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Biosorption of cadmium(II) and copper(II) from aqueous solution using red alga (*Osmundea pinnatifida*) biomass

H. El Hassouni*, D. Abdellaoui, S. EL Hani, R. Bengueddour
Laboratoire de Nutrition et Santé, biology departement, Faculty of Sciences, Ibn Tofail University, Kenitra, Morocco.

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** Corresponding author. E-mail: hayatelhassouni.pr@gmail.com*

Abstract

The biosorption characteristics of Cd(II) and Cu(II) ions from aqueous solution using the red alga (*Osmundea pinnatifida*) biomass were investigated as a function of pH, contact time, biomass dosage and initial metal concentrations at room temperature. Langmuir and Freundlich models were applied to describe the biosorption isotherm of the metal ions by *Osmundea pinnatifida* biomass. Langmuir model fitted the equilibrium data better than the Freundlich isotherm. The metal sorption capacities increased with increase in the initial metal concentration. The maximum biosorption capacity (q_{max}) of that algae for Cd(II) and Cu(II) was found to be 10.02 and 6.94 mg/g, respectively, at optimum conditions of pH 5.0, contact time of 60 min and biomass dosage of 20 g/L. The sorption mechanisms were characterized using Fourier transform infrared spectroscopy (FTIR). All results showed that *Osmundea pinnatifida* biomass represents a potential for metal ions removal from aqueous solution.

Key words: Biosorption; Cadmium; Copper; Isotherm studies; *Osmundea pinnatifida*

1. Introduction

Heavy metal pollution has become a major issue in many countries because their existence in drinking waters and wastewaters often exceed the permissible standards [1]. Metal ions in the environment are biomagnified in the food chain and are accumulated in tissues; therefore, toxic effects of heavy metals in particular are especially found in animals of higher trophic levels and especially in human. Heavy metals discharged into the aquatic environment will be bound predominantly to suspended materials and finally accumulate in the sediment.

The metals hazardous to human include lead, cadmium, mercury, arsenic, copper, zinc, and chromium. Arsenic can cause skin manifestations, visceral cancers and vascular disease. Cadmium can cause kidney damage, renal disorder and human carcinogen. Mercury can cause mutations and genetic damage. Copper can cause liver damage, wilson disease and insomnia. Lead cause damages the fetal brain, diseases of the kidneys, circulatory system and nervous system. While chromium can cause headache, diarrhea, nausea, vomiting and carcinogenic [2,3]. Heavy metals are often derived from industries such as electroplating and battery factories, metal finishing, and chemical manufacturing [4].

The removal and recovery of heavy metal ions from wastewater involve many techniques such as ion exchange, evaporation, precipitation, membrane separation, etc. However, these common techniques are too expensive to treat low levels of heavy metals in wastewater. In addition, they have some disadvantages such as requiring a large area of lands, a sludge dewatering facility, skillful operators, and multiple basin configurations [5].

Biosorption is an innovative technology using living or dead biomasses to remove toxic heavy metals from aqueous solutions. Various biomasses such as bacteria, yeast, fungi and alga for biosorption of metal ions have been widely used [6]. Among the biological materials marine alga have been reported to have high metal uptake capacity due to its physicochemical characteristics [7]. Seaweed biomass contains various chemical groups attached to the cell wall polysaccharides and

proteins, such as amino, carboxyl and hydroxyl groups [8], which are responsible for the interactions with metal cations via complexation, coordination, microprecipitation and ion exchange [9].
The aim of this work was to study the biosorption of copper(II) and cadmium(II) from aqueous solutions using dead biomass of red alga *Osmundea pinnatifida*. Experimental parameters affecting the adsorption process such as pH, biomass dosage, initial metal ion concentration and contact time, were studied, in batch experiments. The equilibrium adsorption data were evaluated by Langmuir, Freundlich isotherm models, and the equilibriums parameters were evaluated. Cadmium(II) and Copper(II) sorption mechanisms were elucidated using Fourier transform infrared spectroscopy (FTIR).

2. Materials and methods

2.1. Seaweed biomass preparation

The biosorbent of red macroalga, *Osmundea pinnatifida* used in this study was collected on the coastal region of Rabat within North latitude of 34°03′ and a west longitude of 6°46′ with an altitude of 79 m. The beach of Rabat is located 35 km away from Kenitra city, on the left bank of the mouth of Bouregreg River. It is bordered by the Atlantic Ocean to the west. The alga was washed several times with tap water and then deionized water to remove impurities and salts and then dried in an oven at 60°C for 48 h. The dried alga biomass was cut, ground in a mortar and subsequently sieved and the particles with an average size of 0.5 mm were used for biosorption experiments.

2.2. Metal solution preparation

Cadmium and copper solutions were prepared by dissolving a weighed quantity of cadmium nitrate tetrahydrate and copper nitrate-2,5-hydrate respectively in deionized distilled water. Before the adsorption study, the pH of the Cd(II) and Cu(II) solution was adjusted to required value with 1M HCl and 1M NaOH solutions using a handheld pH meter provided with a combined glass electrode [10].

2.3. Seaweed biomass characterization

The untreated and metal-treated seaweed biomass samples were analysed using Fourier transform infrared spectrometer (FTIR). The seaweed biomass samples were encapsulated in KBr. The infrared spectroscopy (IR) spectra were collected using an AVATAR 360 Thermo Nicolet spectrophotometer within the range 400–4000 cm^{-1}.

2.4. Batch biosorption studies

Cadmium and copper sorption experiments were conducted in a shake flask. The seaweed biomass (1 g) was added into a flask containing 50 ml metal solution and the mixtures were agitated on a rotary shaker at 500 rpm for 3 hours. The samples were then filtered using filter paper (Whatman No 4). The residual concentration of cadmium and copper in solution was analyzed using Inductively Coupled Plasma Spectrometry (ICP). The following is the some of the most beneficial characteristics of the ICP source: excellent detection limits for most elements (0.1–100 mg mL^{-1}), high stability leading to excellent accuracy and precision and cost-effective analyses.
The performance of alga biomass for removal of Cd^{2+} and Cu^{2+} ions from aqueous solutions was quantitatively evaluated using amount of metal adsorbed on mass unit of algae biomass (q, mg/g):

$$q = (C_i - C_e).V/M \qquad (1)$$

And the percent biosorption of metal ion (R, %) was calculated as follows:

$$R = (C_i - C_e).100 / C_i \qquad (2)$$

Where: C_i is the initial metal concentration (mg/L), C_e is the residual metal concentration (mg/L), V is the volume of metal solution (L) and M is the mass of biosorbent used in the reaction mixture (g) [11].
Batch experiments were carried out at pH ranging from 2-9 to determine the effect of pH on adsorption process. Effect of initial metal concentration was investigated using initial Cd(II) and Cu(II) concentration varied from 50 to 400 mg/L. In experiments concerning the effect of adsorbent dose, a range of algae biomass samples (5, 10, 20, 40, 60 and 80 g/L) were used. For contact time experiments, the procedure was similar with those presented above, with the difference that the phases were separated after a determined period of contact time. All adsorption experiments were performed at room temperature (20 - 23°C).

3. Results and discussion

3.1. FTIR analysis

Many authors have used Fourier transformation infrared (FTIR) spectroscopy to detect vibration frequency changes in algae [12,13]. FTIR offers excellent information on the nature of the bands present on the surface of the algae and also presents three main advantages as an analytical technique: it is fast, nondestructive, and requires only small sample quantities [14]. Fig. 1a, 1b and 1c show the results of FTIR analysis of unloaded, cadmium-loaded and copper-loaded *Osmundea pinnatifida* respectively at pH 5.

The most specific peaks of *Osmundea pinnatifida* biomass before Copper and Cadmium adsorption are the following: 3433 cm^{-1} (–OH and –NH stretching), 2923 cm^{-1} (–CH_2– stretching), 1655 cm^{-1} (C=O stretching), 1543 cm^{-1} (C=C stretching of aromatic rings), 1384 cm^{-1} (Asymmetric –SO_3 bending), 1261 cm^{-1} (–C–O stretching of ester), 1034 cm^{-1} and 1025 cm^{-1} (–C–O stretching of alcohol) and 801 cm^{-1} (S=O stretching).

The shifting of peaks of *Osmundea pinnatifida* biomass after placed in contact with copper and cadmium respectively, indicate that adsorption of both metals was made.

The main functional groups that are responsible for the metal uptake onto algal biomass were carboxyl, amines, and hydroxyl, mainly those from polysaccharidic material which constitutes most of the algal biomass surface wall [15].

Moreover, these functional groups were deprotonated at pH value greater than their acidic dissociation constants and thus interacted with metal ions [16]. In these figures, the significant changes in the vibrational frequencies indicate that carboxyl, amines, and hydroxyl groups bind with copper and cadmium ions respectively through ion exchange and complexation reactions [13].

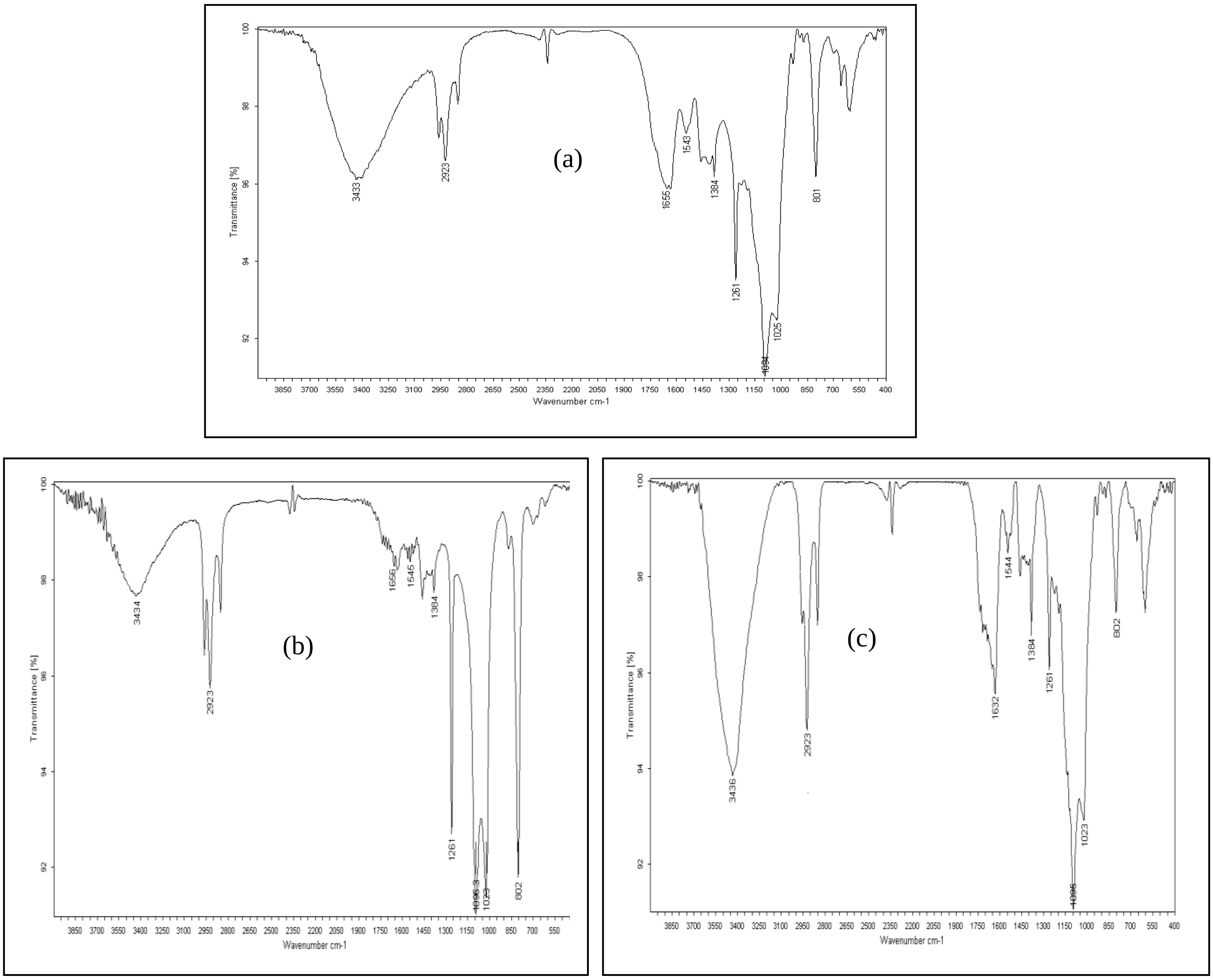

Figure 1: FTIR spectra of unloaded (a), Cd(II)-loaded (b) and Cu(II)-loaded (c) *Osmundea pinnatifida* biomass

3.2. Effect of initial solution pH

The initial solution pH is one of the most important environmental factors in the adsorptive removal of heavy metals from aqueous solutions, because this parameter affects not only the site dissociation, but also the speciation and solubility of metal ions [17]. The effect of pH on the biosorption of Cd(II) and Cu(II) ions onto *O. pinnatifida* biomass was studied by changing pH values in the range, 2–9 and the results were presented in Fig. 2.

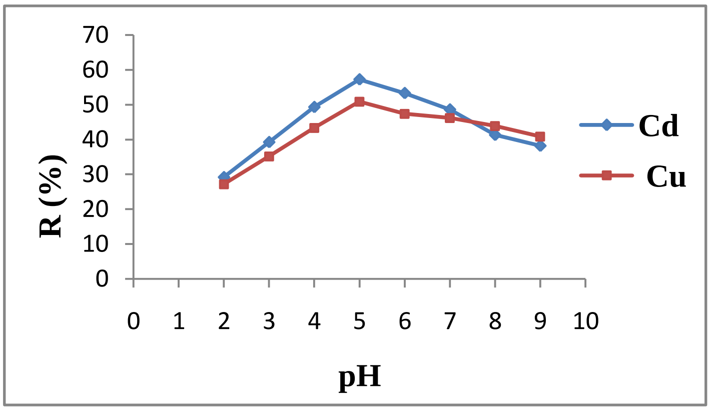

Figure 2: The effect of initial pH on biosorption by *O. pinnatifida* biomass (adsorbent dose 20 g/ L, initial concentration of metals 100 mg/L, contact time 180 min).

The maximum biosorption was found to be 50.89 % for Cu(II) and 57.29 % for Cd(II) ions at pH 5. Therefore, all the biosorption experiments were carried out at pH 5. At higher pH values, the biosorption yield for two metals was dramatically decreased. Increased positive charge (protons) density on the sites of biomass surface at low pH values restricted the approach of metal cations as a result of repulsive force. In contrast, when the pH value increased, biomass surface was more negatively charged and the biosorption of the metal ions with positive charge Cd(II) and Cu(II)) was reached maximum around pH 5. Decrease in biosorption at higher pH (pH > 5) is due to the formation of soluble hydroxilated complexes of the metal ions and their competition with the active sites, and as a consequence, the retention would decrease. Similar findings were reported for other types of biosorbents [18].

3.3. Effect of Contact Time

The effect of contact time on the biosorption of Cu(II) and Cd(II) onto *O. pinnatifida* biomass is shown in Fig. 3. The percent biosorption of metal ion increases with rise in contact time up to 60 min. The equilibrium was reached in 60 min for Cd(II) and Cu(II) and remained nearly constant afterward. The maximum biosorption was found to be 62.90 % for Cd(II) and 69.15 % for Cu(II). Therefore, the optimum contact time was selected as 60 min for further experiments [19].

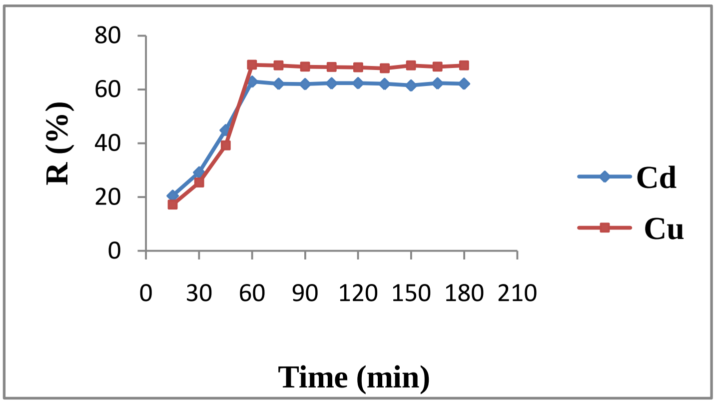

Figure 3: Effect of contact time on the biosorption of Cd(II) and Cu(II) onto *O. pinnatifida* biomass (adsorbent dose 20 g/L, initial concentration of metals 100 mg/L, pH=5).

3.4. Effect of biomass dosage

The effect of biomass dosage on the biosorption of Cd(II) and Cu(II) ions was studied using different biomass dosage in the range, 5- 80 g/L (Fig. 4). Results shows an increase in percentage removal of cadmium and copper ions with the increase in dose of adsorbent up 20 g/L which was 75.36 % for cadmium(II), 70.22 % for copper(II) and then it decrease. Increase in the adsorption with increasing dose of adsorbent is expected due to the increase in adsorbent surface area and the availability of more adsorption sites [20-23]. The decrease in biosorption efficiency with further increase in biomass dose above 1g could be explained as a consequence of a partial aggregation of biomass, which results in a decrease in effective surface area for the biosorption process [24]. On the other hand, uptake capacity or amount of metal adsorbed (q, mg/g) will decrease with the biosorbent dose increased from 5-80 g/L (fig. 4b). This may be due to the fact that some adsorption sites may remain unsaturated during the adsorption process. Hence due to the increased biomass, the amount of active sites unsaturated was increased [25], this can be attributed to an insufficiency of metal ions in solution with respect to available binding [26].

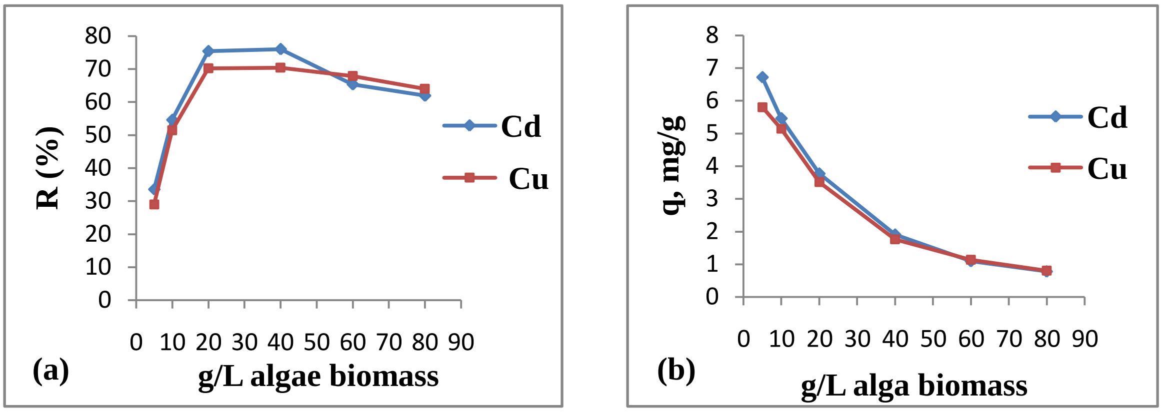

Figure 4: Effect of biomass dosage (a) on percentage Cd(II) and Cu(II) removal, R, and (b) adsorption capacity, q from solution onto *O. pinnatifida* biomass (metal concentration 100 mg/L, PH= 5 and contact time 60 min).

3. 5. Effect of initial metal concentration

The results of heavy metal adsorption at different initial concentration are shown in Fig. 5.The initial concentration of the tow heavy metals had a great effect on biosorption process and as initial concentration increased, biosorption capacity also decreased. In initial concentrations of 50 to 400 mg/L, removal efficiency of cadmium(II) and copper(II) decreased from 75.84 % and 71.64 % to 39.97 % and 29.92 % respectively.

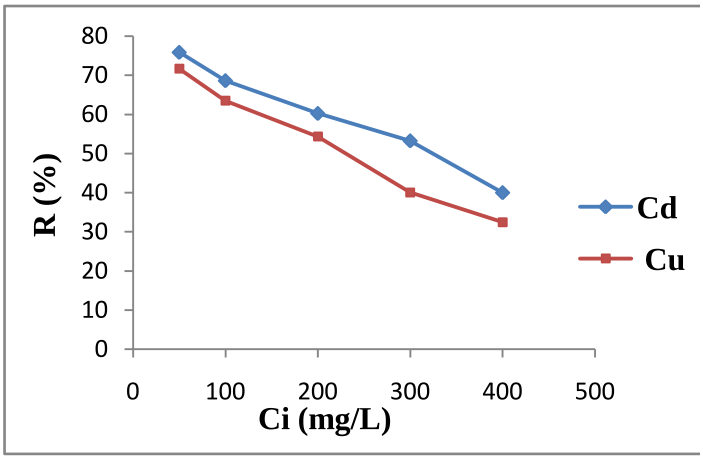

Figure 5: The effect of initial concentration on the percent biosorption of Cd(II) and Cu(II) ions on alga biomass (contact time=60 min, adsorbent dose 20g/L and pH=5).

3.6. Adsorption Equilibrium Study

The sorption capacity of a biosorbent can be described by equilibrium sorption isotherm, which is characterized by definite constants whose values express the surface properties and affinity of the biosorbent [27]. In this study, Langmuir and Freundlich isotherm models were used to describe the adsorption equilibrium. Experimental isotherm data were conducted at room temperature, equilibrium pH=5, dose of biomass 20 g/L and equilibrium time of 60 minutes for different dosages of metals (fig. 6).

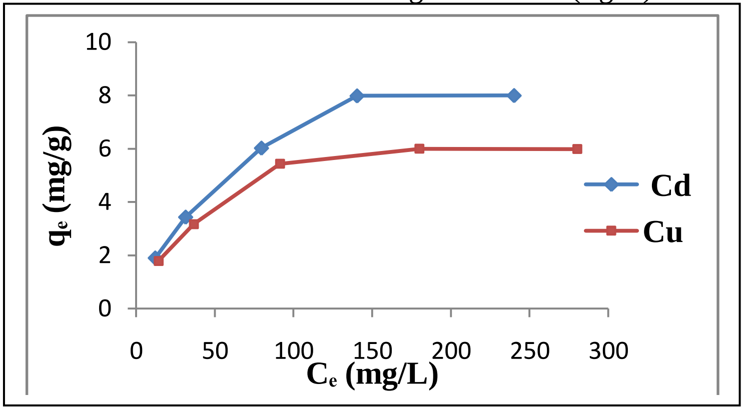

Figure 6: Adsorption isotherm of Cd(II) and Cu(II) on *O. pinnatifida* biomass.

The Langmuir isotherm model [28,29] is based on the monolayer adsorption onto homogeneous surface containing a finite number of accessible sites, and can be used to estimate the maximum adsorption capacity, corresponding to adsorbent surface saturation (q_{max}).The constants of Langmuir model can be determined from linear form, expressed by the relation:

$$\frac{C_e}{q_e} = \frac{1}{K_L . q_{max}} + \frac{C_e}{q_{max}} \qquad (3)$$

Where: q_{max} (mg/g) is the monolayer biosorption capacity of the biosorbent, K_L (L/mg) is the Langmuir biosorption constant relating the free energy of biosorption and C_e (mg/L) is the concentration of metal in solution at equilibrium.

The Freundlich adsorption model [28,29] is refers to the adsorption on highly heterogeneous surface and describe the adsorption process from diluted solutions. The Freundlich constants can be determined from linearized equation:

$$log\ q_e = log\ K_F + \frac{1}{n} log C_e \qquad (4)$$

Where: K_F, $(mg/g).(L/mg)^{1/n}$ is related to the maximum adsorption capacity, and n is a constant that characterized the affinity between adsorbent and metals ions.

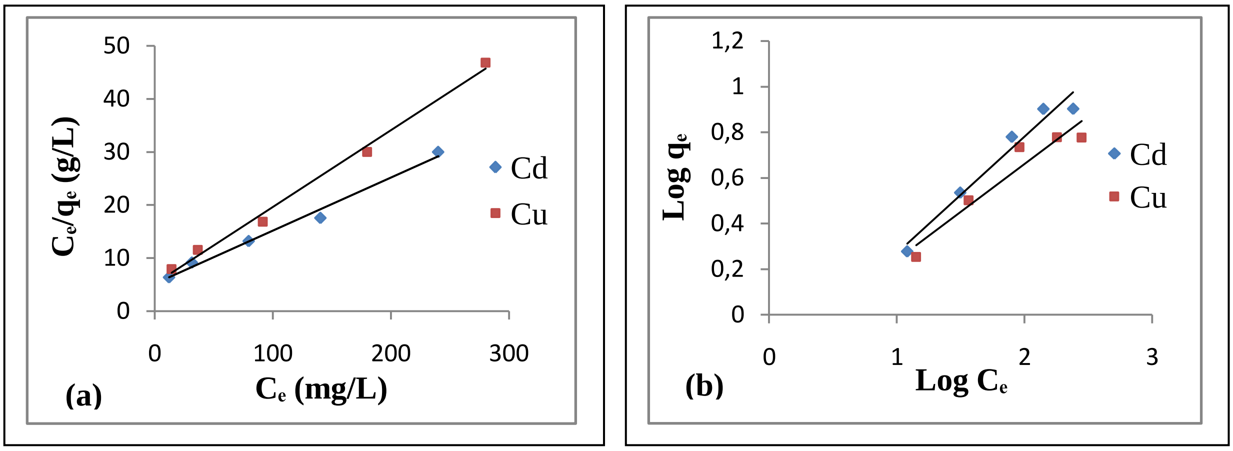

Figure 7: Linear representation of Langmuir (a) and Freundlich (b) isotherm models for Cd(II) and Cu(II) adsorption on *O. pinnatifida* biomass.

Table 1: Adsorption characteristics of Langmuir and Freundlich models on Cd(II) and Cu(II) sorption by means of *O. pinnatifida* biomass

	Langmuir model			**Freundlich model**		
Metals	$q_{max}\ (mg/g)$	$K_L\ (L/mg)$	R^2	$K_F\ (mg/g).(L/mg)^{1/n}$	n	R^2
Cd(II)	10,02	0,019	0,988	0,786	1,957	0,961
Cu(II)	6,94	0,027	0,993	0,835	2,379	0,921

The linearized Langmuir and Freundlich isotherms acquired for Cd(II) and Cu(II) were presented in Fig. 7. The experimental data could better be described by the Langmuir isotherm than the Freundlich isotherm (Table 1). The Langmuir isotherm model fits the adsorption behavior well, indicating monolayer adsorption prevailed. The correlation coefficient $R^2 \geq 0.98$ for the both metals ions. The maximum Cd(II) and Cu(II) uptake values obtained are almost similar to the experimental adsorption capacity. Although K_L is a simple fitting parameter rather than a true adsorption constant, the high value of K_L can indicate a high affinity for adsorption [15]. The good performance of the Langmuir model can also be found in other studies [30-33].

The correlation coefficients R^2 of the Freundlich model are 0.961 and 0.921 for Cd(II) and Cu(II) ions respectively. Compare to the Langmuir isotherm model, the Freundlich model did not fit the adsorption behavior well.

Conclusion

This study focused on the biosorption of Cd(II) and Cu(II) ions onto algal biomass (*Osmundea pinnatifida*) from aqueous solution. The operating parameters, pH of solution, biomass dosage, contact time, and initial metal concentration, were effective on the biosorption efficiency of Cd(II) and Cu(II). The biosorption equilibrium was better described by the Langmuir isotherm model than the Freundlich model. The monolayer biosorption capacity of *O. pinnatifida* biomass for Cd(II) and Cu(II) was found to be 10.02 and 6.94 mg/g ions, respectively. Based on all results, it can be concluded that the *O. pinnatifida* biomass is an alternative biosorbent to treatment wastewater containing Cd(II) and Cu(II) ions, since that alga is natural, abundant available and low cost.

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