Experimental Investigation of Adsorption of Copper from Aqueous Solution using Vermiculite and Clinoptilolite

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ABSTRACT: Considering the point that the existence of heavy metals in the wastewater are so dangerous for the environment and it would have many bad consequences for all the creatures including human beings, we must try out the ways that make us capable of adsorbing these heavy metals. In order to accomplish this goal we should use a method called adsorbing. In this study the adsorption of copper ions in hydrated copper nitrate (Cu $(NO_3)_2$, $3H_2O$) aqueous solution on natural zeolite (Clinoptilolite) and vermiculite was studied in batch reactors. The effect of temperature (25, 50, 75 °C), solution pH (1.00-5.5) and concentration effect on the traditionally defined adsorption isotherm in the adsorbate range 100-325 mg/L for clinoptilolite and 100-650 mg/L for vermiculite on the removal of copper was studied. The results showed that an increase in pH increases the adsorptivity of vermiculite. Pseudo second order model best described the reaction rate. Batch adsorption experiments conducted at room temperature (25±1 °C) showed that the adsorption pattern followed the Langmuir and Freundlich isotherm models. Optimum conditions for adsorption were determined at pH 5.5, and vermiculite and clinoptilolite at a dose of 3g. The concentration of metal ions was measured by Atomic Absorption Spectrometer (AAS). The results indicated that vermiculite and clinoptilolite are appropriate for adsorbing copper ions.

Key words: Heavy metal, Copper, Hydrated copper nitrate, Langmuir, Freundlich, Natural zeolite

INTRODUCTION

In recent years, the removal of heavy metal ions from polluted sources has drawn a great deal of attention for global awareness of the underlying detriment of heavy metals in the environment. In addition, it has been widely recognized that heavy metal ions in aqueous solutions creates many problems for humans, animals and plants (Mahvi, 2008). Although copper is essential to human life and health, it is potentially toxic at higher concentration levels. Copper is extensively discharged from the electrical industry, pulp, paper mills and petroleum refineries (Lgwe *et al.,* 2006).

A number of technologies for the removal of heavy metal ions from aqueous solutions have been developed over the years (Gupta *et al.,* 2006 ; Lu *et al.,* 2008 ; Zvinowanda *et al.,* 2009). The most important of these techniques include chemical precipitation, filtration and reverse osmosis. However, all these

techniques have their inherent advantages and limitations in application. Adsorption has become one of the preferred methods for removal of toxic contaminants from water as it has been found to be very effective , economical , versatile and simple (King *et al.,* 2006 ; Chen *et al.,* 2010). Adsorption has the additional advantages of applicability at very low concentrations, suitability for using batch processes, ease of operation, little sludge generation and low capital cost (Tran *et al.,* 1999 ; Mohanty *et al.,* 2006). The main properties of the adsorbents are strong affinity and high loading capacity for the removal of heavy metals.Biomass,synthetic and natural adsorbents have these properties. Tea residue (Dizadji *et al.,* 2011) and IR93 (Dizadji *et al.,* 2009) are examples of biomass and synthetic adsorbents used to remove heavy metals from aqueous solutions.

Ion-exchange and adsorption mechanisms of clay minerals have been used to remove different heavy

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metals from aqueous solution (Angove *et al.,* 1997; Naseem *et al.,* 2001; Adebowale *et al.,* 2005; Sari *et al.,* 2007).

Clay plays an important role in the environment by acting as a natural scavenger of pollutants by taking up cations and anions either through ion-exchange or adsorption or both (Dizadji *et al.,* 2012; Naseem *et al.,* 2001).

Zeolites are naturally occurring hydrated aluminosilicate minerals. They belong to the class of minerals known as "tectosilicates" (Almaraz *et al.,* 2003). The structure of zeolites consists of the three-dimensional frameworks of SiO_4 and AlO_4 tetrahedra (Inglezakis *et al.,* 2003). The aluminium ion is small enough to occupy the central position of the tetrahedron of four oxygen atoms, while the isomorphous replacement of Si^{4+} by Al^{3+} produces a negative charge in the lattice. The net negative charge is balanced by the exchangeable cations (Na, K or Ca). These cations are exchangeable with certain cations in solutions, such as lead, cadmium and zinc. Vermiculite is a typical clay and consists of tetrahedral-octahedral-tetrahedral sheets. The two tetrahedral silicate layers are bonded together by one octahedral magnesium hydroxide-like layer and the structure is often referred to as 2:1 phyllosilicate. When tetravalent silicon is substituted by trivalent aluminum in the tetrahedral layer of the vermiculite sheet, a negative charge is generated on the layer and, thus, hydrated magnesium is adsorbed on the tetrahedral layer between the sheets to maintain electro neutrality (Pandey *et al.,* 2010). These magnesium ions can be easily cation exchanged with other cationic species such as copper, which partly contribute to the high cation-exchange capacity of vermiculite (Xueyi *et al.,* 2003). Vermiculite can adsorb heavy metals via two different mechanisms: (1) through cation exchange at the planar sites, resulting from the interactions between metal ions and negative permanent charge (outer-sphere complexes) and (2) through the formation of inner-sphere complexes

through Si-O- and Al-O- groups at the clay particle edges. Both mechanisms are pH dependent but the latter is particularly influenced by pH because in acid conditions (pH < 4) most silanol and alominol groups on edges are protonated .

In this study, the adsorption of Cu^{2+} ions from aqueous solutions by vermiculite and clinoptilolite, quarried in Iran at operating condition of temperature (25, 50, 75 °C) and pH (1.00-5.5), and different amounts of adsorbent were studied. In addition, adsorption kinetics and adsorption models of Cu^{2+} ions on said minerals were studied in this survey. The study was done at Science and Research Branch, Islamic Azad University in Tehran.

MATERIALS & METHODS

Two different minerals were used in order to examine the removal of Cu^{2+} from aqueous solutions. The minerals quarried respectively from Amlash Mines in Guilan Province and Semnan Spa in Southeast of Semnan Province was used to carry out this survey. For preparation of adsorbents, these minerals were initially washed, dried in the oven at temperature 50 °C, then smashed, and sieved (Vermiculite <0.5 mm and clinoptilolite <5 µm).

The chemical analyses of the vermiculite and clinoptilolite used have been shown in Tables 1 and 2. The chemical composition of the minerals was measured using X-ray diffraction (XRD).
Adsorbents were used without any chemical pre-treatment. All the chemicals used in the study were of analytical grade.

Solutions were prepared by dissolving precisely measured quantities of copper nitrate ($Cu(NO_3)_2.3H_2O$) in distilled water to obtain various concentration of Cu ions in aqueous solutions. The pH was adjusted using 0.01 M HNO_3 and NaOH solutions.

The ion exchange of Cu^{2+} on clinoptilolite and vermiculite was examined in batch mode experiments.

Table 1. Chemical analysis of Vermiculite (%w/w)

	SiO_2	Al_2O_3	TiO2	Fe_2O_3	MgO	CaO	Na_2O	K_2O
Vermiculite	48.35	17.85	0.60	13.99	12.85	2.26	0.07	0.59

Table 2. Chemical analysis of Clinoptilolite (%w/w)

	SiO_2	Al_2O_3	Fe_2O_3	K_2O	CaO	Na_2O	LOI
Clinoptilolite	68	10.86	1.35	2.56	1.36	3.30	8.36

Copper adsorption as a function of equilibrium time, initial concentration, pH and temperature were studied. Three grams of each adsorbent were shaken with 100 mL of Cu^{2+} solution (300 mg/L) for different time intervals 0, 10, 20, 45, 80, 120 and 240 min. At the end of shaking period the samples were filtered through Whatmann grade No. 3 filter paper. The concentration of Cu in the filtrates was determined using an Atomic Absorption Spectrometer (Varian SpectrAA-200).

For adsorption isotherms studies, each 100 mL of Cu^{2+} solutions at varying concentrations (100-650 mg/L for vermiculite and 100-325 mg/L for clinoptilolite) were introduced into beakers containing 3 g of each adsorbent. The solution was analyzed for Cu^{2+} concentration after a 24 h shaking.

The effect of pH (1.00-5.5) on Cu adsorption was examined. Adsorbent (3g) was equilibrated with 100 mL of 300 mg Cu/L by shaking for 45 min. In the final set, the effect of temperature (25, 50, 75 °C) was examined. After shaking, the extracted solution was filtered through Whatmann grade No. 3 filter paper and analyzed for Cu^{2+} ions.

RESULTS & DISCUSSION

In order to understand the process of adsorption, the kinetic model was applied to analyze the experimental data. The linear form of pseudo second-order kinetic model of Lagergern is expressed as Eq. (1).

$$\frac{t}{q_t} = \frac{1}{K q_e^2} + \frac{t}{q_e} \qquad (1)$$

Where, q_e and q_t, respectively, represent the amount of metal adsorbed on adsorbent at equilibrium and time t, K (g/(mg.min)) is the pseudo second-order rate constant and h (mg/g/min) is the initial adsorption rate equal to $K q_e^2$. q_e and K can be calculated from the slope and intercept of plot $\frac{t}{q_t}$ versus t (Hu *et al.*, 2010).

The amount of copper adsorbed onto the adsorbent, q_e *(mg/g)*, was calculated by a mass balance relationship presented in Eq. (2).

$$q_e = (C_0 - C_e)\frac{V}{W} \qquad (2)$$

Where C_0 *(mg/l)* and C_e *(mg/l)* are the initial and equilibrium liquid-phase concentrations, respectively. *V(L)* stands for the volume of the solution while, *W(g)* corresponds the dry weight of the adsorbent. The results have been shown in Tables 3 and 4. It is observed that the initial adsorption rate (h), increased by the increase of Cu^{2+} initial solution concentration. The driving force for the adsorption is the difference between the Cu^{2+} ion concentration in the solution and that on the solid-liquid interface, which is evidently larger at higher concentrations of Cu^{2+} ions (Tables 3 and 4).

The analysis of the isotherm data is of great importance by fitting them into different isotherm

Table 3. Kinetic parameters of pseudo second-order model for cover onto vermiculite (pH=4)

Cu	100 (mg/*l*)	200 (mg/*l*)	300 (mg/*l*)
Rate constant K (g/ mg hr)	0.144	0.055	0.07
Initial adsorption rate h (mg/g/hr)	1.37	1.46	1.89
Amount adsorbed predicted q_{pre} (mg/g)	2.13	3.01	3.4
Amount adsorbed Experimental q_{exp} (mg/g)	2.08	2.9	3.125
R^2	0.985	0.974	0.926

Table 4. Kinetic parameters of pseudo second-order model for cover onto clinoptilolite (pH=5.5)

Cu	100 (mg/*l*)	200 (mg/*l*)	300 (mg/*l*)
Rate constant K (g/ mg min)	0.104	0.0155	0.042
Initial adsorption rate h (mg/g/min)	1.39	1.52	2.82
Amount adsorbed predicted q_{pre} (mg/g)	3.597	6.88	8.067
Amount adsorbed Experimental q_{exp} (mg/g)	3.59	6.91	8.064
R^2	0.999	0.995	0.999

models to optimize the adsorption system (Seader and Henly., 2006). The most widely used isotherm equations are Langmuir and Freundlich equations (Kim *et al.,* 2004).

Langmuir isotherm is based on the assumption that an active point on the surface of the adsorbent is able to adsorb one molecule, indicating the adsorbed layer is one molecule thick (Chang *et al.,* 2003). It is expressed as the following Eq. (3):

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a}{K_L} C_e \qquad (3)$$

Where, C_e *(mg/l)* is the equilibrium concentration, q_e *(mg/l)* is the amount adsorbed, K_L and *a* are the Langmuir constans.

Freundlich isotherm is valid for non-ideal adsorption on heterogeneous surfaces, suggesting multilayer adsorption on adsorbent surfaces (Safa and Bhatti., 2011). The empirical equation is presented as following Eq. (4):

$$Log\, q_e = log\, K_F + \frac{1}{n} logC_e \qquad (4)$$

where K_F is the Freundlich adsorption constant and the slope of the Freundlich equation $\frac{1}{n}$ ranging between *0* and *1* is a measured of adsorption intensity or surface heterogeneity, which may become more heterogeneous when $\frac{1}{n}$ gets close to zero (Nausha *et al.,* 2010 ; Hu *et al.,* 2010).

The linearized forms of the Langmuir and Freundlich isotherms on copper ion removal by vermiculite and
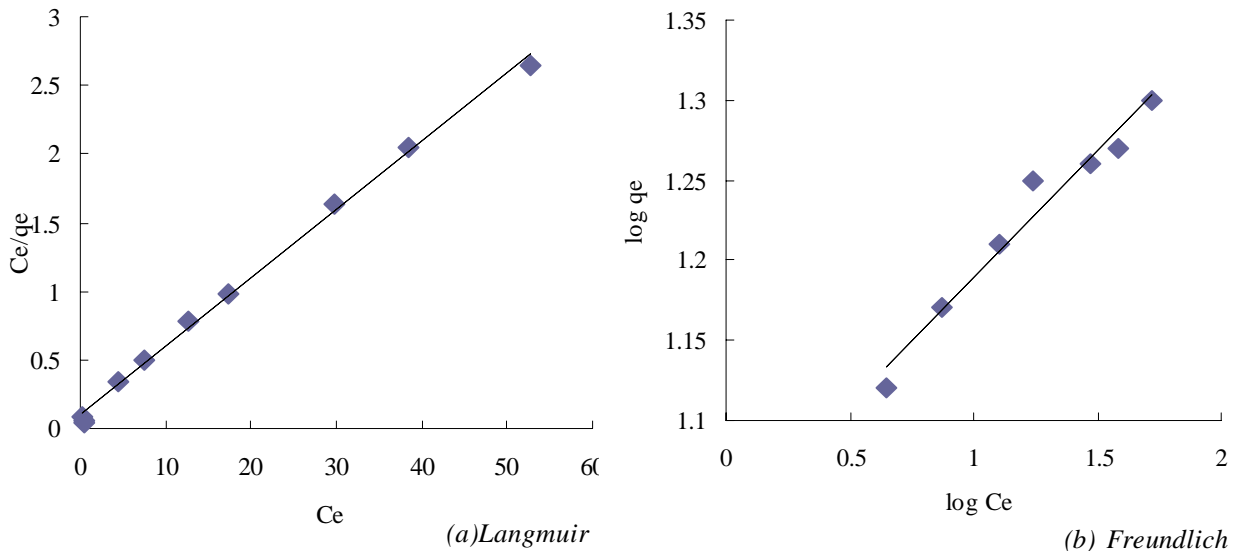

(a)*Langmuir*   (b) *Freundlich*

Fig. 1. Langmuir (a) and Freundlich (b) isotherms of Cu²⁺ ion adsorption by vermiculite (shaking time , 24 h, temperature, 25 °C)
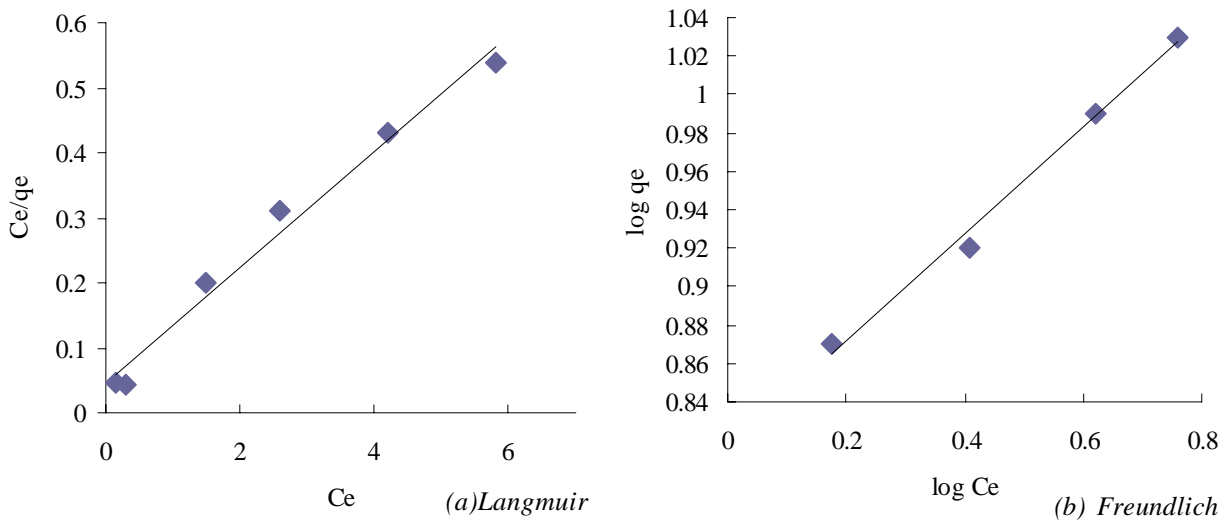

(a)*Langmuir*   (b) *Freundlich*

Fig. 2. Langmuir (a) and Freundlich (b) isotherms of Cu²⁺ ion adsorption by clinoptilolite (shaking time 24 h, temperature 25 °C)

clinoptilolite can be seen in Figs. 1 and 2 and the Langmuir and Freundlich parameters computed from Eqs. (3) and (4) are listed in Tables 5 and 6.

The morphology of vermiculite before and after the removal of Cu^{2+} was photographed by SEM as shown in Fig. 3.

Batch kinetic experiments were studied by agitation 100 ml of three different concentration of Cu^{2+} (100, 200 and 300 mg/*l* with 3 g clinoptilolite and vermiculite at the initial pH. The stirring rate was 200 rpm during the experiments. Samples were collected at 1-300 min (Fig. 4 and Fig. 5).

The larger removal amount of copper caused by a higher initial copper concentration was presumably attributed to the active interaction between adsorbents and copper molecules. The findings probably were also due that an increase in metal concentration could accelerate the diffusion of metal molecules onto the adsorbents as a result of an increase in the driving force of concentration gradient.

The pH of the aqueous solution is an important variable, which controls the adsorption of the metal at the solid-water interfaces as well as the ion exchange of cations. The influence of pH on the adsorption of Cu^{2+} on vermiculite and clinoptilolite were examined. It is observed that acidity influences the removal of Cu^{2+}

Table 5. Langmuir and Freundlich isotherms constans for Cu^{2+} ion adsorbed on vermiculite (shaking time,24 h, temperature, 25 °C)

Parameters	Vermiculite	R^2
K_L (Langmuir)	11.11	0.9967
a (Langmuir)	0.55	0.9967
K_F (Freundlich)	10.69	0.963
$\frac{1}{n}$ (Freundlich)	0.159	0.963

Table 6. Langmuir and Freundlich isotherms constans for Cu^{2+} ion adsorbed on clinoptilolite (shaking time 24 h, temperature 25 °C)

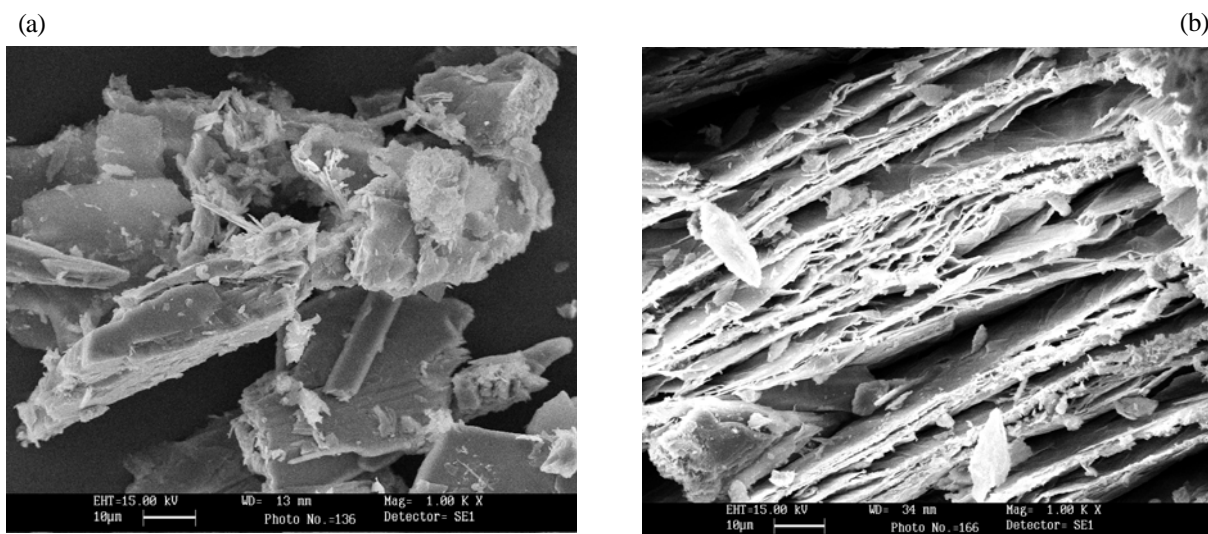| Parameters	Clinoptilolite	R^2
K_L (Langmuir)	23.25	0.9853
a (Langmuir)	2.07	0.9853
K_F (Freundlich)	6.17	0.9911
$\frac{1}{n}$ (Freundlich)	0.325	0.9911

(a) (b)

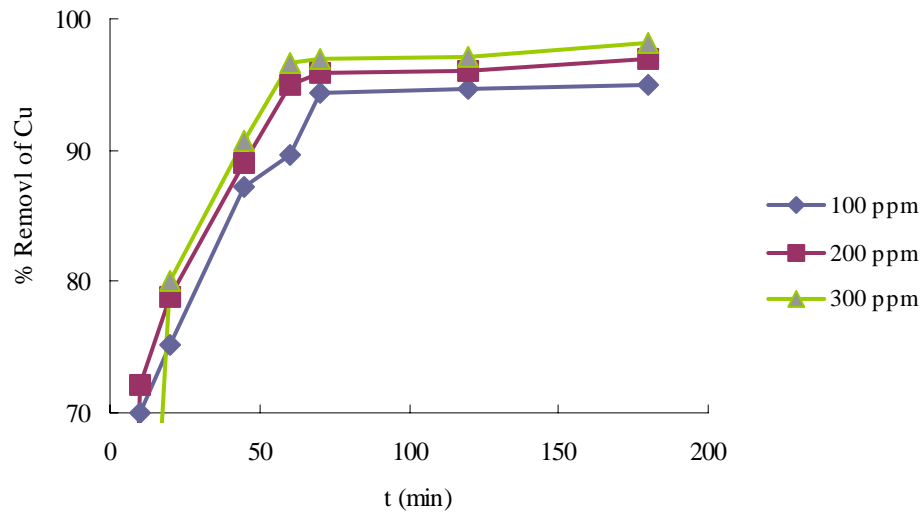**Fig. 3. SEM images of vermiculite before (a) and after (b) the adsorption of Cu^{2+}**

Fig. 4. Percentage removal of copper by clinoptilolite as a function of contact time (T=25 °C , agitation=200 rpm)
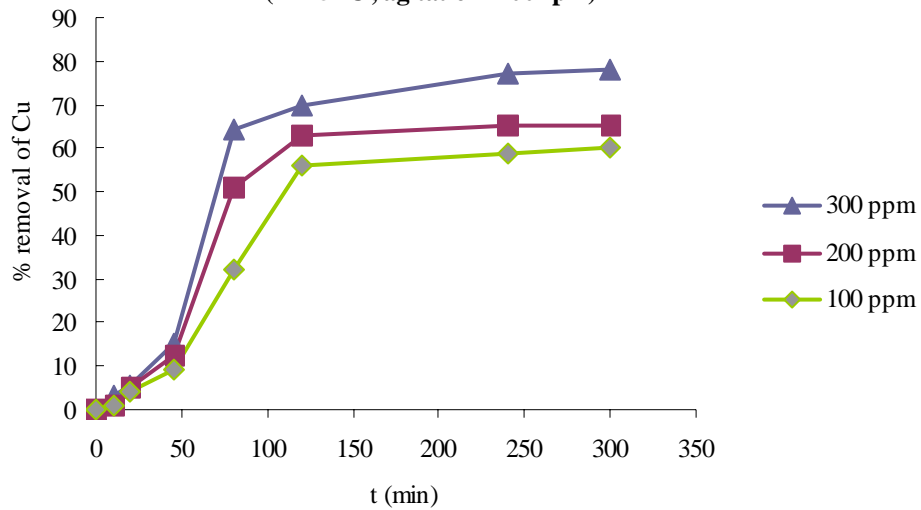

Fig. 5. Percentage removal of copper by vermiculite as a function of contact time (T=25 °C , agitation=200 rpm)
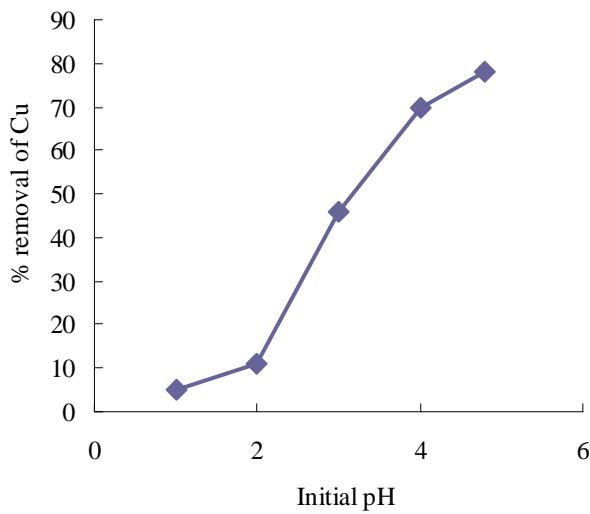

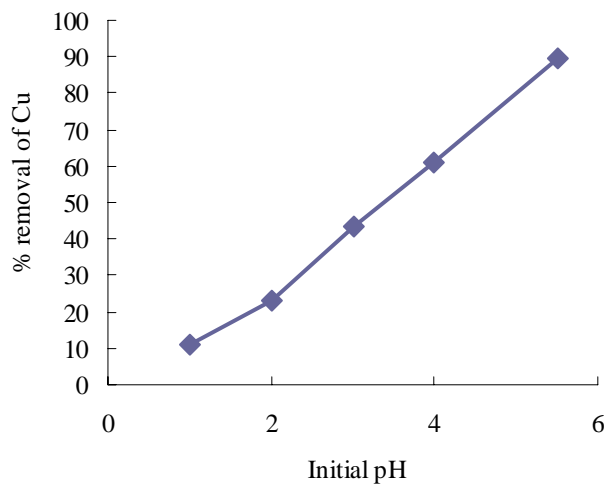**Fig. 6. Effect of pH on removal of copper by vermiculite at 25 °C**

Fig. 7. Effect of pH on removal of copper by clinoptilolite at 25 °C

by the vermiculite (Fig. 6) and by the clinoptilolite (Fig. 7). The copper adsorption on vermiculite was lower with pH<4.00. At pH 1.00 below 6% of the copper was adsorbed. In the present study it was found that Cu^{2+} started precipitating as $Cu(OH)_2$ above pH 5.5. H^+ cations should be considered as competitive ones in ion exchange process and, consequently, ion exchange of metal is favored by high pH values, which should, however, be lower than the minimum pH of precipitation. However, low pH values may also have a beneficial effect as they influence the hydrolysis of the metals. Hydration is followed by hydrolysis, according to the following two-way reversible reaction, giving acidic properties to heavy metal solutions. Consequently, at decreasing pH the above equilibrium is shifted to the left and more highly charged metal complexes are formed, a fact which is beneficial for the exchange (Inglezakis *et al.,* 2003).
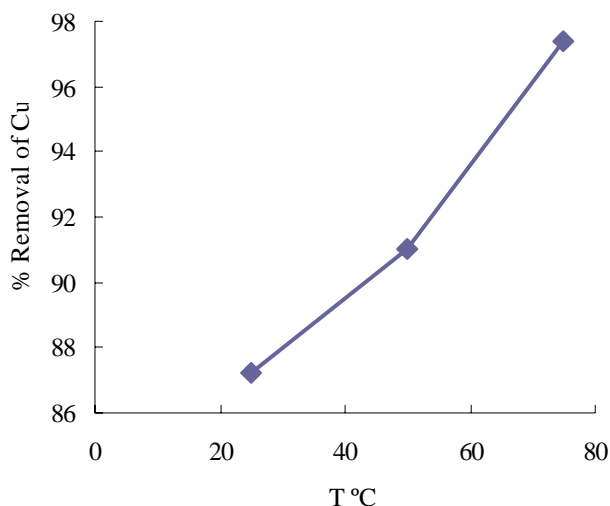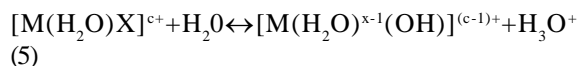
$$[M(H_2O)X]^{c+}+H_2O\leftrightarrow[M(H_2O)^{x-1}(OH)]^{(c-1)+}+H_3O^+ \quad (5)$$

The influence of temperature on the adsorption of copper on vermiculite and clinoptilolite was examined at three different temperatures (25, 50 and 75 °C). An increase in Cu^{2+} removal from the aqueous solution with a raise in temperature was observed (Fig. 8 and Fig. 9).

As far as the effect of the temperature on the adsorption process is concerned, the metal uptake is favored at higher temperatures, since higher temperatures activate the metal ions for enhancing adsorption at the coordinating sites of the minerals (Naseem *et al.,* 2001; Sari *et al.,* 2007). Also it is mentioned that cations move faster when temperature increases. Potential explanations for this are that specific or electrostatic interactions become weaker and the ions become smaller, since solvation is reduced (Inglezakis *et al.,* 2004).
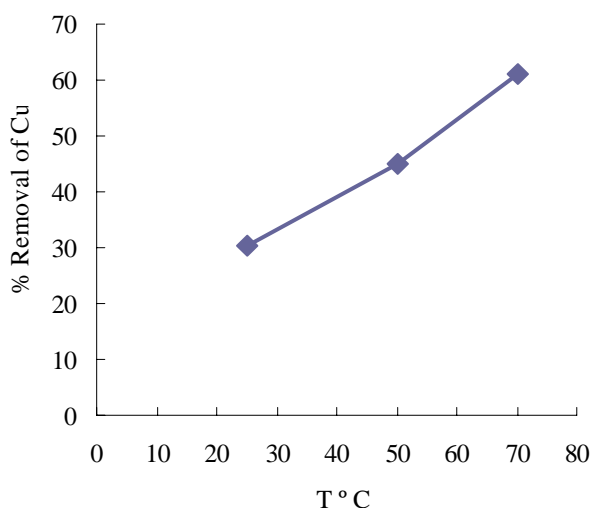

Fig. 8. Effect of temperature on removal of copper by clinoptilolite

Fig. 9. Effect of temperature on removal of copper by vermiculite

CONCLUSION

Based on the present investigation it can be concluded that both of adsorbents vermiculite and clinoptilolite exhibits good adsorption properties for Cu^{2+} ions in aqueous solutions. The adsorption capacity was found to be 11.24 mg/g at pH 5.5 for clinoptilolite and -25 °C and 200 rpm agitation. The adsorption capacity for vermiculite was found to be 20 mg/g at pH 4.8 and 25 °C and 200 rpm agitation.

The adsorption of Cu^{2+} was strongly pH dependent. The pH value of 5.5 seems to give better results than lower pH values for clinoptilolite and the best pH value for vermiculite was 4.8.

The equilibrium isotherm analysis of the experimental data showed that the adsorption Cu^{2+} ions onto the vermiculite and clinoptilolite follows Langmuir and Freundlich isotherms. Therefore it is possible to conclude that both of adsorbents have good potentialities in cost-effective treatments of metal-contaminated aqueous solutions.

The results indicate a better performance of the vermiculite and clinoptilolite in adsorption of Cu^{2+} ions, in comparison to previous studies (Stylianou et al., 2007). It is worth mentioning that an exact comparison could not be made, since operating conditions of the experiment such as temperature, solution pH and the amount of minerals constituents are not the same.

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