#### **ORIGINAL ARTICLE**



# Evaluation efficiency of Iranian natural zeolites and synthetic resin to removal of lead ions from aqueous solutions

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#### Abstract

Heavy metal such as Pb<sup>2+</sup> (lead ions) has high toxicity potential, and it can be dangerous for public health and environment. The ion exchange process is one of the methods that can be used for Pb<sup>2+</sup> removal from aqueous solutions. The aim of this study was to investigate the removal efficiency of Pb<sup>2+</sup> from the synthetic aqueous solutions using Iranian natural zeolite (INZ) (Clinoptilolite) in comparison with a synthetic resin (SR). In this study, the removal of Pb<sup>2+</sup> from aqueous solution investigated by INZ and synthetic resin under different experimental conditions. Parameters like initial Pb<sup>2+</sup> concentration, contact times, adsorbent dosage, pH and size particles of INZ, and best-fitted isotherm were studied. The results showed that the most removal efficiency of Pb<sup>2+</sup> with INZ was obtained at pH 3–5, contact time 15–60 min, adsorbent dosage 20–50 g/L, Pb<sup>2+</sup> initial concentration 25 mg/L, and the removal efficiency was increased with decreasing INZ particle size. The high removal of Pb<sup>2+</sup> with SR was at pH 4–6, for 25 mg/L initial Pb<sup>2+</sup> concentration at 15–60 min and 5–10 g/L SR. Isotherms study with ISOFT software indicates that the Freundlich and Langmuir isotherms expression provides the best fit for Pb<sup>2+</sup> sorption by INZ and SR, respectively. This study indicated that for Pb<sup>2+</sup> ion removal, the SR was more efficient than INZ for high concentration solutions; however, in low concentration of Pb<sup>2+</sup>, the removal efficiency was approximately equal.

Keywords Lead ions · Aqueous solutions · Synthetic resin · Iranian natural zeolites (INZ) · Adsorption isotherm

#### Introduction

Worldwide developments, population growth, and industrialization have caused the accumulation of Pb<sup>2+</sup> to the formation of enormous volumes of wastes and environmental

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pollution (Mahdavi et al. 2017). Special industrial wastes from mining, electroplating, Pb<sup>2+</sup> smelting, and metal finishing industries discharge substantial amounts of heavy metals (Abdel-Halim et al. 2003; Inglezakis et al. 2002) such as mercury, chromium, nickel, copper, zinc, cadmium and Pb<sup>2+</sup> into water resources that are hazardous for the public health, ecosystem, and environment (Kim et al. 2013). Heavy metals are not biodegradable and have a tendency to accumulate in organisms, causing various diseases and disorders (Inglezakis et al. 2003; Mozgawa et al. 2009). Therefore, it is necessary to remove this material before entering the environment. Pb<sup>2+</sup> is one of the materials that have adverse effects on public health (Moazeni et al. 2017).

Chemical treatment, ion exchange, precipitation, filtration, oxidation–reduction, electrochemical recovery, ultrafiltration, reverse osmosis, electrodialysis, and adsorption are being used to remove such metals from water resources (Mier et al. 2001). However, many of these approaches may be ineffective, too expensive, or not easy to apply in developing countries. Hence, ion exchange is considered to be cost-effective if low-cost ion exchangers such as zeolites are used (Hesami et al. 2013). In this regard, the availability



of naturally occurring zeolites in many countries provides low-cost treatment by ion exchange systems to remove heavy metals from industrial wastewater. The main advantages of ion exchange over chemical precipitation are the recovery of metal amounts, selectivity, less sludge volume production, and the meeting of stringent discharge specifications (Ali and El Bishtawi 1997).

Zeolites are a large family of crystalline hydrated aluminosilicates that have unique properties like anions and cations exchangeability (Jha et al. 2008; Mozgawa et al. 2009). Among more than 40 natural zeolites, Clinoptilolite is the most abundant that most often used water and wastewater treatment (Barrera-Diaz et al. 2005; Berber-Mendoza et al. 2006; Calvo et al. 2009; Faghihian et al. 1999; Hamidpour et al. 2010; Hwang et al. 2011; Suh and Kim 2000; Yang et al. 2011). Consistent amounts of this zeolite type are found in volcanic tuffs in different parts of Iran. The zeolite grade, in most cases, is higher than 90% and can reach about 95% (Faghihian et al. 1999). Heavy metals removal by this material is based on the cationic exchanges between heavy metals and cations, such as sodium and potassium or the precipitation of heavy metal hydroxides over the zeolite external surfaces (Castaldi et al. 2008). Based on this, the aim of the present study was to investigate the removal efficiency of Pb<sup>2+</sup> from the synthetic aqueous solutions using Iranian natural zeolite (INZ) (Clinoptilolite) in comparison with a synthetic resin type. Some parameters like the effect of solution pH on Pb<sup>2+</sup> adsorption, contact time, the initial concentration of Pb2+, adsorbent dosage, particle size of INZ, and adsorption isotherms were studied.

#### **Materials and methods**

#### **Instruments**

Pb<sup>2+</sup> analyses were carried out using a flame atomic absorption instrument (PerkinElmer model 2380). A reciprocating shaker was used to agitate the mixtures at room temperature. A Metrohm pH meter model 525A was used for pH measurements. Particle sizes of the INZ samples were determined using a series of laboratory sieves in several meshes.

## **Reagents and solutions**

All the chemicals used were of analytical reagent grade. Deionized water was used throughout the experimental studies. Lead nitrate (Pb(NO<sub>3</sub>)<sub>2</sub>), HCl, and NaOH were purchased from Merck (Darmstadt, Germany), the representative seller in Iran. A 1 g/L concentration of Pb<sup>2+</sup> solutions was prepared and stored for a short time until test implementation.



### Adsorbent compounds

Iranian natural zeolite (INZ), Clinoptilolite, was supplied by the Afrand Tooska Co. in Iran under the trade name of Anzymite. These zeolites were extracted from Semnan mines in the northeast of Iran (Sharghe Haftdareh). In this location, zeolite deposits are found in some horizons of sedimentary volcanic rocks, which were dependent on Eocene. These deposits were situated in anticline structure with a gentle slope, about 10°-15°. The level of utilization of these deposits is widespread in Iran. In some locations, the thickness of zeolite horizons is greater than 20 m. These types of zeolite deposit are Clinoptilolite as well as quartz, halite, sodium sulfate, glubrite, tenardite, and also crystobalite. The position of this mine is illustrated in Fig. 1. An English Purolite strong acid cation exchanger was also purchased and was used as SR. The Anzymite (natural zeolite) and synthetic resin (Purolite) properties which were obtained from manufacturers are shown in Tables 1 and 2.

### **Preparation of INZ samples**

To achieve the desired particle size, INZ prepared using different laboratory meshes, to lie in three sieve granulation sizes (> 1180, 420–1180, and 297–420 µm). A 420–1180µm grading class was used as major grade, and two other classifications were used to determine the effects of particle size on ion exchange capacity of INZ. Then, for eliminating of very fine dust particles, the INZ samples were washed with deionized water, repeatedly, and in order to their increase the cation exchange capacity, 10 g of INZ was placed in reflux (358 K) with 200 mL 1 M NaCl solutions for 48 h, and then the phases were separated. The materials were rinsed with deionized water several times again, to achieve a Cl<sup>-</sup>-free solution and were tested using silver nitrate solution as an indicator. The resultant materials after drying in laboratory air were dried at 110 °C for 24 h and were kept under a desiccator until the experiment was done.

#### **Adsorption procedures**

One at the time technique was used for the sorption experiments by a batch technique at room temperature, and all tests were triplicates (Fig. 2). To compare the results in each series of tests, one blank sample also was considered. To study Pb<sup>2+</sup> sorption, start by an accurate weight of 1.5 g (30 g/L) of this type of zeolite and 0.5 g (10 g/L) of SR which were shaken with 50 mL of 25, 50, 100, 150, 200, and 250 mg/L Pb<sup>2+</sup> solutions for 120 min at constant pH 4.5 (asbuilt pH of synthetic aqueous solutions), laboratory temperature and with 160 times the reciprocating speed of shaker, separately. Thereinafter to survey of adsorbent dose changes

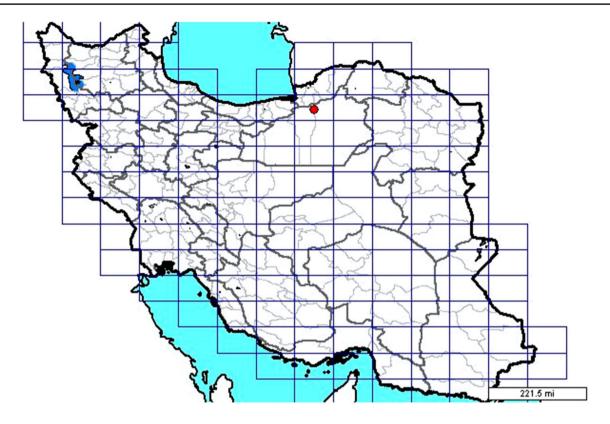


Fig. 1 Semnan mines in the northeast of Iran (Sharghe Haftdareh)

**Table 1** Chemical and physical properties of *Anzymite* 

	Percent (%) in 100 g <sup>a</sup>
Chemical properties	
${ m SiO_2}$	66.5
$Al_2O_3$	11.8
CaO	3.1
$K_2O$	2.1
$Na_2O$	2
$Fe_2O_3$	1.3
MgO	0.8
TiO	0.3
MnO	0.04
$P_2O_5$	0.01
Physical properties	
Color	Light green
CEC in meq/100 g	160–180
Specific gravity in (g/cm <sup>3</sup> )	1
Mineral percent (%)	85–95
Cations adsorption selectivity	$Cs>Rb>K>NH_4>Ba>$ Sr>a>Ca>Fe>Al>M g>Li

<sup>&</sup>lt;sup>a</sup>Remainder including of other impurities that were not analyzed

on Pb<sup>2+</sup> sorption, accurate weights of 1, 1.5, 2, and 2.5 g (20, 30, 40 and 50 g/L) of zeolite with 50 mL of 50 mg/L Pb<sup>2+</sup> solutions and 0.25, 0.5, and 0.75 g (5, 10 and 15 g/L) of SR with 50 mL of 250 mg/L Pb<sup>2+</sup> solutions and with fixed other conditions as above mentioned, were contacted, separately. The influences of solution pH changes were also examined by pH range of 3, 4, 5, 6, and 7, respectively. With respect to the determination of contact time impacts on adsorption phenomenon, series of tests were also implemented in the range of 1-3.5 h with 0.5-h intervals. Finally, an aliquot of the solution was then filtered and Pb<sup>2+</sup> concentration in the supernatant was measured by a flame atomic absorption spectroscopy according to the standard method (APHA 2013). Blank solutions were treated similarly and the final concentrations were taken as the initial ones. For the efficiency removal calculation, the following equation was used:

Removal efficiency = 
$$[(C_0 - C_t)/C_0] \times 100$$
 (1)

where  $C_0$  and  $C_{\rm t}$  (mg/L) are the initial and the final Pb<sup>2+</sup> concentrations.

 ${\rm Pb}^{2+}$  adsorption isotherm experiments using INZ and SR were implemented under of the optimum conditions. The amounts of adsorbed  ${\rm Pb}^{2+}$  on the adsorbents ( $q_{\rm e}$ , mg/g) were calculated as follows:



**Table 2** Chemical and physical properties of synthetic resin

Properties	
Polymer structure	Polystyrene with devinyl side branches
Physical and appearance shape	Transparent spheroid particles
Operational groups	Polystyrene sulfonate
Ionic shape	Na <sup>+</sup>
Approximate weight for carrying	850 g/L
Sieve size range	
English standard sieve	In wet mode, 16–52 Mesh
American standard sieve	In wet mode, 16–50 Mesh
In wet mode, 16–50 Mesh	
	+1.2  mm < 5%
	-0.3  mm < 1%
Moisture content for Na <sup>+</sup> shape	44–48%
Special weight for Na <sup>+</sup> shape in wet mode	1.29
Total ion exchange capacity for Na <sup>+</sup> shape	
In wet mode (volumetric)	2 eq/l min
In dry mode (weighing)	4.5 eq/kg min
Operating temperature for Na <sup>+</sup> shape	Maximum 150 °C
Stability in the range of pH	0–14

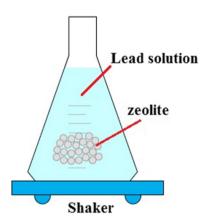


Fig. 2 Scheme of experimental procedure for adsorption study

$$q_{\rm e} = \left(C_0 - C_{\rm t}\right) \times \frac{V}{m},\tag{2}$$

where all parameters have defined as the same above at a certain period of time, V is the initial solution volume (L), and m is the adsorbent weight (g).

#### **Analysis of data**

Data analysis was conducted by SPSS 16 software. Isotherm Fitting Tool (ISOFIT) is a software program that fits isotherm parameters to experimental data via the minimization



of a weighted sum of squared error (WSSE) objective function. ISOFIT supports a number of isotherms, including (1) Brunauer–Emmett–Teller (BET), (2) Freundlich, (3) Freundlich with linear partitioning (F-P), (4) generalized Langmuir–Freundlich (GLF), (5) Langmuir, (6) Langmuir with linear partitioning (L-P), (7) linear, (8) Polanyi, (9) Polanyi with linear partitioning (P-P), and (10) Toth. Observation weights are ideally assigned according to individual estimates of measurement error, such that  $w_i = 1/\text{sd}_i$ , where  $\text{sd}_i$  is the standard deviation of the ith measurement.

#### **Results and discussion**

#### Effect of initial concentration of Pb<sup>2+</sup>

The results of the  $Pb^{2+}$  sorption by INZ and SR at the concentration of 25, 50, 100, 150, 200, and 250 mg/L are shown in Fig. 3. As shown, the removal efficiency by INZ has been dramatically reduced from 94.48 to 14.24% with increasing initial  $Pb^{2+}$  concentrations. Performing one-way ANOVA also showed that there was a significant relationship (p < 0.001) between  $Pb^{2+}$  removal percentage decrease with the increase in its concentration. For SR, raising  $Pb^{2+}$  concentrations in the range of 25–250 mg/L had a very low influence on changing its removal efficiency. So, the highest and the lowest removal efficiencies of 99.96% and 99.4% were related to  $Pb^{2+}$  concentrations of 25 and 250 mg/L, respectively. In other words, with the increase in  $Pb^{2+}$  concentration, its removal efficiency only lost 0.56%. Then, based on Fig. 3, it can be observed that increase in  $Pb^{2+}$ 

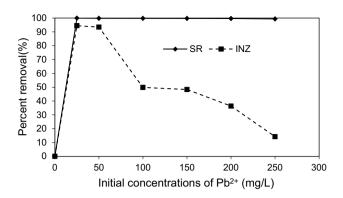


Fig. 3 Removal efficiency of  $Pb^{2+}$  by INZ and SR in several solution concentrations (pH=4.5, contact time=120 min, adsorbent dose: INZ=30 g/L, SR=10 g/L)

concentrations had no significant impact on the removal decrease trend of SR, but this decreasing trend was significant in INZ. Totally, the initial concentrations of solutions effectively control the performance of ion exchange systems. So as the results of this study and other similar studies, the removal of metal ions by cationic synthetic resin almost does not depend on the initial concentration of solutions, and these compounds show the same behavior in removing metal ions, while increasing the initial concentration of metal ions decreases the efficiency of elimination in natural zeolites (Ulmanu et al. 1996, 2003). Kim et al. (2013) surveyed removal of Pb<sup>2+</sup> from aqueous solution by a zeolite-nanoscale zero-valent iron composite, and their results indicated that at the lower concentration (100 mg/L), 99.2% of the Pb<sup>2+</sup> were removed by the Z-nZVI composite. Based on these results, the Pb<sup>2+</sup> removal efficiency was decreased when Pb<sup>2+</sup> initial concentration increased (Kim et al. 2013).

## **Effect of contact time**

To study the effect of contact time of INZ and SR on the removal of Pb<sup>2+</sup>, adsorption conducted at different contact time (Fig. 4). Results showed that the adsorption of the Pb<sup>2+</sup> is increased firstly for SR and then constant gradually, while the results were different for INZ. In this study, with respect to technical and economic conditions, the optimal contact time for Pb<sup>2+</sup> removal was 60 min (1 h). The sorption performance of INZ was low, and it had slight fluctuations during contact times. Final contact time is an important parameter in batch ion exchange processes. According to Donnan membranous phenomenon, the concentration of metal ions in solution always is more than solid phase. So, there was never equilibrium point, and sorption and desorption of metal ions occur especially in low contact times, continuously But, it is an important factor for natural zeolite that has very low exchange kinetics in long contact times, and it can increase the metal removal by these adsorbents.

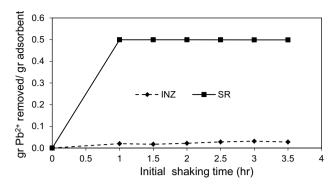


Fig. 4 Effect of contact time on  $Pb^{2+}$  adsorption with INZ and SR (pH=4.5, initial concentration=50 mg/L, adsorbent dose: INZ=30 g/L, SR=10 g/L)

In total, based on results of this study, we can say that contact time 60 min can be suitable for resin exchanger in the removal of Pb<sup>2+</sup> from wastewater. Some researchers (Mier et al. 2001; Sawyer et al. 2003) have confirmed our results, and it showed that absorption equilibrium could be accessed in contact times of 18–72 h only in experimental conditions. Also, they concluded that more than 90% of the removal has occurred in the first 15 min of the 24 h contact time using Clinoptilolite zeolite. Salem and Sene 2011 surveyed removal of Pb<sup>2+</sup> from solution by a combination of natural zeolite–kaolin–bentonite, and they reported that amount of Pb<sup>2+</sup> adsorption increases with residence time, and it remains relatively constant after about 4 h, reaching equilibrium condition.

#### Effect of adsorbents dosage

The effect of adsorbent dosage on Pb<sup>2+</sup> removal is presented in Fig. 5. For INZ, with the increase in its dose in the range of 0-50 g/L, there is more removal observed until a dose of 20 g/L. Also, for SR with the increase in its dose in the range of 5-15 g/L, it is observed the same trends but in the lower ranges. One-way ANOVA showed that there was a significant relationship (p < 0.001) between Pb<sup>2+</sup> ions removal percentage and the increase in both INZ and SR amounts. Based on the Duncan test, it was cleared that the removal percentage increase has a fast trend for Pb<sup>2+</sup> in the range of 5–10 g/L resin, but this increasing was lost in the range of 10-15 g/L. Also, it was observed that with the increasing INZ dosage in the range of 20-50 g/L, Pb<sup>2+</sup> removal has increased that it was significantly based on one-way ANOVA test. Then, the increase in Pb<sup>2+</sup> removal is observed with raising ion exchange; however, the loading amounts were decreased during the addition of dosage, resulting from the higher availability of the exchange sites rather than available ions in solution and the ion exchange efficiency was general reduced. Finally, lower Pb<sup>2+</sup> ions amounts will there was in



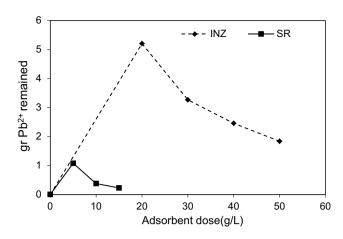


Fig. 5 Influence of adsorbent dose on  $Pb^{2+}$  removal (pH=4.5, initial concentration=50 mg/L, contact time=120 min)

comparison with the available ion exchange sites. This subject is not in an economic way for batch systems. The dispersion of adsorbent particles is good if the adsorbent dosage was low because all active sites on the adsorbent surface are completely disclosed, and they cannot quicken the accessibility of Pb<sup>2+</sup> to a large number of the adsorbent active sites (Arshadi et al. 2014). Jamil et al. (2010) reported that the equilibrium concentration in solution phase decreases with increasing the zeolite amount since the fraction of Pb<sup>2+</sup> removed from the aqueous phase increases as the sorbent amount is increased (Jamil et al. 2010).

## Effect of pH solution on Pb2+ removal

The results of the effect of pH in the range of 3–7 on the removal of Pb<sup>2+</sup> are presented in Fig. 6. High removal efficiency was obtained at pH 3 for INZ, while the least removal efficiency of SR was obtained at this pH. But, the changes of removal percentages were very low in the range of 3–7. Oneway ANOVA showed that there was a significant relationship (p < 0.0001) between Pb<sup>2+</sup> removal percentages with pH changes. While the Duncan test showed that there was not a significant difference between pH in the range of 3–7 with Pb<sup>2+</sup> removal percentages and for SR, the pH range of 4–6 is the most suitable pH for Pb<sup>2+</sup> removal percentages of the solution. Kocaoba et al. (2007) study showed that the adsorption percentages of a natural zeolite were increased sharply after pH 4 for Ni, Cu, and Cd metals. The pH 6 was chosen as the optimum pH for all metals for avoiding the precipitation of metals because most of the heavy metal ions tend to form precipitation at pH higher than 6, which limits this process greatly (Kocaoba et al. 2007). Hamdi and Srasra 2012 showed that the adsorption of phosphate ions by the two clays and the synthetic zeolite samples could be efficiently removed at acidic pH (between 4 and 6) condition.

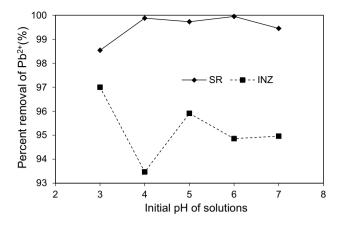


Fig. 6 Influence of pH changes on  $Pb^{2+}$  removal efficiency (initial concentration = 50 mg/L, contact time = 120 min, adsorbent dose: INZ = 30 g/L, SR = 10 g/L)

The difference in pH would have a minimal effect on the surface charge of zeolite (Ponizovsky and Tsadilas 2003). Kim et al. (2013) indicated the removal ranged from 99.9% when the initial pH was 4 and 93.5% when it was 6 (Kim et al. 2013). The results of this study presented that the Pb<sup>2+</sup> ions have high removal efficiency in acidic pH (pH = 3-5 and 4-6 for INZ and SR, respectively). These results were endorsed the Pb<sup>2+</sup> dominate in solution at acidic pH (Zhang et al. 2010). Inglezakis et al. (2002) study showed that ion exchange of Pb<sup>2+</sup> on natural Clinoptilolite is favorable (Inglezakis et al. 2002).

## **Effect of INZ particle size**

To achieve the desired particle size of INZ, three sieve granulation sizes were used, and results of this step are displayed in Fig. 7. It can be seen that the sorption of Pb<sup>2+</sup> is increased with decreasing particle size. One-way ANOVA showed that there was a significant relationship (p < 0.034) between increasing Pb<sup>2+</sup> removal percentage with reducing the particle size of INZ. As the sorption is a surface phenomenon, the smaller sorbent sizes have comparatively larger surface areas, and hence, there was higher Pb<sup>2+</sup> removal at equilibrium conditions. The results are similar to Bektaş and Kara 2004 and Faghihian et al. (1999) studies. Natural zeolites can be considered as one of the best amendment material for co-composting with sewage sludge taking into account their high efficiency and low cost. Utilization of synthetic zeolite (Zeolite P) as an amendment for compost derived from sewage sludge also demonstrated satisfactory results (Wang and Peng 2010).



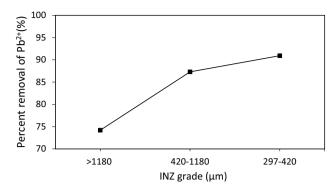


Fig. 7 Effect of particle size for  $Pb^{2+}$  removal capacity of INZ (initial concentration = 50 mg/L, contact time = 120 min, pH = 4.5, adsorbent dose: INZ = 30 g/L, SR = 10 g/L)

## **Adsorption isotherms**

The adsorption equilibrium data of Pb<sup>2+</sup> on INZ and SR adsorbent were fitted by several well-known isotherm models to assess their efficacies. For this matter, ISOFIT was applied to prediction of the adsorption isotherm for Pb<sup>2+</sup> removal. Isotherm experiment conducted with Pb<sup>2+</sup> concentration of 25-250 mg/L (interval 50 mg/L) by INZ and SR. Water solubility  $(S_w)$  of Pb(NO<sub>3</sub>)<sub>2</sub> was estimated 0.53 mg/L at pH 4.5. Some studies have considered one or more of the supported isotherms in the background of a water and wastewater system. The dual-mode isotherms reflect recently developed models for the adsorption of hydrophobic organic solutes (Matott and Rabideau 2008). Table 3 summarizes some of the diagnostic statistics parameters that computed by ISOFIT and reported in the output file for Pb<sup>2+</sup> adsorption by INZ and SR. The AICc values indicate that the Freundlich and Langmuir isotherms expression provides the best fit of Pb<sup>2+</sup> adsorption by INZ and SR, respectively. This result is in agreement with various researchers who used Langmuir equation to represent Pb<sup>2+</sup> removal by Clinoptilolite (Bektaş and Kara 2004). The agreement of the Langmuir model with the experimental results suggests that a monolayer coverage of Pb<sup>2+</sup> ions on the outer surface of INZ and SR. Based on the same study on adsorption of phosphate ions by the two clays and the zeolite samples, the isotherms showed that the zeolite has the highest rate of uptake (52.9 mg P/g). Equilibrium data of this study were well fitted with Langmuir and Freundlich isotherm (Hamdi and Srasra 2012). For the removal of Pb<sup>2+</sup> from solution by a combination of natural zeolite-kaolin-bentonite, the Langmuir isotherm showed the acceptable accuracy in prediction of adsorption data (Salem and Sene 2011). In this study, the best-fitted isotherm for Pb2+ removal by INZ was Freundlich isotherm. The Freundlich isotherm, as an experimental model, can be applied to non-ideal adsorption on

**Table 3** Summary of selected diagnostics parameters and coefficients for Pb<sup>2+</sup> adsorption by INZ and SR

Adsorbents	Adsorbents Selected diagnostics Isotherms	Isotherms									
		GLF	Toth	Linear	Langmuir	F-P	L-P	Freundlich	p-P	BET	Polanyi
INZ	AICca	88.36	78.36	76.08		73.36	78.35	73.35	1	76.29	ı
	$R_{ m y}^{2b}$	0.734	0.000	0.703		0.000	0.862	0.000	ı	0.859	ı
	$R_{ m N}^{2 m c}$	0.724	0.724	0.774		0.724	0.724	0.724	ı	0.724	ı
	$M^{2 m d}$	$9.62 \times 10^{-2}$	I	$5.29 \times 10^{-2}$	$1.18 \times 10^{6}$	$7.22 \times 10^{-3}$	$6.67 \times 10^4$	$7.22 \times 10^{-3}$	I	$7.56 \times 10^{-2}$	ı
	Linearity assessment	Uncertain	Uncertain	Uncertain		Linear	Nonlinear	Linear	Uncertain	Uncertain	Uncertain
SR	$AICc^a$	110.48		95.41		110.40	95.40	100.40	ı	121.38	ı
	$R_{ m y}^{ m 2b}$	0.957	0.956	0.959		0.959	0.959	0.959	ı	0.758	I
	$R_{ m N}^{2c}$	0.841	0.810	0.870		0.870	0.870	0.870	ı	0.991	ı
	$M^{ m 2d}$	$2.73 \times 10^2$	$3.38 \times 10^{-1}$	$3.60 \times 10^{-9}$	$3.39 \times 10^{-9}$	$8.91 \times 10$	$2.98 \times 10^{-9}$	2.73	I	$7.56 \times 10^{-2}$	ı
	Linearity assessment	Nonlinear	Nonlinear	Linear	Linear	Nonlinear	Linear	Nonlinear	Uncertain	Uncertain	Uncertain



<sup>&</sup>lt;sup>b</sup>Correlation between measured and simulated observation

<sup>&</sup>lt;sup>c</sup>Correlation between residual and normality
<sup>d</sup>Linssen measure of nonlinearity



heterogeneous surfaces as well as multilayer sorption. The basic assumption in this model is an exponentially decaying sorption site energy distribution (Anari-Anaraki and Nezamzadeh-Ejhieh 2015).

## **Conclusion**

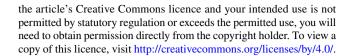
In this study, it was concluded that the rates of Pb<sup>2+</sup> removal for initial concentrations were rapid at initial times for SR and then kept decreasing gradually. The removal efficiency of two adsorbents was increased with increasing initial Pb<sup>2+</sup> concentrations until 50 mg/L. But, the removal efficiency by INZ has been dramatically reduced with increasing initial Pb<sup>2+</sup> concentrations in the range of 50-250 mg/L. The removal efficiency by SR has been increased with increasing initial Pb2+ concentrations in this range. The removal efficiency of Pb<sup>2+</sup> with increasing contact times was increased firstly for SR and then constant gradually, while it has not increased removal efficiency for INZ. The both of INZ and SR have similar removal efficiency for Pb<sup>2+</sup> with increasing adsorbents dosage, and in this the suitable INZ adsorbent dosage was 20 g/L and for SR was 5 g/L. The removal of Pb<sup>2+</sup> was increased with pH increasing; high removal efficiency was obtained at pH 3 and 4-6 for INZ and SR, respectively. Effect of INZ particle size showed that Pb<sup>2+</sup> removal was increased with reducing the particle size of INZ. This study indicated that for Pb2+ removal the SR was more efficient than INZ for high concentration solutions; however, in low concentration of Pb<sup>2+</sup>, the removal efficiency was approximately equal. The Freundlich and Langmuir isotherm models based on ISOFIT software for removal of Pb<sup>2+</sup> by INZ and SR showed better correlation with the experimental data, respectively.

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## **Compliance with ethical standards**

**Conflict of interest** The authors declare that there is no conflict of interest regarding the publication of this paper.

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