

## **BIOSORPTION OF SELECTED HEAVY METALS BY THE BIOMASS OF THE GREEN ALGA *SPIROGYRA* SP.**

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**Abstract.** *In this paper, the influence of contact time, initial pH and metal ion concentrations on the adsorption properties of a freshwater green alga (*Spirogyra* sp.) biomass was studied. Several model solutions of selected heavy metals (Cd, Cu, Cr, Pb) were put into contact with the green algae-based sorbent for different time periods. After the treatment, the concentrations of heavy metals in model solutions were determined using flame atomic absorption spectrometry (FAAS) and inductively-coupled plasma-optical emission spectrometry (ICP-OES). Fourier transform infrared spectroscopy (FTIR) was used to reveal which functional groups were responsible for the green algae biosorption properties. Adsorption capacities were found to be 22.52, 38.19, 35.59 and 94.34 mg/g for Cd, Cr, Cu and Pb, respectively, at contact times of 15-50 minutes and initial metal ion concentrations of 500-700 µg/g. The optimum pH for biosorption of Cd, Cr, Cu and Pb were 5.5, 5.8, 5.9 and 5.0, respectively. The biosorption process followed second order kinetics and fitted the Langmuir isotherm model. Biomonitoring studies suggested the possible use of this freshwater green alga as a bioindicator, with mean concentration factors for the selected elements in the range of 367-7154.*

**Key words:** *Green algae, biosorption, biomonitoring, toxic metals, FAAS, ICP-OES, FTIR*

### 1. INTRODUCTION

Heavy metals such as cadmium, chromium, copper and lead are among the most important pollutants because of their toxicity and non-biodegradability [1]. These metals may reach the environment mainly from industrial plating baths, acid mine-drainage and metal cleaning baths. Important sources of Cd pollution are the plastics industry, Ag-Cd

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batteries and paints and pigments; paper and fertilizer industry are common sources of Cu pollution; Pb enters environment throughout the combustion of fossil fuels and the smelting of sulfide ores [2].

Cadmium may cause renal dysfunction, hypertension, hepatic injury, lung damage and have teratogenic effects [3]. Excessive intake of copper results in its accumulation in liver and may produce gastro-intestinal catarrh. It is also toxic to aquatic organisms even at very small concentrations in the natural waters [4]. Chromium(VI) is more harmful than Cr(III): it has higher mobility and is an acute carcinogen. Lead accumulates mainly in bones, brain, kidney and muscles and may cause many serious disorders like anemia, kidney diseases, nervous disorders, mental retardation and sickness even death [5]. Thus, removal of these metals from the environment is an important issue.

Numerous processes have been used for the removal of heavy metal ions from aqueous solution. Among others, these include ion exchange, precipitation, reverse osmosis, phytoextraction, ultra-filtration and electro-dialysis [6]. However, these methods are either inefficient in removing trace metal concentrations or quite expensive [7,8]. Biosorption, which uses biological materials for removal of pollutants, is a relatively new technology. It is suitable for removing even trace concentrations of heavy metals from polluted water. Biosorbent materials, such as naturally occurring green algae or other seaweeds, are generally less costly than existing technologies [9]. Removal of pollutants is either based on physical sorption (ion exchange, complexation, chemisorption related to polysaccharides, proteins or lipid on their cell wall surfaces) or is mediated by appropriate metabolic pathways [10]. Algae (these are particularly useful because of their widespread distribution), moss, aquatic plants and leaf-based adsorbents have proved to possess high metal binding capacities [1,11-13].

Biomonitoring is the science of inferring the ecological condition of an area by examining the organisms that live there. Biomonitoring involves the quantitative measurement of an organism's exposure to toxic substances in the environment by determining the substances or their metabolites in specified parts of the organism. Biomonitoring measurements indicate the amount of pollutant that actually gets into the organism from all environmental sources such as air, soil, water, dust and food. It is most often used to assess water quality of rivers, lakes, streams, and wetlands [14]. A good bioindicator should be sedentary, of suitable dimensions, easy to identify and collect, widely distributed, and be able to accumulate metals to a satisfactory degree [15].

The aim of this work was to investigate whether (and under which experimental conditions: pH, contact time, *etc.*) green algae (*Spirogyra* sp.) are suitable biosorbent for the removal of Cd, Cr, Cu and Pb from several model solutions and whether they might be used in heavy metal biomonitoring studies around Thika and Juja, Kenya. Concentration of heavy metals in treated model solutions were determined using flame atomic absorption spectrometry (FAAS) and inductively-coupled plasma-optical emission spectrometry (ICP-OES). Fourier transform infrared spectroscopy (FTIR) was used to reveal which functional groups were carriers of green algae biosorption properties. The adsorption capacities were evaluated from equilibrium adsorption isotherms.

## 2. MATERIALS AND METHODS

### 2.1. Equipment and reagents

Flame Atomic Absorption Spectrophotometer (210VGP, UK) using air acetylene flame system and hollow cathode lamps and a Perkin Elmer Optima 5300D ICP – OES spectrophotometer operating in axial mode were used for metal determination. pH measurements were done using a digital pH meter fitted with a temperature probe and a glass electrode (pH 211, HANNA Instruments) while vacuum filtration was done using a Millipore filter funnel equipped with a 0.45  $\mu\text{m}$  cellulose acetate filter membrane. The algae spectra were generated from a Fourier Transform Infrared Spectrophotometer 8400CE (Shimadzu, Japan) fitted with a pellet cell. All chemicals used in this work, were of analytical grade and were used without further purification. All solutions were prepared using distilled water. Stock solutions were prepared by dissolving appropriate amounts of analytical grade salts in 250 mL distilled water, acidified by adding 5mL of concentrated nitric acid and the solution finally made to a liter using distilled water. Working solutions were made by diluting stock solutions.

### 2.2. Sampling

Fresh green algae was collected from a stationery fresh water pond in Juja, Kenya, washed in tap water several times and rinsed with distilled water. The algae samples were sun-dried in the open for two days then oven-dried at 60 °C for eight hours. Finally it was grinded, sieved to 0.5mm particle size and stored in a plastic bottle at room temperature until use. A second batch of algae samples was collected from various water ponds along Thika road, Juja and around Thika town and treated as described above. Water samples were also collected from each site, acidified to a pH 2 by addition of concentrated nitric acid. The water samples were stored in a refrigerator at 4 °C in plastic bottles until use.

### 2.3. Optimization of pH

Batch biosorption experiments were conducted on model solutions of Cd, Cr, Cu and Pb. For each element, the stock solution was diluted to 200 mg/L using 0.1 molar acetate buffer and divided into two series of appropriate number of 50 mL batches, for which pH values were adjust to 2.0, 3.0, 4.0, 4.5, 5.0, 5.5, 6.0 or 7.0 using concentrated sodium hydroxide and nitric acid solutions. The samples from the first series were equilibrated with 0.20 g of crushed algae for two hours while the second series (control) was allowed to stand for two hours without addition of biosorbent. Both solutions were filtered through a 0.45  $\mu\text{m}$  membrane and the filtrate analyzed for residual metal ion concentration by FAAS and ICP-OES. All experiments were done in triplicate and the mean values reported. A plot of biosorption against pH was used to determine the optimum pH.

### 2.4. Optimization of contact time

The stock solutions of the selected metal ions were each diluted with acetate buffer solution to obtain 500 mL of 100 and 200 mg/L solutions of Cd, Cr, Cu and Pb. The pH of the solutions was adjusted to 5.5, 5.8, 5.9 and 5.0 for cadmium, chromium, copper and lead, respectively. Exactly 2.00 g of crushed algae was weighed out and added to 500 mL of each solution and equilibrated for 140 minutes with magnetic stirring at 300 rpm.

Mixture (10 mL) was withdrawn at measured time intervals between 0 and 140 minutes. Each portion was immediately filtered through a 0.45  $\mu\text{m}$  membrane and the residual metal ion concentration determined by FAAS. All experiments were done in triplicate.

To determine the order of the reaction, the experimental data was fitted to both 1<sup>st</sup> and 2<sup>nd</sup> order rate equations. Linear correlation coefficient ( $R^2$ ) values were used to deduce the order of reaction.

### 2.5. Optimization of initial metal concentration

The initial concentration which gives rise to the highest metal uptake was determined. Initial concentrations ranging from 50 to 1000 mg/L and the respective optimum pH values were used for each metal. 50 mL of each solution was equilibrated with 0.2g of finely crushed algae for two hours with stirring at 300rpm. The solution was filtered through a 0.45 $\mu\text{m}$  membrane and the residual metal ion concentration determined by FAAS and ICP-OES. The data was fitted to the linearized Freundlich and Langmuir adsorption isotherms from which the adsorption capacity was calculated. A plot of metal uptake (mg/g) against initial metal ion concentration was done for all metals and used to determine the optimum initial metal concentration.

### 2.6. Biomonitoring studies

The metal concentrations in acid – leached algae, digested algae and in the water samples where the algae material was collected from were determined. Leaching was done by shaking 1 g of ground algae sample with 20 mL of 0.1M hydrochloric acid for five minutes, filtering and rinsing the residue with enough distilled water to make 50 mL of filtrate while the digestion was done on dried algal biomass using a 3:1:1 mixture of concentrated perchloric, nitric and hydrochloric acids, respectively. The digested and acid – leached samples were filtered through a 0.45  $\mu\text{m}$  membrane filter and the filtrate made up to 50 mL before analysis by FAAS and ICP-OES. Concentration factors were calculated from the total metal ion concentration in digested algae and that in the water samples.

**Table 1** FTIR peaks and their possible assignments

Peak position before loading ( $\text{cm}^{-1}$ )	Peak position after loading ( $\text{cm}^{-1}$ )	Possible assignment
3386.8	3355.9	O-H <sub>str</sub> , alcohols/phenols, N-H, amines
2931.6	2923.9	O-H <sub>str</sub> , carboxylic acids
2376.1	-	C $\equiv$ N
1651.0	1651.0	C=N, C=O <sub>vib</sub> , C=C, N-H <sub>bend</sub>
1380.9	1380.9	O-H <sub>bend</sub> , S=O <sub>str</sub> , CH <sub>3</sub> bend and ss, N-O
1041.5	1033.8	C-N <sub>str</sub> , aliphatic amines
678.9	540.0	-C $\equiv$ C-H: C-H <sub>bend</sub> alkynes
617.2	470.6	-C $\equiv$ C-H: C-H <sub>bend</sub> alkynes, C-Br <sub>str</sub> , alkyl halides

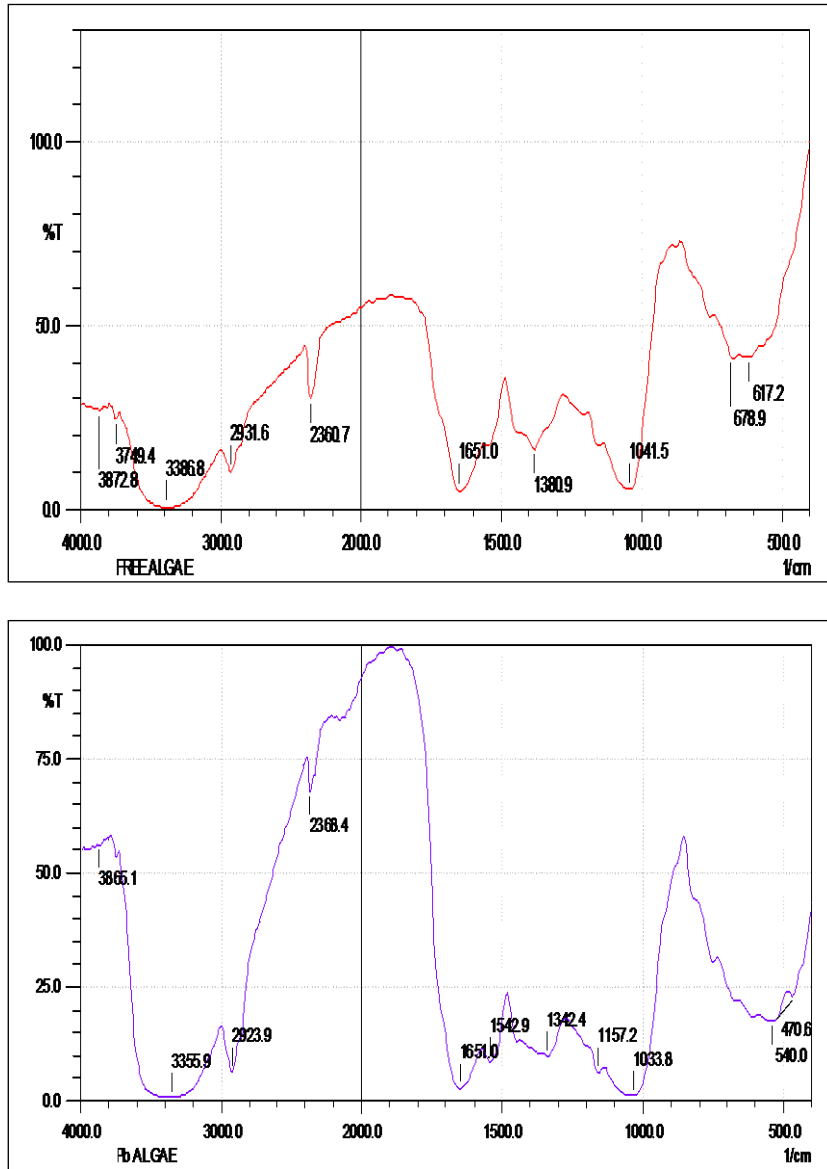


Fig. 1 FTIR Spectra of free (top) and metal loaded algae (bottom).

### 3. RESULTS AND DISCUSSION

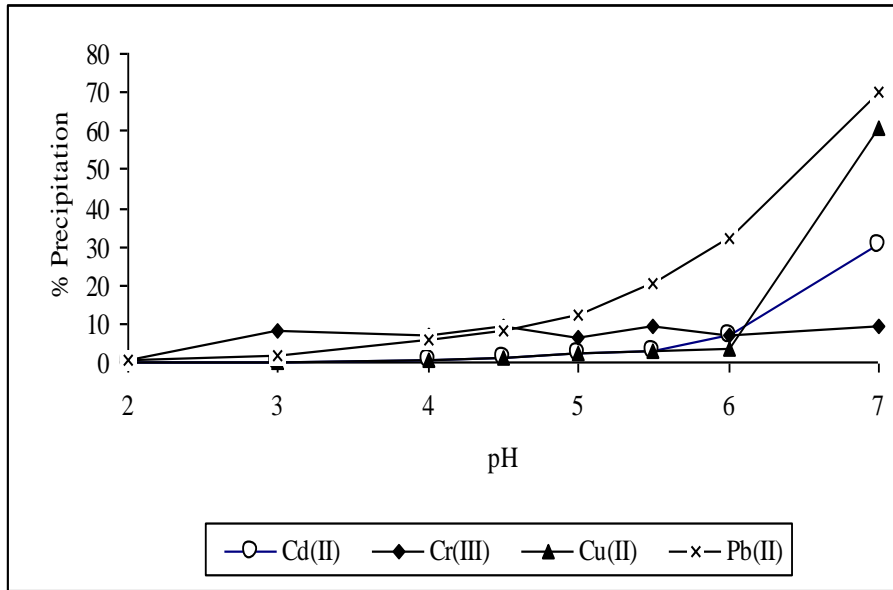
#### 3.1. Functional groups in green algae

The functional groups involved in biosorption of heavy metal by green algae were investigated by FTIR analysis. The spectrum of free algae and algae loaded with chromium metal is shown in Fig. 1. The position of absorption bands and corresponding functional groups able to interact with metal ions are summarized in Table 1. The results of FTIR analysis confirm the presence of carboxylic, amino, hydroxyl and carbonyl groups on the algal surface as suggested in literature [16,17]. After adsorption of lead, slight changes were observed in the absorption peak frequencies between 2000 and 4000  $\text{cm}^{-1}$ . For instance, the peak at 2360.7  $\text{cm}^{-1}$  attributed to a cyanide group completely disappears. This was probably due to the coordination of the heavier metal atom to an active functional group resulting in a vibration frequency below the selected range. Other peaks (3386.8, 2931.6, 1380.9, 1041.5, 678.9  $\text{cm}^{-1}$ ) are also observed to shift to lower frequencies (3355.9, 2923.9, 1342.4, 1033.8, and 540.0  $\text{cm}^{-1}$  respectively) after loading the algae with lead. This was probably due to the attachment of the heavier metal atom to an active functional groups resulting in lower vibration frequency. Similar trends are observed for all other selected metals.

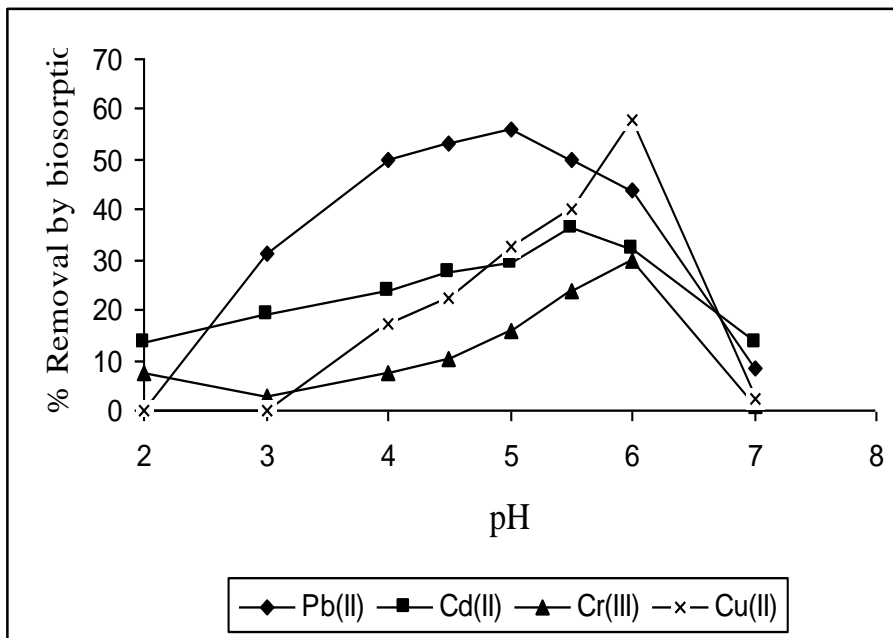
#### 3.2. Effect of pH

The residual metal ion concentrations after batch equilibration with algae at various pH values were determined. The metal removal is a combination of biosorption and precipitation. The relative proportion due to each process was determined. Plots of the relative removal by precipitation are shown for each metal in Fig. 2. For all the metals considered, metal removal by all processes was low at low pH. For biosorption the removal rises to a peak between pH 5 and 6 then starts to decline.

This is probably because at low pH there is high competition for adsorption sites between metal ions and protons. Furthermore, at low pH both the hydrogen ion and the metal ion concentration are high since the metals are not precipitated but are available in solution. This explains why both processes are ineffective at low pH values. Since algal biomass has a high content of carboxyl groups on its cell walls, biosorption process can be affected by changes in the solution pH [18]. Change in pH affects both the nature of the functional groups as well as the metal chemistry. As the pH rises, the hydrogen ion concentration falls resulting in an increase in biosorption of heavy metals. The high pH also leads to precipitation of low solubility metal hydroxides as shown in Figure 2a. Precipitation and complexation interfere with the biosorption process because they immobilize the metal ions thus making them unavailable for biosorption. Precipitation is due to the formation of low solubility metal hydroxides [4, 5, 17], while complexation may occur between the acetate ions in the buffer and the metal ions in solution. The optimum pH for biosorption is thus a compromise between interference from precipitation at high pH, a competition with hydrogen ions for sorption sites at low pH and complexation. To obtain the optimum pH, a graph of percentage of metal removal by biosorption against pH was plotted. Plot (Fig. 2b) shows the difference between the total metal removal (biosorption/precipitation/complexation, *etc.*) and metal removal by processes other than biosorption (precipitation/complexation, *etc.*). According to these curves (Fig. 2b), the optimum pH values for the selected metals were found to be 5.5, 5.8, 5.9 and 5.0 for cadmium, chromium, copper and lead, respectively.



(a)



(b)

**Fig. 2** Percent metal uptake from solution (a) other processes and (b) biosorption.

### 3.3. Effect of contact time

The minimum time required for quantitative uptake of metal ions from solution was determined. The contact time was obtained by plotting the mean percentage metal ion uptake against time as shown in Figure 3. For all metals considered, metal adsorption was very rapid and went to completion in less than an hour. Cadmium adsorption was the fastest with quantitative uptake being achieved in fifteen minutes while chromium and copper took forty minutes. For lead, quantitative uptake occurred in fifty minutes. Hence the contact times for the selected metals were found to be 15 minutes for cadmium, 40 minutes for both chromium and copper and 50 minutes for lead. The short contact times demonstrate the potential of algae as a suitable biosorbent for fast removal of heavy metals from contaminated water.

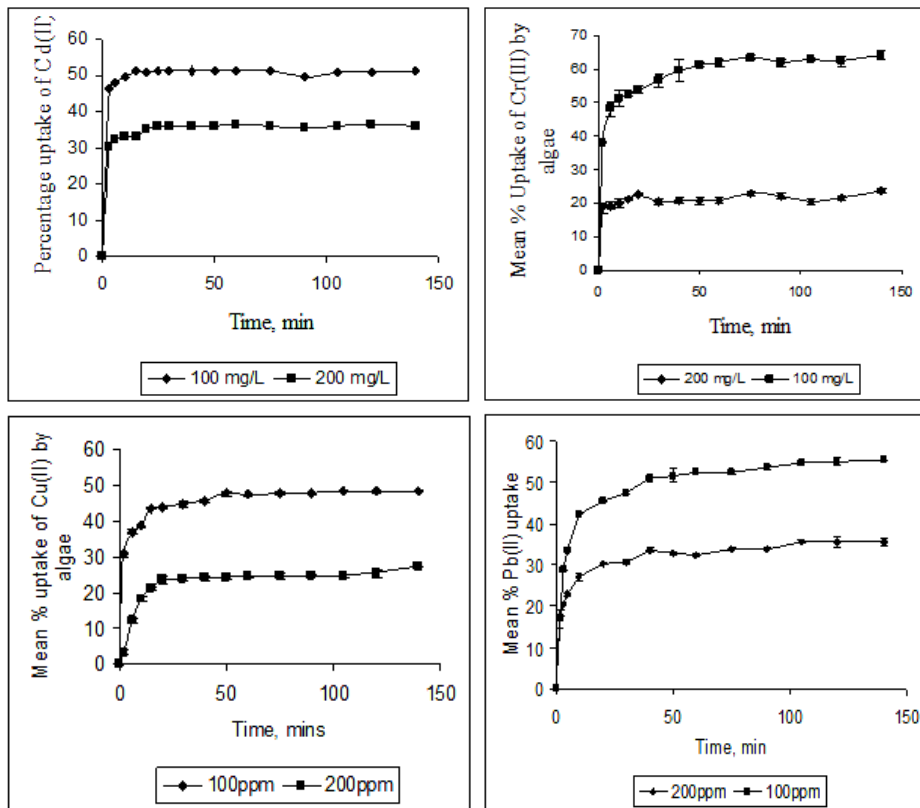


Fig. 3 Percentage of metal uptake as a function of time.

### 3.4. Order of reaction

The first and second-order kinetics of biosorption processes are described by the rate equations (1) and (2), respectively, which upon integration yield the following solutions (3) and (4). Linear plots of  $t$  versus  $\ln(q_e - qt)$  and  $t/q_t$  versus  $t$  were used to test the data for first and second order kinetics. Linear correlation coefficients ( $R^2$  values) were used to deduce the order of reaction. For all studied metals (the kinetic parameters are summarized



in Table 2), the results fit better in to second order integrated rate equation (plot for lead is given in Fig. 4). These results agree with the previously published data [2,19].

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (1)$$

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (2)$$

$$k_1 t = \ln q_e - (\ln q_e - q_t) \quad (3)$$

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \quad (4)$$

**Table 2** Kinetic parameters for Cd, Cr, Cu and lead

Metal	Initial metal concentration ( $\mu\text{g/mL}$ )	Calculated metal uptake $q_e$ in (mg/g) at equilibrium	$R^2$ values for 1 <sup>st</sup> order linearity test	$R^2$ values for 2 <sup>nd</sup> order linearity test
Cd(II)	200	3.64	0.338	1.000
	100	2.55	0.159	1.000
Cr(III)	200	8.06	0.598	0.999
	100	5.60	0.884	0.996
Cu(II)	200	26.39	0.719	0.998
	100	24.45	0.944	0.999
Pb(II)	200	35.97	0.904	0.999
	100	27.55	0.948	0.997

**Table 3** Equilibrium concentration  $C_e$ (mg/L) and metal uptake  $q_e$ (mg/g) data fitted to Langmuir and Freundlich isotherms

Metal ion $C_i$ ( $\mu\text{g/mL}$ )	Cd(II)		Cr(III)	
	$C_e$	$q_e$	$C_e$	$q_e$
50	14.3 $\pm$ 0.6	8.9 $\pm$ 0.2	4.2 $\pm$ 0.5	5.7 $\pm$ 0.1
150	87.4 $\pm$ 0.5	15.6 $\pm$ 0.1	30.8 $\pm$ 1.9	14.9 $\pm$ 0.2
300	214.0 $\pm$ 0.4	21.5 $\pm$ 0.1	104.2 $\pm$ 1.7	24.5 $\pm$ 0.2
500	410.9 $\pm$ 1.0	22.3 $\pm$ 0.3	257.6 $\pm$ 4.6	30.3 $\pm$ 0.6
600	517.9 $\pm$ 0.5	20.5 $\pm$ 0.1	349.2 $\pm$ 1.6	31.4 $\pm$ 0.2
700	616.7 $\pm$ 0.3	20.8 $\pm$ 0.1	424.1 $\pm$ 7.8	34.5 $\pm$ 1.0
850	760.2 $\pm$ 0.5	22.5 $\pm$ 0.1	559.7 $\pm$ 4.2	36.3 $\pm$ 1.8
1000	859.3 $\pm$ 0.6	35.2 $\pm$ 0.2	713.3 $\pm$ 5.7	35.8 $\pm$ 0.7
Metal ion $C_i$ ( $\mu\text{g/mL}$ )	Cu(II)		Pb(II)	
	$C_e$	$q_e$	$C_e$	$q_e$
50	12.1 $\pm$ 0.8	9.5 $\pm$ 0.2	30.3 $\pm$ 0.5	34.8 $\pm$ 0.3
150	84.2 $\pm$ 0.5	16.5 $\pm$ 0.1	83.2 $\pm$ 8.5	58.4 $\pm$ 4.3
300	208.6 $\pm$ 0.8	22.9 $\pm$ 0.2	146.7 $\pm$ 12.4	76.7 $\pm$ 1.2
500	389.0 $\pm$ 2.6	27.8 $\pm$ 0.6	338.2 $\pm$ 2.4	80.9 $\pm$ 3.0
600	485.54 $\pm$ 0.6	28.6 $\pm$ 0.2	426.0 $\pm$ 6.0	87.0 $\pm$ 0.3
700	574.7 $\pm$ 13.4	31.3 $\pm$ 3.4	537.6 $\pm$ 1.8	81.2 $\pm$ 0.9
850	721.6 $\pm$ 0.3	32.1 $\pm$ 0.1	631.5 $\pm$ 3.0	84.3 $\pm$ 1.5
1000	869.6 $\pm$ 4.6	32.6 $\pm$ 1.2	713.2 $\pm$ 11.2	93.4 $\pm$ 5.6

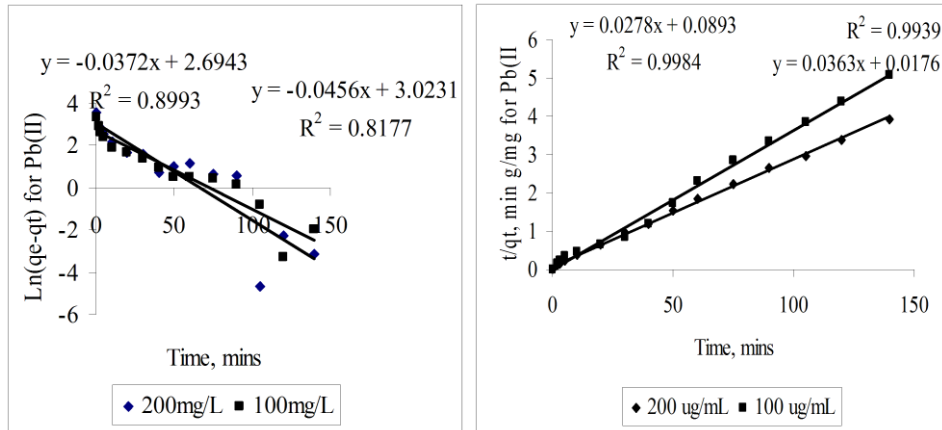


Fig. 4 First and second order linearity plots for lead.

### 3.5. Adsorption capacity

The analytical forms of Langmuir and Freundlich isotherms are given below (equations (5) and (6)). Here,  $q_e$  and  $q_{max}$  are the equilibrium and maximum metal uptake in mg per gram of biosorbent, respectively;  $C_e$  is the equilibrium metal ion concentration,  $b$ ,  $K_F$  and  $n$  are Langmuir and Freundlich constants, respectively. However, better fit of experimental results are obtained for the linearized Langmuir and Freundlich isotherms (equations (7) and (8)). The resulting linear plots in the case of lead are given in Fig. 5. The values of linear regression coefficients of the linearized isotherms revealed that the experimental data fitted better to the Langmuir isotherm, Fig. 5. Thus, the adsorption capacities were determined from the Langmuir adsorption isotherm. The data are summarized in Table 3.

$$q_e = q_{max} \left( \frac{bC_e}{1 + bC_e} \right) \quad (5)$$

$$q_e = k_F (C_e)^{1/n} \quad (6)$$

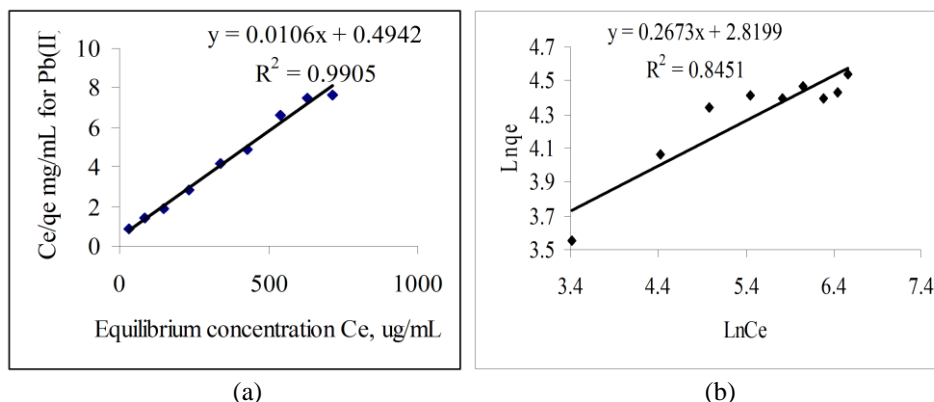
$$\frac{C_e}{q} = \frac{1}{q_{max} b} + \frac{C_e}{q_{max}} \quad (7)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (8)$$

Table 4 Comparison of adsorption capacity of green algae for Cd, Cr, Cu and Pb ions with that of different biomasses

Biomass	Adsorption capacity (mg/g)				Reference
	Cd	Cr	Cu	Pb	
<i>Caulerpa lentillifera</i>	4.7	-	-	28.7	[20]
<i>Mucor rouxii</i>	8.5	-	-	35.7	[21]
<i>Chlorella minutissima</i>	11.1	-	-	9.7	[22]
<i>Palmaria palmate</i> (red algae)	-	-	6.6	-	[9]
<i>Pseudomonas aeruginosa</i> (bacteria)	-	-	23.0	68.4	[1]
Alfalfa biomass	-	6.2	-	-	[21]
Green algae	2.5	8.2	5.6	4.3	Present results

The adsorption capacity,  $q_{max}$  was calculated from the linearized Langmuir isotherm and found to be 22.52, 38.19, 35.59 and 94.34 mg/g for cadmium, chromium, copper and lead, respectively.



**Fig. 5** Data for Pb fitted to Langmuir (a) and Freundlich (b) isotherms.

**Table 5** Comparison of experimentally observed metal uptakes  $q_e$  (mg/g) against the Langmuir capacities for selected metals

Metal ion	Cd(II)	Cr(III)	Cu(II)	Pb(II)
Langmuir adsorption capacity (mg/g)	22.5	38.2	35.6	94.3
Experimentally observed adsorption capacity (mg/g)	$22.29 \pm 0.26$	$34.49 \pm 0.97$	$31.32 \pm 3.35$	$93.42 \pm 5.59$

**Table 6** Average concentrations of the selected metals in environmental samples

Metal	Water		Algae
	Total concentration ( $\mu\text{g/L}$ )	Leachable concentration ( $\mu\text{g/g}$ )	Total concentration ( $\mu\text{g/g}$ )
Cd	$1.82 \pm 0.11$	$0.01 \pm 0.09$	$2.30 \pm 0.09$
Cr	$64.33 \pm 0.35$	$4.43 \pm 1.86$	$12.17 \pm 0.20$
Cu	$17.14 \pm 0.15$	$8.23 \pm 0.59$	$25.61 \pm 0.74$
Pb	$12.08 \pm 1.80$	$0.19 \pm 0.01$	$60.50 \pm 1.57$

Table 4 gives a comparison of the adsorption capacity of algae with those of other biosorbents from literature. From the table it is clear that the adsorption capacity of freshwater green algae for the selected metals is high compared to other biosorbents. Green algae are therefore suitable for the biosorption of Cd, Cr, Cu and Pb from polluted water. Green algae are therefore suitable for the biosorption of Cd, Cr, Cu and Pb from polluted water. The adsorption capacity calculated from the linearized Langmuir isotherm was compared with the experimentally observed values. The results are reported in Table 5. The results show good agreement between the Langmuir values and the observed values. This further confirms that the Langmuir isotherm best describes the process.  $\text{Pb}^{2+}$  ions generally show high sorption capacity because they have a polarizable soft ion character.

The other ions (Cd (II), Cr (II) and Cu (II)) are classified borderline metal ions. In soft ions covalent interactions as well as electrostatic attractions play significant roles in metal uptake while for the borderline to hard ions only electrostatic attraction is important [23].

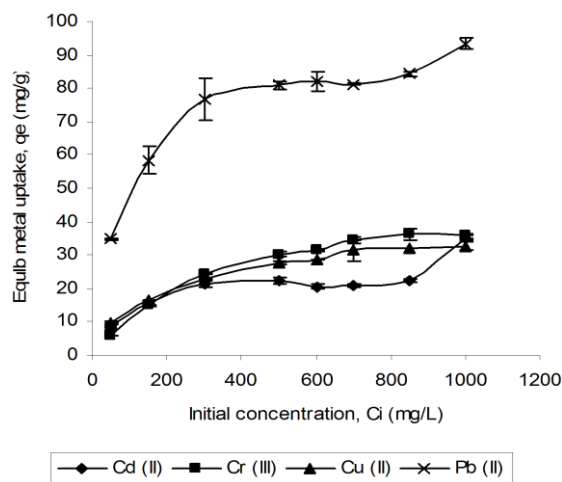


Fig. 6 Metal uptake as a function of initial concentration.

### 3.6. Effect of initial metal concentration

The trend in metal uptake  $q_e$  (mg/g) by green algae at various initial concentrations was determined. The uptake increased with increasing initial metal concentration to a limiting value at initial concentrations between 500 – 700 mg/L, Figure 6. At concentrations above 800 mg/L the observed uptake started to rise again perhaps as a result of the onset of precipitation. Thus the optimum initial metal ion concentrations range from 500 to 700 mg/L for all the metals considered.

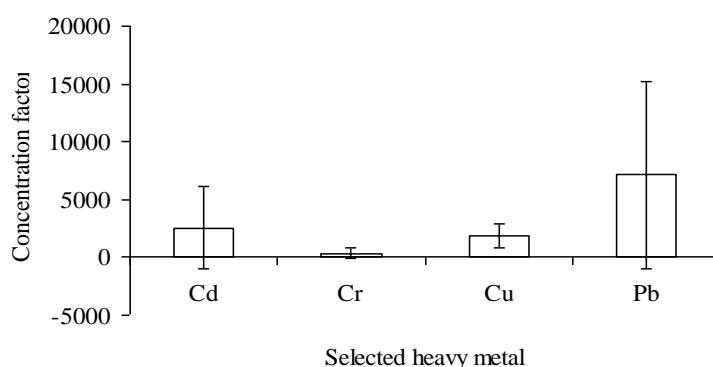
### 3.7. Concentrations in water, acid - leached and digested algae

The concentration of the heavy metals in environmental water samples and in algae collected from the water were determined. The summary of these concentrations is reported in Table 6. Concentration factors were calculated from the ratio of metal concentration in green algae to that in the parent water. The mean concentration factors were 2547.01 (Cd), 367.02 (Cr), 1843.59 (Cu) and 7154.95 (Pb). The results are reported graphically in Fig. 7. Lead had the highest concentration factor and chromium the lowest. The values of concentration factors could also possibly indicate the trend in the strengths of active metal transport by the algae. The high concentration factors confirm that algae are a good biosorbent and bioindicator for the studied metals.

#### 4. CONCLUSIONS

The biosorption and biomonitoring study conducted in this work provides significant information regarding the suitability of green algae as a biosorbent and a biomonitor for the selected heavy metals in solution. Adsorption parameters were determined. The best pH for adsorption of the selected metals was found to be 5.0, 5.5, 5.8 and 5.9 for lead, chromium, copper and cadmium, respectively and the times required for metal adsorption equilibrium to be established in model solutions were 15 minutes for cadmium, 40 minutes for both chromium and copper, and 50 minutes for lead. The adsorption process was found to be second order and the data fitted better to the Langmuir than the Freundlich isotherm. The adsorption capacities were found to be 22.52, 35.59, 38.19 and 94.34 mg/g for cadmium, copper, chromium and lead, respectively. The initial metal concentrations which resulted in highest metal adsorption onto green algae were between 500 – 700 mg/L for all the metals considered. The average concentrations of cadmium, lead, copper and chromium in water were  $1.82 \pm 0.11$ ,  $12.08 \pm 1.80$ ,  $17.14 \pm 0.15$  and  $64.33 \pm 0.35$  ng/mL, respectively while in the digested algae, cadmium, chromium, copper and lead concentrations were  $1.36 \pm 0.10$ ,  $12.42 \pm 1.74$ ,  $14.88 \pm 0.99$  and  $14.98 \pm 1.01$  µg/g, respectively. The adsorbed metal (leachable) fraction concentrations were found to be  $0.74 \pm 0.09$ ,  $4.95 \pm 1.86$ ,  $8.23 \pm 0.59$  and  $9.41 \pm 0.74$  µg/g, for cadmium, chromium, copper and lead, respectively.

There was correlation between the total and leachable metal concentrations, ( $R = 0.88$ ,  $0.55$ ,  $0.95$  and  $0.94$  for cadmium, chromium, copper and lead respectively). As expected, little correlation was found between the heavy metal concentration in algae and the parent water ( $R \leq 0.11$ ). This observation points towards an active transport assisted sorption process as opposed to diffusion mediated one. Furthermore average concentration factors in the range of 2547.01 for cadmium, 367.02 for chromium, 1843.59 for copper and 7154.95 for lead were observed.



**Fig. 7** Average concentration factors of Cd, Cr, Cu and Pb by green algae.

From this work, green algae were found to be a suitable biosorbent for effectively removing heavy metals from polluted water. The algae are also suitable as a bioindicator because it is able to accumulate metals to a satisfactory degree. While the metal concentration in the water samples was negligible for all metals considered, the algae were much richer in heavy metal content. This is evidence for pre-concentration of heavy metals from water.

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## **BIOSORPCIJA ODABRANIH TEŠKIH METALA POMOĆU BIOMASE ZELENE ALGE *SPIROGYRA SP.***

*U ovom radu je proučavan uticaj kontaktnog vremena, početnog pH i početne koncentracije metalnih jona na sorpcione karakteristike slatkovodne zelene alge Spirogyra sp. Nekoliko model-rastvora odabranih teških metala (Cd, Cu, Cr, Pb) je tretirano, u različitim vremenskim intervalima, sorbentom pripremljenim od zelenih algi. Plamena atomska apsorpciona spektrometrija (FAAS) i induktivno kuplovana plazma sa optičkom emisionom spektrometrijom (ICP-OES) su korišćene za određivanje sadržaja teških metala u model-rastvorima Nakon tretmana. Furijeova transformaciona infracrvena spektroskopija (FTIR) je pokazala koje funkcionalne grupe su nosioci biosorpcionih osobina zelenih algi. Pri kontaktnim vremenima u opsegu 15-50 minuta i polaznoj koncentraciji metala 500-700 µg/ml, sorpcioni kapacitet je iznosio 22,52, 38,19, 35,59 i 94,34 mg/g za Cd, Cr, Cu i Pb. Optimalni pH za biosorpciju Cd, Cr, Cu i Pb je bio 5,5, 5,8, 5,9 i 5,0. Proces biosorpcije prati kinetiku drugog reda i zakonitosti Lengmirovog izotermalnog modela. Rezultati biomonitoringa ukazuju da zelene alge imaju veliki potencijal kao bioindikator; srednji koncentracioni faktori za proučavane metale su bili u opsegu 367-7154.*

Ključne reči: zelene alge, biosorpcija, biomonitoring, toksični metali, FAAS, ICP-OES, FTIR