and could extend the range of pH values for Fenton-type oxidation. The hydrolysis products of iron ions, such as $Fe(OH)^{2+}$, $Fe(OH)_2{}^{+}$, $Fe_2(OH)_2{}^{4+}$, have high photochemistry activity [20,21]. Through cation exchange reaction, these ions could intercalate bentonite and be fixed as pillars to form hydroxyl-Fe pillared bentonite (H-Fe-P-B) [22–24]. And the H-Fe-P-B may be a novel and cheap catalyst for heterogeneous UV-Fenton.

In this study, the H-Fe-P-B was developed as a new photo-Fenton catalyst for catalytic degradation of azo-dye. The effects of some conditions such as initial pH, H_2O_2 concentration, catalyst dosage, temperature and the stability of catalyst were also examined in detail. Acid Light Yellow G (ALYG) was employed as a probe of azo-dye, which has been used extensively in dyeing industry. Its chemical structure was shown in Fig. 1.

2. Experiment

2.1. Materials

The bentonite used was primarily Ca^{2+}-montomorillonite from Inner Mongolia Autonomous Region, China. Its cation exchange capacity (CEC) was 108.4 mmol/100 g. Bentonite was prepared from original mineral by drying, grinding into powder (0.074 mm). The azo-dye, Acid Light Yellow G, was of industrial grade and used without further purification. And others reagents used were of analytical grade.

2.2. Hydroxyl-Fe pillared bentonite synthesis and characterization

The hydroxyl-Fe pillared bentonite catalyst was prepared by pillaring the bentonite through cation exchange process.

Firstly, Na_2CO_3 was added slowly as powder into the solution of $Fe(NO_3)_3$ under magnetic stirring and N_2 atmosphere, until the ratio of $[Na^+]/[Fe^{3+}]$ became 1:1. Then the solution was aged at 60 °C for 1 day. Secondly, the pillaring solution was added to the clay suspension under stirring. The final $[Fe^{3+}]$/clay ratio was equal to 10 mol/kg of dry clay. The product was then filtered, washed with deionized water several times. Finally, the hydroxyl-Fe pillared bentonite was dried at 105 °C overnight, ground to about 200-mesh (0.074 mm).

The d_{001}-spacing was measured by XRD analysis on a (Rigaku) D/max-2550 diffractometer. Specific surfaces area was determined by N_2 adsorption (BET method) on a NOVA2000e instrument. The element of raw bentonite and solid catalyst was analyzed by X-ray fluorescence (XRF) spectrometer (ZSX100e).

2.3. Degradation of azo-dye ALYG

The experiments were carried out in a photocatalytic oxidation reactor, which was shown in Feng's experiments [14]. In the center of the cylindrical reactor, one UVA light tube (6 W 365 nm) was used as light resource. The temperature was controlled to 30 °C during the experiments and solution pH was adjusted to 3.0 except otherwise specified. The initial concentration of ALYG was 50 mg/L, the concentration of catalyst was 1.0 g/L and the concentration of H_2O_2 was 10 mmol/L except otherwise specified. All experiments were carried out under constantly stirring to make the catalyst good dispersion. Deionized water was used throughout the work. The reaction was initiated when the UVA light was turned on and H_2O_2 was added to the ALYG solution. And the pH was measured by a Mettler Toledo pH meter (Seven Multi) in solution.

At given intervals of degradation, a sample was analyzed by UV–vis spectroscopy using Shimadzu UV-2450 at a wavelength of 402 nm, which is the maximum absorption wavelength of ALYG. The concentration of ALYG was converted through the standard curve method of dyes. Total organic carbon (TOC) was analyzed in a TOC analyzer (Shimadzu TOC-Vcph) to evaluate the mineralization of dye. Before analysis, all the samples were immediately treated with scavenging reagent [15] to obtain accurate TOC data. To evaluate the leaching of the catalyst, the iron concentration in the solution after reaction was determined by ICP-AES (IRIS IntrepidIIXSP). The discoloration degree and mineralization degree were defined by the Eqs. (1) and (2), respectively.

$$X_{\mathrm{DIS}}\,(\%) = \left(\frac{1 - C_t}{C_0}\right) \times 100 \qquad (1)$$

$$X_{\mathrm{TOC}}\,(\%) = \left(\frac{1 - \mathrm{TOC}_t}{\mathrm{TOC}_0}\right) \times 100 \qquad (2)$$

3. Results and discussion

3.1. Characterization of H-Fe-P-B catalyst

In Table 1, the characteristics of bentonite and H-Fe-P-B were given. The results indicated that the pillaring process had beneficial effects on the characteristics of bentonite. The interlamellar distance ($d_{0\,0\,1}$) of bentonite was 1.52 nm, which was a criteria interlamellar distance of Ca^{2+}-montomorillonite. During the preparation of H-Fe-P-B, the molar ratio of $[Na^+]/[Fe^{3+}]$ was 1:1 in pillaring solution, which meant that the value of B (OH^-/Fe^{3+}) was 1.0 [24]. In such solution, the iron ions will build up large polymers such as Fe_6, Fe_9 and Fe_{24}, which could be described as $Fe_x(OH)_y^{(3x-y)+}$ [25]. As a result, the interlamellar distance ($d_{0\,0\,1}$) of H-Fe-P-B increased up to 5.45 nm after these polycations exchanged the Ca^{2+}. The result was analogous to that reported by Mandalia who observed a d-spacing of 7.6 nm in the XRD pattern of Fe-pillared montmorillonite with an OH^-/Fe ratio of 1.0 [23]. Furthermore, the content of iron of H-Fe-P-B reached 17.1%, which was much more than expected from the CEC of the bentonite, conforming that the Fe^{3+} ions was present as polycations (hydroxyl-Fe species). The specific surface area and the micropore volume of H-Fe-P-B were 138.30 m^2/g and 0.044 ml/g separately. The results indicated that the iron polycations intercalated the bentonite successfully.

3.2. Degradation of ALYG by heterogeneous UV-Fenton process with H-Fe-P-B as catalyst

The relative concentration removal efficiency of ALYG versus time under different conditions was shown in Fig. 2. From the results, it is clear that the dye was resistant to direct photolysis of UVA light (curve a) and oxidation of H_2O_2 in dark (curve b). After 120 min treatment, only 5.2% and 6.5% discoloration of ALYG was observed, respectively. It was interesting that the adsorption of ALYG on H-Fe-P-B could not achieved equilibrium in 120 min, since the concentration of ALYG decreased continuously (curve c). The H_2O_2 and H-Fe-P-B composed a heterogeneous Fenton like system (curve d). In Fenton like system, the formation of hydroxyl radical is due to Fe^{2+} catalyzed decomposition of H_2O_2 (Eqs. (3) and (4)).

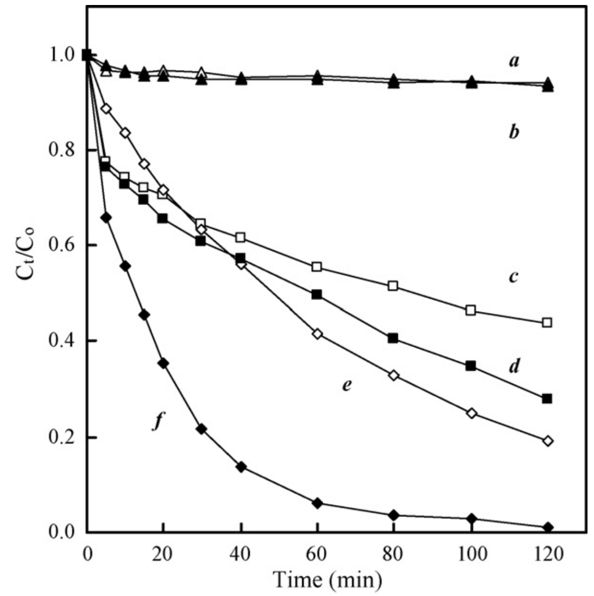


Fig. 2. Degradation of 50 mg/L ALYG at initial pH of 3.0 and 30 °C: (a) 6 W of UVA, (b) 10 mmol/L H_2O_2, (c) 1.0 g/L of H-Fe-P-B, (d) 1.0 g/L of H-Fe-P-B + 10 mmol/L H_2O_2, (e) 6 W of UVA + 10 mmol/L H_2O_2, and (f) 6 W of UVA + 1.0g/L of H-Fe-P-B + 10 mmol/L H_2O_2.

$$\equiv Fe^{3+} + H_2O_2 \rightarrow \equiv Fe^{2+} + HOO^{\bullet} + H^+ \qquad (3)$$

$$\equiv Fe^{2+} + H_2O_2 \rightarrow \equiv Fe^{3+} + {}^{\bullet}OH + OH^- \qquad (4)$$

The rate of Eq. (4) is relatively low and the oxidation of ALYG by hydroxyl radical could not proceed effectively. In the first 15 min, the curve of adsorption (curve c) and the curve of heterogeneous Fenton like process (curve d) were almost overlapped. With the process proceeding, the difference between curve c and curve d became more and more obvious. And at 120 min, the color removal by adsorption and heterogeneous Fenton like process were 56.2% and 72.1%, respectively. For heterogeneous UV-Fenton process (curve f, with H-Fe-P-B and H_2O_2 and UVA), the decrease of the ALYG concentration was quite fast in the first 40 min. And the color removal was 64.6%, 86.3%, 93.8%, 98.8%, at 20 min, 40 min, 60 min, 120 min, respectively. In the heterogeneous UV-Fenton system, Fe^{2+} could be formed following Eq. (5), and then the ALYG could be oxidized effectively by hydroxyl radical which was generated from the decomposition of H_2O_2 with Fe^{2+} (Eq. (4)).

$$\equiv Fe^{3+} + UVA \rightarrow \equiv Fe^{2+} + {}^{\bullet}OH \qquad (5)$$

$$H_2O_2 + UV \overset{(\lambda < 320\mathrm{nm})}{\longrightarrow} \cdot OH + \cdot OH \qquad (6)$$

Table 1
The characteristic of bentonite and H-Fe-P-B

	Specific surface area (m^2/g)	Micropore volume (ml/g)	Fe (wt.%)	Fe/Al	Fe/Si	XRD $d_{0\,0\,1}$(nm)
Bentonite	55.44	0.009	3.12	0.37	0.12	1.52
H-Fe-P-B	138.3	0.044	17.09	2.41	0.74	5.45

It is well known that hydroxyl radical could be formed from the direct photolysis of H_2O_2 when the wavelength of light irradiation is below 320 nm (Eq. (6)) [8]. With the combined action of UVA (365 nm) and H_2O_2 (curve e), the color removal efficiency of 80.9% was obtained at 120 min. As the direct photolysis of H_2O_2 will not occur under UVA (365 nm) irradiation, the degradation of ALYG was not due to the oxidation of ALYG by the hydroxyl radical. It was reported that Fe^{3+} ions could be reduced to Fe^{2+} by excited dye molecules under visible light irradiation [1,26]. The H_2O_2 is a more powerful oxidant than Fe^{3+}, since the standard oxidation potential (E^o) of Fe^{3+} and H_2O_2 are 0.771 V and 1.78 V, respectively [27]. A probable degradation mechanism of ALYG under UVA (365 nm) irradiation and H_2O_2 is suggested as follows:

$$\text{ALYG} + h\nu(\text{UVA}) \rightarrow \text{ALYG}* \quad (7)$$

$$\text{ALYG}* + H_2O_2 \rightarrow \text{organicintermediates} \quad (8)$$

The degradation of ALYG under UVA (365 nm) irradiation and H_2O_2 involves dye excitation (Eq. (7)) and oxidation of excited dye molecules by H_2O_2 (Eq. (8)). The absorption characteristic of ALYG at 365 nm was shown in Fig. 3, which also presented the absorption spectra of an aqueous solution of ALYG in heterogeneous UV-Fenton process during 120 min period. Generally, the azo-dye is characterized by nitrogen to nitrogen bond (–N=N–), and the absorption at 402 nm is due to the color of ALYG solution (*n*–π* transition in N=N group). The results showed that the intensity of the 402 nm absorption peaks decreased rapidly following photolysis, without new adsorption peaks appeared in visible light region. ALYG contains one azo bond, which is more active site for oxidative attack by hydroxyl radial. The discoloration of ALYG is due to the electrophilic cleavage of its chromophoric azo bond.

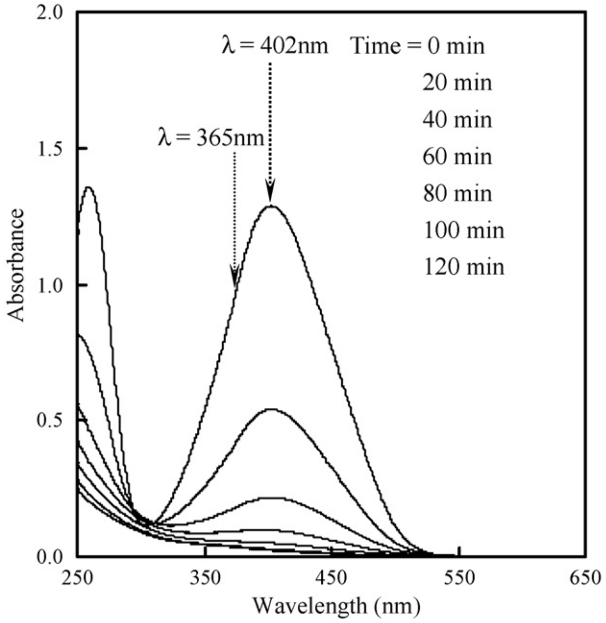


Fig. 3. UV–vis spectral changes of ALYG in heterogeneous UV-Fenton process as a function of irradiation time.

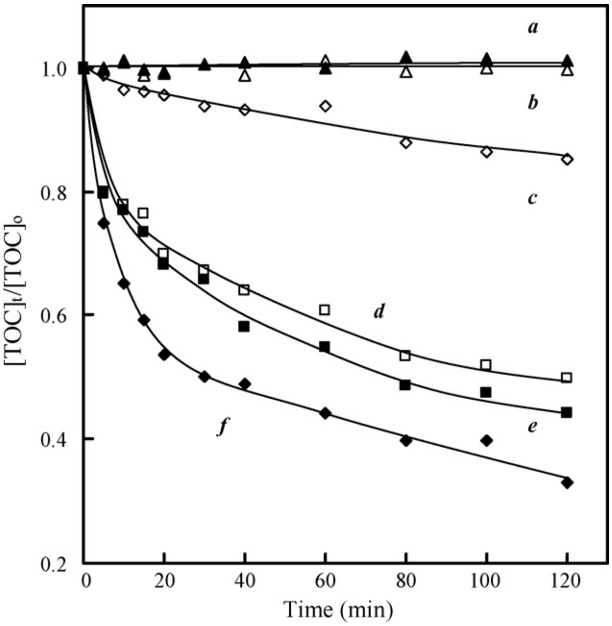


Fig. 4. TOC removal efficiency of 50 mg/L ALYG at initial pH of 3.0 and 30 °C: (a) 6 W of UVA, (b) 10 mmol/L H_2O_2, (c) 6 W of UVA + 10 mmol/L H_2O_2, (d) 1.0 g/L of H-Fe-P-B, (e) 1.0 g/L of H-Fe-P-B + 10 mmol/L H_2O_2, and (f) 6 W of UVA + 1.0 g/L of H-Fe-P-B + 10 mmol/L H_2O_2.

The relative TOC removal efficiency of ALYG versus time under different conditions was illustrated in Fig. 4. As expected, there was no mineralization of ALYG with H_2O_2 only (curve b) or UVA only (curve a) after 120 min treatment. With UVA (365 nm) and H_2O_2 (curve c), only around 15% of TOC was removed while more than 80% discoloration was obtained after 120 min. The result implied that the oxidation of excited dye molecules by H_2O_2 could not lead to effective mineralization of dye. The phenomenon of TOC removal by adsorption (curve d) and heterogeneous Fenton like process (curve e) were similar to discoloration of ALYG (Fig. 2). With H_2O_2, UVA and H-Fe-P-B (curve f), the TOC decreased rapidly in the first 20 min and then decreased slowly. More than 65% TOC removal of ALYG could be achieved after 120 min irradiation.

3.3. Effect of H_2O_2 and H-Fe-P-B concentration on degradation of ALYG

In general, the Fenton and photo-Fenton reaction rates on the degradation of organic pollution have been described well by the pseudo-first-order equation [14,15,28,29]:

$$-\ln\left(\frac{C_t}{C_0}\right) = k_a t \quad (9)$$

where C_0 is the initial concentration of the reactant (mg/L), C_t the concentration of the reactant at different degradation time (mg/L), t the degradation time (min), and k_a is the reaction rate constant (min^{-1}).

Initial concentration of H_2O_2 is important for Fenton and photo-Fenton process. The effect of H_2O_2 concentration (2–14 mmol/L) on degradation of ALYG was studied. And the

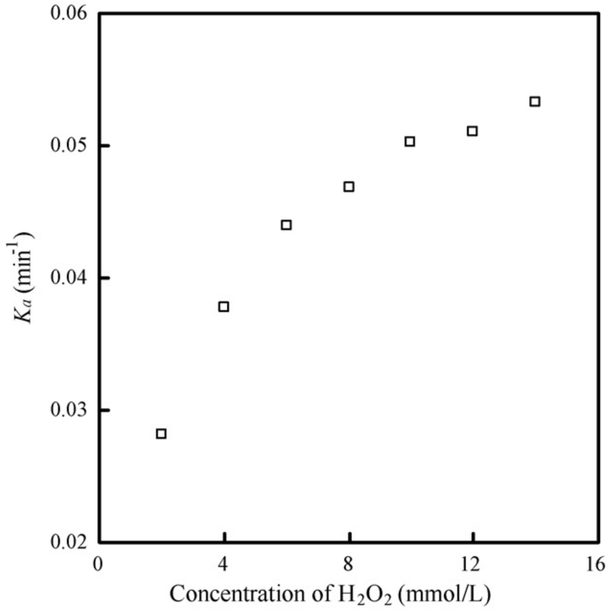


Fig. 5. Effect of the concentration of H_2O_2 on k_a (experimental conditions: 50 mg/L ALYG, initial pH 3.0, 30 °C, 6 W of UVA, 1.0 g/L H-Fe-P-B catalyst).

relationship between k_a and concentration of H_2O_2 was presented in Fig. 5. In heterogeneous UV-Fenton process, the concentration of H_2O_2 varied from 2 mmol/L to 10 mmol/L could increase the reaction rate constant, while further increase from 10 to 14 mmol/L cause no significant increase of reaction rate constant. This is due to the fact that the $^{\bullet}$OH radical concentration increased with the increase of H_2O_2 and caused the degradation rate of ALYG faster. At the same time, the hydroxyl radical will be scavenged by H_2O_2 itself (Eqs. (10) and (11)) [10,30]. At high H_2O_2 concentration, the reaction between H_2O_2 and hydroxyl radical became more obvious, which made the $^{\bullet}$OH radical concentration for ALYG degradation increase slowly.

$$H_2O_2 + {}^{\bullet}OH \rightarrow H_2O + HOO^{\bullet} \qquad (10)$$

$$HOO^{\bullet} + {}^{\bullet}OH \rightarrow H_2O + O_2 \qquad (11)$$

$$C_{16}H_{13}N_4NaO_4S + 48H_2O_2 \rightarrow 16CO_2 + 52H_2O + 4HNO_3 + NaHSO_4 \qquad (12)$$

The mineralization of ALYG by H_2O_2 could be written as Eq. (12). According to this chemical formula, when the initial concentration of ALYG was 50 mg/L, the theoretically concentration of H_2O_2 should be 6.3 mmol/L. In this experiment, the optimal concentration of H_2O_2 was around 10 mmol/L, which was higher than the theoretical value. In the one hand, some H_2O_2 will be oxidized by the hydroxyl radical in heterogeneous UV-Fenton process. In the other hand, the adsorption of H_2O_2 on the surface of H-Fe-P-B was important since the decomposition of H_2O_2 and degradation of ALYG mostly occurred on the surface of H-Fe-P-B. The result indicated that the suitable excess amount of H_2O_2 was needed to keep enough $^{\bullet}$OH radical for effective degradation of ALYG.

Table 2
Rate constants under different conditions

Conditions	k_a (min^{-1})	R^2
Catalyst dosage (g/L)		
0.2	0.0324	0.994
0.4	0.0373	0.993
0.6	0.0424	0.996
0.8	0.0443	0.992
1.0	0.0512	0.988
Temperature (K)		
303	0.0512	0.988
308	0.0583	0.990
313	0.0748	0.995
318	0.0904	0.993
323	0.1067	0.990

Concentration of catalyst is also one of main parameters to influence on the heterogeneous photo-Fenton. The effect of addition of H-Fe-P-B from 0.2 g/L to 1.0 g/L on degradation of ALYG has been studied and the reaction rate constants, which were obtained from the slopes of the straight lines, were displayed in Table 2. The correlation coefficient R^2 values were superior to 0.98 in all cases. The results revealed that the value of k_a was positive relative to H-Fe-P-B dosage. Generally, with the increase of catalyst dosage, the adsorption capacity and active site number of catalyst increase. So faster degradation of ALYG could be obtained when the concentration of catalyst increased.

3.4. Effect of initial pH on degradation of ALYG

The influence of the pH on the degradation of ALYG was presented in Fig. 6. The degradation curves of ALYG were displayed as time-dependent normalized dye concentration in

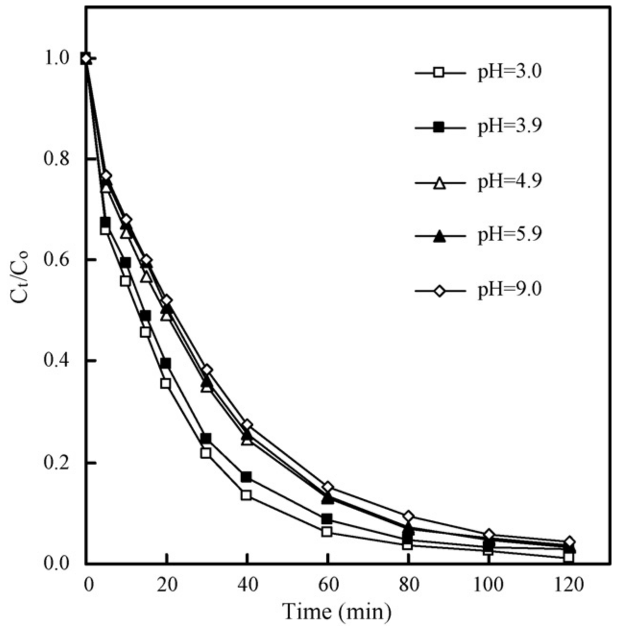


Fig. 6. Effect of initial pH on degradation of ALYG (experimental conditions: 50 mg/L ALYG, 30 °C, 6 W of UVA, 1.0 g/L H-Fe-P-B catalyst, 10 mmol/L H_2O_2).

the solution. Compared with the results shown in Fig. 6, about 84.6% and 93.7% of ALYG were degraded at an initial solution pH of 9.0 and 3.0 respectively after 60 min treatment. The results showed that even up to initial pH 9.0, the heterogeneous photo-Fenton process could proceed effectively with H-Fe-P-B as catalyst. This observation is most important since it is well known that one major drawback of homogeneous photo-Fenton is the tight range of pH. And the acidification is more costly than the energy and oxidant used in Fenton degradation [12], which limits its practical industrial application of wastewater treatment.

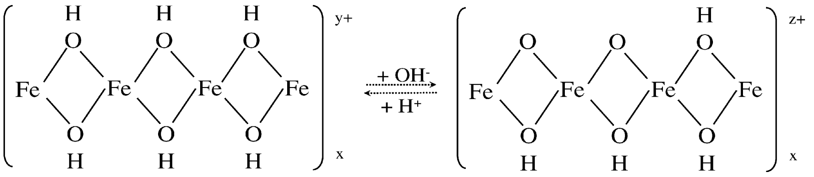
The phenomenon that the PILCs could extend the range of pH values for Fenton-type oxidation was also reported by Catrinescu et al. [18]. Depending on the electronegativity of the pillared clay surface, the condensation reaction of iron ions could be prevented or slow down over a wide range of pH [18]. Moreover, the pillared clay has unique characteristics of surface acidity. Fig. 7 showed the titration curves of the H-Fe-P-B and bentonite suspended in HCl solution with NaOH solution. The experiments demonstrated that the bentonite had acid–base buffering capacity, while the H-Fe-P-B had strong acidic properties. It was assumed that the surface hydroxyls of bentonite have acidic-basic properties (Eq. (13)) [31]. In the acidic aqueous solution, the exchange between the cations (Ca^{2+}, K^+, Na^+) in the bentonite interlayer and the H^+ in the solution resulted in increase of pH (Eq. (14)). And in the alkaline aqueous solution, part of base will be consumed by surface hydroxyls of bentonite, which decrease the pH of solution (Eq. (13)).

$$\text{Bentonite}{-}\text{OH}_2^+ \underset{+\text{H}^+}{\overset{+\text{OH}^-}{\rightleftarrows}} \text{Bentonite}{-}\text{OH} \underset{+\text{H}^+}{\overset{+\text{OH}^-}{\rightleftarrows}} \text{Bentonite}{-}\text{O}^- \qquad (13)$$

$$\text{Bentonite}{-}\text{M}^{n+} \xrightarrow{+\text{H}^+} \text{Bentonite}{-}\text{H}^+ + \text{M}^{n+} \qquad (14)$$

The Fe-pillared clays have not been investigated extensively and their structure is not well understood [32]. However, considering of hydrolysis process of Fe(III) salts [33,34], we believed that the added base was mainly consumed by Fe polycation in the bentonite interlayer (Eqs. (15) and (16)). At the same time, part of hydroxo edge (Fe–OH–Fe) of Fe polycation changed into oxo corner (Fe–O–Fe). As a result, the pH of solution dropped and the degradation of ALYG could proceed effectively by heterogeneous UV-Fenton process.

$$\text{Fe}_x(\text{OH})_y^{(3x-y)+} \underset{+\text{H}^+}{\overset{+\text{OH}^-}{\rightleftarrows}} \text{Fe}_x\text{O}_z(\text{OH})_y^{(3x-2z-y)+} \qquad (15)$$



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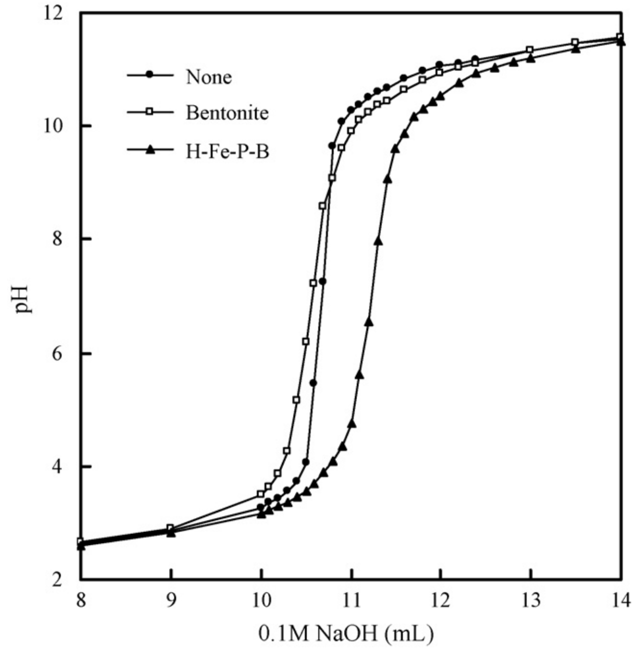

Fig. 7. Titration curves of 1.0 g/L bentonite and H-Fe-P-B suspended in 100 mL 0.01 M HCl solution with 0.10 M NaOH solution.

3.5. Effect of temperature on degradation of ALYG

The effect of temperature on degradation of ALYG was studied. The reaction rate constant values were obtained and showed in Table 2. The relationship between ln k_a and $1/T$ was illustrated in Fig. 8. The result implied that the value of k_a was positive relative to temperature. In the Fenton or photo-Fenton process, the reaction activity of $^{\bullet}OH$ radical increases with the increase of temperature, that is beneficial to the degradation of organic pollutant. According to Arrhenius equation, the reaction activation energy could be calculated, and the value is 31.0 kJ/mol. The value is similar to the result reported by Lin and Gurol [35]. As the reaction activation energy of ordinary thermal reactions is usually between 60 kJ/mol and 250 kJ/mol, the result implied that the oxidation of ALYG in UV-Fenton system needed low activation energy when H-Fe-P-B was used as catalyst.

3.6. The stability of H-Fe-P-B catalyst on degradation of ALYG

Stability is an important property for effective catalyst. Fig. 9 depicted the repetitive ALYG degradation in 120 min cycles. After each recycling, the catalyst was treated by centrifugation,

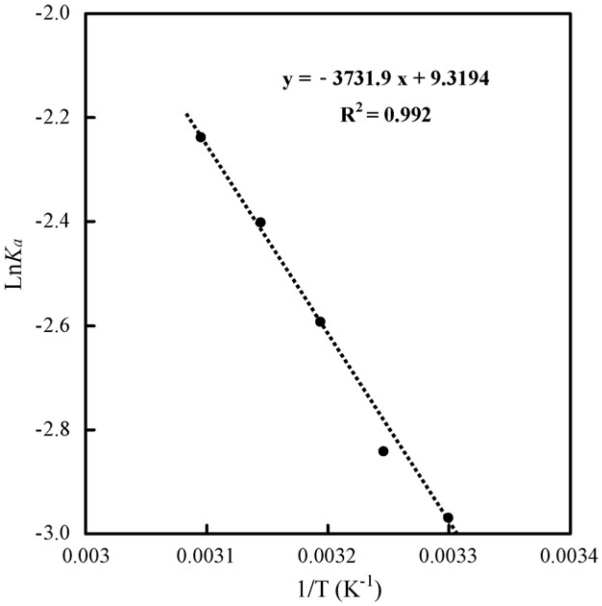

Fig. 8. Arrhenius plot for heterogeneous UV-Fenton catalytic degradation of ALYG.

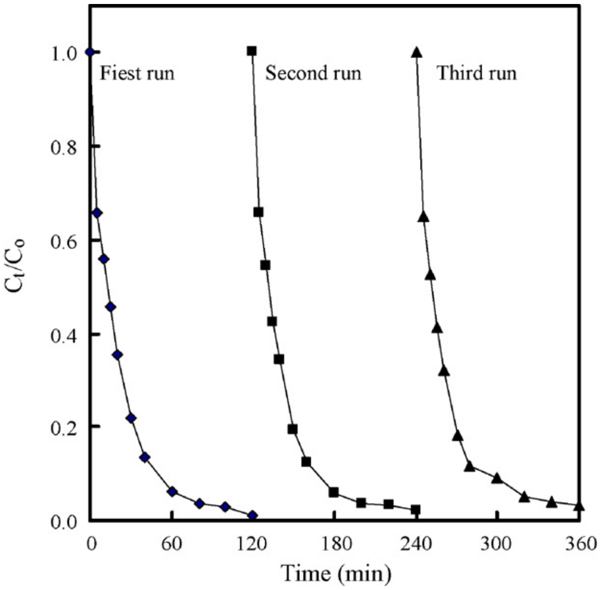

Fig. 9. Degradation of ALYG as a function of the time up to the third cycle (experimental conditions: 50 mg/L ALYG, initial pH 3.0, 30 °C, 6 W of UVA, 1.0 g/L H-Fe-P-B catalyst, 10 mmol/L H_2O_2).

dried and reused. Compared with the results displayed in Fig. 9, it could be found that the kinetics and efficiency of the ALYG degradation did not vary. The concentrations of iron ions detected by ICP in the solution after each recycling were 0.91 mg/L, 0.76 mg/L, 0.75 mg/L, respectively. And the leaching rates of iron from the H-Fe-P-B were 0.53%, 0.45%, 0.44%, which were negligible. These results confirmed that the catalyst had a good long-term stability and activity.

4. Conclusions

Through the cation exchange process, hydroxyl-Fe pillared bentonite was developed as heterogeneous catalyst for UV-Fenton system. The results indicated that the H-Fe-P-B had high catalytic activity in the degradation of ALYG. It was found that almost 100% discoloration and more than 65% TOC removal of 50 mg/L ALYG could be achieved by heterogeneous UVA-Fenton system in 120 min. The catalyst also had good long-term stability and could be reused. In multi-run experiments, the iron leaching rates of H-Fe-P-B and the concentrations of iron ions in solution were below 0.6% and 1 ppm, respectively. Because of the strong surface acidity on H-Fe-P-B, the range of pH for heterogeneous UV-Fenton could extend from 3.0 to 9.0, which indicated that the costly pre-adjustment of solution pH for Fenton-type oxidation could be avoided by using H-Fe-P-B as catalyst. Furthermore, the results also showed that the temperature, concentration of H_2O_2 and catalyst dosage in solution could influence the degradation of ALYG by heterogeneous UV-Fenton process.

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