

Effect of pH on the Zinc Adsorption Pattern and Breakthrough Point in a Zeolite-loaded Column

Elvis Fosso-Kankeu, Leandri Dekker and Hlanganani Tutu

Abstract -Column experiments were conducted to study the adsorptive capacity of the zeolite clinoptilolite for zinc uptake. The effect of pH on the breakthrough point (and hence the ion exchange and saturation of the clinoptilolite surface) was studied. The results indicated that the adsorption capacity of the clinoptilolite is better at neutral pH metal solutions, than more acidic solutions. The best fit kinetic and isotherm models were identified. The adsorption isotherm models that were tested was the Langmuir and Freundlich models. It was found that the Freundlich isotherm model was best fit for the adsorption capacity of clinoptilolite. For kinetic adsorption studies, pseudo-first- and second-order models were tested. It was found that the pseudo-second-order model was the better fit. It was also observed that the acidic conditions resulted in faster breakthrough reducing the exchange capacity of zeolite bed for zinc.

Keywords - Zinc Adsorption Pattern, Breakthrough Point, Zeolite-loaded Column

I. INTRODUCTION

Water as a resource has many uses in the agricultural, domestic, industrial and environmental sectors. In many countries around the world the water demand already exceeds the supply and it is expected that many more areas will experience this imbalance in the near future [1]. In the 20th century the global population tripled, and water use increased six-fold [2]. It is estimated that about 1.2 billion people lack access to affordable and safe water required for domestic use. The lack of access to water has massive impacts on people's well-being [2-17].

Groundwater is considered to be the main source of potable water for one-third of the global population. This water is used for drinking, sanitation and other domestic purposes [18]. Groundwater is defined as the water that is found in aquifers located beneath the earth's surface [19]. Unfortunately, the increase in mining activities have led to the increase of groundwater pollution. Heavy metals that can be found in polluted mining water include Pb^{2+} , Cd^{2+} , Cu^{2+} , Zn^{2+} and Mn^{2+} [20].

Elvis Fosso-Kankeu is with the Water Pollution Monitoring and Remediation Initiatives Research Group in the School of Chemical and Minerals Engineering of the North West University, Bult area-Potchefstroom-South Africa.

Leandri Dekker is with the Water Pollution Monitoring and Remediation Initiatives Research Group in the School of Chemical and Minerals Engineering of the North West University, Bult area-Potchefstroom-South Africa.

Tutu Hlanganani is with the School of Chemistry of the Witwatersrand University, Bult area-Johannesburg, South Africa.

Excessive heavy metal pollution of groundwater is very dangerous to humans as well as the environment. Heavy metals are dangerous mainly due to their tendency to bioaccumulate [21]. In short, bioaccumulation means that there is an increase in the concentration of a chemical or a biological organism over a period of time, compared to the chemical's concentration in that environment. Metals are considered as conservative contaminants that are not readily transformed in a way that removes them from the ecosystem [22]. The magnitude of groundwater contamination is partly depended on the characteristics of the leachate or waste. These characteristics include the leachate volume, concentration, composition, time rate of the release of the contaminate, the size of the area from which the contaminants are derived as well as the density of the leachate [23].

The toxicity of heavy metals does not only depend on their total concentration, but also on their mobility and reactivity with the other components in the ecosystem [24]. Natural zeolites (including clinoptilolite) have the ability to influence the mobility of these heavy metals. This study will review the adsorptive nature of the clinoptilolite and the influence of pH on the adsorption capacity of the clinoptilolite in a column.

II. EXPERIMENTAL

A. Chemicals

All materials were commercial grade and were stored under dry conditions. The clinoptilolite used (VLTR Creek Clinoptilolite 0.8-4mm), was ordered from ChemLite Technologies. The zinc chloride ($ZnCl_2$), sodium hydroxide pellets and hydrochloric acid were ordered from ACE. Stock solutions were made with distilled water.

B. Equipment and instruments

Four clear columns (height: 23cm, diameter: 2.5cm), pH meter (HANNA, HI 8424), ICP-EOS (Agilent Technologies, USA), peristaltic pump, shaking incubator (Labcon), magnetic stirrer, pipette and centrifuge (Hettich Zentrifugen, ROTOFIX 32 A).

C. Preparation of clinoptilolite

To activate the raw clinoptilolite for maximum adsorption 5kg of raw clinoptilolite was weighed and mixed with a 5L of 100g/L salt solution. The salt solution was prepared with normal table salt. The excess liquid was drained from the mixture and the wet clinoptilolite was spread evenly in two baking sheets. It was dried in the oven at 110°C for 24 hours. After the clinoptilolite was removed from the oven and cooled, all the large clumps that formed were broken down by hand to achieve

a similar particle size distribution.

D. Determining the pore volume of the clinoptilolite

The pore volume was determined by pouring a given amount of clinoptilolite in the column into a volumetric cylinder and measuring the volume of the dry clinoptilolite. The volume was recorded and 100 mL of distilled water was added to the volumetric cylinder. The contents of the volumetric cylinder

$$\text{Pore volume} = (\text{volume of dry clinoptilolite} + 100 \text{ ml distilled water})$$

$$- \text{Total volume of contents in cylinder after settling}$$

were left to settle for 15 minutes and the final volume of the contents in the cylinder was recorded. The formula used to determine the pore volume is as follow (1):

(1)

E. Preparing the metal solution

For adsorption experiments, a constant solution of 500ppm zinc chloride was used. First, a batch solution of 1000ppm zinc chloride was made by mixing 2.08g of ZnCl_2 to 1L of distilled water. The solution was continuously stirred using a magnetic stirrer. To make 0.1L of a 500ppm ZnCl_2 solution, 50mL of the 1000ppm ZnCl_2 solution was added to 50mL of distilled water and continuously mixed with the magnetic stirrer.

To make different metal solution concentrations, the bulk solution of 1000ppm ZnCl_2 was still used and different ratios of the bulk solution and distilled water were mixed to create the concentration of choice.

F. Preparing different pH solutions

Three pH solutions were made, namely pH3.5 and 7. The pH solutions were made by adding droplets of sodium hydroxide (to increase the pH) and hydrochloric acid (to decrease the pH) until the desired pH was reached.

G. Column loading for the effect of pH

Three columns were loaded with clinoptilolite to the height of 5cm. 10 pore volumes of each specific pH metal solution was pumped to the column at 5mL/min. Each pore volume of filtrate was collected and sent for ICP-EOS testing- testing for zinc and sodium.

H. Testing the effect of concentration for isotherm models

To determine the effect of concentration, five variations of ZnCl_2 solutions were prepared, namely 20 mg/L, 40 mg/L, 60 mg/L, 80 mg/L and 100 mg/L. All the samples were put into the shaking incubator at 25°C and 160rpm for 90min. Once the samples were removed from the incubator, it was poured into a centrifuge tube and put into the centrifuge at 4000 rpm for 5 minutes to separate the liquids from the solids. The separated liquid for each sample, was sent for ICP testing. The experiments were conducted in triplicates.

I. Testing the effect of time for kinetic models

A batch adsorption system using 250 mL capacity Erlenmeyer flasks were made by filling these flasks with 0.5 g of activated clinoptilolite and 100 mg/L ZnCl_2 . The exposure times that were tested included 15, 30, 45, 60, 75 and 90 minutes. The experiment was conducted in triplicate to improve

the accuracy of the results. All the samples were inserted into the shaking incubator at 25°C and 160 rpm for its allocated time. Once the samples were removed from the incubator, they were poured into centrifuge tubes and centrifuged at 4000 rpm for 5 minutes to separate the liquids from the solids. The separated liquid for each sample was sent for ICP-EOS testing.

J. Adsorption Kinetics

The pseudo first- and second-order models were used to determine the adsorption rate. The pseudo first-order kinetic model is given in equation (2):

$$\log(q_e - q_t) = \log q_e - k_1 \frac{t}{2.303} \quad (2)$$

The pseudo second-order kinetic model is given by equation (3):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

The symbol q_t is the amount of metal adsorbed at time t in (mg/g). The first order rate constant (min^{-1}) is represented by the symbol k_1 and the rate constant in ($\frac{\text{g}}{\text{mg}} / \text{min}$) is represented by the symbol k_2 . t is the time in (min).

K. Adsorption Isotherm

The Langmuir isotherm model assumes monolayer adsorption in a single solute system [10]. The linear form of the Langmuir isotherm model is given by equation (4):

$$\frac{C_e}{q_e} = \frac{1}{k q_m} + \frac{C_e}{q_m} \quad (4)$$

The Freundlich model is usually applied to heterogeneous systems and it is therefore not limited to monolayer adsorptions. The linear form of the Freundlich model is given by equation (5):

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \quad (5)$$

In both models, C_e refers to the concentration of the metal solution after adsorption has taken place in (mg/L). q_e represents the concentration of the metal solution at equilibrium (mg/g). q_m is known as the Langmuir constant that is associated with the adsorption capacity measured in (mg/g). k indicates the Langmuir constant associating to the amount of energy that is released during the adsorption process in (L/mg). Referring to the Freundlich isotherm model, the symbol k_F refers to the Freundlich adsorption capacity parameter in (mg/g). The symbol n indicates the deviation of adsorption to linearity [25].

III. RESULTS AND DISCUSSION

A. Pore volumes

The pore volumes of the variations in height of the clinoptilolite in the column was determined using the method discussed in the methodology. Refer to Table 1 for the results. The pore volumes were determined, to indicate what volume increments of filtrate should be collected with each run.

TABLE I: Pore Volumes

Height of Clinoptilolite (cm)	Pore Volume (mL)
5	15
10	35
15	40
20	51

B. Effect of pH

For metal solutions of pH 3 and 5, it can be observed that the breakthrough point is reached very fast and the amount of sodium in the filtrate decreases with the increase of pore volumes moving through the clinoptilolite (refer to Figure 1). In other words, although more sodium is washed out in the first few pore volumes (for all the pH's) the zinc concentration in the filtrate does not increase, therefore it is an indication that the zinc is binding to the surface of the clinoptilolite exchanging with sodium ions. It is therefore an indication that the ion exchange process does occur on the surface of the clinoptilolite, but the zinc molecules have to compete with the proton molecules of the acidic solutions to bind to the surface of the clinoptilolite. Therefore, the surface of the adsorbent is quickly saturated, and the zinc is adsorbed less under acidic conditions, indicating that more zinc will be present in the filtrate. For the results of the neutral solution, it is clear that the breakthrough point only occurs at the 5th pore volume that moved through the column of clinoptilolite. This is due to the fact that the zinc molecules do not have to compete with protons in the solution when the ion exchange occurs on the surface of the clinoptilolite. Therefore, more zinc molecules are adsorbed to the surface of the adsorbent. This indicates that the retention of the zinc by the clinoptilolite is longer and less zinc is present in the filtrate. Therefore, the adsorption capacity of the clinoptilolite zeolite is more effective with more neutral solutions and less with acidic solutions.

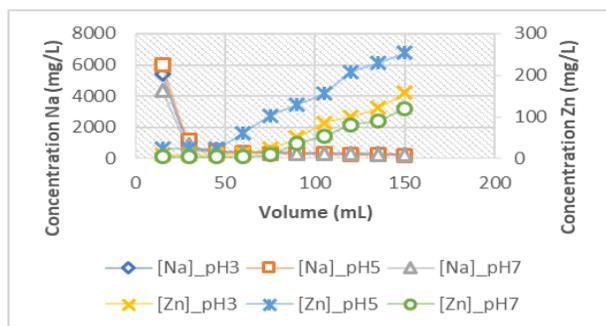


Fig. 1: Effect of pH on [Zn] and [Na] in filtrate

C. Isotherm and kinetic models result

The Langmuir and Freundlich isotherms were considered to better understand the mechanism of adsorption of zinc onto clinoptilolite. The Langmuir isotherm plot for the adsorption of the zinc onto the clinoptilolite is depicted in Figure 2.

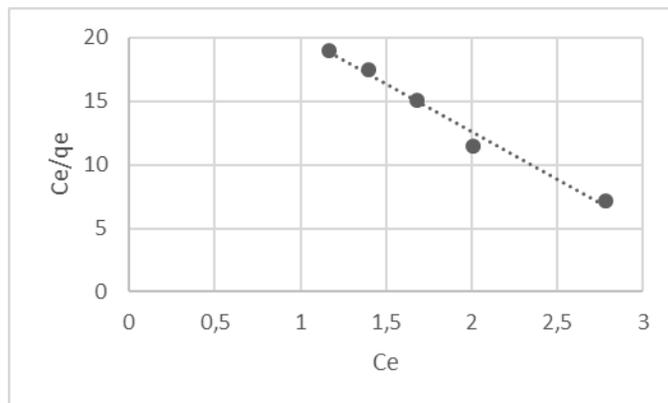


Fig. 2: Langmuir isotherm

The plot was constructed by plotting C_e/q_e vs. C_e . The Freundlich plot was constructed by plotting $\ln(q_e)$ vs. $\ln(C_e)$. Refer to figure 3 for the Freundlich plot.

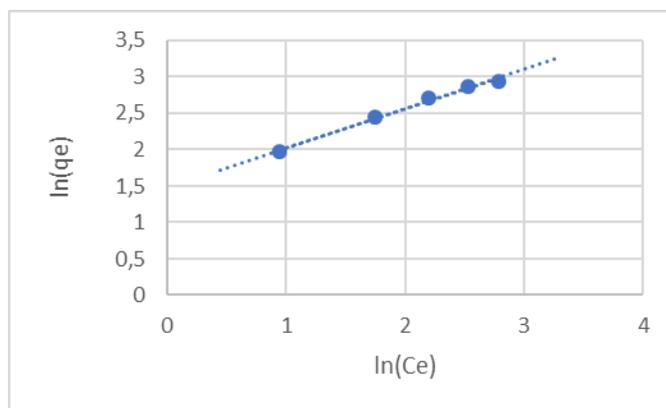


Fig. 3: Freundlich plot

To determine the isotherm parameters (Table 2), the intersects and the slopes of the various plots were calculated. The best isotherm model for the adsorption of zinc onto clinoptilolite was determined by considering the coefficient of determination (R^2 values). From these values, it was concluded that the Freundlich isotherm model is the best fit as the coefficient of determination was closer to unity. This indicated that the adsorption process occurs through a heterogeneous binding to the surface and therefore implying that there are many layers involved in the adsorption.

TABLE II: Langmuir and Freundlich isotherm constants

Adsorbent	Q_m (mg/g)	k (L/mg)	R^2	n	K_f	R^2
Clinoptilolite	-7,643	-0,036	0,98	0,54	0,06	0,99
e			4	6	7	2

A prediction of the rate at which zinc is adsorbed onto the clinoptilolite is very important to have an idea of the success of

the treatment of the heavy metal polluted water. A kinetic study provides this information, as well as the determination of the capacity of the adsorbent. The pseudo-first and pseudo-second-order models are among the kinetic models that are frequently used for predicting the adsorbent's behavior [25]. The values of the kinetic parameters (Table 3 & 4) were calculated by plotting $\ln(q_e - qt)$ vs. t as well as t/qt vs. t . (Figure 4 & 5) represents the pseudo-pseudo and -second-order models, respectively.

TABLE III: Pseudo-first-order parameters

Adsorbent	q_e (exp) (mg/g)	q_e (cal) (mg/g)	k_1 (min^{-1})	R^2
Clinoptilolite	20	3,1248	0.0093	0.9321

TABLE IV: Pseudo-second-order parameters

Adsorbent	q_e (exp) (mg/g)	q_e (cal) (mg/g)	k_2 (g/mg/min)	R^2
Clinoptilolite	20	18,0363	24,3488	0,9996

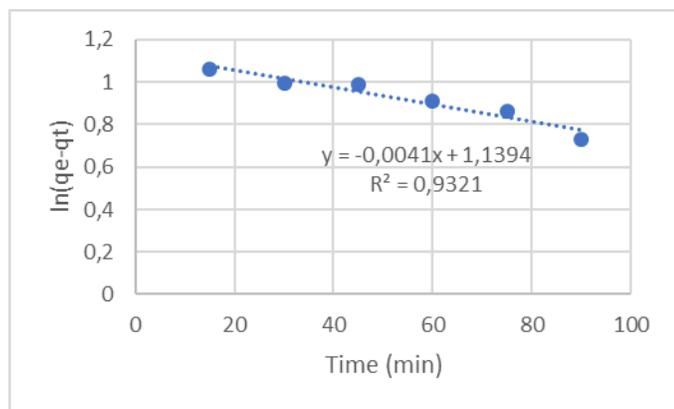


Fig. 4: Pseudo-first-order model

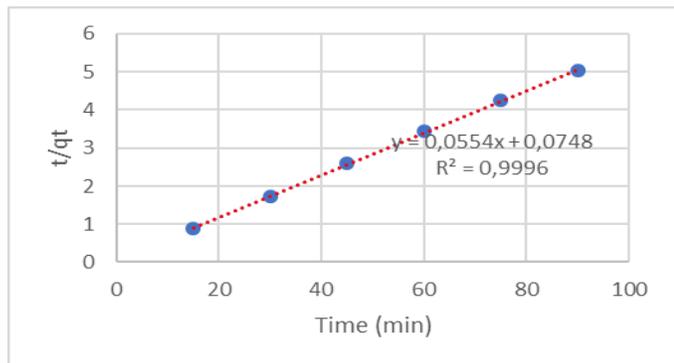


Fig. 5: Pseudo-second-order model

To determine which model is best suited to predict the adsorption behaviour, the value of the coefficient of determination (R^2) was considered. The pseudo-second-order was found to be the better fit, seeing that the coefficient of determination was closer to unity. This indicates that the surface adsorption involving chemisorption, is the rate-limiting step [26-37]. This result therefore indicates that there is a stronger interaction between the surface of the clinoptilolite and the zinc ions.

IV. CONCLUSION

In this study, the adsorptive nature of the clinoptilolite and the influence of pH on the adsorption capacity of the clinoptilolite was investigated. The kinetic studies indicated that the pseudo-second-order was the best fit and therefore concluding that the surface adsorption that involves chemisorption, is the rate-limiting step. The batch isotherm studies indicated that the Freundlich isotherm model could better to explain the adsorption of the zinc molecules onto the clinoptilolite, which implies that the adsorption process occurs onto a heterogeneous surface and therefore, there are many layers involved in the adsorption. It was demonstrated throughout this study that ion exchange does occur on the surface of the clinoptilolite as the zinc ions exchange for the sodium ions which are released in solution. However, a decrease in pH of the metal solution showed the breakthrough point being reached quicker, indicating that the adsorption capacity of the clinoptilolite decreases as the pH decreases. This implies that the zinc in an acidic leachate will not be effectively retained by the soil, which will result in faster contamination of groundwater.

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