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Enhanced hydrodechlorination of 4-chlorophenol by Cu/Fe bimetallic system via ball-milling

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ABSTRACT

A stable and cheap Cu/Fe bimetallic system was first prepared by ball-milling (BM) to dechlorinate 4-chlorophenol (4-CP). The enhanced hydrodechlorination activity of the resulting bimetallic system was mainly attributed to the homogenous distribution of Cu catalyst in the bulk Fe particles. The homogeneity increases the speed of electron transfer and takes advantage of hydrogenation. The prepared and used BM Cu/Fe bimetallic systems were visualized through scanning electron microscopy/energy-dispersive X-ray spectrometry (SEM/EDS) with image mapping. Dechlorination benefited the metal content, BM time and initial solution pH because there is an overall kinetic equilibrium between the rate of electron generation by Fe and the rate of hydrogenation by Cu. We note over 93% dechlorination efficiency for 50 ppm 4-CP at pH 3.0 by 100 g/L of 5% Cu/Fe (wt%) ball-milled for 8 h. The BM Cu/Fe bimetallic system showed high sustainability to coexisting ions. It is stable. Its dechlorination reactivity remained high and reproducible during five successive applications. No Cu was dissolved during the experiments. The remaining Cu can be completely recovered by re-ball-milling with Fe powders, and they showed stable dechlorination activity.

Keywords: 4-chlorophenol; Hydrodechlorination; Ball-milling; Bivalent; Wastewater; Degradation

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1. Introduction

Chlorophenols are very common environmental pollutants with high toxicity, extreme stability and resistance to natural biodegradation [1–3]. Hydrodechlorination (HDC) by zero valent metal (ZVM) is an efficient method to treat chlorophenols to the non-toxic and environment-friendly products after reduction [4–7]. Zero valent iron (ZVI) is the most frequently used metal in HDC as its reductive reactivity ($E^\theta = -0.44$ V) and environmentally friendly chemical characteristics [8]. However, several studies have found that dechlorination by ZVI alone is incomplete because some chloroogranic compounds (COCs) are recalcitrant toward ZVI reduction [9–12]. To improve its dechlorination ability, the second metal is added to promote the reaction via hydrogenation or corrosion. The second metal has a higher standard redox potential and acts as a catalyst or reaction accelerator. Precious metals such as Pd, Ag, Pt, Ni, Zn, etc. [3,5,6,13–15] are added as the catalyst and offer superior hydrogenation activity. However, these composite metal materials cannot handle the organochlorine pollutants in environmental water. The catalytic activity can be easily inhibited by inorganic salts [16], and this coexists in environmental water supplies. Copper has a relatively modest catalytic property and may solve the deactivation problem because the adsorption between copper and inorganic is weak.

Cu presents a distinct advantage over other metals in that the standard redox potential of Cu^{2+} is +0.34 V — well above that of Ni^{2+} (–0.257 V), Zn^{2+} (–0.762 V), and Fe^{2+} (–0.44 V). Obviously, Cu is more stable in thermodynamics. Transition

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metals such as Ni may cause secondary pollution due to dissolution. The Ni^{2+} was reported to reach 160 μmol L^{-1} in Ni/Cu bimetallic system [17] and 20 μmol L^{-1} in Ni/Fe bimetallic system [12] (Ni^{2+}, LD_{50}: 180–470 μmol L^{-1} for amphibians [Registry of Toxic Effects of Chemical Substances, RTECS]). The loss of material not only causes secondary pollution but also decreases its stability and durability. However, it is critical to further improve copper's activity. As shown in Table 1, the pseudo-first-order rate constant for the dechlorination of chlorophenols by Cu-catalyzed Fe is much lower than that of Ni/Fe and Pt/Fe.

Cu is normally reduced onto the Fe bulk by chemical solution deposition (CSD) [18]. From this method, Cu nanoparticles have a higher catalytic activity for the HDC reaction. Thus, the catalyst on the surface can easily flack off during Fe dissolution resulting in lower or no dechlorination activity. The desorption of Cu was significant on Cu/Fe surface prepared from CSD. This result does not meet the needs of environmental engineering. New methods for the preparation of Cu/Fe bimetallic systems with stable and higher dechlorination activity are needed. In recent years, ball-milling (BM) has been successfully used to prepare Ni–Fe bimetallic system [19,20]. BM is effective in preparing the bimetallic system with homogenously distribution and controllable mass fraction ratios. It is effective in preparing bimetallic systems with good performance for HDC of 4-chlorophenol (4-CP) [20] and monochloroacetic acid [19]. To date, only bimetallic systems containing precious metals such as Pd–Mg [21], and Ni–Fe [19,20] bimetallic system were prepared by BM for HDC. No study has yet reported cheap BM bimetallic systems via HDC reactions. In fact, versus Ni, copper has a high standard redox potential. High redox potential improves the stability as the copper ions and prevents facile flow out. Therefore, Cu/Fe BM bimetallic systems are more likely to avoid secondary pollution to the environment. It is possible to apply the actual organochlorine sewage treatment.

The primary objective of this study is to prepare a cost-effective Cu/Fe bimetallic system for 4-CP dechlorination. The dechlorination activity and material stability were evaluated. The influence of material synthesis and reaction experiments on dechlorination activity were investigated. The effects of coexisting inorganic salts in the aqueous solution were detected. The long-term performance of BM metallic system was evaluated by successive reaction and accelerated longevity experiments.

Table 1
Pseudo first-order rate constant for the dechlorination of chlorophenols by metal-catalyzed hydrodechlorination

Material	K_{obs} (h^{-1})	Particles	Reference
Cu/Fe	0.40	Ball-milling marcoparticles	This paper
Cu/Fe	0.09	Nanoparitcles	[18]
Ni/Fe	4.8	Ball-milling marcoparticles	[19]
Ni/Cu	3.8	Mechanical mixing marcoparticles	[17]
MWCNTs-Fe_3O_4–Pd/Fe	0.90	Nanoparticles	[6]
Pb/Fe	9.6	Nanoparticles	[3]
Fe with humic acid	0.081	Nanoparticles	[20]

2. Experimental

2.1. Materials

Iron (>99%, 325–400 mesh) and copper (>99%, 325–400 mesh) powders were purchased from Beijing Xingrongyuan Technology Co., Ltd. (Beijing, China). The 4-CP (>99%) and phenol (>99%) were obtained from Sigma-Aldrich Corporation. HPLC-grade methanol was purchased from Fisher Chemical (USA). All other chemicals were of reagent grade.

2.2. Preparation of BM Cu/Fe bimetallic system

BM was carried out in a planetary ball-mill (XQM-0.4A, Hunan Tenan Power Co. Ltd., China) consisting of four grinding jars (100 mL each) at a rotation speed of 500 rpm without inert gas protection under dry conditions. The weight ratio of steel balls to metal powder was 37.5:1 (wt%). The Cu and Fe mixtures at different weight ratios (wt%) were added to the jar and milled at different times. To remove passivating films that may form during milling, 10 g of the metal after BM were weighted and washed in 100 mL of HCl solution (pH 1.0) in a shaker at 200 rpm for 15 min and then washed 3 times with deionized water before use.

2.3. Dechlorination experiments

The 50 ppm 4-CP solutions were prepared by dissolving 4-CP in Milli-Q water. All dechlorination experiments were carried out in 50 mL flasks containing 30 mL of a 4-CP solution and certain amounts of BM Cu/Fe. All batch systems were carried out in conical flasks with a ground glass stopper; the reaction solutions were not protected from the atmosphere. The flasks were shaken at 220 rpm in a constant temperature shaker at 25°C. The 4-CP and phenol concentrations were measured.

2.3.1. Effects of metal contents

The Cu weight ratios in bimetallic systems were 0%, 2%, 5%, 10%, 15%, 20%, 30%, 40%, and 50%. They were milled for 6 h. Next, 3 g of the prepared bimetallic system were added to a 50 ppm solution of 4-CP at pH 2.0, and the residual 4-CP concentration was measured 10 h later.

2.3.2. Effects of BM time

A Cu:Fe weight ratio of 5%:95% was milled for 1, 3, 6, or 9 h after which 3 g of the prepared BM Cu/Fe were added to a 50 ppm 4-CP at pH 2.0. The residual 4-CP concentration was measured after 8 h of reaction.

2.3.3. Effects of initial pH

The 3 g of BM Cu/Fe (Cu content = 5 wt%, milled for 3 h) were added to 50 ppm 4-CP solutions with pH values ranging from 1.0 to 6.0. The 4-CP concentrations were measured 10 h later, and solution pH was measured every 2 h.

2.3.4. Effects of dosage

The effect of 10, 50, 100, and 200 g/L BM Cu/Fe was examined by adding the BM Cu/Fe (Cu content = 5 wt%, milled for 6 h) to 30 mL of 4-CP solution (pH = 3, 50 ppm concentration). The reaction time was 2, 4, 6, 8, or 10 h.

2.3.5. Effects of coexisting substances

The potential effects of coexisting substances were examined by adding 50 ppm Cl^-, NO^{3-}, SO_4^{2-}, Mg^{2+}, or Ca^{2+} to 50 ppm 4-CP solutions at pH 3 at a microparticle dose of 100 g/L. The residual 4-CP concentration was measured at 8 h later.

2.3.6. Successive dechlorination experiments

The 3 g of BM Cu/Fe (Cu content = 5 wt%, milled for 6 h) were added to 30 mL of 4-CP solution (50 ppm, pH = 3). The residual 4-CP concentration was detected after the 10 h reaction time. Five successive dechlorination cycles were tested. At the end of every cycle, the metal was filtered and dried using a rotary evaporator to a constant weight. The percentage loss of the material was calculated over the course of the reaction.

2.3.7. Acceleration longevity experiment

The 2.63 g of leftover BM Cu/Fe after the successive experiments were dissolved in pH = 1 HCl. The remaining metal were then filtered and dried using a rotary evaporator to a constant weight of 1.70 g. Another 1.30 g Fe powder was added to bring the Cu weight ratio to 5%, and the mixed powder was milled for another 6 h. The second-generation BM Cu/Fe were used for another five successive dechlorination cycles. The residual metal weighed 2.40 g. This was again dissolved in pH = 1 HCl solution to 1.40 g, and 1.60 g Fe powder were added for third-generation BM. Five cycles of successive dechlorination were then performed with these materials.

2.4. 4-CP and phenol analysis

Residual 4-CP and phenol concentrations in the solutions were measured using HPLC with an Inertsil ODS-SP column (5 μm, 250 × 4.6 mm id; GL Sciences Inc., Japan) at 40°C and a flow rate of 1.5 mL/min with 70% (v/v) methanol. A UV detector monitored the absorbance of the solutions at 254 nm, and the dechlorination rate was calculated using the following equation:

$$\text{Dechlorination} = C_{\text{phenol}}/(C_{\text{phenol}} + C_{\text{4-CP}}) \times 100\% \qquad (1)$$

where C_{phenol} is the molar concentration of phenol after dechlorination (μmol/L), and $C_{\text{4-CP}}$ denotes the molar concentration of 4-CP after dechlorination (μmol/L).

Dissolved Fe and Cu ions were measured with inductively coupled plasma-atomic emission spectroscopy (ICP-AES, IRIS Intrepid, Thermo Electron Corporation, USA). The scanning electron microscope (SEM; LEO-1530, LEO, Germany) was equipped with an energy-dispersive X-ray spectroscopy (EDS). It characterized the morphology and elemental mapping of the BM Cu/Fe before and after BM as well as Fe and Cu contents in different positions.

3. Results and discussion

3.1. Characterization of BM Cu/Fe bimetallic system

The prepared BM Cu/Fe bimetallic system (6 h of BM, Cu content = 5 wt%) were characterized by SEM. The SEM image in Fig. 1(a) and EDS data in Fig. 1(b) show that Fe and Cu particles can be easily distinguished from each other via their morphologies prior to BM mixing. Before BM, the Fe particles exhibited irregular shapes with a smooth surface. Cu presented a large number of small grains. After BM, the grain-like particles disappeared, and uniform particles were observed after milling for 6 h (Figs. 1(c) and (d)). The Fe and Cu contents in the selected regions of the BM microparticles were analyzed by EDS. As shown in Table 2, the Cu and Fe contents in different regions of the BM Cu/Fe were very close to the

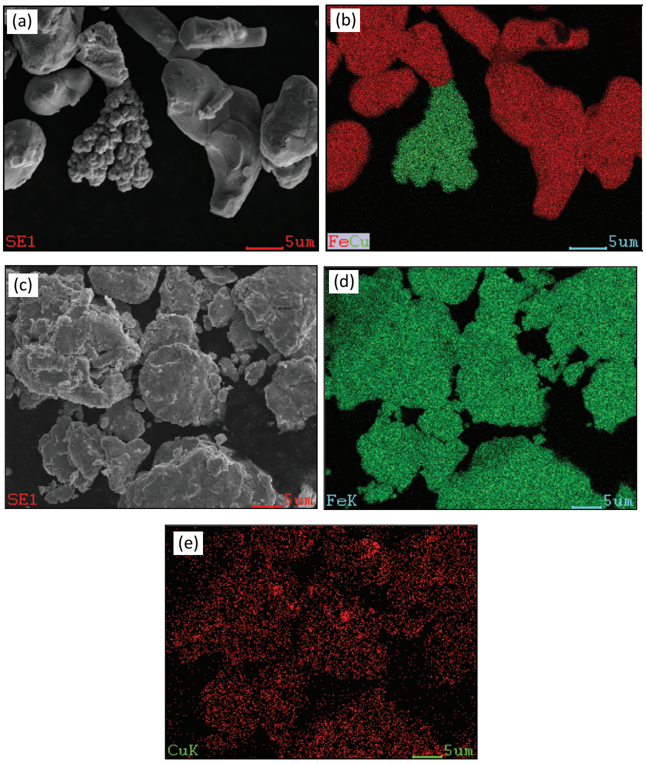

Fig. 1. (a) SEM micrograph of mixed Cu and Fe prior to BM (Cu content = 5 wt%); (b) EDS mappings of Cu/Fe; (c) SEM micrograph of the Cu/Fe bimetallic system after 6 h of BM; and (d) and (e) EDS mappings of the Fe and Cu.

Table 2
SEM-EDS analysis results of Fe, Cu, and O contents in newly prepared BM Cu/Fe bimetallic system

Metals	Weight percentage (%)
Fe	93.70
Cu	4.93
O	1.37

theoretical value of 5%. This reflects the homogenous composition in the BM bimetallic particles. To further illustrate the distribution of Fe and Cu in the BM Cu/Fe, SEM-EDS mapping was employed to characterize the Cu/Fe system. As shown in Fig. 1(d), the Cu particles were dispersed homogeneously into the Fe phase. The particles were in several microns size as seen in the enlarged micrograph in Fig. 1(c). Full homogeneity of Fe–Cu bimetallic systems with low Cu concentrations (2.5–10 wt%), which were prepared using planetary ball-mill equipment, was shown by Wille et al. [22]. They pointed out that the miscibility region was extended by BM in comparison with the traditional Fe–Cu equilibrium phase diagram. This homogeneity results in close and effective contact between Cu and Fe. Many bimetallic corrosion cells were formed through BM, which increases the speed of electron transfer during galvanic corrosion. More hydrogen will be released to participate in the dechlorination. Another advantage of these bimetallic microparticles is efficient utilization of hydrogen, which increases significantly because of the short migration route as the nanosized distribution of Cu and Fe. For the hydrogen overflow mechanism between two metals [17], atomic hydrogen can be readily transferred from the site of generation to adsorption on the Cu surface of the hydrogenation catalyst. This prevents the formation and release of molecular hydrogen. Atomic hydrogen formation is the key step to HDC, and Eqs. (3) and (4) show that dechlorination can be improved by this BM technology vs simple mixing.

Schrick et al. [23] also described the importance of close contact between microparticles for dechlorination when Ni–Fe nanoparticles prepared using the $NaBH_4$ method were used to dechlorinate trichloroethylene.

3.2. Dechlorination behavior of BM Cu/Fe bimetallic system

3.2.1. Effects of metal contents

It was reported by Fang and Al-Abed [13] and Chun et al. [24] that dechlorination was achieved by BM Cu/Fe via a catalytic HDC mechanism. Two composites of Cu and Fe served as hydrogenation catalyst and electron donor, respectively. The whole dechlorination process is shown in Eqs. (2)–(4). Fe and Cu formed galvanic couple. Fe with negative redox potential served as the electron donor (Eq. (2)) and transferred the electrons to Cu. H^+ was reduced to atomic hydrogen on the surface of Cu via accepting the electrons from Fe (Eq. (3)). Subsequently, 4-CP was dechlorinated by the newly reductive atomic hydrogen on Cu (Eq. (4)). It is infered that the best dechlorination activity was obtained when the rates of electron generation by Fe (Eq. (2)) and hydrogenation by Cu (Eqs. (3) and (4)) reach an overall kinetical equilibrium. The effects of the Cu/Fe ratio on the dechlorination were investigated. As expected, the highest dechlorination percentage was observed at Cu:Fe = 0.5:9.5(w/w ratio) (Fig. 2). After 10 h of reaction, the dechlorination of BM Cu/Fe was 76.9%. The mixed powder without BM (Cu:Fe = 0.5:9.5, w/w ratio) with the same dechlorination reaction was only 2.1% (not shown in the figure). This further confirmed that BM increased the dechlorination effect between Cu and Fe. To achieve the best synergistic effect, we studied different Cu amounts in the BM Cu/Fe. This did not benefit dechlorination.

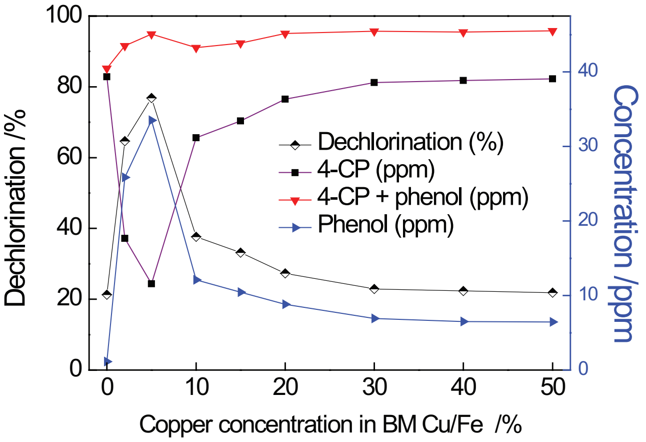

Fig. 2. Effects of Cu content (milling time = 3 h) on 4-CP dechlorination and the degradation product concentrations of phenol. The $C_{Cu/Fe}$ was 100 g/L; $C_{4\text{-CP}}$ was 50 ppm; and the initial pH was 2 for 10 h of reaction time.

$$Fe^0 - 2e^- \rightarrow Fe^{2+} \tag{2}$$

$$2H^+ + 2e^- \rightarrow 2H^* \text{ (atomic hydrogen)} \tag{3}$$

$$RCl + 2H^* \rightarrow RH + Cl^- + H^+ \tag{4}$$

Another result shown in Fig. 2 is that the concentration trend of the degradation product (phenol) is consistent with the dechlorination trend. In fact, the total concentrations of (4-CP + phenol) in all experiments are markedly constant. This implies that phenol is the dechlorination product of 4-CP. Thus, the dechlorination was calculated by $C_{phenol}/(C_{phenol} + C_{4\text{-CP}}) \times 100\%$.

3.2.2. Effects of solution pH

As shown in Eqs. (3) and (4), it can be seen that H^+ directly participated the dechlorination reaction. Therefore, pH is an important influential factor. The effect of pH on the dechlorination was investigated. It can be seen from Fig. 3 that the dechlorination percentage exhibited a first increase and subsequent decrease trend. The best dechlorination was achieved at initial pH 3 (Fig. 3(a)). This result is different from the Ni–Fe system. For Ni–Fe BM system, low pH benefits dechlorination [20] because copper has a lower catalytic activity of copper than Ni. The dechlorination process uses the synergistic effect of hydrogen generation by Fe and atomic hydrogen generation by copper. At more acidic conditions (pH 1), dechlorination rate is decreased due to ineffective dissolution loss of Fe (Eq.(5)), and a lot of hydrogen could not be formed into atomic hydrogen, but hydrogen gas (Eq. (6)), the gas released from the reaction, also may occupy the Cu surface, which inhibited the adsorption of 4-CP and decreased dechlorination. However, in high pH, the dissolution speed of iron is slow, and it inhibits the formation of atom hydrogen as well. The two factors have a unique kinetic equilibrium at pH 3. Fig. 3(b) shows the pH change profiles during dechlorination. The pH of the acid solution rapidly increased within the first hour of dechlorination, gradually

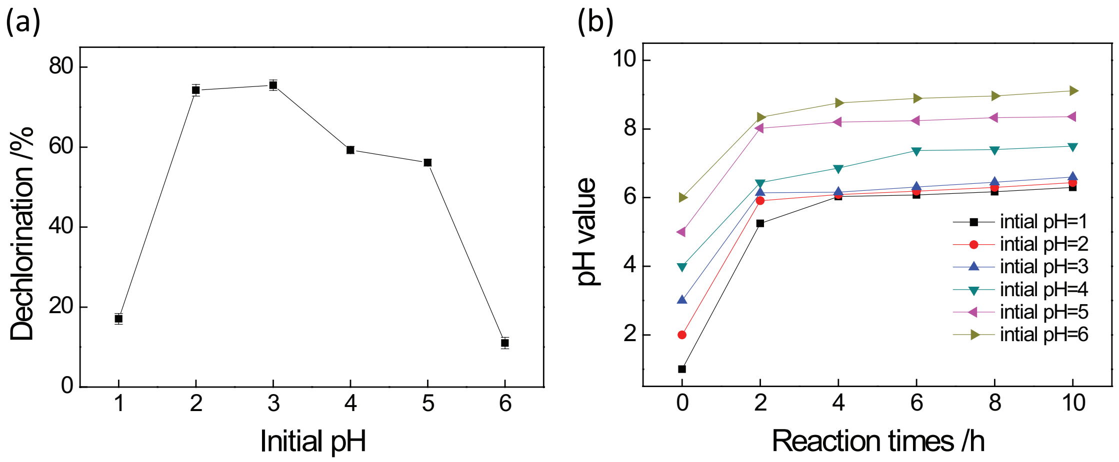

Fig. 3. Effect of initial pH on (a) 4-CP dechlorination for 10 h of reaction. Panel (b) shows the pH change profile during dechlorination. The BM time is 3 h; $C_{Cu/Fe}$ is 100 g/L; and $C_{4\text{-CP}}$ is 50 ppm.

reached a stable pH, and then finally remained relatively stable for 3 h. The dechlorination activity is stable during the reaction.

$$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2 \quad (5)$$

$$2H^* \rightarrow H_2 \quad (6)$$

3.2.3. Effects of BM time

The dechlorination percentage increased with increasing BM time from 1 to 6 h but decreased after 9 h (Fig. 4).

The reason for the influences of milling time on dechlorination is probably related to the variation of bimetallic structure and hydrogen adsorption ability [25]. BM involves heavy deformation of the powders. The formation of internal strain and dislocations in ball-milled powders can substantially increase the adsorption of hydrogen in the materials [26,27], which is beneficial for the dechlorination efficiency improvement. However, once the metal was milled for too long time, the bimetallic systems easily tended to become more intact alloy crystals with less internal strain and dislocations, which inversely decrease the dechlorination ability. The above conjectures still required to be elucidated in the future work. In the experimental conditions, 6 h was identified as the optimal Cu/Fe BM time. The BM Cu/Fe with 5% Cu milled for 6 h were used in the following experiments to balance dechlorination activity and preparation costs. The results indicate the importance of the BM technique for preparing BM Cu/Fe for 4-CP dechlorination.

3.2.4. Effects of Cu/Fe dosages

Dosages of metal are a key factor determining the reactive site amounts, the dechlorination rate and the efficiency. Without side reactions, only a low dose of Cu/Fe BM could completely dechlorinate 50 ppm of 4-CP with an initial pH of 3. However, experimental results show that if the dosage is reduced, it will reduce the rate of dechlorination (Fig. 5). This result showed that not all of the iron dissolution is for dechlorination. Some is in the form of hydrogen release, which had no effect on dechlorination. Fig. 5(a) shows the degradation rates obtained from different dosages in the entire stage follow pseudo-first-order reaction kinetics. The pseudo-first-order rate constant k_{obs} is equal to the slope of the $-\mathrm{Ln}(C_t/C_0)$ over time. The k_{obs} increased as the metal dosage increased. However, as the level of the dose increased, the value of k_{obs} per unit BM Cu/Fe ($k_{obs}/C_{Cu/Fe}$) increased from 0.00275 $L\cdot g^{-1}\cdot h^{-1}$ to 0.00403 $L\cdot g^{-1}\cdot h^{-1}$ to 0.00406 $L\cdot g^{-1}\cdot h^{-1}$ but finally decreased to 0.00323 $L\cdot g^{-1}\cdot h^{-1}$ (Fig. 5(b)). To balance the reaction rate and material efficiency, a 100 g/L metal dose is suitable for dechlorination.

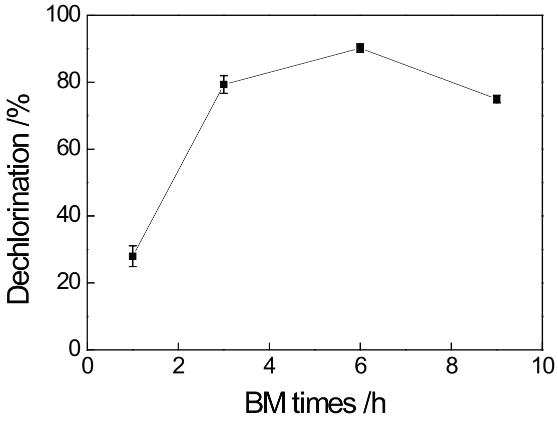

Fig. 4. Effect of BM times on 4-CP dechlorination; $C_{Cu/Fe}$ is 100 g/L; reaction time is 8 h; $C_{4\text{-CP}}$ is 50 ppm; and initial pH ~ 3.

3.2.5. Effects of coexisting substances

In real world water samples, 4-CP pollutants often coexist with interfering substances such as the anions Cl^-, SO_4^{2-}, and NO^{3-} and the cations Ca^{2+} and Mg^{2+}. To determine possible interfering species, Cl^-, SO_4^{2-}, NO_3^-, Ca^{2+}, and Mg^{2+} were added to the 4-CP solution at 50 ppm and reacted with BM Cu/Fe for 8 h. Versus the control experiment, the NO_3^-, Mg^{2+}, Ca^{2+}, and Cl^- have little influence on the

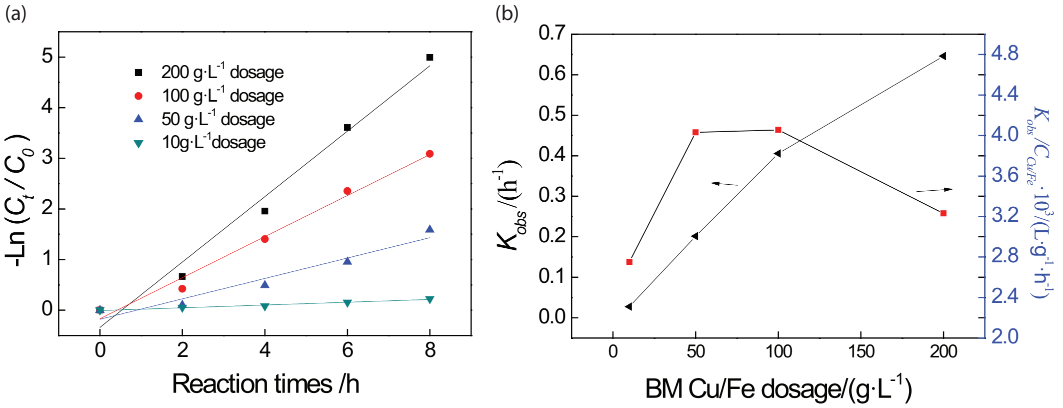

Fig. 5. (a) Kinetic fitting at different BM Cu/Fe concentrations and (b) relationship between k_{obs} and BM Cu/Fe dosage including bimetal with 6 h of BM time. The $C_{4\text{-CP}}$ was 50 ppm with an initial pH of 3.

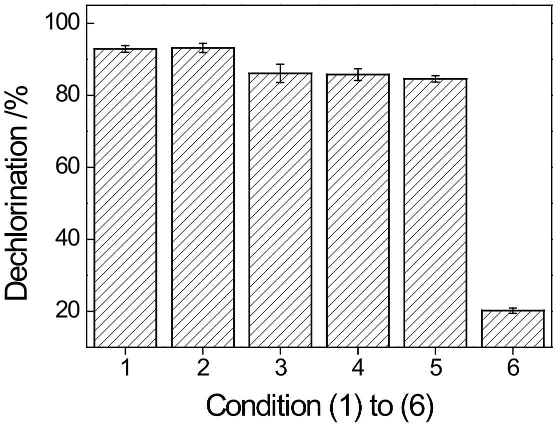

Fig. 6. Effect of coexisting cations and anions on dechlorination. Condition (1) was without any added ions; Condition (2) to (6) were 50 ppm NO_3^-, Mg^{2+}, Ca^{2+}, Cl^-, or SO_4^{2-}. The reaction conditions were $C_{Cu/Fe}$ at 100 g/L, $C_{4\text{-CP}}$ at 50 ppm, an initial pH of 3, and a reaction time of 8 h.

dechlorination (Fig. 6). However, SO_4^{2-} seriously inhibited dechlorination; the dechlorination of control experiment was nearly fourfold vs. the experiment with SO_4^{2-}. This is because SO_4^{2-} may form inner-sphere complexes that adsorb on the metal surface and impede 4-CP from progressing to the metal surface to degrade [28]. Even if passivation occurs, washing with pH 1 HCl is a suitable strategy to recover activity.

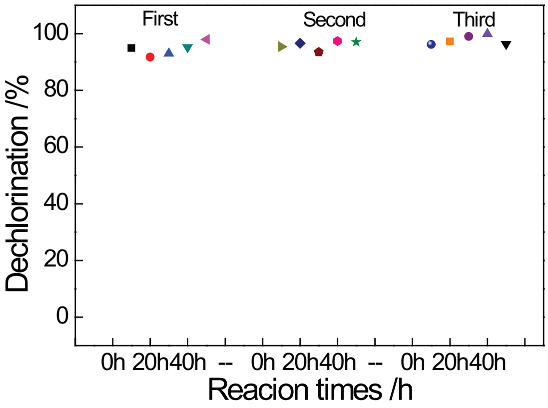

Fig. 7. Dechlorination activity of the BM Cu/Fe over five successive uses (First), successive dechlorinations for the second BM (Second), and the third BM (Third).

Table 3
SEM-EDS analysis results of Fe, Cu, and O contents in used BM Cu/Fe bimetallic system

Metals	Weight percentage (%)
Fe	87.26
Cu	5.81
O	5.03

3.2.6. Successive reduction activity

During the dechlorination, the iron dissolution is low with an initial pH ~ 3, and with a 100 g/L dose of BM Cu/Fe. According to the calculations, there can be multiple batches of water treatment, which is the advantage of the result. Another problem is whether the copper in the bimetallic system could be used repeatedly. To evaluate the stability and longevity of the BM Cu/Fe, the bimetallic powder was used repeatedly in five successive cycles. Stable dechlorination percentages were achieved. The percentage of dechlorinated 4-CP remained between 93% and 98% over five successive cycles (Fig. 7 shows the first cycle). After the five cycles of dechlorination, 2.63 g BM Cu/Fe were left over (initial metal amount was 3 g); the average material loss per cycle was 2.7%. Copper and iron ions were detected at the end of every cycle, and iron ion concentrations were 36–40 ppm. The remaining powder was characterized with SEM-EDS. The Cu and Fe continued to show a homogenous distribution. Versus composites of the fresh BM Cu/Fe (Table 2), the Fe content clearly decreased while O obviously increased. The Cu in the residual BM Cu/Fe increased (Table 3).

Copper ion was not detected out in the solution, due to the high standard redox potential of Cu^{2+} ions (+0.34 V). Two metals can make a galvanic couple with greater potential difference. This makes it faster for the metal with a high potential to accelerate the corrosion of the metal with low potential. Thus, copper accelerates the loss of Fe and protects itself [29,30]. Versus Ni–Fe and Ni–Cu, the Cu/Fe avoids the secondary pollution of material. Iron ions are not toxic. The test results once again confirm that the material could avoid secondary pollution of heavy metal ions.

As shown in Fig. 2, the degradation activity would be reduced when the copper content increased over 5%. This would affect the dechlorination, with the loss of Fe during the successive dechlorination.

To further prove the recyclability of copper and the long-term use of BM Cu/Fe, the 2.63 g leftover BM Cu/Fe were dissolved in pH = 1 HCl until 1.70 g metal left. And another 1.30 g Fe powder was added to it for the second BM preparation. The second-generation BM Cu/Fe was used for another 5 successive dechlorination experiments. At the same step, third-generation BM Cu/Fe was prepared and used for next 5 cycles of dechlorination. 93%–97% dechlorinations were got in the second and third 5 successive cycles (Fig. 7). Cu can be used repeatedly during the preparation and dechlorination. The results showed the high stability of the BM material.

4. Conclusion

The BM Cu/Fe bimetallic system showed good catalytic activity and stable dechlorination properties for 4-CP. It can be used repeatedly without passivation. The stable and extensive dechlorination of 4-CP may be attributed to the homogeneous distribution of nanosized Cu catalysts in Fe as well as the synergistic effect between Cu and Fe. The BM Cu/Fe bimetallic system proposed here can accommodate some anions and cations. Cu could not be dissolved. However, the presence of SO_4^{2-} anions must be controlled. Acid washing is effective for regenerating deactivated materials once a passivating film forms over the BM Cu/Fe. This study demonstrated that BM is a promising method to improve the dechlorination activity of cheap metal microparticles. The long-term reuse experiments showed that BM Cu/Fe were stable with dechlorination. Copper can be used repeatedly. BM Cu/Fe bimetallic system could be used as a potential material to remediate COCs in water because it can avoid secondary pollution of heavy metal ions.

Acknowledgments

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