

Selective Adsorption of Heavy and Light Metals by Natural Zeolites

Elvis Fosso-Kankeu, Magdali Reitz, and Frans Waanders

Abstract—Recent studies have shown that zeolite can be applied through an ion-exchange process to remove metals from solutions. In this paper the potential of two zeolites to perform as sorbents for treatment of multi-metal system is investigated. Parameters such as initial metal concentration, contact time, zeolite type and affinity for heavy versus light metals are taken into consideration. All the samples were prepared and characterized by XRD, XRF and FTIR. Evaluating suitable model for the determination of binding affinity, the results showed that the pseudo second order kinetic model was adequate for such prediction. The binding affinity followed the order $\text{Co} > \text{Cu} > \text{Ca} > \text{Mg}$ which was mainly correlated to the electronegativity of the metals. The FT-IR spectra revealed that the functional group –OH was mostly responsible for the binding of metals on the two zeolites.

The zeolites studied have shown preferential binding of heavy metals and can therefore be used to mitigate the level of such pollutant in multi-metal water system.

Keywords—Attapulgit, clinoptilolite, water pollution, adsorption affinity, heavy and light metals

I. INTRODUCTION

THE pollution of water sources with heavy metals has become an increasing problem worldwide [1]. The government in correlation with environmentalists have therefore effected rigid environmental regulations to which industrial activities must conform [2]. Techniques applied to achieve the removal of heavy metals include; adsorption, reverse osmosis, chemical precipitation, ion-exchange and evaporation. According to Shinzato *et al.*[1] most of these processes are difficult and not cost-effective for developing countries. These processes do not only require high operational and capital costs, but also produces a residual metal sludge which is an additional burden.

Naturally occurring zeolite therefore offers a great potential, as it is a simple ion treatment strategy which addresses local constraints and resources. Adsorption and ion-exchange methods are environmental friendly, sustainable and South Africa has abundant zeolite reserves in the form of clinoptilolite [3].

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However, the complexity of environmental water solutions which beside heavy metals also contain larger concentrations of light metals, hinders the adsorption process. The presence of light metals in solutions affects negatively the removal of toxic heavy metals by competing for the binding sites on the adsorbents [4]; it is therefore important to identify adsorbents with high affinity for heavy metals of interest in order to improve the remediation process.

The aim of this study is to investigate the adsorption affinity of natural zeolites during the removal of heavy (Cu^{2+} and Co^{2+}) and light metals (Mg^{2+} and Ca^{2+}) from solutions.

II. METHODOLOGY

A. Characterization of adsorbents

Natural Clinoptilolite and Attapulgit both considered as zeolites, were obtained from the West Rand and North West of South Africa, respectively. The zeolites were grinded to $-75\mu\text{m}$ prior to experimentation. The zeolite's mineralogical composition was determined by XRD (X-ray diffraction); the diffractometer used was the Philips model X'Pert pro MPD, at a power of 1.6 kW used at 40 kV; Programmable divergence and anti-scatter slits; primary Soller slits: 0.04 Rad; 2θ range: 4-79.98; step size: 0.017° . The XRF (x-ray fluorescence) was used to identify the elements in the zeolites; it was performed on the MagiX PRO & SuperQ Version 4 (Panalytical, Netherland); a rhodium(Rh) anode was used in the X-ray tube and operated at 50 kV and current 125 mA; at power level of 4 kW.

The ATR-FTIR (Perkin-Elmer Spectrum 100 spectrometer) to ascertain the different functional groups of the clay in the spectral range of $4000-400\text{ cm}^{-1}$ with a resolution of 4 cm^{-1} .

B. Preparation of synthetic solutions

Stock solutions of 1000mg/L of metals were prepared by weighing adequate mass of the corresponding salt of Mg, Cu, Co and Ca ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$; CuSO_4 ; $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; $\text{Ca}(\text{NO}_3)_2$) which was dissolved in 100ml of sterile distilled water. The main stock solutions were then diluted into various working solutions (20, 50, 75 and 100 mg/L) as required.

C. Metal removal experiments

This experiment was conducted in a batch system using flasks of 250 ml capacity.

Impact of initial metal concentration

Working solutions of 20, 50, 75 and 100mg/L were diluted from the main stock solutions at an optimum pH of 7 and a mass of 0.3 g of the zeolite added to the solution. All the samples were mixed on orbital shaker at 150 rpm for 2 hours, then centrifuged for 6min at 4000rpm and the residual metals in the supernatant were analysed using the atomic adsorption spectrophotometer (AAS).

Removal of metals at various contact time

To determine the adsorption rate the exposure time of the metals to 0.3 g of zeolite was varied between 30 min, 1 h, 2 h and 3h,. The working solutions contained 75 mg/L of metals and were prepared at pH of 7. The mass transfer was maintained by mixing at a speed of 150 rpm. The mixture was then centrifuged for 6min at 4000rpm and analysed as above.

D. Experimental calculations

The adsorption capacity at equilibrium was calculated by the equation below;

$$q_e = \frac{(C_o - C_e)V}{m}$$

Where: q_e (mg/g) is the adsorption capacity; C_o (mg/L) is the initial metal ion concentration in the solution; C_e (mg/L) is the metal concentration at equilibrium; m (g) is the amount zeolite; V (L) is the solution volume

Langmuir and Freundlich isotherms were used to determine the adsorption affinity of the bentonite clay for the metals;

The linear expression of the Langmuir model is as follow:

$$\frac{C_e}{q_e} = \frac{1}{q_m k} + \frac{C_e}{q_m}$$

where: C_e is the metal's equilibrium constant in (mg/L), q_e is the amount of adsorped metal at equilibrium in (mg/g), q_m is a Langmuir constant associated with the adsorption capacity in (mg/g), k is a Langmuir constant associated with the energy released during adsorption in (L/mg

The linear expression of the Freundlich model is as follow:

$$\log q_e = \log k_f + \frac{1}{n} \log C_e$$

where: q_e is the concentration of the metal at equilibrium in its solid form (mg/g), C_e is the concentration of the metal at equilibrium in the solution (mg/L), k_f is the adsorption capacity measured (mg/g), n is the intensity of adsorption

The pseudo-first order is expressed by the following equation:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$$

where: q_e is the adsorped amount of metal at equilibrium in (mg/g), q_t is the adsorped amount of metal at a certain time t (mg/g), k_1 is the rate constant for the first order adsorption in (min^{-1})

The pseudo-second order can be described by the following equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

where: q_e is the adsorped amount of metal at equilibrium in (mg/g), q_t is the adsorped amount of metal at a certain time t (mg/g), k_2 is the rate constant for the second order adsorption in ($\text{g/mg} \cdot \text{min}^{-1}$)

III. RESULTS AND DISCUSSION

A. Element and phase composition

X-ray fluorescence (XRF) analysis was done to determine the elemental composition; SiO_2 and Al_2O_3 dominate in both zeolites, the binding sites in attapulgite were occupied by K_2O (5.28%) as well as CaO and Fe_2O_3 . The clinoptilolite contained 11.34% Fe_2O_3 and elements such as K_2O , CaO and TiO_2 were also present. The phase composition of the zeolite - attapulgite contained three phases namely SiO_2 , Fe_2B and Ag_2Na ; whereas in the clinoptilolite, the two phases observed included $\text{Ca}_{1.54} \text{MgNa}_{3.28} \text{K}_2$ (clinoptilolite) and $\text{Li}(\text{N}(\text{S} \text{O}_2\text{F})_2)$.

B. Uptake of heavy and light metals from synthetic solutions

(Zeolite 1=attapulgite, Zeolite 2=Clinoptilolite).

Cobalt and copper are some of the main heavy metals present in the industrial wastewater in South Africa; hence they were considered in this study. According to [5], light metals such as Mg^{2+} and Ca^{2+} can also be found at high concentrations in industrial water. Light metals may have an effect on the removal of heavy metals from solutions; the extent of competition for binding sites must therefore be evaluated to predict the behaviour of a given sorbent during treatment of polluted water.

C. Adsorption behaviour of zeolites

The adsorption behaviour of sorbents is generally determined using the parameters derived from the isotherm and kinetic studies.

Adsorption isotherms

The Langmuir and Freundlich adsorption models were applied to study the relationship between the equilibrium ion concentration remaining in the solution (C_e) and the adsorped amount of metal per unit weight of adsorbent (q) used.

Langmuir isotherm model

This isotherm assumes a homogenous binding of the adsorbate at a monolayer surface. The intercept and slope of the plot between C_e and C_e/q are used to calculate the maximum adsorption capacity (q_m mg/g) and Langmuir constant (k). The results in Table 1 show that this model only fit the adsorption of heavy metals on the zeolites as indicated by the values of the coefficient of determination (R^2) which were close to the unit. The maximum adsorption for Cu Z1, Cu Z2 and Co Z1 was 27.54, 35.58 and 555.55 mg/g respectively. All the calculated values of R^2 , q_m and k are listed in Table 1.

Freundlich isotherm model

It is considered in this model that a heterogeneous adsorption process takes place and that the adsorption

capacity mainly relies on the concentration of the adsorbate. This model is applicable for solutions with relatively low adsorbate concentrations [6]. In Table 1 the Freundlich constants such as K_f , $1/n$ and R^2 , which were calculated from the slope and intercept of the plot $\log q_e$ and $\log C_e$, are listed. The R^2 values determined in Table 1 are mostly close to the

unit indicating that the model fit the interpretation of adsorption data, implying that the binding of metals resulted from adsorption at the surface of the zeolites and inter-layer diffusion.

TABLE I
CALCULATED PARAMETERS OF THE ISOTHERM AND KINETIC MODELS

| Model | Parameter | Heavy Metals | | | | Light Metals | | | |
|------------------|----------------------|---------------|---------|----------|---------|--------------|---------|---------|---------|
| | | Cu Z1 | Cu Z2 | Co Z1 | Co Z2 | Ca Z1 | Ca Z2 | Mg Z1 | Mg Z2 |
| Langmuir | q_m | 27.5482 | 35.5872 | 555.5556 | NA | NA | NA | NA | NA |
| | k | 0.0589 | 0.0145 | 0.0009 | NA | NA | NA | NA | NA |
| | R^2 | 0.9787 | 0.9962 | 0.967 | 0.9388 | 0.3295 | 0.8234 | 0.9108 | 0.9646 |
| Freundlich | $1/n$ | 0.3574 | 0.2461 | 0.9679 | 1.5268 | 0.8328 | 0.6244 | 2.7949 | 1.6952 |
| | K_f | 5.0956 | 5.3555 | 0.5609 | 0.0451 | 0.3400 | 0.8705 | 0.0006 | 0.0390 |
| | R^2 | 0.9816 | 0.8828 | 1 | 0.9977 | 0.953 | 0.9593 | 0.9894 | 0.9992 |
| Pseudo 1st order | $k_1 \times 10^{-2}$ | 0.0230 | 0.02303 | 0.0018 | 0.0046 | 0.0092 | NA | -0.0069 | 0.0069 |
| | q | 69.6786 | 73.4006 | 72.7947 | 75.544 | 65.5994 | NA | 32.1366 | 31.4629 |
| | R^2 | 0.9061 | 0.9021 | 0.5837 | 0.7235 | 0.9506 | 0.0203 | 0.5681 | 0.9688 |
| Pseudo 2nd order | $k_2 \times 10^{-3}$ | 5.0567 | 3.6865 | 102.6397 | 21.8845 | 18.3997 | NA | NA | 64.2322 |
| | q | 18.8679 | 16.1290 | 18.5873 | 16.5563 | 10.2145 | 10.2986 | 4.4385 | 5.9241 |
| | R^2 | 0.9923 | 0.9821 | 1 | 0.999 | 0.9984 | 0.9982 | 0.9985 | 0.9999 |

For $1/n < 0$, the adsorption process was thus favourable over the entire range of the concentrations of adsorbates; this was the case for the adsorption of almost all the metals, except in the case of the adsorption of Mg on both zeolites and the adsorption of Co on zeolite 2 which were favourable at larger concentrations ($1/n > 0$).

Kinetic studies

The pseudo first and second order models were applied to study the kinetics for the adsorption. From the intercepts of the plots $\log(q_e - q_t)$ vs. t and t/q vs. t , the values of k_1 and k_2 were calculated respectively and listed in Table 1. All the R^2 values of the pseudo second order rate equation were above 0.98, indicating that the pseudo second order model is most appropriate for the kinetic study.

D. Binding affinity

Adsorption capacity

The adsorption of metals in multi-system is quite complex as the species involved tend to compete for the functional groups at the surface of the sorbent; aiming to remove heavy metals from solutions, it was important to determine which of the heavy or light metals the zeolites will preferably attach to. From the above results, the pseudo second order kinetic model was found suitable for the prediction of the binding affinity. Figures 1a and b show the plots of t/qt vs t for the adsorption of heavy and light metals on zeolite 1 (a) and zeolite 2 (b); it can be observed that there was good fit in the expression of data using this model as confirmed by the

coefficient of determination ($R^2 \sim 1$); the two zeolites had almost similar trend for the adsorption of heavy metals but they behave differently for light metals adsorption.

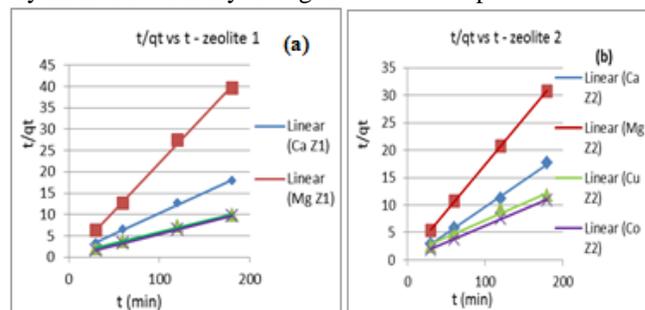


Fig. 1 Pseudo-second order kinetic plots for the adsorption of heavy and light metals on zeolite 1 (a) and zeolite 2 (b)

The adsorption capacity values (q) calculated in Table 1, clearly show that the two zeolites preferably bind the heavy metals than the light metals; for zeolite 2 the adsorption affinity follows the order ($Co > Cu > Ca > Mg$); this order respects the principle of increase affinity with higher electronegativity as stipulated by previous authors [4, 7]. No major difference was observed for the adsorption of cobalt and copper by zeolite 1. It is also observed that zeolite 1 adsorbed more heavy metals than zeolite 2 while there is an opposite trend for light metals adsorption.

Binding groups

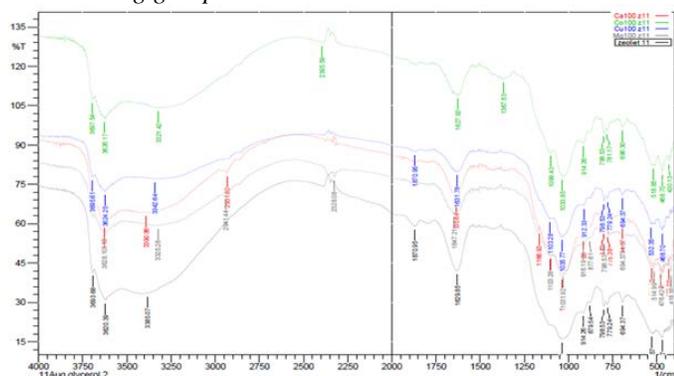


Fig. 2 FT-IR spectra of raw and loaded zeolite 1

In Figure 2, a shift of bands intensity can be observed in the zone 3700-3200, following attachment of metals. The functional groups involved in the binding of metals on zeolite 1 are therefore likely to be alcohol, alkyne and amine.

Figure 3 shows some similarities with regard to the types of binding groups involved during metal adsorption by zeolite 2. A shift was mainly observed in the zone 3640-3610 which correspond to the involvement of the alcohol group

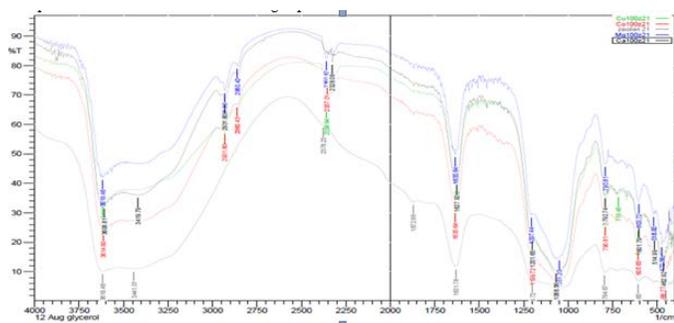


Fig. 3 FT-IR spectra of raw and loaded zeolite 2

It therefore ensues that the binding groups of zeolites 1 and 2 involved in the adsorption of the metals studied are located in the same region hence no major difference in their adsorption capacity; the few differences involved may be ascribed to the poisoning level.

IV. CONCLUSION

The determination of the binding affinity is important for the optimum use of the sorbent. It was observed in this study that the zeolites used have higher affinity for the heavy metals than the light metals; these sorbent may therefore be suitable for the removal of toxic heavy metals from environmental water containing relatively high amount of light metals. Zeolite 1 could be preferred to zeolite 2 since it removes more heavy metals.

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