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Unrevealing the biosorption capacity of freshwater algae biomasses for toxic heavy metals in aqueous solutions

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ABSTRACT

Freshwater contamination is one of the major global environmental problems especially in developing countries due to low economic and high population growth rates. Bioremediation is a cost-effective, onsite, green technology and environmentally friendly method. The present study investigated freshwater algal biomasses for biosorption potential of various toxic heavy metals (HM) including cadmium (Cd), lead (Pb), nickel (Ni) and chromium (Cr) in aqueous solution at different concentrations and dosages. For this purpose, four algal species named *Oedogonium westii, Cladophora glomerata, Vaucheria debaryana* and *Zygnema insigne* were used to remove the HM from aqueous solution. The HM biosorption capability was significantly ($p \leq 0.05$) changed with changes in biomass dosage. The *C. glomerata* biosorptions were very effective for the removal of Pb (73.2%), followed by Cd (67%) and Ni (65.2%) and the *Z. insigne* showed higher biosorption for Cr (79%), Pb (59.2%) and Ni (38.2%). Therefore, this study recommends the utilization of *Z. insigne* and *C. glomerata* algae for industrial and mining wastewater treatments.

Keywords: Heavy metals; Wastewater; Biosorption isotherm; Algal biomass; Bioremediation

1. Introduction

Toxic heavy metals (HM) contamination has become one of the serious environmental problems due to their essential use in emerging epidemic industrialization [1–5]. These HM are discharged into the aquatic ecosystem from the domestic and industrial effluents, mining and agriculture activities [6,7]. In an aquatic ecosystem, the HM contaminate drinking water and pose a direct threat to human being via ingestion of contaminated water [8]. The HM could accumulate in aquatic and terrestrial food and pose an indirect threat when such contaminated food is consumed by humans [9,10]. The HM in the environment was observed with deleterious effects due to their hazardous, persistent and bio-accumulative nature [11–13]. The toxic effects of HM include a variety of life-threatening problems including poisoning, neurological, depression problems and cancer, and memory loss in children [14–16].

Recently, the global annual discharge of HM reached millions of tons [17]. Therefore, it is very imperative to decontaminate the wastewater effluents before released into the ecosystem [18,19]. Conventional methods for decontamination of HM enriched wastewater, including chemical precipitation, ion exchange and membrane adsorption has limitations due to high cost, less effectiveness and environmental problems in dealing with a large quantity of water [20–22]. To cope the limitation of conventional methods, the biosorbents such as algae has been introduced. The biosorbents such as algae are a very cost-effective,

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alternative method and had the ability for on-site sorption of HM [19,23–25]. The biosorption of HM and other compounds in algae mainly take place in the cell wall that is composed of cellulose, protein, alginic acid and several functional groups such as carboxyl, hydroxyl, amino and sulphate [26].

Wastewater treatment using biosorbent becomes an attractive field due to low cost, low residue and environmental friendly operation. The uses of dead and inactive biomasses of algae or any plant species for biosorption is an innovative method for the decontamination of HM from the wastewater. Environmental studies had focused to unravel new biosorbent especially algae due to their higher sorption capacity, abundance in various ecosystems and ability of adaptation to environmental conditions [26–28]. Therefore, this study was aimed to evaluate the biosorption capacity of indigenous freshwater algae for HM including cadmium (Cd), lead (Pb), nickel (Ni) and chromium (Cr) decontamination from aqueous solution. For this purpose, algal biomass such as *Oedogonium westii, Cladophora glomerata, Zygnema insigne* and *Vaucheria debaryana* was used at various dosages for HM treatment at different concentrations.

2. Materials and methods

2.1. Algal biomass preparation and characterization

Algal species including *C. glomerata, O. westii*, *Z. insigne* and *V. debaryana* samples were collected from freshwater ponds in Islamia College University (ICU), Peshawar of Khyber Pakhtunkhwa, Pakistan. Samples were thoroughly washed five and three times with tap water and deionized water to remove any adhering debris. Algal samples were oven-dried at 60°C for 24 h, ground and sieved (500–850 mm) of particle size [29,30]. Samples were stored in air-tight plastic bottles for further process.

2.2. Chemicals

Standard stock solutions containing Pb, Cr, Ni and Cd were prepared by dissolving salts $Pb(NO_3)_2$, $Cr(NO_3)_3{\cdot}9H_2O$, $Ni(NO_3)_2$ and $Cd(NO_3)_2$ in deionized water. Wastewater stock solutions were diluted to the desired concentrations of each experiment.

2.3. Experiment design

Biosorption experiments were performed in 500 mL Erlenmeyer flasks that were rinsed with 10% nitric acid (HNO_3) and deionized water to remove any attached contamination. Controls; one without dry algae, and another with dry algae and without HM solution, were added to the experiment. The initial concentrations of Cd, Cr and Ni and Pb were 1, 2, 4, 8, 10 mg L^{-1} were mixed with a labeled flask of wastewater experiment. Each flask has 0.5 g of dry algae biomass and shaken for 2 h at 200 rpm at room temperature 25°C ± 1°C [30]. Second, the range of biomass dosage (0.5, 1.0, 1.5, 2.0 and 2.5 g) was used, adjusted at pH 5 and shaken as aforementioned. Each experiment including control was performed in triplicate.

2.4. Heavy metals

The contents of the flask were filtered through whatman filter paper no. 42 and analyzed for HM concentrations [31]. Briefly, filtrate was taken in beakers and mixed with HNO_3 and hydrogen peroxide (H_2O_2, 3:1, V/V). Then solution in beaker was heated at 110°C on a hot plate. After complete digestion, the solution of each sample was filtered. To get 50 mL of each solution, deionized water was added. Solution was analyzed for HM using the atomic absorption spectrometer (AAS, Analyst 700 PerkinElmer, USA).

2.5. Quality control

Standard reference materials (GBW10015 [GSB-6]) of the plant were used to check precision and accuracy. Blank reagents were digested and analyzed in each batch. The recovery rates for selected toxic HM ranged from 92.4% ± 6.2% to 103% ± 8.3%.

2.6. Data analysis

2.6.1. Adsorption equilibrium

The amount of HM sorbed by algal biomass has calculated accordingly to the formula adopted from Xin et al. [32]:

$$q = \frac{V(C_i - C_e)}{W} \tag{1}$$

where q, V, C_i, C_e and W were the adsorption amount at equilibrium (mg^{-1}), the volume of solution, the initial and final concentration of HM in solution at equilibrium (mg L^{-1}) and the dry weight of biosorbent dosage (g L^{-1}), respectively.

2.6.2. Biosorption removal efficiency

The efficiency (%) to remove HM was calculated accordingly to the formula adopted from Xin et al. [32]:

$$r = \frac{(C_i - C_e)}{C_i} \times 100 \tag{2}$$

where r, C_i and C_e was removal percentage at each testing time, initial and final concentration of HM (mg L^{-1}).

2.6.3. Biosorption isotherm

Langmuir isotherms model was used for quantification of HM sorption of tested algae as follows [33,34]:

$$q_e = q_m \frac{bC_e}{1 + bC_e} \tag{3}$$

where Q_e, C_e, Q_m, b and c were the metal sorbed at equilibrium (mg g^{-1}), ion concentration metal at equilibrium, maximum metal sorbed (mg g^{-1}) and Langmuir constants, respectively.

2.7. Statistical analysis

Data were evaluated using the SigmaPlot 12.5 and SPSS 25 (SPSS Inc., Chicago, IL, USA).

3. Results and discussion

3.1. HM biosorption and algal biomass

3.1.1. Cladophora glomerata

The biosorption capacity of algal biomass to HM in wastewater was summarized (Fig. 1). Among algal species, the *C. glomerata* showed the highest biosorption capabilities for the selected HM, especially Cr and Ni as compared with other algal species. Various biomass ranges (0.5, 1.0, 1.5, 2.0 and 2.5 g) of the *C. glomerata* were studied for the biosorption of HM in wastewater. Results showed that the HM biosorption capability was decreased with the increase of biomass dosage. At 1.5 and 2.0 g dosage, the biosorption potential of *C. glomerata* was almost the same for Cr and Ni (Fig. 1). This could be attributed to the partial aggregation of biomass which had decreased effective surface area for the biosorption of HM [30,35].

3.1.2. Zygnema insigne

The biosorption of *Z. insigne* for the selected HM was in the order of Cr > Ni > Cd > Pb at biomass dosage of 0.5–2.0 g (Fig. 1). These results showed a high HM biosorption at a low biomass dosage of 0.5 g and decreased with an increase of *Z.*

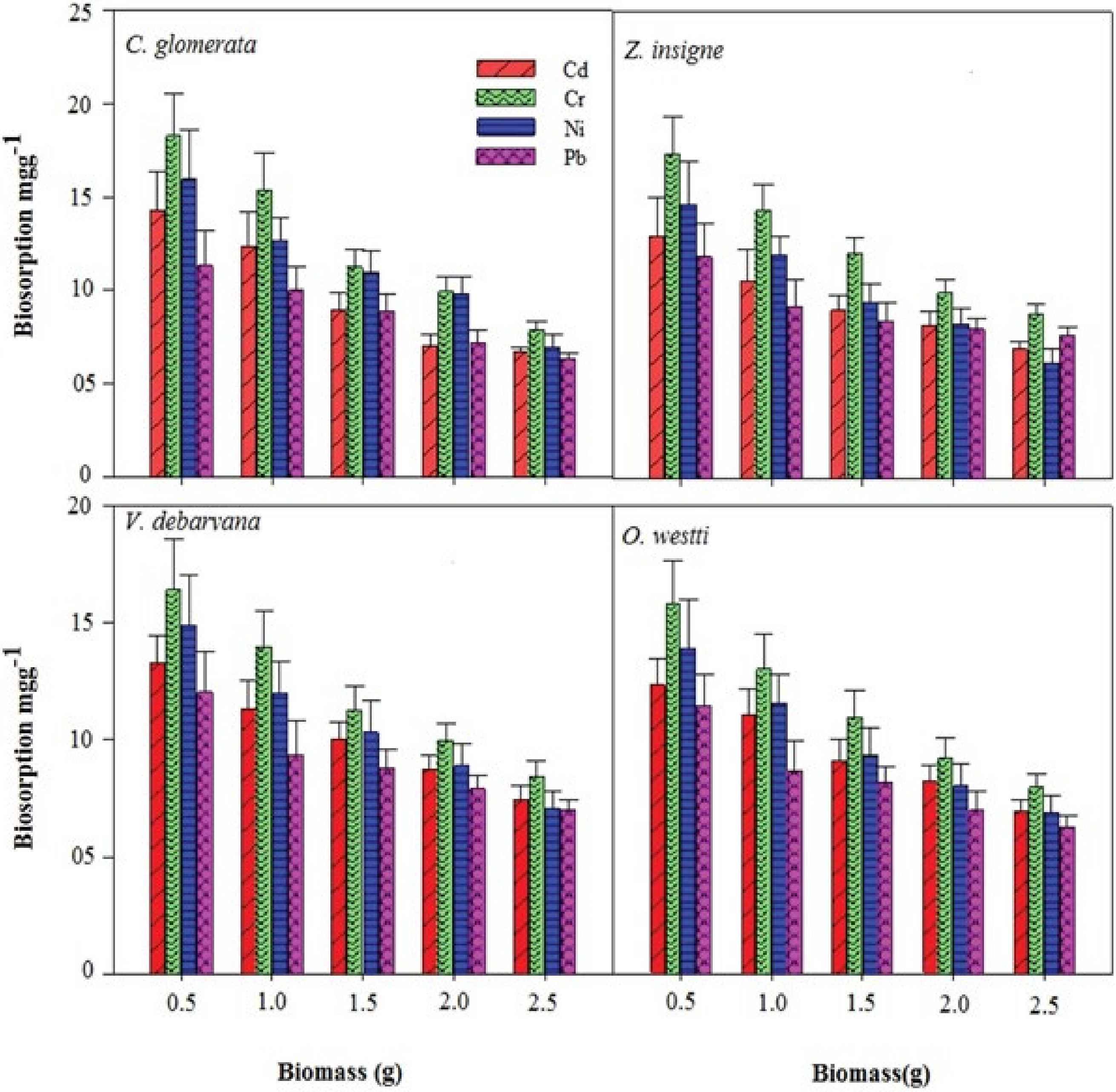

Fig. 1. Uptake capacity of algal species for heavy metals.

insigne biomass dosage. This may be linked with the partial gathering of biomass which reduce the effective surface area for the biosorption [30,35].

3.1.3. Vaucheria debaryana

The *V. debaryana* biosorption capabilities were tested for the studied HM and results are summarized in Fig. 1. This algal species showed the highest biosorption capacity for Cr (16.4 mg g^{-1}) and followed by Ni (14.9 mg g^{-1}) at 0.5 g biomass dosage. However, algal biosorption capacity for Cr remained highest at different dosages and the increases in the biomass dosage led to decreased biosorption capacity (Fig. 1). The dosage of biomass is a very important parameter during metal biosorption. The algae biomass takes up more HM at a given equilibrium concentration [26,36] and electrostatic interactions are very significant factor in the relationship between metal sorption and biomass dosage. Lower the biomass dosage in suspension, the higher will be the metal biosorbent ratio and the metal hold by sorbent unit, unless the biomass reached saturation. High biomass can serve as a shield protecting the active sites from being occupied by HM. Results of this study of algal biosorption of HM were in support of previous studies [37,38].

3.1.4. Oedogonium westii

The effect of *O. westii* biosorption capabilities was studied for the selected HM using different biomass dosage in the range of 0.5–2.5 g. This algal species also showed the highest biosorption capacity for Cr (15.8 mg g^{-1}), followed by Ni and lowest for Pb at 0.5 g dosage. The algal biosorption capacity for Cr was highest at all dosages of biomasses tested in the study. Like other algal species, with an increase in biomass dosage, the biosorption capacity was decreased (Fig. 1). The amount adsorbed of HM per unit weight of algal adsorbent was decreased as reported by Fraile et al. [39]. This trend of algal biomass for biosorption of HM was in support of other previous studies [37,38].

3.2. HM biosorption efficiency

The biosorption efficiency of *C. glomerata* greatly changed with variation in HM concentrations of an aqueous solution. At low concentration (1 mg L^{-1}), the biosorption efficiency for Pb and Cd contaminants was 73.2% and 67.2%, respectively, followed by Ni 65.2% and lowest by Cr 48%. The biosorption efficiency of *C. glomerata* slightly decreased with an increase in HM concentrations (2 mg L^{-1}) in aqueous solution (Table 1). At highest concentrations (10 mg L^{-1}) of HM,

Table 1
Equilibrium absorbing amount of selected HM by algal species

Algae species	Q_e (mg g^{-1})				Removal efficiency (%)			
Initial concentration (mg L^{-1})	Cd	Cr	Ni	Pb	Cd	Cr	Ni	Pb
Cladophora glomerata								
1	0.336	0.24	0.326	0.366	67.2	48	65.2	73.2
2	0.573	0.47	0.535	0.678	57.3	47	53.5	67.8
4	0.967	0.748	1.098	1.08	48.4	37.4	54.9	54
8	2.629	1.805	2.589	2.901	65.7	45.1	64.7	72.5
10	2.94	2.244	3.221	3.277	58.8	44.9	64.4	65.5
Oedogonium westii								
1	0.335	0.26	0.24	0.275	67	52	48	55
2	0.55	0.385	0.428	0.454	55	38.5	42.8	45.4
4	0.933	0.756	0.82	0.908	46.7	37.8	41	45.4
8	2.296	1.847	1.888	2.109	57.4	46.2	47.2	52.7
10	2.317	1.874	2.087	2.744	46.3	37.5	41.7	54.9
Vaucheria debaryana								
1	0.135	0.21	0.19	0.175	27	42	38	35
2	0.216	0.316	0.28	0.295	21.6	31.6	28	29.5
4	0.424	0.6	0.511	0.564	21.2	30	25.6	28.2
8	1.036	1.445	1.391	1.56	25.9	36.1	34.8	39
10	1.283	1.459	1.344	1.711	25.7	29.2	26.9	34.2
Zygnema insigne								
1	0.249	0.395	0.191	0.296	49.8	79	38.2	59.2
2	0.429	0.615	0.296	0.45	42.9	61.5	29.6	45
4	0.723	1.037	0.524	0.875	36.2	51.9	26.2	43.8
8	1.916	2.399	1.517	2.015	47.9	60	37.9	50.4
10	1.874	2.396	1.625	2.324	37.5	47.9	32.5	46.5

the biosorption efficiency was in order of Pb (65.5%) > Ni (64.4%) > Cd (58.8%) > Cr (44.9%). Results of higher biosorption efficiency for HM were consistent with the previous study for industrial wastewater [40].

O. westti showed that at low concentrations in aqueous solution (1, 2 mg L^{-1}), the biosorption was recorded high for the HM such as Cd (46.3%–67%) and Pb (45.4%–55%). This specie showed high biosorption effect for Cd and Cr at low concentrations. However, when the HM concentrations in the aqueous solution increased to 10 mg L^{-1}, the biosorption capacity reduced was and were in the order of Pb (54.9%) > Cd (46.3%) > Ni (41.7%) > Cr (37.5%) (Table 1). Results of higher biosorption efficiency for HM were consistent with the previous study on wastewater [25].

V. debaryana showed high algal biosorption for the Cr and Ni at low concentrations (Table 1). The Cr biosorption reached 42%, followed by Ni (38%) > Pb (35%) > Cd (27%) at low concentration 1 mg L^{-1}. At 2 mg L^{-1}, the biosorption capacity was in order of Cr > Ni > Pb > Cd. This specie showed that the biosorption efficiency slightly decreases at high concentration (10 mg L^{-1}) in the aqueous solutions the biosorption for the contaminant was in the order of Pb (34.2%) > Cr (29.2%) > Ni (26.9%) and Cd (25.7%). Results of higher biosorption efficiency for HM were consistent with the previous study on industrial wastewater [40].

Table 1 summarizes the equilibrium biosorption of *Z. insigne* for each contaminant in aqueous solution; the removal efficacy was ranged 47.9%–79%, 43.8%–59.2%, 36.2%–49.8% and 26.2%–38.2% for Cr, Pb, Cd and Ni at range of 1–10 mg L^{-1}, respectively. This algal showed high biosorption at a low concentration (1 mg L^{-1}) for Cr (79%), followed by Pb (59.2%) > Cd (49.8%) and Ni (38.2%). At low concentration (2 mg L^{-1}), the biosorption for Cr (61.5%) and Pb (45%) was in the order Cd > Ni. The initial concentration of HM

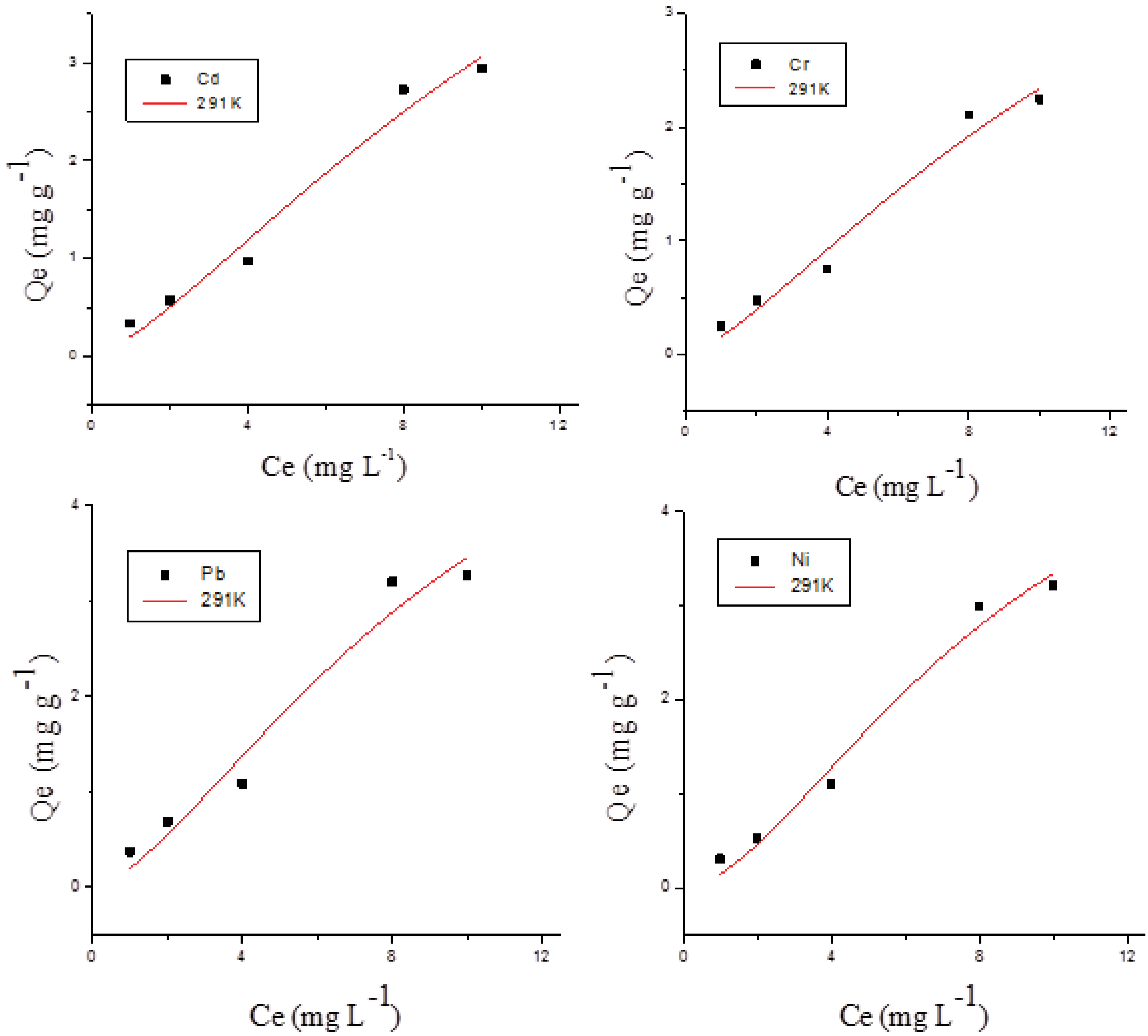

Fig. 2. Adsorption isotherms of Cd, Cr, Ni and Pb by *Cladophora glomerata*.

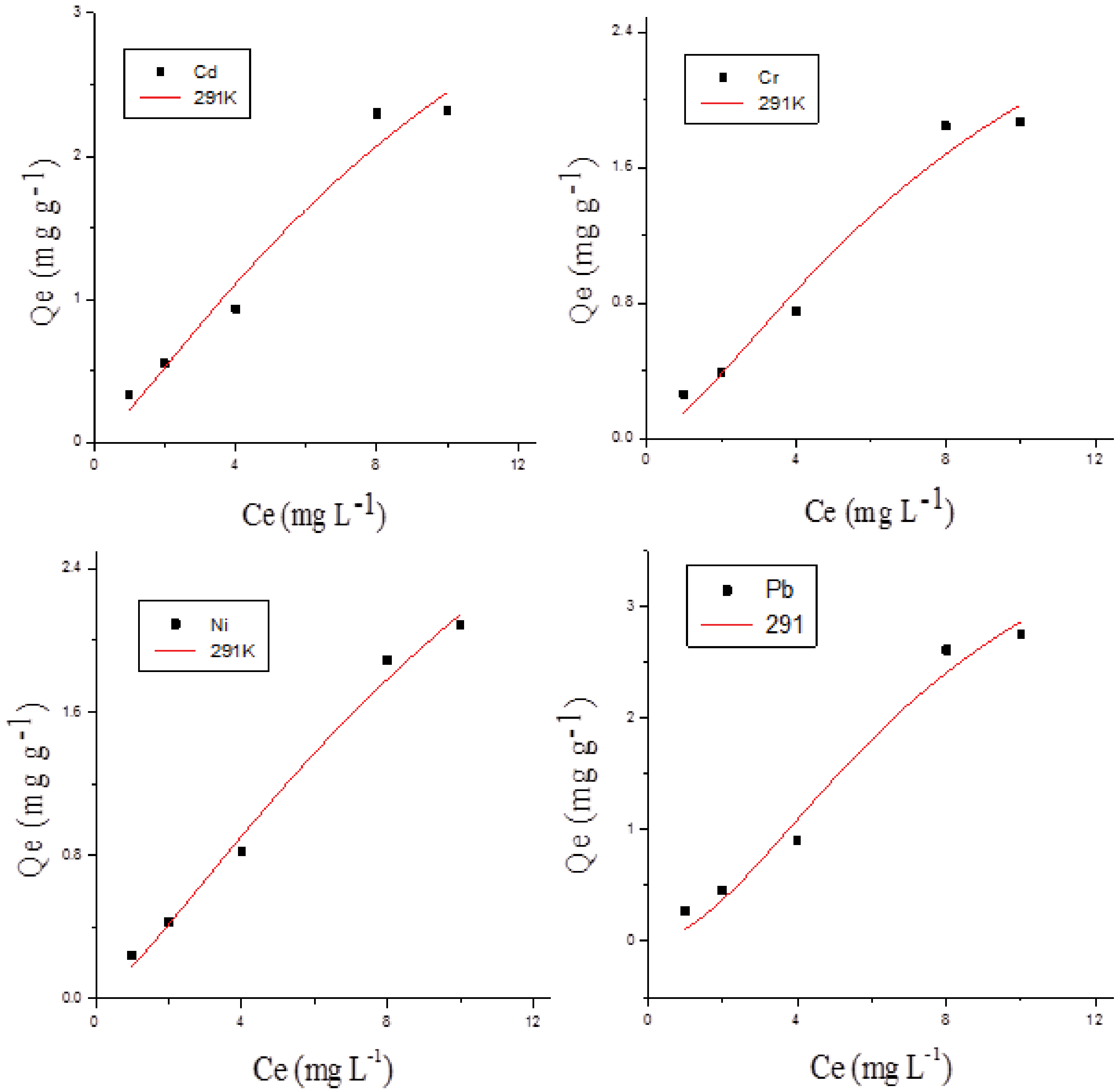

Fig. 3. Adsorption isotherms of Cd, Cr, Ni and Pb by *Oedogonium westii*.

increased in the aqueous solution, the biosorption slightly decreased and within the order of Cr > Pb > Cd > Ni.

Algal biomasses host the biomolecules including lipids, proteins and carbohydrates distributed on the surface of the cell wall that reacts with the HM ions. The interactions of algal biomass protons and HM ions represented that metal ions were sorbed through electrostatic attraction to negative sites algal surface [41,42]. Previously, Jaafari and Yaghmaeian [43] reported high effectiveness of algal specie *Chlorella* for bio-accumulation of HM more efficiently at low doses. An increase in the algal biomasses resulted in more binding sites availability and decreased HM biosorption has been reported if algal biomass quantities were higher than a specific amount that was attributed to the partial accumulation of biomass, a cooperative process that limits the available effective binding site for HM biosorption [43,44].

3.3. Biosorption isotherm Langmuir model

Langmuir isotherm model is used worldwide for biosorption because this assumes that sorption process occurs at a specific sorption surface. This model basic postulated mechanism is illustrated by certain constants values that can be applied to compare diverse biosorbent for various pollutants and the sorption process occurs at a specific sorption surface [34,40,45,46]. The pull between molecules lower

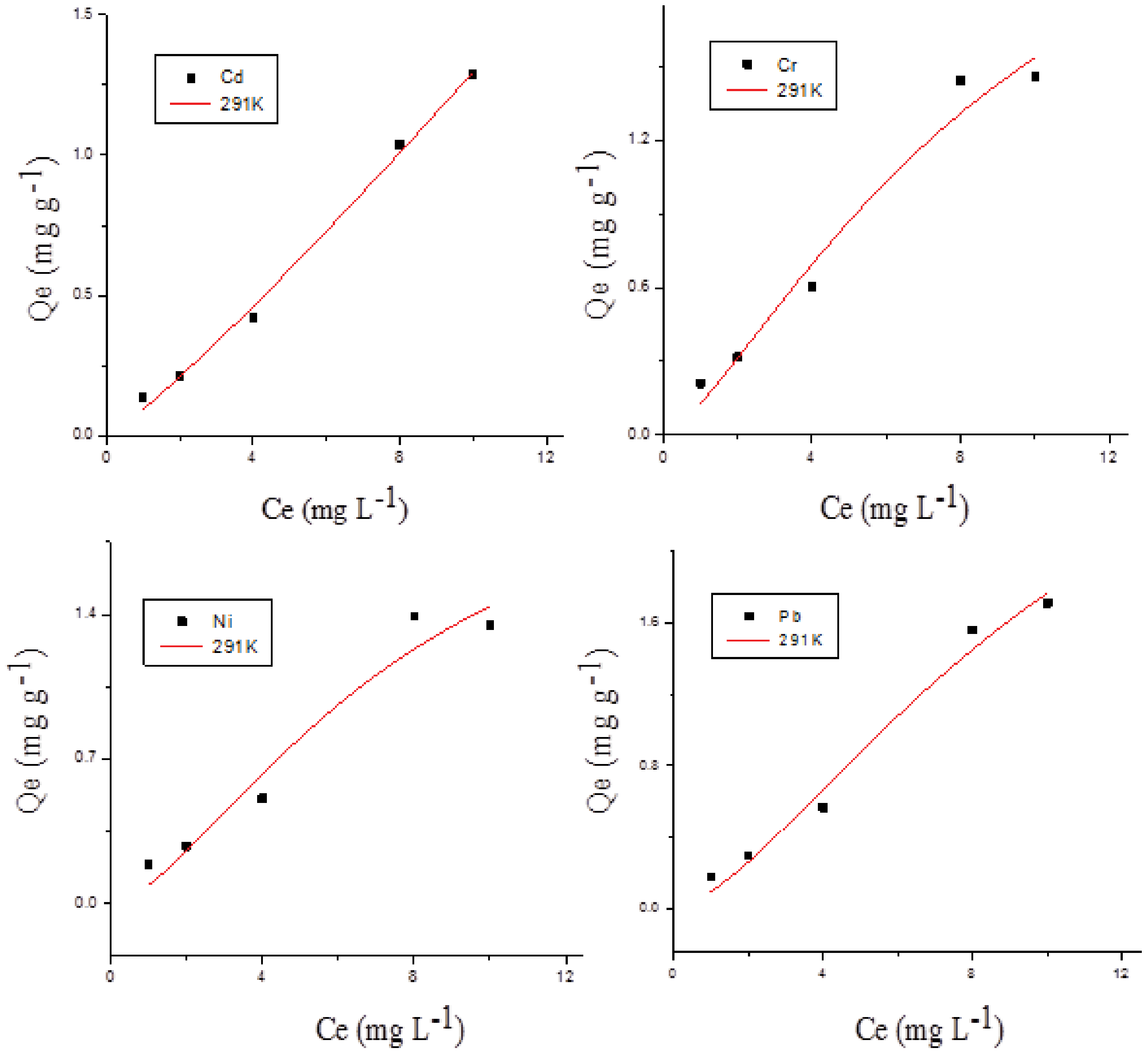

Fig. 4. Adsorption isotherms of Cd, Cr, Ni, and Pb by *Vaucheria debaryana*.

as distance increase from the sorption surface. In this study, Langmuir equation was used to fit the experimental data for algal biomasses (Figs. 2–5). The high correlation coefficients (R^2) are the evident and constants Q_m, b and c were determined.

Table 2 summarizes the high changes in the model constants for Pb, Cr, Cd and Ni sorption by *C. glomerata*. The high Q_m value of Cd was followed by that of Pb. The Cr, Ni and Pb achieve the conditions that a high metal sorbent should have high value of Q_m [32,47] particularly for Cd and for *O. westii* Q_m value for Ni was high in the order Cd > Pb > Cr. The Q_m value for *V. debaryana* was recorded highest for the Cd followed by Pb > Cr > Ni. Similarly, the Q_m value for *Z. insigne* was recorded highest for Pb followed by Cr > Ni > Cd (Table 2).

The observation that biomass showed a high affinity for an HM and less sorption capacity, may be linked with the degree of affinity of particular biomass for each HM. The total amount of HM adhered to its surface depending on the number of the active sites and how easily it can be reached [31,45,48]. The studied algal species showed high HM accumulation from aqueous solution and could be very useful to decontaminate the hazardous HM from wastewater effluents. The specific concentration of Cr is very essential to mammals because it helps in the control of the blood-sugar levels but unsafe to fish and human when the threshold limit 0.05 mg L^{-1} in water is surpassed [49]. Similarly, the ingestion of a higher concentration of Ni-chloride and Ni-sulfate causes fatal heart and other severe health problems [50]. Pb is one of the hazardous carcinogenic metals and results in

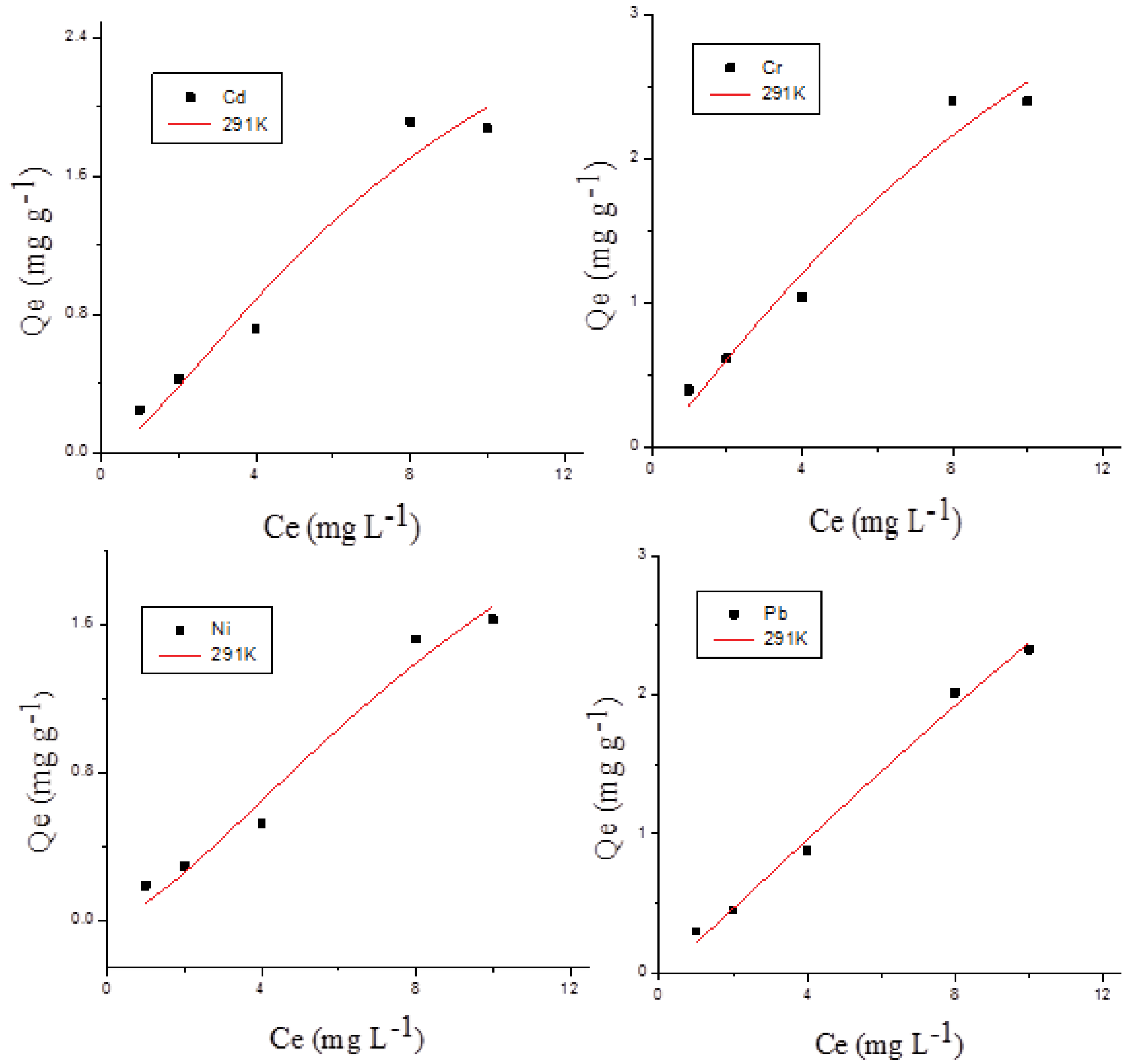

Fig. 5. Adsorption isotherms of Cd, Cr, Ni and Pb by *Zygnema insigne*.

health risks problems such as abdominal pain, headache, blood pressure, irritability, kidney and nerve damages, stomach and lung cancer [51,52], and intellectual problems in children [15]. Zn has essentially required elements of the human body. However, it causes toxicity such as sideroblastic anemia at higher doses [53].

4. Conclusions

The algae species were studied for the biosorption of HM from solution at variable concentrations and biomass dosage. The removal efficiency varied with metal concentration and different biomass dosage. The *C. glomerata* biosorptions were very effective for the removal of Pb (73.2%), followed by Cd (67%) and Ni (65.2) at a low concentration from the aqueous solution. The *O. westii* with an efficiency of 67% can be used for the removal of Cd from the wastewater. Similarly, in this study Z. *insigne* showed high biosorption efficiency for the removal of Cr, Pb, Cd and Ni at low concentration and the biosorption reached 79%, 59.2% 49.8% and 38.2%, respectively. Therefore, this study recommends the growth of algal species including *C. glomerata* and Z. *insigne* along wastewater effluent streams.

Acknowledgments

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Table 2
Langmuir constant for the sorption of test metals by algal species

Algae species	Langmuir constant			
	Q_m (mg g^{-1})	b	c	R^2
Cladophora glomerata				
Cd	7.940	0.026	–0.389	0.954
Cr	5.840	0.028	–0.384	0.951
Ni	5.851	0.027	–0.699	0.969
Pb	6.752	0.030	–0.539	0.932
Oedogonium westii				
Cd	5.435	0.044	–0.269	0.940
Cr	3.633	0.043	–0.440	0.948
Ni	5.558	0.033	–0.276	0.982
Pb	4.641	0.025	–0.809	0.957
Vaucheria debaryana				
Cd	100.094	0.001	–0.132	0.993
Cr	2.956	0.046	–0.377	0.946
Ni	2.404	0.040	–0.569	0.914
Pb	3.820	0.025	–0.533	0.968
Zygnema insigne				
Cd	3.629	0.043	–0.453	0.923
Cr	6.017	0.050	–0.162	0.939
Ni	3.854	0.026	–0.485	0.951
Pb	15.126	0.015	–0.106	0.986

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