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Original Research

Removal of Lead and Cadmium Ions from Water Using Cladophora Biomass

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Abstract

Cladophora biomass has been treated and used for the removal of Lead and Cadmium ions from water, and the characterization of Cladophora biomass by Fourier transform infrared (FTIR) and energy-dispersive x-ray analysis (EDS) indicate the presence of functional groups of different components such as polysaccharides, amino acids, fatty acids and others. Scanning electron microscopy (SEM) and surface area analysis (BET) confirm nonporous algal biomass with small surface area. The parameters affecting metal ions removal from water such as adsorbent-solution contact time, pH of metal ion solution, algal biomass dose and mesh sizes have been studied. Isothermal study has been applied using Freundlich and Langmuir models.

Keywords: Cladophora biomass; water treatment; lead; cadmium; isothermal study

Introduction

Deterioration of water resources due to heavy metal pollutants, such as lead and cadmium and other metals, have become an emerging concern for environmental agencies and governmental authorities around the world. The accumulation and persistence of such heavy metals in the food chain elevate its threat of toxicity, even when found at low concentrations in water [1, 2]. The increment of heavy metals pollution comes from industrial revolution and transportation activities that contribute heavily with heavy metal discharge to the environment.

Different methodologies have been applied to minimize heavy metals pollution in water resources, such as precipitation, coagulation [1], nanomaterials [3] ion exchange [4], adsorption [5], oxidation/reduction [6] and biosorption methods, which is being applied in this study.

In the biosorption method, pretreated natural substances such as seaweed or algae are used as sorbents of pollutants and become a promising alternative to the traditional physicochemical methods used for water treatment [7–12]. The Red Sea area features an important biodiversity hotspot for marine life organisms that is still being explored [13]. New algal species have been recorded in the western shores of Saudi Arabia over the past few decades [14, 15], especially in industrial areas such as Jeddah and Yanbu, where pollution, eutrophication and overfishing occur [16, 17].

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The genus Cladophora is a member of the Ulvophyceae alga class, recorded in shallow waters of Jeddah and Obhor regions on the western shores of Saudi Arabia [14]. *Cladophora* has many species that are difficult to classify due to its high morphological variations, which is greatly affected by age, habitat and temperature [18]. Nevertheless, the green algae species are characterized by its branchy, filamentous, long and setaceous green fronds [14] with thick cellulose layers in its cell wall [19] and growth limitation by both nitrogen and phosphorus [18]. Both micro- and macro- green algae have been used in the area as indicators for heavy metal pollution in wastewater [20] due to their ability to adsorb heavy metals from the surrounding environment [21]. Previous studies have shown that green algae possess a superior capability of heavy metal adsorption among different species collected and analyzed from the Red Sea area [22].

Isotherm Models

The importance of sorption isotherm comes from its representation of how metal ions distribute between the solution and biosorbents at equilibrium [23]. Several isothermal models were used for this purpose, including Langmuir and Freundlich, which are considered the most common models [24]. Selecting a suitable model depends on fitting the experimental data onto model equations, and the correlation coefficient helps by indicating the models that are suitable to fit the data.

Langmuir Isotherm

It is simply represented by the linear equation:

$$\frac{Ce}{Qe} = \frac{1}{XmK} + \frac{1}{Xm}Ce$$

…where C_e (mg/L) is the metal ion concentration at equilibrium, Q_e (mg/g) is the amount of metal ion adsorbed per gram adsorbent, and Xm and k are the Langmuir constants representing the sorption capacity and rate of sorption, respectively [23].

Freundlich Isotherm

The linear equation of the Freundlich model [23] is:

$$\ln Qe = \ln Kf + \frac{1}{n}\ln Ce$$

In this equation; Q_e is the amount of metal ion adsorbed at equilibrium (mg/g) and Ce (mg/L) is the metal ion concentration at equilibrium. KF and n are Freundlich equation constants, where n value indicates how favorable the sorption process and KF represents the sorption capacity of the adsorbent.

In the present study, treated Cladophora sp. are characterized for its ability in lead and cadmium ion removal, considering the parameters affecting the removal of heavy metals from water such as pH, algal biomass dose and mesh size. The adsorption of metal ions on adsorbent is illustrated by the isothermal study.

Experimental

Cladophora Sampling and Sample Preparation

Samples of *Cladophora* sp. green algae were collected from three different locations, heavily contaminated with boat oil and wastewater, at Yanbu in fall 2016. The algae were kept in plastic bags at a cool temperature and sent to the lab. Samples were immediately soaked and washed with tap water and then rewashed three times with distilled water. The biomass was dried overnight in a 45°C oven and ground using a commercial blender. Powdered *Cladophora* biomass was sieved through different mesh sizes <0.125, 0.125-0.212, 0.212-0.5, 0.5-1.0 and 1.0-2.0 mm.

Chemicals and Equipment

All glass and plasticware used were previously soaked overnight in 10% nitric acid, rinsed with distilled water, and finally with deionized water. Cadmium stock solution 1000 ppm was prepared from cadmium nitrate (Sigma-Aldrich). Lead stock solution 1000 ppm was prepared from lead nitrate (Fluka). Nitric acid was bought from Riedel-de'Haën (65%, Puriss, Germany), while AA Cd and Pb elements standards were bought from Panreac (1000 μg mL^{-1}). Metal ions determinations were done using atomic absorption spectroscopy (Agilent Technology, 200 series). 0.1M HNO_3 and 0.2 M NaOH were used to adapt the required pH.

Scanning electron microscopy (SEM) was performed using a NOVA NANO SEM instrument. Elemental analysis was conducted using energy-dispersive X-ray spectroscopy (EDS) of Superscan SSX-550 Shimadsu Company. Fourier transfer infra-red (FTIR) characterization was done by (IR Affinity-1) Shimadsu Company and surface area by BET (Micromeritics ASAP 2020).

Results and Discussions

Algal Biomass Characterization

Fourier Transfer Infra-Red (FTIR)

FTIR spectra (Fig. 1) shows the functional groups that are responsible candidates for metals adsorption such as hydroxyl, carbonyl, sulfonate and carboxylic. According to the FTIR spectra in (Fig. 1), peaks show that algal biomass sample contains a mixture of different components such as polysaccharides, amino acids, fatty acids and others. Bands at 3618

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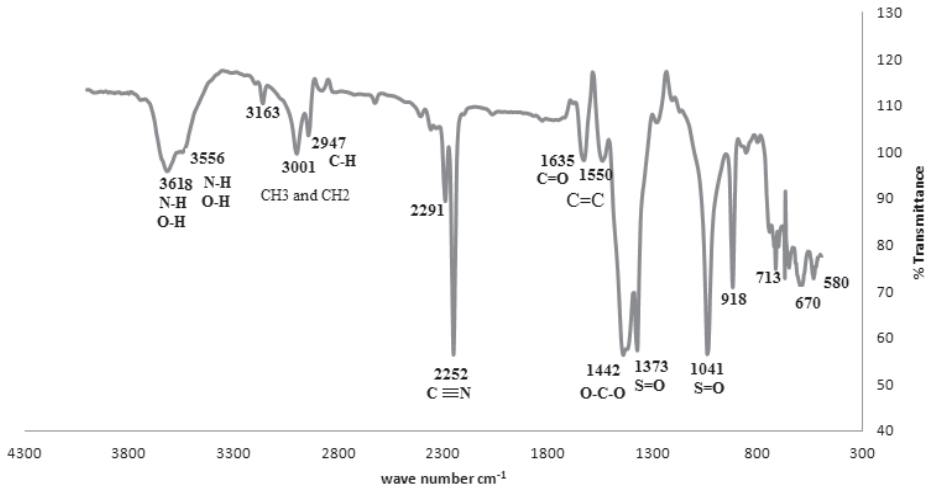

Fig. 1. FTIR spectra of Cladophora biomass.

and 3556 cm^{-1} indicate the presence of O-H and N-H stretching vibrations, whose groups resemble the presence of amino acids [25]. The presence of chlorophyll groups is confirmed by CH3 and CH2 stretching bands at 2947 and 2893 cm^{-1}[25]. 2337, 2360 cm^{-1} stands for C-O and P-H stretching bands of carboxylic group and phosphine, respectively. The sharp peak at 2252 cm^{-1} stand for CN bond of acetonitrile added to the sample for FTIR analysis. The 1635 cm^{-1} peak is due to C=O stretching and 1550 cm^{-1} is due to C=C stretching, which is indicative of the presence of pectin and lignin, respectively. 1373 cm^{-1} 1041 cm^{-1} peaks are stretching bands of S=O related to sulfonamides and sulfone, respectively. The 1442 cm^{-1} shows a peak due to O-C-O symmetric stretching vibration amino acids [26]. The appearance of 670 cm^{-1} reveals C-H bonds of aromatic or vinyl compounds [27]. Strong 920 cm^{-1} stand for P-O-C stretching, and the weak absorption bands observed near 580 and 670 cm^{-1} are due to C-S and C=S stretching vibrations (sulfides) [27].

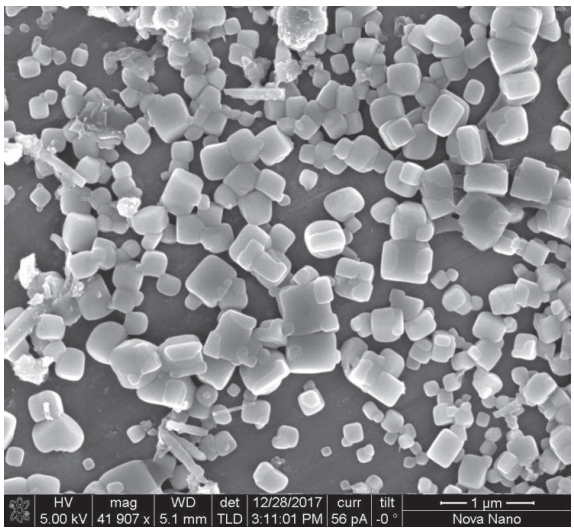

Fig. 2. SEM image of *Cladophora* biomass.

Scanning Electron Microscopy (SEM) and BET (Surface Area)

BET surface area analysis of *Cladophora* showed that the surface area is 1.7062 m^2/g, this small surface area synchronized with the scanning electron microscopy SEM image (Fig. 2), which showed that *Cladophora* algal biomass is nonporous material.

Energy-Dispersive x-ray Analysis (EDS)

EDS analysis results in (Table 1 and Fig. 3) shows the presence of O, C, N, S and P elements, which synchronizes with the FTIR analysis data and illustrates the functional groups that should contain these elements, in addition to other alkali and alkaline earth metals that are usually available in algal biomass [24].

Factors Affecting Metal Ion Removal Study

Effect of Contact Time

The effect of contact time on the removal of metal ions are shown in (Fig. 4). The equilibrium time was around 45 and 60 minutes for Cd and Pb ions, respectively. Generally, the equilibrium time depends on

Table 1. EDS results of Cladophora biomass.

Element	Weight %	Atom %	Element	Weight %	Atom %
O	36.73	40.29	Cl	10.09	4.94
Na	7.76	5.92	N	4.5	4.91
Mg	3.79	2.73	K	2.75	1.23
Al	1.36	0.88	Ca	3.25	1.42
Si	2.1	1.31	Fe	0.59	0.19
S	3.2	1.75	P	0.51	0.34

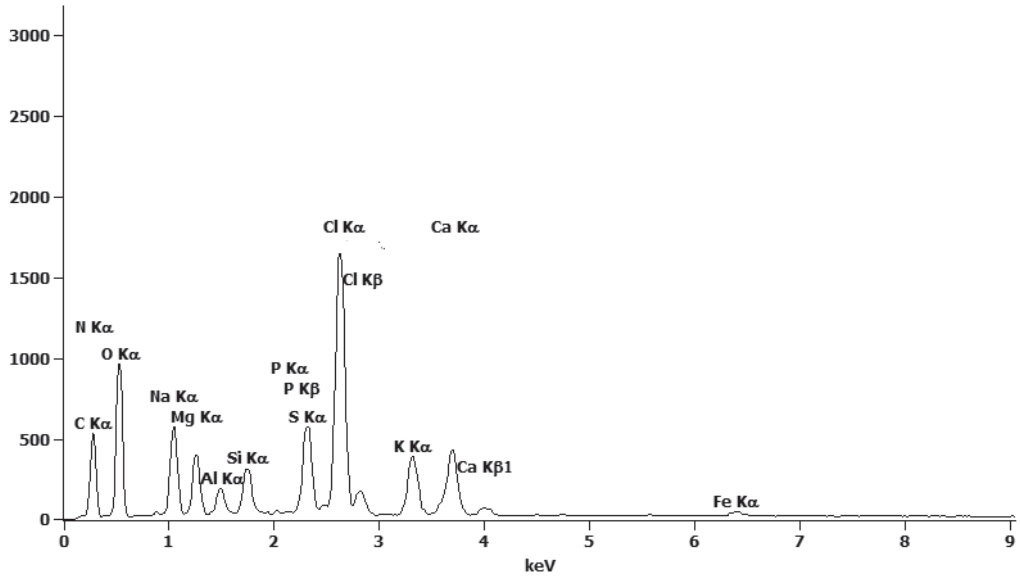

Fig. 3. EDS spectra of Cladophora biomass.

the nature of adsorbent and the availability of sorption sites.

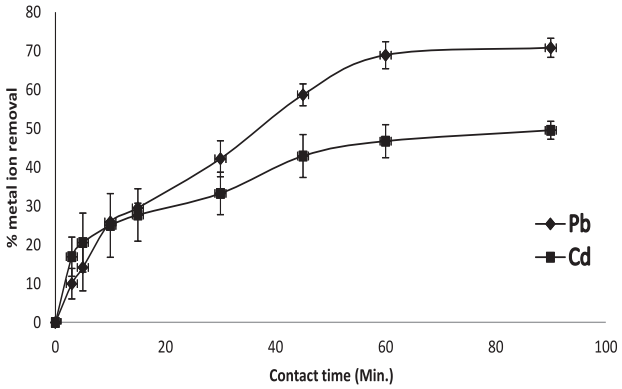

Fig. 4. Effect of contact time on metal ion removal (mean±RSD) (50 mL, 50 ppm) using *Cladophora* (0.2 g, 0.212-0.5 mm) (120 RPM, pH 4, 25ºC).

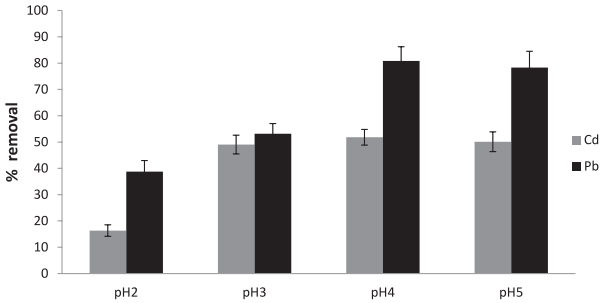

Fig. 5. Effect of solution pH on metal ion removal (mean±RSD) (50 mL, 50 ppm) using *Cladophora* (0.2 g, 0.212-0.5 mm) (120 RPM, 60 Min, 25ºC).

Effect of pH

The effect of metal ion solution pH has been studied in the range pH (2-5), higher pH not applied since higher pH values metal hydroxide form (Fig. 5) shows clearly that metal ion removal increased significantly between pH 2 and 3 for both Cd and Pb ions, and for Cd ion there no significant difference between pH 3, 4 and 5 with removal percentage reaching around 50%. On the other hand, Pb ion removal reaches the value of 80% at pH 4, with no significant difference from pH 5.

Effect of Algal Biomass Dosage

Metal ion removal has been studied by a wide range of algal biomasses, as shown in (Fig. 6), the maximum dose used is 0.75 g, since at higher doses the solution becomes like emulsion. As shown in (Fig. 6), increasing doses have no significant effect on Pb ion removal, which falls in the range of 70 to 80%.

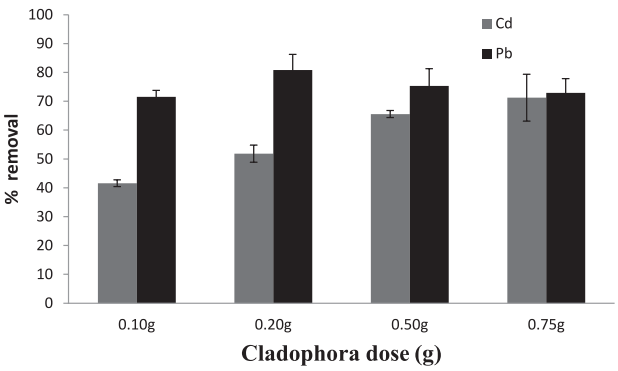

Fig. 6. Effect of Cladophora dose (0.212-0.50 mm) on metal ion removal (mean±RSD) (50 mL, 50 ppm, pH 4) (120 RPM, 60 Min, 25ºC).

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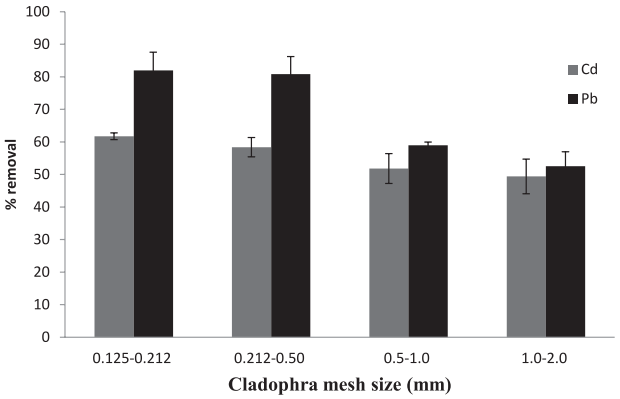

Fig. 7. Effect of Cladophora mesh size (0.20 g) on metal ion removal (mean±RSD) (50 mL, 50 ppm, pH 4) (120 RPM, 60 Min, 25ºC).

For Cd ion removal increases clearly as dose increases, Cd ion removal reaches around 70% for 0.75 g dose.

Effect of Algal Biomass Mesh Size

Using different mesh sizes reflects directly on surface area, which increases as mesh size decreases. Pb ion removal increases with the decrease of mesh size, as shown in (Fig. 7). On the other hand, Fig. 7 shows no significant difference in Pb ion removal between (0.125-0.212 mm) and (0.212-0.50 mm) with around 80%, and Pb ion removal decreases to around 55% at higher mesh sizes. On the other hand, the removal of Cd ion reaches around 60% at mesh sizes less than 0.5 mm, which is higher but not significantly different from mesh sizes 0.5-2.0 mm, which reach around 50% Cd ion removal, as shown in Fig. 7.

Adsorption Isotherms

Adsorption isothermal study has been conducted in order to estimate the maximum adsorption capacity of algal biomass, furthermore isothermal study results predict how metal ions adsorbed on algal biomass surface. Initial metal ion concentrations used were 100 to 500 mg\L.

According to the trend line equations in (Fig. 8) that represents Langmuir and Freundlich for Cd and Pb ions, R^2 values for Langmuir are higher than Freundlich isotherm for both ions, which indicated the metal ions adsorbed as a homogenous monolayer on algal biomass surface. Sorption capacities according to Langmuir isotherm equation are 60.97 and 18.87 mg/g algal biomass for Pb and Cd ion, respectively.

Effect of Contact Time and Adsorption Kinetic Models

(Fig. 9a) shows the effect of contact time between Cladophora biomass and metal ions on the adsorption capacity, and it is clear from Fig. 9a) that the adsorption of both metal ions increases sharply in the first 30 minutes. Furthermore, adsorption reaches equilibrium plateau after one hour contact time for both metal ions.

Adsorption kinetic models were applied to study how metal ions are adsorbed on the Cladophora biomass surface.

The first-order model for physisorption process, in this model the adsorption rate relates to the vacant

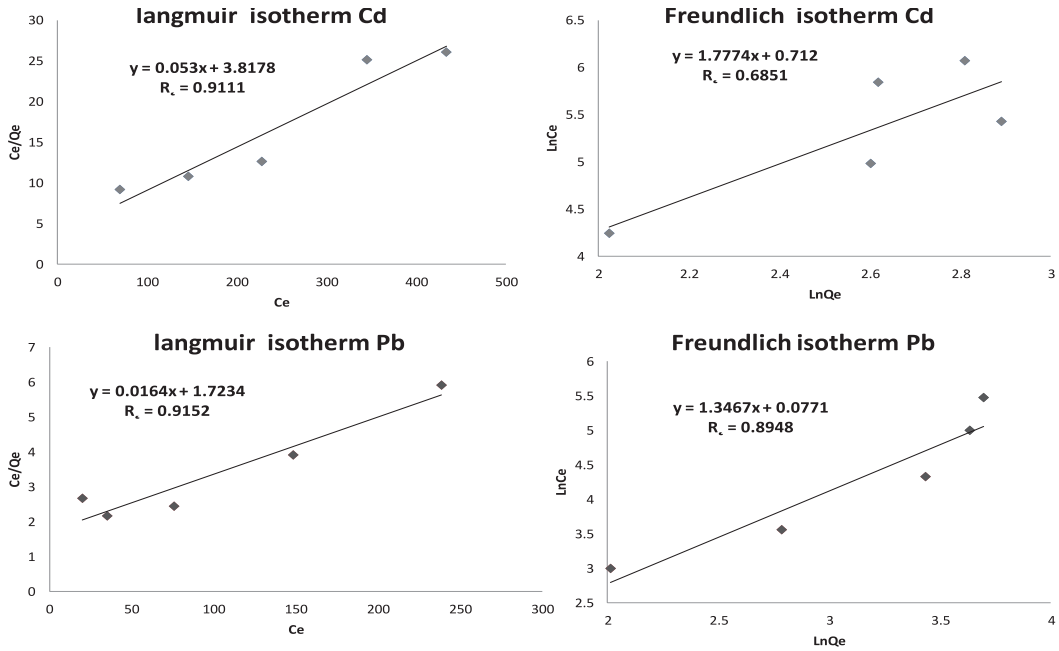

Fig. 8. Langmuir and Freundlich isotherms of Pb and Cd ions, 0.20 g Algal biomass, 50-500 mg/L initial concentration (50mL, pH 4,120 RPM, 60 Min, 25ºC).

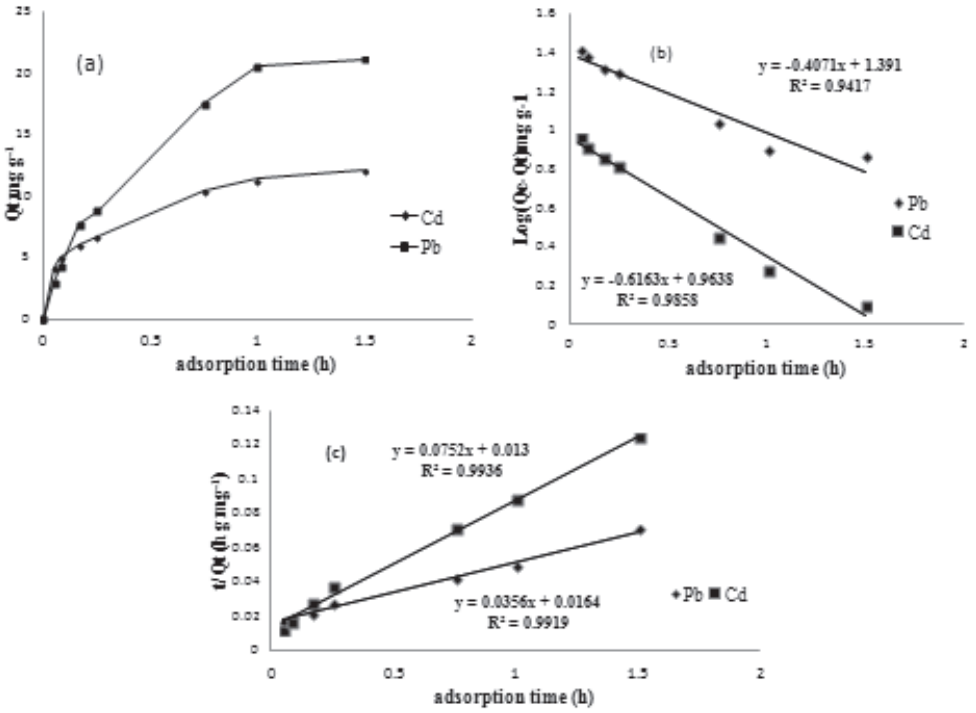

Fig. 9. a) Effect of time on the adsorption capacity of Cd and Pb ions on Cladophora biomass, b) first-order kinetic model, c) second-order kinetic model.

adsorptive sites on the adsorbent [28, 29]. The linear form of this model can be expressed by the following equation:

$$\log (Qe - Qt) = \log Qe - \frac{k1t}{2.303}$$

…where Qt is the adsorption capacity at a certain time t (mg g^{-1}) and k1 is the first-order rate constant (h^{-1}). From the kinetic model data in Table 2 (Fig. 9b) for the adsorption of Pb and Cd ions, it can be concluded that data are poorly fitted to the kinetic model for both metal ions.

However, the second-order kinetic model (Fig. 9c), which expresses the presence of chemisorption process, is related to the difference between the equilibrium vacant adsorptive sites and the occupied sites [28, 30]. The second-order kinetic model can be expressed by the following linear equation:

$$\frac{t}{Qt} = \frac{1}{k2Qe^2} + \frac{t}{Qe}$$

…where k_2 is the second-order rate constant (g $mg^{-1}h^{-1}$). Data shown in Table 2 indicated that the adsorption of Pb and Cd ions fit with the second-order kinetic model, with correlation coefficient (R^2>0.99) for both metal ions. Furthermore, differences between Qe calc and Qe exp are lower in the second-order kinetic model than the first-order kinetic model for Cd ion, counter to Pb ion. According to the fitness of the data to the second-order kinetic model, the adsorption of Pb and Cd ions by Cladophora biomass may be chemisorption.

Conclusion

The ability of *Cladophora* biomass to remove metal ions from water samples reached 80% and 50% of Pb and Cd ions, respectively. Moreover, metal ion removal reached equilibrium within 60 minutes contact time for both Pb and Cd ions. The optimum pH of metal ion solutions is 4 for both Cd and Pb. Nevertheless, algal biomass dose of 0.20 g was shown to be the optimum

Table 2. First- and second-order kinetic models for the adsorption of lead and cadmium ions on Cladophora biomass.

Metal ion	First order kinetic model			
	$Q_{e,\,exp}$ (mg g^{-1})	$Q_{e,\,calc}$ (mg g^{-1})	k_1 ($^{h-1}$)	R^2
Pb	20.56	24.60	0.9375	0.9417
Cd	12.07	9.20	1.419	0.9858
	Second order kinetic model			
	$Q_{e,\,exp}$ (mg g^{-1})	$Q_{e,\,calc}$ (mg g^{-1})	k_2 (g $mg^{-1}h^{-1}$)	R^2
Pb	20.56	28.4	0.0348	0.9919
Cd	12.07	13.33	0.0741	0.9936

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dose for Pb ion removal, and the 0.50 g dose showed better performance for Cd ion removal. Smaller algal biomass mesh sizes showed better Pb ion removal than bigger ones, and no significant effect of mesh sizes for Cd ion removal. Isothermal study results correlate with the Langmuir model for both Pb and Cd ions, which means that metal ions form a homogenous monolayer on algal biomass surface. Adsorption kinetic study showed experimental adsorption capacity of 20.56 and 12.07 mg/g algal biomass for Pb and Cd ions, respectively. Furthermore, kinetic models indicated that both metal ions fit the second-order kinetic model, so adsorption by Cladophora biomass may be chemisorption.

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Conflict of Interest

The authors have not declared any conflict of interest.

References

1. PENG Q., CHEN W., WU L., BAI L. The Uptake, Accumulation, and Toxic Effects of Cadmium in Barnyardgrass (*Echinochloa crus-galli*). Polish Journal of Environmental Studies. **26** (2) 779, **2017**.
2. ABU AL-RUB F.A., El-NAAS M.H., ASHOUR I., Al-MARZOUKI M. Biosorption of copper on Chlorella vulgaris from single, binary and ternary metal aqueous solutions. Process Biochemistry. **41**, 457, **2006**.
3. AMIN M.T., AlAZBA A.A., MANZOOR U. A Review of Removal of Pollutants from Water/Wastewater Using Different Types of Nanomaterials. Advances in Materials Science and Engineering, **1**, 1, **2014**.
4. GAIKWAD R.W., SAPKAL V.S., SAPKAL R.S. Ion exchange system design for removal of heavy metals from acid mine drainage wastewater. Acta Montanistica Slovaca. **15** (4) 298, **2010**.
5. AMRO A.N., YOUSEF R.I., MUSLEH S.M. Chemical Treatment of Jordanian Zeolitic Tuff Using Dimethyl Sulfoxide and Thiourea. Asian Journal of Chemistry. 21, (4) 2973, **2009**.
6. CHAKRABARTI S., CHAUDHURI B., BHATTACHARJEE S., RAY A.K., DUTTA B.K. Photo-reduction of hexavalent chromium in aqueous solution in the presence of zinc oxide as semiconductor catalyst. Chemical Engineering Journal. **153**, 86, **2009**.
7. SAEED A., IQPAL M., AKHTAR M.W. Removal and recovery of lead (II) from single and multi metal (Cd, Cu, Ni, Zn) solutions by crop milling waste (black gram husk). J. Hazard. Mater. **117**, 65, **2005**.
8. GONG R., DING Y.D., LIU H., CHEN Q., LIU Z. Lead biosorption by intact and pretreated spirulina maxima biomass. Chemosphere. **58**, 125, **2005**.
9. ABU AL-RUB F.A., El-NAAS M.H., BENYAHYA F., ASHOUR I. Biosorption of nickel on blank alginate beads, free and immobilized algal cells. Process Biochemistry. **39**, 1767, **2004**.
10. DAVIS T., VOLESKY B., MUCCI A. A review of the biochemistry of heavy metal biosorption by brown algae. Water Res. **37**, 4311, **2003**.
11. DENG Y., WANG L., LUO K., PENG D., JIANG H., JIN C., ZHOU X., BAI L. Screening and identifying a cadmium-resistant fungus and characterizing its cadmium adsorption. Polish Journal of Environmental Studies. **26** (3) 1011, **2017**.
12. AMIN M.T., AlAZBA A.A., AMIN M.N. Absorption behaviors of copper, lead, and arsenic in aqueous solution using date palm fibers and orange peel: kinetics and thermodynamics. Polish Journal of Environmental Studies. **26** (2) 543, **2017**.
13. SONNEWALD M., El-SHERBINY M.M. Editorial: Red Sea biodiversity, Marin Biodiversity. **47**, 991, **2017**.
14. ALEEM A.A. Marine Algae from Obhor, in the vicinity of Jeddah, Saudi Arabia. Bulletin Faculty of Science K.A. U. Jeddah. **2**, 539, **1978**.
15. HARIRI M. The present status of the Red Sea coral reefs between Haql and Yanbu, Saudi Arabia. Life Science Journal. **9** (4) 3852, **2012**.
16. PAIMPILLIL J., SE J., DAHALAWI M. Impact of treated industrial effluents on Yanbu (Red Sea) Coral Reefs and the Efficiency of Coastal Ecosystems Conservation. The Changing Coast. EUROCOAST / EUCC, Porto – Portugal Ed. EUROCOAST – Portugal. 311, **2002**.
17. ERTFEMEIJER P. Seawater intake and outfall channel and thermal pollution study in northern and southern sector at MYAS (Yanbu), Saudi Arabia. Report prepared for the Saudi Consulting Services. **2006**.
18. GESTINARI L.M., SONIA P.M., YOCIE Y.V. Distribution of Cladophora Species (*Cladophorales, Chlorophyta*) along the Brazilian Coast. Phytotaxa. **14**, 22, **2010**.
19. SARGIN I., ARSLAN G., KAYA M. Efficiency of chitosan-algal biomass composite microbeads at heavy metal removal. Reactive and Functional Polymers. **98**, 38, **2016**.
20. Al-HOMAIDAN A., Al-GHANAYEM A., ALKHALIFAH A. Green algae as bio indicators of heavy metal pollution in Wadi Hanifah stream, Riyadh, Saudi Arabia. International Journal of Water Resources and Arid Environments. **1** (1) 10, **2011**.
21. DWIVEDI S. Bioremediation of heavy metal by algae: current and future perspective. J. Adv. Lab. Res. Bio. **3** (3) 228, **2012**.
22. El-NAGGAR M., Al-AMOUDI O. Heavy metal levels in several species of marine algae from the red sea of Saudi Arabia. Journal of King Abdulaziz University: Science. **1**, 5, 1989.
23. HARARAH M.A., Al-NASIR F., El-HASAN T., AL-MUHTASEB A.H. Zinc adsorption-desorption isotherms: possible effects on the calcareous vertisol soils from Jordan, Environ Earth Science. **65**, 2079, **2012**.
24. AHMADY S., MOHAMMADI M. Biosorption of Copper Ions by Marine Brown Alga Fucus vesiculosus, Journal of Biological and environmental science. **5** (15), 121, **2011**.
25. KANNAN S. FT-IR and EDS analysis of the seaweeds Sargassum wightii (brown algae) and Gracilaria corticata (red algae). International Journal of Current Microbiological Application Science. **3** (4), 341, **2014**.

26. MARIA A.P.C., MAYER D.A. POZDNIAKOVA T.A., MAZUR L.P., BOAVENTURA R.A.R., DE SOUZA A.A.U., DE SOUZA S.M.A., VILAR V.J.P. Removal of Metal Ions from a Petrochemical Wastewater using Brown Macro-algae as Natural Cation exchanger. Chemical Engineering Journal. **286**, 1, **2016**.
27. SON E.B., POO K.M., CHANG J.S., CHAE K. Heavy metal removal from aqueous solutions using engineered magnetic biochars derived from waste marine macro-algal biomass. J. Science of the Total Environment. **615**, 161, **2018**.
28. AL HAMOUZ O.C.S., AKINTOLA O.S. Chemistry Removal of lead and arsenic ions by a new series of aniline based polyamines. Process Safety and Environmental Protection. **106**, 180, **2017**.
29. SHEN S., GUISHEN L., PAN T., HE J., GUO Z. Selective adsorption of Pt ions from chloride solutions obtained by leaching chlorinated spent automotive catalysts on ion exchange resin Diaion WA21J. J. Colloid Interface Sci. **364**, 482, **2011**.
30. SHAABAN A.F., FADEL D.A., MAHMOUD A.A., ELKOMY M.A., ELBAHY S.M. Synthesis of a new chelating resin bearing amidoxime group for adsorption of Cu(II), Ni(II) and Pb(II) by batch and fixed-bed column methods. J. Environ. Chem. Eng. **2**, 632, **2014**.

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