



Biosorption of lead from aqueous solutions by algae biomass: optimization and modeling

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Received 3 April 2018; Accepted 11 January 2019

ABSTRACT

The present work represents the biosorption of lead from aqueous solution by using mixed-culture of algae biomass. The effect of four numerical independent variables (initial pH, biosorbent dosage, contact time, and initial concentration of lead) on the lead removal efficiency were investigated. The operational conditions were statistically optimized using central composite design (CCD) through response surface methodology (RSM). The maximum Pb removal was 95.43% at conditions including, pH of 6, 110 min of contact time, and 5.52 g/L of adsorbent dosage and 100 mg/L concentration of Pb. Adsorption kinetics follows the pseudo-second-order model and equilibrium is well described by Freundlich isotherm.

Keywords: Lead; Biosorption; Algae biomass; Adsorption kinetics

1. Introduction

The discharge of heavy metal ions into the environment by industrial activities is a serious problem in industrial countries, because they are difficult to degrade and have the ability to bio-magnified in the food chain and accumulate in living organisms [1]. Lead is a non-biodegradable contaminant that is considered as one of the most toxic heavy metal and hazardous to the environment [2,3]. Lead is currently applied in many industries such as cables, batteries, pigments, paints, steels and alloys, metal, glass, and plastic industries [4]. The lead contamination of the aquatic environment has been caused by the release of these industries effluent [4]. The awareness of increasing lead discharging has implied studies regarding water and wastewater treatment to achieve the level of standards for drinking water [5]. The heavy metals removal has been considered as a serious issue with respect to the environmental and economical aspects [6]. Chemical precipitation, ion exchange, chemical oxidation or reduction, reverse osmosis, evaporation, membrane separation etc. are common methods used

for the heavy metals removal from aqueous solution [7–9]. Nevertheless, the feasibility of economical and technical features may limit the use of these techniques [2]. Adsorption of toxic heavy metals is a technology, commonly used for the removal of heavy metal ions from industrial discharge, which can apply low-priced adsorbents. It is a fast, reversible, economical and environmental friendly methodology, in contrast with listed conventional technologies of removing heavy metals from aqueous solutions [10]. Different types of biomass, such as algae, fungi or bacteria, have been reported to have significant capacities for the adsorption of various heavy metals from aqueous effluents [11]. Application of different biomass with the aim of finding an efficient and cost effective adsorbent has been reported by many researchers [12]. Among them, algae have demonstrated high metal uptake capacities because of functional groups such as amino, hydroxyl, carboxyl and sulphate of polysaccharides, proteins or lipid binding sites on the surface of their cell walls [6]. There are many researches on the biosorption of lead metal on marine algae [13,14], green seaweed [15,16], and fresh water green algal species [17,18] with different metal uptake efficiency. Many studies have already investigated the effect of espe-

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cial specie of algae for lead removal. A study performed by Hammud and his coworker (2014) showed that 95.5% lead removal achieved at 200 mg/L initial concentration of lead and pH of 3 by *Enteromorpha* Algae [19]. Gupta and Rastogi (2008) investigated bioadsorption of lead by algae biomass (*Spirogyra* species), that results showed 80% of lead was adsorbed at pH of 5, 10 mg/L adsorbent and 100 min contact time [20].

This paper explored the sorption potential of algae biomass (mixed-culture) for the removal of Pb(II) ions from an aqueous solution. The main objective of the current study was molding and optimization of biosorption process. The effect of operating factors such as pH level, biosorbent dosage, initial metal ion concentration and contact time on the sorption process onto the algae biomass were studied and modeled by CCD through RSM. Langmuir and Freundlich isotherm were used to evaluate and modeling the equilibrium adsorption data.

2. Materials and methods

2.1. Preparation of sorbate and sorbent

A synthetic solution was prepared by $Pb(NO_3)_2$ from AR, Sinopharm Chemical Reagent Co., Ltd. In order to achieve 1,000 mg/L stock solution 1.598 g of lead nitrate (E. Merck company, Germany) was dissolved in 1,000 mL distilled water. It was then diluted into different concentrations based on experimental designed values. Algae biomass (mixed-culture) was collected from the wastewater treatment plants of the Eslamabad-e Gharbtown, Kermanshah, Iran. The raw material was washed several times by both tap and distilled water to remove its active ingredients, and was dried at 60°C in an oven for 3 h. The dried algae biomass was powdered and then was screened through sieve mesh of 50.

2.2. Biosorption experiments

According to CCD 30 batch experiments were carried out at room temperature ($25^\circ C \pm 2^\circ C$).

In all experiments, 100 mL of the sorbent-sorbate mixtures was taken in a 250 mL flask and agitated at 200 rpm by a magnetic shaker from IKA (Staufen, Germany). The samples were centrifuged at 3,800 rpm for 5 min in a lab centrifuge (Shimifan, Iran) and the supernatant was used for analysis of metal concentrations using AAS. Each experiment was repeated 3 times.

2.3. Experimental design and mathematical modeling

The experimental design was conducted using RSM. The RSM used in this work was a central composite design (CCD) with four numerical variables at 5 levels. The CCD is the standard RSM, which lets the use of second-degree polynomial in the estimation of relationships between the independent and dependent variables. Also information on the interaction between variables based on the dependent variables can be provided by CCD [21,22].

The statistical method of DOE (version 8.0.0) software was applied to evaluate the effect of independent variables, namely adsorbent dosage (A), adsorbate concentration

(B), contact time (C), pH (D). The range of the variables was selected based on previous studies and a preliminary study. The variables range was adsorbent dosage (1–19 g/L), adsorbate concentration (10–100 mg/L), contact time (10–210 min) and pH (2–10). The experimental conditions for biosorption process from synthetic wastewater based on CCD are presented in Table 1. The significance of the variables was recognized based on the confidence levels above 95% ($P < 0.05$) in the polynomial model. The quadratic model based on Eq. (1) was used to estimate the coefficients of the statistical model [21,23]:

$$Y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_{i < j}^k \beta_{ij} x_i x_j + e \quad (1)$$

where i represents linear coefficient, j stands for the quadratic coefficient, β is regression coefficient, x represents independent variables, k is the number of studied and optimized factors in the experiment, and e is the random error.

Table 1
Experimental condition and results

Run No.	Factor 1A: Adsorbent, g/L	Factor 2B: Lead, mg/L	Factor 3C: Contact time, min	Factor 4D: pH	R1: Pb removal (%)
1	19	100	210	10	88.1
2	10	10	110	6	99.1
3	19	100	10	10	99.6
4	10	55	110	6	80.61
5	10	55	110	6	76.89
6	10	55	10	6	95.2
7	19	10	10	10	98.99
8	10	55	210	6	79.78
9	10	55	110	2	97.45
10	10	100	110	6	93.58
11	10	55	110	6	78.87
12	10	55	110	6	95.5
13	1	10	10	2	40.8
14	1	10	210	2	36
15	1	100	10	10	99.7
16	1	100	210	2	73.49
17	1	100	210	10	87.66
18	10	55	110	6	77.52
19	1	100	10	2	80.53
20	19	10	210	10	92.36
21	19	100	210	2	90.28
22	19	100	10	2	97.6
23	19	55	110	6	68.96
24	1	55	110	6	80.76
25	10	55	110	10	91.55
26	10	55	110	6	85.63
27	1	10	210	10	84.11
28	1	10	10	10	74.63
29	19	10	210	2	89.46
30	19	10	10	2	57.99

2.4. Measurement and apparatus

Surface morphology of algae was studied by scanning electron microscopy (SEM). The samples were sited under a JEOL JSM field-emission SEM. During operation, the accelerating voltage of the instrument was maintained at 20 kV, and varying magnifications were used. Fourier transform-infrared (FT-IR) spectroscopy analysis was performed to identify the functional groups of algae biomass in the range of 400–4000 cm^{-1} using a FT-IR spectrophotometer (model: FTIR 2000, Shimadzu IR Prestige, Japan). The concentration of Pb in the sample solution was determined using atomic absorption spectrophotometer (AAS) (Shimadzu AA, Japan). The pH of solutions was measured using a pH meter (WTW-Germany) and adjusted by adding 1N HCl and 1N NaOH. In order to calculate the removal efficiency of lead the following equation was used:

$$\text{Removal} = \frac{C_0 - C_e}{C_0} \cdot 100 \quad (2)$$

and the biosorption capacity (q_e) was obtained using the following equation [24]:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (3)$$

where C_0 is the initial concentration of Pb (mg/L), C_e is the equilibrium concentration of Pb (mg/L), V is the volume of the solution (l), and m is the mass of the biosorbent (g).

3. Results and discussion

3.1. Characterization of algae biomass

Fig. 1 illustrates the morphological characterization of algae that has been carried out by SEM. Irregular and porous structure of adsorbent - areas cause an increase in biosorption capacity that is a main factor in increasing the absorption potential. Based on SEM, micrograph of biosorbent shows uneven surfaces and porous texture, resulting high affinity for Pb uptake. The FTIR peaks show the pres-

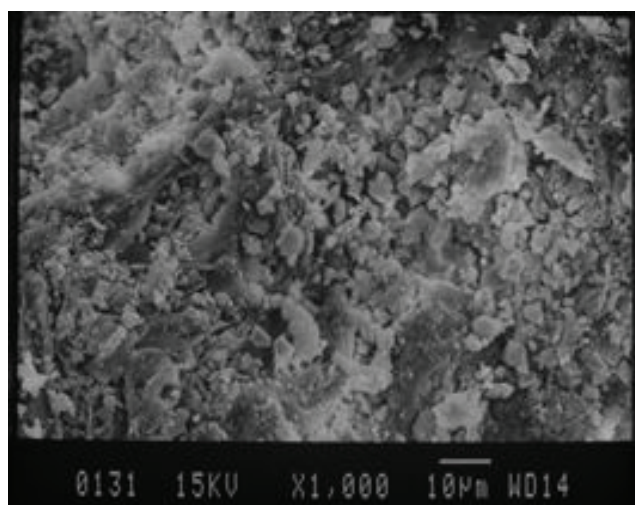


Fig. 1. The electron micrograph (SEM) of algae biomass.

ence of functional groups such as, OH, CO and carbonyl groups. Stretching vibration band around 900–1600 cm^{-1} confirm C–O group. The strong band at 1000–1500 cm^{-1} may be due to C–C band. The peaks appearing between 1900 and 2900 cm^{-1} are allocated to the C–H stretching mode in structure of carbon. The broad band around 3400–3900 cm^{-1} is assigned to OH group (Fig. 2). The band around 2900 cm^{-1} reveals the presence C–H group in algal biomass [25]. Presence of these reactive sites indicate the algae biomass (mixed-culture) is a suitable material for strong interaction with various contaminate and suitable them for wastewater treatment. As previous studies confirmed that the carboxyl, carbonyl, methylene and carbonate, were the main groups involved in the Pb^{2+} ions biosorption process [26]. Also alcoholic groups have an important role in metal uptake [27].

3.2. Statistical analysis and modeling

The removal of lead was evaluated based on the CCD with 30 experiments and the results obtained are given in Table 1. The final model can be expressed by the following equation:

$$Y = 86.01 + 6.98 A + 7.62 B - 1.32C + 8.51D - 4.32AB - 4.47AD - 4.21BC - 5.79BD - 2.06CD - 14.65A^2 + 6.83B^2 - 2.02C^2 + 4.99D^2 \quad (4)$$

where Y is the percentage removal of Pb (II) and A–D are the coded values of sorbent dosage (g/L), concentration of Pb(II) ion (mg/L), contact time (min) and pH value, respectively. ANOVA was used to study the adequacy of the quadratic model for Pb(II) removal by algae. The ANOVA results are presented in Table 2. The statistical significance of model was checked by p-value and F-value. The model F-value of 3.25 implies the model is significant. There is only a 1.52% chance that a model F-value this large could occur due to noise. The p-value less than 0.05 indicate model terms are significant. As can be seen from Table 2, A, B, D, A^2 are significant model terms, other model terms are not significant due to P-value > 0.05. As illustrated in Table 2, the lack of fit was not significant as the f-value and p-value were 3.1 and 0.1119, respectively, which shows an adequate fit between predicted values and the experimental data. Based on the ANOVA results, the coefficient of determination (R^2) of the model and adjusted R^2 were 0.75 and 0.52 respectively. High

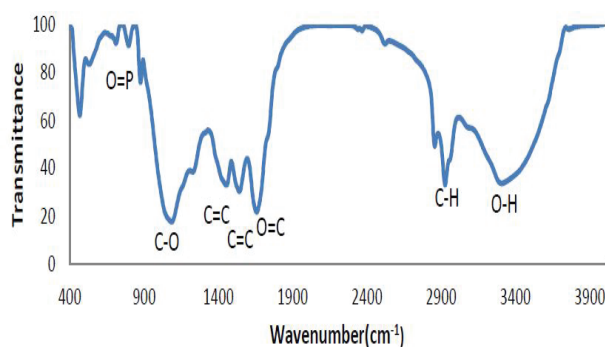


Fig. 2. FTIR spectra of natural adsorbent of algae biomass.

Table 2
ANOVA results for lead removal

Source	Sum of squares	df	Mean Square	F-value	P-value	Significant
Model	5491.95	14	392.28	3.25	0.0152	Significant
A-Adsorbent	877.25	1	877.25	7.26	0.0166	
B-Lead (C_0)	1044.24	1	1044.24	8.64	0.0101	
C-Contact time	31.45	1	31.45	0.26	0.6173	
D-pH	1302.20	1	1302.20	10.78	0.0050	
AB	298.08	1	298.08	2.47	0.1371	
AC	26.06	1	26.06	0.22	0.6490	
AD	320.05	1	320.05	2.65	0.1244	
BC	284.09	1	284.09	2.35	0.1460	
BD	536.85	1	536.85	4.44	0.0523	
CD	68.06	1	68.06	0.56	0.4645	
A ²	556.43	1	556.43	4.61	0.0486	
B ²	120.69	1	120.69	1.00	0.3334	
C ²	10.57	1	10.57	0.088	0.7714	
D ²	64.39	1	64.39	0.53	0.4766	
Residual	1811.97	15	120.80			
Lack of fit	1560.16	10	156.02	3.10	0.1119	Not significant
Pure error	251.82	5	50.36			
Corr total	7303.92	29				

values of R^2 are essential for modeling the experimental design space, while in identification of significant factors R^2 value does not matter and for significant factors will remain significant [28,29]. Adequate precision measures the signal-to-noise ratio and compares the range of the predicted values at the design points to the average prediction error [21]. The ratio greater than 4 is desirable and indicates adequate model discrimination [30]. In this study, the ratio of adequate precision was 8.026, which showed the reliability of the achieved data. The coefficient of variation (CV) and standard deviation (SD) were 13.23 and 10.99, respectively, that state the degree of precision.

3.3. Effect of variables on Pb(II) removal

The effect of different variables on the removal of lead from solution was explored by three-dimensional response surface and two-dimensional contour plots. And also the effects of factors were compared at a particular point using the perturbation plot [29]. It has been proved that some parameter like pH, sorbent dosage, contact time, initial concentration of metal ions etc. affected on the sorption efficiency [31]. Therefore, the rustles of investigation of aforementioned variables have been discussed as below.

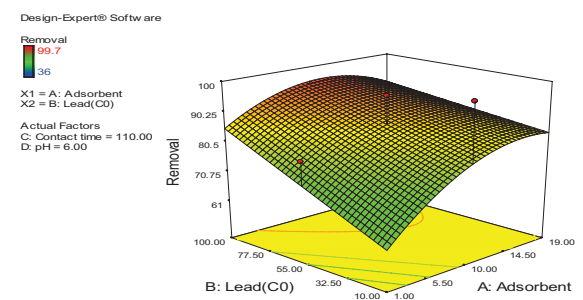
3.3.1. Effect of initial concentration of Pb(II)

Figs. 3a and 4a illustrate the effect of Pb(II) concentration on sorption efficiency. As can be seen from the figures by increasing the initial adsorbate concentration, the lead removal efficiency increased. In addition, perturbation plot (Fig. 5) has shown the significant influence adsorbate concentration on the removal efficiency. Initial concentra-

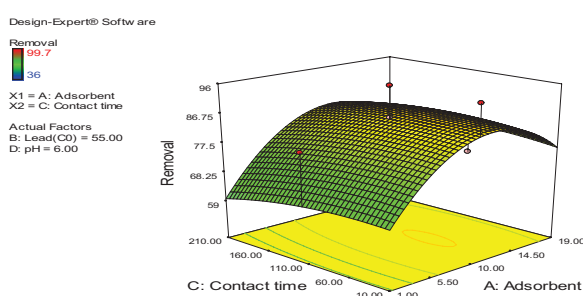
tion as the major driving force to overcome the limitations of lead mass transfer between the solid and liquid showed that at higher concentrations of lead the biosorption was improved [32]. The results of previous studies showed that the adsorbent capacity by increasing the concentration of lead is likely to increase interaction and contact between the adsorbent and adsorbent [33]. Another factor that can increase the capacity by increasing the initial concentration of lead is that under such conditions increase the mass transfer, the phenomenon has overcome the resistance force against absorption, causing a significant thrust of transfer of the liquid phase pollutants to the solid-liquid interface [34].

3.3.2. Effect of sorbent dose

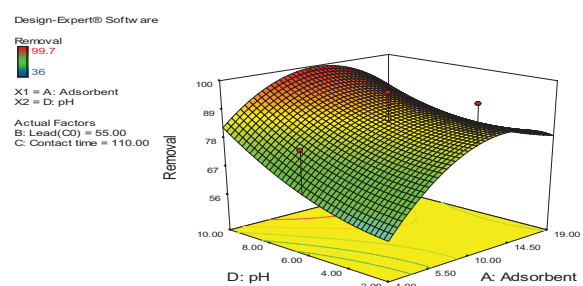
The effect of sorbent dosage on the removal efficiency of Pb(II) was studied using varying amounts of sorbent dosages (1–19 g/L) and the results are shown in Figs. 3a and 4a. The maximum removal efficiency was attained as the dosage was 10 g/L. The sorption percentage increases with increase in sorbent dosage and almost constant at dose higher than 10 g/L at lower concentration of initial Pb(II) ion. Identical behavior was observed by Hammud et al. [19] using *Enteromorpha* algae for removal of Pb metal from an aqueous solution. This behavior may be due to a consequence of partial aggregation of biomass at higher biomass concentration, which results in the decrease in effective surface area for the sorption [35]. However, at higher values of initial Pb(II) ion by increasing adsorbent dose more than 10 g/L, the removal efficiency of lead declined. This trend could be explained as at higher adsorbent dose, the availability of higher energy sites decreases with a larger fraction



(a)



(b)



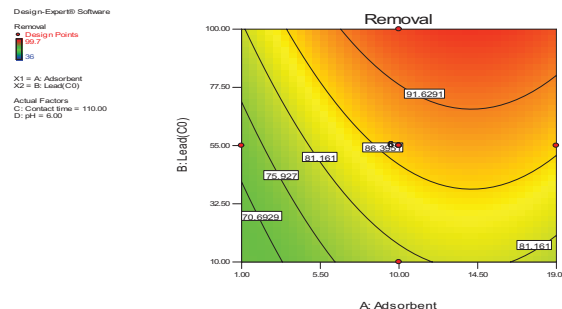
(c)

Fig. 3. Three-dimensional response surface for lead removal efficiency (%) onto algae biomass in term of independent variables: (a) initial concentration of Pb(II) and adsorbent dose, (b) contact time and adsorbent dose (c) pH and adsorbent dose.

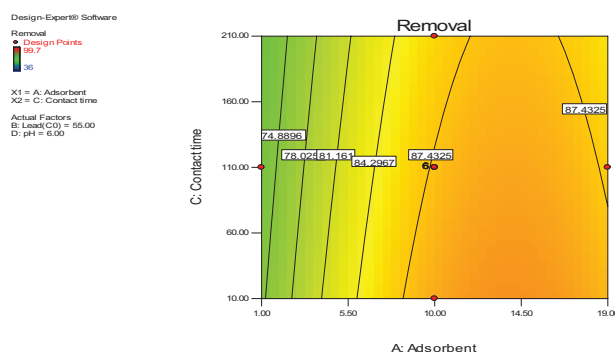
of lower energy sites occupied, resulting in a lower removal efficiency [20].

3.3.3. Effect of contact time

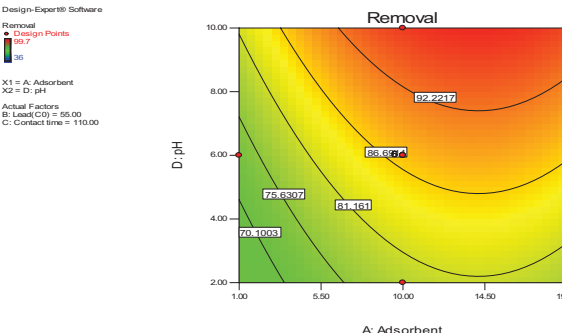
Figs. 3b and 4b illustrate lead removal efficiency as function of contact time. According to figures removal efficiency slowly increased with an increase in contact time within the first minutes of process. Then, the rate of biosorption was found to be relatively slow and then constant. This is because of a large number of adsorption sites at the beginning of process, the big difference between the concentration of lead in the absorbing solution, and its value in the adsorbent surface that lead uptake is increased.



(a)



(b)



(c)

Fig. 4. Two-dimensional contour plots for lead removal efficiency (%) onto algal biomass in term of independent variables: (a) initial concentration of Pb(II) and adsorbent dose, (b) contact time and adsorbent dose (c) pH and adsorbent dose.

Nevertheless, over time, the gentle slope sat tract to itself that this is due to the formation of a layer of lead onto the adsorbent. Also over time, occupy the place left vacant surface simply is not possible. Because the adsorption of molecules on the surface of other molecules in the solution phase is attractive, this can be case of repulsive onto adsorbent surface [36]. Contact time slightly influenced the process efficiency. Results have confirmed that there are no significant changes on the lead biosorption removal with the increase of contact time (Fig. 3b). Perturbation plot (Fig. 5) clearly shows this trend. As removal efficiency only increased 0.3% with increase of contact time from 10 to 110 min at pH of 6 and lead concentration of 55 mg/L. The same result was obtained by Mousavi et al. [37] using

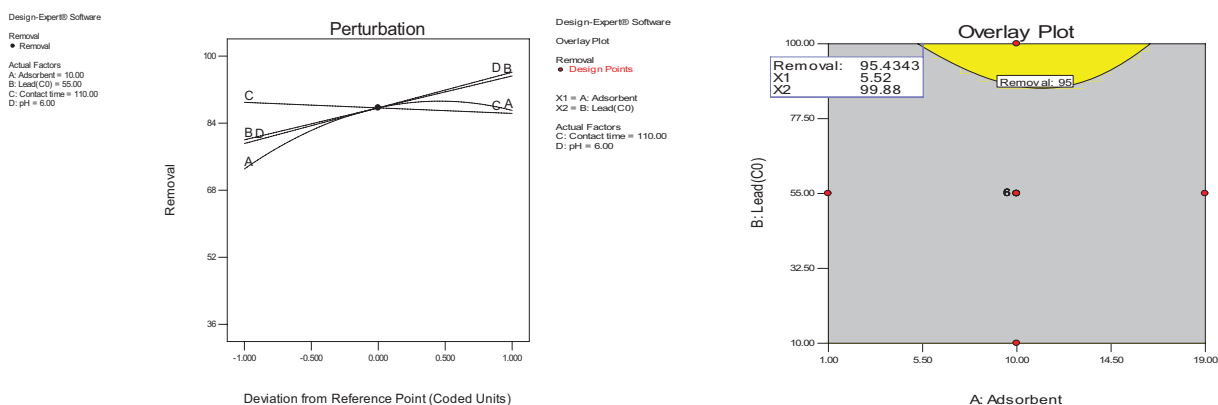


Fig. 5. (a) Perturbation plot for lead removal. (b) Overlay plot for the optimal region.

Nasturtium Officinale for the removal of lead from aqueous solution.

3.3.4. Effect of pH

The effect of pH on the removal efficiency is shown in Figs. 3c and 4c. According to the figures with increase in pH the biosorption increased, as Pb removal efficiency was 97% at pH of 6. At higher value of pH, the precipitation of insoluble metal hydroxides takes place restricting the true biosorption studies [18,38]. Due to precipitation of lead as lead hydroxide the experiments with pH value higher than 6 ignored. pH slightly influenced the process efficiency as can be seen in Fig. 3c, when pH increased from 2 to 6 about 2% Pb removal increased at the conditions (110 min contact time, 55 mg/L initial lead concentration and 10 mg/L adsorbent). A study carried out by Gupta and Rastogi [20] in which bioadsorption of lead by algae biomass (*Spirogyra* species) were investigated showed that 80% of lead removal at pH of 5, 10 g/L adsorbent and 100 min contact time was achieved. Perturbation plots were analyzed in order to identify the most effective parameter for lead removal. Perturbation plot (Fig. 5) revealed a sequence of relative influence of the operating parameters on the Pb^{2+} removal as follows: adsorbent dose > initial lead concentration > pH > contact time. Contour plots were used to show the interaction of parameter. Elliptical contours are obtained when there is a perfect interaction between the independent variables [39]. As can be seen in Fig. 4 they are in the not perfectly elliptical. This indicates that there are fewer interactions among the independent variables. However, based on contour plots the interaction between adsorbent dose with pH and initial concentration of lead is much more than its interaction with contact time.

3.4. Process optimization

Graphical optimization was used to determine the optimum process parameters for maximum removal of lead. Graphical optimization displays the area of feasible response values in the factor space and the regions that do fit the optimization criteria would be shaded [40]. By defining the value of the response, the shaded portion of the overlay plot as shown in Fig. 5, defines the permissible

values of the dependent values. The optimum region was identified by considering the highest lead removal (>95%). Two independent variables, pH and contact time were kept constant while concentration of adsorbent and adsorbate and, were used in x and y-axes to construct the graph. Using this overlay plot a point was selected in the optimum region to obtain optimum value for the response as well as value for the varied independent variables (lead concentration and adsorbent dose). As can be seen in Fig. 5 a maximum removal of 95.43% was predicted by model under the following optimum conditions: adsorbent dose (5.52 mg/L), contact time (110 min), initial lead (99.88 mg/L) and pH 6. These finding was consistent with the result of verifying experiment at this conditions that 94% Pb removal was achieved. A comparison between the results of present study and others work is presented in Table 3. The value of lead removal obtained in this study is higher than reported for other biosorbents. Consequently, the algae biomass (mixed-culture) is an efficient biosorbent for lead removal from aqueous solution.

3.5. Adsorption kinetic

Pseudo-first-order and pseudo-second-order models were used to investigate the mechanism of biosorption process. The linear forms of pseudo-first order [Eq. (5)] and pseudo-second-order [Eq. (6)] kinetics models can be written as [42,43]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (5)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (6)$$

where q_t (mg/g) is the amount of adsorbed Pb(II) on the algae biomass at time t (min) and k_1 (min^{-1}) is the rate constant of first order adsorption, and q_e is the equilibrium adsorption capacity (mg/g), k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) is the rate constant of second-order adsorption. Fig. 6 illustrates the kinetics plot for biosorption process. According to the Table 4 and Fig. 6 the correlation coefficient R^2 value for pseudo-first-order and pseudo-second-order models was 0.97 and 0.99 respectively and the value of q_e was 5.59 mg/g. As presented in Table 4 the value of rate constant for the

Table 3
Percentage of Pb removal: optimum results obtained from present study, comparison with literature

Removal (%)	Contact time (min)	pH	Initial Pb(II) (mg/L)	Biosorbent dose (g/L)	Biosorbent type	Reference
80	100	5	200	10	Green algae <i>Spirogyra</i> species	[20]
93	30	5	175.6	8	Marine algae <i>Ulva Lactuca</i> species	[10]
88.94	20	3	200	12	<i>Enteromorpha</i> algae	[19]
60	180	6	20	1.5	<i>Chaetoceros</i> algae	[41]
78	180	6	20	1.5	<i>Chlorella</i> algae	[41]
Predicted: 95.43	110	6	100	5.52	Algae (mixed-culture)	Present study
Experiment data: 94						

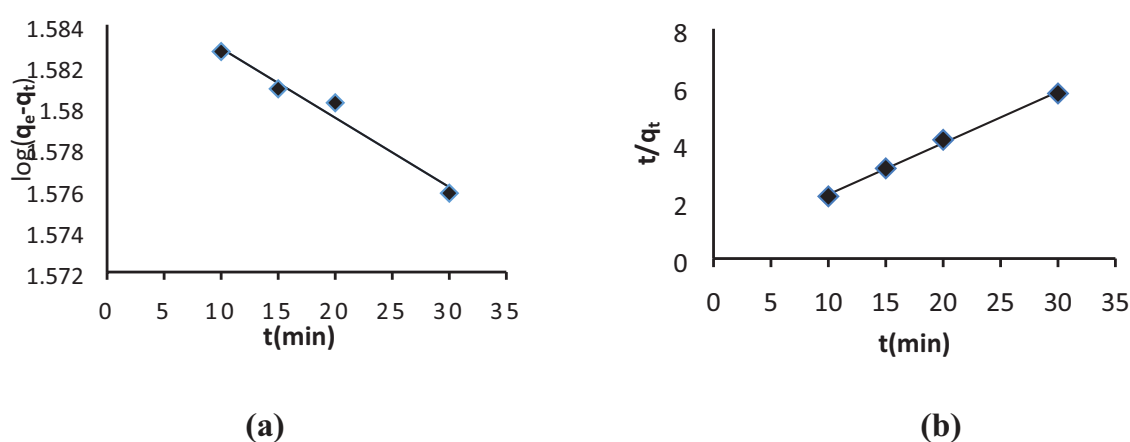


Fig. 6. Kinetics plot: first-order kinetic (a) and second-order kinetic (b)

Table 4
Kinetic constants for lead onto algae biomass

Models	Kinetics parameters	
	R ²	K(×10 ⁻³)
First-order	0.97	0.7 min ⁻¹
Second-order	0.99	70 (g mg min ⁻¹)

pseudo-first-order and pseudo-second-order models was $0.7 \times 10^{-3} \text{ min}^{-1}$ and $70 \times 10^{-3} \text{ g mg min}^{-1}$ respectively.

The correlation coefficients, R², showed that the pseudo second order model fits better with the experimental data than the pseudo-first order model [44]. In a study performed by Jayakumar et al. [24] in which marine algae was used for Pb removal, the results indicated that adsorption kinetics was best described as pseudo-second order with R² value of 0.99. However, R² value of pseudo-first-order was 0.97.

3.6. Adsorption isotherm model

Two linear isotherm models equations, namely, Langmuir and Freundlich, were applied to determine the mechanism of Pb(II) sorption on to algae biomass. The Langmuir isotherm is based on the adsorption of a monolayer onto homogeneous surface, and the maximum adsorption capacity,

Table 5
Langmuir and Freundlich isotherm constants and correlation coefficients

Adsorbent	Freundlich			Langmuir		
	R ²	1/n	K _f	R ²	b (L/mg)	q _{max} (mg/g)
Algae biomass	0.81	0.92	1.85	0.1	0.16	42.9

can be estimated by this isotherm model [45,46]. The linear form of Langmuir isotherm is expressed as [42]:

$$\frac{c_e}{q_e} = \frac{c_e}{q_{\max}} + \frac{1}{bq_{\max}} \quad (7)$$

where q_e is equilibrium adsorption capacity (mg/g), C_e is equilibrium ion concentration in the solution (mg/L), q_{\max} is the maximum sorption capacity (mg/g), and b (L/mg) is the Langmuir isotherm constant related to affinity of adsorptive sites.

The Langmuir model was applied to investigate the Pb(II) sorption mechanism by algae biomass at different initial metal ion concentration. As can be seen in Table 5 the amount of q_{\max} and b were 42.9 and 0.16 respectively. In this study a low correlation coefficients (R² = 0.1) indicate the data are not fitted to Langmuir model. The important characteristics of the Langmuir isotherm can be expressed

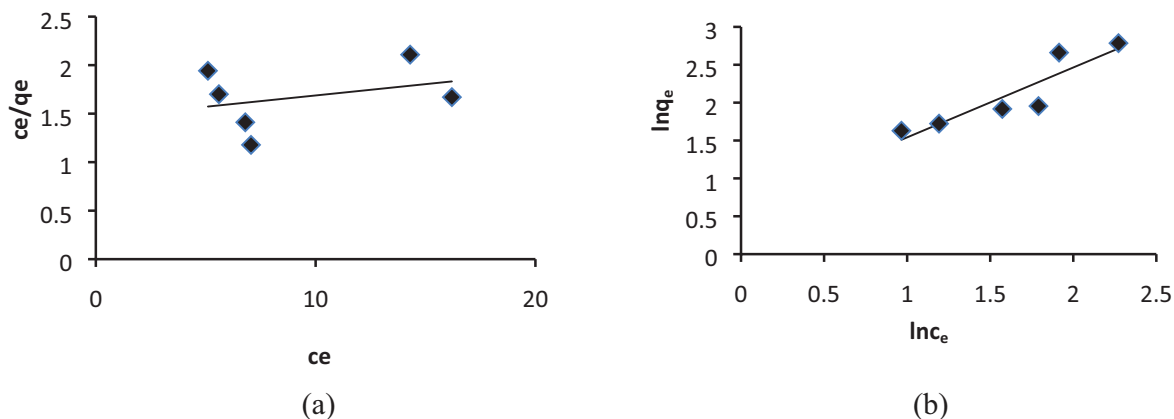


Fig. 7. Linear isotherm plots: a) Langmuir model, b) Freundlich models.

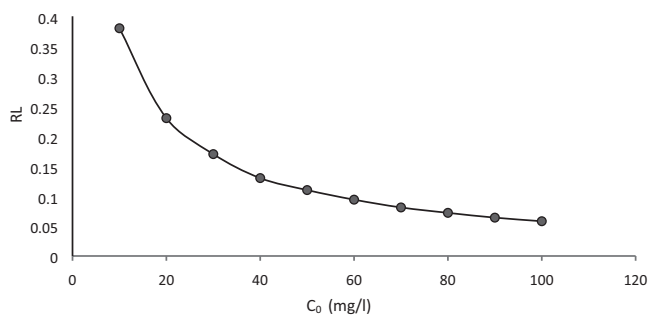


Fig. 8. Variation of separation factor as a function of initial lead concentration.

in terms of separation factor (R_L), which is given by the following equation [47]:

There are four probabilities for the R_L value: unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$) [47]. Fig. 8 illustrates the variation of separation factor with initial lead concentration. As can be seen in the Fig. 8 the R_L values were in the range of 0–1 indicating that the biosorption of lead on algae biomass is favorable.

The Freundlich isotherm which describe the adsorption process on heterogeneous surface [46] was also applied for the sorption of Pb(II) ion onto algae biomass. The liner form of the Freundlich model is represented as the following equation [20]:

$$\ln q_e = \ln k_f + \frac{1}{n} \ln c_e \quad (8)$$

where K_f is a constant relating to the sorption capacity and $1/n$ is an constant relating the sorption intensity, From Table 5, K_f and $1/n$ values were found to be 1.85 and 0.92 respectively. Usually, $1/n$ values between 0 and 1 specify favorable sorption [24]. In the present study, a value of 0.92 showed that the sorption of lead by algae biomass was good and high values of K_f indicate that the biosorbent is suitable. Figs. 7a and b demonstrate the Langmuir and Freundlich plots of lead sorption for algae biomass at different initial lead concentration. From Fig. 7 R^2 for Freundlich model was 0.81, which indicated it fits the experimental data better than the Langmuir model with R^2 of 0.1.

4. Conclusion

In the present study, the applicability of algae biomass for lead adsorption from aqueous effluents was investigated, and its operational conditions were statistically optimized using CCD with RSM. The effects of four main independent variables including pH, adsorbent dose, lead metal concentration, and contact time were studied. The results indicated the lead biosorption is extremely dependent on adsorbent dose, initial lead concentration, the initial pH and contact time slightly influenced the process efficiency. The pseudo second order was found to be the applicable kinetic model in the current study. The data were in good agreement with Freundlich isotherm. The maximum predicted bioadsorption efficiency was 95.43% at optimum conditions (5.52 g/L adsorbent dose, 110 min contact time, 100 mg/L initial lead and initial pH of 6). This results of study demonstrated that the algae biomass from stabilization ponds that is cheap and available has relatively high lead uptake capacity.

Acknowledgment

The authors would like to thank the Faculty of Health, Kermanshah University of Medical Science for financially supporting this research.

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