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Chemosphere 57 (2004) 1173–1180

CHEMOSPHERE

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Removal of Cu(II) from aqueous solution in a fluidized-bed reactor

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Received 14 August 2003; received in revised form 6 August 2004; accepted 10 August 2004

Abstract

In this study, a fluidized-bed reactor (FBR) was employed to treat copper-containing wastewater by mean of copper precipitation on the surface of sand grains. The conditions for optimum copper removal efficiency were also investigated. This technology was controlled so as to keep supersaturation low to induce the nucleated precipitation of copper coating on the sand surface in an FBR. The effects of relevant parameters, such as the pH value, the molar ratio of $[C_T]$ to $[Cu^{2+}]$, hydraulic loading and the types of chemical reagents used, were examined. The experimental results indicated that 96% copper removal efficiency could be achieved when the influent copper concentration was $10\,mg\,l^{-1}$. The optimum chemical reagent was Na_2CO_3; the molar ratio of $[C_T]/[Cu^{2+}]$ was 2, and the optimal hydraulic loading was not be more than $25\,m\,h^{-1}$. In addition, preventing homogeneous nucleation in the FBR was an important operation parameter. Homogeneous nucleation and molecular growth would lead to undesirable microparticle formation in the effluent. A good mixture of carbonate and copper in the presence of sand grains could reduce the level of homogeneous nucleation in the bottom of the reactor. Energy dispersive analysis (EDS) of X-rays provided insight into the copper coating on the sand surface, and element analysis indicated the weight percentages of $CuCO_3$ and $Cu(OH)_2$ in precipitate.

Keywords: Fluidized-bed reactor; Copper; Supersaturation; Precipitation; Homogeneous nucleation

1. Introduction

With industrial advances, copper has become one of the most widely used metals. The primary sources of copper discharge from industries include printed circuit boards, metal finishing industries, tannery operations, chemical manufacturing and mining drainage. As copper is a highly toxic element, the removal of Cu^{2+} from wastewater has been the subject of many studies (Sarfarazi and Ghoroghchian, 1994; Keane, 1998; Ho, 2003; Lai and Lin, 2004).

The most commonly used treatment method for copper removal from industrial wastewater is based on the chemical precipitation process. In this process, copper generally forms hydroxide precipitate, to which caustic is added to adjust the wastewater to alkaline pH. This process usually generates huge amounts of sludge, which have to be disposed off. An alternative method for minimizing the generation of sludge has been developed and applied.

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0045-6535/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.chemosphere.2004.08.028

The fluidized-bed reactor (FBR) technique process has been used in various water and wastewater treatment plants. The process of crystallizing $CaCO_3$ in FBR has been applied to soften drinking water (van Dijk and Wilms, 1991; Harms and Robinson, 1992). Nielsen et al. (1997) tested the fluidized-bed technique at a coal-fired power station using wastewater from a flue gas de-sulphuration unit to study the removal of heavy metals from the wastewater. With this technique, manganese or ferrous ions and an oxidation agent (e.g., O_2, H_2O_2, $KMnO_4$) are continuously added to the wastewater. An adsorptive granule of either FeOOH or MnO_2 is generated as a coating on the surface of the carrier material. Ferric oxyhydroxide and manganese dioxide have significant adsorptive properties in relation to dissolved metals. Aktor (1994) used a similar process to coat catalyzing FeOOH on a carrier medium in FBR to catalyze the redox reaction between ferrous iron and chromate. Chou and Huang (1999) prepared the supported FeOOH in an FBR and applied the catalyst to oxidize benzoic acid. For the recovery of heavy metals, a precipitation reagent of carbonate was dosed into a reactor to remove heavy metals through the crystallization of metal carbonate on the surface of sand grains (Scholler et al., 1987; Wilms et al., 1992; Chen and Yu, 2000). These metal carbonates can be reused after the pellets are dissolved in acid. Anions have been used by the semiconductor industry to remove fluoride through calcium fluoride crystallization (van den Broeck et al., 2003), and phosphate removal from wastewater by using calcium phosphate crystallization and struvite (MAP, $MgNH_4PO_4$) in an FBR (Seckler et al., 1996; Battistoni et al., 2002) has also been studied.

The essential condition for heavy metal removal in an FBR is supersaturation of the reactant solution. Supersaturation acts as a driving force for crystallization on the media in an FBR. When the reactant solution reaches supersaturation, nucleation occurs immediately, but the supersaturation level should not be so high to prevent homogeneous nucleation.

In this study, we aimed to use the method of nucleated precipitation in an FBR to remove copper from industrial wastewater. In the FBR operation, a seed material (e.g., quartz sand) was placed into the reactor, and the chemicals were pumped vertically to fluidize the sand bed. The fluidized sand provided a large specific area for copper nucleation and crystallization. Copper was removed in the form of copper precipitate and coated onto the surface of the sand grains.

2. Materials and methods

2.1. Process description

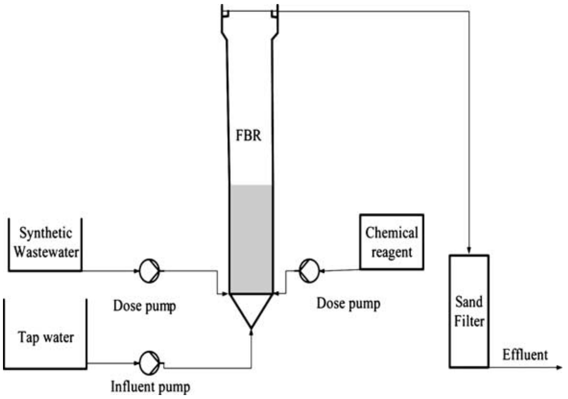

Fig. 1. Schematic diagram of the experimental set-up.

The experimental set-up is shown in Fig. 1. A clear acrylic column which served as the FBR had an inner diameter of 3 cm, a height of 120 cm, and a larger cross-sectional area of weir. A 0.2 mm stainless steel net was installed at the bottom of the reactor to distribute the influent flow smoothly. The reactor was filled with quartz sand that was 0.25–0.42 mm in diameter and had a density of $1560\,kg\,m^{-3}$. The static height of the original packed sand in the reactor was 45 cm. A sand filter which in an acrylic column having a height of 20 cm and a diameter of 10 cm was used to polish the effluent quality. The media (sand) with an average diameter of 1.0 mm was packed to a height of 10 cm from the bottom.

A stock solution of copper ions and precipitation reagent were prepared by dissolving $CuCl_2 \cdot 2H_2O$ and Na_2CO_3 in tap water. The synthetic copper-containing wastewater and precipitation reagent (Na_2CO_3) were injected into the reactor from the sides of the reactor at the bottom using a peristaltic pump (Cole-Parmer Instrument Co., USA), and tap water was fed constantly from the bottom of the reactor using a pump (Cole-Parmer Instrument Co., USA) at a given flow rate in order to dilute the chemical concentration and fluidize the sand bed. During this operation, all the influent (Cu^{2+}, chemical reagent and tap water) was added at a constant flow rate. The samples were taken from the effluent of the FBR and the sand filter reactor at every 24 h interval. The pH values of the solutions in the FBR effluent were also measured.

2.2. Batch experiment

Batch experiments were carried out in a 1000 ml beaker, and no sand was added to determine the pure precipitate composition. $CuCl_2 \cdot 2H_2O$ and Na_2CO_3 were dissolved in deionized water. The initial copper concentration was $20\,mg\,l^{-1}$, and the $[C_T]/[Cu^{2+}]$ ratio was 2 (C_T is the total carbon concentration). After standing for 24 h, the precipitate was collected and freeze-dried, and then analyzed using elemental analyzer (HERAEUS

VarioEL-III, Germany) to determine the C and H content.

2.3. Determination of the copper content

For filtered copper, the samples were filtered through Whatman 41 filter paper (20–30 μm), and filtrates were acidified using HNO_3 and stored in a refrigerator at 4 °C and then analyzed. The total copper concentration was determined by using an unfiltered sample after vigorous digestion with concentrated HNO_3. The copper concentration was analyzed using an atomic absorption spectrometry spectrophotometer (Perkin Elmer AAnalyst 800). The amount of copper removed was calculated indirectly based on the difference between the influent and effluent concentrations of the solutions.

2.4. Analysis of the characteristics of copper-coated sand

After an operation time of 178 h, the copper-coated sand grains were saturated and drained. The sand grains were then air dried and analyzed to determine the surface shape and composition using a scanning electron microscope with an energy dispersive X-ray spectrum (SEM-EDS, Philips). The copper-coated sand grains subjected to EDS analysis were coated with a thin carbon film to prevent a charge from having any effect during the EDS operation.

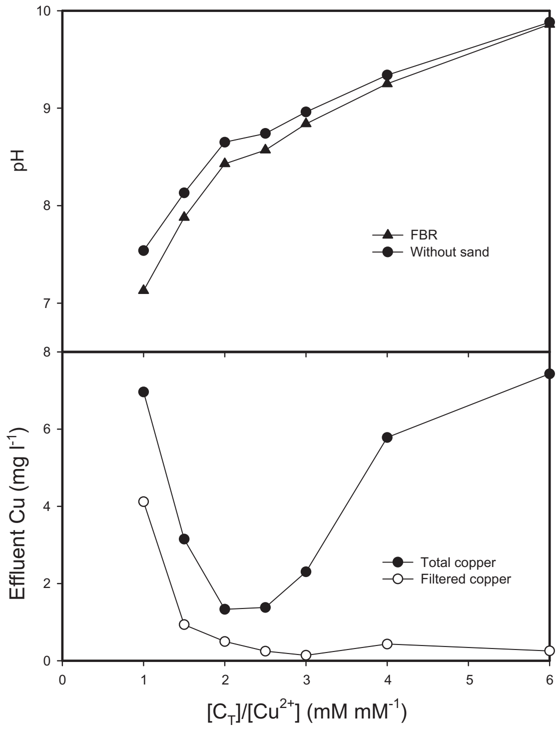

Fig. 2. Variation of the pH value of the effluent from the FBR with and without sand and of the copper concentration in the effluent under different molar ratios of $[C_T]$ to $[Cu^{2+}]$ (influent $Cu^{2+} = 10\,mg\,l^{-1}$, hydraulic loading = $20\,m\,h^{-1}$).

3. Results and discussion

3.1. Effects of the $[C_T]/[Cu^{2+}]$ ratio and pH value

The change of the pH value of the effluent from the FBR with and without sand and the variation of the effluent copper concentration with the molar ratio of $[C_T]/[Cu^{2+}]$ are shown in Fig. 2. The pH value of the effluent from the FBR without sand was measured by collecting the samples which flowed through the empty FBR (no sand was added). The difference between the total copper concentration and filtered copper concentration in the effluent from the FBR is a measure of the microparticle concentration in the water phase of the fluidized bed.

From the results of the pH change between the sand bed and empty bed, it can be seen that the pH decreased slightly after the solution passed through the FBR, and that the change became less noticeable when the $[C_T]/[Cu^{2+}]$ molar ratio increased. The lower the $[C_T]/[Cu^{2+}]$ ratio, the lower the pH of the solution and the higher the HCO_3^- concentration. The result indicated at pH 8 even though bicarbonate was predominant (Stumm and Morgan, 1996), the copper carbonate could be precipitated, which was confirmed by the pH decrease caused by CO_2 released into the sand bed. Equilibrium was achieved when

$$Cu^{2+} + 2HCO_3^- \leftrightarrow CuCO_3 + CO_2 + H_2O. \qquad (1)$$

From the copper removal results, the effluent total copper concentration decreased as the $[C_T]/[Cu^{2+}]$ ratio increased from 1.0 to 2.0 and then increased at $[C_T]/[Cu^{2+}]$ ratio >2.5; the effluent pH value also increased with the molar ratio. It should be noted that when the molar ratio was 2.0 and the respective pH value was 8.4, the total copper concentration in the FBR effluent was $1.33\,mg\,l^{-1}$ and the copper removal efficiency was 87%. When the ratio exceeded 3, the effluent copper concentration increased rapidly with the increased $[C_T]/[Cu^{2+}]$ ratio.

Fig. 2 shows that the optimum molar ratio of $[C_T]/[Cu^{2+}]$ was between 2 and 2.5, and the optimum effluent pH was between 8.4 and 8.6. Copper precipitate coated onto the surface of sand is a fundamental part of the copper removal method described herein and is explained by the following equations:

$$Cu^{2+} + CO_3^{2-} \rightarrow CuCO_3; \quad K_{sp} = 10^{-9.9}, \qquad (2)$$

$$Cu^{2+} + 2OH^- \rightarrow Cu(OH)_2; \quad K_{sp} = 10^{-19.7}. \qquad (3)$$

In theory, copper precipitate is formed when the degree of solubility exceeds the solubility product constant (K_{sp}) of copper carbonate and hydroxide. Rising pH values cause a shift to the left in the chemical equilibration described by Eq. (4) and causes the concentrations of hydroxide and carbonate to increase, thereby increasing the degree of supersaturation of the copper carbonate and hydroxide:

$$CO_3^{2-} + H_2O \leftrightarrow HCO_3^- + OH^-. \qquad (4)$$

The rise in pH increased the driving force of heterogeneous nucleation which caused nucleated precipitate to be coated onto the sand surface, leading to a lower copper concentration in the reactor effluent. However, when the pH increased too much, this resulted in a highly supersaturated solution. Under high supersaturation, homogeneous nucleation of copper carbonate and copper hydroxide tended to occur and molecules were not coated onto the sand surface. These precipitates then went through the sand bed and appeared in the effluent. Homogeneous nucleation occurred when the effluent became turbid and the total copper concentration increased.

3.2. The effects of the hydraulic loading

Fig. 3 shows that the effluent copper concentration of the effluent from the FBR increased as the hydraulic loading increased from 10 to 40 m h^{-1}. The filtered copper concentration in the FBR effluent and the total copper concentration from the sand filter were less than 1 mg l^{-1} under different hydraulic loadings. Under different hydraulic loadings, the filtered copper concentration was almost the same as the total copper concentration from the sand filter.

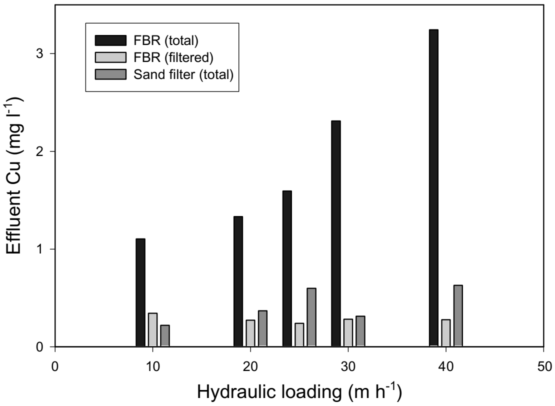

Fig. 3. Effects of the hydraulic loading on the copper concentration in the effluent (influent Cu^{2+} = 10 mg l^{-1}, [C_T]/[Cu^{2+}] molar ratio = 2).

Due to the pore size of filtered paper was 20–30 μm, the results revealed that the size of the microparticles uncoated on sand surface was about 20–30 μm. To prevent higher effluent copper concentration, the hydraulic loading should not be greater than 25 m h^{-1}, and the empty bed detention time should not be less than 2.88 min.

The factors which caused the total copper concentration to increase with the hydraulic loading in the FBR included the erosion of granulates in the fluidized bed and the increasing porosity of the microparticles in the water phase among the fluidized grains (van Dijk and Wilms, 1991; Wang et al., 1993; Seckler et al., 1996). There was always competition between the copper coated onto the sand surface and the microparticles that formed in the water phase. As the hydraulic loading increased, the surface area of the sand per column volume decreased, and the porosity of the fluidized bed increased. The bed porosity and expansion ratio can be calculated as follows:

$$\text{B.P(bed porosity)} = \left[1 - \frac{V}{H \times A}\right], \qquad (5)$$

$$\text{E.R. \%(expansion \%)} = \frac{H}{h} * 100, \qquad (6)$$

where V = the volume of sand in the FBR; H = the height of expanded fluidized bed; A = the cross-section area of the FBR; h = the static height of the FBR.

The bed porosity and expansion ratio under various hydraulic loadings are shown in Table 1. It indicates that an increase in the fluidized velocity caused the surface area per volume to decrease and the porosity to increase, thus causing the particle growth and particle discharge in the effluent. On the other hand, when the hydraulic loading was lower, the microparticles were not washed out and the erosion of granulates did not increase, thus resulting in copper precipitation on the sand surface.

Table 1
The bed porosity and expansion ratio under different hydraulic loadings

Hydraulic loading (m h^{-1})	h (cm)	H (cm)	Bed porosity	E.R. (%)
10	45	60	0.25	133
20	45	76	0.40	169
25	45	80.5	0.44	179
30	45	85	0.47	189
40	45	97	0.54	216

3.3. The selection of chemical reagents

In this experiment, we used different chemical reagents (Na_2CO_3, NaOH and Na2S) as the base source and compared the copper concentrations resulting from these different reagents. The molar ratio of the chemical reagent to copper was 2, the influent copper concentration $10\,\mathrm{mg\,l^{-1}}$, and the hydraulic loading at $20\,\mathrm{m\,h^{-1}}$. The results are shown in Fig. 4, indicate that the optimum chemical reagent for copper removal in the FBR was Na_2CO_3. In this case, it was found that the CuS particles were very fine and could easily pass through the pores of the filter paper (20–30m), thus increasing the concentration in the filtered solution. In addition, the concentration after sand filtering was high.

In the FBR, precipitation was carried out to remove copper ions. For copper sulphide, the pK_{sp} was about 35 and was much greater than that for hydroxide or carbonate. That is, a very small concentration of copper could react with sulphide to form copper sulphide. In theory, the copper concentration of the sulphide in the FBR effluent should be lower than that of hydroxide or carbonate. However, in this study, we used nucleated precipitation technology to carry out the copper precipitation onto the sand surface. In the case of copper sulphide, a very low copper concentration and sulphide would lead to supersaturation. Under the experimental conditions used in our experiment, the level of supersaturation was too high; hence, homogeneous nucleation occurred and particle growth in water phase was dominant during coating of the sand surface. The microparticles went through the sand bed, thus increasing the copper concentration in the effluent.

The saturation index (SI) was also considered (van den Broeck et al., 2003). The SI is a measure of the local saturation at the bottom of the reactor before any reaction occurs. The SI values for $CuCO_3$, $Cu(OH)_2$ and CuS can be calculated as follows:

$$\mathrm{SI} = \log\frac{[\mathrm{Cu}^{2+}][\mathrm{CO}_3^{2-}]}{K_{sp}} = \log\frac{[\mathrm{Cu}^{2+}][\mathrm{CO}_3^{2-}]}{10^{-9.9}}, \tag{7}$$

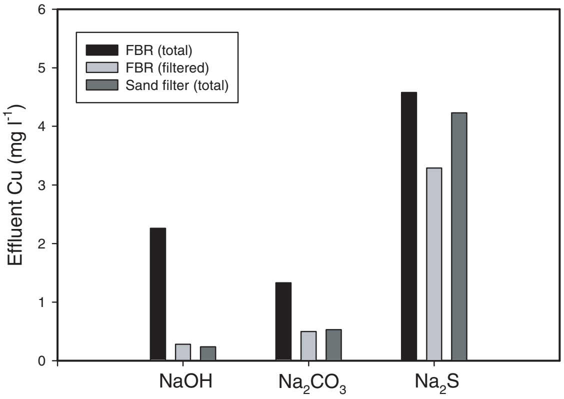

Fig. 4. Effects of different chemical reagents on the copper concentration in the effluent (influent $Cu^{2+} = 10\,\mathrm{mg\,l^{-1}}$, $[C_T]/[Cu^{2+}]$ molar ratio = 2, hydraulic loading = $20\,\mathrm{m\,h^{-1}}$).

$$\mathrm{SI} = \log\frac{[\mathrm{Cu}^{2+}][\mathrm{OH}^-]^2}{K_{sp}} = \log\frac{[\mathrm{Cu}^{2+}][\mathrm{OH}^-]^2}{10^{-19.7}}, \tag{8}$$

$$\mathrm{SI} = \log\frac{[\mathrm{Cu}^{2+}][S^{2-}]}{K_{sp}} = \log\frac{[\mathrm{Cu}^{2+}][S^{2-}]}{10^{-35.2}}, \tag{9}$$

where [·] = the molar concentration in M before any reaction occurs.

When the concentration of the influent Cu^{2+} was $10\,\mathrm{mg\,l^{-1}}$ and the molar ratio was 2, the calculated SI values for $CuCO_3$, $Cu(OH)_2$ and CuS were 2.6, 8.9 and 27.9, respectively. When the molar ratio was 1 for both $[OH^-]/[Cu^{2+}]$ and $[S^{2-}]/[Cu^{2+}]$, the SI values for $Cu(OH)_2$ and CuS were 8.3 and 27.6, respectively, that is much higher than 2.6.

A high SI value will led to higher homogeneous nucleation and lower coating efficiency. Microparticles easily appeared at the bottom of FBR. The results indicate that the K_{sp} was an important factor for selecting a suitable chemical reagent, and that the K_{sp} should not be so low as to prevent homogeneous nucleation.

In addition, we used NaOH to control the effluent pH value and reduce the chemical reagent concentration of C_T. We also compared the copper removal efficiency achieved by using only Na_2CO_3 to control the pH value.

The effect of a molar ratio of $[C_T]/[Cu^{2+}]$ of 1.5 with a fixed pH value (pH = 8.4, the same as when the molar ratio of $[C_T]/[Cu^{2+}]$ was 2) on the copper concentration in the effluent is shown in Fig. 5. From these results, it can be seen that when the pH of the effluent was fixed, using Na_2CO_3 as a base source only for copper removal was better than using NaOH or Na_2CO_3, but that the copper removal efficiency with these two was almost the same.

From the results, we compared the supersaturation of copper carbonate. At the same pH, the driving force at the molar ratio of $[C_T]/[Cu^{2+}]$ 1.5 was not high enough for the crystallization on the sand compared with the case when the molar ratio of $[C_T]/[Cu^{2+}]$ was 2.0. In this case, it was found that the pH value needed to be kept within a suitable range, and that the SI value needed to be high enough to provide enough driving force as discussed in Section 3.1 but not so high as to promote homogeneous nucleation.

3.4. The effects of homogeneous nucleation

In an FBR, homogeneous nucleation is an unwanted process that may occur in the bottom of the reactor (van Dijk and Wilms, 1991; Chou et al., 2004). In order to determine the effects of homogeneous nucleation on copper removal efficiency, two different dosing conditions were examined as follows: one involved a 10cm

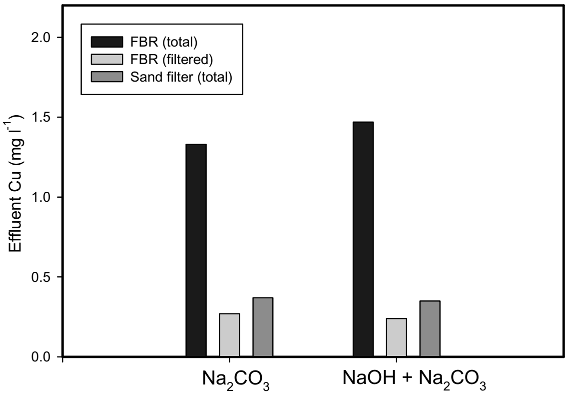

Fig. 5. The copper concentration in the effluent at a fixed pH value under different molar ratios of $[C_T]/[Cu^{2+}]$ (influent $Cu^{2+} = 10\,mg\,l^{-1}$, hydraulic loading $= 20\,m\,h^{-1}$; when $[C_T]/[Cu^{2+}] = 1.5$, the pH value was controlled at 8.4, the same as when the molar ratio was 2).

diameter FBR and a dose of carbonate in a copper-containing wastewater storage tank before FBR to result in homogeneous nucleation; the other involved normal operation. After the operation reached saturation, the sand grains were withdrawn and air dried. The dried sand grains were then subjected to SEM analysis.

Fig. 6 shows the SEM graphs depicting the different patterns of copper precipitate that formed on the sand surface. It can be seen from the microphotographs that when homogeneous nucleation occurred while carbonate was reacted with copper ions before operation of the FBR, powder precipitate formed on the surface of the sand, and the mechanical stability was weak (Fig. 6a). Grains sampled following normal operation in which copper was reacted with carbonate in the sand bed showed an irregular surface on which aggregated particles formed (Fig. 6b).

Analysis revealed several findings regarding homogeneous nucleation in the FBR. One was homogeneous nucleation and growth, resulting in a breakthrough in the FBR. The others were that the small particles during homogeneous nucleation could be coated onto the sand surface, but that the mechanical stability of the grains was weak, and that as the hydraulic loading increased, erosion in the fluidized bed reactor increased and small fragments of copper precipitate appeared in the effluent of the reactor, thus increasing the total copper concentration.

The method used to mix carbonate and copper was important to prevent homogeneous nucleation. When carbonate and copper were mixed in the sand bed, the turbulence motion of the sand could effectively reduce the local supersaturation and prevent homogeneous nucleation.

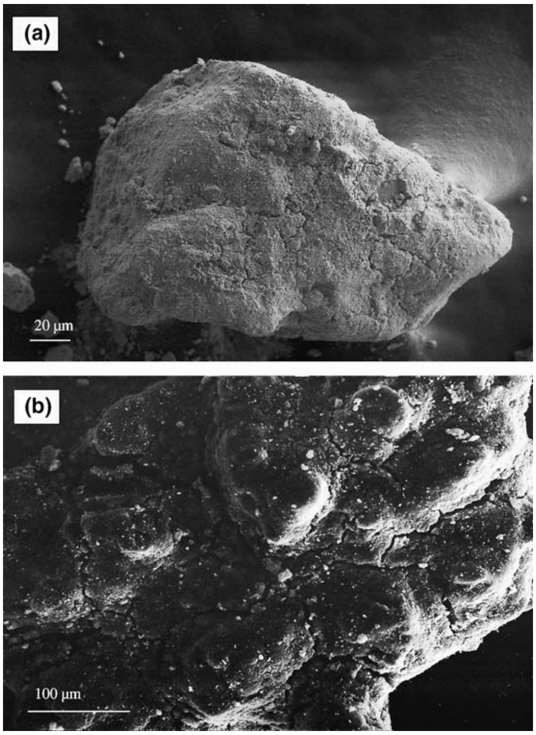

Fig. 6. (a) SEM view of a grain taken after carbonate and copper were pre-mixed then pumped into the FBR; (b) SEM view of a grain taken following normal operation.

3.5. Determination of precipitate composition

To determine the composition of the copper precipitate, two experiments were conducted. In one, deionized water was used in batch tests to prevent interference from other ions, and in the other, copper-coated sand grains were collected and analyzed to determine the precipitate composition. The results for freezed-dry pure precipitate are shown in Table 2, where the percentages of C and H were measured using an element analyzer, while the percentages of copper carbonate ($CuCO_3$%) and copper hydroxide ($Cu(OH)_2$%) were calculated. The percentages of copper carbonate and copper hydroxide were calculated based on C and H contents.

Table 2 shows that the total weight percentages of $CuCO_3$ and $Cu(OH)_2$ were over 99%, which indicated that the pure copper precipitate was composed of $CuCO_3$ and $Cu(OH)_2$.

Table 2
Composition of the pure precipitate from batch test

Cu^{2+} ($mg\,l^{-1}$)	$[C_T]/[Cu^{2+}]$ ($mM\,mM^{-1}$)	C (%)	H (%)	$CuCO_3$ (%)	$Cu(OH)_2$ (%)
20	2	4.44	1.10	46	54

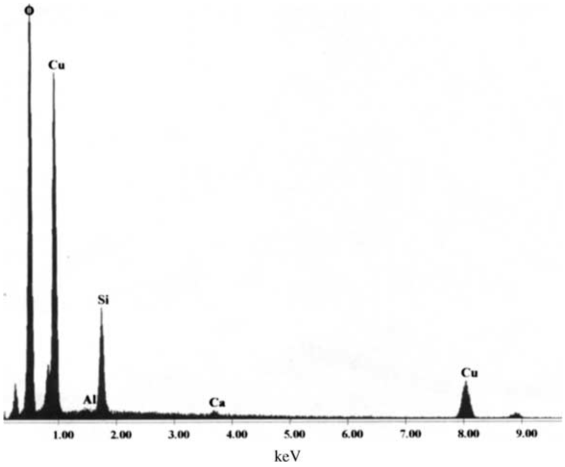

Fig. 7. EDS spectrum of the copper coated sand grains.

Furthermore, EDS analysis was performed to analyze the elemental constitution of copper-coated sand grains. Fig. 7 displays a spectrum of virgin sand coated with copper ions and indicates that copper was the principal metal element coated onto the sand. Although an overdose of the chemical reagent $\mathrm{Na_2CO_3}$ was added, no Na signal was detected in this analysis. In addition, the calcium in tap water also reacted with carbonate and coated on the sand surface. In short, EDS analysis provided direct evidence that copper precipitates were coated onto the surface of the sand.

4. Conclusions

Based on the findings obtained in this study, the following conclusions can be drawn:

1. The optimum molar ratio of $[\mathrm{C_T}[/[\mathrm{Cu}^{2+}]$ was 2–2.5, and the respective pH range was 8.4–8.6. In this pH range, the copper removal efficiency that could be reached as 96% when the influent copper concentration was $10\,\mathrm{mg\,l^{-1}}$.
2. As for the effect of the hydraulic loading on copper removal, copper removal decreased as the hydraulic loading increased. This was caused by erosion of the granulates in the fluidized bed and the porosity that caused microparticles to form in the water phase among the fluidized grains. Under these circumstances, the hydraulic loading should not be exceeded $25\,\mathrm{m\,h^{-1}}$.
3. As for the selection of chemical reagents, K_{sp} has been found to be an important parameter. When K_{sp} is too high, heavy metal becomes soluble, and when K_{sp} is too low, homogeneous nucleation can easily take place. In this investigation, the optimum chemical reagent was $\mathrm{Na_2CO_3}$, and when the influent Cu^{2+} was $10\,\mathrm{mg\,l^{-1}}$ the optimum $[\mathrm{C_T}]/[\mathrm{Cu}^{2+}]$ molar ratio was 2.
4. Homogeneous nucleation is an undesirable process that can occur in the bottom of the reactor. In our experiment, small particles during of homogeneous nucleation could be coated onto the sand surface, but the mechanical stability of the sand grains was weak. Mixing carbonate and copper in the presence of sand grains could effectively reduce the local supersaturation and prevent homogeneous nucleation.

Acknowledgments

The authors express their gratitude to the Ministry of Economic Affairs of the Republic of China (Contract No: 91-EC-17-A-10-S1-0007) for its financial support.

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