Sardinian natural clinoptilolites for heavy metals and ammonium removal: experimental and modeling

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Abstract

Sardinian natural clinoptilolites are examined to evaluate their performance for metals, i.e. copper, cadmium, lead and zinc, as well as ammonium removal. The natural material is either used as received or once converted into the sodium form. Equilibrium data for each species and the natural material are obtained. The corresponding behavior is quantitatively correlated using classical isotherms, whose parameters are estimated by fitting the equilibrium data. Breakthrough experiments of lead solutions are also performed. Fixed-bed runs are simulated using a mathematical model which includes axial dispersion as well as a new approximate rate law for non-linear adsorption and diffusion in spherical adsorbent particle based on an equivalent film resistance model.

Keywords: Clinoptilolites; Adsorption; Equilibria; Diffusion; Dynamics; Pollutant Removal

1. Introduction

Zeolites have been recognized for more than 200 years, but only during the middle of the twenty-th century have attracted the attention of scientists and engineers who demonstrated their technological importance in several fields [1-5]. Although most of the effort was devoted to synthetic zeolites, in recent years increasing attention has been directed towards natural zeolites, whose status changed from that of museum curiosity to an important mineral commodity. Several hundred thousands tons of natural zeolite bearing materials are mined in the United States, Japan, Italy, Bulgaria, Cuba, Yugoslavia, Mexico, Korea and Germany but only those containing chabazite, clinoptilolite, erionite, ferrierite, phillipsite, mordenite and analcime are available in sufficient quantity and purity to be considered as exploitable natural resources [6]. The main reason of the interest for natural zeolite-bearing materials is the increasing demand of low-cost ion exchange and adsorbent materials in fields such as energy production, pollution control and metal recovery as well as their wide availability on the earth. Some of the attractive applications of natural zeolites are listed in Table 1, where it may be seen that pollution prevention and control represents one of the most important area of exploitation.

Equilibrium uptake as well as fixed-bed dynamic investigations have been carried out involving natural zeolites and pollutants from either gas or liquid phase including heavy metals, pesticides, explosives, SO_2 [1]. From Table 1 it may be seen that natural zeolites-bearing materials have been extensively used for a variety of applications such as the removal of ammonium ions in wastewater treatment plants and from landfill leachate. The adsorption capacity of natural clinoptilolites is currently being exploited for H_2S, SO_2, CO, N_2 and CH_4 uptake [7-10]. The performance of natural clinoptilolites for heavy metal removal has been also compared with precipitation processes, adsorption on activated carbon and solvent extraction processes.

In order to effectively design natural zeolite-bearing materials units, the development of mathematical models that can successfully simulate their operation is required. These models should be able to predict the dynamics of both adsorption and desorption processes in order to also facilitate the development of novel applications such as the design of hybrid system which combined biological degradation and adsorption treatment [11]. However, the dynamics of fixed-bed adsorption-elution processes involving natural zeolite-bearing materials cannot be described using the mass transfer zone approach [12-14]. This goal can be on the other hand obtained by writing transient conservation equations in spherical coordinates for the adsorbent particles and coupling these equations with overall transient balances through boundary conditions at the particle-fluid interface [15, 16]. Appropriate diffusion mechanisms relevant to adsorption processes which include pore and solid (or surface) diffusion are then used to quantitatively describe the intraparticle diffusion rates [17 and references therein]. Because of mathematical and numerical complexities associated with such equations, a new approximate rate law for non-linear adsorption and diffusion in a spherical adsorbent particle based on an equivalent film resistance model has been developed recently [18]. The approximation provides a quantitatively correct description of the effect of the adsorption isotherm for parallel pore and solid diffusion as well as of the effect of a variable adsorbed-phase diffusivity. A similar approach has been successfully adopted for the prediction of batch and column breakthrough curves for both irreversible and reversible ion-exchange processes [19].

The objective of this paper is to test the validity of the model described above to quantitatively describe the performance of Sardinian natural clinoptilolites for metals, i.e. copper, cadmium, lead and zinc, as well as ammonium removal. To this aim, equilibrium data for each species with the natural material used either as received or once converted into the sodium form are obtained. The corresponding behavior is quantitatively correlated using

classical isotherms, whose parameters are estimated by fitting the equilibrium data. Breakthrough experiments of lead solutions are also performed and the corresponding behavior is quantitatively correlated using the model proposed by Carta and Cincotti [18] while accounting for interparticle mass transfer phenomena previously neglected.

2. Experimental section

The natural material used in this work was characterized by X-Ray diffractometry (XRD) on a Rigaku Geirflex fully automated apparatus employing the Cu-kα, Ni filtered radiation of power settings of 30 kV and 30 mA, while the assignments of peaks were from a JCPDS file. As it can be seen from Figure 1, the material is constituted not only by clinoptilolite but also illite and quartz. In this work we used the Sardinian natural zeolite-bearing material characterized by two different clinoptilolite contents, i.e. 20 and 50 % wt, as evaluated using standard chemical analysis. The cation exchange capacity (CEC) of the material was determined according with the "cross exchange method" [20] as follows. Nine samples of 1g each of the zeolite in sodium form were first equilibrated at 25 ^{o}C with a 1M solution of KCl until the complete conversion in potassium form was accomplished. To assure the complete exchange, the process was repeated by renewing the solution until the sodium concentration at equilibrium resulted below 1 mg/L. The obtained zeolite samples in potassium form were then re-exchanged into the sodium one using a 1M solution of NaCl and according to the previous exchange procedure. The equilibrium solutions collected were used to calculate the average CEC value which was found to be about 0.7 meq/g, for the zeolite with 50% wt clinoptilolite content.

The density of the natural material measured using a gas picnometer (ACCUPIC 1330 V201) was found to be 2.425 g/cm^3, while the intraparticle porosity obtained through a Porosimeter 4000 (Carlo Erba Instruments) was equal to 0.2.

The natural material was used as received and is identified by Z_1 or Z_2 depending upon the clinoptilolite content equal to 20 or 50% wt, respectively. The natural material Z_2 was also used once converted into the sodium form. The exchange was performed by repeatedly equilibrating the natural material with renewed 1M NaCl solutions until the potassium and calcium concentration in the final solution resulted to be less than 1 mg/L. The material obtained following the procedure above is identified by the symbol Z_2-Na.

Equilibrium tests were carried out in a temperature controlled shaker at 25°C by contacting known weights (1-5 g) of the natural material in the Z_1, Z_2 and Z_2-Na form, with a solution of known solute (Cu^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, and NH_4^+) concentration and volume in suitable flasks. In particular, $CdCl_2$, $CuCl_2 \cdot 2H_2O$, and NH_4Cl from Aldrich Chemical Company and $PbCl_2$ and $ZnCl_2$ from Carlo Erba Reagents were employed. The flasks were sealed and shaken for 24 h, which were proved experimentally to be sufficient to reach equilibrium. Finally, the solutions were sampled in order to determine the solute concentration and pH. The equilibrium solute concentration in the zeolite phase q is determined through the following mass balance:

$$q^e = \frac{\left(C^0 - C^e\right) V_s}{W} \tag{1}$$

where the symbols significance is reported in the Nomenclature. The experimental values of the solute concentration were determined using an Atomic Absorption Spectrophotometer (Video 12, Instruments Laboratory) for the metal ions, while the ammonium ion was measured with the Antek technique (a chemilumiscent nitrogen system).

Breakthrough experiments were also carried out at 25°C using lead solutions and the apparatus schematically shown in Figure 2. The natural material was slurry packed in a glass column (50 g of adsorbent, 1.6 cm diameter and 23 cm depth). Quartz wool was placed at the bottom to avoid adsorbent entrainment. A bed void fraction of about 0.44 was measured.

Lead solutions containing 65 mg/l of Pb^{2+} were percolated at 1.2 L/h through a bed constituted by either Z_2 or Z_2-Na adsorbent material. Samples of the column effluent were collected at selected time intervals, and the composition was measured using the same analytical techniques employed for batch equilibrium runs.

3. Mathematical model

The transient behavior of the fixed-bed column was simulated by means of an heterogeneous axial-dispersion model. The column was assumed isothermal and monodimensional flux is considered. Parallel pore and surface diffusion is considered to take place in spherical and uniformly sized adsorbent particles. Local equilibrium between pore fluid and adsorbent surface is assumed.

The solid diffusion coefficient is supposed to depend, in general, on the adsorbate concentration in the adsorbed phase with the form $D_s^0 \cdot g(q)$, where q represents the concentration of the pollutant in the solid phase. Thus, the mass balance equation in the aqueous phase is given by:

$$\varepsilon \frac{\partial C}{\partial t} = -\varepsilon \, \mathrm{v}_{\mathrm{int}} \frac{\partial C}{\partial z} + \varepsilon \, E_D \frac{\partial^2 C}{\partial z^2} - \frac{3(1-\varepsilon)}{R_p} k_f \left(C - C_p^*\right) \tag{2}$$

along with the initial and Dankwerts's boundary conditions:

$$\mathrm{t} = 0 \qquad C = C_p^* = 0 \tag{3}$$

$$\mathrm{z} = 0 \qquad \mathrm{v}_{\mathrm{int}} C^f = \mathrm{v}_{\mathrm{int}} C - E_D \frac{\partial C}{\partial z} \tag{4}$$

$$\mathrm{z} = \mathrm{L} \qquad \frac{\partial C}{\partial z} = 0 \tag{5}$$

where C represents the aqueous phase concentration of the pollutant, while the meaning of other symbols is reported in the Nomenclature.

Following [18] the intraparticle diffusional resistance is represented by pseudo-steady state diffusion through an hypothetical flat film of thickness $\delta = R_p/5$, where R_p represents the particle radius.

Therefore, the mass balance equation of the pollutant in the solid phase is given by:

$$\frac{\partial \overline{q}}{\partial t} = \frac{15/R_p^2}{\rho_p + \varepsilon_p \dfrac{d\left(f_{eq}^{-1}\left(\overline{q}\right)\right)}{d\overline{q}}} \left[\varepsilon_p D_p \left(C_p^* - \overline{C}_p\right) + \rho_p D_s^0 \int_{\overline{q}}^{q^*} g(q)\, dq \right] = \\ = \frac{3/R_p}{\rho_p + \varepsilon_p \dfrac{d\left(f_{eq}^{-1}\left(\overline{q}\right)\right)}{d\overline{q}}} k_f \left(C - C_p^*\right) \tag{6}$$

where, due to the local equilibrium assumption,

$$q^* = f_{eq}\left(C_p^*\right) \tag{7}$$

and

$$\overline{q} = f_{eq}\left(\overline{C}_p\right) \tag{8}$$

being f_{eq} the expression of the equilibrium isotherm obtained as discussed in the next section. $\overline{q}$ and $\overline{C}_p$ represent the average solid phase and pore fluid concentration of the pollutant, respectively, and are defined as follows:

$$\overline{q} = \frac{\int_0^{R_p} q\ 4\pi r^2 dr}{4/3\ \pi R_p^3} \tag{9}$$

$$\overline{C}_p = \frac{\int_0^{R_p} C_p\ 4\pi r^2 dr}{4/3\ \pi R_p^3} \tag{10}$$

The appropriate initial condition of equation (6) is given by:

$$t = 0 \qquad \overline{q} = \overline{C}_p = q^* = C_p^* = 0 \tag{11}$$

Equations (2) to (8) and (11) represent a system of nonlinear partial differential equations that was solved by the “method of lines”, which consists in adopting a central finite difference scheme for the spatial derivatives in order to convert the equations above into a set of ordinary differential equations at the internal node points. The resulting system of ordinary differential equations was integrated numerically as an initial value problem with Gear’s method (subroutine DIVPAG of the IMSL libraries). During the computation, the number of the internal node points of the spatial domain was kept as 50. Higher values were tested without causing any perceptible variation in the results.

4. Results and discussion

Equilibrium uptake isotherms of copper, cadmium, lead, zinc and ammonium with the Z_1, Z_2 and Z_2-Na form of the natural material are reported in Figures 3 to 7, respectively, in terms of species concentration in the solid phase as a function of its value in solution. It is seen that the natural material converted into the sodium form gives rise to better adsorption capacity for all ions investigated.

Adsorption capacities of the natural material considered in this work may be compared in Table 2 for each species investigated with the corresponding values reported in the literature for other natural clinoptilolite based adsorbents. It may be seen that the natural materials Z_1 and Z_2 display adsorption capacity values for copper, cadmium, lead and zinc species invariably lower than those reported in the literature for similar materials. This consideration holds true also for the sodium form of the natural material used in this work, i.e. Z_2-Na, for the case of copper and zinc ions. On the contrary, adsorption capacities of the Z_2-Na material with respect to cadmium and lead fall within the corresponding range reported in the literature.

The experimental data above were quantitatively correlated using several well known isotherms, i.e. the Langmuir, Freundlich, Toth, Radke and Prausnitz, Fritz and Schlünder ones [17, 25]. The adjustable parameters of these isotherms have been estimated by fitting directly the experimental data using standard procedures. As an example, the comparison between model results and experimental data is shown in Figure 8 for the system Z_2-Na/Pb^{2+}. The Langmuir isotherm was selected with respect to the other ones, since it invariably provides a reasonable accuracy in reproducing the experimental data as clearly shown in Table 3, where the estimated values of the corresponding adjustable parameters are reported together with the resulting correlation coefficients. Figures 3 to 7 compare the experimentally determined adsorption isotherm data to the fit following the Langmuir isotherm. It should be noted that the ion selectivity scale reported in the literature [1] for natural clinoptilolites, i.e. Pb>NH_4>Cd, Cu, Sr>Zn>Co, is satisfied for the case of Z_1, Z_2 and Z_2-Na materials as it may be seen from Figure 3 to 7, except for the ammonium ion.

As reported in the literature [1, 26-29], several factors can contribute to determine the selectivity scale. In particular, molecular sieving, presence of impurities, free energy of hydration and volume steric effect are found to play an important role in the cations uptake of natural zeolites. Although in this work, these and related phenomena are not further investigated, it should be noted for example that the observed preference of the natural material for lead may be explained in terms of its relatively lower hydration energy if compared with the other cations [26]. It is also important to note that, although classical adsorption isotherms are considered in this work, more appropriate equilibrium ion exchange models based on previous works [30, 31] are currently being adopted to interpret the experimental data.

Next we consider the adsorption experiments performed using the natural adsorbents Z_2 and Z_2-Na and the apparatus depicted in Figure 2. The complete experimental

breakthrough curves corresponding to a 65 mg/L lead solution fed at an inlet flow rate equal to 1.2 L/h, for both natural adsorbents Z_2 and Z_2-Na, are shown in Figure 9, where the lead outlet concentration is also reported as a function of the bed volumes. Using the model parameters values reported in Table 4, the solid diffusion coefficient, D_s^0, has been fitted through a direct comparison between experimental data and model results, for the case of Z_2-Na/Pb^{2+} system by assuming constant solid diffusivity, i.e. $g(q)=1$ in equation (6).

The corresponding fitting results shown in Figure 9 are satisfactory, thus supporting the reliability of the proposed model. In particular, it is worth noting that the fitted value of D_s^0, i.e. $2.0 \cdot 10^{-12}$ m^2 s^{-1} is coherent with typical values reported in the literature for solid diffusion coefficients under similar conditions [25]. The capability of the proposed mathematical model in reproducing the experimental data is further tested by considering the breakthrough curve for lead solution and the natural material Z_2. By keeping constant the value of D_s^0 as obtained above, and changing only the equilibrium isotherm parameters according to the values reported in Table 3 for the system Z_2/Pb^{+2}, the model is able to predict fairly well the corresponding breakthrough curve, as clearly shown in Figure 9.

From this figure, the bed volumes for the Z_2/Pb^{2+} and Z_2-Na/Pb^{2+} systems corresponding to the so-called breakpoint, i.e. when the 5% of the inlet pollutant concentration is reached in the outlet stream, result to be equal to 250 and 700, respectively. It should be noted that these values are of the same magnitude of typical bed volume values reported in the literature for the removal of various pollutants using natural zeolite-bearing materials [22, 34, 35].

This observation clearly supports the exploitation of the Sardinian natural clinoptilolite considered in this work as a potential adsorbent for lead removal.

Besides, the proposed mathematical model, due to its capability of reproducing the experimental data, provides a useful tool for the optimal design of the adsorption process. However, the model may be improved by incorporating multicomponent equilibrium isotherms in order to be able to properly simulate elution experiments. This goal may be also achieved by considering a recently developed model for the simulation of ion exchange equilibria [30, 31]. As shown by Melis *et al.* [36], the ion-exchange equilibrium model should be also coupled with the appropriate dissociation equilibria in aqueous solution as well as a lumped description of the intraparticle diffusion according to the Nernst-Plank mechanism. While for the intraparticle diffusion description we consider the approximation recently proposed by Carta *et al.* [19], work is under way along the lines outlined above to obtain a comprehensive model involving multicomponent system which can be used to properly design suitable and cost-effective adsorption processes for the immobilization of heavy metals from abandoned mines based on the exploitation of natural resources such as Sardinian zeolites.

5. Concluding remarks

In the present work, we evaluate the capabilities of Sardinian natural clinoptilolite for the uptake of heavy metals, i.e. copper, cadmium, lead and zinc, and ammonium ions. It was found that the equilibrium performance of this zeolite, once converted in the sodium form, is comparable to the one reported in the literature for the case of cadmium and lead ions. Despite the fact that natural clinoptilolites have been extensively used for ammonium ion removal, the corresponding performance of the zeolite considered in this work cannot be compared due to the lack of literature data.

Breakthrough experiments related to lead uptake have been performed and the corresponding behavior quantitatively correlated or predicted using the model proposed by Carta and Cincotti [18], while accounting for interparticle mass transfer phenomena.

It is worth noting that, although classical adsorption isotherms are considered in this work, more appropriate equilibrium ion exchange models [30] are currently being adopted to interpret the experimental data.

6. Nomenclature

C	concentration of pollutant in the liquid phase	kmol m^{-3}
D	pore liquid-phase diffusivity	m^2 s^{-1}
D_m	molecular diffusivity	m^2 s^{-1}
D_s^0	solid diffusivity	m^2 s^{-1}
d_p	diameter of zeolite particle	m
E_D	dispersion coefficient	m^2 s^{-1}
f_{eq}	equilibrium isotherm	—
$g(q)$	function appearing in equation (6)	—
k_f	interparticle diffusion coefficient	m s^{-1}
K	equilibrium constant of Langmuir isotherm	L mg^{-1}
L	zeolite bed height	m
q	concentration of pollutant in the solid phase	$mg\,g^{-1}_{Zeolite}$
q_{max}	monolayer coverage of adsorbent of Langmuir isotherm	$mg\,g^{-1}_{Zeolite}$
r	radial coordinate in the particle	m
R	correlation coefficient	—
Re	Reynolds number $(v_{int}\varepsilon d_p / v)$	—
R_p	particle radius	m
Sc	Schmidt number (v/D_m)	—
t	time	s
V_s	volume of the solution	L
v_{int}	interstitial fluid velocity	m s^{-1}
W	zeolite weight	kg

z	distance through the bed	m

Greek Symbols

δ	thickness of the hypothetical flat film $(R_p / 5)$	m
ε	bed void fraction	—
ε_p	intraparticle porosity	—
ρ_p	zeolite particle density	kg m^{-3}
τ	tortuosity	—
v	kinematic viscosity	kg m^{-1} s^{-1}

Superscripts

0	initial conditions
e	equilibrium conditions
f	feed conditions
p	pore liquid phase
*	fluid-solid interface condition
–	volume average over the particle

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Table 1. Technological applications of natural zeolites.

Adsorption	**Catalysis**
	Isomerization
Heavy Metals (Ag, Ba, Cd, Co, Cs, Cu, Fe, Hg, Mn, Ni,	Hydration and dehydration
Pb, Pd, Sr, Zn)	Disproportion
Organic Compounds (Aflatoxin, Benzene,	Hydrocracking
Ethylbenzene, Methane, Methyl alcohol, *p*-Xylene,	Hydromethylation
Toluene, 1-1-1-Trichloroethane)	Hydrodesulfurisation
Fungicide	Dewaxing
Pesticide	Alkylation and Acylation
Other (Water, Ammonia, N_2, Ca, CO, CO_2, Mg, Na, K,	Nitration
Phosphates, H_2S, Li, Nitrates, SO_2)	Dimerization
	Reduction

Table 2. Adsorption capacity of natural clinoptilolite based materials for copper, cadmium, lead, zinc and ammonium species

Adsorption Capacity [meq/g]					
Cu^{2+}	Cd^{2+}	Pb^{2+}	Zn^{2+}	NH_4^+	**References**
—	1.07 - 1.24	0.6 - 0.96	—	—	[6]
0.7	0.7	0.7540	—	—	[21]
0.88 - 1.42	0.84 - 1.24	—	—	—	[22]
—	0.24 - 0.42	0.76 - 0.88	—	—	[23]
—	—	—	0.52 - 0.76	—	[24]
0.093	0.06	0.161	—	0.18	Z_1, this work
0.15	0.17	0.31	0.14	0.45	Z_2, this work
0.38	0.25	0.62	0.25	0.68	Z_2-Na, this work

Table 3. Values of the adjustable parameters of Langmuir ($q = q_{max} KC/(1+KC)$) isotherm and corresponding correlation coefficient (R) obtained by fitting the equilibrium data.

System	q_{max}	K	R
Z_1/Cu^{2+}	2.96	0.29	0.9980
Z_1/Cd^{2+}	3.49	0.38	0.9752
Z_1/Pb^{2+}	16.75	0.08	0.9426
Z_1/NH_4^+	3.23	0.10	0.9357
Z_2/Cu^{2+}	4.78	0.45	0.9948
Z_2/Cd^{2+}	9.50	0.19	0.9834
Z_2/Pb^{2+}	32.65	0.09	0.9906
Z_2/Zn^{2+}	4.54	0.09	0.9841
Z_2/NH_4^+	8.15	0.04	0.9930
Z_2-Na/Cu^{2+}	12.11	0.53	0.9995
Z_2-Na/Cd^{2+}	14.30	6.68	0.9956
Z_2-Na/Pb^{2+}	64.52	0.14	0.9951
Z_2-Na/Zn^{2+}	8.14	0.34	0.9997
Z_2-Na/NH_4^+	12.26	0.10	0.9994

Table 4. Model parameters.

Parameter	Value	Reference
C^f	$3.18 \cdot 10^{-1}$ mol m^{-3}	This work
D_m	$1.46 \cdot 10^{-9}$ m^2 s^{-1}	[32]
d_p	$1.2 \cdot 10^{-3}$ m	This work
D_p	$\frac{D_m}{\tau}$	[17]
E_D	$\frac{\varepsilon\, d_p v_{int}}{0.2 + 0.011\,(Re)^{0.48}}$	[33]
f_{eq}	See Table 3	This work
k_f	$\frac{1.09}{\varepsilon}\ \mathrm{Re}^{0.33}\, Sc^{0.33}\cdot\left(\frac{D_m}{d_p}\right)$, 0.0015<Re<55 $\frac{0.25}{\varepsilon}\ \mathrm{Re}^{0.69}\, Sc^{0.33}\cdot\left(\frac{D_m}{d_p}\right)$, 55<Re<1050	[15]
L	$2.3 \cdot 10^{-1}$ m	This work
v_{int}	$3.75 \cdot 10^{-3}$ m s^{-1}	This work
ε	0.44	This work
ε_p	0.2	This work
ρ_p	$1.94 \cdot 10^{3}$ kg m^{-3}	This work
τ	5	[17]
V	$1.07 \cdot 10^{-3}$ Kg $m^{-1}s^{-1}$	[17]

Captions for figures

Figure 1 XRD spectrum of the Sardinian natural bearing-clinoptilolite material.

Figure 2 Experimental set-up for adsorption runs: 1) lead solution tank; 2) peristaltic pump; 3) glass column; 4) natural material bed; 5) quartz wool.

Figure 3 Equilibrium uptake isotherms of copper with the Z_1, Z_2 and Z_2-Na form of the natural adsorbent.

Figure 4 Equilibrium uptake isotherms of cadmium with Z_1, Z_2 and Z_2-Na form of the natural adsorbent.

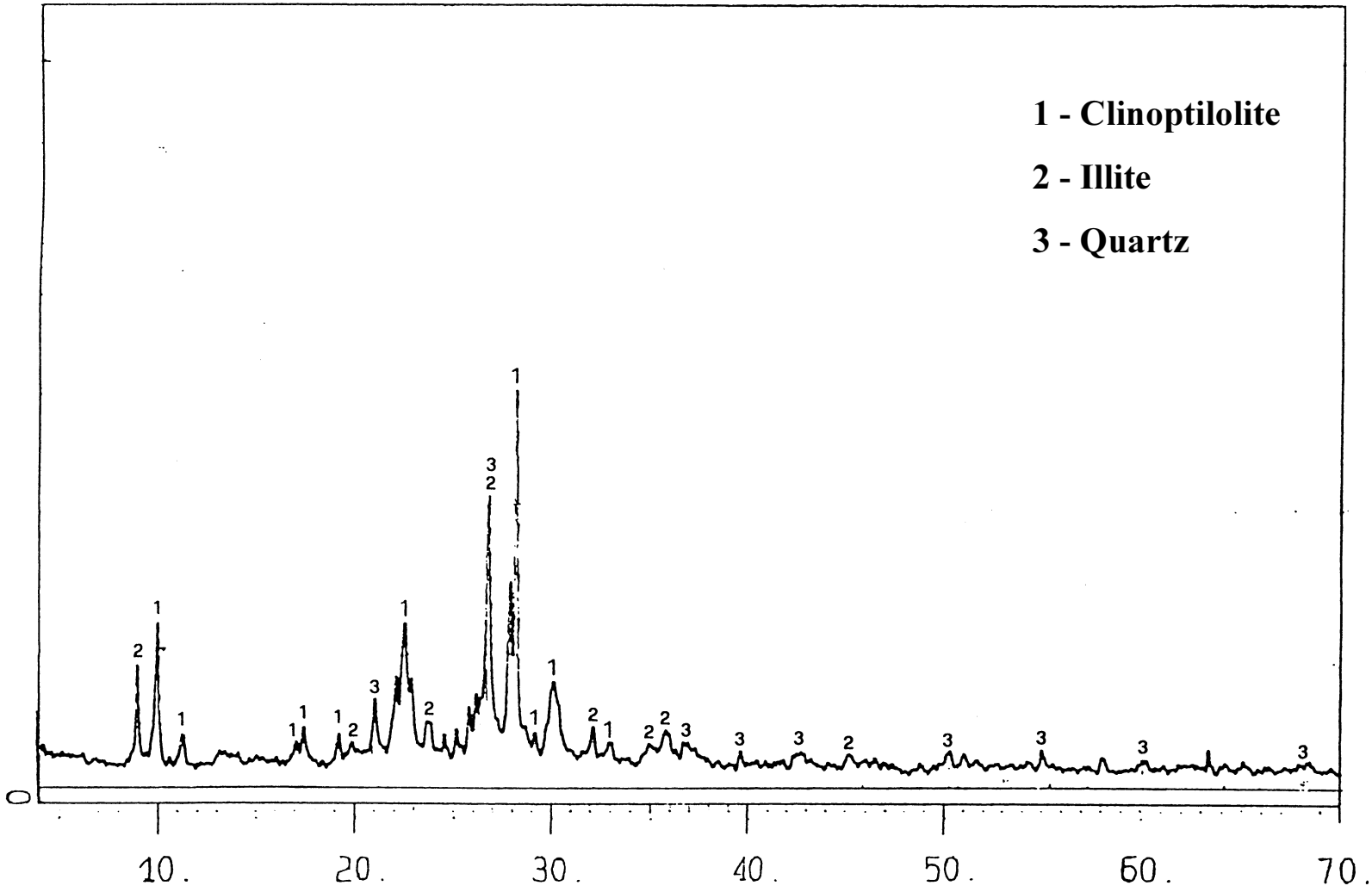
Figure 5 Equilibrium uptake isotherms of lead with Z_1, Z_2 and Z_2-Na form of the natural adsorbent.

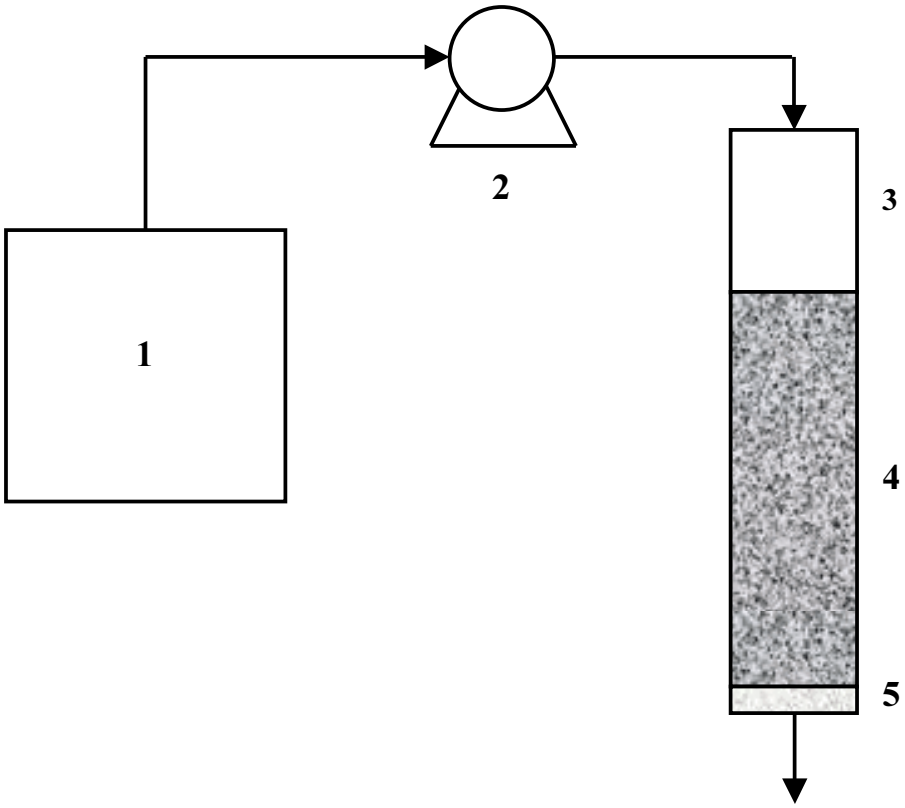
Figure 6 Equilibrium uptake isotherms of zinc with Z_2 and Z_2-Na form of the natural adsorbent.

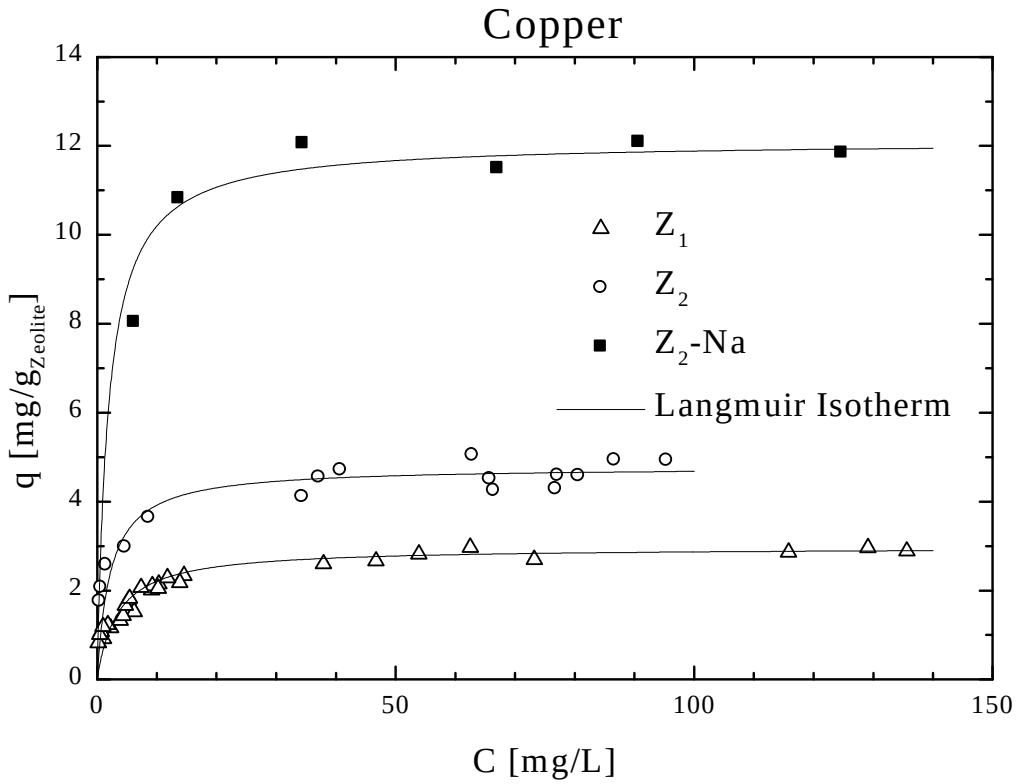
Figure 7 Equilibrium uptake isotherms of ammonium with Z_1, Z_2 and Z_2-Na form of the natural adsorbent.

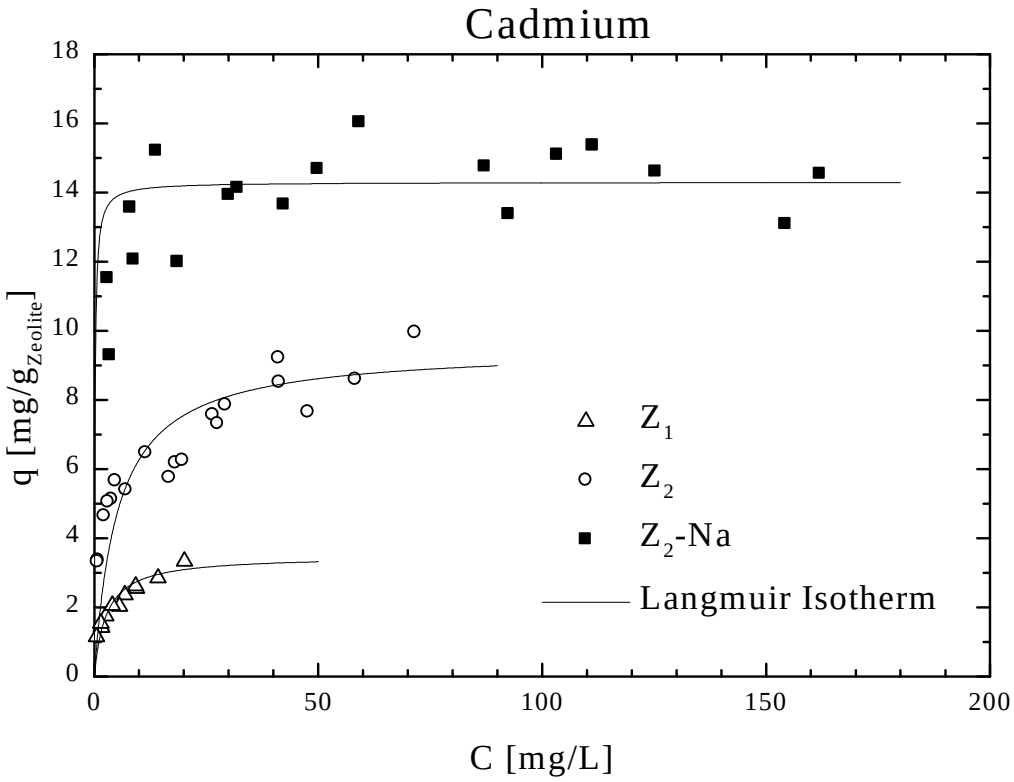
Figure 8 Equilibrium uptake of lead with the Z_2-Na form of the natural adsorbent and possible quantitative interpretation using different isotherms.

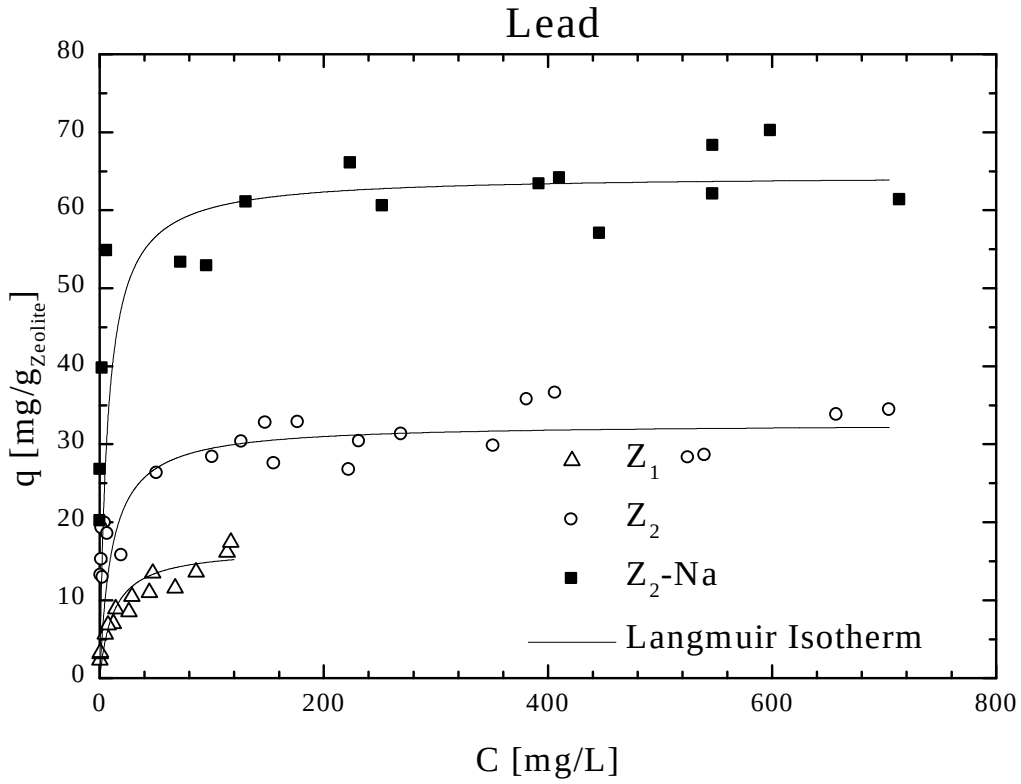
Figure 9 Breakthrough curves of lead solution with the Z_2 and Z_2-Na form of the natural adsorbent and corresponding model fit and prediction.

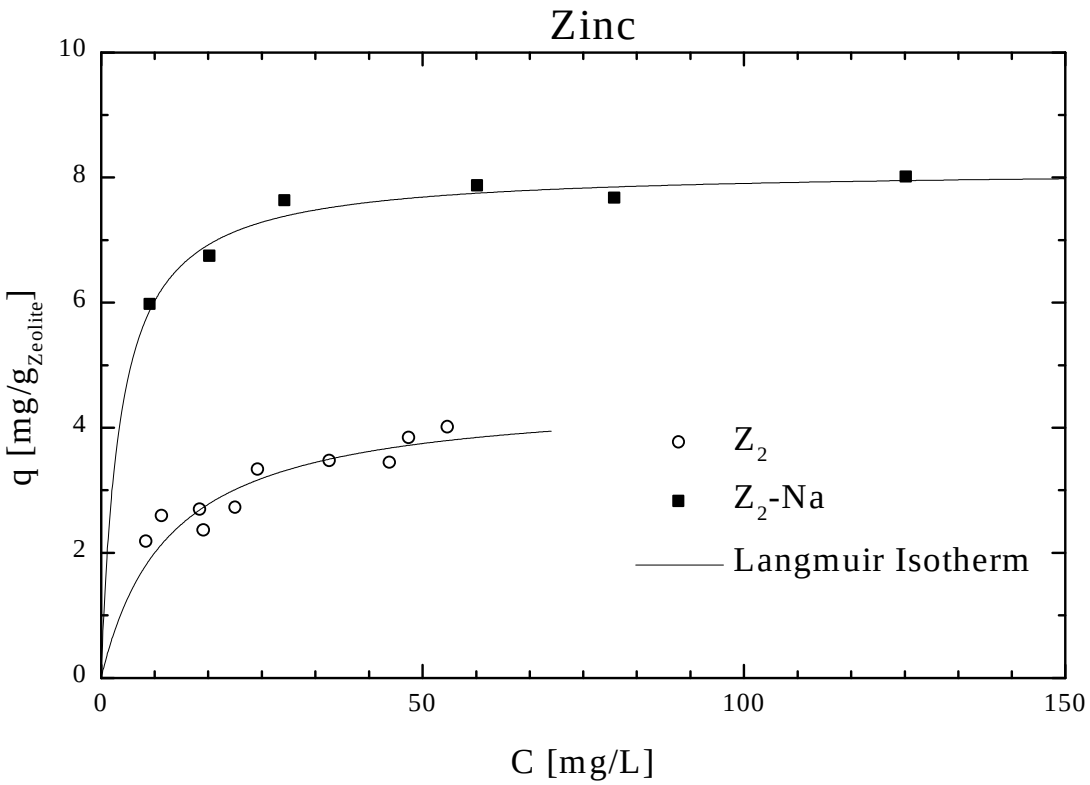

1 - Clinoptilolite
2 - Illite
3 - Quartz
0
10.
20.
30.
40.
50.
60.
70.
Diffraction Angle,

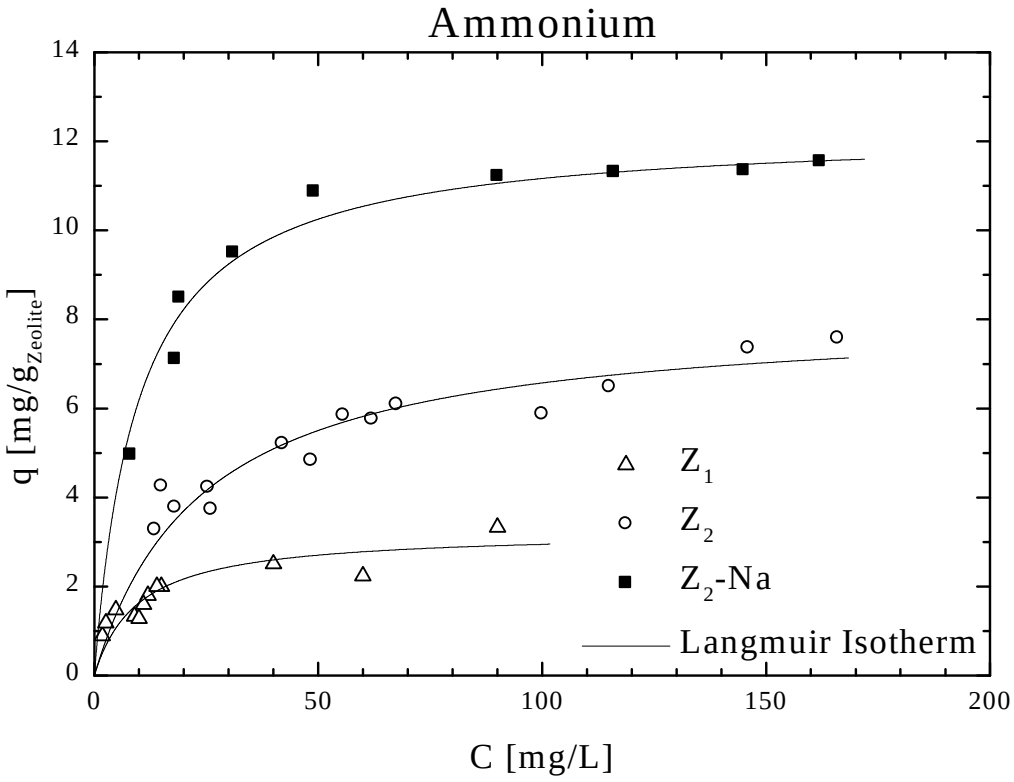

1
2
3
4
5

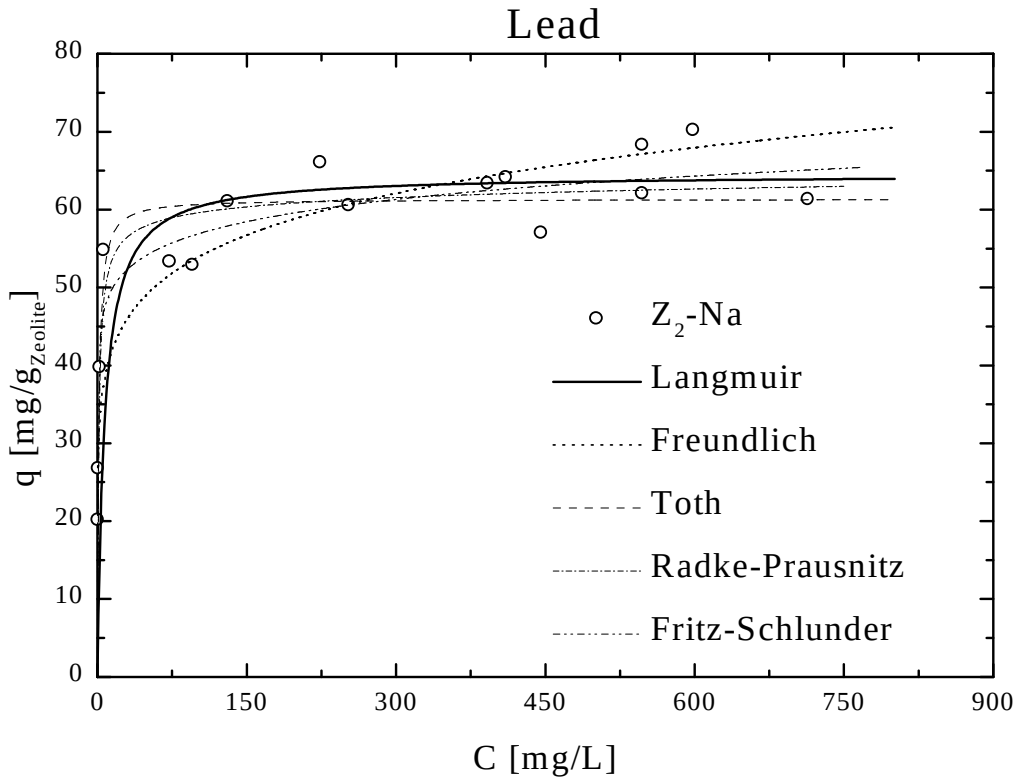

Copper
14
12
10
8
6
4
2
0
0
50
100
150
q [mg/g$_{Zeolite}$]
C [mg/L]
Z$_1$
Z$_2$
Z$_2$-Na
Langmuir Isotherm

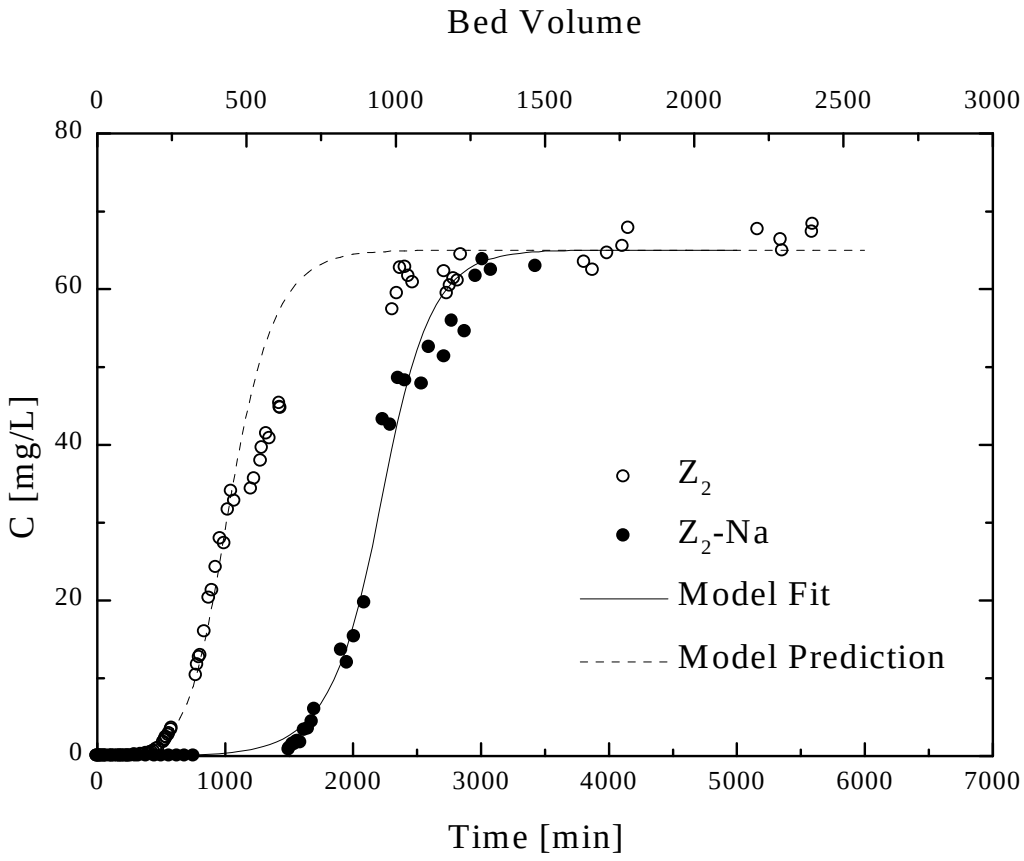

Cadmium
q [mg/g$_{Zeolite}$]
C [mg/L]
0
2
4
6
8
10
12
14
16
18
0
50
100
150
200
Z$_1$
Z$_2$
Z$_2$-Na
Langmuir Isotherm


Lead
80
70
60
50
40
30
20
10
0
0
200
400
600
800
q [mg/g$_{Zeolite}$]
C [mg/L]
Z$_1$
Z$_2$
Z$_2$-Na
Langmuir Isotherm


Zinc
10
8
6
4
2
0
0
50
100
150
q [mg/g$_{Zeolite}$]
C [mg/L]
Z$_2$
Z$_2$-Na
Langmuir Isotherm


Ammonium
14
12
10
8
6
4
2
0
0
50
100
150
200
q [mg/g$_{Zeolite}$]
C [mg/L]
Z$_1$
Z$_2$
Z$_2$-Na
Langmuir Isotherm


Lead
80
70
60
50
40
30
20
10
0
0
150
300
450
600
750
900
q [mg/g$_{Zeolite}$]
C [mg/L]
Z$_2$-Na
Langmuir
Freundlich
Toth
Radke-Prausnitz
Fritz-Schlunder


Bed Volume
0
500
1000
1500
2000
2500
3000
80
60
40
20
0
C [mg/L]
Z2
Z2-Na
Model Fit
Model Prediction
0
1000
2000
3000
4000
5000
6000
7000
Time [min]