

Biosorption Of Cu, Zn And Pb By Eichhornia Crassipes: Thermodynamic And Isotherm Studies

P. Vijetha, K. Kumaraswamy, Y. Prasanna Kumar, N. Satyasree, K. Siva Prasad

Abstract: The present work mainly concentrates on biosorption studies of Cu, Zn and Pb by Eichhornia crassipes. The biosorption data of Cu, Zn and Pb by Eichhornia crassipes were fit on the Freundlich and Langmuir adsorption isotherms at 297 K. The Cu and Zn solutions were adjusted to pH 4.0 and the Pb solution was adjusted to pH 3.0. The correlation coefficient values indicated that the data fit better the Freundlich model. The maximal capacities (KF) were found to be 5.75×10^{-2} , 3.20×10^{-2} , and 1.10×10^{-2} mol/g for Cu, Zn and Pb respectively. Similar results were obtained using the Langmuir and the Dubinin–Radushkevich equations. Thermodynamic parameters calculated from the Khan and Singh equation and from the q_e vs. ce 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 Cu and Zn indicated that these ions were biosorbed spontaneously. The mean free energy values calculated from the Dubinin–Radushkevich equation (10.75, 9.40, and 9.00) for Zn, Pb and Cu respectively suggest that the binding of Cu, Zn and Pb by Eichhornia crassipes occurs through an ionic exchange mechanism.

Index terms: Biosorption, Correlation coefficient, Eichhornia crassipes, Equilibrium, Freundlich, Isotherm, Langmuir.

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[17]. This type of bioremediation is referred to as phytoremediation. This technology is gaining interest of many researchers as it is more economic and poses less health risks than many of the current techniques[18-20,6]. The bioadsorption of metals to the biomass surface occurs mainly as a result of either physical binding involving London–Van der Waals forces or electrostatic attraction, or by chemical binding such as ionic or covalent binding between the adsorbent and the adsorbate[17,6]. 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[17,19,20,7-10]. 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[7]. 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 eichhornia crassipes has significant phytoremediation potential for Cu, Zn and Pb[11,12]. These three metal species are widely used in industrial activities, all of them are toxic but Cu is considered the most toxic of them [13-16]. The objectives of the present study were to obtain a better understanding of the Cu, Zn and Pb biosorption mechanisms by eichhornia crassipes. The experimental data obtained were fit into the Freundlich and Langmuir isotherms and the obtained isotherms and thermodynamic parameters are reported herein.

METHODOLOGY:

The eichhornia crassipes were collected from plants grown around Takkellapady Lake, 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 [21]. 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 bio- mass, hand shaken, and centrifuged for 5 min. The washings were evaporated in an oven at 750 ° 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 4.0 for the Cu and Zn isotherm experiments and for the Zn experiment the pH was adjusted to 3.0. 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 77×10^{-5} mol/dm³) 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

- P.vijetha, currently working as assistant professor, chemical engineering department, vignan university, india, PH -09494414528, E-mail: vijetha.ponnam@gmail.com
- K.Kumaraswamy, Assistant professor, chemical engineering department, vignan university
- N.satyasree, Assistant professor, sciences and humanities department, vignan university
- Y.prasanna kumar, principal, sanketika vidya parishad engineering college, vizag
- K.SivaPrasad, Asst proff, R.V.R & JC college of engineering.)

solution was prepared in 0.01 M sodium acetate buffer and the other eight concentrations were prepared from this solution. 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 and the supernatants were saved for metal quantification using an atomic absorption spectrometer (AAS) Perkin–Elmer model 3110.

RESULTS AND DISCUSSION:

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 [17-19,6-10]. The Langmuir model is a non-linear model that suggests a mono- layer 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 [22,23]. Traditionally, the Langmuir model is represented as

$$q_e = \frac{QL bC_e}{1 + bC_e} \tag{1}$$

Where q_e is the amount of metal adsorbed per mass of adsorbent biomass. In Eq. (1) q_e is given in mol/g, QL 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/dm³). Equation (2) shows the linearized form of the Langmuir model, and the plots of C_e/q_e versus C_e for the Cu, Zn and Pb are shown in Figs. 1A and 1B (the plot for Cr(III) (Fig. 1B) is shown separately due to the scale),

$$\frac{C_e}{q_e} = \frac{C_e}{QL} + \frac{1}{bQL} \tag{2}$$

The dimensionless adsorption intensity (RL) is calculated using the following formula [23],

$$RL = \frac{1}{1 + bC_0} \tag{3}$$

where C_0 is the initial metal concentration in the solution (mol/dm³). The calculated average RL value for different initial metal concentrations indicates favorable isotherm if this value is between 0 and 1 [23]. 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 [17,22]. 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 [17]. The Freundlich isotherm is expressed using Eq. (4), and this formula is linearized as shown in Eq. (5) as follows:

$$q_e = KFC_e \tag{4}$$

$$\ln q_e = \ln KF + \frac{1}{n} \ln C_e \tag{5}$$

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

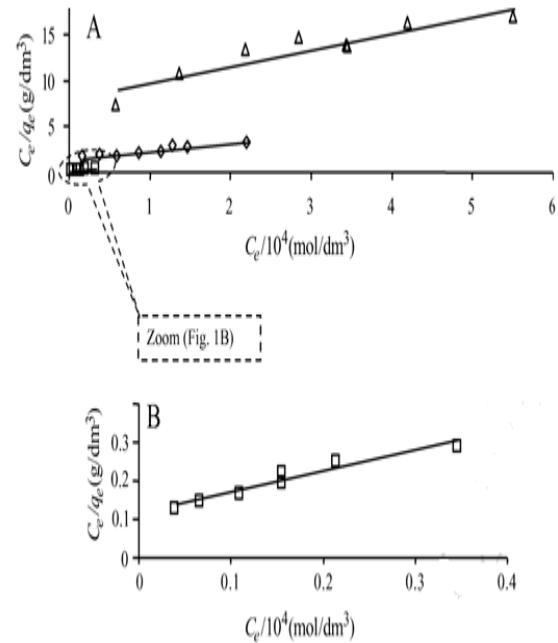
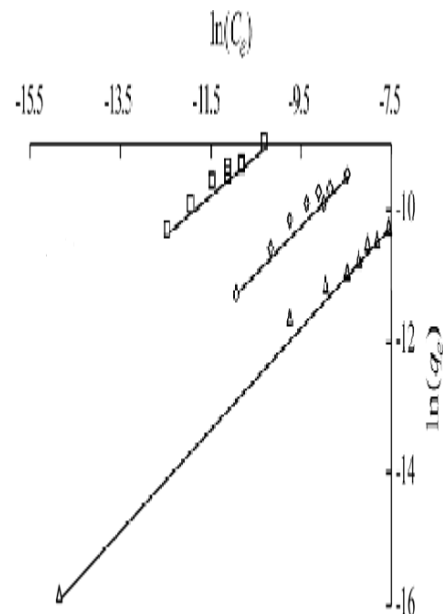


Figure 1. (A) Langmuir isotherms for the biosorption of Cu(◇),Zn(□) and Pb(Δ) on Eichhornia crassipes at 297K ;(B) biosorption of Pb on Eichhornia crassipes (enlarged scale). The Cu and Zn solutions were adjusted at pH 4.0 and the Pb solution at pH 3.0.



are presented in Table 1. As shown in Table 1, the correlation coefficients for the Langmuir isotherms had $R^2 > 0.850$, but for the Freundlich isotherms R^2 were higher than 0.9620, which suggests that the differences in binding capacity showed by eichhornia crassipes

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.

Figure. 2. Freundlich isotherms for the biosorption of Cu(\diamond),Zn(\square) and Pb(Δ) on eichhornia crassipes at 297k. The Cu and Zn solution were adjusted at pH 4.0 and the Pb solution at pH 3.0.

Table 1 Isotherm models parameters for the biosorption of Cu, Zn and Pb on eichhornia crassipes biomass at 297k

Metal	Freundlich			Langmuir			
	KF *10 ⁻² (mol/g)	N	R2	QL *10 ⁻² (mol/g)	b (l/mg)	RL	R2
Cu	3.20	1.4	0.96	2.2	35.28	0.98	0.89
Zn	5.8	1.7	0.98	3.3	260.42	0.9	0.94
Pb	1.10	1.3	0.99	0.75	23.5	0.99	0.85

The Cu and Zn solutions were adjusted at pH 4.0 and the Pb solution at pH 3.0. KF is adsorption capacity, n is adsorption intensity, R2 is the correlation coefficient, QL and b are the Langmuir constants, and RL is adsorption intensity. The parameters resulted from the Langmuir and Freundlich plots for Cu, Zn and Pb (Figs. 1 and 2)

Thermodynamic parameters:

The biosorption equilibrium constants (Kc) for the binding data of Cu, Zn and Pb by eichhornia crassipes are calculated either from the intercept of Khan and Singh plot [17] (ln qe /Ce versus qe, Fig. 3) or from the slope of plotting qe versus Ce, Eq. (6) (Fig. 4). The real equilibrium constant is expected to be in the range of the values presented in Table 2.

$$Kc = qe /Ce \tag{6}$$

The change in Gibbs free energy G0 (kJ/mol) for the biosorption of the metals on the eichhornia crassipes 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):

$$G0 = -RT \ln Kc \tag{7}$$

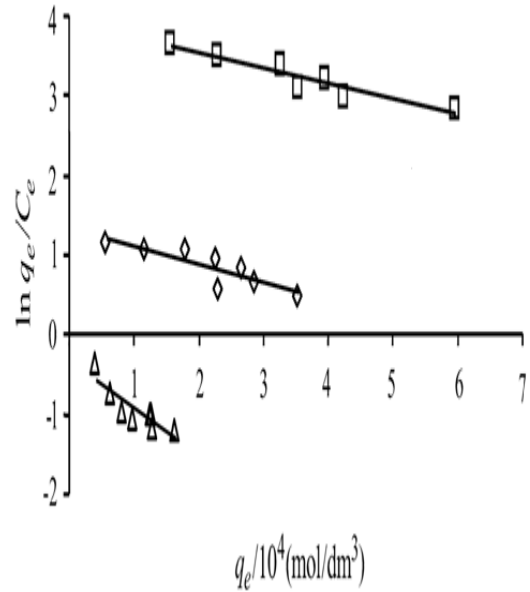


Figure. 3. Adsorption of Cu(\diamond),Zn(\square) and Pb(Δ) on eichhornia crassipes biomass using the Khan and Singh plots of ln qe/Ce versus qe . The Cu and Zn solutions were adjusted at pH 4.0 and the Pb solution at pH 3.0.

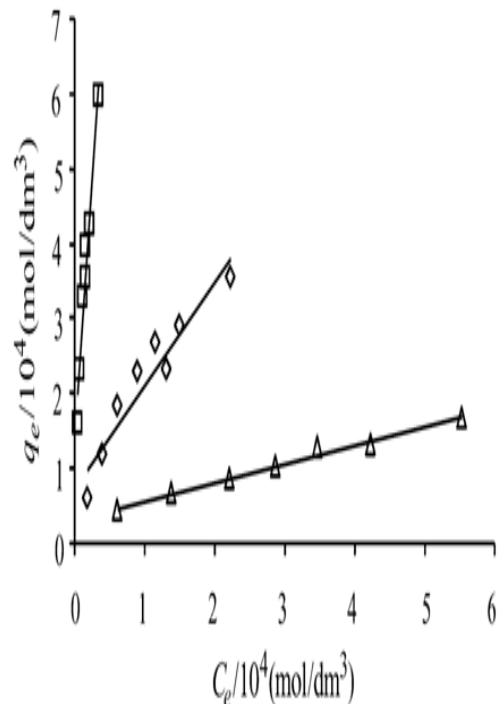


Figure. 4. Adsorption of Cu (\diamond), Zn (\square) and Pb (Δ) on eichhornia crassipes biomass using qe versus Ce plot for the purpose of calculating the distribution coefficient. The Cu and Zn solutions were adjusted at pH 4.0 and the Pb solution at pH 3.0.

Table 2 Thermodynamic parameters for the biosorption of Cu, Zn and Pb on eichhornia crassipes biomass at 297k.

Khan and singh qe versus Ce plot				
Metal	kc	ΔG0(kJ/mol)	kc	ΔGo(kJ/mol)
Cu	1.334	-0.7121	1.380	-0.7957
Zn	3.934	-3.3837	13.522	-6.4340
Pb	0.095	5.8075	0.251	3.4160

The Cu and Zn solutions were adjusted at pH 4.0 and the Pb solution at pH 3.0. Kc is equilibrium constant; ΔG0 is the Gibbs free energy. The negative ΔG0 values for Cu and Zn shown in Table2 indicate that the sorption of these metals on the eichhornia crassipes is a spontaneous process. This result corroborates the KF values for the studied metals (Zn > Cu > Pb). Probably this result is due to the fact that the negatively charged carboxyl group is the main group in the eichhornia crassipes biomass that binds Cu and Zn[11,12].

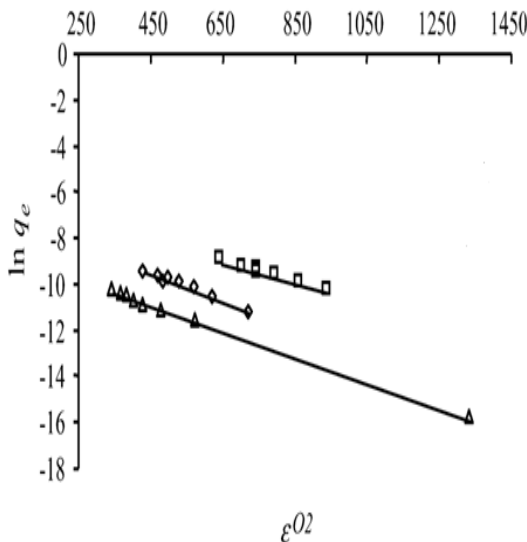


Figure 5. Dubinin–Radushkevick plots for the biosorption of Cu, Zn and Pb on eichhornia crassipes biomass at 297k. The Cu and Zn solutions were adjusted at pH 4.0 and the Pb solution at pH 3.0.

Table 3 Dubinin–Radushkevick parameters for the biosorption of Cu, Zn and Pb on eichhornia crassipes biomass at 297k.

Metal	KE (mol/kj)2	Qm (mol/kg)	E (kJ/mol)	R2
Cu	-6.1(10-3)	1.06	9.00	0.97
Zn	-4.3(10-3)	1.92	10.75	0.99
Pb	-5.6(10-3)	0.21	9.40	1.00

The Cu and Zn solutions were adjusted at pH 4.0 and the Pb solution at pH 3.0. KE is a constant related to sorption energy, qm is the monolayer capacity, E is the mean free energy sorption, R2 is the correlation coefficient. The biosorption mean free energy (E) [27,1] was calculated from Eq. (8),

$$E = (-2KE)^{-1/2} \tag{8}$$

where KE is a constant related to the biosorption energy (mol2/kJ2), that is calculated from the Dubinin–Radushkevick (D–R) Eq. (9), where qm is the monolayer capacity (mol/g),

$$\ln qe = \ln qm - KE(\epsilon_0)^2 \tag{9}$$

ε0 is the Polanyi potential that is calculated from Eq. (10)

$$\epsilon_0 = RT \ln(1 + 1/Ce), \tag{10}$$

Where the KE and ln qm are calculated from the slope and the intercept of plotting ln qe versus (ε0)2 (Fig. 5). Table 3 shows that the mean free energy was between 9.00 and 10.75 kJ/mol for the three studied metals, which suggests that the biosorption of Cu, Zn and Pb occurs via ionic exchange mechanism in which the sorption energy lies within 9–17 kJ/mol.

Conclusions:

The results of this study show that the biosorption of Cu, Zn and Pb on eichhornia crassipes 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 Zn > CU > Pb. 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 Zn and Cu, the adsorption of Zn was privileged compared to that of Cu, and that the biosorption of Pb was non- spontaneous. The mean free energy calculated from the D–R equation suggests that the binding of the Cu, Zn and Pb by eichhornia crassipes biomass occurs through an ionic exchange mechanism.

References:

- [1]. J.P. Hobson, J. Phys. Chem. 73 (8) (1969) 2720.
- [2]. F. Helfferich, Ion Exchange, McGraw–Hill, New York, 1962.
- [3]. K.J. Tiemann, Study of alfalfa phytofiltration technology to clean heavy metal contaminated waters, Doctoral Dissertation, University of Texas at El Paso, Chemistry Department, 1998.
- [4]. M.E. Vallejo, F. Persin, C. Innocent, P. Sstat, G. Pourcelly, Sep. Purif. Technol. 21 (1–2) (2000) 61.

- [5]. G. de la Rosa, J.R. Peralta-Videa, J.L. Gardea-Torresdey, J. Hazard. Mater. 97 (1–3) (2003) 207–218.
- [6]. S.S. Ahluwalia, D. Goyal, Eng. Life Sci. 5 (2) (2005) 158.
- [7]. O. Altun, H.O. Ozbelge, T. Dogu, J. Colloid Interface Sci. 198 (1) (1998) 130.
- [8]. B.S. Krishna, D.S.R. Murty, B.S. Jai Prakash, J. Colloid Interface Sci. 229 (1) (2000) 230.
- [9]. N. Goyal, S.C. Jain, U.C. Banerjee, Adv. Environ. Res. 7 (2) (2003) 311.
- [10]. I. Villaescusa, M. Martinez, N. Miralles, J. Chem. Technol. Biotechnol. 75 (9) (2000) 812.
- [11]. M.F. Sawalha, J.L. Gardea-Torresdey, J.G. Parsons, G. Saupe, J.R. Peralta-Videa, Microchem. J. 81 (1) (2005) 122.
- [12]. M.F. Sawalha, J.R. Peralta-Videa, J.G. Parsons, J.H. Gonzalez, J.L. Gardea-Torresdey, Int. J. Environ. Pollut., in press.
- [13]. E.T. Snow, Environ. Health Perspect. 92 (1991) 75.
- [14]. F. Forster, J. Wase (Eds.), Biosorbents for Metal Ions, Taylor & Francis, London, 1997.
- [15]. L. Bucio, V. Souza, A. Albores, A. Sierra, E. Chavez, A. Carabez, M.C. Gutierrez-Ruiz, Toxicology 102 (3) (1995) 285.
- [16]. R.S. Bai, T.E. Abraham, Water Res. 36 (2002) 1224.
- [17]. T.A. Davis, B. Volesky, A. Mucci, Water Res. 37 (18) (2003) 4311.
- [18]. A. Benhammou, A. Yaacoubi, L. Nibou, B. Tanouti, J. Colloid Interface Sci. 282 (2) (2005) 320.
- [19]. K. Chojnacka, A. Chojnacki, H. Gorecka, Chemosphere 59 (1) (2005) 75.
- [20]. J.L. Gardea-Torresdey, G. de la Rosa, J.R. Peralta-Videa, Pure Appl. Chem. 76 (4) (2004) 801.
- [21]. J.L. Gardea-Torresdey, K.J. Tiemann, V. Armendariz, L. Bess-Oberto, R.R. Chianelli, J. Rios, J.G. Parsons, G. Gamez, J. Hazard. Mater. 80 (1–3) (2000) 175.
- [22]. J. Romero-Gonzalez, J.R. Peralta-Videa, E. Rodriguez, S.L. Ramirez, J.L. Gardea-Torresdey, J. Chem. Thermodyn. 37 (4) (2005) 343.
- [23]. S.H. Lin, R.S. Juang, J. Hazard. Mater. 92 (3) (2002) 315.
- [24]. J. Romero-Gonzalez, J.R. Peralta-Videa, E. Rodriguez, M. Delgado, J.L. Gardea-Torresdey, Bioresour. Technol. 97 (1) (2006) 178.
- [25]. A. Demirbas, E. Pehlivan, F. Gode, T. Altun, G. Arslan, J. Colloid Interface Sci. 282 (1) (2005) 20.
- [26]. R.E. Sievers, J.C. Bailar Jr., Inorg. Chem. 1 (1962) 174.
- [27]. S.A. Khan, Riaz-ur-Rehman, M.A. Khan, Waste Manage. 15 (4) (1995) 271.