

Thermodynamics of Cu (II) Adsorption onto South African Clinoptilolite from Synthetic Solution by Ion Exchange Process

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Abstract. The adsorption of Cu (II) ions from aqueous solution onto clinoptilolite from synthetic solutions by ion exchange was investigated. The effects of solution pH and temperature were examined. The Langmuir isotherm model was employed to calculate the different thermodynamics parameters. Thermodynamics studies revealed that the adsorption behavior of Cu (II) ions onto clinoptilolite was a spontaneous and endothermic process, resulting in higher adsorption capacities at higher temperatures.

Keywords: adsorption, clinoptilolite, thermodynamics, Langmuir isotherm

1. Introduction

Clinoptilolite is known for its ion exchange and adsorption properties [1]. Ion-exchange processes have been widely used to remove heavy metals from wastewater due to their many advantages, such as high treatment capacity, high removal efficiency and fast kinetics [2]. Clinoptilolite has the specific ability to exchange its cations with metals in the wastewater and many researchers have demonstrated that clinoptilolite is one of the most frequently studied natural zeolite which has received extensive attention due to its selectivity for heavy metals [2,3,4]. The uptake of metals ions by ion-exchange using clinoptilolite is rather affected by certain variables such as pH, temperature, initial metal concentration and contact time [5]. The objective of this study was to use modified clinoptilolite for the adsorption of Cu (II) ions from aqueous solution and to study the thermodynamics of the ion exchange process.

2. Materials and Methods

2.1. Preparation of the adsorbent and synthetic wastewater

The adsorbent and synthetic solution were prepared as described in Mamba et al. [6]. The clinoptilolite used in this study was sourced from the Vulture Creek, KwaZulu-Natal Province of South Africa. The clinoptilolite was crushed and milled into powder with average particle sizes of approximately 75 μ m. The powder was then analysed using an X-ray powder diffractometer (XRD) Phillips X'pert Model 0993 to determine its composition. Its elemental composition was determined using X-ray fluorescence spectroscopy (XRF, Phillips Magix Pro) while the surface area was analyzed using BET (Tristar 3000). The measurements were done under a nitrogen atmosphere. Prior to porosity and surface area analysis, 2g of sample was first degassed and the synthetic Cu solution was prepared at five different Cu²⁺ ion concentrations namely; 0.361, 1.099, 1.969 and 2.748 g/l. The solution was analysed using atomic adsorption spectroscopy (AAS), (Model Varian Spectra (20/20)).

3. Results and Discussion

3.1. Effect of pH on the removal of Cu²⁺

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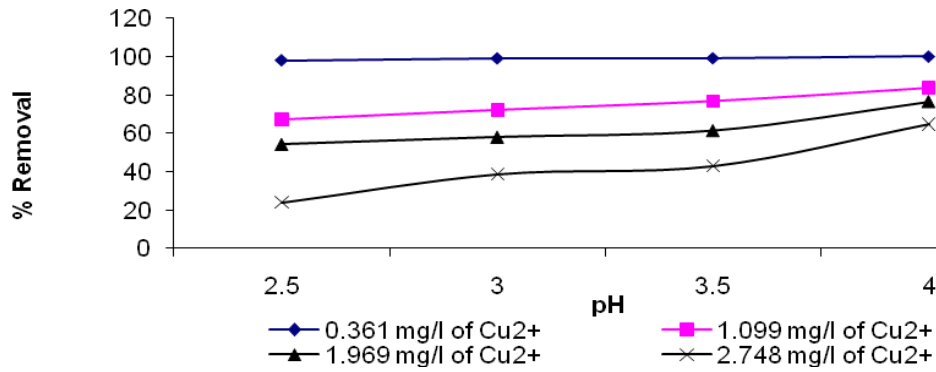


Fig.1: Effect of pH in Cu²⁺ removal from water

The effect of pH on the adsorption of metals is shown in Fig. 1 and it can be seen that the uptake capacity of Cu²⁺ using natural clinoptilolite zeolite was found to be higher at a pH of 4.0. Studies done at higher pH solutions showed that after pH of 4.5 the adsorption starts to decrease [4]. For this reason a pH of 4 was selected for the rest of the experiments.

3.2. Effect of temperature on the removal of Cu²⁺

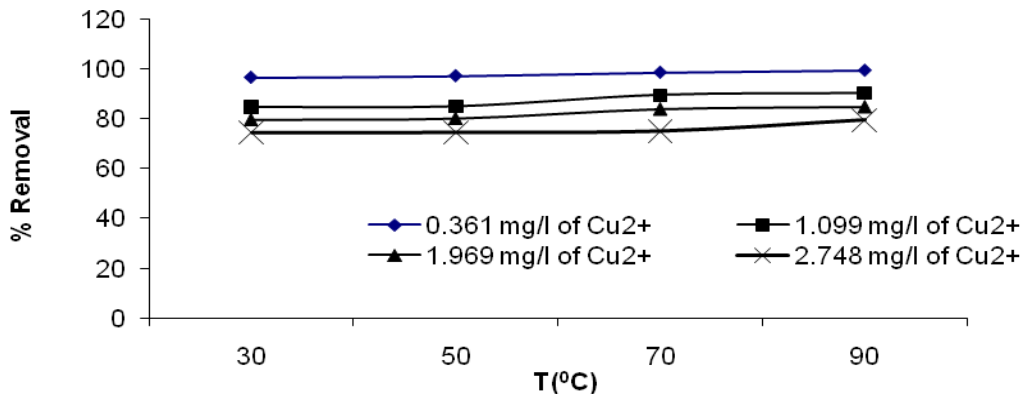


Fig. 2: Effect of Temperature in Cu²⁺ absorption studies

Fig. 2 shows the effect of temperature on adsorption of Cu (II) ions at different initial concentrations of Cu (from 0.361 to 2.748 mg/l), and at different temperatures i.e. 30, 50, 70 and 90°C. It was observed that the adsorption of Copper ions increases with increase in temperature due to increase in the collision of particles. However, increasing the temperature from 50 - 90°C did not significantly increase the % removal of Cu ions from solution.

3.3 Langmuir isotherm

The Langmuir isotherm assumes that adsorption happens at specific homogeneous sites within the adsorbent, and there is no interaction between the adsorbate molecules [7]. The isotherm equation is given by Eqn 1:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_{\max}} + \frac{1}{K_L Q_{\max}} \quad (1)$$

Where C_e is the equilibrium concentration of Cu in solution, q_e is the amount adsorbed at C_e , Q_{\max} is the maximum adsorption capacity and K_L is the binding constant for the Langmuir isotherm which is related to

the energy of adsorption. Plotting C_e/q_e against C_e gives straight line with slope and intercept equal to $1/Q_{\max}$ and $1/K_L Q_{\max}$ respectively. The values of K_L and Q_{\max} at different temperatures are shown in Table 1

Table 1: Isotherm constants, maximum adsorption capacity and regression data at the different temperatures

Temperature (°C)	Q_{\max}	K_L	R^2
30	0.1923	23.998	0.992
50	0.1056	7.213	0.986
70	0.0793	3.974	0.961
90	0.0400	1.490	0.937

3.4. Thermodynamic studies

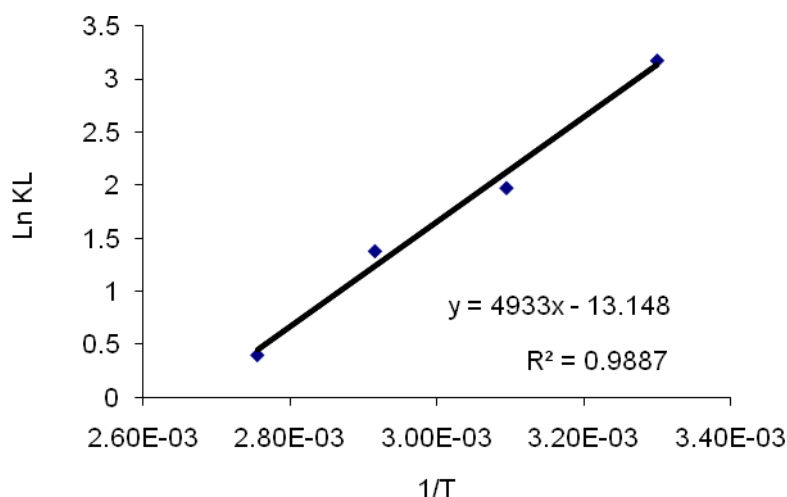


Fig. 3: Plot of $\ln K_L$ vs. $(1/T)$ for Cu (II)

The thermodynamic parameters of the adsorption reaction were calculated using Van't Hoff equation (Eqn. 2):

$$\ln K_L = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (2)$$

Plotting of $\ln K_L$ against $1/T$ gives a straight line with slope and intercept equal $-\Delta H^\circ/R$ and $\Delta S^\circ/R$, respectively (Figure 3). The Gibbs free energy ΔG° of the adsorption reaction was obtained using the equation $\Delta G^\circ = -RT \ln K_L$ and is given in Table 2.

Table 2: Thermodynamic parameters on the adsorption of Cu (II) at different temperatures.

Temperature (K)	$\Delta H^\circ / \text{kJ mol}^{-1}$	$\Delta S^\circ / \text{kJ mol}^{-1}$	$\Delta G^\circ / \text{kJ mol}^{-1} \text{K}^{-1}$
303	- 41.013	- 0.10931	- 8.005
323	-	-	- 5.306
343	-	-	- 3.935
363	-	-	- 1.207

Considering the thermodynamic parameters in Table 2, the negative values of both ΔH° and ΔS° indicate an exothermic adsorption reaction accompanied with a more ordered state. The negative values of ΔG° indicate that the adsorption is spontaneous, with the affinity of Cu (II) to clinoptilolite increasing with increasing temperature. This indicates that the process of adsorption of Cu (II) was favorable at higher temperature.

4. Conclusion

This study established that the adsorption of Cu (II) ions from aqueous solution onto clinoptilolite from synthetic solution by ion exchange process was spontaneous and endothermic. Thermodynamic parameters such as ΔH° , ΔS° and ΔG° were calculated using the Langmuir isotherm model from the experimental results.

5. Acknowledgements

The authors would like to express their appreciation and thanks to the Department of Chemical Engineering, University of Johannesburg.

6. References

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