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Equilibrium, Kinetic and Thermodynamic Studies on Biosorption of Cd (II) and Pb (II) from Aqueous Solution Using a Spore Forming Bacillus Isolated from Wastewater of a Leather Factory

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***Abstract*—**The equilibrium, thermodynamics and kinetics of the biosorption of Cd (II) and Pb(II) by a Spore Forming Bacillus (MGL 75) were investigated at different experimental conditions. The Langmuir and Freundlich, and Dubinin-Radushkevich (D-R) equilibrium adsorption models were applied to describe the biosorption of the metal ions by MGL 75 biomass. The Langmuir model fitted the equilibrium data better than the other models. Maximum adsorption capacities q_{max} for lead (II) and cadmium (II) were found equal to 158.73mg/g and 91.74 mg/g by Langmuir model. The values of the mean free energy determined with the D-R equation showed that adsorption process is a physiosorption process. The thermodynamic parameters Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) changes were also calculated, and the values indicated that the biosorption process was exothermic and spontaneous. Experiment data were also used to study biosorption kinetics using pseudo-first-order and pseudo-second-order kinetic models. Kinetic parameters, rate constants, equilibrium sorption capacities and related correlation coefficients were calculated and discussed. The results showed that the biosorption processes of both metal ions followed well pseudo-second-order kinetics.

***Keywords*—**biosorption, kinetics, Metal ion removal, thermodynamics

I. Introduction

THE intensification of industrial activity during the recent years is greatly contributing to the increase of the heavy metal levels in the environment, mainly in the aquatic systems [1]. Lead and cadmium are the two most abundant heavy metals in the environment [2]-[4]. The term heavy metal refers to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations. In order to protect the environment animals and human beings, the concentration of lead, cadmium and other heavy metal ions in wastewater has to be reduced to fulfill the stringent water quality criteria [5], [6].

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Metal biosorption is a solution for such situations. An biosorbent, both living and nonliving, is derived from suitable biomass can be used for the effective removal and recovery of heavy metal ions from wastewater streams, These include bacteria, fungi, yeast, marine algae and others [7]. Among the biological materials According to Beveridge [8], bacteria make excellent biosorbents because of their high surface-to-volume ratios and a high content of potentially active chemosorption sites such as on teichoic acid in their cell walls. The major advantages of biosorption technology are highly selective, more efficient, easy processing, and cost effective for the treatment of large volumes of wastewaters containing low metal concentrations. In addition, the process does not produce chemical sludge [9], [10].

The aim of the present work was to investigate the possible use of MGL 75 biomass as a biosorbent material for removal of Cd and Pb ions from aqueous solutions. This bacterium is a spore forming bacillus isolated from wastewater of a leather factory (Varamin, Iran). Equilibrium data were attempted by various adsorption isotherms including Langmuir, Freundlich, and D-R in order to select an appropriate isotherm model. A kinetics study of the adsorption process was also considered in the present study to describe the rate of sorption. In addition thermodynamic parameters such as ΔG°, ΔH° and ΔS° for biosorption process was valuated.

II. Materials And Methods

A. Biomass Preparation Isolated

Bacterial cells of MGL 75 were cultivated in a glucose mineral salt medium composed of 5.35g Na_2HPO_4, 2.67g NH_4Cl, 3g yeast extract, 10g glucose, 0.0006g $CaCl_2.2H_2O$, 0.06g $MgSO_4.7H_2O$, 0.00045g $MnSO_4.7H_2O$, and 0.0024g $FeSO_4.7H_2O$ in 1l distilled water for 72 hours. Before autoclaving, pH of the growth medium was adjusted to 7 using 0.1N HCL and NaOH. Then 100 ml of the medium was transferred to a 250 ml Erlenmeyer flask and autoclaved at 121°C for at least 20 min. Subsequently bacteria were added to each flask shaken at 125rpm at 30°C for 3 days.

Finally, the biomass was separated from the growth medium by centrifuging at 5000 rpm for 20 min.

B. Preparation of Standard Stock Solution

Standard stock solutions of Pb (II) and Cd (II) (1000 ppm) were prepared by dissolving analytical grade salts (Pb $(NO_3)_2$) and $CdCl_2.2H_2O$ supplied by Merck. Other concentrations were prepared from the stock solution by dilution varied between 15 to 200 ppm for Pb (II) and 10 to 120 ppm for Cd (II).

C. Biosorption Studies

5 ml of bacterial suspension containing 0.2 g of dry biomass was mixed with 15 ml of solution of 60 ppm of Pb (II) or Cd (II). Then, the solution was shaken at 150 rpm. The pH of the solutions was adjusted using 0.1N HCL and NaOH. The amount of adsorbed metal ions per gram of the biomass was obtained using the general following equation:

$$q = (C_i - C_f) * V / M \quad (1)$$

where q is the amount of metal ions biosorptioned onto the biomass (mg/g), C_i is the initial metal ion concentration in solution (mg/l), C_f is equilibrium metal concentration in solution (mg/l), V is volume of medium (l) and M is amount of biomass used in reaction mixture (g).

After biosorption process, the samples were centrifuged at 5000 rpm for 20 min and then were analyzed by atomic adsorption spectrophotometer (Perkin Elmer 603). All the experiments were carried out in triplicate and the arithmetical mean values were used in calculations.

III. Result And Discussion

A. Equilibrium Studies

The dependence of the adsorption capacity of MGL 75 on the equilibrium concentrations of Cd (II) and Pb (II) is presented in Fig. 1. The results reveal that adsorption capacities increased steadily with metal concentration. This can be attributed to the increase in the concentration gradient which acts as a driving force for the adsorption process. Nevertheless, the increase in adsorption capacity becomes less significant at C_f>23.5 ppm for Cd (II) and C_f>40 ppm for Pb (II). This is probably because the active sites on the adsorbent become saturated at this concentration and subsequent increase in concentration does not affect the adsorption capacity.

Experimental data in Fig. 1 can be obtained in linear form by adsorption isotherms. Three isotherm equations have been tested in the present study, namely, Langmuir, Freundlich, and D-R isotherm. The goodness of fit between experimental data and the model predicted values is expressed by the correlation coefficient (R^2, value close or equal 1). A relatively high R^2 value indicates that the model successfully describes the isotherm of Cd (II) or Pb (II) adsorption.

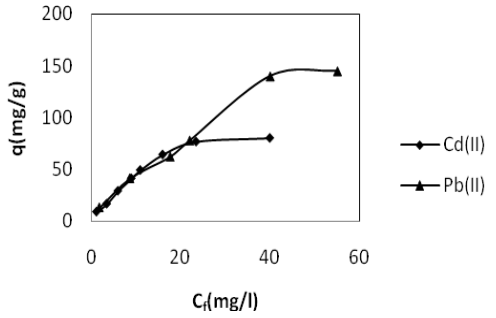

Fig. 1 adsorption isotherms of Cd (II) and Pb (II) by MGL 75 biomass

1. Langmuir isotherm

The Langmuir isotherm model was chosen for the estimation of maximum adsorption capacity corresponding to complete monolayer coverage on the biomass surface. The widely used Langmuir isotherm has found successfully application in many real sorption processes [9]-[12], and is expressed in linear form as:

$$1/q = 1/(q_{max}\, bC_f) + 1/q_{max} \quad (2)$$

where q is milligrams of metal accumulated per gram of the adsorbent material, C_f is the metal residual concentration in solution at equilibrium, q_{max} and b are the Langmuir constants. From the linear plot of $1/q_e$ versus $1/C_f$ (not shown), was calculated the Langmuir constants. These values and correlation coefficient are shown in table I.

The R^2 values of table I suggested that the Langmuir isotherm provides a good model of the sorption system.

The sorption capacity, q_{max}, which is a measure of the maximum adsorption capacity corresponding to complete monolayer coverage showed that the MGL 75 biomass had higher mass capacity for Pb^{2+} (158.73mg/g) than for Cd^{2+} (91.74 mg/g).

The adsorption coefficient, b, which is related to the apparent energy of adsorption for Cd^{2+} (0.09 l/mg), was greater than that of Pb^{2+} (0.05 l/mg) and this could mean that the energy of adsorption is more favorable for Pb^{2+} than Cd^{2+}. This indicates that not all binding sites may be available for cd^{2+} binding due to its relatively larger hydration energy.

2. The Freundlich Isotherm

The well known Freundlich isotherm is often used for heterogeneous surface energy systems.

The linear Freundlich equation is as follows:

$$\ln q = \ln K_f + 1/n \ln C_f \quad (3)$$

where k_f is a constant relating the biosorption capacity and 1/n is an empirical parameter relating the biosorption intensity, which varies with the heterogeneity of the material[9]-[12].

The values of kf and 1/n were found to be 8.16 and0.74 for pb (II) biosorption and 8.1 and 0.69 for cd (II) biosorption (table I).

The 1/n values were between 0 and 1 indicating that the biosorption of pb (II) and cd (II) onto MGL biomass was favorable at studied conditions. However, compared to the R^2 values, 0.992 for pb (II) and 0.965 for cd (II), with that obtained from the Langmuir model, It can be seen that Langmuir isotherm fit the data slightly better than the Freundlich isotherm**.**

3. The D-R Isotherm

The equilibrium data were also applied to the D-R isotherm model to determine the nature of biosorption processes as physical or chemical. The D-R equation has the following linear form:

$$Lnq=lnq_m- \beta \varepsilon^2 \quad (4)$$

Where q is the amount of metal ions sorbed on per unit weight of biomass (mg/g), q_m is the maximum biosorption capacity (mg/g), β is the activity coefficient related to mean biosorption energy (mg^2/J^2) and ε is Polanyi potential $\varepsilon=RT \ln (1+1/C_f)$ [9]-[11].

The D-R isotherm model not well fitted the equilibrium data science the R^2 value was found to be 0. 757 For Pb (II) biosorption and 0.692 for Cd (II) biosorption (table I). From the intercept of the plots ε^2 versus lnq, the q_m value was found to be 87.62 for Pb (II) biosorption and 50.05 for Cd (II) biosorption (table I). The mean biosorption energy is as follow:

$$E=1/\sqrt{-2 \beta} \quad (5)$$

The mean free energy of biosorption gives information about biosorption mechanism, physical or chemical. If E value is between 8 and 16 (kJ/mol), the biosorption process follows chemically and if E<8 (kJ/mol), the biosorption process is of a physically. The mean biosorption energy was calculated as 0.77 and 0.53 kJ/mol for the biosorption Cd (II) and Pb (II) ions, respectively. These results indicated that the biosorption process of both metal ions onto MGL 75 biomass may be the physical.

B. Biosorption Kinetics

The rate of biosorption is important for designing batch adsorption experiments. Therefore, the equilibrium biosorption time of Pb (II) and Cd (II) onto MGL 75 biomass was investigated in a batch system. The adsorbed metal ions on the biosorbent (q) were plotted as a function of time, as shown in Fig.2. It can be observed that Pb (II) or Cd (II) uptake was rapid in initial 5 min and thereafter it proceeded at a slower rate and finally attained saturation. The higher sorption rate at the initial period might be due to an increased number of vacant sites available at the initial stage, which resulted in an increased concentration gradient between sorbate in the solution and sorbate in the biosorbent surface. As time passed, the concentration gradient was reduced due to the sorption of metal ion onto the vacant sites, leading to decrease in sorption rate at later stages.

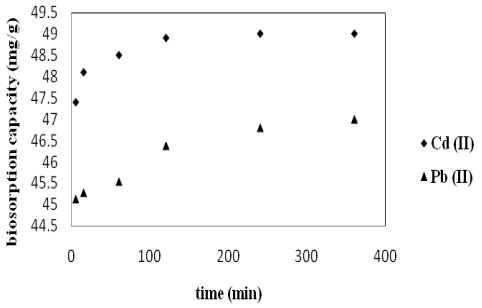

Fig. 2 The effect of time contact on Pb (II) and Cd (II) biosorptions by MGL 75

TABLE I
ISOTHERM CONSTANTS FOR THE BIOSORPTION OF PB (II) AND CD (II) BY MGL 75

Metal ions	models								
	Langmuir			**Freundlich**			**D-R**		
	q_{max} (mg/g)	**b (l/mg)**	**R^2**	**1/n**	**k_f (mg/g)(mg/l)^n**	**R^2**	**q_m (mg/g)**	**E (kJ/mol)**	**R^2**
Cd(II)	91.74	0.09	0.974	0.69	8.10	0.965	50.05	0.77	0.692
Pb(II)	158.73	0.05	0.994	0.74	8.16	0.992	87.62	0.53	0.757

1. Pseudo-First-Order Model

The sorption kinetics may be described by a pseudo-first-order equation. This equation has been traditionally the most conventional model often used for liquid sorption modeling. The linearized form of the pseudo first order rate equation is given as [13]:

$$Ln(q_e-q_t)=lnq_e-k_1t \quad (6)$$

Where q_t and q_e (mg/g) are the amounts of the metal ions biosorbed at equilibrium (mg/g) and t (min), respectively and k_1 is the rate constant of the equation (min -1).

The slopes and intercepts of plots of ln (q_e-q_t) versus t were used to determine the pseudo-first-order constant k_1 and equilibrium adsorption density q_e. These values (k1 and q_e) and correlation coefficient are shown in table II. Although the correlation were not low but the theoretical q_e values found from the pseudo-first-order kinetic model did not give reasonable values for both metal ions. This suggests that this adsorption system is not a pseudo-first-order reaction for Pb (II) and Cd (II).

2. Pseudo-Second-Order Model

The pseudo-second- order kinetic model can be represented in the following form:

$$t/q_t=1/k_2q_e^2+1/q_et \quad (7)$$

where k_2 (mgg^{-1} min^{-1}) is the second order rate constant, q_t (mgg^{-1}) is the amount of biosorption time t(min) and q_e is the amount of biosorption equilibrium (mgg^{-1}) [13].

C. Biosorption Thermodynamics

In order to describe thermodynamic behavior of the biosorption of the Cd (II) and Pb (II) ions by MGL 75 biomass, thermodynamic parameters including the changes in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) of biosorption process were determined by using following equations [9]:

$$K_D=q/C_f \quad (8)$$

$$\Delta G°=-RT \ln K_D \quad (9)$$

$$\ln K_D=(\Delta S°/R)-(\Delta H°/RT) \quad (10)$$

a Vant hoff plot of ln K_D as a function of 1/T (Fig. 3) yields a straight line the ΔH° and ΔS° parameters were calculated from the slope and intercept of the plot, respectively. The Gibbs energy change ΔG° was calculated to be -3.1982, -3.1171, and -2.1381 kJ/mol for Pb (II) biosorption and -3.9137, -3.7653, and -2.7178 for Cd (II) biosorption at 15, 30, and 50 °C, respectively. The negative ΔG° values indicated thermodynamically feasible and spontaneous nature of the biosorption. The decrease in ΔG° values shows a decline in feasibility of biosorption as temperature is increased. The ΔH° parameter was found to be -12.1114 and -13.9417 kJ/mol for Pb (II) and Cd (II) biosorption, respectively. The negative (ΔH°) indicates the exothermic nature of the biosorption processes at 15-50 °C. The (ΔS°) was found to be -0.0305 J/mol K for Pb (II) biosorption and -0.03437 J/mol K for Cd (II) biosorption. The negative (ΔS°) value means a decrease in the randomness at the solid/solution interface during the biosorption process.

TABLE II
PARAMETERS PSEUDO–FIRST- ORDER AND PSEUDO–SECOND- ORDER MODELS FOR THE BIOSORPTION OF PB (II) AND CD (II) BY MGL 75.

	C_i (mg/l)	q_e exp. (mg/g)	Pseudo 1st Order			Pseudo2st Order		
			K1 (1/min)	qe cal. (mg/g)	R^2	K2 (g/mg.min)	qe cal. (mg/g)	R^2
Pb (II)	60	47	0.0092	2.1135	0.983	0.0192	47.61	0.9999
Cd(II)	60	49	0.0207	1.5922	0.974	0.0571	50	0.9999

The slops and intercepts of plots t/q_t versus t were used to calculate the pseudo-second-order rate constants k_2 and q_e. Table II lists the computed results obtained from the pseudo-second-order kinetic model. The correlation coefficient for pseudo-second-order kinetic model obtained were 0.9999 for both metal ions. The calculated q_e values also agree very well with the experimental data. These indicate that the adsorption system studied belongs to the second order kinetic model.

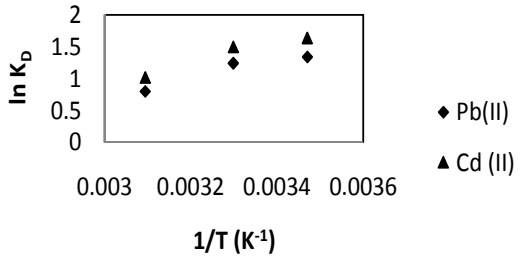

Fig. 3 plot of ln K_D vs 1/T for the estimation of thermodynamic parameters for biosorption of Pb (II) and Cd (II) by MGL 75

IV. Conclusion

This study was focused on the biosorption of Pb (II) and Cd (II) by MGL 75 biomass from aqueous solution. The equilibrium sorption data analyzed according to the Freundlich, Langmuir, and D-R models.

The Langmuir isotherm represented best the equilibrium sorption data; the maximum monolayer biosorption capacity of MGL 75 biomass for Pb (II) and Cd (II) was found to be 158.73 mg/g and 91.74 mg/g, respectively. The sorption process was found to be physiosorption process, as confirmed by the values of the mean free sorption energy calculated by the D- R equation for Cd and Pb metal ions. Kinetic examination of the equilibrium data showed that the biosorption of Pb and Cd ions by MGL 75 followed well the pseudo-second-order kinetic model. The calculated thermodynamic parameters showed the feasibility, exothermic and spontaneous nature of the biosorption of Pb (II) and Cd (II) ions by MGL 75 biomass. Thus, it may be concluded that MGL 75 biomass exhibited the potential for application in treatment of aqueous solutions containing Cd (II) and Pb (II) ions.

References

[1] H. Ucun, Y.K. Bayhana, Y. Kaya, A. Cakici, O.F. Algur, "Biosorption of lead (II) from aqueous solution by cone biomass of Pinus sylvestris," *Desalination*, vol. 154, no. 3, pp. 233-238, May 2003.

[2] M. Athar, S. Vohora, "Heavy metals and environment," New Age. International Publishers, New Dehli, 1995.

[3] S. Tunali, T. Akar, A.S. Özcan, I. Kiran, A. Özcan, "Equilibrium and kinetics of biosorption of lead(II) from aqueous solution by cephalosporium," *Separation and Purification Technology*, vol. 47, no. 3, pp. 105-112, January 2006.

[4] Y. Pingh, Y. Qiming, J. Bo, L. Zaho, "Biosoration removal of cadmium from aqueous solution by using pretreated fungal biomass cultured from starch wastewater," *Wat. Res.*, vol. 33, no. 8, pp. 1960-1963, June 1999.

[5] M.T. Ganji, M. Khosravi, R. Rakhshaee, "Biosorption of Pb, Cd, Cu and Zn from the wastewater by treated Azolla filiculoides with H2O2/MgCl2," *International Journal of Environmental Science & Technology*, vol. 1, no. 4, pp. 265-271, winter 2005.

[6] H. Xu, Y. Liu, J.H. Tay, "Effect of pH on nickel biosorption by aerobic granular sludge," *Bioresource technol.*, vol. 97, no. 3, pp. 359-363, February 2006.

[7] T. Bahadir, G. Bakan, L. Altas, H. Buyukgungor, "The investigation of lead removal by biosorption: An application at storage battery industry wastewaters," *Enzyme and Microb. Tech.*, vol. 41, no. 1-2, pp. 98-102. July (2007).

[8] T.J. Beveridge, "The role of cellular design in bacterial metal accumulation and mineralization," *Annu Rev Microbiol*, vol. 43, pp. 147–171, October 1989.

[9] M. Venkata Subbaiah, Y. Vijaya, A. Subba Reddy, G. Yuvaraja, A. Krishnaiah, "Equilibrium, kinetic and thermodynamic studies on the biosorption of Cu(II) onto Trametes versicolor biomass," *Desalination*, vol. 276, no. 1-3, pp. 310–316, August 2011.

[10] C. Shamik, C. Sagnik, S. Papita , "Biosorption of Basic Green 4 from aqueous solution by Ananas comosus (pineapple) leaf powder," *Colloids and Surfaces B: Biointerfaces*, vol. 84, no. 2, pp. 520-527, Jun 2011.

[11] A. Sule, T. Alkim, G. Cem, "Biosorption of uranium(VI) by bi-functionalized low cost biocomposite adsorbent," *Desalination*, vol. 280, no. 1-3, pp. 354-362, October 2011.

[12] H. J.Michael, I. S. Ayebaemi, "Effect of metal ion concentration on the biosorption of Pb2+ and Cd2+ by Caladium bicolor (wild cocoyam)," *African Journal of Biotechnology*, vol. 4, no. 2, pp. 191-196, August 2005.

[13] M. A. María, H. Sergio, D. Jorge, D. María, A.Santos, "Biosorption of Cu(II), Zn(II), Cd(II) and Pb(II) by dead biomasses of green alga Ulva lactuca and the development of a sustainable matrix for adsorption implementation," *Journal of Hazardous Materials*, vol. 213-214, pp. 123-132. April 2012.