Desalination and Water Treatment
www.deswater.com

doi:10.5004/dwt.2018.22309

135 (2018) 330–340
December

Adsorption of Pb^{2+} and Zn^{2+}from aqueous solutions using dried powder of cactus *Opuntia:* characterization, adsorption capacity and kinetics

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Received 28 December 2017; Accepted 31 March 2018

ABSTRACT

Dried powder of the cactus *Opuntia* was used as an adsorbent to remove Pb^{2+} and Zn^{2+} from aqueous solution. The characteristics of the adsorbent were studied using Brunauer–Emmett–Teller (BET), point of zero charge (pH$_{pzc}$), Fourier transform infrared spectroscopy (FTIR),and energy dispersive spectroscopy (EDS) analyses. Adsorption efficiency experiments were conducted on single-metal aqueous systems, including variations in dose, contact time, initial adsorbate concentration, initial solution pH, and temperature. The maximum removal efficiencies of Pb^{2+}and Zn^{2+} were found to be 90.6% and 37.6%, respectively, with adsorbent doses of 0.5 and 2.0 g. The maximum amount adsorbed onto *Opuntia* adsorbent for Pb^{2+} (119.0 mg/g) was found to be higher than that of Zn^{2+} (32.3 mg/g) at the 300 and 200 mg/L initial concentrations of Pb^{2+}and Zn^{2+} ions, respectively. A rapid rise in binding efficiency was observed with increasing pH up to 4, and Pb^{+2} ions adsorbed preferentially compared to Zn^{2+}. The pseudo-second-order and Elovich models best fit the experimental data on the adsorption of Pb^{2+}and Zn^{2+} onto *Opuntia* powder. The energy dispersive spectroscopy (EDS) analysis was employed to confirm the adsorption process. In isotherm studies, the maximum adsorption capacity (q_{max}) was calculated to be 62.9 mg/g for Pb^{2+} and 21.6 mg/g for Zn^{2+}. The adsorption data for both Pb^{2+} and Zn^{2+}obeyed the Freundlich model. A thermodynamic study showed that the adsorption process was spontaneous and endothermic. The results of the present study indicate that dried *Opuntia* powder as low-cost adsorbent could be useful and effective for the removal of heavy metals, especially in developing countries.

Keywords: Dried cactus powder; *Opuntia*; Heavy metal removal; Adsorption capacity; Kinetic studies

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1. Introduction

Water pollution by heavy metals is becoming a subject of attention worldwide. In developing countries, industries such as tanning, chemical manufacturing, textiles, and fossil fuels lack proper waste treatment facilities and are therefore exposed to heavy metals poising [1–3]. The consequence of trace metal ions such as Pb^{2+} heads the list of environmental threats because,it causes venomous effects on brain, kidney, cardiovascular, and other important body parts [4].

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Presented at the 10th International Conference on Challenges in Environmental Science & Engineering (CESE-2017), 11–15 November 2017, Kunming, China

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Excessive ingestion of zinc can cause gastrointestinal distress and diarrhea [5]. For their removal from wastewater, some physicochemical approaches have been suggested, such as electro-chemical precipitation [6,7], ultrafiltration [8], and reverse osmosis [9]. However, such approaches are often ineffective and/or very expensive when used for the removal of heavy metal ions. Therefore, new technologies are required that can affordably reduce heavy metal concentrations to environmentally acceptable levels [10,11].

The application of plant-material adsorbents (biosorbents) for heavy metal removal is a viable choice for developing countries and is showing good progress as a sustainable environmental technology [12–18]. Biosorbents have the comparative advantages of non-polluting nature, low cost, good efficiency, and ease of operation, making them promising for wastewater treatment [19–21]. Several plant-based adsorbents have been reported for the removal of heavy metals from aqueous solution, such as rice husk [12], *Sporopollenin* [13], *Lactarius piperatus macrofungus* [14] *Codium vermilara* [16], *Cladophora fascicularis* [15], valonia tannin resin [17], and *corn silk* (*Zea mays* L.) [18]; Table 3 lists the maximum adsorption capacities of these materials. It is worthwhile to study these low-cost and environmentally suitable plant-material adsorbents.

The cactus *Opuntia*is inexpensive [22] and abundant natural material [23], have been suggested for water treatment in developing countries [24]. However, little work has been done in that respect. In the present study, *Opuntia* was used as an adsorbent for removing Pb^{2+} and Zn^{2+} from aqueous solution.

The purpose of this preliminary study was to investigate the feasibility of using dried *Opuntia* powder as a low-cost and environmentally friendly adsorbent for the removal of metal ions (Pb^{2+} and Zn^{2+}) from aqueous solution. The effects of adsorbent dose, contact time, initial metal ion concentration, initial solution pH, and temperature were studied. FT-IR spectroscopy, EDX, BET, and pH_{pzc} were used to characterize the adsorbent surface characteristics and morphology. To understand the adsorption process, the kinetics for the Pb^{2+} and Zn^{2+} removal by *Opuntia* was investigated and adsorption models were used to fit the experimental data.

2. Material and methods

2.1. Preparation and characterization of adsorbent

Opuntia was collected from an area near Mekelle city, Tigray regional state, Northern Ethiopia. Prior to use, the fresh *Opuntia* pads were washed several times with tap water and then distilled deionized water to remove dirt and surface impurities, cut into smaller pieces, and dried at 80°C for 1440 min. The dried *Opuntia* was ground and sieved using a 1.25 mm sieve and stored at 4°C before use. This sieved powder was used as the adsorbent in all experiments.

Points of zero charge (pH_{pzc}) were determined using 0.5 g samples of *Opuntia* adsorbent in 40 mL of 0.01 mol/L aqueous NaCl solution, adjusted to various pH values from 2 to 11 using 0.1 mol/L HCl or NaOH [25]. After adding *Opuntia* powder to the solution, it was shaken at 150 rpm and at 25°C for 1440 min. The pH was measured after filtration, and the change in pH was calculated from pH_{final} and $pH_{initial}$, with the intersection point representing the pH_{pzc} value. Surface areas of *Opuntia* powder samples were determined using nitrogen adsorption data acquired at 77.35 K using an ASAP 2020 adsorption analyzer (Micromeritics) after activating the samples at 673K under vacuum. Samples of virgin *Opuntia* powder and used *Opuntia* powder (separated from Pb or Zn solution after adsorption) were analyzed using Fourier transform infrared spectroscopy (FTIR) and energy dispersive spectroscopy (EDS).

2.2. Adsorption experiments

Adsorption experiments were conducted by adding dried *Opuntia* powder to Pb^{2+} and Zn^{2+} metals in aqueous solution. The experiments included various adsorbent doses, contact times, initial metal ion concentrations, solution pHs, and temperatures. Lead (II) nitrate (Kanto Chemical Co.) and zinc (II) chloride (Duksan Chemical) were used to prepare stock solutions (1,000 mg/L) of Pb^{2+} and Zn^{2+}, which were diluted with water to the required concentrations before use. A dose experiment was carried out by varying the amount of dried *Opuntia* powder adsorbent (from 0.1 to 4.0 g/L) under the fixed experimental conditions of 40 mL aqueous solution of Pb^{2+} or Zn^{2+} of 10 mg/L initial concentration, placed in 50 mL conical tubes, and shaken at 150 rpm at 25°C for 1,440 min. To evaluate the effect of contact time on Pb^{2+} and Zn^{2+} adsorption, 0.5 g/L doses of *Opuntia* adsorbent were used in samples of 10 mg/L concentration of metal ion; samples were shaken during the experiments, and the contact time for adsorption was varied from 30 to 2,880 min. To evaluate the effect of initial metal ion concentration, the concentrations were varied between 5 and 300 mg/L under the fixed experimental conditions of 0.5 g/L adsorbent dose, 150 rpm shaking, 25°C temperature, and 1,440 min contact time.

To investigate the effect of solution pH on Pb^{2+} and Zn^{2+} adsorption by *Opuntia* adsorbent, standard solutions of 10 mg/L Pb^{2+} and Zn^{2+} were prepared, samples of which were adjusted to vary in pH from 2–5 by adding 0.1 mol/L HCl at the beginning of each experiment. Adsorption isotherm experiments were conducted at different temperatures (5, 25 and 45°C) by mixing 0.5 g/L of *Opuntia* adsorbent into 10–300 mg/L solutions of Pb^{2+} or Zn^{2+}; these experiments were conducted at pH 4 with 1,440 min contact time. At the end of the predetermined contact time, each adsorption sample was filtered using a 0.45 µm filter (cellulose acetate, Hyundai Micro Co., Ltd.) and analyzed with inductively coupled plasma–atomic emission spectrometry (ICP–AES; IRIS, Thermo Jarrel Ash Co., USA) to measure the concentration of Pb^{2+} or Zn^{2+} ions. The ICP–AES apparatus was calibrated using standard metal ion solutions.

The amount of Pb^{2+} or Zn^{2+} at equilibrium (q_e, mg/g) with the *Opuntia* adsorbent was calculated using the following equation:

$$q_e = V \times \frac{(C_i - C_e)}{m} \quad (1)$$

where C_i and C_e are the initial and equilibrium ion concentrations in solution (mg/L), respectively; V is the volume of the aqueous solution (L); and m is the mass of the adsorbent (g).

The removal percentages of Pb^{2+} and Zn^{2+} were calculated using the following equation.

$$\% \ removal = \frac{C_i - C_e}{C_i} \times 100\% \tag{2}$$

3. Results and discussion

3.1. Effect of adsorbent dose and characterization of *Opuntia* powder

The effect of adsorbent dose on the removal of Pb^{2+} and Zn^{2+} metal ions from aqueous solution was evaluated by varying the dose under the fixed conditions of 1440 min contact time, pH 4, ambient temperature, and 10 mg/L initial concentrations of Pb or Zn. The Pb^{2+} and Zn^{2+} removal efficiencies in this system increased exponentially with increasing adsorbent dose, over the range of 0.1–0.5 g dose for Pb^{2+} and over the range of 0.1–2.0 g dose for Zn^{2+}. The removal efficiencies did not notably increase with increasing dose above 0.5 g for Pb^{2+} or above 2.0 g for Zn^{2+}. Thus, there appeared to exist maximum adsorption levels at which further addition of adsorbent had little or no effect. Similar trends have been reported by other researchers regarding zinc and lead adsorption [26–28]. This might be due to decreased adsorption sites for Pb^{2+} and Zn^{2+}. According to Fig. 1, the maximum removal efficiencies were 90.6% for Pb^{2+} at 0.5 g adsorbent dose and 37.6% for Zn^{2+} at 2.0 g adsorbent dose. It can also be seen from Fig. 1 that the adsorption capacity tended to decrease with increasing adsorbent dose. This decrease could arise from aggregation of sorbent sites, resulting in a low adsorptive surface area [23,29,30]. For ease of comparison, 0.5 g adsorbent doses were used for both metal ions in all further experiments.

To investigate the chemical functional groups present in the dried *Opuntia* powder, both before and after adsorption of Pb^{2+}or Zn^{2+} metal ions, FTIR spectra of virgin and used powder samples were acquired (Fig. 2). FTIR spectra of all sample types showed peaks at 3466, 3384, 2917, and 2862 cm^{-1}, attributed to hydroxyl groups, and peaks at 1616, 1363, 1320, 1160, 1089, 784, and 663 cm^{-1}, attributed to amide or C=O groups. These peaks were slightly less intense for the used powders relative to the virgin powder. These results are in agreement with previously reported observations [23].

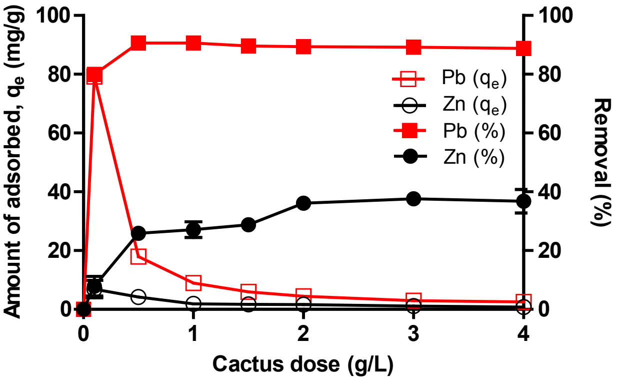


Fig. 1. Effect of dose on the Pb^{2+} and Zn^{2+} adsorption capacities and removal efficiencies of *Opuntia* adsorbent (Initial concentration: 10 mg/L; dose: 0.1–4.0 g/L; temperature: 25°C; pH: 4; contact time: 1,440 min).

EDS spectra of virgin and loaded *Opuntia* powder adsorbents were acquired to confirm the adsorption process for Pb^{2+} and Zn^{2+} metal ions by *Opuntia*. The virgin powder showed the presence of C, O, Mg, Ca, Pb and K (Fig. 3a). A stronger Pb peak was observed for the powder loaded as a Pb *Opuntia* (Fig. 3b), and a new Zn peak was observed for the powder loaded as a Zn *Opuntia* (Fig. 3c), confirming the binding of these metals to the *Opuntia* adsorbent. The specific surface area of the *Opuntia* adsorbent was estimated to be 0.67 m^2/g using the BET method.

3.2. Kinetics study

The adsorption of Pb^{2+} and Zn^{2+} metal ions onto *Opuntia* adsorbent at various contact times from 30 to 2880 min was studied for the initial Pb^{2+} and Zn^{2+} concentrations of 5, 10, and 50 mg/L.

The pseudo-first-order, pseudo-second-order, and Elovich models were each fit to the experimental data in order to elucidate the adsorption mechanism. The pseudo-first-order kinetics for adsorption of Pb^{2+}or Zn^{2+} onto dried *Opuntia* powder was calculated using the Lagergren model, which can be expressed as follows [31,32]:

$$\log\left(q_e - q_t\right) = \log q_e - \frac{k_1}{2.303}t \tag{3}$$

where q_e is the amount adsorbed (mg/g), t is the time (min), and k_1 is the adsorption rate constant.

The pseudo-second-order kinetics for the adsorption of Pb^{2+} or Zn^{2+} onto dried *Opuntia* powder was calculated using the Ho model [33] as follows:

$$\frac{t}{q_t} = \frac{t}{k_2\left(q_e\right)^2} \frac{t}{k_2\left(q_e\right)^2} + \frac{t}{q_e} \tag{4}$$

where k_2 is the adsorption rate constant.

The Elovich equation is another rate determining equation, which is suitable to describe adsorption behavior that concurs with the nature of chemical adsorption based on the adsorption capacity [34,35]. The Pb^{2+} and Zn^{2+} adsorp-

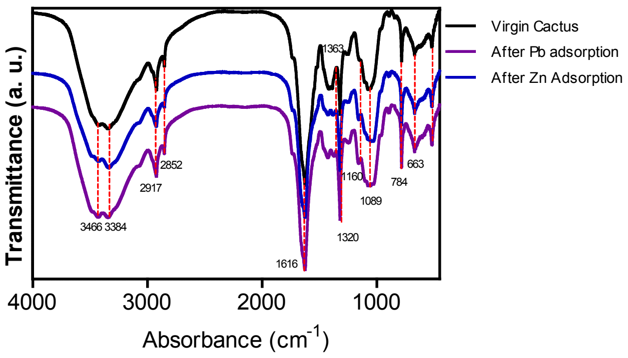
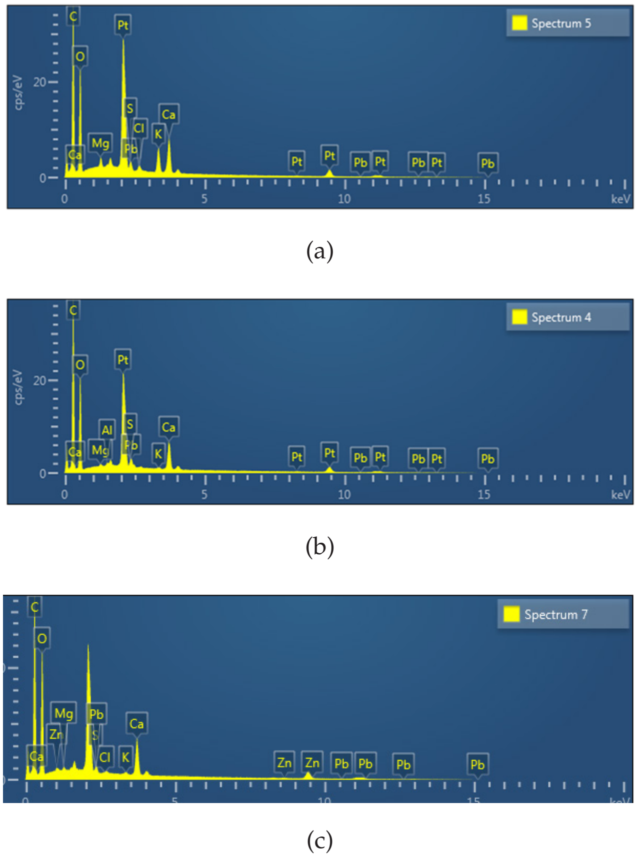


Fig. 2. FTIR spectra of virgin and used *Opuntia* adsorbents.



(a)

(b)

(c)

Fig. 3. EDS spectra of (a) virgin *Opuntia* adsorbent and (b, c) *Opuntia* adsorbents after adsorption of (b) Pb^{2+} and (c) Zn^{2+}.

tion capacities of the *Opuntia* adsorbent were calculated using the following equation [33,36,37]:

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}lnt, \tag{5}$$

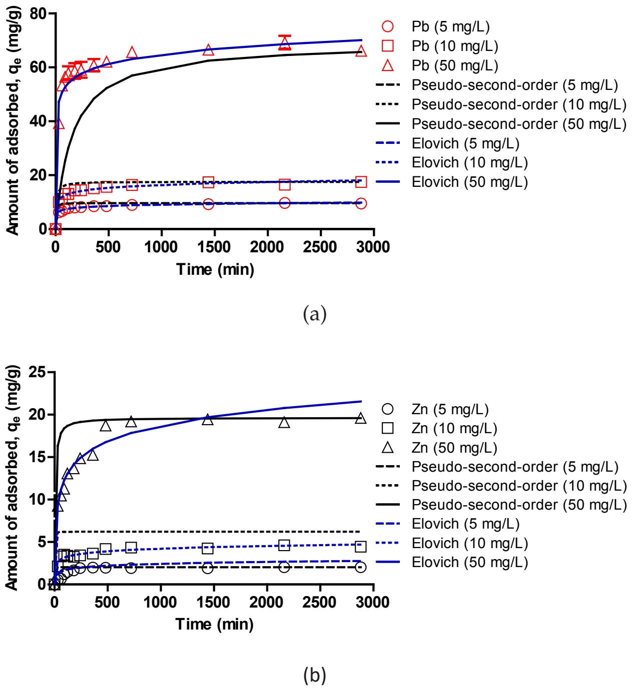
where α (mg/g/min) is the initial adsorption rate, and β (g/mg) is the adsorption constant.

Linear regression analysis (coefficient of determination R^2) was used to analyze the linear forms of each kinetic model. Kinetic constants were determined using the slope and intercept values of the linear plots. In addition, to quantitatively compare the models' suitability, the normalized standard deviation (Δ*q*)of each model was determined as follows:

$$\Delta q(\%) = 100 \times \sqrt{\frac{\Sigma\left[\left(q_{e,exp} - q_{e,cal}\right)/q_{e,\exp}\right]^2}{n-1}} \tag{6}$$

where $q_{e,cal}$ is the calculated equilibrium uptake of adsorbate (mg/g), $q_{e,exp}$ is the measured equilibrium uptake of adsorbate (mg/g), and *n* represents the number of data points. Because Δ*q* represents the agreement between the experimental and prophesied data points, it offers a numerical measure to interpret a mathematical model's goodness of fit to the data [38,39].

Determination of the order of adsorption process was based on three criteria: first, R^2; second, predicted q_e; and third, Δ*q* [40].



(a)

(b)

Fig. 4. Effect of contact time on the adsorption of (a) Pb^{2+} and (b) Zn^{2+} onto *Opuntia* adsorbent (Dose: 0.5 g/L; contact time: 30–2,880 min; temperature: 25°C; pH: 4; initial concentration: 5, 10, or 50 mg/L).

Figs. 4a and 4b show the effect of contact time on Pb^{2+} and Zn^{2+} adsorption onto *Opuntia* adsorbent. Rapid adsorption kinetics within 240 min was observed for both Pb^{2+} and Zn^{2+} metal ions, and equilibrium states were reached by 1440 min. This result might be due to the fact that all adsorbent sites were initially unoccupied, and the solute concentration gradient was high. These findings are in agreement with previous work by other researchers [27,41].

To study the adsorption kinetics of Pb^{2+} and Zn^{2+} ions onto *Opuntia* adsorbent, the pseudo-first-order, pseudo-second-order, and Elovich models were fit to the experimental data to determine which fit best as a means of elucidating the adsorption mechanism. Table 1 lists the kinetic parameters calculated for each model using Eqs. (4)–(6).

Straight line plots (not shown) of the pseudo-first-order (log (q_e–q_t) vs. *t*), pseudo-second-order (t/q_t vs. *t*), and Elovich models (q_t vs. ln *t*) indicated that the pseudo-second-order and Elovich models were most relevant to the adsorption of Pb^{2+} and Zn^{2+} onto the *Opuntia* adsorbent. Table 1 presents the rate constants and R^2 values for each model, as well as the q_e and Δ*q* values.

Detailed analysis of the data indicated that the pseudo-second-order and Elovich models showed good agreement (Fig. 4).Therefore, these models are more appropriate than the pseudo-first-order model to explain the processes whereby Pb^{2+} and Zn^{2+} adsorb onto *Opuntia* adsorbent. Given that, in the pseudo-first-order model, adsorbate concentration is assumed to be the controlling factor, these results suggest that the adsorption of Pb^{2+} and Zn^{2+} was controlled not by the Pb^{2+} and Zn^{2+} concentrations, but rather by the availability of adsorption sites on the *Opuntia*

Table 1
Experimental and calculated values of q_e, k_1, k_2, α, β, and R^2

	q_e (exp) (mg/g)	Pseudo-first-order				Pseudo-second-order			
		k_1 (L/min)	q_e (calc) (mg/g)	R^2	Δq	k_2 (g/mg/min)	q_e (exp) (mg/g)	R^2	Δq
Pb	17.576	0.00115	4.565	0.790	0.68	0.0564	17.576	0.999	0.22
Zn	6.226	0.00092	3.658	0.84	0.86	0.2137	6.226	0.998	0.88
	q_e (exp) (mg/g)		Elovich						
			α (g/mg/min)		β (exp) (mg/g)			R^2	Δq
Pb	17.576		50.01		0.63			0.929	0.05
Zn	6.226		0.72		1.49			0.8575	0.10

powder. The high R^2 values of Elovich model and low value of surface area revealed that the main driving force between *Opuntia* adsorbent and metal ions (Pb^{2+} and Zn^{2+}) adsorption might be not Van der Waals force, could be chemisorption. At this step, more investigations are needed to fully elucidate the adsorptions mechanisms.

3.3. Isotherm studies

The effects of initial Pb^{2+} and Zn^{2+} metal ion concentration on the adsorption efficiency of *Opuntia* adsorbent were studied for initial concentrations of Pb^{2+} and Zn^{2+} ranging between 5 and 300 mg/L, under the fixed conditions of 1,440 min contact time, 150 rpm shaking in a shaker incubator, and 25°C temperature. The Langmuir and Freundlich equations were used to determine the adsorption behaviors of Pb^{2+} and Zn^{2+} onto *Opuntia* adsorbent and their equilibrium concentration in solution.

Langmuir isotherms for the adsorption of Pb^{2+} and Zn^{2+} onto *Opuntia* adsorbent were calculated using the following equation [42]:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} b} + \frac{C_e}{q_{\max}} \tag{7}$$

where q_e is the amount adsorbed (mg/g), C_e is the equilibrium concentration (mg/L), $q_{\max}$ is the maximum amount adsorbed (mg/g), b is the rate of adsorption (L/mg).

Freundlich isotherms were estimated using the following equation[43]:

$$q_e = K_F C e^{1/n} \tag{8}$$

where K_F and $1/n$ are Freundlich constants related to adsorption capacity and adsorption intensity, respectively.

Fig. 5 shows the effect of initial concentration on the adsorption of Pb^{2+} and Zn^{2+} onto *Opuntia* adsorbent. The amounts of Pb^{2+} and Zn^{2+} adsorbed increased with increasing initial metal ion concentration. The maximum amounts of Pb^{2+} and Zn^{2+} adsorbed onto the *Opuntia* were 119.0 mg/g at 300 mg/L initial Pb^{2+} concentration and 32.3 mg/g at 200 mg/L Zn^{2+} concentration. Pb^{+2} adsorbed preferentially over Zn^{2+} onto the *Opuntia* adsorbent. The higher removal efficiency of Pb^{+2} compared to Zn^{2+} under the same experimental conditions might have arisen from their differences in electronegativity, chemical affinity with chemical functional groups on the surface of the adsorbent, and/or molecular weight [27].

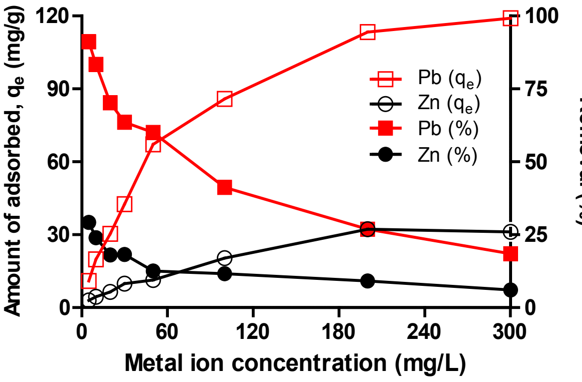


Fig. 5. Effect of initial ion concentration on the removal efficiency of (a) Pb^{2+} and (b) Zn^{2+} by *Opuntia* adsorbent (Dose: 0.5 g/L; initial concentration: 5–300 mg/L; temperature: 25°C; pH: 4; contact time: 1,440 min).

As shown in Fig. 6, the amount of adsorbed metal ions increased with increasing initial metal concentration. This could have arisen from enhanced mass transfer of metal ions [29]. Fig. 6 also shows that increasing metal ion concentration increased the amount of metal ion uptake per unit weight of *Opuntia* adsorbent (mg/g). This result is in agreement with previous adsorption studies of Pb^{2+} and Zn^{2+} [27,44,45].

The Langmuir and Freundlich isotherm models were used to evaluate the Pb^{2+} and Zn^{2+} adsorption capacity of *Opuntia* adsorbent. The Langmuir model represents an adsorption process on a homogenous surface by monolayer adsorption without interaction between adsorbed molecules [19]. The linearized Langmuir model was used herein, as expressed in Eq. (7). The Langmuir constants were calculated, and the values of $q_{\max}$ and b were calculated from the slope and intercept of the Langmuir plot of C_e vs. C_e/q_e [10]; $q_{\max}$ and b were calculated to be 62.89 and 0.37 for Pb^{2+}, respectively, and 21.59 and 0.04 for Zn^{2+}. For the Langmuir model, the correlation coefficient (R^2) values for Pb^{2+} and Zn^{2+} were found to be 0.92 and 0.96, respectively (Table 2).

The Freundlich model can be applied for multilayer adsorption onto heterogeneous surfaces. The linearized

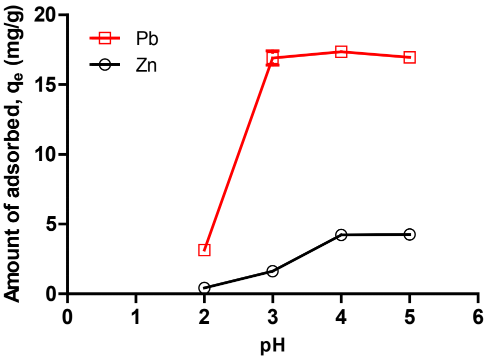


Fig. 6. Effect of initial solution pH on Pb^{2+} and Zn^{2+} adsorption capacities of *Opuntia* adsorbent (Dose: 0.5 g/L; initial concentration: 10 mg/L; temperature: 25°C; pH: 2–5; contact time: 1,440 min).

Table 2
Isotherm parameters of Langmuir and Freundlich models for Pb^{2+} and Zn^{2+} adsorption by *Opuntia* adsorbent

Isotherm type	Isotherm parameters	25°C
Langmuir (Pb)	q_{max}(mg/g)	62.89
	b (L/mg)	0.37
	R^2	0.921
	Δq	0.36
Freundlich (Pb)	K_F(mg/g)(L/mg)$^{1/n}$	15.23
	$1/n$	0.401
	R^2	0.980
	Δq	0.12
Langmuir (Zn)	q_{max} (mg/g)	21.60
	b (L/mg)	0.04
	R^2	0.962
	Δq	0.25
Freundlich (Zn)	K_F(mg/g)(L/mg)$^{1/n}$	1.42
	$1/n$	0.59
	R^2	0.986
	Δq	0.10

Freundlich model was used for the adsorption process as expressed in Eq. (8). Table 2 lists the values of K_F and $1/n$, Freundlich parameters that incorporate all factors affecting the adsorption process. The magnitudes of K_F and $1/n$ are related to the adsorption capacity of the adsorbent to the adsorbate and to a function of adsorbent heterogeneity, respectively. The parameter $1/n$ is related to the distribution of adsorption site energies, and values of $1/n$ between 1 and 0.1 represent beneficial adsorption [46,47]. The $1/n$ values for the *Opuntia* adsorbent were within this range for both Pb^{2+} and Zn^{2+}, indicating favorable adsorption of these species. This result is in agreement with previous adsorption studies of zinc [14].

Table 2 lists the isotherm parameters obtained from both the Langmuir and Freundlich models. The R^2 values of the Freundlich model were higher than those of the Langmuir model for both Pb^{2+} and Zn^{2+}, indicating that the adsorptions of Pb^{2+} and Zn^{2+} onto the *Opuntia* adsorbent obey the Freundlich isotherm model and thus are multilayer adsorption processes.

Table 3
Pb^{2+} and Zn^{2+} adsorption capacities of various plant-based adsorbents

Adsorbent	Pb(II)	Zn(II)	Reference
Cactus *Opuntia*	62.89	21.60	Present study
Valonia tannin resin	68.36	12.28	[17]
Rice husk	58.1	8.14	[12]
Sporopollenin	8.52	–	[13]
Lactarius piperatus macrofungus	–	7.54	[14]
Codium vermilara	63.30	23.80	[16]
Cladophora fascicularis	58.08	–	[15]
Corn silk (*Zea mays* L.)	–	13.98	[18]

The q_{max} calculated in the present study was compared with the results of previous studies on different untreated plant material adsorbents for Pb^{2+} and Zn^{2+} removal from aqueous solution; Table 3 summarizes the results. The *Opuntia* adsorbent used in the present study has relatively good capacity, making it suitable for removal of Pb^{2+} and Zn^{2+} from water contaminated with these heavy metals.

3.4. Effect of initial solution pH

The initial pH of a solution is considered to be an important parameter controlling the adsorption of heavy metals from aqueous solutions, because pH impacts the ionization of the functional groups present on the surface of the adsorbent and the chemical speciation of the metal ions [29]. Thus, experiments to investigate the effect of solution pH on adsorption efficiency of Pb^{2+} and Zn^{2+} metal ions were carried out by varying the initial solution pH between 2 and 5. The adsorption efficiencies of Pb^{2+} and Zn^{2+} metal ions were found to be low at pH below 3and increased gradually with increasing pH from 3 to 4. However, the adsorption percentage decreased for pH 5. The optimum pH yielding maximum metal ion adsorption was found to be 4 for both Pb^{2+} and Zn^{2+} ions. Therefore, pH 4 was considered to be the optimum pH of aqueous solutions in subsequent experimental studies.

As shown in Fig. 6, the adsorption of Pb^{2+} and Zn^{2+} ions was low in low pH and increases with increasing the solution pH. The low removal at low pH might be due to the more highly protonated surface area of the adsorbent and competition between Pb^{2+} and Zn^{2+} ions and H_3O^+ [48,49] toward the binding sites, and the rapid increase in binding efficiency with pH up 4 could be due to the presence of negative charge on the surface of the adsorbent that might be responsible for metal binding [27,30].

The pH_{pzc} of the *Opuntia* adsorbent was found to be 6.3 (Fig. 7). The surface of the adsorbent was positively charged for pH below the pH_{pzc} value and negatively charged for pH above pH_{pzc}. Because the greatest adsorbed amount of metal ions occurred at pH of around 4, which was less than the pH_{pzc}, it can be concluded that electrostatic forces (attractive

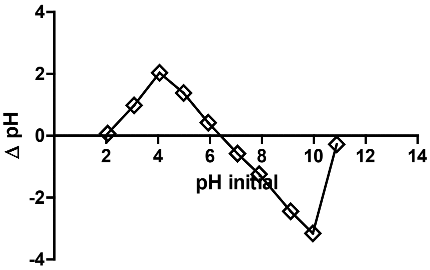


Fig. 7. pH_{pzc} plot for *Opuntia* adsorbent (Dose: 0.5 g/L; contact time: 1,440 min; temperature: 25°C; pH: 2–11; solvent: 0.01 mol/L NaCl solution).

and repulsive) do not contribute to the adsorption of Pb^{2+} and Zn^{2+} onto *Opuntia* adsorbent [50].

3.5. Thermodynamic study

Temperature influences the possibility of diffusion of solutes onto the adsorbent surface and affects the number of active surface sites [5]. Thus, study on the effect of temperature on adsorption efficiency of *Opuntia* adsorbent was carried out at various initial metal ion concentrations and various temperatures from 4 to 45°C, under the fixed conditions of 1,440 min contact time and pH 4. The result indicated that, the adsorption efficiency of Pb^{2+} and Zn^{2+} ions enhanced with increasing temperature from 5 to 45°C. The increase of metal ion removal with increasing temperature indicates that the process of Pb^{2+} and Zn^{2+} adsorption by the *Opuntia* adsorbent is an endothermic process. Similar observations were reported in previous studies [13,41].

Thermodynamic parameters are considered as important parameters in providing thorough information related to internal energy changes about adsorption. To predict the adsorption process, the standard free energy change ($\Delta G°$), the standard enthalpy change ($\Delta H°$), and the standard entropy change ($\Delta S°$) were calculated from the temperature-dependent adsorption isotherms. The standard free energy change ($\Delta G°$) for adsorption of Pb^{2+} and Zn^{2+} adsorption capacity of *Opuntia* adsorbent were calculated using the following equation [51]:

$$\Delta G^{\circ} = -RT \ln K^{\circ} \tag{9}$$

The K_c distribution adsorption coefficient is calculated from the following equation [52]:

$$K_c = \frac{1000 q_e}{C_e} \tag{10}$$

where R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T is the absolute temperature (K), q_e is the adsorption capacity (mg/g), and C_e is the equilibration concentration after centrifugation (mg/L). To make K_c dimensionless, q_e is multiplied by 1000 before calculating the logarithm [52]. The $K°$ adsorption equilibrium constant of *Opuntia* adsorbent can be calculated by plotting ln K_c vs. C_e and extrapolating C_e to zero, taking the value of the intercept as ln $K°$. The standard enthalpy change ($\Delta H°$) and the standard entropy change ($\Delta S°$) are calculated from the following equation [51].

$$\ln K^{\circ} = -\frac{\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R} \tag{11}$$

The slope and intercept of the plot of ln $K°$ vs. $1/T$ are $-\Delta H°/R$ and $\Delta S°/R$, respectively. Table 4 lists the thermodynamic parameters calculated from Eqs. (10)–(12) for three different temperatures. The negative sign of the standard free energy change ($\Delta G°$) indicated that the adsorption was a spontaneous process; also, the value of $\Delta G°$ became more negative with increasing temperature, indicating that heat facilitated the adsorption of Pb^{2+} and Zn^{2+} onto *Opuntia* adsorbent. The positive sign of $\Delta H°$ suggested the endothermic nature of adsorption process, which was also supported by the increment in the adsorption capacity of Pb^{2+} and Zn^{2+} with increasing temperature. The positive entropy change ($\Delta S°$) for this reaction also indicated an increase in the number of species at the solid–liquid interface, hence the randomness in the interface that is presumably due to the release of water molecules when the Pb^{2+} and Zn^{2+} were adsorbed on the surface of the adsorbent. The values of the thermodynamic parameters gave us insight into the interaction between the *Opuntia* adsorbent and the metal ions Pb^{2+} and Zn^{2+}.

3.6. Competitive adsorption of metal ions from binary metal aqueous solution

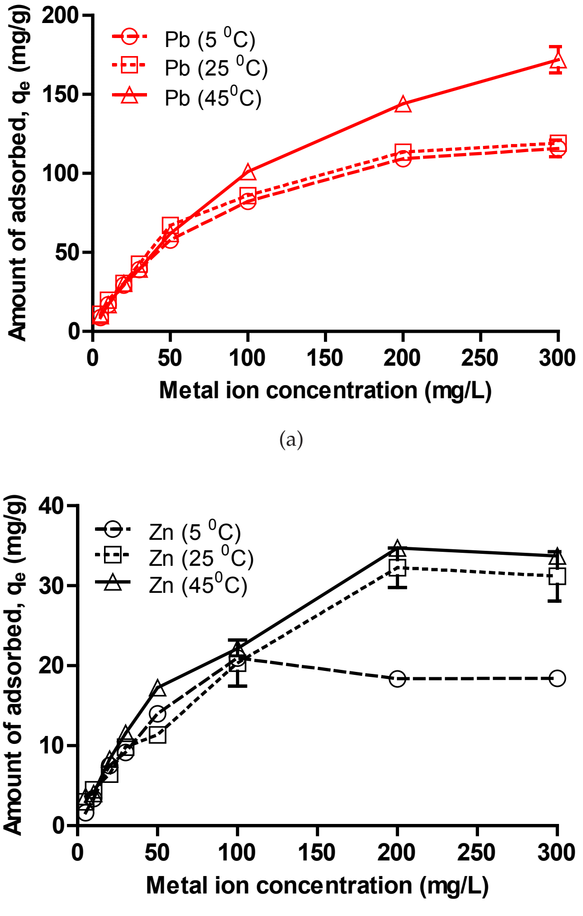
The competitive adsorption efficiencies for the Pb^{2+}/Fe^{2+}, Pb^{2+}/Mn^{2+}, Zn^{2+}/Fe^{2+}, and Zn^{2+}/Mn^{2+} binary systems were studied by fixing the initial concentration of Pb^{2+} or Zn^{2+} to 10 mg/L in each system. The adsorption efficiencies of Pb^{2+} and Zn^{2+} ions onto *Opuntia* adsorbent in the presence of the competing metal ions Fe^{2+} or Mn^{2+} at varied initial concentrations (5, 10, and 20 mg/L) were investigated in terms of removal efficiency. The competitive adsorption experiments were conducted under the conditions of 1,440 min contact time, pH 4, 0.5 g/L adsorbent dose, and 150 rpm shaking.

In both the Pb^{2+}/Fe^{2+} and Pb^{2+}/Mn^{2+} systems, Pb^{2+} removal efficiency decreased with increasing concentration of either Fe^{2+} or Mn^{2+} (Fig. 9). In the Pb^{2+} single system, a maximum Pb^{2+} removal efficiency of about 90.6% was obtained at 0.5 g/L adsorbent dose and 10 mg/L initial concentration, whereas in the Pb^{2+}/Fe^{2+} binary metal system under the same initial concentration of Pb^{2+} and adsorption conditions, the removal efficiencies were found to be 89.0%, 88.4%, and 83.1% for the initial Fe^{2+} concentrations of 5, 10, and 20 mg/L, respectively (Fig. 9a). In the Pb^{2+}/Mn^{2+} binary metal system, the Pb^{2+} removal efficiencies were found to be 83.9%, 80.6%, and 76.9% for the initial Mn^{2+} concentrations of 5, 10, and 20 mg/L, respectively (Fig. 9b).

In both the Zn^{2+}/Fe^{2+} and Zn^{2+}/Mn^{2+} systems, Zn^{2+} removal efficiency decreased with increasing concentration of either Fe^{2+} or Mn^{2+} (Fig. 9). In the Zn^{2+} single system, the maximum Zn^{2+} removal efficiency of 25.9% was obtained at the 0.5 g/L adsorbent dose and 10 mg/L initial concentration, whereas in the Zn^{2+}/Fe^{2+} binary metal system under the same initial concentration of Zn^{2+} and adsorption conditions, the removal efficiencies were found to be 23.1%, 20.4%, and 15.5% for the initial Fe^{2+} concentrations of 5, 10, and 20 mg/L, respectively (Fig. 10a). In the Zn^{2+}/Mn^{2+} binary metal system, the Zn^{2+} removal effi-

Table 4
Thermodynamic parameters of Pb^{2+} and Zn^{2+} adsorption on *Opuntia* adsorbent

	Temperature (K)	ΔG⁰ (kJ/mol)	ΔH⁰ (kJ/mol)	ΔS⁰ (J/mol/K)
Pb	278.15	–19.35	14.92	122.99
	298.15	–21.61		
	318.15	–24.29		
Zn	278.15	–14.19	4.37	66.83
	298.15	–15.61		
	318.15	–16.86		



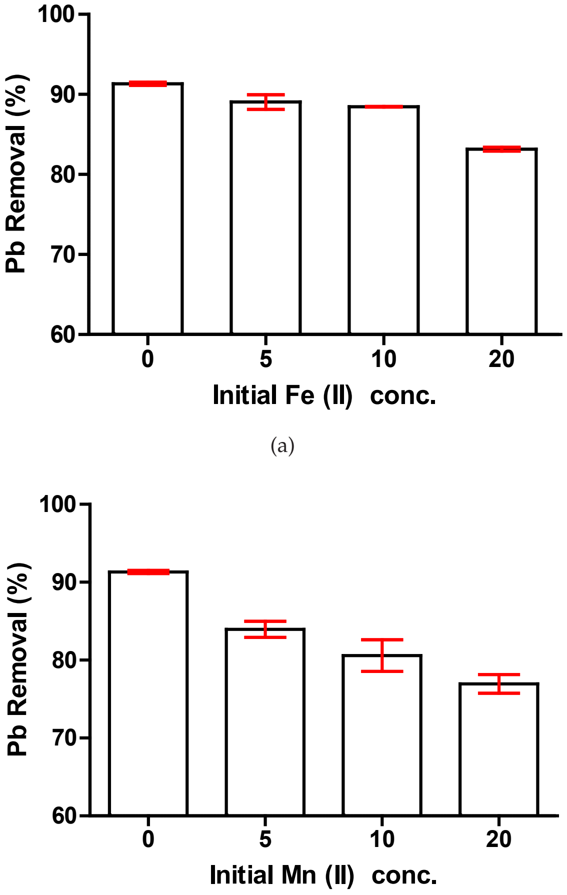
(a)

(b)

Fig. 8. Effect of temperature on (a) Pb^{2+} and (b) Zn^{2+} adsorption capacities of *Opuntia* adsorbent (Dose: 0.5 g/L; contact time: 1,440 min; temperature: 5, 25, or 45°C; pH: 4; initial concentration: 5–300 mg/L).

ciencies were found to be 16.1%, 15.9%, and 12.9% for the initial Mn^{2+} concentrations of 5, 10, and 20 mg/L, respectively (Fig. 10b).

As can be seen in Figs. 9 and 10, the removal capacity of Pb^{2+} and Zn^{2+} tended to decrease with increasing initial concentration of the competing metal (Fe^{2+} and Mn^{2+}) ions. These decreasing trends probably arose from competition between the metals in saturating the finite surface bridging sites available on the *Opuntia* adsorbent. In addition, it could also arise from the ability of the metal ions to compete for the adsorption sites available in the adsorbate. This result is in agreement with previous observations [17,53].



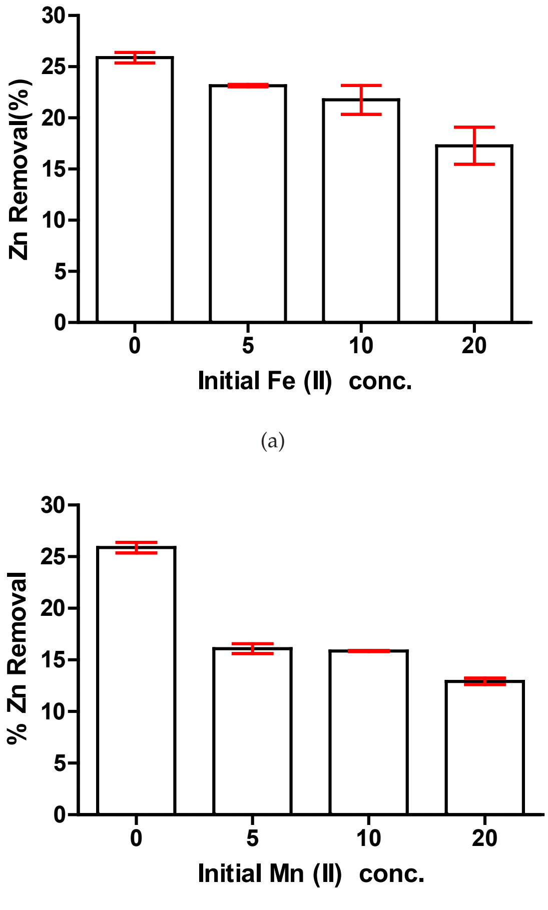
(a)

(b)

Fig. 9. Trends in Pb^{2+} removal efficiency by *Opuntia* adsorbent: removal with Pb^{2+} present as a single metal and in binary systems with (a) Fe^{2+} and (b) Mn^{2+} ions in increasing initial concentrations (Dose: 0.5 g/L; contact time: 1,440 min; temperature: 25°C; pH: 4; initial concentration: 0, 5, 10, 20 mg/L).

4. Conclusions

In the present work, we studied the adsorption efficiency of *Opuntia* adsorbent as a low-cost adsorbent and its mechanism of adsorbing metal ions (Pb^{2+} and Zn^{2+}) from aqueous solution. The maximum metal ion removal efficiencies of Pb^{2+} and Zn^{2+} were found to be 90.6% and 37.6%, respectively, at doses of 0.5 and 2.0 g/L. The maximum amounts of Pb^{2+} and Zn^{2+} adsorbed onto *Opuntia* adsorbent were 119.0 and 32.3 mg/g, respectively, at initial concentrations of 300 and 200 mg/L. Adsorption of Pb^{2+} and Zn^{2+} was affected by pH, and the optimum pH giving maximum adsorption was found to be approximately 4.



(a)

(b)

Fig. 10. Trends in Zn^{2+} removal efficiency by *Opuntia* adsorbent: removal with Zn^{2+} present as a single metal and in binary systems with (a) Fe^{2+} and (b) Mn^{2+} ions in increasing initial concentrations (Dose: 0.5 g/L; contact time: 1,440 min; temperature: 25°C; pH: 4; initial concentration: 0, 5, 10, 20 mg/L).

A kinetic study of Pb^{2+} and Zn^{2+} adsorption onto *Opuntia* adsorbent showed that the pseudo-second-order and Elovich models best fit the adsorption data. The adsorption of Pb^{2+} and Zn^{2+} onto *Opuntia* was verified by EDS. In isotherm studies, the adsorptions of Pb^{2+} and Zn^{2+} onto *Opuntia* adsorbent were better fit by the Freundlich isotherm model than by the Langmuir isotherm model, indicating that both were multilayer adsorption processes. Calculated thermodynamic parameters indicated that the adsorption processes were spontaneous and endothermic. Competition adsorption studies showed high removal efficiencies of Pb^{2+} and Zn^{2+} in the presence of the interfering ions Fe^{2+} and Mn^{2+}, with decreasing trends in removal efficiency with increasing concentrations of the interfering metal ions. This preliminary study concludes that dried powder of cactus *Opuntia* can be used as an effective, low-cost,and environmentally friendly adsorbent for the removal of Pb^{2+} and Zn^{2+} from aqueous solution. Because of the promising Zn^{2+} and Pb^{2+} removal efficiencies demonstrated in the present work, we plan to investigate surface modifications of this adsorbent, as well as the potential application and detail adsorption mechanism of this adsorbent for the removal of other heavy metal ions.

Symbols

C_i	—	Initial ion concentrations (mg/L)
C_e	—	Equilibrium ion concentrations (mg/L)
V	—	Volume of aqueous solution (L)
m	—	Mass of the adsorbent (g)
q_e	—	Amount adsorbed (mg/g)
t	—	Time (min)
k_1	—	Adsorption first order rate constant
k_2	—	Adsorption second order rate constant
α	—	Initial adsorption rate (mg/g/min)
β	—	Adsorption constant (g/mg)
$q_{e,cal}$	—	Calculated equilibrium uptake of adsorbate (mg/g)
$q_{e,exp}$	—	Measured equilibrium uptake of adsorbate (mg/g)
n	—	The number of data points
Δq	—	The agreement between the experimental and prophesied data points
$q_{\max}$	—	Maximum amount adsorbed (mg/g)
b	—	Rate of adsorption (L/mg)
K_F	—	Freundlich constants related to adsorption capacity
$1/n$	—	Freundlich constant related to adsorption intensity
$\Delta G°$	—	Standard free energy change
$\Delta H°$	—	Standard enthalpy change
$\Delta S°$	—	Standard entropy change
R	—	Universal gas constant (8.314 J mol^{-1} K^{-1})
T	—	Absolute temperature (K)
$K°$	—	Adsorption equilibrium constant
K_c	—	Distribution adsorption coefficient

Acknowledgements

This work was supported by the Ministry of Education of the Republic of Korea and the National Research Foundation of Korea (NRF-2016S1A5B8925203).

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