

# Equilibrium and Kinetic Analysis for $\text{Cu}^{2+}$ and $\text{Ni}^{2+}$ Adsorption Onto Na-Mordenite

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**Abstract:** In the present study, the adsorption behaviors of mordenite (a common zeolite) with respect to  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  from aqueous solutions were investigated. The sorption data followed the Freundlich and Langmuir isotherms. The maximum sorption capacities were found to be 9.778 and 5.371 mg/g at pH 6, initial concentration of 40 mg/L and temperature of 30°C for  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$ , respectively. The kinetic experimental data fitted the pseudo-second order equation very well and the values of rate constant of adsorption were evaluated. The Na-mordenite could be used as low-cost sorbent to remove copper and nickel ions from aqueous solutions.

**Keywords:** Mordenite, Diffusion, Wastewater treatment.

## 1. INTRODUCTION

Nickel (Ni) may be found in wastewater discharges from mining, electroplating, pigments and ceramic industries, battery and accumulator manufacturing [1]. Nickel is toxic to a variety of aquatic organisms, even at very low concentration. The most common adverse health effect of nickel in humans is an allergic reaction; large amounts of nickel can cause lung and nasal sinus cancers. Copper (Cu), which is widely used, is one of the principal heavy metals responsible for causing hemolysis, liver and kidney damage, irritation of upper respiratory tract, gastrointestinal disturbance, diarrhea [2]. The main anthropogenic pathway through which Cu (II) enters the water bodies is via wastes from industrial processes such as dyeing, paper, petroleum, copper/brass-plating and copper-ammonium rayon [3]. The US EPA requires nickel and copper in drinking water not to exceed 0.04, 0.015 mg/L [4].

Conventional treatment technologies such as precipitation, ion exchange, and activated adsorption have been employed to remove heavy metal ions from aqueous solution. However, these processes have significant disadvantages such as incomplete metal removal, particularly at low concentrations and high operational costs [5]. Cost-effective treatment technologies, therefore, are needed to meet these requirements. Ion exchange process based on zeolites has been considered to be a cost-effective approach for waste decontamination. Recently, natural zeolites have started gaining interest for removing undesirable heavy metal ions from industrial and processing effluent water [6]. Clinoptilolite and chabazite for example has received extensive attention due to their attractive selectivities for certain heavy metal ions such as  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  [6-10]. However, to authors' knowledge, studies on heavy metal ions removal by using mordenite (a naturally occurring zeolite) are still scarce. Moreover, the mordenite samples

from different regions show different adsorption behavior in ion-exchange processes. With this in mind, the aim of this work is to evaluate the usefulness of mordenite as low cost sorbent material for the removal of copper and nickel ions from single aqueous solution.

## 2. MATERIALS AND METHODS

Naturally occurring mordenite was provided for study by China University of Mining and Technology. The mordenite was lightly ground and sieved. Fine particles with a diameter < 150  $\mu\text{m}$  were used to prepare the Na-mordenite. To prepare homoionic Na-mordenite, 30g of mordenite was mixed with 500 mL of 1 M NaCl. After 24h end-over-end shaking, the mordenite suspension was centrifuged at 3000rpm and the supernatant was replaced with fresh 1 M NaCl solution. This procedure was repeated three times, followed by a three-fold washing with 500 mL de-ionized water. The Na-mordenite was dried at 60°C overnight and stored in polyethylene flask for further experiments.

XRD measurement was done with X-Ray Diffraction (D/Max-3B) using Cu K $\alpha$  radiation (Fig. 1). Sears' method was chosen to estimate the surface areas of the Na-mordenite. The copper bisethylenediamine complex method was used to determine the cation exchange capacity of the Na-mordenite [11]. Other physical properties were determined by the usual analytical methods. The results of the sample properties are presented in Table 1.

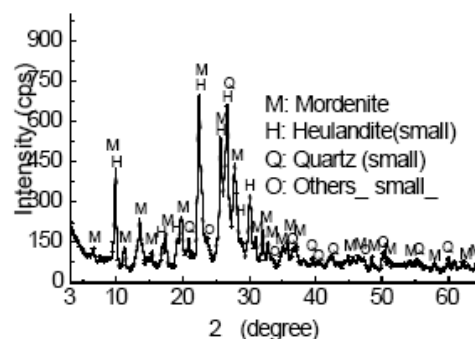


Fig. (1). XRD pattern of adsorbent.

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Table 1. Physical Properties of Natural Mordenite Sample

Bulk density (g/cm <sup>3</sup> )	1.50
Particle density (g/cm <sup>3</sup> )	2.31
Porosity (%)	35
pH	6.98
Cation exchange capacity (mmol/100g)	187
Mean particle diameter (μm)	107.2
Specific area (m <sup>2</sup> /g)	7.0

The stock solutions of Cu<sup>2+</sup> and Ni<sup>2+</sup> (2000mg/L) were prepared in deionized water using copper sulfate and nickel sulfate (analytical grade reagent). All working solutions were prepared by diluting the stock solution with deionized water.

Batch adsorption experiments were carried out by shaking 0.25g of sorbent with 50 mL aqueous solution of the desired concentration (20 to 100 mg/L) in a temperature-controlled water-batch shaker (30°C). The flasks were shaken for 240 min to reach equilibrium. A known volume of the solution was removed and filtered for Cu<sup>2+</sup> and Ni<sup>2+</sup> analysis with atomic absorption spectrophotometer (AAS). Effect of sorbent dose on uptake of Cu<sup>2+</sup> and Ni<sup>2+</sup> were investigated by varying the range of Na-mordenite doses from 1.0 to 5.0 g/L with an initial concentration 40 mg/L and agitation speed of 200 rpm. Kinetic studies were carried out at constant pH 6 with initial concentration (40 mg/L) and adsorbent dose of 2 g/L at 30°C. After shaking, the samples were withdrawn at suitable time intervals, filtered through a 0.45 μm membrane filter and then analyzed for Cu<sup>2+</sup> and Ni<sup>2+</sup> concentrations.

The amounts of Cu<sup>2+</sup> and Ni<sup>2+</sup> sorbed by Na-mordenite ( $q$ ) in the sorption system were calculated using the mass balance:

$$q = \frac{V(C_i - C_e)}{m} \quad (1)$$

where  $V$  is the solution volume (L),  $m$  is the amount of sorbent (g), and  $C_i$  and  $C_e$  (mg/L) are the initial and equilibrium metal concentrations, respectively.

The percent removal (%) and distribution coefficient ( $K_D$ ) (mL/g) were calculated using the following equations:

$$\text{Removal\%} = \frac{C_i - C_e}{C_i} \times 100 \quad (2)$$

and

$$K_D = \frac{C_i - C_e}{C_e} \times \frac{V}{m} \quad (3)$$

The percent removal (%) and  $K_D$  (mL/g) can be correlated by the following equation:

$$\text{Removal\%} = \frac{100K_D}{K_D + V/m} \quad (4)$$

### 3. RESULTS AND DISCUSSION

#### 3.1. Adsorption of Cu<sup>2+</sup> and Ni<sup>2+</sup> Ions Onto Na-Mordenite

The adsorption of Cu<sup>2+</sup> and Ni<sup>2+</sup> onto Na-mordenite as a function of their concentrations was studied at 30 °C by varying the initial concentration from 20 to 100 mg/L while keeping all other parameters constant and the results are shown in Figs. (2) and (3). Percentage removals for Cu<sup>2+</sup> and Ni<sup>2+</sup> decrease with increasing metal concentrations in aqueous solutions. The  $K_D$  values increase with the decreasing initial concentrations of metal ions. These results show that energetically less favorable sites are involved with increasing metal concentrations in the aqueous solution. These results are in accordance with those obtained by Erdem *et al.* [10] in the study of removal of heavy metal cations (Cu<sup>2+</sup>, Co<sup>2+</sup>, Zn<sup>2+</sup>, Mn<sup>2+</sup>) by natural clinoptilolite.

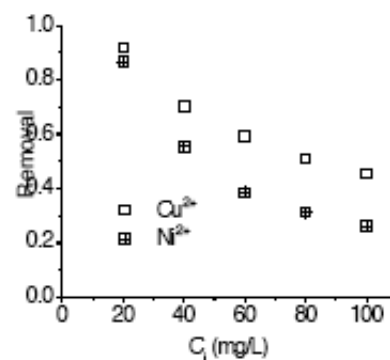


Fig. (2). Removal of Cu<sup>2+</sup> and Ni<sup>2+</sup> ions by Na-mordenite as a function of initial concentrations ( $C_i$ ):  $m=0.25$ g,  $V=50$  ml, pH 6, reaction time 4 h.

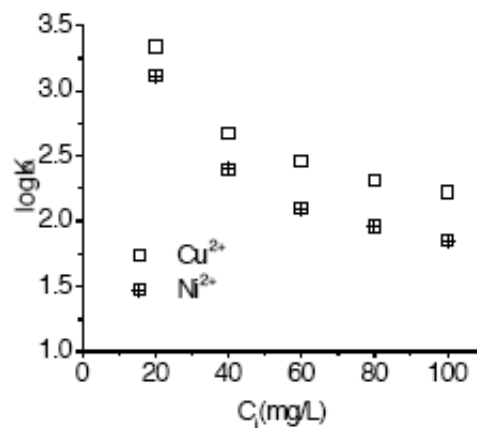


Fig. (3). Distribution coefficients ( $K_D$ ) of Cu<sup>2+</sup> and Ni<sup>2+</sup> as a function of initial concentrations ( $C_i$ ):  $m=0.25$ g,  $V=50$  ml, pH 6, reaction time 4 h.

#### 3.2. Isotherm Models

The sorption data have been subjected to two sorption isotherms, namely, Freundlich and Langmuir. The Freundlich isotherm based on sorption on a heterogeneous surface is as follows:

$$q_e = K C_e^{\frac{1}{n}} \quad (5)$$

**Table 2.** Freundlich Constants log *K* and 1/*n* Together with the Correlation Coefficient (*R*)

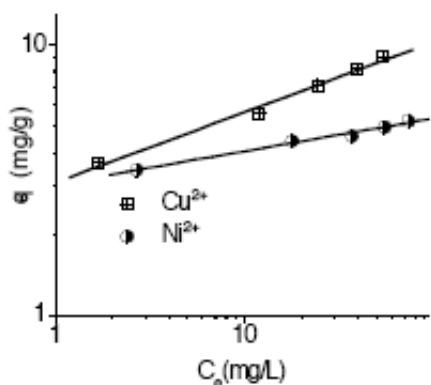
Metal	log <i>K</i>	1/ <i>n</i>	<i>R</i>
Cu <sup>2+</sup>	0.4938	0.2595	0.9947
Ni <sup>2+</sup>	0.4883	0.1211	0.9927

where  $q_e$  is the amount adsorbed at equilibrium (mg/g),  $C_e$  the equilibrium concentration (mg/L).  $K_F$  and  $n$  are equilibrium constants, respectively. The linearized form of Freundlich sorption isotherm is:

$$\log q_e = \log K + \frac{1}{n} \log C_e \quad (6)$$

Freundlich plots for Cu<sup>2+</sup> and Ni<sup>2+</sup> adsorption onto Na-mordenite at 30°C are given in Fig. (4). It illustrates that adsorption of these two metal ions onto Na-mordenite obeys the Freundlich isothermal model very well. The corresponding Freundlich isotherm constants log *K* and 1/*n* together with the correlation coefficients (*R*) is listed in Table 2. The parameter *n* is a characteristic constant for the adsorption system. Values of *n* between 2 and 10 indicate good adsorption [10]. The numerical values of *n* in Table 2 suggest favorable adsorption of Cu<sup>2+</sup> and Ni<sup>2+</sup> onto Na-mordenite.

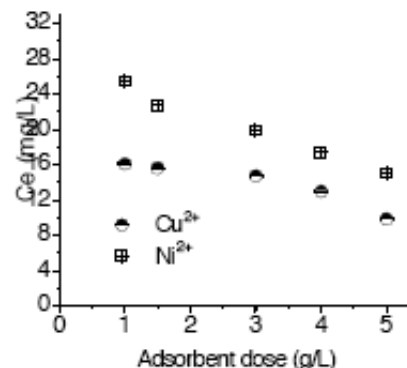
Lower 1/*n* values indicate the effective removal with increasing sorbent concentrations [12]. However, in this study, this effect can not be found in Fig. (5) in which illustrates the effect of sorbent concentrations on equilibrium metal ions concentrations. The higher value of 1/*n*, the more effective removal is.

**Fig. (4).** Freundlich plots for metal ions adsorption onto Na-mordenite.

The Langmuir equation was developed by Irving Langmuir in 1916 to describe the adsorption of gas molecules on a planar surface. The Langmuir model suggests, as a hypothesis, that uptake occurs on a homogenous surface by monolayer sorption without interaction between sorbed molecules. This Langmuir equation has the form:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (7)$$

where  $q_e$  is the amount adsorbed at equilibrium (mg/g),  $C_e$  the equilibrium concentration (mg/L),  $b$  a constant related to the adsorption energy (L/mg), and  $q_m$  the maximum adsorp-

**Fig. (5).** Effect of sorbent doses on equilibrium metal ions concentrations with an initial metal ions.

tion capacity (mg/g). The Langmuir equation can be described by the linearized form as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (8)$$

By plotting ( $C_e/q_e$ ) versus  $C_e$ ,  $q_m$  and  $b$  can be determined if a straight line is obtained.

The Langmuir plots for Cu<sup>2+</sup> and Ni<sup>2+</sup> isothermal adsorption data at 30°C are shown in Fig. (6). The calculated constants  $q_m$  and  $b$  together with correlation coefficients are given in Table 3. The *R* values suggest that the Langmuir isotherm provides a good model of the sorption system as well. The Langmuir constant,  $q_m$ , which is a measure of maximum sorption capacity corresponding to complete monolayer coverage, shows the Na-mordenite had a higher adsorption capacity for Cu<sup>2+</sup> (9.778 mg/g) than for Ni<sup>2+</sup> (5.371 mg/g). The affinity constant,  $b$ , which is related to the adsorption energy, for Ni<sup>2+</sup> (0.2996 L/mg) is greater than that of Cu<sup>2+</sup> (0.1516 L/mg), indicating probably that not all binding sites on the surface of Na-mordenite may be available for Ni<sup>2+</sup> binding due to its relatively higher hydration energy (Table 4). This is in agreement with the result obtained by Jnr and Spiff in the study of effect of metal ion concentration on the biosorption of Pb<sup>2+</sup> and Cd<sup>2+</sup> by *Caladium bicolor* (wild cocoyam) [13]. Table 4 also shows that the affinity constant,  $b$ , positively correlates with the  $pK_h$  value. The large difference in the  $pK_h$  values may be another important factor which results in the discrepancy in affinity for Cu<sup>2+</sup> and Ni<sup>2+</sup> adsorption onto Na-mordenite. It should be noted that the order of  $q_m$  for Cu<sup>2+</sup> and Ni<sup>2+</sup> do not follow the sequence of Langmuir affinity constant,  $b$ . This is in agreement with the results derived by Lv *et al.* [16].

The essential characteristic of the Langmuir equation can be expressed in terms of a dimensional separation factor  $R_L$ , which is defined by the following equation:

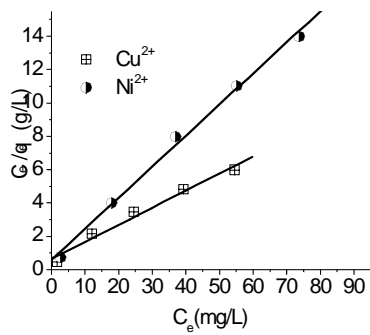


Fig. (6). Langmuir plots for metal ions adsorption onto Na-mordenite.

Table 3. Langmuir Constants  $q_m$  and  $b$  Together with the Correlation Coefficients ( $R$ )

Metal	$q_m$ (mg/g)	$b$ (L/mg)	$R$
Cu <sup>2+</sup>	9.778	0.1516	0.9902
Ni <sup>2+</sup>	5.371	0.2996	0.9977

Table 4. Some Physical Parameters for Cu<sup>2+</sup> and Ni<sup>2+</sup> in Solution [14-18]

Metal	Ionic Radius (nm)	Hydrated Radius (nm)	Hydration Energy (kJ/mol)	Solubility of Hydroxides (pK <sub>s</sub> )	Constants of Hydrolysis (pK <sub>h</sub> )	Electro-Negativity (X <sub>n</sub> )	Covalent Index (X <sub>n</sub> <sup>2</sup> r)
Cu <sup>2+</sup>	0.071	0.419	-2100	19.6	7.53	2.0	3.0
Ni <sup>2+</sup>	0.069	0.302	-2105	14.7	9.40	1.91	2.5

r: ionic radius.

$$R_L = \frac{1}{1 + bC_i} \tag{9}$$

where  $C_i$  is the initial metal concentrations (mg/L) and  $b$  is the Langmuir constant.

The value of  $R_L$  indicates the shape of the isotherm to be either unfavorable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favorable ( $0 < R_L < 1$ ) or irreversible ( $R_L = 0$ ). The  $R_L$  values for Cu<sup>2+</sup> and Ni<sup>2+</sup>

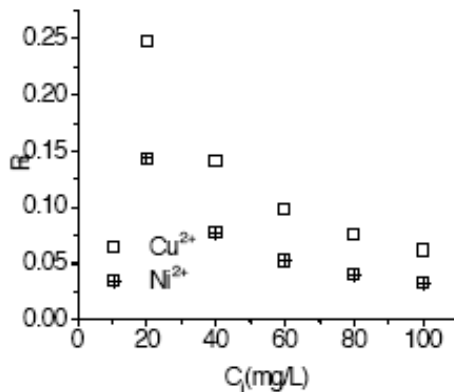


Fig. (7). Plots of  $R_L$  as a function of initial concentrations ( $C_i$ ).

(Fig. 7) were found to be between 0 and 1, indicating favorable adsorption of Cu<sup>2+</sup> and Ni<sup>2+</sup> onto Na-mordenite. The Ni<sup>2+</sup> adsorption onto Na-mordenite was found to be more favorable and closer to the irreversible adsorption edge of  $R_L = 0$  as evidenced from relatively lower  $R_L$  values. Aktas and Cecen [12] concluded that Langmuir isotherm can be used to obtain an idea on the reversibility of adsorption and to make comparisons by using the dimensionless separation factor  $R_L$  from the Langmuir equation. Consequently, according to the  $R_L$  values, the affinity for Ni<sup>2+</sup> adsorption onto Na-mordenite is higher than that for Cu<sup>2+</sup>.

### 3.3. Adsorption Kinetics

The rate constant ( $k_{ad}$ ) (mg/g min) for Cu<sup>2+</sup> and Ni<sup>2+</sup> adsorption onto Na-mordenite were determined using the

pseudo-second order kinetic model [19]. The linearized form of the model is as follows:

$$\frac{t}{q_t} = \frac{1}{q_{max}^2 k_{ad}} + \frac{t}{q_{max}} \tag{10}$$

where  $q_t$ ,  $q_{max}$  are the amount adsorbed at time  $t$  and at equilibrium, respectively. The linear plots of  $t/q_t$  versus  $t$  (Fig. 8) suggested the pseudo-second order kinetics of the Cu<sup>2+</sup> and Ni<sup>2+</sup> adsorption. The values of  $k_{ad}$  were calculated from the slopes of the plots and are represented in Table 5.

Table 5 indicates that the order of the sorption rates was Cu<sup>2+</sup> > Ni<sup>2+</sup>. Cu<sup>2+</sup> was easily and rapidly adsorbed by Na-mordenite. This order is possibly related to the differences in electro-negativity and ionic radius of the atoms. The values of ionic radius and electronegativity of Cu<sup>2+</sup> are higher than those for Ni<sup>2+</sup>. Jiang *et al.* [20] reported that the sorption (molar basis) of metals having a larger ionic radius was greater than for those with a smaller ionic radius.

### 4. CONCLUSIONS

The adsorption capacity of Na-mordenite for Cu<sup>2+</sup> and Ni<sup>2+</sup> is in the order of Cu<sup>2+</sup> > Ni<sup>2+</sup> and this may be related to the difference in metal ion hydration energy and pK<sub>h</sub>. The

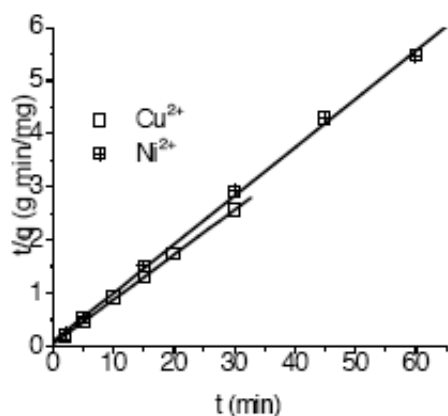


Fig. (8). Plots of  $t/q_t$  versus  $t$  for  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  adsorption onto Na-mordenite at  $30^\circ\text{C}$ .

Table 5. Adsorption Rate Constants and Correlation Coefficients

	$k_{ad}$ (mg/g min)	R
$\text{Cu}^{2+}$	0.1422	0.9999
$\text{Ni}^{2+}$	0.0770	0.9993

sequence of pseudo-second order kinetic rate constants also follows the order of  $\text{Cu}^{2+} > \text{Ni}^{2+}$ . The Na-mordenite could be used as low-cost sorbent to remove copper and nickel ions from aqueous solutions.

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