Ion-Exchange Equilibria Studies of Cu^{2+} and Co^{2+} Ions on Clinoptilolite-Na in Industrial Wastewater

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Abstract—**Ion-exchange equilibria of Na$^+$/Cu^{2+} and Na$^+$/Co^{2+} on clinoptilolite-Na in aqueous medium at (298, 328 and 359) K have been determined in order to assess the possibility of using ion-exchange to remove heavy metal ions from industrial wastewater. The varied parameters such as initial concentration, pH, particle size and adsorbent dosage were discussed. The clinoptilolite equilibrium data were analyzed by Lagmuir and Freundlich adsorbent isotherms. Wilson and Debye-Hückel equations have been used to calculate activity coefficients in the solid and the liquid phase, respectively. The thermodynamic parameters such as Gibbs free energy change (ΔG^o), enthalpy change (ΔH^o) and entropy change (ΔS^o) were calculated using the constant K$_{AB}$.**

Index Terms— **clinoptilolite, cobalt, copper, ion-exchange equilibria, industrial wastewater**

I. INTRODUCTION

INDUSTRIAL wastewater contains high amount of heavy metal ions which are non-biodegradable, toxic, and easy to accumulate at low concentrations in living organisms in general and in the human body in specific. They can cause serious illnesses, such as cancer, nervous system damage, and kidney failures and can be deadly at high concentrations [1]. Therefore, it is mandatory to treat metal contaminated wastewater prior to its discharge to the environment. Various treatment techniques are currently implemented to remove heavy metals from industrial wastewater and these include ion exchange, adsorption, phytoextraction, electrodialysis, ultrafiltration and reverse osmosis [2]. Ion-exchange is the most frequently employed in industrial water treatment, among the heavy metal removal techniques [3]. Ion-exchange is a process whereby a solid substance (the ion-exchanger) and some aqueous solution exchange ions [4]. Natural zeolites have ascendancy over other ion exchange materials such as resin, because they are lost-cost material and exhibit excellent selectivity for different ions at low temperatures, which is accompanied with a release of non-toxic exchangeable ions to the environment [4]. Clinoptilolite is the most abundant and cosmopolitan natural zeolites with hydrated microporous crystalline material and it has been widely exploited for its ion-exchange

capabilities, since it can easily exchange its interstitial cations for external cations in solution. Natural zeolites such as clinoptilolite are able to lose and gain water in a reversible manner and to exchange their extra framework cations, both without changing the crystal structure [5].

The general chemical formula of clinoptilolite is (Na, Li, K)$_\alpha$(Mg, Ca, Sr, Ba)$_d$ [Al$_{\alpha + 2d}$- Si $_{n-(\alpha+ 2d)}$ O$_{2n}$]. mH$_2$O [6]. The Na$^+$ ion is the weakest bound ion in clinoptilolite and this it can be easily exchanged with the cations in solution [7]. 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 [4]. 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.

For the effective utilization of clinoptilolite as an ion-exchanger material, it is essential to have chemical models that help to describe accurately heavy metals exchange equilibria [8]. The target heavy metals in this study are Co^{2+} and Cu^{2+} which are frequently find in industrial effluents.

However, Co^{2+} and Cu^{2+} are usually found at high concentrations in industrial wastewater, because it is considered as the most valuable and commonly used heavy metals in many industrial applications, such as metal finishing, electroplating, plastics and etching.

In addition to removing heavy metals from industrial wastewater, clinoptilolite can facilitate heavy metal removal by shifting the thermodynamic equilibrium and binary interactions parameters. Wilson and Debye Hückel equations were used to calculate activity coefficients in the solid and liquid phase, respectively.

The objective of this study is to assess the ion-exchange equilibrium of Na$^+$/Cu^{2+} and Na$^+$/Co^{2+} on clinoptilolite for the removal of Co^{2+} and Cu^{2+} from industrial wastewater.

II. MATERIALS AND METHODS

A. Preparation of clinoptilolite and synthetic wastewater

Clinoptilolite was prepared as described by Kabuba [4]. Clinoptilolite was washed with 20 Vol % HCl and then with deionized water. Resulting material was dried in an oven at 80°C for 24 hrs to remove the moisture content, crushed with jaw crushers and sieved through screens to a size of 1.7, 2.0- and 2.8-mm for the experiments. Sieving was

repeated several times to minimize the retention of smaller grains in a sample with a large size range. 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 130 rpm then dried for another 24 hrs at 70°C.

The synthetic solutions were prepared by dissolving CoSO$_4$.7H$_2$O and CuSO$_4$.5H$_2$O (analytical grade) in deionized water at pH 6.5 to generate solutions that contained Cu^{2+} and Co^{2+}, respectively at the concentration of 150, 300 and 600 ppm. These synthetic solutions were stored at room temperature (approximately 25°C). The solutions were essayed using atomic adsorption spectroscopy (AAS), (Model varian spectra (20/20)). The samples were used within 48 hrs after preparation to minimize errors from precipitation and container plating of the metal ions. The pH of the solution was adjusted by adding 0.1 M sulphuric acid or 0.1 M sodium hydroxide solution.

B. Ion-exchange equilibrium and Experimental procedure

The experimental procedure was done as described by Kabuba [4]. Equilibrium clinoptilolite loading data were generated for Na$^+$/Cu^{2+} and Na$^+$/Co^{2+} systems at desired temperature 298, 328 and 358K. 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 ion-exchange equilibrium was achieved. Then, the mixture was filtered to remove the clinoptilolite and the filtrate was analyzed for the removal content. The metal concentration exchanged onto the clinoptilolite was calculated using mass balance relation (1):

$$q = \left(C_i - C_f\right)\frac{V}{W} \qquad (1)$$

Where C$_i$ and C$_f$ are the initial and final concentrations in the solution phase, respectively; q is the metal concentration in the clinoptilolite phase (mmol/g), V is the solution volume, and W is the mass dry weight of clinoptilolite (g).

Co^{2+} and Cu^{2+} in ion-exchange processes on the clinoptilolite was conducted at room temperature. A glass column (2 cm in diameter and 30 cm 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 solutions were 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 and assayed. The solutions were collected at 30, 60, 90 and 120 mins 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 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 solution 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 solution 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 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 H$_2$SO$_4$ 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 5.3. The pH was adjusted using KOH and H$_2$SO$_4$. 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 clinoptilolite (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 clinoptilolite is partially replaced by B (see 2).

$$\beta A_r^{\alpha+} + \alpha B_s^{\beta+} \leftrightarrow \beta A_s^{\alpha+} + \alpha B_r^{\beta+} \qquad (2)$$
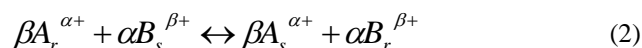
In equilibrium, both the clinoptilolite and the solution contain competing counterion species, A and B. The ionic fraction for a binary system can be introduced as presented in (3) and (4).

$$x_A = \frac{C_A}{N} ; \ x_B = \frac{C_B}{N} \qquad (3)$$

$$y_A = \frac{q_A}{q_o} ; \ y_B = \frac{q_B}{q_o} \qquad (4)$$

Where C_i represents the normality concentration of the ionic species in solution, N is the total ionic concentration in the solution phase, qi 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 (K_{AB}) for the exchange reaction (2) assuming real behavior for both phases could be calculated from (5):

$$K_{AB}(T) = \frac{\left(y_B \bar{\gamma_B} \right)^\alpha \left[(1 - x_B) N \gamma_A \right]^\beta}{\left[(1 - y_B) \bar{\gamma_A} \right]^\beta \left(x_B \gamma_B N \right)^\alpha} \qquad (5)$$

Where $\bar{\gamma}$ and γ are the activity coefficient of each ion in the clinoptilolite and in the solution and y_B and x_B are the ionic fraction of ion B in the solid phase and A in the solution. The activity coefficients in the solid phase were calculated using the Wilson Equation as described by Valverde et al. [9].

$$\bar{\gamma_A} = \left[\exp(1 - \ln(y_A + (1 - y_A)\Lambda_{AB})) - \left(\frac{y_A}{y_A + (1 - y_A)\Lambda_{AB}} \right) - \left(\frac{(1 - y_A)\Lambda_{BA}}{(1 - y_A) + y_A \Lambda_{BA}} \right) \right]$$
$$(6)$$

$$\bar{\gamma_B} = \left[\exp(1 - \ln((1 - y_A) + y_A \Lambda_{AB})) - \left(\frac{1 - y_A}{(1 - y_A) + y_A \Lambda_{BA}} \right) - \left(\frac{y_A \Lambda_{AB}}{y_A + (1 - y_A)\Lambda_{AB}} \right) \right]$$
$$(7)$$

Where Λ_{AB} and Λ_{BA} are the Wilson coefficients.

The activity coefficients in the liquid phase were determined from the Debye-Hückel limiting law [10]:

$$\gamma_i = \exp\left(-\frac{A\sqrt{I}}{1 + Ba\sqrt{I}} \right) \qquad (8)$$

Where A and B denote the Debye-Hückel equation parameters, I is the ionic strength and a refers to the average ionic diameter (Å) of the hydrated ions Na^+, Cu^{2+} and Co^{2+}.

$$T(1 - \ln \Lambda_{AB} - \Lambda_{BA}) = C_{AB}^A \qquad (9)$$

$$T(1 - \ln \Lambda_{BA} - \Lambda_{AB}) = C_{AB}^A \qquad (10)$$

Where Λ_{AB} and Λ_{BA} are Wilson coefficients, T is the absolute temperature, and C_{AB}^A and C_{AB}^B are the constants of the Gilliland relationship [11].

$$\Lambda_{AB} = \frac{V_B}{V_A} \exp\left(-\frac{A_{AB}}{RT} \right) \qquad (11)$$

$$\Lambda_{BA} = \frac{V_A}{V_B} \exp\left(-\frac{A_{BA}}{RT} \right) \qquad (12)$$

Where V_A and V_B (cm^3/mol) are the molar volumes of component A and component B. A_{AB}, A_{BA} interaction energy parameters (Cal/mol) between unlike molecules.

III. RESULTS AND DISCUSSION

A. X-Ray Fluorescence (XRF)

TABLE I
XRF RESULTS OF NATURAL CLINOPTILOLITE AND CLINOPTILOLITE-NA

Component	Clinoptilolite	Clinoptilolite-Na
SiO_2	77.24	77.36
Al_2O_3	13.30	13.18
Fe_2O_3	0.14	0.13
FeO	1.09	1.01
MnO	0.04	0.01
MgO	0.86	0.71
CaO	1.40	0.77
Na_2O	1.94	3.84
K_2O	3.78	2.94
TiO_2	0.14	0.14

The elemental analysis of the natural clinoptilolite and clinoptilolite-Na given in Table I revealed that clinoptilolite is mainly composed of SiO_2, Al_2O_3 and Fe_2O_3 with very low amounts of MnO and TiO_2 in the framework. In clinoptilolite-Na, it was observed a significant increase amount of Na_2O (3.84%). This is due to the conditioning of natural clinoptilolite with NaCl. Some consideration changes were observed because the total should be 100%.

B. Metal Removal from a Double Component System

By varying some 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. It is possible that there were Cu^{2+} affinitive sites immediately available on the clinoptilolite's surface, such that the uploading started off very fast, these Cu^{2+} affinitive sites then became depleted with time as the Cu^{2+} adopted another uploading mechanism that probed to be slower than ion-exchange [5]. The most likely mechanism to have occurred at first is the ion-exchange mechanism which is known to be quick. It is suggested that the latter part of the metal ion loading takes place inside the clinoptilolite and is slow due to the percolation of the solution through the clinoptilolite channels. In light of the fact that there was more Cu^{2+} than Co^{2+} in solution there were freer and more available Cu^{2+} ions in solution for exchange, such that the Cu^{2+} ions were uploaded first. As time went by the Cu^{2+} ions that had formed Co-Cu non-stable complexes in a dynamic fashion were later uploaded as they broke away from their Co^{2+} ion counterparts in a manner allowed by their complex formation dynamics.

C. 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.

The difference of the adsorption capacity of clinoptilolite for heavy metal ions may be due to a number of factors which include hydration diameter and solubility of cation. The hydrated radii of Cu (II) and Co (II) are 0.419 and 0.423 nm, respectively [5]. The Cu^{2+} particles should ideally be adsorbed in larger quantities compared to the Co^{2+} particles, since the smaller particles can pass through the micropores of the clinoptilolite structure with ease.

The increase of adsorbed Co^{2+} is directly connected with a decrease in the particles size. Initially this is attributed to a larger specific surface area which leads to a more effective contact between adsorbent and adsorbates.
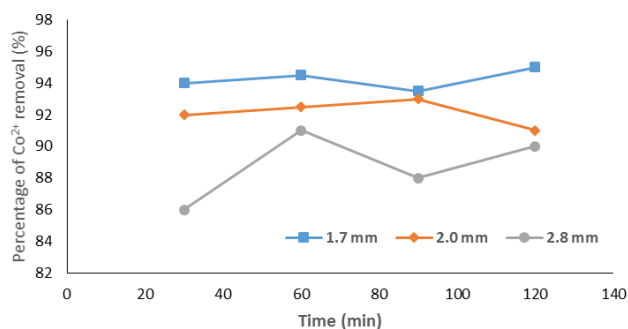
more slowly in concentrated solutions. In Fig. 3, the results show that for the Co^{2+} percentage metal removal, the diluted aqueous solution shows the highest metal removal percentage which ranges from 95 – 92% (for 150ppm solution) and 83 – 81% for the 600pm solutions. This can also be seen in Fig. 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. It was also observed that at low concentration of both metal ions, a unit mass of the clinoptilolite is exposed to small number of metal ions and consequently the adsorption is independent of the initial metal ion concentration. The extent of adsorption comes down for a fixed adsorbent content at high metal ions concentration due to deceased number of available adsorption sites on clinoptilolite.

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

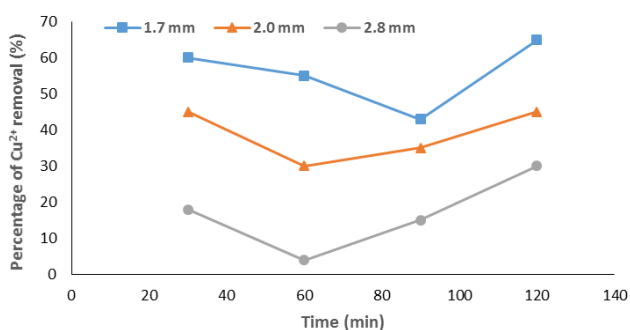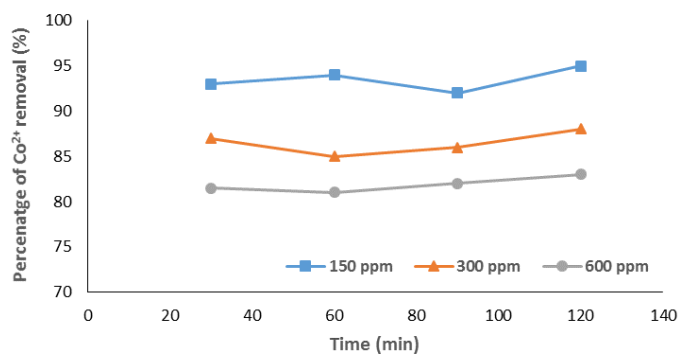Fig. 3. Percentage removal of Co^{2+} after 120 min investigating the effect of initial concentration on the metal percentage removal

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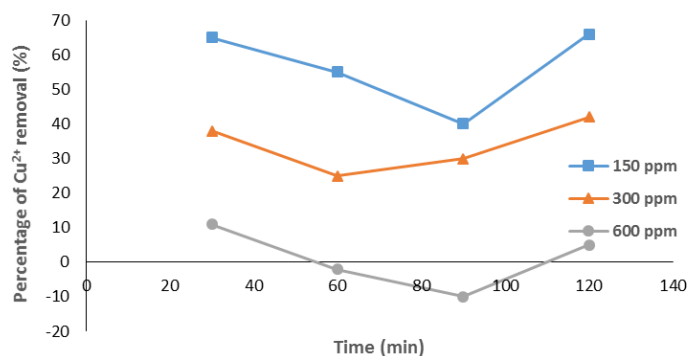

Fig. 4. Percentage removal of Cu^{2+} after 120 min investigating the effect of initial concentration on the metal percentage removal

D. 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

E. Effect of Clinoptilolite Dosage

Figs. 5 and 6 show that the metal percentage increased with an increase in clinoptilolite dosage. This is due to the fact that as the clinoptilolite dosage increased, it provides more area for the ion exchange to take place. This can be 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.

The number of active sites increases with the amount of clinoptilolite, so adsorption takes place in a major extension. However, when the dosage is very high, a partial aggregation of clinoptilolite occurs, which results in a constant adsorption percentage independently of the amount of adsorbent used. The opposite situation occurs with the adsorption capacity (q), because, when the dosage increases, there is a greater number of active adsorption sites, but the concentration of ions remains the same, so, the adsorbed quantity per weight unit decreases.
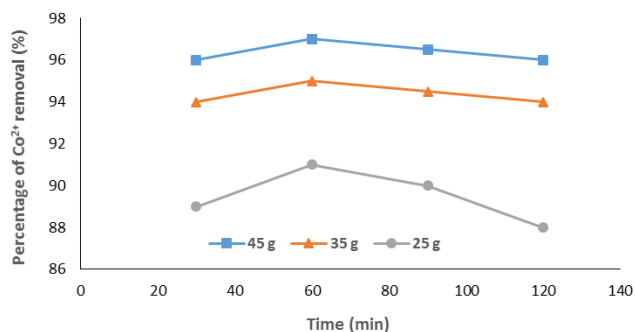

Fig. 5. Percentage removal of Co^{2+} after 120 min investigating the effect of clinoptilolite dosage on the metal percentage removal
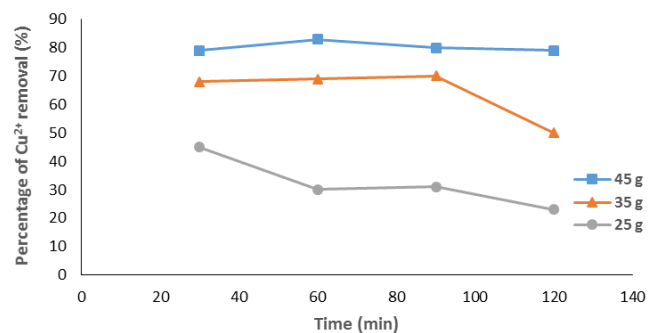

Fig. 6. Percentage removal of Cu^{2+} after 120 min investigating the effect of clinoptilolite dosage on the metal percentage removal

F. Effect of pH

The effect of the initial pH was also evaluated. This variable is one of the most important parameters affecting Co^{2+} adsorption because it can affect either the active sites of the adsorbent or the metal chemistry in water. Under acidic conditions, the metal removal capacity is lower because there is a competition between the H^+ and Co^{2+} for the active site on the clinoptilolite. In this case, the clinoptilolite adsorb firstly the H^+ due to its ionic mobility and ionic radius. However, at higher pH values, the

competition from the protons becomes less important, so the vast majority of Co^{2+} can be exchanged with exchangeable cations or adsorbed onto the clinoptilolite surface.

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+}.

A decrease in metal removal at pH higher 8 may be due to the fact that a high concentration of H^+ ions compete with metal for active site at low pH, with an apparent preponderance of H^+ ions. This results in the suppression of Cu^{2+} adsorption on the surface of clinoptilolite. The uptake capacity of clinoptilolite was found to be a maximum at pH 4. At low pH value, strong competition exists between protons and Cu^{2+} for adsorption sites, so the removal efficiency is low. As the pH value increases, linked H^+ is released from the active sites and the amount of adsorbed Cu (II) ions increases. However, when the pH value higher than 6.0, Cu2+ ions are precipitated because of higher concentration of OH^- ions in the medium. Literature indicates that cobalt precipitates as hydroxide when the pH is above 8 [17].
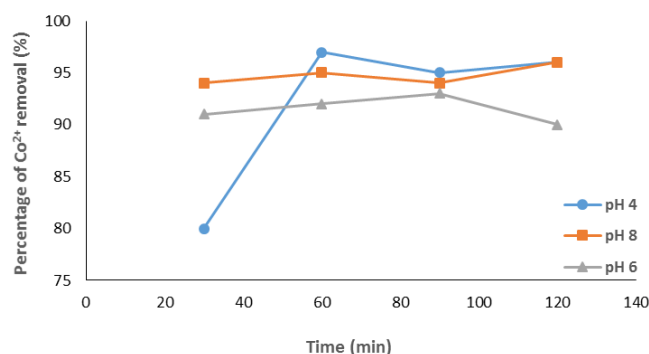

Fig. 7. Percentage removal of Co^{2+} after 120 min investigating the effect of pH on the metal percentage removal
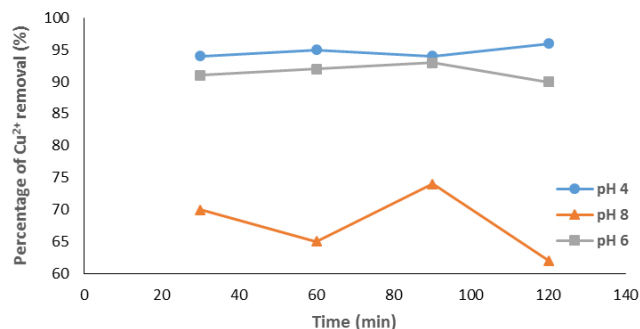

Fig. 8. Percentage removal of Cu^{2+} after 120 min investigating the effect of pH on the metal percentage removal

G. Thermodynamic properties

TABLE II
EQUILIBRIUM PARAMETERS OF THE BINARY SYSTEMS NA⁺/CU²⁺ AND
NA⁺/CO²⁺ ON CLINOPTILOLITE-NA

T (K)	K_{AB}	Λ_{AB}	Λ_{BA}	C_{AB}^A	C_{AB}^B
283	5.60	3.123	0.102	-1.211	-1.531
328	8.21	5.251	0.038	-2.117	-3.062
358	9.28	7.012	0.023	-3.312	-5.311

Calculated values (Table II) of the equilibrium constant K_{AB} in (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 temperatures (283, 328 and 358K) (See 13-15).

The values of K_{AB} in Table II were calculated as the ratio of the equilibrium concentration of Cu^{2+} and Co^{2+} on the clinoptilolite and in solution attained after 24 hrs of adsorption.

$$\Delta G^o{}_{AB} = -RT \ln K_{AB} \tag{13}$$

$$\Delta H^o{}_{AB} = -(RT / \alpha\beta)d(\ln K_{AB}) / dt \tag{14}$$

$$\Delta S^o{}_{AB} = (\Delta H^o{}_{AB} - \Delta G^o{}_{AB}) / T \tag{15}$$

Where R (8.314 J mol⁻¹ K⁻¹) and T (K) are the universal gas constant, temperature and distribution coefficient reflecting the selectivity for metal adsorption.

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

T (K)	K_{AB}	$\Delta G^o{}_{AB}$ (kJ.mol⁻¹)	$\Delta H^o{}_{AB}$ (kJ.mol⁻¹)	$\Delta S^o{}_{AB}$ (kJ.mol⁻¹)
283	5.60	-7.01	12.03	27.58
328	8.21	-5.38	14.70	33.22
358	9.28	-4.06	16.20	41.12

In Table III, the negative values of the Gibbs free energy change (ΔG^o) indicate that the ion-exchange process is spontaneous. ΔG^o was negative, suggesting that the spontaneity of the process increased with increasing temperature. The negative values indicate that metal cations would be preferably bound to the clinoptilolite as compared to Na^+. The positive enthalpy (ΔH^o) reveals energy is absorbed as ion-exchange proceeds, and the reaction is said to be endothermic resulted in the equilibrium extent of reaction increase with increasing temperature. ΔH was positive in all forms of clinoptilolite which indicates that the sorption reaction is endothermic for Co^{2+} and Cu^{2+}. These values were calculated from plots of $\ln K_{AB}$ versus $1/T$. The linear nature of the plot indicates that the mechanism of ion-exchange is not changed as temperature is changed. But the amount of adsorption is changed because the supply of thermal energy is different. The endothermic nature of the ion-exchange processes shows that these processes are not energetically stable.

The enthalpy of exchange is positive for the Cu^{2+}/Na^+ and Co^{2+}/Na^+ clinoptilolite. This positive value is explained on the one hand by the substitution of Na^+ cation by Cu^{2+} and Co^{2+} cations, which have a greater heat of hydration in the aqueous phase, and on the other hand by the greater interaction energy of the Cu^{2+} and Co^{2+} cations with the exchange centres of clinoptilolite as a result of their similarity in size.

The positive entropy change may be due to the release of water molecule produced by ion-exchange reaction [16]. The entropy changes in this study are found to be positive, it means that the increased randomness appeared on the clinoptilolite -solution interface during the exchange of heavy metals.

H. Langmuir and Freundlich Adsorption Isotherms

The sorption data were analyzed by the Langmuir and Freundlich adsorption isotherms. The equilibrium for Co^{2+} and Cu^{2+} metal solutions was linked with the Langmuir isotherm according to (17):

$$q_e = \frac{q_m K_L C_f}{1 + K_L C_f} \tag{16}$$

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).

$$\frac{1}{q_e} = \frac{1}{q_m K_L} \frac{1}{C_f} + \frac{1}{q_m} \tag{17}$$

To make the Langmuir plots, $\frac{1}{q_e}$ was plotted against $\frac{1}{C_f}$ a straight-line graph was attained for this plot [14]. 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 Cu^{2+}, 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 adsorption isotherm 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:

$$q_e = K_F C_f^{1/n} \tag{19}$$

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 (19) can be reorganized in a linear equation form (see 20).

$$\log q_e = \log K_F + \frac{1}{n} C_f \tag{20}$$

To make the Freundlich plots, log q_e was plotted against log C_f and a straight-line graph was attained for this plot [15]. 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+}).
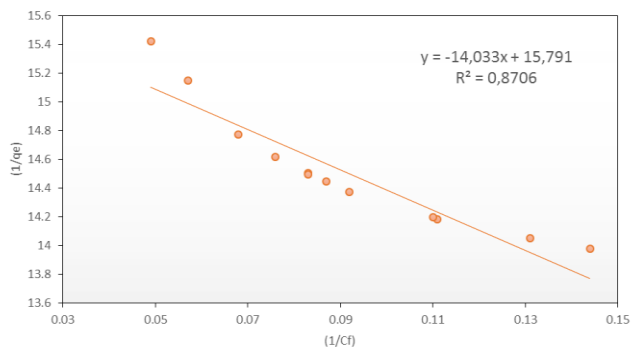

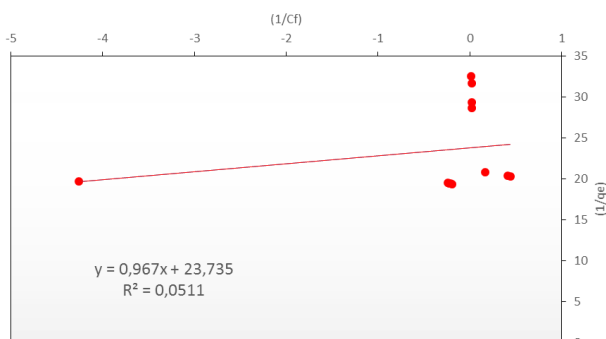Fig. 9. Langmuir plot for Co^{2+} after 120 min.
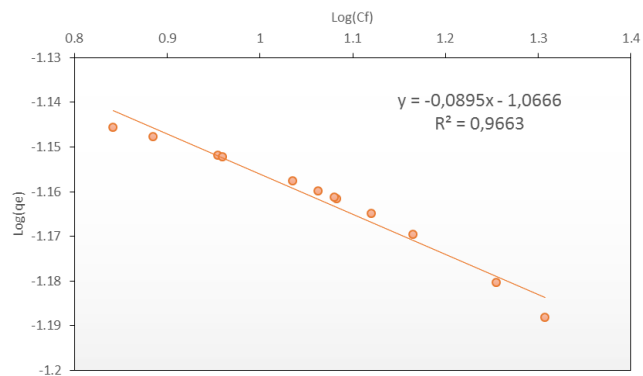

Fig. 10. Langmuir plot for Cu^{2+} after 120 min.

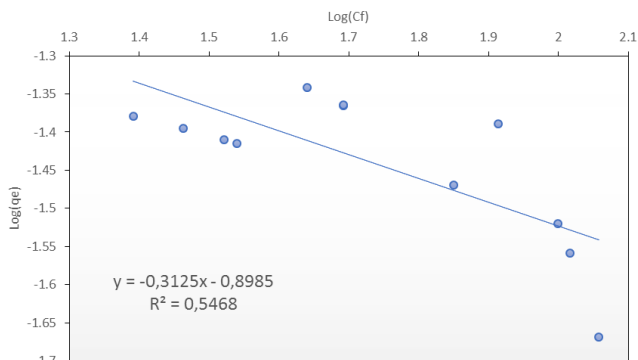
Fig. 11. Freundlich plot for Co^{2+} after 120 min.

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

IV. CONCLUSION

Ion-exchange equilibria Na^+/Cu^{2+} and Na^+/Co^{2+} systems using clinoptilolite-Na have been measured at (298, 328 and 358) K. Experimental equilibrium data can be satisfactory correlated to the homogenous mass active model using Wilson and Debye-Hückel equation to calculate activity coefficients in the solid and the liquid phase, respectively. The effect of particle size, initial concentration, adsorbent dosage and pH were investigated. Adsorption isotherms were performed in this study, the Freundlich isotherm ($R^2 = 0.97$) fits better than the Langmuir approach ($R^2 = 0.87$). The thermodynamic parameters of the ion-exchange process were calculated and found to be spontaneous. The positive values of the enthalpy and entropy change confirm that the ion-exchange process is endothermic and randomness, respectively.

REFERENCES

[1] V.J. Inglezakis, A.A. Zorpas, M.D. Loizidou & H.P. Grigolopoulou, "The Effect of Competitive Cations and Anions on Ion-Exchange of Heavy metals", *Separation Purification Techno*logy 46, 2005, pp. 202-207.

[2] J. Kabuba, A. Mulaba-Bafubiandi, K. Battle. "Neural Network Techniques for Modelling of Cu (II) removal from aqueous solution by clinoptilolite". *Arabian Journal for Science and Engineering*, 39, 2014, pp. 6793-6703.

[3] A. Amankwah & J. Kabuba, "Comparison of Neural Network and Kalman Filter for the Modelling of Ion-Exchange Process" *Life Science Journal,* 10, 2003, pp. 1012-1015.

[4] J. Kabuba, "Ion-Exchange Equilibria of Na^+/Cu^{2+} and Na^+/Co^{2+} using Clinoptilolite". *Lecture notes in Engineering and Computer Science: Proceedings of the World Congress on Engineering and Computer Science 2018, 23-25 October 2018, San Francisco, USA*, pp. 492-497.

[5] B.B. Mamba, D.W. Nyembe and A.F. Mulaba-Bafubiandi, "The effect of conditioning with NaCl, KCl and HCl on the performance of natural clinoptilolite's removal efficiency of Cu^{2+} and Co^{2+} from Co/Cu synthetic solutions" *Water SA*, 36,2010, pp. 437-444.

[6] E.P. Favvas, C.G. Tsanaktsidis, A.A. Sapalidis, G.T. Tzilantonis, S.K. Papageorgiou, A.Ch. Mitropoulos, "Clinoptilolite, a natural zeolite material: Structural characterization and performance evaluation on its dehydration properties of hydrocarbon-based fuels". *Microporous and Mesoporous Materials* 225, 2016, pp. 385-391.

[7] B.B. Mamba, D.W Nyembe & A.F Mulaba-Bafubiandi, "Removal of copper and cobalt from aqueous solutions using national clinoptilolite'. *Water SA*, 35, 2009, pp. 307-313.

[8] J. Kabuba, A. Mulaba-Bafubiandi, K. Battle "Binary Mixture of Copper-Cobalt Ions Uptake by Zeolite using Neural Network" *International Journal of Materials and Metallurgical Engineering*, 6, 8, 2012, pp. 727-732.

[9] J.L. Valverde, A. Lucas, M. Ganzalez, J.F. Rodriguez, "Ion-Exchange Equilibrium of Cu^{2+}, Cd^{2+}, Zn^{2+} and Na^+ ions on the cationic Exchanger Amberlite IR-120" *Journal of Chemical & Engineering Data*, 46, 2001, pp. 1404-1409.

[10] A. Lucas, J.L. Valverde, M.C. Romero, J. Gomez, J.F. Rodriguez, "The ion exchange equilibria of Na^+/K^+ in nonaqueous and mixed solvents on a strong acid cation exchanger" *Chemical Engineering Science,* 57, 2002, pp. 1943-1954.

[11] K.S. Pitzer, "Thermodynamics of Electrolyte Solutions" 2nd ed.; CRC. Press; Boca Raton, FL, 1991.

[12] J.P.S Aniceto, D.L.A. Fernandes, C.M. Silva. "Modelling ion exchange equilibrium of ternary systems using neural networks", *Desalination*, 309, 2013, pp. 267-274.

[13] M. Jaina, V.K. Gorg, K. Kadirvelu. "Adsorption of hexavalent chromium from aqueous medium onto carbonaceous adsorbents prepared from waste biomass". *Journal of Environmental Management*, 91, 2010, pp. 949-957.

[14] I. Langmuir, "The adsorption of gases on plane surfaces of glass, micro and platinum", *Am. Chem. Soc.*, 40, 1918, pp. 1361-1402.

[15] O. Altin, H. Ozbelch & T. Dogu, "Use of General Purpose Adsorption Isotherms for Heavy Meta-clay Mineral Interactions", *Journal of Colloid and Interface Sci*ence, 198, 1998, pp. 130-140.

[16] I.H. Lee, Y.C. Kuan, J.M. Chern, "Equilibrium and Kinetics of heavy metal ion exchange". *Journal of the Chinese Institute of Chemical Engineers*, 38, 2007, pp. 71-84.

[17] R.N. Collins & A.S. Kinsela "The aqueous phase speciation and chemistry of cobalt in terrestrial environments" *Chemosphere*, 79, 2010, pp. 763-771.