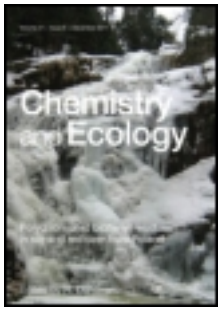

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Biosorption of lead and cadmium using marine algae

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The use of algae (*Ulva fasciata*, green and *Sargassum* sp., brown) to reduce lead and cadmium levels from mono-metal solutions was investigated. The brown algae showed higher efficiency for the accumulation of lead (∼1.5 times) and cadmium (∼2 times) than green algae. The optimum pH value is found to be between 4 and 5.5. Regarding biomass concentration, an increase in metals percentage removal and a decrease in metal uptake capacity coincided with the increase in biomass concentration. All light metals (Ca, Mg and Na) showed a suppressive effect on biosorption capacity. The enhancement of biosorption in the case of NaOH was obvious. The biosorption process (65–90%) occurred within 3 min. Experimental data were in high agreement with the pseudo-second-order kinetic model and Freundlich model for lead and cadmium biosorption using different biosorbents. In the desorption study, 0.2 $mol \cdot L^{-1}$ HCl recorded the best concentration for the elution of metals from the biomass. The biosorption capacity decreased over the four operational cycles for both lead and cadmium. Infrared analysis showed that amino, hydroxyl and carboxyl functional groups provide the major biosorption sites for metal binding. Use of the above-mentioned algae for cheap metal absorbance is considered as one water treatment criterion.

Keywords: biosorption; green algae; brown algae; lead; cadmium; Freundlich isotherm

1. Introduction

As our population and industry have grown, increased levels of treatment prior to the discharge of wastewater have become necessary [1]. Wastewater treatment is becoming ever more critical due to diminishing water resources, increasing wastewater disposal costs and stricter discharge regulations that have lowered permissible contaminant levels in waste streams [2]. Industrial wastewater now contains larger quantities of heavy metals, which are a significant environmental problem because of their mobility in the liquid phase of ecosystems, toxicity to higher life forms and accumulation throughout the food chain. Moreover, these ions are non-degradable and thus persistent, leading to both ecological and health problems [3]. The 'big three' metals, lead, mercury and cadmium, are known for their toxicity and impact, and share negative publicity as major toxins [4].

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Chemical methods for the removal of metals are not economical for treating a large volume of water body with a dilute metal concentration. Biosorption has proven to be quite effective at removing metal ions from contaminated solutions in a low-cost and environmentally friendly manner [5]. Biosorption is essentially the passive or physico-chemical binding of chemical species to biopolymers. The existence of this phenomenon has been reported for a broad range of biomass types such as bacteria, fungi and algae [6]. It is believed that phosphate, carboxyl, amine and amide groups found in carbohydrates, lipids, proteins and other biopolymers of the microbial cell envelope represent the main sites for metal adsorption [7]. Marine algae have been identified as good biosorbents because of their low cost, renewable nature and high metal biosorption capacity [8]. The heavy-metal biosorption characteristics of different marine algae have been studied [9–14]. It was found that the obtained values are often comparable with synthetic chelating resins and there is a similarity between experimental values and theoretical isotherm models.

The principal objective of this study is to investigate the possibility of using marine algae (*Ulva fasciata* and *Sargassum* sp.) for heavy-metal removal from individual metal solutions that contain lead and cadmium. Biosorption properties, as functions of operational conditions (e.g. pH, initial metal concentration, biomass concentration, light-metal interference and rotation speed), were determined. Different modifications of the biomass for the enhancement of heavy-metal removal were tested. A number of experiments were conducted to determine biosorption kinetics, isotherms and desorption. A multicycle biosorption/desorption experiment was performed. The biosorption mechanism was studied using Fourier transform infrared (FTIR) spectroscopy. Finally, application of the biosorption process to waste- and seawater was completed using a binary metals solution of lead and cadmium.

2. Material and methods

2.1. *Biomass preparation*

Green algae (*U. fasciata*) samples were collected from the Alexandria shore during summer 2007 and brown algae (*Sargassum* sp.) were collected from Suez Bay shore during spring 2008. The collected algae were washed with excess tap water and finally with distilled water to remove salt and particulate materials from the surface, dried at room temperature, milled with a blender and sieved to particle sizes ranging from 0.055 to 0.150 mm.

2.2. *Preparation of heavy metals solution*

Individual stock metal solutions of $1\ g \cdot L^{-1}$ of Pb(II) as $Pb(NO_3)_2$ and Cd(II) as $CdCl_2.1.1/2H_2O$ were prepared (analytical grade chemicals). The desired concentrations were prepared through the adequate dilution of stock solution with deionised water. The initial pH was adjusted with concentrated HCl or $1\ mol \cdot L^{-1}$ NaOH. Initial metal concentrations were measured using a Shimadzu atomic absorption spectrophotometer AA6800 with autosampler Shimadzu ASC-6100 (AAS). Samples were diluted before the required analysis to set the calibration linear range.

2.3. *Laboratory biosorption experiments*

2.3.1. *Metal removal efficiency*

Biosorption capacity (q_e), the amount of metal adsorbed per gram of biosorbent, can be calculated at equilibrium in $mg \cdot g^{-1}$ as follows:

$$q_e = (C_0 - C_e)V/m \quad (1)$$

Where C_0 is the initial concentration of metal ions in the solution ($mg \cdot L^{-1}$), C_e is the equilibrium concentration of metal ions in the solution ($mg \cdot L^{-1}$), V is the volume of solution (in litres) and m is the mass of biosorbent applied, in grams.

Metal uptake can also be displayed by the percentage of metal removal given by:

$$\text{Metal removal } (\%) = 100(C_0 - C_e)/C_0 \tag{2}$$

2.3.2. *Factors affecting biosorption*

In this section, the influence of several operational parameters such as pH value, initial heavy metal concentration, biomass concentration, light-metal interference and rotation speed on the biosorption characteristics of metals (Pb and Cd) were assessed using raw *U. fasciata*. The experimental conditions were changed according to the parameter under investigation.

2.3.3. *Test of chemical modification methods*

U. fasciata was treated with 0.1 mol · L^{-1} NaOH, 0.1 mol · L^{-1} HCl and 0.1% formaldehyde solution before use. One gram of dry *U. fasciata* was reacted with 100 mL of chemical solutions for 24 h. The resulting modified biosorbents were then filtered from the mixture, washed with deionised water several times until the washing solution reached pH 7 and dried in an oven overnight at 60 °C.

One gram of the modified biosorbents in 1 L of metal solution was used to remove Pb(II) and Cd(II) in a rotatory shaker at a rotation speed of 150 rounds per min (rpm). The contact time was controlled at 6 h. The metal removal efficiency of different modified biosorbents was determined.

2.3.4. *Time-dependence studies*

One gram of biosorbents was added to 1 L of metal solution at pH 5. The solution was stirred at a constant speed and temperature. Samples were taken at different time intervals of 0, 1, 3, 5, 7, 10, 15, 30, 45, 60, 120, 240 and 360 min, filtered and analysed by AAS.

2.3.5. *Isotherm studies*

Biosorbents (0.1 g) were added to 100 mL of metal solutions with different initial metal concentrations varying from 10 to 750 mg · L^{-1}. The solution was controlled at pH 5, 25 °C and 150 rpm for 6 h.

2.3.6. *Desorption experiments*

In order to remove bound metal ions from the *U. fasciata* biomass, desorption experiments were performed using HCl as a stripping agent. The lead- and cadmium-loaded biosorbents were prepared. To study the effect of different concentrations of desorption agent, 0.1 g of dry metal-loaded biosorbents was mixed with 10 mL of different concentrations of HCl (0.05–1 mol · L^{-1}). A solid-to-liquid value (S/L) of 10 g · L^{-1} was maintained. The eluted metal was determined and the elution efficiency by desorption agent can be defined as follows:

$$\text{Elution efficiency } (\%) = 100(C_s V_s)/(q_e m) \tag{3}$$

Where C_s is the concentration of metal ions in the desorbed solution ($mg \cdot L^{-1}$), V_s is the volume of solution in the desorption (L), m is the mass of biosorbent used in desorption studies (g) and q_e

is defined in Equation (1). The time needed to complete the desorption process was also estimated at different time intervals (0–30 min) using 0.2 mol · L^{-1} HCl.

2.3.7. *Multicycle biosorption/desorption*

Four biosorption/desorption cycle batch experiments were performed to determine the reusability of biomass. The biosorption and desorption experiments were the same as above and conducted for 6 and 2 h, respectively. After each cycle, the biosorbent was washed with deionised water and dried in the oven. The metal solutions were filtrated and analysed.

2.3.8. *FTIR*

The *U. fasciata* biomass was analysed in different forms obtained throughout the biosorption approach (raw, NaOH modified, metal-loaded and metal-desorbed biomass). Spectra were collected using a model Perkin–Elmer spectrometer within the wave number 400–4000 cm^{-1} under ambient conditions.

2.3.9. *Application to waste- and seawater*

The adsorption behaviour of the raw and modified *U. fasciata* in treating wastewater and seawater samples was studied. The wastewater and seawater samples were collected from El-Umum Drain and El-Mex Bay (Alexandria, Egypt), respectively. Owing to the low concentrations of lead and cadmium, quantities of both metals were added as a binary metal solution to obtain 10 mg · L^{-1} of both lead and cadmium. The metal solution was adjusted to pH 5 and filtrated. The biosorption process was performed as mentioned above.

2.3.10. *Kinetic models*

2.3.10.1. *Reaction-based system.* Lead and cadmium adsorption on different biosorbents was analysed using pseudo-first-order and pseudo-second-order kinetics.

The pseudo-first order is given by Ho et al. [15].

$$\log(q_e - q_t) = \log q_e - k_1 t/2.303 \tag{4}$$

Where q_e and q_t (mg · g^{-1}) are the adsorption capacity at equilibrium and time t, respectively. k_1 (min^{-1}) is the rate constant of pseudo-first-order adsorption. When values of $\log(q_e - q_t)$ are linearly correlated with t, we have a good fit for the pseudo-first-order reaction. Values of k_1 and q_e are determined from the slope and intercept of the kinetic model, respectively.

The pseudo-second order is given by Ho et al. [15].

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

Where k_2 (g · mg^{-1} · min^{-1}) is the pseudo-second-order rate constant of sorption.

Plots of t/q_t against t should give a linear relationship from which the values of q_e and k_2 can be determined from the slope and intercept, respectively.

2.3.10.2. *Diffusion-based system.* The most widely intraparticle diffusion equation for biosorption system is given by Weber and Morris [16]:

$$q_t = k_d t^{0.5} \tag{6}$$

McKay and Poots [17] proposed another model for intraparticle diffusion, given as:

$$q_t = X_i + k_d t^{0.5} \tag{7}$$

Where X_i ($mg \cdot g^{-1}$) is the boundary layer diffusion effect and k_d ($mg \cdot g^{-1} \cdot min^{-0.5}$) is the rate constant for intraparticle diffusion. The values of X_i and k_d can be determined from the intercept and slope, respectively.

2.3.11. *Isotherm models*

2.3.11.1. *Langmuir model.* The Langmuir isotherm assumes monolayer coverage of metal ions over a homogeneous sorbent surface. The adsorption of each molecule onto the surface has equal adsorption activation energy, each site can accommodate only one molecule and there is no interaction between neighbouring sorbed molecules or atoms [18]. The isotherm is presented by the following equation:

$$q_e = q_{max} b C_e / (1 + b C_e) \tag{8}$$

Where q_e ($mg \cdot g^{-1}$) is the observed biosorption capacity at equilibrium, q_{max} ($mg \cdot g^{-1}$) is the maximum biosorption capacity corresponding to the saturation capacity (representing total binding sites of biomass), C_e ($mg \cdot L^{-1}$) is the equilibrium concentration and b ($L \cdot mg^{-1}$) is a coefficient related to the affinity between the sorbent and sorbate (b is the energy of adsorption). The linear relationship can be obtained by plotting ($1/q_e$) vs. ($1/C_e$):

$$1/q_e = 1/(b q_{max} C_e) + 1/q_{max} \tag{9}$$

In which b and q_{max} are determined from slope and intercept respectively. The different biosorbents can be compared by its respective q_{max} values which are calculated from fitting the Langmuir isotherm model to actual experimental data.

2.3.11.2. *Freundlich model.* The Freundlich isotherm assumes a heterogeneous surface with non-uniform distribution of adsorption heat over the surface (binding sites are not equivalent) and/or a multilayer adsorption [19]. The mono-component Freundlich isotherm equation is given by:

$$q_e = K_f C_e^{1/n} \tag{10}$$

Where K_f is the Freundlich isotherm constant related to the sorption capacity and n is the constant related to affinity of metal ions on adsorbent. The Freundlich model can be easily linearised by plotting it in a logarithmic form:

$$\log q_e = \log K_f + 1/n \log C_e \tag{11}$$

By plotting $\log q_e$ vs. $\log C_e$, the constant n and K_f can be determined from the slope and intercept, respectively.

2.3.11.3. *Error analysis.* To evaluate the fit of isotherm equations to the experimental data, the sum of square errors squared (SSE) was used. SSE can be defined as [15]:

$$\mathrm{SSE} = \sum [(q_{e(exp)} - q_{e(theo)})^2 / q_{e(exp)}^2] \tag{12}$$

Where $q_{e(exp)}$ and $q_{e(theo)}$ are the experimental and theoretical biosorption capacity respectively. If data from the isotherm models are similar to the experimental data, SSE will be a small value [15].

3. Results and discussion

3.1. *Factors affecting biosorption capacity*

3.1.1. *pH*

The pH value has large effect in biosorption studies, because it influences not only the activity of functional groups in the biomass, but also the metal solution chemistry [20]. At pH values >5.5 for lead and 8.3 for cadmium, the metal will precipitate in the form of metal hydroxides [21]. Therefore, the biosorption capacity of heavy metals was studied at a pH range from 2.0 to 5.5 to avoid metal ions precipitation. The metal biosorption capacity increased remarkably for Pb(II) and Cd(II) over a pH range of 2.0–3.5 until it reached a plateau at pH 4.0. Similar results have been reported previously [22,23]. The pH dependence of metal biosorption can be explained as follows: at low pH, heavy metals and hydrogen ions compete for a place in ligands with an apparent prevailing of hydrogen ions. Consequently, binding sites in the biomass are generally protonated or positively charged, and repulsion occurs between the metal cations and the active groups of the biomass. At higher pH (above the isoelectric point; pH 3.0) [24], binding sites begin to deprotonate which makes different functional groups available for positively charged metal binding.

3.1.2. *Initial heavy metal concentration*

The biosorption capacity of Pb(II) and Cd(II) increased with the initial concentration of both metals up to almost 500 and 180 $mg \cdot L^{-1}$ with biosorption capacities of ~270 and 47 $mg \cdot g^{-1}$ respectively. The developing uptake capacity tends to diminish with further increase in metals concentration (<725 $mg \cdot L^{-1}$) to almost constant saturation levels of 295 and 66 $mg \cdot g^{-1}$ for lead and cadmium, respectively. Effective thrusting force (concentration gradient) increased with the increase in differences in metal ion concentrations on the cell surface and in the bulk solution, which facilitates biosorption [25]. The decrease in the rate of lead and cadmium uptake with further increases in concentration reflects the saturation of available binding sites. This appears to be due to an increase in the number of ions competing for available binding sites in the biomass [26].

3.1.3. *Biomass concentration*

The assessment of metal-binding capacity displayed by metal removal (%) and biosorption capacity ($mg \cdot g^{-1}$) at different concentrations of raw dried *U. fasciata* is illustrated in Figure 1. With regard to metal removal percentage, an increase in biomass concentration from 0.5 to 4.0 $g \cdot L^{-1}$ enhanced lead removal from 42.7 to 75.4%, followed by a decrease to 61.6% at a biomass concentration of 6.0 $g \cdot L^{-1}$. Cadmium removal increased from 43.6 to 73.4% with an increase in biomass concentration from 0.5 to 6.0 $g \cdot L^{-1}$, as shown in Figure 1. A similar trend in metal removal (%) with variations in biosorbent concentrations has been reported for cadmium biosorption by activated sludge [27] and lead biosorption by two bacterial strains [28]. Increased metal removal percentage at higher biomass concentration is simply due to the greater availability of metal binding sites [29].

By contrast, a reduction in biosorption capacity was observed with increasing biomass concentration (Figure 1). Values decreased from 159.1 to 19.1 $mg \cdot g^{-1}$ for Pb(II) and from 68.9 to 9.7 $mg \cdot g^{-1}$ for Cd(II), coinciding with an increase in biomass concentration (0.5–6.0 $g \cdot L^{-1}$). Similar observations have been reported [28,30]. It seems that the highest biosorption capacity was found at the lowest tested biomass concentration (0.5 $g \cdot L^{-1}$). High biosorbent concentrations are known to cause cell agglomeration and a consequent reduction in intercellular distance. This

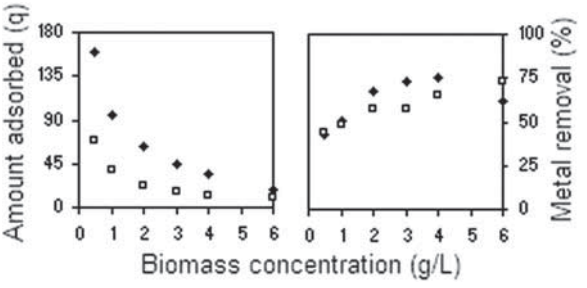

Figure 1. Effect of biomass concentration on biosorption capacity ($mg \cdot g^{-1}$) and metal removal (%) of raw dried *Ulva fasciata*: contact time, 6 h; rotation speed, 150 rpm; temperature, 25 °C; pH 5; $[Pb]_o$, 186.3 $mg \cdot L^{-1}$, $[Cd]_o$, 79.0 $mg \cdot L^{-1}$. (♦) Lead, (□) cadmium.

is reported to produce 'screen effect' among dense layer of cells, leading to the 'protection' of binding sites from metal ions [31].

3.1.4. *Light-metal interference*

Biosorption is mainly used to treat wastewater in which more than one metal would be present. Among such metals, light-metal ions exist in most industrial effluents and they greatly affect the metal sorption potential of biosorbents [32]. Therefore, it was necessary to determine the effects of various concentrations of these cations (Ca^{2+}, Mg^{2+}, Na^{+}) individually on the metal-binding ability of biomass while maintaining constant concentrations of Pb(II) and Cd(II). Calcium ions showed the most pronounced light-metal effect on the biosorption process with a 59.7% and 78.6% reduction in lead and cadmium uptake, respectively, observed at an initial calcium concentration of 200 $mg \cdot L^{-1}$ (Figure 2. Moreover, Na showed the lowest effect on the biosorption process because the reduction in metal uptake was 30.2 and 33.0% for lead and cadmium, respectively (Figure 2). Sodium, a monovalent cation, does not compete directly with covalent binding of heavy metals by the biosorbents and consequently reflects relative lower reduction. The inhibitory effect of Na is more pronounced with weakly bound metals such as Zn or Ni [33]. With respect to Mg, an intermediate effect on lead and cadmium biosorption was estimated (Figure 2). These findings agreed with those of Nabizadeh et al. [34].

Even though a decrease in overall metal-uptake capacity was observed at high concentrations of light metals, cadmium showed more pronounced response to calcium and magnesium than did

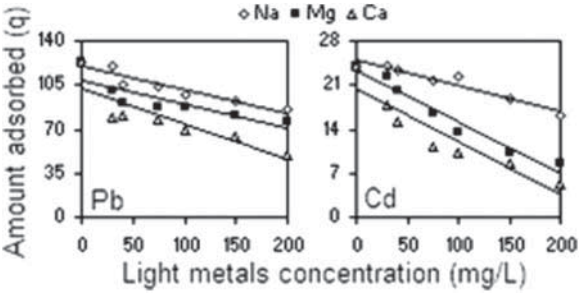

Figure 2. Effect of initial light metals concentration on heavy metals biosorption capacity ($mg \cdot g^{-1}$) of raw dried *Ulva fasciata*: biomass concentration, 1 $g \cdot L^{-1}$; contact time, 6 h; rotation speed, 150 rpm; temperature, 25 °C; pH 5; $[Pb]_o$, 209.2 $mg \cdot L^{-1}$; $[Cd]_o$, 81.4 $mg \cdot L^{-1}$.

lead (Figure 2). The most logical reason for reduced metal uptake is the competition for cellular binding sites on the biomass and the screening effect by the other metal ions [35].

3.1.5. *Rotation speed*

A low uptake of lead and cadmium was estimated at zero rotation. The rotation speed in the studied range (50–250 rpm) is sufficient to ensure that all the cell wall binding sites are readily available for metal uptake by reducing the film thickness to a minimum. Rotation decreases the film thickness and eventually eliminates film resistance [36]. Similar trends in biosorption of cadmium and lead have been reported previously [37,38].

3.2. *Modification methods*

The biomass biosorption capacity can be manipulated by pretreatment of the biomass with alkalis, acid and organic solvent. For this purpose, the biomass was subjected to chemical treatment by sodium hydroxide, hydrochloric acid and formaldehyde. Modification methods apparently alter the manner of metal uptake of raw *U. fasciata.* Figure 3 illustrates the metal uptake values of raw and modified *U. fasciata*. Sodium hydroxide increased the metal-uptake capacity of biomass by 37.4 and 44.6% for lead and cadmium, respectively. The enhancement of biosorption in the case of alkaline treatment could be attributed to the removal of surface impurities, rupture of cell membrane and the exposure of new binding sites for metal biosorption [39]. A decrease in metal uptake of 36.2 and 52.0% for lead and cadmium, respectively was produced by HCl-modified biomass (Figure 3). Hydrogen ions may bind to the negatively charged binding groups on the surface of the biomass and reduce the chances for metal binding [40]. However, a strong enhancement of biosorption capacity for *Aspergillus oryzae* by HCl modification was reported by Huang and Huang [41]. Different behaviour was observed using formaldehyde modified biomass because the biosorption capacity of cadmium and lead maintained similar or decreased levels, respectively (Figure 3). Kapoor and Viraraghavan [42] reported that the biosorption of lead and cadmium by *A. niger* was increased after formaldehyde treatment.

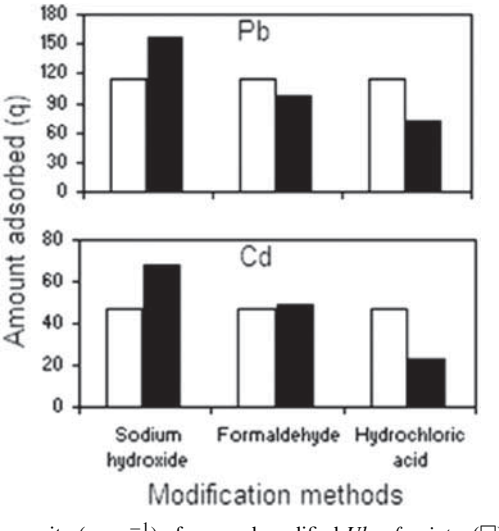

Figure 3. Metals biosorption capacity (mg·g^{-1}) of raw and modified *Ulva fasciata*. (□) Raw biomass, (■) modified biomass.

3.3. *Time-dependence studies*

3.3.1. *Time-concentration profile*

The sorption of metals by different biosorbents occurred in two stages. The first stage, the initial rapid sorption (65–90%) of total lead and cadmium uptake, can be achieved by different biosorbents within the first 3 min. A second, slower stage reached equilibrium within ~4 h. The fast biosorption kinetic is typical for the biosorption of metals involving no energy-mediated reactions in which metal removal from solution is due to metal adsorption onto the biomass surface [43]. This rapid metal uptake has desirable and significant practical importance.

3.3.2. *Kinetic modelling*

The kinetics of lead and cadmium adsorption on different biosorbents was analysed using pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetics models. Conformity between the experimental data and model-predicted values was expressed by the coefficient of determination (R^2 values close or equal to 1). Table 1 gives a description of the main approaches to determine rate equations for sorption systems using different biosorbents.

3.3.2.1. *Reaction-based system.* The kinetics of heavy metals biosorption from wastewater has been studied using mostly pseudo-first-order and pseudo-second-order reaction models. It was found in this study that pseudo-first-order kinetics does not correlate linearly with experimental data over the whole time range with determination coefficient <0.689 for both lead and cadmium, as per Table 1. Experimental data, however, are closely aligned with the second-order equation because the determination coefficient is >0.998 (Table 1). The second-order rate parameter q_e indicated that this model was successful in estimating q_e because the experimental values of q_e agree with $q_{e(theo)}$. Similar results were obtained by Yu et al. [44].

3.3.2.2. *Diffusion-based system.* The relationship between q_t and $t^{0.5}$ was not linear over the whole time range, indicating that there are several processes affecting the adsorption. The initial curved portion of the plot is attributed to boundary layer diffusion effects. The curved portion

Table 1. Kinetic models for lead and cadmium biosorption by *Ulva fasciata* and *Sargassum* sp.

		Ulva fasciata		*Sargassum* sp.	
		Raw		Raw	
Models	Parameters	Pb	Cd	Pb	Cd
First-order kinetic	$q_{e(exp.)}$	171.8	29.3	203.7	45.2
	$q_{e(theo)}$	23.0	5.8	23.7	14.2
	$k_1 \times 10^{-3}$	14.74	9.21	12.21	7.60
	R^2	0.625	0.555	0.643	0.689*
Second-order kinetic	$q_{e(theo)}$	172.4	29.9	204.1	44.3
	$k_2 \times 10^{-3}$	5.25	16.06	5.34	5.79
	R^2	1*	0.999*	1*	0.998*
Intraparticle diffusion kinetic	X_i	153.4	24.4	189.8	36.8
	k_d	1.2	0.3	0.9	0.4
	R^2	0.806*	0.817*	0.869*	0.911*

Notes: $q_{e(exp.)}$, experimental biosorption capacity at equilibrium ($mg \cdot L^{-1}$); $q_{e(theo)}$, theoretical biosorption capacity at equilibrium ($mg \cdot L^{-1}$); $k_1 \times 10^{-3}$, pseudo-first-order rate constant (min^{-1}); $k_2 \times 10^{-3}$, pseudo-second-order rate constant ($g^{-1} \cdot mg^{-1} \cdot min^{-1}$); X_i, boundary layer diffusion ($mg \cdot g^{-1}$); k_d, rate constant for intraparticle diffusion ($mg \cdot g^{-1} \cdot min^{-0.5}$). * Significant at the 1.0% level.

represents intraparticle diffusion controlled by the rate constant k_d. Higher values of X_i depict higher adsorption capacities [43]. The obtained boundary layer thickness for lead and cadmium reflected a high tendency of adsorption, as shown in Table 1.

3.4. *Sorption isotherm*

3.4.1. *Langmuir isotherm*

The fitting of experimental data with Langmuir model was emphasised by high R^2 values of >0.908. NaOH modification of *U. fasciata* and *Sargassum* sp. was intended to improve the maximal uptake capacity (q_{max}) for lead and cadmium as per Table 2. However, a higher affinity coefficient (b) between lead and biosorbents was recorded for unmodified biosorbents, which reflects a good uptake value at a low metal concentrations. For overall biosorbents, the highest affinity coefficient for lead was observed for unmodified *U. fasciata* and the lowest for NaOH-modified *Sargassum* biomass. It seems that chemical modification enhances the content of functional groups but reduces its affinity for metal ions [45]. In the case of cadmium, the affinity coefficient fluctuated with the highest affinity for NaOH-modified *Sargassum* sp. and the lowest for NaOH-modified *U. fasciata*. Functional groups on the surface of the biomass differed from one organism to another, leading to variability in the maximum uptake capacities [46].

Apparently, the q_{max} values of Pb biosorption are higher than those of Cd. By contrast, the affinity of most biosorbents toward each ion follows the order Cd(II) > Pb(II).

3.4.2. *Freundlich isotherm*

The experimental data obeyed the Freundlich model, as confirmed by the high determination coefficient ($R^2 > 0.867$). As can be seen from the results, the n values were found to be greater than unity for different biosorbents for both Pb(II) and Cd(II) (Table 2). According to Kadirvelu and Namasivayam [47], n values between 1 and 10 represent beneficial biosorption.

3.4.3. *Error analysis*

The values of SSE are represented in Table 2. The comparison between different isotherms and experimental data for lead and cadmium using different biosorbents is displayed in Figure 4.

Table 2. Isotherm models for lead and cadmium biosorption by *Ulva fasciata* and *Sargassum* sp.

		Ulva fasciata				*Sargassum* sp.			
		Raw		NaOH modified		Raw		NaOH modified	
Models	Parameters	Pb	Cd	Pb	Cd	Pb	Cd	Pb	Cd
Langmuir isotherm	q_{max}	80.7	43.1	149.3	119.1	119.1	79.4	185.2	94.3
	b	0.221	0.068	0.032	0.060	0.020	0.116	0.012	0.321
	R^2	0.908*	0.927*	0.949*	0.954*	0.963*	0.987*	0.965*	0.987*
	SSE	4.04	0.97	2.01	0.43	1.78	0.44	1.83	0.72
Freundlich isotherm	K_f	11.3	4.2	4.9	13.1	2.2	10.8	1.8	18.1
	n	1.95	2.08	1.20	2.79	1.15	2.43	1.00	2.72
	R^2	0.920*	0.991*	0.951*	0.867*	0.958*	0.957*	0.962*	0.974*
	SSE	1.53	0.06	0.92	1.02	0.58	0.28	0.65	0.22

Notes: *Significant at the 1.0% level. Note: q_{max}, maximum biosorption capacity (mg·g^{-1}); b, affinity coefficient (L·mg^{-1}); SSE, sum of square errors squared; K_f, Freundlich sorption capacity constant; n, Freundlich affinity constant.

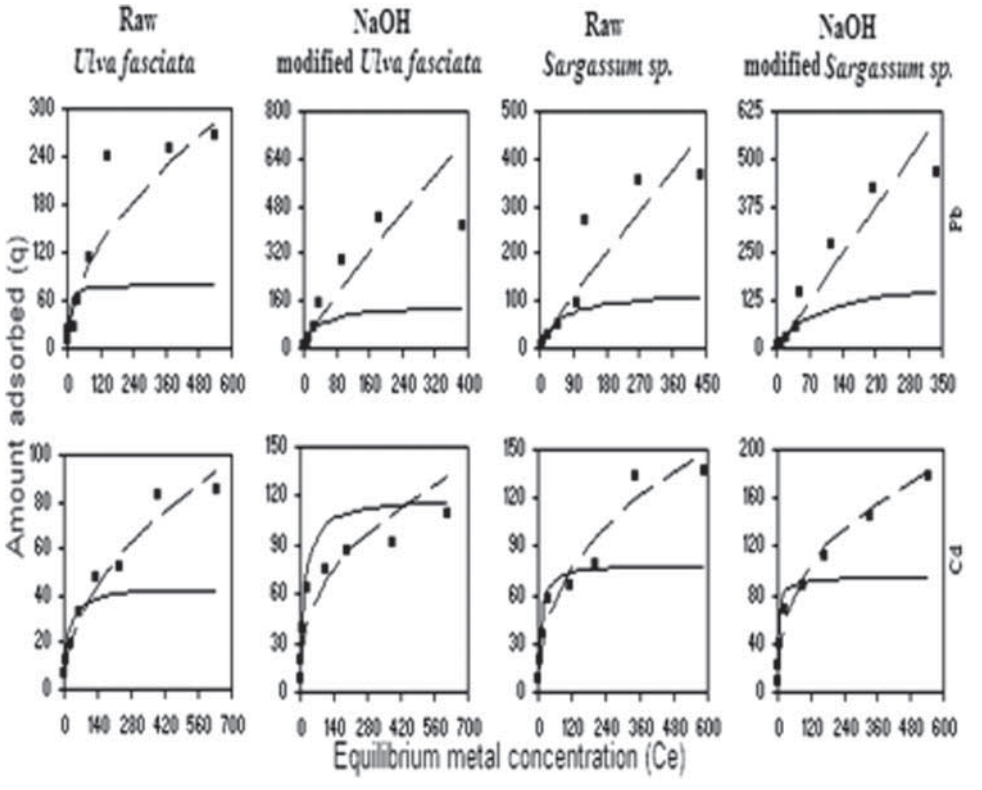

Figure 4. Comparison between different isotherms and experimental data for lead and cadmium biosorption using raw and NaOH modified biosorbents. (■) Experimental data, (—) Langmuir model, (- - -) Freundlich model.

By comparing the values of SSE, it was found that the Freundlich model has lower SSE values than that the Langmuir model, except for cadmium biosorption by NaOH-modified *U. fasciata*. This demonstrates that a heterogeneous surface adsorption occurred with different biosorbents.

3.5. *Desorption experiments*

3.5.1. *HCl concentration*

When increasing the concentration of HCl from 0.05 to 0.2 mol·L^{-1}, the elution efficiency of lead and cadmium was increased. Insignificant changes in the elution efficiency were evaluated with a further increase in HCl concentration >0.2 mol·L^{-1}. Consideration of elution efficiency led to the selection of 0.2 mol·L^{-1} HCl for the recovery of heavy metals from biosorbents.

3.5.2. *Desorption kinetics*

Desorption increased over a few minutes; almost 97% of maximum desorption occurred within 2.5 min. The optimum elution was achieved within ∼15 min for both lead and cadmium. The rapid desorption kinetics elevated the applicability of the biosorption process.

3.6. *Multicycle biosorption/desorption*

Four repeated cycles of biosorption/desorption were performed to estimate the reusability of raw and NaOH-modified *U. fasciata*. The lead uptake capacities and the metal eluted over the four cycles are illustrated in Figure 5. Lead uptake decreased over the four operational biosorption cycles from 93.8 to 6.8 $mg \cdot g^{-1}$ for raw biomass, whereas for modified biomass it declined from 163.9 to 13.6 $mg \cdot g^{-1}$. The eluted lead concentration ranged from 816.8 to 53.4 $mg \cdot L^{-1}$ and from 944.8 to 123.4 $mg \cdot L^{-1}$ for raw biomass and modified biomass respectively.

As shown in Figure 5, the cadmium uptake decreased from 32.0 to 4.7 $mg \cdot g^{-1}$ for raw biomass over the four biosorption cycles, whereas the modified biomass recorded a decrease in cadmium uptake from 49.9 to 6.5 $mg \cdot g^{-1}$. The eluted cadmium concentrations ranged from 141.8 to 36.7 $mg \cdot L^{-1}$ and 151.4 to 36.3 $mg \cdot L^{-1}$ for raw and modified biomass, respectively. The diminishing biosorption of metals over the four cycles was brought about by the destructive effect of stripping agents and the weight loss in the biomass. In addition, resident of metal ions in the biomass (irreversible binding) resulted in a decrease in the number of available binding sites.

The eluted lead and cadmium in the stripping solution are present in high concentrations and can easily be recovered using chemical reduction approaches [48].

3.7. *FTIR*

The spectrum for raw and modified *U. fasciata* was complex due to numerous functional groups on the surface biomass (Table 3).

Different peaks were observed for raw *U. fasciata*. Upon modification of raw *Ulva* sp. with NaOH, a slight shift in the wave number was observed as well as the creation of absorption bands at 2362.3 and 2339.6 cm^{-1}.

FTIR analysis shows the coordination of metals with functional groups present in the modified biomass. The band at 3406.6 cm^{-1} represents pendent O–H and N–H groups in the virgin modified biomass. The shift in the band to 3412.4 and 3434.7 cm^{-1} indicates changes in the hydroxyl and amino group positions during lead and cadmium sorption, respectively. The carbonyl group

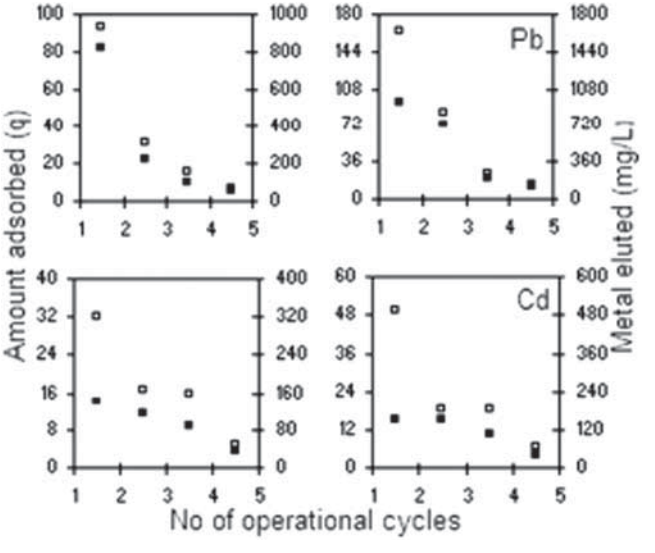

Figure 5. Process performance as a function of four operational cycles for metals biosorption/desorption using raw and NaOH modified *Ulva fasciata.* (□) Metals biosorption capacity, (■) metals elution.

Table 3. Assignments of infrared bands to the corresponding functional groups in *Ulva fasciata*.

Functional groups (γcm^{-1})	*Ulva fasciata*					
	Raw	NaOH modified	Pb loaded	Pb desorbed	Cd loaded	Cd desorbed
γ_{O-H} & γ_{N-H}	3415.9	3406.6	3412.4	3417.6	3434.7	3389.8
γ_{N-H}	–	–	–	1537.2	1555.6	1542.7
$\gamma_{C=O}$	1660.6	1657.3	1652.7	1646.2	1642.9	1653.1
$\gamma_{C=O}$	1442.1	1440.7	1418.1	1450.6	1446.0	1457.3
γ_{C-O} & γ_{C-N}	1109.1	1115.4	1112.6	–	1258.1	1258.3
γ_{C-O} & γ_{C-N}	–	–	–	–	1047.8	–
γ_{C-H}	2924.9	2924.7	2920.8	2920.9	2920.4	2924.1
γ_{C-H}	850.6	854.0	849.2	848.6	850.0	669.3

exhibits dual bands at 1657.3 and 1440.7 cm^{-1} for the virgin modified biomass. Both observed bands were shifted to different extents after metal biosorption to 1652.7–1418.1 cm^{-1} for lead and 1642.9–1446.0 cm^{-1} for cadmium. This shift can be explained by the association of the carboxyl group with metal ions. The band at 1115.4 cm^{-1} is due to C–O and C–N. After the lead ions are adsorbed into the biosorbent, this band was shifted to 1112.6 cm^{-1}. In the case of cadmium loaded biomass, disappearance of this band coincided with the appearance of two bands 1258.1 and 1047.8 cm^{-1} corresponding to C–O and C–N groups. No chemical bonds are destroyed or created because of the presence of lead ions in the biomass, as shown in Table 3. By contrast, cadmium-loaded biomass shows bond creation and destruction. Table 3 demonstrates the appearance of different bands at 2476.9, 1555.6, 1258.1, 1047.8 and 790.4 cm^{-1} and the disappearance of the absorption band at 1115.4 cm^{-1}, indicating the participation of both N–H and O–H groups in the presence of cadmium ions in the biomass.

FTIR spectra of the virgin modified biomass that have undergone lead and cadmium biosorption and elution (0.2 mol·L^{-1} HCl; S/L=10 g·L^{-1}) are given in Table 3. After the desorption process, the absorption bands indicate no restoration of binding sites to their original wave number as observed in virgin modified biomass, indicating the decrease in the biosorption efficiency through biosorption/desorption cycles. Table 3 demonstrates one type of N–H absorption band at 1537.2 and 1542.7 cm^{-1} for lead and cadmium, respectively, with no prior peaks observed for reference spectra associated with the virgin modified biomass.

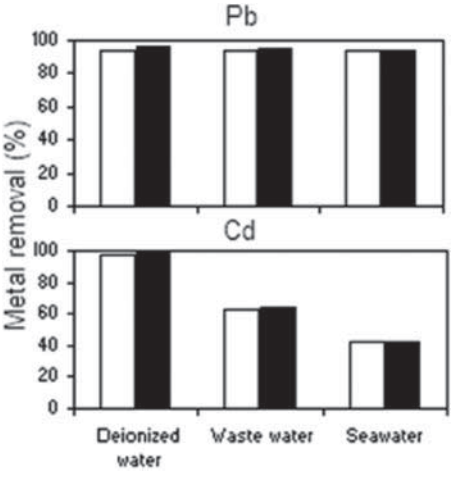

Figure 6. Effect of different waters on metals removal percentage of raw and NaOH modified *Ulva fasciata.* (□) Raw biomass, (■) modified biomass.

3.8. *Application to wastewaters*

Figure 6 compares different types of waters. Both raw and NaOH-modified *Ulva* sp. might be able to take up Pb in nearly identical percentages from different types of waters, whereas Cd showed a lower removal percentage in wastewater and much lower in seawater. The low effect of interfering ions in the case of lead biosorption might be due to the high affinity of binding sites for lead. Cadmium tends to be more affected by interfering ions present in waste water and increases in magnitude in seawater that retards cadmium biosorption.

4. Conclusions

Consistent with this study, the biosorption process was influenced by various parameters such as initial pH, metal ion concentration, light-metal interference, biomass amount and rotation speed. The biosorption capacity of biomass can be increased by pretreatment of the biomass with alkalis. The amino and carboxyl functional groups provide the major biosorption sites for the metal binding (lead or cadmium). Other functional groups such as alcoholic groups also have an important role in metal uptake. It might be concluded that the biosorption process applied for removal of Pb from wastewater using raw or treated *U. fasciata* is an efficient and economic method in which 93.9 and 95.2% of metal could be removed for raw and NaOH-modified biomass respectively. The biosorption of cadmium was relatively lower (62.3–63.5%) due to interference problems. These results agree with the results obtained by Olga et al. [49] who reported that the observed biosorption capacities for cadmium, zinc and lead ions were in the ranges of 23.9–39.5, 18.6–32.0 and 32.3–50.4 $mg \cdot g^{-1}$, respectively, when using *Laminaria hiperborea*, *Bifurcaria bifurcata*, *Sargassum muticum* and *Fucus spiralis* at the Portuguese coast. Kinetic studies revealed that the metal uptake rate was rather fast, with 75% of the total amount occurring in the first 10 min for all algal species.

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