



Adsorption Kinetics and Isotherms of Copper Ion in Aqueous Solution by Bentonite Supported Nanoscale Zero Valent Iron

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ABSTRACT

Copper ions discharged into the water can cause serious damages to the plants and living organisms in water. Therefore, it is very important to develop effective technologies to treat copper ions polluted wastewaters before their discharge into the natural environment. The main objective of this study was to evaluate copper ions removal by bentonite supported nanoscale zero valent iron (nZVI). In this work, the bentonite supported nZVI was synthesized by direct mixing of bentonite pretreated with nZVI. A range of experiments were conducted to evaluate the sorption ability of bentonite supported nZVI to copper ions in aqueous solutions. Results showed that the contact time, pH in solution and initial concentration of copper ions had an important effect on the removal of copper ions from aqueous solution by bentonite supported nZVI. The Freundlich and pseudo-second-order kinetic models can preferably describe the adsorption process.

INTRODUCTION

With the rapid development of industrial activities, a large amount of industrial effluents containing heavy metals is released into surface and underground water, which has resulted in a number of environmental problems (Aleksandra et al. 2015). Heavy metals, such as lead, copper, and cadmium, are toxic and nonbiodegradable. They can accumulate in living organisms, and may thus pose a threat to human health (Jiang et al. 2016). Copper ions have been frequently detected in waste streams and natural waters, as copper is widely used in electrical, machinery, semiconductor, and many other industries. Extensive studies have demonstrated that copper ions discharged into the water can cause serious damages to the plants and living organisms in water (Lukáš et al. 2014). Epidemiological investigation shows that excessive copper intake can result in a series of negative effects to human health, including liver cirrhosis, kidney damage, haemolysis, vomit and cramps (Jin et al. 2016). Therefore, it is very important to develop effective technologies to treat copper ion polluted wastewater before their discharge into the natural environment (Lia et al. 2013).

Several methods, such as chemical precipitation, ion exchange, solvent extraction, electrochemical treatment, reverse osmosis and the application of biological materials, have been proposed for treating copper ions (Regmi et al. 2012, Zuo et al. 2016). However, applications of these methods have been limited because of high capital costs, high

operational costs and ineffective means of disposal of the resulting sludge (Ding et al. 2016). The use of sorbents to remove and recover heavy metals from contaminated industrial effluents has emerged as a potential alternative to conventional methods (Wang et al. 2015). Development of a practical method for effective removal of toxic metal ions from water is still an urgent need and of vital significance to environmental remediation and pollution control (Park et al. 2016).

Nanoscale zero-valent iron (nZVI) is a reducing agent with a significantly large surface area and colloidal effect (Shen et al. 2015). Due to its high activity, nZVI has received increasing attention for the removal of a variety of heavy metals and chlorinated organic contaminants through chemical reduction processes (Tong et al. 2013). However, nZVI often forms aggregates and easily reacts with water and other substances in soil and groundwater environments, which leads to its instability and the rapid loss of reactivity in the subsurface (Su et al. 2016). These significant efforts have focused on the modification of aggregation alleviation of nZVI (Marcio et al. 2017). It has been demonstrated that the support of nZVI by many materials, such as clay minerals, zeolite, carbonaceous materials, biopolymers, Fe_3O_4 and resin, is effective for dispersing the nZVI and reducing its agglomeration, thus increasing the reactivity (Kerkez et al. 2014). Among these stabilizing materials, porous carbon and minerals are commonly used for nZVI. As carbon materials have a large specific surface area and, a

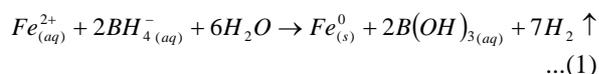
porous and stable structure, they are often used as supporting materials for nZVI (Wang et al. 2016).

The main objective of this study was to evaluate copper ions removal for bentonite supported nZVI. In this work, the bentonite supported nZVI was synthesized through direct mixing of bentonite pretreated with nZVI. A range of experiments were conducted to evaluate the sorption ability of bentonite supported nZVI to copper ions in aqueous solutions. Furthermore, the mechanisms of copper ions in aqueous solution removal by bentonite supported nZVI were explored and discussed.

METHODS AND MATERIALS

Materials: The adsorbate in this study was copper prepared by dissolving $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ into 1000 mL of deionized water to stock solution concentrations of 1000 mg/L. The adjustment of pH in solution was achieved by adding 10% NaOH and 1 mol/L HCl.

The nZVI was synthesized in the laboratory using a modified method from previous liquid phase method by adding the macromolecule stabilizer. The basic principle of the synthesis process was that ferrous ion was rapidly reduced to the nanoscale zero valent iron by borohydride solution following the equation below:



The concentration of 100 mL 0.02 M ferrous chloride solution was prepared and then 4 g PVP was added into the ferrous chloride solution in a beaker with vigorous stirring till PVP was completely dissolved. The 5 g bentonite was swiftly added to the above solution and the mixture was agitated in a water bath shaker with a shaking rate of 120 rpm at room temperature for 20 minutes. Then the product was separated by filtration, washed with alcohol three times AND vacuum dried for 12 hr at 60°C. The dry bentonite supported nZVI was gained and used for the following experiments.

Experimental process: Adsorption experiments were conducted in a set of 250 mL Erlenmeyer flasks containing 0.1 g bentonite supported nZVI and 200 mL of Cu^{2+} ion solution with various initial concentrations (between 10 mg/L and 50 mg/L). The initial pH was adjusted to 4.0 with 1 mol/L HCl. The flasks were placed in a shaker at a constant temperature of 298 K and 200 rpm. The samples were filtered and analyzed.

Analytical methods: The BET surface area of the bentonite supported nZVI was analyzed with an ASAP2020 system. The particle size, morphology and structure of the bentonite supported nZVI were characterized by scanning electron

microscopy (SEM) and transmission electron microscopy (TEM). The concentration of Cu^{2+} ion was analyzed by atomic absorption spectrophotometry.

The amount of adsorbed Cu^{2+} ion q_t (mg/g) at different times, was calculated as follows:

$$q_t = \frac{(C_0 - C_t) \times V}{m} \quad \dots(2)$$

Where, C_0 and C_t (mg/L) are the initial and equilibrium liquid-phase concentrations of Cu^{2+} ion respectively. V (L) is the solution volume and m (g) is the mass of adsorbent used.

Statistical analyses of data: All experiments were repeated in duplicate and the data of results were the mean and the standard deviation (SD). The value of the SD was calculated by Excel Software. All error estimates given in the text and error bars in figures are standard deviation of means (mean \pm SD). All statistical significances were noted at $\alpha=0.05$ unless otherwise noted.

RESULTS AND DISCUSSION

Characterization of bentonite supported nZVI: The specific surface area is the main indicator reflecting the adsorption capacity of adsorbent. The BET surface area of the bentonite supported nZVI was analyzed with an ASAP2020 system. The specific surface area of bentonite supported nZVI was 31.15 m^2/g , which was larger than that of bentonite. The result was similar to surface areas of other supported nanoscale iron materials (Pang et al. 2014).

The morphology and particle distribution of bentonite and bentonite supported nZVI was analyzed by SEM. The results are shown in Fig. 1.

From Fig. 1, it can be concluded that the bentonite had a layered structure, and there were a lot of crevices between different layers, which provided enough space for supporting nanoscale iron particles. The bentonite supported nanoscale zero valent iron was aggregated as a chain-like clusters.

The TEM image of bentonite and bentonite supported nZVI is shown in Fig. 2. The bentonite supported nZVI has a core shell structure.

Effect of contact time: The contact time is one of the important parameters in this experiment. The effect of contact time on the removal of copper ion in aqueous solution by bentonite supported nZVI was carried out at pH 4.0, initial concentration of copper ion 40 mg/L and a constant temperature of 298 K and 200 rpm. The experimental results are shown in Fig. 3.

The efficiency of copper ions removal from the aqueous

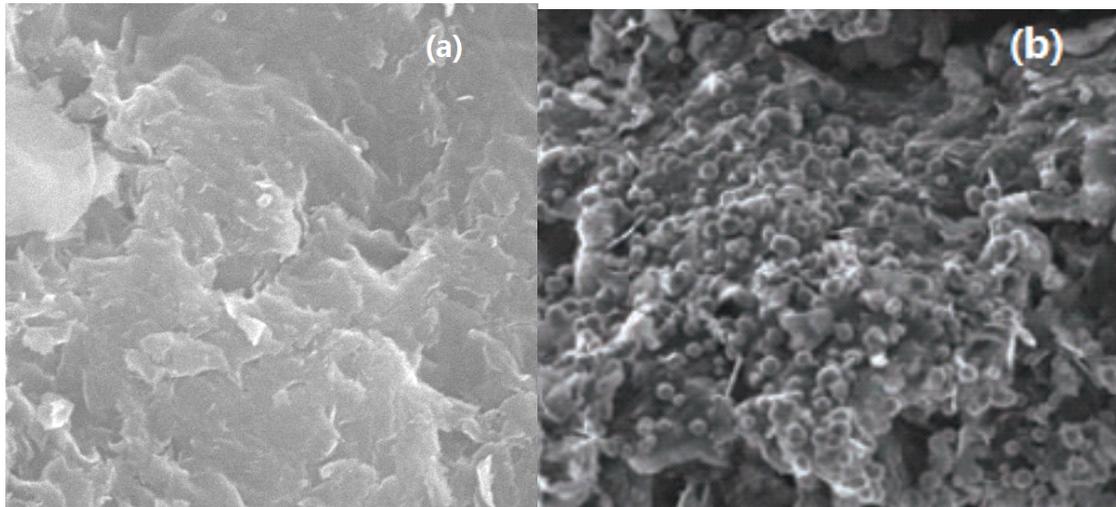


Fig. 1: SEM images of bentonite and bentonite supported nZVI, (a) bentonite and (b) bentonite supported nZVI.

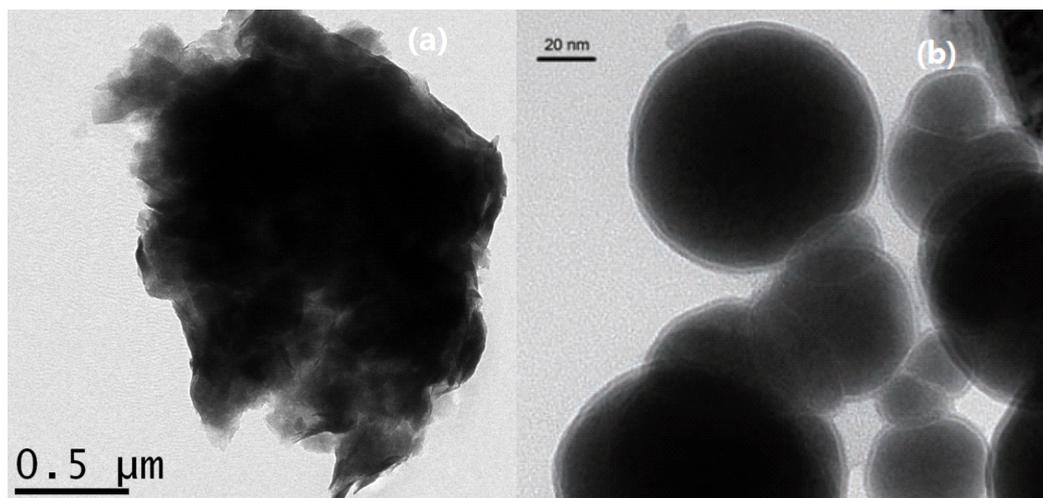


Fig. 2: TEM images of bentonite and bentonite supported nZVI, (a) bentonite and (b) bentonite supported nZVI.

solution increased rapidly as the contact time increased. At first stage, the removal process was very quick. When the contact time was 120 minutes, the efficiency of copper ions removal from aqueous solution was similar. It may be inferred that the contact time of 120 minutes was equilibrium time and adsorption process reached a saturation state.

Effect of pH: The initial pH of the electroplating effluent is a key factor determining the efficiency of copper ion in aqueous solution removal. The effect of pH on the removal of copper ion in aqueous solution by bentonite supported nZVI was carried out at a contact time of 120 minutes, initial concentration of copper ion 40 mg/L and a constant temperature of 298 K and 200 rpm. The experimental re-

sults are shown in Fig. 4.

As shown from Fig. 4, the removal rate of copper ion in aqueous solution increased significantly as the initial pH was increased. At low solution pH values, oxygen containing groups (e.g., carboxyl and hydroxyl) on the surfaces of bentonite supported nZVI might be positively or neutrally charged, which hindered the adsorption of positively charged metal ions (Liu et al. 2011). As a result, increase in pH promoted the removal the heavy metals in this work.

Effect of initial concentration of copper ions: In order to test the effect of initial concentration of copper ions, the following experiments were carried out. The initial concentration of copper ions was ranged from 10 mg/L to 50 mg/L.

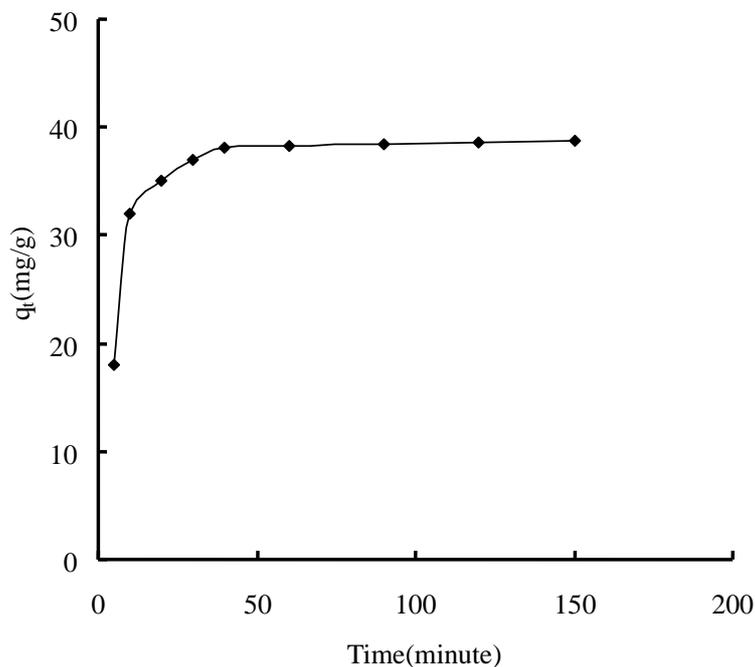


Fig. 3: Effect of contact time on the removal of copper ion in aqueous solution by bentonite supported nZVI.

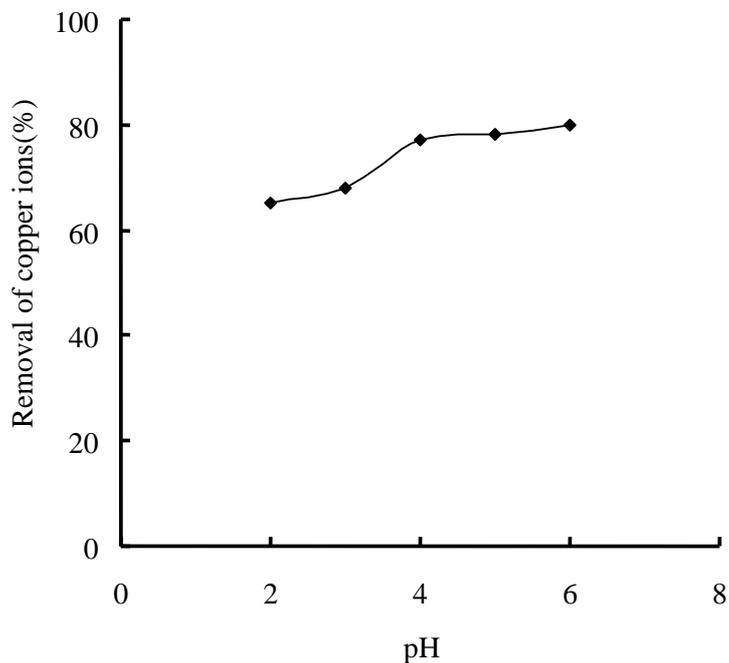


Fig. 4: Effect of pH on the removal of copper ion in aqueous solution by bentonite supported nZVI.

The other parameters were pH 4.0, contact time of 120 minutes and a constant temperature of 298 K and 200 rpm. The results are shown in Fig. 5.

The sorption of copper ions decreased with the initial

concentration of copper ions in aqueous solution.

Sorption isotherms: Langmuir and Freundlich adsorption isotherms suggested that the main adsorption mechanism usually involved the integrative effects of several kinds of

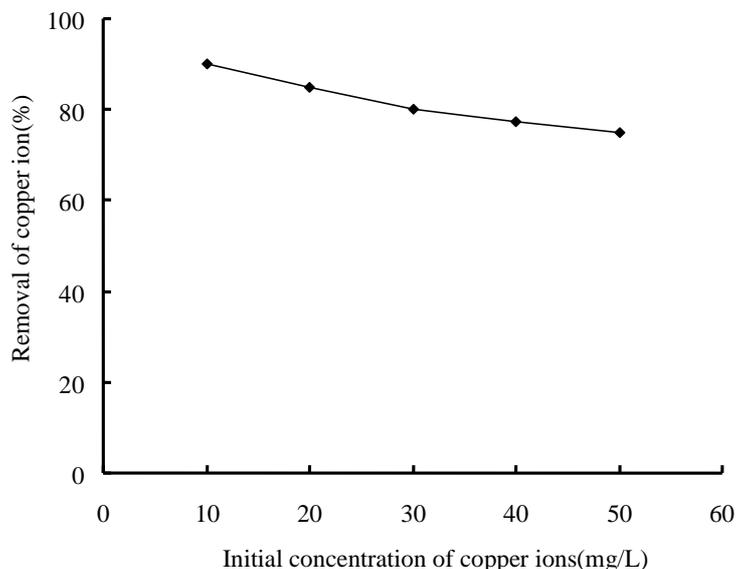


Fig. 5: Effect of initial concentration of copper ions on the removal of copper ion in aqueous solution by bentonite supported nZVI.

interactions, including electrostatic attraction, ion-exchange, physical adsorption, surface complexation and/or precipitation. The experimental data were fitted by Langmuir and Freundlich isotherms as follows.

The Langmuir model and Freundlich model of linear forms are (Liu & Zhang 2011):

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}} \quad \dots(3)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad \dots(4)$$

Where, C_e (mg/L) is the equilibrium concentration in the solution, q_e (mg/g) is the adsorbate adsorbed at equilibrium, q_{max} (mg/g) is the maximum adsorption capacity, n is the Freundlich constant related to adsorption intensity, K_L (L/mg) and K_F ((mg/g)^{1/n}) are the adsorption constants for Langmuir and Freundlich models respectively. The results are given in Table 1.

As seen from Table 1, the value of R^2 is 0.9571 according to the Langmuir isotherm model. The value of R^2 is 0.9991 according to the Freundlich isotherm model. Therefore, the adsorption process of the Cu²⁺ ion in aqueous solution by the bentonite supported nZVI fitted well with the Freundlich isotherm model. This indicated that chemisorption on heterogeneous surface played a dominating role in adsorption of copper ions.

Kinetics of copper ion adsorption: Two kinetic models, pseudo-first-order and pseudo-second-order were used to analyse the adsorption processes.

Table 1: Parameters of Langmuir isotherm model and Freundlich isotherm model for the description of Cu²⁺ ion adsorption onto the bentonite supported nZVI.

qm(mg/g)	Langmuir		Freundlich		
	K_L	R^2	K_F	n	R^2
52.63	0.17	0.9571	9.03	1.79	0.9991

The pseudo-first-order model:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad \dots(5)$$

The pseudo-second-order model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad \dots(6)$$

Where, q_t (mg/g) is the amount of copper ions adsorbed at time t , k_1 (h⁻¹) and k_2 (g/mg/h) are the pseudo-first-order reaction rate constant and the pseudo-second-order reaction rate constant, respectively. The results are presented in Table 2.

From Table 2, it can be seen that the adsorption process fits well with the pseudo-second-order kinetics model according to the value of R^2 . It implies that the predominant process is chemisorption, which involves a sharing of electrons between the adsorbate and the surface of the adsorbent.

CONCLUSIONS

In this work, the bentonite supported nanoscale zero valent iron was synthesized through direct mixing of bentonite

Table 2: Parameters of the pseudo-first-order kinetic model and the pseudo-second-order kinetic model for the description of Cu²⁺ ion adsorption onto bentonite supported nZVI.

Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
k ₁ (min)	q _e (mg/g)	R ²	k ₂ (mg/g min)	q _e (mg/g)	R ²
0.042	8.65	0.8745	0.0085	39.68	0.9994

pretreated with nZVI. A range of experiments were conducted to evaluate the sorption ability of bentonite supported nZVI to copper ions in aqueous solutions. The results showed that the contact time, pH in solution and initial concentration of copper ions had an important effect on the removal of copper ions from aqueous solution by bentonite supported nZVI. The Freundlich and pseudo-second-order kinetic model can preferably describe the adsorption process.

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