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Cadmium removal from aqueous solution by brown seaweed, *Sargassum angustifolium*

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Abstract−Four kinds of indigenous seaweed were employed for assessing their soluble cadmium biosorption performance. *Sargassum angustifolium* revealed the greatest capacity in the range of equilibrium cadmium concentration lower than 0.5 mmol l^{-1}. It was further examined by optimization, equilibrium, kinetic and thermodynamic studies. It was found that1 g l^{-1} biosorbent at initial pH of 6 and 38 °C revealed the highest Cd^{2+} uptake. Kinetic studies revealed that the Cd^{2+} biosorption included a two-stage mechanism with an initial rapid stage during the first 30 min where ion exchange was the dominant mechanism. The process gradually reached equilibrium after 40-50 min of contact where the metal adsorption occurred too low due to the intraparticle diffusion. However, it was not the sole rate-limiting step. The pseudo-second order kinetic model, unlike the pseudo-first order, excellently described the experimental data in the whole range of contact time. The Langmuir isotherm model was more successful in describing the equilibrium data than the Freundlich and D-R models. Using this isotherm model, a relationship was proposed to predict the dose of biosorbent needed for removing specific initial cadmium concentration from aqueous solution or to meet a desire equilibrium cadmium concentration. The spontaneity and endothermicity as well as increasing randomness at the solid/solution interface during the biosorption were revealed by means of the thermodynamic studies.

Keywords: Biosorption, *Sargassum*, Kinetic Model, Ion Exchange, Iintraparticle Diffusion

INTRODUCTION

The presence of cadmium ions in the environment has caused irreparable damage to organisms and humans. It readily enters the tissues of living organisms through the food chain [1]. A wide variety of industrial processes, e.g., cadmium electroplating, battery manufacturing, ceramic industries waste waters, and metallurgy of cadmium, release significant amounts of cadmium into the environment [2,3]. Therefore, more attention is increasingly being paid to treating cadmium-contaminated environments.

Many traditional physicochemical techniques such as precipitation, evaporation, adsorption, ion exchange, membrane processing, and solvent extraction have been employed for heavy metal removal from aqueous solutions. However, these become inefficient or expensive especially at metal concentrations less than 100 mg l^{-1} [4,5]. In recent decades, the use of living and nonliving agents has proved to be an excellent alternative for elimination of heavy metals from aqueous solutions. However, treatment using dead biomass, which is known as biosorption, has many advantages over living biomass, as they do not need nutrition for growth as well as the fact that contamination control is not required [6,7]. Biosorption technique, as an inexpensive and effective alternative for heavy metals removal from aqueous solutions, has received considerable attention due to its good efficiency and environmentally friendly nature [3].

Biosorbent selection can directly affect the economy of a biosorption process. A good biosorbent should be naturally available in high amounts [8]. Seaweeds, as abundant biomass in Bushehr coastal waters, Persian Gulf, can serve as promising agents for treating heavy metal contaminated waters. However, their sorption capacities over metal ions should also be considered in biosorbent screening. Various studies have been reported on heavy metal biosorption by seaweed biomasses [9-11]. They are known as cheap biosorbents and the brown ones have been introduced as impressive biosorbents for heavy metal sequestering, probably due to their polysaccharide and alginic acid content [12,13].

Studying the behavior of a biosorbent in batch systems using equilibrium, kinetic, and thermodynamic modeling can help us in deciding the most efficient biosorbent. Moreover, further considerations on packed-bed column experiments or mathematical modeling require such predetermined batch evaluations. In the present research, the four most abundant kinds of seaweeds in Bushehr coastal waters, Persian Gulf, were employed for comparing their Cd^{2+} removal capacities. On this basis, the most efficient one was selected and further examined under optimization, equilibrium, kinetic and thermodynamic studies. The obtained results will be used in future column studies.

MATERIALS AND METHODS

1. Materials

All chemicals were of analytical grade and purchased from Merck. Solutions were prepared in distilled water. All glassware was soaked in 10% nitric acid and rinsed several times with distilled water prior to the experiments to avoid metal contamination. A stock solution (1,000 mg l^{-1}) of Cd^{2+} was prepared by dissolving the required quantity of cadmium salt in distilled water. The pH of the solutions was adjusted to required values using 0.1 M NaOH or 0.1 M

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HNO_3.

2. Biosorbent Preparation

Four different kinds of fresh seaweed, including *Sargassum angustifolium* (brown), *Acanthophora nayadiformis* (red), *Gracilaria corticata* (red), and *Botryocladia leptopoda* (red) were harvested from Bushehr coastal waters (Iran), Persian Gulf, and washed several times with tap water and 0.1 M HCl to remove salt and sands, followed by rinsing with distilled water until the pH of the wash became neutral. They were then dried in a conventional oven at 60 °C for 48 hrs. The dried biomass was crushed and sieved to achieve the required size.

3. Selection of the Most Effective Seaweed for Cadmium Biosorption

Selection of a suitable biosorbent for heavy metal removal process is a complex problem. In this way, using sorption isotherm derived from equilibrium batch contact experiments under the same environmental conditions (e.g. pH, temperature) is a scientific basis [13]. For this purpose, a vast range of initial Cd^{2+} concentrations were prepared from 0.045 to 2.67 mmol l^{-1} (5 to 300 mg l^{-1}) in 100 ml Erlenmeyer flasks containing 50 ml cadmium solution. The initial pH of the solutions was adjusted to 6 and controlled during the experiments. After adding 0.1 g biosorbent, the flasks were incubated in a shaker incubator at a fixed temperature of 28 °C and 160 rpm for 180 min of contact in order to ensure attaining the equilibrium conditions. The equilibrium biosorption capacities, q_e (mol Cd^{2+} g biomass^{-1}), were calculated at the end of experiments according to Eq. (1):

$$q_e = \frac{(C_i - C_e)}{C_b} \quad (1)$$

where C_i and C_e are the initial and equilibrium concentrations of cadmium (mol l^{-1}), respectively, and C_b is the biomass concentration (g l^{-1}). Finally, the most effective biosorbent was selected by drawing the plots of C_e versus q_e.

4. Optimization Experiments

A series of batch experiments were performed by the selected biomass to determine the optimum contact time, initial pH and dose of biomass for cadmium biosorption process. These experiments were performed as above in 100 ml Erlenmeyer flasks containing 50 ml Cd^{2+} solution. The effect of biomass dosage on the biosorption capacity, Eq. (1), as well as on the cadmium removal percentage, Eq. (2), was assessed by employing biomass concentrations of 0.2, 0.5, 1, 2 and 5 g l^{-1} in 10 mg l^{-1} Cd^{2+} solution at initial pH of 6, 28 °C, 180 min contact and 160 rpm.

$$\%R = \frac{(C_i - C_e)}{C_i} \times 100 \quad (2)$$

The effect of contact time was studied by adding 1 g l^{-1} biomass in three different cadmium solutions of 0.045, 0.134, and 0.222 mmol l^{-1} (5, 15, and 25 mg l^{-1}). Samples were withdrawn at regular time intervals up to 180 min of contact. The pH of the solutions was initially adjusted to 6.0 (not controlled during the experiments) and the solutions were incubated at a fixed temperature of 28 °C and 160 rpm. The effect of initial pH was investigated in the range of 2 to 8 in flasks containing 0.045 mmol l^{-1} Cd^{2+} (5 mg l^{-1} Cd^{2+}) and 60 min contact. Metal-free and biosorbent-free blanks were used as controls.

The biomass was harvested by Whatman No. 42 filter papers and the residual Cd^{2+} concentration in the solution was analyzed with a flameless atomic absorption spectrophotometer (PG instruments, AA500). All the adsorption experiments were performed in triplicate and confidence intervals (C.I.) of 95% were determined for each set of samples.

5. Equilibrium Isotherms

This part of the experiments is of great importance in a batch process. The equilibrium models include useful information for comparing the maximum sorption capacities of different biosorbents as well as the affinity of the biosorbents toward specific metal ions [7].

The equilibrium isotherm experiments were performed under fixed optimum conditions determined by previous experiments. Three commonly used and successful isotherm models, Langmuir, Freundlich, and Dubinin-Radushkevich (D-R), were employed to describe the equilibrium data between metal ions in the solution and adsorbed metal ions on the biomass surface. In this set of experiments a wide range of initial Cd^{2+} concentrations (0.045 to 2.67 mmol l^{-1}) were considered with preparing fixed conditions of pH and temperature during the experiments.

6. Kinetics Modeling

The effects of initial cadmium concentrations and contact time were assessed on the rate of cadmium removal by the biosorbent. Two common kinetic models including pseudo-first order and pseudo-second order models were utilized for describing the experimental adsorption of Cd^{2+} ions in the whole range of contact time. For this purpose, several cadmium concentrations were considered in the range of 0.045 to 0.222 mmol l^{-1} (5 to 25 mg l^{-1}) at an initial pH of 6 and temperature of 28 °C during 120 min of contact. The intraparticle diffusion mechanism was also investigated by evaluating the linearity of the sorption capacities over the square root of time. On the other hand, the ion exchange mechanism seems to be an important mechanism in cadmium removal process by seaweeds [10,11,14,15]. Here, this phenomenon was investigated by recording the initial and final pH of the solutions after 60 min of contact between the solid and metal phases. The Boyd et al. [16] rate equation was also employed to describe the experimental data if such mechanism is dominant.

7. Thermodynamic Studies

Undoubtedly, the metal sorption performance would be affected by temperature variations. Appropriate decisions were made using the thermodynamic parameters including enthalpy change (ΔH^0), entropy change (ΔS^0), and free energy change of the sorption (ΔG^0). The equilibrium experiments were repeated under several temperatures of 15, 28, 38 and 45 °C for achieving these thermodynamic parameters.

RESULTS AND DISCUSSION

1. Biomass Selection

As previously mentioned, the sorption isotherms derived from equilibrium batch experiments under the same environmental conditions are needed for quantitative comparison of different biosorbents. This comparison in terms of metal sorption capacity should

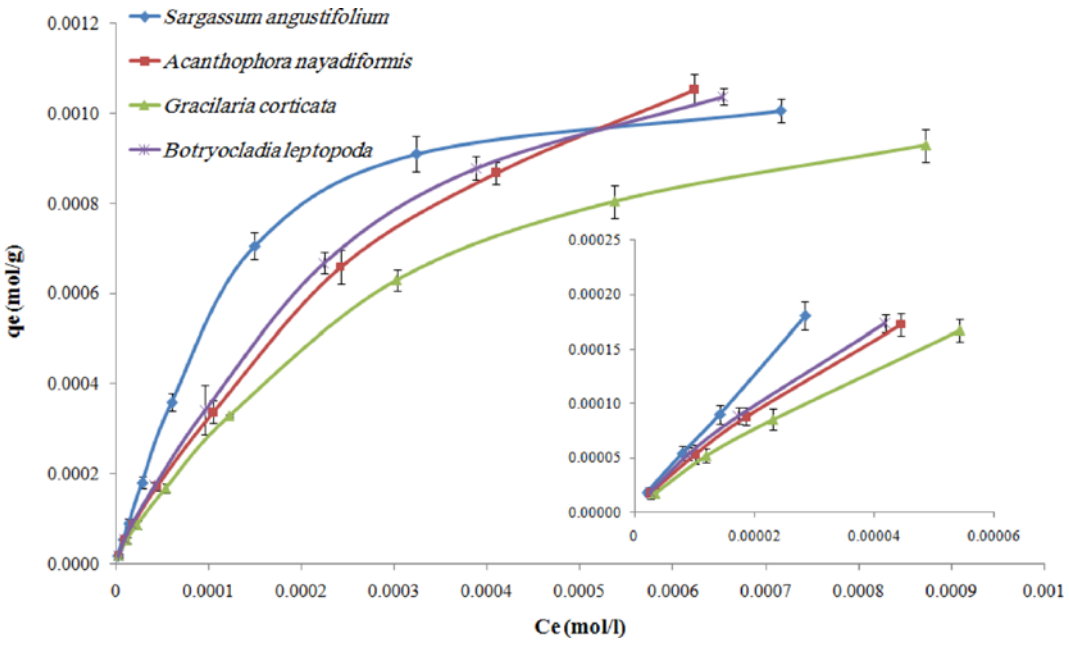

Fig. 1. Isotherm plots for comparing Cd^{2+} biosorption performances using four indigenous seaweeds, *Sargassum angustifolium* (◆), *Gracilaria corticata* (▲), *Acanthophora nayadiformis* (■) and *Botryocladia leptopoda* (*). Initial metal concentration in the range of 4 to 300 mg l^{-1} at 28 °C. Confidence intervals=95%.

be made at the same low or high equilibrium (final, residual, or equilibrium) concentrations [8,12,13,17]. Any other comparison of sorbent performance based on metal removal percentage can only result in a qualitative and relative comparison and does not indicate the concentration range. Removal percentage often is used for quick and approximate screening of sorbent materials [13].

Fig. 1 illustrates that the brown seaweed, *Sargassum angustifolium*, has located on top of the others. This implies that it has the greatest performance among the others, especially at equilibrium cadmium concentrations lower than 0.5 mmol l^{-1} (corresponding to initial cadmium concentration of almost 2.44 mmol l^{-1}). For example, when the initial cadmium concentration was fixed at 2.14 mmol l^{-1} for all these seaweeds, *Sargassum* removed cadmium ions more than others did and reached an equilibrium cadmium concentration down to 0.30 mmol l^{-1}, while it was 0.39, 0.41 and 0.54 mmol l^{-1} for *Botryocladia, Acanthophora*, and *Gracilaria*, respectively. It means a higher metal uptake capacity for *Sargassum* seaweed (0.91 mmol g^{-1}). On the contrary, *Gracilaria Corticata* has located at the lowest level, which suggests the lowest biosorption performance for this seaweed (0.80 mmol g^{-1}). According to Fig. 1, other studied seaweeds, *Acanthophora nayadiformis* and *Botryocladia leptopoda*, are in the middle position. This trend of capacities was reversed at equilibrium cadmium concentrations higher than 0.5 mmol l^{-1} (or initial concentration of almost 2.44 mmol l^{-1}). *Acanthophora nayadiformis* featured the highest capacity and *Botryocladia*, *Sargassum*, and *Gracilaria* were the next, respectively.

Low equilibrium metal concentrations are good measures for sorbent selection since very high metal concentrations are not likely to be encountered in reality. In addition, in these high concentration ranges, probably phenomena other than sorption (like precipitation, adherence, etc.) are encountered.

Brown seaweeds are known as promising adsorbents and their metal uptake capacities normally are much higher than other seaweeds, bacteria, fungi, activated carbon, natural zeolite, and synthetic ion exchange resins [1,6,10,13,18]. *Sargassum* species possess a relatively high metal binding capacity in comparison with other brown seaweeds [11,19]. Presence of alginic acid (20-40% on a dry-weight basis) or negatively charged carboxylate groups of alginate in the cell walls of brown seaweeds are largely responsible for higher metal cations uptakes [10]. So the biomass of *Sargassum* was selected for further experiments.

The cadmium biosorption process has satisfactory efficiency under lower initial metal concentrations. In the case of *Sargassum*, increasing the initial cadmium concentrations from 0.045 to 2.67 mmol l^{-1} (5 to 300 mg l^{-1}) decreased the process efficiency from 94 to 73%. Thus, the use of low concentrations is preferred for the following experiments.

2. Effect of Biosorbent Dosage on the Biosorption

The biomass dosage is another important factor during metal uptake. There should be an optimum concentration of biosorbent in the solution. The lower the biosorbent concentration in the solution, the lower surface area, and subsequently, the contribution of sorbent unit will increase for sequestering metal ions. This increases the metal adsorption capacity, q. However, the premature saturation of the biosorbent is expected. A reverse effect will occur when higher biomass concentrations are employed due to the high available vacant sites. On the other hand, excessive biomass concentration may interfere with each other and block the vacant sites for sorption metal ions. This most probably leads to a low sorption capacity as well as low removal percentage.

Five different biosorbent concentrations of 0.2, 0.5, 1, 2 and 5 g l^{-1} were employed to evaluate these effects on 10 mg l^{-1} cadmium solu-

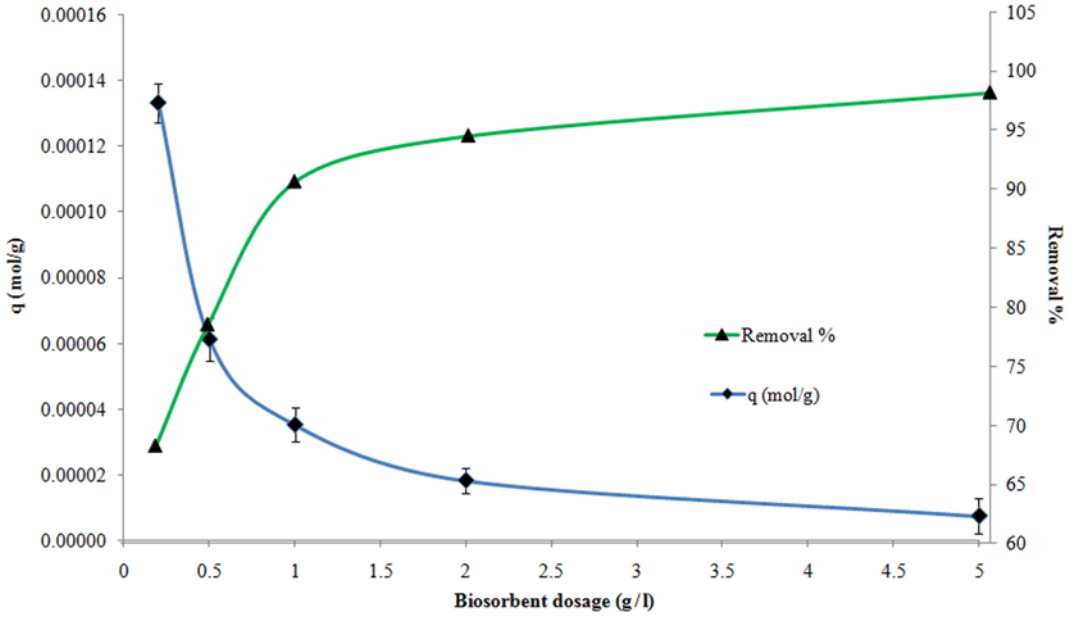

Fig. 2. Effect of dried *Sargassum angustifolium* concentration on Cd^{2+} removal capacity, q (◆), and Cd^{2+} removal percentage, %R (▲). 10 mg l^{-1} cadmium solution at 28 °C, 160 rpm and initial pH 6. Confidence intervals=95%.

tion. As can be seen in Fig. 2, increasing the biomass concentration decreases the metal adsorption capacity from 0.133 to 7.65× 10^{-3} mmol g^{-1}. However, it led to simultaneous increase in process efficiency from 68 to 98%. The same trends in removal efficiencies as well as adsorption capacities were also observed by Romera et al. [18] and Vimala and Das [20] for heavy metal removal by *Ascophyllum nodosum* and mushrooms, respectively. Chatterjee and Ray [21] reported that biomass aggregation in high concentrations reduced the Cu(II) biosorption percentage by immobilized *Bacillus cereus*. It was due to the ligands' interference with each other.

To achieve an appropriate sorption capacity along with high process efficiency the optimum value of 1 g l^{-1} biomass was considered for the following experiments.

3. Effect of Contact Time on Cd^{2+} Biosorption

Cadmium removal by dried biomass of *Sargassum* exhibited a very rapid kinetic under different metal concentrations of 0.045, 0.134, and 0.222 mmol l^{-1} (5, 15, and 25 mg l^{-1}). It was found that there is a two-stage kinetic behavior in cadmium biosorption by

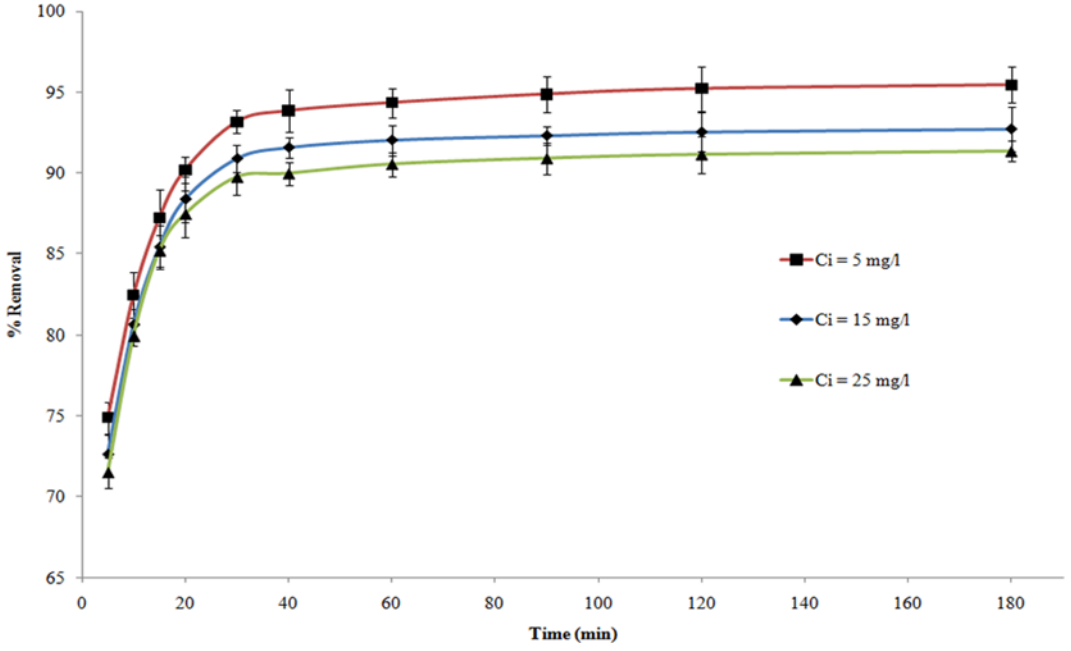

Fig. 3. Effect of contact time on Cd^{2+} removal percentage by dried biomass of *Sargassum angustifolium* in the presence of 5 (■), 15 (◆) and 25 (▲) mg l^{-1} Cd^{2+}. 1 g l^{-1} biomass dosage, 28 °C, 160 rpm and initial pH 6. Confidence intervals=95%.

studied *Sargassum* (Fig. 3). A very rapid cadmium sorption (during the first 30 min of contact) resulted in the elimination of more than 90% of the initial metal concentration, followed by the next 15 min biosorption where the process reached a relative equilibrium. The amount of adsorbed Cd^{2+} ions did not significantly change with time during this phase. Some literature reported the same fast cadmium biosorption from aqueous solution during the first 5 to 30 min contact of different marine macro algae by cadmium ions [1, 10,22]. However, there were some other reports that cadmium biosorption lasted for a longer time of 160 min up to 60 hr [6,23,24]. If column operation is needed for removing metal ions from aqueous solution, using biosorbent with fast metal uptake would be advantageous since it needs shorter height of bed, which directly affects the process economy.

In the present work, different initial Cd^{2+} concentrations did not significantly affect the equilibrium contact time so that all of the concentrations reached equilibrium at about 45-50 min of contact. Only the equilibrium sorption capacities increased from 0.019 to 0.089 mmol g^{-1} by increasing the initial Cd^{2+} concentrations from 0.045 to 0.222 mmol l^{-1} (5 to 25 mg l^{-1}).

Further experiments were conducted for 60 min to ensure attaining the equilibrium conditions.

4. Effect of Initial pH of the Solution on Cd^{2+} Removal

The pH of solution has two main effects on the metal biosorption process: metal solution chemistry or metal speciation and the change in the ionic state of the functional groups on biosorbent [1,6,18]. Therefore, the process efficiency is a direct function of the initial pH of the solution.

Fig. 4 illustrates the metal biosorption capacity changed with the variation in the initial pH of the solution when the initial metal concentration was adjusted to 5 mg l^{-1}. As can be seen, the maximum cadmium removal was achieved in pH values higher than 5 and less than 7. There was only a small metal uptake at pH value of 2 (25% removal). Increasing the initial pH from 2 to 6, increased the sorption capacity from 6.6×10^{-3} to 0.018 mmol g^{-1} (95% removal). However, further increase in the initial pH of the solution resulted in a 5% drop in the sorption capacity. According to Aksu [3], the isoelectric point plays a key role in surface charge of the adsorbents, and this could be found at pH 3.0 for algal biomass. At lower pH values, the cell wall ligands carry positive charges due to close association with proton ions. This restricts metal access to surface ligands due to repulsive force between proton and metal cation. However, surface ligands carry negative charges above pH 3. It promotes the attraction of positively charged cadmium ions [24,25]. From Fig. 4, a step rise observed after pH 3 can be attributed mainly to this tendency. On the other hand, there is an intense competition between Cd^{2+} and H^{+} ions for the active sites at low pH values. High concentration of proton ions does not allow the metal cations to occupy the binding sites on the biomass. However, increasing the initial pH decreases this competing effect and more ligands on the biomass are available for Cd^{2+} ions [4,6,25]. The presence of isoelectric point is a great advantage of the biomass since it can be easily regenerated by acid in practical uses such as column processes.

The theoretical cadmium speciation diagram presented by Leyva-Ramos et al. [26] shows that cadmium is present in the ionic form of Cd^{2+} at pH levels up to 6-7. However, increasing the pH gradually changes the predominant species of cadmium (e.g., cadmium hydroxides). They are less prone to being attracted by the surface ligands. These complexes turned the medium turbid due to the precipitation. The biosorbent free experiments verified it. This phenomenon is presumably the main reason for metal uptake depletion observed at pH values higher than 6 [2,19].

The optimum pH of 6 was considered for the following experiments. Other researchers also achieved this value for cadmium biosorption by some fungus species [4], immobilized *Zoogloea ramigera* cells [27], dealginated seaweed waste [9], some species of mushroom [20] and different algae [18]. However, the optimal pH values of 5 [1,6,28] and 4 [24] have also been reported in several papers.

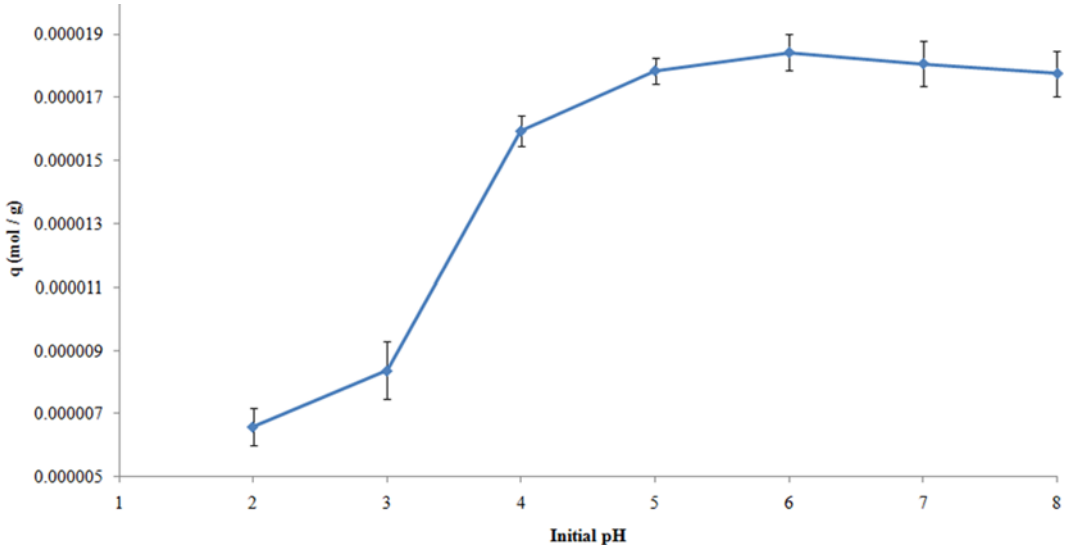

Fig. 4. Effect of initial pH of solution in the range of 2 to 8 on Cd^{2+} removal capacity by *Sargassum angustifolium*. 1 g l^{-1} biomass dosage, 5 mg l^{-1} cadmium solution, and 60 min contact time. Confidence intervals=95%.

5. Ion Exchange Mechanism

As was found earlier, the sorption capacity was highly influenced by pH variations. Many investigators identified the ion exchange as a mechanism responsible for cationic metal sorption onto the *Sargassum* [10,11,14,15].

Recording the final pH of the Cd^{2+} solution at the end of the process (after 60 min of contact) revealed that the final values were not the same as the initial ones. The changes were not significant in the free metal and free biosorbent blank tests. This means that the concentration of proton ions had changed in the solution due to the removing or releasing proton ions into the solution for cadmium sorption. The initial washing of the biomass with HCl (even in a short time) attached some H^+ ions to the surface ligands, which must be released to the solution during the cadmium biosorption experiments. The changes in the proton ion concentration, ΔH^+, were calculated by subtracting the initial proton ion concentration, $[H^+]$, from the final one. Table 1 shows the rate of changes in proton ions at the end of the experiments and the corresponding q_e values. As can be seen, increasing the initial pH of the solution up to 6 increased ΔH^+ due to the more proton ions released into the solution for exchange by cadmium ions. It is in accordance with the findings of literature [29,30]. The loss in ΔH^+ values at pH levels greater than 6 suggests the lower ion exchange in the solution, since the cadmium hydroxides become the predominant species at this range of pH. These anions have no interest in rushing toward the negatively charged biomass, and consequently less ion exchange occurs. A direct relationship between ΔH^+ and q_e values was also found, as reported in Table 1. Except for first and last points, which have significant deviation, the other data points are well fitted by a linear relationship as Eq. (3) with convincing correlation coefficient of R^2=0.987:

Table 1. Effect of initial pH variations on the changes in hydrogen ion concentration and Cd^{2+} sorption capacity. Initial Cd^{2+} concentration 5 mg l^{-1} (0.045 mmol l^{-1}) and 60 min of contact

pH_i	pH_{60}	ΔH^+ (mM)	$q_e \times 10^{-3}$ (mmol g^{-1})[a]
2	2.2	−3.690	6.59±0.43
3	3.1	−0.206	8.37±0.66
4	3.9	0.026	15.93±0.35
5	4.2	0.053	17.85±0.29
6	4.1	0.078	18.42±0.42
7	4.3	0.050	18.07±0.51
8	4.6	0.025	17.76±0.52

[a]Average value C.I., n=3

$$q_e = 4.05\ \Delta H^+ + 1.77 \quad (3)$$

The slope of Eq. (3), 4.05 mg gmM^{-1}, is the ion exchange rate, which is low but comparable to similar cases reported in other literature: 15.04 mg gmM^{-1} for mercury biosorption onto dried bacterial biosorbent *Vibrio parahaemolyticus* PG02 [7], 33.22 mg gmM^{-1} for biosorption of lead(II) onto mansonia wood sawdust [30], 0.289 mg gmM^{-1} for cadmium(II) adsorption onto coconut copra meal [29], and 10.60 mg gmM^{-1} for lead(II) transfer onto tree fern [31].

It can be concluded that the ion exchange mechanism is one of the most important mechanisms in Cd^{2+} biosorption by *Sargassum*. Probably, the initial rapid metal uptake during the first 30 min

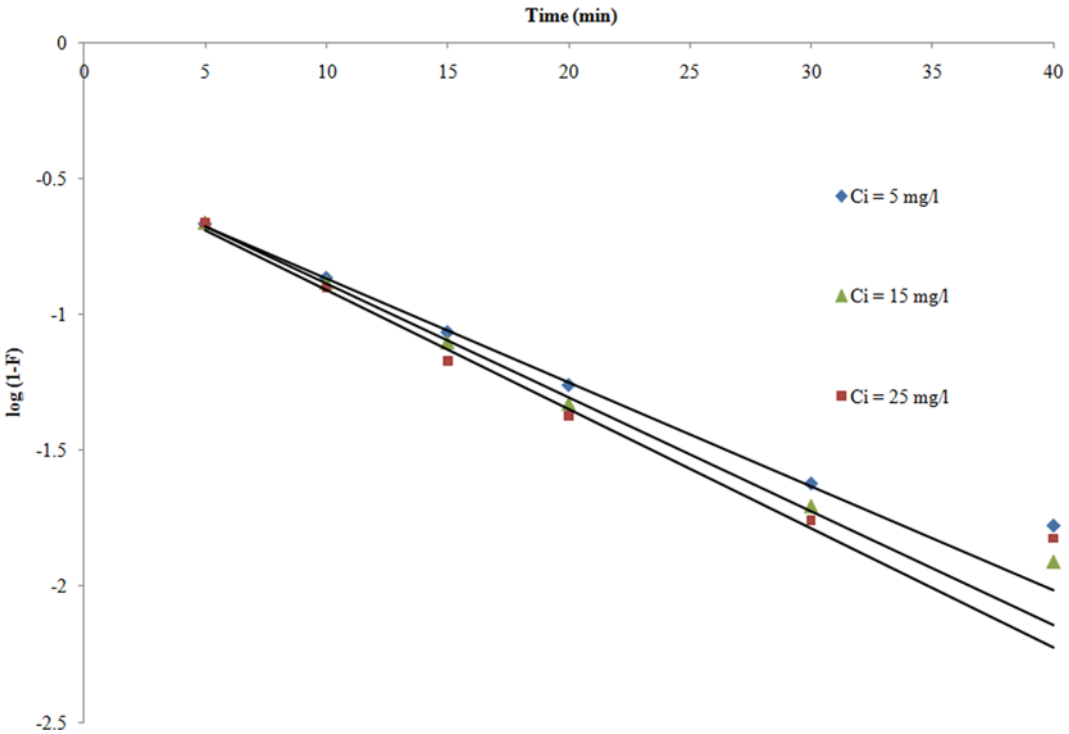

Fig. 5. Ion-exchange biosorption kinetics of Cd^{2+} onto dried *Sargassum angustifolium* at various initial Cd^{2+} concentrations of 5 (◆), 15 (▲) and 25 (■). 1 g l^{-1} biomass dosage, initial pH 6.0, and 28 °C.

Table 2. The Boyd et al. rate constants at different studied concentrations. Initial pH of 6, 28 °C and 30 min contact

C_i, mg l^{-1} (mmol l^{-1})	S (min^{-1})[a]	R^{2a}	pH_i	pH_{60}	ΔH^+ (mM)[b]	q_e (mmol g^{-1})[b,c]	R^{2b}
5 (0.045)	0.088	0.999	6	4.2	0.062	$0.0184\pm8.9\times10^{-3}$	
15 (0.133)	0.096	0.998	6	3.6	0.250	$0.0545\pm1.5\times10^{-2}$	0.993
25 (0.222)	0.100	0.994	6	3.3	0.500	$0.0903\pm1.6\times10^{-2}$	

[a]Values during the first 30 min of contact
[b]Values after 60 min of contact
[c]Average value C.I., n=3

of contact can be attributed to this phenomenon, but this needs some verification. Boyd et al.'s [16] rate equation, Eq. (4), was employed to prove this fact. This model, which considers rates of ion exchange adsorption by organic zeolites, is known as follows:

$$\log(1-F)=-\left(\frac{S}{2.303}\right)t \tag{4}$$

where F is the fractional attainment of equilibrium, F=qt/qe, and S (min^{-1}) is rate constant. The model validation has been previously conducted in literature for heavy metal biosorption [7,29,31]. According to Fig. 5, there is a good fitting of the experimental data by theoretical curves in the first 30 min of contact at all metal concentrations. However, some deviation is observed after that. It strongly suggests that the initial rapid cadmium uptake during the first 30 min of contact can be attributed to the ion exchange mechanism and certainly is not a rate-limiting step. Table 2 presents the rate constants at various studied concentrations and corresponding ΔH^+ values as well as sorption capacities. As can be seen, increasing initial metal concentrations from 0.045 to 0.222 mmol l^{-1} (5 to 25 mg l^{-1}) increased andvalues from 0.088 to 0.100 min^{-1} and 0.062 to 0.500 mM, respectively. This implies that increasing the initial driving force due to increasing initial metal concentration increases the number of replacements of proton and Cd^{2+} ions. The same linear relationship was also observed in Table 2 between ΔH^+ values and the equilibrium sorption capacities (R^2=0.993). Therefore, all the results obtained support the involvement of the ion exchange mechanism in the biosorption of cadmium cations onto *Sargassum* biomass during the initial rapid phase.

6. Equilibrium Isotherm Modeling

Equilibrium is established when the concentration of a metal ion in the solution is in balance with that of the biosorbent surface. In such cases, an equilibrium isotherm model is employed to describe the experimental data in order to give useful information about the biosorbent. Three of the most common and most successful isotherm models in describing biosorption equilibrium data are Langmuir, Freundlich and Dubinin-Radushkevich (D-R). Metal sorption on a homogeneous surface, as a monolayer, without interaction between adsorbed molecules is the basis of the Langmuir model [7]. Eq. (5) shows the nonlinear form of the Langmuir isotherm model:

$$q_e=\frac{q_m\cdot b\cdot C_e}{1+b\cdot C_e} \tag{5}$$

where q_{max} is the maximum metal uptake (mmol g^{-1}) to form a complete monolayer on the surface at high metal concentrations. This factor is used in the comparison of adsorption performance; b is the Langmuir equilibrium constant (l $mmol^{-1}$) that represents the affinity between the sorbent and metal ions. The q_{max} and b values were determined by a nonlinear least-squares method using MATLAB software. Note that C_e in Eq. (5) must be expressed as the molar concentration [32].

The Freundlich isotherm is an empirical model that proposes a monolayer sorption with heterogeneous energetic distribution of active sites. The nonlinear form is given by Eq. (6):

$$q_e=k_F\cdot C_e^{1/n} \tag{6}$$

where k_F (mmol g^{-1}) and are the Freundlich constant and Freundlich exponent, respectively. The k_F value is an indicator of the biosorption capacity and 1/n represents the surface heterogeneity, calculated by nonlinear least-squares method using MATLAB software. The D-R isotherm model also assumes monolayer adsorption and is employed to estimate the characteristic porosity of the biomass and the mean free energy of adsorption. However, it does not assume a homogeneous surface or constant sorption potential. Distinguishing the chemisorption and physisorption of metal ions is another advantage of the D-R model [33]. It has the following nonlinear form:

$$q_e=q_m\cdot\exp(-\beta\varepsilon^2) \tag{7}$$

where q_m is the maximum sorption capacity (mmol g^{-1}), β is a constant related to the sorption energy (mol^2 J^{-2}) and ε=RT ln(1+1/C_e) is the Polanyi potential where R is the gas constant (8.314 J mol^{-1} K^{-1}) and T is the absolute temperature (K).

The parameters β and q_m are also achieved by nonlinear least-squares method.

β gives the mean free energy, E (kJ mol^{-1}), according to Eq. (8). It is a change in free energy when one mole of ion migrates to the surface of the sorbent from infinite distances in the bulk solution, and is calculated as follows:

$$E=(2\beta)^{-0.5} \tag{8}$$

This parameter gives information about chemical or physical adsorption.

To compare the validity of each model more efficiently, a normalized standard deviation, Δq, is calculated by using the following equation [34]:

$$\Delta q=\left(\frac{\sum[(q_e^{exp}-q_e^{mod})/q_e^{exp}]^2}{n-1}\right)^{1/2}\times100 \tag{9}$$

where the superscripts exp and mod are the experimental and model

Table 3. The Langmuir, Freundlich and Dubinin-Radushkevich parameters for Cd^{2+} biosorption by *Sargassum angustifolium* biomass under different temperatures of 15, 28, 28 and 45 °C

Temperature (°C)	Langmuir constants				Freundlich constants				Dubinin-Radushkevich				
	q_{max} (mmol g^{-1})	b (l $mmol^{-1}$)	R^2	Δq%	k_F (mmol g^{-1})	n	R^2	Δq%	q_{max} (mmol g^{-1})	β (mol^2 kJ^2)	R^2	E (kJ mol^{-1})	Δq%
15	1.09	5.064	0.991	11.8	23.9	2.16	0.935	127	3.6	0.0048	0.957	10.21	75
28	1.24	7.497	0.994	18.7	31.3	2.18	0.934	144	4.4	0.0042	0.956	10.92	86
38	1.31	6.970	0.994	11.4	38.0	2.09	0.944	128	4.9	0.0040	0.963	11.11	73
45	1.20	6.146	0.992	13.3	29.7	2.14	0.938	137	4.2	0.0039	0.959	11.37	81

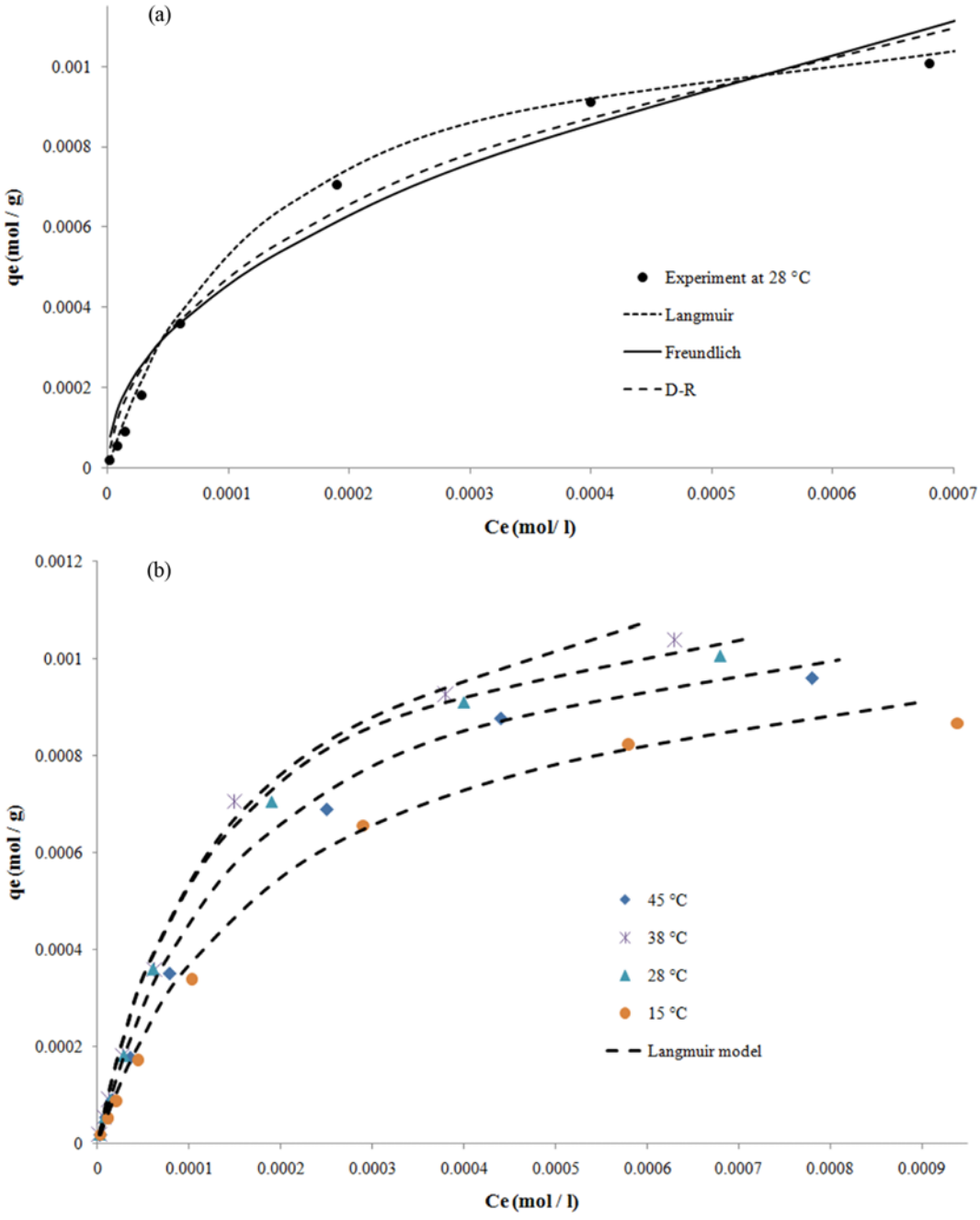

Fig. 6. (a) The precision of Langmuir, Freundlich and Dubinin-Radushkevich isotherm models for describing experimental q_e at 28 °C and (b) data description by the preferred isotherm model, Langmuir, at 15, 28, 38 and 45 °C.

Table 4. Comparison of the maximum Cd^{2+} biosorption capacities as well as the Langmuir affinity parameters, b, for different sorbents

(bio)Sorbent	q_{max} (mmol g^{-1})	pH	b (l $mmol^{-1}$)	Reference
Synthetic zeolite A	1.6		0.991	[34]
Sargassum angustifolium	1.24	6	7.497	This study
Pretreated *Durvillaea potatorum*	1.12	5.4	6.150	[25]
Sargassum	1.07	5.5	-	[19]
Padina	0.76	5.5	5.650	[6]
Sargassum	0.75	5.5	11.340	[6]
Sargassum baccularia	0.74	5	4.670	[10]
Sargassum siliquosum	0.73	5	6.600	[10]
Cystoseira baccata	0.69	4.5	11.000	[22]
Sargassum hemiphyllum	0.69	5	5.080	[11]
Chondrus crispus *(red)*	0.67	-	6.370	[18]
Fucus ceranoides	0.65	4.5	-	[1]
Padina tetrastomatica (Brown)	0.53	5	4.650	[10]
Bagasse activated carbon	0.34	4.5	13.200	[35]
Pleurotus platypus	0.31	6	9.094	[20]
Asparagpsis armata *(red)*	0.29	-	10.610	[18]
Moroccan stevensite	0.26	6	0.002248	[33]
Peat moss	0.20	-	-	[36]
Codium vermilara (green)	0.19	-	11.150	[18]
Gracilaria salicornia (red)	0.16	5	9.040	[10]
Papaya wood	0.15	5	36.983	[28]
Granulated activated carbon	0.07	-	8.064	[26]

prediction values, respectively, and n is the number of data points.

Table 3 represents the obtained equilibrium isotherm parameters by Langmuir, Freundlich and D-R models for *Sargassum* biomass under various temperatures of 15, 28, 38 and 45 °C. As can be seen, the equilibrium sorption data were satisfactorily described by the Langmuir model (R^2 values over 0.99 and $\Delta q \leq 18.7\%$). Fig. 6(a) illustrates the experimental and predicted equilibrium data at 28 °C to better distinguish data description by these three models. Bold points represent the experimental q_e values and dashed lines are predicted ones by the models using parameters listed in Table 3. The Langmuir model has also been reported in literature as a dominant model for predicting the equilibrium experimental data of Cd^{2+} biosorption by *Sargassum* and other biosorbents [6,11,19, 20,24]. Fig. 6(b) illustrates the Langmuir fitting well at all studied temperatures. Dashed lines represent the predicted q_e values by the Langmuir model using parameters listed in Table 3. It is clear from the figure that the highest sorption capacities did not meet the full saturation values. So the predicted values of 1.09, 1.24, 1.31, and 1.20 mmol g^{-1} were achieved by this model as the maximum sorption capacities, q_{max}, at the corresponding temperatures of 15, 28, 38, 45 °C, respectively. These values for maximum sorption capacities are conditional [1]. It means that they are valid solely for the experimental conditions under which they are obtained. Changing environmental condition such as pH achieves other values for q_{max}.

The parameter q_{max} is not the only parameter that must be taken into account for comparing the biosorbent performances under different conditions. The parameter b, presented in Table 3, is another key factor. A high value for this parameter is desirable, which appears as the steep initial slope at low residual concentration range. According to Fig. 6(b), the highest b value is expected for 38 °C. This means that the best affinity for Cd^{2+} ions is rather established at 38 °C than other temperatures. These two parameters, q_{max} and b, are also good measures for comparing different biosorbents performances. Table 4 compares the maximum cadmium sorption capacities for several biosorbents in literature. Most of them have been achieved in the range of 25 to 30 °C. It was found that the studied *Sargassum angustifolium* is in good position among the others, at the top of Table 4.

Obtaining the biomass needed in grams for treating a metal contaminated water containing specific initial metal concentration or reaching a certain final metal concentration is another aspect of possessing equilibrium parameters. For this purpose, the selected equilibrium isotherm model, nonlinear Langmuir model, should be combined with Eq. (1) to achieve an equation as follows:

$$C_b = \frac{(C_i - C_e)(1 + b \cdot C_e)}{q_{max} \cdot b \cdot C_e} \tag{10}$$

This equation is used to estimate the biosorbent concentration required to achieve a specific final concentration in a batch process. However, sometimes it is desirable to supply a biomass dose to meet a given metal removal percentage. Therefore, by placement Eq. (2) in Eq. (10), the following equation, Eq. (11) is obtained, which can be used to determine the biomass dosage required to remove a specific percentage of metal from solution as a function of C_i.

$$C_b = \frac{\%R\ (100 + 100 \cdot b \cdot C_i - b \cdot C_i \cdot \%R)}{100 \cdot q_{max} \cdot b \cdot (100 - \%R)} \tag{11}$$

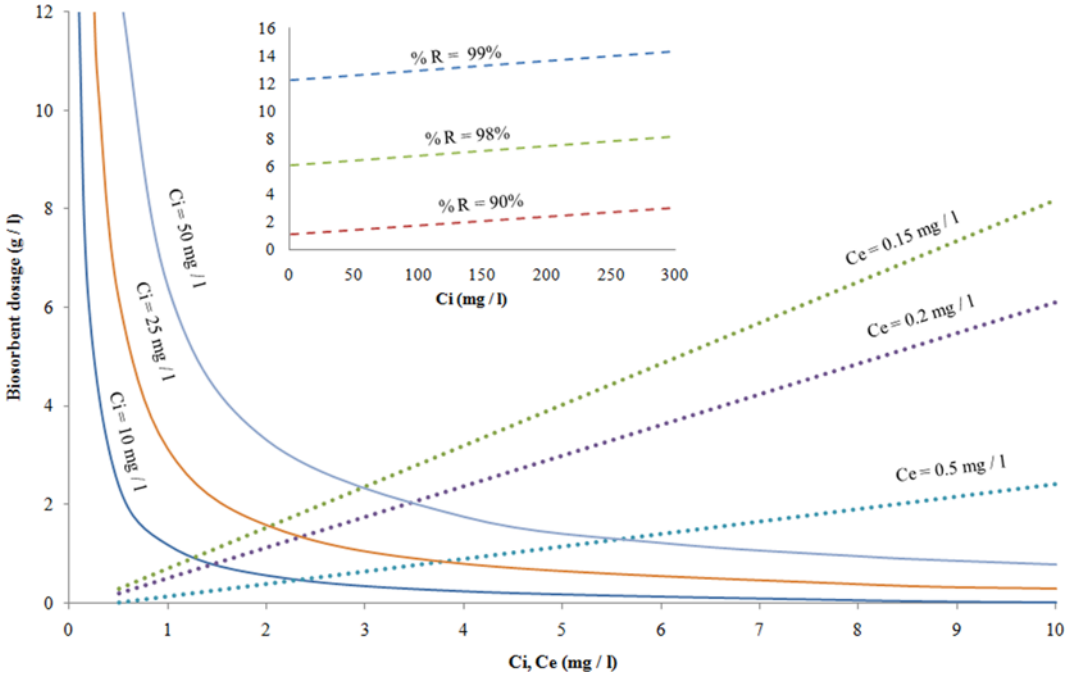

Fig. 7. Estimating the dried *Sargassum angustifolium* concentration needed using Eqs. (10) and (11) either to treat a known initial Cd^{2+} concentration or to meet a given final Cd^{2+} concentration under a batch process at 28 °C.

Table 5. The experimental and predicted equilibrium concentrations, C_e, according to Eqs. (10) and (11) under several initial Cd^{2+} concentrations and 2 g l^{-1} biomass dosage at 28 °C and 120 min contact time

C_i, mg l^{-1} (mmol l^{-1})	C_b (g l^{-1})	Experimental		Predicted			E%[b]
		$C_e\times10^{-3}$ (mmol l^{-1})[a]	%R	$C_e\times10^{-3}$ (mmol l^{-1})	%R	Reference	
4 (0.036)	2	2±0.2	93.30	2	94.11	Eq. (10)	12.3
10 (0.089)	2	6±1.0	93.10	5	94.00	Eq. (10)	13.0
50 (0.445)	2	34±2.5	92.40	31	93.12	Eq. (11)	9.5
100 (0.889)	2	86±6.0	90.32	74	91.65	Eq. (11)	13.7

[a]Average value±C.I., n=3

[b]Error value %=$(C_e^{exp}-C_e^{prd})/C_e^{exp}\times100$, where the superscripts "exp" and "prd" are experimental and predicted, respectively

Fig. 7 depicts how to determine the *Sargassum* biomass concentration required for treating a batch process according to the parameters C_e, C_i or %R (both Eqs. (10) and (11)). For instance, if the initial cadmium concentration in a batch process is 8 mg l^{-1} (0.071 mmol l^{-1}), 1.9 g l^{-1} *Sargassum* biomass is required to reach a final concentration of 0.5 mg l^{-1} (4.45×10^{-3} mmol l^{-1}) at 28 °C. Similarly, for more sensitive processes, 6.5 g l^{-1} biosorbent is needed to meet the final critical concentration of 0.15 mg l^{-1} (1.33×10^{-3} mmol l^{-1}). On the other hand, 1.6 g l^{-1} biomass is needed for 90% cadmium elimination at 28 °C in a batch process with initial cadmium concentration of 80 mg l^{-1} (0.712 mmol l^{-1}); however, this value rises sharply to 12.7 g l^{-1} if 99% removal is desired. Obviously, increasing the initial metal contamination increases the required biosorbent dosage to meet the same final concentration. On the other hand, when a very low final metal concentration is considered, the amount of required adsorbent increases exponentially. Therefore, when it is not essential to over-decrease the metal concentration in an aqueous solution, additional charge can be saved by avoiding the use of excess biosorbent concentration. It seems to be very useful, especially in the case of expensive adsorbents when a cost-effective batch biosorption process is desired.

Table 5 reports the results of some verification tests that were conducted with 2 g l^{-1} *Sargassum* at 28 °C to verify the predicted C_b values by Eqs. (10) and (11). As can be seen, the small error values, E% ≤13.7%, suggest a good agreement between the experimental and predicted C_e for both equations.

The following sections investigate the mechanism of biosorption process, since the prior empirical equilibrium models do not reflect any one of the mechanisms of metal uptake [6,13].

7. Effect of Temperature and Thermodynamic Studies

Contradictory reports in literature provide different interpretations of the effect of temperature on cadmium biosorption using different biosorbents. It is due to the immense variety of biosorbents that each utilizes specific mechanisms for heavy metal uptake. For example, Lodeiro et al. [22] found that temperature variation in the range of 15 to 45 °C was practically negligible on cadmium

removal by brown seaweed *Cystoseira baccata*. Only a small increase was observed in sorption capacity at 45 °C. Cruz et al. [19] reported decreasing cadmium biosorption capacity of *Sargassum* by increasing temperature in the range of 25 to 55 °C. Aksu [3] showed an exothermic cadmium biosorption by green microalgae *C. vulgaris* under temperature of 20 to 50 °C.

It seems that the nature of cadmium biosorption by the studied *Sargassum* biomass is temperature dependent and endothermic. The reported q_{max} values in Table 3 imply that increasing temperature from 15 °C to 38 °C raised the maximum biosorption capacity. However, a slight decline in q_{max} value was observed at 45 °C, which can be attributed to an increasing tendency to desorb metal ions from the interface to the solution at higher temperatures.

The endothermicity of the biosorption can be proved by thermodynamic study and calculating the enthalpy change, ΔH^0. For this purpose, the free energy change of the adsorption, ΔG^0 kJ mol^{-1}, as the fundamental criterion of spontaneity, was determined from Eq. (12):

$$\Delta G^0 = -RT \ln K \quad (12)$$

where R is the gas constant, T is the absolute temperature, and K is the thermodynamic equilibrium constant without unit. It is a common application in literature which uses the Langmuir equilibrium constant b instead of the dimensionless thermodynamic equilibrium constant in Eq. (12) [7,37,38]. The b constant with the unit *l* mol^{-1}, can be changed to dimensionless K by multiplying with 55.5, number of moles of water per liter of solution [37]. The Langmuir equilibrium constant with units of *l* mol^{-1} can be used directly for determination of ΔG^0 without any modification only if neutral or weak charge adsorbates or a dilute solution of charged adsorbate are used [38].

The free energy change of the adsorption is also expressed as follows:

$$\Delta G^0 = \Delta H^0 - T\,\Delta S^0 \quad (13)$$

where ΔH^0 is the enthalpy change (kJ mol^{-1}) and ΔS^0 is the entropy change (j mol^{-1} K^{-1}), that are evaluated from the intercept and the slope of a plot of ΔH^0 versus T, respectively. As can be seen in Table 6, the R^2 value is so close to 1 (0.968) that it implies a good linear relation among the experimental data by Eq. (13). The positive low value of ΔH^0 (10.75 kJ mol^{-1}) signifies the endothermic biosorption of Cd^{2+} ions by dried *Sargassum* and proves the previous results. This value is also in the range of heats of condensation, from 2.1 to 20.9 kJ mol^{-1}. It is far from heats of chemisorption, which are generally in the range of 80 to 200 kJ mol^{-1} [38,39]. This suggests weak forces between adsorbates and adsorbents. However, the presence of chemical reaction such as valence forces, ion exchange, complexation and/or chelation in metal biosorption mechanism cannot be ignored [29]. On the other hand, the magnitude of mean free energy values, from Eq. (8), are approximately similar and were found to be in the range of 8-16 kJ mol^{-1} (Table 3), which is within the energy range of chemisorption. However, if it was less than 8 kJ mol^{-1}, it would suggest a physisorption [34,40].

According to Table 6, the negative values obtained for free energy change, ΔG^0, for all studied temperatures signify a spontaneous biosorption process which increased with temperature. The positive value of ΔS^0 (142.15 j mol^{-1} K^{-1}) indicates an increased randomness at the solid/solution interface during the adsorption of Cd^{2+} ions onto biomass and some structural changes in the cell wall.

Although the process performance was established better at 38 °C, the lower level, 28 °C, was considered as an optimum temperature for further experiments as well as for future related column studies. Process control under ambient temperature is preferred due to reducing operational costs.

8. Kinetic Modeling and the Effect of Cd^{2+} Concentration on the Biosorption

Kinetic modeling is used to investigate the overall rate of metal biosorption from aqueous solution onto the biosorbent surface as well as characterizing the rate controlling step such as mass transport and chemical reaction processes [3,30]. The most widely used kinetic models for metal biosorption processes are Lagergren's pseudo-first and pseudo-second order models. Their unknown parameters are usually achieved with the aid of linear forms. But the nonlinear forms achieved more accurate results. The nonlinear form of pseudo-first order rate equation is expressed as follows:

$$q_t = q_e(1 - \exp(-k_1 t)) \quad (14)$$

where q_t and q_e are the amounts of Cd^{2+} adsorbed at time t (min) and equilibrium (mmol g^{-1}), respectively, and k_1 is the rate constant of the pseudo-first order adsorption process (min^{-1}). The values of k_1, and q_e are determined by nonlinear least-squares method using MATLAB software. The nonlinear form of the pseudo-second order kinetic model is given as Eq. (15):

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (15)$$

where k_2 is the equilibrium rate constant for pseudo-second order biosorption (g mmol^{-1} min^{-1}) and $k_2 q_e^2$=h, the initial sorption rate (mmol g^{-1} min^{-1}). Values of k_2 and q_e are also calculated using MATLAB. The data fitting by the kinetic models was conducted during the first 60 min of contact and avoided the step of equilibrium.

Note that the first-order models are usually capable of describing the experimental data only for the first minutes of process. Contrary to the first-order model, the pseudo-second order model can

Table 6. Thermodynamic parameters for Cd^{2+} biosorption process by brown seaweed *Sargassum angustifolium*

Temperature (°C)	ΔG^0 (kJ mol^{-1})	K	ΔH^0 (kJ mol^{-1})	ΔS^0 (j mol^{-1} K^{-1})	R^2
15	−30.04	281105	10.75	142.15	0.968
28	−32.38	416111			
38	−33.27	386884			
45	−33.68	341116			

Table 7. Pseudo-first order, pseudo-second order and intraparticle diffusion parameters for Cd^{2+} biosorption onto dried *Sargassum angustifolium* at several initial concentrations and 60 min contact

C_i, mg l^{-1} (mmol l^{-1})	$q_{e,exp}$ (mmol g^{-1})[a]	Pseudo-first order model			Pseudo-second order model				Intraparticle diffusion	
		k_1 (min^{-1})	$q_{e,mode}$ (mmol g^{-1})	R^2	k_2 (g $mmol^{-1}$ min^{-1})	h (mmol g^{-1} min^{-1})	$q_{e,mode}$ (mmol g^{-1})	R^2	k_{int} (mmol g^{-1} min)	R^2
5 (0.045)	0.0186±0.0027	0.314	0.0168	0.807	34.7	0.012	0.0188	0.985	0.0032	0.813
15 (0.133)	0.0542±0.0063	0.308	0.0413	0.836	11.3	0.035	0.0555	0.989	0.0095	0.793
25 (0.222)	0.0890±0.0085	0.307	0.0791	0.874	6.9	0.058	0.0912	0.991	0.0156	0.753

[a]Average value C.I., n=3

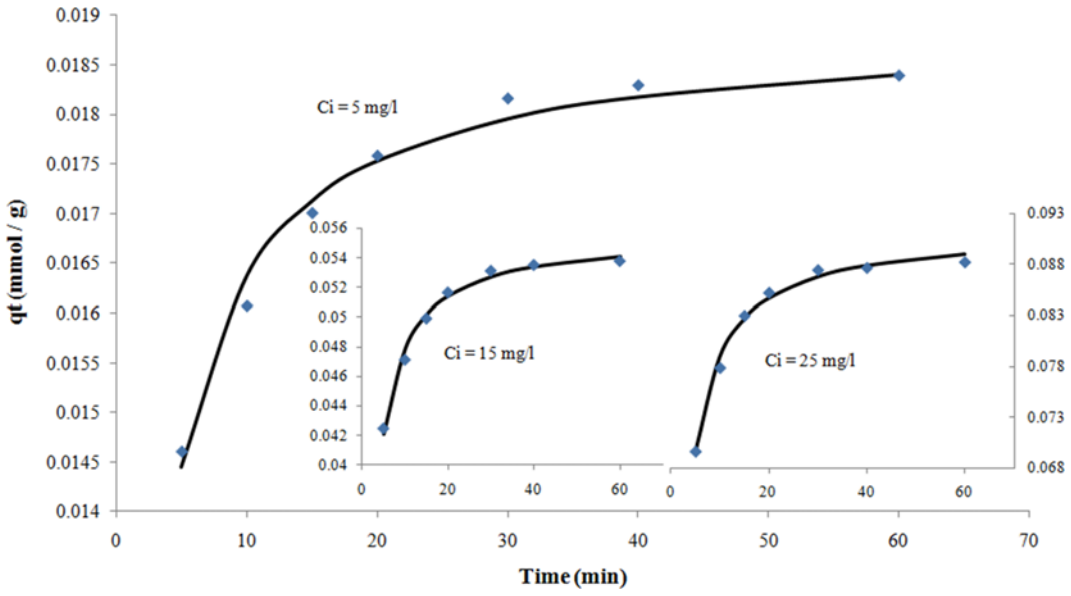

Fig. 8. Plots of nonlinear pseudo-second order model for the biosorption kinetics of Cd^{2+} onto dried *Sargassum angustifolium* at initial Cd^{2+} concentrations of 0.045 to 0.222 mmol l^{-1} (5 to 25 mg l^{-1}). 1 g l^{-1} 0biomass dosage, initial pH 6.0, 28 °C and at the first 60 min of contact before attaining equilibrium.

describe the experimental data during the whole range of contact time (data not shown) [3,19,41]. From data reported in Table 7, the poor values of R^2 (less than 0.874) in the case of pseudo-first order model as well as significantly good data fitting for pseudo-second order model ($R^2 \geq 0.986$) clearly indicate that the pseudo-first order model is not successful in predicting the entire experimental data. Fig. 8 illustrates the significantly good description of the experimental kinetic data by the nonlinear pseudo-second order model during the first 60 min of contact time. Comparing the experimental and predicted q_e values in Table 7 also confirms the accuracy of the pseudo-second order model for data fitting. The predicted q_e values by pseudo-first order do not match the experimental ones. According to Sinha et al. [42], if the experimental q_e is not equal to the theoretical q_e, the considered kinetic equation will not correspond to experimental data, even if the plot has a high correlation coefficient. Therefore, both facts imply that the biosorption of cadmium ions follows the pseudo-second order kinetic model, and chemisorption seems significant in the rate-controlling step [22]. Many authors have shown that pseudo-second order model is a reliable model for describing the cadmium biosorption data [1,24, 28,29].

As can be seen in Table 7, the k_2 value decreased from 35 to 7.5 g $mmol^{-1}$ min^{-1} by increasing the initial metal concentration, and inversely the h value increased from 0.012 to 0.064 mmol g^{-1} min^{-1}, which is consistent with the findings of other papers [7,29,30]. It can be interpreted by initial driving force. Increasing the initial metal concentration increases the initial driving force between bulk solution and biomass surface, which induces the initial rate of metal uptake, h. However, metal ion collision at high concentrations makes diffusion toward the surface ligands or micro pores difficult and so reduces the overall rate of kinetic, k_2.

Other possible mechanisms such as bulk transport in the liquid phase, external film diffusion, and intraparticle diffusion could also be considered in the biosorption process. Since the batch process was conducted under a well-agitated condition, the effect of bulk transport and external film diffusion on biosorption rate can be assumed insignificant [1,3,22], and the intraparticle diffusion into the sorbent pores could be considered as a rate-limiting step [34]. In addition, as El-Sikaily et al. [43] reported, the non-linearity relation between the initial metal concentration and the k_2 val-

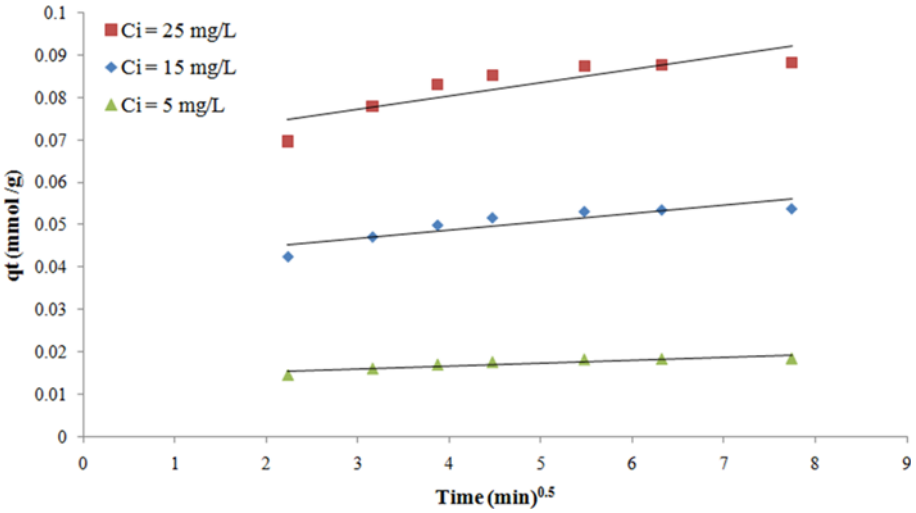

Fig. 9. The multi-linearity behavior of intraparticle diffusion mechanism for Cd^{2+} biosorption by dried *Sargassum angustifolium* at initial Cd^{2+} concentrations of 5 (◆), 15 (▲) and 25 (■) mg l^{-1}. 1 g l^{-1} biomass dosage, initial pH 6.0, 28 °C and at the first 60 min of contact before attaining equilibrium.

ues (Table 7) emphasizes the intraparticle diffusion mechanism as rate-limiting step in cadmium biosorption process by *Sargassum angustifolium*. It will be discussed in the following section.

9. Intraparticle Diffusion

Intraparticle diffusion rate parameter is defined to characterize the rate of diffusion after the initial rapid stage of metal biosorption. This prolonged phase is usually the main rate controlling step, as McKay et al. [44] have pointed; the intraparticle diffusion is the rate controlling step after an initial rapid dye uptake by fired clay. Weber and Morris model, Eq. (16), was employed to study the intraparticle diffusion during the cadmium biosorption process:

$$q_t = k_{int}\, t^{0.5} \tag{16}$$

where k_{int} is the intraparticle diffusion rate constant (mmol g^{-1} $min^{-0.5}$) and is characteristic of intraparticle diffusion within adsorption system. The linear plot of q_t versus $t^{0.5}$ yields this constant.

As it is clear from Fig. 9, there is no linear relation between the variables at all initial cadmium concentrations. The poor R^2 values reported in Table 7, for intraparticle diffusion, indicate it. In addition, the overall line for each metal concentration, in Fig. 9, does not pass through the origin. However, there is multi-linearity in the shape of the intraparticle diffusion plots. Therefore, it can possibly be concluded that the intraparticle diffusion is not the sole rate-limiting step [30,34,43]. Similar results have been previously reported by Ofomaja [30] in the biosorption of lead(II) onto mansonia wood sawdust, by Gialamouidis et al. [39] for biosorption of Mn(II) onto *Pseudomonas* sp., *Staphylococcus xylosus*, and *Blakeslea trispora* cells and by Jafari and Cheraghi [7] for mercury removal by *Vibrio parahaemolyticus* PG02. The intraparticle diffusion rate values reported in Table 7 are directly proportional to the initial mercury concentration, so that increasing the initial metal concentration from 5 to 25 mg l^{-1} (0.045 to 0.222 mmol l^{-1}) makes this parameter more important and promotes it from 0.0032 to 0.0156 mmol g^{-1} $min^{-0.5}$. This finding is in accordance with the results reported by Jafari and Cheraghi [7], Ofomaja [30], and McKay et al. [44].

CONCLUSIONS

The brown seaweed, *Sargassum angustifolium*, had the best Cd^{2+} biosorption performance in comparison with other studied strains, in the range of equilibrium cadmium concentration lower than 0.5 mmol l^{-1} or corresponding initial cadmium concentration lower than 2.1 mmol l^{-1}. To evaluate its characteristics in cadmium biosorption process, this seaweed was further examined. First, the environmental conditions were optimized to improve the process performance. The optimization experiments revealed that when the initial pH of solution, temperature, biomass concentration, and contact time were adjusted to 6, 38 °C, 1 g l^{-1}, and 60 min, respectively, maximum process performance was achieved. According to the kinetic studies, the Cd^{2+} biosorption included a two-stage mechanism with a rapid initial stage during the first 30 min of contact where almost 90% of initial Cd^{2+} concentration was eliminated. With the help of Boyd et al. rate equation, it was found that the ion exchange was a dominant mechanism during this period. A direct relationship between ΔH^+ and q_e values gave the ion exchange rate of 4.05 mg gmM^{-1} for cadmium removal. In addition, the magnitude of mean free energy was found to be in the range of 8-16 kJ mol^{-1}, which was within the energy ranges of chemisorption. Increasing the biosorption contact time formed a surface monolayer and led to equilibrium between metal ion in the solution and solid surface after about 45-50 min of contact. The pseudo-second order kinetic model, unlike the pseudo-first order, excellently described the experimental data during the reaction time. The equilibrium isotherm study at various temperatures revealed that the Langmuir model better described the experimental data than the Freundlich and D-R models. The maximum sorption capacity improved to 1.31 mmol g^{-1} with rising temperature up to 38 °C. This implied an endothermic process. However, further increase in temperature decreased a little the sorption capacity possibly due to the destruction of surface ligands. The positive obtained value for ΔH^0, 10.75 kJ mol^{-1} also signified the endothermic nature of Cd^{2+} bio-

sorption by dried *Sargassum*. The low magnitude of this parameter as well as locating the magnitude of mean free energy in the range of 8-16 kJ mol^{-1} suggests a weak chemisorption process. Other thermodynamic parameters revealed that this process was spontaneous with increasing randomness at the solid/solution interface during biosorption.

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