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Adsorptive removal of Pb(II), Ni(II), and Cd(II) from aqueous media and leather wastewater using *Padinasanctae-crucis* biomass

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ABSTRACT

In this study, a $CaCl_2$-treated biomass of the *Padinasanctae-crucis* algae was used for bio-adsorption of lead, cadmium, and nickel removal from aqueous solution. The properties of bio-adsorbent were analyzed using SEM, FTIR, and methylene blue surface area. The effect of physical parameters on the bio-adsorption process was investigated and it was revealed that the solution pH has the most effective role in the bio-adsorption process. The increasing of temperature led to an increase in the bio-adsorption efficiency of nickel, lead,and cadmium. Bio-adsorption kinetics showed that the pseudo second order model can describe the kinetics of the process better than the pseudo first order model. The adsorption diffusion model stated that the bio-adsorption of metal ions was controlled by the intra-particle diffusion model. Based on the Langmuir model, the maximum bio-adsorption capacity of lead, nickel, and cadmium was determined to be 80.64, 78.74, and 93.45 mg/g, respectively. After desorption of toxic metals, the spent bio-adsorbent was recycled six times. A leather factory wastewater was successfully treated by the *P.sanctae-crucis* bio-adsorbent. The results revealed that the adsorption process was spontaneous and endothermic and temperature increase can improve the spontaneous degree of the process.

Keywords: Aqueous solution; Bio-adsorption; Desorption; Heavy metals; Kinetics; Leather factory

1. Introduction

Heavy metals are known as non-degradable pollutants in the environment and harmful to living organisms. Thus, the metals removal from water and wastewater is critical in terms of the protection of public health and the environment [1]. The wastewater of industrial processes like plating, photography, aerospace, atomic energy, and petrochemical facilities can result in heavy metals pollution of the water resources if the metal content is not suitably treated [2,3]. Among the metals, lead and nickel are accounted as a serious threat to living organisms even with low concentrations because of accumulative, carcinogenic, and mutagenic properties [4]. The World Health Organization (WHO) has reported that the amount of allowable nickel and lead ions

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in drinking waters must be less than 0.5 mg/L and 10 μg/L, respectively [5]. Another important heavy metal from health and environmental point of view is cadmium. Cadmium is one of the toxic metals in the environment and its allowable level in wastewater treatment plants effluent and drinking water is 0.1 mg/L and 0.05 mg/L, respectively [6]. Therefore, it is mandatory to reduce the concentration of Cd, Ni, and Pb ions in waste waters under their standard values.

Common removal techniques of heavy metals from industrial waste waters are chemical precipitation, ion change, solvent extraction, reverse osmosis, electro dialysis, and adsorption [7,8]. The adsorption process is usually used for metal ions removal as it has a number of advantages. In the conventional adsorption process, the activated carbon adsorbent is used which is expensive [9]. Nowadays, the biological adsorption (bio-adsorption) is used for heavy metals removal and is highly favorable. In bio-adsorption processes, many biomaterials are applied including sea algae [10], fungi biomass [11,12], and agricultural wastes such as cellulose made from orange peel [13], olive stone [14], and dew melon peel [2]. Although algae biomass has been widely tested for the removal of metals [15–19], limited studies have been conducted on the removal capacity of heavy metals by *Padinasanctae-crucis* algae [20]. The capacity of the *P.sanctae-crucis* brown algae for bio-adsorption of heavy metal is contributed to biochemical compounds of the cell wall. Cellular walls of these type algae mainly consist of three biopolymer types of alginate, fucoidan, and cellulose [18]. Alginate which is 10–40% of the dry weight of brown algae has also a main role in the adsorption process.

The purpose of this study was to determine the bio-adsorption potential of the chemically modified biomass of *P. sanctae-crucis* algae for removal of Pb, Ni, and Cd from the aqueous solution. The algae are easily accessible in the inter-tidal to sub-tidal zones up to 10 m deep waters of seas. The effect of physical parameters such as pH and bio-adsorbent dose on the bio-adsorption process was studied. Kinetic, equilibrium, and thermodynamic behavior of the bio-adsorption process were also investigated. To the best of author's knowledge, this is the first report of the application of chemically modified biomass of *P. sanctae-cruces* algae for removal of Pb, Ni, and Cd ions from the aqueous solution.

2. Materials and methods

2.1. Bio-adsorbent preparation

The brown algae of *P. sanctae-crucis* were collected from the coasts of the Persian Gulf, Bushehr, Iran. The algae biomass were transferred to the laboratory within 1 h, washed with double-distilled water to remove sediment particles on the surfaces, and was kept in the oven with 80°C temperature for 48 h to be fully dried. Afterward, a Moulinex mill (LM2211 model) was applied to powder the dried alga.

The chemical treatment of the powdered *P. sanctae-crucis*was performed with 0.1 M calcium chloride. For this purpose, 20 g of the powdered product was mixed with 200 mL of 0.1 M calcium chloride solution and stirred with a magnetic stirrer (200 rpm) for about 60 min. The output mixture was passed through the 0.42 μm- Whatman filter, washed with double distilled water, and then oven-dried at 70°C for 24 h. Modified alga was again milled and 0.71 mm-size fractions were separated by a sieve Grade 25 (ASTM E11) and finally preserved in polyethylene bottles in the fridge at 4°C for usage in batch bio-adsorption experiments.

2.2. Preparation of working solutions

The preliminary stock solution (1000 mg/L) of lead, cadmium, and nickel was prepared by dissolution of 1.598 g $Pb(NO_3)_2$, 2.744 g $Cd(NO_3)_2{\cdot}4H_2O$, and 4.34 g $Ni(NO_3)_2{\cdot}4H_2O$, respectively in double distilled water. Solutions with required initial concentrations were also prepared by dilution of the stock solution with double distilled water. All chemicals were purchased from Merck Company (Germany) and double distilled water utilized for preparing all solutions.

2.3. Bio-adsorption experiments

Batch bio-adsorption experiments were performed in 200 mL-Erlenmeyer flasks which contained 80 mg/L of lead, cadmium, and nickel. The effects of physical parameters like initial pH and bio-adsorbent dosage on the adsorption process were examined.

In order to study the effect of pH on the metals bio-adsorption with the treated biomass, the pH range of 2–8 was considered. The initial pH adjustment was done using 0.1 M HCl/NaOH. At pH > 6, some metals precipitation was observed and we did not record this type of metal removal as the bio-adsorption efficiency. The pH test was done at the conditions of a bio-adsorbent dose of 3 g/L, mixing rate of 200 rpm, contact time of 60 min, and temperature of 35°C. Similarly, the effect of bio-adsorbent concentration (2–8 g/L) was assessed at the conditions of temperature: 55°C, pH: 5 for Pb, pH: 6 for Ni and Cd, C_o: 80 mg/L, mixing rate: 200 rpm, contact time: 60 min. In all tests, the bio-adsorption percentage of metal ions (R%) and bio-adsorption capacity (q_e, mg/g) were calculated with Eqs. (1) and (2):

$$R(\%) = \frac{(C_i - C_e)}{C_i} \times 100 \tag{1}$$

$$q_e = \frac{(C_i - C_e)}{W} \times V \tag{2}$$

where C_i and C_e are the initial and equilibrium concentration of heavy metal ions (mg/L), respectively, V is the volume of the working solution (L), and W is the weight of utilized bio-adsorbent (g).

All tests are repeated three times and the average of measurements are presented here in. For each test, the control sample (to determine the effect of the amount of metal precipitation at pH > 6) was also considered.

2.4. Desorption study

The used bio-adsorbent was subjected to study desorption of heavy metals ions with 0.2 N to 0.8 N concentration of HCl. The given spent adsorbent (0.50 g) was put in Erlenmeyer flasks containing 100 mL of the HCl solution. The mixture was stirred at 30°C for 1 h in a shaker incubator

(Parsazma, Iran). The desorbed mass was passed through a filter and the concentration of metal ions in the filtrate was analyzed. The desorbed mass as a bio-adsorbent was used for 2–4 times to purify the effluent containing heavy metals. All cycles were done in the same order to maintain the consistency.

2.5. Measurements

A digital pH-meter (model Metrohm 744) was used for pH measurements and a flame atomic absorption spectrometry (Plus SpectrAA-10, Varian) was applied to measure the ions content before and after bio-adsorption tests. Moreover, the surface examination of *P. sanctae-cruces* brown algae before and after chemical treatment and also after metal ion bio-adsorption was done by Scanning Electron Microscope (SEM, model Hitachi S4160). Functional groups of the bio-adsorbent were determined by Fourier transform infrared spectroscopy (FT-IR, Broker Victor 22). Heater with a magnetic stirrer (Yellow MAG HS 7) used to supply heating and stirring of the solution.

In order to measure the specific area of the bio-adsorbent prepared from $CaCl_2$-treated *P. sanctae-curces*, the methylene blue adsorption method was applied. First of all, the methylene blue solution with concentrations of 1–20 mg/L was prepared to plot a calibration graph. The methylene blue concentration was measured using a spectrophotometer with a 600 nm wavelength. Then, 1 g of bio-adsorbent was added to 15 mg/L methylene blue solution and stirred at 200 rpm for 1 h. The biomass then separated with Whatman filter and the final concentration of methylene blue in the filtrate was measured. The specific area of the bio-adsorbent (S_{MB}, m^2/g) was calculated using the following equation [21]:

$$S_{MB} = \frac{C_{opt} \times A_{MB} \times A_V}{MV_{MB}} \tag{3}$$

where C_{opt} is the number of molecules adsorbed by the $CaCl_2$-treated *P. sanctae-curces*in mg/mg, A_{MB} is the area occupied by a molecule of methylene blue, and A_v is Avogadro's number (6.02 × 10^{23} molecules per).

3. Results and discussion

3.1. Analysis of FTIR, SEM, and specific surface area

To examine the changes on the surface of *P. sanctae-cruces* before and after metal removal, the SEM test was applied. Fig. 1 shows the apparent surface of treated algae before and after bio-adsorption of lead, nickel, and cadmium. The surface of the fresh bio-adsorbent has no additional wastes and it appears to be smooth and flaky structure. On the bio-adsorbent surface, there are few rudimentary-pores.

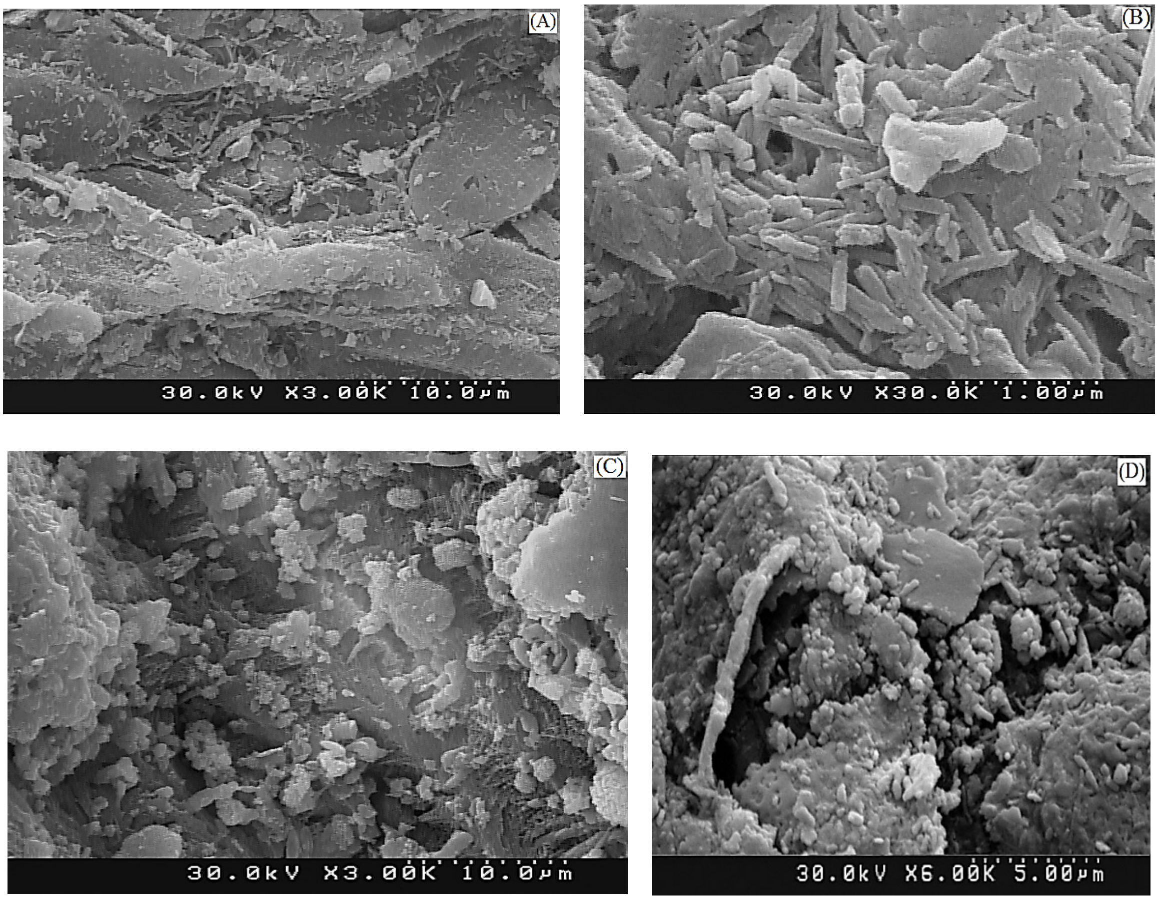

Fig. 1. SEM images of (A) fresh *P. sanctae-cuces* biomass and after bio-adsorption of (B) Pb, (C) Cd, and (D) Ni.

After the metals bio-adsorption process, the flaky structures were shirked and some patches with different shapes were found at the surface of the bio-adsorbent that reveal the adsorption of the metal pollutants.

The FT-IR analysis was performed to determine the functional groups of raw and calcium chloride-modified algae, as well as their interactions with metal ions. The results are depicted in Fig. 2. In the raw alga biomass in the range of 3395 cm^{-1}, a courier has appeared that extends to the tensile vibrations of the -OH or -N-H functional group contained in the algal structure [22]. The vibrations of the -CH$_2$ functional group appear in the raw algal structure at 2929 cm^{-1}. Before modifying algae with calcium chloride, in the range of 2524 cm^{-1}, a peak is also observed, which is related to the vibrations of the -NH$^+$, -NH$_2^+$, and -NH group in algae biomass [16]. In the structure of raw algae in the range of 1030 cm^{-1}, 1415 cm^{-1}, and 1798 cm^{-1}, vibrations have been observed that can be attributed to C-O and C=O. This group has also been observed in previous studies in the structure of algae [23]. In the range of 875 cm^{-1}, 715 cm^{-1}, 661 cm^{-1}, and 469 cm^{-1}, vibrations were observed which can be attributed to the -C-N-C, S=O, P-O, and -OH groups. After treatment of algae using calcium chloride solution, the vibration intensity and range of peaks in the structure of raw algae were altered. After modifying raw algae, the peak varied from 3395 cm^{-1} to 3444 cm^{-1}, which could be due to interactions between the OH-group or -NH with calcium. It is also worth noting that, after modification of the algae biomass, in the range of 3848–3848 cm^{-1}, vibrations have also been observed that can be attributed to the -OH or -NH functional groups in the structure of algae [16]. The correction of algae with calcium chloride resulted in significant changes in the range of peaks of 417–1030 cm^{-1}. For example, peaks of 469 cm^{-1}, 522 cm^{-1}, 661 cm^{-1}, 715 cm^{-1}, and 1030 cm^{-1} in raw algae were changed to 465 cm^{-1}, 516 cm^{-1}, 671 cm^{-1}, 820 cm^{-1}, and 1035 cm^{-1} after modification, which can show the correction of raw algae by calcium chloride solution. After using modified algae biomass in the lead, nickel, and cadmium bio-adsorption process, the range of vibrations of functional groups also varied, which could be due to the interaction between the active ingredient groups in the algae biomass with the metal ions. After the bio-adsorption of nickel, lead, and cadmium ions by using CaCl$_2$-modified algae biomass, the peak of 3444 cm^{-1} was changed to 3446 cm^{-1}, 3445 cm^{-1},and 3443 cm^{-1}, respectively. It should be noted that after bio-adsorption of nickel ions by modified biomass, a peak at 2850 cm^{-1} appeared due to the vibrations of the C-H functional group. Also, the range of couriers in the region of 2922 cm^{-1} was also changed after the bio-adsorption of metal ions. The peak of 1518 cm^{-1} in the structure of modified algae biomass has changed to 1521 cm^{-1}, 1522 cm^{-1}, and 1524 cm^{-1} after the adsorption of Ni, Pb, and Cd, respectively, indicating the effectiveness of the C-O and C=O functional groups in the metals adsorption process. It is worth noting that the range of peaks belonging to other functional groups has also been altered after the bio-adsorption process (see Fig. 2). Therefore, based on the above results, it can be stated that the -OH, -NH, CO, C=O, and -NH$_2$ functional groups in the structure of modified biomass have been effective in the metal bio-adsorption process. In previous studies, the effectiveness of these functional groups has also been reported [24].

The specific area of *P. sanctae-cruces* bio-adsorbent was determined to be 30.73 m^2/g, which is greater than those obtained for calcined *Cardita bicolor* oyster shell (17.40 m^2/g) [21] and *Tamarixhispida* (1.12 m^2/g) [25] confirming the effectiveness of biomass production method.

3.2. Effect of CaCl$_2$ treatment on the bio-adsorption potential of *P. sanctae-crucis* biomass

The treatment of the bio-adsorbent mass with calcium chloride, in addition to improve the stability of the adsorbent mass [26], also leads to an increase in the adsorption efficiency of heavy metals. The efficiency of cadmium, lead, and nickel bio-adsorption by two raw and CaCl$_2$- treated *P. sanctae-crucis* biomass is depicted in Fig. 3. As shown in Fig. 3, the bio-adsorption efficiency of metals by the CaCl$_2$-treated adsorbent has a remarkable difference with the untreated one. The CaCl$_2$-treatment of the *P. sanctae-crucis* biomass leads to the conversion of the active binding sites from the H$^+$ to the Ca^{2+} form. This substitution may suitable the bio-adsorption reaction of heavy metals (Cd, Ni, and Pb) because, due to the size of the metal ions, it should be

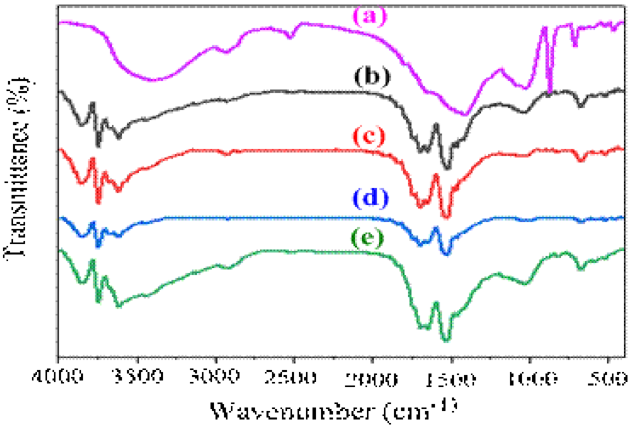

Fig. 2. FTIR analysis for (a) raw *P. sanctae-cuces* biomass, (b) CaCl$_2$- treated *P. sanctae-cuces* biomass, and after bio-adsorption of (c) Ni, (d) Pb, and (e) Cd.

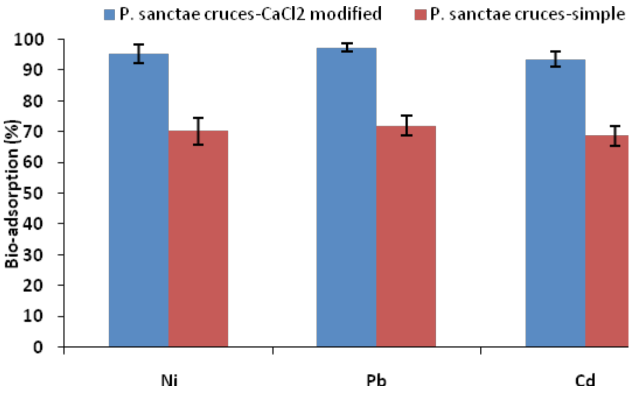

Fig. 3. Comparision of untreated and CaCl$_2$-treated *P. sanctae-cuces* biomass for metals bio-adsorption (dose: 3 g/L, temperature: 55°C, pH$_{opt}$, C_o: 80 mg/L, mixing rate: 200 rpm, contact time: 60 min).

easier to exchange cadmium, nickel, and lead for calcium than for hydrogen ions.

3.3. Effect of pH

The solution pH is one of the effective parameters in the bio-adsorption of metal ions because hydrogen ion competes with metal ions to relocate active sites of the bio-adsorbent [27]. The adsorption highly depends on the concentration of hydrogen ion in the solution. The effect of initial pH was studied and the results are depicted in Fig. 4. The maximum removal of nickel (=87.6%), lead (=88.34%), and cadmium (=86.45%) were obtained at the solution pH of 6, 5, and 6, respectively. At pH range of 2–4, the removal percentage decreased owing to the high concentration of hydrogen ions in the solution and relocate on active sites [28]. Occupying active sites of the bio-adsorbent by hydrogen ions would repulse metal cations and prevent them from to be adsorbed. By increasing the solution pH from 2 to 6, the bio-adsorption of pollutants was increased; because the negative charges on the bio-adsorbent surface were increased and consequently more attraction of metal ions was occurred [29]. Therefore, optimum initial pH for the bio-adsorption of lead, nickel, and cadmium was selected 5, 6 and 6, respectively.

3.4. Effect of bio-adsorbent dosage

Bio-adsorbent dosage is considered as an important parameter because this parameter defines the capacity of the adsorbent for a definite initial metal concentration [30]. The effect of bio-adsorbent dosage was investigated at pH = 6 for cadmium and nickel and at pH = 5 for lead and results are shown in Fig. 5. The results revealed that as the adsorbent dosage went up, the bio-adsorption also increased owing to the rise in the number of active sites [16]. The main increase in the bio-adsorption took place in the range of 1–4 g/L of bio-adsorbent concentration and higher increase in dose did not accompany with a considerable increase in the bio-adsorption efficiency and thus, the process rate continued slowly. A plausible reason for remaining the removal rate at bio-adsorbent dosage >4 g/L is aggregation and overlapping the biomass particles.

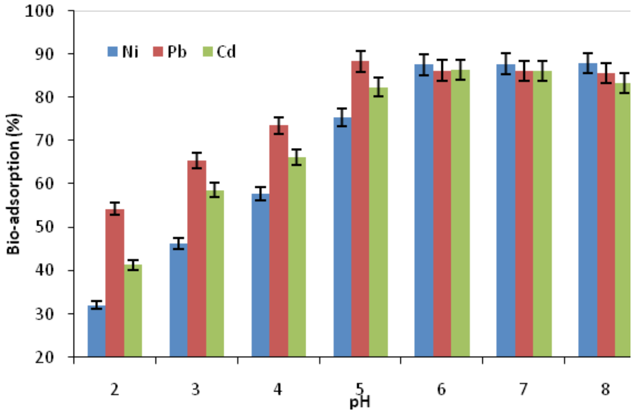

Fig. 4. Effect of solution pH (dose: 3 g/L, C_o: 80 mg/L, contact time: 60 min, temperature: 35°C, mixing rate: 200 rpm).

3.5. Effect of solution temperature and contact time

The effect of contact time in the range of 5 to 180 min was studied and the results are shown in Fig. 6. According to the results, longer contact time can enhance the bio-adsorption of metals ions by the $CaCl_2$-treated *P. sanctae-cuces*. The rate of bio-adsorption of metal ions was higher at earlier contact times (i.e., 5–60 min) due to the abundance and availability of active sites on the bio-adsorbent surface. But as time passes (t > 60 min) the adsorption rate decreased which can be ascribed by saturation of active sites of the sorbent.

The initial temperature of the solution is a parameter with an intermediate effect on contamination removal from aqueous solutions [31]. Temperature can provide appropriate energy for the system and affect the capacity of the system whether it is exothermic or endothermic [32]. To do this test, the temperature, pH, and metal concentration in the solution was set at 25–55°C,optimal value, and 80 mg/L, respectively (see Fig. 6). Temperature increase improves the bio-adsorption of lead, nickel, and cadmium ions showing that this process is endothermic. The reason for such behavior is dedicated to an increase in the number of suitable active sites for the metal ions adsorption. Besides, rising the temperature causes a reduction in the thickness of the boundary layer around the bio-adsorbent and this result in the higher ability of the biomass to uptake the studied pollutants [32].

3.6. Bio- adsorption kinetics

The bio-adsorption kinetic is used to determine the control mechanism involved in the bio-adsorption process. The pseudo first order kinetic model is one of the frequent models being used in previous studies for describing of adsorption kinetics. The linear form of this model is:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{4}$$

where: q_t (mg/g) is the adsorbed ions content per gram of adsorbent during the contact time (t) and k_1 (1/min) is the bio-adsorption constant. In order to calculate k_1, the plot of $ln(q - q_t)$ versus t is drawn and the slope of the graph is measured. Comparing the adsorption capacity ($q_{e.cal}$) measured

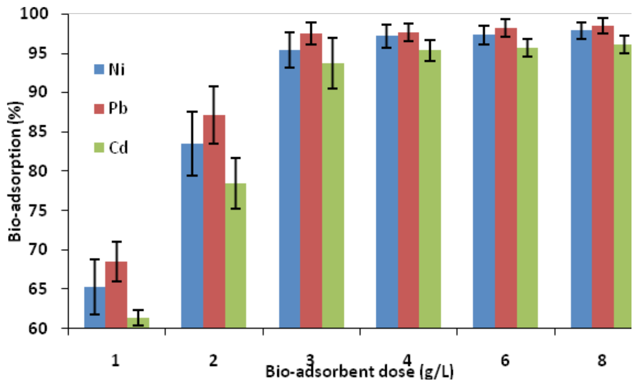

Fig. 5. Effect of bio-adsorbent dose (temperature: 55°C, pH_{opt}, C_o: 80 mg/L, mixing rate: 200 rpm, contact time: 60 min).

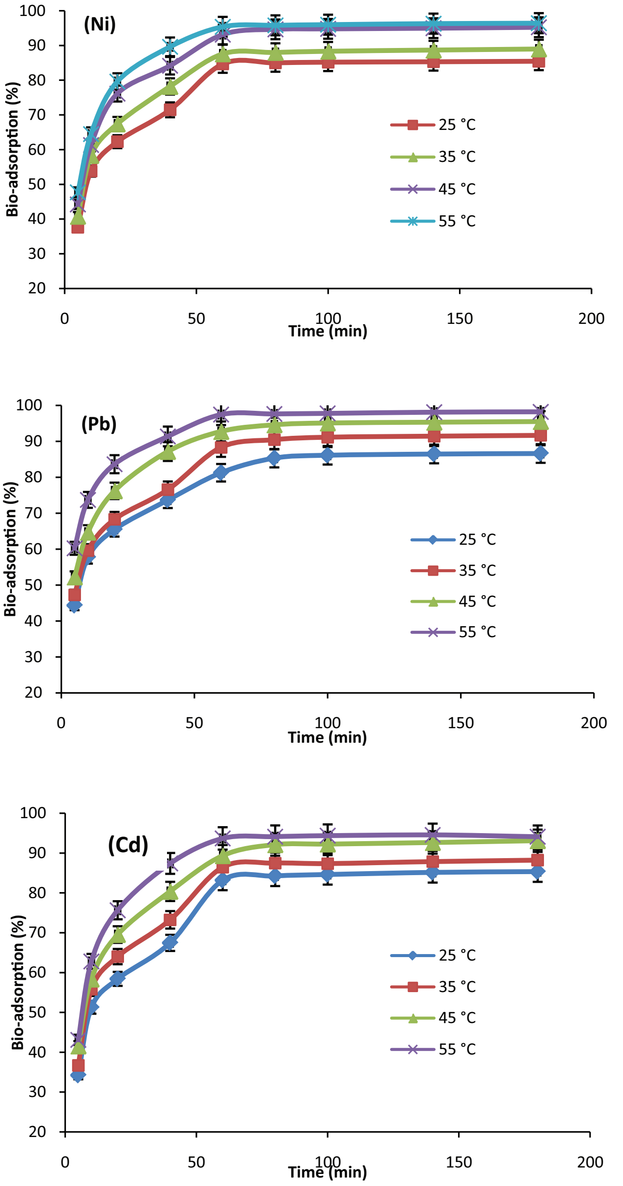

Fig. 6. Effect of temperature and contact time on bio-adsorption efficiency (dose: 3 g/L, pH$_{opt}$, mixing rate: 200 rpm, C_o: 80 mg/L).

from data analyses and those obtained from the experiments ($q_{e.exp}$) is revealed that the pseudo first order model cannot describe the kinetic behavior of the bio-adsorption process. Correlation coefficients (R^2) for pseudo first order model in the temperature range of 295.15–328.15 K for lead, cadmium, and nickel adsorption were attained 0.9862, 0.909–0.9622, and 0.8838–0.909, respectively. These values confirmed that the bio-adsorption data did not follow the pseudo first order model. It is also noticeable that the experimental adsorption capacity value ($q_{e.exp}$) was higher than the calculated adsorption capacity value ($q_{e.cal}$) by pseudo first order model. Therefore, this model sounds not to be suitable for metal ions adsorption. The constant values and other parameters of this model are listed in Table 1.

The pseudo second order model was also used for modeling the bio-adsorption kinetic. This model is described as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{5}$$

where k_2 is the constant of pseudo second order model (g/mg·min). The q_e and k_2 parameters can obtain from the slope and the intercept of the plot of t/q_t versus t.

The value of constants and other parameters of the second order model are reported in Table 1. Correlation coefficients (R^2) of this model for lead, cadmium, and nickel adsorption were determined 0.9994–0.9998, 0.998–0.9998, and 0.9994–0.9997, respectively. These values are higher than the pseudo first order model showing that the pseudo second order model is more suitable. Further, the calculated adsorption capacity of second order model ($q_{e2.cal}$) was very close to experimental value ($q_{e2.exp}$). This confirms better fittingness of pseudo second order model in comparison with pseudo first order model.

Pseudo first and second order kinetic models do not provide information on the stage of controlling the adsorption process, which is why experimental data are analyzed using the interaparticle diffusion (Weber-Morris) kinetic model. The interaparticle diffusion model is an experimental model and assumes that the bio-adsorption capacity varies with $t^{1/2}$. In this model, the heavy metal bio-adsorption mechanism is assumed to be based on four steps:

(a) Migration and transfer of metal ions from soluble mass to the bio-adsorbent surface (mass penetration);
(b) the penetration of metal ions from the boundary layer to the bio-adsorbent surface by the penetration of the film;
(c) the transfer of metal ions from the bio-adsorbent surface to the internal pore (interaparticle diffusion); and
(d) the bio-adsorption of metal ions by adsorbent active sites occurs through chemical reactions, ion exchange, complexation or chelation [33].

The linear form of interaparticle diffusion model is as follows:

$$q_t = k_i t^{0.5} + I \tag{6}$$

where q_t(mg/g) is the amount of lead, nickel, and cadmium adsorbed at time t by bio-adsorbent and k_i (mg/g·min$^{0.5}$) is the constant interaparticle diffusion rate, and I is the parameter that gives ideas about the thickness of the boundary layer (its high value indicates the high effect of the boundary layer). The values of k_i and I are determined from the slope and intercept of the q_t versus $t^{1/2}$ graph, respectively. If the relation q_t versus $t^{1/2}$ is linear, it shows that the process controller stage is the only interaparticle diffusion step [34]. According to the results, the linear equation of interaparticle diffusion for the bio-adsorption of Pb, Ni, and Cd using modified algae biomass is not linear (Fig. 7), which shows that the bio-adsorption process is not controlled solely by interaparticle penetration, and the diffusion of the pollutants from the liquid film and other conditions are also

Table 1
Kinetic modeling parameters (temperature: 25–55°C, time: 5–180 min, adsorbent dose: 3 g/L, C_o: 80 mg/L, and pH_{opt})

Temperature (K)	$q_{e.exp}$ (mg/g)	Pseudo-first-order			Pseudo-second-order		
		k_1 (1/min)	$q_{e1.cal}$ (mg/g)	R^2	k_2 (g mg^{-1} min^{-1})	$q_{e2.cal}$ (mg/g)	R^2
Pb(II)							
298.15	23.101	0.0436	14.247	0.9862	0.0066	24.038	0.9994
308.15	24.448	0.0416	13.497	0.9706	0.00603	25.51	0.9998
318.15	25.477	0.0408	11.59	0.9771	0.0081	26.315	0.9998
328.15	26.192	0.0455	8.866	0.9496	0.0114	26.809	0.9998
Cd(II)							
298.15	22.757	0.0434	15.015	0.9622	0.00481	24.096	0.998
308.15	23.528	0.0395	11.971	0.909	0.0056	24.69	0.9998
318.15	24.826	0.0378	12.446	0.9425	0.0058	25.9067	0.9995
328.15	25.256	0.0446	8.9539	0.9151	0.0076	26.178	0.9995
Ni(II)							
298.15	22.792	0.0479	12.321	0.909	0.00612	23.923	0.9987
308.15	23.733	0.0398	10.755	0.9266	0.0068	24.69	0.9994
318.15	25.405	0.0417	11.053	0.931	0.0072	26.315	0.9996
328.15	25.717	0.0401	8.86	0.8838	0.0085	26.525	0.9997

effective [22]. The results show that the bio-adsorption process has two stages: the first step is the adsorption process associated with the penetration of the liquid film in which metal ions pass through the liquid layer surrounding the adsorbent, and this step is carried out at a high rate. The second step is the gradual adsorption in which the penetration within the particle restricts the velocity. In some cases, there is a third stage, which is the final adsorption stage, and it is very slow due to the low concentration of metal ions in the aqueous solution and the occupation of active sites of adsorbent [34]. In Table 2, the constants and parameters of the kinetic model of interaparticle diffusion for the bio-adsorption process of lead, nickel, and cadmium using modified algae biomass were reported.

3.7. Bio-adsorption isotherms

Adsorption isotherms are indicated the relation between adsorbent and solution at the equilibrium time. Thus, adsorption isotherms are useful for description of the adsorption process. Also, adsorption isotherms provide the basic requirements for designing the adsorption process [35]. Two important isotherm models were selected in this study: Langmuir and Freundlich.

The Langmuir adsorption isotherm is applied to equilibrium adsorption assuming monolayer adsorption onto a surface with a finite number of identical sites [36]. The linear form of the Langmuir model is written as follows:

$$\frac{1}{q_e} = \left(\frac{1}{K_L q_{\max}}\right)\frac{1}{C_e} + \frac{1}{q_{\max}} \tag{7}$$

where K_L (L/g) and q_{max} (mg/g)are the energy of bio-adsorption and Langmuir constant relating to the adsorption capacity, respectively. These constants are determined from the slope and intercept of the linear plots of $1/q_e$ versus $1/C_e$, respectively.

Based on the Langmuir equation, the dimensionless parameter of the equilibrium or adsorption intensity $\left(R_L = \frac{1}{1+K_L C_i}\right)$ can be used. The value of R_L defines the state and goodness of the isotherm model. If $R_L > 1$, $R_L = 0$, $R_L = 1$, and $0 < R_L < 1$, the process is undesirable, irreversible, linear, and desirable, respectively [36].

Table 3 shows the results of the isotherm study. Correlation coefficients for lead, cadmium, and nickel were obtained 0.8935, 0.8776, and 0.9086, respectively indicating the Langmuir isotherm model is an appropriate model for the description of the bio-adsorption process. The adsorption capacity of lead, cadmium, and nickel by the bio-adsorbent was attained 80.64, 93.45, and 78.74 mg/g, respectively. According to Table 3, the value of R_L for the bio-adsorption process of lead, cadmium, and nickel were achieved 0.0837, 0.2083, and 0.113, respectively which confirms that the process is desirable ($0 < R_L < 1$). Table 4 compares the adsorption capacity of the bio-adsorbent prepared from *P. sanctae-cruces* with other natural bio-adsorbents and shows that the adsorbent of this study has an acceptable adsorption capacity.

Freundlich model is an empirical model and can describe the adsorption capability of adsorbents. This model is applied for non-ideal adsorption on heterogeneous surfaces [43]. The linear form of this model is expressed by Eq. (7):

$$\ln q_e = \ln K_f + \frac{1}{n}\ln C_e \tag{8}$$

where K_f((mg/g)(L/mg)$^{1/n}$) and n are the Freundlich constants showing the adsorption capacity and adsorption strength, respectively.

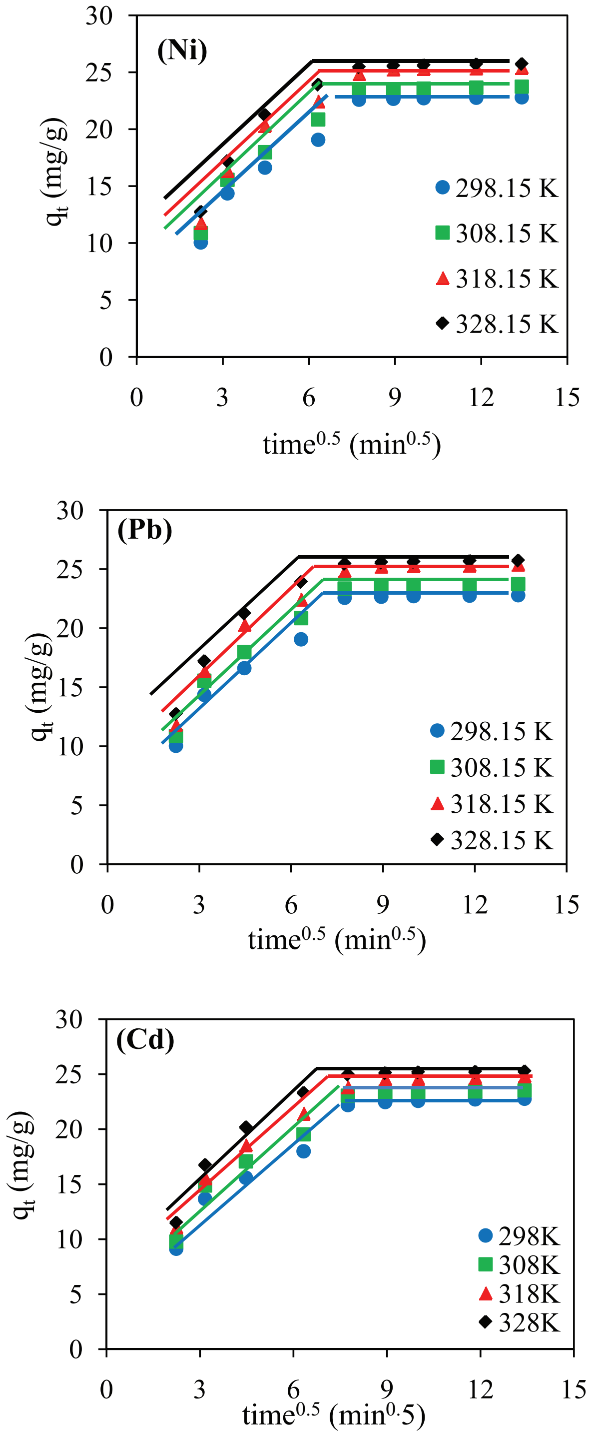

Fig. 7. Intra-particle diffusion model for metals bio-adsorption.

The K_f and n constant in the Freundlich model are determined by plotting $ln(q_e)$ versus $ln(C_e)$. Correlation coefficients for lead, cadmium, and nickel bio-adsorption using this model were obtained as 0.8328, 0.8198, and 0.8679, respectively (see Table 3). Thus, the Freundlich model cannot justify isotherm behavior of the equilibrium data.

3.8. Thermodynamic behavior

Thermodynamic parameters like Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°), equilibrium constant of ‘$K_D = q_e/C_e$’ could be determined from the experimental data obtained as a function of temperature using following equations [5]:

$$\Delta G° = -RT \ln K_D \tag{9}$$

where R (8.314 J/mol·K) is the universal gas constant and T (K) is the temperature.

Enthalpy and entropy are also calculated by the following equation:

$$\ln K_D = \frac{\Delta S^{o}}{R} - \frac{\Delta H^{0}}{RT} \tag{10}$$

where the values of enthalpy and entropy are attained by plotting $ln\ K$ vs. $1/T$ which the slope of the line is enthalpy and the intercept is entropy.

Table 5 shows thermodynamic parameters identified in the bio-adsorption process for the metal ions in the temperature range of 298.15–328.15 K. As seen in Table 5, the value of Gibbs free energy of the metal bio-adsorption was negative showing the process is spontaneous and feasible. In addition, increasing the temperature led to increasing of the ΔG° values and speed up the spontaneous situation of the process. The enthalpy (ΔH°) parameter for nickel, lead, and cadmium was obtained 37.88, 57.95, and 29.23 J/mol, respectively. These values affirmed that the bio-adsorption process in the range of 298.15–328.15 K is endothermic. Furthermore, entropy values were measured as 131.303, 196.268, and 101.505 J/mol·K for nickel, lead, and cadmium, respectively. The positive value of entropy (ΔS°) indicates that the degrees of unrestraint of the bio-adsorbed Ni, Pb, and Cd ions were increased [2].

3.9. Desorption and reusability of the bio-adsorbent

An important economic and environmental point of view in the treatment of wastewater/water using adsorbents is their reusability. In addition, the final disposal of the spent adsorbents containing toxic metals in landfills could lead to groundwater contamination. It is, therefore, necessary to separate heavy metals from the adsorbent before disposal [44]. If it is possible to recover nickel, cadmium, and lead from the utilized adsorbent, then the environment can be preserved from secondary contamination, as well as the wastewater treatment (since metals and the adsorbent are recycled) also become more economical. Here in this paper, the different concentrations of hydrochloric acid (0.2–0.8 N HCl) were applied to regenerate the spent *P. sanctae-cruces*biomass. By increasing the acid concentration, the percentage of desorption increased for all metals and maximized at 0.8 Normal (figure not shown). Maximum desorption for all three metals was obtained in the range of 93–97%. The recovery of nickel, lead, and cadmium metals was maintained above 90% for the 6 desorption cycles.

Table 2
Parameters and constants of interaparticle diffusion model

Metal	Parameter	Temperature			
		25°C	35°C	45°C	55°C
Ni(II)	$K_{i,1}$ (mg/g min$^{1/2}$)	2.0554	2.0815	2.202	2.2
	I_1 (mg/g)	6.689	7.7592	8.6058	9.5655
	R^2	0.9572	0.9472	0.9271	0.9211
	$K_{i,2}$ (mg/g min$^{1/2}$)	0.0265	0.0573	0.0355	0.0375
	I_2 (mg/g)	22.441	22.971	24.922	25.223
	R^2	0.9582	0.9799	0.9907	0.9819
Pb(II)	$K_{i,1}$ (mg/g min$^{1/2}$)	1.6475	1.8284	1.9061	1.6842
	I_1 (mg/g)	9.3098	9.3856	10.775	13.614
	R^2	0.9501	0.9717	0.9573	0.9346
	$K_{i,2}$ (mg/g min$^{1/2}$)	0.0717	0.0654	0.0509	0.036
	I_2 (mg/g)	22.179	23.594	24.809	25.722
	R^2	0.8221	0.876	0.8972	0.9609
Cd(II)	$K_{i,1}$ (mg/g min$^{1/2}$)	2.1018	2.1428	2.1576	2.2923
	I_1 (mg/g)	5.6451	6.6044	7.7596	8.3625
	R^2	0.9515	0.9392	0.9506	0.9206
	$K_{i,2}$ (mg/g min$^{1/2}$)	0.0656	0.0501	0.0595	0.0337
	I_2 (mg/g)	21.9	22.852	24.016	24.811
	R^2	0.962	0.8847	0.9854	0.958

Table 3
Isotherm modeling results

Isotherms	Parameters	Heavy metal ions		
		Pb(II)	Ni(II)	Cd(II)
Langmuir	q_{max} (mg/g)	80.64	78.74	93.45
	K_L (l/mg)	0.1367	0.098	0.0475
	R_L	0.0837	0.113	0.2083
	R^2	0.8935	0. 9086	0.8776
Freundlich	n	2.164	1.984	1.787
	K_f(mg/g)(L/mg)$^{1/n}$	12.459	9.996	7.1857
	R^2	0.8328	0.8679	0.8198

Table 4
Comparison of the bio-adsorption capacity of modified *P. sanctae-cruces* for Pb(II), Ni(II), and Cd(II) with different bio-adsorbents

Bio-adsorbent	Bio-adsorption capacity (mg/g)			Reference
	Pb(II)	Cd(II)	Ni(II)	
P. simplicissimum	76.9	52.5	–	[37]
Lactarius scrobiculatus	56.2	53.1	–	[38]
Modified apple pomace	178.57	112.35	51	[39]
Olive cake	19.53	10.56	–	[40]
Oedogonium hatei	–	–	44.2	[17]
Gracilaria caudata	–	–	50.1	[41]
Rhizoclonium hookeri	74.8-81.7	–	55.4–65.8	[42]
Modified Padina sanctae cruces	80.64	93.45	78.74	This study

Table 5
Thermodynamic parameters

Metal ions	T (K)	ΔG° (kJ/mol)	ΔH° (J/mol)	ΔS° (J/mol·K)
Ni(II)	298.15	–1.515	37.88	131.30
	308.15	–2.194		
	318.15	–3.997		
	328.15	–5.268		
Pb(II)	298.15	–0.914	57.95	196.26
	308.15	–2.373		
	318.15	–3.840		
	328.15	–6.964		
Cd(II)	298.15	–1.238	29.23	101.50
	308.15	–1.933		
	318.15	–2.717		
	328.15	–4.358		

3.10. Treatment of leather factory wastewater

Upon completion of the laboratory tests, the field application of modified *P. sanctae-cruces* was examined by treatment of the leather factory wastewater. To do this, a bulk of wastewater (10 L) was collected from an equalization tank of a leather factory - wastewater treatment plant, Shiraz, Iran. The characteristics of the wastewater before and after treatment by the *P. sanctae-cruces* algae are depicted in Table 6. As shown in this table, the amount of all metals effectively reduced. The final pH value was slightly increased to around neutral which reduce the total cost of effluent neutralization before discharge to the water bodies

Table 6
Treatment of the leather wastewater (bio-adsorbent dose: 3 g/L, contact time: 60 min, temperature: 35°C, mixing rate: 200 rpm)

Component	Unit	Before treatment	After treatment
pH	pH unit	6.1	6.9
COD	mg/L	284	179
Ni(II)	mg/L	14.5	1.4
Pb(II)	mg/L	6.6	< detection limit
Cd(II)	mg/L	20.2	3.8
Cr(VI)	mg/L	27.3	7.9

and make the bio-adsorbent more beneficial. Another note from Table 6 is the partially COD removal from real wastewater using the adsorbent which affirms the suitability of the $CaCl_2$-treated*P. sanctae-cruces* for industrial wastewater treatment.

4. Conclusions

In the present study, the $CaCl_2$-treated biomass of the *P. sanctae-cruces* brown algae was applied as bio-adsorbent for removal of nickel, cadmium, and lead from the aqueous solution. According to the FTIR analysis, the functional groups of the bio-adsorbent are including a mine, carboxyl, and hydroxyl. The bio-adsorption process was carried out in the batch mode and effect of initial pH and bio-adsorbent dosage was investigated. Maximum removal of lead, cadmium, and nickel took place at initial pH of 5, 6, and 6, respectively. Kinetics behavior of the bio-adsorption process showed that the pseudo second order model well-described data. Maximum bio-adsorption capacity of nickel, lead, and cadmium was calculated 78.74, 80.64, and 93.45 mg/g, respectively. The thermodynamic study confirmed that the process was spontaneous and endothermic. Overall, the *P. sanctae-cruces* biomass can be easily used as a low cost, recyclable, available, renewable, and effective bio-adsorbent for nickel, lead, and cadmium removal from aqueous solution and leather factory wastewater.

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