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RESEARCH ARTICLE

BIOSORPTION OF PB(II) IONS FROM AQUEOUS SOLUTION ONTO FREE AND IMMOBILIZED CELLS OF BACILLUS MEGATERIUM

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ABSTRACT

In present study, the free and immobilized cells of Bacillus megaterium were used as biosorbent for the removal of Pb(II) ions from the aqueous solution. The adsorption studies of bacterium were compared in batch mode. Optimum biosorption conditions were determined as a function of pH, temperature and contact time. The equilibrium adsorption data was analyzed by the Langmuir, Freundlich, Tempkin, Dubinin-Radushkevich, Redlich-Peterson and Sips isotherm models. The values of the regression coefficient of the isotherms gave the best fit (free cells R^2=0.998 and immobilized cells R^2=0.999) with the Langmuir isotherm. The maximum monolayer adsorption capacity (q_e) of the biosorbents (free and immobilized cells), as obtained from the Langmuir adsorption isotherm, was found to be 166 and 200 mg/g, respectively at 5h contact time, 7.0 pH, 0.4 g/L bacterial dose, and 30^0C temperature. The energy of adsorption, E (free = 9.911KJ/mol and immobilized = 11.174 KJ/mol) obtained from the Dubinin-Radushkevich isotherm suggested a chemical ion exchange mechanism. Kinetics of adsorption followed both first- and second-order rate equations with intra-particle diffusion processes. Biosorbent could be regenerated using 0.1 M NaOH solution, with up to 60% recovery. The performance of this biosorbent was compared with many other reported biosorbents for lead removal and it was observed to be most effective.

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INTRODUCTION

Heavy metals continue to pose a serious threat to biota, due to their acute toxicity, nonbiodegradable nature, and build up of high concentrations in water bodies all over the world. Hence, developing strategies for their control and reducing the levels of heavy metals to their permissible limits in waste waters are major challenges for environmental scientists (Tang. 2013). Pb(II) ion is one such toxic heavy metal frequently encountered in raw wastewater streams from industries such as electroplating, battery manufacturing, mineral processing and paint formulation (Han . 2006). Pb accumulates mainly in the bones, brain, kidney, and muscles and may cause many serious disorders, including anemia, kidney diseases, nervous disorders, and even death (Chua . 2012). It is therefore, essential to remove Pb (II) from wastewater before disposal. Many adsorbents, either in the raw state or modified state have been used for removal of lead ions (Ibrahim . 2010; Teoh . 2013, Lalhruaitluanga . 2010; Liao . 2011; Depci . 2012; Mouni . 2011; Ghafarab . 2013; Kumar and Rao 2011). Thus, there is a growing demand to find relatively efficient, low cost and easily available adsorbents for lead removal. One of the promising alternative that is receiving more attention is biosorption using microbial biomass as the adsorbent for the removal of heavy metals (Ozturk 2007). Microbial and plant origin biomasses were successfully used as biosorbent material in many biosorption studies (Ahluwalia and Goyal 2007; Borba . 2006; Kumar . 2008; Mane . 2011). The major advantages of the biosorption technology are its effectiveness in reducing the concentration of heavy metal ions to very low levels and the use of inexpensive biosorbent materials (Wong 2000). The high affinity, rapid metal uptake and maximum loading capacity are some of the important factors to consider when selecting a biosorbent (Akhtar. 2007). Bacteria have the largest surface area to volume ratio of any independent life form. The structural polymers in the bacteria cell wall provide acidic functional groups like carboxyl, phosphoryl and amino groups that are directly responsible for the reactivity of bacterial cells (Kulczycki . 2002). Although there are reports of biosorption of lead metal ion by various bacteria (Vegilo . 1997; Konig-Peter . 2011; Pardo . 2003; Dorian . 2012; Lu . 2006; Sag and Kutsul 1996; Friss and Meyers 1986; Vecchio . 1988) showing varying removal efficiencies, maximum adsorption capacities (q_e) and binding constants but there are no reports on the removal of Pb(II) from aqueous solutions using the gram positive bacterium *Bacillus megaterium*. This new material was chosen as biosorbent in this study as it is natural, easily available, and thus a low-cost biomass for dissolved metal ions. The purpose of the present study is to evaluate the biosorption capacity of Bacillus megaterium in free and immobilized cell state for the removal of lead(II) ions from aqueous solutions. In addition, kinetics and adsorption isotherms were also evaluated.

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MATERIALS AND METHODS

Biomass used

Pure culture of Bacillus megaterium was readily available in the Department of Microbiology at G.B. Pant University of Agriculture and Technology Pantnagar. The slant cultures were prepared with Nutrient agar (NA) medium containing peptone 0.5% and yeast extract 0.3%. The slant cultures were incubated at 35^0 C for 24h.

Immobilization of Biosorbent

5% sodium alginate was prepared by dissolving 5g of sodium alginate in 100ml distilled water. The resultant solution was autoclaved at 120^0C temperature and 15 lb pressure for about 20 minutes. 40 mg of *Bacillus megaterium* was dissolved in sodium alginate and immobilized cell composites are prepared by adding the slurry drop wise to 2% calcium chloride solution. The immobilized cell composites approximately 40 were used for sorption studies.

Lead ion solution

A stock solution for lead ions (1000 ppm) was prepared by dissolving an accurate quantity of $Pb(NO_3)_2$ in deionized water. Diluted concentrations were obtained from the stock solution. The pH of working solutions was adjusted to 7 by addition of the necessary amount of either 1.0 M HCl or 0.1 M NaOH solution.

Biosorption studies

The biosorption of Pb ions was studied in batch system. All experiments were carried out with 40 mg biosorbent and 50 mL solution in a 250 mL flask at 30^0C and with a stirring speed of 120 rpm for 5h. Each experiment was conducted in triplicate, and average values were used for the data analysis. In the experiments, the biosorption capacity of immobilized and free cells of Bacillus megaterium for Pb(II) ions was determined separately. Initial heavy metals concentrations were varied from 50 to 250 ppm for different contact time (1, 3, 5, 7 and 9 h). The saturation value for the sorption was found to be about 50 ppm initial concentration of the metal ions and further experiments were carried out at this initial concentration. To determine the optimum temperature for biosorption, the temperature was varied from 20 to 40^0C. The effect of pH on the biosorption capacity of the bacterium was investigated in the pH range from 3 to 11 at 30^0C for 5h with 250 ppm of initial metal ion loading. After incubation the cultures were centrifuged at 1500 rpm for 10 min. After centrifugation, the supernatants were digested using nitric acid-perchloric acid digestion according to APHA (1995) and were used for determination of residual metal ion concentration by using Atomic Absorption Spectrophotometer (AAS). The amount of metal ions adsorbed per gram of *B. megaterium* was calculated as follows:

$$q_e = (C_e\text{-}C_0)V/m \quad (1)$$

where q_e is the amount of metal ions adsorbed (mg/g) onto *B.* megaterium, C_o is the initial metal ion concentration in solution (ppm), C_e is the concentration of non-adsorbed metal ions in solution (ppm), V is the volume of the medium (L) and *m* is the amount of *B.* megaterium used in the reaction mixture (g).

Kinetic Experiments

Kinetic studies were carried out in order to determine the contact time required to reach the equilibrium. 200 mL samples of various concentrations(50-250 mg/L) of metal ion solutions were adjusted to desired pH and temperature and then mixed with 40 mg of each sorbent.

Adsorption Experiments

Experiments were carried out in batch mode. 200 mL samples of aqueous solutions of Pb(II) ions at different initial concentrations (50–250 mg/L) and at adjusted pH were transferred into 250 mL Erlenmeyer flasks. At every 1h, 3 mL of solutions were filtered and metal ion concentrations in the filtrate were determined. During the adsorption, a rapid equilibrium is established between adsorbed metal ions on the adsorbent (q_e) and unadsorbed metal ions in solution (C_e). This equilibrium data were analyzed using Freundlich isotherm, Langmuir isotherm, Temkin isotherm, Dubinin-Radushkevich, Sips model, and R-P model presented in Table 1.

Desorption

The recycling of an adsorbent is a most important aspect for an economical technology. Adsorption–desorption experiments were carried with 10 ml of 0.1 M NaOH up to three cycles. A single cycle sequence consists of adsorption followed by desorption (temperature, 30^0C; agitation, 200 rpm; biosorbent mass, 0.4 g; metal concentration, 250 mg/L; adsorption contact time 5h; and desorption contact time 2 h). After adsorption, the resultant metal-loaded algal biomass was filtered and reintroduced into the desorption solvent and agitated.

Quality control

For each experiment, blanks were run and corrections applied if necessary. All the observations were replicated thrice and average values were reported. The accuracy and reliability of the collected data was confirmed using known standards. All jars, conical flasks, and containers used in the study were prepared by being soaked in a 5% HNO_3 solution for a period of 3 days before being double rinsed with distilled, deionized water and oven dried.

RESULTS AND DISCUSSION

Effect of contact time

The results obtained from the adsorption of Pb ions onto the free and immobilized cells showed that the biosorption increased with increase in contact time (Fig. 1). The adsorption of Pb (II) ions was gradually increased for the first 5 h and equilibrium was nearly reached after 5 h for five different initial Pb(II) ion concentrations. A further increase in the contact time has a negligible effect on the removal percentage of lead because the active sites of the biosorbent gets exhausted due to the repulsive forces between the metal ions in the solid and bulk phases (Chen . 2008). The active sorption sites in a system have a fixed number and each active site can absorb only one ion in a monolayer. The metal uptake by the sorbent surface was rapid initially and geared as the competition for the decreasing availability of active sites intensified by the metal ions remaining in the solution (Saravanan. 2012).

Effect of temperature

The effect of temperature on the adsorption of Pb(II) ion was investigated at different temperatures (20^0C – 40^0C) for both

bacterial biomasses and is given in Fig. 2. Studies reveal that the biomass exhibited maximum sorption capability in the temperature range between 30^0C - 35^0C. For an increase in temperature from 30^0C to 40^0C the adsorption capacities of the free and immobilized bacterial cells for Pb(II) showed a decrease from 89.63–71.6 to 67.98–52.31 mg/g, respectively, thus indicating the exothermic nature of the biosorption process (Padmavathy . 2003). This is due to either the damage of active binding sites in the biomass (Ozer and Ozer 2003) or the increasing tendency to desorb metal ions from the interface to the solution (Saltali . 2007). The optimum solution temperature was selected as 30^0C for further biosorption experiments.

affects the competition ability of hydrogen ions with metal ions to active sites on the biosorption surface (Lodeiro. 2006). The initial pH optimum for biosorption is also microorganism dependent because of different adsorptive sites of different species of microorganisms. The effect of initial pH on the equilibrium uptake of Pb(II) ions was investigated between pH 3.0 to 11.0 as presented in Fig. 3. The maximum removal (86.61%) was observed at pH 7.0 while minimum removal (63.14%) was observed at pH 3.0. The low level of Pb (II) uptake at lower pH values could be attributed to the increased concentration of hydrogen (H^+) and hydronium (H_3O^+) ions competing for Pb(II) binding sites on the biomass (Segel 1976;

Table 1 Equilibrium isotherm models used to represent lead biosorption

Isotherm model	Equations	Nomenclature	References
Langmuir	$q_e=(q_{max}bC_e)/(1+bC_e)$	q_e(mg/g) is amount of metal ion sorbed at equilibrium, q_{max}(mg/g) is maximum metal sorption, C_e(mg/L) is metal ion concentration at equilibrium and b(l/mg) is Langmuir adsorption equilibrium constant	Langmuir (1918)
Freundlich	$\log q_e=\log K_F+(1/n)\log C_e$	K_F(mg/g) and n(g/L) are Freundlich constants indicating adsorption capacity and adsorption intensity	Freundlich (1906)
Dubinin-Radushkevich	$\ln (q_e)= \ln(q_S)- K_{DR}\varepsilon^2$	K_{DR} is a constant related to mean free energy E_S(kJ/mol) as $E_S=(1/\sqrt{2}\ K_{DR})$ q_s is theoretical saturation capacity, ε is Polanyi potential equal to RT $\ln(1+(1/C_e))$	Dubinin (1960)
Temkin	$q_e=(RT/B_T)\ln A_T + (RT/B_T)\ln C_e$	R is universal gas constant(8.314 J/mol/K), T is absolute temperature in Kelvin, A and B(L/g) represents Temkin constants	Tempkin & Pyzhev (1940)
Redlich-Peterson	$q_e=(K_RC_e)/(1+a_RC_e^{\beta})$	K_R(l/g), a_R(l/mg) and β represents Redlich-Peterson constants and are empirical parameters with no physical meaning, β varies between 0 and 1	Reddlich & Peterson (1959)
Sips	$qe=(K_SC_e^{\ 1+b_S}) / (1+a_SC_e^{\ 1+b_S})$	K_S (l/mg/g), a_S(l/mg) and b_S are Sips constants	Sips (1948)

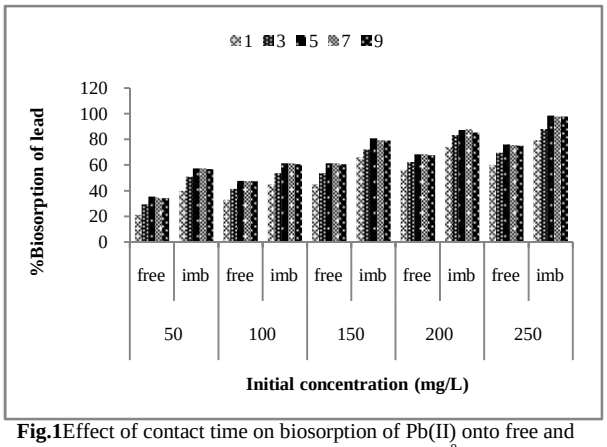

Fig.1 Effect of contact time on biosorption of Pb(II) onto free and immobilized cells of B. megaterium (Temperature, 30^0C; pH 7.0; initial Pb(II) concentration 50-250 mg/L.)

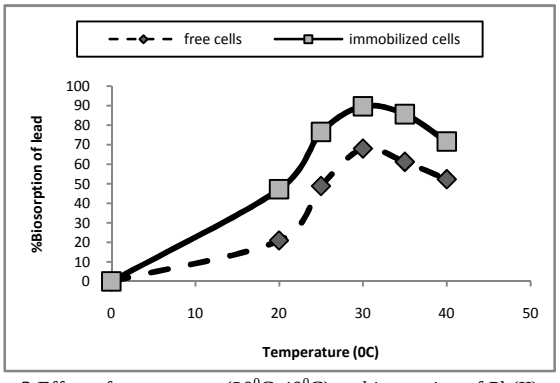

Fig. 2 Effect of temperature (20^0C-40^0C) on biosorption of Pb(II) onto free and immobilized cells of *B.megaterium* at pH 7.0

Effect of pH

One of the most important factors affecting biosorption of metal ions is acidity of solution. The acidity of the medium

Cabuk . 2005). The increase in Pb(II) biosorption at higher pH values (5–7) may be explained by the ionization of functional groups on the cell surface which serve as the binding sites related to the isoelectric point of the cells (Hetzer . 2006). Decrease in biosorption at higher pH (pH > 7) is due to the formation of soluble hydroxylated complexes of the metal ions and their competition with the active sites, and as a consequence, the retention would decrease again (Sari . 2007).

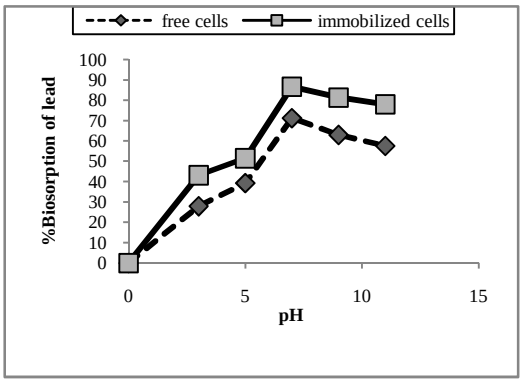

Fig. 3 Effect of pH on biosorption of Pb(II) onto free and immobilized cells of *B. megaterium* (Temperature, 30^0C; initial Pb(II) concentration 250 mg/L.)

Adsorption isotherms

The analysis of adsorption data is important for developing an equation which accurately represents the results and which could be used for design purposes. Out of several isotherm equations, the Langmuir, Freundlich, Temkin, D-R, R-P and Sips isotherms were used to fit the experimental data. The linear regression was used to determine the most fitted model among all the six above written isotherms. The values of Langmuir, Freundlich, Tempkin, D-R, R-P and Sips isotherm constants are given in Table 2 and on comparing the linear regression values it is concluded that the Langmuir (R^2= 0.998

and 0.999) isotherm is capable of representing the data more satisfactorily than the other isotherms.

Table 2 Equilibrium constants for lead on free and immobilized cells of B.megaterium

	Free cells	Immobilized cells
Langmuir isotherm		
q_e (mg/g)	166.66	200.00
b (L/mg)	0.003	0.023
R^2	0.998	0.999
Freundlich isotherm		
n (g/L)	1.272	2.941
K_F (mg/g)	0.408	0.306
R^2	0.811	0.843
Dubinin-Radushkevich isotherm		
K_{DR}	0.012	0.001
q_S	0.805	1.293
E_S (kJ/mol)	8.841	10.443
R^2	0.864	0.861
Tempkin isotherm		
A_T	1.479	1.788
B_T (L/g)	102	191
R^2	0.720	0.728
Redlich-Peterson isotherm		
a_R (L/mg)	2.864	3.203
β	0.979	0.418
K_R (L/g)	1.642	4.527
R^2	0.881	0.884
Sips isotherm		
a_S (L/mg)	0.128	0.049
K_S (L/mg/g)	0.221	0.279
b_S	0.786	0.171
R^2	0.832	0.836

Table 3 Sorption capacity of lead on different bacterial biomasses

Biosorbent	e(mg/g)	Reference
Arthrobacter sp.	130	Vegilo *et al.* (1997)
Pseudomonas aeruginosa	164	Konig-Peter *et al.* (2011)
Pseudomonas putida	56.2	Pardo *et al.* (2003)
Delftia tsuruhatensis	44.8	Dorian *et al.* (2012)
Enterobacter sp. J1	50.9	Lu *et al.* (2006)
Bacillus sp.	92.3	Sag and Kutsul (1996)
Streptomyces longwoodensis	100	Friss and Meyers (1986)
Brevibacterium sp.	74.6	Vecchio *et al.* (1988)
B. megaterium(free)	166.66	This study
B.megaterium(immobilized)	200	This study

the Langmuir parameter, b, can be used to predict the affinity between the sorbate and the sorbent using the dimensionless separation factor, R_L, defined by Hall. (1966) as

$$R_L=1/ (1+bC_0) \quad (2)$$

Where b is the Langmuir constant (mg/L) and C_0 is the initial Pb (II) concentration (mg/L). If the R_L values are equal to 0 or 1, the adsorption is either linear or irreversible; if the values are in between 0 and 1, adsorption is highly favorable; and R_L values greater than 1 indicate unfavorable sorption.

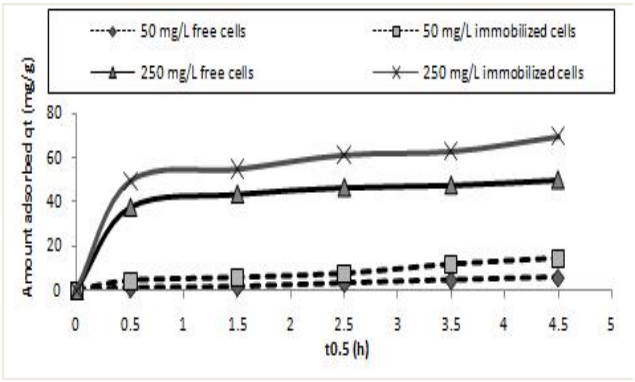

Fig.4 Intraparticle diffusion model plot of Pb(II) adsorption on B. megaterium

The values of R_L for sorption of Pb (II) on free and immobilized bacterium B. megaterium are less than 1 and greater than 0 (0.158 and 0.034), indicating the favorable uptake of Pb(II) by the biosorbents. The adsorption of Pb(II) on bacterial surface is thus a highly favorable process. Moreover, it is observed that the sorption of lead is more favorable at higher lead initial concentration (250 mg/L) than for the lower ones (50 mg/L). The data illustrated in Table 2 represent the D–R values of the biosorption of Pb(II) onto B. megateriuum biomass.

It is well known that the mean free energy of biosorption gives information about biosorption mechanism, physical or chemical. If the E value lies between 8 and 16 kJ/mol, the biosorption process occurs chemically and if E < 8 kJ/mol, the

Table 4 Kinetic models for free and immobilized cells of bacterium *B.megaterium*

Free cells									
	First order model				Second order model	Intraparticle model			
C^0 (mg/L)	$q_{e,exp}$ (mg/g)	K_I (g/mg/h)	$q_{e,cal}$ (mg/g)	R^2	K_{II} (g/mg/h)	$q_{e,cal}$ (mg/g)	R^2	K_w (mg/gh$^{0.5}$)	R^2
50	31.655	0.002	43.029	0.942	1.222	37.226	0.985	0.221	0.903
100	48.512	0.020	57.394	0.946	1.532	52.937	0.993	0.803	0.993
150	66.145	0.023	78.257	0.905	1.402	72.899	0.996	0.983	0.909
200	97.582	0.055	112.58	0.927	1.761	102.825	0.999	1.112	0.947
250	167.22	0.207	174.76	0.913	1.839	158.701	0.997	1.439	0.914
Immobilized cells									
	First order model				Second order model	Intraparticle model			
C^0 (mg/L)	$q_{e,exp}$ (mg/g)	K_I (g/mg/h)	$q_{e,cal}$ (mg/g)	R^2	K_{II} (g/mg/h)	$q_{e,cal}$ (mg/g)	R^2	K_w (mg/g h$^{0.5}$)	R^2
50	38.681	0.004	48.274	0.996	0.081	43.422	0.987	0.365	0.934
100	60.764	0.023	73.265	0.904	0.254	65.163	0.994	1.062	0.947
150	74.143	0.025	84.235	0.926	0.629	77.149	0.996	0.725	0.924
200	120.301	0.027	129.181	0.932	0.829	124.364	0.994	1.074	0.908
250	203.973	0.347	222.427	0.921	0.887	180.333	0.998	2.433	0.975

The extent of adsorption of Pb(II) by different other bacteria as biosorbents, collected from the literature, along with the results of the present study is included in Table 3 in the form of monolayer adsorption capacity. The data in the table indicate that bacterium in free and immobilized forms have comparable adsorption capacities compared to many biosorbents. Further,

Ho. 2002). In the current study, the mean biosorption energy was calculated as 8.84 and 10.44 kJ/mol for the biosorption of Pb onto the free and immobilized *B. megaterium* biomasses, respectively. These results indicated that the biosorption process of Pb(II) onto both biomasses may be carried out chemically via involving valence forces through sharing or

exchange of electrons between sorbent and sorbate (Mar Areco and Dos Santos Afonso 2010).

Biosorption kinetics

The prediction of adsorption rate gives important information for designing batch adsorption systems. Information on the kinetics of solute uptake is required for selecting optimum operating conditions for full-scale batch process. The kinetics of the adsorption data was analyzed using pseudo-first order, pseudo-second order and intra-particle diffusion, which can be represented in their nonlinear forms, as follows:

Pseudo-first-order model,

$$\log(q_e - q_t) = \log q_e - K_I t \quad (3)$$

Pseudo-second-order model,

$$t/q_t = 1/ k_{II} q_e^2 + t/ q_e \quad (4)$$

Where q_e is the amount of solute sorbed at equilibrium (mg/g); q_t the amount of solute sorbed at time t (mg/g); k_I the first-order equilibrium rate constant (g/mg/h) and k_{II} is the second-order equilibrium rate constant (g/mg/h). The adsorption rate constant K_I for Pb(II) sorption was calculated from the slope of the linear plot of $\ln(q_e - q_t)$ vs. time. In the later case, kinetic data were plotted between t/q_t against t. The kinetic rate constants obtained from first and second-order kinetic model were given in Table 4. Though, both first-order and pseudo-second-order kinetics possess high correlation coefficient values but the later fits better with highest R_2 values ranging from 0.985-0.997 and 0.987–0.998 for free and immobilized biomasses. Besides, Table 4 data indicate that the $q_{e,cal}$ values for the second-order model are more close to $q_{e,exp}$ values (167.22 and 203.97 mg/g for free and immobilized cells, respectively) in comparison to first-order values. So, it can be concluded that lead sorption onto the biosorbent seems to be more pseudo-second order.

The Intra-particle Diffusion (Weber and Morris) Model

The intra-particle diffusion model is characterized by a linear relationship between the amount of metal adsorbed (qt) and the square root of the time and is expressed as,

$$q_t = (K_w)t^{0.5} \quad (5)$$

Where q_t (mg/g) is the amount of metal ions adsorbed at time t (h) and K_w is the initial rate of the intra-particle diffusion (mg/g $h^{0.5}$). The intra-particle diffusion rate constants were found to increase for Pb with different concentrations (Table 4 and Fig. 4). It gives the conclusion that the intra-particle diffusion is the rate determining step in the adsorption of the metals on free and immobilized bacterial cells.

Desorption

The reusability of bacterial biomass B. megaterium for Pb(II) uptake was examined by repeating adsorption- desorption cycles four times using 0.1M NaOH as elutant. About 60% of the adsorbed Pb(II) ions were desorbed from the biosorbent. Moreover, the adsorption capacities of the biosorbents changed by only about 10-15% suggesting the reusability of the biosorbents repeatedly for 4-5 cycles with little change in their initial adsorption capacities.

CONCLUSIONS

The batch studies conducted in the present study provide significant information regarding the biosorption of Pb(II) ion onto free and immobilized B. megaterium in terms of optimum pH, temperature, and contact time for the maximum removal of lead from the aqueous solutions. The results indicated that *B.* megaterium is an effective biosorbent for Pb(II) removal. The maximum adsorption capacity of free and immobilized bacterial cells (166.66 and 200.00 mg/g) was found to have greater or comparable values compared to other similar biosorbents reported in the literature. The adsorption equilibrium data fit the Langmuir model better than the other five models. The sorption kinetics followed both the first and the pseudo- second-order rate equation with the later being best fited. A 0.1 M NaOH efficiently desorbed metal from the metal-loaded biomass during successive sorption/desorption cycles. The results of this study will serve as basis for the development of cost-effective and robust indigenous technology for biosorption of lead from aqueous solutions. Moreover, this organism has a potential for future use as a biosorbent particularly when metal concentration in the waste streams is very high. However, pilot-scale experiments need to be conducted so that commercial exploitation of *B.* megaterium as a metal biosorbent can be ascertained.

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