Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1095683

57 (2016) 18799–18805
August

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Taylor & Francis Group

Removal of lead(II) ions from aqueous solutions using diatomite nanoparticles

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Received 7 April 2015; Accepted 2 September 2015

ABSTRACT

In the present study, the performance of diatomite nanoparticles was investigated for the lead(II) ions sorption in a batch mode. The diatomite nanoparticles were characterized using X-ray fluorescence, scanning electron microscopy, dynamic light scattering, and Brunauer–Emmet–Teller analysis. The influence of sorption parameters including pH, contact time, initial concentration, and temperature on the lead ions sorption was evaluated. The maximum adsorption capacity of lead ions onto the diatomite nanoparticles was found to be 103.1 mg g^{-1} at equilibrium time of 90 min and temperature of 45°C. The kinetic data were analyzed by pseudo-first-order and pseudo-second-order kinetic models. The Freundlich and Langmuir isotherm models were applied to describe the equilibrium data. The kinetic data of lead ions were found to follow the pseudo-first-order kinetic model and the equilibrium data of lead ions sorption were well described by Langmuir isotherm model. Evaluation of thermodynamic parameters indicated that the lead adsorption onto the diatomite nanoparticles was endothermic and spontaneous process. The reusability studies indicated that the lead adsorption capacity did not change remarkably after five sorption–desorption cycles.

Keywords: Diatomite nanoparticles; Lead; Adsorption; Kinetic; Isotherm; Thermodynamic

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1. Introduction

Lead is one of the major environmental pollutants which is harmful for the nervous system, liver, and brain [1]. Lead is observed in a variety of industrial wastes such as battery manufacturing, printing and pigment, ceramic and glass industries, ammunition, and mine tailing [2]. So, the removal of lead ions from wastewater is very important with respect to the environmental issue and public health. Several methods including chemical precipitation, ultrafiltration, reverse osmosis, electrodialysis, ion-exchange, flotation, and adsorption have been used for the treatment of lead ions from wastewater [3]. Among all, the adsorption process due to its simplicity, moderate operational conditions, and economic feasibility is commonly considered for the removal of metal ions [3,4].

The most important property of any adsorbent is the surface area and structure. Furthermore, the chemical nature and polarity of the adsorbent surface can influence the attractive forces between the adsorbent

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and adsorbate. Additionally, the use of alternative low-cost materials for heavy metal removal is required. In recent years, the search for locally available low-cost adsorbents has been intensified [5]. In recent researches, silica-based adsorbents were widely used for the removal of heavy metal ions [6]. The natural materials such as perlite [7], diatomite [3], dolomite [3], sawdust [8], clay [9], and zeolite [10] have been used for metal ions sorption. Diatomite is fine grained, low-density biogenic sediment, which consists essentially of amorphous silica ($SiO_2 \cdot nH_2O$) derived from opalescent frustules of diatoms. Due to the presence of silanol groups that spread over the matrix of silica, diatomite can react with many polar functional groups [11]. The performance of diatomite for the heavy metal ions sorption was reported in the literature [12–17]. Kamelabad area (Iran) is particularly rich in the diatomite resources.

The nano-sized particles due to the higher specific area are more favorable for wastewater treatment compared with micro-sized particles. In the previous studies, the researchers have used the natural mineral adsorbents with micro size particles for heavy metal removal [18]. However, there is no study about the application of diatomite nanoparticles for lead(II) ions sorption from aqueous solutions.

In this work, the diatomite nanoparticles were prepared from Iranian diatomite mines. The prepared nanoparticles were characterized using X-ray fluorescence (XRF), scanning electron microscopy (SEM), dynamic light scattering (DLS), and Brunauer–Emmet–Teller (BET) analysis. The nature of the adsorption process with respect to its kinetics, isotherms, and thermodynamic aspects has been also evaluated.

2. Experiments

2.1. Materials

The raw diatomite was obtained from Kamelabad mines of Iran. At first, natural diatomite particles were washed with distilled water to remove impurities, and dried at 110°C for 8 h. Then, the dried samples were powdered in a ball mill consisting of distilled water at 250 rpm for 5 h. Finally, slurry samples were dehumidified using a spray dryer at 140°C. The prepared diatomite nanoparticles were used in the adsorption process. The chemical composition of the prepared diatomite particles was determined by XRF analysis and the result is presented in Table 1.

The lead ions solutions were prepared by dissolving weighed amounts of lead nitrates (Sigma–Aldrich, Germany) in distilled water.

2.2. Characterization tests

The morphology of the prepared diatomite nanoparticles was determined using a scanning electron microscopy (SEM, JEOL JSM-6380) after gold coating.

The hydrodynamic diameter of the diatomite nanoparticles was determined by DLS using a Malvern Zetasizer Nano (Malvern Instruments, Worcestershire) (Wavelength: 632.8 nm, Scattering Angle: 173°).

The average pore diameter, specific surface area, and pore volume of the prepared diatomite particles were measured with nitrogen adsorption and BET method on a Quantachrome Autosorb-1 instrument.

The final concentration of lead ions in the adsorption medium was determined using an inductivity coupled plasma atomic emission spectrophotometer (ICP-AES, Thermo Jarrel Ash, Model Trace Scan). Analytical wavelength was set to 220.5 nm for lead ions.

2.3. Batch adsorption experiments

The performance of prepared diatomite nanoparticles for lead ions sorption was investigated as a function of pH (2–7), contact time (0–240 min), initial concentration (10–500 mg L^{-1}), and temperature (298–318 K) in a batch system. For this, 50 mg of nanoparticles were placed in a flask containing 100 mL of lead ions solution on a rotary shaker at 200 rpm for 2 h. Each experiment was repeated in triplicate and the results were given as averages. The amount of the metal ions adsorbed was calculated as follows:

$$q_e = \frac{(C_0 - C_e)V}{1,000\,M} \tag{1}$$

where q_e is the adsorption capacity in mg g^{-1}, C_0 and C_e are the initial and equilibrium concentrations of

Table 1
Chemical composition of prepared diatomite nanoparticles

Sample	SiO_2	Al_2O_3	K_2O	Na_2O	CaO	Fe_2O_3	MgO	P_2O_5
Diatomite	90.30	5.10	0.62	1.18	0.70	1.50	0.50	0.10

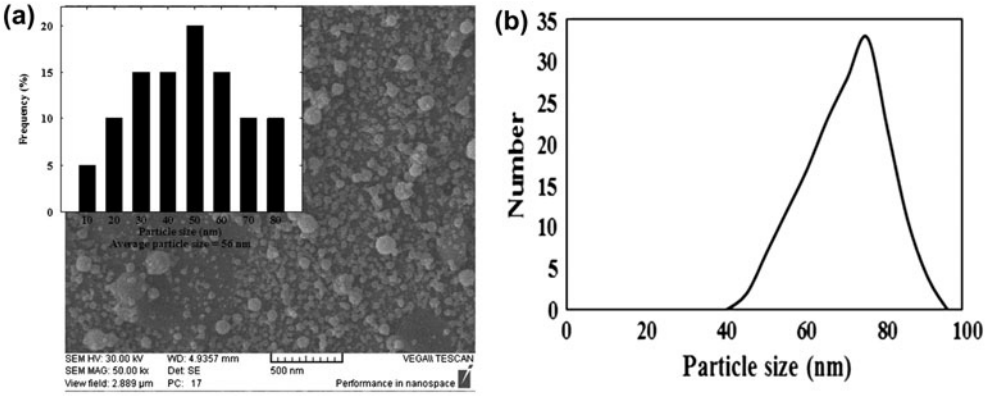

Fig. 1. (a) SEM image and size distribution of diatomite nanoparticles and (b) DLS of diatomite nanoparticles.

lead ions solution in mg L^{-1}, V is the volume of the solution in mL, and M is the weight of the dry absorbents in g.

3. Results and discussion

3.1. Characterization of diatomite nanoparticles

The SEM image of the diatomite nanoparticles is presented in Fig. 1. As shown, the diatomite nanoparticles with the average particle size of 56 nm were produced. DLS analysis was used to evaluate the hydrodynamic diameter and particle size distribution of synthesized diatomite nanoparticles (Fig. 1(b)). The particle size of 72 nm with narrow size distribution was obtained for the diatomite nanoparticles. The results of DLS analysis was in good agreement with the result of SEM analysis. The results of BET analysis indicated that the average pore diameter of diatomite nanoparticles was 2.12 nm. The BET surface area was 119 $m^2\ g^{-1}$ and the pore volume was 0.187 $cm^3\ g^{-1}$.

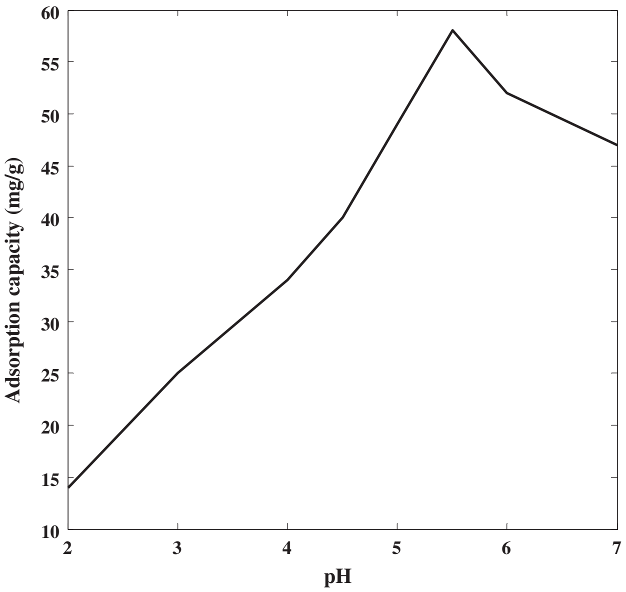

Fig. 2. Effect of pH on the lead sorption onto the diatomite nanoparticles.

3.2. Effect of pH on the lead sorption

The effect of pH on the lead sorption by the prepared diatomite nanoparticles in the pH range of 2–7 at 25˚C for the initial metal concentration of 100 mg L^{-1} lead solution is illustrated in Fig. 2. As shown, the sorption capacity increased by increasing the pH values for lead ions up to 5.5; and then declined by further increase in pH values. The lower adsorption of lead ions at lower pH values could be attributed to the increasing H^+ concentration, which reduced the ability of anion functional groups on the

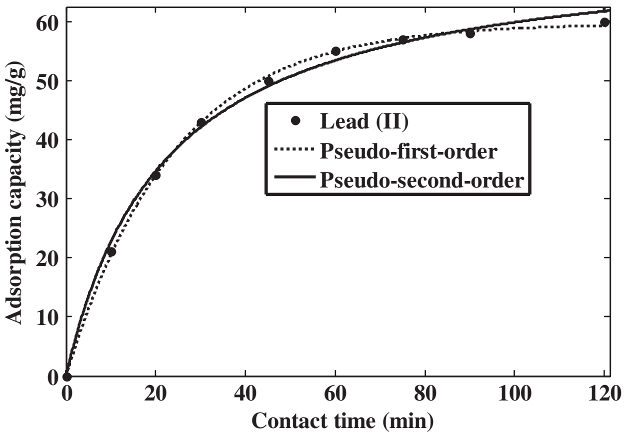

Fig. 3. Adsorption kinetics of lead onto the diatomite nanoparticles.

Table 2
Kinetic parameters of lead sorption onto the diatomite nanoparticles

Metal ion	Pseudo-first-order model			Pseudo-second-order model		
	q_{eq} (mg g^{-1})	k_1 (min^{-1})	R^2	q_{eq}	k_2 (mg g^{-1} min^{-1})	R^2
Pb^{2+}	56.69	0.0421	0.999	73.10	0.000617	0.992

adsorbent surface. By increasing the pH values up to 5.5, the positive charge density on the surface sites of nanoparticles was decreased, which resulted in an increase in the lead sorption by the prepared diatomite nanoparticles. The decrease in the lead ions sorption at pH values higher than 5.5 was due to the formation of hydroxylated complexes of the lead ions in the form of $Pb(OH)_2$, which decreased the adsorption capacity of the diatomite nanoparticles. Similar trends were reported by other researchers [19,20]. Consequently, the pH of 5.5 was selected as an optimum value for further experiments.

3.3. Effect of contact time on the lead sorption

The effect of contact time on lead sorption onto the diatomite nanoparticles in the initial concentration 100 mg L^{-1} and 25˚C is shown in Fig. 3. As shown, the diatomite nanoparticles reached the equilibrium time after 90 min. More than 90% of total adsorption of lead occurred within the first hour. Therefore, the equilibrium time of 90 min was selected for further experiments.

Kinetic models, namely pseudo-first-order and pseudo-second-order models were used to describe the adsorption kinetics of lead ions onto the diatomite nanoparticles.

The pseudo-first-order kinetic model is given as follows:

$$q_t = q_e(1 - \exp(-k_1 t)) \tag{2}$$

The pseudo-second-order kinetic model is given as follows:

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \tag{3}$$

where q_t and q_e (mg g^{-1}) are the adsorption capacity at time t and equilibrium time. k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are the pseudo-first-order and pseudo-second-order models constants. The results are presented in Table 2. By comparing the coefficient of determination (R^2) values for pseudo-first-order ($R^2 = 0.999$) and pseudo-second-order ($R^2 = 0.992$), it was found that the pseudo-first-order model fitted better than the pseudo-second-order model with kinetic data.

3.4. Isotherm models

The known Freundlich and Langmuir isotherm models were used to describe the equilibrium data of metal ions sorption using diatomite nanoparticles.

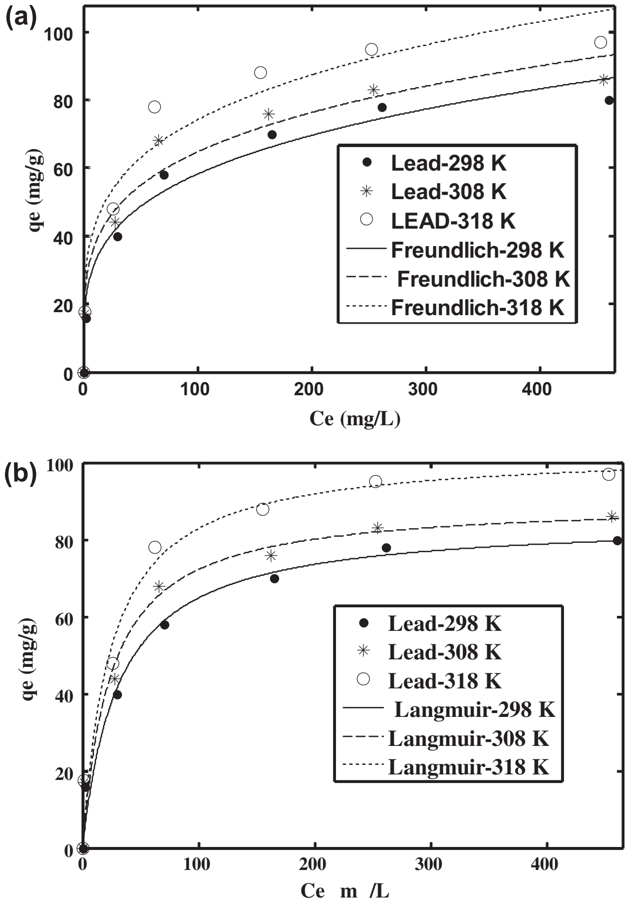

Fig. 4. (a) Freundlich and (b) Langmuir isotherm plots for lead sorption onto the diatomite nanoparticles.

Table 3
Isotherm parameters for lead sorption onto the diatomite nanoparticles

		Freundlich isotherm			Langmuir isotherm		
Metal	T (°C)	k_F (mg g^{-1})	n	R^2	q_{max} (mg g^{-1})	K_L (L mg^{-1})	R^2
Pb^{2+}	25	17.67	3.865	0.975	85.06	0.03211	0.980
	35	21.59	4.196	0.963	89.94	0.04081	0.976
	45	24.90	4.220	0.952	103.1	0.04101	0.977

Table 4
Thermodynamic parameters of lead sorption onto the diatomite nanoparticles

	k_C					ΔG° (kJ mol^{-1})		
Metal	25°C	35°C	45°C	ΔH° (kJ mol^{-1})	ΔS° (kJ mol^{-1} k)	25°C	35°C	45°C
Pb^{2+}	8.36	14.33	21.80	37.78	0.1445	–5.261	–6.817	–8.148

The Freundlich isotherm equation is expressed as follows:

$$q_e = k_F C_e^{\frac{1}{n}} \tag{4}$$

The Langmuir isotherm model is expressed as follows:

$$q_e = q_m \frac{bC_e}{1 + bC_e} \tag{5}$$

where k_F (mg g^{-1}) and n are Freundlich parameters related to the sorption capacity and intensity of the sorbent, respectively. q_{max} (mg g^{-1}) and b (mg^{-1}) are the Langmuir model constants. q_m is the maximum value of metal ion adsorption per unit weight of adsorbent that is related to the monolayer adsorption capacity, and b is related to the enthalpy of adsorption. The parameters of isotherm models were calculated by nonlinear regression of q_e vs. C_e using MATLAB software. The results are shown in Fig. 4 and are listed Table 3. By comparing the coefficient of determination (R^2) values, it was found that the equilibrium data was best described by Langmuir isotherm model ($R^2 > 0.976$) compared with Freundlich ($R^2 > 0.952$) isotherm model.

3.5. Thermodynamic parameters

The thermodynamic parameters including Gibbs free energy change (ΔG°), entropy change (ΔS°), and enthalpy change (ΔH°) for lead ions sorption by the diatomite nanoparticles were evaluated by the following equations:

$$k_C = \lim_{C_{el} \to 0} \frac{C_{es}}{C_{el}} \tag{6}$$

$$\Delta G^\circ = -RT \ln k_C \tag{7}$$

$$\ln k_C = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{8}$$

where R (kJ mol^{-1} K^{-1}) is the gas constant, and T (K) is the temperature. C_{es} and C_{el} (mg L^{-1}) are the equilibrium values of lead concentration in solid phase and liquid phase, respectively. The thermodynamic parameters are listed in Table 4. The negative values of ΔG° and positive value of ΔH° showed the spontaneous and endothermic nature of the lead sorption by the

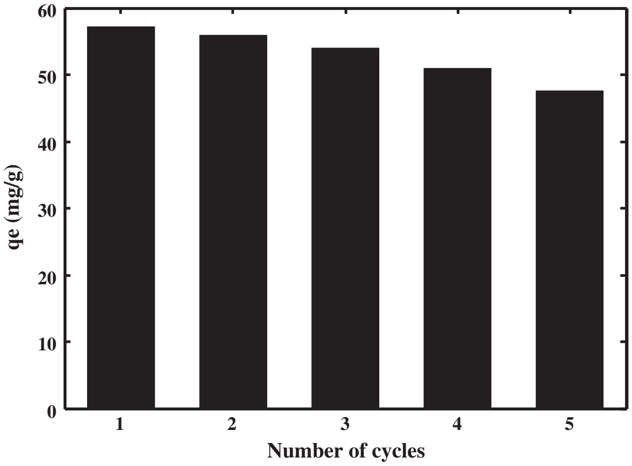

Fig. 5. Five cycles of lead adsorption–desorption with 0.5 M HNO_3.

Table 5
Comparison of adsorption capacity (mg g^{-1}) of diatomite nanoparticles for lead ions sorption with other adsorbents reported in the literature

Adsorbent	Adsorption capacity of Pb(II) (mg g^{-1})	Refs.
Diatomite	25.01	[3]
Diatomite	24.00	[20]
Mn–diatomite	99.00	[20]
Raw diatomite	24.94	[11]
Expanded perlite	13.39	[21]
Montmorillonite	10.40	[22]
Natural calcite	19.92	[23]
Kaolinite	11.52	[24]
Bentonite	16.66	[25]
Diatomite nanoparticles	103.10	This study

diatomite nanoparticles. The positive value of ΔS° showed that the randomness was increased at the solid–solution interface.

3.6. Reusability of diatomite nanoparticles

The five cycles of adsorption–desorption of lead ions onto the diatomite nanoparticles were performed at initial lead concentration of 100 mg L^{-1} and 25°C. The result is shown in Fig. 5. The desorption step of lead ions from diatomite nanoparticles was treated with 0.5 M HNO_3. Desorption time was fixed as 1.5 h throughout the adsorption period. The adsorption capacity of lead ions onto the diatomite nanoparticles from 57.2 mg g^{-1} in the first step decreased to 47.6 mg g^{-1} in the fifth step. This showed that the diatomite nanoparticles could be reused without almost any significant loss in the adsorption performance.

3.7. Comparison of diatomite nanoparticles with other natural adsorbents

In Table 5, the maximum adsorption capacity of prepared diatomite nanoparticles was compared with other adsorbents reported in the literature [3,11,21–26]. It can be concluded that the maximum adsorption capacity of lead ions onto the diatomite nanoparticles was higher than all of the adsorbents in these literatures, therefore, diatomite nanoparticles has a significant potential for adsorption of lead ions from aqueous systems.

4. Conclusion

The potential of diatomite nanoparticles as an adsorbent was investigated for the removal of lead ions from aqueous solutions. The SEM image of diatomite nanoparticles indicated that the average particle size of 56 nm was produced. The kinetic data of lead sorption were best described by pseudo-first-order model at equilibrium time of 90 min and optimum pH value of 5.5. The equilibrium data followed well the Langmuir isotherm model with maximum monolayer sorption capacity of 103.1 mg g^{-1} at a temperature of 45°C. The obtained thermodynamic parameters indicated the spontaneous and endothermic nature of lead sorption onto the diatomite nanoparticles. The diatomite nanoparticles were regenerated with 0.5 M HNO_3 and was not observed to be significantly lost in adsorption performance after five adsorption–desorption cycles.

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