Biosorption of Selected Heavy Metals Using Green Algae, Spirogyra Species

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Abstract
Biosorption studies were conducted to determine the adsorption parameters (pH, contact time and adsorption capacity) of cadmium, chromium, copper and lead in model aqueous solutions using green algae, *spirogyra* species. pH was optimized for each heavy metal. The optimum pH values were found to be 5.5, 5.8, 5.9 and 5.0 for cadmium, chromium, copper and lead, respectively. The adsorption process was second order and fitted the Langmuir isotherm better than the Freundlich. Adsorption capacities were found to be 22.52, 38.19, 35.59 and 94.34 mg/g for cadmium, chromium, copper and lead, respectively. The biosorption process was rapid with contact times of 15 minutes for cadmium, 40 minutes for chromium and copper and 50 minutes for lead. The optimum initial concentrations for metal adsorption ranged from 500 - 700 µg/mL. Adsorption kinetics of the metals on green algae were also investigated. The experimental data was tested for biosorption kinetics using first and second order kinetic models and was found to follow second order kinetics. The concentration of the selected metals was determined in algae and in the parent water. The results in both samples by ICP – OES were 1.81 ± 0.11, 64.33 ± 0.35, 17.14 ± 0.155 and 12.08 ± 1.80 µg/L in water and 2.30 ± 0.09, 12.17 ± 0.20, 25.61 ± 0.74 and 60.50 ± 1.57 µg/g for cadmium, chromium, copper and lead in algae, respectively. The average concentration factors were Cd (2547.01), Cr (367.02), Cu (1843.59) and Pb (7154.95). Little correlation was found between the heavy metal concentration in parent water and in algae from the same water ($R \leq 0.32$). The concentration of the acid-leached metal fraction from the algal surface, correlated well with the total metal taken up by the algae, ($0.55 \leq R \leq 0.94$). This work demonstrates the potential of green algae as both a biosorbent and bioindicator of water pollution by the selected heavy metals.
Keywords: biosorption, algae, adsorption, biosorbent, isotherm.

1.0 Introduction

A heavy metal is a collective term for metals of high atomic mass, particularly those that are toxic and cannot be processed by living organisms. These include lead, mercury and cadmium among others. Many other definitions of heavy metals have been proposed based on density, atomic number and atomic weight. Depending on the context, the term can include elements lighter than carbon and can exclude some of the heaviest metals (Duffus, 2002). At one time, an IUPAC technical report described the term *heavy metal* as a "meaningless and misleading term" due to its contradictory definitions, lack of a "coherent scientific basis" and unclear boundaries (Duffus, 2002). Recently, the definition has been based on chemical properties particularly toxicity.

Heavy metals can be broadly classified into three groups; those that are essential for certain biochemical processes, but are toxic when their concentration exceeds certain thresholds. These include copper, zinc, cobalt, selenium and iron. The second group consists of metals with no known biological function and toxic if present in concentrations above trace amounts. These include arsenic, bismuth, indium, antimony and thallium. The last and evidently the most dangerous group includes lead, cadmium and mercury which serve no known biological function and are toxic at all concentrations (Fernandez *et al.,* 1992).

The toxicity of trace metals arises from their interference with an organisms' uptake of essential metal ions such as sodium and calcium. For instance, cadmium and zinc block the uptake of calcium ions which is essential for bone and teeth development. The interaction of some heavy metals with enzymes and their tendency to bind to protein and other biological tissues also cause trace metal poisoning in organisms (Campbell, 1995). The common results of trace metal toxicity to living organisms include brain disorder, gross deformities in development, carcinogenic effects and generally, disruption of biological processes.

In most cases these elements find their way into the environment through human industrial processes such as mining, electroplating, battery manufacture, leather tanning, and manufacture of printing pigments and paints, among others. A high concentration of heavy metals in the environment is of great health concern because they are non-biodegradable and end up accumulating in food chains in various forms such as organic, inorganic or organometallic species (Cordero *et al.*, 2004) with disastrous consequences. Due to the toxicity of trace metals, it is important to remove them from water in particular and the environment in general.

1.1 Removal of Heavy Metals from Wastewater

The most common technologies used for removing heavy metals from industrial and agricultural wastewater before it is discharged to the environment include precipitation, ion exchange and reverse osmosis (Deng *et al.,* 2006). Though these methods are effective in removing heavy metal contaminants, they are quite

expensive.

1.1.1 Biosorption

Biosorption is a term that describes the removal of heavy metals from an aqueous solution by passive binding to non-living biomass. This implies that the removal mechanism is not metabolically mediated. Bioaccumulation on the other hand, describes an active process where removal of metals requires the metabolic activity of a living organism (Davies *et al.,* 2003). In recent years research on biosorption has intensified with a view to using biomass to remove heavy metals from industrial effluents or to recover precious metals from processing wastewater. Of the many types of biosorbents recently investigated, algal biomass has proven to be highly effective, reliable and predictable in the removal of heavy metal ions from aqueous solutions (Davies *et al.,* 2003). While having a performance similar to ion exchange, biosorption is more advantageous because biosorbents are quite abundant, less costly and easily biodegradable.

Some biosorbents, among many, which have been used used, are Cystine-modified biomass, (Yu *et al.*, 2007); *Rhizopus Arrhizus* (fungi) (Bahadir *et al.*, 2007); *Sargassum glaucescens* (brown algae) (Yang and Chen, 2008); Chaff (Han *et al.*, 2005).

Besides the low cost and abundance, biosorbents can be recycled. This makes them even more attractive. With advancement in chemical modification techniques, there are prospects of achieving analyte specificity with chemically modified biosorbents (Volesky, 2003).

1.1.2 Biosorption by green Algae

Green algae are the most diverse group of algae. *Spirogyra* species are unbranched filamentous freshwater green algae. Their cell wall is characteristically straight and parallel-sided. Green algae are commonly found in clean water and produce food through the process of <u>photosynthesis</u>. They can be easily identified from their green filamentous structure and fresh water habitat. The uptake of trace metals by green algae occurs through biosorption and bioaccumulation processes (Davis *et al.,* 2003). Carboxylate groups are generally the most abundant acidic functional groups in the algae.

1.2 Adsorption Isotherms

An adsorption isotherm is an equation that describes how the amount of a substance adsorbed onto a surface depends on its concentration or its pressure at a constant temperature. Adsorption isotherms focus mainly on systems where the adsorbate particles are mostly concentrated on the surface of an adsorbent. The Langmuir isotherm describes the dependence of the surface coverage of an adsorbed species on the pressure/concentration of the species at a fixed temperature. The Freundlich describes physical adsorption in solution while the BET isotherm applies to multi-layer adsorption.

1.2.1 Langmuir Isotherm

The Langmuir isotherm has been widely used to describe and determine the adsorption capacity q_{max} of metal ions during biosorption processes. The Langmuir adsorption isotherm is useful in quantifying and contrasting the performance of different biosorbents. In its formulation, binding to the surface is primarily by physical forces mainly electrostatic and implicit in its derivation is the assumption that all sites possess equal affinity for the adsorbate. It has been used to empirically describe equilibrium relationships between a bulk liquid phase and a solid phase. The Langmuir equation is frequently used to fit experimental data.

Experimental results can most easily be compared with the Langmuir theory the equation above is expressed in its linear form as follows;

$$\frac{C_e}{q} = \frac{1}{q_{max}b} + \frac{C_e}{q_{max}}$$

where q, q_{max}, C_e and b is the metal uptake at any time (in milligrams of heavy metal per gram of biosorbent), the maximum metal uptake, the final equilibrium concentration of the heavy metal in solution and the Langmuir empirical constant, respectively. If the experimental data agrees with the theory, a plot of C_e/q versus C_e yields a straight line. From this curve the adsorption capacity q_{max} and the Langmuir constant b can be obtained.

1.2.2 Freundlich Isotherm

The Freundlich isotherm was originally of an empirical nature, but was later interpreted as sorption to heterogeneous surfaces or surfaces supporting sites of varied affinities. It is assumed that the stronger binding sites are occupied first and that the binding strength decreases with increasing degree of site occupation. In this model, the energy of a metal ion binding to a site on an adsorbent depends on whether or not the adjacent sites are already occupied. The Freundlich equation takes the form:

$$q_e = K_F \left(C_e \right)^{1/n}$$

where q_e and C_e is the mass of solute adsorbed per gram of the adsorbent and the solute concentration at equilibrium respectively. K_F and n are empirical constants characteristic of the system and are indicators of

the adsorption capacity and intensity, respectively. Large values of K_F and *n* indicate high adsorption capacity and intensity, respectively. This equation is most conveniently used in its linearized form namely;

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$

Experimental results agree with the Freundlich isotherm if a plot of *lnq_e* versus *lnC_e* yields a straight line. The Freundlich constants K_F and *n* can be calculated from the linear plot.

1.3 Kinetics of metal adsorption
The dependence of a chemical reaction on initial reactant concentration can be shown by a rate equation. The rate equation once integrated gives expressions for the variation of concentration of a reactant with time. The order of reaction is deduced from the integrated rate equation.

2.0 Methodology
2.1 Apparatus and equipments
A Millipore filter funnel equipped with a 0.45 µm cellulose acetate filter membrane and attached to a vacuum pump was used for the filtration processes. The ground algae were sieved through a 0.5 mm sieve. Atomic Absorption Spectrophotometer (AAS) was used for metal determination. pH measurements were done using a digital pH meter fitted with a temperature probe (pH 211, HANNA Instruments).

2.2 Reagents
Analytical grade concentrated nitric acid, hydrochloric acid and perchloric acid were used to digest the algae samples.

2.3 Sampling
The fresh green algae samples used for the investigation of adsorption parameters were collected from a fresh water pond, washed with tap water several times and rinsed with distilled water. They were sun-dried in the open for twenty-four hours then oven-dried at 60 ^{0}C for eight hours. Finally the sample was ground, sieved to 0.5 mm particle size and stored in a plastic bottle at room temperature until use.

Table 4. Parameters used for metal ion loading onto green algae.

Metal ion	pH used	Initial concentration, ppm
Cd^{2+}	5.5	500
Cr^{3+}	5.8	600
Cu^{2+}	5.9	600
Pb^{2+}	5.0	500

2.4 Optimization of pH
Batch biosorption experiments were conducted on model solutions of cadmium, chromium, copper and lead to determine the optimum pH for metal uptake by algae. For each element, the stock solution was diluted to 200 µg/mL using 0.1 M acetate buffer solution and divided into two 50 mL batches. Both batches were adjusted to pH values of 2.0, 3.0, 4.0, 4.5, 5.0, 5.5, 6.0 and 7 using sodium hydroxide and nitric acid. One batch was equilibrated with 0.20 g of ground algae for two hours. The solution was filtered through a 0.45 µm filter membrane and the metal ion concentration in the filtrate determined by flame atomic absorption spectrometry (FAAS). The second batch (control) was treated like the first one but no algae was added. This was used to determine the amount of metal lost due to precipitation. All experiments were done in triplicate.

2.5 Initial metal ion concentration and adsorption capacity
The initial concentration which gives rise to the highest metal uptake was investigated. 50 mL of standard metal ion solution at concentrations between 50 – 1000 µg/mL were equilibrated with 0.2 g of dried and ground algae at their respective optimum pH for two hours with stirring at 300 revolutions per minute (rpm). After equilibration, each solution was filtered through a 0.45 µm membrane filter and the residual metal ion concentration in the filtrate determined by FAAS. The data was fitted to both Freundlich and Langmuir adsorption isotherms and the adsorption capacity calculated from the linearized Langmuir isotherm. A plot of equilibrium metal uptake (mg/g) against initial metal ion concentration was done to determine the optimum initial metal concentration for all metals.

3.0 Results and discussion
3.1 Effect of pH on metal uptake
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. The results are shown in table 1. Plots of the relative removal by precipitation are shown for each metal in figure 1.

Table 1. Percentage metal removal by precipitation and biosorption at different pH values

Metal removal (%)		pH							
		2.0	3.0	4.0	4.5	5.0	5.5	6.0	7.0
Cd	Total removal	13.47 ± 0.98	19.39 ± 1.11	24.20 ± 1.90	28.38 ± 2.30	31.56 ± 2.61	38.87 ± 1.99	39.23 ± 0.88	43.61 ± 3.13
	Precipitation	0.02 ± 0.00	0.10 ± 0.05	0.62 ± 0.04	1.03 ± 0.07	2.12 ± 0.13	2.63 ± 0.16	7.11 ± 0.08	30.22 ± 2.71
	Biosorption	13.45	19.28	23.59	27.35	29.44	36.24	32.11	13.40
Cr	Total removal	8.30 ± 0.60	10.93 ± 0.57	14.53 ± 0.67	19.23 ± 1.51	22.47 ± 1.90	33.26 ± 2.20	14.53 ± 2.04	19.23 ± 1.47
	Precipitation	0.63 ± 0.68	8.33 ± 0.40	7.00 ± 1.54	9.17 ± 0.72	6.47 ± 0.32	9.60 ± 2.26	7.00 ± 0.33	9.17 ± 0.29
	Biosorption	7.67	2.60	7.53	10.07	16.00	23.66	7.53	10.07
Cu	Total removal	0.03 ± 0.53	0.10 ± 0.64	18.02 ± 0.92	23.32 ± 1.17	34.90 ± 0.85	42.71 ± 0.59	61.39 ± 1.12	62.93 ± 1.32
	Precipitation	0.02 ± 0.03	0.10 ± 0.03	0.62 ± 0.11	1.03 ± 0.36	2.12 ± 0.17	2.63 ± 0.19	3.42 ± 0.06	60.60 ± 0.76
	Biosorption	0.01	0.00	17.40	22.29	32.78	40.07	57.97	2.33
Pb	Total removal	13.40 ± 0.59	33.03 ± 0.84	55.67 ± 0.43	61.33 ± 0.26	67.80 ± 0.48	70.67 ± 0.47	76.19 ± 0.18	78.33 ± 0.03
	Precipitation	0.64 ± 0.10	1.84 ± 0.62	5.63 ± 0.94	8.22 ± 0.71	12.02 ± 0.78	20.58 ± 0.24	32.08 ± 2.16	70.02 ± 0.20
	Biosorption	0.23	31.19	50.04	53.11	55.77	50.09	44.10	8.32

For all the metals considered, metal removal by both precipitation and biosorption 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 sorption sites between metal ions and protons and that metals do not form precipitates at low pH. 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 (Matheickal and Yu, 1999). 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.
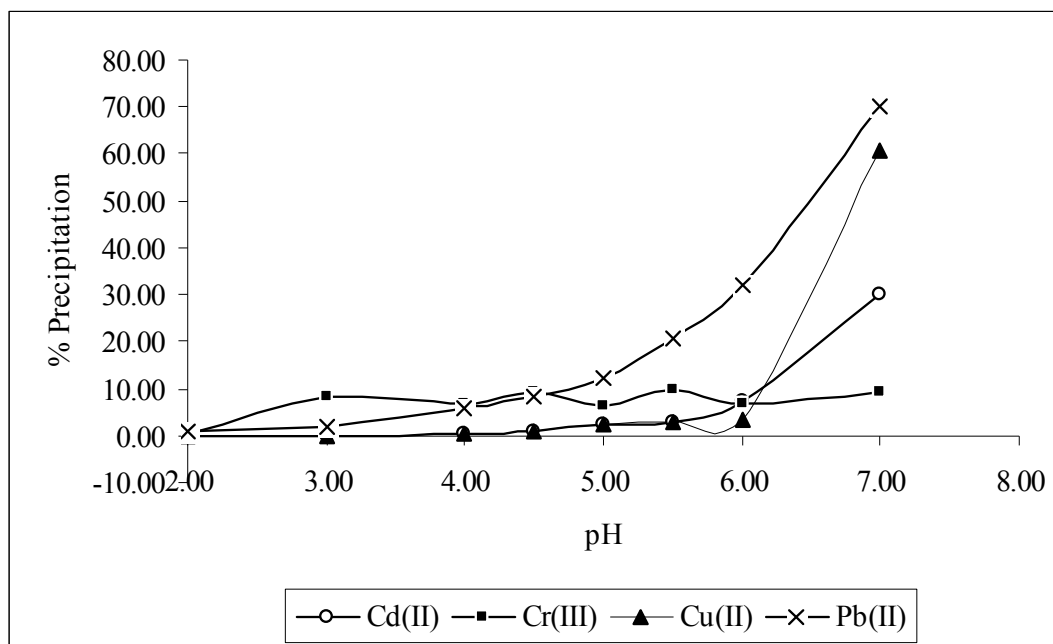

Figure 1. Percentage precipitation of Cd, Cr, Cu and Pb at pH values 2 – 7.

To obtain the optimum pH, a graph of percentage metal removal by biosorption against pH was plotted. The curves obtained for the selected metal ions are shown in figure 2. From these curves 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.
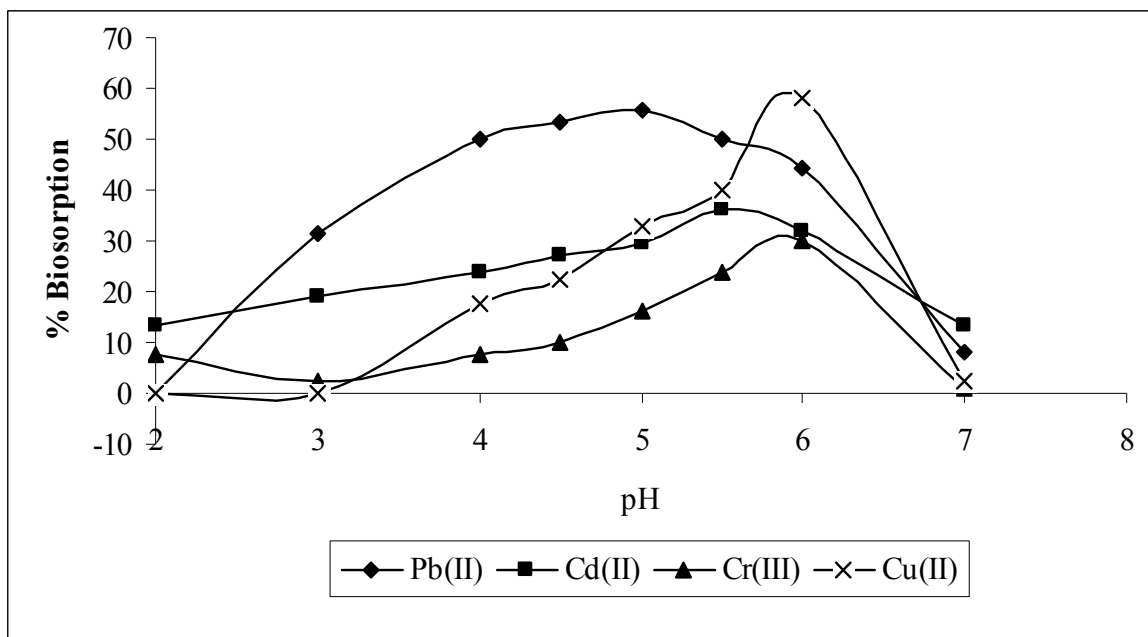
Figure 2. Percentage removal of metal ions from model aqueous solution by biosorption

3.2 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 the process ending in fifteen minutes while chromium and copper took forty minutes. For lead, quantitative uptake occurred in fifty minutes.

Table 2. Variation of concentration (µg/mL) of Cd, Cr, Cu and Pb in solution with contact time.

Contact time, (min)	Cd (II)		Cr (III)		Cu (II)		Pb (II)	
0	200.00 ± 0.00	100.00 ± 0.00	200.00± 0.00	100.00 ± 0.00	200.00± 0.00	100.00± 0.00	200.00 ± 0.00	100.00 ± 0.00
2	149.71± 0.55	63.89 ± 0.02	198.89± 0.04	94.50 ± 1.40	193.60± 1.52	99.93 ± 0.02	199.85 ± 0.03	94.24 ± 0.65
6	135.75± 0.73	51.97 ± 0.12	162.90± 1.66	71.94 ± 0.19	175.89± 1.13	69.27 ± 0.67	164.23 ± 0.45	83.18 ± 2.15
10	134.13± 0.62	50.23 ± 0.02	161.32± 1.02	61.72 ± 1.13	163.63± 1.27	62.87 ± 0.74	159.15 ± 0.40	71.17 ±0.18
15	133.54± 0.92	48.85± 0.07	159.92± 1.34	58.76 ± 1.23	157.46± 0.94	61.40± 0.25	154.12 ± 0.87	66.57 ± 0.27
20	129.72± 0.55	49.32 ± 0.02	158.40± 0.43	57.44 ± 0.32	152.59± 0.83	56.31 ± 0.40	146.10 ± 0.14	57.75 ± 0.12
25	128.56± 1.22	48.67 ± 0.05	155.02± 0.51	56.10 ± 0.60	152.46± 2.29	56.14 ± 0.45	139.37 ± 0.44	54.69 ± 0.17
30	127.97± 0.87	48.66 ± 0.03	158.98± 0.80	53.34 ± 0.92	152.24± 0.82	55.07 ± 0.80	138.61 ± 0.43	52.43 ± 0.49
40	127.79± 0.95	48.81 ± 0.05	158.68± 0.85	50.32 ± 1.59	151.70± 1.22	54.32 ± 0.37	132.93 ± 0.39	49.15 ± 0.64
50	128.15± 1.17	48.32 ± 0.07	158.72± 1.02	48.68 ± 0.31	151.22± 1.17	52.35 ± 0.74	134.39 ± 0.46	48.35 ± 1.67
60	127.58± 0.66	48.79 ± 0.03	158.32± 0.89	48.14 ± 0.56	150.84± 0.38	52.68 ± 0.24	135.16 ± 0.32	47.65 ± 0.05
75	128.32± 0.3	48.76 ± 0.04	154.26± 0.61	46.54 ± 0.33	150.17± 1.63	52.10 ± 0.42	132.50 ± 0.53	47.46 ± 0.27
90	129.33± 0.44	50.48 ± 0.04	156.22± 0.84	48.06 ± 0.48	150.09± 0.28	52.39 ± 0.02	132.21 ± 0.47	46.42 ± 0.49
105	127.91± 0.73	49.04 ± 0.04	159.16± 0.84	47.10 ± 0.29	150.44± 0.55	51.60 ± 0.30	128.76 ± 1.14	45.27 ± 0.39
120	127.12± 0.28	48.93 ± 0.04	156.96± 0.69	47.52 ± 0.73	149.05± 1.90	51.73 ± 0.31	128.95 ± 0.94	45.01 ± 0.89
140	127.75± 0.91	48.63 ± 0.03	152.30± 0.89	45.70 ± 0.63	145.33± 0.27	51.60 ± 0.26	128.83 ± 1.18	44.65 ± 0.06

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 waters. The standard deviations were low hence the y-error bars are not prominent.
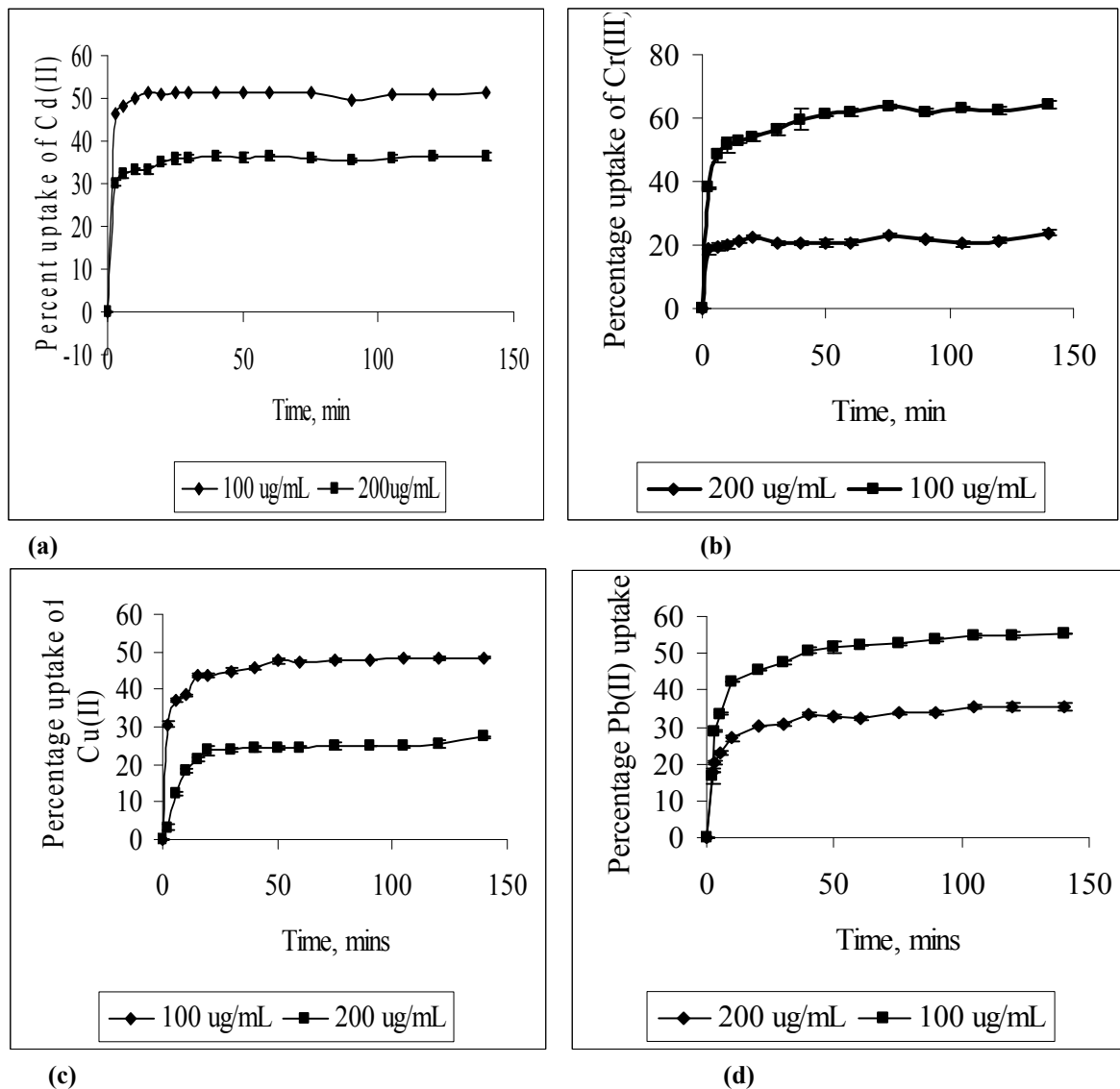
(a)

(b)

(c)

(d)

Figure 3. Variation of metal uptake by green algae with time

3.3 Order of reaction
The variation of metal ion concentration with time during the adsorption process (Table 2) was used to follow the kinetics of the adsorption until equilibrium was achieved. The mass q_t of metal adsorbed after time t is related to the equilibrium metal uptake q_e by the integrated first and second order equations

$$k_1 t = \ln q_e - \ln\left(q_e - q_t\right) \text{ and } \frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^{2}}$$ respectively, where k_1 and k_2 are the first and second

order rate constants. A plot of $\text{Ln}(q_e - q_t)$ against time (minutes) was used for the first order linearity test, while a

plot of $\dfrac{t}{q_t}$ (min g/mg) against time (minutes) was used for the second order linearity test and the calculation of

q_e, which is the metal uptake in milligrams per gram of biosorbent at equilibrium. The order of reaction for each metal was deduced from the linearity of the respective plots. Figure 7 gives the slopes and the R^2 values from which q_e and the linear correlation coefficients may be obtained. The second order plots for all metals have higher R^2 values than the corresponding first order plots as shown in table 8. The process is therefore second order for all metals. This agrees with litreature (Gupta and Rastogi 2007, Sari and Tuzen 2007, Patel and Suresh, 2008).
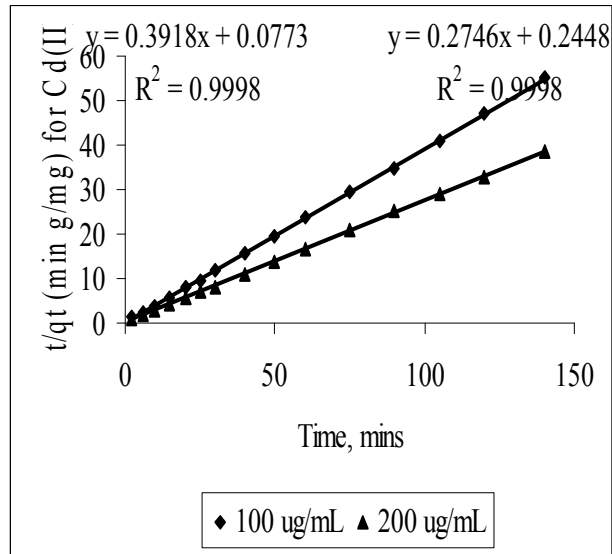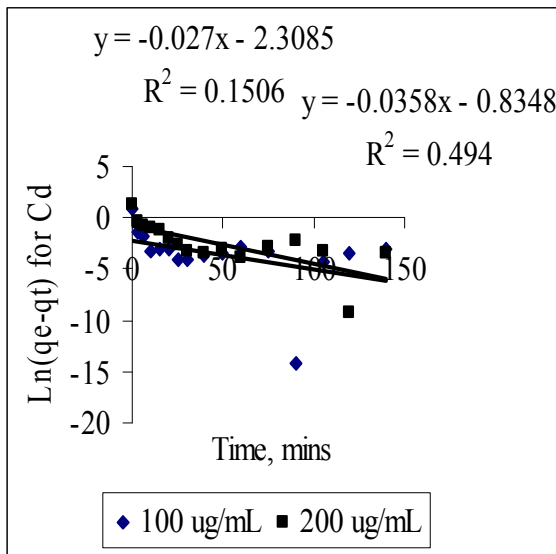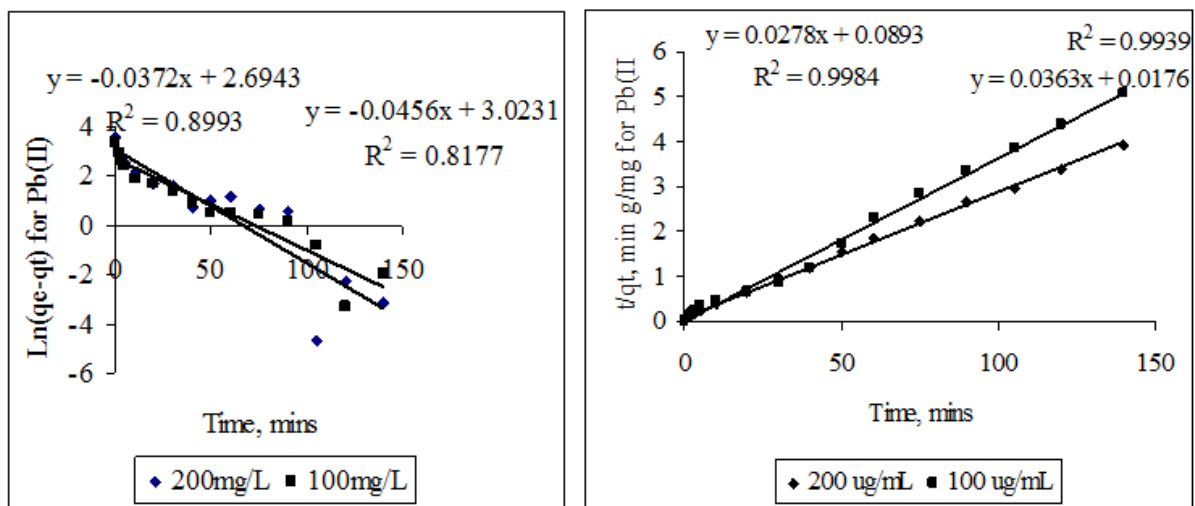
(a) First and second order linearity test for cadmium adsorption on green algae
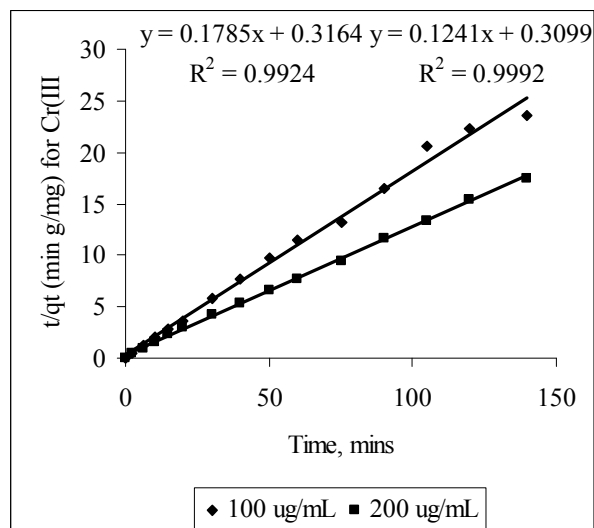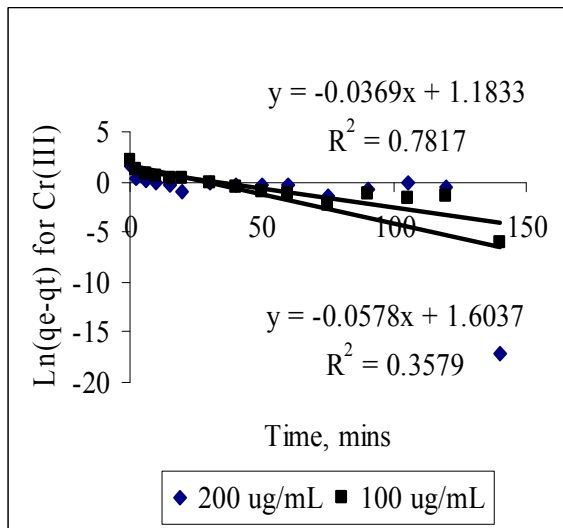
(b) First and second order linearity test for chromium adsorption on green algae
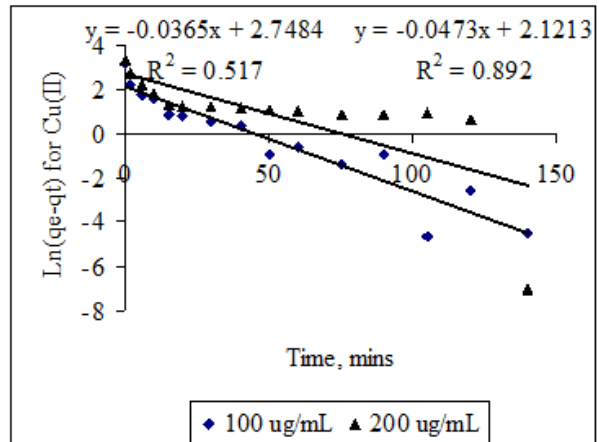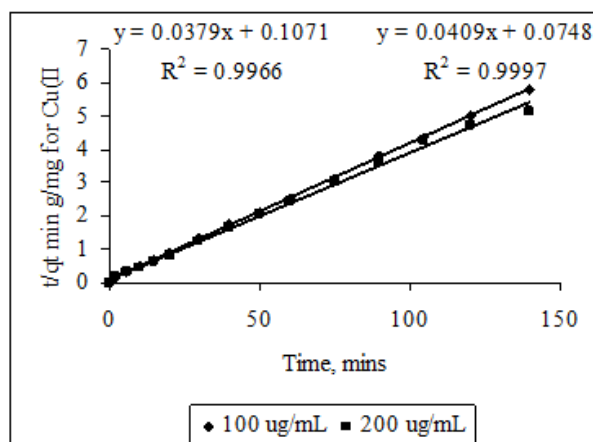
(c) First and second order linearity tests for copper adsorption on green algae

 (d) First and second order linearity tests for lead adsorption on green algae.
Figure 4. First and second order linearity tests for Cd, Cr, Cu and Pb

Table 8. Kinetic parameters for Cd, Cr, Cu and Pb metal adsorption on green algae

Metal	Initial concentration, (µg/mL)	Calculated metal uptake at equilbrium q_e, (mg/g)	R value for first order linearity test	R value for second 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

3.4 Adsorption capacity and optimum initial metal ion concentration
The equilibrium concentrations C_e of cadmium, chromium, copper and lead in the filtrates were determined by FAAS and reported in Table 9 together with the corresponding initial concentrations, C_i and the calculated metal uptake at equilibrium, q_e. The data was fitted to the linearized Freundlich and Langmuir isotherms represented by

the equations $\ln q_e = \ln K_F + \dfrac{1}{n} \ln C_e$ and $\dfrac{C_e}{q_e} = \dfrac{1}{q_{max}b} + \dfrac{C_e}{q_{max}}$, respectively, where q_{max} is the adsorption

capacity, b is a Langmuir constant, K_F and n are Freundlich constants. Linear regression coefficients (R^2) were used to deduce which isotherm best fitted the data.

Table 9. Equilibrium concentrations C_e (µg/mL) and metal uptake q_e (mg/g) at equilibrium

Metal ion	Cd (II)		Cr (III)		Cu (II)		Pb(II)	
$C_{i,}$ (µg/mL)	C_e	q_e	C_e	q_e	C_e	q_e	C_e	q_e
50	14.25 ± 0.59	8.94 ± 0.15	4.21 ± 0.51	5.72 ± 0.06	12.12 ± 0.79	9.47 ± 0.20	30.33 ± 0.50	34.83 ± 0.25
150	87.43 ± 0.48	15.64 ± 0.12	30.75 ± 1.93	14.91 ± 0.24	84.20 ± 0.48	16.45 ± 0.12	83.17 ± 8.50	58.42 ± 4.25
300	213.95 ± 0.38	21.51 ± 0.10	104.18 ± 1.73	24.48 ± 0.22	208.56 ± 0.80	22.86 ± 0.20	146.67 ± 12.35	76.67 ± 1.18
500	410.85 ± 1.03	22.29 ± 0.26	257.63 ± 4.56	30.30 ± 0.57	388.99 ± 2.57	27.75 ± 0.64	338.17 ± 2.35	80.92 ± 3.01
600	517.85 ± 0.53	20.54 ± 0.13	349.20 ± 1.64	31.35 ± 0.20	485.54 ± 0.61	28.62 ± 0.15	426.00 ± 6.03	87.00 ± 0.25
700	616.73 ± 0.28	20.82 ± 0.07	424.07 ± 7.75	34.49 ± 0.97	574.70 ± 13.41	31.32 ± 3.35.	537.61 ± 1.84	81.19 ± 0.92
850	760.21 ± 0.48	22.45 ± 0.12	559.71 ± 14.16	36.28 ± 1.77	721.58 ± 0.30	32.11 ± 0.08	631.50 ± 3.00	84.25 ± 1.50
1000	859.33 ± 0.59	35.17 ± 0.15	713.32 ± 5.70	35.84 ± 0.72	869.55 ± 4.56	32.62 ± 1.15	713.17 ± 11.18	93.42 ± 5.59

The adsorption capacity q_{max} was obtained as the reciprocal of slope of the linearized Langmuir plot $\dfrac{C_e}{q_e}$ against the equilibrium concentration C_e, and the Langmuir constant b from the y – intercept. The adsorption capacities of green algae were found to be 22.52, 38.19, 35.59 and 94.34 mg/g for cadmium, chromium, copper and lead, respectively (Table 10). These results show green algae has a higher adsorption capacity for all metals studied in this work as compared to other biosorbents that have been studied (Table 1). Different metals have different adsorption capacities to a particular biosorbent due to differences in their ions. The ability of a metal ion to form a strong ligand with the biosorbent is important in adsorption (Remacle, 1990; Brady and Tobin, 1995). The trend in biosorption capacity obtained in this work agrees with literature (Kogej and Pavko, 2001 and Reddad *et al*, 2002) who used *Saccharomyces cerevisiae*, *Rhizopus nigricans and* sugar beet pulp waste, respectively and found the adsorption capacity varied as; $Pb^{2+} > Cu^{2+} > Cd^{2+}$.
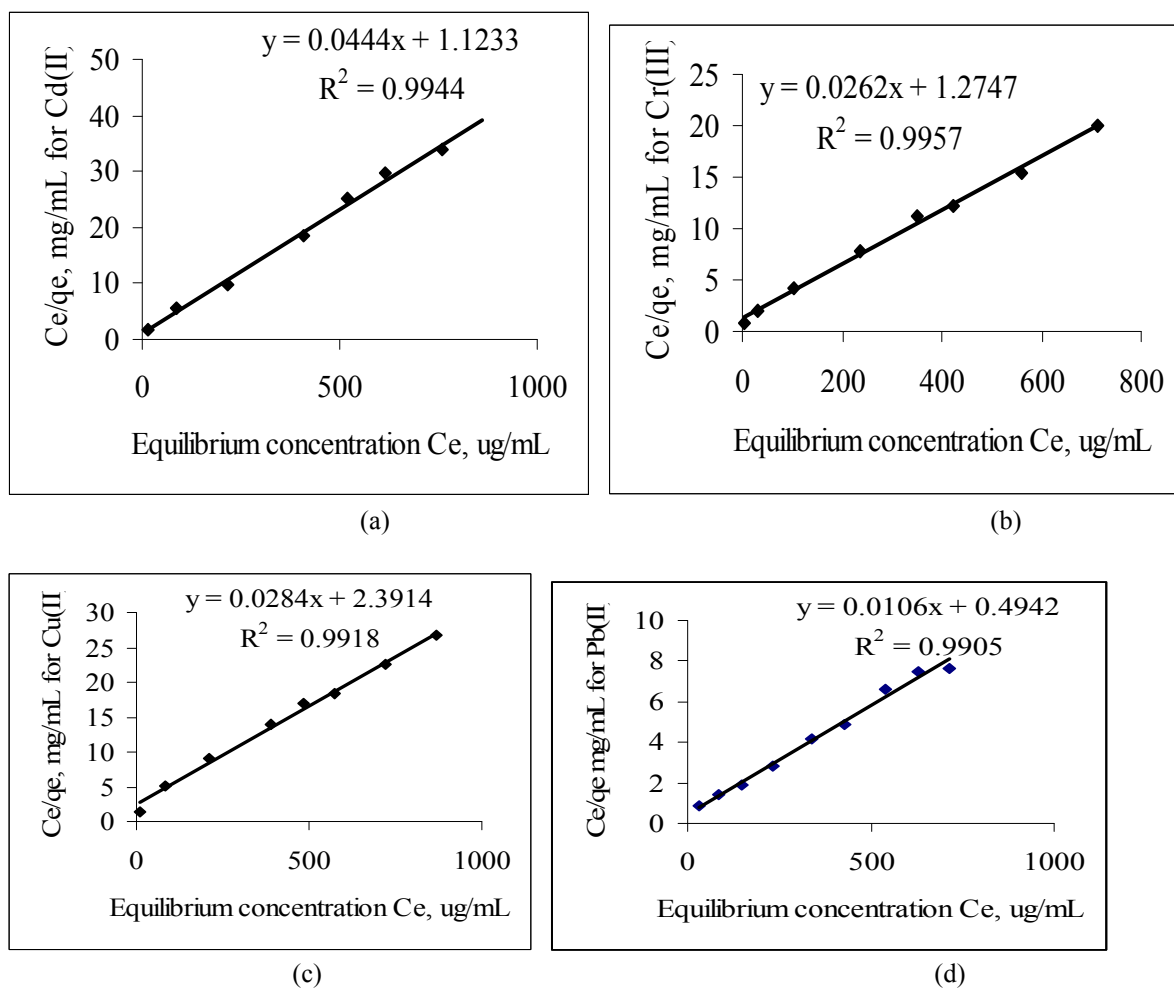
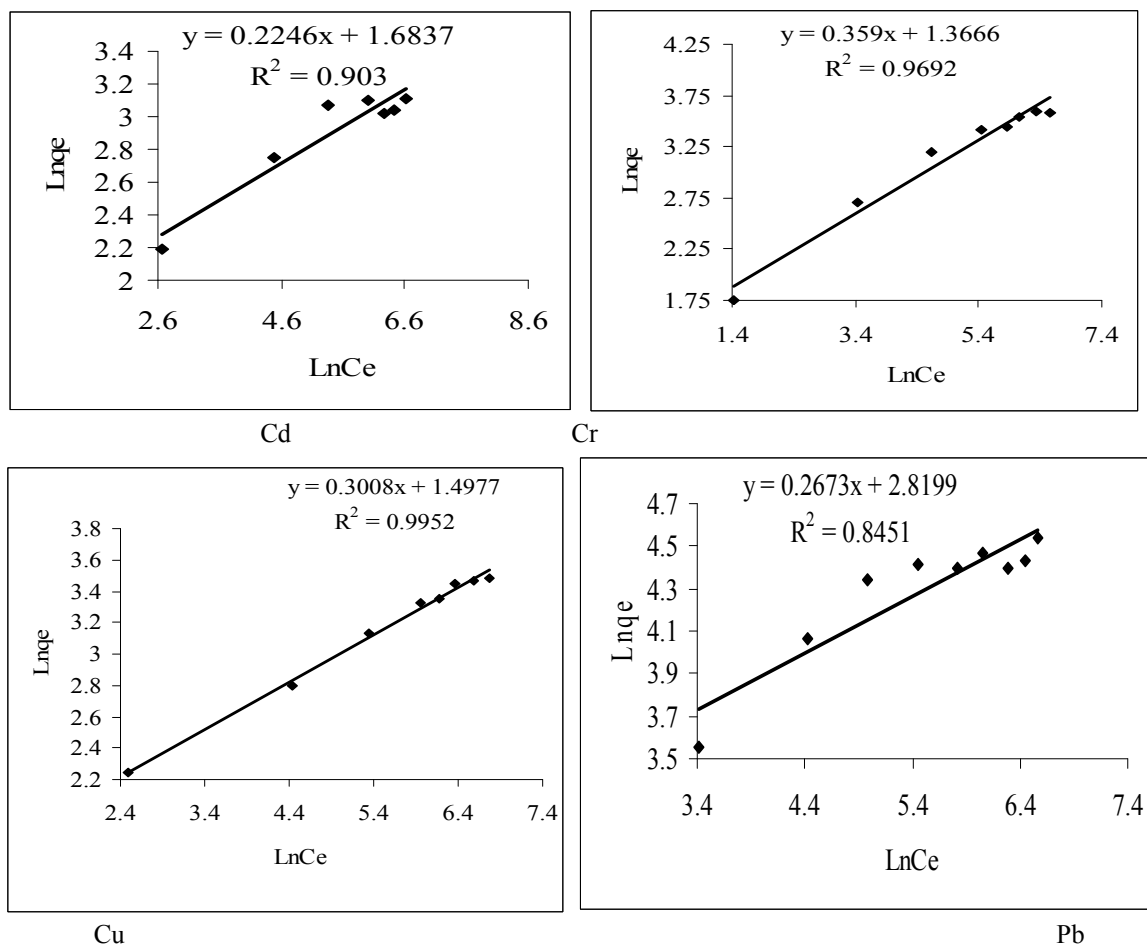**Figure 5.** Linearized Langmuir plots for Cd, Cr, Cu and Pb

Figure 6. Linearized Freundlich plots for Cd, Cr, Cu and Pb respectively

The magnitude of the Freundlich constants was used to asses the adsorption intensity. Freundlich constants were obtained from a plot of lnq_e against lnC_e in which n is the reciprocal of the slope and lnK_F is the y – intercept. The large values (greater than unity), of the Freundlich constants K_F and n (Table 10), indicate a high affinity of the metal ions for the sorbent sites hence a good surface coverage at equilibrium. Figure 9 shows the linearized Freundlich plots for cadmium, chromium, copper and lead. The Langmuir and Freundlich constants obtained from figures 8 and 9 are reported in table 10. The higher linear correlation coefficients for the Langmuir plots (Table 10), suggest that the experimental data fits better to the Langmuir isotherm than the Freundlich isotherm.

Table 10. Calculated adsorption isotherm parameters for metal adsorption

Metal	Langmuir parameters			Freundlich parameters		
	R	b (L/mg)	q_{max} (mg/g)	R	K_F	n
Cd (II)	0.997	0.035	22.52	0.950	5.40	4.45
Cr (III)	0.998	0.021	38.19	0.984	3.93	2.79
Cu (II)	0.998	0.011	35.59	0.996	4.47	3.32
Pb (II)	0.995	0.021	94.34	0.919	16.78	3.74

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 and leveled off at initial concentrations between 500 – 700 mg/L (Figure 10). At concentrations above 800 mg/L the uptake started to rise again perhaps as a result the onset of precipitation. Thus the optimum initial metal ion concentrations ranges from 500 to 700 mg/L for all the metals considered.
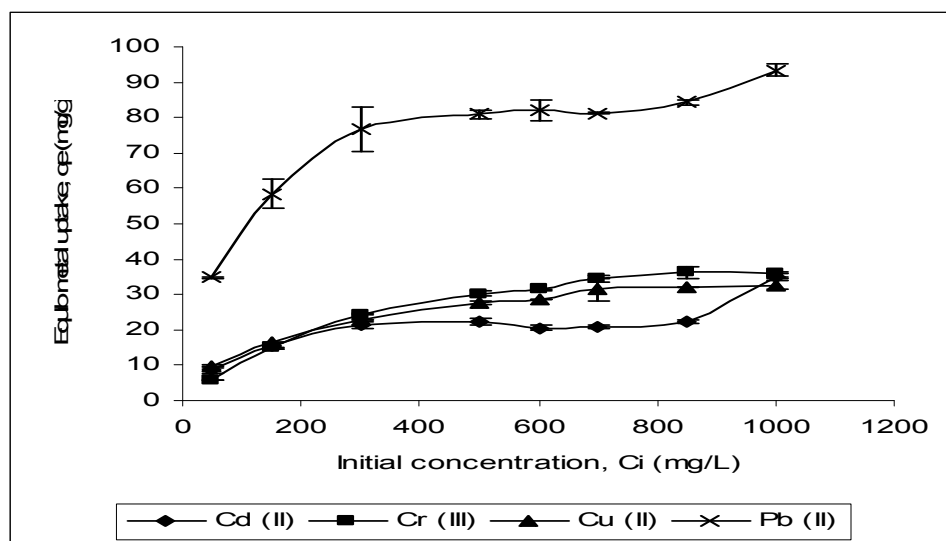
Figure 7. Variation of metal ion uptake with initial concentration of Cd, Cr, Cu and Pb ions.

4.0 Conclusion and recommendations

The biosorption and biomonitoring study conducted in this work provides significant information regarding suitability of green algae as a biosorbent and a bioindicator for the selected heavy metal pollution. Adsorption parameters were determined. The optimum pH was found to be 5.5, 5.8, 5.9 and 5.0 for cadmium, chromium, copper and lead, respectively and the contact times required for quantitative metal uptake 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 isotherm than the Freundlich. The adsorption capacities were found to be 22.52, 38.19, 35.59 and 94.34 mg/g for cadmium, chromium, copper and lead, respectively. The initial metal concentrations which resulted in highest metal adsorption onto green algae were between 500 and 700 mg/L for all the metals considered.

The heavy metal concentrations in water samples were in the range of 0.519-40.03, 8.41-202.20, 6.47-55.71 and 2.54-40.89 μg/L for cadmium, chromium, copper and lead, respectively. The adsorbed metal (leachable) fraction concentrations were found to be Cd (0.00-5.78 μg/g), Cr (0.00-21.53 μg/g), Cu (0.26-43.50 μg/g) and Pb (0.63-62.21 μg/g). Correlation between the total and leachable metal concentrations was fairly good (R = 0.88, 0.55, 0.95 and 0.94 for cadmium, chromium, copper and lead respectively).

From this work, green algae was found to be a reasonably good biosorbent which can be used for effectively removing heavy metals from polluted water. The algae is a suitable 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 was much richer in heavy metal content.

Due to removal of heavy metals from polluted water by biosorbents, determination of heavy metal pollution in any water body by direct analysis of water samples may not be accurate because it will not reflect the real bioavailable pollutant level in the water. This is because most of the heavy metals will be removed from the water to biota and sediments resident in the same water. Use of a bioindicator like green algae would be more accurate.

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