



## Removal Process of Cu<sup>2+</sup> from Aqueous Solutions using Expanded Vermiculite

J.H. WANG<sup>1,2,3,\*</sup>, S.Y. YAN<sup>1</sup>, Y.W. FAN<sup>1,2,3</sup>, Z.Y. CHEN<sup>1,\*</sup> and L. WANG<sup>1,2,3</sup>

<sup>1</sup>Xinjiang Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Urumqi 830011, P.R. China

<sup>2</sup>Xinjiang Key Laboratory of Electronic Information Materials and Devices, Urumqi 830011, P.R. China

<sup>3</sup>Graduate School of the Chinese Academy of Sciences, Beijing 100049, P.R. China

\*Corresponding author: Fax: +86 991 3838957; Tel: +86 991 3850821; E-mail: czy@ms.xjb.ac.cn

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The adsorption of Cu<sup>2+</sup> from aqueous solution by expanded vermiculite was studied in batch mode. The sorption process was fast and equilibrium was achieved in *ca.* 50 min of contact. The effect of adsorbent dosage, contact time, temperature and initial Cu<sup>2+</sup> concentration was investigated. The removal efficiency of Cu<sup>2+</sup> using expanded vermiculite reached 99 % in low Cu<sup>2+</sup> concentration. Experimental results indicated that a pseudo-second-order reaction model provided the best description of the data with a correlation coefficient 0.99 for different temperatures. The rate constants of adsorption by expanded vermiculite were defined by second-order kinetics of rate constant 0.0228, 80.878 and 120.280 g/mg/min<sup>-1</sup> at 298, 303 and 323 K, respectively. The results indicated that this system was an endothermic process.

**Key Words:** Adsorption, Copper, Expanded vermiculite, Kinetics.

### INTRODUCTION

Environmental pollution by heavy metals such as lead, copper and cadmium is of great concern since their increasing trend in discharge, nondegradation in nature and high toxicity to plants, animals and human being<sup>1-3</sup>. Copper is a commonly used metal, however, it is very harmful if it is discharged into natural water resources and causes a serious health hazard<sup>4</sup>. Inhalation acute doses of copper produce symptoms similar to those of silicosis and allergic contact dermatitis and chronic copper poisoning cause hemolytic anemia, neurological abnormalities and corneal opacity<sup>5</sup>. A number of processes exist for the removal of metal pollutions from wastewater, *e.g.* precipitation, electroplating, ion-exchange, solvent extraction and membrane separation. But they have several disadvantages such as incomplete metal removal, high reagent and energy requirement and generation of toxic sludge/waste products that require disposal and further treatments<sup>6</sup>. As a result, in the last few decades, different adsorbents for the treatment of heavy metal contamination have been studied<sup>7-10</sup>. A low-cost adsorbent is defined as one which is abundant in nature, or is a by-product or waste material from another industry<sup>11,12</sup>. Clays can remove pollutants from aqueous solutions owing to their high cation exchange capacity and high specific surface area associated with their small particle sizes<sup>13</sup>. The cost of clays is relatively low as compared to other alternative adsorbents, including

activated carbon, natural and synthetic zeolites, ion-exchange resins and other adsorbent materials. Activated carbon is most widely used at present in spite of high cost of production and regeneration. Therefore, research has been focused on finding new, preferably natural, abundant and cheap materials for replacing activated carbon<sup>14</sup>.

Vermiculite has already been used for the adsorption of different elements and substances from water and wastewaters in its natural form (raw), presenting very promising and positive results. In its expanded form, vermiculite has a very low density and thermal conductivity, which makes it attractive for use as a soil amendment, lightweight construction aggregate and thermal insulation filler<sup>15</sup>. Expanded vermiculite also has a very large chemically active surface area, which makes it useful as an absorbent in some chemical processes. The expanded vermiculite is very cheap and easily available in market. This could make it a viable candidate as an economical adsorbent for removing heavy metals such as lead, copper, cadmium and chromium. The utilization of vermiculite as an adsorbent material to replace activated carbon will greatly reduce costs in wastewater treatment<sup>16</sup>.

In this study, expanded vermiculite has been tested for the adsorption of Cu<sup>2+</sup> from aqueous solution. The effect of concentration of adsorbent, contact time, temperature and initial Cu<sup>2+</sup> concentration has been explored in present study.

## EXPERIMENTAL

Vermiculite obtained from Yuli Mine in Xinjiang, China, was washed with distilled water three times, dried at 373 K for 12 h, calcinated at 1173 K for 1 min and then kept in desiccators. The expanded vermiculite was ground and then sieved to a size < 0.150 mm. The cation exchange capacity (CEC) of expanded vermiculite was 110 meq/100 g (NH<sub>4</sub>OAc method). Solution of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O was prepared using analytical grade reagent and high-purity deionized water. Other agents used were all analytical grade and all solutions were prepared with deionized water. The pH was initially adjusted during all ion exchange experiments using nitric acid.

**Procedure:** A 50 mL polypropylene container was first cleaned with 0.2 N HNO<sub>3</sub> and then consecutively rinsed with deionized water three times. All the experiments were carried out in polyethylene test tubes by using batch technique. For the copper adsorption test, 0.3 g expanded vermiculite was contacted with a specified concentration of copper in a 45 mL of deionized water using centrifugal tube. Solutions were centrifuged at 8000 rpm during 5 min after predetermined time intervals to remove suspension particles. And the final metal concentration was analyzed for Cu<sup>2+</sup> content by an inductively couple plasma emission spectroscopy (ICP-ES). The solution pH was measured by PHS-3B pH meter.

The adsorption capacity (*q*) and sorption efficiency (*R*) of the expanded vermiculite for Cu<sup>2+</sup> were calculated through the following equation, respectively:

$$q = \frac{V(C_{\text{init}} - C_{\text{eq}})}{m}; R\% = \frac{C_{\text{init}} - C_{\text{eq}}}{C_{\text{eq}}} \times 100$$

Kinetics for clay-metal interaction was studied thoroughly in this work by applying the first assuming pseudo-first-order kinetics, where the number of metal ions outnumbers the number of adsorption sites on clay surface:

$$\ln(q_{\text{eq}} - q_t) = \ln(q_{\text{eq}}) - k_1 t$$

If the validity of the first-order kinetics is weak, the kinetics can be tested for following second-order mechanism as per the rate law expressed as<sup>17</sup>

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

where, *q<sub>e</sub>* and *q<sub>t</sub>* (mg/g) are the adsorption capacities at equilibrium and at time *t*, respectively, *k<sub>1</sub>* (min<sup>-1</sup>) is the rate constant of the pseudo-first order adsorption, *k<sub>2</sub>* (gmg<sup>-1</sup> min<sup>-1</sup>) is the rate constant of the pseudo-second order adsorption.

## RESULTS AND DISCUSSION

**Effect of initial concentration of Cu<sup>2+</sup>:** The sorption % of Cu<sup>2+</sup> by expanded vermiculite was studied in aqueous solutions at 298 K by varying the initial metal ion concentrations from 10 to 211 mg/L while keeping all other parameters constant. The experiments were conducted using 20 g/L adsorbent. The metal uptake by expanded vermiculite, in respect to the different initial metal concentrations is shown in Fig. 1. The adsorbed amount of metal ions per unit mass of clay gradually increases as the initial concentration of Cu<sup>2+</sup> solution increases,

while the lower the initial concentration is, the higher the percentage removal becomes (Fig. 1A). With the initial solution at a low concentration, the ratio between the number of ions and the number of adsorptive sites available is small. Consequently, adsorption depends on the initial concentration. Therefore, as the concentration of ions increases, adsorption increases as well. At high ion concentrations, each unit mass of adsorbent is subjected to a larger number of ions, which gradually fill up the sites. Thus, an increase in *q* and a reduction in the adsorbed percentage are observed in Fig. 1B.

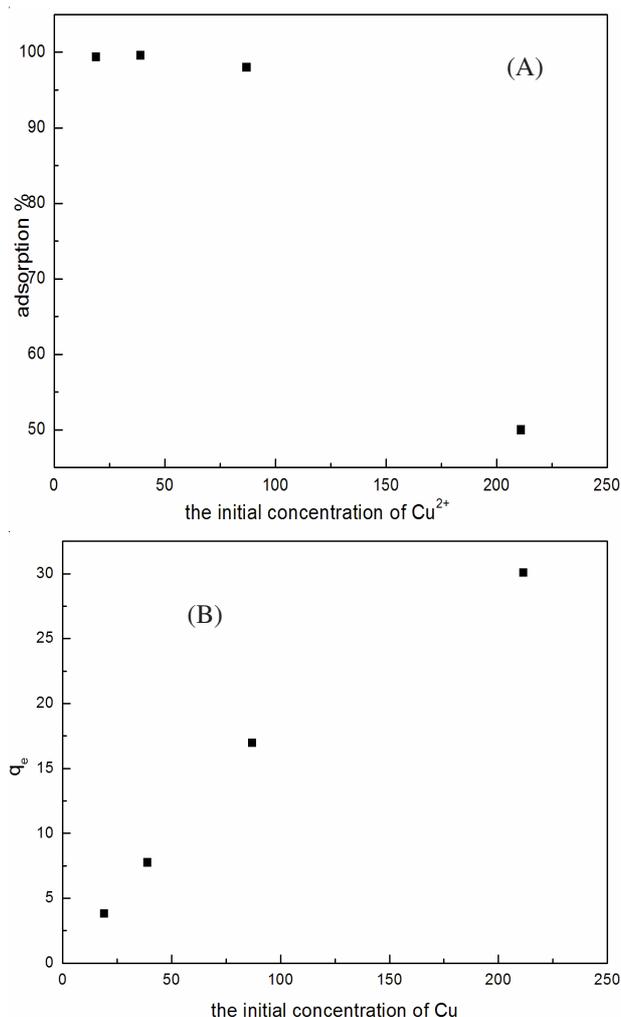


Fig.1. Effect of initial concentration on metal uptake

**Effect of adsorbent dosage:** To determine the effect of the adsorbent dosage on the removal efficiency of Cu<sup>2+</sup> by expanded vermiculite, the amounts of adsorbent in solution were varied from 5 to 50 g/L with all other parameters constant at 298 K (Fig. 2). The removal efficiency of Cu<sup>2+</sup> increased with increase of the adsorbent dosage as expected. The maximum removal efficiency was attained at 20 g/L and reached a saturation level at higher dosages.

**Effect of pH:** The pH of a solution is an important parameter in adsorption process that controls cationic adsorption onto the clay surface. Fig. 3 shows the variation of copper uptake at different pH. The removal efficiency increased with an increase in pH. In acid conditions of pH < 4, most silanol and aluminol groups on edges in expanded vermiculite are

protonated<sup>18</sup>.  $\text{H}^+$  cations should be considered as competitive ones in ion-exchange processes, leading to a low removal of  $\text{Cu}^{2+}$  and, consequently, ion exchange of metals is favoured by high pH values, which should, however, be lower than the minimum pH of precipitation. At the same time, the force of electrostatic attraction were weakened because of the increasing fraction of  $\text{Cu}(\text{OH})^+$  with the rise of pH. But this effect may be insignificant compared with those positive effects<sup>19</sup>.

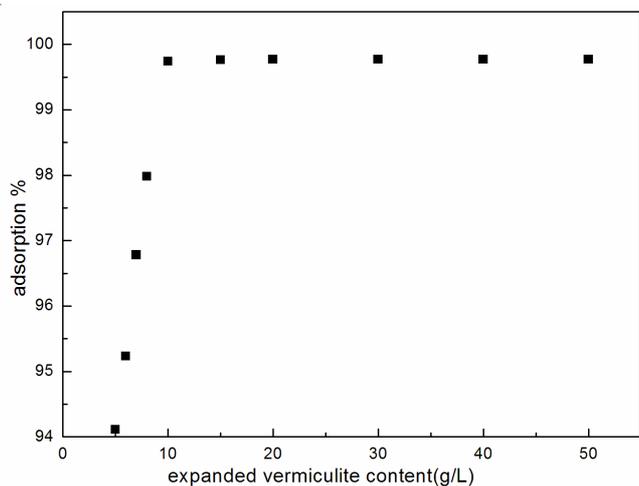


Fig. 2. Effect of adsorbent dosage on metal uptake

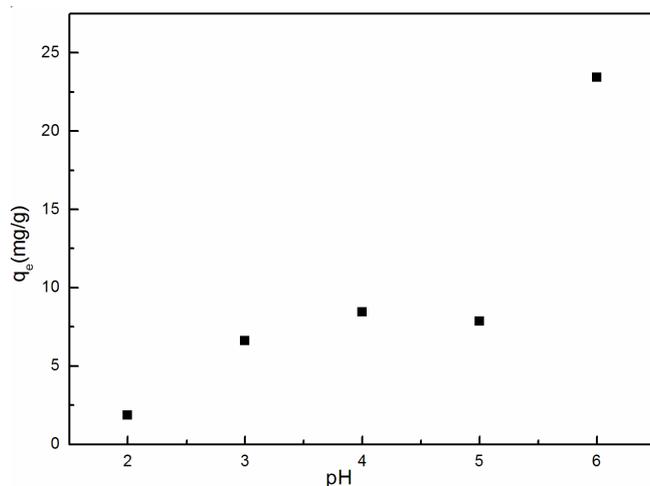


Fig. 3. Effect of pH on metal uptake

**Effect of contact time and temperature:** Copper uptakes at different temperatures were evaluated as a function of time to determine an optimal contact time. The time course of adsorption equilibrium of  $\text{Cu}^{2+}$  onto expanded vermiculite at 298 K was depicted in Fig. 4. The removal efficiency increased with increase of contact time till equilibrium. The sorption was rapid at first and equilibrium at each temperature was obtained within 50 min. And there was almost no adsorption beyond this time. It can be attributed to the fact that at the initial stage the adsorption sites are abundant and the metal ions can interact easily with the sites and the slow adsorption rate in later stage is due to slower diffusion of metal ions into the interior of the adsorbent. With increasing temperature, the rate of the sorption process was increasing, indicating this system was an endothermic process.

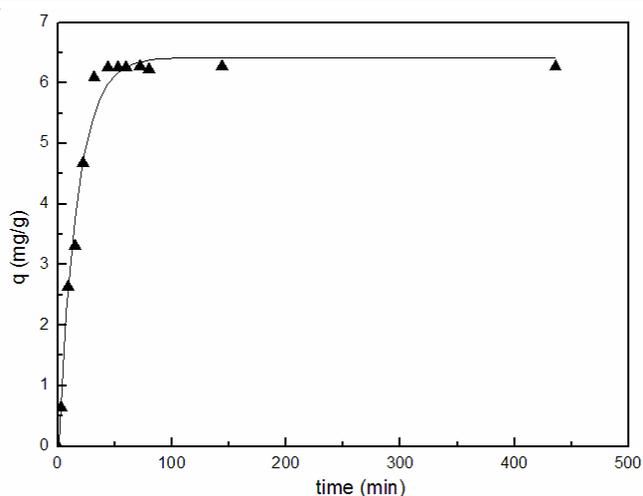


Fig. 4. Effect of contact time on metal uptake at 298 K

**Adsorption kinetics:** The kinetic data were analyzed in terms of pseudo-first order and pseudo-second order rate equation and the results are shown in Fig. 5 and 6, respectively. Actually, pseudo-first order rate equation can only provide good fitness of the original sorption stages instead of the whole processes. It seems the kinetic behaviour could be satisfactorily explained by pseudo-second order rate equation, of which the regression coefficients are higher than 0.99 and the  $q$  values calculated are in good agreement with the results of experiments. It can be seen clearly from the rate constant of the pseudo-second order adsorption. The increase in adsorption capacity of the expanded vermiculite with temperature indicates the adsorption process is endothermic in nature. The increase in adsorption with temperature may be attributed to increasing tendency to adsorb metal ions from the interface to the solution. Adsorption by expanded vermiculite is defined by second-order kinetics of rate constant 0.0228, 80.878 and 120.280  $\text{g}/\text{mg}/\text{min}^{-1}$  at 298, 303 and 323 K, respectively. High sorption rates are clearly desired, because a shorter contact time eventually translates to smaller contact equipment, which, in turn, directly affects both the capacity and operation cost of the process.

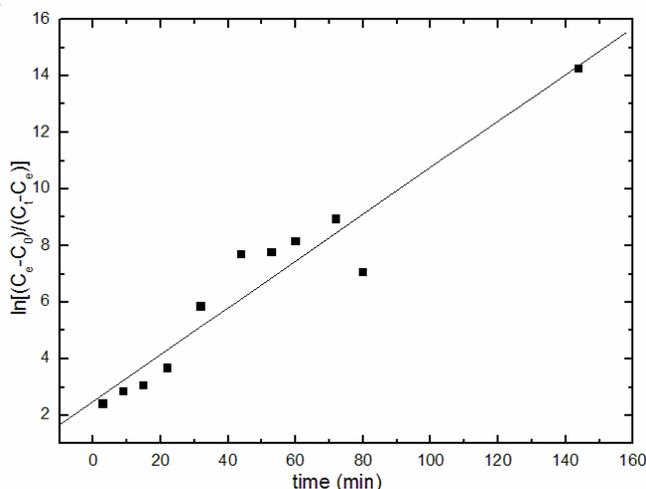


Fig. 5. Pseudo-first-order kinetic plots at 298 K

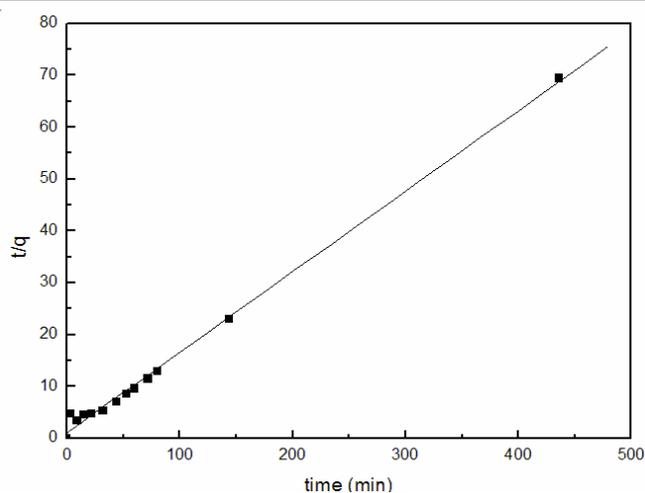


Fig. 6. Pseudo-second-order kinetic plots at 298 K

## Conclusion

In this work, the adsorption of copper ions from aqueous solution by expanded vermiculite was investigated systematically. The effects of concentration of adsorbent, contact time, temperature and initial  $\text{Cu}^{2+}$  concentration on the adsorption process were studied respectively. It was found that the pH of the solution can greatly influence the sorption capacity of the expanded vermiculite. The removal efficiency could reach 99 % under appropriate conditions, indicating the expanded vermiculite has great potential to be applied in heavy-metal-ion contained waste water treatment process.

The sorption kinetics study suggests the adsorption process follows pseudo-second order rate equation. The regression coefficients are higher than 0.99 and the  $q$  values calculated are in good agreement with the observation of experiments. The changes of sorption kinetics and isotherms with the increase in temperature have similar trend. The initial sorption rate and sorption equilibrium capacity increase with the rise in temperature from 293 to 303 K and the adsorption process is endothermic.

## ACKNOWLEDGEMENTS

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