Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1067831

57 (2016) 14544–14551
July

Taylor & Francis
Taylor & Francis Group

Biosorption of Pb(II), Cu(II), and Ni(II) ions onto novel lowcost *P. eldarica* leaves-based biosorbent: isotherm, kinetics, and operational parameters investigation

Sevna Asgarzadeh[a], Roshanak Rostamian[b], Elham Faez[c], Afshin Maleki[d], Hiua Daraei[e,*]

[a]*Department of Chemistry, Tehran Shomal Azad University, Tehran, Iran, Tel. +98 21 22977862; email: sevna.asgarzadeh@yahoo.com*
[b]*Department of Chemistry, Razi University, Kermanshah, Iran, Tel. +98 83 34274559; email: roshanak_rostamian@yahoo.com*
[c]*School of Health, Safety & Environment, Shahid Beheshti University of Medical Sciences, Sanandaj, Iran, Tel. +98 21 77309960; email: jobin_es2000@yahoo.com*
[d]*Kurdistan Environmental Health Research Center, Kurdistan University of Medical Sciences, Sanandaj, Iran, Tel. +98 871 6131504; email: Maleki43@yahoo.com*
[e]*Kurdistan Environmental Health Research Center, Kurdistan University of Medical Sciences, Sanandaj, Iran, Tel. +98 871 6131466; Fax: +98 871 6625131; email: Hiua.Daraei@muk.ac.ir*

Received 20 October 2014; Accepted 23 June 2015

ABSTRACT

In this study, the novel low-cost *Pinus eldarica* leaves-based biosorbent (Pe) was introduced to remove heavy metal ions from aqueous media. The Pe ability of Pb(II), Cu(II), and Ni(II) ions biosorption was investigated in aqueous solutions. The maximum sorption capacity was 40, 26, and 33 mg g^{-1} for Pb(II), Cu(II), and Ni(II), respectively, that was so promising. Experiments were carried out in lab-scale batch reactors as function of initial pH (pH$_0$), initial concentration of heavy metal ions (C_0), and contact time (t). The statistical analysis was applied to determine the significant parameters, rank of parameter influences, and type of influences. The adsorption kinetics data were modeled using the pseudo-first, pseudo-second-order, and intraparticle diffusion kinetics equations. The pseudo-first-order and pseudo-second-order kinetics equations described the adsorption kinetics very well. Finally, the equilibrium data were described by 15 isotherm models with different number of parameters from two to five. The results revealed that the Langmuir and Fritz–Schlunder models provided the best correlation of the experimental data.

Keywords: Biosorption; *Pinus eldarica* leaves; Heavy metals; Isotherm; Kinetics

1. Introduction

Heavy metals are among the main pollutants of water and wastewaters in Iran and in other countries [1,2]. Industrial wastewaters of a variety of industries usually contain harmful heavy metal ions that can damage the aquatic life and human health [3]. Heavy metals are non-biodegradable pollution. Heavy metal ions accumulate in living tissues causing several

---

*Corresponding author.

diseases and disorders; therefore, heavy metal must be removed before discharge into the environment [4].

There are several treatment methods for effluents containing heavy metals including precipitation [5], filtration [6], reduction [7], extraction, ion exchange [8], and adsorption [9,10]. In recent years, application of biosorption in removing heavy metal pollution has gained more attention [11,12]. Since Iran as a developing country has a lot of problems with heavy metal pollution of water sources, the application of low-cost technology to solve the problems will be promising.

Since biosorbents effectively and quickly possess dissolved metal ions, sequestering their property, and decrease the concentration of heavy metal ions in solution from ppm to ppb level, they are an ideal candidate for the treatment of high-volume and low-concentration complex wastewaters [13–16]. Various natural materials of biological origin, including different plant species [17,18], bacteria [19], fungi [20], yeast, algae, etc., have been utilized as biosorbents.

Pine tree as the local plant of Iran shows a high ability to absorb heavy metal from the environment [21]. Their efficiency in application as the heavy metal pollution bioindicator confirms their ability to heavy metal absorption [22]. The leaves of plants such as pine trees can be used as low-cost precursor to produce biosorbent [23]. Although there are a lot of studies on pine bark [24] and pine cone [25]-based biosorbent, pine leaves have rarely been applied to produce biosorbent [26]. It could therefore be promising to produce efficient biosorbent based on pine tree leaves.

Adsorption equilibrium and kinetics information are the necessary requirements for the adsorption process. Sorption capability is an important parameter for process cost estimation [12,27,28]. The sorption efficiency is determined experimentally at constant temperature, and the results are presented as isotherms. The adsorption data may be described by empirical equations called isotherm models with estimated constants. The description of the sorption isotherms can be based on models with different numbers and arrangements of parameters. The simplest and usual method for determination of constants in two parametric models is transformation to a linear equation form; however, non-linear regression can be used as an alternative method [28–30].

In this work, the biosorption of Pb(II), Cu(II), and Ni(II) onto *Pinus eldarica*-based biosorbent was studied focusing on kinetics and sorption isotherms of the process. Also, the influence of operational parameters including initial pH (pH_0), initial concentration of heavy metal cations (C_0), and contact time (t) was studied experimentally.

2. Materials and methods

2.1. Biosorbent preparation and biosorption experiments

Fresh leaves of *P. eldarica* were collected in June from Tehran pine trees. The leaves were washed by warm deionized water several times and then dried at room temperature. The dried materials were powdered and sieved with mesh 35–60 μm. The synthetic wastewaters containing Pb(II), Cu(II), and Ni(II) were prepared by diluting their 1,000 ppm spectroscopy-grade stock solution of nitrate salts. Deionized double-distilled water was used for diluting the solution. Since the solutions pH_0 was adjusted using nitric acid, the nitrate salts were used to prevent more counter ion influences. The biosorption experiments were carried out in 100-ml flask batch reactor. The reactor was supported by a 100-rpm shaker. The experiments were started by pouring 50 ml of prepared synthetic wastewater, pH adjustment, and adding 0.5 g of biosorbent (10 g L^{-1}). Spectrophotometer (Shimadzu, AA-6800) was applied for determination of remaining and initial concentration. All experiments were triplicated and the mean values have been reported.

2.2. Operational parameter influences investigation

Three operational parameters including contact time, initial pH, and initial concentrations were studied. The experiments were designed using one-factor-at-a-time method. The contact time was investigated in the range of 5–360 min. The experiments were carried out in 25℃ and adsorbent dose of 10 (g L^{-1}). The initial pH was studied in the range of 2–6 when initial concentration and contact time were fixed at 10 ppm and 360 min, respectively. The initial concentrations (C_0) were probed in the range of 10–1,000 ppm when the pH_0 and contact time were fixed at 4 and 120 min, respectively. Finally, two-way analysis of variance (ANOVA), multiple linear regression, and rank estimation were used to statistically determine the significance, rank, and type of parameter influences.

2.3. Isotherm and kinetics modeling

There are a number of isotherm model equations with different numbers and arrangements of parameters to describe the adsorption process. In this study, 15 adsorption isotherm models were examined for Pb^{2+} adsorption onto *P. eldarica*-based biosorbent (as a sample process) to assess their modeling ability. These 15 isotherm equations were two, three, four, and five parametric equations. The equation of explored isotherm models is tabulated in Table 1.

Table 1
The equations of explored isotherm models[a]

Models	Models equation	Notes
Two parametric Freundlich model	$Q_e = K_\mathrm{F} C_e^{\left(\frac{1}{n}\right)}$	K_F: the adsorption capacity
Linearized Freundlich	$\log(Q_e) = \log(K_\mathrm{F}) + \left(\frac{1}{n}\right)\ \log(C_e)$	n: intensity of adsorption
Langmuir	$Q_e = \dfrac{Q_\mathrm{max} b C_e}{1 + bC_e}$	Q_max: the maximum of adsorption (mg g^{-1})
Linearized Langmuir	$\left(\frac{1}{Q_e}\right) = \left(\frac{1}{Q_\mathrm{max}}\right) + \left(\frac{1}{bQ_\mathrm{max}}\right)\left(\frac{1}{C_e}\right)$	b: the Langmuir adsorption equilibrium constant (L mg^{-1})
Dubinin and Radushkevich	$Q_e = q_\mathrm{D}\ \exp\left(-B_\mathrm{D}\left(RT\ \ln\left(1 + \frac{1}{C_e}\right)\right)^2\right)$	q_D: theoretical isotherm saturation capacity (mg g^{-1})
Linearized Dubinin and Radushkevich	$\ln(Q_e) = \ln(q_\mathrm{D}) - B_\mathrm{D}\left(RT\ \ln\left(1 + \frac{1}{C_e}\right)\right)^2$	B_D: the mean free energy of sorption per gram of the adsorbate as it is transferred to the surface of the solid from infinite distance in the solution R: the universal gas constant T: the temperature (K)
Temkin	$Q_e = \dfrac{RT}{Q_m}\ln(KC_e)$	R: the universal gas constant (8.314 J moL^{-1} K^{-1})
Linearized Temkin	$\ln(C_e) = \dfrac{Q_m}{RT}Q_e - \ln\ K$	T: temperature at 298 K K: Temkin isotherm equilibrium binding constant (L g^{-1}) Q_m: Temkin isotherm constant
Three parametric isotherm model		
Redlich and Peterson	$Q_e = \dfrac{AC_e}{1 + BC_e^{\beta}}$	A: the Redlich–Peterson isotherm constant (L g^{-1}), B: a constant having unit of (L mg^{-1})
Sips	$Q_e = \dfrac{Q_m K_\mathrm{S} C_e^m}{1 + KC_e^m}$	Q_m: the Sips maximum adsorption capacity (mg g^{-1}) K_S: the Sips equilibrium constant (L mg^{-1}) m: the Sips model exponent
Toth	$Q_e = \dfrac{Q_m C_e}{(1/K + C_e^m)^{1/m}}$	Q_m: the Toth maximum adsorption capacity (mg g^{-1}) K: the Toth equilibrium constant m_T: the Toth model exponent
Langmuir–Freundlich	$Q_e = \dfrac{Q_m (KC_e)^m}{1 + (KC_e^m)^m}$	Q_m: the Langmuir–Freundlich maximum adsorption capacity (mg g–1) K: the equilibrium constant for a heterogeneous solid m: the heterogeneity parameter lies between 0 and 1
Radke–Prausnitz 1	$Q_e = \dfrac{Q_m KC_e}{(1 + KC_e)^m}$	Q_m: the Radke–Prausnitz maximum adsorption capacities (mg g^{-1})
Radke–Prausnitz 2	$Q_e = \dfrac{Q_m KC_e}{1 + KC_e^m}$	K: the Radke–Prausnitz equilibrium constants
Radke–Prausnitz 3	$Q_e = \dfrac{Q_m KC_e^m}{1 + KC_e^{m-1}}$	m: the Radke–Prausnitz models exponents
Jossens model	$C_e = \dfrac{Q_e}{H}\ \exp(FQ_e^P)$	H, F, and P: the parameters of the equation of Jossens. H and F depend only on temperature. The equation can be reduced to Henry's law at low capacities

(*Continued*)

Table 1 (*Continued*)

Models	Models equation	Notes
Four and five parametric Isotherm model		
Fritz–Schlunder	$Q_e = \frac{AC_e^{\alpha}}{1 + BC_e^{\beta}}$	A and B: the Fritz–Schlunder parameters α and β: the Fritz–Schlunder equation exponents $(\alpha, \beta) \leq 1$
Baudu	$Q_e = \frac{Q_m K C_e^{(m_1+m_2+1)}}{1 + KC_e^{(m_1+1)}}$	Q_m: the Baudu maximum adsorption capacity (mg g^{-1}) K: the equilibrium constant m_1 and m_2: the Baudu parameters
Fritz–Schlunder	$Q_e = \frac{Q_m K_1 C_e^{m_1}}{1 + K_2 C_e^{m_2}}$	Q_m: the Fritz–Schlunder maximum adsorption capacity (mg g^{-1}) K_1, K_2, m_1, and m_2: the Fritz–Schlunder parameters. $(m_1, m_2) \leq 1$

[a] C_e is the equilibrium liquid-phase concentration of the adsorbate (mg L^{-1}) and Q_e is the equilibrium adsorbate loading onto the adsorbent (mg g^{-1}).

Transformation to linear form and then linear regression as the usual method to explore two parametric isotherms was investigated. The results of linear equations were compared with the non-linear exploration of the models. The comparison can present a clear insight about the linear transformation method and its deficiencies. The model parameters were estimated using the least square algorithm by programming in MATLAB software (*regress* and *curve-fitting* functions).

The kinetics of sorption process was investigated using the gathered data-set of contact time influences study. The Lagergren first-order, pseudo-second-order, and intraparticle diffusion kinetics models were analyzed in this study. The equation of the explored kinetics models is tabulated in Table 2.

3. Results and discussions

3.1. *Influences of contact time (t) on biosorption*

Fig. 1 illustrates the influences of *t* on the heavy metals removal. A two-step kinetics behavior was identified from Fig. 1 including a very rapid step due to the larger surface area and more available active sites for adsorption (over 30 min for Ni^{2+} and

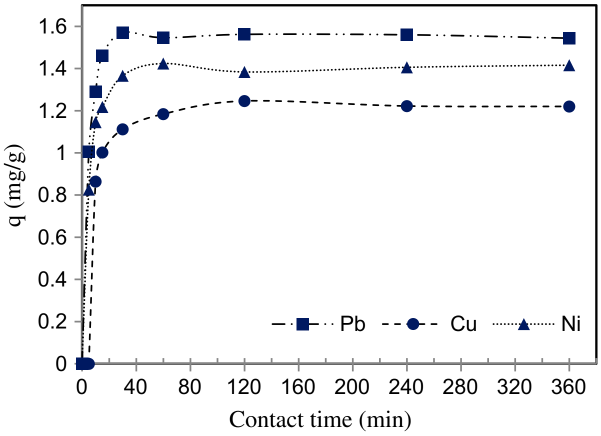

Fig. 1. The influences of t on the adsorption capacity (*q*) for Pb(II), Cu(II), and Ni(II) in room temperature, 100 rpm shaker, C_0 10 mg^{-1}, pH_0 4, and 10 g L^{-1} adsorbent dose.

Table 2
The equation of explored kinetics models[a]

Kinetics model	Model equation	
Lagergren first-order equation	$Q_t = Q_e(1 - e^{-Kt})$	Q_m: the amounts of adsorbed cations per weight unit of biosorbent at equilibrium (mg g^{-1})
Second-order equation	$Q_t = \frac{KQ_e^2 t}{1 + KQ_e t}$	k: the rate constant (min^{-1})
Intraparticle diffusion	$Q_t = Kt^{0.5} + C$	K: the intraparticle diffusion rate constant (g (mg $min^{0.5})^{-1}$) C: the intercept

[a] Q_e is the equilibrium adsorbate loading onto the adsorbent (mg g^{-1}).

Pb^{2+} and over 60 min for Cu^{2+}). The initial step is followed by a slower step when the active sites for adsorption become occupied. In the slow step, the process rate is controlled by the transportation of adsorbates from the exterior to the interior sites of adsorbent.

3.2. Influences of initial pH (pH_0) on biosorption

Fig. 2 illustrates the influences of pH_0 on the biosorption capacity (q). As presented in Fig. 2, the initial pH is one of the effective factors which influences the heavy metal ions biosorption. It was observed that biosorption was very small in pH 2 in our experiments (17.33, 12.6, and 11.7% for Pb(II), Ni(II), and Cu (II), respectively). In low pH_0, not only is the solubility higher but also the occupation of the negative sites of the adsorbent by H^+ (H_3O^+) leads to decline q. The values of q increased as the initial pH increased from 2 to 4. In higher pH, the ability of metal ions for competition with H^+ ions was also increased. The further increasing of pH to 6 does not influence the biosorption significantly.

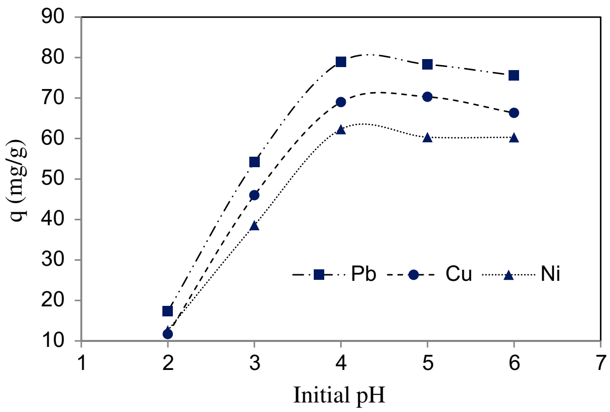

Fig. 2. The influences of pH_0 on the adsorption capacity (q) for Pb(II), Cu(II), and Ni(II) in room temperature, 100 rpm shaker, C_0 10 mg^{-1}, t 120 min, and 10 g L^{-1} adsorbent dose.

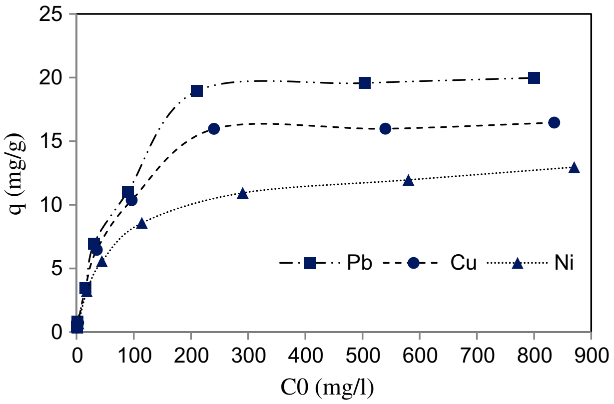

Fig. 3. The influences of C_0 on the adsorption capacity (q) for Pb(II), Cu(II), and Ni(II) in room temperature, 100 rpm shaker, pH_0 4, t 120 min, and 10 g L^{-1} adsorbent dose.

3.3. The influences of initial concentration (C_0) on biosorption

Since the initial concentration (C_0) affects the mechanism of adsorption, in this study, the influences of C_0 on biosorption were studied. The results of the influences of C_0 on q are shown in Fig. 3. The q is increased with increasing C_0 until C_0 400 mg L^{-1}. It results in the maximum q of 25, 32, and 39 mg g^{-1} for Ni, Cu, and Pb, respectively. The initial concentration provided the necessary driving force to overcome the

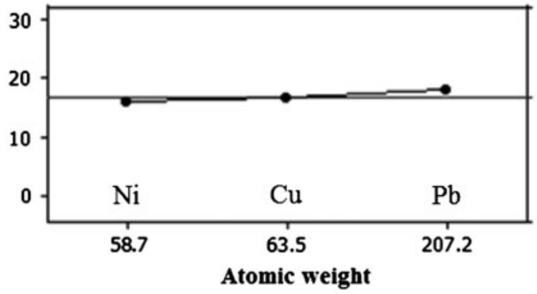

Fig. 4. The comparison of mean adsorption for three adsorbates.

Table 3
The ANOVA analysis of q (mg g^{-1}) vs. (three operational parameters and atomic weights of cations (A))

Statistical parameters		q vs. (1. A and 2. C_0)	q vs. (1. A and 2. pH_0)	q vs. (1. A and 2. T)
First input variable	P-value	0.007	0.000	0.000
	F-value	7.12	31.52	86.29
Second input variable	P-value	0.000	0.000	0.000
	F-value	43.1	223	43.1
ANOVA model accuracy parameters	R^2(adj)	0.93	0.99	0.95

Table 4
Rate constant, experimental, and predicted adsorption capacity for whole three kinetics models

	Kinetics model									
	Experimental	Pseudo-first-order			Pseudo-second-order			Intraparticle diffusion		
Adsorbent	Q_e/m (mg g^{-1})	k (min^{-1})	Q_e/m (mg g^{-1})	R^2	k (min^{-1})	Q_e/m (mg g^{-1})	R^2	k	C	R^2
Pb	1.56	0.20	1.55	0.99	0.25	1.61	0.92	0.020	1.28	0.36
Cu	1.22	0.22	1.20	0.90	0.37	1.25	0.96	0.015	1.01	0.44
Ni	1.40	0.17	1.39	0.98	0.22	1.46	0.96	0.023	1.08	0.46

Table 5
The results of exploring 15 isotherm models for Pb^{2+} adsorption data-set

	Model parameters					Model goodness parameters				Fitting parameters				
Model	P_1	P_2	P_3	P_4	P_5	R^2	Q^2	APE	MSE	P_1	P_2	P_3	P_4	P_5
Freundlich	k_F	n				0.92	0.90	83	27	4.38	2.87			
Langmuir	Q_{max}	b				0.98	0.98	18	5	45.3	0.01			
Dubinin and Radushkevich	q_D	B_D				0.93	0.92	46	28	36.6	0.00			
Temkin	Q_m	K				0.90	0.89	114	32	398	0.70			
Linearized Freundlich	k_F	n				0.85	0.82	23	79	1.38	1.76			
						0.97	0.96	27	0					
Linearized Langmuir	Q_{max}	b				0.84	−0.42	32	158	19.5	0.07			
						0.99	0.99	51	0					
Linearized Dubinin and Radushkevich	q_D	B_D				0.46	−1.55	95	181	18.6	0.00			
						0.67	0.51	85	1					
Linearized Temkin	Q_m	K				0.37	−1.79	90	1×10^5	360	0.21			
						0.90	0.89	57	0.56					
Redlich and Peterson	A	B				0.99	0.99	21	4	0.45	0.00	1.19		
Sips	Q_m	K_S	m			0.99	0.99	22	6	0.35	0.87	0.01		
Toth	Q_m	K	m			0.99	0.99	20	4	517	180	0.74		
Langmuir–Freundlich	Q_m	K	m			0.95	0.44	174	79	8.04	-77×10^{12}	0.68		
Radke–Prausnitz 1	Q_m	K	m			0.99	0.99	21	4	0.45	0.00	1.19		
Radke–Prausnitz 2	Q_m	K	m			0.93	0.88	115	36	5.68	-25×10^7	0.69		
Radke–Prausnitz 3	Q_m	K	m			0.84	0.68	195	76	0.01	−1.00	0.00		
Jossens model	H	F	P			0.96	0.00	1×10^7	42×10^7	89×10^{17}	0.84	1.02		
Fritz–Schlunder	A	α	B			0.99	0.99	10	4.2	1,295	−0.47	1,367	−1.24	
Baudu	Q_m	K	m_1	m_2		0.92	0.91	61	42.5	4.5	−0.12	0.56	1.34	
Fritz–Schlunder	Q_m	K_1	m_1	K_2	m_2	0.99	0.99	10.37	5.62	359	3.59	−0.48	1,367	−1.24

R^2: Coefficient of determination.
APE: Average pure error.
MSE: Mean square error.

resistances to the mass transfer. Also, the increase in C_0 enhances the interaction between adsorbent and adsorbate. As present in Fig. 3, further increase in C_0 causes no considerable changes in q.

It is well known that atomic weights of adsorbed cations affect the q. In order to investigate the influences of atomic weights of adsorbed cations, the statistical analysis was applied to compare the mean of adsorption results for the cations. Fig. 4 graphically illustrates the comparison of cations mean adsorption.

The two-way ANOVAs were applied to the statistical assessment of the results of operational parameter influences, and the results are summarized in Table 3. The statistical results confirmed the significant influences of the whole three operational parameters as well as the atomic weights of cations on the *q*.

An additional statistical test was applied to determine the rank of each parameter influence. The results show the ordering of C_0, pH_0, *t*, and *A* (atomic weights of cations). Then, the C_0 and pH_0 have more influence on adsorption.

3.4. Kinetics study

A study of the kinetics of adsorption is desirable as it provides information about the mechanism of adsorption, which is important for the efficiency of the process. The pseudo-first-order, pseudo-second-order, and intraparticle diffusion model equations were used in this study to assess the kinetics of the process. The values of rate constant *k* and the experimental and predicted adsorption capacity (q/m) for kinetics equations are presented in Table 4. The high correlation coefficient (R^2) values presented in Table 4 confirm that pseudo-first- and pseudo-second-order equations can model the experimental data very well. The predicted *q* near the experimental value confirms the validity of the pseudo-first- and second-order equations.

3.5. Adsorption isotherms

The results of the adsorption isotherm study are tabulated in Table 5. The results confirm that non-linear fitting outperformed linear regression for two parametric isotherm equations. The comparison between the goodness of linearized models and transformed to non-linear of same model shows that goodness parameters of linear model dramatically present illusive viewpoint in linearized forms. The results confirm that Q^2 and APE are good alternative for R^2 and MSE as goodness of model parameters when the R^2 and MSE present no confident viewpoint about the models. Increase in the number of parameters does not considerably improve the model quality. Among the four two parametric isotherm, the Langmuir isotherm can precisely describe the experimental data. It refers to the one-layer adsorption mechanism. Among the isotherm with more than two fitting parameters, the four parametric Fritz–Schlunder presents better fitting quality than the Langmuir isotherm.

4. Conclusions

The ability of *P. eldarica* has been probed for removing three heavy metal cations including Pb(II), Cu(II), and Ni(II) from aqueous solutions. The experimental studies showed the different optimum conditions including pH 4, 30 min *t*, and 300 ppm C_0 for Pb(II), pH 4, 60 min *t*, and 400 ppm C_0 for Cu(II), and pH 4, 30 min *t*, and 200 ppm C_0 for Ni(II). The experimental data were analyzed using 15 isotherm models as well as the three kinetics models. The equilibrium biosorption isotherms showed that *P. eldarica* possess promising affinity and sorption capacity for Pb(II), Cu(II), and Ni(II).

References

[1] E. Bazrafshan, F.K. Mostafapour, M. Esmaelnejad, G.R. Ebrahimzadeh, A.H. Mahvi, Concentration of heavy metals in surface water and sediments of Chah Nimeh water reservoir in Sistan and Baluchestan province, Iran, Desalin. Water Treat. (2015) 1–11, doi: 10.1080/19443994.2015.1027958.

[2] M. Fahiminia, M. Mosaferi, R.A. Taadi, M. Pourakbar, Evaluation of point-of-use drinking water treatment systems' performance and problems, Desalin. Water Treat. 52 (2014) 1855–1864.

[3] D. Belhaj, S. Ghrab, M. Medhioub, M. Kallel, Performance evaluation of an industrial wastewater treatment plant in South-Eastern Tunisia, Desalin. Water Treat. 52 (2014) 2174–2179.

[4] W.W. Wan Ngah, M. Hanafiah, Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review, Bioresour. Technol. 99 (2008) 3935–3948.

[5] D. Kavak, Removal of lead from aqueous solutions by precipitation: statistical analysis and modeling, Desalin. Water Treat. 51 (2013) 1720–1726.

[6] H. Daraei, A. Mittal, J. Mittal, H. Kamali, Optimization of Cr(VI) removal onto biosorbent eggshell membrane: experimental & theoretical approaches, Desalin. Water Treat. 52 (2014) 1307–1315.

[7] A.L. N'Guessan, H.A. Vrionis, C.T. Resch, P.E. Long, D.R. Lovley, Sustained removal of uranium from contaminated groundwater following stimulation of dissimilatory metal reduction, Environ. Sci. Technol. 42 (2008) 2999–3004.

[8] F.J. Alguacil, I. Garcia-Diaz, F. Lopez, The removal of chromium(III) from aqueous solution by ion exchange on Amberlite 200 resin: Batch and continuous ion exchange modelling, Desalin. Water Treat. 45 (2012) 55–60.

[9] M. Du, Q. Li, L. Wang, Adsorption removal of Pb^{2+} and Cd^{2+} on lignocellulose-g-acrylic acid/montmorillonite nanocomposite from aqueous solutions, Desalin. Water Treat. (2014) 1–9, doi: 10.1080/19443994.2014.984338.

[10] X. Sun, C. Hu, J. Qu, Adsorption and removal of arsenite on ordered mesoporous Fe-modified ZrO_2, Desalin. Water Treat. 8 (2009) 139–145.

[11] A.H. Sulaymon, S.E. Ebrahim, S.M. Abdullah, T.J. Al-Musawi, Removal of lead, cadmium, and mercury ions using biosorption, Desalin. Water Treat. 24 (2010) 344–352.

[12] A.H. Sulaymon, A.A. Mohammed, T.J. Al-Musawi, Removal of lead, cadmium, copper, and arsenic ions using biosorption: equilibrium and kinetic studies, Desalin. Water Treat. 51 (2013) 4424–4434.

[13] M. Karnib, A. Kabbani, H. Holail, Z. Olama, Heavy metals removal using activated carbon, silica and silica activated carbon composite, Energy Proc. 50 (2014) 113–120.

[14] G.J. Rincón, E.J. La Motta, Simultaneous removal of oil and grease, and heavy metals from artificial bilge water using electro-coagulation/flotation, J. Environ. Manage. 144 (2014) 42–50.

[15] I. Sheet, A. Kabbani, H. Holail, Removal of heavy metals using nanostructured graphite oxide, silica nanoparticles and silica/graphite oxide composite, Energy Proc. 50 (2014) 130–138.

[16] D. Prithviraj, K. Deboleena, N. Neelu, N. Noor, R. Aminur, K. Balasaheb, M. Abul, Biosorption of nickel by *Lysinibacillus* sp. BA2 native to bauxite mine, Ecotoxicol. Environ. Saf. 107 (2014) 260–268.

[17] J.A. Baig, T.G. Kazi, L. Elci, Biosorption characteristics of indigenous plant material for trivalent arsenic removal from groundwater: Equilibrium and kinetic studies, Sep. Sci. Technol. 47 (2012) 1044–1054.

[18] D.C. Tadic, F.V. Lozano, M.E.Z. Maza, P.L.V. Elicer, Plant for the removal of metals by biosorption from mining or industrial effluents, Google Patents, 2009.

[19] A. Zouboulis, M. Loukidou, K. Matis, Biosorption of toxic metals from aqueous solutions by bacteria strains isolated from metal-polluted soils, Proc. Biochem. 39 (2004) 909–916.

[20] N.S. Maurya, A.K. Mittal, P. Cornel, E. Rother, Biosorption of dyes using dead macro fungi: Effect of dye structure, ionic strength and pH, Bioresour. Technol. 97 (2006) 512–521.

[21] A. Ofomaja, E. Naidoo, S. Modise, Removal of copper (II) from aqueous solution by pine and base modified pine cone powder as biosorbent, J. Hazard. Mater. 168 (2009) 909–917.

[22] B. Kord, A. Mataji, S. Babaie, Pine (*Pinus Eldarica* Medw.) needles as indicator for heavy metals pollution, Int. J. Environ. Sci. Technol. 7 (2010) 79–84.

[23] U. Shafique, A. Ijaz, M. Salman, W. uz Zaman, N. Jamil, R. Rehman, A. Javaid, Removal of arsenic from water using pine leaves, J. Taiwan Inst. Chem. Eng. 43 (2012) 256–263.

[24] B. Acemioglu, Removal of Fe(II) ions from aqueous solution by Calabrian pine bark wastes, Bioresour. Technol. 93 (2004) 99–102.

[25] A. Ofomaja, E. Naidoo, S. Modise, Surface modification of pine cone powder and its application for removal of Cu(II) from wastewater, Desalin. Water Treat. 19 (2010) 275–285.

[26] M. Rahman, S. Gul, M. Ajmal, A. Iqbal, A. Achakzai, Removal of cadmium from aqueous solutions using excised leaves of Quetta pine (*Pinus halepensis* Mill.), Bangladesh J. Bot. 43 (2015) 277–281.

[27] D. Bulgariu, L. Bulgariu, Equilibrium and kinetics studies of heavy metal ions biosorption on green algae waste biomass, Bioresour. Technol. 103 (2012) 489–493.

[28] M. Ghaedi, S. Hajati, F. Karimi, B. Barazesh, G. Ghezelbash, Equilibrium, kinetic and isotherm of some metal ion biosorption, J. Ind. Eng. Chem. 19 (2013) 987–992.

[29] A.R. Khataee, F. Vafaei, M. Jannatkhah, Biosorption of three textile dyes from contaminated water by filamentous green algal *Spirogyra* sp.: Kinetic, isotherm and thermodynamic studies, Int. Biodeterior. Biodegrad. 83 (2013) 33–40.

[30] M. Torab-Mostaedi, M. Asadollahzadeh, A. Hemmati, A. Khosravi, Equilibrium, kinetic, and thermodynamic studies for biosorption of cadmium and nickel on grapefruit peel, J. Taiwan Inst. Chem. Eng. 44 (2013) 295–302.