Ion-Exchange Equilibria of Na^+/Cu^{2+} and Na^+/Co^{2+} using Clinoptilolite

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Abstract— **Equilibrium ion-exchange of Na^+/Cu^{2+} and Na^+/Co^{2+} on clinoptilolite in solution have been determined in order to assess the possibility of using ion-exchange to remove heavy metal ions from industrial wastewater. Clinoptilolite competences as an ion exchanger with respect to Co^{2+} and Cu^{2+} was examined to deliberate conceivable application at eliminating metals from aqueous solutions. The open-column method was utilized in the cation exchange procedures with synthetic wastewater solution concentrations of 150ppm, 300ppm and 600ppm. The varied parameters were initial concentration, pH, particle size and clinoptilolite dosage. The maximum recorded metal-removal percentage was 98%, this was achieved by conditioning the clinoptilolite with 0.05M NaCl. Thermodynamic properties using the constant K_{AB} show the preferably bound to the clinoptilolite as compared to sodium cation.**

Keywords: Clinoptilolite, Cobalt, Copper, Ion-exchange Equilibrium, Wastewater

I. INTRODUCTION

Water pollutant emerging from metallurgical operations have been accentuated as one of the paths by which groundwater can be polluted therefore threatening valuable water sources [1]. However, industrial waters often hold a cuisine of metals such as copper and cobalt that may enforce cost implications when it comes to purification. The necessity for the removal of metal species in water and the general purification of these waters cannot be overemphasized. Various purification methods are currently employed in the water purification industry and these include ion exchange, phytoextration, electrodialysis, ultrafiltration and reverse osmosis. Ion-exchange is the most commonly employed in industrial water treatment, among the water purification technologies [2]. Ion-exchange is a process whereby a solid substance (the ion-exchanger) and some aqueous solution exchange ions [3]. Clinoptilolite has been widely exploited as solid substance for water pollution remediation because of its ion-exchange capabilities. Clinoptilolite is hydrated microporous crystalline material, the most abundant and cosmopolitan natural zeolite with the general chemical formula of $(Li, Na, K)_\alpha (Mg, Ca, Sr, Ba)_d [Al_{\alpha + 2d} - Si_{n-(\alpha+2d)}O_{2n}].mH_2O$.

Clinoptilolites are low cost material and exhibit excellent selectivity for different cations at low temperatures over other cation exchange materials such as resins, which is followed with a release of non-toxic exchangeable cations to the environment [4]. The ion-exchange is made feasible by the existence of extra-framework cations which are in the well-ordered array of channels and cages that make up the rigid anionic framework. Cations are linked to the lattice and to water molecules which normally load the clinoptilolite micropores [5]. When the clinoptilolite comes across an electrolytic solution, the exchangeable cations in the clinoptilolite can be released from their sites and replace by cations in the solution. The objective of this study is to assess the equilibrium ion-exchange of Na^+/Cu^{2+} and Na^+/Co^{2+} on clinoptilolite for the removal of copper and cobalt from industrial wastewater.

II. MATERIALS AND METHODS

A. Preparation of clinoptilolite and synthetic wastewater

Clinoptilolite was washed with 20 Vol % HCl and then with deionized water. Resulting material was dried in an oven at 80ºC for 24 hrs, crushed in 1.7, 2.0 and 2.8 mm mesh sizes for the experiments. The clinoptilolite was then conditioned with 0.05M NaCl at ratio 40g clinoptilolite and 100 mL NaCl solution. The solid and liquid mixture was stirred for 24 hrs at 130rpm then dried for another 24 hrs at 70ºC.

The synthetic solution was prepared at the concentration of 150, 300 and 600 ppm for both cobalt (II) chloride hexahydrate and copper (II) sulphate pentahydrate solutions. The solutions were mixed at ration of 1:1 per concentration for 12hrs.

B. Experimental Procedure

Equilibrium clinoptilolite loading data were generated for Na^+/Cu^{2+} and Na^+/Co^{2+} systems. To obtain these data, 0.1 L of a known composition solution were weighed and added into each of several flasks. Solution and clinoptilolite were maintained at room temperature under vigorous stirring, until the equilibrium was achieved. Then, the mixture was filtered to remove the ion-exchange clinoptilolite and the filtrate was analyzed for the removal content. The Co^{2+} and Cu^{2+} ion exchange processes on the clinoptilolite was conducted at room temperature. A glass column (2cm in diameter and 30cm in length) was installed into the retort stand. A beaker was place under the glass column to collect the elute. The glass column was loaded

with the clinoptilolite and the parameters were tested while some are kept constant. The synthetic solution was poured into the glass column for a specified amount of time. Each parameter was tested for a period of 2 hrs and the samples were collected, then diluted (which will be explained further) and assayed. The effluent solutions were collected at 30, 60, 90 and 120 min intervals and analyzed for final metal content using AAS.

Experiment 1

In this experiment, all the parameters were kept constant except for the particle size of the clinoptilolite. The columns were loaded with 30g of clinoptilolite each as follows:

Column 1: 1.7mm, Column 2: 2.0mm, Column 3: 2.8mm

After loading the clinoptilolite, a volume of 60ml of synthetic water with a concentration of 150ppm was poured in each column. Samples of 15mL were collected from each column after every 30 mins. The experiment was running for 2 hrs.

Experiment 2

In this experiment, all the parameters were kept constant except for the initial concentration of the synthetic water solution. The columns were loaded with 30g of clinoptilolite with a uniform size of 1.7mm in each column. Column 1: 150ppm, Column 2: 300ppm, Column 3: 600ppm

After loading the clinoptilolite, volumes of 60mL of synthetic water with different concentrations, as shown above, were poured in each column respectively. Samples of 15mL were collected from each column after every 30 mins. The experiment was running for 2 hrs.

Experiment 3

In this experiment, all the parameters were kept constant except for the dosage of the clinoptilolite in each column. Each column was loaded with different amounts of clinoptilolite, but with a uniform size of 1.7mm as follows: Column 1: 25g, Column 2: 35g, and Column 3: 45 g

After loading the clinoptilolite, a volume of 60mL of synthetic water with a concentration of 150ppm was poured in each column. Samples of 15mL were collected from each column after every 30 minutes. The experiment was running for 2 hrs.

Experiment 4

In this experiment, all the parameters were kept constant except for the pH of the synthetic water solutions. The columns were loaded with 45g of clinoptilolite each, with uniform size of 1.7mm in each column as follows: Column 1: pH of 4, Column 2: pH of 6, Column 3: pH of 8

To increase the pH of the synthetic water, a solution of 0.1 M potassium hydroxide (KOH) was prepared as follows:

Then the mass of KOH was dissolved in a volume of 250mL of deionized water.

To increase the pH of the synthetic water, a solution of 0.1 M sulphuric acid (H_2SO_4) was prepared as follows:

After loading the clinoptilolite, a volume of 80mL of synthetic water with a concentration of 150ppm was measured for each column. A pH meter was used to measure the pH of the original synthetic water, and the pH was 5.301. The pH was adjusted using KOH and H_2SO_4.

Then a volume of 60 mL was measured from the 80ml solution and poured into the columns with their respective pH readings. Samples of 15mL were collected from each column after every 30 mins. The experiment was running for 2 hrs.

Suppose that the ion-exchanger (r) is initially in the A form and that the counterion in the solution (s) is B. Counterion exchange occurs, and the ion A in the ion exchanger is partially replaced by B (see Eq. 1).

$$\beta A_r{}^{\alpha+} + \alpha B_s{}^{\beta+} \leftrightarrow \beta A_s{}^{\alpha+} + \alpha B_r{}^{\beta+} \qquad (1)$$
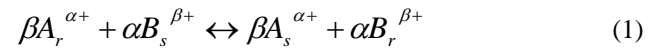
In equilibrium, both the ion-exchanger and the solution contain competing counterion species, A and B. The ionic fraction for a binary system can be introduced as presented in Eqs. (2) and (3).

$$x_A = \frac{C_A}{N} ; \; x_B = \frac{C_B}{N} \qquad (2)$$

$$y_A = \frac{q_A}{q_o} ; \; y_B = \frac{q_B}{q_o} \qquad (3)$$

Where C represents the normality concentration of the ionic species in solution, N is the total ionic concentration in the solution phase, q_i is the solute concentration in the solid phase and q_o is the useful capacity of the clinoptilolite in the system studied.

The equilibrium constant for the exchange reaction (Eq. 1) assuming real behavior for both phases could be calculated from the Eq. (4):

$$K_{AB}(T) = \frac{(y_B \bar{\gamma}_B)\left[(1-x_B)N\gamma_A\right]^\beta}{\left[(1-y_B)\bar{\gamma}_A\right]^\beta (x_B \gamma_B N)^\alpha} \qquad (4)$$

Where $\bar{\gamma}$ and γ are the activity coefficient of each ion in the ion-exchanger and in the solution and y_B and x_B are the ionic fraction of ion B in the solid phase and in the solution. The activity coefficients in the solid phase were calculated using the Wilson Equation as described by Valverde et al. [6].

$$\bar{\gamma}_A = \left[\exp(1 - \ln(y_A + (1-y_A)\Lambda_{AB})) - \left(\frac{y_A}{y_A + (1-y_A)\Lambda_{AB}}\right) - \left(\frac{(1-y_A)\Lambda_{BA}}{(1-y_A) + y_A \Lambda_{BA}}\right)\right]$$

$$(5)$$

$$\bar{\gamma}_B = \left[\exp(1 - \ln((1-y_A) + y_A \Lambda_{AB})) - \left(\frac{1-y_A}{(1-y_A) + y_A \Lambda_{BA}}\right) - \left(\frac{y_A \Lambda_{AB}}{y_A + (1-y_A)\Lambda_{AB}}\right)\right]$$

$$(6)$$

$$T(1 - \ln \Lambda_{AB} - \Lambda_{BA}) = C^A_{AB} \qquad (7)$$

$$T(1 - \ln \Lambda_{BA} - \Lambda_{AB}) = C^A_{AB} \qquad (8)$$

Where Λ_{AB} and Λ_{BA} are Wilson coefficients, T is the absolute temperature, and C^A_{AB} and C^B_{AB} are the constants of the Gilliland relationship [7].

III. RESULTS AND DISCUSSION

A. Metal removal from a double component system

By varying some certain parameters with time and keeping other parameters constant, the ion kinetics of Co^{2+} and Cu^{2+} as a function of their parameters in their respective solutions were studied at room temperature. From the results shown from Figs. 1 to 8, it can be established that Co^{2+} ions were removed more than the Cu^{2+} ions. This may be due to the fact that Co^{2+} is more reactive compared to Cu^{2+}, so it can be pulled towards the clinoptilolite faster than the Cu^{2+} ions.

B. Effect of particle size

The smaller the size of the particle, the greater the interfacial area between the solid and the liquid, and thus the higher the rate of exchange of ions and the smaller the distance the ions must diffuse. In simple terms, there will be increase surface area for ion exchange to occur. The metal removal percentage decreased with an increase in particle size. From the results shown in Figs. 1 and 2, it can be confirmed that the smaller clinoptilolite particles showed the best metal removal percentage, with Co^{2+} percentage removal ranging from 95 – 94% for the particle size of 1.7mm and 91 – 86% for the particle size of 2.8mm, this is shown in Fig. 1. This was also seen in the Cu^{2+} percentage removal in Fig. 2, with the smallest clinoptilolite particle size having the highest percentage removal which ranges from 65 – 43% for the particle size of 1.7mm and 28 – 4% for the particle size of 2.8mm.
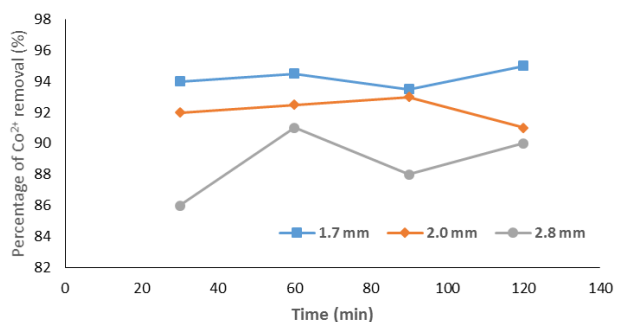

Fig. 1. Percentage removal of Co^{2+} after 120 min investigating the effect of particle size on the metal percentage removal.
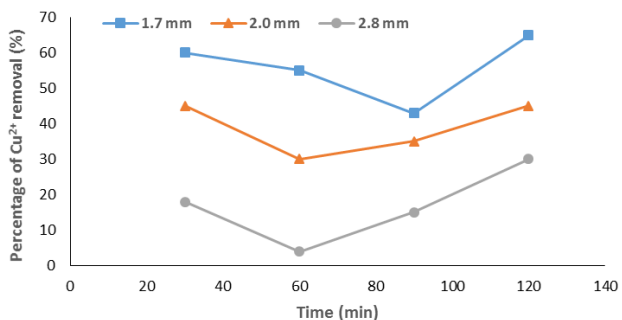

Fig. 2. Percentage removal of Cu^{2+} after 120 min investigating the effect of particle size on the metal percentage removal.

C. Effect of initial concentration

From the Figs. 3 and 4, it can be confirmed that the percentage metal removal decreased with an increase in metal concentration in the aqueous solutions. This may be since particles continuously disuse faster when they are less packed, therefore they move faster in dilute solutions and more slowly in concentrated solutions. In Fig. 3, the results show that for the Co^{2+} percentage metal removal, the diluted aqueous solution shows the highest metal removal percentage which ranges from 95 – 92% (for 150ppm solution) and 83 – 81% for the 600pm solutions. This can also be seen in Fig. 4 where the best Cu^{2+} percentage metal removal was established from the less concentrated solution (which is the 150ppm solution), which ranges from 66 – 40% and 11 – 5% for the concentrated solution (which is the 600ppm). There were abnormalities when the results for the Cu^{2+} percentage removal were assayed. Some concentration obtained from the AAS were higher than the initial concentration. This may be due to impurities in the solutions, or the solution was unstable or the concentration couldn't fit in the standard solution range.
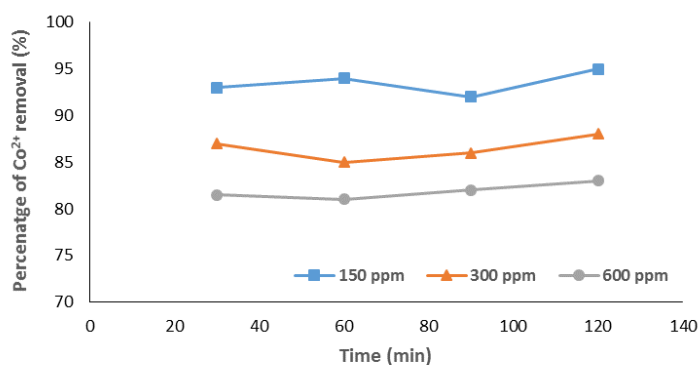

Fig. 3. Percentage removal of Co^{2+} after 120 min investigating the effect of initial concentration on the metal percentage removal.
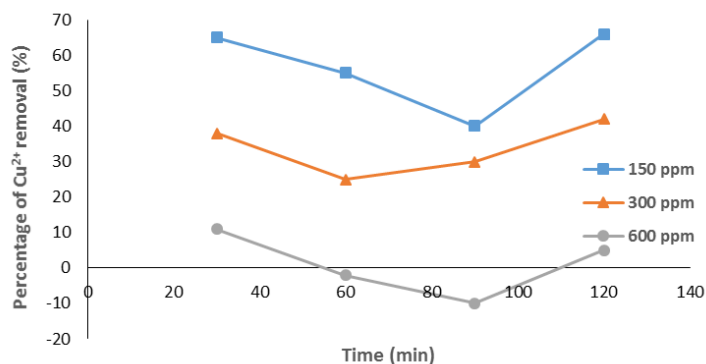

Fig. 4. Percentage removal of Cu^{2+} after 120 min investigating the effect of initial concentration on the metal percentage removal.

D. Effect of clinoptilolite dosage

Figs. 5 and 6 show, the metal percentage increased with an increase in clinoptilolite dosage. This is due to the fact that as the clinoptilolite dosage is increased it provides more area for the ion exchange to take place. This is seen in Fig. 5, where the best Co^{2+} percentage metal removal is

seen where 45g of clinoptilolite was used, wherein the percentage metal removal ranges from 97 – 96% and 91 – 88% where 25g of clinoptilolite was used. Fig. 6 also gave similar results to Fig. 5, where the best Cu^{2+} percentage metal removal is seen where 45g of clinoptilolite was utilized, wherein the percentage metal removal ranges from 83 – 76% and 45 – 23% where 25g of clinoptilolite was utilized.
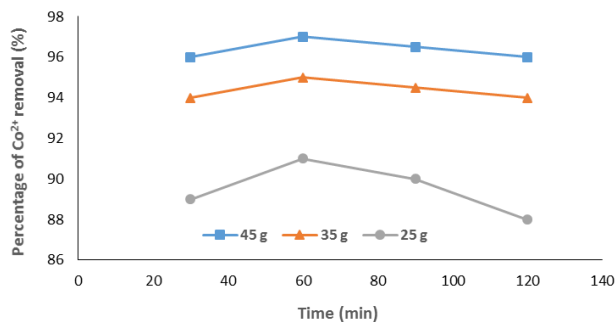

Fig. 5. Percentage removal of Co^{2+} after 120 min investigating the effect of clinoptilolite dosage on the metal percentage removal.
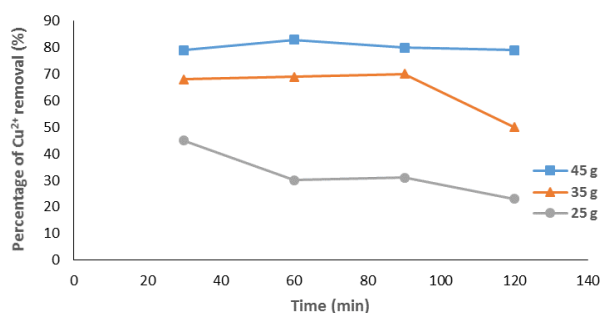

Fig. 6. Percentage removal of Cu^{2+} after 120 min investigating the effect of clinoptilolite dosage on the metal percentage removal.

E. Effect of pH

Figs. 7 to 8 show, the highest percentage metal removal was seen in solution with a pH of 4 and 8. In Fig. 7, there is no convincing trend or a relationship between the pH and the percentage metal removal. This is also seen in Fig. 8, in theory, a base is more viscous than an acid, in this case a potassium hydroxide, KOH solution is more viscous than a sulphuric acid, H_2SO_4 solution. A viscous solution will move slowly within the exchange medium, as in, the time of contact between the solid and the liquid is increase which result in a high percentage metal removal. This is evident in Figs. 7 and 8 where a solution with pH 4 exhibited the highest percentage removal for both Co^{2+} and Cu^{2+}.
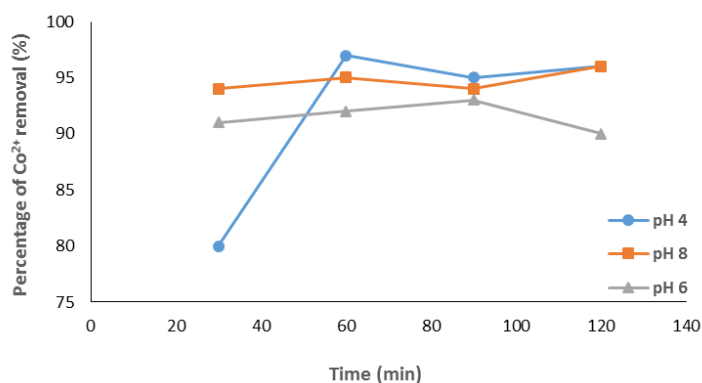

Fig. 7. Percentage removal of Co^{2+} after 120 min investigating the effect of pH on the metal percentage removal.
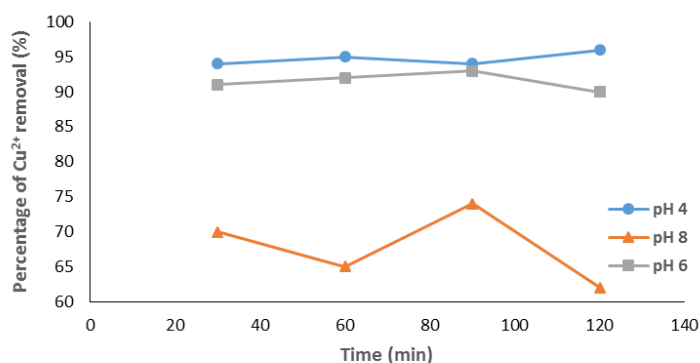

Fig. 8. Percentage removal of Cu^{2+} after 120 min investigating the effect of pH on the metal percentage removal.

F. Thermodynamic properties

TABLE I
EQUILIBRIUM PARAMETERS OF THE BINARY SYSTEMS NA^+/CU^{2+} AND NA^+/CO^{2+} ON CLINOPTILOLTE

System A/B	T/K	K_{AB}	Λ_{AB}	Λ_{BA}	$10^{-2}\,C_{AB}^{A}$	$10^{-2}\,C_{AB}^{B}$
NA^+/CU^{2+}	283	5.60	3.123	0.102	-1.211	-1.531
NA^+/CO^{2+}	283	8.21	5.251	0.038	-2.117	-3.062

Calculated values of the equilibrium constant K_{AB} in Eq. (4) show that clinoptilolite is exhibits different orders of selectivity being $Cu^{2+} > Co^{2+}$.

Thermodynamic properties of the binary systems constituted by Na^+/Cu^{2+} and Na^+/Co^{2+} and clinoptilolite could be evaluated from the thermodynamic constant K_{AB} and the temperature (See Eqs. 9-11).

$$\Delta G^o{}_{AB} = -RT \ln K_{AB} \qquad (9)$$

$$\Delta H^o{}_{AB} = -(RT/\alpha\beta)d(\ln K_{AB})/dt \qquad (10)$$

$$\Delta S^o{}_{AB} = (\Delta H^o{}_{AB} - \Delta G^o{}_{AB})/T \qquad (11)$$

Where R (8.314 J mol^{-1} K^{-1}), T (K), K_d (mL g^{-1}) are the universal gas constant, temperature and distribution coefficient reflecting the selectivity for metal adsorption. The K_d value was calculated using Eq. (12) [8]:

$$K_d = \frac{q_e}{C_e} \tag{12}$$

Table II contains these thermodynamic properties at room temperature. The negative standard free energy would indicate that metal cations would be preferably bound to the clinoptilolite as compared to sodium cation. On the other hand, the negative value of the standard entropy could suggest that metal cation would be more strongly bound to the clinoptilolite than sodium cation. Furthermore, the exchange process is exothermic, as the negative enthalpy indicates.

TABLE II
THERMODYNAMIC PROPERTIES OF THE BINARY SYSTEMS NA+/CU2+ AND NA+/CO2+ ON CLINOPTILOLITE

System (A/B)	T/K	K_{AB}	ΔG^o_{AB} kJ.mol^{-1}	ΔH^o_{AB} kJ.mol^{-1}	ΔS^o_{AB} kJ.mol^{-1}
NA^+/CU^{2+}	283	5.60	-4.06	-16.20	-41.12
NA^+/CO^{2+}	283	8.21	-5.38	-14.70	-33.22

G. Langmuir and Freundlich adsorption isotherms

The sorption data was exposed to Langmuir and Freundlich adsorption isotherms. The equilibrium for double metal solutions was linked with the Langmuir isotherm according to the Eq. (13):

$$q_e = \frac{q_m K_L C_f}{1 + K_L C_f} \tag{13}$$

Where: q_e is the adsorption capacity adsorbed at equilibrium (mg/g); q_m is the maximum adsorption capacity (mg/g); K_L is the Langmuir adsorption constant and C_f is the final equilibrium concentration (mg/L).

The application of the Langmuir model to the data is show in Figs. 9 and 10. The Langmuir equation can be reorganized in a linear equation form and rewritten as follows:

$$\frac{1}{q_e} = \frac{1}{q_m K_L} \frac{1}{C_f} + \frac{1}{q_m} \tag{14}$$

To make the Langmuir plots, $\dfrac{1}{q_e}$ was plotted against $\dfrac{1}{C_f}$ and a straight-line graph was attained for this plot [9]. The data attained fit the Langmuir model for Co^{2+} with R^2 highest value of 0.87 and for Cu^{2+} which did not fit the Langmuir model that well. For copper, R^2 values ranged from the lowest value of 0.051. According to the Langmuir model and R^2 correlation values, Co^{2+} uptake is favored than Cu^{2+}. The ion exchange capacity of Co^{2+} and Cu^{2+} specifies that the clinoptilolite favors Co^{2+} over Cu^{2+}. This may be since Co^{2+} are more reactive than the Cu^{2+} ions and ions that are more reactive possess a lot of kinetic energy. The Langmuir model successfully pronounces the adsorption data obtained in these experiments for Co^{2+} with values of R^2 being as high as 0.87 and it was less successful for Cu^{2+} with values of R^2 being as high as 0.87, which is much lower compared to Co^{2+}. The isotherm also established the selectivity of the clinoptilolite as being more favorable for Co^{2+} than Cu^{2+}. The clinoptilolite was observed to generally have a good selectivity for cobalt cations. Another mathematical model utilized to fit the data attained in this study is known as the Freundlich isotherm. This model is acknowledged for its good fit of data over an extensive range of concentrations. It gives an equation that comprises the heterogeneity of the surface of the ion exchange and the exponential distribution of active sites and their energies. The Freundlich equation is given by:

$$q_e = K_F C_f^{1/n} \tag{15}$$

Where q_e is the adsorption capacity adsorbed at equilibrium (mg/g); K_F is a constant related to temperature; C_f is the final equilibrium concentration (mg/L) and n is a characteristic constant for any system under study.

The Freundlich equation (15) can be reorganized in a linear equation form (see Eq. 16).

$$\log q_e = \log K_F + \frac{1}{n} C_f \tag{16}$$

To make the Freundlich plots, $\log q_e$ was plotted against $\log C_f$ and a straight-line graph was attained for this plot [10]. It was observed that the data tailed the Freundlich model as well, especially data obtained for Co^{2+} with R^2 values of 0.97 and for Cu^{2+} which improved from the Langmuir model with R^2 value of 0.54, which is a huge improvement. The application of this model is seen in Figs. 11 and 12. Every metal in the solution possesses a hydrated layer which has a characteristic thickness and degree of stability. It has been proven that ions with large radii often, not always, show large rejections while smaller ions are often favored by exchanges. This is not the case in this study, an ion with a larger radius (Co^{2+}) is favored compared to the ion with a smaller radius (Cu^{2+}).
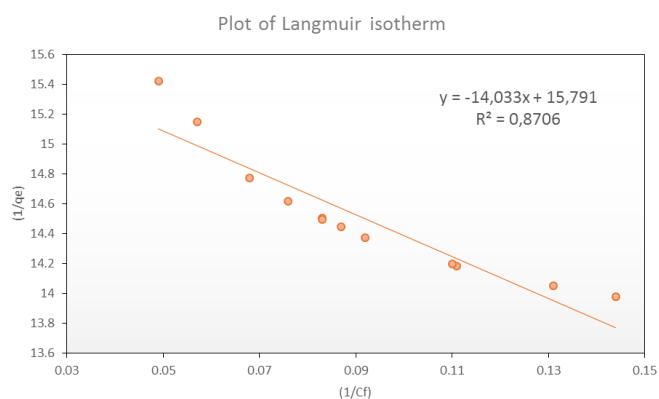

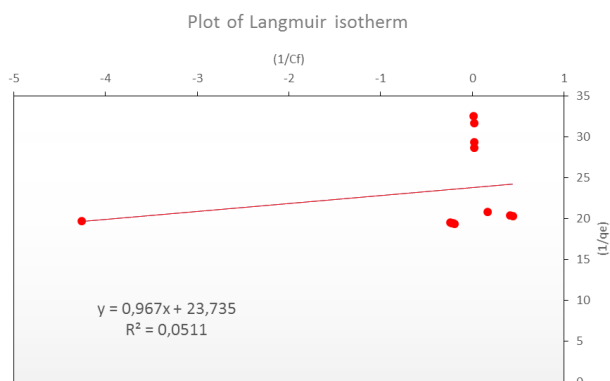Fig. 9. Langmuir plot for Co^{2+} after 120 min.

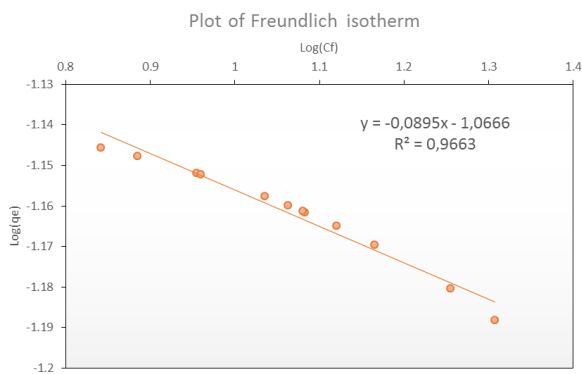Fig. 10. Langmuir plot for Cu^{2+} after 120 min.

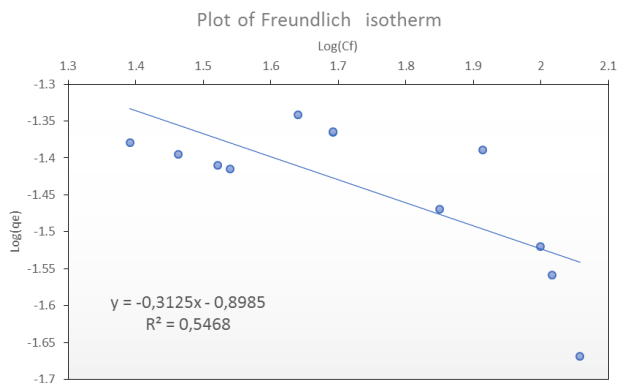Fig. 11. Freundlich plot for Co^{2+} after 120 min.

Fig. 12. Freundlich plot for Cu^{2+} after 120 min. (Effect of dosage)

IV. CONCLUSION

Although in most cases the clinoptilolite showed preference for both the cations and were effectively removed from the solution. Most of the results obtained for the percentage metal removal are sensible in the sense that the obtained percentages ranged for 80 – 95% in most cases. The Langmuir and Freundlich agree with this notion as most of the R^2 obtained are as high as 0.97. There were a few abnormalities were the percentage metal removal was above 100% or it was found to be negative. This may be due to impurities in the solutions, or the solution was unstable or the concentration couldn't fit in the standard solution range. Thermodynamic properties show that the preferably bound to the clinoptilolite as compared to sodium cation.

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