

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/264556111>

Influence of Preparation Conditions on Characteristics, Reactivity, and Operational Life of Microsized Fe/Cu Bimetallic Particles

ARTICLE in INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH · AUGUST 2014

Impact Factor: 2.59 · DOI: 10.1021/ie501756m

CITATION

1

READS

41

5 AUTHORS, INCLUDING:



Bo Lai

Sichuan University

25 PUBLICATIONS 196 CITATIONS

SEE PROFILE



Yue Yuan

Sichuan University

8 PUBLICATIONS 8 CITATIONS

SEE PROFILE



Ping Yang

45 PUBLICATIONS 842 CITATIONS

SEE PROFILE

Influence of Preparation Conditions on Characteristics, Reactivity, and Operational Life of Microsized Fe/Cu Bimetallic Particles

Bo Lai,* Yun-Hong Zhang, Yue Yuan, Zhao-Yu Chen, and Ping Yang

Department of Environmental Science and Engineering, School of Architecture and Environment, Sichuan University, Chengdu, Sichuan 610065, China

S Supporting Information

ABSTRACT: The effect of the preparation conditions on the physicochemical characteristics, operating life, and reactivity of Fe/Cu bimetallic particles was studied significantly by using a model pollutant (*p*-nitrophenol), scanning electron microscopy–energy dispersive spectrometry, and X-ray diffraction spectrometry. The results suggest that the higher reactivity and longer operating life of Fe/Cu bimetallic particles were obtained under the optimal preparation conditions. Furthermore, under the optimal preparation conditions, Cu was not easily dropped from the Fe⁰ particle, and the weight ratio of Cu on the surface of the Fe/Cu bimetallic particles increased significantly. Moreover, their optimal theoretical Cu mass loading could be decreased from 0.89 to 0.41 g Cu/g Fe, which favors the reduction of production costs. In addition, two batch experiments with Fe/Cu bimetallic particles prepared under optimal and nonoptimal conditions were set up to comparatively investigate the improvement of operating life and reactivity of Fe/Cu particles when optimized preparation conditions were carried out. As a result, it was proven that the reactivity and operating life of Fe/Cu bimetallic particles could be improved significantly through the optimization of preparation conditions.

1. INTRODUCTION

In recent years, there has been increasing interest in the study of the degradation of toxic and refractory pollutants in industrial wastewater by zerovalent iron (ZVI), Fe/GAC, and Fe/Cu bimetallic systems, which are environmental physicochemical processes based on the in situ generation of Fe²⁺, atomic hydrogen (*H, anoxic conditions), or hydroxyl radical (*OH, oxic conditions).^{1–4} On one hand, under the anoxic conditions, both the newly generated Fe²⁺ and atomic hydrogen are strong reductants that could reduce the pollutants in wastewater.^{4–6} On the other hand, under the oxic conditions, the generated hydroxyl radical is the second strongest oxidant known after fluorine, with a high standard oxidation potential that can nonselectively mineralize the pollutants (i.e., overall conversion into CO₂, H₂O, and inorganic ions).^{7–10}

ZVI and Fe/GAC systems have been used to treat toxic and refractory industrial wastewater including dye wastewater,⁸ pharmaceutical wastewater,¹¹ pesticide wastewater,¹² and ABS resin wastewater.^{13,14} Despite the widespread studies on these treatment technologies, their practical applications are still suffering from many limitations.^{14,15} Recently, it has been shown that the micron-scale Fe/Cu bimetallic particles prepared by planting Cu on the iron surface can significantly enhance the reduction rates of the pollutants.^{4,5} In our previous work, it was also proven that the planted Cu could improve the reactivity of Fe⁰ remarkably.⁶ Meanwhile, the reduction reactions with high efficiency occurred even in a much wider range of pH (3.0–9.0) when the *p*-nitrophenol (PNP) aqueous solution was treated by the prepared Fe/Cu bimetallic particles.⁶ Also, the Cu distributional characteristics on the surface of Fe⁰ significantly affected the reactivity of the prepared Fe/Cu bimetallic particles.^{5,6} Furthermore, the preparation conditions, such as temperature, mixing intensity, Cu²⁺

concentration, and pH, might have an influence on the distributional characteristics of Cu. Therefore, the reactivity of Fe/Cu bimetallic particles might be affected by the preparation conditions. In the previous studies, however, the effect of these preparation conditions was not studied yet. In other words, the previous preparation process of Fe/Cu bimetallic particles was too simple. In particular, after the CuSO₄ solution was added to the iron particles, the slurry was mixed manually, and then the prepared Fe/Cu bimetallic particles were deposited, cleared, and dried.^{4–6} Therefore, it is necessary to investigate the effect of the preparation conditions on the reactivity of Fe/Cu bimetallic particles.

In this study, PNP was used as a model pollutant to investigate the reactivity of Fe/Cu bimetallic particles that were prepared under different conditions. Also, the Cu distributional characteristics on the surface of Fe⁰ were observed by using scanning electron microscope (SEM) and energy dispersive spectrometry (EDS). Furthermore, the optimal preparation conditions were obtained based on the results of PNP removal efficiency and SEM-EDS analysis. Finally, the reactivity and operational life of Fe/Cu bimetallic particles prepared under optimal conditions were compared with those of Fe/Cu bimetallic particles prepared under nonoptimal conditions.

2. EXPERIMENTAL SECTION

2.1. Reagents. Zero valent iron powders, CuSO₄ (analytical reagent), CuCl₂ (analytical reagent), Na₂SO₄ (analytical reagent), and PNP (99%) from Chengdu Kelong chemical

Received: April 29, 2014

Revised: July 13, 2014

Accepted: July 22, 2014

Published: July 22, 2014

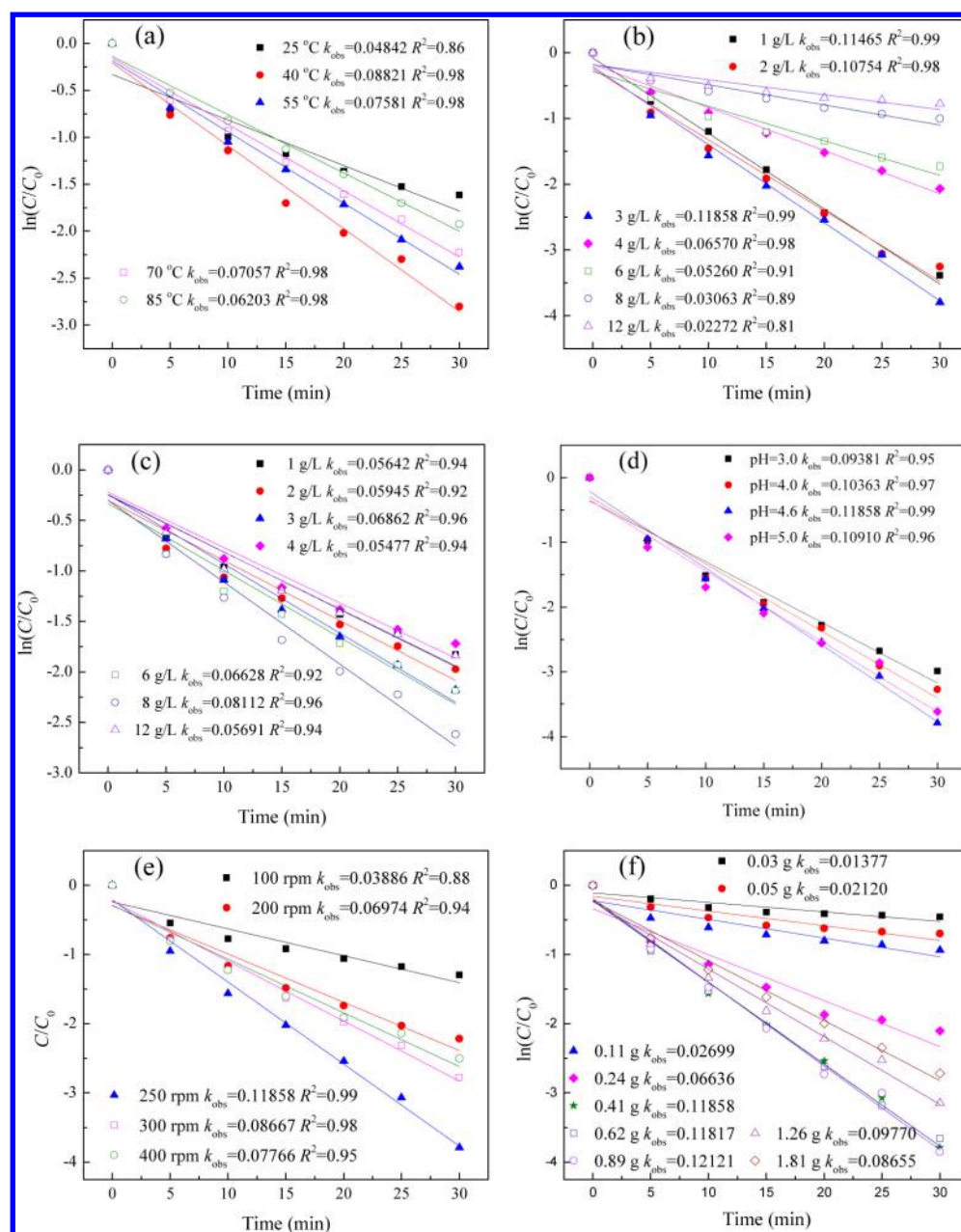


Figure 1. Effect of preparation parameters on the reactivity of Fe/Cu bimetallic particles: (a) temperature, (b) Cu^{2+} concentration (CuSO_4), (c) Cu^{2+} concentration (CuCl_2), (d) pH of planting solution, (e) mixing speed, and (f) TML_{Cu} .

reagent factory were used in the experiment. The zerovalent iron powders have mean particle size of approximately $120\ \mu\text{m}$, and their iron content reaches approximately 97%. Other chemicals used in the experiment were of analytical grade.

2.2. Preparation of Fe/Cu Bimetallic Particles. 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.⁶ In this study, the main preparation conditions including temperature, mixing intensity, initial pH, Cu^{2+} concentration of planting solution, types of copper salt, and theoretical Cu mass loading (TML_{Cu}) were optimized thoroughly.

First, the Fe/Cu bimetallic particles were prepared under different temperatures (i.e., 25, 40, 55, 70, and $85\ ^\circ\text{C}$). Next, under the obtained optimal temperature, the Fe/Cu bimetallic particles were prepared under different Cu^{2+} concentrations

(i.e., 1, 2, 3, 4, 6, 8, and 12 g/L). Meanwhile, to investigate the effect of copper salt, two typical copper salts (i.e., CuSO_4 and CuCl_2) were used to prepare planting solutions. Furthermore, under the above optimal conditions, the preparation processes were performed in the planting solutions with different initial pH (i.e., 3.0, 4.0, 4.6, and 5.0). Moreover, the effect of stirring speed (i.e., 100, 200, 250, 300, and 400 rpm) was further investigated under other optimal conditions. Additionally, under the above optimal conditions, the effect of TML_{Cu} (i.e., 0.03, 0.05, 0.11, 0.24, 0.41, 0.62, 0.89, 1.26, and 1.81 g Cu/g Fe) was investigated. Finally, to observe the effect of the preparation conditions on the physicochemical characteristics of the prepared Fe/Cu bimetallic particles, these particles obtained under different preparation conditions were analyzed using SEM-EDS.

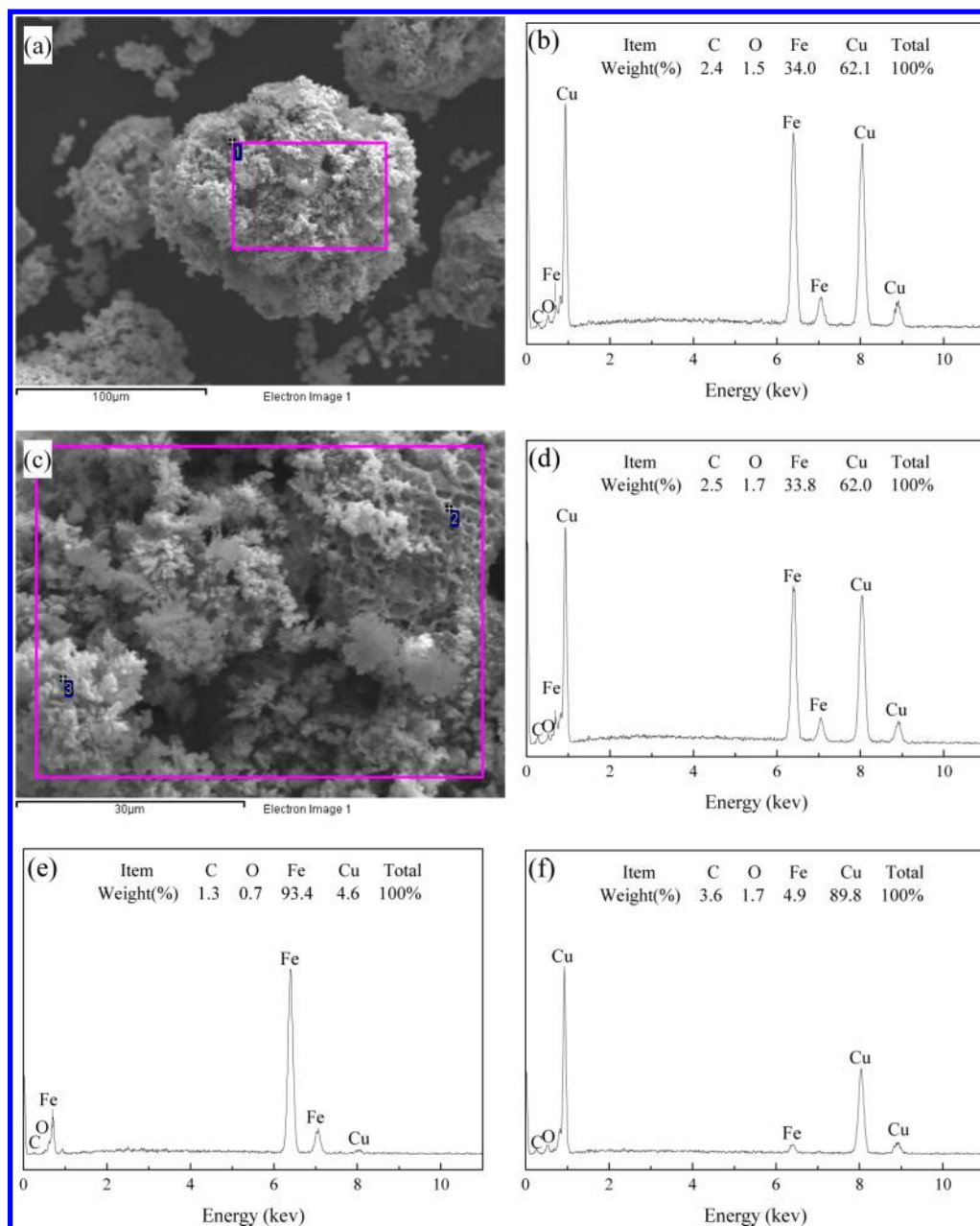


Figure 2. Characteristics of the prepared Fe/Cu bimetallic particles under the optimal conditions: (a) SEM image of Fe/Cu bimetallic particles; (b) EDS spectrum of area in the purple frame of the SEM in panel a; (c) SEM image of Fe/Cu bimetallic particles; (d) EDS spectrum of area in the purple frame of the SEM in panel c; (e, f) EDS spectra of points 2 and 3 in the SEM in panel c. (Optimal conditions: temperature, 40 °C; mixing speed, 250 rpm; Cu^{2+} concentration, 3 g/L (CuSO_4); TML_{Cu} 0.41 g Cu/g Fe; and pH of planting solution, 4.6.)

2.3. Batch Experiments. In the experimental process, PNP was used as a model pollutant to evaluate the reactivity of the prepared Fe/Cu bimetallic particles. A 500 mg/L PNP aqueous solution was prepared by simple dissolution in deionized water, filtered by the 0.45 μm glass fiber membranes, and stocked in amber bottles. The Na_2SO_4 as an electrolyte (50 mmol/L) was added into the PNP aqueous solution. Furthermore, the PNP stock solutions were not buffered, and the initial pH was adjusted to approximately 6.7.

In each batch experiment, 6 g of Fe/Cu bimetallic particles and 300 mL of PNP aqueous solution (500 mg/L) were added into a 500 mL beaker and the slurry was stirred by a mechanical stirrer with a stirring speed of 400 rpm. The whole experiment process was performed at a running temperature of 25 ± 1 °C

through water bath heating. Then, the Fe/Cu bimetallic particles obtained under different preparation conditions were used to treat the 500 mg/L PNP aqueous solution at the same operating conditions. The reactivity of the prepared Fe/Cu bimetallic particles could be evaluated through the PNP removal efficiencies. Samples (1 mL) were taken at 5 min intervals for 30 min, diluted by deionized water, and filtered through a PTFE syringe filter disc (0.45 μm). Finally, the PNP concentration of the influent and effluent were measured by reversed-phase high-performance liquid chromatography (HPLC) chromatography (Agilent, U.S.).

2.4. Analytical Methods. The concentration of PNP in the samples was achieved by reversed-phase HPLC chromatography (Agilent U.S.) equipped with the Eclipse XDB C-18 (5

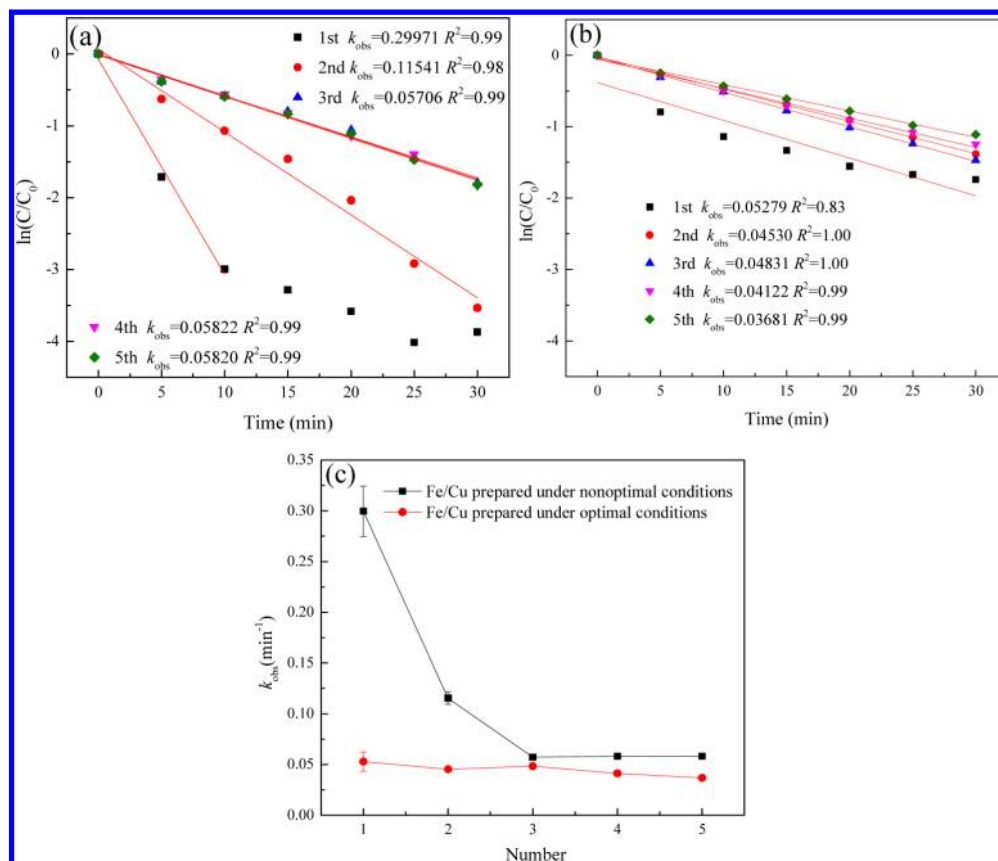


Figure 3. Operating life of the Fe/Cu bimetallic particles prepared under optimal or nonoptimal conditions: (a) optimal conditions, (b) nonoptimal conditions, and (c) correlation of k_{obs} and number of batch experiments. (Optimal conditions: temperature, 40 °C; mixing speed, 250 rpm; Cu^{2+} concentration, 3 g/L ($CuSO_4$); TML_{Cu} 0.41 g Cu/g Fe; and pH of planting solution, 4.6. Nonoptimal conditions: temperature, 25 °C; mixed by hand; Cu^{2+} concentration, 8 g/L ($CuSO_4$); TML_{Cu} 0.41 g Cu/g Fe; and pH of planting solution, 4.5.)

μm , 250×4.6 mm²).⁶ The surface morphologies and elementary composition of the prepared Fe/Cu bimetallic particles were observed by an S-3500N scanning electron microscope (Hitachi, Japan) and an energy dispersive spectrometer (Oxford Instruments).¹⁶ On the basis of the elemental composition analysis of the prepared Fe/Cu bimetallic particles by EDS, its compound composition was further investigated by X-ray diffraction (XRD) analysis.^{6,16}

2.5. Kinetics Analysis. The removal efficiency of PNP in aqueous solution by the Fe/Cu bimetallic system was treated by a pseudo-first-order equation:

$$\ln \frac{C}{C_0} = -k_{obs}t \quad (1)$$

where C_0 is the initial concentration of PNP in aqueous solution (mg/L), C the residual PNP concentration in aqueous solution after the treatment (treatment time is t), k_{obs} the measured rate constant (min⁻¹), and t the treatment time (min). The k_{obs} were calculated by the method of linear regression.

3. RESULTS AND DISCUSSION

3.1. Effect of Preparation Temperature. In previous work, the preparation process of Fe/Cu bimetallic particles usually was performed at room temperature (25 ± 3 °C),^{4,17,18} and the effect of preparation temperature on the reactivity of Fe/Cu bimetallic particle has not yet been investigated. Figure 1a shows that k_{obs} increased sharply from 0.04842 to 0.08821

min⁻¹ when the preparation temperature increased from 25 to 40 °C. The k_{obs} decreased gradually from 0.08821 to 0.06203 min⁻¹ when the preparation temperature further increased from 40 to 85 °C. The results suggest that the optimal preparation temperature was 40 °C, as the lower or higher preparation temperature would be unfavorable to the reactivity of Fe/Cu bimetallic particles. In the literature, it is noted that the accelerating temperature usually could enhance the mass-transfer rate and overcome the activation energy barrier to improve the heterogeneous chemical reaction at the surface or the diffusion of reactant and product.^{19–22} Therefore, the displacement reaction rate between Fe^0 and Cu^{2+} could be accelerated significantly with the preparation temperature increase. Subsequently, the high or low displacement reaction rate might have a negative effect on the distribution of Cu on the surface of Fe^0 particles, which would limit the reactivity of Fe/Cu bimetallic particles.

3.2. Effect of Cu^{2+} Concentration. Previous authors usually used $CuCl_2$ or $CuSO_4$ to support Cu^{2+} for the displacement reaction.^{17,23,24} However, the Fe–Cu displacement reaction rate might be affected by Cu^{2+} concentration and type of copper salt, which would indirectly affect the Cu distribution characteristics on the surface of Fe^0 . Figure 1b shows that high k_{obs} (0.10754–0.11858 min⁻¹) were obtained when the Cu^{2+} concentration of planting solution was below 3 g/L. k_{obs} decreased sharply from 0.11858 to 0.02272 min⁻¹ when the Cu^{2+} concentration of planting solution increased from 3 to 12 g/L. The results suggest that the reactivity of the

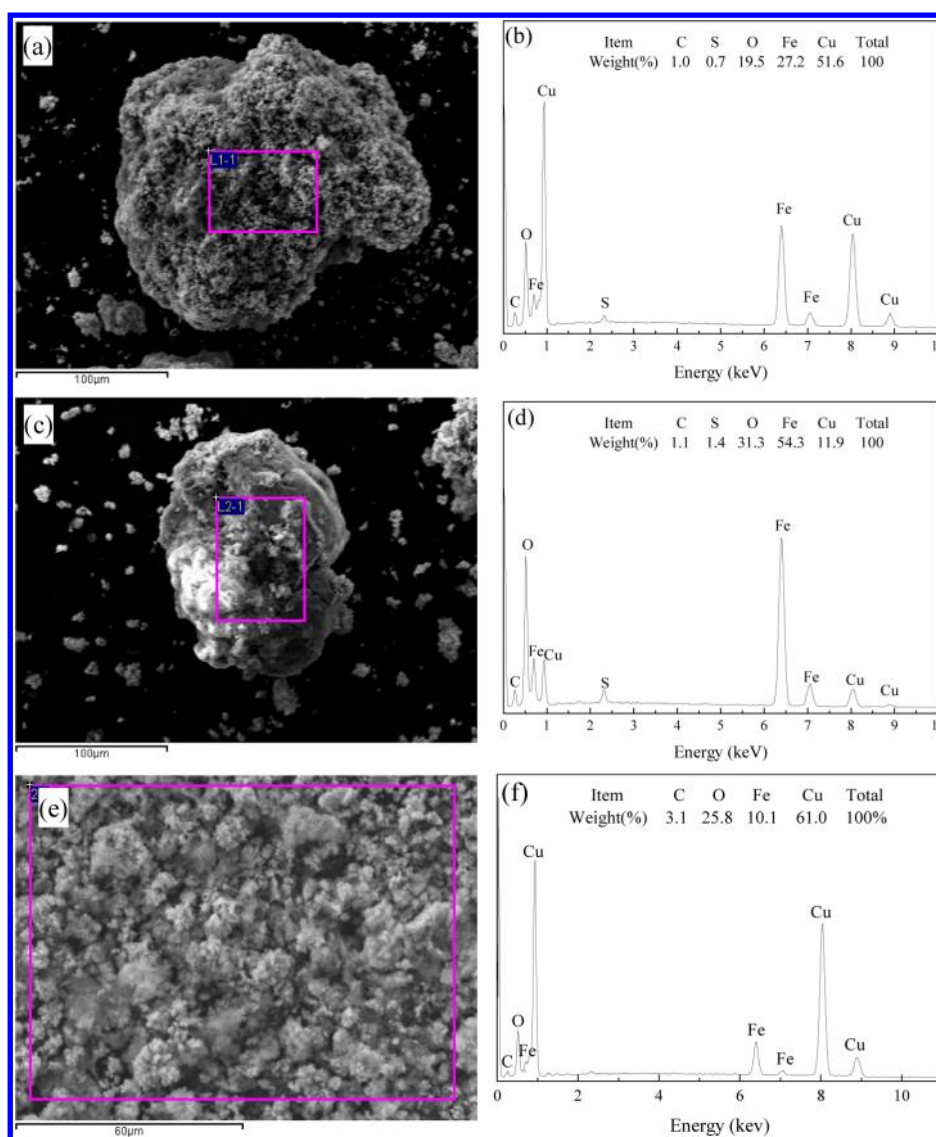


Figure 4. Characteristics of Fe/Cu bimetallic particles after 5 batch experiments. (a) SEM image of Fe/Cu bimetallic particles prepared under optimal conditions. (b) EDS spectrum of area in the purple frame of the SEM in panel a. (c) SEM image of Fe/Cu bimetallic particles prepared under nonoptimal conditions. (d) EDS spectrum of area in the purple frame of the SEM in panel c. (e) SEM image of casting of the Fe/Cu prepared under nonoptimal conditions. (Optimal and nonoptimal conditions are the same as those in Figure 3).

prepared Fe/Cu bimetallic particles would be improved by using a lower Cu^{2+} concentration planting solution (<3 g/L), whereas a higher Cu^{2+} concentration planting solution (>3 g/L) would significantly decrease its reactivity.

Figure 1c shows the effect of CuCl_2 on the reactivity of Fe/Cu bimetallic particles. Their k_{obs} maintained between 0.05642 and 0.08112 min^{-1} when the Cu^{2+} concentration increased from 1 to 12 g/L. It is clear that if the Fe/Cu bimetallic particles were prepared at a lower Cu^{2+} concentration (<3 g/L), the obtained k_{obs} (0.10754 – 0.11858 min^{-1}) when CuSO_4 was used to support Cu^{2+} were much higher than those (0.05642 – 0.06862 min^{-1}) obtained when CuCl_2 was used to support Cu^{2+} . The results suggest that the reactivity of Fe/Cu bimetallic particles could be significantly improved by the lower Cu^{2+} concentration (<3 g/L) when the CuSO_4 were used to support Cu^{2+} , while it could not be improved when the CuCl_2 were used to support Cu^{2+} . This phenomenon can be explained from two aspects: (a) The lower Cu^{2+} concentration (<3 g/L) would limit the Fe–Cu displacement reaction rate, which was

favorable to the Cu deposition on the surface of Fe^0 . (b) Cl^- could significantly accelerate the corrosion rate of Fe^0 ,^{25,26} and the rapid corrosion of Fe^0 was harmful to the Cu deposition on the surface of Fe^0 . Therefore, the reactivity of Fe/Cu bimetallic particles prepared by using CuSO_4 was much higher than that prepared by using CuCl_2 when the Cu^{2+} concentration of the planting solution was below 3 g/L.

3.3. Effect of Initial pH of the Planting Solution. Figure 1d indicates the effect of initial pH of the planting solution on the PNP degradation by the prepared Fe/Cu bimetallic particles. It is clear that k_{obs} of the PNP degradation increased gradually from 0.09381 to 0.11858 min^{-1} with increasing pH from 3.0 to 4.6. Then it decreased to 0.10910 min^{-1} when the pH further increased to 5.0. When the pH was above 5.0, Cu^{2+} precipitated in the form of $\text{Cu}(\text{OH})_2$. Therefore, the effect of the higher pH (>5.0) was not investigated in this study. Additionally, the Fe–Cu reaction time increased rapidly from 1.7 to 6.5 min with increasing pH from 3.0 to 5.0. The results suggest that the decrease of the initial pH of the planting

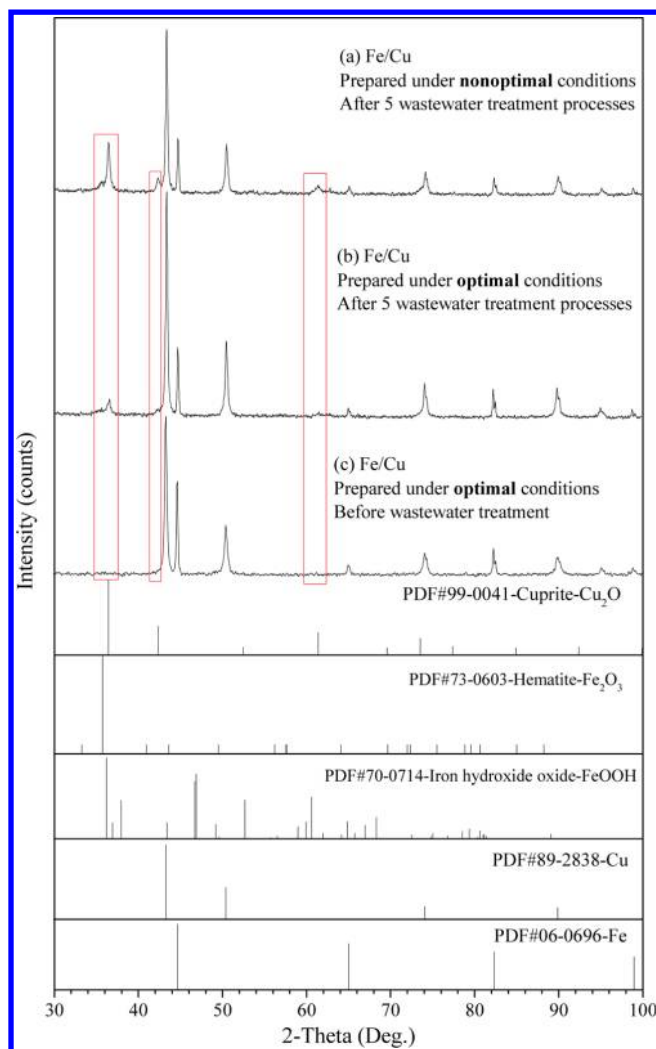


Figure 5. XRD patterns of Fe/Cu bimetallic particles before and after 5 batch experiments: prepared under (a) nonoptimal conditions and (b, c) optimal conditions. (Optimal and nonoptimal conditions are the same as those in Figure 3.)

solution would accelerate the Fe–Cu displacement rate, which would affect the reactivity of the prepared Fe/Cu bimetallic particles; the optimal initial pH of the planting solution was 4.6.

3.4. Effect of Mixing Intensity. The mass-transfer rate of the reacting substance usually was controlled by the mixing intensity of the reaction system.^{27,28} The Fe–Cu displacement reaction rate might be limited by the mixing intensity. Figure 1e shows that the k_{obs} increased sharply from 0.03886 to 0.11858 min^{-1} when the rotation speed increased from 100 to 250 rpm. The k_{obs} decreased gradually from 0.11858 to 0.07766 min^{-1} with the further increase in rotation speed from 250 to 400 rpm. Thus, the optimal rotation speed was 250 rpm during the preparation process of the Fe/Cu bimetallic particles. Finally, this phenomenon could be explained from two aspects: (a) When the rotation speed was below 250 rpm, the increase of mixing intensity could improve the mass-transfer rate of reactant (Cu^{2+}) and corrosion products (Fe^{2+} or Fe^{3+}). It could avoid the effect of the residual corrosion products (Fe^{2+} or Fe^{3+}) on the Cu deposition. (b) When the rotation speed was above 250 rpm, the higher shearing force produced from the higher rotation speed could drop off some Cu deposited on

the surface of Fe^0 , which could decrease the reactivity of the prepared Fe/Cu bimetallic particles.

3.5. Effect of Theoretical Cu Mass Loadings. Figure 1f shows that k_{obs} of the PNP degradation increased rapidly from 0.01377 to 0.11858 min^{-1} when TML_{Cu} increased from 0.03 to 0.41 g Cu/g Fe. The value of k_{obs} maintained between 0.11858 and 0.12121 min^{-1} with the further increase of TML_{Cu} from 0.41 to 0.89 g Cu/g Fe. Finally, k_{obs} began to decrease gradually from 0.12121 to 0.08655 min^{-1} when TML_{Cu} continued to increase from 0.89 to 1.81 g Cu/g Fe. Therefore, the optimal TML_{Cu} was between 0.41 and 0.89 g Cu/g Fe when the Fe/Cu bimetallic particles were prepared under the above optimal conditions. When these results are compared with our previous work,⁶ it is clear that the optimal TML_{Cu} could be decreased to 0.41 g Cu/g Fe, which could decrease the addition of Cu and reduce production costs. Also, the decrease of the optimal TML_{Cu} mainly resulted from the optimization of the other preparation parameters, including temperature, mixing speed, Cu^{2+} concentration, and initial pH of the planting solution.

3.6. Characteristics of the Prepared Fe/Cu Bimetallic Particles. To further confirm the effect of preparation, the characteristics of Fe/Cu bimetallic particles prepared under different conditions were observed thoroughly using SEM-EDS.

3.6.1. Under the Optimal Preparation Conditions. Figure 2 shows SEM images and EDS spectra of Fe/Cu bimetallic particles that were prepared under the optimal conditions. Figure 2a,b shows that two main elements (Fe, 34.0 wt % and Cu, 62.1 wt %) were observed on the surface of the prepared Fe/Cu bimetallic particle. It is clear that the weight ratio of Cu (62.1 wt %) obtained in this study was much higher than that (29.9 wt %) obtained in our previous work.⁶ The results indicate that the Cu was much easier to deposit on the surface of Fe^0 under the optimal preparation conditions and that the planted Cu was not easy to drop off. Under the above optimal conditions, therefore, the Fe/Cu bimetallic particle with a lower TML_{Cu} (i.e., 0.41 g Cu/g Fe) also had strong reactivity. Figure 2c–f shows that the planted Cu was a heterogeneous film on the surface of the prepared Fe/Cu bimetallic particles. The Cu distribution characteristics were in accord with those in our previous work.⁶ The heterogeneous Cu layer was favorable for the formation of Fe/Cu galvanic corrosion, which could significantly improve the reactivity of the Fe/Cu bimetallic particles.^{5,6}

3.6.2. Effect of the Preparation Temperature. Figure S1 in the Supporting Information illustrates the characteristics of Fe/Cu bimetallic particles prepared at a lower or a higher temperature (i.e., 25 or 70 °C). It is clear that a low weight ratio of Cu (25.0 wt %) was obtained on the surface of some Fe/Cu bimetallic particles (Figure S1a,b), whereas a high weight ratio of Cu (>80.0 wt %) was obtained on the surface of other Fe/Cu bimetallic particles (Figure S1c–f). The results indicate that the Cu loading on each Fe/Cu bimetallic particle was obviously different, which would bring about the following shortcomings: (a) The low Cu loading (<30.0 wt %) would limit the formation number of Fe–Cu galvanic cell (Figure S1a,b). (b) The high Cu loading (>80.0 wt %) would form a thick and compact copper layer on the surface of Fe^0 particles, which could inhibit the formation of Fe–Cu galvanic cell and protect Fe^0 from corrosion (Figure S1c–f). Additionally, it is clear that only the heterogeneous copper distribution on the surface of Fe^0 could form a large number of Fe–Cu galvanic cells and improve the reactivity of Fe/Cu bimetallic particles.^{4–6} Also, in the field of anticorrosion, a compact and homogeneous metal

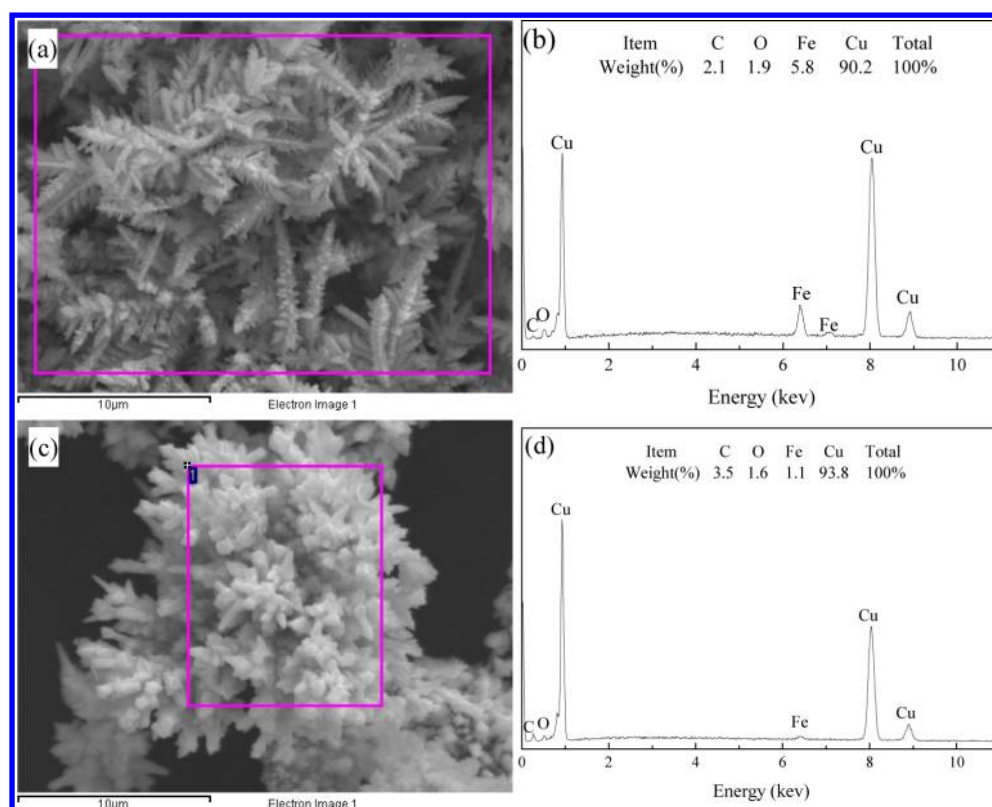


Figure 6. Characteristics of the fine Cu particles generated from Fe–Cu displacement reaction. Panels a and c are SEM images, and panels b and d are EDS spectra of area in the purple frame of the SEM images in panels a and c, respectively.

layer was usually used to protect other metals from dust.²⁹ Therefore, either the lower or the higher preparation temperature was harmful to the reactivity of Fe/Cu bimetallic particles.

3.6.3. Effect of Cu^{2+} Concentration in the Planting Solution. Figure S2 in the Supporting Information shows the characteristics of Fe/Cu bimetallic particles prepared at a high Cu^{2+} concentration of planting solution (i.e., 30 g/L). It is clear that only a part of Fe^0 particles were covered by planting Cu layer (Figure S2a–c), and a large number of fine Cu particles were generated during the preparation process (Figure S2d). The SEM-EDS results further confirmed that the low reactivity of Fe/Cu bimetallic particles prepared using high Cu^{2+} concentration of planting solution (i.e., 30 g/L) mainly resulted from two aspects: (a) High Cu^{2+} concentration would affect the mass-transfer rate of Cu^{2+} and corrosion products (Fe^{2+} or Fe^{3+}) between planting solution and the surface of Fe/Cu bimetallic particles. (b) High Cu^{2+} concentration would significantly accelerate the displacement reaction rate and quickly produce a large amount of Cu. Additionally, plenty of the newly generated Cu was difficult to fully distribute on the surface of Fe^0 particles. The Cu easily dropped off the surface of Fe^0 particles to form fine Cu particles (Figure S2d). Thus, the high Cu^{2+} concentration of the planting solution was harmful to the reactivity of the Fe/Cu bimetallic particles.

3.6.4. Effect of Mixing Intensity. Figure S3 in the Supporting Information shows the characteristics of Fe/Cu bimetallic particles prepared at a lower rotation speed of 100 rpm. It is clear that the weight ratios of Cu on the surface of Fe/Cu bimetallic particles fluctuated between 12.1% and 87.3% (Figure S3a–d), and a large number of fine Cu particles were generated during the preparation process (Figure S3e,f). The

results suggest that the lower mixing intensity (i.e., 100 rpm) would limit the Cu uniform distribution on each Fe^0 particle, and the newly generated Cu easily dropped off, which would decrease the reactivity of the prepared Fe/Cu bimetallic particles. This phenomenon could be explained by the fact that the lower mixing intensity would limit the mass-transfer rate of Cu^{2+} , Fe^{2+} , and other reaction products between Fe^0 and the planting solution; the different Fe^0 particles would react with a different amount of Cu^{2+} , resulting in the different Cu mass loadings on each Fe^0 particle.

Figure S4 in the Supporting Information shows the characteristics of the Fe/Cu bimetallic particles prepared at a higher rotation speed of 400 rpm. Although the Cu mass loadings on each Fe^0 particle were not completely different, the Cu weight ratio (34.0 wt %) of the prepared Fe/Cu bimetallic particle was much lower than that (62.0 wt %) obtained under the optimal rotation speed of 250 rpm (Figure 2 and Figure S4). The higher mixing intensity could enhance the mass-transfer rate of Cu^{2+} , Fe^{2+} , and other reaction products between Fe^0 and the planting solution and make the Cu distribute uniformly on each Fe^0 particle. However, the higher shearing force produced from the higher rotation speed could drop off some Cu deposited on the surface of Fe^0 , which could decrease the reactivity of the prepared Fe/Cu bimetallic particles.

3.6.5. Effect of Theoretical Cu Mass Loadings. Figure S5 in the Supporting Information shows the characteristics of Fe/Cu bimetallic particles prepared with a lower TML_{Cu} (i.e., 0.05 g Cu/g Fe). It is clear that the Cu weight ratio reached about 21.1%, which was much higher than that (15.1 wt %) obtained in our previous work even if the Fe/Cu bimetallic particles had a higher TML_{Cu} of 0.11 g Cu/g Fe.⁶ Although optimal preparation conditions could improve the Cu mass loading on

the surface of Fe^0 particles, the lower TML_{Cu} still limited the formation number of Fe–Cu galvanic cells on the surface of Fe/Cu bimetallic particles. Bransfield et al. also found that the copper loading and surface coverage could significantly affect the reactivity of Fe/Cu bimetallic particles.⁴

Figure S6 in the Supporting Information shows the characteristics of Fe/Cu bimetallic particles prepared with a higher TML_{Cu} (i.e., 1.81 g Cu/g Fe). It is clear that the Cu weight ratio reached approximate 86.6%, which was much higher than that (48.5 wt %) obtained in our previous work.⁶ The results suggest that under the optimal preparation conditions, the Cu was not easily dropped off from Fe^0 particles even if the Fe/Cu bimetallic particles had a higher TML_{Cu} (i.e., 1.81 g Cu/g Fe). However, plenty of Cu covered on the surface of Fe^0 particles and protected Fe^0 from dust, which also limited the formation of Fe–Cu galvanic cells and decreased the reactivity of Fe/Cu bimetallic particles.

3.7. Improvement of Operating Life and Reactivity of Fe/Cu Particles. In the literature, although the effect of operating parameters on Fe/Cu bimetallic system was investigated, the effect of preparation conditions was not studied yet.^{5,6,17,30} To confirm the improvement of operating life and reactivity of Fe/Cu bimetallic particles prepared under the optimal conditions, two batch experimental systems were set up: (a) PNP wastewater was treated by the Fe/Cu bimetallic particles prepared under the optimal conditions (temperature, 40 °C; mixing speed, 250 rpm; Cu^{2+} concentration, 3 g/L (CuSO_4); TML_{Cu} , 0.41 g Cu/g Fe; pH of planting solution, 4.6), and (b) this wastewater was treated using Fe/Cu bimetallic particles prepared under nonoptimal conditions (temperature, 25 °C; mixed by hand; Cu^{2+} concentration, 8 g/L (CuSO_4); TML_{Cu} , 0.41 g Cu/g Fe; pH of planting solution, 4.5). Additionally, under the same operating conditions, the same PNP wastewater was treated by the two batch experimental systems separately. Furthermore, both experimental systems continuously ran five times.

Figure 3a shows that k_{obs} of the degradation of PNP decreased from 0.29971 to 0.05706 min^{-1} after three batch experiments when the wastewater was treated by using Fe/Cu particles prepared under the optimal conditions, and then it was maintained at approximately 0.058 min^{-1} with the increase of running time. It can be seen from Figure 3b that k_{obs} of the degradation of PNP decreased gradually from 0.05279 to 0.03681 min^{-1} with the increase of running time when the wastewater was treated by using Fe/Cu particles prepared under the nonoptimal conditions. Figure 3c illustrates that during five continuous batch experiments, k_{obs} values obtained using the Fe/Cu particles prepared under the optimal conditions were always much higher than those obtained by using the Fe/Cu particles prepared under the nonoptimal conditions. As a result, the optimal conditions were favorable to the deposition of Cu on the surface of Fe^0 and formed many more Fe–Cu galvanic cells, which could improve the operating life and reactivity of Fe/Cu bimetallic particles.

3.8. Characteristics of Fe/Cu Particles after Repeated Running. Figure 4a,b shows that the weight ratios of Fe and Cu of the Fe/Cu particles prepared under the optimal conditions decreased from 34.0% and 62.1% (panels a and b of Figure 3) to 27.2% and 51.6% (panels a and b of Figure 4), respectively, after five continuous runs. However, the weight ratio of oxygen element increased significantly from 1.5% to 19.5% on the surface of Fe/Cu particles after five continuous runs. The results suggest that some corrosion products (oxide

compounds of Fe or Cu) were generated on the surface of Fe/Cu particles, which resulted in the decrease of reactivity of the Fe/Cu bimetallic particles after repeated runs. Even if the preparation conditions were optimized completely, the Fe/Cu bimetallic particles' reactivity and operating life would be affected after repeated runs. Panels c and d of Figure 4 show the SEM image and EDS spectrum, respectively, of the Fe/Cu bimetallic particles prepared under nonoptimal conditions after repeated runs. It is clear that the surface of these particles contained three elements, including Fe (54.3 wt %), O (31.3 wt %), and Cu (11.9 wt %). The results indicate that corrosion products were generated, and most of the planted Cu was dropped off after repeated runs. Furthermore, it could be seen from Figure 4e,f that plenty of slight casting containing O (25.8 wt %), Fe (10.1 wt %), and Cu (61.0 wt %) was found after repeated runs. When the SEM-EDS results of Fe/Cu particles prepared under optimal and nonoptimal conditions are compared, the planted Cu was much more easily dropped off after repeated runs when the Fe/Cu particles were prepared under the nonoptimal conditions.

The XRD pattern in Figure 5c indicates that the chemical composition of Fe/Cu bimetallic particles prepared under optimal conditions was predominantly iron and copper. It was also proven in our previous work that they had the same chemical composition even if their preparation conditions were not optimized.⁶ However, plenty of cuprite (Cu_2O) and a little hematite (Fe_2O_3) and iron hydroxide oxide (FeOOH) were generated when the Fe/Cu particles prepared under nonoptimal conditions were used to repeatedly treat wastewater (Figure 5a). Additionally, these products also were found on the surface of Fe/Cu particles prepared under optimal conditions (Figure 5b). However, the peak intensity of these products in Figure 5b was much lower than that in Figure 5a. In other words, the yield of these corrosion products in the Fe/Cu particles prepared under optimal conditions was much lower than that in the Fe/Cu particles prepared under nonoptimal conditions. Therefore, the results also confirm that the optimal conditions could improve the operating life and reactivity of Fe/Cu particles.

In the literature, the corrosion products found in ZVI or Fe/C systems usually were iron oxides or phosphate such as Fe_3O_4 , Fe_2O_3 , FeOOH , and $\text{Fe}_3(\text{PO}_4)_2$.^{16,31–33} However, the main corrosion product found in the Fe/Cu bimetallic system was Cu_2O . The results suggest that Cu planted on the surface of Fe/Cu bimetallic particles could be oxidized by dissolved oxygen (DO) and PNP in wastewater. Additionally, the fine Cu particles generated from the direct Fe–Cu displacement reaction had a dendritic morphology (Figure 6) and might be broken into copper nanoparticles by mechanical agitation during the repeated wastewater treatment process, resulting in their high specific area. A similar Cu powder with a dendritic morphology had been prepared by the electrolysis method.^{34,35} Additionally, the activation energy for the oxidation of nano-Cu into Cu_2O was only 1–2 kJ/mol,³⁶ leading to the generation of Cu_2O when the Fe/Cu bimetallic system was operated repeatedly. According to Figure 5a,b, it is clear that the yield of Cu_2O in the Fe/Cu particles prepared under optimal conditions was much lower than that in the Fe/Cu particles prepared under nonoptimal conditions after five repeated runs. The results suggest that the planted Cu obtained under the nonoptimal conditions was easily dropped off and formed fine Cu particles that were easily oxidized into Cu_2O . Because the dropped off Cu was easily oxidized into Cu_2O , according to the

yield of Cu_2O , it is indirectly proven that the planting of Cu on the surface of Fe^0 obtained under the optimal conditions was not easy to be dropped off during the process of repeated runs.

According to the above discussion, it is clear that although the optimal conditions could improve the reactivity and operating life of Fe/Cu particles, their reactivity would still decrease with the increase of number of runs. Even if the Fe/Cu bimetallic particles were prepared under optimal conditions, the planting Cu would still be dropped off by mechanical agitation. In our previous work, it was found that a uniform and condensed Cu layer was formed on the surface of Fe^0 when EDTA was added into the planting solution.⁶ Nekouie et al. also found that some organic additives would affect the morphology and pattern of copper nano powders.³⁴ Therefore, in order to prepare the Fe/Cu bimetallic particles with high operating life and reactivity, the effect of additives in the planting solution will be investigated significantly in future work.

4. CONCLUSIONS

In this study, the effect of the preparation conditions on the physicochemical characteristics, reactivity, and operating life of the Fe/Cu bimetallic particles were investigated thoroughly. The results suggest that the highest k_{obs} (0.11858 min^{-1}) of PNP degradation could be obtained when the Fe/Cu bimetallic particles were prepared under the optimal conditions (preparation temperature, 40°C ; mixing speed, 250 rpm; Cu^{2+} concentration, 3 g/L (CuSO_4); pH of planting solution, 4.6; theoretical Cu mass loading, 0.41 g Cu/g Fe). Also, four elements including C (2.4 wt %), O (1.5 wt %), Fe (34.0 wt %), and Cu (62.1 wt %) were observed on the surface of the Fe/Cu bimetallic particles prepared under the optimal conditions. Meanwhile, the optimal theoretical Cu mass loading of the prepared Fe/Cu bimetallic particles could be decreased from 0.89 to 0.41 g Cu/g Fe, which was favorable for the reduction of production costs. During five continuous batch experiments, k_{obs} obtained by using the Fe/Cu particles prepared under the optimal conditions were always much higher than those obtained by using the Fe/Cu particles prepared under the nonoptimal conditions. According to the results of SEM-EDS and XRD analysis, it is clear that the planting Cu of Fe/Cu particles prepared under nonoptimal conditions was easily dropped off and oxidized into Cu_2O , which would limit the reactivity and operating life. Thus, the reactivity and operating life of Fe/Cu bimetallic particles could be improved significantly when they were prepared under the optimal preparation conditions.

■ ASSOCIATED CONTENT

Supporting Information

Pseudo-first-order rate constants of PNP degradation by Fe/Cu bimetallic particles with different theoretical Cu mass loadings (Table S1); effect of preparation temperature on the characteristics of Fe/Cu bimetallic particles (Figure S1); effect of high Cu^{2+} concentration (30 g/L) on the characteristics of Fe/Cu bimetallic particles (Figure S2); effect of lower mixing speed (100 r/min) on the characteristics of Fe/Cu bimetallic particles (Figure S3); effect of higher mixing speed (400 r/min) on the characteristics of Fe/Cu bimetallic particles (Figure S4); characteristics of the preparation of Fe/Cu bimetallic particles with a lower theoretical Cu mass loading, 0.05 g Cu/g Fe (Figure S5); characteristics of the preparation of Fe/Cu bimetallic particles with a higher theoretical Cu mass loading,

1.81 g Cu/g Fe (Figure S6). This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*Tel./fax: +86 18682752302. E-mail: laibo@scu.edu.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors acknowledge the financial support from National Natural Science Foundation of China (21207094) and China Science Foundation Special Funded Project (2013T60854).

■ REFERENCES

- (1) Venkatapathy, R.; Bessingpas, D. G.; Canonica, S.; Perlinger, J. A. Kinetics models for trichloroethylene transformation by zero-valent iron. *Appl. Catal., B* **2002**, 37 (2), 139–159.
- (2) Lai, B.; Zhou, Y. X.; Yang, P.; Yang, J. H.; Wang, J. L. Degradation of 3,3'-iminobis-propanenitrile in aqueous solution by Fe^0/GAC micro-electrolysis system. *Chemosphere* **2013**, 90 (4), 1470–1477.
- (3) Reardon, E. J. Anaerobic corrosion of granular iron: Measurement and interpretation of hydrogen evolution rates. *Environ. Sci. Technol.* **1995**, 29, 2936–2945.
- (4) Bransfield, S. J.; Cwiertny, D. M.; Rorerts, A. L.; Fairbrother, D. H. Influence of copper loading and surface coverage on the reactivity of granular iron toward 1,1,1-trichloroethane. *Environ. Sci. Technol.* **2006**, 40 (5), 1485–1490.
- (5) Bransfield, S. J.; Cwiertny, D. M.; Livi, K.; Fairbrother, D. H. Influence of transition metal additives and temperature on the rate of organohalide reduction by granular iron: Implications for reaction mechanisms. *Appl. Catal., B* **2007**, 76 (3–4), 348–356.
- (6) Lai, B.; Zhang, Y. H.; Chen, Z. Y.; Yang, P.; Zhou, Y. X.; Wang, J. L. Removal of *p*-nitrophenol (PNP) in aqueous solution by the micron-scale iron-copper (Fe/Cu) bimetallic particles. *Appl. Catal., B* **2014**, 144, 816–830.
- (7) Wang, K. S.; Lin, C. L.; Wei, M. C.; Liang, H. H.; Li, H. C.; Chang, C. H.; Fang, Y. T.; Chang, S. H. Effects of dissolved oxygen on dye removal by zero-valent iron. *J. Hazard. Mater.* **2010**, 182 (1–3), 886–95.
- (8) Chang, S. H.; Wang, K. S.; Chao, S. J.; Peng, T. H.; Huang, L. C. Degradation of azo and anthraquinone dyes by a low-cost Fe^0/air process. *J. Hazard. Mater.* **2009**, 166 (2–3), 1127–1133.
- (9) Chang, S. H.; Chuang, S. H.; Li, H. C.; Liang, H. H.; Huang, L. C. Comparative study on the degradation of I.C. Remazol Brilliant Blue R and I.C. Acid Black 1 by Fenton oxidation and Fe^0/air process and toxicity evaluation. *J. Hazard. Mater.* **2009**, 166 (2–3), 1279–88.
- (10) Joo, S. H.; Feitz, A. J.; Sedlak, D. L.; Waite, T. D. Quantification of the Oxidizing Capacity of Nanoparticulate Zero-Valent Iron. *Environ. Sci. Technol.* **2005**, 39 (5), 1263–1268.
- (11) Segura, Y.; Martínez, F.; Melero, J. A. Effective pharmaceutical wastewater degradation by Fenton oxidation with zero-valent iron. *Appl. Catal., B* **2013**, 136–137, 64–69.
- (12) Kim, G.; Jeong, W.; Choe, S. Dechlorination of atrazine using zero-valent iron (Fe^0) under neutral pH conditions. *J. Hazard. Mater.* **2008**, 155 (3), 502–6.
- (13) Lai, B.; Zhou, Y. X.; Yang, P. Treatment of wastewater from acrylonitrile–butadiene–styrene (ABS) resin manufacturing by Fe^0/GAC –ABFB. *Chem. Eng. J. (Amsterdam, Neth.)* **2012**, 200–202, 10–17.
- (14) Lai, B.; Zhou, Y. X.; Qin, H. K.; Wu, C. Y.; Pang, C. C.; Lian, Y.; Xu, J. X. Pretreatment of wastewater from acrylonitrile–butadiene–styrene (ABS) resin manufacturing by microelectrolysis. *Chem. Eng. J. (Amsterdam, Neth.)* **2012**, 179, 1–7.

- (15) Ma, L. M.; Ding, Z. G.; Gao, T. Y.; Zhou, R. F.; Xu, W. Y.; Liu, J. Discoloration of methylene blue and wastewater from a plant by a Fe/Cu bimetallic system. *Chemosphere* **2004**, *55* (9), 1207–12.
- (16) Lai, B.; Zhou, Y. X.; Yang, P. Passivation of sponge iron and GAC in Fe⁰/GAC mixed-potential corrosion reactor. *Ind. Eng. Chem. Res.* **2012**, *51* (22), 7777–7785.
- (17) Zheng, Z.; Yuan, S.; Liu, Y.; Lu, X.; Wan, J.; Wu, X.; Chen, J. Reductive dechlorination of hexachlorobenzene by Cu/Fe bimetal in the presence of nonionic surfactant. *J. Hazard. Mater.* **2009**, *170* (2–3), 895–901.
- (18) Koutsospyros, A.; Pavlov, J.; Fawcett, J.; Strickland, D.; Smolinski, B.; Braida, W. Degradation of high energetic and insensitive munitions compounds by Fe/Cu bimetal reduction. *J. Hazard. Mater.* **2012**, *219–220*, 75–81.
- (19) Lien, H. L.; Zhang, W. X. Nanoscale Pd/Fe bimetallic particles: Catalytic effects of palladium on hydrodechlorination. *Appl. Catal., B* **2007**, *77* (1–2), 110–116.
- (20) Brezonik, P. L. *Chemical Kinetics and Process Dynamics in Aquatic Systems*. Lewis Publishers: Boca Raton, FL, 1994.
- (21) Ahn, S. C.; Oh, S. Y.; Cha, D. K. Enhanced reduction of nitrate by zero-valent iron at elevated temperatures. *J. Hazard. Mater.* **2008**, *156* (1–3), 17–22.
- (22) Oh, S. Y.; Chiu, P. C.; Kim, B. J.; Cha, D. K. Enhanced reduction of perchlorate by elemental iron at elevated temperatures. *J. Hazard. Mater.* **2006**, *129* (1–3), 304–7.
- (23) Ghauch, A.; Tuqan, A. Catalytic degradation of chlorothalonil in water using bimetallic iron-based systems. *Chemosphere* **2008**, *73* (5), 751–759.
- (24) Ghauch, A.; Assi, H. A.; Bdeir, S. Aqueous removal of diclofenac by plated elemental iron: Bimetallic systems. *J. Hazard. Mater.* **2010**, *182* (1–3), 64–74.
- (25) Kwok, C. T.; Cheng, F. T.; Man, H. C. Synergistic effect of cavitation erosion and corrosion of various engineering alloys in 3.5% NaCl solution. *Mater. Sci. Eng., A* **2000**, *290* (1–2), 145–154.
- (26) Hamdy, A. S.; Sa'eh, A. G.; Shoeib, M. A.; Barakat, Y. Evaluation of corrosion and erosion–corrosion resistances of mild steel in sulfide-containing NaCl aerated solutions. *Electrochim. Acta* **2007**, *52* (24), 7068–7074.
- (27) Lai, B.; Chen, Z. Y.; Zhou, Y. X.; Yang, P.; Wang, J. L.; Chen, Z. Q. Removal of high concentration *p*-nitrophenol in aqueous solution by zero valent iron with ultrasonic irradiation (US-ZVI). *J. Hazard. Mater.* **2013**, *250–251*, 220–8.
- (28) Epolito, W. J.; Yang, H.; Bottomley, L. A.; Pavlostathis, S. G. Kinetics of zero-valent iron reductive transformation of the anthraquinone dye Reactive Blue 4. *J. Hazard. Mater.* **2008**, *160* (2–3), 594–600.
- (29) Zhang, Y. D. *Corrosion and Protection Manual*. Chemical Industrial Press: Beijing, 2008.
- (30) Zhu, N. R.; Luan, H. W.; Yuan, S. H.; Chen, J.; Wu, X. H.; Wang, L. L. Effective dechlorination of HCB by nanoscale Cu/Fe particles. *J. Hazard. Mater.* **2010**, *176* (1–3), 1101–1105.
- (31) Mielczarski, J. A.; Atenas, G. M.; Mielczarski, E. Role of iron surface oxidation layers in decomposition of azo-dye water pollutants in weak acidic solutions. *Appl. Catal., B* **2005**, *56* (4), 289–303.
- (32) Rao, P.; Mak, M. S.; Liu, T.; Lai, K. C.; Lo, I. M. Effects of humic acid on arsenic(V) removal by zero-valent iron from groundwater with special references to corrosion products analyses. *Chemosphere* **2009**, *75* (2), 156–62.
- (33) Reardon, E. J. Zerovalent Irons: styles of corrosion and inorganic control on hydrogen pressure buildup. *Environ. Sci. Technol.* **2005**, *39* (18), 7311–7317.
- (34) Nekouie, R. K.; Rashchi, F.; Joda, N. N. Effect of organic additives on synthesis of copper nano powders by pulsing electrolysis. *Powder Technol.* **2013**, *237*, 554–561.
- (35) Orhan, G.; Hapçı, G. Effect of electrolysis parameters on the morphologies of copper powder obtained in a rotating cylinder electrode cell. *Powder Technol.* **2010**, *201* (1), 57–63.
- (36) Liu, C. Y.; Li, Z. Y.; Zhai, Y. C.; Gong, P. W. Study on kinetics of nano-Cu powder oxidize reduction. *J. Mol. Sci. (Int. Ed.)* **2007**, *23* (1), 22–27.