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## Adsorption Mechanisms of $\text{Co}^{2+}$ and $\text{Cu}^{2+}$ from Aqueous Solutions using Natural Clinoptilolite: Equilibrium and Kinetic Studies

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**Abstract:** The study was aimed at determining the adsorption mechanisms involved in the ion-exchange of  $\text{Co}^{2+}$  and  $\text{Cu}^{2+}$  in their aqueous solutions using Southern African natural clinoptilolite in its original (non-activated form). The clinoptilolite was characterized with FTIR and XRF and was found to consist of quartz, alumino-silicates calcite and dolomite was shown to be effective at removing  $\text{Co}^{2+}$  and  $\text{Cu}^{2+}$  ions from an aqueous solution. Both  $\text{Co}^{2+}$  and  $\text{Cu}^{2+}$  were readily adsorbed from dilute solutions (0.0020 M) followed by a 0.0698 M solution and the least removal was recorded with 0.2000 M solution. After mixing  $\text{Co}^{2+}$  and  $\text{Cu}^{2+}$  to generate a mixed Co/Cu synthetic solution the removal rates variable results and depended on the salt concentration ratios of the mixed solution. It was observed that  $\text{Co}^{2+}$  was generally easily removed from these solutions compared to  $\text{Cu}^{2+}$ . The adsorption data of the metal ions were postulated by Langmuir and Freundlich isotherms over the entire concentration range. Kinetic data for adsorption kinetics accurately fitted the pseudo-first order with external diffusion models indicating that the ion-exchange of  $\text{Co}^{2+}$  and  $\text{Cu}^{2+}$  ions could be happening on the exterior surface of the sorbent while the contribution of internal diffusion mechanism was considered to be minimal.

**Key words:** Clinoptilolite,  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$  solutions, ion-exchange, isotherms, kinetics

### INTRODUCTION

The presence of heavy metals in aquatic systems can threaten various living species that depend on such an environment. Metallurgical operations and manufacturing industries discharge aqueous effluents containing heavy metals which are non biodegradable. These non biodegradable species tend to accumulate in living organisms, causing various kinds of metabolic disorders. Innovative methods for water and wastewater treatment are continuously being developed to remediate water containing metallic species. However, these methods are unable to achieve the standards which have been recommended by international water standards bodies (Garcia-Sanchez and Alvarez-Ayuso, 2002; Bailey *et al.*, 1999).

In recent years, many natural adsorbents have been investigated for the removal of heavy metals from water. Calcite, magnetite and dolomite which fall under the category of carbonate minerals have been investigated for possible use in the removal of heavy and radio-active metals from aqueous solutions (Zachara *et al.*, 1991;

Papadopoulos and Rowell, 1988). Carbonate rich minerals are effective at removing heavy metals through a mechanism of interaction proposed to be a combination between ion-exchange and precipitation on the carbonate surface (Garcia-Sanchez and Alvarez-Ayuso, 2002). Natural silicate minerals, of which zeolites are a typical form, have also been investigated as potential low-cost sorbents for removing toxic heavy metals (Al-Degs *et al.*, 2006; Sheta *et al.*, 2003). Sorbents can either be organic or inorganic ion-exchangers. Among the inorganic ion exchangers zeolites are the most abundant. Inorganic exchangers such as zeolites have useful properties such as resistance to decomposing in the presence of ionizing radiation or at high temperatures and compatibility with the environment (El-Kamash, 2008). They also, show high selectivity towards heavy metal ions which make them suitable for ion exchange process (El-Kamash, 2008).

Clinoptilolite is the most abundant and cosmopolitan natural zeolite and it has been widely exploited for its ion-exchange capabilities since, it can easily exchange its interstitial cations for external cations in solution

(Kuronen *et al.*, 2006). 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 the change of crystal structure (Rezaei and Movahedi, 2009). Ion-exchange is made possible by the presence of extra-frame-work cations which are located in the regular array of channels and cages that constitute the rigid anionic framework. Cations are bound to the lattice and to water molecules, which normally fill the zeolite micropores (Dyer and Townsend, 1981). When the zeolite comes into contact with an electrolytic solution, the exchangeable cations in the zeolite can be removed from their sites and replaced by ions in the solution. The substitution is stoichiometric and depends on the parameters provided during experimental procedures.

In addition to high mechanical strength, natural zeolites have good porosity and high surface area (Inglezakis *et al.*, 2005). The determination of the exact type of mechanism for metal sorption by natural adsorbents such as zeolites is a complex procedure (Frimmel and Huber, 1996). In this study, the chemical and mineralogical characteristics of South African clinoptilolite were investigated in order to assess the feasibility of this zeolite as a low cost sorbent for the removal of  $\text{Cu}^{2+}$  and  $\text{Co}^{2+}$  from aqueous solutions and mine water solutions. The objectives of the study were to: assess the removal efficiency and the mechanism of metal removal, to determine the effect of solution concentration on  $\text{Co}^{2+}$  and  $\text{Cu}^{2+}$  removal in single and mixed solutions, determine the adsorption mechanisms, to apply the sorption kinetics and equilibrium studies.

## MATERIALS AND METHODS

All chemicals used in this study were of analytical reagent grade and were obtained from Sigma Aldrich and Merk. The clinoptilolite used was supplied by Prattely South Africa and was sourced from the Vulture Creek, KwaZulu-Natal Province of South Africa. The study was conducted between April, 2007 and December 2008. The experimental procedures are as outlined by Nyembe *et al.* (2009).

**Preparation of clinoptilolite:** Original clinoptilolite was crushed with jaw crushers and sieved through screens to a size range of 2.8-5.6 mm. A fraction of this average particle size was rinsed with distilled water and air-dried for 24 h. In addition to original forms, conditioned forms of Southern African clinoptilolite were also used in this study.

**Thermogravimetric analysis (TGA):** The physical and chemical changes brought about by heat to matter have been scientifically proved to be characteristic to that particular type of matter. There are techniques used in studying these changes and Thermogravimetric analysis (TGA) is one of them. This technique is used to measure the change in mass of a sample in a specified atmosphere as the temperature of the sample is programmed.

For thermal analysis, the TGA (Perkin Elmer Pyris 1) analysis was carried out in this study. The aim was to determine the stability of the zeolite by examining its weight loss with increasing temperatures. The clinoptilolite used was dried at  $50^{\circ}\text{C}$  for 24 h and therefore, it was important to know its thermal stability at very high temperatures. About 10 mg of the original clinoptilolite was used for the analysis. A constant heating rate of  $10^{\circ}\text{C min}^{-1}$  in air for a range of  $50\text{-}900^{\circ}\text{C}$  under a  $\text{N}_2$  atmosphere was configured.

**Infrared spectroscopy:** Infra red radiation may be absorbed by covalent bonds present in a sample resulting in the vibration of the bond at specific amplitude unique to that type of a covalent bond due to the absorbed frequency. The absorbed frequency largely depends (among other factors) on the geometry and the weights of the atoms present in the vibrating covalent bond (Skoog *et al.*, 1998).

The FTIR technique was used for the HCl-activated, NaCl-activated, KCl-activated and the original forms of clinoptilolite in order to ascertain the effects of chemical conditioning on original clinoptilolite. This was to aid in giving possible explanations about the performances of the clinoptilolite. Dry pellets were prepared by mixing finely milled clinoptilolite (approx.  $75\ \mu\text{m}$ ) with a bromide binder in a ratio of 1:10 of sample to binder (0.05 g clinoptilolite: 0.5 g binder) and mixing using a pestle and mortar until homogeneity of the mixture was achieved. The pellet was analyzed for its peaks. Results of IR spectra were obtained using a Midac FT-IR 5000 spectrophotometer on  $\text{CaF}_2$  plates. The IR data are listed with their individual characteristic peaks in wavenumber ( $\text{cm}^{-1}$ ).

**X-ray Fluorescence (XRF):** For XRF analysis, sample preparation was done by mixing 8 g of dry finely milled ( $<75\ \mu$ ) clinoptilolite sample with 20 pellets of HPMA40 binder (approx. 4.1 g) using a milling machine until the mixture was homogeneous. A pressed pellet of the mixed sample was prepared by setting the pressure at 20 tones for 60 sec. The pellet's elemental composition was determined using X-ray Fluorescence spectroscopy (XRF, Phillips Magix Pro).

**Preparation of synthetic solutions:** For AAS analysis solutions of copper and cobalt were prepared by dissolving  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in deionised water to generate solutions that contained  $\text{Cu}^{2+}$  and  $\text{Co}^{2+}$  concentrations of 0.0020, 0.0698 and 0.2000 M. These concentrations were arbitrarily chosen on the basis of generating low, middle and high concentrated solutions. These synthetic aqueous solutions were stored at room temperature (approx.  $25^\circ\text{C}$ ). The samples were used within 48 h after preparation to minimize errors due to precipitation and container plating of the metal ions. The non-mixed  $\text{Cu}^{2+}$  and  $\text{Co}^{2+}$  aqueous solutions of concentrations 0.0020, 0.0698 and 0.2000 M which corresponded to 0.032, 1.109 and 3.177 g of  $\text{Cu}^{2+}$  and 0.030, 1.028 and 2.947 of  $\text{Co}^{2+}$  were prepared by dissolving  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  salts in deionised water in 250 mL volumetric flasks. The effects of one cation on the other's removal efficiency were studied by varying the metal ion concentration in solution. Studies on the Co/Cu mixed synthetic solutions were done with solutions of copper and cobalt prepared at stoichiometric ratios of Co:Cu -1:1, 1:5, 1:9, 5:1 and 9:1 which corresponded to these concentrations of Co:Cu-0.0020:0.0020 M, 0.0020:0.0698, 0.0020:0.2000, 0.0698:0.0020 and 0.2000:0.0020 M, respectively.

**Mine water sampling:** In order to assess the applicability of clinoptilolite used in this study for the removal of  $\text{Cu}^{2+}$  and  $\text{Co}^{2+}$  and other metals from real aqueous solutions, the clinoptilolite's capabilities were tested on mine water samples containing other cations and exhibiting a variety of physical parameters. The mine water used was sampled from a gold mining are in Nigel in the Gauteng Province, South East of Johannesburg. The schematic locations of the sampling sites are depicted in Fig. 1. A total of 9 sampling points (Fig. 1) were arbitrarily chosen around the site.

Samples were collected in two instances, before and after rains in 2008. Effluents from metallurgical operations were collected from all sites. Physical parameters such as conductivity, pH and turbidity of the water were measured

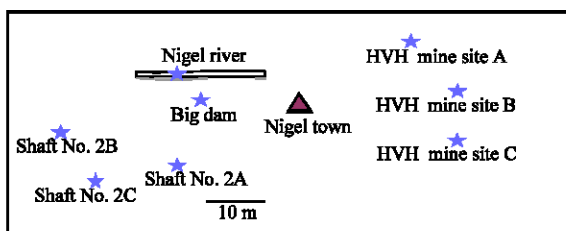


Fig. 1: Site map showing the sampling points around Nigel town

on site per sampling point and the overall activities noticed around the sampling point were noted. The water samples were drawn within 5 cm below the surface, using glass sampling bottles. Samples were placed in glass jars and chilled at  $6^\circ\text{C}$  before laboratory analysis which was done within 72 h. The samples were then decanted and assayed for the presence and content of  $\text{Co}^{2+}$  and  $\text{Cu}^{2+}$  metal ions. Assay of samples was done using Atomic Absorption Spectroscopy (AAS Varian 20/20).

**Adsorption models of  $\text{Cu}^{2+}$  and  $\text{Co}^{2+}$  onto clinoptilolite:** Sorption kinetic models can be divided into two main types, namely diffusion-based models and reaction-based models (Ho *et al.*, 2000).

**Diffusion based models**

**External diffusion model:** If external diffusion of metal cations within the diffuse layers outside the sorbent is the rate determining step then, the Eq. 1 can be fitted into the absorption data (Lee *et al.*, 1990):

$$\ln\left(\frac{C_t}{C_o}\right) = -kt \tag{1}$$

Where:

- $C_o$  = The initial concentration of adsorbate at time  $t$  ( $\text{mol g}^{-1}$ )
- $C_t$  = The surface concentration of adsorbate at time  $t$  ( $\text{mol g}^{-1}$ )
- $k$  = The external diffusion coefficient ( $\text{mol g}^{-1}$ )
- $t$  = The sorption time

This model showed that the ion-exchange of  $\text{Cu}^{2+}$  and  $\text{Co}^{2+}$  ions occurred mainly on the external surface of the adsorbent and this can be described by an external diffusion model.

**Internal diffusion mechanism:** When internal surface and pore diffusion of metal cations inside the sorbent are the rate determining steps, then the absorption data can be presented by the Eq. 2 (Ho *et al.*, 2000):

$$C_t = k_d t^{1/2} \tag{2}$$

Where:

- $C_t$  = The surface concentration of adsorbate at time  $t$  ( $\text{mol g}^{-1}$ )
- $k_d$  = The internal diffusion coefficient ( $\text{mol g}^{-1}, \text{min}^{1/2}$ )
- $t$  = The sorption time (min)

**Reaction-based models:** A simple kinetic analysis of  $\text{Co}^{2+}$  and  $\text{Cu}^{2+}$  absorption can be employed using pseudo-first-order equation.

$$\log(C_e - C_t) = \log C_e - \frac{k_1}{2.303} t \quad (3)$$

Where:

$C_e$  = The surface concentration at equilibrium ( $\text{mol g}^{-1}$ )

$C_t$  = The surface concentration at time  $t$  ( $\text{mol g}^{-1}$ )

$k_1$  = The pseudo-first-order rate constant ( $\text{l min}^{-1}$ )

$t$  = The time of reaction (min)

### Adsorption isotherms and equilibrium studies

**Langmuir and freundlich:** Two of the most commonly used isotherm theories have been adopted in this study, namely, the Langmuir and Freundlich equilibrium isotherm theories. The Langmuir equation can be represented by the Eq. 4:

$$q_e = \frac{bQ_{\max}C_e}{1 + bC_e} \quad (4)$$

Where:

$C_e$  = The equilibrium concentration of remaining metal in the solution ( $\text{mmol dm}^{-3}$ )

$q_e$  = The amount of a metal adsorbed per mass unit of sorbent at equilibrium ( $\text{mmol g}^{-1}$ )

$Q_{\max}$  = The amount of solution at complete monolayer coverage ( $\text{mmol g}^{-1}$ )

$b$  ( $\text{dm}^3 \text{mmol}^{-1}$ ) is a constant that relates to the heat of adsorption.

Freundlich isotherm equation is represented as follows:

$$q_e = k_F C_e^n \quad (5)$$

$$\log q_e = \log k_F + n \log C_e \quad (6)$$

## RESULTS

**X-ray Fluorescence (XRF):** The XRF showed a typical mineralogical diffraction pattern of a crystallite with a composition of 70%  $\text{SiO}_2$ , 12%  $\text{Al}_2\text{O}_3$ , 2%  $\text{Na}_2\text{O}$ , 5%  $\text{K}_2\text{O}$ , 2%  $\text{CaO}$  and 2.5%  $\text{Fe}_2\text{O}_3$  and traces (0.2%) of  $\text{TiO}_2$ . The X-Ray Fluorescence (XRF) technique revealed the following composition for the alumino-silicate natural clinoptilolite: 0.2%  $\text{TiO}_2$ , 74%  $\text{SiO}_2$ , 1.3%  $\text{Na}_2\text{O}$ , 1.1%  $\text{MgO}$ , 3.8%  $\text{KO}$ , 1.5%  $\text{Fe}_2\text{O}_3$ , 1.5%  $\text{CaO}$  and 12.4%  $\text{Al}_2\text{O}_3$ .

**FTIR analysis:** The FTIR spectra in Fig. 2 show the functionalities that are present in the various forms of clinoptilolite, natural and activated forms. The wavelength measured ranged between 500 and 4000  $\text{cm}^{-1}$  for the original, 0.04 M and the 0.02 M Hcl-activated forms

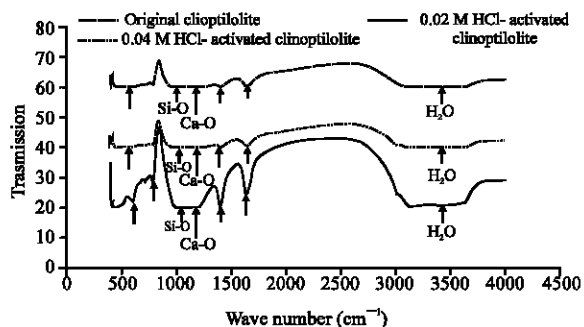


Fig. 2: The FTIR spectra for original and HCl-activated clinoptilolite forms at concentrations of 0.02 and 0.04 M, showing quartz, calcite and  $\text{H}_2\text{O}$  peaks and bands

of clinoptilolite. The distinct stretchings between 300 and 4000  $\text{cm}^{-1}$  are typical of water adsorption (Madejova, 2003). This shows that water adsorption and retention by clinoptilolite is increased by HCl activation at 0.02 M concentration

At the range of 2000 and 1500  $\text{cm}^{-1}$ , the 0.02 M HCl-activated clinoptilolite showed two intensive peaks and yet again the original and the 0.04 M activated forms showed none. This could be as a result of 0.02 M activation washes out the non zeolitic impurities present in the original clinoptilolite as confirmed by XRD, XRF and SEM-EDS. There were peaks observed for all the clinoptilolite forms at 1558  $\text{cm}^{-1}$  which may be due to the bending vibrations of adsorbed water. This is expected since given its porous structure, desiccation of the zeolite at high temperatures 50°C will increase its hydrophilic (water absorption) properties (Ng and Mintova, 2008). The stretching between 1500 and 1000  $\text{cm}^{-1}$  observed indicates the presence of a high content of calcite in the sample as confirmed by SEM-EDS. The strong band at 1341  $\text{cm}^{-1}$  (due to Si-O stretching) is the main characteristic band for quartz (Al-Degs *et al.*, 2003). The peaks observed between 1000 and 600  $\text{cm}^{-1}$  are present in all the forms of clinoptilolite, one characteristic band appears at 836  $\text{cm}^{-1}$  for all the forms. This is the quartz band which is common with zeolites, especially those of the Heulandite family (Al-Degs *et al.*, 2003).

The absorbed water in zeolites is driven off by heating at temperatures greater than 450°C without the structure being decomposed (Mondale, 1995).

In order to assess the thermal stability of the clinoptilolite, thermogravimetric analysis was carried out over a temperature range exceeding 800°C as shown in Fig. 3. In the temperature range from 25-100°C, the weight loss due to desorption of physically absorbed water for a 100% weight is rapid at about 2.5% as it is attributed to

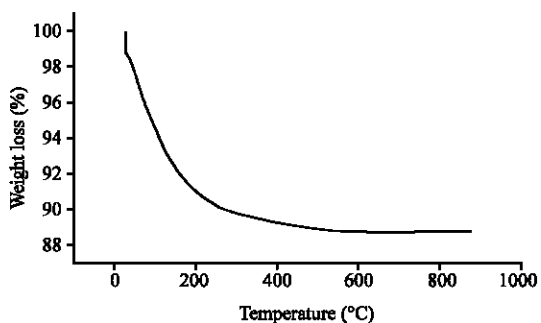


Fig. 3: A typical TGA curve of South African clinoptilolite. Individual points are not showing due to the proximity of points to one another

the loss of loosely bonded water. In the temperature range from 100 to 200°C, the weight loss is about 3% whereas, between 200 and 400°C it is 1%. Between, 400 and 600°C the weight loss was 0.5%. The effective total weight loss when 600°C was reached is 7%. The dehydration rate in the temperature range from 100 to 400°C is similar to that of other zeolites characterized as heulandite type-II (Elaiopoulos *et al.*, 2008). The clinoptilolite was found to be very stable over a wide range of temperatures which is very important since in this study the zeolite was dried at 50°C for 24 h from preliminary studies.

**Adsorption experiments:** The ion exchange kinetics of  $\text{Co}^{2+}$  and  $\text{Cu}^{2+}$  as a function of their concentrations in their respective solutions were studied at room temperature by varying their concentrations with time and keeping all other parameters constant. From the results shown in Fig. 4 and 5, it can be confirmed that the percentage metal removal decreased with an increase in metal concentration in the aqueous solutions.

**Effects of solution concentration on cation removal efficiency:** In general, natural clinoptilolite appeared to remove the metals more efficiently from dilute solutions than from concentrated ones. There was a 56%  $\text{Cu}^{2+}$  removal from the more dilute (0.0020 M)  $\text{CuSO}_4$  solution (Fig. 4).

There was a 46 and 28% removal of  $\text{Cu}^{2+}$  from aqueous  $\text{CuSO}_4$  solutions whose concentrations were 0.0698 M and 0.2000, respectively. On the other hand, there was a 36% removal of  $\text{Co}^{2+}$  from a  $\text{CoSO}_4$  synthetic solution whereas, a 14% removal of  $\text{Co}^{2+}$  from the 0.2000 M  $\text{CoSO}_4$  and a 27% removal of  $\text{Co}^{2+}$  from a 0.0698  $\text{CoSO}_4$  aqueous solution were obtained as shown in Fig. 5.

Percentage removal for  $\text{Cu}^{2+}$  and  $\text{Co}^{2+}$  was observed to decrease with increasing metal concentration in the

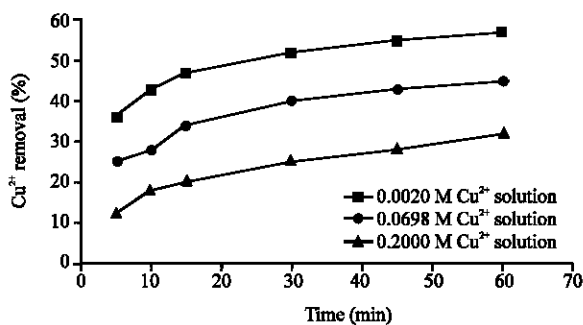


Fig. 4:  $\text{Cu}^{2+}$  removal from 0.0020, 0.0698 and 0.2000 M  $\text{CuSO}_4$  synthetic solutions using original clinoptilolite

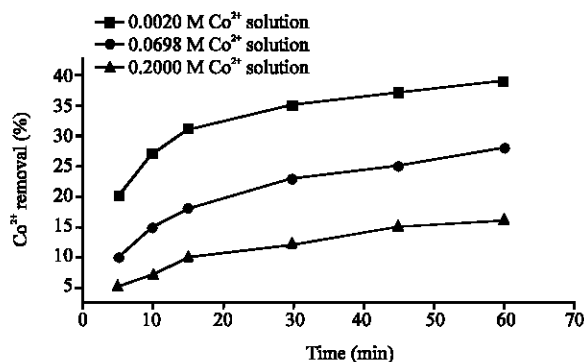


Fig. 5:  $\text{Co}^{2+}$  removal from 0.0020, 0.0698 and 0.2000 M  $\text{CoSO}_4$  synthetic solutions using original clinoptilolite

aqueous solutions. Similar results were obtained with  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Mn}^{2+}$  removal from their aqueous synthetic in a study by Erdem *et al.* (2004).

**Effects of Co/Cu mixing on removal efficiency of  $\text{Co}^{2+}$  and  $\text{Cu}^{2+}$  removal:** The concentration ratios of 1:1 Co:Cu showed the highest removal of  $\text{Co}^{2+}$  (40%) and the least removal of in  $\text{Cu}^{2+}$  (37%) shown in Fig. 6 and 7, respectively.

The highest  $\text{Cu}^{2+}$  removal recorded was 35% and was recorded with a 1:9 Co:Cu ratio. The lowest removal efficiency recorded for  $\text{Co}^{2+}$  was 26% and was recorded with the 9:1 Co:Cu synthetic solution where the  $\text{Co}^{2+}$  concentration was at its highest while  $\text{Cu}^{2+}$  recorded a removal efficiency of 23% with the 1:1 Co:Cu ratio. Another solution where,  $\text{Co}^{2+}$  concentration was higher than that of  $\text{Cu}^{2+}$  (5:1) also recorded only 31% removal.

**Mine water:** From the results in Table 1 it can be deduced that the degree of removal must be dependent upon the complexity of the aqueous solution's matrix since, the

clinoptilolite was observed to be capable of effective removal of both  $\text{Cu}^{2+}$  and  $\text{Co}^{2+}$ . The concentration levels of copper and cobalt ions at the various sites in the sampling zone vary. In site HVH, site A had copper concentration levels exceeding 20 ppm. Since, the Nigel mine is a gold mine one would generally find copper in the soil samples. Since, the sampling was also done during the rainy period, most of the copper had been

washed into the nearby small water table where the sampling was carried out. When considering all the sites where copper and cobalt were found, it can be noted that there was quantitative adsorption of both copper and cobalt, in all cases exceeding 95% removal. Although, there were other ions, such as silver ions present in solution, this did not seem to affect the adsorption capability of the clinoptilolite.

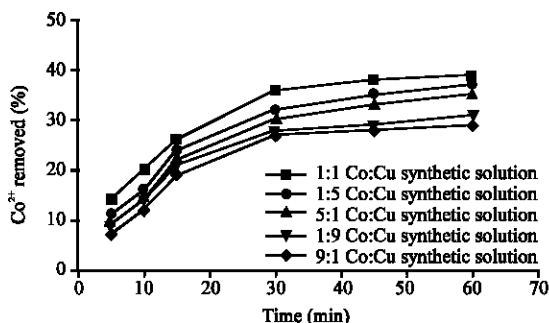


Fig. 6:  $\text{Co}^{2+}$  removal from Co/Cu mixed synthetic solutions of different Co:Cu concentrations using original clinoptilolite

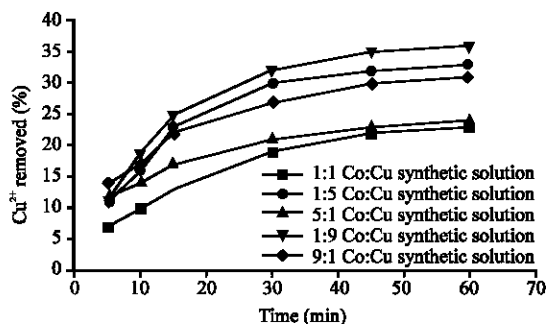


Fig. 7:  $\text{Cu}^{2+}$  removal from Co/Cu mixed synthetic solutions of different Co:Cu concentrations using original clinoptilolite

**Adsorption models of  $\text{Cu}^{2+}$  and  $\text{Co}^{2+}$  onto clinoptilolite:** It can be noted that for  $\text{Cu}^{2+}$  the  $k_F$  values (external diffusion), are much greater than those observed in  $k_d$  values (internal diffusion) in Table 2 and 3 under the same conditions.

This indicates the dominance of the external diffusion model for  $\text{Cu}^{2+}$  adsorption regardless of the concentrations of Co/Cu or Si/Fe in solution were. On the other hand, the  $k_F$  values for  $\text{Co}^{2+}$  adsorption were only lower where Co:Cu was in a 1:1 concentration ratio and were higher than  $k_d$  values in all the other solutions, regardless of the amount of Si/Fe added. This means that the Si/Fe added did not influence the type of diffusion model of the two ions ( $\text{Cu}^{2+}$  and  $\text{Co}^{2+}$ ). Therefore, the external diffusion model was dominant one.

Table 1:  $\text{Co}^{2+}$  and  $\text{Cu}^{2+}$  AAS assay before and after adsorption experiments

Site	Before adsorption experiments		After adsorption experiments	
	Cu	Co	Cu	Co
	----- (ppm) -----			
Nigel river	5	2	1	0
Nigel dam	1	1	0	0
HVH site A	>20	8	2	1
Shaft No 2A	2	2	0	0
B	2	2	0	0
C	4	1	0	0
Piet farm A	6	1	0	0
C	3	0	0	0
D	2	0	0	0
E	6	0	0	0
Artisanal point 169	2	8	0	1

Table 2: Parameters for  $\text{Cu}^{2+}$  and  $\text{Co}^{2+}$  for external ( $K_F$ ) and internal ( $K_d$ ) diffusion models in the synthetic solutions

Conc. ratio (M) of Co:Cu	Sorbent mass (g)	Solution volume (mL)	Impurities Si:Fe	$K_d(\text{Cu})$	$K_d(\text{Co})$	$K_F(\text{Cu})$	$K_F(\text{Co})$
0.07:0.07	25	25	1:1	0.0027	0.0153	0.0077	0.0036
	25	25	1:2	0.0031	0.0145	0.0075	0.0038
	25	25	2:1	0.0023	0.0137	0.0079	0.0040
0.07:0.33	25	25	1:1	0.1217	0.0083	0.0942	0.0645
	25	25	1:2	0.0145	0.0078	0.1123	0.0607
	25	25	2:1	0.0148	0.0055	0.1149	0.0426
0.33:0.07	25	25	1:1	0.0160	0.0092	0.1239	0.0710
	25	25	1:2	0.0153	0.0078	0.1188	0.0607
	25	25	2:1	0.0147	0.0075	0.1136	0.0581
0.07:0.66	25	25	1:1	0.0128	0.0112	0.0994	0.0865
	25	25	1:2	0.0135	0.0108	0.1046	0.0839
	25	25	2:1	0.0138	0.0103	0.1072	0.0800
0.66:0.07	25	25	1:1	0.0128	0.0092	0.0994	0.0710
	25	25	1:2	0.0135	0.0078	0.1046	0.0607
	25	25	2:1	0.0140	0.0075	0.1084	0.0581

Table 3: Parameters for Cu<sup>2+</sup> and Co<sup>2+</sup> for external (K<sub>F</sub>) and internal (K<sub>d</sub>) diffusion models in the mine water samples

Sorbent mass (g)	Mine water volume (mL)	K <sub>d</sub> (Cu)	K <sub>d</sub> (Co)	K <sub>F</sub> (Cu)	K <sub>F</sub> (Co)
25	25	0.0027	0.0153	0.0077	0.0036
25	25	0.0031	0.0145	0.0075	0.0038
25	25	0.0023	0.0137	0.0079	0.0040

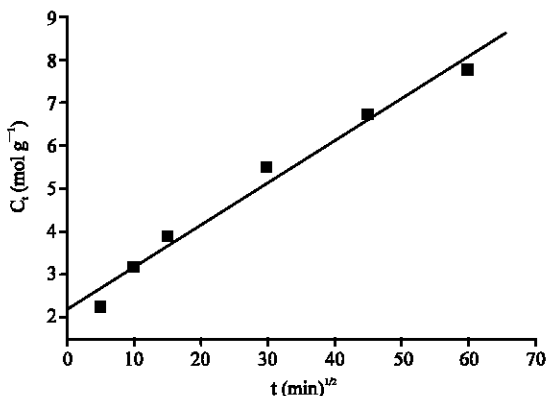


Fig. 8: Plot of Co<sup>2+</sup> internal diffusion model of time against C

Considering, the mine water samples and the sorbent used in Table 3, it can be inferred that Cu<sup>2+</sup> was still adsorbed externally. However, Co<sup>2+</sup> appeared to be mainly adsorbed internally since, the k<sub>F</sub> values for external diffusion were lower than the k<sub>d</sub> values.

In general the external diffusion model k<sub>F</sub> values show good correlation with the sorption data obtained with the synthetic solutions where, high correlation coefficients were obtained, thus indicating that the adsorption of Co<sup>2+</sup> and Cu<sup>2+</sup> was mainly a surface phenomenon that occurs on the external surface of the clinoptilolite. This was further confirmed by a plot of the Co<sup>2+</sup> internal diffusion model of concentration (C) versus time (t). At higher concentrations, the competition for the surface active sites on the clinoptilolite is high and consequently lower sorption rates were obtained for both Cu<sup>2+</sup> and Co<sup>2+</sup>. The linear plot shown in Fig. 8 indicates the dominance of internal diffusion alongside external diffusion since it does not pass through the origin.

**Adsorption isotherms for Co<sup>2+</sup> and Cu<sup>2+</sup>**

**Freundlich isotherms:** Even though, high R<sup>2</sup> values were obtained for Cu<sup>2+</sup> and Co<sup>2+</sup> in Fig. 9 and 10, respectively, the values indicate higher deviations from linearity using the Freundlich isotherm model for describing Co<sup>2+</sup> and Cu<sup>2+</sup> compared to Langmuir models in Fig. 11 and 12.

From the Freundlich isotherm, the K<sub>F</sub> value obtained for Cu<sup>2+</sup> and Co<sup>2+</sup> were 2.534 and 2.7188, respectively (Fig. 13, 14). The R<sup>2</sup> values obtained were Cu<sup>2+</sup> and

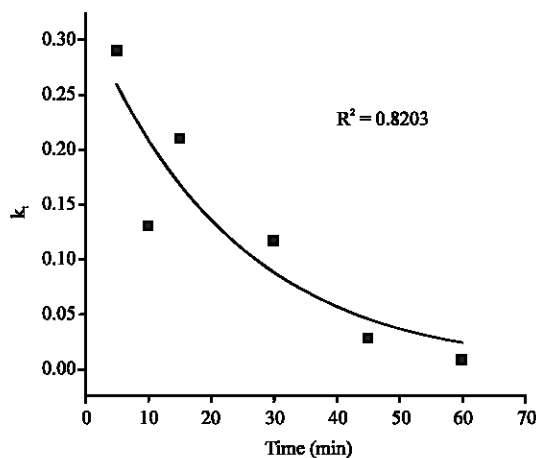


Fig. 9: Graph of Cu<sup>2+</sup> from the Co/Cu mixed solutions shows first order kinetics with a correlation value of R<sup>2</sup> = 0.8203

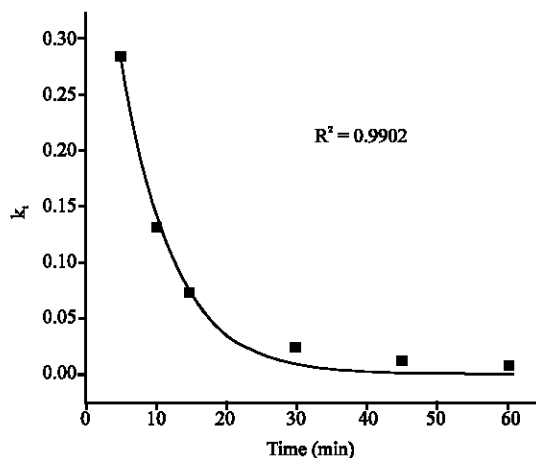


Fig. 10: Graph of Co<sup>2+</sup> from the Co/Cu mixed solutions shows first order kinetics with a correlation value of R<sup>2</sup> = 0.9902. solutions shows first order kinetics with a correlation value of R<sup>2</sup> = 0.8203

Co<sup>2+</sup> 0.9445 and 0.9006, respectively while, the 1/n (intercept) values obtained for the two ions were 0.4406 and 0.7185.

From the results of R<sup>2</sup> (0.9445 for Cu<sup>2+</sup> and 0.9006 for Co<sup>2+</sup>) obtained the accession that Cu<sup>2+</sup> was easier to remove from these solutions can be made.

**Langmuir isotherms:** The Langmuir isotherms were observed to fit the ion-exchange data of Co<sup>2+</sup> and Cu<sup>2+</sup> more than the Freundlich did. The Langmuir gave higher correlation values than did the Freundlich isotherms and from these results it can be deduced that the ion-exchange of Co<sup>2+</sup> was more efficient than that of Cu<sup>2+</sup>.



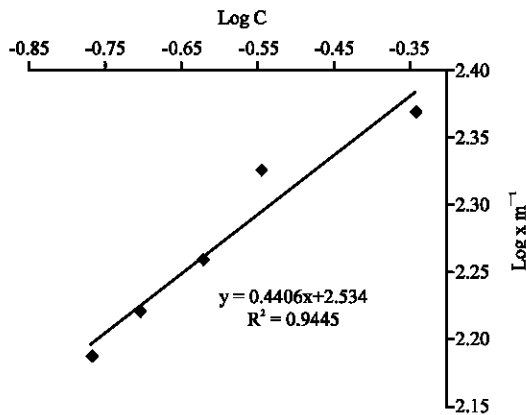


Fig. 11: Freundlich plot of Cu<sup>2+</sup> obtained from the non-mixed solutions a correlation value of  $R^2 = 0.9445$

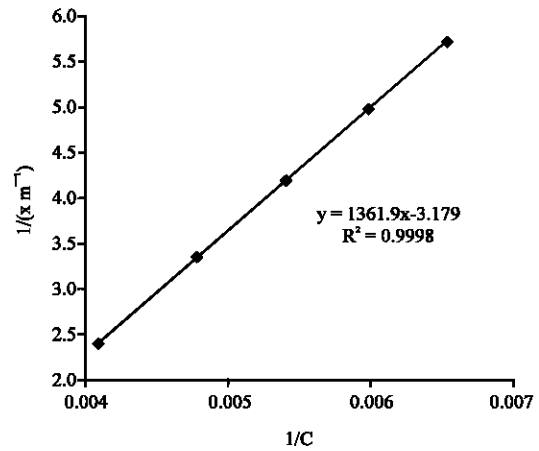


Fig. 14: Langmuir plot of Co<sup>2+</sup> obtained from the mine water with a correlation value of  $R^2 = 0.9998$

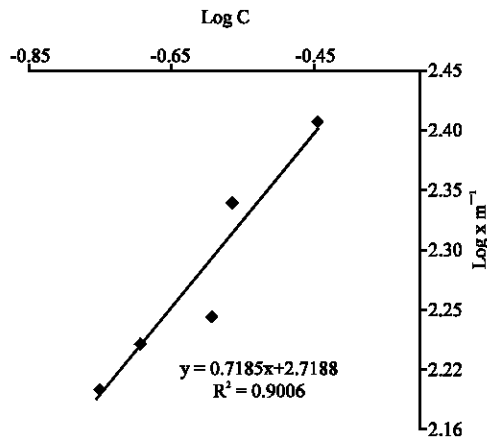


Fig. 12: Freundlich plot of Co<sup>2+</sup> obtained from the non-mixed solutions a correlation value of  $R^2 = 0.9006$

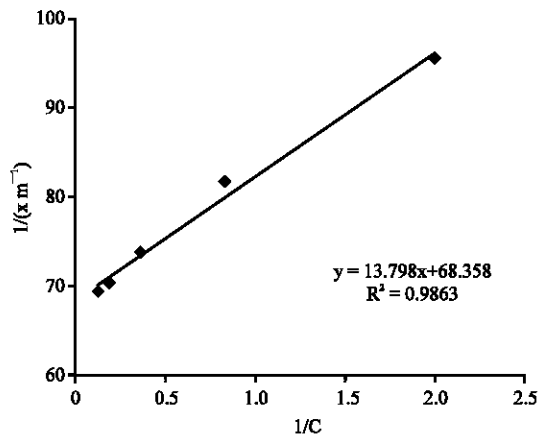


Fig. 13: Langmuir plot of Cu<sup>2+</sup> obtained from the mixed Co/Cu solutions with a correlation value of  $R^2 = 0.9863$

## DISCUSSION

### FTIR analysis

#### Effects of solution concentration on removal efficiency:

Athanasiadis *et al.* (2004) reported that high metal solution concentrations showed low ion exchange rates compared to solutions of lower concentration. These researchers concluded that this was due to the high concentration of the counter ion in the solution which was generally true for all the analytes. It is possible that more of the smaller size range of particles was present in this batch. Small particle size increases exchange efficiency due to surface area to volume ratio. The cation being exchanged moves a shorter distance in smaller grains than in larger ones thus speeding up the exchange rate. In Fig. 4 and 5 the percentage removal for Cu<sup>2+</sup> and Co<sup>2+</sup> was observed to decrease with increasing metal concentration in the non-mixed aqueous solutions.

The results in Fig. 4 and 5 indicate that energetically less favourable sites become involved with increasing metal concentrations in the aqueous solution (Zachara *et al.*, 1991). Heavy metal uptake is attributed to different mechanisms of ion-exchange process as well as to the adsorption process. The phenomena of ion-exchange is also said to be dependent on the concentration of the aqueous solutions (Zachara *et al.*, 1991). This is such that the more dilute solutions upload mainly by means of ion-exchange which proves to be a fast process, while the more concentrated solutions also use precipitation to upload, which is a slow process (Papadopoulos and Rowell, 1988). During the ion-exchange process, metal ions migrate not only through the pores of the zeolite mass, but also through channels of the zeolite lattice structure and

replace exchangeable cations accessible to them in the clinoptilolite (McBride, 1980). In concentrated solutions, the cation diffusion process is faster through the pores and is slowed down when the ions move through the smaller diameter channels of the exchanger such that the ion-exchange process takes place at a slower pace (McBride, 1980).

The ease of removal observed with the mixed 1:1 Co:Cu solutions must have been due to that the  $\text{Cu}^{2+}$  formed more bulky and stable complexes with the water molecules in solution which probably then resulted in the availability of  $\text{Co}^{2+}$  ions for sorption. The discrepancies observed in the metal removal efficiencies could be due to the original zeolite's heterogeneous structure since there was no modification applied to it. It is also possible that the clinoptilolite surface and pore openings were partially covered by dust produced during the crushing of the clinoptilolite, resulting in pore clogging which led to smaller ion-exchange capacity and slower ion-exchange rates (Inglezakis *et al.*, 1999). Pore clogging by fine particles, which can be reduced by chemical conditioning of the zeolite, has also been reported as a possible cause of smaller ion exchange capacity and slower exchange rates (Mondale *et al.*, 1995). According to literature, pore clogging can affect the ion-exchange capacity by up to 15%. The distribution of the minerals in original zeolite is non homo-ionic and is very likely to cause discrepancies in metal loading. This could also mean that the locations of exchangeable ions are not ideally distributed within the zeolite, such that there are delays in the ion exchange process due to exchangeable ions being hindered with other ions not partaking in the ion-exchange process. The rate at which these metal ions were being up-loaded into the clinoptilolite was such that the more dilute solutions were at a high rate than in the more concentrated ones. Such was the case because more efficient utilization of the adsorption capability of the ion-exchanger is expected due to a greater driving force by a higher concentration gradient pressure (Erdem *et al.*, 2004).

**Possible adsorption mechanisms of  $\text{Co}^{2+}$  and  $\text{Cu}^{2+}$ :** Different physico-chemical reactions such as dissolution, ion-exchange, adsorption and possibly surface precipitation are known to prevail in a heavy metal solution-clinoptilolite interaction. Investigation of this interaction is important for their application in environmental chemistry such as in heavy metal removal from industrial waste waters and in acid mine drainage remediation. Surface ion-exchange is one of the processes in a heavy metal solution-clinoptilolite interaction. The forces involved in this process range

from weak vander waals forces and electrostatic outer-sphere complexes, such as strong chemical interactions. Chemical interactions can include inner-sphere complex formation that involves a ligand exchange mechanism, covalent bonding, hydrogen bridges and steric effects (Doula and Ioanoo, 2003). During the initial stages of surface ion-exchange, outer-sphere complexes form on the external surface sites of the sorbent. The outer-sphere complex formation process involves ion-exchange reactions between metal ions in the aqueous solution and surface counterbalance cations on the ion-exchanger. As the metal concentration increases on the surface of the ion-exchanger, metal ions are forced into the internal surface sites, thus, forming inner-sphere complexes that form during internal ion-exchange.

An increase in the amount of metal cations absorbed on the surface of the clinoptilolite to a higher surface coverage during adsorption causes the metal ions to exchange on the clinoptilolite surface. At low surface coverage, complex formation tends to dominate. As surface coverage increases the formation of distinct aggregates on the absorbent's surface occurs and as surface loading increases surface ion exchange become the dominant mechanism. Surface ion-exchange is a method of metal loading common with more concentrated solutions than dilute ones. The predominant mechanism of sorption of metal ions from dilute solutions is internal ion-exchange, although both mechanisms occur simultaneously at different rates in the same solution (Scheidegger and Sparks, 1996).

Dissolution also takes place in a heavy metal solution-clinoptilolite interaction. The complexes formed on the zeolite's surface sites can cause dissolution of  $\text{Al}^{3+}$  and/or  $\text{Si}^{4+}$ . The tendency of a sorbent's surface to dissolve depends on the type of surface species that make up an inner-sphere complex. A highly electronegative ligand such as a halide e.g.,  $\text{Cl}^-$  ions facilitates the detachment of a central metal ion and enhances dissolution. This is due to the electron density shift from the ligands towards the central metal ion at the surface (Doula and Ioanoo, 2003). This excess of electron density brings the negative charge into the coordination sphere of the Lewis acid centre and simultaneously enhances the surface protonation and can labilize the critical Si-O lattice bonds of the clinoptilolite, thus causing detachment of the central metal ion. This may then result in the total collapse of the zeolite structure (Scheidegger and Sparks, 1996).

Calcite is a principal component of the clinoptilolite as confirmed by FTIR in this study and therefore the

cation exchange capacity may be due to the targeted metal ions affinity to the surface of calcite (Bolto and Pawlowski, 1987). The ionic radius of  $M^{2+}$  cations and metals of ionic radius close to that of  $Ca^{2+}$  display stronger displacement than other metals during ion-exchange. This can provide a reasonable explanation for the higher adsorption capacity of  $Co^{2+}$  compared to  $Cu^{2+}$ . During ion-exchange, the cations saturate natural zeolites. This means that the metal ions exhaust all available possible sites of the zeolite and further adsorption can only be possible at new clinoptilolite surfaces. The cation exchange capacities of  $Co^{2+}$  and  $Cu^{2+}$  indicate the selectivity to be in favour of  $Co^{2+}$  over  $Cu^{2+}$  in the Co/Cu synthetic solutions. These metal cations are present in solution as hexa-aqua ( $Cu^{2+}$ ) and tetra-aqua ( $Co^{2+}$ ) complexes with six and four, respectively, surrounding water molecules in their non-mixed solutions (Jama and Yucel, 1990). However, in multi-component systems, such as the Co/Cu solutions, the complexes formed by these ions may not be as simple as the ones in the non-mixed cation solutions. They may be attached to other cations which may also be attached to others leading to even bulkier complexes.

The occupation of active sites of clinoptilolite during ion-exchange is a competitive process whereby one cation is more favoured over the other. This could be attributed to cation-cation interactions as well as to the water molecules that surround the cations in solution. Inglezakis *et al.* (2005) documented that selectivity of a zeolite for one ion over the other in a matrix is a result of physico-chemical and stereo-chemical factors which are hydrated radii, hydration enthalpy of the cation and the space requirements in the micropores of clinoptilolite in connection with the incoming ions. The rate of  $Cu^{2+}$  and  $Co^{2+}$  ions-exchange on clinoptilolite was determined as a function of the initial metal concentrations. The plots show that the kinetics of adsorption of  $Cu^{2+}$  and  $Co^{2+}$  consisted of two phases; an initial rapid phase where the adsorption process was fast and contributed significantly to equilibrium uptake and a slower second phase with a relatively small contribution to the total metal adsorption. The first phase is the instantaneous adsorption stage or external surface ion-exchange. The second phase is the gradual adsorption stage is the intra-particle diffusion which controls the adsorption rate and finally the metal uptake reaches equilibrium.

**Kinetic models:** The kinetic models outlined in Eq. 1-3 were applied to the kinetic data of  $Co^{2+}$  and  $Cu^{2+}$  adsorption by the clinoptilolite forms. The internal diffusion theorem states that external diffusion is the dominant adsorption mechanism if the straight line

obtained from the equation does not pass through the origin. This was true with the plot obtained for the  $Co^{2+}$  plot. The plot indicates the dominance of external diffusion at the earlier stages of interaction. Due to the heterogeneous nature of the adsorbent and the presence of active materials, i.e., calcite and zeolite minerals, the molecular movement of  $Co^{2+}$  and  $Cu^{2+}$  deep inside the sorbent particles is likely to be restricted though not totally excluded.

The external and internal diffusion models confirmed that external ion-exchange occurring mainly on the surface of the clinoptilolite. The  $K_F$  values were observed to increase with a decrease in the initial cation concentration, which can be attributed to the lower competition among the cationic species for the sorption surface sites at lower concentration as observed with the mine water samples in Table 3 (Lee *et al.*, 1999; Ho *et al.*, 2000). At the early stages of adsorption, the process appears to be largely controlled by external diffusion mechanism. This serves to confirm that external ion-exchange was the controlling mechanism during  $Co^{2+}$  and  $Cu^{2+}$  adsorption. The correlation values of  $Co^{2+}$  and  $Cu^{2+}$  in the first order kinetics plot (Fig. 9, 10) show that the high correlation of this model to the sorption data is an indication that Eq. 3 gives an accurate estimation for the equilibrium capacity for the two cations. The adsorption mechanism was confirmed to follow first order kinetics.

**Adsorption isotherms:**  $K_F$  and  $n$  are the Freundlich parameters that show the favorability of the type of adsorption of a particular ion under study (Frimmel and Huber, 1996). If the slope is high and the value of  $n$  is high, it is a clear indication that adsorption intensity is favorable over a wide range of the concentrations studied, while a steep slope where the value of  $n$  is low is an indication that the adsorption intensity is favorable at high concentrations but much less at dilute concentrations (Mohan *et al.*, 2006). A high value of the intercept  $K_F$ , indicates high adsorption potential (Mohan and Singh, 2000; Hasany *et al.*, 2002). In this study, the  $K_F$  values obtained were quite low and this indicates a low adsorption potential and the adsorption potential of the clinoptilolite over the recorded time was indeed low. The  $1/n$  values for the systems in this study fall in the range of  $1/n < 1$  (0.4406 for  $Cu^{2+}$  and 0.7185), which indicates minimal metal ion adsorption as confirmed by the percentages removed by the clinoptilolite. A lower description for  $Cu^{2+}$  adsorption data was evident ( $R^2 = 0.9006$ ) according to the  $b$  mol  $g^{-1}$  parameter. Using the Langmuir model, the maximum adsorption capacity for the metals can be estimated as  $Co^{2+} > Cu^{2+}$  from the Co/Cu mixed solutions.

## CONCLUSIONS

The natural clinoptilolite investigated in this study is an effective sorbent for removing  $\text{Cu}^{2+}$  and  $\text{Co}^{2+}$  ions from aqueous solution. The natural sorbent is especially suited to retaining  $\text{Co}^{2+}$ , as  $\text{Co}^{2+}$  was found to be more mobile than  $\text{Cu}^{2+}$ . It was also found that mixing the cations in solution greatly influences metal removal efficiency and this largely depended on the dissolved ratios of these metals. The adsorption data proved that sorption is faster in dilute solutions than in concentrated solutions. It was also found that the main mechanism of adsorption is ion-exchange. Kinetic data showed good correlation to a pseudo-first order and external diffusion models which indicated that sorption of  $\text{Co}^{2+}$  and  $\text{Cu}^{2+}$  occurred on the external surface of the sorbent with internal diffusion being less significant in the experimental systems investigated. The Langmuir equation fitted the kinetic data better than the Freundlich equation and it also indicated that  $\text{Co}^{2+}$  was adsorbed much faster than  $\text{Cu}^{2+}$ . This implies that the ion-exchange process occurred more on the surface of the clinoptilolite than it did in its inner sites.

## REFERENCES

- Al-Degs, Y., M. Tutunji and H. Baker, 2003. Isothermal and kinetic adsorption behaviour of  $\text{Pb}^{2+}$  ions on natural silicate minerals. *Clay Miner.*, 38: 501-509.
- Al-Degs, Y.S., M.I. El-Barghouthi, A.A. Issa, M.A. Khraisheh and G.M. Walkert, 2006. Sorption of Zn(II), Pb(II) and Co(II) using natural sorbents: Equilibrium kinetics and studies. *Water Res.*, 40: 2645-2658.
- Athanasiadis, K., B. Helmreich, C. Peter, R. Hilliges and P.A. Wilderer, 2004. On-site treatment of runoff from roofs and prior to infiltration. *Water Environ. Manage. Ser.*, pp: 61-68.
- Bailey, S.E., T.J. Olin, R.M. Brica and D.D. Adrin, 1999. A review of the potential low cost sorbents for heavy metals. *Water Res.*, 33: 2469-2479.
- Bolto, B.A. and L. Pawlowski, 1987. *Waste Water Treatment by Ion Exchange*. E. and F.N.Spon, London, UK.
- Doula, M.K. and A. Ioanou, 2003. The effect of electrolyte anion on Cu adsorption-desorption by clinoptilolite. *Microporous Mesoporous Mater.*, 58: 115-130.
- Dyer, H.E. and R.P. Townsend, 1981. The plotting and interpretation of ion-exchange isotherms in zeolite systems. *Separation Sci. Technol.*, 16: 173-183.
- El-Kamash, A.M., 2008. Evaluation of zeolite A for the sorptive removal of  $\text{Cs}^+$  and  $\text{Sr}^{2+}$  ions from aqueous solutions using batch and fixed bed column operations. *J. Hazard. Mater.*, 151: 432-445.
- Elaiopoulos, K., T.H. Perraki and E. Grigoropoulou, 2008. Mineralogical study and porosimetry measurements of zeolites from Scaloma area, Thrace, Greece. *Microporous Mesoporous Mater.*, 112: 441-449.
- Erdem, E., N. Karapinar and R. Donat, 2004. The removal of heavy metal cations by natural zeolites. *J. Colloid Interface Sci.*, 280: 309-314.
- Frimmel, F.H. and L. Huber, 1996. Influence of humic substances on the adsorption of heavy metals on defined mineral phases. *Environ. Int.*, 22: 507-517.
- Garcia-Sanchez, A. and E. Alvarez-Ayuso, 2002. Sorption of Zn, Cd and Cr on calcite: Application to purification of industrial wastewaters. *Min. Eng.*, 15: 539-547.
- Hasany, S.M., M.M. Saeed and M. Ahmed, 2002. Sorption mechanism of  $\text{Cs}^+$ ,  $\text{Co}^{2+}$  and  $\text{Eu}^{3+}$  ions onto EGIB sorbent. *J. Radioanal. Nucl. Chem.*, 252: 477-484.
- Ho, Y.S., J.C.Y. Ng and G. McKay, 2000. Kinetics of pollutant sorption by biosorbents: Review. *Separ. Purif. Methods*, 29: 189-232.
- Inglezakis, V.J., N.A. Diamandis, M.D. Loizidou and H.P. Grigoropoulou, 1999. Effect of pore clogging on kinetics of lead uptake by clinoptilolite. *J. Colloid Interface Sci.*, 215: 54-57.
- Inglezakis, V.J., A.A. Zorpas, M.D. Loizidou and H.P. Grigoropoulou, 2005. The effect of competitive cations and anions on ion exchange of heavy metals. *Separation Purificat. Technol.*, 46: 202-207.
- Jama, M.A. and H. Yucel, 1990. Equilibrium studies of sodium-ammonium, potassium-ammonium and calcium-ammonium on clinoptilolite zeolite. *Separation Sci. Technol.*, 24: 1393-1416.
- Kuronen, M., M. Weller, R. Townsend and R. Harjula, 2006. Ion exchange selectivity and reactive and functional polymers. *React. Funct. Polym.*, 66: 1350-1361.
- Lee, C.K., K.S. Low and S.L. Chew, 1999. Removal of anionic dyes by water hyacinth roots. *Adv. Environ. Res.*, 3: 343-351.
- Madejova, J., 2003. FTIR techniques in clay mineral studies. *Vib. Spectrosc.*, 31: 1-10.
- McBride, M.B., 1980. Chemisorption of  $\text{Cd}^{2+}$  on calcite surfaces. *Soil Sci. Soc. Am. J.*, 44: 26-28.
- Mohan, D. and K.P. Singh, 2000. Removal of Cu(II), Pb(II) and Ni(II) by adsorption onto activated carbon cloths. *Water Res.*, 36: 2304-2318.

- Mohan, D., K.P. Singh and V.K. Singh, 2006. Trivalent chromium removal from wastewater using low cost activated carbon derived from agricultural waste material and activated carbon fabric cloth. *J. Hazard. Mater.*, 135: 280-295.
- Mondale, K.D., R.M. Carland and F.F. Alpan, 1995. The Comparative ion exchange capacities of natural sedimentary and synthetic zeolites. *Minerals Eng.*, 8: 535-548.
- Ng, E.P. and S. Mintova, 2008. Nanoporous materials with enhanced hydrophilicity and high water sorption capacity. *Microporous Mesoporous Mater.*, 114: 1-26.
- Nyembe, D.W., B.B. Mamba and A.F. Mulaba-Bafubiandi, 2009. Removal of copper and cobalt from aqueous solutions using natural clinoptilolite. *Water SA.*, 35: 307-314.
- Papadopoulos, P., D.L. Rowell, 1988. The reactions of cadmium with calcium carbonate surfaces. *J. Soil Sci.*, 39: 23-36.
- Rezaei, M. and S.A.R. Movahedi-Naeini, 2009. Kinetics of potassium desorption from the loes soil, soil mixed with zeolite and the clinoptilolite zeolite as influenced by calcium and ammonium. *J. Applied Sci.* 9: 3335-3342.
- Scheidegger, A.M. and D.L. Sparks, 1996. A critical assessment of sorption-desorption mechanisms at the soil mineral/water interface. *Soil Sci.*, 161: 813-831.
- Sheta, A., A. Falatah, M. Al-Sewailem, E. Khaled and A. Sallam, 2003. Sorption characteristics of zinc and iron by natural zeolite and bentonite. *Microporous Mesoporous Mater.*, 61: 127-136.
- Skoog, D.A., F.J. Holler and T.A. Nieman, 1998. *Principles of Instrumental Analysis*. 5th Edn., Saunders College of Publishing, Philadelphia, PA., pp: 13-14.
- Zachara, J.M., C.E. Cowan and C.T. Resch, 1991. Sorption of divalent metals on calcite. *Geochim. Cosmochim. Acta*, 55: 1549-1562.