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Biosorption of heavy metal ions from aqueous solution by red macroalgae

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ABSTRACT

Biosorption is an effective process for the removal and recovery of heavy metal ions from aqueous solutions. The biomass of marine algae has been reported to have high biosorption capacities for a number of heavy metal ions. In this study, four species of red seaweeds *Corallina mediterranea*, *Galaxaura oblongata*, *Jania rubens* and *Pterocladia capillacea* were examined to remove Co(II), Cd(II), Cr(III) and Pb(II) ions from aqueous solution. The experimental parameters that affect the biosorption process such as pH, contact time and biomass dosage were studied. The maximum biosorption capacity of metal ions was 105.2 mg/g at biomass dosage 10 g/L, pH 5 and contact time 60 min. The biosorption efficiency of algal biomass for the removal of heavy metal ions from industrial wastewater was evaluated for two successive cycles. *Galaxaura oblongata* biomass was relatively more efficient to remove metal ions with mean biosorption efficiency of 84%. This study demonstrated that these seaweeds constitute a promising, efficient, cheap and biodegradable sorbent biomaterial for lowering the heavy metal pollution in the environment.

1. Introduction

Heavy metals are the important environmental pollutants throughout many countries and many of them are toxic at very low concentration. Many industrial activities such as metal plating, fertilizer industry, mining operations, and textile introduce heavy metals to environment via their waste effluents [1,2]. Heavy metal toxicity can be observed by a variety of syndromes and effects including renal dysfunction, hypertension, hepatic injury, lung damage, cancer and adverse potential to modify the DNA transcription process [3–5].

Increasing discharge limits of heavy metals have accelerated the search for highly efficient yet economically attractive treatment methods for their removal. Biosorption is one of the most applicable technologies in recent years. Biosorption have a potential marketing advantage over other traditional wastewater treatment technologies as it is cheaper and environmental friendly, particularly when natural biomass is used [6–9]. Different biomass types such as bacteria, fungi, and algae have been screened and studied extensively in the last decades with the aim of identifying highly efficient metal removal biosorbents. Many of the studies to date on metal biosorption by seaweeds have largely been restricted to various species of brown seaweeds. On the other hand, green and red seaweed species have not been evaluated to a great extent.

However, according to author' survey, there is no extensive study on the biosorption of heavy metals from industrial wastewater using *Corallina mediterranea*, *Galaxaura oblongata*, *Jania rubens* and *Pterocladia capillacea* in literature. Therefore, the present work aims to investigate the experimental parameters affecting the biosorption process such as pH, contact time and biomass dosage. In addition, the biosorption potential of low-cost natural red macroalgae for the removal of Co(II), Cd(II), Cr(III) and Pb(II) ions from aqueous solution and industrial wastewater was evaluated.

2. Materials and methods

2.1. Biomass preparation

Four red macroalgal species were used in this investigation; *C. mediterranea* (Aresch.), *G. oblongata* (Ellis & Solander) Lamouroux, *J. rubens* (L.) Lamour., and *P. capillacea* (Gmelin) Bornet & Thuret. Samples of the biomass were collected from the Mediterranean Sea at Abu Quir beach, Alexandria, Egypt, during summer season (July, 2009). The collected algal species, once returned to the laboratory, were rinsed thoroughly with distilled water in order to remove any adhering debris. Samples were oven dried at 60 °C for 24 h, then ground and sieved to a particle size of 500–850 mm. The biomass was stored in airtight polyethylene bottles until required.

2.2. Reagents and equipments

Standard metal solutions (analytical grade) containing 1000 mg/L of Co(II), Cd(II), Cr(III) and Pb(II) (as nitrate) were

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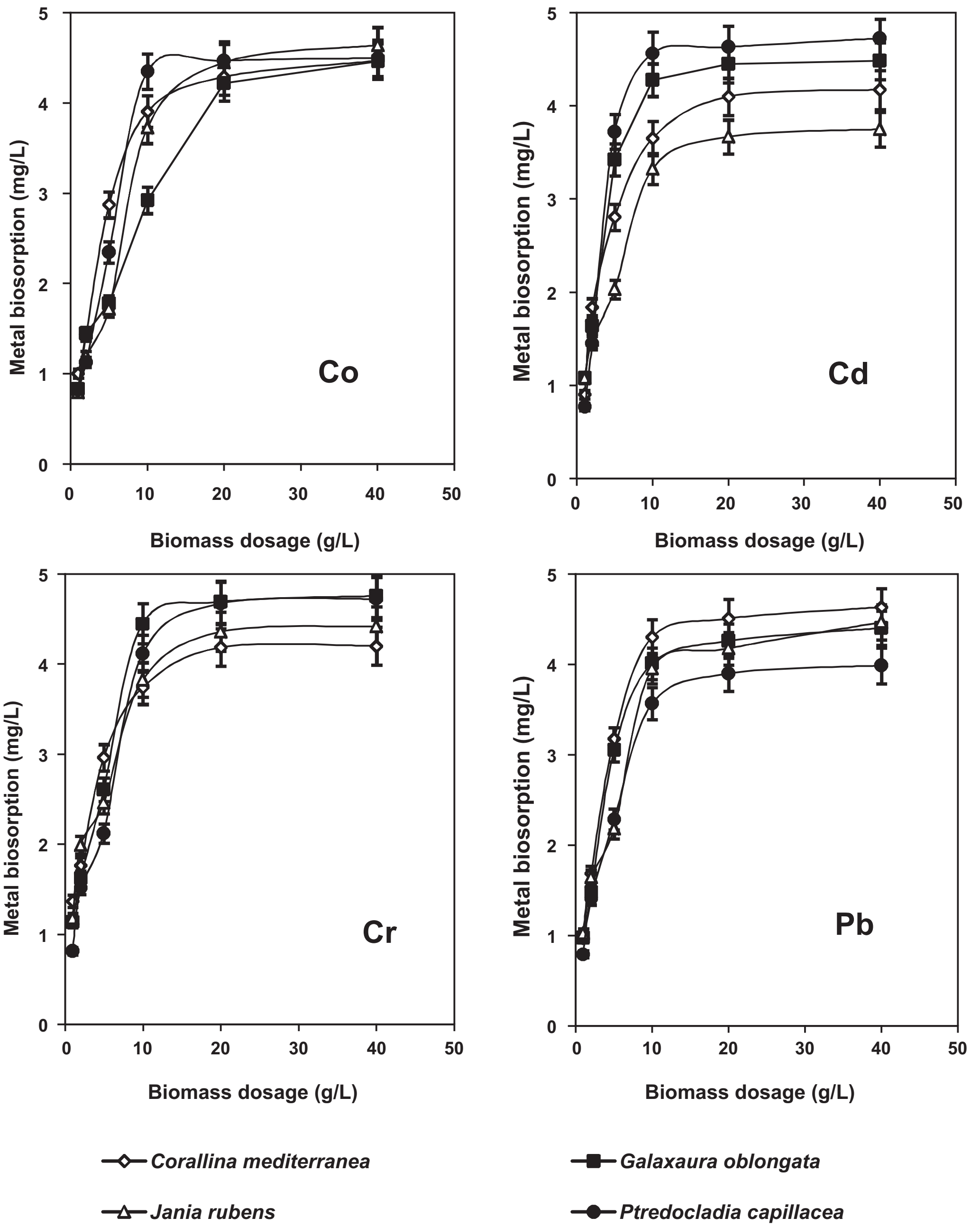

Fig. 1. Optimum biomass dosage determination for heavy metal ions sorption. Error bars are calculated based on triplicate runs with 95% confidence intervals (metal concentration 5 mg/L).

purchased from Sigma–Aldrich (Ireland). Working solutions were prepared by diluting the stock solution with distilled water. The metal concentrations in solution were determined using Perkin-Elmer AAnalyst 700 flame atomic absorption spectrophotometer with deuterium background corrector. All measurements were carried out in an air/acetylene flame.

2.3. Determination of optimum biomass dosage

In order to investigate the optimum biomass dosage for heavy metal biosorption, biomass dosages in the range 1–40 g/L were added to different flasks containing 5.0 mg/L from each metal solution. Flasks were shaken for 2 h at 200 rpm and room temperature (25 ± 1 °C). The samples were analyzed via AAS and the percentage of biosorption was calculated according to the following equation:

$$\text{Biosorption}\quad(\%) = \left(\frac{C_i - C_f}{C_i}\right) \times 100$$

where C_i and C_f are the initial and final metal ion concentrations (mg/L), respectively [5].

2.4. Optimum pH determination

The optimum pH for heavy metal biosorption was investigated by adding 10 g/L algal biomass to heavy metal solution adjusted to various pH values (2–8) using 0.1 M NaOH or 0.1 M HNO_3. Flasks were shaken for 2 h at 200 rpm and room temperature (25 ± 1 °C).

Table 1
Independent *t*-test for the differences in biosorption efficiency by algal biomass.

Treatment	*Corallina mediterranea*		*Galaxaura oblongata*		*Jania rubens*		Ptredocladia capillacea	
	T	S	T	S	T	S	T	S
Biomass dosage (g/L)								
1	–	–	–	–	–	–	–	–
2	4.56	**	6.59	***	3.01	*	6.61	***
5	10.6	***	3.26	*	2.28	NS	3.26	*
10	5.73	**	3.43	*	7.81	***	3.57	*
20	2.18	NS	1.35	NS	2.04	NS	0.96	NS
40	0.69	NS	0.91	NS	0.58	NS	0.26	NS
PH value								
2	–	–	–	–	–	–	–	–
3	0.09	NS	3.11	*	2.86	*	1.40	NS
4	2.62	*	2.72	*	2.28	NS	0.90	NS
5	4.36	**	5.18	**	2.61	*	1.59	NS
6	−2.05	NS	−1.32	NS	−0.91	NS	−0.76	NS
7	−4.41	**	−2.12	NS	−2.93	*	−1.36	NS
8	−3.26	*	−3.01	*	−1.75	NS	−1.52	NS
Contact time (min)								
5	–	–	–	–	–	–	–	–
10	4.13	**	5.95	***	1.51	NS	5.48	**
30	4.14	**	3.17	*	1.71	NS	3.75	**
60	4.63	**	3.97	**	2.48	**	2.47	*
90	0.54	NS	0.10	NS	0.06	NS	0.18	NS
120	0.78	NS	0.16	NS	0.09	NS	0.38	NS

$T = t$ value of t-test; NS = non significant – no preceding value to compare with: *significant ($P \leq 0.05$), **high significant ($P \leq 0.01$), ***very high significant ($P \leq 0.001$).

The samples were analyzed via AAS and the percentage of biosorption was calculated as before.

2.5. Determination of optimum contact time

A quantity of 0.5 g biomass was added to 50 mL metal solution adjusted to pH 5. Flasks were shaken at 200 rpm and room temperature (25 ± 1 °C). Samples were taken at $t = 5, 10, 30, 60$ and 120 min and the samples were analyzed by AAS.

2.6. Industrial effluent sampling

Effluent samples were collected from El-Fayoum for chemical production company outfalls during working hours. The collected samples were filtered through GF/C Whatman glass filters and stored at 4 °C in dark.

2.7. Batch biosorption procedure

Batch biosorption of effluent heavy metals was carried out in stoppered conical flask at the optimum pH, biomass dosage and contact time. The contents of the flask were filtered through filter paper and the filtrate was analyzed for metal concentration by using flame AAS. After biosorption experiments, the loaded biomass was regenerated using 25 mL of 0.1 M HNO_3 for 10 min [10]. The procedures for collection and analysis of samples were the same used for biosorption experiments. After elution, the biomass was washed with distilled water until effluent pH stabilization near the inlet pH and the regenerated biomass was reused in a next cycle.

2.8. Statistical analyzes

Data were presented as mean of replicates from three runs and were analyzed statistically using Student's *t*-test for independent samples. Statements of significant differences were based on accepting $P \leq 0.05$. To validate the boisorption efficiency of algal biomass, two identical series of linear regression curves were established for effluent biosorption experiments.

3. Results and discussions

3.1. Effect of biomass dosage

The effect of biomass dosage on the biosorption of heavy metal ions was studied using different biomass dosage in the range, 1–40 g/L (Fig. 1). Results showed that the biosorption efficiency was highly dependent on the increase in biomass dosage of solutions up to 10 g/L where the maximum biosorption (60–91%) of the metal ions was attained. This can be expected because the higher dose of biosorbent in the solution, the greater availability of exchangeable sites for the ions. However, the biosorption efficiency was almost the same at biomass dosages higher than 10 g/L (Table 1). This could be attributed to a partial aggregation of biomass which reduces effective surface area for the biosorption [11]. Therefore, the optimum biomass dosage was selected as 10 g/L for further experiments. In this context, the maximum biosorption of Cd(II) and Cr(III) ions using different biomass dosage of red alga *Ceramium virgatum* in the range 0.4–40 g/L was attained at 10 g/L [5,12].

3.2. Effect of solution pH

One of the important factors affecting the biosorption of metal ions is acidity of solution. Solution pH affects the cell wall metal binding sites and the metal ion chemistry in water. Various authors [13,14] have shown that solution pH greatly influences metal biosorption by algal biomass. To examine the effect of pH on the biosorption efficiency, several experiments were performed at different pH ranges from 2 to 8 as shown in Fig. 2. The sorption capacity progressively increases up to pH 5 where the maximum biosorption efficiency was obtained (98%). At higher pH values, the biosorption of metal ions were significantly decreased (Table 1). Therefore all further biosorption experiments were carried out at pH 5.

The phenomenon of protonation/deprotonation which occur on surface of the biomass explains the relation between uptake of metals and solution pH. Algal biomasses contain high content of carboxyl groups from mannuronic and guluronic acids on the cell wall polysaccharides, which suggests that the biosorption process could be affected by changes in the solution pH [15]. Carboxyl groups are acidic, so at low pH values (2–4) they will be protonated

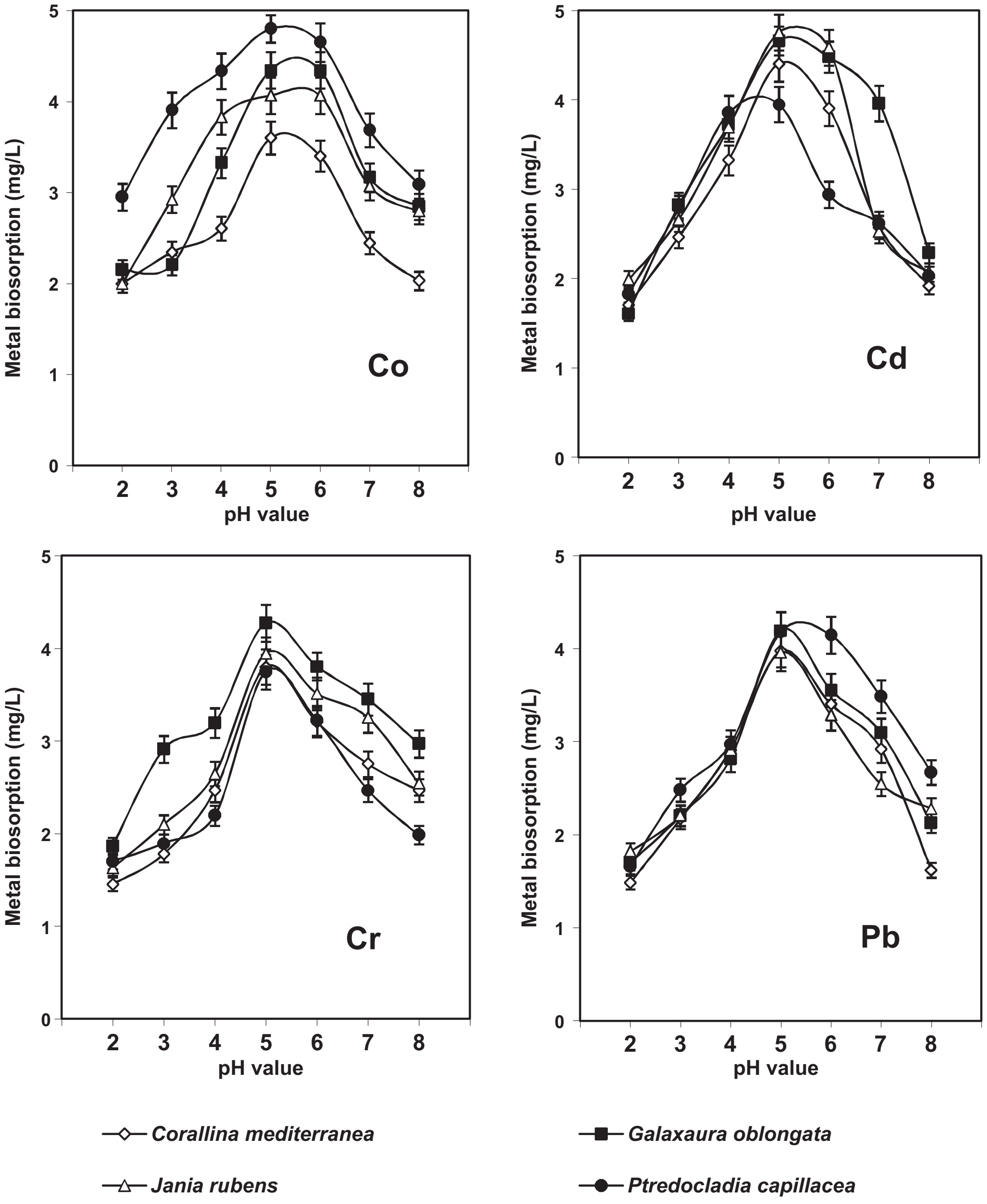

Fig. 2. Optimum pH value determination for heavy metal ions sorption. Error bars are calculated based on triplicate runs with 95% confidence intervals (metal concentration 5 mg/L, biomass dosage 10 g/L).

due to the high concentration of the positively charged H^+ and H_3O^+ ions and thereby become less available for binding metals [16,17]. The increment in the biosorption at pH 5 could be associated with deprotonation of carboxyl or other negatively charged groups leading to electrostatic attraction of positively charged metals [10,18]. The decrease in the biosorption efficiency at higher pH values (6–8) may be attributed to the formation of anionic hydroxide complexes which decrease the dissolved metal concentration in solution and their competition with the active sites [19,20].

3.3. *Effects of contact time*

The contact time was also evaluated as one of the most important factors affecting the biosorption efficiency. Fig. 3 shows the biosorption efficiency of metal ions by algal biomass as a function of contact time. The biosorption efficiency significantly enhanced by increasing the contact time up to 60 min and above that it was more or less constant (Table 1). Therefore, the optimum contact time was selected as 60 min for further experiments. In accordance with these results the biosorption efficiency of Cd(II) ion from aqueous solution by red alga *C. virgatum* increases with rise in contact time up to 60 min after then it is almost constant [5]. Many biosorption studies have also indicated that the majority of test algae attained maximum metal ions biosorption within periods fluctuated between 30 and 90 min [4,12,15,21].

3.4. *Biosorption isotherm model*

A biosorption isotherm is characterized by certain constant values, which express the surface properties and affinity of the biosorbent and can also be used to compare the biosorptive capacities of the biosorbent for different pollutants [22]. In this study, Langmuir isotherm model was selected to fit experimental data. This model supposes that the sorption process takes place at a spe-

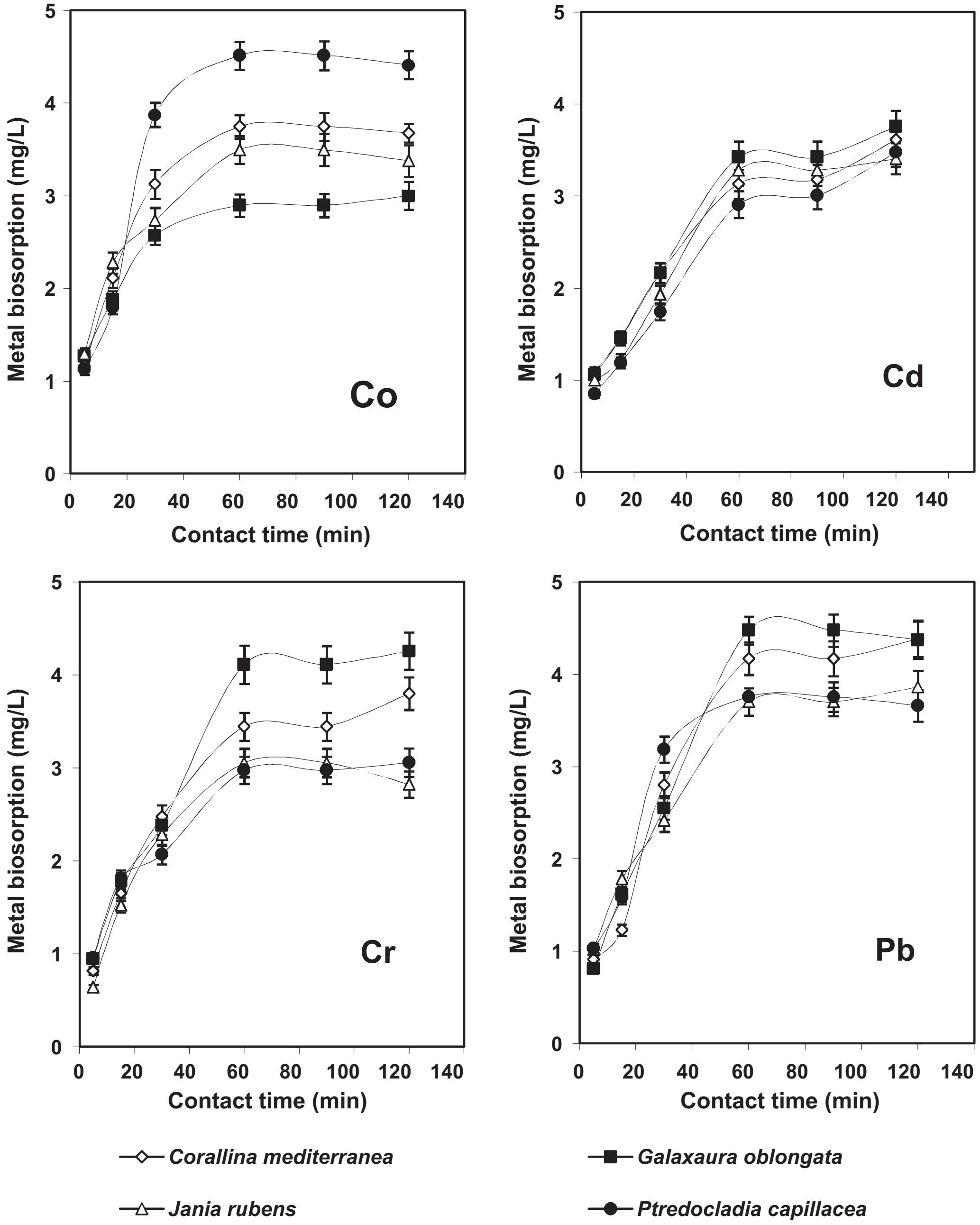

Fig. 3. Optimum contact time determination for heavy metal ions sorption. Error bars are calculated based on triplicate runs with 95% confidence intervals (metal concentration 5 mg/L, biomass dosage 10 g/L, pH 5).

cific sorption surface. The attraction between molecules decreases as getting further from the sorption surface. Langmuir isotherm can be defined according to the following equation [23]:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m}$$

where q_e is the equilibrium metal ion concentration on the adsorbent (mg/g), C_e is the equilibrium metal ion concentration in the solution (mg/L), q_m is the monolayer biosorption capacity of the adsorbent (mg/g), and K_L is the Langmuir biosorption constant (L/mg) relating the free energy of biosorption.

Fig. 4 indicates the linear relationship between the amount (mg) of heavy metal ions sorbed per unit mass (g) of *C. mediterranea*, *G. oblongata*, *J. rubens* and *P. capillacea* against the concentration of heavy metal ions remaining in solution (mg/L). The correlation coefficients (R^2) ranged from 0.919 to 0.998 for metal biosorption (Table 2). This high R^2 values indicated that the equilibrium data well fitted to the Langmuir model. As shown from Table 2, the maximum biosorption capacities (q_m) ranged from 28.5 mg/g to 105.2 mg/g. These q_m values were compared with other biosorbents in order to validate *C. mediterranea*, *G. oblongata*, *J. rubens* and *P. capillacea* as a suitable metal ions adsorbent. Table 3 shows the q_m values for the biosorption of metal ions on different algal species and other biomasses in the literature. The biosorption capacities of the tested red algal biomasses for heavy metals are higher than that of the majority of the biomasses given in this table. Therefore, it can be noteworthy that the *C. mediterranea*, *G. oblongata*, *J. rubens* and *P. capillacea* have considerable potential for the removal of metal ions from aqueous solution.

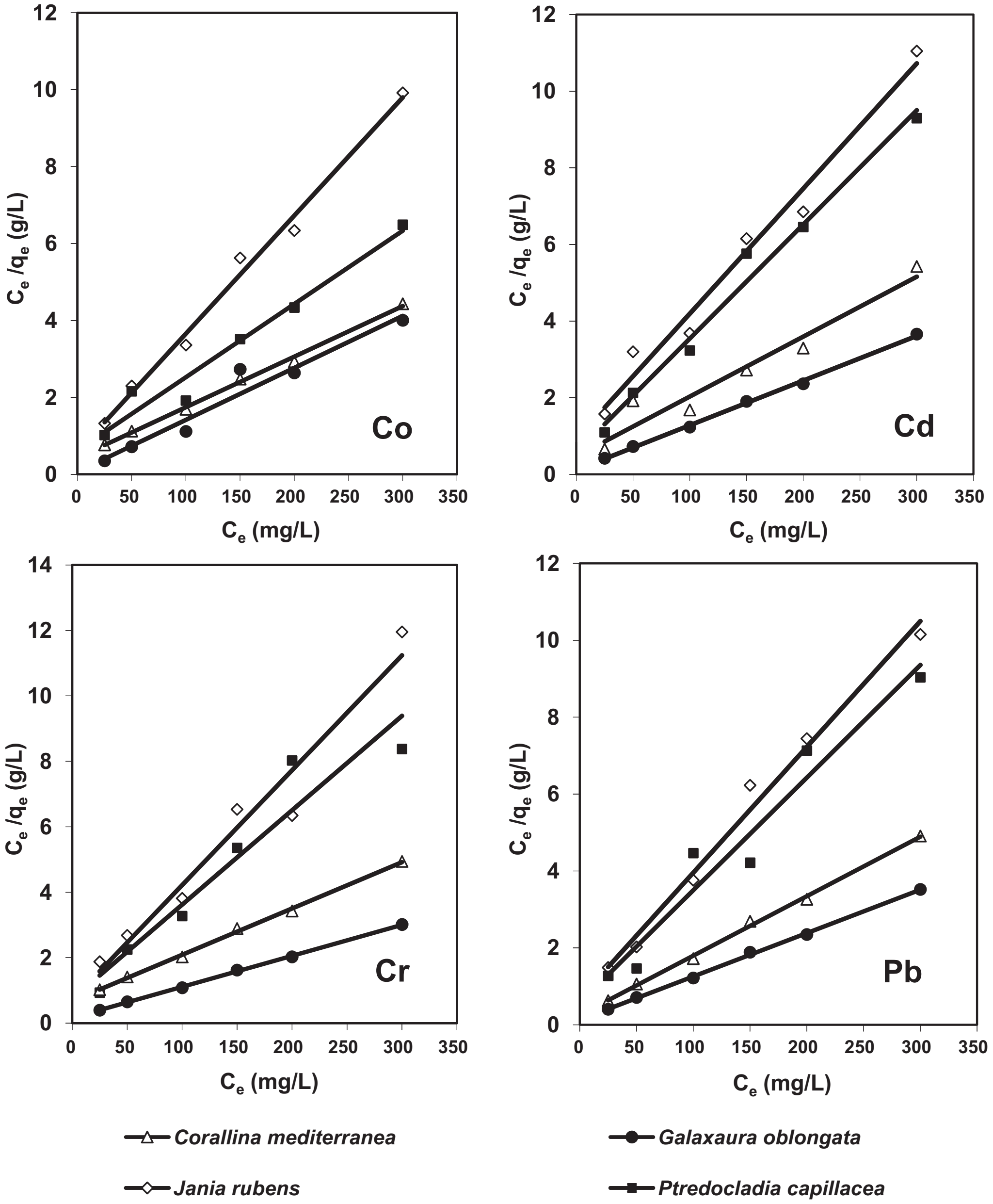

Fig. 4. Langmuir isotherm plots for biosorption of heavy metals onto different algal biomasses (biomass dosage 10 g/L, contact time 60 min, pH 5, temperature 25 °C).

Table 2
Langmuir isotherm constants for the biosorption of Co(II), Cd(II), Cr(III) and Pb(II) on red algal biomasses.

Metal ions	Biosorbent	Langmuir constants		
		q_m (mg/g)	K_L (L/mg)	R^2
Co(II)	*J. rubens*	32.6	0.0396	0.990
	P. capillacea	52.6	0.0283	0.962
	C. mediterranea	76.2	0.0567	0.996
	G. oblongata	74.2	0.1136	0.947
Cd(II)	*J. rubens*	30.5	0.0422	0.977
	P. capillacea	33.5	0.0444	0.984
	C. mediterranea	64.1	0.0675	0.942
	G. oblongata	85.5	0.0984	0.998
Cr(III)	*J. rubens*	28.5	0.0453	0.955
	P. capillacea	34.7	0.0430	0.919
	C. mediterranea	70.3	0.0614	0.998
	G. oblongata	105.2	0.0799	0.995
Pb(II)	*J. rubens*	30.6	0.0422	0.987
	P. capillacea	34.1	0.0437	0.948
	C. mediterranea	64.3	0.0671	0.997
	G. oblongata	88.6	0.0951	0.998

Table 3
Comparison of biosorption capacity (q_m) of red algae for metal ions with that of different algal species and other biomasses.

Biosorbent	pH	Biosorption capacity (mg/g)				Reference
		Cd	Pb	Cr	Co	
Ulva lactuca (green algae)	5	29.2	34.7	–	–	[24]
Caulerpa lentillifera (green algae)	5	4.7	28.6	–	–	[25]
Sargassum wightii (brown algae)	4.5	–	–	–	20.6	[26]
Padina tetrastomatica (brown algae)	5	59.5	–	–	–	[21]
Fucus vesiculosus (brown algae)	4–6	107.9	211.3	–	–	[27]
Palmaria palmate (red algae)	2	–	–	33.8	–	[28]
Ceramium virgatum (red algae)	5	39.7	–	–	–	[5]
Gracilaria salicornia (red algae)	5	17.9	–	–	–	[21]
Chondracanthus chamissoi (red algae)	4	85.2	283.5	–	–	[29]
Galaxaura marginata (red algae)	3.5	–	26.9	–	–	[30]
Chroococcus sp.	4	–	–	21.3	–	[31]
Nostoc muscorum	3	–	–	22.9	–	[32]
Alternanthera philoxeroides	2	–	–	17.7	–	[33]
Geobacillus thermodenitrificans	4–6	42.9	32.2	70.7	69.7	[7]
Pinus sylvesteris	5	19.1	22.2	–	–	[34]
Rhytidiadelphus squarrosus (moss)	6	–	–	–	7.2	[35]
J. rubens (red algae)	5	30.5	30.6	28.5	32.6	Present study
P. capillacea (red algae)	5	33.5	34.1	34.7	52.6	Present study
C. mediterranea (red algae)	5	64.1	64.3	70.3	76.2	Present study
G. oblongata (red algae)	5	85.5	88.6	105.2	74.2	Present study

Table 4
Physico-chemical properties of the industrial effluent.

Parameter	Value
pH	9.2 ± 0.2
Temperature (°C)	30.7 ± 2.4
Conductivity (μs/cm)	1463 ± 52
COD (mg/L)	56.0 ± 7.9
BOD$_5$ (mg/L)	35.0 ± 4.7
Turbidity (NTU)	6.52 ± 0.68
Hardness (mg/L)	148.0 ± 9.2
TDS (mg/L)	762.0 ± 26.1
TSS (mg/L)	46.0 ± 3.1
DO (mg/L)	5.7 ± 0.5
Alkalinity (mg/L)	247.0 ± 19.5

Values are means ± S.E for 3 samples ($n = 3$).

3.5. Efficiency of algal biomass to remove metal ions from industrial effluent

Table 4 indicates the physico-chemical properties of El-Fayoum for chemical production company effluent. The efficiency of algal biomass to remove metal ions from this industrial effluent varied according to the metal ion and the algal biomass (Figs. 5 and 6). After two biosorption–elution cycles, the efficiencies of *C. mediterranea*, *G. oblongata*, *J. rubens*, and *P. capillacea* biomasses to remove metal ions ranged from 57% to 94% (Fig. 5, Table 5). The highest metal ions removal efficiency was *G. oblongata* biomass followed by *C. mediterranea, P. capillacea* and *J. rubens* biomasses with mean metal ion biosorption efficiencies of 84%, 80%, 76% and 72%, respectively (Figs. 5 and 6). The capacity of 0.1 M HNO_3 to elute metal ions from loaded biomasses ranged between 74.4% and 95.3% for the two cycles (Table 5).

Table 5
Biosorption–elution cycles of heavy metal ions from El-Fayoum for chemical production company effluent.

Biosorbent	Conc.of metal in effluent (mg/L)	First biosorption-elution cycle			Second biosorption–elution cycle		
		Biosorbed metal (mg/L)	Eluted metal (mg/L)	Elution (%)	Biosorbed metal (mg/L)	Eluted metal (mg/L)	Elution (%)
Corallina mediterranea							
Co	1.34	1.26 ± 0.05[a]	1.08 ± 0.03	86.2	1.04 ± 0.04	0.89 ± 0.03	85.2
Cd	1.21	0.97 ± 0.04	0.83 ± 0.04	85.5	0.84 ± 0.04[b]	0.74 ± 0.04	89
Cr	0.72	0.56 ± 0.02[b]	0.51 ± 0.03	90.2	0.56 ± 0.02[a]	0.44 ± 0.02	79.8
Pb	0.68	0.59 ± 0.03	0.55 ± 0.02	93.8	0.5 ± 0.02	0.41 ± 0.02	83
Galaxaura oblongata							
Co	1.34	1.23 ± 0.06[a]	1.08 ± 0.04	87.6	1.10 ± 0.05	0.92 ± 0.05	83.41
Cd	1.21	1.05 ± 0.05[b]	0.94 ± 0.05	89.1	0.94 ± 0.05[b]	0.72 ± 0.03	76.59
Cr	0.72	0.64 ± 0.03	0.54 ± 0.03	85.2	0.56 ± 0.03	0.42 ± 0.02	76.59
Pb	0.68	0.61 ± 0.03	0.57 ± 0.03	93.4	0.56 ± 0.02[a]	0.52 ± 0.02	94.11
Jania rubens							
Co	1.34	1.15 ± 0.05 [a]	1.04 ± 0.05	90.6	0.96 ± 0.05	0.76 ± 0.04	79.46
Cd	1.21	0.95 ± 0.04	0.90 ± 0.04	94.7	0.72 ± 0.03[b]	0.54 ± 0.03	74.46
Cr	0.72	0.53 ± 0.02 [b]	0.47 ± 0.02	89.5	0.41 ± 0.02	0.30 ± 0.01	74.46
Pb	0.68	0.53 ± 0.03	0.48 ± 0.02	91.3	0.50 ± 0.02[a]	0.43 ± 0.02	86.27
Ptredocladia capillacea							
Co	1.34	1.26 ± 0.06[a]	1.2 ± 0.03	95.3	1.07 ± 0.05	0.96 ± 0.05	89.63
Cd	1.21	0.92 ± 0.05[b]	0.83 ± 0.04	90	0.72 ± 0.03[b]	0.65 ± 0.03	89.36
Cr	0.72	0.55 ± 0.02	0.51 ± 0.02	93	0.43 ± 0.02	0.37 ± 0.01	87.23
Pb	0.68	0.58 ± 0.03	0.52 ± 0.02	89	0.55 ± 0.03[a]	0.50 ± 0.02	92.15

[a] Maximum biosorption of heavy metal ions.
[b] Minimum biosorption of heavy metal ions.

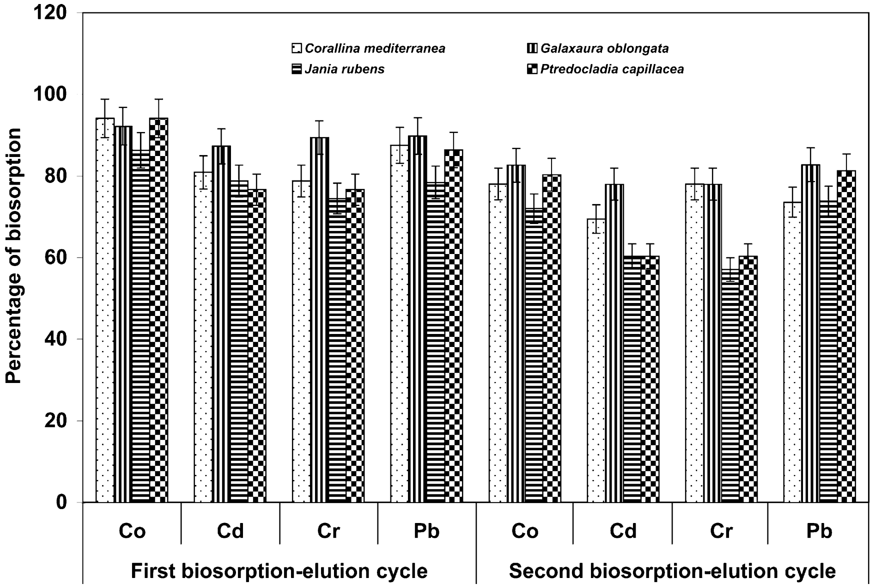

Fig. 5. Percentage of biosorption from El-Fayoum for chemical production company effluent. Error bars are calculated based on triplicate runs with 95% confidence intervals (biomass dosage 10 g/L, pH 5, contact time 60 min).

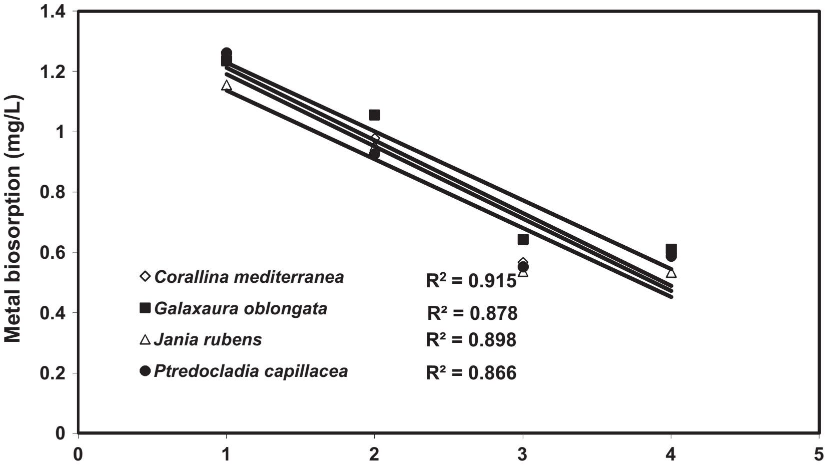

Fig. 6. Biosorption-response linear regression curves of heavy metal ions of El-Fayoum for chemical production company effluent (where 1 = Co, 2 = Cd, 3 = Cr, 4 = Pb).

The efficiency of the red alga *Mastocarpus stellatus* for cadmium uptake reaches over 90% in the first 9 min and HNO_3 as desorbent agent has elution efficiencies around 90% for the first 10 min of contact [36]. Also, the biosorption of lead by nonliving biomass of eight brown, green and red marine algae after the 10th sorption–desorption cycle was similar to that after the first cycle (98%) and the removal of lead from algal biomass was successfully achieved (95%) by eluting with 0.1 M HNO_3 for 15 min [37].

The regenerated algal biomasses were reused in two biosorption–elution cycles and the results are shown in Table 5. The efficiency of the biosorption process was the same for the two consecutive cycles and the elution percentage for the two cycles are very similar, which means that the metal-loaded on the biomass is equal in the two consecutive cycles. This result indicates that the algal biomass maintains the same efficiency of metal uptake after two biosorption–elution cycles.

4. Conclusions

This study focused on the biosorption of Co(II), Cd(II), Cr(III) and Pb(II) ions onto red algal biomass from aqueous solution. The operating parameters such as pH of solution, biomass dosage and contact time affected the biosorption efficiency of metal ions. The red algal biomass demonstrated a high capacity of metal biosorption, highlighting its potential for treating some effluents. The efficiencies of *C. mediterranea*, *G. oblongata*, *J. rubens*, and *P. capillacea* biomass for the removal of different metal ions from industrial effluent reached to 94% after two biosorption–elution cycles. According to these results, the red algal biomass can be used as an effective and alternative biomass for the removal of heavy metal ions from industrial effluents due to its high biosorption capacity, being of natural, renewable and thus cost-effective biomass.

Conflict of interest

The author has declared that no conflict of interest exists.

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