Utilization of water clarifier sludge for copper removal in a liquid fluidized-bed reactor

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Abstract

A method was used to investigate the potential for using water clarifier sludge to remove copper in a fluidized-bed reactor (FBR). This study was conducted to evaluate the removal of copper in an aquatic system without prior treatment. Chemical analyses of water clarifier sludge through inductively coupled plasma-atomic emission spectrophotometry indicated that silicon, aluminum and iron oxides made up more than 84% of this average composition, similar to the composition of clay. The experimental results indicated that the copper removal efficiency was highly dependent on the pH. pH values also influence the character of the water clarifier sludge. After the copper was adsorbed by the water clarifier sludge, the pH of the solution was slightly increased. In the FBR, the copper removal efficiency reached 90% when the initial copper concentration was 20 mg/L, the pH was 4 and the operating time was 60 min. In addition, copper precipitation occured on the surface of clarifier sludge when the initial copper concentration was 20 mg/L and the pH was 7.0. The kinetics of copper ion adsorption at pH 5 showed that 94% copper ion was removed in 60 min and the adsorption equilibrium was attained in 5 h. The mechanisms of adsorption of copper ions on water clarifier sludge including the formation of surface complexation and surface precipitate.
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1. Introduction

In the process of water treatment, huge amounts of sludge are formed. The proper disposal, regeneration, or reuse of water clarifier sludge has become significant environmental issues of concern to the public. Generally speaking, landfilling is the main disposal method for water clarifier sludge, but with the land space being limited and treatment costs rising, alternative methods of disposal or recycling are being investigated [1,2].

The primary sources of copper discharge from industries including printed circuit board production, metal finishing processes, tannery operations, chemical manufacturing, and mining drainage. Copper may cause stomach and intestinal distress, liver and kidney damage, and anemia [3]. As copper is a highly toxic element, removing copper ions from water bodies is an important process.

Conventional methods for treating metal-bearing water that contains copper ions employ the alkaline precipitation process. This process can only reduce the dissolved metal concentration to the solubility product level, which often cannot meet the discharge permit standard, thus necessitating further polishing stages. Cost-effective alternative techniques or materials for the removal of copper ions from low-contaminated water and waster are, hence, needed.

Adsorption processes for the treatment of metal-bearing drinking water or wastewater are becoming attractive. In recent years, research interested in finding different adsorbents that are low in cost and locally available has been increasing. Industrial waste is one of the available low-cost adsorbents for heavy metal removal, and adsorption using the industrial waste has been studied extensively [4–13].

Generally, most adsorbents are available only as fine powders or are generated in aqueous suspension as hydroxide floc or gel. In such forms, these adsorbents retain adsorptive properties for heavy metals, but a sedimentation basin or filtration unit is needed for solid/liquid separation. In order to solve the solid/liquid separation problem and apply the above adsorption

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technology in practice, a cheap adsorbent of water clarifier sludge and the fluidized-bed reactor (FBR) are used. Compared to the batch adsorption process, the treated water can separate with the adsorbent directly in the FBR and the adsorption sites of absorbent could be used efficiently by the FBR is demonstrated [14]. Moreover, compared to the fixed-bed adsorption process, using an FBR can increase the adsorption rate. The flow velocity has been found to be less than 3 m/h in a fixed-bed [15,16], which is low. Using an FBR has been studied to adsorb heavy metals from wastewater [14,17,18] and found that the velocity was 6–30 m/h. The flow rate in an FBR is higher than that in a fixed bed, and the adsorption time is reduced.

Due to the composition of water clarifier sludge, which is rich with silicon and aluminum oxides, we propose employing water clarifier sludge as adsorption material for copper removal from wastewater. In this study, we aimed to investigate the feasibility of reusing water clarifier sludge as an adsorbent to remove copper ions from industrial wastewater in an FBR. During operation, the copper containing wastewater was only subjected to pH value adjustment and was pumped vertically upward through the water clarifier sludge bed. The adsorption sites of water clarifier sludge could be used efficiently in the fluidized reactor. Copper ions were removed by means of adsorption and precipitation on the surface of water clarifier sludge in the FBR. When the adsorptive capacity was saturated, the adsorbent could be withdrawn via a side-tube near the reactor bottom and replaced from the top of the reactor.

2. Materials and methods

2.1. Materials

The water clarifier sludge samples used in this study were collected from Ban-Xin Water Treatment Plant, Taipei County, Taiwan. The Ban-Xin Plant performs coagulation, sedimentation, filtration and disinfection. The sludge is treated using a gravity thickener and belt filter press. The water treatment plant use polyaluminum chloride (PAC, $Al_2(OH)_nCl_{6-n}$) as coagulant. In this study, the sampled dewater sludge cake was shredded and screened using a 0.5 mm sieve. Some of the screened samples were further dried at 300 °C.

The screened samples were used as a carrier material (or absorbent), and placed in the reactor. Synthetic wastewater was prepared by dissolving $CuCl_2\cdot2H_2O$ in deionized water.

2.2. Methods

The experimental set-up is shown in Fig. 1. The FBR had an inner diameter of 3 cm and a height of 120 cm with a cross-sectional area of weir, and it was filled with a fixed amount of water clarifier sludge. The experiment was begun with 5 L of a solution containing a fixed concentration of copper, and the solution pH was adjusted to a desired value of 0.1N NaOH or 0.1N HNO_3.

The copper solution was pumped into the reactor vertically and fluidized the water clarifier sludge bed at a flow velocity of 10 m/h by a peristaltic pump (Cole-Parmer Instrument Co.,

USA), and the temperature kept at room temperature, that is, about 25 °C. For measurement of the copper concentration, samples were taken from the influent and effluent of the FBR. After a specified period of time, the effluent solution was taken.

The adsorption isotherms of water clarifier sludge for copper removal were carried out in 250 mL high-density polyethylene bottles. One hundred milliliters of the solution containing a copper concentration of 100 mg/L was introduced into each bottle, and a fixed amount of water clarifier sludge was added. In order to prevent the precipitation of hydroxides, pH values of solutions were adjusted to 5.0 with HNO_3 and NaOH. The bottles were shaken (DENG YNG, Taiwan, Model DKW- 40 L) at 25 °C and immersed in a water bath for 24 h to attain an equilibrium state. The oscillatory velocity was 100 rpm.

The pH of the solutions at the beginning and end of the experiments was measured. The pH measurements were performed with HTC-201U, HOTEC, and a combination electrode. The meter was standardized using buffer solutions with the following pH values: 4.0, 7.0, and 10.0.

The taken solution was filtered through Whatman 42 filter paper (the pore size is 2.5 μm), and the filtrates were acidified using HNO_3 and stored in a refrigerator at 4 °C. The copper concentration in each filtrate was analyzed using a flameless 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.

2.3. Analysis of the characteristics of water clarifier sludge

The water clarifier sludge samples were analyzed to determine their chemical compositions using inductively coupled plasma-atomic emission spectrometry (ICP-AES). Powderized samples were analyzed as X-ray diffractometry (XRD) diagrams with a diffractometer (XRD, PHILIPS) in the 2θ range of 20–80° using Ni filtered Cu Kα radiation (40 KV, 20 mA). The specific surface area was tested using the nitrogen adsorption method, and the BET adsorption model was used in the calculation. The cation exchange capacity (CEC) of water clarifier sludge was determined by following the standard method released by Environmental Protection Agency, Republic of China (cation-exchange capacity of soils (sodium acetate)) [19]. The surface shape was analyzed using a scanning electron microscope (SEM, PHILIPS). The pH value of water clarifier sludge was measured by adding 5 g samples to a beaker and diluting with distilled water to obtain a final volume of 100 mL.

3. Results and discussion

3.1. The characteristics of water clarifier sludge

The water clarifier sludge samples had common features, including silica sand and a brown color. The water content of dried and un-dried water clarifier sludge was 0 and 21.7%. The specific surface areas were 61 and 67 m^2/g, respectively, obtained using the nitrogen adsorption method and the BET adsorption model. The CEC of the water clarifier sludge was
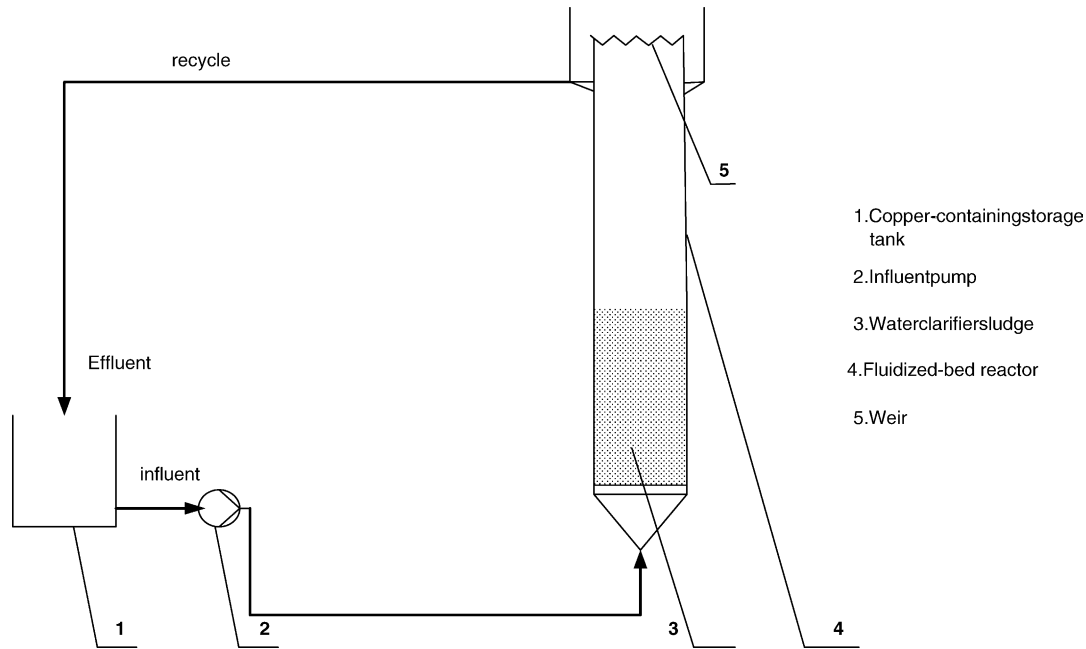
Fig. 1. Schematic drawing of the fluidized-bed reactor. (1) Copper containing storage tank; (2) influent pump; (3) water clarifier sludge; (4) fluidized-bed reactor; (5) Weir.

48.2 meq/100 g, greater than 16.2 meq/100 g of Illite and lower than 81 meq/100 g of Montmorillonite [20]. The SEM images of these two water clarifier sludge are shown in Fig. 2. This figure re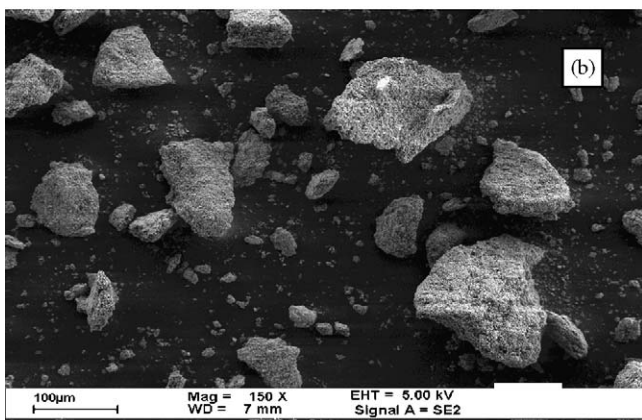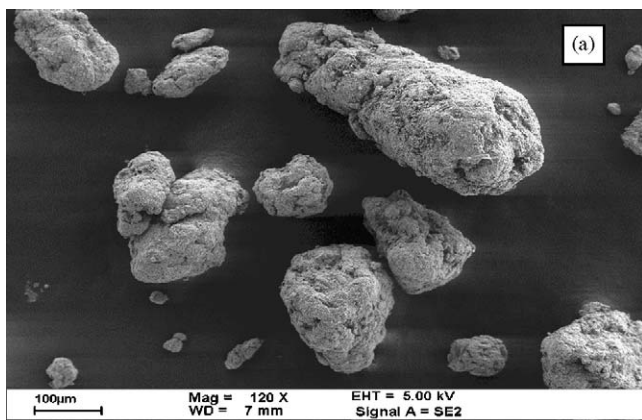veals the common features of the water clarifier sludge sur-face, which is a porous and irregular surface with aggregated particles. Furthermore, the dried sludge was more powdery than the un-dried samples.

XRD showed a small signal for quartz in the samples (Fig. 3). The chemical analysis for the water clarifier sludge indicates that the predominant chemical elements included silicon oxide (56.35%), aluminum oxide (21.53%), and iron oxide (6.63%). The chemical composition of the water clarifier sludge was sim-ilar to the average composition of clay [21]. In this case, silicon, aluminum and iron oxides made up more than 84% of the aver-age composition.

3.2. Adsorption equilibrium of water clarifier sludge

This test of the adsorption equilibrium for water clarifier sludge included an experiment on the adsorption rate of the

Fig. 2. SEM images of dried (a) and un-dried (b) water clarifier sludge.
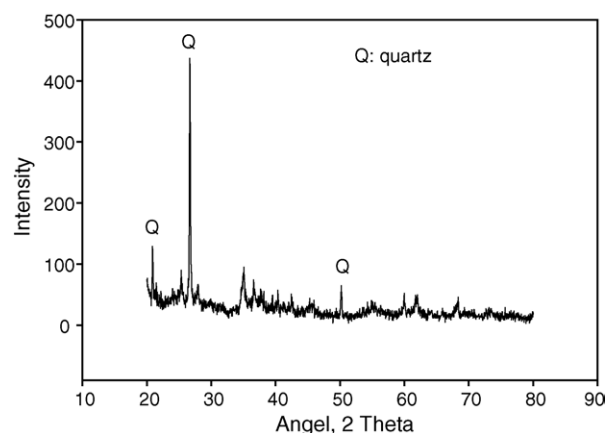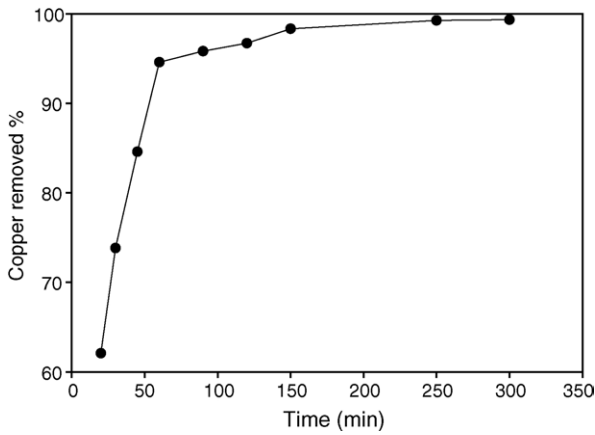

Fig. 3. XRD diagram of water clarifier sludge.

Fig. 4. The adsorption kinetic of copper in the FBR (pH 5, $C_0 = 21$ mg/L, sludge concentration = 20 g/L).

Fig. 5. Freundlich adsorption isotherms of copper on water clarifier sludge (pH 5, $C_0 = 100$ mg/L).

water clarifier sludge in the FBR and an adsorption isotherm test performed using a thermo-stated shaker.

Fig. 4 shows the adsorption kinetic of copper ions in the FBR under a water clarifier sludge concentration of 20 g/L. The copper adsorption efficiency increased rapidly from 62 to 94% with an increase in the effluent time from 20 to 60 min. When the effluent time reached 250 min, the copper removal efficiency reached 99%.

The amount of copper adsorbed by water clarifier sludge versus the equilibrium concentration of copper ions was calculated based on the Langmuir and Freundlich adsorption models. Both the Langmuir and Freundlich adsorption isotherms were determined when the equilibrium state was reached.

The Langmuir model is expressed as

$$q_e = \frac{Q^0 b C_e}{1 + b C_e}, \tag{1}$$

where q_e is the amount of copper ions adsorbed per unit weight of the water clarifier sludge (mg/g), C_e the equilibrium concentration of copper ions (mg/L), and Q^0 and b are the Langmuir constants.

The Freundlich adsorption isotherm was determined as follows:

$$q_e = k C_e^n, \tag{2}$$

where k and n are the Freundlich constants.

The constant values and the correlation coefficients (R^2) obtained for the Freundlich and Langmuir isotherms are shown in Table 1. The R^2 values of dried sludge and un-dried water clarifier sludge for the Langmuir isotherm were 0.91 and 0.81 and for the Freundlich isotherm were 0.97 and 0.99, respec-

tively. The results reveal that copper ions adsorption on water clarifier sludge is consistent with the Freundlich isotherms. The Freundlich isotherms obtained at pH 5 is shown in Fig. 5.

3.3. Effect of pH on copper removal

Fig. 6 shows the removal of copper onto dried and un-dried sludge over a pH range of 2.0–8.0 in the FBR. The adsorption amount of copper increased as the pH value increased from pH 2–4, and at pH 4, the percentages of adsorbed copper on
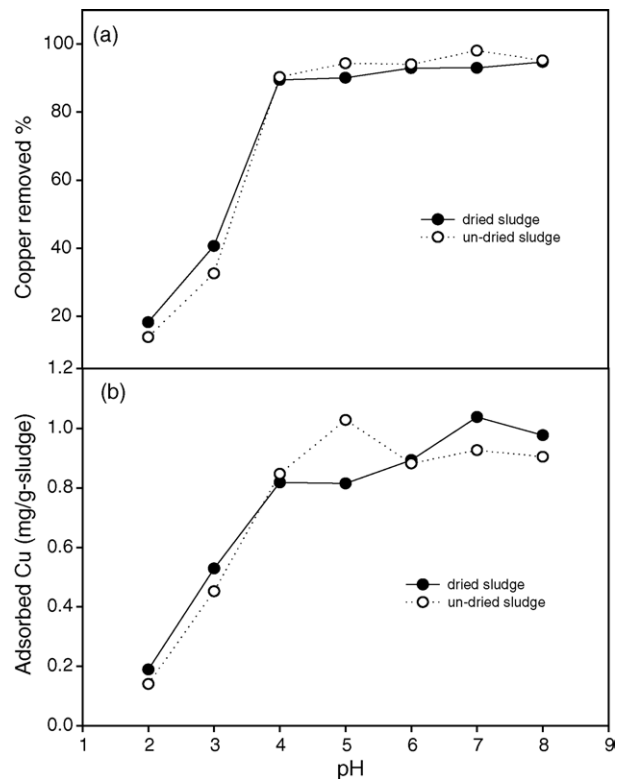

Fig. 6. Variation of the copper adsorption under different pH values ($C_0 = 20$ mg/L, sludge concentration = 20 g/L): (a) copper removed percent at pH 2.0–8.0 (b) The adsorption of copper on water clarifier sludge as a function of the pH value.
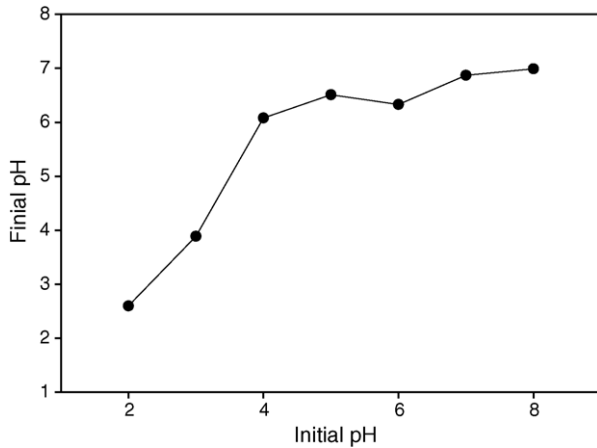
Table 1
Fitting constants and coefficients of the Langmuir and Freundlich isotherms

Water clarifier sludge	Langmuir			Freundlich		
	Q^0 (mg/g)	b	R^2	k	n	R^2
Dried (300 °C)	3.94	0.66	0.91	1.56	0.25	0.97
Un-dried	3.94	1.11	0.81	1.82	0.22	0.99

Fig. 7. The pH values before and after the adsorption process for an initial copper concentration of 20 mg/L.
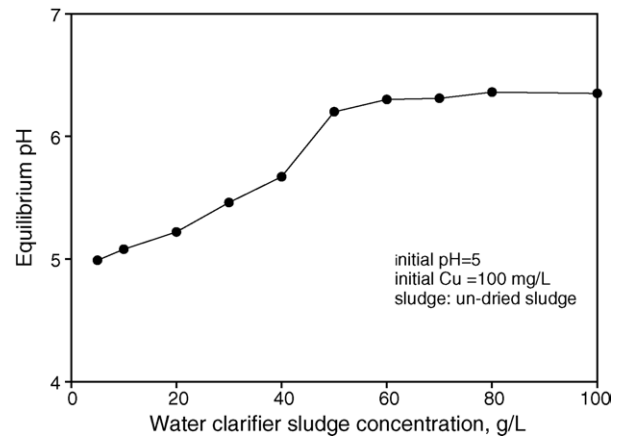

Fig. 8. Variation of the equilibrium pH with the water clarifier sludge concentration.

dried and un-dried sludge were both about 90%. When the pH was greater than 4, the copper removal efficiency stayed at a nearly constant value. At pH 4, the copper adsorptivity of dried and un-dried sludge were 0.82 and 0.85 mg/g, respectively.

The results reveal that pH had a significant impact on copper removal by water clarifier sludge because it could influence both the character of the copper ions and the character of the water clarifier sludge. Chemically, the pH of the solution influenced copper speciation. At high pH, copper precipitation could occur, or the copper ions could form complexes with OH^-.

Theoretical calculation shows that under an initial copper concentration of 20 mg/L, free ions of Cu are the dominant species when pH < 6.1. On the other hand, the precipitate $Cu(OH)_2$ forms when pH > 6.1. According to the results for copper removal, at pH 7, when the initial copper concentration was 20 mg/L and after 60 min, the total copper concentration in the residual solution was 0.95 mg/L. The result indicated that at pH 7, 95% of copper ions took the form of $Cu(OH)_2$, and precipitated onto the surface of the water clarifier sludge.

Moreover, the surface character of the water clarifier sludge was influenced by the ambient pH, which was not equal to the external solution value. Fig. 7 shows the pH values of the solution before and after the adsorption process. The final pH value meant the pH value of the residual solution after an operation time of 1 h. It can be seen from this table that the initial pH of the aqueous solutions increased remarkably after adsorption. This increase can be attributed to the property of the alkaline water clarifier sludge (pH 7.14). Note also from Fig. 8 that the extent and nature of the pH drift over the course of the experiment was a function of the water clarifier sludge concentration. The equilibrium pH of the solution increased with the water clarifier sludge concentration increased. When the initial pH was 5, the equilibrium pH was 5.0 and 6.4 while the water clarifier sludge concentration was 5 and 60 g/L, respectively. When the concentration was over 60 g/L, the equilibrium pH remained constant.
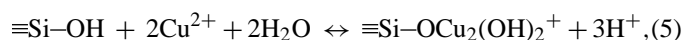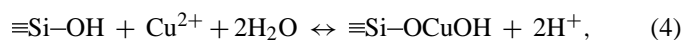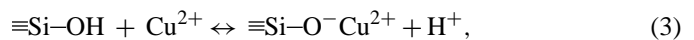
3.4. Mechanisms of adsorption of copper ions on water clarifier sludge

The experimental results obtained from the FBR and the thermostat shaker were important and were directly associated with the mechanism of copper ion removal by means of water clarifier sludge. The mechanisms of copper ion removal by means of water clarifier sludge are described in the following.

3.4.1. Surface complexation adsorption

The correlation coefficients obtained for the Freundlich and Langmuir isotherms are 0.99 and 0.81, respectively. Chen et al. [22] studied the fixation of peat and found that correlation coefficient of 0.98–0.99 when the Langmuir isotherm was used to simulate the ion-exchange reactions and the Freundlich isotherm was used to simulate the adsorption complexation reactions. The results indicate that the surface complexes reaction is more important than ion-exchange by which copper ions be bound to the water clarifier sludge. Similar results were also reported at the Illite [23] and activated carbon [24,25] surfaces. Surface complexation adsorption is a surface reaction, where a positively charged ion is attracted to a negatively charged surface without the exchange of ions or electrons. Since the weight percentage of Si in the water clarifier sludge was 56%, the silica surface sites on the surface of the water clarifier sludge should have predominated.

The mononuclear and multinuclear surface complex reactions of copper with hydrous silica oxide may be written as follows:

$$\equiv Si-OH + Cu^{2+} \leftrightarrow \equiv Si-O^- Cu^{2+} + H^+, \tag{3}$$

$$\equiv Si-OH + Cu^{2+} + 2H_2O \leftrightarrow \equiv Si-OCuOH + 2H^+, \tag{4}$$

$$\equiv Si-OH + 2Cu^{2+} + 2H_2O \leftrightarrow \equiv Si-OCu_2(OH)_2{}^+ + 3H^+, \tag{5}$$

3.4.2. Precipitation on the surface of water clarifier sludge

Under our experimental conditions, when the initial copper concentration was 20 mg/L and the pH greater than 6.1, precipitation occurred. In this case, the total copper concentration in the effluent of the FBR was low, which showed that the copper

precipitate, which was coated onto the water clarifier sludge was more predominate than it was in the water phase.

The formation of surface precipitate is expressed as follow [23]:

$$\equiv Si-OH + 2Cu^{2+} + 3H_2O \leftrightarrow \equiv Si-OCu_2(OH)_3 + 4H^+. \quad (6)$$
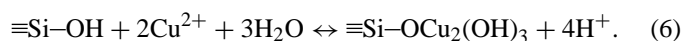
4. Conclusions

The study of utilization of water clarifier sludge for copper removal in a liquid fluidized-bed reactor leads us to the following conclusions:

1. From the chemical composition analysis results, water clarifier sludge is similar to clay and can be reused as an effective and economic adsorbent for copper removal from wastewater.
2. Although the different water content between dried and un-dried sludge (0 and 21.7%, respectively), the copper removal efficiency for dried and un-dried sludge was very similar, but the effluent was turbid in the case of dried sludge. The results showed that the water clarifier sludge did not require pretreatment during the copper adsorption process.
3. The experimental results showed that with FBR used as the reactor, most of copper adsorption took place in the first 1 h, followed a slower process.
4. From the adsorption isotherm test on copper in the water clarifier sludge, the results indicated that adsorption is consistent with the Freundlich isotherm confirms the mechanisms of surface complexation of copper ions on water clarifier sludge.
5. The mechanisms of copper adsorption at aqueous water clarifier sludge surfaces included the formation of surface complexes ($\equiv Si-OCu^+$, $\equiv Si-OCuOH$, $\equiv Si-Cu_2(OH)_2{}^+$), followed by the formation of surface precipitate ($\equiv Si-OCu_2(OH)_{3(sp)}$).

Acknowledgement

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