

Biosorption of Heavy Metals from Aqueous Solution by Green Marine Macroalgae from Okha Port, Gulf of Kutch, India

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Abstract: Recent investigations on the use of biosorbents for heavy metal removal have revealed immense potential of marine algae for biosorption. Five green marine macroalgae namely, *Cladophora fascicularis*, *Ulva lactuca*, *Chaetomorpha* sp, *Caulerpa sertularioides* and *Valoniopsis pachynema* were screened for their metal uptake capacities for Cd, Hg and Pb at various initial concentrations, 20, 40, 60 and 80 mg L⁻¹ and variable contact period of 60 and 120 minutes. Cd reduction was found to be the highest at 20 mg L⁻¹ for all the marine algae except *C. sertularioides*. Hg recorded greater reduction at 20 mg L⁻¹ for *C. fascicularis*, *U. lactuca* and *V. pachynema* whereas; *Chaetomorpha* sp. and *C. sertularioides* exhibited the maximum reduction at 40 and 60 mg L⁻¹, respectively. The highest Pb reduction was observed at 20 mg L⁻¹ for all the algae except *V. pachynema* where it was achieved at 40 mg L⁻¹. With reference to the contact period, all the metals exhibited the highest reduction at 120 minutes for all the studied algae. The values of Freundlich model constants (1/n ranged from 0.112 to 0.773) and Langmuir isotherm indicated good biosorption. The Cd uptake values in the different species were in the order *Chaetomorpha* sp > *C. sertularioides* > *C. fascicularis* > *V. pachynema* > *U. lactuca*. Hg uptake values followed the sequence *C. sertularioides* > *U. lactuca* > *C. fascicularis* > *V. pachynema* > *Chaetomorpha* sp. The metal uptake values for Pb displayed the order *V. pachynema* > *Chaetomorpha* sp > *C. fascicularis* > *U. lactuca* > *C. sertularioides*.

Key words:

INTRODUCTION

Heavy metals released into the environment by technological activities tend to persist indefinitely, circulating and eventually accumulating throughout the food chain, becoming a serious threat to the environment [1]. For more than a decade, researchers have been looking for cheaper and more effective methods to remediate heavy metal-contaminated waters and reduce the growing public health risk. Biosorption is proven to be quite effective at removing metal ions from contaminated solution in a low-cost and environment-friendly manner [2]. The major advantages of biosorption over conventional treatment methods include low cost, high efficiency of metal removal from dilute solution, minimization of chemical and/or biological sludge, no

additional nutrient requirement, regeneration of biosorbent and the possibility of metal recovery [3]. Various biomaterials have been examined for their biosorptive properties and different types of biomass have shown levels of metal uptake high enough to warrant further research [4].

Among the most promising types of biosorbents studied is the algal biomass [5]. These algae possess a high metal-binding capacity [6, 7]. This is due to the presence of various functional groups such as carboxyl, amino, sulphate and hydroxyl groups, which can act as binding sites for metals [8]. Brown algae have been extensively explored worldwide by researchers for their metal biosorption capacities and exhibited promising results. Figueira *et al.* [5] studied the biosorption of Cd by biomass of the brown seaweeds *Durvillaea*, *Laminaria*,

Ecklonia and *Homosira* species presaturated with Ca, Mg and K. Hashim and Chu [9] examined seven species of brown, green and red seaweeds for their abilities to sequester cadmium ions from aqueous solution. Three dried and milled Phaeophyta species, *Ecklonia maxima*, *Macrocystis angustifolia* and *Laminaria pallida* were tested to determine their heavy metal adsorbance capacity [10]. Sheng *et al.* [11] used two locally harvested brown marine algae *Sargassum* sp. and *Padina* sp., for the removal of cations (Cd^{2+} and Cr^{3+}) and anion ($\text{Cr}_2\text{O}_7^{2-}$) from dilute aqueous solutions. Recent investigations on green marine algae have also shown impressive biosorption capacities for the removal of heavy metal [1]. The present study therefore aims to screen five green marine macroalgae for their heavy metal biosorption capacities from aqueous solution at different initial concentrations of the heavy metals Cd, Hg and Pb and at different contact period (time) of dry biomass.

MATERIALS AND METHODS

Collection of Samples: Samples of marine algae *Cladophora fascicularis*, *Ulva lactuca*, *Chaetomorpha* sp, *Caulerpa sertularioides* and *Valoniopsis pachynema* were obtained from Okha Port (22°28'N and 69°05'E) Northwest coast of India. The algae were washed twice with tap water and thereafter with double distilled water thoroughly to remove epiphytes and adhering dirt particles. The washed biomass was first air dried for 24hrs and then at 80°C in an oven to constant weight. The dried biomass was then ground in an analytical mill and sieved through a 2mm mesh size sieve and stored in polyethylene bottles.

Metal Bioadsorption: Batch equilibrium experiments were performed at room temperature in 250 ml Erlenmeyer glass flasks containing aqueous solution of Cd, Hg and Pb of known concentrations, i.e. 20, 40, 60 and 80 mg L⁻¹, prepared using analytical grade cadmium nitrate, mercuric chloride and lead nitrate, respectively. An accurately weighed 100mg portion of biomass was added to each flask and the mixtures were agitated on a rotary shaker at 180 rpm for two different contact periods, 60 and 120 minutes. Controls for each concentration without the addition of heavy metals were also maintained. After the respective contact periods, the solutions were separated from the biomass by filtration and subjected to further analysis. The experiments were conducted in triplicates and the average values were considered.

Instrumentation: Heavy metal content in all the filtrates was quantified using Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES; Perkin Elmer Optima-3300 RL) at Sophisticated Instrumentation Centre for Applied Research and Testing (SICART), Vallabh Vidya Nagar, Gujarat, India. The amount of metal sorbed at equilibrium, q (mg g⁻¹), which represents the heavy metal uptake was calculated from the difference in metal concentration in the aqueous phase before and after adsorption according to the following equation [12]:

$$q = V(C_i - C_{eq})/W$$

where V is the volume of metal solution (L), C_i and C_{eq} are the initial and equilibrium concentration of metal in solution (mg L⁻¹), respectively and W is the mass of dried alga (g). The percentage reduction of the heavy metals by all the macroalgae was estimated.

Adsorption Isotherms: Adsorption from aqueous solutions at equilibrium is usually correlated by Freundlich and Langmuir isotherm. Freundlich equation model is expressed as:

$$q = K C_{eq}^{1/n}$$

In this model, K (L g⁻¹) and $1/n$ are the constants to be determined from the data. For a good adsorbent, $0.2 < 1/n < 0.8$ and a smaller value of $1/n$ indicates better adsorption and formation of rather strong bond between the adsorbate and adsorbent.

Langmuir equation is expressed as:

$$q = q_{\max} b C_{eq} / (1 + b C_{eq})$$

where q_{\max} (mg g⁻¹) is the amount of adsorption corresponding to complete monolayer coverage, i.e., the maximum adsorption capacity and b (L mg⁻¹) is the Langmuir constant.

RESULTS AND DISCUSSION

Five green marine algae *Cladophora fascicularis*, *Ulva lactuca*, *Chaetomorpha* sp, *Caulerpa sertularioides* and *Valoniopsis pachynema* were screened for their metal uptake potentials for Cd, Hg and Pb at various initial concentrations from 20 to 80 mg L⁻¹ and variable contact period. The Cd uptake values (q) for *C. fascicularis* ranged between 4.08 to 18.78 mg g⁻¹, Hg values were between 4.31 to 21.02 mg g⁻¹ and

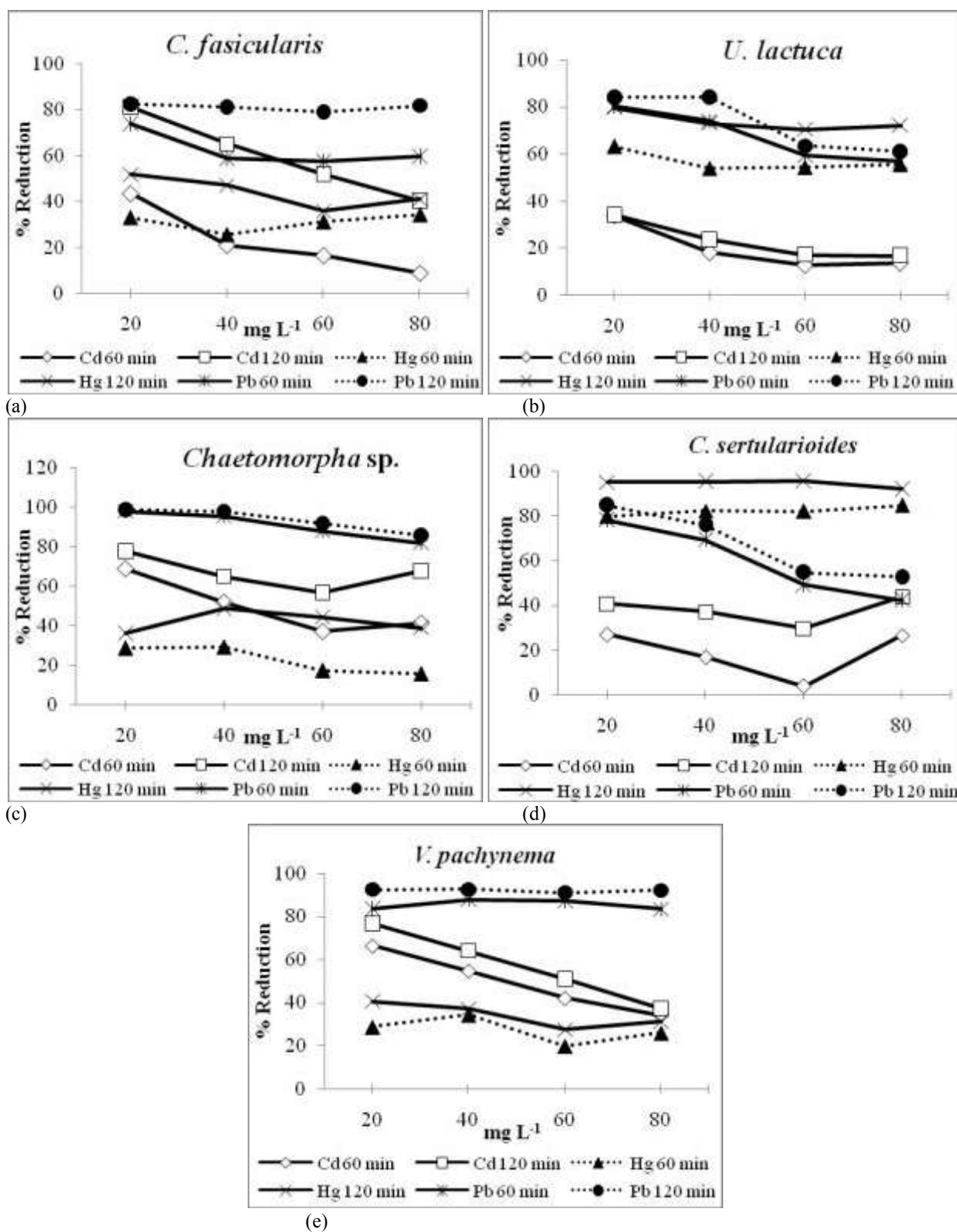


Fig. 1(a-e): Percentage reduction of cadmium, mercury and lead by dried biomasses of various green marine macroalgae

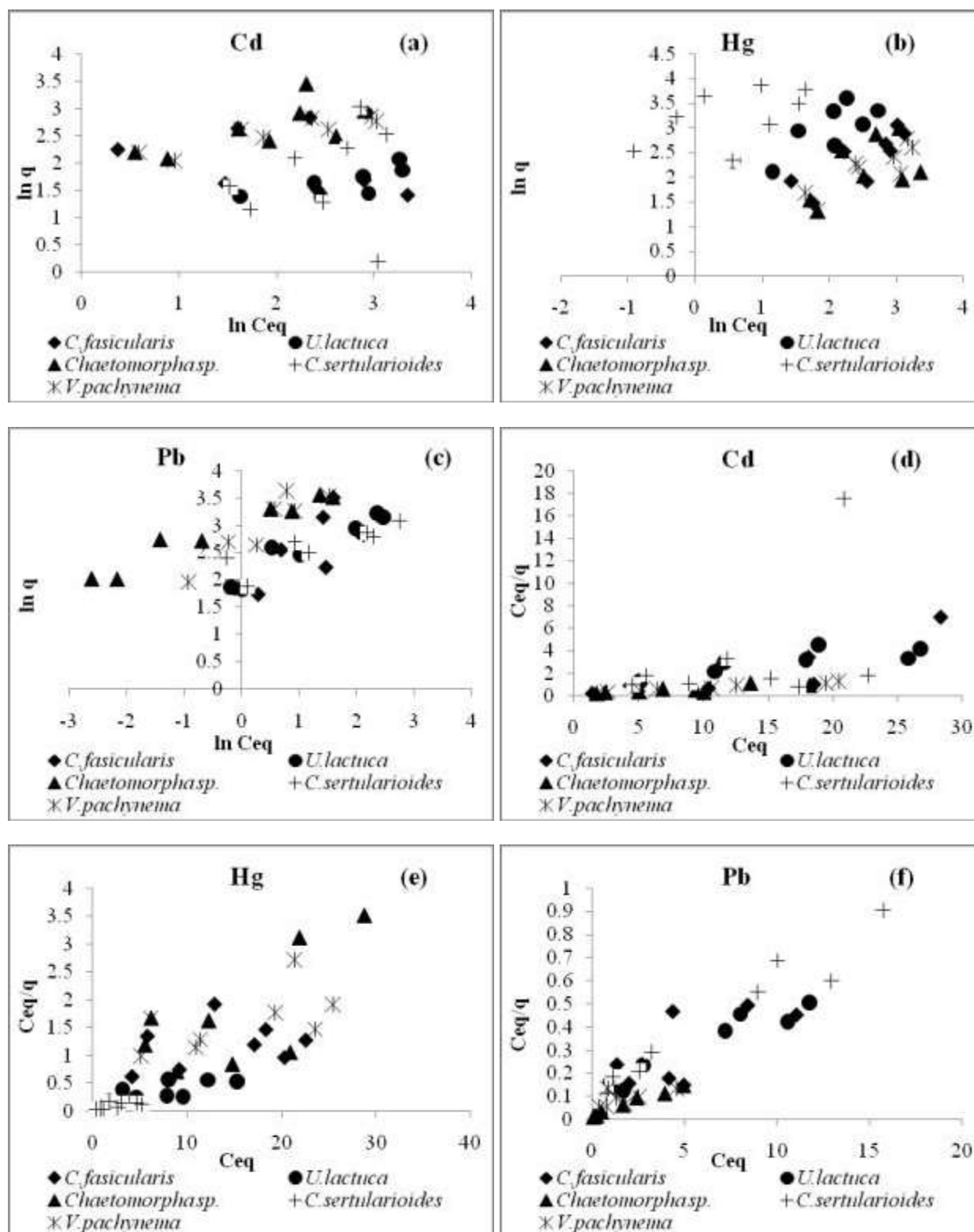


Fig. 2: Freundlich plots for metal removal (a) Cd (b) Hg (c) Pb and Langmuir plots for metal removal (d) Cd (e) Hg (f) Pb by dried biomass of green marine macroalgae

Pb uptake values ranged from 5.68 to 33.53 mg g⁻¹. The Cd uptake values for *U. lactuca* fluctuated from 3.89 to 7.84 mg g⁻¹. For Hg, the values varied from 8.24 to 37.11 mg g⁻¹ and Pb uptake values ranged between 6.19 to 25.07 mg g⁻¹. For *Chaetomorpha* sp, the Cd uptake values were recorded between 7.98 to 31.55 mg g⁻¹, Hg values between 3.73 to 20.02 mg g⁻¹ and Pb values between 7.52 to 35.08 mg g⁻¹. *C. sertularioides* exhibited Cd uptake values in the range of 1.19 to 20.51 mg g⁻¹, Hg uptake values varied from 10.42 to 47.45 mg g⁻¹ and Pb values fluctuated from 6.03 to 21.58 mg g⁻¹. *V. pachynema* displayed Cd values (q) in the range of 7.69 to 17.31 mg g⁻¹, Hg values from 3.73 to 16.11 mg g⁻¹ and Pb uptake values from 6.42 to 37.71 mg g⁻¹. The Cd uptake values in the different species were in the order *Chaetomorpha* sp > *C. sertularioides* > *C. fascicularis* > *V. pachynema* > *U. lactuca*. Hg uptake values followed the sequence *C. sertularioides* > *U. lactuca* > *C. fascicularis* > *V. pachynema* > *Chaetomorpha* sp. The metal uptake values for Pb displayed the order *V. pachynema* > *Chaetomorpha* sp > *C. fascicularis* > *U. lactuca* > *C. sertularioides*.

Percentage reduction for heavy metals for all the marine algae showed considerable differences with reference to various initial concentration and variable contact period (Fig. 1). *C. fascicularis* exhibited maximum reduction at 20 mg L⁻¹ for all the metals at contact time of 120 minutes. The algae also showed higher removal of heavy metals at greater contact period i.e. at 120 minutes. A similar trend was observed for *U. lactuca* which also showed greater reduction at initial concentration of 20 mg L⁻¹ and contact period of 120 minutes for all the three metals. *Chaetomorpha* sp also followed a similar pattern with the highest metal reduction at 20mg L⁻¹, the only exception being Hg which exhibited maximum reduction at 40 mg L⁻¹ for the contact time of 120 minutes. *C. sertularioides* recorded greater reduction at 80 mg L⁻¹ for Cd whereas; Hg exhibited higher reduction at

60 mg L⁻¹ (95.67%) and Pb inversely showed higher reduction (85%) at 20 mg L⁻¹. In reference to contact period all the three metals revealed highest reduction at 120 minutes. For, *V. pachynema*, highest Cd and Hg reduction was observed at 20 mg L⁻¹ whereas; Pb recorded maximum reduction (92.5%) at 40 mg L⁻¹. All the metals exhibited highest reduction at 120 minutes.

Freundlich and Langmuir isotherms were established for the biosorption process for different heavy metals (Fig. 2). The value of *n*, of the Freundlich model, falling in the range of 1 to 10, indicates substantially better sorption. The values of the model constants for the biosorption of metals by all the macroalgae are represented in Table 1. For the Freundlich equation, the values of 1/*n* ranged between 0.112 and 0.773 which indicates good adsorption. R² value varied from 0.030 to 0.952 for the metals studied. Langmuir model served to estimate the maximum metal uptake values where they could not be reached in the experiments. The constant *b* represents affinity between the sorbent and sorbate. Relatively high *q*_{max} value was obtained for Pb biosorption by *V. pachynema*. For Langmuir equation, R² ranged from 0.095 to 0.980. Langmuir model fitted satisfactorily as depicted by high values of correlation coefficients R².

The findings of the study were comparable to the earlier findings of researchers with different species of Chlorophyta. The Cu sorption capacity of *Ulva reticulata* was evaluated by Vijayaraghavan *et al.* [1] and was found to be relatively high (74.63 mg g⁻¹) when compared with other biosorbents. The findings of the current study also inferred similar results with relatively higher Hg uptake values (*q*=47.45) by *C. sertularioides*. Further, Steven and Ryan [13] explored the potential of a local strain of viable *Cladophora* algae to remove cadmium from synthetic wastewater and observed 80-94% removal of the cadmium. In the current study, *C. fascicularis* revealed comparable Cd removal (82%). Özer *et al.* [14] observed that the maximum monolayer coverage capacity of *Enteromorpha*

Table 1: Isotherm constants for heavy metal biosorption by dried biomasses of various green marine macroalgae

	<i>C. fascicularis</i>			<i>U. lactuca</i>			<i>Chaetomorpha</i> sp.			<i>C. sertularioides</i>			<i>V. pachynema</i>		
Isotherm Constants	Cd	Hg	Pb	Cd	Hg	Pb	Cd	Hg	Pb	Cd	Hg	Pb	Cd	Hg	Pb
Freundlich															
<i>n</i>	8.928	1.406	1.733	3.279	1.767	2.096	2.632	1.905	2.695	3.215	2.959	2.659	3.378	1.511	1.293
R ²	0.030	0.650	0.599	0.583	0.608	0.913	0.482	0.284	0.952	0.042	0.287	0.906	0.811	0.729	0.759
Langmuir															
<i>q</i> _{max} (mg g ⁻¹)	4.587	55.556	31.250	8.264	43.478	29.412	20.408	11.494	37.037	2.667	50.000	21.277	18.868	24.390	83.333
<i>b</i> (L mg ⁻¹)	0.321	0.019	0.242	0.121	0.120	0.296	0.371	0.219	2.079	0.264	0.526	0.416	0.358	0.042	0.191
R ²	0.733	0.095	0.532	0.725	0.446	0.934	0.690	0.484	0.980	0.203	0.404	0.944	0.970	0.368	0.254

prolifera, green seaweed for copper (II) ions was found to be 57.14 mg g⁻¹. The maximum adsorption capacity of *Ulva fasciata* for copper and zinc was 26.88 and 13.50 mg g⁻¹, respectively as recorded by Prasanna *et al.* [15]. Sheng *et al.* [16] observed that 90% of the total adsorption of lead, copper, cadmium, zinc and nickel occurred within 60 minutes by the marine algae, *Sargassum* sp., *Padina* sp., *Ulva* sp. and *Gracillaria* from dilute aqueous solutions. Deng *et al.* [17] investigated the biosorption of Cr (VI) from aqueous solutions by nonliving green algae *Cladophora albida* and observed relatively rapid removal rate in the first 60 minutes. Similar observations were made in the present study. The results of the current study thus reinforce the potential of various green marine algae as biosorbent for the removal of heavy metals.

CONCLUSION

The present work evaluated the potential of green marine macroalgae for the removal of Cd, Hg and Pb from aqueous solutions. The results obtained in this study indicated the highest adsorption ability of *Chaetomorpha* sp. for Cd and Pb while maximum Hg sequestration was observed in *C. sertularioides*. The equilibrium sorption data proved that the process conform Langmuir better than Freundlich isotherm model as depicted with high correlation coefficients. The concentration of the heavy metals analyzed during the study decreased significantly during the experimental period, proving the marine macroalgae to be excellent biosorbents. Thus, the use of green marine macroalgae for the development of efficient biosorbent materials can be considered an ecofriendly and cost-effective approach for heavy metal removal.

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