



## Biosorption of lead from aqueous solution onto *Nasturtium officinale*: performance and modeling

Ali Almasi<sup>a</sup>, Fatemeh Navazeshkha<sup>a</sup>, Seyyed Alireza Mousavi<sup>a,b,\*</sup>

<sup>a</sup>Department of Environmental Health engineering, Kermanshah University of Medical Sciences, Kermanshah, Iran, Tel. +9809181317314; emails: alialmasi@yahoo.com (A. Almasi), f.navazeshkha@gmail.com (F. Navazeshkha)

<sup>b</sup>Department of Environmental Health engineering, and Research Center for Environmental Determinants of Health (RCEDH), Kermanshah University of Medical Sciences, Kermanshah, Iran, Tel. +9809188336569; Fax: +980 8318263048; emails: seyedarm@yahoo.com, sar.mousavi@kums.ac.ir

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### ABSTRACT

*Nasturtium officinale* powder (NoP), with leached active ingredients, was used here to adsorb lead (Pb), as a water pollutant. The effects of several variables on the removal of lead including initial pH, contact time, adsorbent dosage and initial concentration of lead were studied. The response surface plots were used for estimating the interactive effects of variables. The statistical analysis and modeling by response surface methodology and central composite design are demonstrated to be effective and reliable in finding the optimal conditions for the adsorption of lead onto NoP. The results showed that the biosorption conditions have significant effects on the removal of lead, and 10 g L<sup>-1</sup> of NoP had the best adsorption efficiency. The equilibrium data was analyzed using Langmuir and Freundlich isotherms models. The pseudo-second-order kinetics model best explained the Pb biosorption by NoP of any dosage.

**Keywords:** Water; Pollutant; *Nasturtium officinale*; Lead; Adsorption; Modeling

### 1. Introduction

The discharge of heavy metals into the environment poses a major challenge to modern societies, because such contaminants are highly persistent and difficult to eliminate. Unlike most organic contaminants, heavy metals such as lead cannot be degraded or detoxified by living beings, and hence, they become a pollution problem over time because they can accumulate in ecological systems, and the gradual increase of the concentration and undesirable adverse effects occur in these systems [1–3]. The awareness of increasing lead releasing implies studies concerning water and wastewater treatment to achieve the level of standards for drinking water and discharge into receiving water [3].

The use of physical–chemical methods for lead removal including electro dialysis processes, chemical precipitation

[4], reverse osmosis [5] and ion exchange [6], due to the high cost, lack of complete elimination of lead as well as waste disposal, has their own limitations. Due to the fact that most of these methods, when the concentrations of heavy metals in the environment are 10–100 ppm, may be ineffective and uneconomical, however, concentrations of less than 1 ppm are permitted to discharge into surface water [7].

Due to the non-biodegradable nature of lead and shortcoming of other methods mentioned above, adsorption has been considered as a suitable method for lead removal. During last decades, researchers tested different materials as activated carbon (i.e., sewage sludge [8], rice husk ash [9–11], fly ash [12], coir pith [13]) but because of high cost of activated carbon preparation, other biological materials as new and cost-effectiveness types of adsorbents were considered such as Pu-erh tea [14], pretreated *Aspergillus*

\* Corresponding author.

niger [15], green algae *Spirogyra* species [16], groundnut hull [17], *Moringa oleifera* pods [18] and alga *Anabaena sphaerica* biomass [19]. Nowadays researchers based on previous results of many studies that have confirmed the ability of aquatic plants, both living and dead, as accumulators of heavy metal, have more focus on use of this type of plants under new term “biosorption”, for water and wastewater treatment [20,21].

Ajmal et al. [22] investigated the effect of sawdust in the removal of copper from industrial wastes. The results confirmed that at 60 min contact time when adsorbent was 4 g/l and pH 6, 60% removal of lead at initial concentration of 17 mg/L achieved. Wang and Qin [23] investigated the equilibrium sorption isotherms for Cu on rice bran, results showed at initial concentration of Cu 100 mg/l, pH 5.5, contact time 240 min, and rice bran 25 g/l; when temperature was 25°C, the adsorption capacity was 19.6 mg/g [23]. Surisetty et al. (2013) studied the ability of *Ficus benghalensis* L., a plant-based material leaf powder, for the elimination of lead ions from aqueous solution. The results showed that lead ions uptake rate increases by increasing the adsorbent dosage and the lead concentration, as well as increases by increasing the pH up to 6 [21].

The present study investigated the potential use of powdered *Nasturtium officinale* as biosorbent for the removal of lead ions from aqueous solution. *Nasturtium officinale* is a very common species in streams and can be found throughout the year. Contaminates accumulation such as azo dye C.I. Acid Blue 92 (AB92) [24] Nickel [25] into *Nasturtium officinale* indicated that the species has ability to remove pollutants specially heavy metal ions from aqueous solutions. The optimization and modeling of data were performed using response surface methodology (RSM). The relationship between lead removal efficiency and four main independent parameters including pH, contact time, lead ion concentration and adsorbent dosage was investigated using central composite design (CCD). The equilibrium adsorption data were modeled by Langmuir and Freundlich isotherm. The biosorption kinetic was conducted based on first- and second-order kinetic models.

## 2. Materials and methods

### 2.1. Adsorbate and adsorbent

The lead nitrate ( $\text{Pb}(\text{NO}_3)_2$ ) was used to prepare synthetic solution, from AR, Sinopharm Chemical Reagent Co., Ltd. Lead nitrate (1.598 g) was dissolved in 1,000 mL distilled water to obtain 1,000 mg/L stock solution, which was provided by E. Merck company (Germany). It was then diluted into different desired concentrations based on designed values. *Nasturtium officinale* is an aquatic perpetual plant. Its leaves and stems are incompletely submerged during growing, and cool running water must be accessible in their environment [26]. *Nasturtium officinale* was collected in summer 2014 from the Gilan-e Gharb town in Kermanshah, Iran. The raw material was washed several times by both tap and distilled water to remove its active ingredients, followed by a drying process at 60°C to constant weight in an oven for 3 h. The dried *Nasturtium officinale* was ground into powder. A sufficient amount of it was screened through sieve mesh of 50 and was stored in airtight containers.

### 2.2. Batch biosorption experiments

The biosorption experiments were carried out by contacting a 100 ml of lead solution with the different concentration of adsorbate (10, 55 and 100 mg/l) and quantity of adsorbent (1, 10 and 19 g/L), when pH was increased from 2 to 10. The solution pH was adjusted using a 537 pH meter (WTW-Germany) by adding 1 M HCl or 1 M NaOH. All flasks were agitated by a magnetic shaker from IKA (Staufen, Germany). Wart, Germany, at 200 rpm at the different contact time (10,110 and 210 min), when other parameters were constant ( $T = 25^\circ\text{C} \pm 2^\circ\text{C}$ ). Finally, the residual concentration of lead was determined using atomic absorption (Shimadzu AA, Japan) after centrifuge of sample at 3,800 rpm for 5 min (Shimifan, Iran).

A control container containing only the lead with no biosorbent was used to control the magnitude of lead removal via biosorption process. The biosorption capacity was evaluated by using the following equation:

$$q_e = \frac{(c_0 - c_e)V}{M} \quad (1)$$

where  $C_0$  and  $C_e$  are the initial and the equilibrium lead concentrations (mg/L);  $V$  is the volume of solution (ml); and  $M$  is the amount of biosorbent used (g).

### 2.3. Analysis methods

Scanning electron microscopy (SEM) was used to study surface morphology of NoP. 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 (FTIR) spectroscopy of the adsorbent was obtained by using an FTIR spectrophotometer (model: FTIR 2000, Shimadzu IR Prestige, Japan) to investigate the surface characteristics of adsorbent.

### 2.4. Experimental design and mathematical modeling

The experimental design was conducted using the statistical method of factorial design of experiments (DOE). The method has the ability to eliminate errors systematically with an estimation of the experiment, reduce the number of experiments and determine an empirical model based on the accomplished experiments. The responses can be affected by a number of variables, and the target is to optimize these responses. In addition, the interaction of feasible effective factors and the efficiency of the biosorption can be appraised using DOE through RSM at a limited number of designed experiments. The CCD is the standard RSM, which allows the use of second-degree polynomial in the estimation of relationships between the independent and dependent variables. The CCD also provides information on the interaction between variables based on the dependent variables [27,28].

The statistical method of DOE (version 8.0.0) software was applied to evaluate the effect of independent variables, namely adsorbent dosage (factor A), adsorbate concentration (factor B), contact time (factor C), pH (factor D), and their interactive influences on lead biosorption. The reasonable range of lead

(actual value = 10, 55 and 100 mg/L) and *Nasturtium officinale* powder (NoP; actual value = 1, 10 and 19 g/L) were selected according to the previous studies and preliminary study that the coded value term was used to represent the independent variables at three levels, which consist of -1 (low level), 0 (central) and +1 (high level). As shown in Table 1, the experimental conditions for biosorption process from synthetic wastewater based on CCD with a factorial matrix of 30 steady-state runs (the reactors steadily was operated in each run for 3 times) were designed in nine factorial points and five experimental runs were approved as center points [27]. In order to perform a comprehensive analysis of the biosorption process, some dependent parameters such as lead removal was evaluated as results of variables interaction (Table 3).

After accomplishing the experiments at a set value of independent variables (concentration of adsorbate, quantity of adsorbent, pH and contact time), the experimental data according to Table 1 were used to develop empirical models based on actual factors (AF) and coded factors (CF), using analysis of variance (ANOVA) via the Design-Expert software. 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. (2) was used to estimate the coefficients of the statistical model [27,29]:

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

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

### 3. Results and discussion

#### 3.1. Characterization of NoP

The morphological characterization has been carried out by SEM that according to Fig. 1, adsorbent (NoP) shows irregular and porous structure, which is areas for

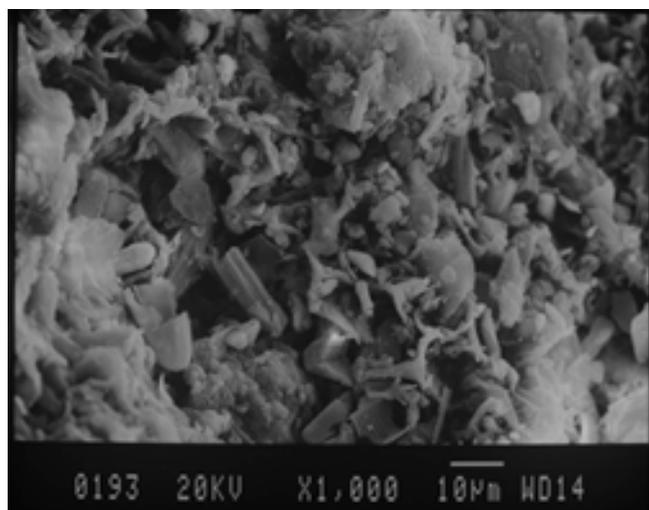


Fig. 1. The electron micrograph (SEM) of NoP.

increasing surface, resulting an increased biosorption of adsorbate, and this is an important factor in increasing the absorption potential. Gupta and Rastogi [16] used green algae as biosorbent of lead, and SEM of it showed intertwined structure that confirms result of present work. Also, based on SEM, micrograph of biosorbent shows uneven surfaces and porous texture, resulting high affinity for Pb uptake.

Using FTIR as an accurate identification technique (Fig. 2) pointed out the distinguished peaks, which indicate presence of functional groups like OH, CO and carbonyl groups. Stretching vibration band around 900–1,600  $\text{cm}^{-1}$  is assigned to C–O group. The strong band at 1,000–1,500  $\text{cm}^{-1}$  may be due to C–C band. The peaks appearing between 1,900 and 2,900  $\text{cm}^{-1}$  are allocated to the C–H stretching mode in structure of carbon. The broad band around 3,400–3,900  $\text{cm}^{-1}$  confirm OH group. The band around 2,900  $\text{cm}^{-1}$  reveals the presence C–H group in NoP. Therefore, existence of these reactive sites and centers makes candidate the present NoP as suitable material for strong interaction with various contaminate and suitable them for wastewater treatment.

#### 3.2. Statistical analysis and modeling

As shown in Table 1, the biosorption for high concentrations of lead was appraised based on the CCD with a factorial matrix of 30 steady-state runs. The results of statistical analysis and modeling by ANOVA through DOE are presented in this section briefly. The significance and adequacy of the model have been approved by ANOVA, and the model and experimental error as source of variations compared with each other to investigate the model significance by using Fisher's  $F$ -test value, which is the ratio between the mean square of the model and the residual error [27]. The achieved results of the statistical analysis indicted the adequacy of the model fits because the  $F$ -value obtained, 3.32, is greater than the  $F$  value (2.47 at 95% significance) obtained from the standard distribution table. According to summarized results in Table 1, the significance of all main variables namely quantity of the adsorbent ( $X_1$ ), initial concentration of the adsorbate ( $X_2$ ), contact time ( $X_3$ ) and pH value ( $X_4$ ) was determined by  $p$ -value ( $\text{Prob} > F$ ), which are  $< 0.002$ ,  $< 0.006$ ,  $< 0.7$  and  $< 0.02$ , respectively. The term contact time ( $X_3$ ) is not significant due to  $p > 0.05$ . The lack-of-fit was not significant as the  $p$ -value is  $> 0.05$ , when the model was highly significant ( $p < 0.05$ ), which is the result of comparing the residual error to the pure error

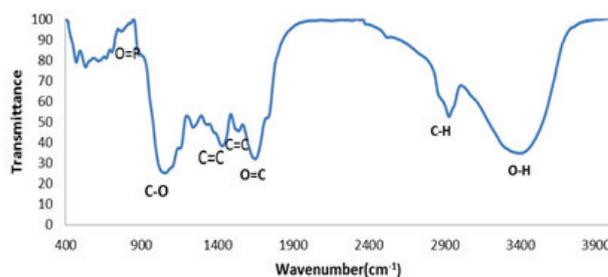


Fig. 2. FTIR spectra of natural adsorbent of NoP.

Table 1

Designing of experiments for two levels of factorial of variables (adsorbent dose, absorber dose, contact time, pH) and CCD results

Run	Factor 1A: Adsorbent, mg/l	Factor 2B: Lead, mg/l	Factor 3C: Contact time, Min	Factor 4D: pH	R1: $C_r$ (mg/l)	R2: Pb (removal %)
1	19	100	210	10	14.88	85.12
2	10	10	110	6	0.75	92.5
3	19	100	10	10	13.46	86.54
4	10	55	110	6	3.97	92.78
5	10	55	110	6	5.69	89.65
6	10	55	10	6	11.39	79.29
7	19	10	10	10	1.47	85.3
8	10	55	210	6	3.46	93.70
9	10	55	110	2	3.26	94.07
10	10	100	110	6	10.37	89.63
11	10	55	110	6	5.69	89.65
12	10	55	110	6	4.93	91.03
13	1	10	10	2	8.13	18.7
14	1	10	210	2	8.1	19
15	1	100	10	10	29.97	70.03
16	1	100	210	2	27.6	72.4
17	1	100	210	10	14.98	85.02
18	10	55	110	6	5.18	90.58
19	1	100	10	2	13.3	86.7
20	19	10	210	10	0.37	96.3
21	19	100	210	2	5.11	94.89
22	19	100	10	2	20.8	79.2
23	19	55	110	6	0.411	99.25
24	1	55	110	6	14.29	74.01
25	10	55	110	10	0.96	98.25
26	10	55	110	6	5.035	90.8
27	1	10	210	10	2.063	79.37
28	1	10	10	10	0.884	91.16
29	19	10	210	2	0.73	92.7
30	19	10	10	2	1.13	88.7

Table 2

Langmuir and Freundlich isotherm constants and correlation coefficients

Adsorbent	Freundlich			Langmuir		
	$R^2$	$n$	$k$	$R^2$	$b$	$Q_{max}$
<i>Nasturtium officinale</i>	1.03	1.8	0.2	0.022	3.13	

from replicated design points. The empirical model based on aforementioned parameters is valid (Eq. (3)):

$$\begin{aligned}
 \text{AF: } & 10.62 + 7.28 (X_1) + 0.62 (X_2) + 0.066 (X_3) + 1.76 (X_4) \\
 & - 0.022 (X_1 X_4) + 1.54 (X_1 X_3) - 0.25 (X_1 X_4) - 9.20 (X_2 X_3) \\
 & - 0.054 (X_2 X_4) - 2.31 (X_3 X_4) - 0.018 (X_1)^2 + 1.029 (X_2)^2 \\
 & - 2.46 (X_3)^2 + 0.47 (X_4)^2
 \end{aligned}
 \quad (3)$$

From Eq. (3), it can be seen that the adsorbent dose, initial concentration, contact time and pH have positive effect on

the bio-adsorption efficiency. The positive value of variables points out an effect that favors the optimization, whereas a negative value presents an inverse relationship between the factors and the responses. The coefficient of determination ( $R^2$ ) of the model was 0.9, which specified a good fit between predicted values and the experimental data points. 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 [27]. The ratio greater than 4 is desirable and indicates adequate model discrimination [30]. In this experimental work, the ratio is found to be 10.063, which shows the consistency of the achieved data. The coefficient of variation (CV) and standard deviation (SD) were 12.78 and 10.70, respectively, that specify the degree of precision. The low values of CV and SD display the adequacy with which the experiment is conducted [31]. Results show the high precision in predicting the lead removal efficiency by NoP based on significant  $F$  value, high  $R^2$  value, an insignificant lack-of-fit  $P$  value and low coefficient of variance and standard deviation.

3.3. Response surface and counter plotting for evaluation of operational parameters

The effects of variables on the removal of lead are indicated in Fig. 3. As illustrated in Fig. 3(a–c), by increasing of initial pH and adsorbent dose, and decreasing of

initial absorbate concentration, the lead removal efficiency improved. Initial concentration 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

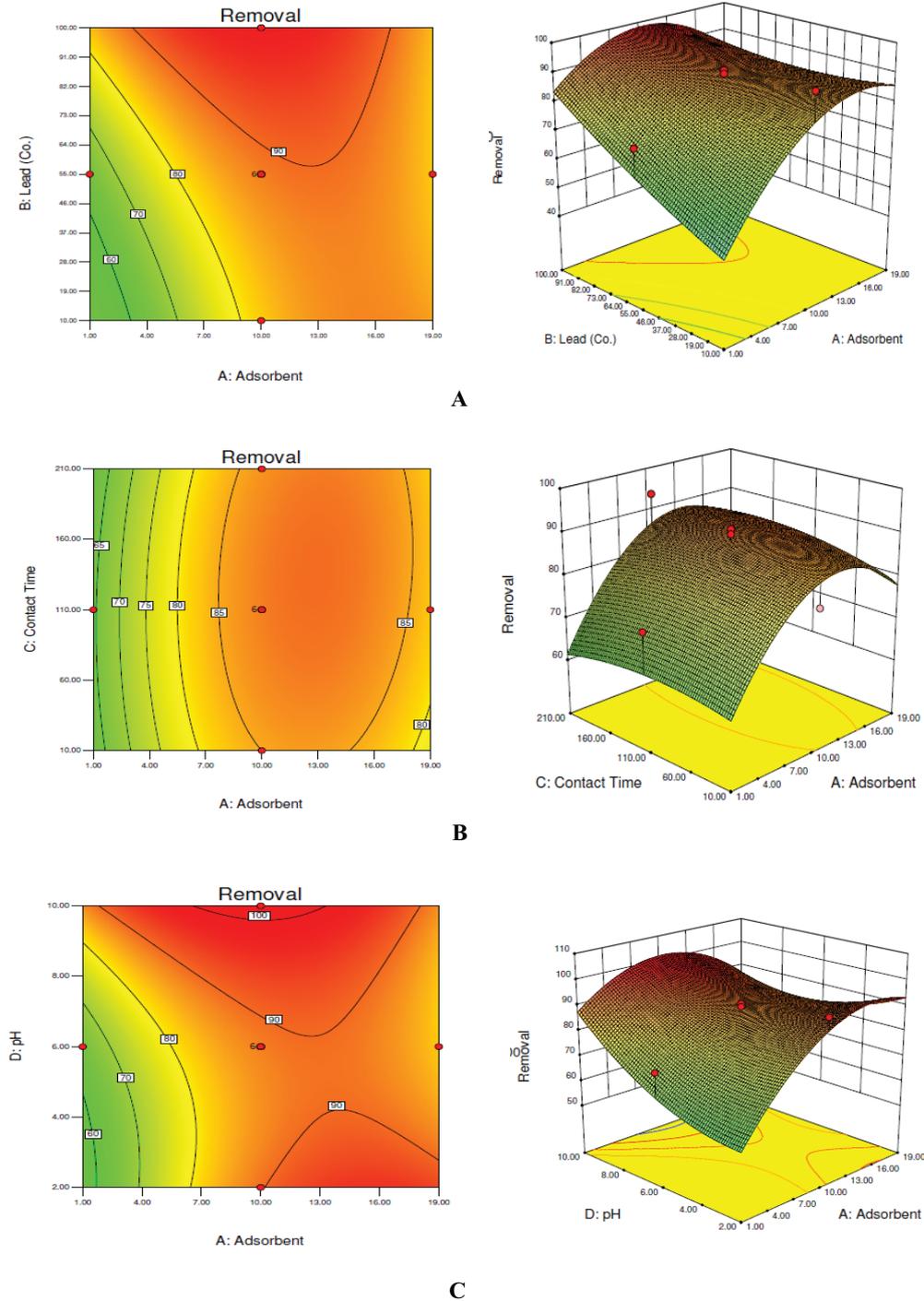


Fig. 3. Response surface plots for lead removal efficiency (%) onto NoP: (a) effect adsorbent dose/initial concentration (contact time = 110 min, pH = 6, ambient temperature 25°C ± 2°C and 200 rpm); (b) effect adsorbent dose/contact time (initial concentration of metal solution = 55 mg/l, pH = 6, ambient temperature 25°C ± 2°C and 200 rpm.); (c) effect pH/adsorbent dose (ambient temperature 25°C ± 2°C, initial concentration of metal solution = 55 mg/l, contact time = 110 min, and 200 rpm).

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 increased 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]. Moreover, as shown in Fig. 3(b), biosorption 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. But 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 [35]. For NoP, balance time occurs in the first 60 min of biosorption and not significant change after that. The result of Gupta and Ali (2004) on the elimination of lead and chromium from water using bagasse ash confirms the result of presence work, as results showed that high removal 95–96% achieved at contact time of 60 min when adsorbent dose, optimal pH were 10 g/L and 6, respectively. For a well description of the independent variables and their interactive effects on the lead removal, 3D plots and its corresponding contour plots are denoted in Fig. 3. According to figure, the lead biosorption is extremely dependent on adsorbent dose and initial lead concentration, and the initial pH and contact time slightly influenced the process efficiency. At constant value of the initial pH (6), when the adsorbent dose and initial absorbate concentration increase, the lead removal efficiency increases and finally reaches more than 90% (Fig. 3(c)). Results have confirmed that there are no significant changes on the lead biosorption removal with the increase of contact time (Fig. 3(b)).

### 3.4. Optimization of experimental condition

According to DOE ability, the possible input optimizations, using numerical optimization, have been investigated that a desirable value for each input variable and response can be selected through this method. The concentration of lead in effluent, lead percentage removal, as responses were each optimized as a function of the studied variables namely concentration of absorbate, quantity of adsorbent, contact time and pH value. Fig. 4 illustrates the overlay plot, where the highlighted spherical surface is the optimum area based on the concentration of lead in effluent (as input variables) for achieving the lead discharged standard (<1 mg/L). To confirm the dependability of the models' predictions, one point within the optimum region was chosen for implementation in verification experiments (55 mg Pb/L in effluent with 99% removal). The obtained experimental results confirmed that the model was able to make a reasonably precise prediction for the optimum conditions, in terms of lead concentration. At the applied values of variables (adsorbent dosage

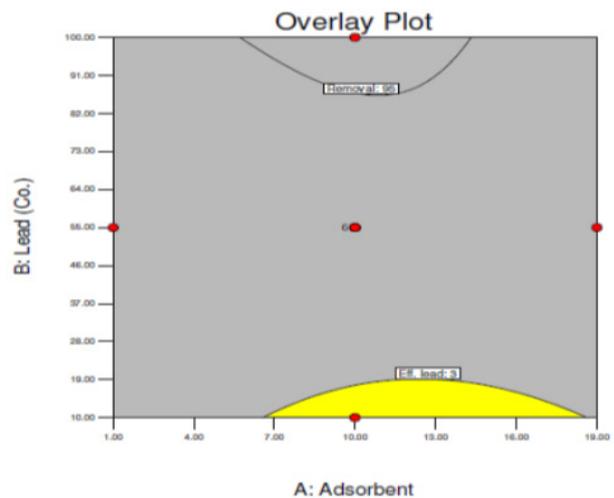


Fig. 4. Determination of optimal points plan (contact time = 110 min, pH = 6).

(19 g/L), initial concentration of lead (55 mg/L), contact time (110 min) and pH (6), the concentration of lead in effluent was 0.411 mg/l. Therefore, the obtained results verified that the model was able to make an acceptable prediction for the optimum conditions.

### 3.5. Adsorption isotherms and kinetics

Finding out an appropriate correlation of the equilibrium data to optimize the design of a biosorption system is importance. In this regard, two models, namely Langmuir and Freundlich models, have been investigated. The correlation coefficient ( $R^2$ ) as a factor to investigate appropriateness of isotherm models has been used in the current study. The Langmuir isotherm can be presented by unimolecular adsorbed layer [36]. The Freundlich adsorption model specifies that the ratio of solute adsorbed to the solute concentration is a function of the solution. The empirical model was revealed to be consistent with an exponential distribution of active centers, characteristic of heterogeneous surfaces [37]. The determined error function values and isotherm parameters are summarized in Table 2. According to results, the Freundlich isotherm displays a better fit to the biosorption data than the Langmuir isotherm in the sorption of lead based on the highest  $R^2$  value.

Pseudo-first-order and pseudo-second-order models have been used to study the rate constants for biosorption of lead onto NoP. The coefficients of correlation for the first-order-kinetic model were not high for biosorbent at different concentrations (Table 3), which proves that the model is not appropriate to explain the biosorption process. Therefore, the pseudo-second-order model has been developed to describe biosorption kinetics. The correlation coefficient was  $R^2 = 0.99$ , recommends a strong relationship between the parameters and also describes that the process follows pseudo-second-order kinetics. Fig. 5 illustrates the kinetic models that are fitted to the experimental data. Analyzing the data, it can be mentioned that the highest  $R^2$  value were found for the pseudo second-order kinetic model.

Table 3  
Kinetic constants for lead onto *Nasturtium officinale*

Models	Kinetics parameters	
	$R^2$	$K_f$
First-order	0.82	1.8
Second-order	0.99	0.08

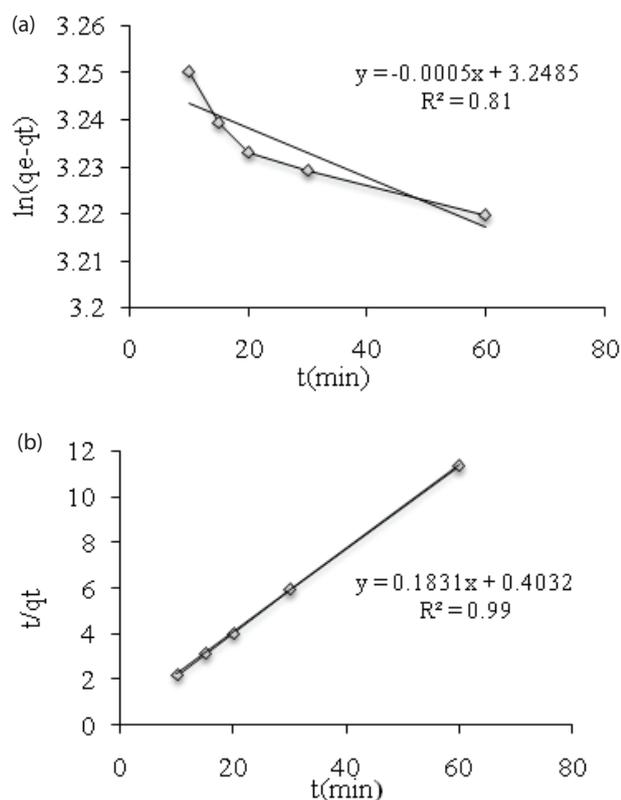


Fig. 5. Kinetics plot: first-order kinetic (a) and second-order kinetic (b).

#### 4. Conclusions

In this study, RSM and CCD were used to find out the optimal conditions for the adsorption of lead onto NoP from aqueous solutions. The second-order mathematical model was developed by regression analysis of the experimental data. The effects of four main variables including pH, adsorbent dose, lead ion concentration, and biosorption time were investigated. The pseudo second order was found to be the applicable kinetic model in the present study. The data were in good agreement with Freundlich isotherm. This study demonstrated that the NoP has relatively high adsorption capacity compared with some other adsorbents and biosorbents reported in the literature.

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#### References

- [1] F.W. Sousa, A.G. Oliveira, J.P. Ribeiro, M.F. Rosa, D. Keukeleire, R.F. Nascimento, Green coconut shells applied as adsorbent for removal of toxic metal ions using fixed-bed column technology, *J. Environ. Manage.*, 91 (2010) 1634–1640.
- [2] C. Namasivayam, K. Ranganathan, Removal of Cd(II) from wastewater by adsorption on “waste” Fe(III)Cr(III) hydroxide, *Water Res.*, 29 (1995) 1737–1744.
- [3] T. Budinova, N. Petrov, V. Minkova, K. Gergova, Removal of metal ions from aqueous solution by activated carbons obtained from different raw materials, *J. Chem. Technol. Biotechnol.*, 60 (1994) 177–182.
- [4] A. Hafez, M. El-Manharawy, M. Khedr, RO membrane removal of unreacted chromium from spent tanning effluent. A pilot-scale study, Part 2, *Desalination*, 144 (2002) 237–242.
- [5] A.B. Ribeiro, E.P. Mateus, L.M. Ottosen, G. Bech-Nielsen, Electrolytic removal of Cu, Cr, and As from chromated copper arsenate-treated timber waste, *Environ. Sci. Technol.*, 34 (2000) 784–788.
- [6] A. Dąbrowski, Z. Hubicki, P. Podkościelny, E. Robens, Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method, *Chemosphere*, 56 (2004) 91–106.
- [7] S. Ahmady-Asbchin, Y. Andres, C. Gérente, P. Le Cloirec, Biosorption of Cu(II) from aqueous solution by *Fucus serratus*: surface characterization and sorption mechanisms, *Bioresour. Technol.*, 99 (2008) 6150–6155.
- [8] A. Zielińska, P. Oleszczuk, Evaluation of sewage sludge and slow pyrolyzed sewage sludge-derived biochar for adsorption of phenanthrene and pyrene, *Bioresour. Technol.*, 192 (2015) 618–626.
- [9] Y. Chen, F. Wang, L. Duan, H. Yang, J. Gao, Tetracycline adsorption onto rice husk ash, an agricultural waste: its kinetic and thermodynamic studies, *J. Mol. Liq.*, 222 (2016) 487–494.
- [10] M.K. Seliem, S. Komarneni, M.R. Abu Khadra, Phosphate removal from solution by composite of MCM-41 silica with rice husk: kinetic and equilibrium studies, *Microporous Mesoporous Mater.*, 224 (2016) 51–57.
- [11] K. Zhu, H. Fu, J. Zhang, X. Lv, J. Tang, X. Xu, Studies on removal of  $\text{NH}_4^+\text{-N}$  from aqueous solution by using the activated carbons derived from rice husk, *Biomass Bioenergy*, 43 (2012) 18–25.
- [12] F. Jiao, L. Zhang, Z. Dong, T. Namioka, N. Yamada, Y. Ninomiya, Study on the species of heavy metals in MSW incineration fly ash and their leaching behavior, *Fuel Process. Technol.*, 152 (2016) 108–115.
- [13] C. Namasivayam, D. Sangeetha, Recycling of agricultural solid waste, coir pith: removal of anions, heavy metals, organics and dyes from water by adsorption onto ZnCl<sub>2</sub> activated coir pith carbon, *J. Hazard. Mater.*, 135 (2006) 449–452.
- [14] P. Li, Y.-J. Su, Y. Wang, B. Liu, L.-M. Sun, Bioadsorption of methyl violet from aqueous solution onto Pu-erh tea powder, *J. Hazard. Mater.*, 179 (2010) 43–48.
- [15] A.Y. Dursun, A comparative study on determination of the equilibrium, kinetic and thermodynamic parameters of biosorption of copper(II) and lead(II) ions onto pretreated *Aspergillus niger*, *Biochem. Eng. J.*, 28 (2006) 187–195.
- [16] V.K. Gupta, A. Rastogi, Biosorption of lead from aqueous solutions by green algae *Spirogyra* species: kinetics and equilibrium studies, *J. Hazard. Mater.*, 152 (2008) 407–414.
- [17] S. Qaiser, A.R. Saleemi, M. Umar, Biosorption of lead(II) and chromium(VI) on groundnut hull: equilibrium, kinetics and thermodynamics study, *Electron. J. Biotechnol.*, 12 (2009) 3–4.
- [18] O. Adelaja, I. Amoo, A. Aderibigbe, Biosorption of lead(II) ions from aqueous solution using *Moringa oleifera* pods, *Arch. Appl. Sci. Res.*, 3 (2011) 50–60.
- [19] A.M. Abdel -Aty, N.S. Ammar, H.H. Abdel Ghafar, R.K. Ali, Biosorption of cadmium and lead from aqueous solution by fresh water alga *Anabaena sphaerica* biomass, *J. Adv. Res.*, 4 (2013) 367–374.
- [20] A. Ucer, A. Uyanik, H.G. Kutbay, Removal of heavy metals using *Myriophyllum verticillatum* (whorl-leaf watermilfoil) in a hydroponic system, *Ekoloji*, 22 (2013) 1–9.

- [21] V.R. Surisetty, J. Kozinski, L. Rao Nageswara, Biosorption of lead ions from aqueous solution using *Ficus benghalensis* L., *J. Eng.*, 2013 (2013) 1–8.
- [22] M. Ajmal, A. Hussain Khan, S. Ahmad, A. Ahmad, Role of sawdust in the removal of copper(II) from industrial wastes, *Water Res.*, 32 (1998) 3085–3091.
- [23] X.-s. Wang, Y. Qin, Equilibrium sorption isotherms for of  $\text{Cu}^{2+}$  on rice bran, *Process Biochem.*, 40 (2005) 677–680.
- [24] S. Torbati, A. Movafeghi, A. Khataee, Biodegradation of C.I. acid blue 92 by *Nasturtium officinale*: study of some physiological responses and metabolic fate of dye, *Int. J. Phytorem.*, 17 (2015) 322–329.
- [25] F. Duman, F. Ozturk, Nickel accumulation and its effect on biomass, protein content and antioxidative enzymes in roots and leaves of watercress (*Nasturtium officinale* R. Br.), *J. Environ. Sci.*, 22 (2010) 526–532.
- [26] D. Aydin, O.F. Coskun, Effects of EDTA on  $\text{Cr}^{+3}$  uptake, accumulation, and biomass in *Nasturtium officinale* (watercress), *Ekoloji*, 22 (2013) 16–23.
- [27] R.H. Myers, D.C. Montgomery, C.M. Anderson-Cook, *Response Surface Methodology: Process and Product Optimization Using Designed Experiments*, 3rd ed., John Wiley & Sons, USA, 2009.
- [28] S.A. Mousavi, A. Almasi, Z. Kamari, F. Abdali, Z. Yosefi, Application of the central composite design and response surface methodology for the treatment of Kermanshah landfill leachate by a sequencing batch reactor, *Desal. Wat. Treat.*, 56 (2015) 622–628.
- [29] S.A. Mousavi, S. Ibrahim, Application of response surface methodology (RSM) for analyzing and modeling of nitrification process using sequencing batch reactors, *Desal. Wat. Treat.*, 57 (2016) 5730–5739.
- [30] S.F.A. Halim, A.H. Kamaruddin, W. Fernando, Continuous biosynthesis of biodiesel from waste cooking palm oil in a packed bed reactor: optimization using response surface methodology (RSM) and mass transfer studies, *Bioresour. Technol.*, 100 (2009) 710–716.
- [31] R. Wang, P. Chen, F. Jia, J. Tang, F. Ma, Optimization of polysaccharides from *Panax japonicus* C.A. Meyer by RSM and its anti-oxidant activity, *Int. J. Biol. Macromol.*, 50 (2012) 331–336.
- [32] E. Malkoc, Ni(II) removal from aqueous solutions using cone biomass of *Thuja orientalis*, *J. Hazard. Mater.*, 137 (2006) 899–908.
- [33] J. Wu, H.-Q. Yu, Biosorption of 2,4-dichlorophenol from aqueous solution by *Phanerochaete chrysosporium* biomass: isotherms, kinetics and thermodynamics, *J. Hazard. Mater.*, 137 (2006) 498–508.
- [34] A. Amalraj, A. Pius, Removal of selected basic dyes using activated carbon from tannery wastes, *Sep. Sci. Technol.*, 49 (2014) 90–100.
- [35] H. Uzun, Y.K. Bayhana, Y. Kaya, A. Cakici, O.F. Algur, Biosorption of lead (II) from aqueous solution by cone biomass of *Pinus sylvestris*, *Desalination*, 154 (2003) 233–238.
- [36] A. Dada, A. Olalekan, A. Olatunya, O. Dada, Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms studies of equilibrium sorption of  $\text{Zn}^{2+}$  onto phosphoric acid modified rice husk, *IOSR-JAC*, 3 (2012) 38–45.
- [37] Y. Kara, Bioaccumulation of Cu, Zn and Ni from the wastewater by treated *Nasturtium officinale*, *Int. J. Environ. Sci. Technol.*, 2 (2005) 63–67.