BIOSORPTION OF Hg (II) FROM AQUEOUS SOLUTIONS USING BUTEA MONOSPERMA

Mallappa A. Devani[1], Basudeb Munshi[2], John U. Kennedy Oubagaranadin[3], Bipin Bihari Lal[4]

[1, 2]*Department of Chemical Engineering, National Institute of Technology, Rourkela 769008, Orissa, INDIA*
[3]*Department of Ceramic and Cement Technology, PDA College of Engineering, Gulbarga, Karnataka, INDIA:*
[4]*Department of Civil Engineering, Bheemanna Khandre Institute of Technology, Bhalki, Karnataka, INDIA*
mdevani003@gmail.com and basudebmyahoo.com, ju_kennedy@yahoo.co.in, bipinji@yahoo.com

Abstract

The objective of this study is to investigate the feasibility of using Butea monosperma leaves powder (BMLP) for the removal of mercury from aqueous solution at the normal pH of the solution and at room temperature (30^{o}C). Results show that BMLP has a good biosorption capacity for mercury. The biosorption isotherms were analyzed using Freundlich, Langmuir and Temkin models. The Freundlich model yielded the best fit for the experimental biosorption equilibrium data. The maximum monolayer biosorption capacity as determined from the Langmuir model is 62.235 mg/g of biosorbent for initial concentration of 150 ppm mercury in the solution. The biosorption energy, ΔQ indicates that the biosorption reaction was endothermic. The kinetic data fitted the Ho's pseudo-second-order model with correlation coefficient 0.9985 and 0.9620 for initial concentration of 100 ppm and 150 ppm mercury in the solution. The studies suggest that the sorbent can be used for the removal of mercury from aqueous solutions.

Keywords: *Biosorption, Mercury, Isotherms, Kinetics*

----------***----------

1. INTRODUCTION

Today worldwide heavy metal pollution is a dangerous threat to human and animals both in developed and developing countries. The most toxic metals given in the report by the United States Environmental Protection Agency (USEPA, 1978) are antimony, arsenic, beryllium, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, thallium and zinc. These metals are neither biodegradable nor destroyable; therefore removal of them is extremely necessary from water/wastewater [1].

Biosorption is most emerging technique studied worldwide since last 10 years, due to its potential in treatment of wastewater [2-3]. Biosorbents of agricultural origin have polar functional groups of protein lignin, carbohydrates and phenolic compounds that have carboxyl, hydroxyl, sulfate, and amino groups, polymeric groups like cellulose, hemi-cellulose, pectin, lignin and proteins as active centers for metal uptake [4]. Many researchers have made significant contributions in this area, utilizing a number of agro-based materials such as rice husk, coconut shell, walnut hazelnut and almond shell, cotton seed hull, bagasse pith, papaya wood, sun flower stem, etc. [5-7].

The objective of the present study was to explore the potential of *Butea monosperma leaves powder (BMLP)* for the removal of Hg(II) from the aqueous solutions. The *Butea monosperma* leaves are in enormous supply, inexpensive and easily found around in forest.

2. EXPERIMENTAL

2.1 Biosorption Equilibrium Experiments

50 ml solutions of 100 ppm Hg(II) concentration were dosed with 0.05g, 0.1g, 0.15g, 0.2g, 0.25g, 0.3g, 0.35g, 0.4g and 0.45g of average size 0.5125mm biosorbent and was shaken in an orbital shaker for about 4 hrs for equilibration. The solutions were then filtered and the residual Hg(II) concentrations were determined spectrophotometrically as reported [8]. A similar set of experiments was performed with an initial Hg(II) concentration of 150 ppm.

2.2 Kinetic Experiments

Batch kinetic studies were carried out in a 250 ml glass beaker. 0.1g of average size 0.5125mm biomass was added to 25 ml metal solution of 100 ppm Hg(II) concentration and was shaken in an orbital shaker. Samples were withdrawn at different time intervals of 30 Sec, 1 min, 3 min, 6 min, 10 min, 25 min, 45 min, 60 min, 75 min, and 90 min. Samples were immediately vacuum filtered by using Gooch sintered ware grade G4 and the residual concentration of Hg(II) were determined spectophotometrically. A similar set of experiments was performed with an initial Hg(II) concentration of 150 ppm.

3. RESULTS AND DISCUSSION

3.1 Equilibrium Studies

In this study three isotherm models were to used to test the equilibrium biosorption of Hg (II) onto *BMLP*.

1. Freundlich Isotherm

This model normally gives a better fit mainly for biosorption from liquids and can be expressed as [9]:

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

Where q_e (mg/gm) is the amount of adsorbate biosorbed at equilibrium and C_e (mg/L) is the equilibrium concentration of adsorbate in solution. In this model, the mechanism and the rate of adsorption are functions of the constants, *1/n* and K_F (L/mg) respectively. The value of the plots for the biosorption of Hg(II) on *BMLP* given in the table 1. The plots give good fit (R^2 = 0.9945 for 100 ppm and 0.9921 for 150 ppm). For a good biosorbent, 0.2 <*1/n* <0.8 (0.3368 for 100 ppm and 0.6036 for 150 ppm) A smaller value of *1/n* indicates better biosorption and formation of relatively strong bond between the adsorbate and biosorbent.

2. Langmuir Isotherm

This model is valid for monolayer biosorption onto surface having finite number of similar sorption sites which is presented by the following equation [10]:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \qquad (2)$$

In this model, q_m (mg/g) is the metal biosorbed corresponding to complete monolayer coverage, i.e., the maximum biosorption capacity, C_e is equilibrium concentration of the solution (mg/L), and K_L (L/mg) is the Langmuir constant. From the values of q_m, as shown in the Table No. 1, it is observed that the maximum biosorption capacity of *BMLP* is 26.719 mg/g and 62.235 mg/g for initial concentration of mercury 100 ppm and 150 ppm respectively.

For Langmuir type process, to determine if the biosorption is favorable or not, a dimensionless separation factor is defined as [11]:

$$R_L = \frac{1}{1 + K_L C_0} \qquad (3)$$

If R_L >1, the isotherm is unfavorable

R_L =1, the isotherm is linear

0< R_L <1, the isotherm is favorable

R_L = 0, the isotherm is reversible.

The value of R_L for Butea monosperma (0.01104 for 100 ppm mercury and 0.08025 for 150 ppm mercury) falls between 0 and 1, indicating that the isotherms are favorable. Fig.1 shows a plot of residual equilibrium concentration C_e (ppm) against adsorbate loading q_e (mg/g). The curves are convex upward and so they are favorable because a relatively high adsorbate loading can be obtained at low concentration in the solution.

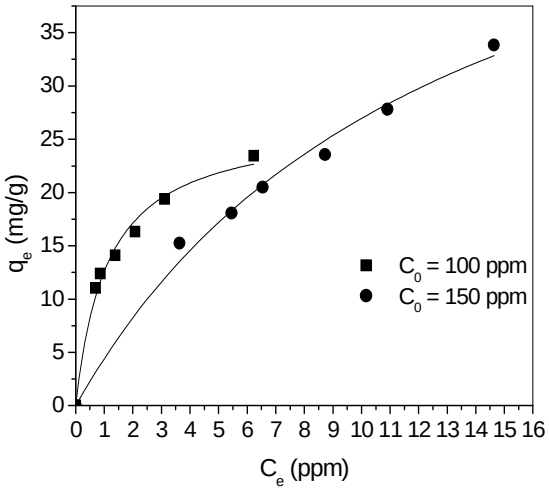

Fig1. Equilibrium data for the biosorption of Hg(II) on Butea monosperma

3. Temkin Isotherm

The derivation of the Temkin isotherm assumes that the fall in the heat of biosorption is linear rather than logarithmic, as implied in the Freundlich equation.

The Temkin isotherm is expressed as [12]:

$$q_e = \frac{RT}{\Delta Q} \ln(K_T C_e) \qquad (4)$$

The parameters of the Temkin model, which takes into account the biosorbing species-biosorbent interactions, gave a satisfactory fit to the experimental data. The biosorption energy, ΔQ (448 kJ/kmol for 100 ppm and 189 kJ/kmol for 150 ppm mercury in the solution), indicates that the biosorption reaction was endothermic. K_T is the equilibrium binding constant (L/mg) corresponding to the maximum binding energy. From the values of K_T (9.7496 and 0.7611 for an initial concentration of 100 ppm and 150 ppm mercury) it is observed that the binding energy is better for *BMLP*.

Table1. Isotherm modeling for the biosorption of Hg (II) onto Butea monosperma

Model	Equation	R^2	χ^2	C_0 (ppm)	Parameter values
1. Freundlich	$q_e = K_F C_e^{1/n}$	0.9945	0.1486	100	*1/n* = 0.3368; K_F = 12.80
		0.9921	0.4574	150	*1/n* = 0.6036; K_F = 6.599
2. Langmuir	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$	0.9894	0.6979	100	q_m = 26.719; K_L = 0.8954
		0.9912	1.2169	150	q_m = 62.235; K_L = 0.0764
3. Temkin	$q_e = \frac{RT}{\Delta Q}\ln(K_T C_e)$	0.9903	0.2636	100	ΔQ = 448 kJ/kmol; K_T = 9.7496
		0.9553	2.5904	150	ΔQ = 189 kJ/kmol; K_T = 0.7611

3.2 Kinetic Studies

Information about the biosorption mechanism is provided by kinetic study of biosorption. In this study, two different kinetic models were applied in order to establish which of them shows the best fit with experimentally obtained data.

1. Pseudo-first-order (Lagergren) model

This model is frequently used in kinetic studies and is the earliest known one explaining the rate of biosorption based on the biosorption capacity [13]. It is given by:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (5)$$

Where, q_t is uptake at any time't', q_e is equilibrium uptake and k_1 is first order rate constant. The experimental data gives good fit for *BMLP* (R^2 = 0.9963 and 0.9247 for 100 ppm and 150 ppm mercury concentration). The values of the first-order rate constant (k_1) are 4.898 and 2.457min^{-1} for 100 ppm and 150 ppm mercury.

2. Pseudo second-order (Ho) model

The kinetic equation is written in the form [14]:

$$q_t = \frac{q_e^{\,2} k_2 t}{1 + q_e k_2 t} \qquad (6)$$

The data gives perfect fit for this model for *BMLP* (R^2 = 0.9985 and 0.9625 for initial concentration of 100 ppm and 150 ppm mercury) as shown in Fig.2 compared to Lagergren's first-order rate equation. The values of the second-order rate constants found from of the graphs for *BMLP* (k_2 = 0.8261 gm/(mg-min) and 0.1490 gm/(mg-min) for 100 ppm and 150 ppm mercury) indicate that Hg(II) removal rate is very fast.

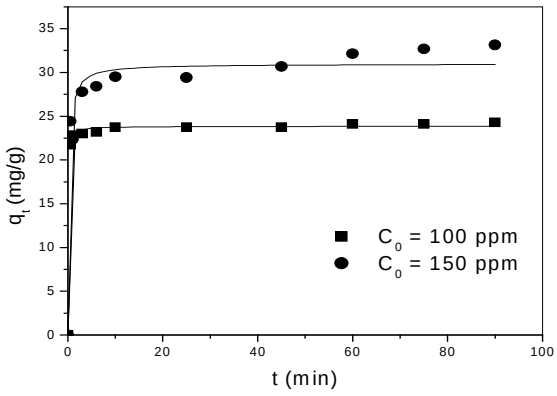

Fig2. Kinetic data for the biosorption of Hg(II) on Butea monosperma

Table2. Kinetic modeling of biosorption of Hg (II) by Butea monosperma

Model	Equation	R^2	χ^2	C_0 (ppm)	Parameter values
1. Pseudo-first-order (Lagergren)	$q_t = q_e(1 - e^{-k_1 t})$	0.9963	0.2087	100	q_e = 23.66; k_1 = 4.898
		0.9247	7.3495	150	q_e = 30.15; k_1 = 2.457
2. Pseudo-second-order (Ho)	$q_t = \frac{q_e^{\,2} k_2 t}{1 + q_e k_2 t}$	0.9985	0.0870	100	q_e = 23.86; k_2 = 0.8261
		0.9620	3.7061	150	q_e = 30.97; k_2 = 0.1490

CONCLUSIONS

In the present study, the potential of using *BMLP* was assessed for the removal of Hg(II) from aqueous solutions. The Freundlich model fitted the experimental data well. The *BMLP* exhibits a maximum biosorption capacity of 62.235mg/g for initial metal concentration of 150 ppm. Biosorption followed pseudo-second order rate model as indicated by very high value of coefficient of correlation 0.9912. Since the raw material (Butea monosperma) is freely available in large quantities as a waste, it can be used economically for Hg(II) removal from polluting waters.

REFERENCES

[1] T. Akar and S. Tunali, "Biosorption Performance of Botrytis Cinerea Fungal by Products for Removal of Cd(II) and Cu(II) Ions from Aqueous Solutions", *Minerals Engineering*, Vol.18, 2005, pp.1099-1109.

[2] K. H. Chong and B. Volesky, "Description of Two Metal Biosorption Equilibria by Langmuir type Models", *Biotechnology and Bioengineering*, Vol. 47, 1995, pp. 451-60.

[3] [3] A. D. Crowall, "Surface and Solid Gas Interface", New York, *Marcel Dekker*, 1966.

[4] F. Pagnanelli, S. Mainelli, F. Veglio and L. Toro, "Heavy Metal Removal by Olive Pomace: Biosorbent Characterization and Equilibrium Modeling," *Chemical Engineering Sci*ence, Vol. 58, pp. 4709-4717, 2003.

[5] D. Sud, G. Mahajan and M. P. Kaur, "Agricultural Waste Material as Potential Adsorbent for Sequestering Heavy Metal Ions from Aqueous Solutions - A Review," *Bioresource Technolology*, Vol. 99, pp. 6017-6027, 2008.

[6] T. Altun and E. Pehlivan, "Removal of Copper(II) Ions from Aqueous Solutions by Walnut, Hazelnut and Almond shells," *Clean-Soil Air Water*, Vol. 35, pp. 601-606, 2007.

[7] N. A. Khan, S. Ibrahim, P. Subramaniam, "Elimination of Heavy Metals from Wastewater using Agricultural Wastes as Adsorbents," *Malays Journal of Science*, Vol. 23, pp. 43-51, 2004.

[8] T. V. Ramakrishna, G. Aravamudan and M. Vijayakum ar, "Spectrophotometric Determination of Mercury (II) as the Ternary Complex with 6G and Iodide," Analytica Chimica Acta, Vol. 84, pp. 369-375, 1976

[9] H. M. F. Freundlich, "Over the Adsorption in Solution," *Journal of Physical Chemistry*, Vol. 57, pp. 385-471, 1906

[10] Langmuir, "The Adsorption of Gases on Plane Surfaces of Glass, Mica and Platinum," *Journal of American Chemical Society*, Vol. 40, pp. 1361-1368, 1918.

[11] T. W. Weber and R. K. Chakkravorti, "Pore and Solid Diffusion Models for Fixed Bed Adsorbents", *American Institute of Chemical Eng. Journal*, Vol. 20, pp. 228-238, 1974

[12] F. Xian-cai and C. Qui-hui, "*Physical Chemistry*", Higher Education Press, China, pp. 303-321, 1988

[13] John U. Kennedy Oubagaranadin and Z.V.P. Murthy, "Modeling of Adsorption of Chromium(VI) on Activated Carbons Derived from Corn (Zea mays) Cob," *Chemical Product and Process Modeling*, Vol. 4, Issue 1, 2009.

[14] Y. Ho, and A. E. Ofemaja, Pseudo – Second order Model for Lead Ion Sorption from Aqueous Solutions onto Palm Kernel fiber," *Journal of Hazardous Materials*, Vol. 129, pp. 137-142, 2006.