# Kinetics and equilibrium studies on biosorption of cadmium, lead, and nickel ions from aqueous solutions by intact and chemically modified brown algae

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## ARTICLE INFO

## ABSTRACT

The present study deals with the evaluation of biosorptive removal of Cd (II), Ni (II) and Pb (II) ions by both intact and pre-treated brown marine algae: *Cystoseira indica, Sargassum glaucescens, Nizimuddinia zanardini* and *Padina australis* treated with formaldehyde (FA), glutaraldehyde (GA), polyethylene imine (PEI), calcium chloride ($CaCl_2$) and hydrochloric acid (HCl). Batch shaking adsorption experiments were performed in order to examine the effects of pH, contact time, biomass concentration, biomass treatment and initial metal concentration on the removal process. The optimum sorption conditions for each heavy metal are presented. One-way ANOVA and one sample *t*-tests were performed on experimental data to evaluate the statistical significance of biosorption capacities after five cycles of sorption and desorption. The equilibrium experimental data were tested using the most common isotherms. The results are best fitted by the Freundlich model among two-parameter models and the Toth, Khan and Radke-Prausnitz models among three-parameter isotherm models for Cd (II), Ni (II) and Pb (II), respectively. The kinetic data were fitted by models including pseudo-first-order and pseudo-second-order. From the results obtained, the pseudo-second-order kinetic model best describes the biosorption of cadmium, nickel and lead ions.

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## 1. Introduction

The increase of industrial activities has accentuated environmental pollution problems [1] causing the deterioration of several ecosystems with the accumulation of many pollutants, such as toxic metals [2]. Heavy metals are discharged from various industries such as storage batteries, textile, pigment, fertilizer, plastic, ceramic and glass manufacturing, mining, electroplating, and metallurgical processes [3]. Heavy metals are persistent environmental contaminants since they cannot be degraded or destroyed. Heavy metal pollution represents an important problem due to its toxic effect and accumulation throughout the food chain leading to serious ecological and health problems [4].

Removal and recovery of heavy metals are very important with respect to environmental and economical considerations [5]. Conventional physicochemical methods such as electrochemical treatment, ion-exchange, precipitation, reverse osmosis, evaporation and oxidation/reduction for heavy metal removal from waste streams are expensive, not eco-friendly and inefficient for metal removal from dilute solutions containing from 1 to 100 mg/L of dissolved metal.

In the past few decades, biosorption using microorganism biomass as the adsorbent has emerged as a potential alternative technique to the existing methods for metal removal. The use of biological materials, including living and non-living microorganisms, in the removal and possibly recovery of toxic or precious metals from industrial wastes has gained important credibility during recent years, because of the good performance, minimization of chemical/biological sludge and low cost of these materials. The main advantages of biological substrates are: (a) the diversity of biological active binding sites, (b) small and uniform size, and (c) being less subject to interference from alkali and alkali-earth metals than ion exchange resins. Microorganisms including bacteria, algae, fungi and yeast take up metals either actively (bioaccumulation) and/or passively (biosorption) [6].

The term biosorption indicates a metabolism-independent binding of heavy metals by dead (inactive) or living (active) biological materials. The biosorption mechanism, which is complex and still not well understood, depends on whether the organism is living or dead, the type of microorganism and the elemental species [7]. The use of non-living microbial cells as biosorbents has been shown to be an effective means for removal or recovery of heavy metals from aqueous solution. Biomass acts as a chemical substance or ion exchange agent of biological origin. It is particularly the cell wall structure of certain algae, fungi and bacteria, which is responsible for this phenomenon. The metal

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ions in solution are adsorbed on the surface through interaction with the chemical functional groups such as carboxylate, amine, amide, imidazole, phosphate, hydroxyl and other functional groups found in the cell walls of the biopolymers. Biosorption includes a combination of several mechanisms including electrostatic attraction, complexation, ion-exchange, covalent binding, Van der Waals' attraction, adsorption and microprecipitation [8,9].

Even though the brown algae are among the most common biosorbents used for heavy metal recovery, they may cause secondary pollution due to organic substance release, such as alginate dissolving from biosorbents during the biosorption process. Another problem encountered is that the leaching of some adsorptive components may also lead to a loss of biosorption capacity [10]. These phenomena may hinder their industrial application. Some studies [10–12] have shown that surface modification by calcium chloride, formaldehyde (FA) and glutaraldehyde (GA) can prevent leaching of adsorptive components from biomass and increase the stability of the biosorbent material. Polyethylene imine (PEI) is well known for its metal chelating characteristic due to the presence of a large number of amine groups in a molecule and it is often used to modify the adsorbent surface to increase the adsorption capacity [13].

In the present study, the ability of four species of the Persian Gulf (Iran) brown algae to remove the cadmium (II), nickel (II) and lead (II) ions are compared and then the effect of chemical modification and pH on biosorption is studied. Finally, to optimize the separation process design, the appropriate isotherm models (Langmuir, Freundlich, Khan, Toth and Radke-Prausnitz) are established and then in order to investigate the sorption behaviour, pseudo-first and pseudo-second kinetic models are studied.

## 2. Methods

### 2.1. Materials and preparation of pre-treated biomass

Stock metal solutions were prepared by dissolving cadmium, nickel and lead nitrate, $Cd(NO_3)_2 \cdot 4H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$, $Pb(NO_3)_2$ in double-distilled water (DDW). All the reagents were obtained from Merck (Germany).

Samples of brown marine algae, *Cystoseira indica, Sargassum glaucescens, Nizimuddinia zanardini* and *Padina australis* were collected from coastal areas of the Persian Gulf, Iran. They were washed with tap water to remove sand and other impurities and were sun-dried for 48 h. The biomass was crushed and sieved (RETSCH AS-200, Germany) to a particle size of 0.5–1.0 mm and then washed with double-distilled water (DDW) and dried in an oven (Heraeus CH 20P, Germany) at 80 °C for 24 h. This material will be referred to as intact biomass. Surface modification by $CaCl_2$, HCl, PEI, GA and FA followed a modified protocol of Brierley [14].

### 2.2. Batch biosorption experiments

Experiments were conducted by introducing 0.06 g (2 g/L) of algal biomass into a series of Erlenmeyer flasks containing 30 mL of solutions having a metal concentration of 0.5 mmol/L. The flasks were agitated at 150 rpm in an incubator shaker (INFORS multitron, Switzerland) at 25 °C for 2 h. The algal biomass was separated from the metal solution by centrifugation (Sigma203, Germany) at 4000 rpm for 15 min. The concentration of the metal in the remaining solution was measured by an ICP-OES (inductively coupled plasma-optical emission spectrometer, PerkinElmer-Optima 2100, USA).

The amount of metals adsorbed $q$ (mg/g), by intact and modified biomass was calculated using the following equation [15]:

$$q = \frac{\nu(C_i - C_f)}{m} \tag{1}$$

where $C_i$ and $C_f$ (mg/L) are the initial and final metal ion concentrations in the solution, respectively. $\nu$ (L) is the solution volume and $m$ (g) is the mass of the biosorbent.

## 3. Results and discussion

The influence of various parameters will be discussed below. These parameters have been studied in the literature for other algae and contaminants but the results presented for brown algae in intact and pre-treated forms used for treating aqueous solutions containing three different metal ions namely, nickel, cadmium and lead are presented here for the first time.

### 3.1. Influence of solution pH

Experiments were conducted with intact and modified biomass for cadmium (II), nickel (II) and lead (II) biosorption in batch systems. The adsorption characteristic of metal biosorption at various pH values in the range of 2.5–7.0 was examined. Experiments were not conducted beyond a pH of 7.0 to avoid metal precipitation. The range of pH selected for experiments of pH influence is based on the data in the literature [16–18]. Although all the experiments have been carried out for all intact and pre-treated algae, for brevity reasons only the optimum modifier has been plotted. As shown in Fig. 1, the biosorption of these metals is highly pH-dependent and adsorption of cadmium, nickel and lead is highest at pH values of 5.5, 6.0 and 5.5, respectively, and then decreases as the pH increases.

### 3.2. Influence of treatment on biomass

Since significantly high amounts of organic materials are emitted from algal sorbents during the biosorption process, organic leaching creates secondary pollution. Surface modification by hydrochloric acid, calcium chloride, FA and GA can prevent leaching of adsorptive components from biomass. It also increases the stability of the biosorbent material and enhances the biosorbent properties without affecting the biosorption kinetics [10,11]. Polyethylene imine (PEI) is a well known treating agent and is often used to modify the biosorbent surface to increase the adsorp-
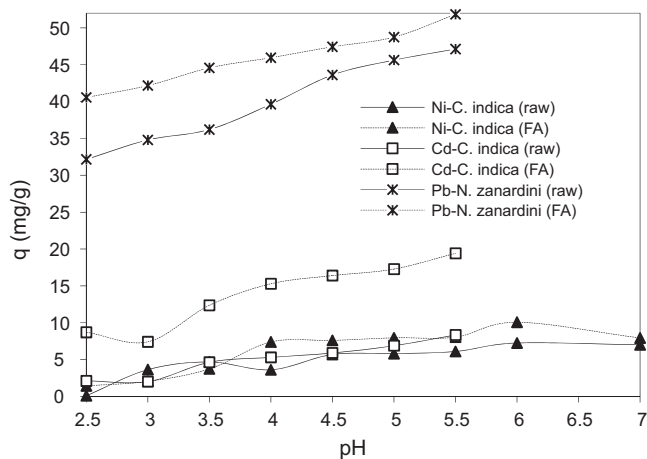


**Fig. 1.** Effect of pH on Cd (II) and Ni (II) biosorption by intact and FA-treated *C. indica* biomass and Pb (II) biosorption by intact and FA-treated *N. zanardini* biomass (metal conc.: 0.5 mmol/L; contact time: 2 h; *T*: 25 °C; biomass dosage: 2 g/L).

**Table 1**
Comparison between biosorption of various species of intact and chemically modified brown algae for Cd (II), Ni (II) and Pb (II) at different pH values (metal conc.: 0.5 mmol/L; contact time: 2 h; $T$: 25 °C; biomass dosage: 2 g/L).

| Brown algae | Chemical modifier | $q$ (mg/g) | | | | | | | | |
| | | pH | | | | | | | | |
| | | Cd | | | Ni | | | Pb | | |
| | | 2.5 | 4.0 | 5.5 | 2.5 | 4.0 | 6.0 | 2.5 | 4.0 | 5.5 |
| *N. zanardini* | Intact | 2.29 | 3.15 | 4.04 | 0.79 | 2.11 | 6.38 | 32.25 | 29.3 | 50.41 |
| | FA | 9.78 | 11.08 | 17.17 | 0.15 | 0.85 | 6.60 | 40.64 | 45.93 | 51.83 |
| | GA | 6.62 | 11.25 | 17.09 | 0.15 | 2.58 | 6.50 | 40.92 | 41.27 | 46.23 |
| | CaCl$_2$ | 6.11 | 15.77 | 18.17 | 0.31 | 2.43 | 4.90 | 49.61 | 50.23 | 51.70 |
| | PEI | 0.71 | 3.93 | 8.66 | 5.31 | 3.96 | 6.30 | 29.56 | 31.65 | 32.51 |
| | HCl | 1.85 | 7.59 | 9.06 | 5.99 | 4.80 | 6.41 | 36.20 | 37.75 | 39.73 |
| *P. australis* | Intact | 0.44 | 3.07 | 3.49 | 0.02 | 2.44 | 5.96 | 19.56 | 21.53 | 46.51 |
| | FA | 10.56 | 16.93 | 16.81 | 0.01 | 0.97 | 4.06 | 31.41 | 41.27 | 50.62 |
| | GA | 3.76 | 15.90 | 17.40 | 1.55 | 3.26 | 7.01 | 35.72 | 43.78 | 45.21 |
| | CaCl$_2$ | 13.60 | 15.53 | 17.27 | 0.16 | 5.80 | 6.91 | 44.49 | 46.73 | 48.25 |
| | PEI | 1.71 | 4.50 | 7.70 | 6.22 | 5.45 | 7.40 | 29.43 | 30.96 | 32.14 |
| | HCl | 4.04 | 7.59 | 8.74 | 6.43 | 6.06 | 6.86 | 32.88 | 33.68 | 35.32 |
| *S. gluacescens* | Intact | 3.73 | 5.72 | 4.23 | 0.04 | 3.08 | 6.35 | 31.77 | 21.53 | 45.84 |
| | FA | 11.48 | 17.83 | 14.50 | 0.87 | 6.49 | 8.10 | 38.11 | 44.91 | 51.25 |
| | GA | 12.29 | 14.71 | 17.23 | 1.98 | 3.86 | 7.81 | 39.53 | 40.47 | 42.60 |
| | CaCl$_2$ | 13.09 | 14.89 | 18.66 | 0.09 | 5.07 | 6.26 | 46.52 | 48.95 | 49.58 |
| | PEI | 3.76 | 3.97 | 7.43 | 5.87 | 4.82 | 6.66 | 28.75 | 31.53 | 31.92 |
| | HCl | 2.36 | 10.45 | 9.65 | 6.81 | 6.52 | 6.72 | 34.22 | 34.91 | 35.53 |
| *C. indica* | Intact | 2.12 | 5.31 | 8.35 | 0.09 | 3.63 | 7.00 | 32.12 | 30.21 | 47.22 |
| | FA | 8.71 | 15.29 | 19.42 | 1.44 | 7.39 | 10.06 | 36.73 | 44.53 | 51.31 |
| | GA | 11.29 | 15.31 | 17.74 | 2.56 | 3.54 | 9.03 | 36.44 | 40.67 | 41.44 |
| | CaCl$_2$ | 13.98 | 15.99 | 18.92 | 2.35 | 3.46 | 7.35 | 46.36 | 48.65 | 50.36 |
| | PEI | 4.45 | 4.79 | 6.79 | 6.77 | 6.07 | 8.99 | 30.12 | 30.58 | 32.41 |
| | HCl | 3.70 | 10.38 | 12.72 | 7.42 | 7.67 | 9.32 | 32.51 | 32.97 | 33.77 |

tion capacity. The PEI molecules are chemically bonded to the biomass through a simple crosslinking reaction during modification. Since many amine groups are present in one PEI molecule, the PEI molecules on the biomass surface can stretch in solution and provide many active adsorption sites leading to high sorption capacities [13,16,19]. The four types of brown algae were treated with five chemicals, 0.1 M CaCl$_2$, 0.1 M HCl, FA, GA and PEI. Table 1 shows the effect of pH on the biosorption capacity of both intact and pre-treated algae for Cd, Ni and Pb at three pH values. Results indicate that the FA-treated *C. indica* biomass has the highest biosorption capacity of 19.42 mg/g and 10.06 mg/g for Cd (II) and Ni (II), respectively. The highest sorption of Pb (II) is obtained for FA-treated *N. zanardini* as 51.83 mg/g, therefore, the remaining experiments were carried out using these optimum values. From Fig. 1 and Table 1 it is obvious that modification causes a significant increase in metal biosorption.

Other studies [20] report the same results for cadmium, nickel and lead ions biosorption at this optimum pH. Moreover, the influence of pH is very similar for various types of algae (red, green and brown algae). The biosorption capacities of Cd (II) ions on *Padina* sp. and *Sargassum* sp. are 61.82 mg/g and 67.44 mg/g (C$_0$ of 1 mmol/L and optimum pH of 5.5). The reported Ni (II) and Pb (II) removal capacity on *Padina* sp. and *Sargassum* sp. are 26.41 mg/g and 182.07 mg/g, respectively (C$_0$ of 1 mmol/L and optimum pH of 6 for Ni and 5.5 for Pb) [21].

### 3.3. Influence of biosorbent dosage

Biosorbent dosage has a great influence on the biosorption process and determines the potential of biosorbent through the number of binding sites available to remove metal ions at a specified initial concentration. The effect of biomass dosage on Cd, Ni and Pb ion removal is indicated in Fig. 2. At equilibrium, metal biosorption capacity decreases with an increase in biomass dosage from 0.006 to 0.48 g. This decrease can be due to the concentration gra-

dient between the sorbent and the sorbate; an increase in seaweed concentration causes a decrease in the amount of metal sorbed onto a unit weight of the algae. Moreover, the increase in biosorption of metals by increasing the biomass dosage is due to an increase in the number of active sites and available surface area. In Fig. 2 the scale of *y* axis is logarithmic because the data for lead are about 10 times bigger than the other two. Similar trends have been reported in the literature [22–25].

### 3.4. Influence of initial metal concentration

The biosorption capacity of *C. indica* and *N. zanardini* as a function of the initial concentrations of cadmium, nickel and lead have been studied at five different concentrations of 0.0625, 0.125, 0.25,
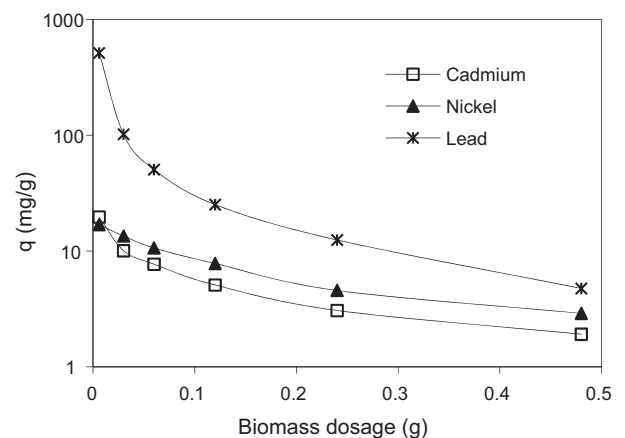


**Fig. 2.** Effect of biomass dosage on biosorption of Cd (II), Ni (II) and Pb (II) at 25 °C and a contact time of 3 h, Cd conc.: 0.5 mmol/L; pH: 5.5, Ni conc.: 1.0 mmol/L; pH: 6.0 onto FA-treated *C. indica* biomass and Pb (II) conc.: 0.5 mmol/L; pH: 5.5 onto FA-treated *N. zanardini* biomass.
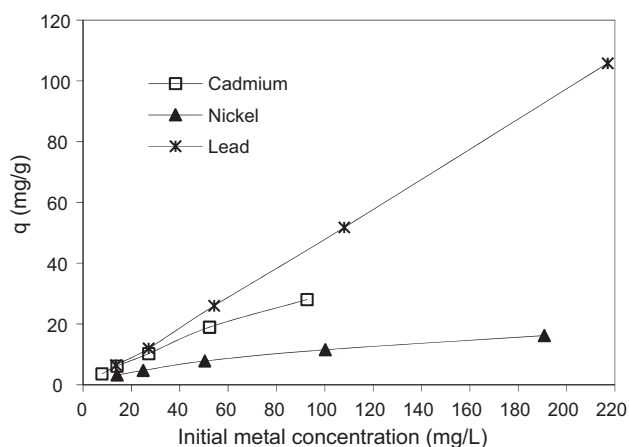
**Fig. 3.** Effect of initial metal concentration on biosorption of Cd (II) and Ni (II) onto FA-treated C. indica biomass and Pb (II) onto FA-treated N. zanardini biomass at 25 °C, a contact time of 3 h, biomass dosage of 2 g/L and at the optimum pH.

0.5 and 1 mmol/L for Cd (II) and Pb (II) and 0.25, 0.5, 1, 2, 4 mmol/L for Ni (II) in batch experiments. The sorption of cadmium and lead was tested at lower concentrations because of their higher toxicity. Fig. 3 indicates that the metal sorption capacity increases with an increase in the initial metal ion concentration. This is due to an increase in the initial ion concentration providing a larger driving force to overcome all mass transfer resistances between the solid and the aqueous phase, thus resulting in higher metal ion adsorption. Similar results have been reported [26–28].

### 3.5. Influence of contact time

As the adsorption process proceeds, the sorbent reaches the saturation state and then the sorbed solute tends to desorbs back into the solution. Eventually, the rates of adsorption and desorption will be equal at equilibrium. When the system reaches sorption equilibrium, no further net adsorption occurs. The time at which adsorption equilibrium occurs was determined [29]. In industry, this time is very important for process optimization.

The adsorption rate tests were performed on an equilibrium batch basis. 0.06 g/L of the biomass was contacted with a solution bearing a metal concentration of 0.25, 1 and 0.5 mmol/L for Cd (II), Ni (II) and Pb (II), respectively at 25 °C and the optimum pH. The biomass was kept in contact with the metal-bearing solution for different time periods (15, 30, 60 min, 2, 3, 6, 12 and 24 h). From the experimental data represented in Fig. 4, the process of biosorption reaches the equilibrium state after approximately 3 h of contact. The reaction rate is rather fast at first and 90% of total biosorption of cadmium (II), lead (II) and nickel (II) occurs in the first 60 min and thereafter it proceeds at a lower rate and finally no further significant adsorption is noted beyond 3 h. The very fast sorption and settling of the anaerobic biomass make this material suitable for continuous flow water treatment systems.
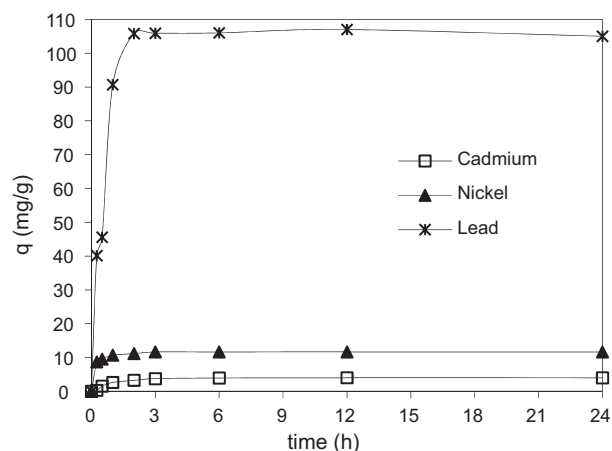


**Fig. 4.** Effect of contact time on biosorption of Cd (II), Ni (II) and Pb (II) at 25 °C and Biomass dosage of 2 g/L, Cd conc.: 0.25 mmol/L; pH: 5.5, Ni conc.: 1.0 mmol/L; pH: 6.0 onto FA-treated *C. indica* biomass and Pb (II) conc.: 0.5 mmol/L; pH: 5.5 onto FA-treated *N. zanardini* biomass.

### 3.6. Sorption and desorption experiments

Because of economic reasons, regeneration of biomass is necessary. For desorption of Cd (II), Ni (II) and Pb (II) ions from biomass, three desorbing agents 0.1 M $CaCl_2$, 0.1 M $CH_3COOH$ and 0.1 M NaCl were used [30]. The biomass biosorption capacity was tested in five repeated cycles at optimum pH values of 5.5, 6.0 and 5.5 for Cd (II), Ni (II) and Pb (II), respectively. The biosorption capacity of the biomasses for Cd (II), Ni (II) and Pb (II) removal in the five cycles are indicated in Table 2. To test the significance and adequacy of the model, statistical testing of the model in the form of analysis of variance (ANOVA) and the one-sample $t$-test were done. For a 5% level of significance, the ANOVA data are given in Table 1 of supplementary data. From this table for Cd (II) and Ni (II), $P$ value is higher than 0.05 and also the values of $F$ are lower than the critical $F$: 0.55 < 3.89 for Cd (II) ($P$ value: 0.590), 2.32 < 3.80 for Ni (II) ($P$ value: 0.141). These values indicate the region of acceptance with 95% confidence; in other words, the variation of sorption capacities of the three desorbents is not significant after five washing cycles. But for Pb (II), the $P$ value is lower than 0.05 and the $F$ value is higher than the critical $F$: 7.16 > 3.89. Therefore, the type of desorbent affects the sorption capacity and there is significant difference between the three desorbing agents in Pb (II) removal.

For a 5% level of significance $T$ values for NaCl, $CH_3COOH$ and $CaCl_2$ are given in Table 2 of supplementary data. For all three metals, the $P$ value is higher than 0.05 and also the values of $T$ are lower than the critical $T$ (3.18): [0.61, 1.66 and 4.44 for Cd (II), 0.85, 1.42 and 3.91 for Ni (II) and 0.85, 1.42 and 1.44 for Pb (II), respectively]. It is obvious from the $t$-tests that for NaCl, $CaCl_2$ and $CH_3COOH$, the number of elution times does not affect the biosorption process [31]. Biosorption results show that the effect of $CaCl_2$ on the biosorbent is significant and $CaCl_2$ causes the highest increase in

**Table 2**
Biosorption capacity of Cd (II) and Ni (II) onto FA-treated *C. indica* biomass and Pb (II) biosorption on FA-treated *N. zanardini* at optimum pH ($T$: 25 °C; sorption time: 45 min; desorption time: 20 min; 5 cycles; Cd (II) conc.: 0.05 mmol/L, Ni (II) conc.: 1.0 mmol/L and Pb (II) conc.: 1.0 mmol/L).

| | $q$ (mg/g) | | | | | | | | |
| | Cd | | | Ni | | | Pb | | |
| Cycle | NaCl | $CH_3COOH$ | $CaCl_2$ | NaCl | $CH_3COOH$ | $CaCl_2$ | NaCl | $CH_3COOH$ | $CaCl_2$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.11 | 0.27 | 0.14 | 10.91 | 11.77 | 11.21 | 49.43 | 49.97 | 49.83 |
| 2 | 0.08 | 0.48 | 0.21 | 9.71 | 11.40 | 12.18 | 50.46 | 50.12 | 51.09 |
| 3 | 0.31 | 0.69 | 0.63 | 11.07 | 11.93 | 13.55 | 50.67 | 51.59 | 52.76 |
| 4 | 0.52 | 1.25 | 1.02 | 12.18 | 13.15 | 14.80 | 51.32 | 50.86 | 54.19 |
| 5 | 0.79 | 1.07 | 1.54 | 13.32 | 14.31 | 13.36 | 51.68 | 52.47 | 53.23 |

**Table 3**
Comparison between adsorption rate constants, the estimated $q_e$ and the coefficients of correlation associated with the Lagergren pseudo-first-order and the pseudo-second-order kinetic models at 25 °C.

| Metal | $q_{e,exp}$ (mg/g) | Pseudo-first-order kinetic model | | | Pseudo-second-order kinetic model | | |
|---|---|---|---|---|---|---|---|
| | | $q_{e,cal}$ (mg/g) | $K_1$ (min$^{-1}$) | $R^2$ | $q_{e,cal}$ (mg/g) | $K_2 \times 10^3$ (g mg$^{-1}$ min$^{-1}$) | $R^2$ |
| Cadmium | 3.80 | 5.11 | 0.02 | 0.96 | 4.22 | 3.79 | 0.99 |
| Lead | 106.00 | 152.59 | 0.04 | 0.97 | 106.39 | 0.72 | 0.99 |
| Nickel | 11.65 | 5.73 | 0.02 | 0.83 | 11.67 | 4.32 | 0.99 |

the sorption capacity. Hence, CaCl$_2$ is recommended as the best desorbent for elution and desorption of cadmium, lead and nickel from the biosorbent. Of course the much lower cost of NaCl should also be taken into consideration. The statistic analysis of one-way ANOVA and one-sample $t$ were carried out using MINITAB®.

### 3.7. Kinetic study

Kinetic study provides valuable information about the mechanism of adsorption and subsequently investigation of the controlling mechanism of the biosorption process as either mass transfer or chemical reaction in order to obtain the optimum operating conditions for industrial-scale batch processes [23].

In batch systems, adsorption kinetics is described by a number of models based on adsorption equilibrium such as the pseudo-first-order and the pseudo-second-order kinetic models. The linearized pseudo-first-order kinetic model takes the following form [26,32]:

$$q_t = q_e - q_e \exp(-K_1 t) \tag{2}$$

where $q_t$ and $q_e$ are the amounts of metal adsorbed at time $t$ and equilibrium, respectively, and $K_1$ (min$^{-1}$) is the first-order reaction rate constant.

The pseudo-second-order kinetic model considered in this study is given as [26,32]:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

where $K_2$ (g mg$^{-1}$ min$^{-1}$) is the second-order reaction rate constant.

The experimental data and the parameters of both models are tabulated in Table 3. It is obvious that the coefficient of correlation ($R^2$: 0.99) for the pseudo-second-order kinetic model is higher in comparison with the pseudo-first-order kinetic model ($R^2$: 0.96, 0.97 and 0.83 for cadmium, lead and nickel biosorption, respectively) and the calculated value of $q_e$ for the pseudo-second-order kinetic model is very close to the experimental value.

Similar experimental results indicate that the pseudo-second-order kinetic model fits the equilibrium data for heavy metal ion sorption on biomasses from aqueous solutions quite well [26,33,34].

### 3.8. Biosorption isotherms

For optimization of the biosorption process design, it is necessary to obtain the appropriate correlation for the equilibrium curve. In this study, the relationship between metal biosorption capacity and metal concentration at equilibrium has been described by four two-parameter sorption isotherm models: Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) and five three-parameter isotherm models: Toth, Khan, Sips, Redlich-Peterson and Radke-Prausnitz. The constants, residual root mean square error (RMSE), chi-square ($\chi^2$) and coefficient of determination ($R^2$) of the two and three-parameter models are given in Tables 4 and 5, respectively.

All model parameters were evaluated by non-linear regression using the MATLAB® software. Furthermore, RMSE, $\chi^2$ and $R^2$ were

used to measure the goodness of fit. RMSE and $\chi^2$ are defined as:

$$RMSE = \sqrt{\left(\frac{1}{m-2}\right) \sum_{i=1}^{m} (q_{i,exp} - q_{i,cal})^2} \tag{4}$$

$$\chi^2 = \sum_{i=1}^{m} \frac{(q_{i,exp} - q_{i,cal})^2}{q_{i,exp}} \tag{5}$$

where $q_{i,exp}$ and $q_{i,cal}$ are the observation from the batch experiment and the estimate from the isotherm for the corresponding $q_{i,exp}$, respectively, and m is the number of observations in the experimental isotherm. A smaller RMSE value indicates a better curve fitting, moreover, if the data obtained from the model are close to the experimental results, $\chi^2$ will be a small number [35].

#### 3.8.1. Two-parameter isotherms
The Langmuir isotherm model is as follows:

$$q_e = q_m \frac{bC_e}{1 + bC_e} \tag{6}$$

where $q_m$ is the maximum metal biosorption and $b$ (L/mg) is the Langmuir constant. These constants are related to monolayer adsorption capacity and energy of adsorption, respectively [35].

Maximum monolayer adsorption capacity ($q_m$) was obtained as 19.56 mg/g, 16.17 mg/g and 110.35 mg/g for Cd (II), Ni (II) and Pb (II) sorption, respectively. The $b$ values of Cd (II), Ni (II) and Pb (II)

**Table 4**
Isotherm constants of two-parameter models for Cd (II) and Ni (II) biosorption on FA-treated *C. indica* biomass and Pb (II) biosorption on FA-treated *N. zanardini* biomass at 25 °C.

| | Metal | | |
|---|---|---|---|
| Two-parameter models | Cadmium | Lead | Nickel |
| *Langmuir* | | | |
| $q_m$ (mg/g) | 19.56 | 110.35 | 16.17 |
| $b$ (L/mg) | 0.05 | 0.03 | 0.04 |
| $R^2$ | 0.90 | 0.79 | 0.99 |
| RMSE | 7.75 | 59.92 | 2.38 |
| $\chi^2$ | 18.74 | 208.98 | 2.57 |
| *Freundlich* | | | |
| $K_F$ | 0.007 | 0.99 | 0.56 |
| $n$ | 0.52 | 0.55 | 1.27 |
| $R^2$ | 0.99 | 0.99 | 0.99 |
| RMSE | 5.62 | 30.83 | 1.72 |
| $\chi^2$ | 10.77 | 89.47 | 1.42 |
| *Dubinin-Radushkevich* | | | |
| $q_{DR}$ (mg/g) | 12.19 | 7.27 | 15.74 |
| $B_{DR}$ | 0.0002 | 1.005 | 0.0001 |
| $R^2$ | 0.73 | 0.52 | 0.87 |
| RMSE | 8.62 | 262.00 | 2.34 |
| $\chi^2$ | 12.97 | 702.00 | 4.36 |
| *Temkin* | | | |
| $b_{Te}$ (J/mol) | 15.45 | 8.76 | 0.04 |
| $a_{Te}$ (L/g) | 0.03 | 0.18 | 15.39 |
| $R^2$ | 0.94 | 0.99 | 0.20 |
| RMSE | 37.97 | 37.54 | 104.24 |
| $\chi^2$ | 182.93 | 276.51 | 102.47 |

**Table 5**
Isotherm constants of three-parameter models for Cd (II) and Ni (II) biosorption on FA-treated *C. indica* biomass and Pb (II) biosorption on FA-treated *N. zanardini* biomass at 25 °C.

| Three-parameter models | Metal | | |
|---|---|---|---|
| | Cadmium | Lead | Nickel |
| *Toth* | | | |
| $q_{m,T}$ (mg/g) | 2.62 | 3.37 | 0.06 |
| $b_T$ (L/mg) | 0.101 | 4.26 | 3.67 |
| $n_T$ | 0.16 | 0.02 | 0.21 |
| $R^2$ | 0.79 | 0.73 | 0.99 |
| RMSE | 7.34 | 72.85 | 1.71 |
| $\chi^2$ | 32.57 | 165.00 | 1.26 |
| *Radke-Prausnitz* | | | |
| $a_{R-P}$ (L/g) | −0.27 | 15.37 | 1.02 |
| $r_{R-P}$ (L/mg) | 0.0004 | 0.02 | 0.37 |
| $\beta_{R-P}$ | 2.55 | 4.39 | 0.99 |
| $R^2$ | 0.99 | 0.99 | 0.87 |
| RMSE | 2.41 | 28.75 | 3.12 |
| $\chi^2$ | 1.75 | 74.72 | 9.62 |
| *Khan* | | | |
| $q_{m,K}$ (mg/g) | 0.28 | 2.59 | 0.95 |
| $b_K$ (L/mg) | 0.05 | 0.61 | 0.54 |
| $a_K$ | −2.67 | 0.77 | 0.21 |
| $R^2$ | 0.96 | 0.99 | 0.99 |
| RMSE | 4.08 | 24.06 | 1.77 |
| $\chi^2$ | 5.77 | 0.99 | 1.39 |
| *Redlich-Peterson* | | | |
| $K_{RP}$ (L/g) | 0.05 | 3.07 | 0.86 |
| $a_{RP}$ (L/mg) | −0.15 | 0.06 | 1.03 |
| $\beta_{RP}$ | 0.43 | 0.72 | 0.17 |
| $R^2$ | 0.93 | 0.99 | 0.83 |
| RMSE | 5.24 | 35.23 | 1.95 |
| $\chi^2$ | 6.20 | 106.59 | 1.72 |
| *Sips* | | | |
| $a_S$ (L/mg) | 0.46 | 4.22 | −0.01 |
| $K_S$ (L/g) | −0.45 | 0.008 | 0.34 |
| $\beta_S$ | 0.19 | 1.19 | 0.86 |
| $R^2$ | 0.72 | 0.99 | 0.88 |
| RMSE | 4.55 | 29.79 | 3.31 |
| $\chi^2$ | 16.67 | 227.12 | 3.82 |

biosorption were estimated from the isotherms to be 0.05 L/mg, 0.04 L/mg and 0.03 L/mg, respectively.

The Freundlich isotherm model is as follows [35]:

$$q_e = k_F C_e^{1/n} \tag{7}$$

where $k_F$ (L/g) is the Freundlich constant and n is the Freundlich exponent. Values of *n* greater than 1 show the favorable nature of adsorption [36]. It is assumed that the stronger binding sites are occupied first. The $k_F$ and *n* values in the Freundlich equation were calculated as 0.007 L/g, 0.56 L/g, 0.99 L/g and 0.52, 1.27, 0.55 for Cd (II), Ni (II) and Pb (II), respectively.

The Dubinin-Radushkevich (D-R) equation is generally expressed as follows:

$$q_e = q_{DR} \exp(-B_{DR}\varepsilon_{DR}^2) \tag{8}$$

$$\varepsilon_{DR} = RT \ln\left(1 + \frac{1}{C_e}\right) \tag{9}$$

where $\varepsilon_{DR}$, the Polanyi potential, is a constant related to the biosorption energy, *R* is the gas constant (8.314 kJ/mol) and *T* is the absolute temperature (K). $q_{DR}$ and $B_{DR}$ are the D–R isotherm constants in mg/g and mol²/kJ², respectively.

The Polanyi sorption theory assumes a fixed volume of sorption space close to the sorbent surface and the existence of a sorption potential over these spaces. The mean free energy of biosorption

(*E*) can be calculated from the following equation:

$$E = \frac{1}{\sqrt{2B_{DR}}} \tag{10}$$

The Temkin isotherm can be represented as:

$$q_e = \frac{RT}{b_{Te}} \ln(K_{Te}C_e) \tag{11}$$

where $K_{Te}$ is the equilibrium binding constant (L/g), $b_{Te}$ is the Temkin constant related to the heat of adsorption (J/mol). All isotherm constants are tabulated in Table 4. It is apparent that equilibrium data of biosorption are fitted well by the Freundlich isotherm for all studied metals, the values of $R^2$ of the Freundlich isotherm model are 0.99 for the three metal ions and the values of RMSE and $\chi^2$ obtained from the Freundlich model are lower than those of the other models. Therefore, among the four two-parameter models, the Freundlich model is the best model for describing the adsorption behaviour.

In previous studies [21] the maximum biosorption capacity calculated by Langmuir isotherm are in the range of 33.72–84.30 mg/g, 16.43–84.30 mg/g and 93.28–302.65 mg/g for Cd (II), Ni (II) and Pb (II), respectively on various species of green, red and brown algae.

### 3.8.2. Three-parameter isotherms

The Toth isotherm, derived from the potential theory, is expressed as:

$$q_e = \frac{q_{m,T}b_T C_e}{[1 + (b_T C_e)^{1/n_T}]^{n_T}} \tag{12}$$

where $b_T$ is the Toth model constant and $n_T$ is the Toth model exponent. It is obvious that for $n_T = 1$ this isotherm reduces to the Langmuir equation.

The Toth model constant $b_T$ and exponent $n_T$ values for Cd (II), Ni (II) and Pb (II) were found to be 0.10 L/mg, 3.67 L/mg, 4.26 L/mg and 0.16, 0.21, 0.02, respectively.

The Radke-Prausnitz isotherm can be expressed as [32,35]:

$$q_e = \frac{a_{R-P}r_{R-P}C_e^{\beta_{R-P}}}{a_{R-P} + r_{R-P}C_e^{\beta_{R-P}-1}} \tag{13}$$

where $a_{R-P}$ and $r_{R-P}$ are Radke-Prausnitz model constants and $\beta_{R-P}$ is the Radke-Prausnitz model exponent.

The Radke-Prausnitz isotherm constants, $a_{R-P}$ and $r_{R-P}$ for Cd (II), Ni (II) and Pb (II) were calculated as −0.27 mg/g, 1.02 mg/g, 15.37 mg/g and 0.0004 L/g, 0.37 L/g, 0.02 L/g, respectively.

The Khan isotherm is simplified as follows:

$$q_e = \frac{q_{m,K}b_K C_e}{(1 + b_K C_e)^{a_K}} \tag{14}$$

where $b_K$ is the Khan model constant and $a_K$ is the Khan model exponent. The maximum biosorption values ($q_{m,K}$) are predicted well using this model with relatively high coefficients of determination and low RMSE and $\chi^2$ values (Table 5).

The Khan isotherm constants, $a_K$ and $b_K$ for Cd (II), Ni (II) and Pb (II) were −2.67, 0.21, 0.77 and 0.05 L/mg, 0.54 L/mg, 0.61 L/mg, respectively.

The Redlich–Peterson isotherm approximates the Henry's law at low sorbate concentrations, and at high concentrations it behaves like the Freundlich isotherm. It is given as [35,36]:

$$q_e = \frac{K_{RP}C_e}{1 + a_{RP}C_e^{\beta_{RP}}} \tag{15}$$

where $K_{RP}$ and $a_{RP}$ are the Redlich-Peterson model constants in L/g and L/mg, respectively and $\beta_{RP}$ is the Redlich-Peterson model exponent which lies between 0 and 1.

The Sips isotherms is a combination of the Langmuir and Freundlich isotherm type models and is expected to describe heterogeneous surfaces much better. At low sorbate concentrations it

reduces to the Freundlich isotherm, while at high sorbate concentrations it predicts a monolayer adsorption capacity characteristic of the Langmuir isotherm. The model can be presented as [35,36]:

$$q_e = \frac{K_S C_e^{\beta_S}}{1 + a_S C_e^{\beta_S}} \qquad (16)$$

where $K_S$ and $a_S$ are the Sips model constants in L/g and L/mg, respectively and $\beta_S$ is the Sips model exponent.

As the results given in Table 5 indicate, the experimental results of Cd (II) biosorption are best fitted by the Radke–Prausnitz isotherm model, the Ni (II) and Pb (II) biosorption data are best correlated by the Toth and Khan models, respectively as confirmed by small values of RMSE and $\chi^2$; and $R^2$ values close to 1.0.

## 4. Conclusions

The present study on biosorption of Cd (II), Ni (II) and Pb (II) from aqueous solutions using brown algae, *C. indica*, *S. glaucescens*, *N. zanardini* and *P. australis* in batch systems indicates that the adsorption of metal ions is significantly dependent on the pH of solution. Comparison of cadmium (II), nickel (II) and lead (II) biosorption capacities of brown algae in intact and chemically modified forms shows that the maximum sorption capacity of FA-treated *C. indica* for Cd (II) at an optimum pH of 5.5 is 19.42 mg/g, the maximum Ni (II) biosorption capacity at an optimum pH of 6.0 is 10.06 mg/g and the maximum sorption capacity for lead is observed on FA-treated *N. zanardini* at an optimum pH of 5.5 to be 51.83 mg/g ($Ci$ = 0.5 mmol/L and 2 g/L biomass). Sorption and desorption cycles have no adverse effect on the biosorption capacity and CaCl$_2$ is the best desorbent, cost considerations notwithstanding.

Among the two-parameter biosorption isotherms, the Freundlich model describes Cd (II), Ni (II) and Pb (II) biosorption better. The maximum monolayer biosorption capacity for Cd (II), Ni (II) and Pb (II) is 19.56 mg/g, 16.17 mg/g and 110.35 mg/g, respectively. The Toth isotherm best describes the adsorption of Ni (II) and the Radke–Prausnitz model is found to provide the closest fit to the biosorption data of Cd (II). For Pb (II), the Khan model describes the equilibrium condition better than the other models. The pseudo-second-order kinetic model fits the experimental data well ($R^2$: 0.99 for all metals). It may be concluded that the FA-treated *C. indica* can be used as a low cost and abundant source for Cd (II), Ni (II) removal from aqueous solutions and *N. zanardini* is suitable for removing Pb (II) ions from wastewaters.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2010.09.047.

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