*Int. J. Environ. Res., 9(3):1001-1010, Summer 2015*
*ISSN: 1735-6865*

# Kinetics and Thermodynamics of Lead Adsorption from Aqueous Solutions Onto Iranian Sepiolite and Zeolite

**Sharifipour, F.[1], Hojati, S.[1*], Landi, A.[1] and Faz Cano, A.[2]**

[1]Department of Soil Science, College of Agriculture, Shahid Chamran University, Ahvaz 6135783151, Khuzestan, Iran

[2] Research Group for Sustainable Use, Management and Reclamation of Soil and Water, Technical University of Cartagena, Murcia, Spain

Received 10 Sep. 2014; Revised 14 Nov. 2014; Accepted 14 Nov. 2014

**ABSTRACT:** A good understanding of adsorption equilibrium and thermodynamics is required to design and operate an adsorption process. This study was conducted to assess the adsorption percentage of $Pb^{2+}$ ions as a function of contact time, solution pH and temperatures, and adsorbent dosage through a series of batch experiments. The methods including zeta potentials, specific surface area measurements and the analysis of adsorption kinetics thermodynamics were introduced to analyze the adsorption mechanisms of the $Pb^{2+}$ ions on sepiolite and zeolite minerals. Results showed that the sorption of $Pb^{2+}$ on Iranian sepiolite and zeolite is a relatively fast process with the equilibrium being attained within 6 hours after the sorbents application. Sepiolite and zeolite yield adsorption capacities ($Q_e$) was found to be 30.5 and 24.4 mg/g for lead ions, respectively. The results also showed that the adsorption of lead metal ions onto sepiolite and zeolite minerals increased with contact time, solution pH, and the amount of adsorbent; but decreased as the temperature of the system increased. The experimental data fitted very well the pseudo-second- order kinetic model. The thermodynamics parameters such as Gibbs free energy, enthalpy, and entropy were also evaluated. The negative values of enthalpy ($\Delta H°$) illustrated the exothermic nature of $Pb^{2+}$ sorption. The activation energy (Ea) of $Pb^{2+}$ sorption onto the sepiolite (17.00 kJ/mol) and zeolite (7.60 kJ/mol) indicated that $Pb^{2+}$ ions were more strongly sorbed onto sepiolite than zeolite.

**Key words:** Sepiolite, zeolite, pH, Thermodynamics, kinetics.

## INTRODUCTION

Environmental pollution from industrial waste streams is one of the hot topics of environmental sciences (Huang *et al*., 2011; Liang *et al*. 2013). Industrial waste streams frequently contain high levels of heavy metals; thus, in order to avoid water pollution, treatment is needed before disposal (Kocaoba and Akyuz, 2005). Lead is one of the most toxic heavy metals being released into the environment from battery manufacturing, acid metal plating and finishing, ammunition, tetraethyl lead manufacturing, ceramic and glass industries, printing, painting, dying, etc (Wang *et al*., 2007). Lead poisoning in human causes severe damage to the kidney, central nervous system, reproductive system, liver, basic cellular processes and brain functions (Wang *et al*., 2007). The toxic symptoms are anemia, insomnia, headache, dizziness, irritability, weakness of muscles, hallucination and renal damages (Naseem and Tahir, 2001).Due to the relative simplicity of application, adsorption techniques can be considered as a useful method for removing dissolved heavy metals from liquid wastes (Potgieter *et al*., 2006). However, the main disadvantage of the adsorption technique is the high price of the adsorbents (e.g. activated C), which increase the price of wastewater treatment. Because of the abundance and low price of natural mineral sorbents, their usage for wastewater treatments is increasing (Huang *et al*., 2011; Hojati and Landi, 2013).

Sepiolite and zeolite are clay minerals widely distributed in arid and semiarid regions of the world (Singer, 1989). Sepiolite is a fibrous hydrated magnesium silicate and a natural clay mineral comprised of two tetrahedral silica sheets enclosing a central magnesia sheet. The silica sheets are segmented and inversion of silica sheets gives rise to tunnels in the structure. These characteristics make sepiolite a powerful adsorbent for heavy metals. In addition, isomorphic substitutions in the tetrahedral sheets of the lattice of the sepiolite, such as $Al^{3+}$ for

---

*Corresponding author E-mail: s.hojati@scu.ac.ir

$Si^{4+}$, form negatively charged adsorption sites, which are occupied by exchangeable cations that compensate for the electrical charge (Murray, 2000; Galan, 1996).

The primary building block of zeolite is the tetrahedron, the center of which is occupied by a silicon or aluminum atom, with four atoms of oxygen at the corners. The ion-exchange capacity is basically a function of the degree of substitution of aluminum for silicon in the framework structure. The greater the substitution, the greater the charge deficiency, and the greater the number of cations required for electrical neutrality (Bernal and Lopez-Real, 1993; Wang and Peng, 2010).

Based on the above structural characteristics, both zeolite and sepiolite are capable of exchanging ions with external media. Previous studies showed that both sepiolite (Brigati *et al*., 1996; Brigati *et al*., 2000; Bektas *et al*., 2004; Liang *et al*., 2013) and zeolite (Ahmed *et al*., 1998; Zou *et al*., 2006; Inglezkias *et al*., 2007; Yang *et al*., 2011; El-Makkawi and Salim, 2014) can retain significant amount of $Pb^{2+}$ ions from aqueous solutions. The main core of these studies is that parameters such as ionic strength, pH, metal ions concentration and size, as well as the concentration of other adsorbing species and complexing ions or ligands play key roles in the adsorption process. However, for the process design and control of adsorption systems, it is important to understand the underlying mechanism that results in the dynamic behavior of the system. As a result, the study of the kinetics and thermodynamics of the adsorption process can provide such valuable information (Adebowale *et al*., 2008; Boparai *et al*., 2011). Due to the abundance and low cost of the minerals sepiolite and zeolite in arid and semi-arid regions of the world (e.g. Iran), along with their chemical and mechanical stability, they can be used to remove hazardous materials from waste waters (Wang *et al*., 2008; Kragovic *et al*. 2012). Although efficiency of natural zeolite and sepiolite for heavy metals removal is well known; little information is available about the Iranian counterparts and no comparative study was carried out to investigate the ability of sepiolite and zeolite to remove Pb from aqueous solutions. This study aims to (1) investigate the influence of factors such as contact time, initial pH of suspension, suspension temperature, and dose of adsorbents on removal capacity of sepiolite and zeolite for lead ions, (2) compare removal efficiency of zeolite and sepiolite minerals for lead ions, (3) determine thermodynamic parameters of the Pb sorption reactions, and (4) investigate the effects of temperature on the kinetics of Pb sorption onto zeolite and sepiolite.

## MATERIALS & METHODS

Sepiolite and zeolite samples used in this study were taken from two mines in Fariman and Semnan regions, northeastern and central Iran, respectively. The chemical composition and physicochemical characteristics of the minerals used in this study are given in Table 1.

The mineralogical composition of the samples was determined by a Philips PW 1840 X-ray diffractometer, and the semi-quantitative analysis was based on the XRD pattern of non-oriented powder sample using the method described by Schultz (1965) (Fig. 1). Total elemental analysis of sepiolite and zeolite minerals was determined using X-ray Fluorescence Spectrometer, Bruker S4 Pioneer. The specific surface area and cation

**Table 1. Chemical composition and physicochemical properties of sepiolite and zeolite samples (20-53 µm) employed in the study.**

| Property | Sepiolite | Zeolite |
|---|---|---|
| **Chemical Composition** | | |
| $SiO_2$ (%) | 55.32 | 68.85 |
| $Al_2O_3$ (%) | 0.30 | 10.34 |
| MgO (%) | 15.73 | 0.59 |
| $Na_2O$ (%) | 0.02 | 4.71 |
| $K_2O$ (%) | 0.01 | 2.33 |
| $TiO_2$ (%) | 0.02 | 0.18 |
| MnO (%) | 0.00 | 0.00 |
| CaO (%) | 2.74 | 0.27 |
| $P_2O_5$ (%) | 0.00 | 0.01 |
| $Fe_2O_3$ (%) | 0.59 | 1.21 |
| $SO_3$ (%) | 0.00 | 0.00 |
| LOI (%) | 25.11 | 10.13 |
| Total (%) | 99.84 | 98.61 |
| **Physicochemical characteristics** | | |
| Specific surface area ($m^2$/g) | 179.9 | 39.9 |
| Specific total volume pore ($cm^3$/g) | 0.378 | 0.154 |
| Cation exchange capacity (cmol (+)/kg) | 11.8 | 163.1 |

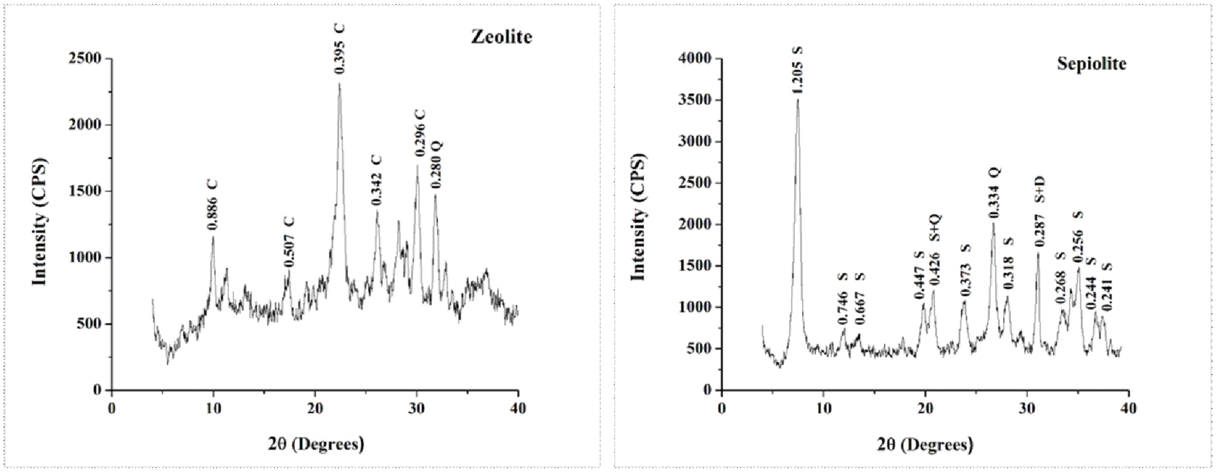

**Fig. 1. XRD pattern analysis of sepiolite and zeolite minerals used in the study (S: sepiolite; D: Dolomite; Q: Quartz; C: Clinoptilolite).**

exchange capacity of the samples were measured by $N_2$-BET sorption analysis and $NH_4$-acetate method, respectively. All chemicals employed in this study were analytical grade with no pretreatment.

Since there is no experimental method for determining both the surface potential and stern layer potential, the zeta potential is the measurable surface potential at the shear plane between the particle and the surrounding liquid (Kara *et al*. 2003). Accordingly, the zeta potentials of sepiolite and zeolite suspensions were measured as a function of equilibrium pH ranging from 2-10 using a ZEN 3600 equipped with a microprocessor unit. The unit automatically calculates the electrophoretic mobility of the particles and converts it to the zeta potential. A suspension of 0.1 g sepiolite or zeolite in 80 mL distilled water, was shaken in an orbital shaker incubator and rinsed for 24 h at 20±1 C. The average of 5 measurements was used to represent the measured potential. The applied voltage during the measurements varied from 50 to 150 mV (Demirbas *et al*., 2007).

Batch adsorption is a simple technique commonly used to assess the adsorptive capacities of natural and synthetic sorbents. Aside from the ease of manipulation, it helps obtain information about the efficiency of a given sorbent to remove adosrbate(s) in static conditions (Sdiri *et al*., 2012). The experiments were performed to investigate the effect of initial pH of solution (2, 3, 4, 5, 6, 7, 8, and 9), dose of sorbents (2, 4, 8, 16, and 20 g /l), contact time (5, 10, 20, 30, 60, 120, 240, 480, 720, 1440, and 2880 minutes) and temperature (20, 30 and 40 ºC), on the adsorption process.

In order to investigate the effects of initial pH of solution on the percentage of removal of Pb from aqueous solutions, a constant mass of sepiolite or zeolite (as adsorbent) (0.1 g) and 50 ml of 300 mg/l concentration of Pb solution (after adjustment of its pH to the desired value using dilute NaOH and HCl solutions) was added to 80 ml polypropylene centrifuge tubes. The mixtures were shaken vigorously on an orbital shaker (200 rpm) at 2880 minutes. The bottles were removed from the shaker and centrifuged at 2500 rpm for 25 min. Then, Pb concentration in the supernatants was measured using a Savaant GBC Atomic Absorption Spectrophotometer (AAS). The detection limit of AAS machine for Pb was 9 ppb.

The above experiments were also carried out in varying contact times and temperatures (in a thermostatic shaker bath) and adsorbent dose while keeping all other parameters constant.

The blank experiments were simultaneously carried out without addition of adsorbent to test possible adsorption and/or precipitation of Pb onto the container walls. Preliminary experiments showed that metal losses due to the adsorption onto the container walls were negligible.

The amount of Pb (II) adsorbed onto sepiolite and zeolite minerals was calculated from the difference between the initial and the residual concentration in solution as follows:

$$Q_e = \frac{\left[(C_0 - C_e)\right] \cdot V}{M} \tag{1}$$

where $C_0$ and $Ce$ (mg/l) are the initial and final (equilibrium) concentrations of Pb, respectively, V (ml) is the volume of solution and M is the mass of sorbent (mg). All measurements were carried out with three replications.

Satisfactory conformity between experimental data and the model predicted values was assessed using correlation coefficient ($r^2$) and non-linear Chi-square ($\chi^2$) criteria. The $\chi^2$values were calculated from Eq. (2):

$$\chi^2 = \sum \frac{[Q_e - Q_{e(Calc)}]^2}{Q_{e(Calc)}} \qquad (2)$$

where, $Q_e$ and $Q_e^{'}$ are observed and model estimated amounts of Pb which sorbed at equilibrium (mg/g), respectively; and *n* is the number of measurements. If model estimated data are similar to those of the experimental data, $\chi^2$ would be small and if they differ, it would be large.

A number of kinetic models have been described to find suitable mechanism explaning solid/liquid adsorption systems, in which pseudo first-order and pseudo second- order kinetic models are the two most widely applied models. These two kinetic models were used to correlate experimental data for the adsorption process of Pb (II) on sepiolite and zeolite.

Pseudo-first-order equation (Eq. 3) is the most popular kinetics equation. The equation assumes that the number of metal ions outnumbers the number of adsorption sites on clay surface. The differential form of equation is:

$$\frac{dQ}{dt} = K_1(Q_e - Q_t) \qquad (3)$$

After definite integration by applying the conditions $Qt$ =0 at t = 0 and $Qt = Qt$ at t = t, Eq. (3) becomes the following (Lagergren, 1898):

$$Ln(Q_e - Q_t) = LnQ_e + K_1 t \qquad (4)$$

where *t* and $K_1$ are the time and rate constant of the equation (1/min), respectively. The adsorption rate constant $K_1$, can be determined experimentally by plotting of $Ln(Q_e - Q_t)$ versus t.

The second-order equation (Eq. 5) is in the following form:

$$Q = K_2 Q_e^{\,2} t \qquad (5)$$

The differential equation is as follows:

$$\frac{dQ_t}{dt} = \frac{K_2(Q_e - Q_t)^2}{1 + K_t} \qquad (6)$$

After definite integration by applying the conditions $Qt$ =0 at t = 0 and $Qt = Qt$ at t = t, Eq. (6) becomes the following (Ho and McKay, 1999):

$$\frac{1}{Q_e - Q_t} = \frac{1}{Q_e} + K_t \qquad (7)$$

When this is linearized, it gives:

$$\frac{t}{Q_t} = \frac{1}{K_2 \cdot Q_e^{\,2}} + \frac{t}{Q_e} \qquad (8)$$

where $K_2$ (g/mg min) is the rate constant of the second-order equation and can be determined from the slope and intercept of the plot $\frac{t}{Q_t}$ versus t (Eq. 8).

The activation energy of $Pb^{2+}$ adsorption on sepiolite and zeolite minerals was calculated using Arrehenius equation as expressed below:

$$k_2 = k \exp(-E_a/RT) \qquad (9)$$

where k is the temperature-independent factor (g / mg min), $E_a$ the activation energy of sorption (KJ/ mol), *R* the universal gas constant (8.314 J /mol K) and *T* the solution temperature (K).

Rate constants of Pb adsorption on sepiolite and zeolite minerals were determined at 20, 30 and 40 $^0$C using the pseudo- second order kinetic model. Then using Arrhenius equation parameters, adsorption type and the temperature independent rate parameters were determined. A plot of $\ln k_2$ versus $1/T$ yields a straight line, with slope $-E_a/R$.

Thermodynamic parameters of sorption including Gibbs free energy ($\Delta G^0$), change in enthalpy ($\Delta H^0$) and change in entropy ($\Delta S^0$) were calculated using the following equations (Eqs. 10-12:

$$\Delta G^0 = -RT \ln K_0 \qquad (10)$$

$$Ln\, K_0 = \Delta S^0/R - \Delta H^0/RT \qquad (11)$$

$K_0$ can be defined as:

$$K_0 = C_{solid} / C_{liquid} \qquad (12)$$

where $C_{solid}$ is the amount of Pb adsorbed by sepiolite or zeolite at equilibrium and $C_{liquid}$ is the equilibrium concentration of Pb in solution. According to Eq. (11), $\Delta S^0$ and $\Delta H^0$ parameters can be calculated from the slope and intercept of the plot of $Ln\, K_0$ versus $1/T$, respectively.

## RESULTS & DISCUSSION

The pH of solution is one of the most important parameters affecting metal adsorption onto adsorbents. The effect of pH on the removal efficiency of Pb (II) by sepiolite and zeolite particles is presented in Fig. 2. The adsorption of Pb (II) ions onto the both minerals is lowest at pH = 3, but increases with an increase in pH of the solution. The low adsorption percentage of $Pb^{2+}$ at lower pH values could be explained by the competition between $H^+$ and $Pb^{2+}$ ions on the available exchange sites of the minerals (Sari *et al.*, 2007; Wang *et al.*, 2008).

In general, protons can mainly compete with metal cations for sorption variable charge sites (Eloussaif and Benzina, 2010; Hojati and Landi, 2013). Due to their structure and morphology, Sepiolite and zeolite have a great number of terminal silica tetrahedrons present in their external surfaces and consistently a great number of silanol groups (Kocaoba and Akyuz, 2005). At low pH values (pH 2–6), the low adsorption observation could be attributed to the increase in

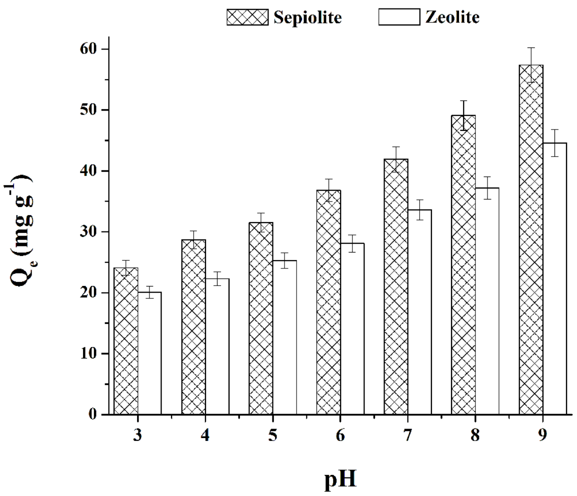

**Fig. 2. Effect of the initial pH of suspension on the percentage removal of $Pb^{2+}$ ions.**

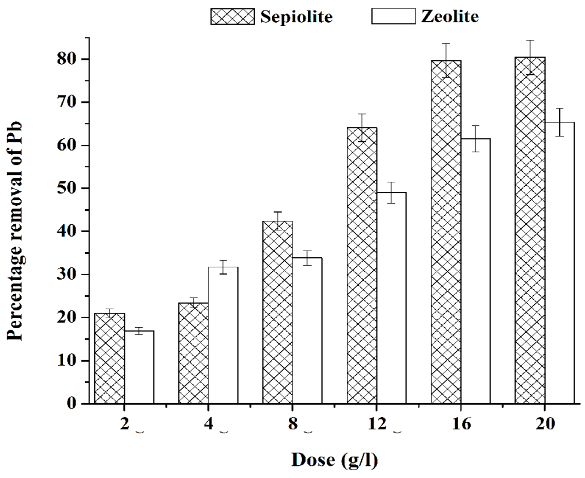

**Fig. 4. Effect of sepiolite and zeolite dose of application on percentage removal of $Pb^{2+}$ ions.**

positive charge density on the surface sites of sepiolite and zeolite minerals and thus, electrostatic repulsion occurs between $Pb^{2+}$ ions and the edge groups with positive charge ($Si\text{-}OH_2^+$) on the surface of zeolite and sepiolite particles as follows:

$$Si\text{-}OH + H^+ \dashrightarrow Si\text{-}OH_2^+ \quad (13)$$

$$Si\text{-}OH + OH^- \dashrightarrow Si\text{-}O^- + H_2O \quad (14)$$

Furthermore, at low pH values, where there is an excess amount of $H_3O^+$ ions in the solution, competition between the positively charged hydrogen ions and the lead ions for the available adsorption sites on the clay surfaces increases. Therefore, the efficiency of removal by both sepiolite and zeolite minerals decreases. Therefore, the decrease in sorption with the decrease in pH has to be mainly attributed to the suppression of sorption on these groups.

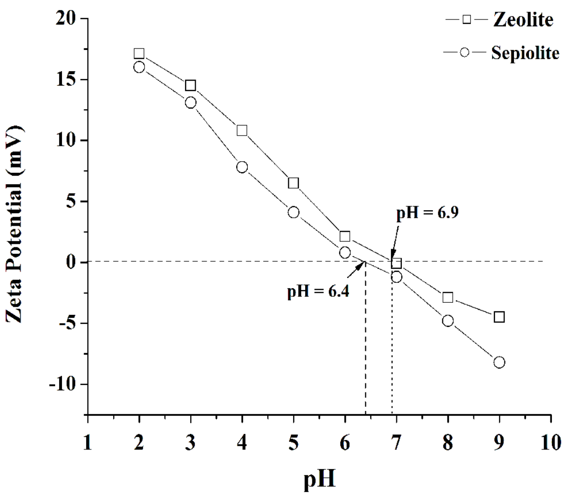

**Fig. 3. Zeta potential of sepiolite and zeolite particles as a function of equilibrium pH.**

The sepiolite and zeolite used in this study have an experimental PZC of 6.4 and 5.9, respectively (Fig. 3). Therefore, at a pH value above their PZC, the net charge on sepiolite and zeolite becomes negative while at a pH value below their PZC the net surface charge becomes positive (Eqs. 13 and 14). Based on this, the negative charges increase with the increase in the solution pH. Hence, the adsorbent gains a high charge resulting from the spread of isomorphous substitution in tetrahedral and octahedral sheets for sepiolite and zeolite. It could also be concluded that both sepiolite and zeolite particles have a higher adsorption affinity to adsorb metal cations at high pH values. As the pH increases and the balance between $H_3O^+$ and $OH^-$ becomes equal, more of the positively charged metal ions in the solution are adsorbed on the negative clay surface and; thus, the removal percentage of the metal ions increases. Heavy metal ions tend to form a precipitate at pH higher than 6.0, and therefore the adsorption of $Pb^{2+}$ ions by both zeolite and sepiolite minerals are difficult to quantify at pH values higher than 6.0; the “true” adsorption at this pH is masked by precipitation (McKay *et al.*, 1985).

The amount of adsorbent is an important factor, which determines the sorption capacity of an adsorbent for a given initial concentration of adsorbate (Chen and Wang, 2007, Hamidpour *et al.*, 2010; Hojati and Khademi, 2013). The influence of sepiolite and zeolite dosage on the removal efficiency of Pb is given in Fig. 4. As expected, the removal percentage of Pb increases as the amount of the sepiolite and zeolite increases. With increasing adsorbent dosage, more surface area is available for adsorption due to increase in active sites on the adsorbent and thus making penetration of metal ions to the sorption sites easier (Kaya and Ören,

**Table 2. Rate constants of Pb adsorption on sepiolite and zeolite particles as estimated from the pseudo first- and second-order kinetic models at different temperatures.**

| | | Pseudo first-order | | | | Pseudo second-order | | | |
|---|---|---|---|---|---|---|---|---|---|
| Temp. (°C) | $Q_e$ (Experiment) (mg/g) | $K_1$ (1/min) | $Q_e$ (calculated) (mg/g) | $R^2$ | $\chi^2$ | $K_2$ (g/mg min) | $Q_e$ (calculated) (mg/g) | $\chi^2$ | $R^2$ |
| Sepiolite | | | | | | | | | |
| 293.15 | 30.5 | 0.0046 | 11.29 | 0.870 | 32.68 | 0.0032 | 31.25 | 0.018 | 0.999 |
| 303.15 | 27.6 | 0.0023 | 10.69 | 0.827 | 26.74 | 0.0039 | 28.57 | 0.032 | 0.999 |
| 313.15 | 23.0 | 0.0046 | 7.46 | 0.788 | 32.37 | 0.0050 | 23.80 | 0.026 | 0.999 |
| Zeolite | | | | | | | | | |
| 293.15 | 24.4 | 0.0046 | 8.12 | 0.842 | 32.64 | 0.0045 | 25.00 | 0.014 | 0.999 |
| 303.15 | 23.2 | 0.0023 | 8.33 | 0.797 | 26.54 | 0.0050 | 23.80 | 0.015 | 0.999 |
| 313.15 | 21.0 | 0.0046 | 7.43 | 0.749 | 24.78 | 0.0055 | 21.27 | 0.003 | 0.999 |

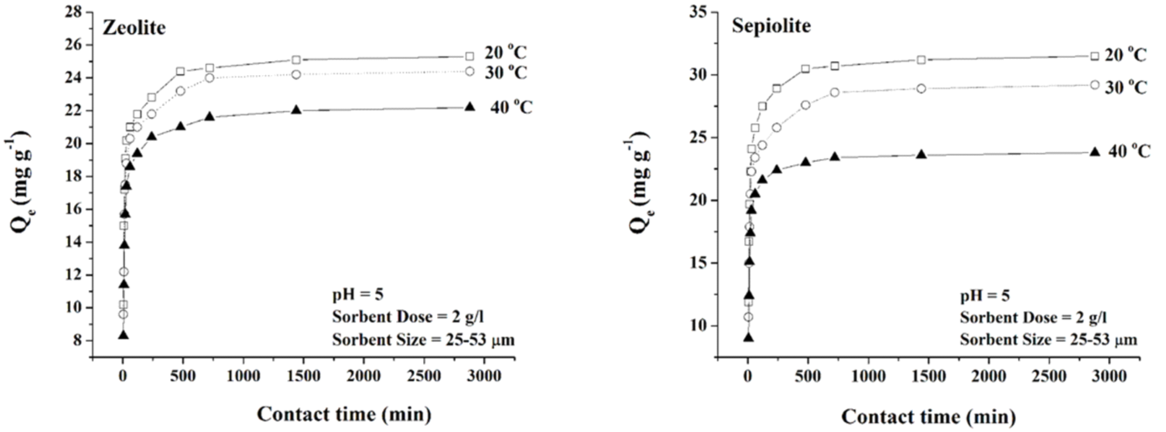

**Fig. 5. Effects of contact time and suspension temperature on the adsorption capacity of sepiolite and zeolite particles for $Pb^{2+}$ ions.**

2005; Sari *et al*. 2007). The results also clearly indicate that the removal efficiency of lead ions by both sepiolite and zeolite minerals increases up to the optimum dosage beyond which the removal efficiency is negligible. Contact time is an important parameter because it can reflect the adsorption kinetics of an adsorbent for a given concentration of the adsorbate (Wang *et al.*, 2007). Fig. 5 shows the effect of contact time on the adsorption capacity of sepiolite and zeolite for Pb(II) ions. This Figure shows that the adsorption capacities of zeolite and sepiolite for Pb(II) ions increase with a rise in the contact time, indicating that the adsorption process is highly time dependent (Potgieter *et al.*, 2006; Sdiri *et al.*, 2012; Hojati and Landi, 2013).

Kinetic studies also indicated that Pb (II) adsorption was characterized by a rapid initial adsorption (with about 80% of the adsorption capacity realized within 1 h) followed by a much slower, continuous uptake. A 6 hour contacting period was found to be sufficient to achieve equilibrium and that further increase of the contact duration did not influence the sorption process (Kubilay *et al.*, 2007; Gupta and Bhattacharyya, 2011).

Predicting the kinetic models for a given adsorption process is probably the most important factor in adsorption system design (Gupta and Bhattacharyya, 2011). The theoretical $Q_{e\,(\text{calculated})}$ values estimated from the pseudo-first order model gave significantly different values compared to experimental values, the correlation coefficients being also low (Table 2). These results showed that the pseudo-first order kinetic model did not describe the sorption systems well (Fig. 6 and 7). The correlation factors are high for the adsorption of $Pb^{2+}$ cations onto the sepiolite and zeolite. Moreover, the values of $Q_{e\,(\text{calculated})}$ estimated from the pseudo-second order model are close to those experimentally found (Table 2). Therefore, it could be suggested that the adsorption of $Pb^{2+}$ ions onto both sepiolite and zeolite minerals follows the pseudo-second order model better than the pseudo-first order one. Our findings are in agreement with the results reported by other workers (Aytas *et al.*, 2004; Dragan and Dinu, 2009; Humelnico *et al.*, 2011).

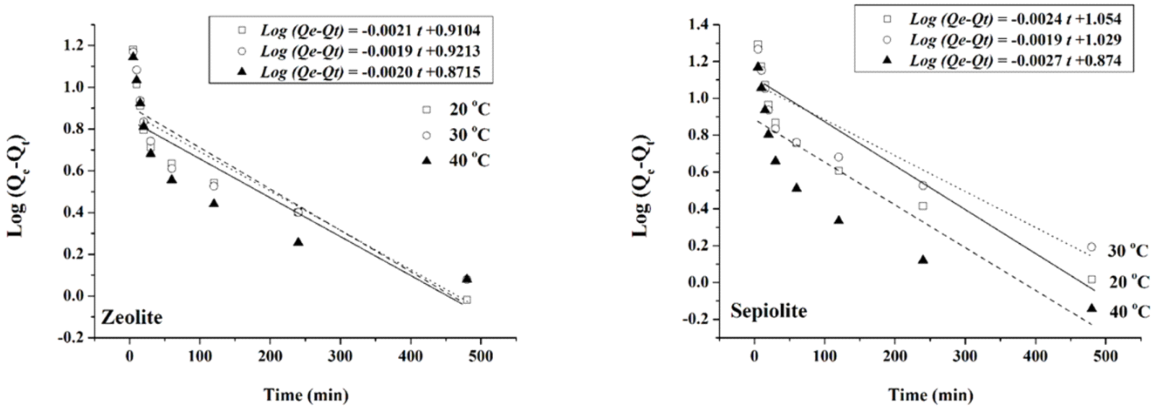

**Fig. 6. Pseudo first-order plots for the removal of $Pb^{2+}$ ions using sepiolite and zeolite at different temperatures.**

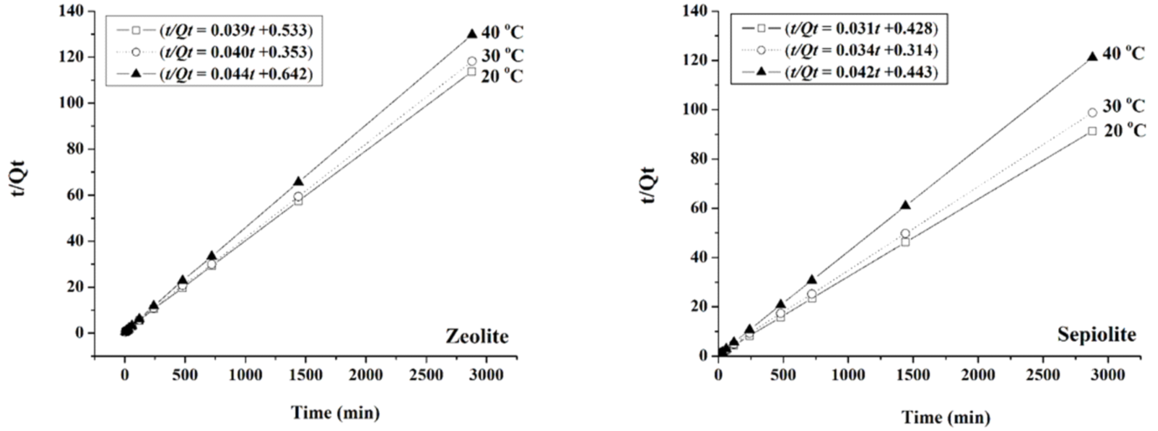

**Fig. 7. Pseudo second-order plots for the removal of $Pb^{2+}$ ions using sepiolite and zeolite at different temperatures.**

**Table 3. Comparison of the maximum adsorption capacities (Qe) of Pb on different clays.**

| Clays | $Q_{max}$ (mg/g) | References |
|---|---|---|
| Fariman sepiolite | 31.5 | This Study |
| Semnan zeolite | 25.3 | This Study |
| Wyoming bentonite | 31.1 | Gupta and Bhattacharyya (2008) |
| Georgia kaolinite | 11.5 | Gupta and Bhattacharyya (2008) |
| Zeolite | 27.7 | Sprynskyy *et al.* (2006) |
| Palygorskite | 62.1 | Potgieter *et al.* (2006) |
| Turkish sepiolite | 93.4 | Bektas *et al.* (2004) |

The maximum adsorption capacities ($Q_e$) calculated from the pseudo-second order kinetic model is comparable with those reported in literature (Table 3). The dissimilarities are due to the type of sepiolite and zeolite we used, and due to the preparation process which was different from other studies. Also, the experimental conditions employed in this study, such as Pb concentration, background solution composition, pH values, size of sorbents and the temperatures were different from those employed in other studies.

As Fig. 5 shows, by increasing temperature from 20 to 40 $^0$C, the adsorption capacities of sepiolite and zeolite particles for the lead ions decrease, indicating that at elevated temperatures less metal sorption onto the minerals takes place. The decrease in the removal efficiency of $Pb^{2+}$ions with the rise in temperature was probably due to an increase in desorption of $Pb^{2+}$ions from the minerals interface to the solution. This also confirms that at high temperatures adsorption of $Pb^{2+}$onto sepiolite and zeolite could be considered an

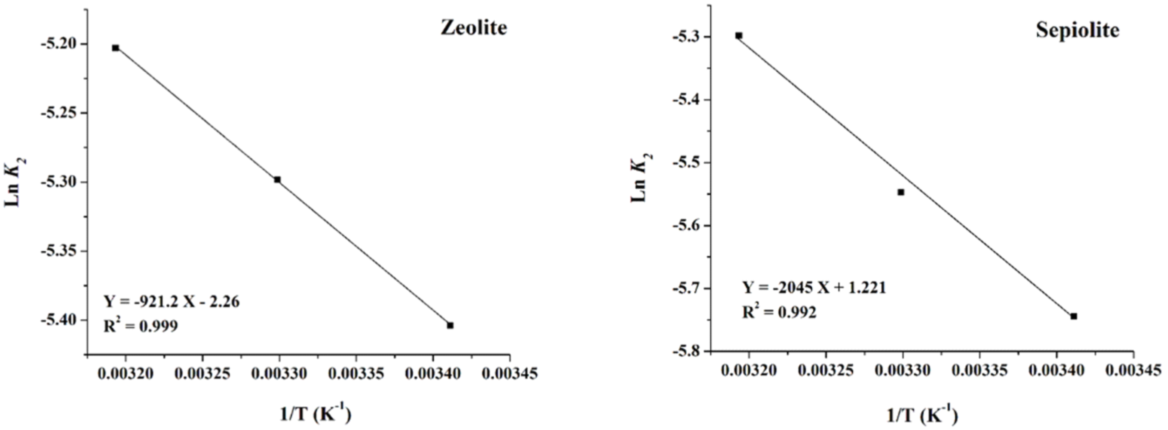

**Fig. 8. Relationship between pseudo-second order rate constants (K2) and absolute temperature (T) of Pb adsorption on sepiolite and zeolite.**

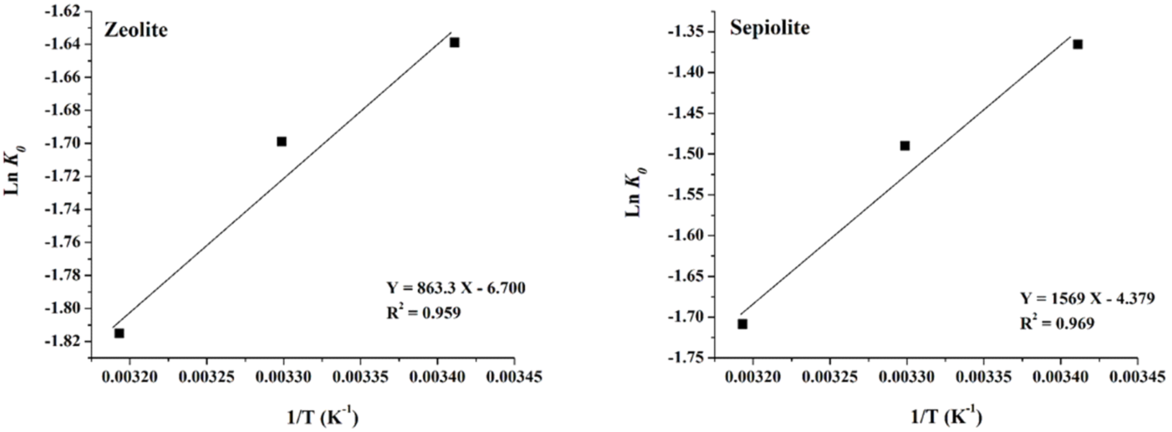

**Fig. 9. Determination of thermodynamic parameters for the sorption of $Pb^{2+}$ ions onto sepiolite and zeolite particles.**

**Table 4. Thermodynamic parameters for the sorption of lead onto sepiolite and zeolite.**

| **Mineral** | **$\Delta H^0$ (KJ/mol)** | **$\Delta S^0$ (J/mol K)** | **$\Delta G^0$ (KJ/mol)** | | |
|---|---|---|---|---|---|
| | | | **293.15 K** | **303.15 K** | **313.15 K** |
| Sepiolite | -13.04 | -36.40 | 3.33 | 3.76 | 4.45 |
| Zeolite | -6.70 | -55.70 | 3.99 | 4.28 | 4.73 |

exothermic phenomenon (Eloussaief and Benzina, 2010; Saltali *et al*., 2007). At all the temperatures, sorption of $Pb^{2+}$ ions by sepiolite particles was greater than that by zeolite. The greater adsorption capacities of sepiolite particles could be attributed to its greater specific surface area and more pore volume compared to that of zeolite (Table 1). In order to fully understand the nature of adsorption, the thermodynamic parameters were calculated (Table 4; Figs. 8 and 9). The Gibbs free energy ($\Delta G^0$) indicates the degree of spontaneity of the adsorption process and the lower values reflect a more energetically favorable adsorption process. The lower values of $\Delta G^0$ for the adsorption of lead ions onto sepiolite in comparison to that of zeolite (Table 4; Figs. 8 and 9) indicate a more spontaneous nature of lead sorption by sepiolite than zeolite. Moreover, the values of $\Delta G^0$ become less positive with decreasing the temperature. This shows that the removal process is favoured by decreasing the temperature. Moreover, the values obtained from the sepiolite-lead system are less than those obtained from zeolite-lead system, which suggests that, the removal process of lead ions is mostly favored by sepiolite particles especially at lower temperatures. The negative value of $\Delta H^0$ confirms that the sorption process was exothermic in nature and a given amount of heat is evolved during the binding $Pb^{2+}$ ions on the surface of adsorbents. Enthropy ($\Delta S^0$) has been defined as the degree of chaos of a system. The more negative values of $\Delta S^0$, the more decrease in degree of randomness at solid/liquid interface during the sorption process (Boparai *et al*., 2011; Sheikhhosseini *et al*., 2014). The $\Delta G^0$ parameter of lead adsorption by sepiolite and zeolite was found to be -36.40 and -55.70 J/mol K, respectively. This implies that $Pb^{2+}$ ions in aqueous solution of zeolite treated samples were in a much more chaotic distribution compared to the relatively ordered state of solid phase at the surface of adsorbents (Sari *et al.*, 2007). The magnitude of the activation energy is commonly used for differentiating between physical and chemical adsorption. Physical adsorption reactions, i.e. diffusion-controlled transport and electrostatic attractions, are readily reversible, equilibrium is attained rapidly and thus energy requirements are small, ranging from 5 to 40 KJ/ mol (Boparai *et al*., 2011). Chemical adsorption is specific, involves stronger forces and thus requires larger activation energies (e.g., 40 –800 KJ/mol) (Boparai *et al*., 2011). The activation energies for Pb adsorption onto sepiolite and zeolite particles were 17.00 and 7.66 KJ/mol, respectively; suggesting that Pb ions were physically adsorbed onto sepiolite and zeolite surfaces (Boparai *et al*., 2011). The lower activation energy (Ea) for zeolite compared to sepiolite indicates that Pb was more strongly sorbed onto sepiolite.

## CONCLUSIONS

The results showed that both sepiolite and zeolite clays can be used to remove $Pb^{2+}$ ions from aqueous solutions and sorption of $Pb^{2+}$ ions onto sepiolite and zeolite is temperature dependent. The adsorption capacity of both sepiolite and zeolite minerals for $Pb^{2+}$ ions increases with increasing contact time and pH, but decreases as temperature increases. Furthermore, the adsorption capacity of $Pb^{2+}$ ions was greater on sepiolite than it was on zeolite. Results obtained from the kinetic studies showed that the sorption of $Pb^{2+}$ ions onto both sepiolite and zeolite paricles is a relatively rapid process and can be described well with the pseudo-second-order model. Thermodynamic studies showed that sorption of $Pb^{2+}$ ions onto both sepiolite and zeolite minerals is an exothermic process and the lower $\Delta G^0$ values for the sorption of lead ions onto sepiolite as compared to those of zeolite indicated more spontaneous adsorption of lead ions onto sepiolite.

## ACKNOWLEDGEMENTS

The authors gratefully acknowledge Shahid Chamran University of Ahvaz and Technical University of Cartagena for the financial support they provided for this study.

## REFERENCES

Ahmed, S., Chightai, S. and Keane, M.A. (1998). The removal of cadmium and lead from aqueous solution by ion exchange with Na-Y zeolite. Sep. Purif. Technol., **13**, 57-64.

Adebowale, K.O., Unuabonah, E.I. and Olu-Owolabi, B.I. (2008). Kinetic and thermodynamic aspects of the adsorption of Pb2+ and Cd2+ ions on tripolyphosphate-modified kaolinite clay. Chem. Eng. J., **136**, 99-107.

Aytas, S., Akyil, S. and Eral, M. (2004). Adsorption and thermodynamic of uranium on zeolite. J. Radioanal. Nucl. Chem., **260**, 119-125.

Bektas, N., Akman, B. and Karda, S. (2004). Kinetic and equilibrium studies in removing lead ions from aqueous solutions by natural sepiolite. J. Hazard. Mater., **B112**, 115-122.

Bernal, M. P. and Lopez-real, J. M. (1993). Natural zeolite and sepiolite as ammonium and ammonia adsorbent materials. Bioresource Technol, **43**, 27-33.

Boparai, H. K., Joseph, M. and O'Carroll, D.M. (2011). Kinetics and thermodynamics of cadmium ion removal by adsorption onto nano zerovalent iron particles. J. Hazard. Mater., 186, 458-465.

Brigatti, M.F., Medici, L. and Poppi, L. (1996). Sepiolite and industrial waste-water purification: removal of Zn2+ and Pb2+ from aqueous solutions. Applied Clay Sci., **11**, 43-54.

Brigatti, M.F., Lugli, C. and Poppi, L. (2000). Kinetics of heavy-metal removal and recovery in sepiolite. Applied Clay Sci., **16**, 45-57.

Chen, H. and Wang, A. (2007). Kinetic and isothermal studies of lead ion adsorption onto palygorskite clay. J. Colloid. Interface Sci., **307,** 309-316.

Demirbas, O., Alkan, M., Dogan, M., Turhan, Y., Namli, H. and Turan, P. (2007). Electrokinetic and adsorption properties of sepiolite modified by 3-aminopropyltrieethoxysilane. J. Hazard. Mater., **149**, 650-656.

Dragan, E.S. and Dinu, M.V. (2009). Removal of copper ions from aqueous solution by adsorption on ionic hybrids based on chitosan and clinoptilolite. Ion Exch. Letters., **2**, 15-18.

El-Mekkawi, D. M. and Selim, M. (2014). Removal of $Pb^{2+}$ from water by using Na-Y zeolites prepared from Egyptian kaolins collected from different sources. J. Environ. Chem. Eng., **2**, 723-730.

Eloussaief, M. and Benzina, M. (2010). Efficiency of natural and acid-activated clays in removal of Pb (II) from aqueous solutions. J. Hazard. Mater, **178**, 753-757.

Galan, E. (1996). Properties and applications of palygorskite-sepiolite clays. Clay Miner., **31**, 443-453.

Gupta, S.S. and Bhattacharyya, K.G. (2008). Immobilization of Pb(II), Cd(II) and Ni(II) ions on kaolinite and montmorillonite surfaces from aqueous medium. J. Environ. Manage., **87**, 46-58.

Gupta, S.S. and Bhattacharyya, K.G. (2011). Kinetics of adsorption of metal ions on inorganic materials: A review. Adv. Colloid. Interface Sci., **162**, 39-58.

Hamidpour, M., Kalbasi, M., Afyuni, M. and Shariatmadari, H. (2010). Kinetic and isothermal studies of cadmium sorption onto bentonite and zeolite. Intl. Agrophysics, **24**, 253-259.

Ho, Y.S. and McKay, G. (1999). Comparative sorption kinetic studies of dye and aromatic compounds onto fly ash. J. Environ. Sci. Health, **34**, 1179-1204.

Hojati, S. and Khademi, H. (2013). Cadmium sorption from aqueous solutions onto an Iranian sepiolite: Kinetics and isotherms. J. Central-South Univ. Technol., **20**, 3627-3632.

Hojati, S. and Landi, A. (2013). Removal of zinc from a metal-plating wastewater using an Iranian sepiolite: Determination of optimum conditions. Desalination. Water Treat., DOI:10.1080/19443994.2013.861771

Huang, R., Wang, B., Yang, B., Zheng, D. and Zhang, Z. (2011). Equilibrium, kinetic and thermodynamic studies of adsorption of Cd (II) from aqueous solutions onto HACC-bentonite. Desalination, **280**, 297-304.

Humelinico, D., Dinu, M. V. and Dragan, E. S. (2011). Adsorption characteristics of $UO_2^{2+}$ and Th4+ ions from simulated radioactive solutions onto chitosan/clinoptilolite sorbents. J. Hazard. Mater., **185**, 447-455.

Inglezkias, V.J., Stylianou, M., Gkantzou, D. and Loizidou, M.D. (2007). Removal of Pb(II) from aqueous solutions by using clinoptilolite and bentonite as adsorbents. Desalination, **210**, 248-256.

Kara, M., Yuzer, H., Sabah, E. and Celik, M. E. (2003). Adsorption of cobalt from aqueous solutions onto sepiolite. Water Res., **37**, 224-232.

Kaya, A. and æren, A. H. (2005). Adsorption of zinc from aqueous solutions to the bentonite. J. Hazard. Mater., **125**, 183-189.

Kocaoba, S. and Akyuz, T. (2005). Effects of conditioning of sepiolite prior to cobalt and nickel removal. Desalination, **181**, 313-318.

Kragovic, M., Dakovic, A., Sekulic, Z., Trgo, M., Ugrina, M., Peric, J. and Gatta, G. D. (2012). Removal of lead from aqueous solutions by using the natural and Fe(III)-modified zeolite. Appl. Surf. Sci., **258**, 3667-3673.

Kubilay, S., Gurkan, R., Savran, A. and Sahan, T. (2007). Removal of Cu(II), Zn(II) and Co(II) ions from aqueous solutions by adsorption onto natural sepiolite. Adsorption, 13, 41-51.

Lagergren, S. (1898). Zur theorie der Sogenannten Adsorption Gelöster Stoffe. Kungliga Svenska Vetenskaps akademiens Handlingar, **24**, 1-39.

Liang, X., Xu, Y., Wang, L., Sun, Y., Lin, D., Sun, Y., Qin, X. and Wan, Q. (2013). Sorption of $Pb^{2+}$ on mercapto functionalized sepiolite. Chemosphere, **90**, 548-555.

McKay, G., Bino, M.J. and Altamemi, A.R. (1985). The adsorption of various pollutants from aqueous solutions on to activated carbon. Water Res., **19 (4)**, 491-495.

Murray, H.H. (2000). Traditional and new applications for kaolin, smectite, and palygorskite: a general overview. Appl. Clay Sci., **17**, 207-221.

Naseem, R. and Tahir, S. S. (2001). Removal of Pb (III) from aqueous solutions by using bentonite as an adsorbent. Water Res., 35 (16), 3982-3986.

Potgieter, J. H., Potgieter-Vermaak, S. S. and Kalibantonga, P. D., (2006). Heavy metals removal from solution by palygorskite clay. Minerals Eng., **19**, 463-470.

Saltali, K., Sari, A. and Aydin, M. (2007). Removal of ammonium ion from aqueous solution by natural Turkish (Yildizeli) zeolite for environmental quality. J. Hazard. Mater., **141**, 258-263.

Sari, A., Tuzen, M., Citak, D. and Soylak, M. (2007). Equilibrium, kinetic and thermodynamic studies of adsorption of Pb (II) from aqueous solution onto Turkish kaolinite clay. J. Hazard. Mater., **149**, 283-291.

Schultz, L.G. (1965). Quantitative interpretation of mineralogical composition from X-ray and chemical data for Pierre Shale, U. S. Geol. Surv. Prof. Paper, 391-C.

Sdiri, A., Higashi, T., Hatta, T., Jamoussi, F. and Tase, N. (2011). Evaluating the adsorptive capacity of montmorillonitic and calcareous clays on the removal of several heavy metals in aqueous systems. Chem. Eng. J., **172**, 37-46.

Sheikhhosseini, A.R., Shirvani, M., Shariatmadari, H., Zvomuya, F. and Najafi, B. (2013). Kinetics and thermodynamics of nickel sorption to calcium-palygorskite and calcium-sepiolite: A batch study. Geoderma, **217-218**, 111-117.

Singer A. (1989). Palygorskite and sepiolite group minerals. In: Minerals in Soil Environments (Dixon, J. B., Weed, S.B., editors). Soil Sci. Soc. Am. Madison, WI. pp. 829 - 872

Sprynskyy, M., Buszewski, B., Terzyk, A. P. and Namiesnik, J. (2006). Study of the selection mechanism of the heavy metal ($Pb^{2+}$, $Cu^{2+}$, $Ni^{2+}$ and $Cd^{2+}$) adsorption of clinoptilolite. J. Colloid. Interface Sci., **304**, 21-28

Wang, S. G., Gong, W. X., Liu, X. W., Yao, Y. W. and Gao, B. Y. (2007). Removal of lead from aqueous solution by adsorption onto manganese oxide-coated carbon nanotubes. Sep. Purif. Technol., **58**, 17-23.

Wang, Y., Lan, Y. and Huang, C. (2008). Adsorption behavior of $Pb^{2+}$ and $Cd^{2+}$ ions on bauxite floatation tailings. J. Central-South Univ. Technol., **15**,183-187.

Wang, S. and Peng, Y. (2010). Natural zeolites as effective adsorbents in water and wastewater treatments. Chem. Eng. J., **156**, 11-24.

Yang, Z., Yang, S., Hu, J., Tan, X. and Wang, Z. (2011). Effect of pH, ionic strength and temperature on sorption of Pb(II) on NKF-6 zeolite studied by batch technique. Chem. Eng. J., **168**, 89-93.

Zou, W., Hah, R., Chen, Z., Jinghua, Z. and Shi, J. (2006). Kinetic study of adsorption of Cu(II) and Pb(II) from aqueous solutions using manganese oxide coated zeolite in batch mode. Colloids Surf A. Physic. Eng. Aspects., **279**, 238-246.