REMOVAL OF HEAVY METALS FROM AQUEOUS SOLUTION BY RED ALGA GRACILARIA CORTICATA AS A NEW BIOSORBENT

Abolfazl Teimouri[1], Saeid Eslamian[2], Atefe Shabankare[3]

[1]Department of Chemical Engineering, School of Chemical Engineering, Kherad Institute of Higher Education, Bushehr, Iran

[2]Department of water Engineering, Isfahan University of Technology, Iran

[3]Islamic Azad University, Tehran Medical Branch, Tehran, Iran

ABSTRACT

Red alga *Gracilaria corticata* biosorbent was evaluated as a new biosorbent of heavy metals from aqouse samples. On contacting copper, lead, zinc and cadmium solutions with red alga *Gracilaria corticata* biosorbent, during contact time of 40 min and pH 5. Metal ion biosorption increased as the ratio of metal solution to the biosorbent quantity decreased. Conversely, biosorption increased as the quantity of biosorbent increased to 15 g L^{-1}. The increase in initial metal ion concentration was associated with steep increase in biosorption at lower concentrations, progressively reaching towards plateau at higher metal concentrations. At equilibrium, the affinity of Red alga *Gracilaria corticata* biosorbent to biosorb metals was in the order of zinc> copper> lead> cadmium, which remained the same during the testing of variables of different factors. The biosorption data perfectly fit the Langmuir adsorption isotherms model with 0.985 regression coefficient (r^2) for all the metals. The fit on Freundlich adsorption isotherms model was acceptable but not as good. The metal-loaded Red alga *Gracilaria corticata* biosorbent was completely desorbed with 0.1N HCl. During repeated biosorption–desorption for five cycles, no loss in the efficiency of heavy metal removal from their respective solutions and the metal-loaded biosorbent was noted. The study points to the potential of a novel use of Red alga *Gracilaria corticata* biosorbent.

KEYWORDS: Biosorbent; Red alga *Gracilaria corticata*; Heavy metals; Atomic absorption spectroscopy.

1. INTRODUCTION

Heavy metal pollution of waters has a seriously detrimental impact on people and ecosystems that rely on such bodies of water (Salam et al., 2011; Suzuki et al., 2005). Heavy metals is a general collective term, which applies to the group of metals and metalloids with atomic density greater than 4 g/cm^3, or 5 times or more, greater than water (Otero et al., 2009; Piotrowska-Niczyporuk et al., 2012; Salam et al., 2011; Suzuki et al., 2005; Yu et al., 2001). Water environmental pollution due to toxic heavy metals is a serious environmental and public health issue (Abdel -Aty et al., 2013; Baker et al., 1983; El-Sheekh et al., 2005; Esmaeili et al., 2008; Shaheen et al., 2013). The removal of heavy metals from mine drainage and industrial effluents has become important to maintain water quality standards that are suitable for environmental and human health (Aulio, 1983; Barakat and Kumar, 2015; Kapoor and Viraraghavan, 1998; Otero et al., 2009; Přibyl et al., 2008; Sangi et al., 2008; Xing et al., 2011; Yu et al., 2000).

The main conventional methods used to remove heavy metals from aqueous solution are chemical precipitation, coagulation, ion exchange, solvent extraction and filtration, evaporation and membrane methods (Kapoor and Viraraghavan, 1998; Lazinsky and Sicko-Goad, 1983; Otero et al., 2009; Salam et al., 2011; Wang et al., 2003). However, many of these methods often involves high operational costs, and in many cases, it is insufficient to meet strict regulatory requirements. Adsorption by non-toxic adsorbent has been shown to be a feasible alternative for removing heavy metals from water (Ihsanullah et al., 2016; Wang et al., 2003; Xing et al., 2011; Yu et al., 2000, 2001).

Synthetic adsorbents have extremely high potential for removing metals such as ion exchange resins or chelating resins, but the high cost of these materials limits their application to treatment facilities that process large volumes of wastewater. Therefore, numerous approaches have been studied to develop cheap and effective metal adsorbents. Biosorbents show a high capacity for assimilating heavy metals and are inexpensive materials (Saeed et al., 2005; Suzuki et al., 2005).

Saeed and coworkers have revealed that, among available biosorbent materials, Papaya wood biomass, is highly effective, reliable, and easily available for the removal of heavy metals (Saeed et al., 2005). Among the advantages of this new biosorbent are its rapid and high adsorption–desorption property and reusability in repeated cycles. The

biosorption characteristics and mechanism of metal binding to brown seaweeds have also been understood by Suzuki and coworkers (Suzuki et al., 2005). Moreover, several other biosorbent have been used for removal of heavy metal from aqouse solution. One category of biomaterials on which little attention has been paid as metal biosorbents is the alga that present in seacoast and water. The few reported cases include using of alga's for removal of heavy metal from wastewater (Baker et al., 1983; Esmaeili et al., 2008; Kapoor and Viraraghavan, 1998; Lazinsky and Sicko-Goad, 1983; Piotrowska-Niczyporuk et al., 2012; Saeed et al., 2005; Sangi et al., 2008).

In this study, for the first time, we used nonliving red alga *Gracilaria corticata* biosorbent for the removal of heavy metals from watery samples . Efficient parameters on heavy metal adsorption with red alga *Gracilaria corticata* biosorbent were optimized using one variable at a time method. The Langmuir sorption isotherm model was also applied to the sorptions of copper, lead, zinc and cadmium onto the red alga *Gracilaria corticata* biosorbent. In addition, the removal of heavy metals from artificial wastewater using red alga *Gracilaria corticata* biosorbent was examined.

2. EXPERIMENTAL

2.1. Chemicals and reagents

All chemicals used in this work were of analytical grade, and solutions were prepared using deionized and distilled water. Stock solutions (1000 mg/L) of the target metals were carefully prepared by dissolving $Cd(NO_3)_2$, $CuSO_4:H_2O$, $ZnSO_4:7H_2O$ and $Pb(NO_3)_2$ (Wako Pure Chemical Ind.) in distilled water. They were all stored in the darkness glass container at 2-8 ˚C and working analyte mixtures were daily prepared by dilution with the suitable volume of distilled water. To adjust the pH, 0.1 M HCl and NaOH solutions were used. For all experiments, glassware and bottles were washed with 6.0 M HCl before use and rinsed with distilled water.

2.2. Apparatus

Graphite furnace-atomic absorption spectrophotometry (GF-AAS) Model-240Z (Varian, Inc., Walnut Creek, CA 94598) was used to analyze concentration of heavy metals in samples. The analyzer is equipped with a Varian GTA-120 graphite tube analyzer, a PSD-120 programmable sample dispenser and a Varian UltrAA high intensity boosted hollow cathode lamp that enabled measurement in the range of $\mu g\ L^{-1}$ (parts per billion, ppb) levels in working solutions. Pyrolytically coated Varian graphite partition tubes were used for all GF-AAS analyses. Argon gas (0.3 L min^{-1} flow) was used to protect and purge the graphite tubes during the furnace program procedures, and the data acquisitions were carried out using Varian SpectrAA software. Four standard solution with concentration of copper, lead, zinc and cadmium in linear range of instrument were used to construct each calibration curve. The sampels having concentration of copper, lead, zinc and cadmium beyond linear range of reference were diluted to appropriate concentrations. All measurement were repeated four time.

A pH meter Model 827 pH Lab digital pH meter from Metrohm with combined glass electrode was used for monitoring pH adjustment. Ultrapure water was deionized by an Aqua MAX water purification system from Younglin (Seoul, Korea). Sample solution was stirred using a MR Hei-standard magnetic stirrer from Heidolph (Schwabach, Germany).

2.3. Preparation of Red alga Gracilaria corticata biosorbent

The biosorbent used in this study was Red alga *Gracilaria corticata* that obtained from Iran beaches along Bandar Abbas (Fig. 1). The Red alga *Gracilaria corticata* was cut into small pieces (2 mm × 2 mm), soaked in boiling water for 30 min, thoroughly washed under tap water, and left for 2–3 h in distilled water, changed 3–4 times. The washed Red alga *Gracilaria corticata* pieces were ground into test tube and oven dried at 80 ˚C and used for biosorption studies.

2.4. Biosorption process

weitghed grams of Red alga *Gracilaria corticata* were transferred in centrifuge tube and 15.0 milliliters of sample solution was added to centrifuge tube. The centrifuge tube was then immersed into the ultrasonic water bath. After that the ultrasonic water bath was switched on for 30 min sonication at 40 kHz of ultrasound frequency and 0.138 kW of power at ambinent temperature. Then, the mixture was centrifuged at 3500 rpm for 10 min to complete phase separation. The upper solution, located at the top of the centrifuge tube, was withdrawn using a syringe and collected in glass test tube. Finally, the test tube solution injected into the atomic absorption spectrophotometry for analysis.

Fig. 1. Typical photo from red alga *Gracilaria corticata*.

2.5. Real samples

Three individual watery sample obtained from Persian Gulf, Tajan river and tap water were selected as real sample. The samples were stored at 4˚C.

2.6. Adsorption isotherms models

Analysis of equilibrium data on a specific mathematical equation is of significance for comparing different materials under different sets of operational conditions. The Freundlich and Langmuir adsorption isotherms equations have been extensively applied for this purpose. Langmuir isotherm assumes monolayer adsorption, and is presented by the following equation:

$$q_{eq} = \frac{q_{max}\, b\, C_{eq}}{1 + b\, C_{eq}} \tag{1}$$

where q_{eq} and q_{max} are the equilibrium and maximum uptake capacities (mg/g biosorbent); C_{eq} the equilibrium concentration (mg L^{-1}); b the equilibrium constant. The Freundlich model is presented below:

$$q_{eq} = K_F\, C_{eq}^{1/n} \tag{2}$$

where K and n are Freundlich constants characteristic of the system. Both isotherms consider q_{eq} as a function of the C_{eq}, corresponding to the equilibrium distribution of ions between aqueous and solid phases as the C_i increases. For the calculation of each isotherm constants, C_i was varied (5–30 g L^{-1}) for sorption by the constant weight of red alga *Gracilaria corticata* (20 g L^{-1}) for the sorbate–sorbent contact time of 30 min.

3. RESULTS AND DISCUSSION

3.1. The red alga Gracilaria corticata biosorbent

The red alga *Gracilaria corticata* is one of the common algae of the south of Iran and Persian Gulf coast and occurs predominantly in the lower littoral zone. It also inhabits occasionally in the intertidal rock pools as submerged population. The intertidal algae often get exposed to the atmosphere periodically during low tide regimes and experience an oxidative stress on regular basis with the turning tides.

3.2. Effect of pH on sorption

The adsorption of copper, lead, zinc and cadmium with varying pH using red alga *Gracilaria corticata* biosorbent were examined as shown in Fig. 2. The sorption capacity was evaluated from the residual copper, lead, zinc and cadmium concentration in the solution after mixing the biosorbent. It was determined that the differences in concentrations between control and setups with biosorbent were due to adsorption onto the biosorbent. The sorption capacity of red alga *Gracilaria corticata* biosorbent was low under highly acidic and highly alkaline conditions. The red alga *Gracilaria corticata* biosorbent, which lowered the residual concentration, was the sorbent in the pH range of 6.0–8.0. The chemical form of heavy metals in solution is dependent on pH, and the biosorption is affected by pH. In this study,

however, to obtain information on red alga *Gracilaria corticata* biosorbent for processing a real wastewater, the adsorption characteristics were evaluated from the total metal concentration in the liquid phase.
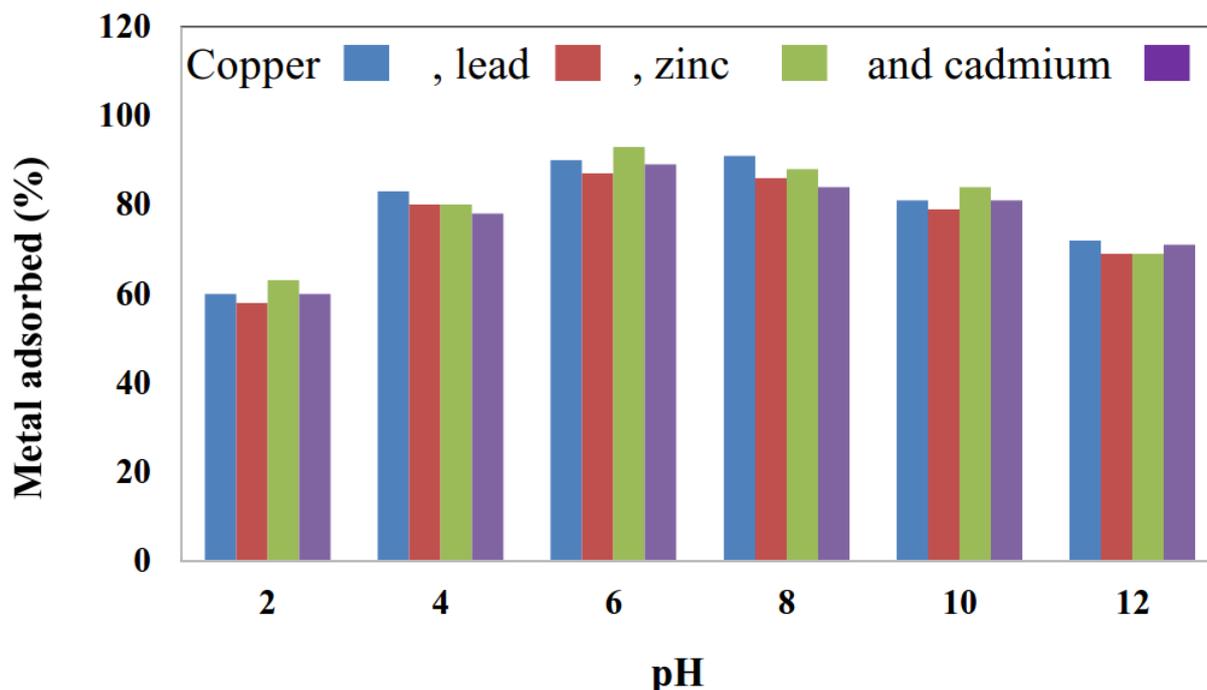

Fig. 2. The effect of pH on the biosorption of copper, lead, zinc and cadmium.

3.3. Effect of biosorbent–biosorbate contact time

The effect of contact time studies on the biosorption of copper, lead, zinc and cadmium ions were performed by contacting 10 mg L^{-1} of the metal solutions at pH 7 with 20 g L^{-1} with red alga *Gracilaria corticata* biosorbent. All the four metals showed a fast rate of sorption during the first 40 min of the sorbate–sorbent contact (Fig. 3). The metal removal from solutions of copper, lead, zinc and cadmium during this rapid phase amounted to 92, 91, 94 and 88% of their respective total sorption at equilibrium in 40 min. The slower phase lasted for the next 20 min. At the contact time of 60 min, the removal of copper, lead, zinc and cadmium, respectively, was 95, 93, 96 and 90%. Further removal of the minor quantities of the metals remaining in solution was not possible, as on the sorbate–sorbent contact for 180 min.

From these observations it was also noted that affinity of *Gracilaria corticata* biosorbent to biosorb the four metals was different. This difference in the maximum uptake level of various metal ions by *Gracilaria corticata* biosorbent has been explained in terms of difference in the ionic size of metals, the nature and distribution of active groups on the biosorbent, and the mode of interaction between the metal ions and the biosorbent. The fast metal uptake by the *Gracilaria corticata* biosorbent may be attributed to it's highly porous and mesh structure, which provides ready access and large surface area for the sorption of metals on the binding sites. The porous structure of the *Gracilaria corticata* biosorbent eliminates the problem of diffusional limitation as would be expected to occur for sorption on *Gracilaria corticata* biosorbent.
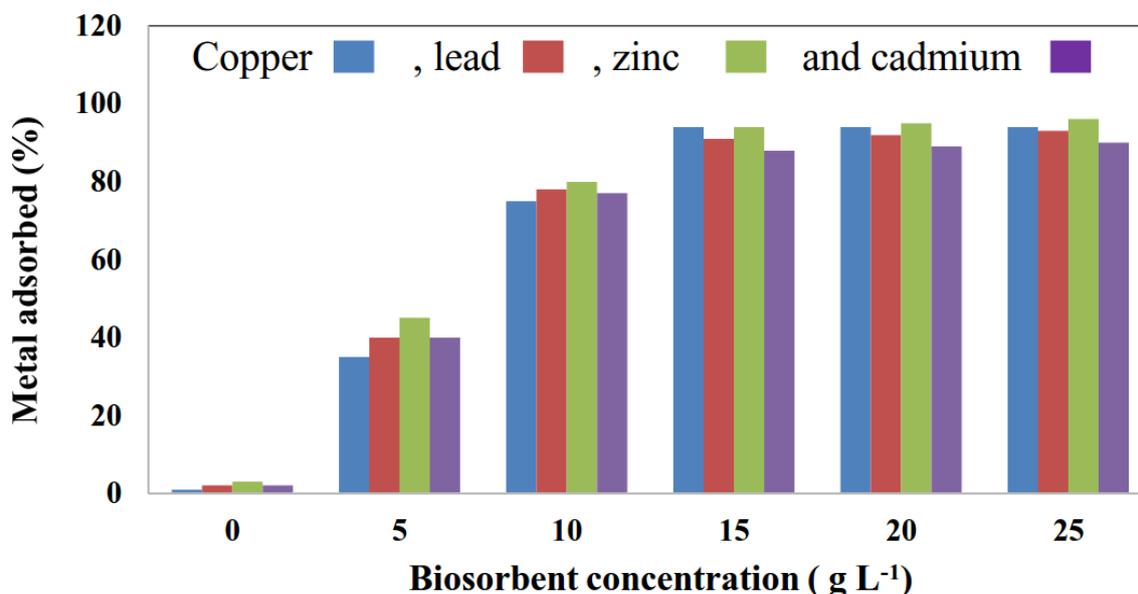
Fig. 3. The effect of biosorbent concentration on the biosorption of copper, lead, zinc and cadmium.

3.4. Relationship of the quantity of red alga Gracilaria corticata with heavy metal

The quantity of red alga *Gracilaria corticata* was varied between 0 to 25 g L^{-1} to determine the optimum quantity of biosorbent needed for maximum sorption. From 10 g L^{-1} metal ion solution, pH 7, the biosorption within 40 min sorbent–sorbate contact time, maximum adsorption was achieved with 15 g L^{-1} red alga *Gracilaria corticata* (Fig. 4). Further increase in the red alga *Gracilaria corticata* weight up to 15 g L^{-1} was associated with marginal, little by little, incremental increases, at each weight change.
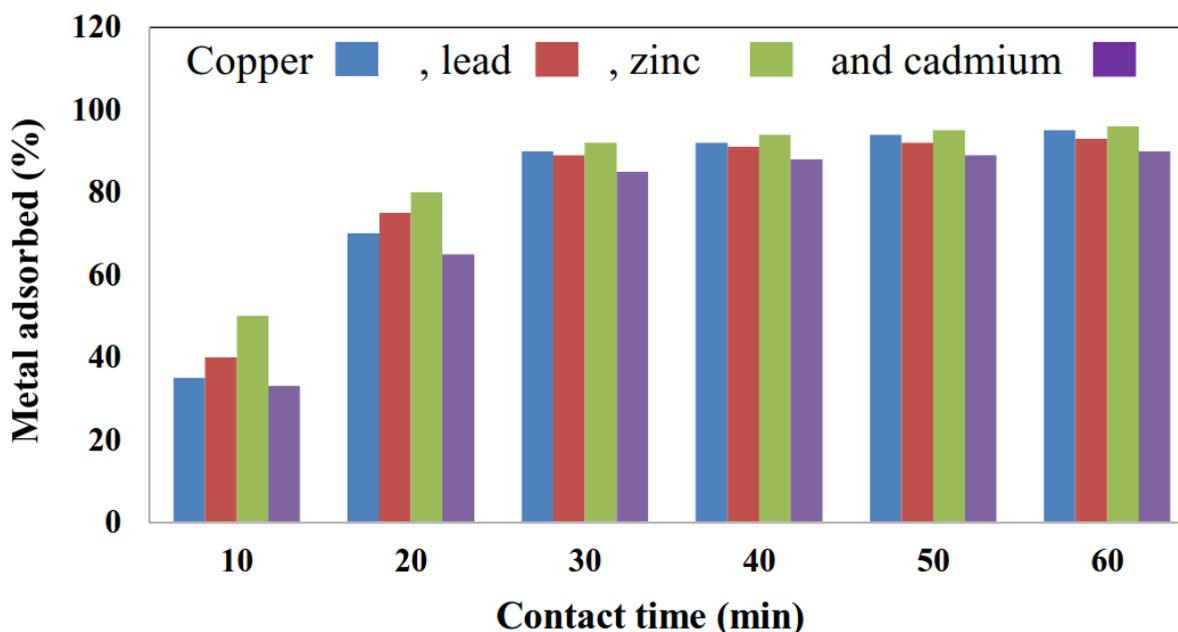

Fig. 4. The effect of contact time on the biosorption of copper, lead, zinc and cadmium.

3.5. Effect of initial metal ion concentration

The metal uptake mechanism is particularly dependent on the initial heavy metal concentration at low concentrations metals are adsorbed by specific sites, while with increasing metal concentrations, the specific sites are saturated and the exchange sites are filled. For determining the sorption capacity of a biosorbent, it is necessary to generate the equilibrium sorption data at various metal solution values. These data are further necessary for modeling on the Langmuir and Freundlich adsorption isotherms, a fit on which is usually used to interpret the efficiency of metal biosorption. For this purpose 5 to 500 mg L^{-1}. After the contact period of 40 min. The results showed that 200 mg L^{-1} has the best adsorption results and used in next experiments (Fig. 5).
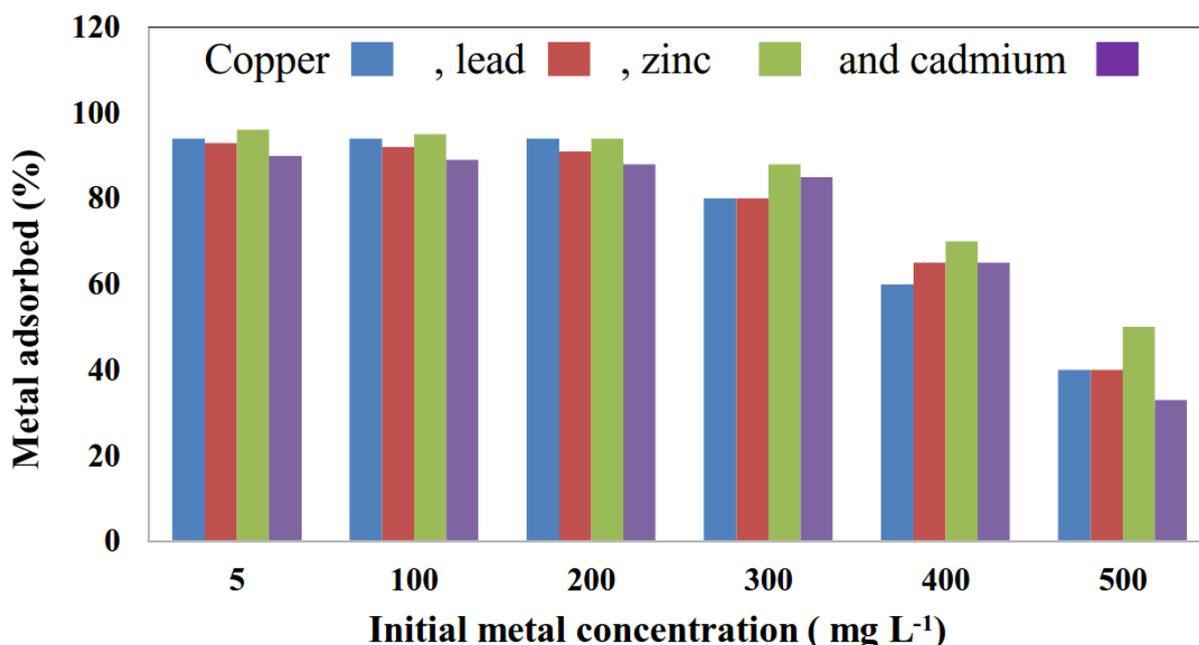

Fig. 5. The effect of initial metal concentration on the biosorption of copper, lead, zinc and cadmium.

3.6. Adsorption isotherms

The Langmuir and Freundlich isotherms describe the adsorption phenomena at the solid liquid interface and the isotherms data were used for the design of adsorption system and to understand the relation between adsorbent and adsorbate. The results of Langmuir model parameters for copper, lead, zinc and cadmium adsorption indicated that the efficacy of adsorption was maximum for zinc and minimum for cadmium as could be noted from the Table 1. The Freundlich copper, lead, zinc and cadmium adsorption capacity increased which was in agreement with the findings of Langmuir isotherms (Table 2). This observation may imply that monolayer adsorption as well as heterogeneous surface conditions could co-exist under the applied experimental conditions and therefore both Freundlich and Langmuir isotherms could be used to model the experimental adsorption data for the four selected heavy metal.

Table 1

Langmuir model parameters for copper, lead, zinc and cadmium adsorption on red alga *Gracilaria corticata* biosobent.

Heavy metal	q_{max} (mmol g^{-1})	b (L $mmol^{-1}$)	r^2
Copper	1.85±0.56	1.21±0.21	0.985
Lead	1.31±0.54	2.19±0.38	0.925
Zinc	2.19±0.21	2.12±0.14	0.945
Cadmium	1.29±0.15	2.18±0.45	0.932

Table 2
Freundlich model parameters for copper, lead, zinc and cadmium adsorption on red alga *Gracilaria corticata* biosobent.

Heavy metal	K_F	1/n	r^2
Copper	2.19	0.376	0.957
Lead	2.21	0.351	0.958
Zinc	1.79	0.412	0.932
Cadmium	2.01	0.521	0.962

4. CONCLUSIONS

The red alga *Gracilaria corticata* has been shown to be highly effective in removing heavy metals from aqueous solution. Among the advantages of this new biosorbent are its rapid and high adsorption–desorption property and reusability in repeated cycles. Furthermore, red alga *Gracilaria corticata* is very cheap, easily available and abundant source of biomaterial generated. The study revealed that this new biosorbent could be used as a tool for the development of low-cost biomaterial-based polishing treatment of heavy metal waste.

REFERENCES

Abdel -Aty A.M., Ammar N.S., Abdel Ghafar H.H., Ali R.K., (2013). Biosorption of cadmium and lead from aqueous solution by fresh water alga Anabaena sphaerica biomass. *J. Advanced Res.* 4(4): 367-374.

Aulio K., (1983). Heavy metals in the green alga Cladophora glomerata as related to shore types in the Archipelago Sea, SW Finland. *Marine Pollution Bull.* 14(9): 347-348.

Baker M.D., Mayfield C.I., Inniss W.E., Wong P.T.S., (1983). Toxicity of pH, heavy metals and bisulfite to a freshwater green alga. *Chemosphere* 12(1): 35-44.

Barakat M.A. and Kumar R., (2015). Synthesis and characterization of porous magnetic silica composite for the removal of heavy metals from aqueous solution. Journal of Industrial and Engineering Chemistry 23, 93-99.

El-Sheekh M.M., El-Shouny W.A., Osman M.E.H., El-Gammal E.W.E. (2005). Growth and heavy metals removal efficiency of Nostoc muscorum and Anabaena subcylindrica in sewage and industrial wastewater effluents. Environ. *Toxicol. Pharmacol.* 19(2): 357-365.

Esmaeili A., Beirami P., Rustaiyan A., Rafiei F., Ghasemi S. and Assadian F. (2008). Evaluation of the marine alga gracilaria corticata for the biosorption of Cu (II) from wastewater in a packed column. *J. Marine Environ. Engineering* 9(1): 65-73.

Ihsanullah Abbas A., Al-Amer A.M., Laoui T., Al-Marri M.J., Nasser M.S., Khraisheh M. and Atieh M.A. (2016). Heavy metal removal from aqueous solution by advanced carbon nanotubes: Critical review of adsorption applications. *Separation Purification Tech.* 157: 141-161.

Kapoor A. and Viraraghavan T. (1998). Removal of heavy metals from aqueous solutions using immobilized fungal biomass in continuous mode. *Water Res.* 32(6): 1968-1977.

Lazinsky D. and Sicko-Goad L. (1983). Ultrastructural modification of three blue-green algae following heavy metal exposure. *Micron and Microscopica Acta* 14(3): 257-258.

Otero M., Rozada F., Morán A., Calvo L.F. and García A.I. (2009). Removal of heavy metals from aqueous solution by sewage sludge based sorbents: competitive effects. *Desalination* 239(1–3): 46-57.

Piotrowska-Niczyporuk A., Bajguz A., Zambrzycka, E. Godlewska-Żyłkiewicz B. (2012). Phytohormones as regulators of heavy metal biosorption and toxicity in green alga Chlorella vulgaris (Chlorophyceae). *Plant Physiol. Biochem.* 52: 52-65.

Přibyl P., Cepák V. and Zachleder V. (2008). Cytoskeletal alterations in interphase cells of the green alga Spirogyra decimina in response to heavy metals exposure: II. The effect of aluminium, nickel and copper. *Toxicol. Vitro* 22(5): 1160-1168.

Saeed A., Akhter, M.W. and Iqbal M. (2005). Removal and recovery of heavy metals from aqueous solution using papaya wood as a new biosorbent. *Separation and Purification Tech.* 45(1): 25-31.

Salam M.A., Makki, M.S.I. and Abdelaal M.Y.A. (2011). Preparation and characterization of multi-walled carbon nanotubes/chitosan nanocomposite and its application for the removal of heavy metals from aqueous solution. *J. Alloys Compounds* 509(5), 2582-2587.

Sangi M.R., Shahmoradi, A., Zolgharnein, J., Azimi, G.H. and Ghorbandoost M. (2008). Removal and recovery of heavy metals from aqueous solution using Ulmus carpinifolia and Fraxinus excelsior tree leaves. *J. Hazardous*

Materials 155(3): 513-522.

Shaheen S.M., Eissa F.I., Ghanem K.M., Gamal El-Din H.M. and Al Anany F.S. (2013). Heavy metals removal from aqueous solutions and wastewaters by using various byproducts. *J. Environ. Management.* 128: 514-521.

Suzuki Y., Kametani T. and Maruyama T. (2005). Removal of heavy metals from aqueous solution by nonliving Ulva seaweed as biosorbent. *Water Res.* 39(9): 1803-1808.

Wang Y.-H., Lin S.-H. and Juang R.S. (2003). Removal of heavy metal ions from aqueous solutions using various low-cost adsorbents. *J. Hazardous Materials.* 102(2–3): 291-302.

Xing, S., Zhao, M., Ma, Z., (2011). Removal of heavy metal ions from aqueous solution using red loess as an adsorbent. *J. Environ. Sci.* 23(9): 1497-1502.

Yu B., Zhang Y., Shukla A., Shukla S.S., Dorris,K.L., (2000). The removal of heavy metal from aqueous solutions by sawdust adsorption — removal of copper. *J. Hazardous Materials* 80(1–3): 33-42.

Yu B., Zhang Y., Shukla A., Shukla S.S. and Dorris K.L. (2001). The removal of heavy metals from aqueous solutions by sawdust adsorption — removal of lead and comparison of its adsorption with copper. *J. Hazardous Materials* 84(1): 83-94.