Degradation of ultrahigh concentration pollutant by Fe/Cu bimetallic system at high operating temperature

Bo Lai*,†, Qingqing Ji*, Yue Yuan*, Donghai Yuan**,†, Yuexi Zhou***, and Juling Wang***

*Department of Environmental Science and Engineering, School of Architecture and Environment,
Sichuan University, Chengdu 610065, China
**Key Laboratory of Urban Stormwater System and Water Environment, Ministry of Education,
Beijing Climate Change Response Research and Education Center,
Beijing University of Civil Engineering and Architecture, Beijing 100044, China
***Research Center of Water Pollution Control Technology,
Chinese Research Academy of Environmental Sciences, Beijing 100012, China

Abstract−To investigate the degradation of high concentration pollutant by Fe/Cu bimetallic system at a high operating temperature, 10,000 mg/L acid orange 7 (AO7) aqueous solution was treated by Fe/Cu bimetallic system at 80 °C. First, the effect of the operating temperature (30-80 °C) on the reactivity of Fe/Cu bimetallic particles was investigated thoroughly. Then, the studies on the effect of theoretical Cu mass loading, Fe/Cu dosage, stirring speed and initial pH on the reactivity of Fe/Cu bimetallic particles at a high temperature (i.e., 80 °C) were carried out, respectively. The degradation and transformation process of AO7 was studied by using COD, TOC and UV-Vis spectra. The results indicate that high concentration pollutant could be removed effectively by Fe/Cu bimetallic system at a high operating temperature. And the removal efficiencies of AO7 by Fe/Cu bimetallic system were in accordance with the pseudo-first-order model. Finally, it was observed that the high temperature could accelerate mass transport rate and overcome the high activation energy barrier to significantly improve the reactivity of Fe/Cu bimetallic particles. Therefore, the higher removal efficiency could be obtained by Fe/Cu system at a high operating temperature. Thus, the high operating temperature played a leading role in the degradation of high concentration pollutant.

Keywords: Operating Temperature, High Concentration Pollutant, Fe/Cu Bimetallic Particles, Wastewater Treatment

INTRODUCTION

Since the toxic and refractory wastewater from industrial production is difficult to treat effectively, industrialization production has led to rapid deterioration of water quality. In particular, high concentration wastewater (COD>8,000 mg/L) is usually released from different industries, such as pharmacy (8000<COD<100,000 mg/L) [1-3], nitra-aromatic explosives (COD≈100,000 mg/L) [4,5] and pesticide manufacturing (COD>10,000 mg/L) [6,7]. Before the biological treatment, the high concentration wastewater was used to be pretreated by physic-chemical process including electro-Fenton [8,9], and adsorption [10]. Although these pretreatment methods could decompose pollutants and improve their biodegradability, their practical application was usually limited by the high cost.

Our previous work found that high concentration *p*-nitrophenol (PNP) in aqueous solution (10,000 mg/L) could be removed effectively by zero valent iron with ultrasonic irradiation (US-ZVI) [11]. But the high removal efficiency could only be obtained under the acidic condition (pH=3.0), and the operating life of ultrasonic

probe would be decreased dramatically because of the cavitation erosion that happened under the acidic condition. In addition, the practical application of US-ZVI was limited by the high energy cost of ultrasonic irradiation. To broaden the pH range, micron-scale Fe/Cu bimetallic particles were developed to remove the pollutants under a neutral condition [12]. The results show that the low concentration PNP (<500 mg/L) could be removed quickly under the neutral condition, but the high concentration PNP (>500 mg/L) could not be removed completely in an easy way. The removal of high concentration pollutants would be limited by the low mass transport rates of pollutants, intermediates, reactants and corrosion products between the solution phase and the Fe/Cu surface. Besides the ultrasonic irradiation, the high operating temperature might also accelerate the mass transport rates as the elevated temperature could enhance molecular motion. Furthermore, Ahn et al. found that a temperature increase could overcome the energy barrier to improve the reduction of nitrate by zero-valent iron (ZVI) [13]. Oh et al. also found that the increased solution temperature may accelerate the reduction of perchlorate by overcoming the high activation energy barrier [14]. Also, as the improved materials of Fe^0, and the Fe/Cu bimetallic particles have similar physical-chemical characteristics. So the elevated temperature might also play a role in the significant improvement of the reactivity of Fe/Cu bimetallic particles. The temperature of the industrial wastewater is usu-

†To whom correspondence should be addressed.
E-mail: laibo@scu.edu.cn, yuandonghai@aliyun.com

ally above 30 °C, and the waste-heating vapor could be used to elevate the wastewater temperature. Therefore, it could be hypothesized that Fe/Cu bimetallic system would become a cost-effective treatment technology for the industrial wastewater.

Nowadays, the negative effect of wastewater containing various dyes on the ecological environment has brought widespread concerns [15-18]. And the dye wastewater was mainly from two aspects: (a) printing and dye wastewater with a lower COD concentration (<4,000 mg/L) from textile plants [19], (b) dye wastewater with a higher COD concentration (>8,000 mg/L) from dye manufacturing. Although there are many studies about the treatment of printing and dye wastewater [20,21], a study on the degradation of high concentration dye wastewater from dye manufacturing industry has not been performed yet.

In this study, we used acid orange 7 (AO7) as a model pollutant to investigate the reactivity of Fe/Cu bimetallic particle at a high temperature. The optimization of the process parameters, such as operating temperature, theoretical Cu mass loading, Fe/Cu dosage, stirring speed and initial pH, was carried out by batch experiments. At the same high operating temperature, the reactivity of Fe/Cu and ZVI was compared by identifying the variation of UV-Vis (190-650 nm), TOC and COD of high concentration AO7 aqueous solution during 60 min treatment process. Our objective was to determine the effectiveness of Fe/Cu bimetallic system, when it was used to treat high concentration dye wastewater at high temperature.

EXPERIMENTAL

1. Reagents

Zero valent iron (ZVI) powders, Na_2SO_4 (analytical reagent) and AO7 (98%) purchased from Chengdu Kelong Chemical Reagent Factory were used in the experiment. The zero valent iron powders have mean particle size of approximately 120 μm, and percentage of iron content approximately 97%. The impurities in iron material can play the role of catalysts to increase the formation of iron corrosion products that contribute to the sequestration and elimination of organic contaminants [22,23]. Other chemicals used in the experiment were of analytical grade. Deionized water was used throughout the whole experiment process.

2. Preparation of Fe/Cu Bimetallic Particle

The Fe/Cu bimetallic particles were prepared through the Fe-Cu displacement reaction in aqueous solution, and the main preparation process was the same as that in our previous work [12]. In this study, the main prepared conditions with theoretical Cu mass loading (TML_{Cu}), temperature, mixing speed and Cu^{2+} concentration ($CuSO_4$) of planting solution were 0.41 g Cu/g Fe, 40 °C, 250 rpm and 3 g/L, respectively.

3. Batch Experiments

The removal of the high concentration pollutant by Fe/Cu bimetallic particles was investigated by batch experiments. AO7 was used as a model pollutant; the AO7 stock solution (10,000 mg/L) was prepared with Na_2SO_4 (50 mmol/L) that was used as an electrolyte. Also, the AO7 aqueous solution was not buffered, and its initial pH (3.0-10.0) was adjusted by adding diluted sulfuric acid (10%) or sodium hydroxide solutions (20%). In addition, the Fe/Cu bimetallic system was mainly comprised of a 500 mL flat bottom beaker,

a mechanical stirrer and a heating bath. The flat bottom beaker with slurry was immersed into the heating bath, and the slurry was mixed by a mechanical stirrer. In addition, a metal ring in the heating bath can fix the beaker to avoid the shaking from the mechanical stirrer. In each batch experiment, 300 mL AO7 aqueous solution (10,000 mg/L) and the desired dosage of Fe/Cu bimetallic particles (5, 10, 15, 20, 25, 30, 35 and 40 g/L) were added in a 500 mL flat bottom beaker, and the slurry was mixed by a mechanical stirrer (0, 100, 200, 300 and 400 rpm). The whole experiment was performed at a desired temperature (30, 40, 55, 70, 75 and 80 °C) by water bath heating.

We first investigated the effect of different operating temperature (30, 40, 55, 70, 75 and 80 °C) by batch experiments. Next, under the optimal temperature condition (80 °C), the other effect factors, including theoretical Cu mass loading (0, 0.05, 0.11, 0.24, 0.41, 0.62, 0.89, 1.26 and 1.81 g Cu/g Fe), Fe/Cu dosage (5, 10, 15, 20, 25, 30, 35 and 40 g/L), stirring speed (0, 100, 200, 300 and 400 rpm) and initial pH (3.0, 5.0, 7.0, 9.0 and 10.0), were investigated thoroughly by batch experiments. Samples were taken from the reactive beaker at different time points (5, 10, 20, 30, 40, 50, 60 min) by withdrawing 2 mL sample solution. The residual AO7 concentration, COD, TOC and UV-Vis spectra of the effluent were measured, respectively. Finally, under the same optimal conditions (initial pH= 7.0, stirring speed at 400 rpm, TML_{Cu}=0.41 g Cu/g Fe, $[AO7]_0$= 10,000 mg/L, $[Na_2SO_4]$=50 mmol/L, [Fe/Cu]=35 g/L, $[Fe^0]$=35 g/L), the reactivity of Fe/Cu and ZVI was compared according to the variation of UV-Vis (190-650 nm), TOC and COD of high concentration AO7 aqueous solution during 60 min treatment process.

4. Analytical Methods

The concentration of AO7 was measured by determining its absorbance at λ max (483 nm) in a cuvette with 1 cm cell length and calculating its weight/volume concentration based on a standard curve [24]. The UV-Vis absorption spectra of the samples were carried out in 10 mm quartz cuvettes, and the UV-Vis spectra were recorded from 190 to 650 nm using deionized water as blank. Before the UV-Vis analysis, the samples were diluted by 200 times due to the ultra-high concentration of AO7. COD and TOC of the samples were measured by COD analyzer (Lianhua, China) and TOC analyzer (Shimadzu, Japan), respectively. To avoid the interference of Fe^{2+}/Fe^{3+} in the samples, these metal ions were removed through adding 20% NaOH solution and filtration (using an aqueous PES needle type filter with a pore size of 0.45 μm).

5. Kinetics Analysis

The removal efficiency of the high concentration AO7 by a Fe/Cu batch system was treated by a pseudo-first-order equation:

$$\frac{dC}{dt} = -k_{obs}C \tag{1}$$

where C is the concentration of AO7 in aqueous solution (mg/L), k_{obs} is the measured rate constant (min^{-1}) and t is the treatment time (min). The k_{obs} were calculated by linear regression method.

RESULTS AND DISCUSSION

1. Effect of Operating Temperature

It has been reported that a temperature increase could overcome
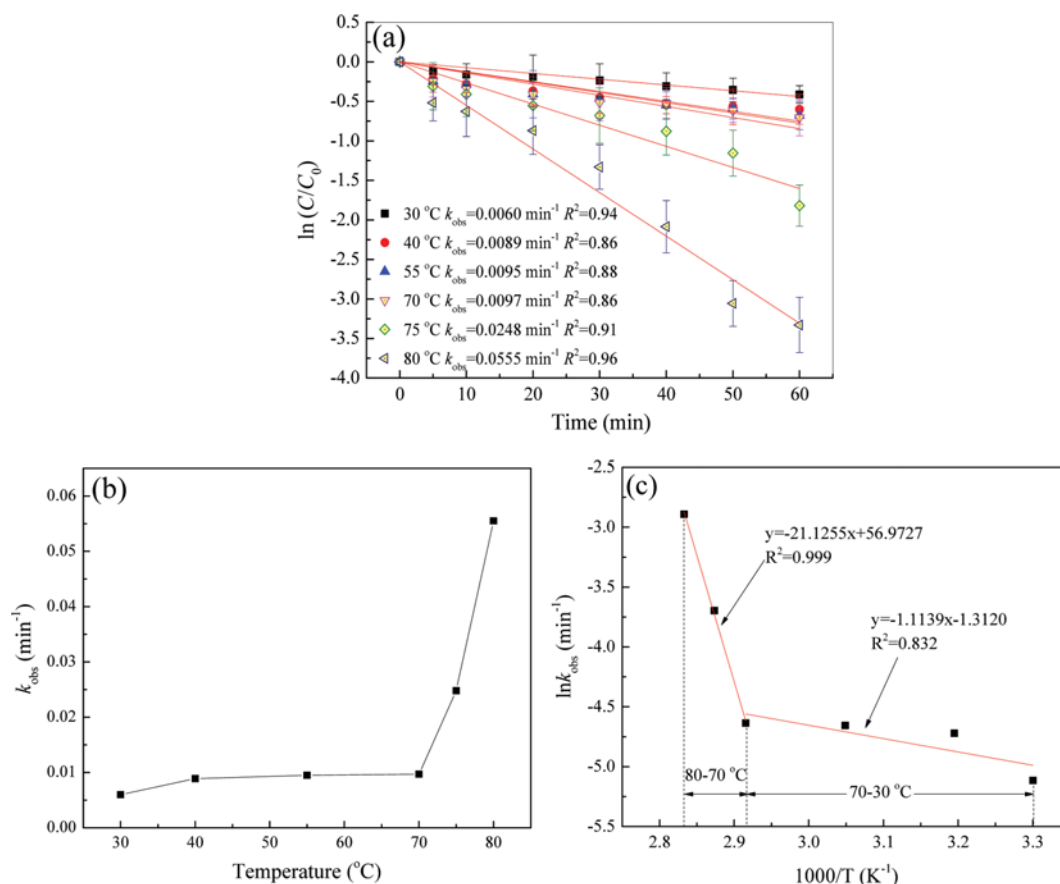
Fig. 1. Effect of temperature on the removal of AO7 by Fe/Cu bimetallic system (volume of AO7 aqueous solution was 300 mL, initial pH was 7.0, stirring speed was 400 rpm, theoretical Cu mass loading was 0.89 g Cu/g Fe, [AO7]$_0$=10,000 mg/L, [Na$_2$SO$_4$]=50 mmol/L, [Fe/Cu]=35 g/L).

the high activation energy barrier to improve the reactivity of zerovalent iron (ZVI) significantly [14]. Besides the chemical reaction process, the physical process was also influenced by increasing temperature. In other words, the effect of temperature on reactivity of heterogeneous reactions mainly results from a chemical reaction at the surface or diffusion of a reactant [25]. Furthermore, both the chemical reaction and diffusion might become a controlled reaction. It was also reported that diffusion-controlled reactions in solution have relatively low activation energy (~8-21 kJ/mol), while the chemical-controlled reactions have higher activation energy (>29 kJ/mol) [26].

Batch experiments on the effect of operating temperature were carried out to evaluate the activation energy for the removal of AO7 by Fe/Cu bimetallic system. An Arrhenius equation was used to describe the relationship between rate constants (k$_{obs}$) and temperature [25,26]:

$$\ln k_{obs} = -\frac{E_a}{RT} + \ln A \qquad (2)$$

where k$_{obs}$ is the measured first-order rate constant, E$_a$ is the activation energy, R is the ideal gas constant, A is a frequency factor and T is the operating temperature. In addition, a plot of lnk$_{obs}$ versus 1/T would result in a linear relationship with the slope equal to $-E_a/R$ [25].

Activation energy for the removal of AO7 was determined in Fe/Cu bimetallic system when its operating temperatures were varied from 30-80 °C. The k$_{obs}$ were obtained by data fitting with the pseudo-first-order model as expressed in Eq. (1). Fig. 1(a) shows a plot of ln(C/C$_0$) vs. time for the removal of AO7 by Fe/Cu bimetallic system at different operating temperatures (30-80 °C). It is clear that the removal of AO7 fit with the pseudo-first-order model, and their correlation coefficients (R^2) were all above 0.85. A plot of k$_{obs}$ versus temperature is shown in Fig. 1(b). It is clear that k$_{obs}$ increased gradually from 0.0060 to 0.0097 min^{-1} when the operating temperature increased from 30 to 70 °C, whereas k$_{obs}$ increased quickly from 0.0097 to 0.0555 min^{-1} when the temperature further increased from 70 to 80 °C. So, the removal efficiency of AO7 was accelerated remarkably when the operating temperature was above 70 °C. It could be hypothesized that the high concentration AO7 (10,000 mg/L) has high activation energy of diffusion-controlled or chemical-controlled reactions, which could only be overcome when the operating temperature was above 70 °C.

Fig. 1(c) gives the Arrhenius plots of k$_{obs}$ versus 1000/T for the removal of AO7 by Fe/Cu bimetallic system. Since the slope of the plots was assigned as a ratio of the activation energy (E$_a$) to the ideal gas constant (R), two E$_a$ of the AO7 removal by Fe/Cu bimetallic system were calculated at different temperature range: (a) E$_a$= 9.3 kJ/mol (30-70 °C), (b) E$_a$=175.6 kJ/mol (70-80 °C). From 30 to

70 °C, k_{obs} of the removal of AO7 only increased from 0.0060 to 0.0097 min⁻¹. Only a little improvement of the AO7 removal rate was obtained by elevated temperature when the operating temperature was below 70 °C. Therefore, the E_a (175.6 kJ/mol) obtained between 70 and 80 °C was the real activation energy, which was much higher than the sum (~37 kJ/mol) of typical minimum activation energy for chemical-controlled (~29 kJ/mol) and diffusion-controlled (~8 kJ/mol) reactions [26]. The high activation energy mainly resulted from the high concentration of AO7 (10,000 mg/L), which would dramatically increase the activation energy of diffusion-controlled and chemical-controlled reactions.

2. Effect of Theoretical Cu Mass Loading

It has been reported that the reactivity of granular iron is affected by the copper loading and surface coverage [27]. Meanwhile, in our previous work, it was also found that the reactivity of Fe/Cu bimetallic particles was influenced remarkably by the theoretical Cu mass loading when it was used to treat the lower concentration PNP (500 mg/L) [12]. However, the effect of theoretical Cu mass loading has not been investigated in the case when the high concentration AO7 (10,000 mg/L) was treated by the Fe/Cu bimetallic system.

Fig. 2(a) shows the logarithmic plots of residual concentration of AO7 in aqueous solution versus the reaction time, and a good linear fitting was observed in each batch experiment. The results suggest that the removal efficiencies of AO7 by using Fe/Cu bimetallic particles with different theoretical Cu mass loadings (0-1.81 g Cu/g Fe) were all described by the pseudo-first-order model, and their R^2 were all above 0.85. Furthermore, k_{obs} of these batch experiments were obtained by calculating the linear regression slope, and a plot of k_{obs} versus theoretical Cu mass loadings is shown in Fig. 2(b). It is clear that k_{obs} increases from 0.0085 to 0.0924 min⁻¹ with the theoretical Cu mass loading increasing from 0 to 0.41 g Cu/g Fe; then it begins to decrease with the further increase of theoretical Cu mass loading. As a result, the optimal theoretical Cu mass loading was 0.41 g Cu/g Fe. The similar variation of k_{obs} was found in our previous work when the low concentration PNP (500 mg/L) was treated by Fe/Cu bimetallic system. However, the obtained optimal theoretical Cu mass loading (0.89 g Cu/g Fe) in our previous work was two-times higher than that (0.41 g Cu/g Fe) obtained in this study [12]. This phenomenon could be explained in an assumption that the high temperature not only accelerated the mass transport rate, but also overcame the high activation energy barrier to improve the reactivity of Fe/Cu bimetallic particles.

3. Effect of Fe/Cu Dosage

At room temperature, degradation of the pollutants was usually influenced seriously by the dosage of Fe⁰ or Fe/Cu bimetallic particles [28,29]. In addition, the increase of the dosage of Fe⁰ or Fe/Cu bimetallic particles could lead to the increase of the reactive sites for the degradation of the pollutants, which could increase the removal efficiencies of the pollutants [30]. At a high temperature (80 °C), the removal efficiency of AO7 (10,000 mg/L) might also be seriously affected by the dosage of Fe/Cu bimetallic particles.

Fig. 3(a) shows that the removal efficiencies of AO7 by using Fe/Cu bimetallic particles with different dosage of Fe/Cu bimetallic particles (10-40 g/L) were all described by the pseudo-first-order model, and their R^2 were all above 0.90. However, it was not described by the pseudo-first-order model ($R^2=0.74$) when small dosage of Fe/Cu bimetallic particles (5 g/L) was used to treat AO7 aqueous solution. The small dosage of Fe/Cu bimetallic particles could only support a few active sites which led to the low removal efficiency of AO7. Furthermore, k_{obs} of these batch experiments were obtained by calculating the linear regression slope, and a plot of k_{obs} versus the dosage of Fe/Cu is shown in Fig. 3(b). It is clear that k_{obs} increases from 0.0133 to 0.0992 min⁻¹ with the increase of Fe/Cu dosage from 10 to 40 g/L. Fig. 3(c) also shows that the removal efficiency of AO7 could reach to 98% after 40 min treatment when the Fe/Cu dosage was above 35 g/L, then the removal efficiency did not increase obviously as the Fe/Cu dosage further increased. As a result, the optimal dosage of Fe/Cu bimetallic particles was 35 g/L.

When these results are compared with our previous work, both of the optimal Fe/Cu dosages were 35 g/L, although the initial concentration of the pollutant (10,000 mg/L) in this study was 20 times higher than that (500 mg/L) in the previous work [12]. The optimal Fe/Cu dosage was not significantly influenced by the increase of the pollutant concentration, which mainly resulted from the improvement of high operating temperature. It can be explained by the theory that the high temperature could accelerate mass trans-
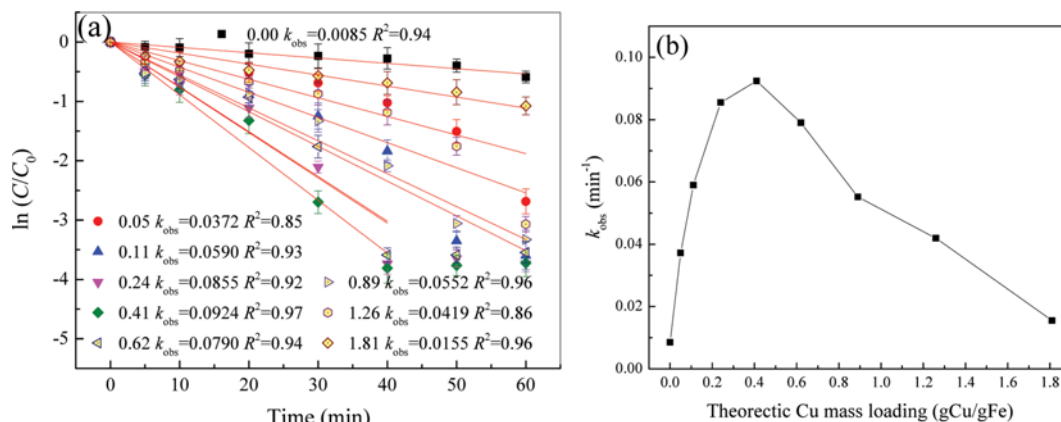

Fig. 2. Effect of theoretical Cu mass loading on the removal of AO7 by Fe/Cu bimetallic system at 80 °C (volume of AO7 aqueous solution was 300 mL, initial pH was 7.0, stirring speed was 400 rpm, [AO7]₀=10,000 mg/L, [Na₂SO₄]=50 mmol/L, [Fe/Cu]=35 g/L).
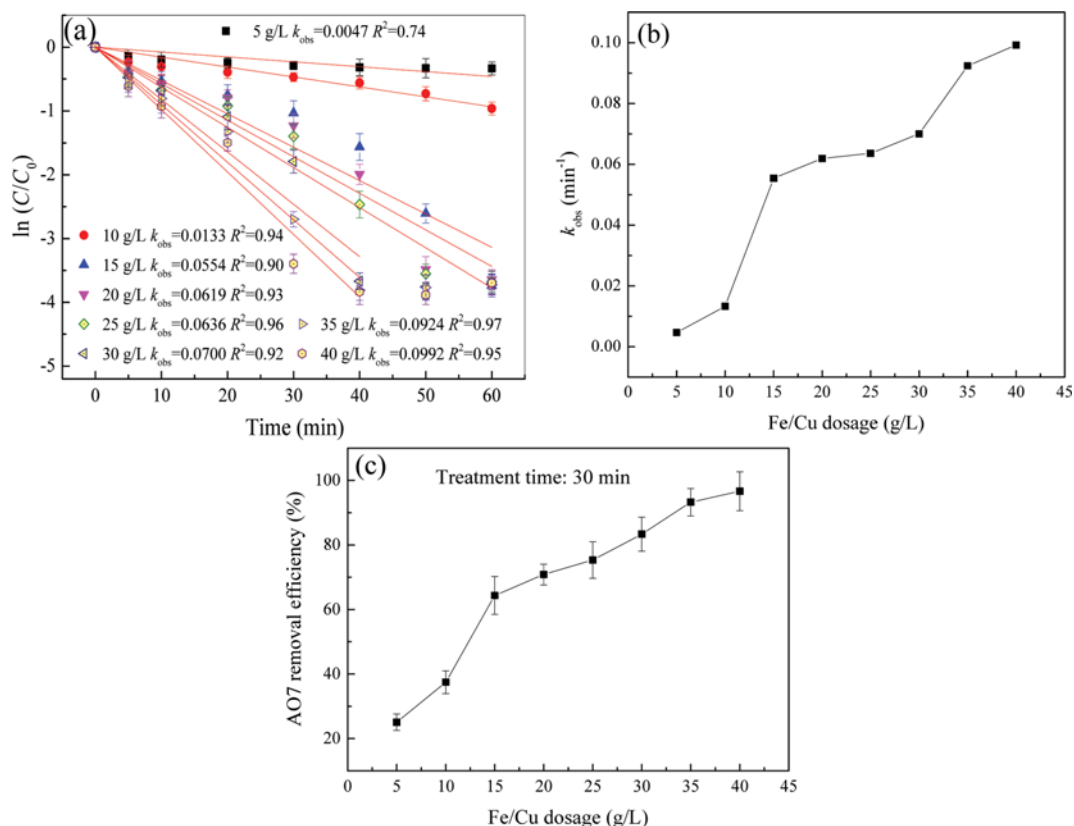
Fig. 3. Effect of Fe/Cu dosage on the removal of AO7 by Fe/Cu bimetallic system at 80 °C (volume of AO7 aqueous solution was 300 mL, initial pH was 7.0, stirring speed was 400 rpm, theoretical Cu mass loading was 0.41 g Cu/g Fe, [AO7]$_0$=10,000 mg/L, [Na$_2$SO$_4$]=50 mmol/L).
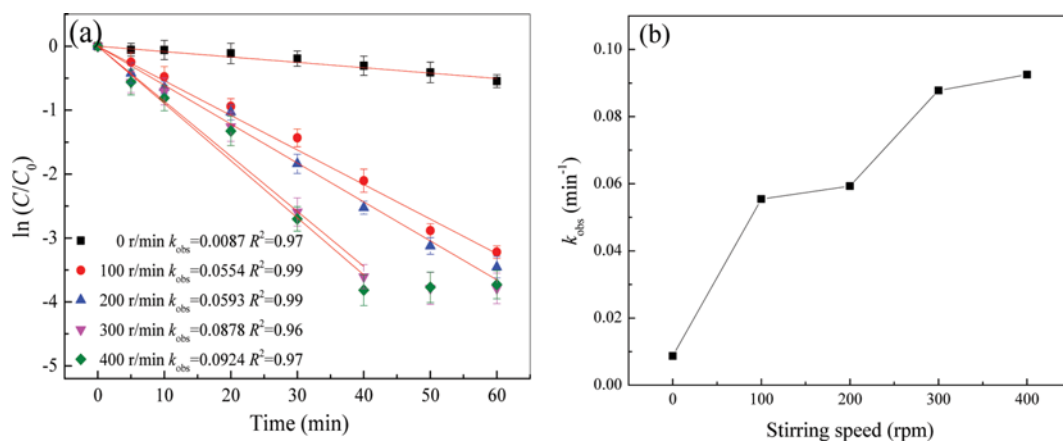

Fig. 4. Effect of stirring speed on the removal of AO7 by Fe/Cu bimetallic system at 80 °C (volume of AO7 aqueous solution was 300 mL, initial pH was 7.0, theoretical Cu mass loading was 0.41 g Cu/g Fe, [AO7]$_0$=10,000 mg/L, [Na$_2$SO$_4$]=50 mmol/L, [Fe/Cu]=35 g/L).

port rate and overcome the energy barrier, which could maintain the number and reactivity of active sites.

4. Effect of Stirring Speed

Mixing intensity of reaction solution would affect the mass transport rates of reactants, intermediates, degradation products and corrosion productions between the solution phase and the catalytic surface [31,32]. So the degradation of the pollutants was usually improved by increasing stirring speed. However, the effect of stirring speed on the degradation of high concentration pollutant

(10,000 mg/L) at high operating temperature (80 °C) was not investigated.

Fig. 4(a) shows that the removal efficiencies of AO7 by using Fe/Cu bimetallic system with different stirring speed (0-400 rpm) were all described by the pseudo-first-order model, and their R^2 were all above 0.96. Furthermore, k$_{obs}$ of these batch experiments were obtained by calculating the linear regression slope, and a plot of k$_{obs}$ versus the stirring speed is shown in Fig. 4(b). It can be seen that k$_{obs}$ increases from 0.0087 to 0.0924 min^{-1} with stirring speed

increasing from 0 to 400 rpm. The k_{obs} obtained at the high stirring speed (400 rpm) was ten times higher than that obtained without mixing (0 rpm). In addition, k_{obs} only increased a little (0.0046 min^{-1}) when the stirring speed increased from 300 to 400 rpm. Meanwhile, AO7 removal efficiency reached 98% at a stirring speed of 300 rpm, and it did not obviously show any further increase when the stirring speed increased to 400 rpm. Therefore, the optimal stirring speed was 300-400 rpm when the high concentration AO7 was treated at high operating temperature (80 °C). Although the high concentration AO7 (10,000 mg/L) was treated in this study, its optimal stirring speed was similar to that obtained in our previous work (treatment of 500 mg/L pollutant) [12]. The results suggest that high operating temperature plays a leading role in the removal of high concentration pollutant.

5. Effect of Initial pH

Reduction of the pollutants by ZVI mainly resulted from atomic hydrogen (•H) generated by the corrosion reaction of Fe at the acidic and anaerobic conditions [33,34]. To broaden the range of solution pH, Cu was added into the ZVI system to form Fe/Cu bimetallic system [35,36]. Furthermore, the high potential difference (0.777 V) between Cu and Fe can accelerate the corrosion rate of Fe^0 [35]. In other words, since the corrosion reaction of Fe^0 could be catalyzed by Cu, it could also be performed even under neutral and basic conditions. Our previous work proved that the Fe/Cu bimetallic particles had a high reaction rate even at neutral condition (pH=6.7) when 500 mg/L PNP was treated at room temperature [12]. However, the effect of initial pH on the degradation of high concentration pollutant (10,000 mg/L) at a high operating temperature (80 °C) was not investigated yet.

Fig. 5(a) shows that the removal efficiencies of AO7 by using Fe/Cu bimetallic particles with different initial pH (3.0-9.0) were all described by the pseudo-first-order model and their R^2 were all above 0.92. However, it was not described by the pseudo-first-order model (R^2=0.37) when the AO7 aqueous solution was treated at pH of 10.0. Furthermore, the k_{obs} of these batch experiments were obtained by calculating the linear regression slope; a plot of k_{obs} versus the initial pH is shown in Fig. 5(b). It is clear that k_{obs} decreased from 0.1537 to 0.0544 min^{-1} with increasing initial pH from 3.0 to 9.0. Although the k_{obs} decreased to 0.0544 min^{-1} when the initial pH increased to 9.0, approximately 97% removal efficiency of AO7 was still obtained after 60 min treatment. Furthermore, only approximately 22% removal efficiency of AO7 was obtained after 60 min treatment when the initial pH increased to 10.0. This phenomenon might be explained in two aspects: (a) at high pH (10.0), the corrosion products of Fe^0 could be quickly transformed into Fe(OH)$_2$ or Fe(OH)$_3$ and immediately deposited on the surface of Fe/Cu bimetallic particles, covering the active site of Fe/Cu bimetallic particles and inhibiting the corrosion reaction, (b) the corrosion reaction between Fe^0 and H$^+$ could be inhibited completely under the high pH condition. In addition, the corrosion of Fe^0 could consume the H$^+$ in the solution, so the solution pH would increase to neutral condition.

At room temperature, despite it was the lower concentration PNP (500 mg/L) aqueous solution that was treated by Fe/Cu bimetallic particles, its removal efficiency decreased rapidly when the initial pH was above 6.7 [12]. However, at high operating temperature (80 °C), even if it was the high concentration AO7 (10,000 mg/L) that was treated by Fe/Cu bimetallic system, its removal efficiency could still maintain at approximate 97% even if its initial pH increased to 9.0. The results also indicate that the high operating temperature played an important role in the removal of high concentration pollutant. Bransfield et al. also considered that the increase of the temperature, as well as the addition of Cu, serves accelerating the corrosion reaction of Fe^0 and increasing the concentration of atomic hydrogen [37].

6. UV-Vis Spectrum

To further confirm the degradation of AO7 by Fe/Cu bimetallic system at high operating temperature, the influent and effluent of Fe/Cu bimetallic system at the optimal conditions (initial pH was 7.0, stirring speed was 400 rpm, theoretical Cu mass loading was 0.41 g Cu/g Fe, operating temperature was 80 °C, [AO7]$_0$=10,000 mg/L, [Na$_2$SO$_4$]=50 mmol/L, [Fe/Cu]=35 g/L) were analyzed by UV-Vis spectrum. Meanwhile, to investigate the improvement of Fe/Cu bimetallic particles, the ZVI control experiment with the same running conditions was set up, and its influent and effluent were also measured by UV-Vis spectrum.

Fig. 6(a) shows the typical UV-Vis spectra obtained during the degradation of AO7 in aqueous solution by Fe/Cu bimetallic parti-
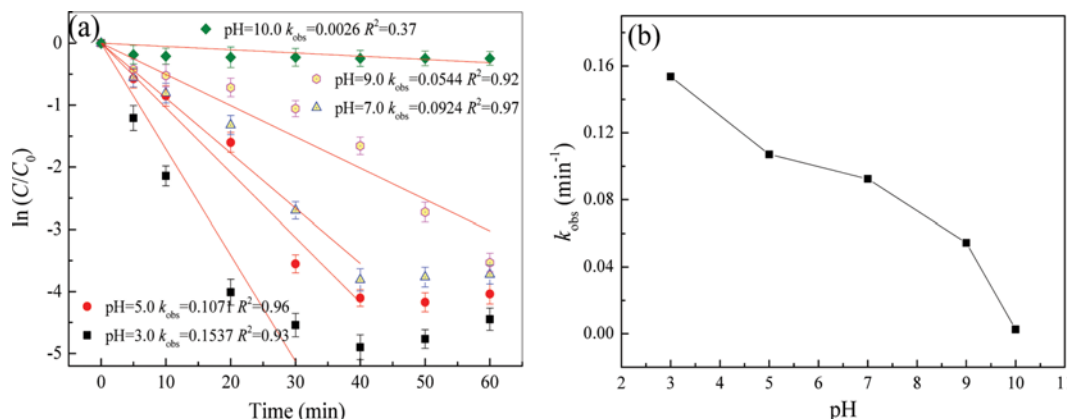

Fig. 5. Effect of initial pH on the removal of AO7 at 80 °C (volume of AO7 aqueous solution was 300 mL, stirring speed was 400 rpm, theoretical Cu mass loading was 0.41 g Cu/g Fe, [AO7]$_0$=10,000 mg/L, [Na$_2$SO$_4$]=50 mmol/L, [Fe/Cu]=35 g/L).
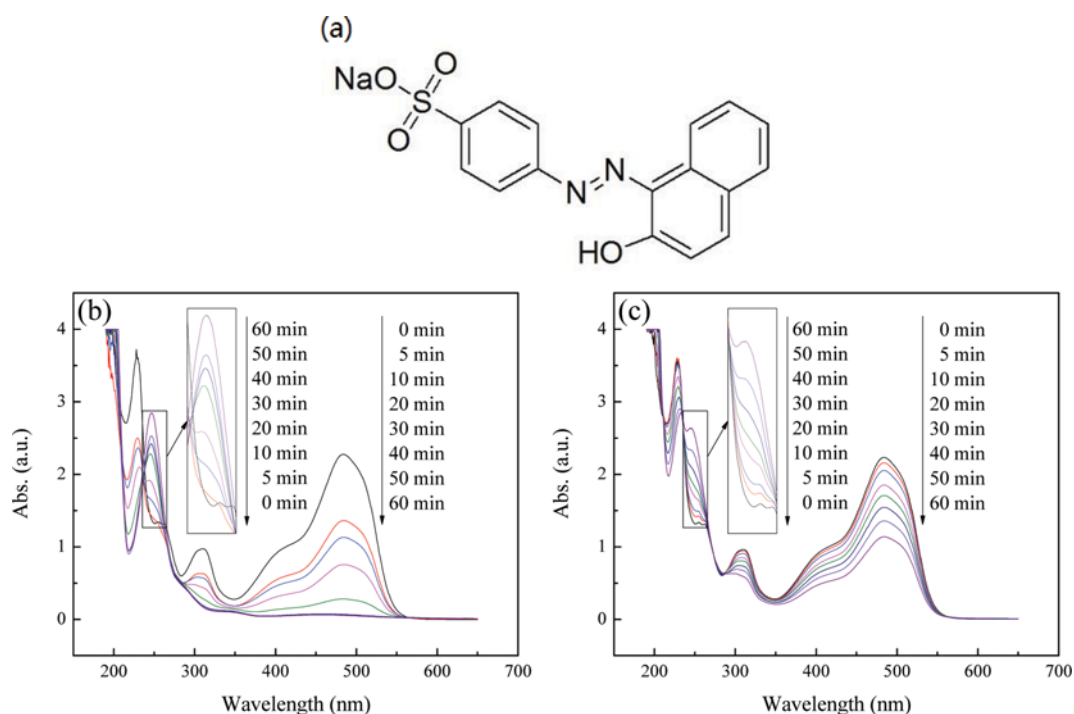
Fig. 6. The variation of UV-vis spectra of AO7 aqueous solution during the treatment process by using (a) structure of AO7, (b) Fe/Cu bimetallic system or (c) Fe^0 system at 80 °C (volume of AO7 aqueous solution was 300 mL, initial pH was 7.0, stirring speed was 400 rpm, theoretical Cu mass loading was 0.41 g Cu/g Fe, $[AO7]_0=10,000$ mg/L, $[Na_2SO_4]=50$ mmol/L, [Fe/Cu]=35 g/L, $[Fe^0]=35$ g/L).

cles under the optimal conditions. The spectrum obtained prior to the degradation process (0 min) is characterized by a peak (485 nm) in the visible region, corresponding to the azo-linkage [38]. Meanwhile, the peaks in the ultraviolet region (310 and 228 nm) correspond to the π-π^* transitions in the naphthalene ring and benzoic ring of AO7 [39]. From Fig. 6(a), the intensity of the peaks at 228, 310 and 485 nm all decreased significantly with the increase of the treatment time. Meanwhile, a new peak at 247 nm was generated and its intensity increased quickly with the increase of the treatment time. The results indicate that at high operating temperature (80 °C), the high concentration AO7 (10,000 mg/L) could be degraded by Fe/Cu bimetallic system and generated some new intermediates. In particular, azo group could be broken quickly by Fe/Cu process, and then AO7 was broken into a naphthalene ring and a benzoic ring. Furthermore, the benzoic ring of these intermediates could be opened and some small molecule products could be generated (e.g., organic acid). Finally, these products might be further mineralized into CO_2 and H_2O. Fig. 6(b) shows that the intensity of all peaks only decreased a little after 60 min ZVI treatment. The results suggest that the Fe/Cu bimetallic system has much stronger treatment capacity for the degradation of AO7 than ZVI do. In other words, Cu deposited on the surface of Fe^0 could enhance the reactivity of Fe^0 significantly.

7. Degradation and Transformation of AO7

To investigate the degradation and transformation of AO7, the COD and TOC of the effluent of Fe/Cu bimetallic system and ZVI were measured during the 60 min treatment process. The high concentration AO7 (10,000 mg/L) aqueous solution was treated by Fe/Cu bimetallic system and ZVI, respectively. Fig. 7 shows the plots
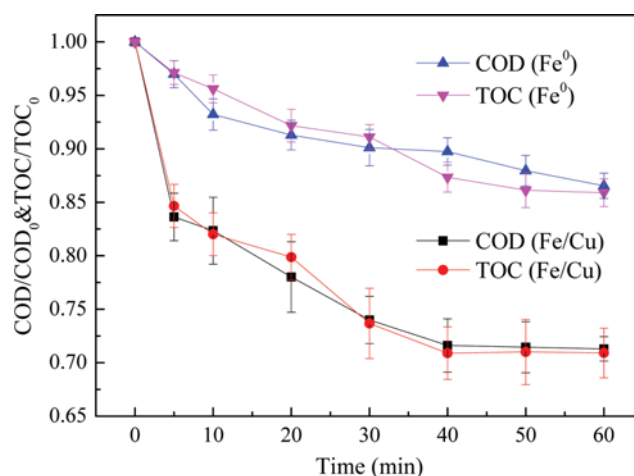

Fig. 7. COD and TOC removal of AO7 aqueous solution by using Fe/Cu bimetallic or Fe^0 system at 80 °C (volume of AO7 aqueous solution was 300 mL, initial pH was 7.0, stirring speed was 400 rpm, theoretical Cu mass loading was 0.41 g Cu/g Fe, $[AO7]_0=10,000$ mg/L, $[Na_2SO_4]=50$ mmol/L, [Fe/Cu]=35 g/L, $[Fe^0]=35$ g/L).

of COD and TOC removal efficiencies versus treatment time.

The curves of Fe/Cu bimetallic system show that COD and TOC removal efficiencies were 28.8% and 29.1%, respectively. After 40 min treatment, the removal efficiencies did not further increase with the increase of the treatment time. The results indicate that AO7 has been completely decomposed and transformed into intermediates after 40 min treatment under the optimal conditions. Mean-

while, after 40 min treatment by Fe/Cu bimetallic system, the obtained UV-Vis spectrum of the effluent also shows that the intensity of three main peaks has decreased to the lowest value. Thus, the results from UV-Vis spectra also proved that AO7 has been completely decomposed and transformed into intermediates after 40 min treatment. Additionally, the removal of COD and TOC was mainly attributed to the oxidation of Fenton-like reaction, the reduction of Fe^0 and the adsorption of corrosion production (Fe^{2+}/Fe^{3+}) [40,41]. The higher COD and TOC removal efficiencies also suggest that some of the intermediates might be mineralized into CO_2 and H_2O.

The curves of ZVI control experiment show that COD and TOC removal efficiencies were 13.5% and 14.1%, respectively, after 60 min treatment (Fig. 7). During the 60 min treatment process by ZVI, the variation of COD and TOC removal efficiencies was similar to that of UV-Vis spectra. The results suggest that only a part of AO7 could be decomposed and transformed into the intermediates. The degradation and transformation of AO7 by Fe/Cu bimetallic system was much higher than that obtained by the ZVI system. The Cu deposited on the surface of Fe^0 can enhance the pollutants degradation capacity of ZVI significantly, which was proved in our previous work and other studies [37].

During the treatment process of the high concentration AO7 (10,000 mg/L) by Fe/Cu bimetallic system at high operating temperature (80 °C), the COD and TOC removal efficiencies (28.8% and 29.1%) obtained were higher than those obtained in our previous work (21.2% and 22.8%) at room temperature. Meanwhile, COD and TOC removal efficiencies (13.5% and 14.1%) obtained by the ZVI system at 80 °C were higher than those obtained by ZVI control experiments in our previous work (~8.8%) at room temperature. Therefore, the results indicate that the high operating temperature plays a leading role in the removal of the high concentration pollutant.

CONCLUSIONS

The effect of operating temperature on the reactivity of Fe/Cu bimetallic system for high concentration pollutants has been investigated thoroughly. At high operating temperature (80 °C), other key operating parameters were also investigated, including theoretical Cu mass loading, Fe/Cu dosage, stirring speed and initial pH on the reactivity of Fe/Cu bimetallic particles. Since high concentration AO7 (10,000 mg/L) has a high activation energy (175.6 kJ/mol), the degradation of AO7 by Fe/Cu bimetallic particles could only be performed under the high temperature condition (i.e., 80 °C). Also, the high temperature could accelerate mass transport rate and overcome the high activation energy barrier to improve the reactivity of Fe/Cu bimetallic particles significantly. Furthermore, the optimal operating parameters (operating temperature was 80 °C, stirring speed was 400 rpm, theoretical Cu mass loading was 0.41 g Cu/g Fe, initial pH=7.0, [Fe/Cu]=35 g/L) were obtained by the batch experiments. Under the optimal conditions, even the high concentration AO7 (10,000 mg/L) that was treated by Fe/Cu bimetallic system, the COD and TOC removal efficiencies (28.8% and 29.1%) were higher than those obtained in our previous work (21.2% and 22.8%) at room temperature. Therefore, the results indicate that

the high operating temperature plays a leading role in the degradation of high concentration pollutant. Finally, if the waste-heating vapor could be used to elevate the operating temperature of Fe/Cu bimetallic system, this system would be a much better cost-effective process for the treatment of the high concentration industrial wastewater, compared with other methods used so far.

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