KINETIC STUDIES OF ZINC IONS REMOVAL FROM AQUEOUS SOLUTION BY ADSORPTION ON NATURAL ZEOLITE

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Abstract: The kinetics of zinc adsorption onto natural zeolite (clinoptilolite) were studied with respect to initial metal ion concentration, adsorbent mass and initial pH value. In order to select the main rate-determining step in the overall uptake mechanism, a series of experiments were performed under batch conditions from single ion solutions. Data obtained from the kinetic experiments are interpreted in terms of Pseudo-second order kinetic model, Weber and Morris model and model proposed by Furusawa and Smith.
The adsorption kinetics is reasonably fast. It means that in the first 20 min approximately 78% of Zn^{2+} is adsorbed from solutions. From the kinetic data can be concluded that adsorption of zinc ions from solution by natural zeolite is more efficiency at high pH value and adsorbent mass, and at lower zinc concentration in solution, but adsorption capacity on zeolite, q_e, increase at higer zinc concentration in solution and pH value.
Keywords: Zincions, adsorption, zeolite, kinetic.

INTRODUCTION

Zeolite is a natural porous mineral in which the partial substitution of Si^{4+} by Al^{3+} results in an excess of negative charge. This is compensated by alkali and alkaline earth cations (Na^+, K^+, Ca^{2+} or Mg^{2+}). Zeolites have been used as adsorbents, molecular sieves, membranes, ion-exchangers and catalysts, mainly because zeolite exchangeable ions are relatively innocuous. Thus, zeolites are particularly suitable for removing undesirable heavy metal ions (e.g. lead, nickel, zinc, manganese, cadmium, copper, chromium and/or cobalt), radionuclides as well as ammoniacal nitrogen (ammonia and ammonium) from municipal wastewaters, metal plating facilities, electroplating, mining operations, fertilizers, battery manufacture, dyestuff, chemical pharmaceutical, electronic device manufactures and many others [1]. Most of heavy metals are highly toxic and are non-biodegradable, therefore they must be removed from the polluted streams in order to meet increasingly stringent

environmental quality standards. The removal of heavy metal cations using natural zeolites were studied by many authors [1][2][3][4][5][6][7][8][9][10].

Most of published paper on adsorption of metallic ions are aimed at assessing the adsorption capacity [1][2][5][6][8][9][10], and only a few attempts have been made to elucidate the mechanism of binding[11]. The adsorption mechanism depends strongly on the nature of the adsorbent. The aim of this work was to investigate the adsorption of zinc ions onto a natural zeolite (clinoptilolite) whereby the main parameters were the adsorption kinetics and the rate-determining step.

EXPERIMENTAL

Adsorbent

The natural zeolite - clinoptilolite was used in the recent study as an adsorbent for adsorption of heavy metals, such as zinc. The particle size range of the natural zeolite used in this study was 0.8 to 2.5 mm.

The chemical composition of natural zeolite are presented in Table 1.

Table 1. Chemical composition of zeolite samples

Typical chemical composition in % wt			
SiO_2	69.68	CaO	2.01
Al_2O_3	11.40	Na_2O	0.62
TiO_2	0.15	K_2O	2.90
Fe_2O_3	0.93	H_2O	13.24
MgO	0.87	P_2O_5	0.02
MnO	0.08	ratio Si/Al	4.0-5.2
Cation exchange per cation		K^+ 41 meq/100g Na^+ 16.10 meq/100g Ca^{2+} 67.14meq/100g Mg^{2+} 3.88 meq/100g	
Total cation exchange capacity		1.8-2.2 meq/g	

X-Ray Difractometer 6100 from Snimadzu was used to investigate the mineralogical structure of natural zeolite samples. This technique is based on observing the scattering intensity of an X – Ray beam hitting a sample as a function of incident and scattered angle, polarization, and wavelength or energy. The diffraction data obtained are compared to the database maintained by the *International Centre for Diffraction Data*, in order to identify the

material in the solid samples. The results of XRD (Fig. 1) shown that the natural zeolite contained clinoptilolite in the majority.
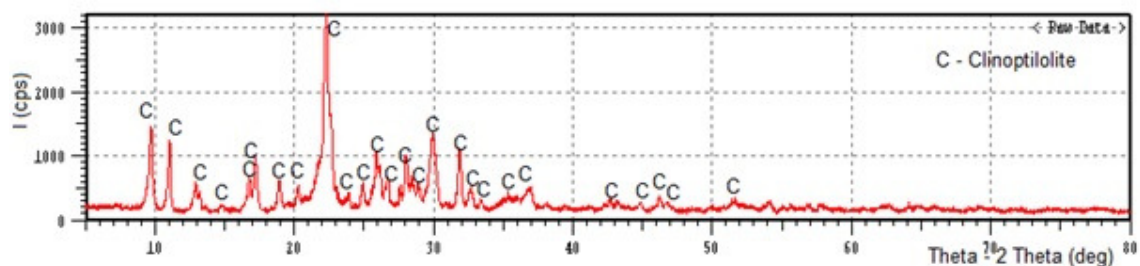

Fig. 1. X–Ray diffractionof natural zeolite

The surface morphology of natural zeolite was studied using a scanning electron microscope,VEGA3 LMU. This particular microscope is also fitted with a Inca 250 EDS system. EDS, stands for Energy Dispersive Spectroscopy, it is an analytical technique used for the elemental analysis of a sample based on the emission of characteristic X – Rays by the sample when subjected to a high energy beam of charged particles such as electrons or protons.

Micrographs of natural zeolite samples obtained from SEM analysis are given in Fig.2. The micrographs clearly show a number of macro-pores in the zeolite structure. The micrographs also show well defined crystals of clinoptilolite.
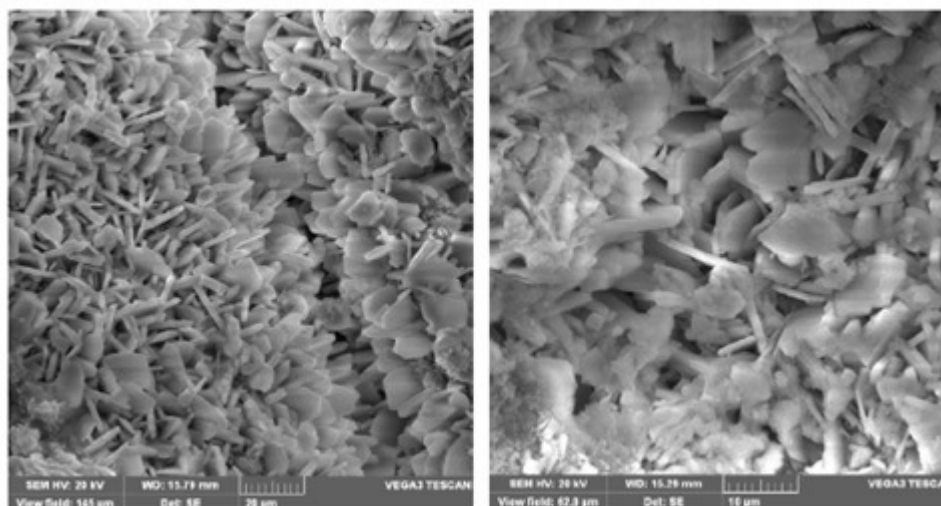

Fig. 2. Micrographs of natural zeolite samples obtained from SEM analysis

An electron beam was directed onto different parts of the samples in order to get a more accurate analysis (Fig.3) and the elemental composition of natural zeolite (clinoptilolite) are presented in Table 2.
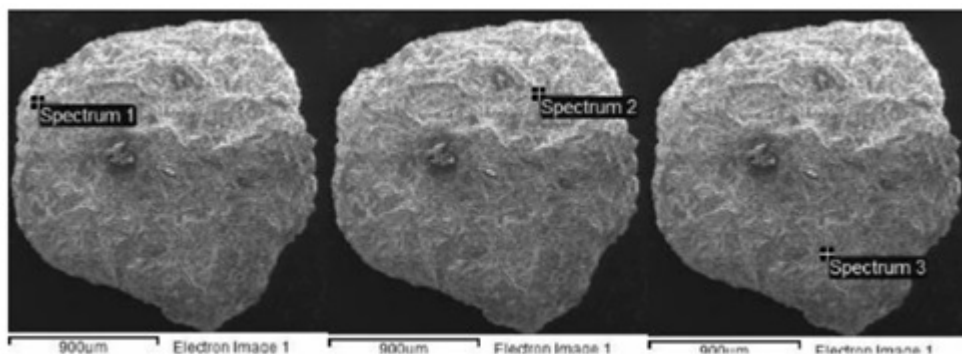
Fig. 3. EDS analysis showing the scanning method fornatural zeolite

Table 2. EDS analysis showing the elemental compositionfornatural zeolite

Element	Spect 1	Spect 2	Spect3	Average	Std. deviation
O	58.46	55.4	58.83	57.56	1.882
Na	0.27	0.15	0.3	0.24	0.079
Mg	0.72	0.66	0.77	0.72	0.055
Al	5.28	5.52	5.03	5.28	0.245
Si	29.55	31.36	29.47	30.13	1.068
K	2.73	2.96	2.44	2.71	0.26
Ca	1.9	2.42	1.66	1.99	0.388
Fe	1.1	1.53	1.5	1.38	0.24
Total	100	100	100	100	

Results of EDS analysis showed that the predominant exchangeable cations in natural zeolite (clinoptilolite) structure wereK^+ and Ca^{2+}.

Adsorbate

The heavy metal, Zn, was used as adsorbate in the recent investigations. Synthetic single component solutions of Zn^{2+}were prepared by dissolving a weighed mass of the analytical grade salt $ZnSO_4 \cdot 7H_2O$ in 1000ml distilled water.

Experimental procedure

Adsorption of zinc ions on zeolite was performed with synthetic single ion solutions of Zn^{2+} ions with different initial concentration. Initial pH of prepared solutions was adjusted by adding 2% sulfuric acid and controlled by 210 Microprocessor pH Meter. The experiments were performed in a batch mode in a series of beakers equipped with magnetic stirrers bycontacting a mass of zeolite with a certain volume of Zn^{2+}ionssolution.Zeolite sample and

aqueous phase were suspended bymagnetic stirrer at 400 rpm. The agitation time was varied up to 360 minutes. At the end of the predetermined time, the suspension was filtered and the filtrate was analyzed. The final pH value was also measured. All experiments were performed at room temperature on 20 ± 1^oC. The initial and remaining concentrations of metal ions were determined by Liberty 110, ICP Emission Spectrometer, Varian.Inductively coupled plasma atomic emission spectroscopy (ICP-AES) is an analytical technique used for the detection of trace metals. It is a type of emission spectroscopythat uses the inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element. The intensity of this emission is indicative of the concentration of the element within the sample.

Based on material balance, the adsorption capacity was calculatedby using the following expression [3]:

$$q_e = \frac{V(C_0 - C_e)}{m}, \ (mg/g) \tag{1}$$

where:q_e is the mass of adsorbed metal ions per unit mass ofadsorbent (mg/g),C_0 and $C_e$are the initial and final metal ionconcentrations (mg/l), respectivly, V is the volume of the aqueousphase (l) and m is the mass of adsorbent used (g).

Degree of adsorption, in percentage, is calculated as:

$$AD\% = \left(1 - \frac{C_e}{C_0}\right) \cdot 100 \tag{2}$$

Kinetic studies

Kinetic studies are important because they supply information about the process dynamics, that is, the adsorption rate, residence time and mass transfer parameters such as external mass transfer coefficients and intraparticle diffusivity. These parameters are essential in the design and operation of any adsorption column in waste water treatment plants. Therefore, kinetic studies help to evaluate the suitability of any material as a potential adsorbent in removing pollutants from solution [12].

A number of kinetic models were identified and used to describe the uptake process/mechanism. The models used in this investigation are the Pseudo second order kinetic model for chemisorption, Weber and Morris model about intraparticle diffusion and the film diffusion model as proposed by Furusawa and Smith.

-Pseudo-second order kinetic model

The pseudo second order kinetic model was used to investigate whether chemical reaction at the adsorption sites of zeolite was rate determining. The experimental data that fits

to this model indicate that chemical reaction is involved in the removal of heavy metals from solution, that is, chemisorption [13], [14].

The pseudo second order kinetic model is given by Eqs.3 and 4:

$$\frac{dq}{dt} = k_2(q_e - q)^2 \tag{3}$$

$$\frac{t}{q} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e} \tag{4}$$

Where q and q_e are the amount of metal adsorbed per unit weight of adsorbent (mg/g) at time t, and at equilibrium respectively. k_2 is adsorption rate constant.

 - Film transfer diffusion control (external mass transfer)

 Film transfer control was determined using a method proposed by Furusawa and Smith, 1973 [15],[16],[11],[17]. The change in metal concentration with respect to time is related to the external mass transfer coefficient, k_s (cm/s), by the Eq. 5:

$$\frac{dC_e}{dt} = -k_s S_s(C_e - C_s) \tag{5}$$

where C_e is the liquid phase solid concentration at a time t, C_s the liquid phase solute concentration at the particle surface; and S_s (1/cm) the specific surface area for mass transfer.

$$S_s = \frac{6m_s}{d_p \rho_t (1 - \varepsilon_p)} \tag{6}$$

where m_s (g/cm^3) is the sorbent mass concentration in the solution, dp is the diameter of the zeolite particles (cm), ρ_t is the density of solid phase (g/cm^3) and ε_p is the porosity of the zeolite particles.

 - Intraparticle diffusion model

 Weber and Morris, 1962 [18] theorized that the rate of intraparticle diffusion varies proportionally with the half power of time and is expressed as:

$$q_t = k_i \cdot t^{1/2} + c \tag{7}$$

where q_t (mg/g) is adsorbate uptake at time t, k_i is the rate constant of intraparticle transport (mg/g-t$^{1/2}$).

 The values of interception, c are related to the boundary layer thickness, i.e., the larger the value of the intercept, the greater is the boundary layer effect [13], [18].

RESULTS AND DISCUSSION

Effect of initial solution concentration

 The results of the kinetic experiments to measure the adsorption of cations from aqueous solutions onto the untreated natural zeolite as a function of initial concentration of Zn in solution and time are shown in Fig. 4. Single component solutions 400ml were mixed

with 5 g natural zeolite and agitated for 120 minutes at the temperature $20 \pm 1^{\circ}C$ and pH value 3,5. The concentration of the single component solution was 5, 25, 50, 200 and 400 mg/lof Zn^{2+}.
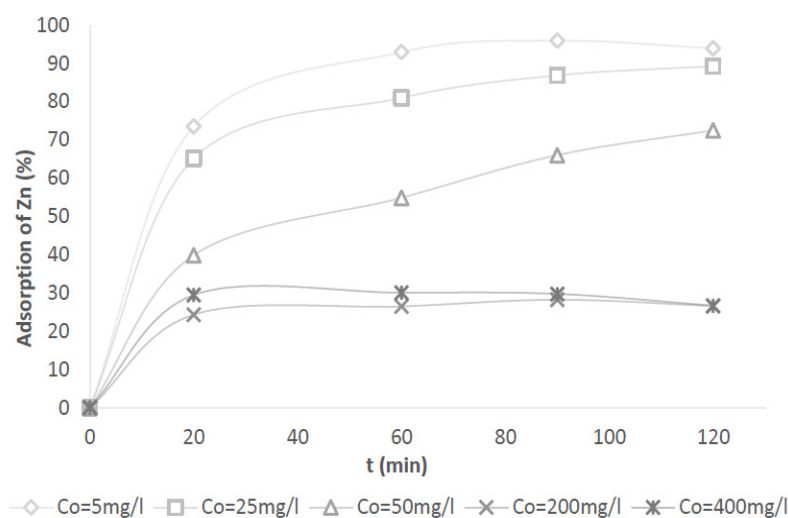

Fig. 4 Effect of initial Zn^{2+} concentration on the adsorption of zeolite

An increase in concentration generally results in an increase in the amount of zinc adsorbed and the rate of adsorption. This may be a result of an increase in collisions between the reactants, leading to the observed increase in reaction rate and capacity according to the *Collision Theory* [12]. The adsorption capacity will increase with an increase in initial concentration until the system reaches a saturation point, at which point further increase of the adsorbate (zinc) concentration will not result in any significant change in the amount adsorbed, q_e. Table 3 presents the results of this investigation.

Table 3: Effect of initial solution concentration on the adsorption capacity of natural zeolite

Heavy Metal	Initial Concentration C_o(mg/l)	Amount Adsorbed q_e (mg/g)	Percentage Adsorbed (%)
	5	0.376	94
	25	1.786	89.32
Zn	50	2.901	72.52
	200	4.256	26.62
	400	8.480	26.69

The above results indicate that the amount of zinc adsorbed by natural zeolite at equilibrium is dependent on the initial zinc concentration. The increase in the amount of zinc adsorbed as initial concentration increases is a consequence of an increase in theconcentration driving force. The concentration driving force is important because it is responsible for overcoming the mass transfer resistance associated with the adsorption of metals from solution by the zeolite [19]. Therefore, as initial concentration increases, the driving force also increases resulting in an increase in zinc uptake by the zeolite.

Table 3 also reveals that an increase in initial concentration not only results in an increase in the amount adsorbed (q_e) but a decrease in the efficiency of natural zeolite for the removal of Zn from solution. Motsi [11] also found a similar trend, that is, a decrease in efficiency, in their work on the adsorption of Cu, Mn, Zn and Fe from solution by clinoptilolite.

Effect of adsorbent mass

A series of kinetic experiments at different adsorbent masses, that is, 2, 5 and 10 g, were performed using fixed initial metal concentrations for the zinc cation (25 mg/l). The other conditions were 400ml solution agitated for 120 minutes at the temperature $20\pm1^{\circ}C$ and pH value 3.5.
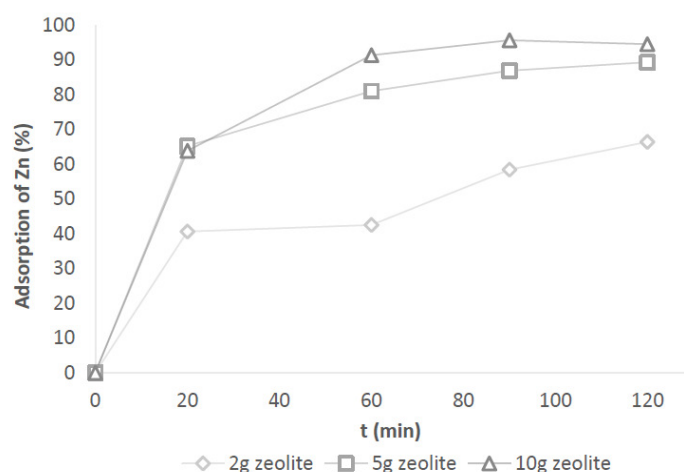

Fig. 5 Effect of adsorbent mass on the adsorption of zeolite

The plots of the amount of metal adsorbed versus time are shown in Fig.5. According to the percentage of zinc adsorbed from solution, we can see that an increase in adsorbent mass resulted in an increase in the adsorption of the zinc (Table 4). This is because as adsorbent mass increases more adsorption sites are available per unit mass of adsorbent added.

Table 4Effect of adsorbent masson the efficiency of natural zeolite for the removal of Zn from solution

Heavy metal	Adsorbent Mass (g)	Percentage Adsorbed (%)
	2	66.44
Zinc	5	89.32
	10	94.52

Effect of initial solution pH

The pH of the solution in contact with natural zeolite has an obvious impact on its ability to remove metals since the acidic solution can influence both the character of the exchanging ions and the character (structure) of the zeolite itself. Fig.6 shows that as solution pH decreases, zinc removal efficiency also decreases.
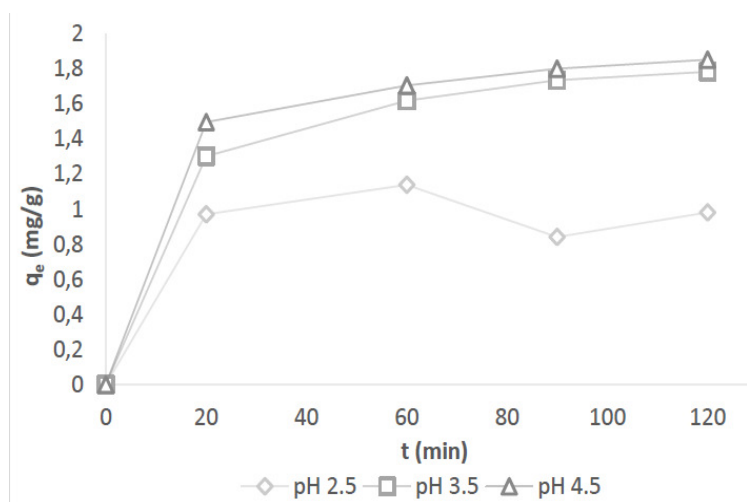

Fig. 6 Effect of pHsolution on the adsorption capacity of natural zeolite

That is because H^+ ions compete with zinc cations for the same exchange sites [20] and electrostatic repulsion between the zinc cations in solution and the protonated zeolite surface increases as more H^+ ions are adsorbed [21]. The efficiency of metal adsorption depends on solution pH levels. This is in agreement with results obtained by Moreno (2001) and Alvarez-Ayuso (2003) [22][20]. Fig.6 shows how the adsorption capacity of natural zeolite is affected by solution pH.

Kinetic modeling

Kinetic modelling was carried out to investigate the rate detemining step in the removal of zinc ions from solution by using natural zeolite.

-Pseudo-second order kinetic model

To test whether the rate of removal of heavy metals from solution by natural zeolite is controlled by chemical reactions (i.e. chemisorption) a number of conditions must be met. These conditions are [23]:

- The rate constant should be constant for all values of initial concentration of counter-ions,

- The rate constant should not change with adsorbent particle size,

- The rate constant is *sometimes* independent of the degree of agitation (stirring rate).

If any of these conditions are not satisfied, chemical reaction kinetics is not rate determining even if rate data is successfully fitted to the pseudo second order kinetic model.

One of the above conditions was tested, that is, whether the rate constant remains constant with a change in initial concentration on Zn^{2+} ion in solution. The results obtained for the adsorption of Zn^{2+} onto natural zeolite were fitted to Eq.4. This was achieved by plotting t/q versus t, as shown in Fig.7.
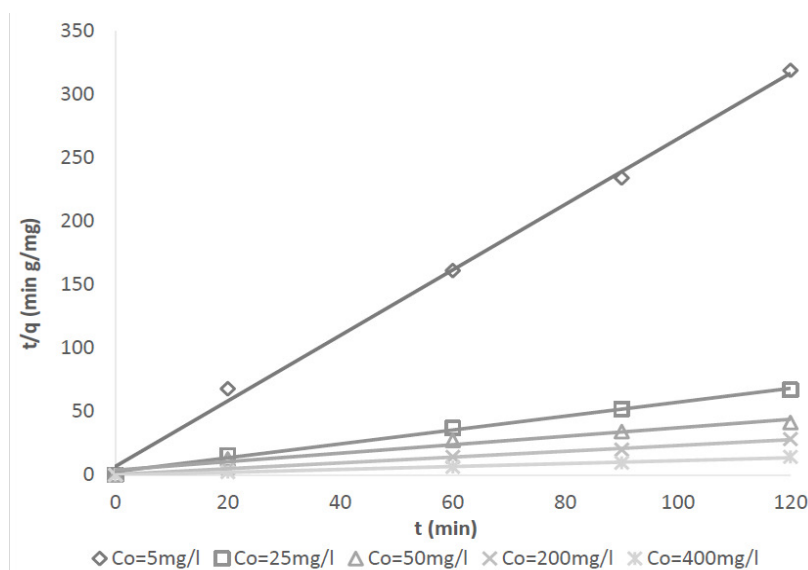

Fig. 7 Effect of initial Zn^{2+} concentration in solution on the reaction rate constant

Table 5 Variation of rate constant with different initial concentration

C_o (mg/l)	5	25	50	200	400
k_2	1.0086	0.1243	0.0303	0.2491	0.0519
q_e	0.3868	1.8215	2.9940	4.3630	8.7032
R^2	0.9974	0.9954	0.9668	0.9974	0.9925

The experimental data (Fig. 7) obtained for the effect of initial concentration on Zn^{2+} ion in solution gave a good fit to the pseudo second order kinetic model as expected, indicating that chemisorption does take place in the removal of zinc from solution by natural zeolite [11]. But from Table5, it is seen that the rate constant, k_2, for the removal of cations from solution, was not constant for different initial concentration on Zn^{2+} ion in solution. This lack of constancy is proof that even though the results gave a good fit to the kinetic model, the rate determining step is not chemisorption. Bektas and Kara (2004) found that the rate constant of the pseudo second order kinetic model varied for different agitation speeds (100 – 225 rpm) and adsorbent particle sizes (0.315-1.6 mm) at removing of lead from solution by clinoptilolite [24].

- Film transfer diffusion control (external mass transfer)

In a well-agitated batch system, the boundary layer surrounding the particle is much reduced, reducing the external mass transfer coefficient k_s, hence, intraparticular diffusion is more likely to be the rate determining step[16].

The results of the experiments were fitted to the model proposed by Furusawa and Smith and presented on Figs. 8, 9 and Table 6. Plotting $In[(C_e/C_o)-(1/ (1+m_sK))]$ vs. time, should give a straight line.The gradient of the straight line is $-[(1+m_sK)/ (m_sK)]k_sS_s$. The external mass transfer coefficient between the bulk liquid and outer surface of the zeolite particle, k_s can then be evaluated.
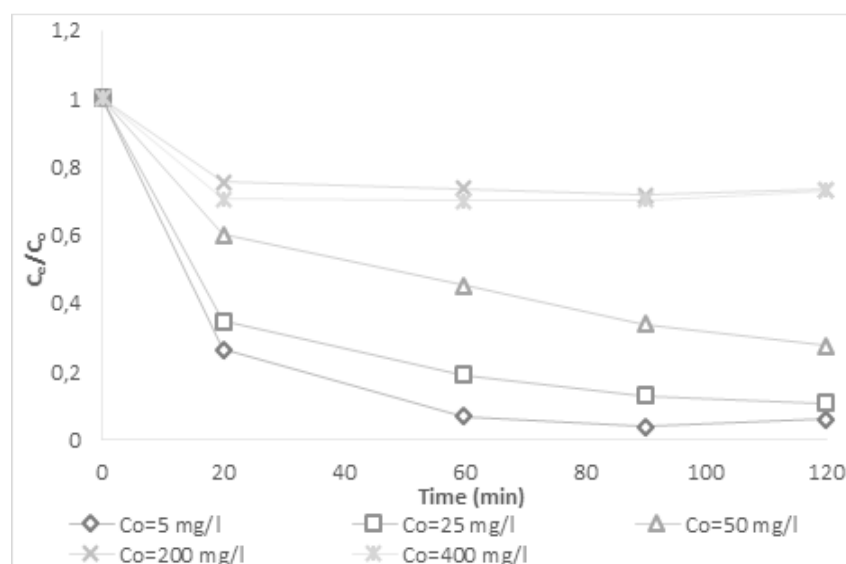

Fig. 8 External mass transfer diffusion model according C_e/C_o vs. time
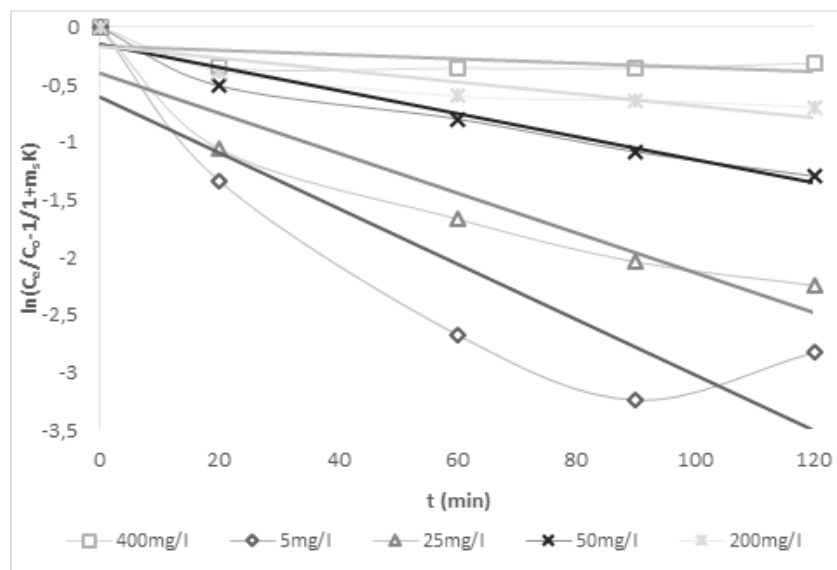
Fig. 9 Fittingexternalmass transfer diffusion model according $In[(C_e/C_o)-(1/(1+m_sK))]$ vs. time

Table 6 Calculated film mass transfer coefficients

C_o (mg/l)	5	25	50	200	400
k_s (cm/s)	0.00098	0.00070	0.00040	0.00021	0.00008
R^2	0.7924	0.8869	0.9474	0.8041	0.3578

From the external mass transfer coefficient,k_s, can be concluded that boundary layer surrounding the particle is reduced and similar at all initial Zn concentration and intraparticular diffusion is more likely to be the rate determining step. Correlation coefficient R^2 is different at all initial Zn concentration and according to R^2 film diffusion does not rate determining step in overall process.

- Intraparticle diffusion model

According to Weber and Morris, if the rate determining step isintraparticle diffusion, a plot of solute adsorbed against the squareroot of the contact time should yield a straight line passing throughthe origin. Also, the rate constant for intraparticle diffusion isobtained from the slope of the curve.
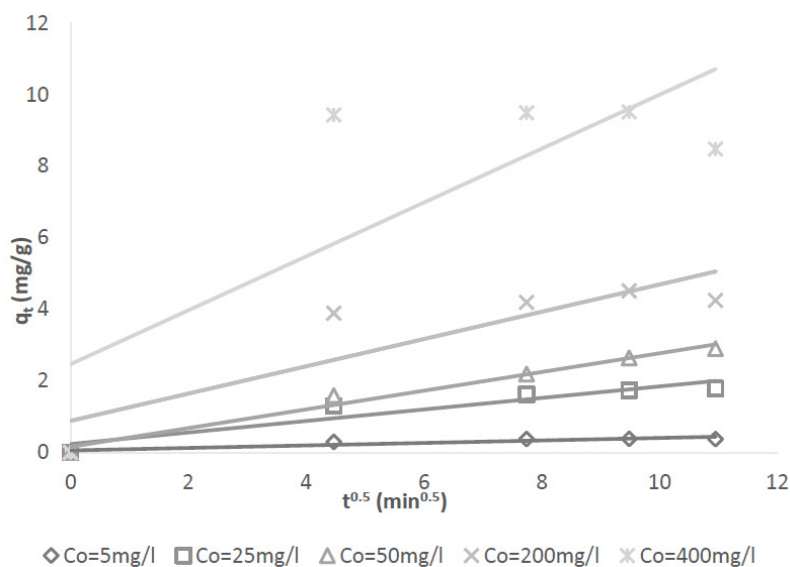
Fig. 10 Intraparticle diffusion control

Table 7 Calculated the rate constant of intraparticle transport

C_o (mg/l)	5	25	50	200	400
k_i	0.0345	0.1606	0.2611	0.3815	0.7531
R^2	0.8522	0.891	0.9791	0.7734	0.6305

According to this theory, C, the intercept gives an idea about the thickness of boundary layer, i.e., the larger the intercept, the greater the boundary layer effect. If intraparticle diffusion occurs, then q_t versus $t^{0,5}$ will be linear and if the plot passes through the origin, then the rate determining process is only due to the intraparticle diffusion. Otherwise, some other mechanism along with intraparticle diffusion is also involved [25], [26].

In this case the intercept gives values different from zero,especially at higher concentrations of Zn ions. These values indicate that intraparticle diffusion does not control the overall rate of adsorption in early stages [25]. And as can be seen from Fig. 10, the graphic is linear, but the plot not pass through the origin and can be concluded that the intraparticle diffusion was not the only rate determining mechanism in the adsorption process. In Table 7 are given the rate constants for intraparticle diffusion and correlation coefficient R^2.

CONCLUSION

The adsorption of zinc ions from diluted solution onto natural zeolite occurs efficiently.

The adsorption kinetics is reasonably fast. It means that in the first 20 min approximately 78% of Zn^{2+} is adsorbed from single ion solutions.

From the kinetic data can be concluded that adsorption of zinc ions from solution by natural zeolite is more efficiency at high pH value and adsorbent mass, and at lower zinc concentration in solution, but adsorption capacity on zeolite, q_e, increase at higer zinc concentration in solution and pH value.

The experimental data obtained for the effect of initial concentration on Zn^{2+} ions in solution gave a good fit to the pseudo second order kinetic model. But the rate constant, k_2, for the removal of cations from solution, was not constant for different initial concentration on Zn^{2+} ions in solution and can concluded that the rate determining step is not chemisorption.

According to the models proposed by Furusawa and Smith and by Weber and Morris it can be concluded that intraparticular diffusion is more likely to be the rate determining step. Except at higher concentration of zinc ions in solution, where film diffusion may take a part in the rate determining step.

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