

# Thermodynamic and isotherm studies of the biosorption of Cu(II), Pb(II), and Zn(II) by leaves of saltbush (*Atriplex canescens*)

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## Abstract

The Freundlich and Langmuir isotherms were used to describe the biosorption of Cu(II), Pb(II), and Zn(II) onto the saltbush leaves biomass at 297 K and pH 5.0. The correlation coefficients ( $R^2$ ) obtained from the Freundlich model were 0.9798, 0.9575, and 0.9963 for Cu, Pb, and Zn, respectively, while for the Langmuir model the  $R^2$  values for the same metals were 0.0001, 0.1380, and 0.0088, respectively. This suggests that saltbush leaves biomass sorbed the three metals following the Freundlich model ( $R^2 > 0.9575$ ). The  $K_F$  values obtained from the Freundlich model ( $175.5 \cdot 10^{-2}$ ,  $10.5 \cdot 10^{-2}$ , and  $6.32 \cdot 10^{-2} \text{ mol} \cdot \text{g}^{-1}$  for Pb, Zn, and Cu, respectively), suggest that the metal binding affinity was in the order  $\text{Pb} > \text{Zn} > \text{Cu}$ . The experimental values of the maximal adsorption capacities of saltbush leaves biomass were  $0.13 \cdot 10^{-2}$ ,  $0.05 \cdot 10^{-2}$ , and  $0.107 \cdot 10^{-2} \text{ mol} \cdot \text{g}^{-1}$  for Pb, Zn, and Cu, respectively. The negative  $\Delta G^\circ$  values for Pb and the positive values for Cu and Zn indicate that the Pb biosorption by saltbush biomass was a spontaneous process.

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## 1. Introduction

Continuous discharges of heavy metals *circa* densely populated areas threaten urban ecosystems and human health [1–3]. Due to that, local and federal authorities derived resources to remove heavy metals and other pollutants from the environment. Scientists and engineers have recently found that several biomaterials can be used to eliminate heavy metals from polluted soil and water [4–6]. This technology has a significant connotation when the heavy metal contaminants exist at trace concentrations or where the current cleaning methods become inefficient and relatively expensive [7,8].

As observed with other materials, the biosorbent process reaches an equilibrium between the biosorbed metal and the bulk concentration of the metal [7,9]. This equilibrium depends on the type of available functional groups on the biomaterial, the target metal, and characteristics of the matrix around the biosorbent species [9–11]. The biosorption can be controlled by physical attraction, chemical complexation with the biomass functional groups, ion-exchange, or hydrate formation at the surface [4,12].

The theoretical aspects of the sorption process have been extensively studied. Adsorption isotherms have been widely used to model the biosorption equilibrium, and to predict the binding at different metal concentrations and environmental conditions [9,13]. The isotherms also produce many thermodynamic and kinetic parameters that could be used for better understanding of the mechanism involved in the biosorption [14,15]. The most common

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equations that are used to describe the experimental isotherm data are the Freundlich and the Langmuir isotherms, both are non-linear models that suggest metal monolayer coverage onto the surface of the biomass [16].

The present investigation includes the heavy metals Cu(II), Pb(II), and Zn(II). Similar to other heavy metals, these metals are released to the environment mainly from industries, they are not biodegradable, and accumulate in living organisms causing diseases, disorders, and other toxic effects [17,18].

Previous studies have shown that saltbush biomass has a high potential for the removal of cadmium and chromium from aqueous solutions [19,20]. Experiments have also shown that this biomass has the capacity to adsorb Cu(II), Pb(II), and Zn(II) from synthetic polluted waters (unpublished data). The present manuscript reports on the Cu(II), Pb(II), and Zn(II) biosorption capacity of the saltbush leaves biomass. In addition, adsorption isotherms were used to describe the biosorption equilibrium and to calculate some kinetic and thermodynamic parameters. The relative binding affinity of the biomass and the main mechanism that could be controlling the biosorption were also discussed.

## 2. Methodology

Saltbush (*Atriplex canescens*) shoots were collected from an area around El Paso, TX, with no previous report on metal contamination. The leaves were separated from the stems, washed with tap water; oven dried at 70 °C for one week, ground using a Wiley-Mill, and sieved to pass through a 100-mesh (0.149 mm) screen to obtain a uniform particle size. The leaves were chosen because they represent the highest percentage of the saltbush biomass.

The isotherms experiments were performed as previously published [16]. A sample of 2.0 g was taken from the ground saltbush leaves biomass, washed once with 0.1 M HCl and twice with deionized (DI) water. After each washing, the biomass was centrifuged for 5 min at 3000 rpm (Fisher Scientific, Marathon 6K). The loss biomass was calculated by evaporating the washings in an oven at 70 °C. The biomass was suspended in DI water to have a concentration of 5 mg biomass per ml. The suspension was adjusted to pH 5.0 (using diluted solutions of HCl and NaOH) because previous equilibrium batch studies showed that the optimum binding of the studied metals (Cu, Pb, and Zn) to the saltbush biomass was at pH 5.0 (data not shown). Two ml of the biomass solution were placed in 5-ml test tubes [27 per each studied metal, Cu from Cu(SO<sub>4</sub>) · 5 H<sub>2</sub>O, Pb from Pb(NO<sub>3</sub>)<sub>2</sub>, Zn from ZnCl<sub>2</sub>], centrifuged, and the supernatants were discarded. Each metal was used at 0.0, 9.6, 19, 29, 38, 48, 58, 67 and 77 × 10<sup>-5</sup> mol · dm<sup>-3</sup> (three replicates per metal concentration, adjusted to pH 5.0). Besides, a fourth tube containing only the metal solution (no biomass) was set as a control. Aliquots of 2 ml (volume

used in the isotherm batch studies) of the different metal solutions were transferred to the respective labeled biomass tubes. The tubes and controls were allowed to equilibrate for 60 min at room temperature (24 ± 2 °C), centrifuged, and the supernatants were saved for metal quantification using an atomic absorption spectrometer with deuterium background subtraction (Perkin–Elmer model 3110, Shelton, CT, USA). The instrument was calibrated using 4 standards and the correlation coefficients ( $R^2$ ) obtained for all analytes were 0.99 or higher. The wavelengths used for the metals were 327.4 nm for Cu, 283.3 nm for Pb, and 213.9 nm for Zn. The coefficients of the used models were computed with linear least-square fitting. The amount of metal bound was calculated from the difference between the amount of metal determined in the corresponding solution control and the plant samples.

## 3. Results and discussion

### 3.1. Sorption isotherms

The Langmuir and Freundlich isotherms are the most widely used models for studying the sorption equilibrium between the metal solution and the solid biomass phase [4,6,7,9–11,15,21]. The Langmuir isotherm is a non-linear model. In this model, represented in equation (1), the biosorbed metal covers a monolayer on the homogeneous solid surface, where all binding sites on the surface have uniform energies of adsorption without any interaction between the adsorbed molecules [14,16]

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

where  $q_e$  is the quantity of metal adsorbed at equilibrium over the mass of adsorbent biomass (mol · g<sup>-1</sup>).  $Q_L$  stands for the monolayer adsorption capacity, defined as the maximum amount of metal ion adsorbed forming a complete monolayer on the biomass surface per mass of adsorbent biomass (mol · g<sup>-1</sup>), and  $b$  is a constant related to the energy of adsorption.  $C_e$  is the concentration of the metal in solution at equilibrium (mol · dm<sup>-3</sup>). The Langmuir model is usually linearized as shown in equation (2). The biosorption data obtained for Cu(II), Pb(II), and Zn(II) were fitted into equation (2) by plotting  $C_e/q_e$  versus  $C_e$  as shown in figure 1:

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

The dimensionless adsorption intensity ( $R_L$ ) is computed using the following equation

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

where  $C_0$  is the initial metal concentration in the solution (mol · dm<sup>-3</sup>);  $R_L$  indicates the type of isotherm; if it is irreversible  $R_L = 0$ , favorable  $0 < R_L < 1$ , linear  $R_L = 1$ , or unfavorable  $R_L > 1$  [14].

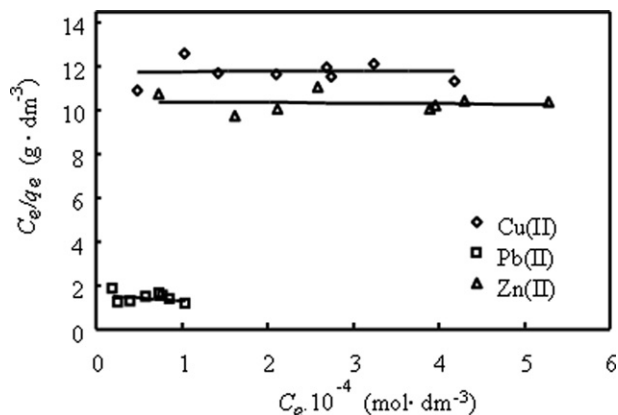


FIGURE 1. Langmuir isotherms for the biosorption of Cu(II), Pb(II), and Zn(II) by saltbush leaves biomass at  $24 \pm 2^\circ\text{C}$  and pH 5.0.

The adsorption trend of the investigated metals onto the saltbush leaves was also fitted into the Freundlich isotherm. The Freundlich model is also a non-linear model that suggests a mono layer sorption of the metal on the biomass. Differing from the Langmuir, the Freundlich model assumes a heterogeneous energetic distribution of the active binding sites on the sorbate surface with interactions between the adsorbed molecules [4,16]. In the Freundlich model, it is considered that the binding sites affinities on the biomass surface vary with the interactions between the adsorbed molecules. Consequently, the sites with stronger affinity are occupied first [4]. The general equation and the linearized form for the Freundlich isotherm is expressed as follows:

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

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

in equations (4) and (5),  $K_F$  is the maximum adsorption capacity ( $\text{mol} \cdot \text{g}^{-1}$ ), and  $n$  is the adsorption intensity, which is related to the affinity or binding strength [4].  $K_F$  and  $1/n$  are determined from the slope and intercept resulting from plotting  $\ln q_e$  versus  $\ln C_e$  as shown in figure 2 for the biosorption of Cu, Pb, and Zn.

The adsorption capacity and affinity of saltbush leaves biomass for Cu(II), Pb(II), and Zn(II) was determined with these two isotherms models (Freundlich and Langmuir), using each metal individually at 0.0, 9.6, 19, 29, 38, 48, 58, 67, and  $77 \cdot 10^{-5} \text{ mol} \cdot \text{dm}^{-3}$  with a volume of the solution of 2 ml at  $24 \pm 2^\circ\text{C}$  and pH 5.0.

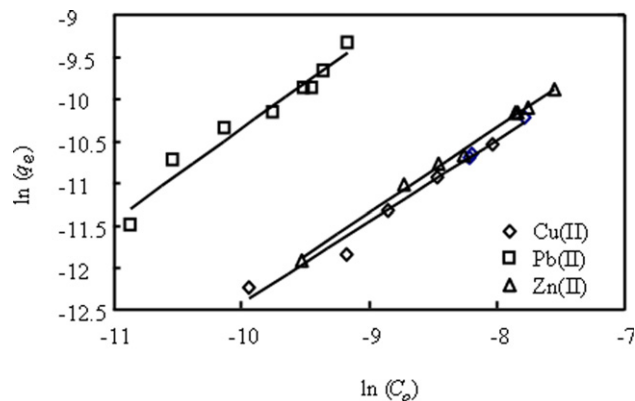


FIGURE 2. Freundlich isotherms for the biosorption of Cu(II), Pb(II), and Zn(II) by the saltbush leaves biomass at  $24 \pm 2^\circ\text{C}$  and pH 5.0.

The parameters obtained from fitting the Langmuir and Freundlich models onto the data obtained from the binding of saltbush leaves biomass with Cu(II), Pb(II), and Zn(II) are presented and confronted in table 1. As shown in table 1, the correlation coefficients ( $R^2$ ) obtained from the Freundlich model were 0.9798, 0.9575, and 0.9963 for Cu, Pb, and Zn, respectively, while for the Langmuir model the  $R^2$  values for the same metals were 0.0001, 0.1380, and 0.0088, respectively. This suggests that saltbush leaves biomass sorbed the three metals following the Freundlich model ( $R^2 > 0.9575$ ). The result also suggests that the biosorption system of saltbush leaves biomass could have more than one functional group which is responsible for the metal binding.

The  $K_F$  values obtained from the Freundlich model ( $175.5 \cdot 10^{-2}$ ,  $10.5 \cdot 10^{-2}$  and  $6.32 \cdot 10^{-2} \text{ mol} \cdot \text{g}^{-1}$  for Pb, Zn, and Cu, respectively), suggest that the metal binding affinity was in the order  $\text{Pb} > \text{Zn} > \text{Cu}$ . The experimental values of the maximal adsorption capacities of saltbush leaves biomass were  $0.13 \cdot 10^{-2}$ ,  $0.05 \cdot 10^{-2}$  and  $0.107 \cdot 10^{-2} \text{ mol} \cdot \text{g}^{-1}$  for Pb, Zn, and Cu, respectively. It was hard to compare the maximum capacity with many reported studies due to differences in experimental conditions and models used to fit the data in each study. However, under similar conditions, the maximum adsorption capacities of Malone/African alfalfa biomass were reported to be ( $\text{mol} \cdot \text{g}^{-1}$ )  $0.031 \cdot 10^{-2}/0.081 \cdot 10^{-2}$ ,  $0.015 \cdot 10^{-2}/0.018 \cdot 10^{-2}$ , and  $0.049 \cdot 10^{-2}/0.041 \cdot 10^{-2}$  for Pb, Zn, and Cu, respectively [22]. The results from the present study clearly showed that the Cu(II) binding capacity of saltbush

TABLE 1

Freundlich and Langmuir isotherm parameters for the biosorption of Cu(II), Pb(II), and Zn(II) on saltbush leaves biomass at  $24 \pm 2^\circ\text{C}$  and pH 5.0

Metal	Freundlich			Langmuir			
	$K_F \cdot 10^{-2}/(\text{mol/g})$	$n$	$R^2$	$Q_L \cdot 10^{-2}/(\text{mol/g})$	$b$ (l/mg)	$R_L$	$R^2$
Cu(II)	6.32	1.04	0.9798	0.93	9.09	0.9971	0.0001
Pb(II)	175.54	0.92	0.9575	-0.04	-3491.20	-0.0221	0.1380
Zn(II)	10.48	0.99	0.9963	-0.39	-24.84	1.0000	0.0088

$K_F$  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.

leaves biomass was higher than the reported capacity for alfalfa biomass.

### 3.2. Thermodynamic parameters

The change in Gibbs free energy,  $\Delta G^\circ$  ( $\text{kJ} \cdot \text{mol}^{-1}$ ) for the biosorption of the studied metals on the saltbush biomass was calculated according to:

$$\Delta G^\circ = -RT \ln K_c, \quad (6)$$

$$K_c = q_e / C_e, \quad (7)$$

where  $K_c$  is the adsorption equilibrium constant,  $q_e$  is the amount of solute (mg) adsorbed on the adsorbent cubic decimeter from the solution at equilibrium, and  $C_e$  is the equilibrium concentration ( $\text{mg} \cdot \text{dm}^{-3}$ ) of the solute in solution,  $T$  is the temperature in Kelvin and  $R$  is the gas constant ( $8.314 \text{ J} \cdot \text{mol}^{-1} \text{ K}^{-1}$ ).

Table 2 shows that the  $K_c$  values obtained from the  $q_e$  versus  $C_e$  plot fit the data of Pb. The biosorption of Pb on saltbush leaves biomass was fast compared to the biosorption of Cu and Zn. Also the negative  $\Delta G^\circ$  values for Pb and the positive values for Cu and Zn shown in table 2 indicate that only the Pb biosorption by saltbush biomass was a spontaneous process. This could be an explanation for the very high Pb binding capacity shown by this biomass compared to the Cu and Zn binding capacities. It has been previously reported that many Pb-complexes with carboxylic containing compounds, such as acetic acid and butanoic acid has higher stability constants compared to Cu and Zn complexes [23]. Thus, the involvement of carboxyl group in the biosorption could be a possible explanation

TABLE 2

Thermodynamic parameters for the biosorption of Cu(II), Pb(II), and Zn(II) on saltbush leaves biomass at  $24 \pm 2^\circ \text{C}$  and pH 5.0

Metal	$K_c$	$\Delta G^\circ$ (kJ/mol)
Cu(II)	0.435	2.0587
Pb(II)	3.970	-3.4062
Zn(II)	0.484	1.7938

$K_c$  is equilibrium constants;  $\Delta G^\circ$  is the Gibbs free energy.

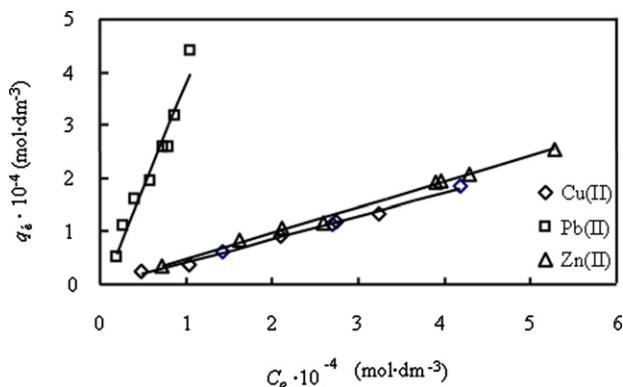


FIGURE 3. Adsorption of Cu(II), Pb(II), and Zn(II) on saltbush leaves biomass at  $24 \pm 2^\circ \text{C}$  and pH 5.0 using  $q_e$  versus  $C_e$  plot.

tion for the Pb maximum banding capacity obtained from the isotherms in this study (see figure 3).

The biosorption mean free energy ( $E$ ) represents the mean free energy of sorption per molecule of the sorbate. When it is transferred to the surface of the sorbate from infinity [15,24], it is calculated from the following equation [13,25]:

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

where  $K_E$  is a constant related to the biosorption energy ( $\text{mol}^2 \cdot \text{kJ}^2$ ) and calculated using the Dubinin–Radushkevick (D–R), equation (9). In this equation  $q_m$  is the monolayer capacity ( $\text{mol} \cdot \text{g}^{-1}$ ),  $\epsilon^0$  is the Polanyi potential that is calculated from:

$$\ln q_e = \ln q_m - K_E \epsilon^{02}, \quad (9)$$

$$\epsilon^0 = RT \ln(1 + 1/C_e). \quad (10)$$

The  $K_E$  and  $\ln q_m$  are calculated from the slope and the intercept of plotting  $\ln q_e$  versus  $\epsilon^{02}$  for the available data as shown in figure 4. Table 3 shows that the mean free energy is between  $5.79 \text{ kJ} \cdot \text{mol}^{-1}$  and  $7.50 \text{ kJ} \cdot \text{mol}^{-1}$  for the three studied metals (D–R equation). This suggests that the biosorption of Cu, Pb, and Zn does not necessarily occur via ion exchange mechanism in which the sorption energy lies within  $8\text{--}16 \text{ kJ} \cdot \text{mol}^{-1}$  [26]. The resulting capacity from the D–R equation does not follow the same order of maximum capacity obtained from the Freundlich isotherm. The difference in the maximal capacities for the two models could be a result of the different assumptions on which each model is based on, as has been previously reported for different sorption systems [11,14].

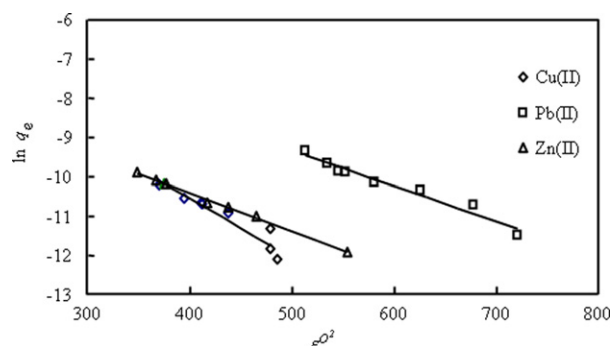


FIGURE 4. Dubinin–Radushkevick plots for the biosorption of Cu(II), Pb(II), and Zn(II) on saltbush leaves biomass at  $24 \pm 2^\circ \text{C}$  and pH 5.0.

TABLE 3

Dubinin–Radushkevick parameters for the biosorption of Cu(II), Pb(II), and Zn(II) on saltbush leaves biomass at  $24 \pm 2^\circ \text{C}$  and pH 5.0

Metal	$K_E$ ( $\text{mol}/\text{kJ})^2$	$q_m$ ( $\text{mol}/\text{kg}$ )	$E$ (kJ/mol)	$R^2$
Cu(II)	$-14.9 (10^{-3})$	$10.11 (10^{-3})$	5.79	0.85
Pb(II)	$-8.9 (10^{-3})$	$7.60 (10^{-3})$	7.50	0.96
Zn(II)	$-9.7 (10^{-3})$	$1.46 (10^{-3})$	7.18	1.00

$K_E$  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.

#### 4. Conclusions

The results of this study show that the biosorption of Pb, Cu, and Zn by the saltbush leaves biomass system fits the Freundlich model, corroborating the assumption of a monolayer adsorption of the three metals on the outer heterogeneous surface of the biomass. The maximal metal binding capacities obtained from the Freundlich model suggest that the capacity follow the order:  $Pb > Zn > Cu$ . The thermodynamic parameters show that the equilibrium constant for the biosorption of Pb (3.970) was higher compared to the other metals (0.435 for Cu and 0.484 for Zn). The Gibbs free energy values show that the biosorption was spontaneous only for Pb. The mean free energy ( $5.79\text{--}7.50 \text{ kJ} \cdot \text{mol}^{-1}$ ) calculated from the D–R equation suggests that the biosorption of Cu, Pb, and Zn does not necessarily occur via ion exchange mechanism in which the sorption energy lies within  $8\text{--}16 \text{ kJ} \cdot \text{mol}^{-1}$ . Further studies have to be done in order to determine the metal binding mechanism(s) in this biomass.

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