

Biosorption of Cd(II), Cr(III), and Cr(VI) by saltbush (*Atriplex canescens*) biomass: Thermodynamic and isotherm studies

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Abstract

The biosorption data of Cd(II), Cr(III), and Cr(VI) by saltbush leaves biomass were fit on the Freundlich and Langmuir adsorption isotherms at 297 K. The Cd(II) and Cr(III) solutions were adjusted to pH 5.0 and the Cr(VI) solution was adjusted to pH 2.0. The correlation coefficient values indicated that the data fit better the Freundlich model. The maximal capacities (K_F) were found to be 5.79×10^{-2} , 3.25×10^{-2} , and 1.14×10^{-2} mol/g for Cr(III), Cd(II), and Cr(VI), respectively. Similar results were obtained using the Langmuir and the Dubinin–Radushkevick equations. Thermodynamic parameters calculated from the Khan and Singh equation and from the q_e vs C_e plot show that the equilibrium constants for the biosorption of the metals follow the same order of the maximal capacities. The negative Gibbs free energy values obtained for Cd(II) and Cr(III) indicated that these ions were biosorbed spontaneously. The mean free energy values calculated from the Dubinin–Radushkevick equation (10.78, 9.45, and 9.05 for Cr(III), Cr(VI), and Cd(II), respectively) suggest that the binding of Cd(II), Cr(III), and Cr(VI) by saltbush leaves biomass occurs through an ionic exchange mechanism.

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1. Introduction

The removal of heavy metals from contaminated solutions using non-living biomass is a physico-chemical process whose mechanism(s) is not metabolically controlled [1]. This type of bioremediation is referred to as phytofiltration. This technology is gaining interest of many researchers as it is more economic and poses less health risks than many of the current techniques [2–5]. The bioadsorption of metals to the biomass surface occurs mainly as a result of either physical binding involving London–Van der Waals forces and electrostatic attraction, or by chemical binding such as ionic or covalent binding between the adsorbent and the adsorbate [1,5]. Studies have shown that the biosorption mechanisms depend on the type of functional

groups on the surface of the biomass, the nature of the metal and the characteristics of the matrix around the biosorbent species [1,3,4,6–9]. However, the exact adsorption mechanism is not well understood yet.

The adsorption isotherms are used to describe the equilibrium of the metal between the aqueous solution and the solid biomass phase. Depending on the nature of the biosorption system, the used isotherm model might determine the maximum biosorption capacity and several kinetic and thermodynamic parameters that can be used for a better understanding of the binding mechanism [6]. The isotherms models are flexible enough to fit over a wide range of experimental conditions; using more than one model helps to understand the mechanism and to quantify more variables. Two of the widely used models are the Freundlich and the Langmuir isotherms.

Previous research and unpublished data have shown that saltbush biomass has significant phytofiltration potential for Cd(II), Cr(III), and Cr(VI) [10,11]. These three metal species

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are widely used in industrial activities, all of them are toxic but Cr(VI) is considered the most toxic of them [12–15]. The objectives of the present study were to obtain a better understanding of the Cd(II), Cr(III), and Cr(VI) biosorption mechanisms by saltbush leaves biomass. For this purpose, metal solutions prepared from $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and $\text{K}_2\text{Cr}_2\text{O}_7$ (adjusted to pH 5.0 for the Cd(II) and Cr(III) and to pH 2.0 for Cr(VI)) were reacted with the ground saltbush leaves biomass. The experimental data obtained were fit into the Freundlich and Langmuir isotherms and the obtained isotherms and thermodynamic parameters are reported herein.

2. Methodology

The saltbush leaves were collected from plants grown around El Paso, TX, USA, from an area without previous report on metal contamination. The leaves were washed with tap water, oven-dried at 70 °C for one week, and ground to pass through a 100-mesh (0.149 mm) screen.

The isotherm experiments were performed as previously reported [16]. Two grams of the ground biomass were washed once with 0.1 M HCl and twice with distilled water. At each washing, 50 ml of either HCl or water were added to the biomass, hand shaken, and centrifuged for 5 min at 3000 rpm (Fisher Scientific 8K, Houston, TX, USA). The washings were evaporated in an oven at 70 °C to account for any biomass loss. The washed biomass was then suspended in deionized (DI) water to give a concentration of 5 mg biomass per ml of water. The pH was adjusted to 5.0 for the Cd(II) and Cr(III) isotherm experiments and for the Cr(VI) experiment the pH was adjusted to 2.0. For each of the studied metals, aliquots of 2 ml of the biomass solution were placed in each of 27 test tubes and centrifuged for 5 min to separate the biomass pellets. Nine concentrations (0.0, 9.6, 19, 29, 38, 48, 58, 67, and $77 \times 10^{-5} \text{ mol/dm}^3$) (three replicates/concentration) were tested for each metal in order to get reproducible results.

For each of the three metals, an aliquot of 50 ml of 1 mM metal solution was prepared in 0.01 M sodium acetate buffer and the other eight concentrations were prepared from this solution. The salts used to prepare the metal solutions were $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and $\text{K}_2\text{Cr}_2\text{O}_7$. The pH was adjusted to 5.0 for the Cd(II) and Cr(III) solutions, while for Cr(VI) it was adjusted to pH 2.0. Aliquots of two ml from each metal solution were transferred into the respective biomass tubes; metal solutions without biomass and biomass solutions without metal were set as controls. The tubes containing the biomass and the controls were shaken on a rocker for 60 min at room temperature (24 ± 2 °C), centrifuged, and the supernatants were saved for metal quantification using an atomic absorption spectrometer (AAS) Perkin–Elmer model 3110 (Perkin–Elmer, Shelton, CT, USA) with deuterium background subtraction. The amount of metal bound was considered to be the difference in concentration between the replicates and the corresponding control. Aliquots of 2 ml of 8.9×10^{-3} and $1.92 \times 10^{-2} \text{ mmol/dm}^3$ for Cd and Cr, respectively, were read every 10 samples to assure the performance of the AAS. The calibration coefficient (R^2) obtained for all analyses was 0.99

or better. Some samples were diluted to fit with the calibration range. The wavelengths used for the analyses were 228.8 nm for cadmium and 257.7 nm for chromium. The coefficients of the used models were computed with linear least-square fit using Microsoft Excel.

3. Results and discussion

3.1. Sorption isotherms

The Langmuir and the Freundlich isotherms have been extensively used to investigate the sorption equilibrium between the metal solution and the solid biomass phase [1–3,5–9]. The Langmuir model is a non-linear model that suggests a monolayer uptake of the metal on a homogeneous surface, having uniform energies of adsorption for all the binding sites without any interaction between the adsorbed molecules [17,18]. Traditionally, the Langmuir model is represented as

$$q_e = Q_L b C_e / (1 + b C_e), \quad (1)$$

where q_e is the amount of metal adsorbed per mass of adsorbent biomass. In Eq. (1) q_e is given in mol/g, Q_L is the adsorption capacity, defined as the maximum amount of metal ion forming a complete monolayer on the biomass surface (mol/g), b is a constant related to the energy of adsorption, and C_e is the equilibrium concentration of the metal in the solution (mol/dm^3). Equation (2) shows the linearized form of the Langmuir model, and the plots of C_e/q_e versus C_e for the Cd(II), Cr(VI), and Cr(III) are shown in Figs. 1A and 1B (the plot for Cr(III) (Fig. 1B) is shown separately due to the scale),

$$C_e/q_e = C_e/Q_L + 1/bQ_L. \quad (2)$$

The dimensionless adsorption intensity (R_L) is calculated using the following formula [18],

$$R_L = 1/(1 + bC_0), \quad (3)$$

where C_0 is the initial metal concentration in the solution (mol/dm^3). The calculated average R_L value for different initial metal concentrations indicates favorable isotherm if this value is between 0 and 1 [18].

The Freundlich isotherm is also a non-linear model that assumes a heterogeneous energetic distribution of the active binding sites on the biomass as well as interactions between the adsorbed molecules [1,17]. The Freundlich model considers different affinities for the binding sites on the biomass surface with interactions between the adsorbed molecules. This model also considers that the sites with stronger affinity are occupied first [1]. The Freundlich isotherm is expressed using Eq. (4), and this formula is linearized as shown in Eq. (5) as follows:

$$q_e = K_F C_e^{1/n}, \quad (4)$$

$$\ln q_e = \ln K_F + 1/n \ln C_e, \quad (5)$$

where K_F is the maximum adsorption capacity (mol/g), and n stands for adsorption intensity; K_F and $1/n$ are determined from the linear plot of $\ln q_e$ versus $\ln C_e$ (Fig. 2).

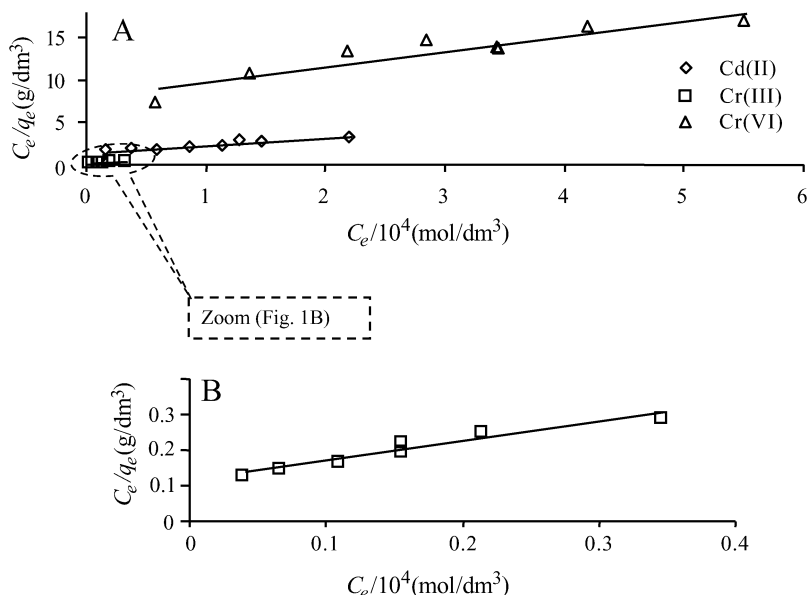


Fig. 1. (A) Langmuir isotherms for the biosorption of Cd(II), Cr(III), and Cr(VI) on saltbush leaves biomass at $24 \pm 2^\circ\text{C}$; (B) biosorption of Cr(VI) on saltbush leaves biomass (enlarged scale). The Cd(II) and Cr(III) solutions were adjusted at pH 5.0 and the Cr(VI) solution at pH 2.0.

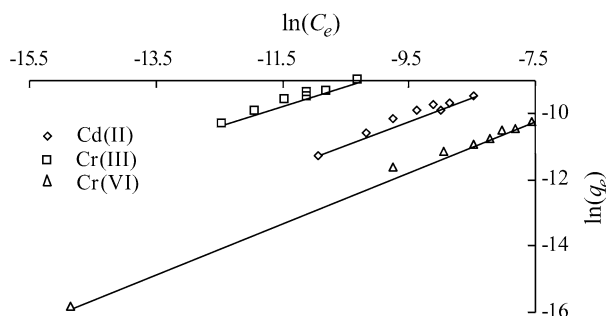


Fig. 2. Freundlich isotherms for the biosorption of Cd(II), Cr(III), and Cr(VI) on saltbush leaves biomass at $24 \pm 2^\circ\text{C}$. The Cd(II) and Cr(III) solutions were adjusted at pH 5.0 and the Cr(VI) solution at pH 2.0.

Table 1
Isotherm models parameters for the biosorption of Cd(II), Cr(III), and Cr(VI) on saltbush leaves biomass at $24 \pm 2^\circ\text{C}$

Metal	Freundlich			Langmuir			
	$K_F \times 10^{-2}$ (mol/g)	n	R^2	$Q_L \times 10^{-2}$ (mol/g)	b (l/mg)	R_L	R^2
Cd(II)	3.25	1.39	0.9624	2.22	33.07	0.9896	0.8991
Cr(III)	5.79	1.66	0.9832	3.34	257.52	0.9138	0.9417
Cr(VI)	1.14	1.30	0.9958	0.79	21.03	0.9916	0.8568

The Cd(II) and Cr(III) solutions were adjusted at pH 5.0 and the Cr(VI) solution at pH 2.0. K_F is adsorption capacity, n is adsorption intensity, R^2 is the correlation coefficient, Q_L and b are the Langmuir constants, and R_L is adsorption intensity.

The parameters resulted from the Langmuir and Freundlich plots for Cd(II), Cr(III), and Cr(VI) (Figs. 1 and 2) are presented in Table 1. As shown in Table 1, the correlation coefficients for the Langmuir isotherms had $R^2 > 0.8568$, but for the Freundlich isotherms R^2 were higher than 0.9624, which suggests that the data fit better the Freundlich model.

The adsorption capacity values (K_F) for Cr(III), Cd(II), and Cr(VI) obtained from the Freundlich model (mol/g) were,

respectively, 5.79×10^{-2} , 3.25×10^{-2} , and 1.14×10^{-2} . These values indicated that saltbush biomass had a better affinity for Cr(III) and Cd(II) ions. According to the literature, lechuguilla biomass had a capacity of 3.9×10^{-2} mol/g for Cr(VI) at pH 2.0, and 4.0×10^{-3} mol/g for Cr(III) at pH 4.0 [17,19]. Under the same conditions, the capacities of Malone/African alfalfa biomass were found to be $0.085 \times 10^{-2}/0.052 \times 10^{-2}$, $0.039 \times 10^{-2}/0.053 \times 10^{-2}$, and $0.025 \times 10^{-2}/0.247 \times 10^{-2}$ mol/g, for Cd(II), Cr(III), and Cr(VI), respectively [25]. On the other hand, in similar conditions the Amberlite IR-120 resin showed a Cd(II) binding capacity of 201.0 mol/g [20]. The differences in binding capacity showed by saltbush biomass compared to other biomasses are due to the fact that each biomass has different types and amounts of functional groups participating in the metal binding. The fact that the biosorption data for the three metals fit with both the Freundlich and the Langmuir isotherms suggests that the binding of the three cations occurs as a monolayer on the surface of the biomass.

3.2. Thermodynamic parameters

The biosorption equilibrium constants (K_c) for the binding data of Cd(II), Cr(III), and Cr(VI) by saltbush leaves biomass are calculated either from the intercept of Khan and Singh plot [17] ($\ln q_e/C_e$ versus q_e , Fig. 3) or from the slope of plotting q_e versus C_e , Eq. (6) (Fig. 4). The real equilibrium constant is expected to be in the range of the values presented in Table 2.

$$K_c = q_e/C_e. \quad (6)$$

The change in Gibbs free energy ΔG^0 (kJ/mol) for the biosorption of the metals on the saltbush biomass is calculated in Table 2 from Eq. (7), where T is the temperature in Kelvin and R is the gas constant (8.314 J/mol K):

$$\Delta G^0 = -RT \ln K_c. \quad (7)$$

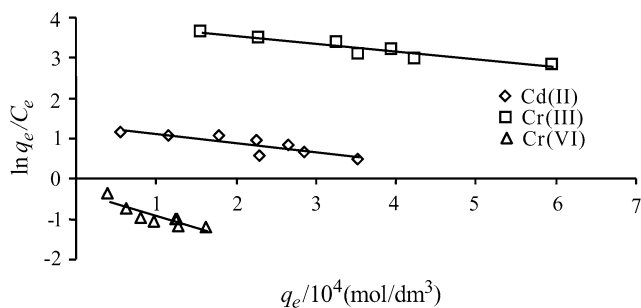


Fig. 3. Adsorption of Cd(II), Cr(III), and Cr(VI) on saltbush leaves biomass using the Khan and Singh plots of $\ln q_e/C_e$ versus q_e . The Cd(II) and Cr(III) solutions were adjusted at pH 5.0 and the Cr(VI) solution at pH 2.0.

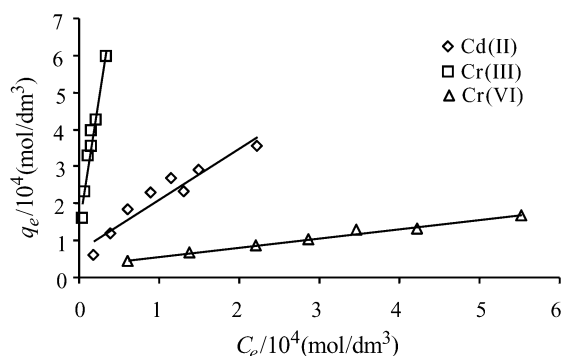


Fig. 4. Adsorption of Cd(II), Cr(III), and Cr(VI) on saltbush leaves biomass using q_e versus C_e plot for the purpose of calculating the distribution coefficient. The Cd(II) and Cr(III) solutions were adjusted at pH 5.0 and the Cr(VI) solution at pH 2.0.

Table 2

Thermodynamic parameters for the biosorption of Cd(II), Cr(III), and Cr(VI) on saltbush leaves biomass at $24 \pm 2^\circ\text{C}$

Metal	Khan and Singh		q_e versus C_e plot	
	K_c	ΔG^0 (kJ/mol)	K_c	ΔG^0 (kJ/mol)
Cd(II)	1.334	-0.7121	1.380	-0.7957
Cr(III)	3.934	-3.3837	13.522	-6.4340
Cr(VI)	0.095	5.8075	0.251	3.4160

The Cd(II) and Cr(III) solutions were adjusted at pH 5.0 and the Cr(VI) solution at pH 2.0. K_c is equilibrium constant; ΔG^0 is the Gibbs free energy.

The negative ΔG^0 values for Cd(II) and Cr(III) shown in Table 2 indicate that the sorption of these metals on the saltbush biomass is a spontaneous process. This result corroborates the K_F values for the studied metals (Cr(III) > Cd(II) > Cr(VI)). Probably this result is due to the fact that the negatively charged carboxyl group is the main group in the saltbush leaves biomass that binds Cd(II) and Cr(III) [10,11]. A higher 'charge over size ratio' for Cr(III) (4.6) compared to Cd(II) (1.9) [21], makes Cr(III) binding more favorable than Cd(II). On the other hand, Cr(VI) exists in the solution as oxo-anion forms ($\text{Cr}_n\text{O}_{3n+1}^{-2}$, n equal 2, 3, or 4) which have larger sizes compared to the other studied metals [26,27]. In addition to that, it has been suggested that Cr(VI) oxidizes part of the functional groups available on the biomass [27]. Further studies are required to investigate this issue in saltbush biomass.

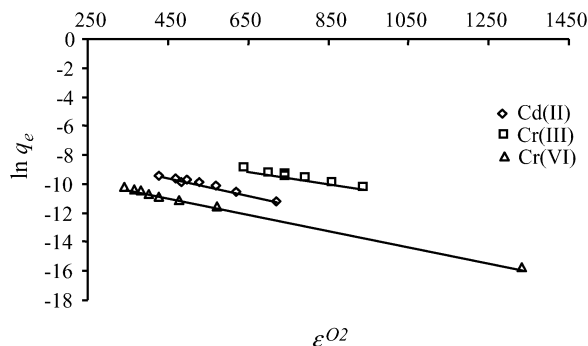


Fig. 5. Dubinin–Radushkevick plots for the biosorption of Cd(II), Cr(III), Cr(VI) on saltbush leaves biomass at $24 \pm 2^\circ\text{C}$. The Cd(II) and Cr(III) solutions were adjusted at pH 5.0 and the Cr(VI) solution at pH 2.0.

Table 3

Dubinin–Radushkevick parameters for the biosorption of Cd(II), Cr(III), and Cr(VI) on saltbush leaves biomass at $24 \pm 2^\circ\text{C}$

Metal	K_E (mol/kJ) ²	q_m (mol/kg)	E (kJ/mol)	R^2
Cd(II)	-6.1 (10^{-3})	1.06	9.05	0.97
Cr(III)	-4.3 (10^{-3})	1.92	10.78	0.99
Cr(VI)	-5.6 (10^{-3})	0.21	9.45	1.00

The Cd(II) and Cr(III) solutions were adjusted at pH 5.0 and the Cr(VI) solution at pH 2.0. K_E is a constant related to sorption energy, q_m is the monolayer capacity, E is the mean free energy sorption, R^2 is the correlation coefficient.

The biosorption mean free energy (E) [22,23] was calculated from Eq. (8),

$$E = (-2K_E)^{-1/2}, \quad (8)$$

where K_E is a constant related to the biosorption energy (mol^2/kJ^2), that is calculated from the Dubinin–Radushkevick (D–R) Eq. (9), where q_m is the monolayer capacity (mol/g),

$$\ln q_e = \ln q_m - K_E (\varepsilon^0)^2, \quad (9)$$

ε^0 is the Polanyi potential that is calculated from Eq. (10)

$$\varepsilon^0 = RT \ln(1 + 1/C_e), \quad (10)$$

where the K_E and $\ln q_m$ are calculated from the slope and the intercept of plotting $\ln q_e$ versus ε^{02} (Fig. 5). Table 3 shows that the mean free energy was between 9.05 and 10.78 kJ/mol for the three studied metals, which suggests that the biosorption of Cd(II), Cr(III), and Cr(VI) occurs via ionic exchange mechanism in which the sorption energy lies within 8–16 kJ/mol [24].

4. Conclusions

The results of this study show that the biosorption of Cd(II), Cr(III), and Cr(VI) on saltbush leaves biomass obeys both the Freundlich and the Langmuir isotherms, which suggests a monolayer adsorption of these three metals on the outer surface of the biomass. According to the D–R equation and the two isotherm models, the maximum capacity for the studied metals follows the order Cr(III) > Cd(II) > Cr(VI). The thermodynamic parameters calculated from the Khan and Singh equation and from the plot of the amount of metal adsorbed versus the

equilibrium concentration show that the equilibrium constants for the biosorption of the studied metals follow the same order of the maximum capacity. The Gibbs free energy values show that, though the biosorption was spontaneous for Cr(III) and Cd(II), the adsorption of Cr(III) was privileged compared to that of Cd(II), and that the biosorption of Cr(VI) was non-spontaneous. The mean free energy calculated from the D–R equation suggests that the binding of the Cd(II), Cr(III), and Cr(VI) by saltbush leaves biomass occurs through an ionic exchange mechanism.

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