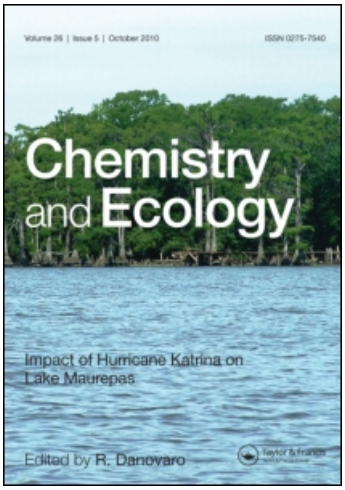

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Heavy-metal adsorption by non-living biomass

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The adsorption of some heavy metals onto the walls of harvested, washed, and dried non-living biomass cells of different *Pseudomonas* strains was studied at optimum experimental conditions using a simplified single component system. The Langmuir adsorption model was found to be a suitable approach to describe the system via multi-step processes. Isotherms measured at 30.0°C and pH 5.5 with $[M]_{total} = 10–100$ mM for tight, reversible $Cr^{6+}(aq)$, $Ni^{2+}(aq)$, $Cu^{2+}(aq)$ and $Cd^{2+}(aq)$ binding by the cell walls of the investigated biomass fit the Langmuir model and give the pH-independent stoichiometric site capacities ν_i and equilibrium constants K_i for metal binding at specific biomass sites i = A, B, C, and D. Tight binding sites A, B, and D of the non-living biomass are occupied by Cr^{VI}, sites A and C by Ni^{II}, sites A and D by Cd^{II}, and only site B by Cu^{II}. It is concluded that ν_i is a stoichiometric parameter that is independent of the magnitude of K_i for binding site i and that the studied heavy metals selectively and tightly bind at different biomass sites.

Keywords: Adsorption; Langmuir; Isotherm; Heavy metals; Non-living biomass; Binding sites

1. Introduction

Toxic heavy-metal contamination of the environment is a significant worldwide phenomenon. The conventional physical and chemical methods for removing heavy metals, such as ion exchange or lime precipitation, are often ineffective and/or very expensive when used for the reduction of heavy-metal ions at very low concentrations [1]. Nowadays, emphasis is given to the utilization of biological adsorbents for the removal and recovery of heavy-metal contaminants [2–5]. Several investigators have reported the potential of living and dead biomass to adsorb heavy-metal ions from solutions [2–7]. The biosorption technology has attracted attention as a cost-effective means for the treatment of metal-bearing wastewater. A variety of toxic heavy metals can be removed from wastewater by non-living biomass of bacteria, fungi, yeast, algae, and higher plants [8–12]. However, the mechanism of metal binding is not clearly understood, and consequently, modelling of the adsorption performance is still raising debates. Non-living biomass can act as a biological chelator. Extensive studies were carried out on biosorption and its dependence on solution chemistry, ionic competition by

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other metals, influence of pH, ionic concentration, kinetics, and also sorption by immobilized biosorbents [13–15]. However, only a few studies were carried out to interpret and establish the actual mechanisms involved in metal ion binding. The biomass binding sites consist of different functional groups, such as amino, thioether, carboxyl, hydroxyl, carbonyl, phosphate, and phenolic groups [16–20]. Theoretically, the Langmuir model relies on a postulated chemical or physical interaction (or both) between a solute and vacant sites on the adsorbent surface. There is no critical reason to use more complex adsorption models if two-parameter models such as the Langmuir isotherm can fit the data reasonably well. The present study was designed to examine the binding characteristics of the investigated heavy metals to the selected non-living biomass. Experiments were performed at optimal value of pH and 30 °C to avoid hydrolysis, polymerization, and precipitation of metal cations in the treatment solutions. The adsorption equilibrium results were tested to fit the Langmuir model, and the binding sites for these biosorption systems were characterized.

2. Materials and methods

2.1 *Biomass preparation*

The four *Pseudomonas* strains used in the experiments were isolated from the western Alexandria sewage treatment plant, Alexandria, Egypt. The strains were characterized and identified according to Burgey's manual of systematic bacteriology as *Pseudomonas fluorrescens* that resists Cr(VI) and three other strains from the species *P. putida*, resistant to Cu(II), Cd(II), and Ni(II) [21]. To produce the biomass for biosorption experiments, the strains were grown in casamino acid media (CAA), composed of casamino acid (Oxoid) 5.0 g L^{-1}; K_2HPO_4 (Merck) and 0.25 g L^{-1} $MgSO_4$ (Merck) [21]. Bacterial cells of each metal resistant strain harvested by centrifugation at 25 °C for 15 min and washed twice with distilled water. The sun-dried biomass was treated with a solution of H_2SO_4 (2 N) [22]. The resulting metal-free biomass was washed with deionized distilled water several times and thereafter dried at 80 °C for 24 h. The biomass was further freeze-dried at 0 °C and reduced pressure, and was used as a biosorbent. All other chemicals employed were of analytical reagent grade.

2.2 *Metal solutions*

$CuCl_2$, $CdCl_2$, $NiSO_4$, and $K_2Cr_2O_7$ salts were dissolved in deionized distilled water to prepare different metal concentrations (10–100 mmol L^{-1}) for each metal. All glassware was washed with 0.1 mol L^{-1} HCl before and after each experiment to avoid the binding to metals.

2.3 *Determination of metal concentration*

The concentrations of copper, chromium, cadmium, and nickel were determined using an atomic absorption spectrophotometer (Perkin Elmer Analyst 300) using a specific lamp for each metal and at a specific wavelength.

2.4 *Biosorption experiments*

Experiments to determine the contact time required for equilibrium sorption experiments were performed in Erlenmeyer flasks, using 1 l of metal solution and 1 g of freeze-dried biomass. The flasks were kept under constant agitation in a rotatory shaker. Samples (1 mL) were removed

at different time intervals, membrane-filtered (Millipore 0.45 μm pore size), and analysed for metals by atomic absorption spectroscopy. Batch equilibrium sorption experiments were carried out by adding 0.10–0.25 g of milled biomass to 50 mL of precisely assigned different concentrations $[M]_{total} = 10–100$ mM of each heavy-metal solution in 125 mL Erlenmeyer flasks for 24 h in a rotary shaker. These experiments were done at pH 5.5 and 30 °C. Solutions of NaOH and H_2SO_4 were used to adjust the pH, and this control was made every hour. After the sorption equilibrium was reached, each solid metal bound biomass product was collected by centrifugation, washed five times for 5 min with water, freeze-dried, digested, and then analysed for the desired metal. The initial and equilibrium metal concentrations in each flask were determined by atomic absorption spectroscopy.

3. Results and discussion

Adsorption of metal ions by non-living biomass is affected by environmental conditions such as pH, temperature, and the concentrations of both metal ions and biomass. The pH of the adsorption medium can affect both the initial adsorption rate of metal ions onto the biomass surface and the mechanism of this adsorption. The initial adsorption rates increase with increasing initial pH up to an optimum pH value. The effect of the pH on the metal precipitation was conducted using 100 mL aliquots of 10–100 mmol L^{-1} of each metal solution. The optimum initial pH values for the biosorption of the investigated metal cations as shown in figure 1 were determined to be 5.5. Metal-binding measurements were made at this optimum pH value to avoid hydrolysis, polymerization, and precipitation of metal cations in the treatment solutions.

At the optimum pH value, electrostatic interactions between cationic species and the negatively charged biomass cell surfaces are responsible for metal binding [23]. To determine the maximum metal-binding capacity of the biomass to sequester certain heavy-metal ions from an aqueous solution, the biomass was shaken with an aqueous 0.1 mol L^{-1} of each metal solution for 24 h until the equilibrium state was characterized. At the equilibrium point, the amount of metal remaining in solution became time-invariant. The metal biosorption experiments were performed as single-component sorption systems for simplicity under optimum conditions. Adding metal cations to the metal free and dry biomass that have different organic binding sites *i* fills the tightest binding sites first, and metals in these sites will be the last to leave on washing the resulting metal-loaded biomass with water or acid [24–28]. When

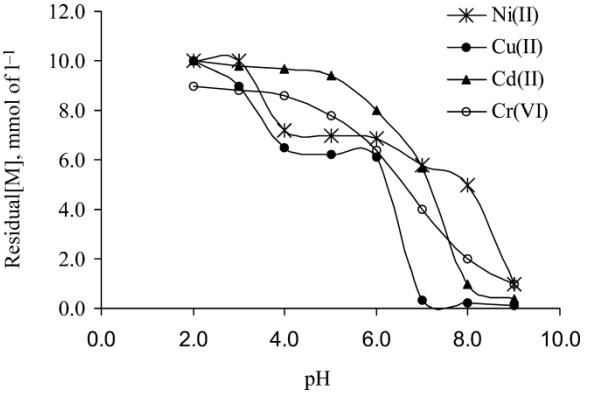

Figure 1. Effect of pH on the precipitation of the investigated metal cations at 30.0 °C.

the metal-loaded biomass is washed with water, any loosely held metal is removed, and only tightly bound metal remains. Reversible reaction of a metal cation, M_{aq}^{n+} with site i in the biomass (BM) equation (1), has equilibrium constant K_i (equation (2)). If the metal binding by the non-living biomass is dissociatively controlled (controlled by the water exchange rate on M_{aq}^{n+}) [29], the rate constant k_f is characteristic of M_{aq}^{n+} in all the equilibria [24–28]. The presence of bound metal after water washing of a metal loaded biomass thus depends on small values of $k_{r,i}$ in equation (2), which determines the rates of metal loss from tight biomass binding sites and the bio-availability of these metals in the environment. When the metal release rates ($k_{r,i}$) are small enough, the loading curve for the adsorbed complex (metal-loaded biomass) that has been washed with water is an isotherm (figure 2) that records the interaction of site i with sufficient excess of M_{aq}^{n+} also to occupy weaker metal-binding sites [24–28].

$$M_{aq}^{n+} + (\text{BM site } i)_{aq} \underset{}{\overset{k_i}{\rightleftharpoons}} M-(\text{BM site } i)_{aq} \tag{1}$$

$$K_i = \frac{k_f}{k_{r,i}} \tag{2}$$

Figure 2 shows the adsorption isotherms for the studied metal binding–biomass systems. Biosorption equilibrium can be represented by the Langmuir adsorption isotherm equation (3) [30]. The amount of metal q_i (mmol g^{-1}) bound at a specific biomass site i to form a complete monolayer on the biomass surface is described by Langmuir equation (3). Here, c (mmol L^{-1}) is the residual metal concentration at equilibrium, K_i (L $mmol^{-1}$) is the metal-binding equilibrium constant, and v_i (mmol g^{-1}) is the stoichiometric capacity of site i for particular metal cation. The equilibrium metal concentration c is calculated from q_i, as measured by metal analysis of the washed solid isolated after treatment of BM with a metal solution of known volume and total concentration. Depending on the magnitude of K_i, equation (3) predicts that a plot of q_i vs. c (the isotherm; figure 2) will curve toward the c axis with increasing c. Such type of curvature indicates specific metal binding by dry BM.

$$q_i = \frac{K_i v_i c}{1 + K_i c} \tag{3}$$

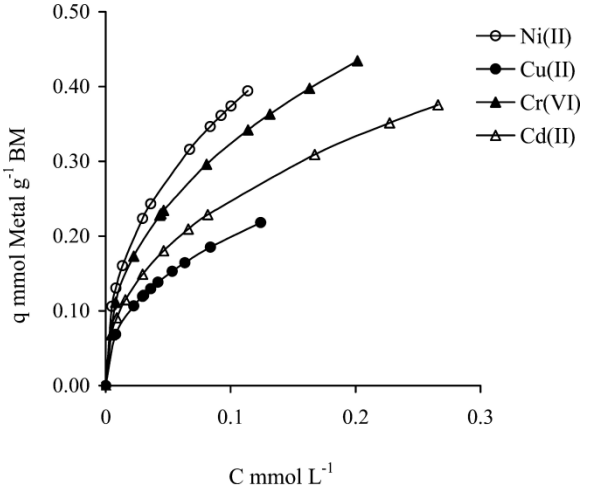

Figure 2. Tight M-BM binding isotherms at 30.0 °C and pH 5.5.

Chromium(VI), nickel(II), copper(II), and cadmium(II) biosorption isotherms have been successfully described by the Langmuir model [24–28,30]. Our previous studies [24–28] showed that the equilibrium data for the adsorption of metal ions onto similar biosorbents such as humic acid biopolymers fit the Langmuir model. The applicability of the Langmuir isotherm in the M–BM systems indicates the monolayer coverage of the metal cations on the surface of the BM. The Langmuir sorption isotherm is the best-known and the most-often-used isotherm for the adsorption of a solute from a liquid solution. However, in order to evaluate the appropriateness of this model, we must look at its underlying assumptions. The Langmuir isotherm was originally developed to describe the gas–solid phase adsorption of activated carbon. In its formulation, binding to the surface was primarily by physical forces (electrostatic, London, or van der Waals forces), and implicit in its derivation was the assumption that all sites possess equal affinity for the adsorbate. Its use was extended to empirically describe equilibrium relationships between a bulk liquid phase and a solid phase. One of the simplest representations of the adsorption phenomenon calls for the migration to and the occupation of a surface site i on a solid BM surface by metal cations. The non-linear equilibrium equations of Langmuir metal binding at specific BM site i can be linearized when a plot of $1/q$ vs. $1/c$ (equation (4)) is done to determine K_i and v_i from the intercept and slope (figure 3) [24]. The existence of equilibrium (1) and the validity of equation (3) are indicated

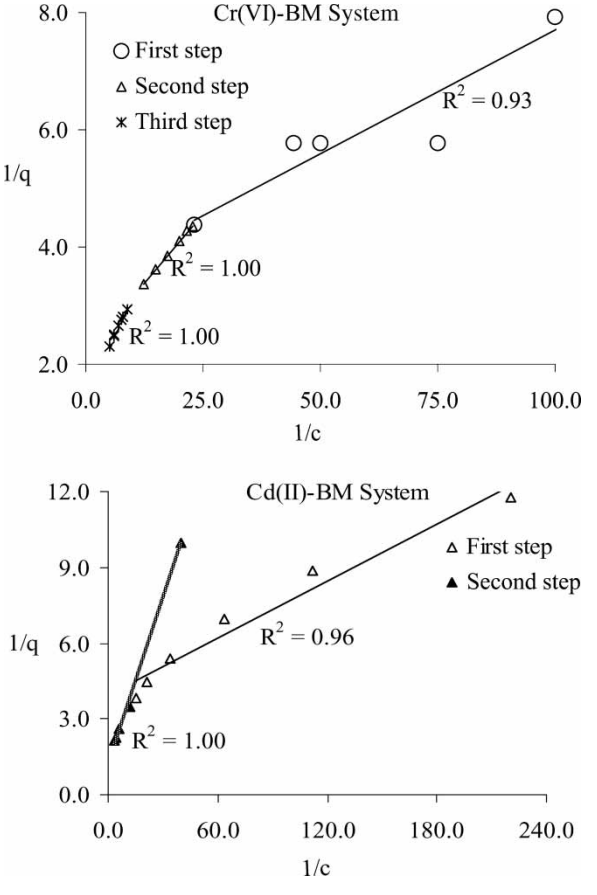

Figure 3. Plots of equation (4) for some data in figure 2.

by positive intercepts $1/\upsilon_i$ (i = A, B, ...) in linear segments of plots of equation (4) as in figure 3 [24].

$$\frac{1}{q_i} = \frac{1}{\upsilon_i} + \frac{1}{K_i \upsilon_i c} \tag{4}$$

Steps on the isotherms in figure 2 can be distinguished by curvature of the plot toward the c axis. Sequential steps in an isotherm indicate that metal cations initially binding to a particular site have reached maximum capacity and that metal binding has moved to a second distinct site on BM cell walls. In order to confirm the number of steps in which a metal binds to a BM surface, a Langmuir plot of c/q vs. c is made (figure 4). The changes of slope in the plot easily allow the number of steps for metal binding to be distinguished.

On applying the preceding methodology, it is concluded that four binding BM sites, assigned as A, B, C, and D, can be recognized in the investigated metal binding systems. The values of the site capacities υ_i and the equilibrium constants K_i, were calculated according to equation (5) from the slopes and intercepts of the straight lines plots of equation (4) for each binding step and recorded in table 1. It is clear in table 1 that the values of the different capacities of those sites are 0.2, 0.3, 0.4, and 0.5 mmol g^{-1}, respectively.

$$\upsilon_i = \frac{1}{\text{intercept}} \quad \text{and} \quad K_i = \frac{\text{intercept}}{\text{slope}} \tag{5}$$

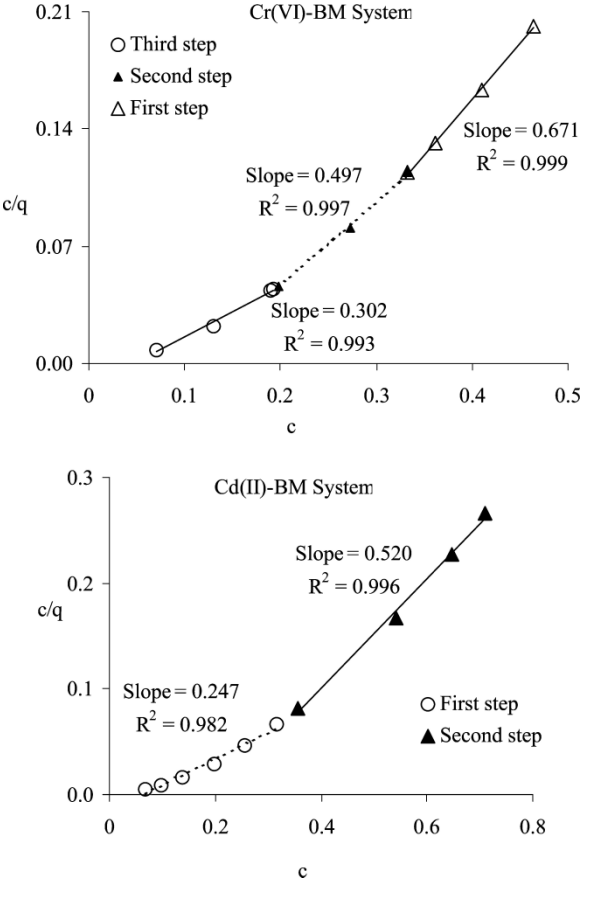

Figure 4. Langmuir plots of c/q vs. c for some metal-binding systems.

Table 1. Tight binding isotherm parameters at 30.0 °C and pH 5.5.

	Site A		Site B		Site C		Site D	
Metal	v_A	$10K_A$	v_B	K_B	v_C	K_C	v_D	K_D
Cr(VI)	0.2	85.5	0.3	29.6			0.5	9.2
Ni(II)	0.2	116.2			0.4	16.2		
Cd(II)	0.2	104.8					0.5	10.1
Cu(II)			0.3	30.1				
Cu(II)*	1.1	4.9	1.6	3.6	3.0	0.13		

*Data from reference [24] for the adsorption on humic acids biopolymers. The site capacity, v_i, is in mmol g^{-1}. The equilibrium constant, K_i, is in L mmol^{-1}.

When the calculated site capacity (v_i) for each of the investigated systems approaches one of those values, this means that the given metal cations bind selectively to the corresponding site. The trend of the site capacities for metal binding to increase as the binding goes from step A to B to C to D is seen for all of these metals and can be rationalized from the equilibrium constants, which are seen to decrease from step A to B to C to D. The plot of $1/q$ vs. $1/c$ (figure 3), in the metal binding of Cr(VI) to BM binding sites i is not a single straight line but three linear segments of positive intercepts $1/v_i$ with excellent R^2 values. This is confirmation of three binding steps for binding of Cr(VI) to BM cell walls. Next, from the values of slope and intercept of the straight lines in plots of equation (4), the metal binding site capacity (v_i) and equilibrium constants (K_i) can be calculated for A, B, and D sites (table 1). These three binding steps are confirmed in the plot of c/q vs. c for this system (figure 4). In the process of Cd(II) binding to BM, the plot of $1/q$ vs. $1/c$ (figure 3) shows that all of the data fit on two lines with distinctive slopes and excellent R^2 values. From the values of the binding capacities (table 1), it is suggested that binding takes place in two steps to sites A and D. These two binding steps are confirmed in the plot of c/q vs. c for this system (figure 4). By the same methodology and from the values of the calculated site capacities, Ni(II) cations prefer to bind in two sequential steps to sites A and C on the BM surface, while for the copper system, the cations bind to only one site assigned B. The largest equilibrium constant, K_A, for Ni(II) binding is due to the high ligand field stabilization energy imparted on a d^8 centre. Bound Cr(VI) in BM is a weak field d^8 centre with no ligand-field stabilization energy, which can account for its low equilibrium constants K_i (table 1). For comparison purposes, the values of the site capacities (v_i) and equilibrium constants (K_i) for copper binding to solid humic acids biopolymers derived from Irish peat [24] are included in table 1. The larger v_i values for the three binding steps in case of humic acids than those for BM indicate that humic acids are much better metal chelators than BM. These large values of v_i for humic acids necessitate smaller K_i values. The same behaviour for all four cations is taken to confirm that the Langmuir model is a suitable approach to describe the adsorption process of the investigated heavy-metal cations onto BM. A number of processes have been considered to describe the binding of any of the investigated metal cations to a site i on BM surface and give its proposed mechanistic profile. First, water associated with a BM binding site needs to be removed before M^{2+}_{aq} cations can bind in an unfavourable enthalpic but favourable entopic step. Second, water also should be removed from M^{2+}_{aq} in order to form an inner sphere complex, with the same thermodynamic considerations as for binding site dehydration. Finally, the metal could form an inner sphere complex in a favourable enthalpic step but an unfavourable entopic step. The overall change for this process may be endothermic or exothermic. It is surmised that BM is functioning as an efficient biological ion exchanger. The effect of isotherm shape can be used to predict whether a sorption system is favourable or unfavourable [31]. The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter K_R that is defined in terms of the equilibrium constant (K_i) and the

Table 2. Shapes of the isotherms.

Values of K_R	Type of isotherm
$K_R > 1$	Unfavourable
$K_R = 1$	Linear
$0 < K_R < 1$	Favourable
$K_R = 0$	Irreversible

Table 3. Values of K_R for the metal ions studied.

Metal cation	Values of K_R
Cr (VI)	0.163
Ni (II)	0.073
Cu (II)	0.339
Cd (II)	0.067

initial concentration (c_o) by equation (6). This parameter indicates the shape of the isotherm according to table 2. The forces between the surface layers are attractive, and the adsorption is more favourable if K_R is less than unity and more than zero while these forces are repulsive, and the adsorption is unfavourable if K_R is greater than unity [32, 33]. The values of K_R for all metals are given in table 3. The K_R values indicate that sorption of chromium, nickel, copper, and cadmium on BM is more favourable for all of the initial concentrations of the metals at the optimal conditions. Also, the K_R values indicate that sorption of copper and chromium is more favourable than that of nickel and cadmium.

$$K_R = \frac{1}{1 + K_i c_o} \tag{6}$$

4. List of symbols

BM	non-living biomass
i	any biomass site
c	residual metal concentration at equilibrium (mmol L^{-1})
v_i	stoichiometric capacity of site i for the given metal (mmol metal g^{-1} BM)
K_i	metal binding equilibrium constant (L $mmol^{-1}$)
k_f	water exchange rate constant on the aqueous metal cation
$k_{r,i}$	rates at which metal cations are lost from the tight metal binding sites of the biomass
q_i	amount of metal bound to a biomass site i (mmol metal g^{-1} BM)
c_o	initial concentration (mmol L^{-1})
K_R	dimensionless constant separation factor or equilibrium parameter
A, B, C, D	binding sites on the cell walls of the non-living biomass
R^2	least-squares fit value
d^8	metal cation containing eight electrons in its d-orbitals

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