

## Determination of Parameters Affecting Copper Removal from Solutions by Clinoptilolite: Adsorption Isotherm and Thermodynamic

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**ABSTRACT:** The clinoptilolite mineral which is a zeolite type is one of the natural cation exchangers. In this study, the removal of copper ions from solutions using Bigadiç clinoptilolite by ion exchange method was investigated. Experiments were carried out in batch mode as a function of the solution pH, temperature, ionic strength and conditioning with NaOH and KOH. The ion exchange reaction reached to the equilibrium within 24 hours. Copper sorption capacity of the clinoptilolite increased with high solution pH, high temperature, and low ionic strength. Conditioning of the raw clinoptilolite with NaOH and KOH provided 10.4 and 10.06 fold capacity increase respectively. The increase of capacity with temperature increase showed that the sorption process was endothermic in nature. Also, the ion exchange reaction between clinoptilolite and copper ions was found as more spontaneous at high temperatures. Maximum sorption capacity of the clinoptilolite sample was calculated as 48.45 mg g<sup>-1</sup> after conditioning with NaOH. Sorption equilibrium data were analyzed by the Langmuir and Freundlich models. It was seen that the fitness of isotherm data to the Langmuir isotherm was very good than Freundlich model. The obtained results showed that the Bigadiç clinoptilolite would be used effectively in removal of copper ions from industrial wastewaters especially after conditioning with NaOH.

**Keywords:** Clinoptilolite, copper, ion exchange, isotherm, thermodynamic

## Klinoptilolit Minerali ile Çözeltilerden Bakır Giderimini Etkileyen Parametrelerin Belirlenmesi: Adsorpsiyon İzotermi ve Termodinamiği

**ÖZET:** Bir zeolit türü olan klinoptilolit minerali doğal katyon değiştiricilerden bir tanesidir. Bu çalışmada iyon değişimi metodu ile Bigadiç klinoptiloliti kullanarak çözeltilerden bakır iyonlarının giderimi araştırılmıştır. Deneyler kesikli modda çözelti pH, sıcaklık, iyon şiddeti, NaOH ve KOH ile şartlandırmanın bir fonksiyonu olarak gerçekleştirilmiştir. İyon değişimi reaksiyonu dengeye 24 saatte gelmiştir. Klinoptilolit adsorpsiyon kapasitesi yüksek pH, yüksek sıcaklık ve düşük iyonik şiddet ile artmıştır. Ham klinoptilolit NaOH ve KOH ile şartlandırılması sırasıyla 10.4 ve 10.06 kat kapasite artışı sağlamıştır. Kapasitenin sıcaklık artışı ile artması prosesin endotermik doğada olduğunu göstermiştir. Ayrıca, bakırın klinoptilolit ile iyon değişimi reaksiyonunun yüksek sıcaklıklarda kendiliğinden daha kolay gerçekleşeceği bulunmuştur. Klinoptilolit maksimum kapasitesi NaOH ile şartlandırma sonrasında 48.45 mg g<sup>-1</sup> olarak hesaplanmıştır. Sorpsiyon denge verileri Langmuir ve Freundlich modelleri ile analiz edilmiştir. İzoterm verilerinin Langmuir izotermine uyumunun Freundlich izoterminden çok daha iyi olduğu görülmüştür. Elde edilen sonuçlar, Bigadiç klinoptilolitinin özellikle NaOH ile şartlandırma sonrasında atık sulardan bakır gideriminde etkili bir şekilde kullanılabileceğini göstermiştir.

**Anahtar kelimeler:** Klinoptilolit, bakır, iyon değişimi; izoterm, termodinamik

## INTRODUCTION

Copper is one of the widely used metals in the industries. Copper mining, petroleum, dye, pigment brass and copper ammonium rayon production industries are the main anthropogenic sources of the copper in the environment (Ekmekyapar et al., 2006). Those industrial activities also cause to contamination of soils (Akgül et al., 2006). Copper in the soil forms insoluble organic copper complexes with humic and fulvic acids (Barancikova and Makovnikova, 2003) and this makes difficult the washing of copper from the polluted soils by rains. On the other hand, the copper limits the use of the waters for drinking and industrial purposes (Petrus and Warchol, 2005). Besides, copper is unbiodegradable and accumulate in the food chain (Kocaoba et al., 2007). Copper species in the industrial and mining wastewaters are  $\text{Cu}^{2+}$ ,  $\text{CuCO}_3$ ,  $\text{CuOH}_2$  and organic copper complexes of which concentrations can reach up to 120-500 mg L<sup>-1</sup> (Ekmekyapar et al., 2006; Hui et al., 2005). Copper intake above 1.3 mg L<sup>-1</sup> by humans may cause to the digestive system problems, kidney and liver damage and DNA mutation (Cojocar and Trznadel, 2007). Therefore an effective method should be developed for removal of copper from wastewaters.

In the last two decades, several methods such as ion exchange (Demirbas et al., 2005), adsorption (Hsieh et al., 2006), electrocoagulation (Escobar et al., 2006), membrane filtration after complexation (Cojocar and Trznadel, 2007) and electrodialysis (Hansen et al., 2005) have been reported for removal of copper ions. These mentioned methods have some advantages and limitations in practical applications. For instance, concentrated metal sludge remains over after those methods except ion exchange and electrodialysis (Hui et al., 2005). To remove heavy metals, the ion exchange method can be cheap and environmentally protective in the case of zeolite usage. Natural cation exchangers like zeolites are also preferable as to synthetic cation exchange resins as most of the targeted heavy metals are economically invaluable (Hui et al., 2005). The most commonly found zeolites in nature are clinoptilolite, mordenite, ferrierite, chabazite, erionite, philipsite and analcime (Akgül et al., 2006). The clinoptilolite belongs to the heulandite group of minerals. Similar to clay minerals, clinoptilolite bears a negative surface charge which results from the replacement of silica

( $\text{Si}^{4+}$ ) with aluminum ( $\text{Al}^{3+}$ ) (Wingenfelder et al., 2005). Also, the broken bonds at the siloxane groups (Si-O-Si) bring a negative charge to the clinoptilolite (Ersoy and Celik, 2002). These negative charges are balanced by the alkaline and alkaline earth cations such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . Therefore clinoptilolite has been used as cation exchanger for removal of heavy metal cations (Akgül et al., 2006). As the clinoptilolite exchangeable cations (i.e.  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) have relatively no effect on water quality, the clinoptilolite mineral can be used safely for removal of heavy metals from industrial effluents (Erdem et al., 2004).

Several experimental studies on copper removal from solutions by zeolites have been reported (Inglezakis et al., 2002; Erdem et al., 2004; Cabrera et al., 2005; Hui et al., 2005; Petrus and Warchol, 2005; Wingenfelder et al., 2005; Sprynskyy et al., 2006; Kocaoba et al., 2007). In the reported studies, generally the cation selectivity sequence of the zeolites has been reported, however; the effects of experimental factors such as temperature, pH, ionic strength and conditioning (with KOH and NaOH) have been reported limitedly (Inglezakis et al., 2002; Erdem et al., 2004; Cabrera et al., 2005; Hui et al., 2005; Petrus and Warchol, 2005; Wingenfelder et al., 2005; Sprynskyy et al., 2006; Kocaoba et al., 2007). Also, the zeolite samples from different regions show different heavy metal sorption characteristics and cation selectivity (Erdem et al., 2004; Hui et al., 2005). Hence, the capacity of the zeolite samples from different regions should be determined as separately. Therefore, copper sorption performance of the Bigadiç clinoptilolite was investigated in this study as a function of solution temperature, pH level, conditioning, concentration and ionic strength.

## MATERIAL AND METHODS

The clinoptilolite mineral was belonging to a deposit in Bigadiç district of Balıkesir city in Turkey. Chemical composition of the clinoptilolite was determined as follows:  $\text{SiO}_2$  (64.99%),  $\text{Fe}_2\text{O}_3$  (1.15%),  $\text{CaO}$  (4.03%),  $\text{K}_2\text{O}$  (2.83%),  $\text{Al}_2\text{O}_3$  (11.66%),  $\text{MgO}$  (1.14%),  $\text{Na}_2\text{O}$  (0.15%),  $\text{MnO}$  (0.008%),  $\text{TiO}_2$  (0.093%),  $\text{P}_2\text{O}_5$  (0.033%),  $\text{BaO}$  (0.24%),  $\text{Cr}_2\text{O}_3$  (0.02%),  $\text{H}_2\text{O}$  (13.00%). The total amount of the exchangeable cations was used in the calculation of the total exchange capacity of the

clinoptilolite. Total exchange capacity of the clinoptilolite was calculated as 2.458 meq g<sup>-1</sup>. The clinoptilolite samples were ground and sieved to 90–180 µm particle size fraction using sieves before being used.

Experiments were carried out in batch mode using a temperature controlled incubator shaker (ZHICHENCG, China). Copper solutions were prepared from CuCl<sub>2</sub>·2H<sub>2</sub>O having 98% purity. A time span of 24 hours was enough for equilibrium. A series of the batch experiments were conducted at equilibrium conditions to obtain isotherm data. For this purpose, 50 mL samples of the copper solutions having a concentration range of 4,9–49 mg/L were treated with 0.1 g clinoptilolite samples at changing temperature conditions. The pH levels of the solutions were adjusted with appropriate droplets of diluted NaOH or HCl solutions. Ionic strength of the solutions was adjusted by diluting appropriate volumes of 1 M NaCl solution. To determine the conditioning effect, the clinoptilolite samples (3 g) were conditioned with 1.5 M 100 mL KOH and NaOH solutions separately. Experiments were carried out at 180 rpm agitation speed. After reaction, the solutions were centrifuged at 10,000 rpm during 5 min. After the centrifugation, an appropriate volume of centrifuged solution was pipetted for dilution. The diluted solutions were analyzed at 324.7 nm by an Atomic Absorption Spectrometer (AAS) (UNICAM, England). The samples were automatically measured three times in one aspiration by the AAS. The Relative Standard Deviation (RSD) during the analyses was in the range of 0 - 2%. The band pass space for copper analysis was 0.5 nm. The flame type of the AAS was air-acetylene. Distilled water was used as blank solution in the analysis of copper concentrations. Copper concentrations for calibration curve were in the range of 0 - 10 mg L<sup>-1</sup>. Copper starts to precipitate at pH range of 7.8 - 14 as function of concentration. The sorption capacity of the clinoptilolite mineral was calculated by the following equation.

$$q_e = (C_o - C_e) \times V/M \quad (1)$$

Where,  $q_e$  is the sorption capacity of the clinoptilolite at equilibrium (mg g<sup>-1</sup>).  $C_o$  and  $C_e$  are initial and liquid phase concentrations at initial and equilibrium (mg L<sup>-1</sup>).  $V$  is the solution volume (L).  $M$  is the mass of the clinoptilolite added to the solutions (g).

### Isotherm Models

The widely used isotherm models in the literature are the Freundlich and Langmuir isotherm models.

The Langmuir isotherm describes the monolayer adsorption. According to the theory of the Langmuir isotherm, the adsorbent surface has homogen binding energy distribution. The linear form of the Langmuir isotherm has been reported as follow (Langmuir, 1918).

$$C_e/q_e = 1/(q_m k_L) + C_e/q_m \quad (2)$$

Where,  $C_e$  is the equilibrium concentration in liquid phase (mg L<sup>-1</sup>).  $q_e$  is the maximum amount of the copper sorbed at equilibrium (mg g<sup>-1</sup>).  $q_m$  is maximum theoretical sorbed amount at equilibrium (mg g<sup>-1</sup>).  $k_L$  is the sorption equilibrium constant (L mg<sup>-1</sup>).

The Freundlich isotherm describes the multilayer adsorption. According to the theory of the Freundlich isotherm, the adsorbent surface has heterogen binding energy distribution throughout the surface. The linear form of the Freundlich isotherm has been reported as follow (Freundlich, 1906).

$$\ln q_e = \ln k_f + \ln C_e/n \quad (3)$$

Where,  $C_e$  is the equilibrium concentration in liquid phase (mg L<sup>-1</sup>).  $q_e$  is the maximum amount of copper sorbed at equilibrium (mg g<sup>-1</sup>).  $k_f$  is the Freundlich adsorption capacity.  $1/n$  is the sorption constant having a value range between 0 and 1.

### Thermodynamic Equations

The thermodynamic properties of a given adsorption process is generally calculated to take information about the spontaneity and nature of the adsorption process. The relation between the gibbs free energy change of the adsorption and equilibrium constant is generally given as follow (Bayramoğlu et al., 2009).

$$\Delta G^\circ = - RT \ln K \quad (4)$$

The gibbs free energy change is also a function of the entropy and enthalpy change of adsorption process at constant temperature as in the following equation.

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (5)$$

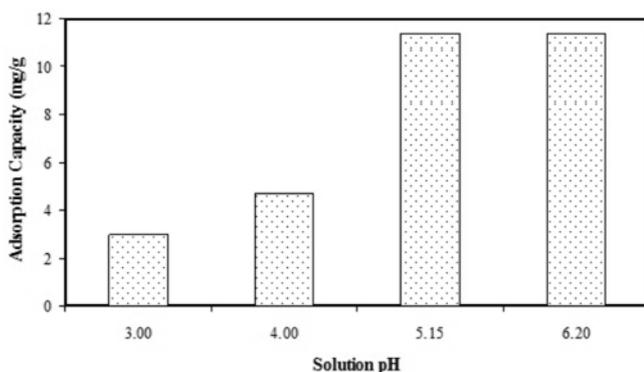
If two equations given above are combined, we get Equation (6),

$$\ln K = -\Delta G^\circ / RT = \Delta S^\circ / R - \Delta H^\circ / RT \quad (6)$$

Where,  $\Delta G^\circ$  is the gibbs free energy change ( $\text{kJ mol}^{-1}$ ).  $\Delta H^\circ$  is the enthalpy change ( $\text{kJ mol}^{-1}$ ).  $\Delta S^\circ$  is the entropy change ( $\text{kJ mol}^{-1} \text{K}^{-1}$ ).  $K = (q_e/C_e)$  is the equilibrium constant ( $\text{L g}^{-1}$ ).  $T$  is absolute temperature ( $\text{K}$ ) and  $R$  is the universal gas constant ( $8.314 \text{ J mol}^{-1} \text{K}^{-1}$ ). Thus  $\Delta H^\circ$  and  $\Delta S^\circ$  can be determined from the slope and intercept of the linear Eq. (6) respectively.

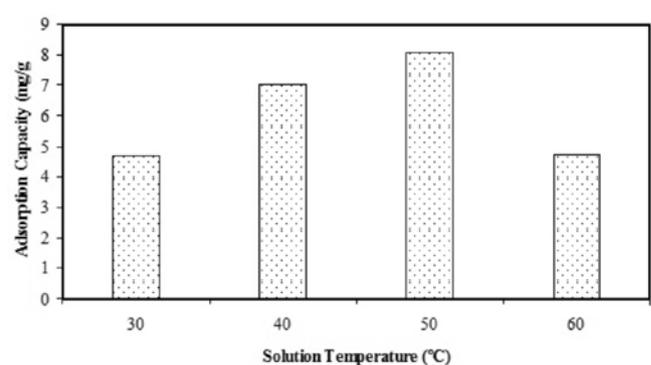
## RESULTS AND DISCUSSION

**Effect of Solution pH:** The solution pH is one of the most important factors affecting the adsorption capacity of the adsorbents because the surface zeta potential of the adsorbent surfaces and ionization degree of the cations is proportional with the solution pH level (Hui et al., 2005). The experiments for pH effect were carried out at pH range of 3–6.20 and other parameters were kept constant, viz. temperature  $30^\circ\text{C}$ , agitating speed 180 rpm, solid-to-solution ratio  $0.1 \text{ g } 50\text{mL}^{-1}$ , concentration  $29.4 \text{ mg L}^{-1}$  and no salt. Experimental results for the pH effect were given in Figure 1. When the solution pH level was increased from 3 to 6.20, the capacity of the clinoptilolite increased from 2.969 to  $11.351 \text{ mg g}^{-1}$ . At high pH values, the negatively charged sites on the clinoptilolite surface increased the negative surface zeta potential and this caused further adsorption of copper ions to the clinoptilolite surface (Doğan and Alkan, 2003). On the other hand, competitive sorption occurred between  $\text{H}^+$  and  $\text{Cu}^{2+}$  ions at low pH levels for negative surface groups and exchangeable cations of clinoptilolite. Therefore the capacity of the clinoptilolite decreased (Özmetin et al., 2009).



**Figure 1.** The effect of solution pH on sorption capacity (Temperature:  $30^\circ\text{C}$ , Concentration:  $29.4 \text{ mg L}^{-1}$ , Salt:  $0 \text{ M NaCl}$ , Solid-to-solution ratio:  $0.1 \text{ g } 50\text{mL}^{-1}$ , Agitation speed: 180 rpm)

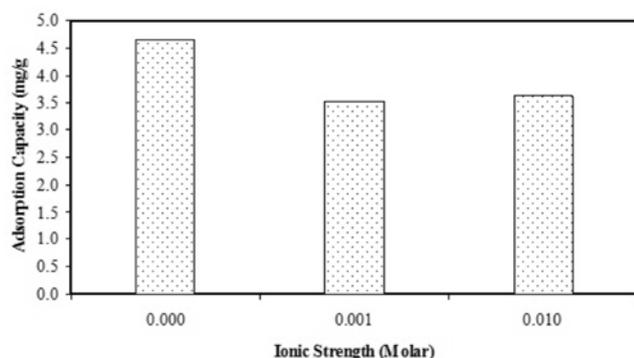
**Effect of Solution Temperature:** Generally, adsorption reactions have either endothermic or exothermic nature. Experiments for temperature effect were carried out at temperature range of  $30\text{--}60^\circ\text{C}$  and other parameters were kept constant, viz. pH 4, agitating speed 180 rpm, solid-to-solution ratio  $0.1 \text{ g } 50\text{mL}^{-1}$ , concentration  $29.4 \text{ mg L}^{-1}$  and no salt. Experimental results for temperature effect were given in Figure 2. When the temperature was increased from  $30$  to  $50^\circ\text{C}$ , the capacity of the clinoptilolite increased from 4.66 to  $8.089 \text{ mg g}^{-1}$ . Increasing temperature caused to sufficient energy gathering by the copper ions for interaction with active sites in the clinoptilolite structure (Özdemir et al., 2006). A similar trend for temperature effect on copper clinoptilolite binary system was also reported (Woinarski et al., 2003). On the other hand, the increased temperature might have caused to swelling in the clinoptilolite structure for easy transmigration of copper ions into the clinoptilolite pores. In addition to this, the capacity of clinoptilolite decreased when temperature was increased from  $50$  to  $60^\circ\text{C}$ . We considered that this result might have been due to increasing osmotic pressure of structural water in clinoptilolite pores with high solution temperature because the used clinoptilolite sample had 13% water content and this structural water prevented copper transmigration into pores at high temperature. Also, thermodynamic parameters such as gibbs free energy change ( $\Delta G^\circ$ ), enthalpy change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ) were calculated using Eq. (6) for temperature range of  $30\text{--}50^\circ\text{C}$ . While the enthalpy value of the process was  $15.553 \text{ j mol}^{-1}$ , the entropy value was  $53.313 \text{ j molK}^{-1}$ . The gibbs free energy change of the process was in the range of  $-608.7$



**Figure 2.** The effect of temperature on sorption capacity (pH:4, Concentration:  $29.4 \text{ mg L}^{-1}$ , Salt:  $0 \text{ M NaCl}$ , Solid-to-solution ratio:  $0.1 \text{ g } 50\text{mL}^{-1}$ , Agitation speed: 180 rpm)

and  $-1674.9 \text{ J mol}^{-1}$ . Positive enthalpy value ( $\Delta H^\circ$ ) indicated that copper sorption on the clinoptilolite was endothermic in nature. The negative gibbs free energy change ( $\Delta G^\circ$ ) indicated that the process was spontaneous at high temperatures ( $50^\circ\text{C}$ ). Positive value of entropy was due to increase in adsorption-desorption rate at clinoptilolite-solution interface (Bayramoğlu et al., 2009). Optimum temperature was found as  $50^\circ\text{C}$ .

**Effect of Ionic Strength:** Generally surface waters and industrial wastewaters contain several types of cations such as  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Fe}^{2+}$ . Experiments for ionic strength effect were carried out at salt ( $\text{NaCl}$ ) concentration range of  $0\text{-}0.01 \text{ M}$  and the other parameters were kept as constant, viz. temperature  $30^\circ\text{C}$ , agitation speed  $180 \text{ rpm}$ , solid-to-solution ratio  $0.1 \text{ g } 50\text{mL}^{-1}$ , concentration  $29.4 \text{ mg L}^{-1}$  and  $\text{pH } 4$ . Experimental results for ionic strength effect were given in Figure 3. As can be seen in Figure 3, when the ionic strength was increased from  $0$  to  $0.01 \text{ M}$   $\text{NaCl}$  concentration, the capacity of the clinoptilolite decreased from  $4.66$  to  $3.633 \text{ mg g}^{-1}$ . The reason of this sorption capacity decrease was due to competitive adsorption of sodium ions with copper ions for the fixation sites in the structure of the clinoptilolite (Wingenfelder et al., 2005). A similar ionic strength effect for heavy metal clinoptilolite binary system was also reported (Wingenfelder et al., 2005). However, the capacity of clinoptilolite for  $0.01 \text{ M}$   $\text{NaCl}$  was found as same with that for  $0.001 \text{ M}$   $\text{NaCl}$ . This might have occurred due to standard deviation of copper analysis which causes on an average  $0.5 \text{ mg g}^{-1}$  capacity change.

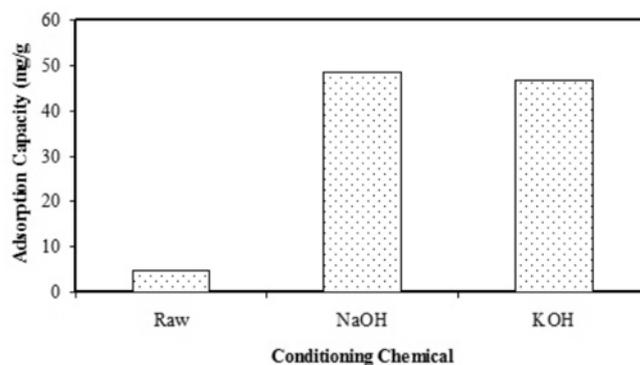


**Figure 3.** The effect of salt concentration on sorption capacity (Temperature:  $30^\circ\text{C}$ , Concentration:  $29.4 \text{ mg L}^{-1}$ ,  $\text{pH } 4$ , Solid-to-solution ratio:  $0.1 \text{ g } 50\text{mL}^{-1}$ , Agitation speed:  $180 \text{ rpm}$ )

### Effect of Conditioning with NaOH and KOH:

The experiments in which the conditioned clinoptilolite samples with  $\text{NaOH}$  and  $\text{KOH}$  were used were carried out at a copper concentration of  $98 \text{ mg L}^{-1}$  and the other parameters were kept as constant, viz. temperature  $30^\circ\text{C}$ , agitation speed  $180 \text{ rpm}$ , solid-to-solution ratio  $0.1 \text{ g } 50\text{mL}^{-1}$  and  $\text{pH } 4$ . The results for conditioning effect were given in Figure 4. As can be seen in Figure 4, the capacity of the clinoptilolite increased with conditioning. In the experiments, the  $3 \text{ g}$  clinoptilolite samples were conditioned with  $8.4 \text{ g}$   $\text{KOH}$  and  $6.0 \text{ g}$   $\text{NaOH}$  solutions which had  $100 \text{ mL}$  volumes,  $15 \text{ meq K}^+$  and  $\text{Na}^+$  amount. When taken into consideration the  $\text{OH}^-$  concentrations in the  $\text{NaOH}$  and  $\text{KOH}$  solutions, the  $\text{KOH}$ -clinoptilolite sample was exposed to more  $\text{OH}^-$  than  $\text{NaOH}$ -clinoptilolite. However, the copper sorption capacity of the  $\text{NaOH}$ -clinoptilolite was found as high than  $\text{KOH}$ -clinoptilolite. The higher copper sorption affinity of  $\text{NaOH}$ -clinoptilolite was attributed to the easy exchange tendency of sodium ions than potassium ions (Hui et al., 2005). Also, this is a sign to that the ion exchange was the main mechanism in the process.

**Determination of Sorption Isotherm:** The results of isotherm experiments were given in Figure 5. Equilibrium experiments were carried out as a function of temperature and other parameters were kept constant, viz. concentration range  $4.9\text{-}49 \text{ mg L}^{-1}$ , agitation speed  $180\text{rpm}$  and solid-to-solution ratio  $0.1 \text{ g } 50\text{mL}^{-1}$ . The obtained data were applied to the Langmuir and Freundlich isotherm models. The fitness of the data to the



**Figure 4.** The effect of  $\text{NaOH}$  and  $\text{KOH}$  conditioning on the capacity of the clinoptilolite (Temperature:  $30^\circ\text{C}$ ,  $\text{pH } 4$ , Concentration:  $98 \text{ mg L}^{-1}$ , Solid-to-solution ratio:  $0.1 \text{ g } 50\text{mL}^{-1}$ , Agitation:  $180 \text{ rpm}$ , Raw clinoptilolite treated with  $29.4 \text{ mg Cu}^{2+}/\text{L}$  copper concentration which was enough for saturation)

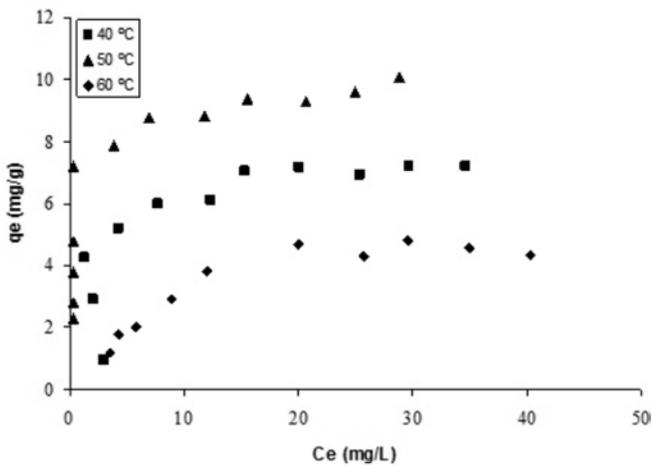


Figure 5. Isotherm plots as a function of temperature

Langmuir and Freundlich isotherms were given in Table 1. As can be seen in Table 1, as the coefficient of determination values ( $r^2$ ) for Langmuir isotherm is higher than Freundlich isotherm, it was determined that the equilibrium data fitted to the Langmuir isotherm. The Langmuir isotherm indicated homogeneous distribution of energetic sites throughout the clinoptilolite surface. Also, the fitness of the data to the Langmuir isotherm is an indicator of mono layer coverage of copper on the clinoptilolite surface and chemisorption (Langmuir, 1918). The clinoptilolite mineral had 2.458 meq  $g^{-1}$  total exchange capacity which was equal to 78.09 mg  $Cu^{2+}/g$  capacity. Maximum exchange capacity of the raw clinoptilolite from the equilibrium experiments was calculated as 10.086 mg  $g^{-1}$  and this was equal to 12.9% capacity usage. 29.4 mg  $L^{-1}$  concentration was enough for entirely saturation.

## CONCLUSION

The main results of this study can be summarized as follows.

- Copper sorption capacity of the clinoptilolite sample increased with increasing pH but decreased with increasing ionic strength. Temperature had increasing effect on capacity from 30 to 50 °C; however, it decreased when temperature was increased from 50 to 60 °C.

- NaOH-clinoptilolite had high sorption capacity than raw and KOH-clinoptilolite due to easy exchange tendency of structural sodium in the clinoptilolite.

Table 1. The coefficient of determination values for the Langmuir and Freundlich isotherms

Isotherm	Temperature (°C)		
	40	50	60
Langmuir ( $R^2$ )	0.922	0.997	0.951
Freundlich ( $R^2$ )	0.449	0.912	0.858

When compared with the raw clinoptilolite, the capacity increase for NaOH-clinoptilolite and KOH-clinoptilolite was 10.4 and 10.06 fold respectively.

- The copper sorption process was endothermic in nature and spontaneous at low concentration and high temperatures.

- Maximum copper sorption capacity of the clinoptilolite sample was calculated as 48.45 mg  $Cu^{2+}/g$  after conditioning with NaOH. The maximum capacity of raw clinoptilolite was 10.08 and this was equal to 12.9% capacity usage.

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## REFERENCES

- Akgul, M., Karabakan, A., Acar, O., Yurum, Y., 2006. Removal of silver (I) from aqueous solutions with Clinoptilolite. *Microporous and Mesoporous Materials*, 94: 99-104.
- Barancikova, G., Makovnikova, J., 2003. The influence of humic acid quality on the sorption and mobility of heavy metals. *Plant Soil Environment*, 49: 565-571.
- Bayramoglu, G., Altintas, B., Arica, M.Y., 2009. Adsorption kinetics and thermodynamic parameters of cationic dyes from aqueous solutions by using a new strong cation-exchange resin. *Chemical Engineering Journal*, 152: 339-346.
- Cabrera, C., Gabaldon, C., Marzal, P., 2005. Sorption characteristics of heavy metal ions by a natural zeolite. *Journal of Chemical Technology and Biotechnology*, 80: 477-481.

- Cojocar, C., Trznadel, G.Z., 2007. Response surface modeling and optimization of copper removal from aqua solutions using polymer assisted ultrafiltration. *Journal Membrane Science*, 298: 56-70.
- Özdemir, Y., Dogan, M., Alkan, M., 2006. Adsorption of cationic dyes from aqueous solutions by sepiolite. *Microporous and Mesoporous Materials*, 96: 419-427.
- Demirbas, A., Pehlivan, E., Gode, F., Altun, T., Arslan G., 2005. Adsorption of Cu(II), Zn(II), Ni(II), Pb(II), and Cd(II) from aqueous solution on Amberlite IR-120 synthetic resin. *Journal of Colloid and Interface Science*, 282: 20-25.
- Dogan, M., Alkan, M., 2003. Adsorption kinetics of methyl violet onto perlite. *Chemosphere*, 50: 517-528.
- Ekmekyapar, F., Aslan, A., Bayhan, Y.K., Cakici, A., 2006. Biosorption of copper(II) by nonliving lichen biomass of *Cladonia rangiformis hoffm.* *Journal of Hazardous Materials*, 137: 293-298.
- Erdem, E., Karapinar, N., Donat, R., The removal of heavy metal cations by natural zeolites. *Journal of Colloid and Interface Science*, 280: 309-314.
- Ersoy, B., Celik, M.S., 2002. Electrokinetic properties of Clinoptilolite with mono- and multivalent electrolytes. *Microporous and Mesoporous Materials*, 55: 305-312.
- Escobar, C., Soto-Salazar, C., Toral, M.I. J., 2006. Optimization of the electrocoagulation process for the removal of copper, lead and cadmium in natural waters and simulated wastewater. *Environmental Management*, 81: 384-391.
- Freundlich, H. M. F., 1906. Over the adsorption in solution. *The Journal of Physical Chemistry*, 57: 385-470.
- Hansen, H.K., Rojo, A., Ottosen, L.M., 2005. Electrodialytic remediation of copper mine tailings. *Journal of Hazardous Materials*, 117: 179-183.
- Hsieh, C.H., Loa, S.L., Kuan, W.H., Chena, C.L., 2006. Adsorption of copper ions onto microwave stabilized heavy metal sludge. *Journal of Hazardous Materials*, 136: 338-344.
- Hui, K.S., Chao, C.Y.H., Kot, S.C., 2005. Removal of mixed heavy metal ions in wastewater by zeolite 4A and residual products from recycled coal fly ash. *Journal of Hazardous Materials*, 127: 89-101.
- Inglezakis, V.J., Loizidou, M.D., Grigoropoulou, H.P., 2002. Equilibrium and kinetic ion exchange studies of Pb<sup>2+</sup>, Cr<sup>3+</sup>, Fe<sup>3+</sup> and Cu<sup>2+</sup> on natural Clinoptilolite. *Water Research*, 36: 2784-2792.
- Kocaoba, S., Orhan, Y., Akyüz, T., 2007. Kinetics and equilibrium studies of heavy metal ions removal by use of natural zeolite. *Desalination*, 214: 1-10.
- Langmuir, I., 1916. The adsorption of gases on plane surface of glass, mica and platinum. *Journal of The American Chemical Society*, 40: 1361-1368.
- Özdemir, Y., Dogan, M., Alkan, M., 2006. Adsorption of cationic dyes from aqueous solutions by Sepiolite. *Microporous and Mesoporous Materials*, 96: 419-427.
- Özmetin, C., Aydın, Ö., Kocakerim, M.M., Korkmaz, M., Özmetin, E., 2009. An empirical kinetic model for calcium removal from calcium impurity-containing saturated boric acid solution by ion exchange technology using Amberlite IR-120 resin. *Chemical Engineering Journal*, 148: 420-424.
- Petrus, R. Warchol, J.K. 2005. Heavy metal removal by clinoptilolite. An equilibrium study in multi-component systems. *Water Research*, 39: 819-830.
- Sprynskyy, M., Buszewski, B., Terzyk, A.P., Namiesnik, J., 2006. Study of the selection mechanism of heavy metal (Pb<sup>2+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>, and Cd<sup>2+</sup>) adsorption on clinoptilolite. *Journal of Colloid and Interface Science*, 304: 21-28.
- Wingenfelder, U., Hansen, C., Furrer, G., Schulin, R., 2005. Removal of Heavy Metals from Mine Waters by Natural Zeolites. *Environmental Science and Technology*, 39: 4606-4613.
- Woinarski, A.Z., Snape, I., Stevens, G.W., Stark, S.C., 2003. The effects of cold temperature on copper ion exchange by natural zeolite for use in a permeable reactive barrier in Antarctica. *Cold Regions Science and Technology*, 37: 159-168.

