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Simultaneous biosorption of nickel and cadmium by the brown algae *Cystoseria indica* characterized by isotherm and kinetic models

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Abstract

Biosorption is an effective way of extracting heavy metal ions from aqueous solutions of various compositions. The brown algae, *Cystoseria indica*, when treated with sodium chloride, demonstrates significant capacity to extract cadmium and nickel, simultaneously, from aqueous solutions. The batch system was running over wide ranges of initial metal ion concentrations (5–150 mg/L), pH (2–6), adsorbent mass (1–4 g/L), and contact times (20–300 min), at a temperature of 25 °C. The results obtained when applying the system in these conditions exhibit higher removal capacities for cadmium than nickel. The optimal conditions of the biosorption process were found as the adsorbent mass of 1 g/L, initial concentration of adsorbates of 100 mg/L and pH of 6. The equilibrium data obtained are better described by the extended-Freundlich isotherm for nickel and cadmium. The maximum biosorption of nickel and cadmium in binary-metal-component system were 18.17 and 55.34 mg/g, respectively. The kinetic data derived from these experiments were evaluated with pseudo-first-order, pseudo-second-order and intra-particle-diffusion kinetic models. Kinetic examination of the equilibrium data derived from these models suggest that the adsorption of nickel and cadmium both follow the intra-particle-diffusion kinetic model.

Keywords: Brown algae, Cadmium nickel extraction, Biosorption

Introduction

Heavy metals constitute significant contaminants in the oceans, in terrestrial water courses and industrial wastewaters. Typically, pollution related to heavy metals is associated with various industries such as batteries, mining, nuclear reactors, oil refineries, and agriculture. Nickel and cadmium are two of the most common heavy-metal contaminants, derived particularly from oil refining, textiles manufacture, batteries, paints, and coatings [1]. The presence of heavy metals in the environment causes damage to many species in the biosphere, including adverse human health impacts and ecosystem disruption [2, 3]. Soluble heavy metal components are

not biodegradable and they tend to accumulate in living organisms as well as oceans, lakes, and rivers [4]. Common methods used to separate heavy metals from industrial wastewaters include chemical precipitation, filtration, reverse osmosis, membranes, ion exchange and adsorption [5]. There are a variety of treatment processes deployed to remove heavy metal ions from the environment, but these, typically, are associated with expensive running costs [6]. Consequently, there is an urgent requirement to develop more-effective and low-cost processes to remove heavy metals from aqueous solutions [7].

Several biomass-based heavy-metal extraction methods have been proposed. A large quantity of materials has been investigated as biosorbents for the removal of metals or organics extensively. The tested biosorbents can be basically classified into the following categories: bacteria (*Bacillus subtilis*), fungi (*Rhizopus arrhizus*),

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yeast (*Saccharomyces cerevisiae*), algae, industrial wastes, agricultural wastes and other polysaccharide materials [3]. Biosorption technology is well known for providing practically-feasible methods for removing heavy metal from the environment [8].

A number of studies have demonstrated that among biosorbents, marine algae, especially the brown algae, are excellent biosorbent for heavy metals [9]. The carboxylic group is known to be the key acidic functional group in the brown algae [10]. This is because of the carboxylic groups constitute the highest percentage of titratable sites in dried brown algae biomass. It is the existence of these active sites that provides the capacity of brown algae to adsorb heavy metals [11]. As brown algae occur in abundance in the biosphere there is the potential to exploit them as cost-effective biosorbents [12]. Despite their valuable biosorbent properties for extracting and recovering heavy metals, brown algae have the potential to cause secondary pollution [13]. Organic substances (e.g., alginate) released as the brown algae biosorption processes proceed are potential pollutants that can hinder their use industrial applications. Moreover, there is the potential for leaching to occur as biosorption proceeds, thereby removing key adsorptive components of brown algae causing degradation their biosorption capacity [14].

The Gulf of Oman is considered as one of the main ecological capitals with the highest biological diversity. Macroalgae is found in the northern coast of the Gulf of Oman is known as the wealthiest sources of macroalgae. Brown algae (*Cystoseria indica*) are vital groups of bioactive complexes in the northern coast of the Gulf of Oman. These algae (*C. indica*) are reputation due to their high density and richness in the region, growth in large sizes and valuable combinations such as alginic acid, iodine vitamins, and minerals. The Gulf of Oman is used for fisheries, aquaculture activities, import and export, economy, urbanization, and industries Heavy metals discharging into the marine ecosystem of the Gulf of Oman have possible to negatively affect marine organism [15].

Here, the surface of brown algae (*Cystoseria indica*), derived from the Oman Sea is treated with sodium chloride to increase the stability of its biosorbent components. The effects of the initial concentrations of nickel and cadmium on the biosorbent performance of *Cystoseria indica* are established and the optimal conditions of the biosorption process were found. Biosorption equilibrium data are evaluated using extended-Langmuir and extended-Freundlich isotherms. The biosorption mechanism is also investigated in terms of its kinetic reaction characteristics at optimum concentrations over a range of contact times.

Methods

Materials and preparations

A set of aqueous metal solutions displaying various concentrations of cadmium (Cd) and Nickel (Ni) were established by diluting cadmium nitrate ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) and nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) with distilled water. The pH of the solutions was adjusted using HCl (0.1 N) and NaOH (0.1 N) to achieve the desired values.

Cystoseria indica samples were gathered from the coastal area of the Oman Sea, Iran. The algal samples were initially washed with deionized water to remove surface contaminants and impurities (e.g. sand and salt). Clean algal samples were then dried by exposure to the sun for 24 h. Dried algal samples were then crushed and subsequently sieved to a particle size of 0.5–1.0 mm. The sieved samples were then washed with deionized water and desiccated in an oven at 70 °C for 24 h. The samples were then subjected to surface alkaline treatment with sodium chloride (NaCl), which, as demonstrated by Brierley [16], disrupts the cell walls of algae potentially exposing additional functional groups to which metal ions are able to bind (Brierley protocol) [16, 17].

Batch biosorption

Bioadsorption experiments were conducted over wide ranges of initial metal ion concentrations (5–150 mg/L), pH (2–6), adsorbent mass (1–4 g/L), and contact times (10–180 min), at a temperature of 25 °C, with the algae added to a series of Erlenmeyer flasks. Previous research has shown that the cadmium and nickel biosorption ability was excellent using brown algae (*Cystoseria indica*) at the pH of 6 [10]. The flasks contained a 100-mL solution of nickel and cadmium simultaneously. The flasks were agitated at 175 rpm in an incubator shaker at 25 °C for 5 h. Algae were separated from the metal solutions by filtration. After each experiment, the remaining metal ions concentrations in solutions after the adsorption experiments were determined using atomic absorption spectroscopy (PinAcle 500, Perkin Elmer, USA). The concentrations of the metals adsorbed (mg/L) by the treated algae was calculated using Eq. (1):

$$q = \frac{V(C_i - C_f)}{m} \quad (1)$$

where: C_i and C_f (mg/L) are the initial and final metal-ion concentrations in the solution, respectively; V is the solution volume in liters; and, m is the mass of biosorbent.

Unlike continuous system, the batch adsorption process is running without input and output.

Biosorption isotherm

Industrial effluents typically contain a combination of several metal contaminants [18]. Consequently, it is usually

necessary to remove more than one metal contaminant during bioadsorption. It is for this reason that we investigate here the efficiency of *Cystoseria indica* in simultaneously removing for nickel and cadmium from aqueous solutions. Published experiments suggest that many adsorbents are less effective in systems contaminated with multiple-metal components than those contaminated with single-metal components [19]. This effect is likely to be caused by metal ions hindering each other during the adsorption process in multi-component systems. The mathematical models considered to best describe biosorption phenomena, are the Langmuir and Freundlich isotherms [20, 21]. The Langmuir isotherm is based on three basic theoretical assumptions:

- Adsorption is monolayer;
- All the active sites are equivalent and the adsorption process is uniform; and,
- The adsorption of a molecule by a free site does not depend on the occupied neighboring sites.

The Langmuir equation is applicable to homogenous adsorption while the Freundlich equation is employed to describe heterogeneous systems and reversible adsorption and is not restricted to the formation of monolayers. The mathematic expression of the extended-Langmuir isotherm can be expressed by Eqs. (2) and (3):

$$q_{e1} = q_{m,1} \left(\frac{K_{L1} C_{e1}}{1 + K_{L1} C_{e1} + K_{L2} C_{e2}} \right) \quad (2)$$

$$q_{e2} = q_{m,2} \left(\frac{K_{L2} C_{e2}}{1 + K_{L1} C_{e1} + K_{L2} C_{e2}} \right) \quad (3)$$

where: K_{L1} , K_{L2} , $q_{m,1}$, $q_{m,2}$ are the Langmuir isotherm constants; C_{e1} (mg/L) and C_{e2} (mg/L) are the unadsorbed concentration of nickel and cadmium, respectively; and q_{e1} (mg/L) and q_{e2} (mg/L) are the equilibrium adsorption values for nickel and cadmium, respectively [22, 23].

On the other hand, for multi-component systems, experimental equilibrium data were difficult to obtain. Therefore, several methods were proposed to estimate multi-component adsorption equilibrium in a mixture on the basis of single-component adsorption isotherms [24]. For example, Freundlich extended model was proposed to predict binary component adsorption systems using known single adsorption isotherms the Freundlich isotherm assumes that the stronger binding sites are occupied first. The mathematic expression of extended-Freundlich isotherm can be expressed as Eqs. (4) and (5):

$$q_{e1} = \frac{K_{F1} C_{e1}^{\frac{1}{n_1} + x_1}}{C_{e1}^{x_1} + y_1 C_{e2}^{x_2}} \quad (4)$$

$$q_{e2} = \frac{K_{F2} C_{e2}^{\frac{1}{n_2} + x_2}}{C_{e2}^{x_2} + y_2 C_{e1}^{x_1}} \quad (5)$$

where: x_1 , y_1 , z_1 , x_2 , y_2 , z_2 are the Freundlich isotherm constants; C_{e1} and C_{e2} are the unadsorbed concentrations of nickel and cadmium, respectively; the unit of C_{e1} and C_{e2} are mg/L. q_{e1} and q_{e2} are the equilibrium adsorption values of nickel and cadmium, respectively; q_{e1} and q_{e2} are equal to mg/L. Suffix 1 indicates nickel and suffix 2 signifies cadmium; and, K_{F1} , K_{F2} , n_1 and n_2 are the Freundlich isotherm constants [25]. These are obtained from the equilibrium data of the single metal components and are listed in Table 1 [26, 27]. These data come from experiments in which nickel and cadmium were adsorbed by the *Cystoseria indica* separately. All the model parameters were evaluated by non-linear regression using MATLAB software. Coefficient of determination (R^2) is used to measure the goodness of fit between the measured data and the theoretical models.

The coefficient of determination (R^2) is defined by Eq. (6):

$$R^2 = 1 - \frac{\sum_{i=1}^m (q_i^{exp} - q_i^{cal})^2}{\sum_{i=1}^m (q_i^{exp} - q_i^{ave})^2} \quad (6)$$

A higher R^2 (i.e. closer to 1.0) indicates a better fitting curve.

Biosorption kinetics

Experimental observations indicate that the adsorption processes for both cadmium and nickel using *Cystoseria indica* reached equilibrium after approximately 180 min of contact. For batch systems, the adsorption process kinetics can be described by a number of models [28, 29]. These models include: pseudo-first-order (Eq. 7), pseudo-second-order (Eq. 8), and intra-particle diffusion (Eq. 9) [30]. The linearized pseudo-first-order,

Table 1 Optimized adsorption isotherm parameters of nickel and cadmium calculated for single-component system with algae *Cystoseria indica* at 25 °C

Isotherms	Parameters	Nickel	Cadmium
Langmuir	q_m (mg/g)	38.601	70.887
	K_L (L/mg)	0.111	0.287
	R^2	0.980	0.90
Freundlich	K_f (mg/g) (L/mg)	17.142	21.302
	n	2.739	1.277
	R^2	0.980	0.980

pseudo-second-order, and intra-particle diffusion kinetic models are defined by Eqs. (7), (8) and (9), respectively [30, 31]:

$$\frac{dq}{dt} = K_1(q_e - q_t) \quad (7)$$

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \quad (8)$$

$$qt = K_p t^{\frac{1}{2}} + C \quad (9)$$

where: q_t (mg/L) and q_e (mg/L) are the metal adsorbed after specific exposure times and at equilibrium conditions, respectively; and K_1 (min^{-1}) and K_2 (g/mg min) are the first-order reaction rate equilibrium constant and the second-order reaction rate equilibrium constant, respectively; and, in Eq. 9, C (mg/g) is adsorption constant and K_p ($\text{mg/g min}^{0.5}$) is the rate of intra-particle diffusion.

Results and discussion

Characterization of *C. indica*

SEM micrographs were obtained using a scanning electron microscope (Hitachi SU-70, Japan). Figure 1 shows SEM images of the *C. indica* at the different magnifications. *C. indica* had a honeycomb structure. Pores greater than 200 nm were observed at surface of *C. indica*. SEM image of *C. indica* showed no uniform pore distribution and high roughness.

Oxygen-containing acidic surface functional groups (hydroxyl, phenolic, aldehydic, ketonic, and carboxylic) on the surface of biochar, which are active binding sites for the adsorption process, were derived from macromolecules in macroalgae [32]. The FTIR spectra of *C. Indica* (Fig. 2) showed the intense bands at ~ 3400 $1/\text{cm}$ (O–H stretching vibration), which can be allocated to hydroxyl functional groups [32]. The absorbance bands at ~ 2900 $1/\text{cm}$, ~ 1640 $1/\text{cm}$, and ~ 1100 $1/\text{cm}$ were assigned to vibration modes of C–H, aromatic CC and, COC= bonds, respectively [33, 34]. Furthermore, the intense peak at 1037 $1/\text{cm}$ (Si–OS-i stretching vibration) is due to high silica content of the biomasses and consequently the ash content of the biochars [35]. The following indices obtained from the integration of absorbance peak regions were utilized to evaluate the chemical properties of biochars, aromaticity, the degree of the aromatic ring, aliphatic chain length, oxygen function groups, and 'C' factor. The ratio of the C=O to CC= stretching group ('C' factor) was used as a criterion for describing oxygen-containing groups in samples [33, 35].

Effect of pH

One of the most important factors affecting the biosorption of metal ions is acidity of solution. Solution pH affects the cell wall metal binding sites and the metal ion chemistry in water. In the present study, the effect of pH and biosorbent pretreatment on two metals biosorption was understandable (Fig. 3). At low pH, metal cations and protons contested for binding sites, resulting in

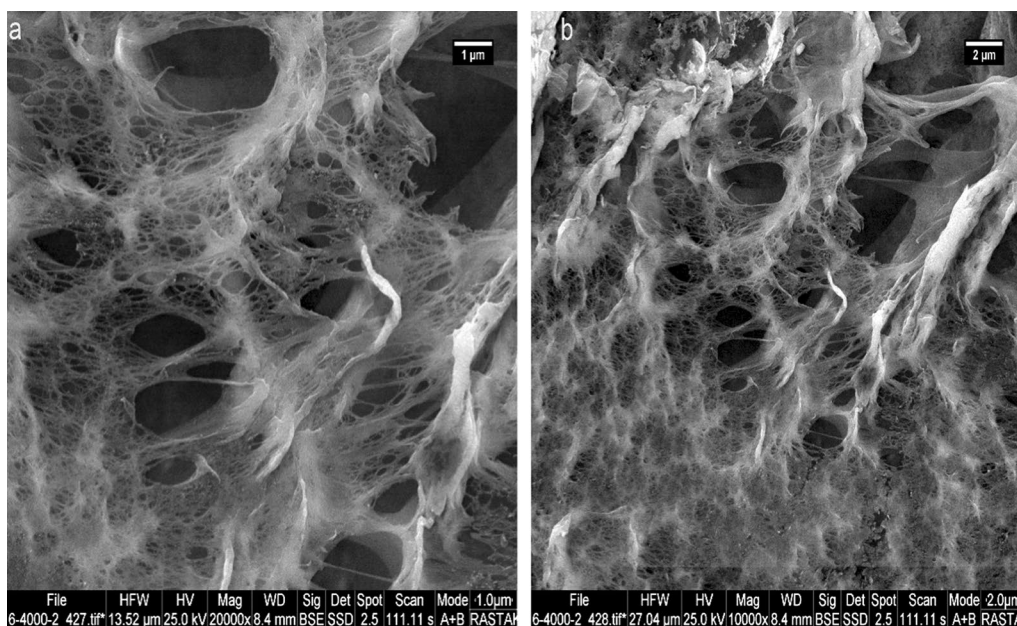


Fig. 1 SEM Image of *C. indica* with different magnifications, 20.0 kx (a), 25.0 kx (b)

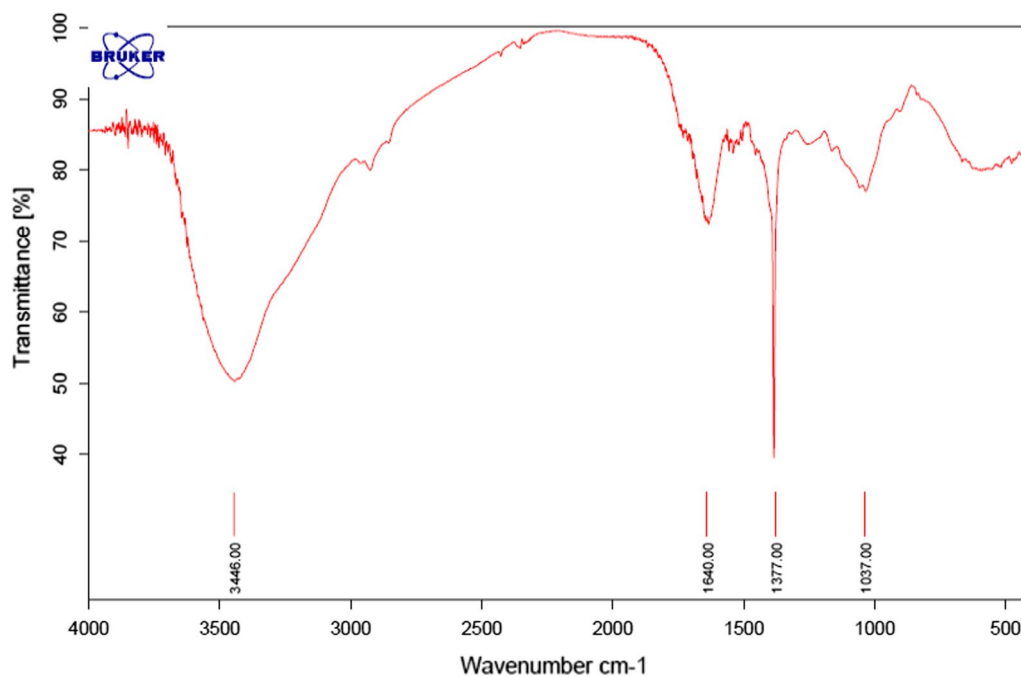


Fig. 2 ATR-FTIR of *C. indica*

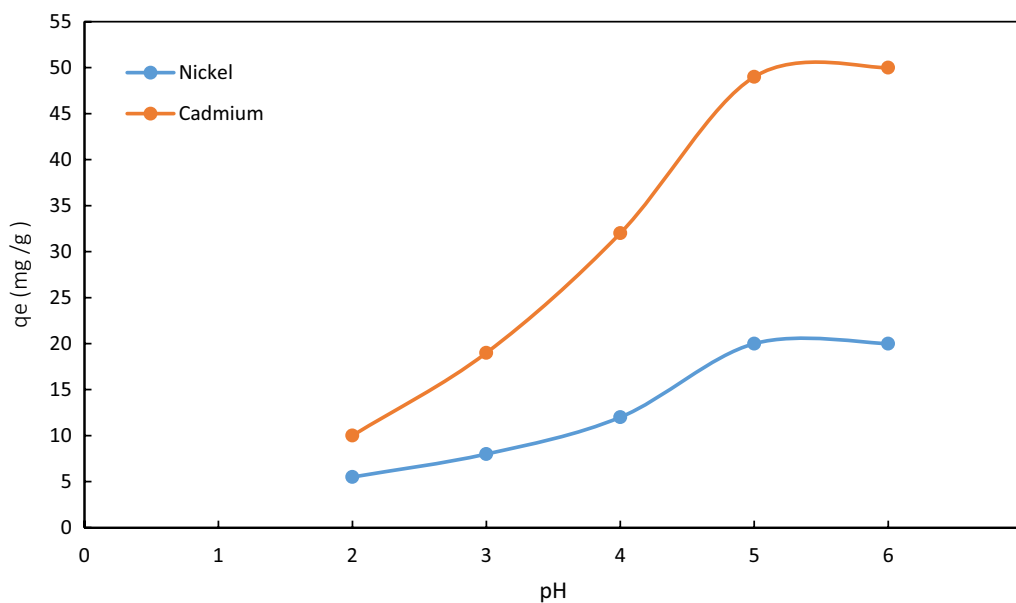


Fig. 3 Effect of pH on Ni (II) and Ca(II) biosorption onto the modified *C. indica* biosorbent

low adsorption of metal ions. Moreover, the number of positively charged surface sites increased, which did not favor the adsorption of positively charged metal cations due to electrostatic repulsion. With an increase in pH, the number of negatively charged active sites also

increased, which would attract more positively charged metal ions for binding. The pH of 6 is the best pH in which both metals reach their highest adsorption capacity. Consequently, this pH (6) was selected for further investigations.

Effect of biosorbent dosage

The biosorbent dosage is an important factor because it can determine the capacity of biosorbent for a given initial metal ion concentration. The effect of biomass dosage in the range of 1–4 g/L on the Ni and Ca uptake by NaCl-pretreated *C. indica* in the initial metal concentration of 100 mg/L and temperature of 25 °C at pH 6 is shown in Fig. 4. According to this Fig. 4, the biosorption capacity of Ni(II) and Ca(II) from an aqueous solution decreased with the increase of the biosorbent dosage, because some of the active sites stayed unsaturated during the biosorption process while the number of sites available on the NaCl-pretreated *C. indica* biomass increased by increasing the biosorbent dosage. Consequently, the dosage of 1 g/L was selected for further investigations.

Effect of contact time

The rate of adsorption is of high importance in modeling and designing the adsorption process in industry. Therefore, the effect of contact time on nickel and cadmium sorption onto the *C. indica* is revealed in (Fig. 5) in the initial concentration of 100 mg/L and 25 °C at pH 6 with the contact time varies from 10 to 180 min. According to Fig. 3, biosorption capacity increased with increasing contact time. More than 95% of the total adsorption of nickel and cadmium occurs within the first 60 min. This behavior might be due to the fact that initially all active sites on the adsorbents surface are vacant and the solution concentration is high. After that period, few surface active sites will be available, so only a very low increase in the metal uptake is observed. Therefore, a contact time of

180 min was selected for all the equilibrium tests. Yinghui and Fang studied the biosorption of Cu(II), Cd(II), Ni(II) and Zn(II) onto pretreated biomass of brown algae [34] and Ibrahim, investigate the biosorption of Co(II), Cd(II), Cr(II) and Pb(II) by red macro-algae [35] and reported similar contact time behavior for Cd(II) and Ni(II) metal ions as observed in current study.

Effect of temperature

The biosorption studies were carried out for both heavy metal at four different temperatures 20, 25, 30 and 35 °C in binary component systems, and the obtained results were presented in Fig. 6. It can be observed that the biosorption capacity of cadmium increased with an increase of temperature from 20 to 25 °C, over 180 min of contact time. Also, the biosorption capacity of cadmium was constant after 25 °C. On the other hand the biosorption capacity of nickel was constant with increasing of temperature.

Effect of initial concentration

Published research [27, 28, 36] indicates that nickel and cadmium achieve their highest capacities of algal adsorption in aqueous solutions with concentrations ranging from 5 to 130 mg/L when they are in the two-component system. The effects of interfering metal ions on the adsorption of cadmium and nickel ions by *Cystoseria indica* are illustrated in Figs. 7 and 8.

Tests were conducted to compare the adsorption performance of *Cystoseria indica* with respect to nickel and cadmium. An initial concentration of nickel of 60 mg/L

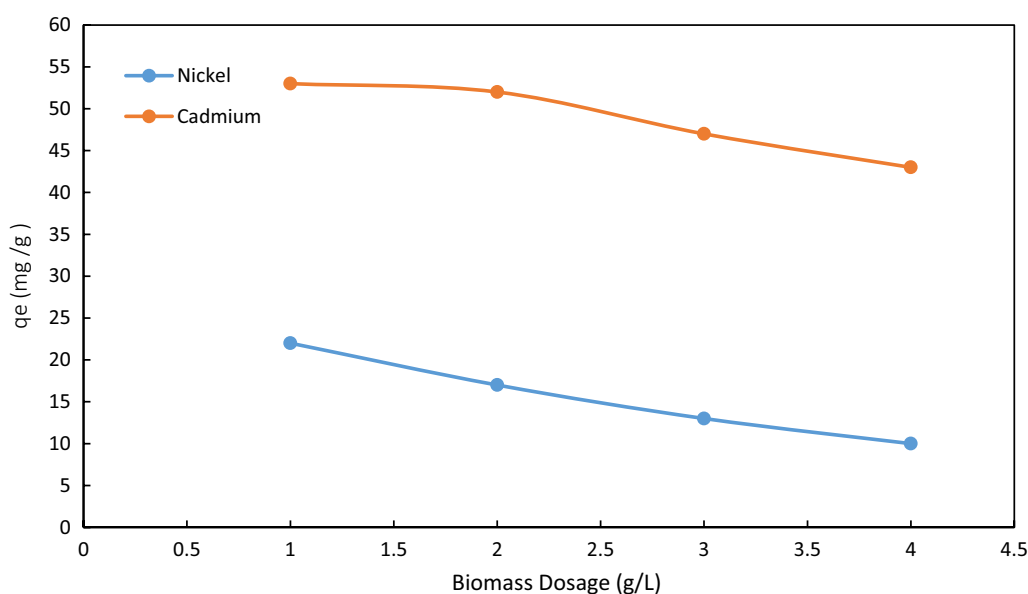


Fig. 4 Effect of biomass dosage on biosorption of Ni(II) and Ca(II) onto NaCl-pretreated *C. indica* biomass

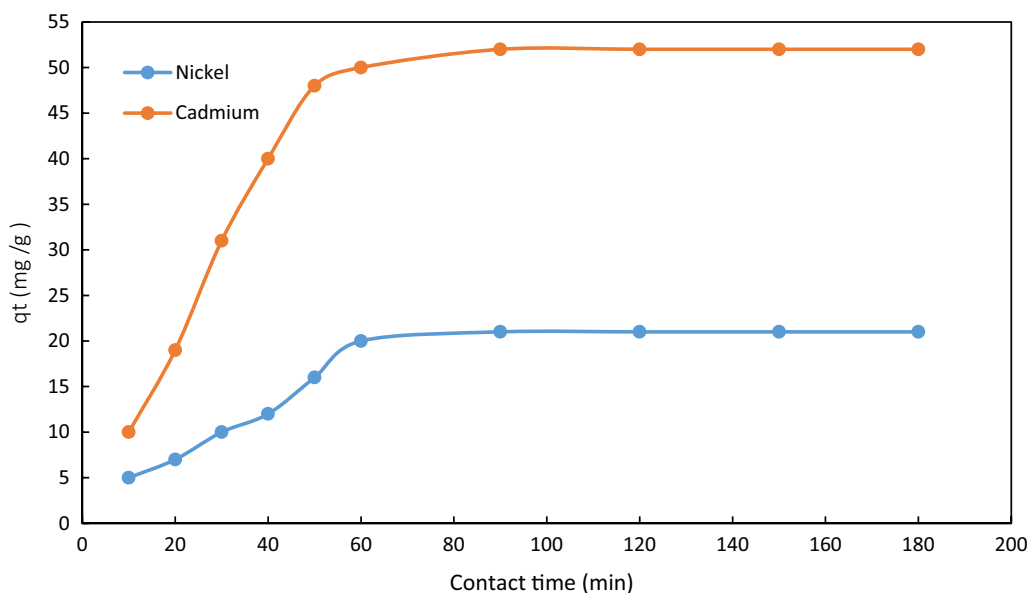


Fig. 5 Effect of contact time on biosorption of Ni (II) and Ca(II) onto *C. indica*

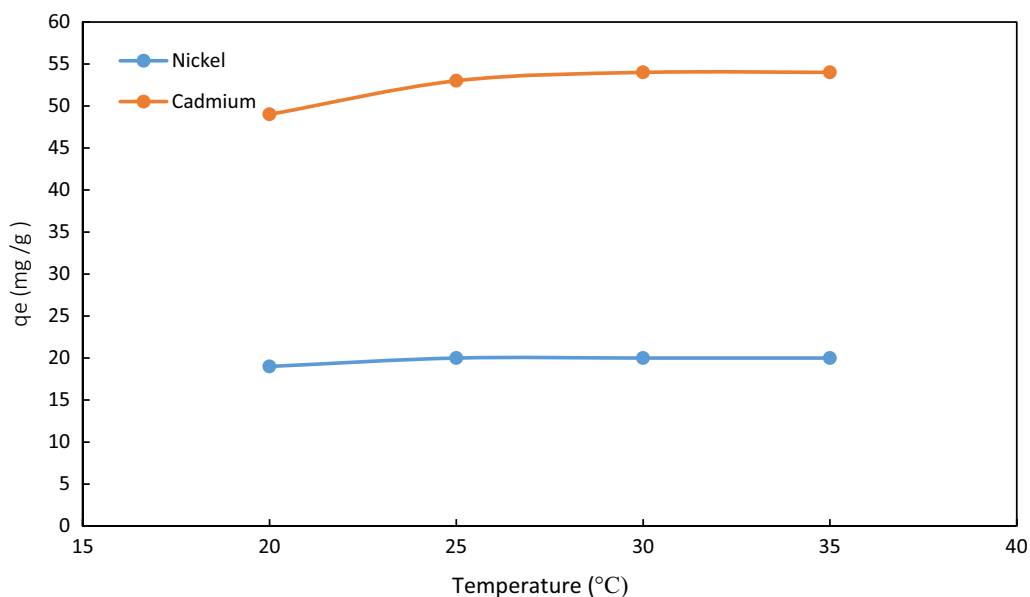


Fig. 6 Effect of temperature on bio sorption of Ni (II) and Ca(II) in binary component systems

was set in three containers. In one of those containers, the initial concentration of cadmium was set at 30 mg/L, in the second container it was set at 60 mg/L, and in the third container it was set at 130 mg/L. The measured adsorption of nickel by *Cystoseria indica* was 17.5, 9.6 and 5 mg/L, respectively in the first, second and third containers. For comparison purposes, an initial

concentration of cadmium of 60 mg/L was set in another three containers. In one of those containers the initial concentration of nickel was set at 30 mg/L, in the second container was set at 60 mg/L, and in the third container it was set at 130 mg/L. The measured adsorption of cadmium by *Cystoseria indica* was 35, 20.6 and 10.1 mg/L, respectively in the first, second and third container. These

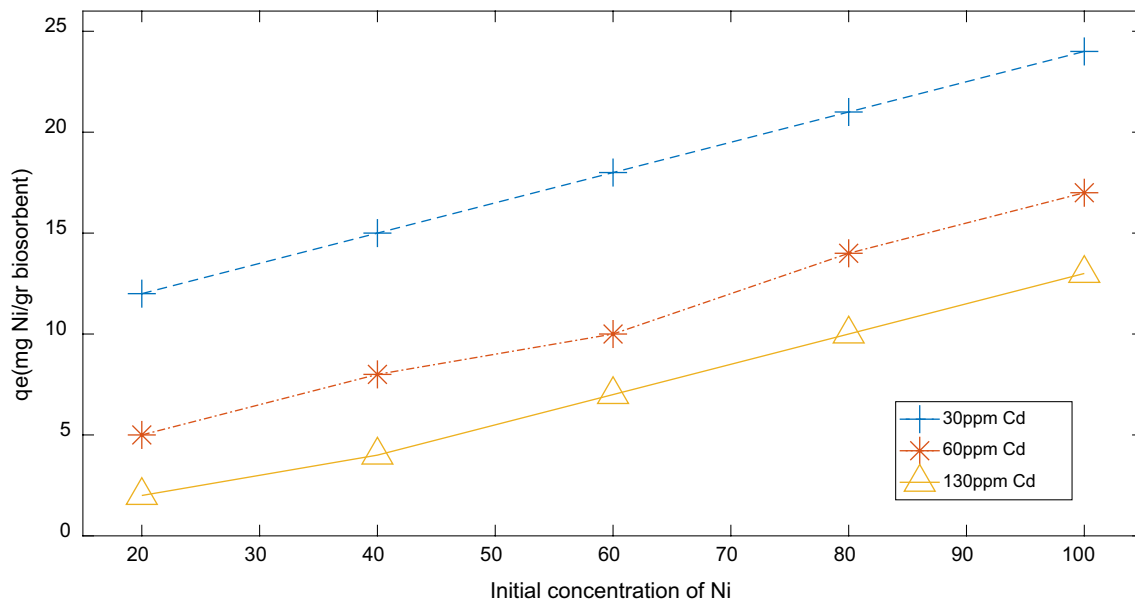


Fig. 7 The effect of interfering nickel ions on cadmium adsorption by *Cystoseria indica*

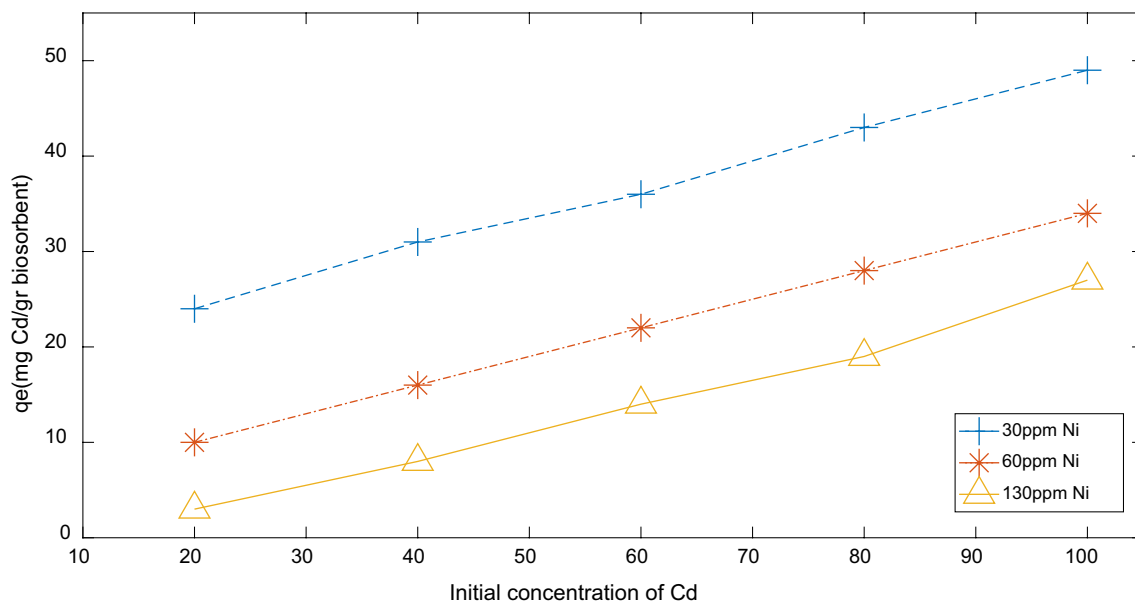


Fig. 8 The effect of interfering cadmium ions on nickel adsorption by *Cystoseria indica*

observations suggest that *Cystoseria indica* clearly has a tendency to adsorb significantly more cadmium than nickel. Adsorption is believed to occur at several functional groups within algae, including carboxyl, sulfonic acid and alginate [37]. There may also be other functional groups in *Cystoseria indica* that are involved in the adsorption of both metal ions. Figures 7 and 8 display the

synergistic effect in the binary system by which cadmium is more successful adsorbed at active sites by *Cystoseria indica*. The alginic acid component, present in alginate within the cell walls of *Cystoseria indica* and other brown algae, has been suggested as the reason for the higher cadmium adsorption potential [29, 38]. Metallic behavior in multi-component systems is believed to strongly

depend on the physical and chemical characteristics of the adsorbent that, in turn, affects the equilibrium behavior of the biosorption processes. The number and type of ions, the concentration of each component ion, pH, and the isotherm models considered will determine the equilibrium constants [39–41].

Adsorption isotherms

The isotherm constants and coefficient of determination (R^2) calculated from the tests for the *Cystoseria indica* tests with the extended-Langmuir and extended-Freundlich isotherms are listed in Table 2. The optimized conditions were obtained from above section following: Initial concentration 100 mg/L, pH 6, biosorbent dosage 1 g/L. Also, all experiments were lasted 180 min at 25 °C. The appropriate parameter values for the isotherm models considered for *Cystoseria indica* adsorption of nickel and cadmium are derived from the experimental data by maximizing the objective function (i.e., R^2). These values are listed in Table 1 for single-metal-component systems and Table 2 for binary-metal-component system. For the nickel and cadmium binary system, the biosorption equilibrium data for *Cystoseria indica* are better described (i.e., higher R^2) using the extended-Freundlich isotherm for nickel. On the other hand, the biosorption

equilibrium data are better described (i.e., higher R^2) using the extended-Freundlich isotherm for cadmium.

Alginate is considered to play a pivotal role in the ability of different brown algae species to adsorb heavy metal ions [42]. Alginate has a non-uniform macromolecular structure providing it with the ability to form a selective bond with cadmium ions. Because of its orientation, shape and the space between dents, glucuronic acid create better complex with cadmium than mannuronic acid in terms of allowing ions to permeate in the structure [31]. The molecular structure of alginate is illustrated in Fig. 9.

Figures 10, 11, 12 and 13 show curve-fitting for the extended-Freundlich and extended-Langmuir isotherms based on the experimental data. The extended-Freundlich isotherm data demonstrates positive correlations between experimental data (q_{exp}) and calculated-adsorption (q_{cal}) for both cadmium and nickel. The extended-Langmuir isotherm data shows low-confident correlation between experimental data (q_{exp}) and calculated-adsorption (q_{cal}) for nickel and cadmium data because of the low value of R^2 . It is apparent that

Table 2 Optimum isotherm parameters of binary-metal-component systems for adsorption of nickel and cadmium using *Cystoseria indica* treated with NaCl (pH=6, contact time 4 h, temperature 25 °C, impeller speed 175 rpm)

Isotherms	Parameters	Nickel	Cadmium
Extended-Langmuir	q_m (mg/g)	18.170	55.341
	K_L (L/mg)	0.166	0.203
	R^2	0.920	0.90
Extended-Freundlich	x	0.004	0.028
	y	1.090	2.880
	z	0.010	0.190
	R^2	0.940	0.970

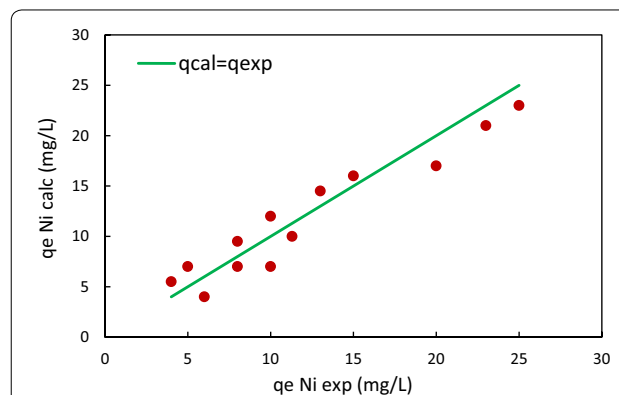


Fig. 10 Parity plot of calculated versus experimental values for Extended-Langmuir isotherm of nickel in the adsorption process of *Cystoseria indica* at different concentrations of the metal ions

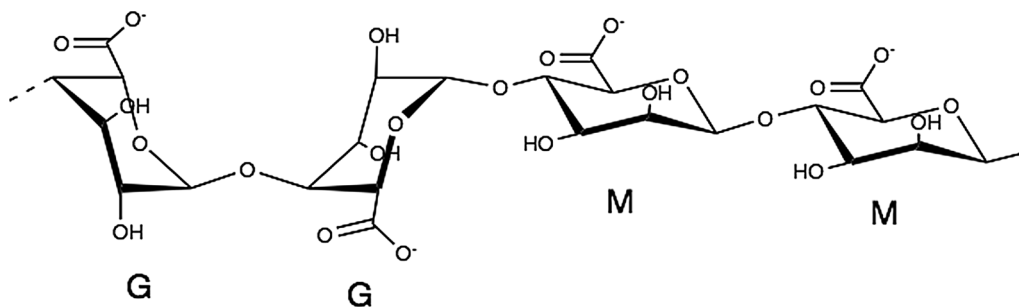


Fig. 9 The molecular structure of alginic acid including glucuronic acid (G) mannuronic acid (M) as it exists within alginate [43]

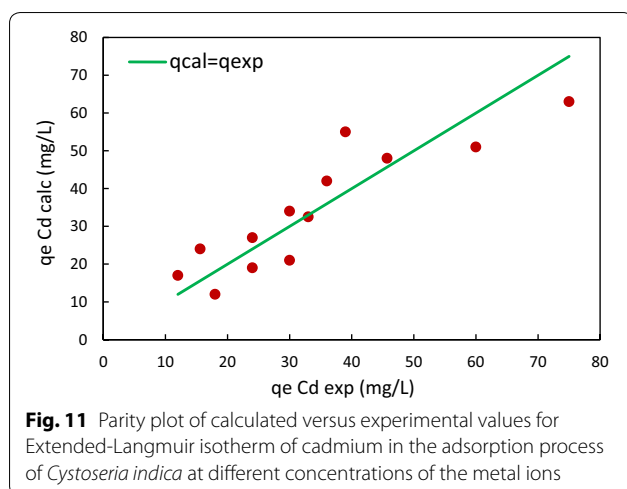


Fig. 11 Parity plot of calculated versus experimental values for Extended-Langmuir isotherm of cadmium in the adsorption process of *Cystoseria indica* at different concentrations of the metal ions

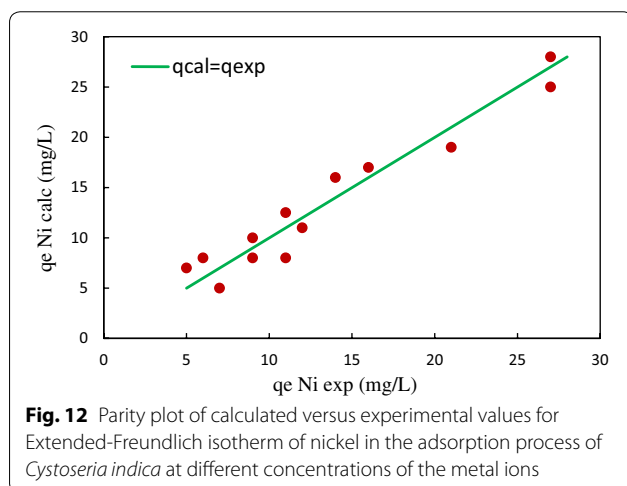


Fig. 12 Parity plot of calculated versus experimental values for Extended-Freundlich isotherm of nickel in the adsorption process of *Cystoseria indica* at different concentrations of the metal ions

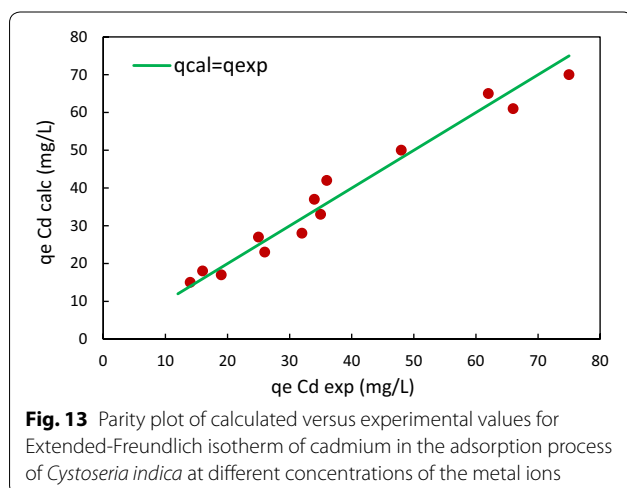


Fig. 13 Parity plot of calculated versus experimental values for Extended-Freundlich isotherm of cadmium in the adsorption process of *Cystoseria indica* at different concentrations of the metal ions

Table 3 Comparison between adsorption rate constant, the estimated q_e and the coefficients of determination associated with pseudo-first-order, pseudo-second-order and intra-particle diffusion kinetic models applied to nickel and cadmium adsorption by *Cystoseria indica* at 25 °C

Kinetic models	Parameters	Nickel	Cadmium
Pseudo-first-order	q_e (mg/g)	18.70	39.201
	k_1 (1/min)	0.112	0.212
	R^2	0.831	0.741
Pseudo-second-order	q_e (mg/g)	24.592	45.272
	k_2 (g/mg.min)	0.003	0.002
	R^2	0.864	0.811
Intra-particle diffusion	C (mg/g)	15.542	32.031
	k_{id} (mg/g.min ^{0.5})	1.726	2.942
	R^2	0.90	0.930

the extended-Freundlich isotherm was a better fit than the extended-Langmuir isotherm equation for nickel and cadmium sorption according to the values of R^2 and, the highest value of R^2 was 0.97 for cadmium in extended-Freundlich isotherm. Also, the highest value of R^2 was 0.94 for nickel in extended-Freundlich isotherm. Two best values suggested that the extended-Freundlich is the best model for nickel and cadmium sorption. It indicates that the sorption of nickel and cadmium ions are similar a multilayer sorption.

Adsorption process kinetics

Table 3 shows that the experimental data using *Cystoseria indica* conform more closely to the intra-particle diffusion model for both nickel and cadmium. However, the fit with that model is only approximate (i.e. $R^2 \leq 0.93$), with the lower-exposure-time data responsible for much of the data spread. On the other hand, the data fit for the pseudo-first-order and pseudo-second-order models is very poor, $R^2 \leq 0.741$ and ≤ 0.811 , respectively. Table 3 lists the coefficient of determination (R^2) values of 0.90 for nickel and 0.93 for cadmium, for the intra-particle diffusion model, values that are significantly higher than those achieved by pseudo-first-order and pseudo-second-order models.

The consequences achieved in this study can be related with to some others reported in the works Comparing uptake capacities of brown marine algae obtained for metal concentrations in the liquid phase similar to that used in the present study, have shown that In spite of some differences in the experimental conditions, cadmium, and nickel uptake capacities are close to those obtained by other researchers. The accumulation profiles obtained for the different brown algae species show that

the metal uptake is rather fast, and more than 75% of the total uptake occurs within the first 20 min and then no further significant adsorption is observed [31, 44].

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Authors' contributions

MK carried out heavy metal sampling, heavy metal solution analyses, and data organization. AH, MK, DAW and NM participated in interpreting the obtained results and organizing the manuscript. All authors read and approved the final manuscript.

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