Kinetic modelling for heavy metal adsorption using Jordanian low cost natural zeolite (fixed bed column study)

Reyad Al Dwairi, Waid Omar and Sura Al-Harahsheh

ABSTRACT

Low cost Jordanian natural zeolite (ANZ1 and ANZ2) of type phillipsite-chabazite obtained from Jabal al Ataitahat south Jordan were tested experimentally as adsorbent material for the removal of lead (Pb) and lithium (Li) ions from the effluent industrial wastewater streams. The experimental breakthrough curves were obtained from fixed bed experiments and analysed using the Thomas and Yoon and Nelson kinetic models to evaluate the adsorbent performance. The rate constants for the Thomas model for the removal of lead ions using the adsorbents ANZ2 and ANZ1 were 0.201 and 0.2345 mL/min/mg, respectively. The Thomas model adsorption capacity for the removal of lead ions using the adsorbents ANZ2 and ANZ1 were 34.7 and 23.64 mg/g, respectively. The estimated rate constants for the Yoon and Nelson model for the two ANZ2 and ANZ1 were 0.038 and 0.05 min^{-1}, respectively. The kinetic data fitted well to both models. The rate constants for the Thomas model for the removal of lithium ions using the adsorbents ANZ1 and ANZ2 were 0.134 and 0.1005 mL/min/mg, respectively, where the Thomas model adsorption capacity for the removal of lithium ions using the adsorbents ANZ1 and ANZ2 were 18.65 and 21.43 mg/g, respectively.

Key words | adsorption capacity, fixed bed colum, natural zeolite, Nelson model, Thomas model

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INTRODUCTION

Nowadays, contamination of water with heavy metals represents a worldwide concern. Lead and lithium are a type of heavy metal which are not biodegradable and gather in the human body. These types of heavy metals are considered as poisonous and dangerous for human health (Nordberg & Nordberg 2009). They cause various illnesses such as renal damage, excess salivation, muscular cramps, nausea, erythrocyte destruction, diarrhea, hypertension and anaemia. Lead and lithium exist in many aqueous waste streams released from different industries such as batteries, metal coating/plating and automobile factories (Yu 2005).

The removal of heavy metals demands high energy or advanced operational requirements. Thus, choosing a technology for the removal of certain type of heavy metal from wastewater often represents a great challenge. The removal of contaminated heavy metals from aqueous waste streams can be achieved by different technologies such as evaporation, coagulation, precipitation, ion-exchange, electrochemical methods, membrane processes, extraction, biosorption (Babel & Kurniawan 2003; Rashed 2006; Hendricks 2010; Kwon *et al.* 2010; Wang & Peng 2010). Most of these methods have weaknesses such as high capital and operational costs. Conversely, the discarding of the remaining sludge which is concentrated with the toxic heavy metal is a main disadvantage of these processes (Tokimoto *et al.* 2005).

Adsorption in fixed-bed column treatment processes is receiving increasing attention because of their simplicity and ease of operation and handling. Generally, the adsorbent material should meet several requirements: low cost; granular type; high capacity, selectivity, and rate of adsorption; high physical strength (not disintegrating) in water and the ability to be regenerated if required (Zeng 2003). Unconventional adsorbents, such as sand, alumina, silica, and zeolite, have attracted the attention of several investigations and

doi: 10.2166/wrd.2014.063

adsorption characteristics and have been widely investigated for the removal of metal ions (Bailey *et al.* 1999; Babel & Kurniawan 2003). Nowadays, natural zeolite found in many environmental applications gains the attention of many researchers due to its properties such as adsorption, catalysis and ion exchange (Adrian 1948; Benefield *et al.* 1982; Weng & Huang 1994; Erdem *et al.* 2004; Zhang 2006).

Natural zeolites are a group of hydrated aluminum silicates of the alkali or alkaline earth metals (sodium, potassium, magnesium, calcium) characterised by low mining cost, availability, bulk density and high resistance to alteration (Mercer & Ames 1978). Ion exchange capacity and cation selectivity are the most important properties for zeolite as a natural molecular sieve material for wastewater treatment. The zeolite prefers, or is more selective for, certain cations and is less selective for others (Colella 1996). Also natural zeolites are excellent adsorbents (Crini 2006; Rawajfiha *et al.* 2010). Natural zeolites have wide applications including environment, agriculture and the pharmaceutical industry (Al Dwairi & Al-Rawajfeh 2012a, b).

Chang *et al.* (2006) studied the adsorption isotherms of water vapour on cornmeal and the breakthrough curves in a packed-bed apparatus for ethanol dehydration. The effective diffusivity was estimated and used to predict breakthrough curves at other adsorption conditions. Purnomo & Prasetya (2007) studied the adsorption breakthrough curves of Cr (VI) on bagasse fly ash. They measured the breakthrough curve at room temperature using a fixed-bed apparatus. They tried to fit the experimental data to fixed-bed model for breakthrough curve. They concluded that if the value of D_e and k can be obtained, it will allow an easier prediction of the behaviour of breakthrough curves in specific adsorption operating conditions and column dimensions without carrying out any adsorption equilibrium experiments.

Nevenka *et al.* (2010) studied the natural zeolite from Serbia as an adsorbent for nickel ions from aqueous solution. They found that the sorption capacity increased three times by increasing the temperature from 298 to 338 K. The sorption was best described by the Sips isotherm model. This was in accord with observations generally encountered in heavy metal sorption studies (Alyuz & Veli 2009; Hsu 2009; Lu *et al.* 2009). They observed that the sorption involved film diffusion, an intra-particle diffusion, and a chemical cation-exchange between the Na^+ ions of zeolite and the Ni^{2+} ions.

Several investigations were carried out on the adsorption behaviour of Jordanian natural zeolite minerals (chabazite, phillipsite and faujasite) as ion exchangeable material for water and wastewater treatment, including: Ibrahim & Inglethorpe (1996); Al Dwairi (2007, 2009); Hussein (2010); Al-Rawajfeh *et al.* (2011); Al Dwairi & Al-Rawajfeh (2012a, b); Taamneh & Al Dwairi (2013); and Al Dwairi *et al.* (2014). The most important of these studies was Taamneh & Al Dwairi (2013), who investigated the removal efficiency and adsorption isotherms for nickel using zeolites from Jabal AL Aritayn NE Jordan. Isotherms were linearized and applied to the prediction of breakthrough curves. By fitting the experimental results of breakthrough curves to the model of Klinkenberg, the experimental results showed that for a given length, the break point time decreases with increasing zeolite grain size and the breakthrough curve becomes steeper. It is also found that the Klinkenberg model parameters include mass transfer coefficients (k) and effective diffusivities (De) can be estimated independently of the experimental data. The model is able to predict the breakthrough curves accurately.

Fixed bed adsorption using Jordanian natural zeolite minerals might be an attractive industrial application for the removal of heavy metals from wastewater streams containing heavy metals. Prediction of the kinetic parameters from the experimental breakthrough curve for the effluent is the predominant factor for the successful design of a column adsorption process. However, there has been no attempt to correlate the fixed bed experimental behaviour for the adsorption of lead and lithium ions on Jordanian natural zeolite minerals with a kinetic model or even modelling the experimental data.

In this study, important kinetic parameters have been investigated to design a column experiment packed with Jordanian natural zeolite beds for the removal of lead and lithium heavy metals. The experimental data were represented using breakthrough curves for the adsorption of metals and modelled using the Thomas model and Yoon and Nelson kinetic models. A comparison study was carried out for the experimental breakthrough curves and the calculated theoretical curves.

MATERIALS AND METHODS

The used fixed bed adsorbent is natural zeolite (ANZ) (phillipsite-chabazite type) obtained from Jabal Al Ataitah, the geology and characterization of this zeolite was studied by Al Dwairi (2007). Two sizes of AZN, summarized in Table 1, were used in the experiments (ANZ1 and ANZ2). The adsorbents ANZ1 and ANZ2 were from the same source and have the same mineral composition, however they differ in their size. Table 1 shows that the adsorbent ANZ2 is smaller in size (0.3–0.7 mm) whereas the adsorbent ANZ1 is larger (0.7–1.0 mm).

EXPERIMENTAL

An adsorption column apparatus was constructed to perform fixed bed column studies for the adsorption of lead and lithium into zeolite. The column was selected from glass material with the dimensions of 1 cm^2 cross-sectional area (i.e. 1.1 cm internal diameter) and length of 40 cm. The granulated zeolite (ANZ1 or ANZ2) was packed in two columns with a layer of glass wool at the bottom. Bed height of 20 cm was fixed in all experiments. The mass of the adsorbent was constant in all experiments at 20 g. Artificial lead or lithium heavy metal solutions prepared with initial ion (lead or lithium) concentration of 200 mg/L which was introduced into the column using the peristaltic pump (Heidolph 6201). A constant flow rate being delivered to the column of 6.7 mL/min was used in all tests. The adsorption study was performed at room temperature 22–25 °C and initial pH of 6.7. The effluent samples were collected at specified intervals and analysed for the residual ion concentration using an atomic adsorption spectrophotometer. Column studies were terminated when the column reached exhaustion. The experiments were conducted under constant conditions and the only variables to be studied are the adsorbates (lead or lithium)/adsorbent material (ANZ1 or ANZ2).

Table 1 | The size and mineral content of the used zeolites (modified by Al Dwairi 2007)

Zeolite type	Size (mm)	Mineral content %	Bed length (cm)
ANZ1	1–0.750	phillipsite-chabazite 50–60	20
ANZ2	0.750–0.300	phillipsite-chabazite 60–70	20

RESULTS AND DISCUSSION

Adsorption column performance

The main target is to evaluate the column performance for the adsorption of the heavy metals (lead and lithium) using the two natural adsorbents which vary only in the size of particles (ANZ1 and ANZ2). The column performance was studied by measuring breakthrough curves under constant conditions (initial pH 6.7; initial concentration 200 mg/L (ppm); flow rate 6.7 mL/min; mass of adsorbent 20 g; bed height 20 cm). The measured experimental breakthrough curve for the adsorption of lead ions on ANZ1, lead ions on ANZ2, lithium ions on ANZ1 and lithium ions on ANZ2 are presented in Figure 1 where the ratio of the effluent concentration (C_e) to the feed concentration (C_0) is plotted against time. It is obvious that the column performance for the adsorption of lead ions on ANZ2 is much better than using the adsorbent ANZ1. It is observed that the breakthrough occurred faster in the case of ANZ1 and the slope of the breakthrough curve is almost the same for both adsorbents (ANZ1 and ANZ2). This can be explained by the fact that more adsorption sites are provided by

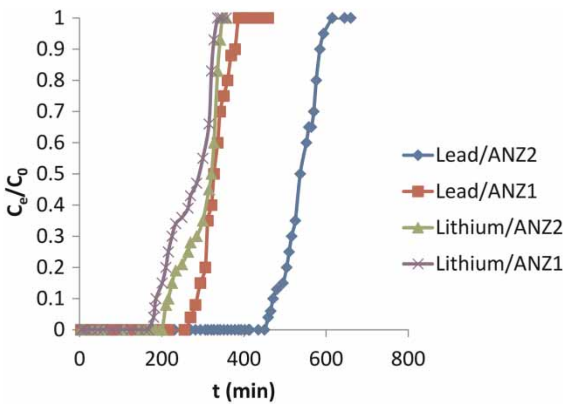

Figure 1 | The measured breakthrough curves for the fixed bed adsorption of the different adsorbate/adsorbent materials.

ANZ2 for the adsorption of lead ions. The breakthrough curves in Figure 1 indicate that in the case of the adsorption of lithium ion on ANZ1, the breakthrough occurred earlier using the adsorbent ANZ1. This means that ANZ2 provides more adsorption sites for lithium ions.

It is clear from the breakthrough curves for ANZ1 that the breakthrough time is faster in the case of the adsorption lithium ions than lead ions and the slope of the breakthrough curve is steeper in the case of lithium ions. In the case of the adsorbent ANZ2, the breakthrough time is much faster in the case of the adsorption of lithium ions than lead ions and the slope is much steeper in the case of the adsorption of lithium ions. This means that ANZ2 has more adsorption capacity to lead ions than lithium ions.

It is clear from the measured breakthrough curves that the consequence of changing particle size during the fixed-bed experiments had a significant consequence on adsorption. The smaller size adsorbent ANZ2 (0.3–0.7 mm) exhibits a better performance than the larger size adsorbent ANZ1 (0.7–1.0 mm). It is clear that increasing the size of adsorbent particles diminishes bed capacities and thus reduces breakthrough time. The diffusion path is shorter for smaller particles, and therefore the adsorbate will be more quickly adsorbed onto the active sites of the zeolite particles. Moreover, smaller particle have larger total external surface area per volume.

The particle size has an important influence on the flow through the column. The smaller size particles lead to greater hydraulic resistance. This significantly influences the residence time of the solute in the column, which can be longer in the case of smaller particles. Therefore, a higher probability for adsorption equilibrium is achieved in the case of the smaller size particles, whereas in the case of larger size particles, the solution is more likely to leave the column before equilibrium is reached.

Analysis using the Thomas kinetic model

The analysis of the breakthrough curves presented in Figure 1 was performed using the Thomas kinetic model. The Thomas model is also referred to as the bed-depth-service-time model. The analysis of experimental breakthrough curves was implemented by many authors to determine the kinetic parameters using the Thomas kinetic model (Baek *et al.* 2007; Sivakumar & Palanisamy 2009). The linearized form of the Thomas model is given by the following equation:

$$\ln\left(\frac{C_0}{C_e}-1\right)=\frac{Mq_0\,K_T}{Q}-\frac{C_0K_T}{Q}V \tag{1}$$

where the kinetic parameters K_T and q_0 are the Thomas rate constant (mL/min/mg) and the maximum adsorption capacity (mg/g), respectively. V is the throughput volume (mL); M is the total mass of the adsorbent (g), C_e and C_0 are the effluent and inlet solute concentrations (mg/L), respectively; Q is volumetric flow rate (mL/min). The kinetic coefficient, K_T and the adsorption capacity of the bed, q_0 can be evaluated by the plot of the experimental breakthrough curves (Figure 1) according to Equation (1).

Thus, a plot of $\ln[(C_0/C_e)–1]$ against V at a given flow rate should give a straight line if the measurements follow the Thomas model. The slope and intercept can be used to evaluate the kinetic parameters K_T and q_0. The literalized Thomas model plot (Equation (1)) of the experimental breakthrough curves (Figure 1) is given in Figure 2. Obviously, the measured breakthrough curves in Figure 1 follows the Thomas model with a correlation coefficient range of $R^2 = 0.9–0.991$ for all the different adsorbate/adsorbent materials. High values of regression coefficients indicate that the experimental kinetic data conformed well to the Thomas model. The evaluated Thomas model kinetic parameters KT and q_o and the regression coefficient R^2 are given in Table 2.

By examining the Thomas model kinetic parameters in Table 2, it can be concluded that the adsorbent ANZ2 has a higher value of adsorption capacity to lead ions than ANZ1. Also, ANZ2 has a higher value of adsorption capacity to lithium ions than ANZ1. Moreover, ANZ1 and ANZ2 possess higher adsorption capacity to lead ions than to lithium ions.

Analysis using the Yoon and Nelson kinetic model

To evaluate the obtained experimental breakthrough curves and to better understand the fixed bed performance and column kinetics, the breakthrough curve of Figure 1 was analysed using the Yoon and Nelson kinetic model. The Yoon and Nelson model is based on the assumption that

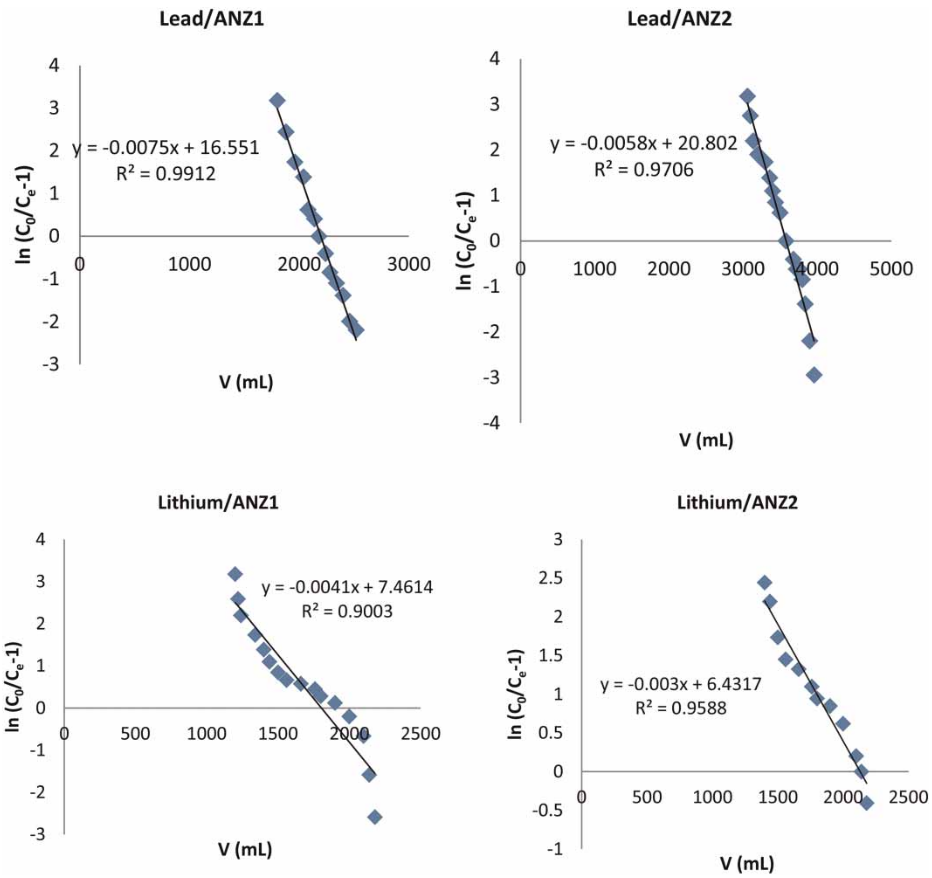

Figure 2 | Kinetic plot according to the Thomas model for the fixed bed adsorption of the different adsorbate/adsorbent materials.

Table 2 | Thomas model kinetic parameters for the fixed bed adsorption of lead and lithium ions on ANZ1 and ANZ2 adsorbents

	Thomas model parameters		
Adsorbate/adsorbent	K_T **(mL/min/mg)**	q_0 **(mg/g)**	R^2 **(–)**
Lead/ANZ1	0.23	23.64	0.99
Lead/ANZ2	0.20	34.67	0.97
Lithium/ANZ1	0.13	18.65	0.90
Lithium/ANZ2	0.10	21.44	0.96

the rate of decrease in the probability of adsorption for each adsorbate molecule is proportional to the probability of adsorbate adsorption and the probability of adsorbate breakthrough on the adsorbent. This model was used previously to analyse different fixed bed adsorption systems (Tsai *et al.* 1999; Sivakumar & Palanisamy 2009). The linear form of the Yoon and Nelson model is given by the following equation:

$$\ln\left(\frac{C_e}{C_0 - C_e}\right) = K_{\mathrm{YN}}t - \tau.K_{\mathrm{YN}} \quad (2)$$

where C_e, C_0 are the effluent and inlet solute concentrations, respectively (mg/L); K_{YN} is the Yoon and Nelson rate constant (min^{-1}); τ is the time required for 50% adsorbate breakthrough (min) and t is the breakthrough time (min).

Thus, a plot of $\ln[(C_e/C_0–C_e]$ against t at a given flow rate should give a straight line with slope of K_{YN}, and intercept of $–\tau.K_{\mathrm{YN}}$ if the measurements follow the Yoon and Nelson model. The plot of the experimental breakthrough curve (Figure 1) according to the linearized Yoon and Nelson model (Equation (2)) is given in Figure 3. Obviously, the measured breakthrough curves in Figure 1 follow the Yoon and Nelson model with a correlation coefficient

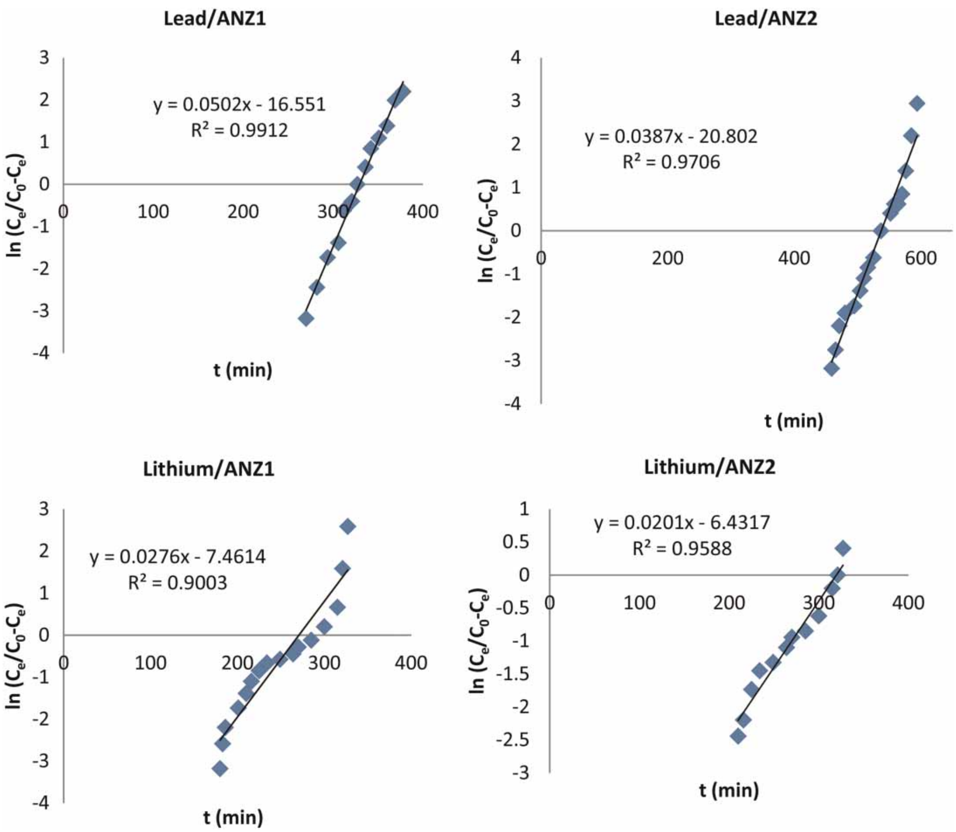

Figure 3 | Kinetic plot according to the Yoon and Nelson model for the fixed bed adsorption of the different adsorbate/adsorbent materials.

$R^2 > 0.90$ for all the adsorbent/adsorbate systems. High determined values of regression coefficients indicate that the kinetic data conformed well to the Yoon and Nelson model. The evaluated Yoon and Nelson model kinetic parameters K_{YN} and τ and the regression coefficient R^2 are given in Table 3.

The time to 50% breakthrough (τ) is an important kinetic parameter of the Yoon and Nelson model. It gives indication about the performance of the adsorbent to adsorb certain adsorbate. Obviously ANZ2 has better adsorption characteristics for lead and lithium ions. Both ANZ1 and ANZ2 have better adsorption to lead ions than to lithium ions.

Table 3 | Yoon and Nelson model kinetic parameters for the fixed bed adsorption of lead and lithium ions on ANZ1 and ANZ2 adsorbents

	Yoon and Nelson kinetic parameters		
Adsorbate/Adsorbent	**K_{YN} (min^{-1})**	**τ Time to (50% breakthrough) (min)**	**R^2 (–)**
Lead/ANZ1	0.05	331.0	0.99
Lead/ANZ2	0.04	547.36	0.97
Lithium/ANZ1	0.02	276.33	0.90
Lithium/ANZ2	0.02	321.55	0.96

Modeling of the experimental breakthrough curves

The measured breakthrough curves (Figure 1) are compared with the calculated values estimated from the Thomas model (Equation (1)) and the Yoon and Nelson model (Equation (2)) using the kinetic parameters in Table 1 for the different adsorbate/adsorbent materials. The theoretical curves are calculated according to both models for the adsorption of lead on ANZ2, lead on ANZ1, lithium with ANZ1 and lithium with ANZ2 and are shown in Figures 4–7, respectively. It can be seen in Figures 4 and 5 that the theoretical curve calculated by the Yoon and Nelson model is in better agreement with the measured

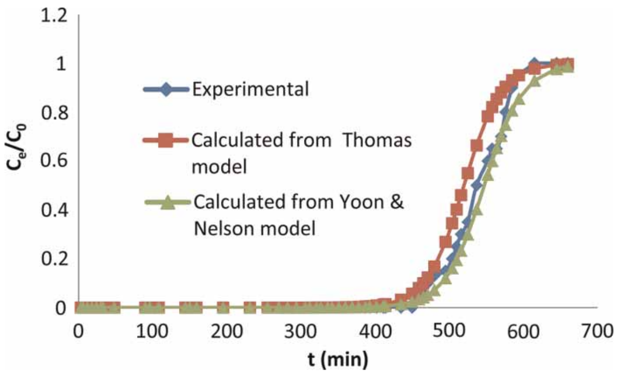

Figure 4 | Comparison of experimental and calculated curves for the adsorption of lead using ANZ2.

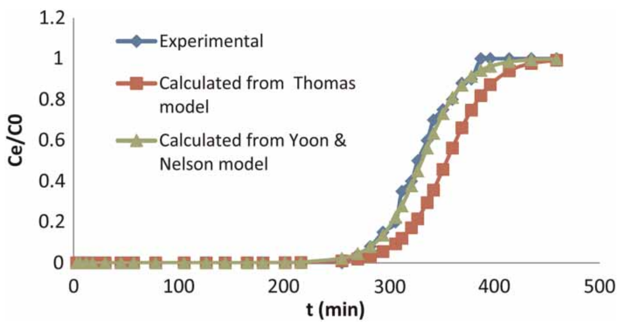

Figure 5 | Comparison of experimental and calculated curves for the adsorption of lead using ANZ1.

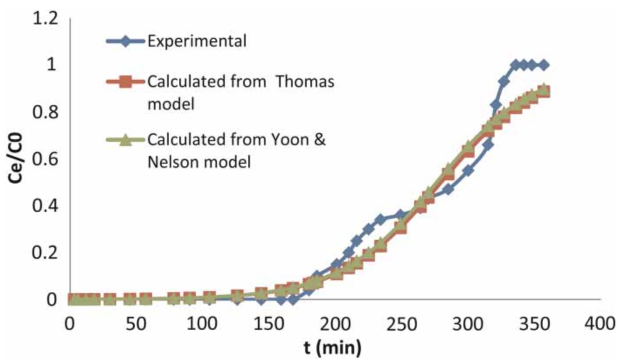

Figure 6 | Comparison of experimental and calculated curves for the adsorption of lithium using ANZ1.

experimental curve than the theoretical curve calculated by the Thomas model in the case of the adsorption of lead ions by ANZ1 and ANZ2. However, the Thomas and Yoon and Nelson models fit the experimental data for the adsorption of lithium ions with the same degree, as can be seen in Figures 6 and 7. Generally the Yoon and Nelson model

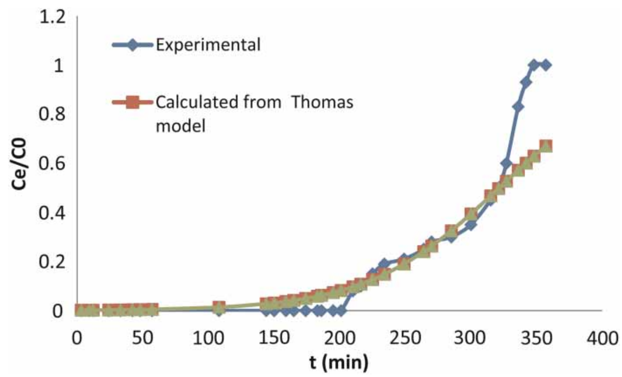

Figure 7 | Comparison of experimental and calculated curves for the adsorption of lithium using ANZ2.

can be used successfully and more accurately to describe the kinetics of adsorption on ANZ1 and ANZ2.

CONCLUSION

The removal of lead and lithium heavy metals from aqueous solution in a fixed bed adsorption column using the natural zeolites (ANZ1 and ANZ2) was studied. The Thomas and Yoon and Nelson kinetic models were used to explain the column adsorption kinetics. The Thomas rate constants, Yoon and Nelson rate constants, adsorption capacities, and the times for 50% adsorbate breakthrough were dependent on the type of adsorbent and adsorbate. The experimental breakthrough curves compared acceptably with the simulated breakthrough profile calculated by the Yoon and Nelson method. The determined column parameters can be further implemented for the fixed bed columns. Further studies are required to investigate the effect of initial concentration, initial pH, and flow rate and bed height on the operation of the fixed bed column.

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First received 30 June 2014; accepted in revised form 13 September 2014. Available online 21 October 2014