# COPPER SORPTION BY CLINOPTILOLITE: EQUILIBRIUM AND THERMODYNAMIC INVESTIGATION

**Mustafa Korkmaz*, Cengiz Özmetin and Elif Özmetin**

**Balıkesir University, Department of Environmental Eng., 10145 Çağış Balıkesir, Turkey, E-mail address: ms_kork@yahoo.com**

## ABSTRACT

Copper is one of the most excavated and used heavy metal cations. Heavy metals such as copper have frequently been reported as toxic substance for the human kind and living organisms in the soil and aqueous environments. Copper forms organo-metal complexes with the soils having fulvic and humic acids and it is hence difficult to washing out the copper complexes that will cause the death of the soil microorganisms. Copper also accumulates in the food chain and is nonbiodegradable. It was therefore investigated the use of clinoptilolite having negatively charged surface for removal of copper from wastewater at various experimental conditions by following the classical batch experimental procedure. Optimum sorption enhancing values of pH level (2.20-6.20), temperature (30-50 $^{o}$C) and ionic strength (0-0.1 M NaCl) were investigated. Copper exchange affinity of the clinoptilolite increased with high pH level, high temperature degree and lower ionic strength. Amoung the applied isotherm models, equilibrium experimental data fitted to the Langmuir model. Thermodynamic parameters were also calculated and the process was found as endothermic in nature. Maximum sorption capacity of the clinoptilolite was calculated as 11 mg$Cu^{2+}$/g. Sorption of the copper by the used clinoptilolite originated by the surface adsorption, surface precipitation and ion exchange.

**Keywords:** Clinoptilolite; Copper; Isotherm; Thermodynamic

## 1. INTRODUCTION

Heavy metals such as copper, lead, zinc are toxic elements for human and animals; however, their concentrations in the surface waters and soils increase as a result of industrial activities day to day. The main sources of the heavy metals in the environment are mining operations, chemical manufacturing factories, agricultural activities, metal manufacturing and petroleum refining plants, pulp industries and textile mill products (Inglezakis et. al. [1]. It is well known that heavy metals accumulate in food chain. Heavy metals form insoluble organic metal complexes with humic and fulvic acids in the soil and, the concentration of heavy metals in the soil increases by the complexlation (Yanhui et. al. [2]). The surface waters contaminated with heavy metals lose their biological properties because the toxin effects of the heavy metals seen in every form of the life within the surface waters as well as the soils.

Copper is one of the most used and mined heavy metals. Metallic copper is widely used in heat and electrical conductors, water pipes, roof coverings, household goods, and chemical equipment, and in many alloys such as brass and bronze (Fawell et. al. [3]). Copper compounds such as oxides, chlorides, sulfates, ethanoates, bromides, and carbonates are widely used in pest control, inorganic dyes, feed additives,

photography, seed disinfectants, fungicides and algicides, and in electroforming (Fawell et. al. [3]). If people are exposed to copper concentrations above 1.3 mg/L, stomach and intestinal problems, kidney and liver damage and DNA mutation occur (Cojocaru et. al. [4])**.** Heavy metals therefore cause great concern throughout the world and an effective method must be improved for removal of them.

Zeolites have been reported as effective cation exchange materials for removal of heavy metals. The most commonly found zeolites in nature are clinoptilolite, mordenite, ferrierite, chabazite, erionite, philipsite and analcime (Çağın et.al [5], Akgül et. al. [6]).The clinoptilolite belongs to the heulandite group of minerals. Similar to clay minerals, clinoptilolite bears a negative charge in the structure that originates from the replacement of silica ($Si^{4+}$) with aluminum ($Al^{3+}$) (Wingenfelder et. al. [7]). These negative charges are balanced by the alkaline and alkaline earth cations, such as $Na^{+}$, $K^{+}$, $Ca^{2+}$ and $Mg^{2+}$. Therefore clinoptilolite has been tested as cation exchanger for removal of heavy metals such as copper (Cu), lead (Pb), zinc (Zn), and etc. (Akgül et. al. [6]). The fact that clinoptilolite exchangeable ions are relatively innocuous (sodium, calcium, potassium and magnesium) makes the clinoptilolite particularly suitable for removal undesirable heavy metal ions from industrial effluents (Erdem et. al. [8]).

In this study, copper exchange performance of the clinoptilolite mineral from Bigadiç-Balıkesir, Turkey was investigated at various experimental conditions. The obtained equilibrium data were applied to the common isotherm models namely the Freundlich and Langmuir. Thermodynamic parameters were also calculated.

## 2. MATERIAL AND METHOD

### 2.1 Clinoptilolite Material

The used clinoptilolite material was supplied from Bigadiç region in Balıkesir, Turkey. Chemical composition of the mineral was determined by X-Ray Fluorescence analysis. The chemical composition of the mineral was given in Table 1. The total cation exchange capacity (TCEC) was calculated as to be 2.458 meq/g by assuming the all exchangeable cations such as sodium, calcium, magnesium and potassium as available for copper ions. The Si/Al ratio was calculated as to be 4.73 (mole/mole) and the typical ratio was reported in the range of 4–5.5 (Çağın et.al [5]). As can be seen from Table 1, the used clinoptilolite sample was calcium clinoptilolite. The specific surface area and pore diameter of the clinoptilolite sample was reported to be 13.4 $m^2/g$ and 17.0 Å by (Çağın et.al [5]).

**Table 1**
**Chemical composition of clinoptilolite.**

| Constituent | Weight,% |
|---|---|
| $SiO_2$ | 64.99 |
| $Fe_2O_3$ | 1.15 |
| CaO | 4.03 |
| $K_2O$ | 2.83 |
| $Al_2O_3$ | 11.66 |

| | |
|---|---|
| MgO | 1.14 |
| $Na_2O$ | 0.15 |
| MnO | 0.008 |
| $TiO_2$ | 0.093 |
| $P_2O_5$ | 0.033 |
| BaO | 0.24 |
| $Cr_2O_3$ | 0.02 |
| $H_2O$ | 13.00 |

## 2.2 Experimental Method

Experiments were carried out in batch mode as a function of solution pH, temperature and salt concentration. Equilibrium time was determined as to be 24 hours. All the experiments were carried out in an temperature controlled orbital incubator shaker (Shangai ZHICHENCG Analytical Instruments Manufacturing Co., Ltd., China). Experiments were carried out at a agitation speed of 180 rpm. Solution pH was measured using a pH meter (WTW, Germany). All used chemical compounds were analytical grade. To prepare solutions, distilled water was used.

Copper solutions were prepared using $CuCl_2{\cdot}2H_2O$ (Merck). The stock solution had a copper concentration of 100 mg/L. A series of 50 mL of copper solutions were reacted with 0.1 g clinoptilolite to obtain isotherm data. Solution salt concentraions were adjusted using appropriate volumes of 1 M NaCl solution. Solution pH values were adjusted using appropriate droplets of 0.5 M HCl and NaOH solutions.

After the reaction reached to the equilibrium, 5 mLs of the centrifugated solutions at 10,000 rpm were taken for dilution and diluted solutions were analyzed at 324.7 nm by Atomic absorption spectrometer (ATI UNICAM 929, England). The samples were automatically measured three times in one aspiration. The flame type was air-acetylene. The adsorption capacity of the used clinoptilolite was calculated by using a mass balance equation. The mass equilibrium equation is expressed as follows:

$$\left(qe = (Co - Ce)V / m\right) \quad (1)$$

## 2.3 Adsorption isotherms

Adsorption equilibrium experiments carried out in batch mode as fuction of concentration are the most common way to find out the isotherms of the adsorption processes. For this purpose, the widely used isotherm models are the Freundlich and Langmuir.

●The Langmuir isotherm generally indicates chemical reaction rather than physical binding. The theory of the Langmuir isotherm assumes that the adsorbent surface is homogeneous with respect to distribution of adsorbing sites throughout all the material surface. Furthermore, in the Langmuir isotherm, the adsorption of adsorbate on the surface is limited by a mono layer (Gimbert et. al. [9]). The widely used linear form of the Langmuir isotherm is given as follow (Günay, [10]).

$$Ce / qe = 1 / q_m k_a + Ce / q_m \quad (2)$$

where *C*e is the equilibrium concentration in liquid phase(mg/L). *q*e is the maximum amount of the dye adsorbed (mg/g). $q_m$ is *q*e for a complete monolayer (mg/g). $k_a$ is a sorption equilibrium constant (L/mg).

●The Freundlich isotherm generally indicates physical binding rather than chemical reaction. The theory of the Freundlich isotherm assumes that the adsorbent surface is heterogeneous with respect to distribution of adsorbing sites throughout the all material surface. Also, in the Freundlich isotherm, adsorption of adsorbate molecules on the adsorbent goes on with increasing concentration and when compared with the Langmuir model, it is difficult that the adsorbent and adsorbate reach to equilibrium (Gimbert et. al. [9]). The widely used linear form of the Freundlich isotherm is given as follow (Günay, [10]).

$$\ln qe = \ln k_F + \ln Ce / n \quad (3)$$

where *Ce* is the equilibrium concentration in liquid phase (mg/L). *qe* is the maximum amount of dye sorbed (mg/g). $k_F$ is the Freundlich adsorption capacity. *1/n* is a sorption equilibrium constant.

## 2.4 Thermodynamic Analysis

The Gibbs free energy change of the adsorption process is related to the equilibrium constant as follow (Bayramoğlu et. al. [11]).

$$\Delta G^0 = -RT \ln K \quad (4)$$

According to thermodynamic, the gibbs free energy change is also related to the entropy and enthalpy change of adsorption process at constant temperature by the following equation.

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (5)$$

Combining above two equations, we get

$$\ln K = -\Delta G^0 / RT = \Delta S^0 / R - \Delta H^0 / RT \quad (6)$$

where $\Delta G^0$ is the free energy change (kJ mol$^{-1}$). $\Delta H^0$ is the enthalpy change (kJ mol$^{-1}$). $\Delta S^0$ is the entropy change (kJ mol$^{-1}$ K$^{-1}$). $K= (q_e/C_e)$ is constant (L g$^{-1}$). T is absolute temperature (K) and *Rg* is the universal gas constant (8.314 J mol$^{-1}$ K$^{-1}$). Thus $\Delta H^0$ and $\Delta S^0$ can be determined from slope and intercept of the linear (Eq.8) respectively.

## 3. RESULTS AND DISCUSSION

In this study, the effects of solution pH, temperature and ionic strength on copper sorption performance of the clinoptilolite was investigated. Adsorption isotherms and thermodinamic of the process were also discussed in this paper.

## 3.1 The effects of pH

The solution pH had a strong effect on zeta potential of the adsorbents and chemistry of solutions. The pH effect on copper adsorption by clinoptilolite was therefore investigated in the range from 2.2 to 6.2 by keeping other parameters as constant. The results of pH effect were given in Figure 1. As can seen in Figure 1, when the pH was increased from 2.2 to 6.2, the sorption capacity of the clinoptilolite increased from 1.899 to 11.009 mg/g. This result was attributed to augmentation in negative zeta potential of the clinoptilolite with high solution pH. Copper precipitation started above

pH 5.15 and precipitation of $CuOH^+$ and CuOH on the clinoptilolite surface and pores occured (Çağın et. al [5]). The optimum pH was proposed as to be 5.15 for this study.

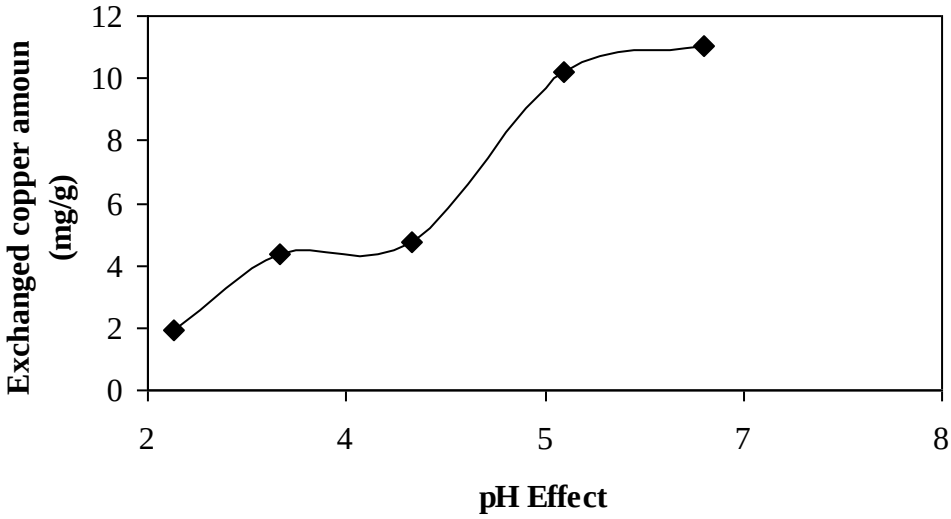


**Figure 1. pH effect on copper sorption**
**(Temperature: 30 $^oC$, solid-to-solution ratio:0.1g/50mL, Concentration:50 mg/L)**

## 3.2 The effects of Salt Concentration

The competing effect of the some cations such as $Na^+$, $Ca^{2+}$, $Mg^{2+}$ as well as heavy metals such as $Zn^{2+}$, $Ni^{2+}$, $Cr^{3+}$ is an important parameter for effectively use of clinoptilolite cation exchange capacity by the target cations. For this purpose, the competing effect of $Na^+$ cations on copper sorption capacity of the clinoptilolite material was investigated at a NaCl concentration range of 0-0.1 M. Experiment results were given in Figure 2. As was given in Figure 2, the copper sorption capacity of the clinoptilolite sample degreased from 4.38 to 2.41 mg/g, when the NaCl concentration was increased from 0 to 0.1 M. The reason of this sorption capacity decrease was due to competitive adsorption of sodium cations with copper cations for the fixation sites in the framework structure of the clinoptilolite (Wingenfelder et. al. [7]).

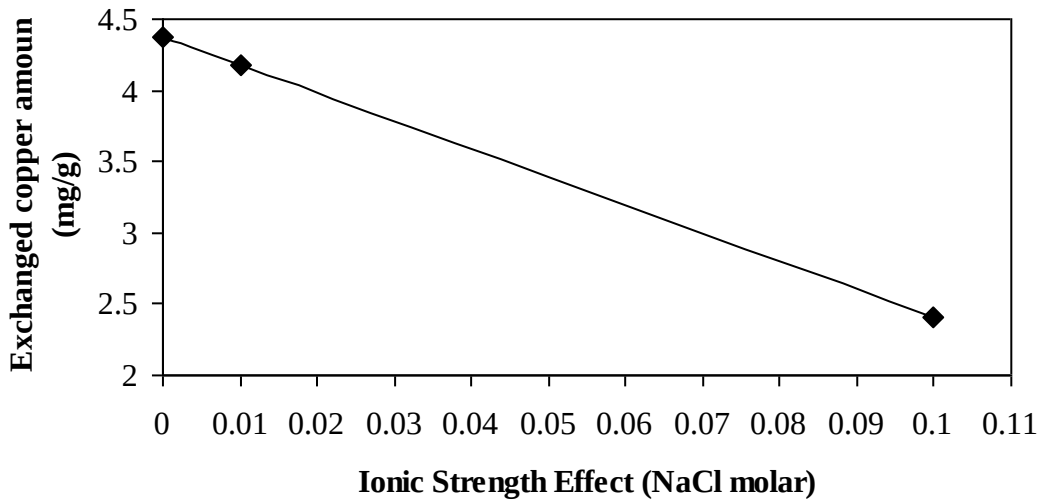

**Figure 2. Effect of salt concentration on copper sorption**
**(Temperature: 30 $^{o}$C, solid-to-solution ratio:0.1g/50mL, Concentration:50 mg/L, pH:4)**

## 3.3 The effects of Temperature

Generally, adsorption reactions are either endothermic or exothermic in nature. The experimental results for temperature effect were given in Figure 3. As was given in Figure 3, the copper sorption capacity of the clinoptilolite material increased from 4.38 to 10.3 mg/g, when the solution temperature was increased from 30 to 50 $^{o}$C. The increased temperature caused to swelling in the clinoptilolite structure for easy transmigration of copper cations into the clinoptilolite pores. On the other hand, with increasing solution temperature, copper cations gained much more energy for reaction with the clinoptilolite fixation sites (Özdemir et. al. [12]). Also, thermodynamic parameters such as gibbs free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) were calculated using equation 6. The calculated thermodynamic parameters were given in Table 2. According to positive enthalpy value given in Table 2, copper sorption on the clinoptilolite was endothermic in nature. Also, positive gibbs free energy change value indicated that the copper sorption process was not spontaneous. Positive value of entropy was due to increase adsorption-desorption rate at clinoptilolite-solution interface.

**Table 2**
**Calculated thermodynamic parameters**

| Temperature (K) | ΔG (kJ/mol) | ΔH (kJ/mol) | ΔS (kJ/mol.K) |
|---|---|---|---|
| 303.15 | 5.42 | 48.827 | 0.143 |
| 313.15 | 3.99 | | |
| 323.15 | 2.56 | | |

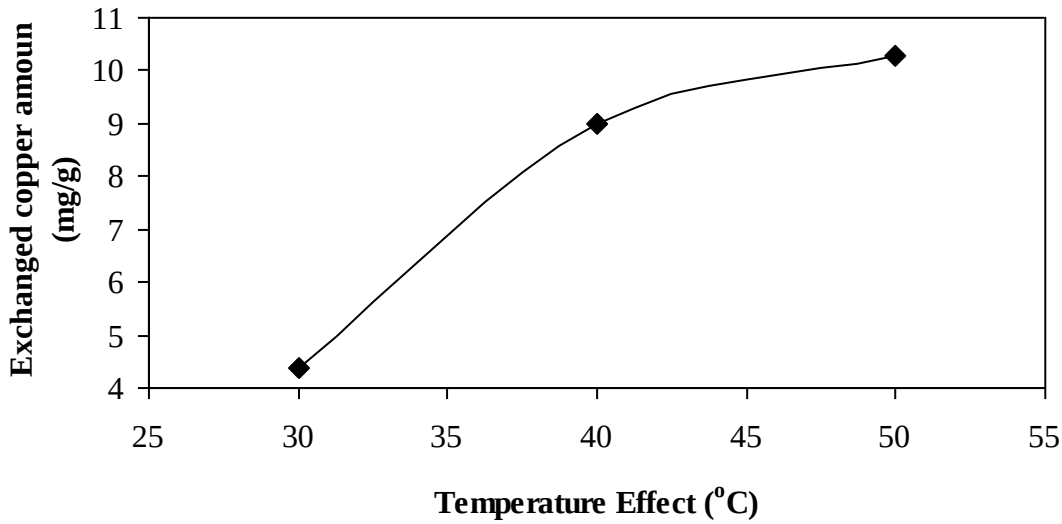


**Figure 3. Effect of temperature on copper sorption**
**(Solid-to-solution ratio:0.1g/50mL, Concentration:50 mg/L, pH:4)**

## 3.4 Evaluation of Adsorption Isotherms

The sorption isotherm data of copper by clinoptilolite were evaluated using the Langmuir and Freundlich models. Adsorption isotherm plots of the copper adsorption

on the clinoptilolite were given in Figure 4. The coeffecient of determination values for the fitness of the data to the Freundlich and Langmuir models were presented in Figure 5a and b. As were given in Figure 5a and b, the obtained data fitted to the Langmuir isotherm rather than Freundlich isotherm. The fitness of data to the Langmuir isotherm indicated that copper sorption by clinoptilolite was chemical reaction rather than physical binding. Also, the distribution of active fixation sites throughout the clinoptilolite surface was found as to be homogeneous according to the Langmuir isotherm.

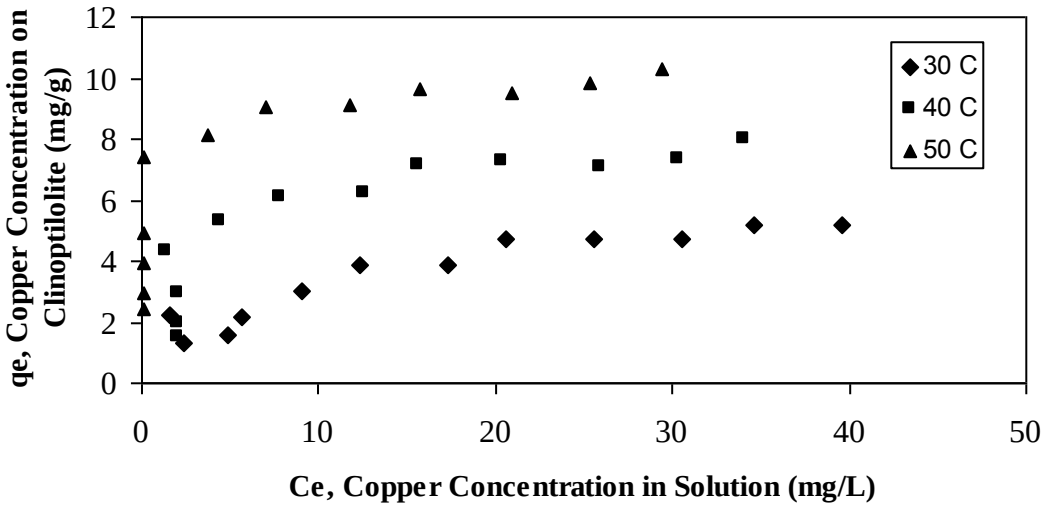


**Figure 4. Adsorption isotherm plots for temperature effect (Solid-to-solution ratio:0.1g/50mL, Concentration range:0-50 mg/L, pH:4)**

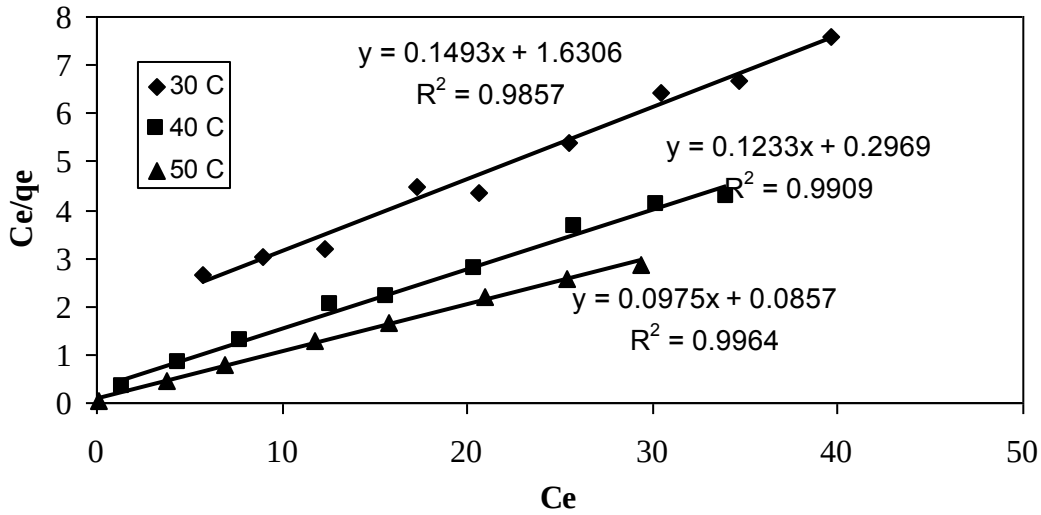


**Figure 5a. The fitness of the data to the Langmuir isotherm**

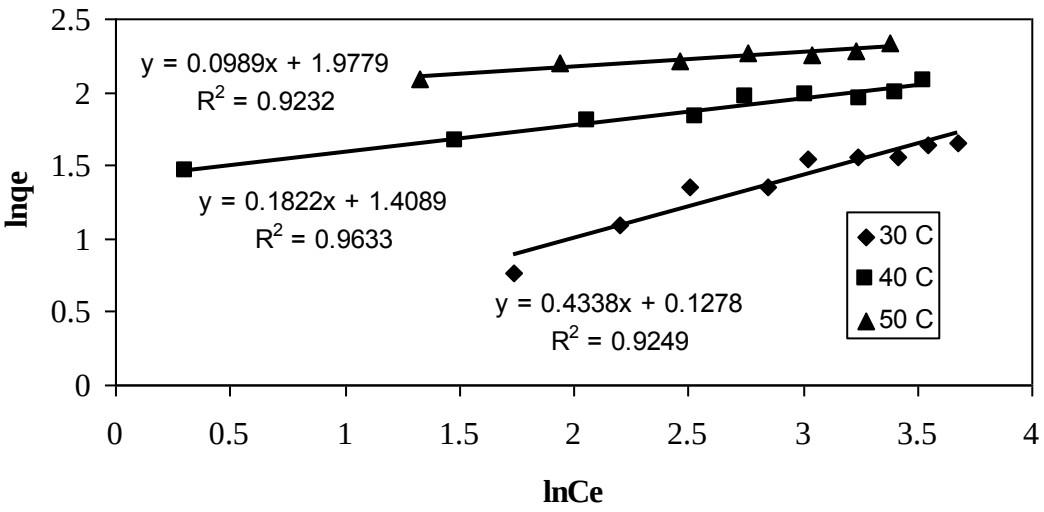


**Figure 5b. The fitness of the data to the Freundlich isotherm**

## 4. CONCLUSION

The main results of this study are given in below.

●The effects of parameters such as pH, temperature and ionic strength on sorption capacity of the clinoptilolite were investigated. The sorption capacity of the clinoptilolite increased with high pH, high temperature and low ionic strength.

●The copper sorption process by the clinoptilolite was endothermic and not spontaneous.

●The equilibrium experimental data fitted to the Langmuir isotherm rather than the Freundlich isotherm.

●In studied experimental conditions, copper sorption reaction by the clinoptilolite was managed by surface adsorption, surface precipitation and ion exchange.

● Maximum sorption capacity of the clinoptilolite was calculated as to be 11 mg/g and this high sorption capacity showed that clinoptilolite was an effective copper adsorbent in place of activated carbon.

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