

Cu (II) Removal from Synthetic Waste Water by Ion Exchange Process

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Abstract— The objective of this study was to investigate the potential of acid activated South Africa clinoptilolite as an adsorbent in the ion-exchange process for the removal of cations from aqueous solutions. The kinetic parameters affecting the adsorption of Cu (II) ions were studied. The adsorption of Cu (II) from synthetic waste water was found to be dependent on pH, temperature, contact time and initial adsorbate concentration. The pH was varied from 2.5 to 6 and the optimum pH for Cu (II) removal was found to be 4.0. The removal of Cu (II) ions increased with time and attained saturation in about 60-70 min. The equilibrium data showed that the adsorption was endothermic nature. Kinetics data showed that at higher temperatures, the rate of adsorption is higher for the clinoptilolite natural zeolite and that Langmuir equation successfully described the adsorption process.

Keywords— *Copper removal, clinoptilolite, adsorption, ion exchange, kinetics*

I. INTRODUCTION

Heavy metals are common pollutants found in various mining and industrial discharges. As environmental regulations on heavy metals discharge are getting stricter and tighter, more efficient remediation methods for waste water are required [1]. Waste streams containing low to medium levels of heavy metals are usually found in metal plating facilities, mining operations, fertilizers, chemical

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pharmaceutical, electronic device manufacturing and many others [2]. The United States Environmental Protection Agency in 1978 published a list of organic and inorganic pollutants including copper found in wastewater and which constitute serious health hazards. Copper is one of the most important metals often found in industrial effluents such as acid mine drainage, galvanizing plants, natural ores and municipal wastewater treatment plants. It is not biodegradable and it travels through the food chain via bioaccumulation [3]. Removal of copper from waste water is crucial and its toxicity for human beings is at levels of 100-500 mg per day [4], [5]. The World Health Organization in 2006 recommended 2.0 mg/l as the maximum acceptable concentration of copper in drinking water. Recently, various studies have focussed on the removal of toxic heavy metal ions from sewage, industrial and mining waste effluents. The presence of heavy metals in streams and lakes has been responsible for several health problems in animals, plants and human beings [6]. Available methods for heavy metal remediation include chemical precipitation, the most economic but inefficient for dilute solutions; adsorption and reverse osmosis, generally effective but have the drawback of fouling as well as high maintenance and operation costs. Ion exchange is among the few promising alternatives for this purpose especially when low cost natural adsorbents such as zeolites, clay material and agricultural wastes are used [7]. Natural zeolites are aluminosilicate minerals with high cation exchange capacities and heavy metals selective properties [8].

The zeolites structure consist of a three dimensional arrangement of SiO_4 and AlO_4 tetrahedral. The aluminum ion is small enough to occupy the position in the center of the tetrahedron of four oxygen atoms, and isomorphous replacement of Al^{3+} for Si^{4+} raises a negative charge in the lattice. The net negative is balanced by the exchangeable cation (sodium, potassium and calcium) and these are exchangeable with certain heavy metal cations in the solution. The relative innocuous nature of zeolite exchangeable ions makes zeolites suitable in the remediation of heavy metals from contaminated streams [2].

Society is eager for new and innovative ideas particularly in health and environmental matters. Zeolites offer a low cost and environmentally safe method of treating municipal water supplies, domestic, industrial and mining waste-water discharge. The aim of this work was to remove copper from synthetic water using South African clinoptilolite zeolite. In

this study the temperature, pH, time and as well as zeolites and synthetic Cu^{2+} solution concentrations were varied.

II. ADSORPTION ISOTHERM STUDIES

Ion-exchange isotherms studies are of fundamental importance in the design of ion-exchange systems because they indicate the nature of partitioning between the adsorbent and liquid phases at equilibrium as a function of ion concentrations [9]. When adsorbent and ion solutions are in contact, the concentration of ions on the adsorbent will increase until a dynamic equilibrium is reached. At this point, a defined distribution of ions between the solid and liquid phases exists [9], [10]. Adsorption isotherms are widely used and of importance in the optimum use of adsorbents. Freundlich and Langmuir isotherms were used in this study to describe the adsorption process.

A. Langmuir Isotherm

The Langmuir isotherm is applied to the ion-exchange data using the linear expression of [11] (1)

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

Where q_e is the amount of cations -exchanged per unit weight of clinoptilolite at the equilibrium (mg/g) and is expressed as (2)

$$q_e = \frac{[(C_o - C_e)V]}{M} \quad (2)$$

V is the volume of solution, M the amount of clinoptilolite added to the solution, C_e is the metal concentration in the aqueous phase, b is the maximum adsorption capacity and K_l is the Langmuir constant related to the ion-exchange capacity and energy of ion-exchange respectively.

B. Freundlich Isotherm

It is one of the widely used mathematical descriptions which fit experimental data of a wide range of concentration. The Freundlich Isotherm [12] expressed as (3) relates the ion exchange capacity to surface heterogeneity as well as the exponential distribution of active sites and their energies.

$$\log q_e = \log k + \frac{1}{n} (\log C_e) \quad (3)$$

Where K is the Freundlich constant related to the ion-exchange capacity of the sorbent, and $1/n$ is the Freundlich constant related to the energy heterogeneity of the system and the size of the exchanged molecule.

III. MATERIAL AND METHODS

A. Synthetic Wastewater

The Natural zeolite used in this study supplied by Prattely South Africa was sourced from the Vulture Creek in KwaZulu Natal province of South Africa. The sample was crashed and pulverized to 75 μm then analyzed using a scanning electron microscope (SEM). Synthetic wastewater was prepared at five different Cu^{2+} ion concentrations of 0.361, 1.099, 1.969 and 2.748 g/l.

B. Experimental Procedure

Fifty two clinoptilolite zeolite samples were prepared and these were exposed to different conditions to optimize the removal of Cu^{2+} ions. For pH variation, 16 zeolite samples of 10 g each were prepared. These were activated at 30°C for 24h at varying HCl concentration of 5.726, 3.181, 1.725 and 0.255 M. The adsorption studies were performed at varying pHs of 2.5 – 6. The rest of the samples were prepared for temperature, zeolite concentration and time variation investigations. These were activated at a pH of 4 corresponding to a concentration of 0.255 M at 30°C for 24 h. The procedure involved the continuous mixing of zeolite samples in aqueous solutions in rolling bottles for 24hours. The solids were separated from solution by filtration. A filtrate was titrated with 0.1M NaOH solution to determine HCl concentration after adsorption. The zeolite solids separated from the solution were dried at 90°C and then analyzed by SEM.

For pH variation, 10 g/l of zeolite were mixed with 1L synthetic water solution at concentration of 0.361, 1.099, 1.969 and 2.748 g/l and held in a closed polyethylene flask at 90°C for 24 h. Zeolite concentration was varied from 4 to 10g for the same pH variation conditions. Temperature was varied from 30 to 90°C at pH of 4 and the same conditions as used to study the influence pH and zeolite concentration were employed. To study the effect of contact time, samples were analyzed at 10 min intervals at pH of 4 and temperature of 90°C. Zeolite and synthetic waste water concentrations were the same as for pH and temperature variation.

IV. RESULTS AND DISCUSSION

A. Clinoptilolite Characterization

The elemental composition for natural and activated clinoptilolite zeolite is shown in Table 1. After the activation with HCl, clinoptilolite was incorporated with significant amount of Cl⁻.

TABLE I
 % CHEMICAL COMPOSITION OF THE NATURAL AND ACTIVATED CLINOPTILOLITE

Component	Natural	Activated
SiO ₂	74	70
Al ₂ O ₃	12.4	11.6
K ₂ O	3.8	2.6
Fe ₂ O ₃	1.5	1
Na ₂ O	1.3	0.9
CaO	1.5	1.3
MgO	1.1	0.8
Cu ²⁺	3.5	3.5
Cl ⁻	-	3.4
TiO ₂	0.2	0.2

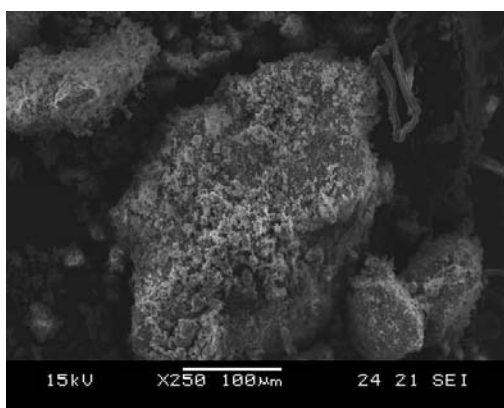


Fig. 1 SEM of original clinoptilolite at X250 magnification

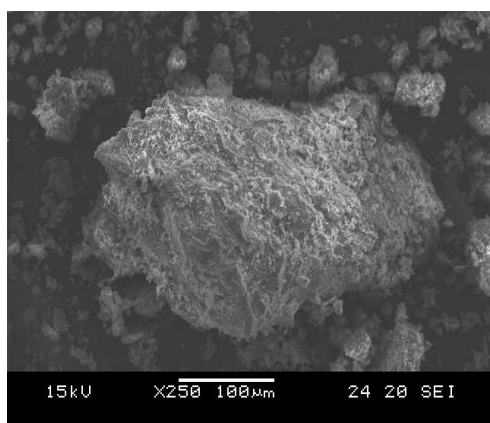


Fig. 2 SEM of activated clinoptilolite at X250 magnification

The SEM micrographs of natural and activated zeolite are shown in figs 1 and 2 respectively. The SEM micrographs show a more open structure of the activated clinoptilolite compared to natural zeolite due morphological changes brought by acid activation.

A. Effect of pH

An optimum pH of 4 was obtained for all initial Cu²⁺ ion concentrations. The mechanism of adsorption at the clinoptilolite zeolite surface reflects the nature of

physicochemical interaction of the metal ions in the solution and zeolite active sites. Acid treatment of natural clinoptilolite improves its adsorbent properties [13] – [15]. This is due to de-cantination, de-alumination and the dissolution of amorphous silica fragments blocking the channels. The availability of sites relates to the equilibrium behaviour whereas accessibility relates to the kinetic behaviour of the ion exchange system.

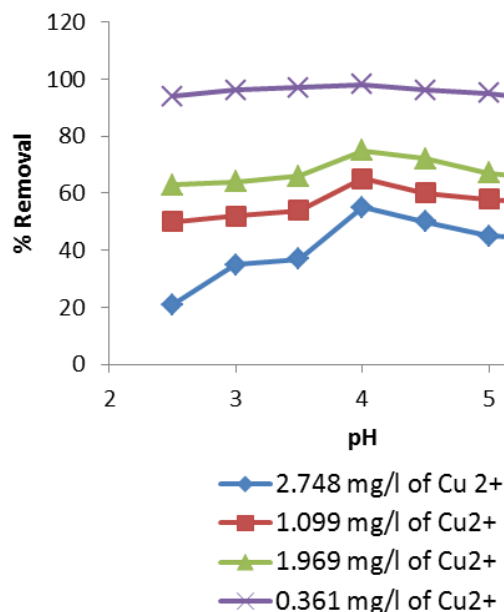


Fig. 3 Effect of pH on adsorption of Cu (II) ions

B. Effect of Temperature

Effect of temperature on adsorption of Cu (II) ions was investigated by varying temperature from 30 to 90°C at various initial concentrations at a pH of 4 for 24 hours and adsorption was found to be temperature dependent. At higher temperatures zeolite pore sizes could increase enhancing the rate of intraparticle diffusion of ions.

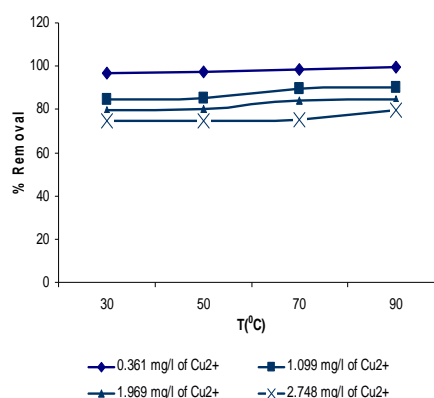


Fig. 1 Effect of temperature on adsorption of Cu (II) ions

C. Effect of Contact Time

The removal of Cu (II) ions increased with time and attained saturation in about 60-70 minutes as observed [14].

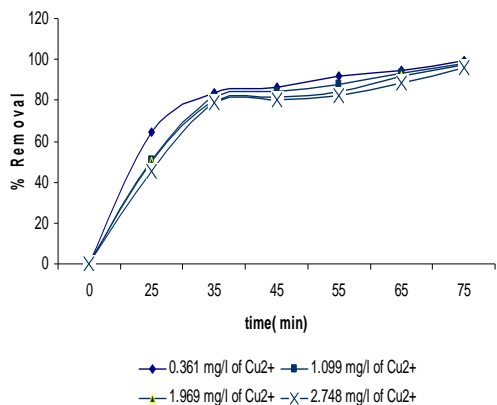


Fig. 2 Effect of contact time on adsorption of Cu (II) ions

D. Effect of Zeolite Concentration

Adsorption increased with increase in zeolite amount for fixed initial concentration. This is because the increase in zeolite amount leads to increase adsorption surface area and available active sites [16].

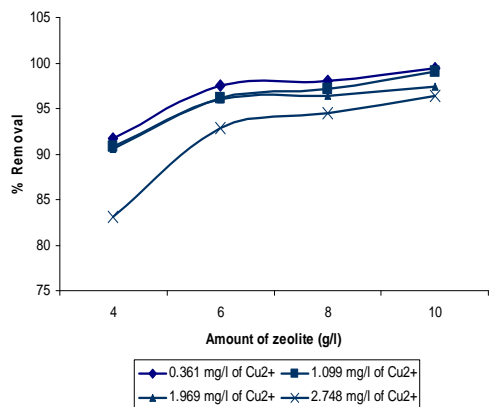


Fig. 6 Effect of zeolite amount on adsorption of Cu (II) at pH 4.0 and 90°C

E. Adsorption Isotherm Studies

The correlation coefficient (R^2) of the adsorption isotherm data shown in Table 2 and fig. 8 confirms that adsorption of Cu (II) ions on clinoptilolite zeolite were better fitted to Freundlich isotherm model. The Langmuir constants, b increase with the increase in temperature as sorption capacities and intensities are enhanced. The nature of adsorption is indicated by the separation factor (R_L) [17] expressed in (4).

$$R_L = \frac{1}{1 + K_L C_o} \tag{4}$$

C_o is the initial cations concentration. For $R_L = 0$ (irreversible), $0 < R_L < 1$ (favourable) and $R_L = 1$ (unfavourable) [18].

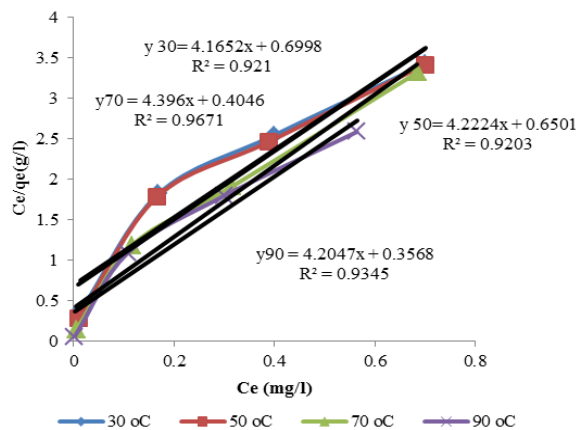


Fig. 3 Langmuir isotherm plots for Cu (II) adsorption at various temperatures.

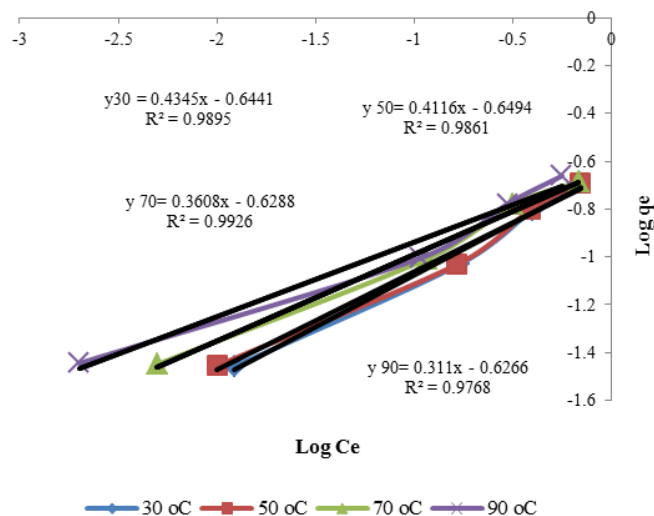


Fig. 4 Freundlich isotherm plots for Cu²⁺ adsorption at various temperatures.

TABLE 2
ESTIMATED THERMODYNAMIC PARAMETERS FOR
Cu²⁺ AT 90°C, pH 4

Isotherm Models	Estimated Isotherm Parameters		
Langmuir Isotherm	R 2	K (mg/g)	b (l/g)
$\frac{C_e}{q_e} = \frac{1}{K_i b} + \frac{C_e}{K_i}$	0.9345	0.24	88.9
Freundlich Equation	R 2	K (mg/g)	n
$\log q_e = \log K + \frac{1}{n} \log c_e$	0.9768	4.23	3.21
Thermodynamic Parameters	ΔG	ΔH	ΔS
	-15.81	8.31	0.0442

V. CONCLUSIONS

The removal of Cu (II) ions from synthetic waste water was dependent on pH, amount of adsorbent, initial concentration of waste water solution and contact time. The optimum pH was 4 and equilibrium saturation was reached after 75 minutes. Thermodynamic parameters such as ΔG, ΔH and ΔS were highly dependent on temperature. The adsorption process was endothermic in nature and the rise in temperature increased the randomness of the solid-solution interface. The Freundlich isotherm model fitted the adsorption of Cu (II) ions into clinoptilolite better compared to the Langmuir model. The calculated values of the dimensionless separation factor R_L from the Langmuir isotherm constants confirm favorable sorption of Cu (II) onto clinoptilolite zeolite.

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