

Biosorption of Pb (II) Ions from Aqueous Solution Using Dry and Immobilized Biomass of *Rhizopus arrhizus*

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Abstract— The biosorption of Pb(II) ions by dry and immobilized cells of *Rhizopus arrhizus* was studied in the aqueous solutions. The effect of contact time (0 – 42 h), pH (2 - 8), initial concentration (50 – 1500 mg/ L) of Pb(II) ions on biosorption were investigated in batch systems. The biosorption rate was established in about 48 h and the adsorbed heavy metal ions did not change further with time. The maximum biosorption capacities of dry and immobilized cells of *Rhizopus arrhizus* biomass were 95.94% and 95.94% respectively at 500 mg/L of Pb(II) ions. The Pb(II) adsorption data were analyzed using the first and the second order kinetic models. The experimental results suggest that the second – order equation is the most appropriate equation to predict the biosorption capacity by dry and immobilized cells of *Rhizopus arrhizus*. Langmuir and Freundlich isotherms were used to evaluate the data and the regression constants were derived. Biosorption equilibrium data were best described by Freundlich isotherm model followed by Langmuir model. The free energy change (ΔG°) obtained for the biosorption of Pb(II) ions at the temperature of 303, 308, 313, 318 and 323 K was – 1076, - 1094, - 1111, - 1129 and – 1147 kJ/mol (dry *Rhizopus arrhizus*) and – 789, - 802, - 815, - 828 and - 841 kJ /mol (immobilized *Rhizopus arrhizus*) respectively at pH – 5. The high negative value of change in Gibbs free energy indicates the spontaneity and feasibility of the biosorption of Pb(II) by kJ/mol dry and immobilized *Rhizopus arrhizus*.

Keywords— *Rhizopus arrhizus*, Pb(II) ions, Kinetic characterization, Immobilized cells, pH.

I. INTRODUCTION

The removal of toxic heavy metal contaminants from industrial wastewater is one of the most important environmental issues to be solved today because a sudden increase in the industrial activities has contributed quantitatively as well as qualitatively to the alarming increase in the metal discharge in to the environmental sink, especially the aqueous environment. Heavy metals released by a number of industrial processes are major pollutants in marine, ground, industrial and even treated wastewaters (Martins 2006). The threat of heavy metal pollution to public health and wild life has led to an increased interest in developing systems that can remove or neutralize its toxic effects in soils, sediments and waste water. Unlike organic contaminants which can be degraded to harmless chemical species, heavy metals cannot be destroyed. Pb(II) ions is a toxic metal which ranks 36th element of abundance in the Earth's crust. Pb(II) ions is emitted in to the environment through a large number of geogenic (wind bloom dusts, forest fires, volcanic emissions, and sea salt sprays) and anthropogenic (mining, oil and gasoline combustion, wood combustion, phosphate fertilizer manufacture, effluents from industries such as battery manufacture, plating, TV tube manufacture, rayon and paper mill, dyes and pigment industry) (Roane & Pepper 2000). Pb(II) ions is non essential for the functioning of human biological systems and it has been recognized as a cumulative poison. It is transported by the blood in the body and stored in teeth, bones and soft tissues including brain. Lead salts are detrimental to brain and immunological function (Dieter &

Finely 1999). The major toxic effects of lead include anemia, neurological dysfunction and renal impairment. High level of exposure produces severe neurological damage, often manifested by encephalopathy and convulsions result in death (Flanngan *et al.* 1978). Conventional methods such as, chemical precipitation, chemical oxidation or reduction, ion exchange, filtration, electrochemical treatment, reverse osmosis, membrane technologies are generally used for removing metals from aqueous solutions (Grau & Bisang 1995). These processes may be ineffective or expensive, especially when the heavy metal ions are in solutions containing in the order of 1-100 mg dissolved heavy metal ions/ L (Volesky 1990 & 1999). Therefore removal of toxic heavy metals by an environmentally friendly manner is of great importance. Microorganisms have evolved resistance mechanisms to deal with heavy metal toxicity, which include volatilization, extracellular precipitation and exclusion, binding to the intracellular sequestration (Roan & Kellogg 1996). Microbial cell surfaces are usually charged and the passive process involving extracellular accumulation of metals on cell walls has been studied (Sahoo *et al.* 1992). Many bacterial species such as *Pseudomonas* K – 62 (Tonomura *et al.* 1968), *Bacillus thuringiensis* (Hassen *et al.* 1998) and *P. fluoresces* BM07 (Noghabi *et al.* 2007) and fungal species such as *Aspergillus nidulans* (Maheswari & Murugesan 2009a), *Aspergillus fumigatus* (Maheswari & Murugesan 2009b) *Rhizopus arrhizus* (Aksu *et al.* 1999), *Phenerochaecte chrysosporium* (Say *et al.* 2001) and *A. niger* (Kapoor *et al.* 1999) have been extensively studied for heavy metal biosorption and the process mechanisms seem to be dependent

upon species. The aim of this study was to investigate the Pb(II) ions biosorption potential of dry and immobilized cells of *Rhizopus arrhizus* from aqueous solution using batch systems.

II. MATERIAL AND METHODS

2.1. Microorganism and Media

Samples collection and isolation of fungi is carried out from the soil samples collected from lead contaminated site, Tamilnadu. From selected soil samples *Rhizopus arrhizus* is isolated by soil dilution method and preserved in laboratory for further heavy metal biosorption analysis. In the collected soil samples, the lead mean concentration was and 65.4 mg/kg respectively

2.2. Immobilization of *Rhizopus arrhizus*

Rhizopus arrhizus cells were immobilized on Biomass Support Particles (BSPs). The BSPs used for immobilization were 6mm cubes of polyurethane foam. Immobilization was effected by placing 1g BSPs inside a flask together with the medium. The cells became well immobilized within the BSPs as a natural consequence of their growth during shake-flask cultivation. The immobilized whole-cell was separated from the culture broth by filtration. After washing with tap water for 1 min, they were treated with 0.1% glutaraldehyde solution for 1 hour.

2.3. Biosorption Studies

The biosorption of Pb(II) ions experiments were conducted in Erlenmeyer flask containing 100ml of heavy metal solution and 0.1g of dry and immobilized cells of *Rhizopus arrhizus* (batch biosorption equilibrium experiments). The effects of the aqueous medium, pH and the initial concentrations of heavy metal ion on the biosorption rate and capacity were studied. The effect of pH on the biosorption rate in aqueous solution (100ml) by the dry and immobilized *Rhizopus arrhizus* was investigated in the pH range (2 – 8). The effect of the initial Pb(II) ions concentrations on the biosorption was studied at the concentration of heavy metal ion in the adsorption medium was varied between 50 to 1500 mg /L. After the desired incubation period the aqueous phase was separated from the fungal biomass. The concentrations of remaining metal ions in biosorption medium were determined by Atomic Absorption Spectrophotometer (PG – 990).

2.4. Data Analysis

The amount of adsorbed heavy metal ions per unit biosorbent (mg metal ions /g dry biosorbent) was obtained by using the following expression (Demirbas *et al.* 2004).

$$q = \frac{[(C_0 - C_t)V]}{M} \quad (1)$$

where q is the amount of heavy metal adsorbed onto the unit amount of the adsorbents (mg/g) and C₀ and C_t are the concentrations of the metal ions in the solution (mg/L) before and after biosorption respectively; V is the volume of the aqueous phase and M is the amount of the adsorbents (g)

2.5. Kinetic Modeling

The study of sorption kinetics describes the adsorbate uptake rate and evidently this rate controls the residence time

of adsorbate at the solid – liquid interface (Demirbas *et al.* 2004). The kinetics of Pb(II) ions sorption on fungal adsorbents were analyzed using different kinetic models, these include, the pseudo first order (Lagergren 1891) and pseudo second order. The agreement between the experimental data and the model predicted values for each model was expressed by the coefficient of determination (r²). A relatively high r² value indicates that the model so examined successfully describes the kinetics of Pb(II) sorption onto the fungal biomass.

2.6. The Pseudo – first order equation

The Pseudo first order equation (Lagergren 1891) is generally expressed as follows,

$$\frac{dq_t}{dt} = K_1(q_{eq} - q_t) \quad (2)$$

where k₁ is the rate constant of pseudo – first – order biosorption (1/min) and q_{eq} and q_t denote the amounts of biosorption equilibrium at time t (mg/g), respectively. After integrating by applying boundary conditions, q_t = 0 at t = 0 and q_t = q_t at t = t, gives

$$\log \frac{q_{eq}}{q_{eq} - q_t} = \frac{(k_1 t)}{2.303} \quad (3)$$

The equation (3) can be rearranged to obtain a linear form

$$\log(q_{eq} - q_t) = \frac{\log q_{eq} - (k_1 t)}{2.303} \quad (4)$$

A plot of log (q_{eq} – q_t) against t should give a straight line to confirm the applicability of the kinetic model. In a true first - order process q_{eq} should be equal to the intercept of a plot of log (q_{eq} – q_t) against t

2.7. The Pseudo – second order equation

If the rate of sorption is a second order mechanism, the pseudo second order chemisorption kinetics rate equation (Ho and McKay 1998) is expressed as Eq, (4)

$$\frac{dq_t}{dt} = k_2(q_{eq} - q_t)k^2 \quad (5)$$

Where, k₂ is the rate constant of pseudo second-order adsorption (g/mg/min). For the boundary conditions t = 0 to t = t and q_t = 0 to q_t = q_t, the integrated form of the equation (5) becomes:

$$\frac{1}{(q_{eq} - q_t)} = \frac{1}{q_{eq}} + k_2 t \quad (6)$$

This is the integrated rate law for a pseudo second order reaction. The above equation (6) can be rearranged to obtain a linear form:

$$\frac{t}{q_t} = \frac{1}{(k_2 q^2_{eq})} + \frac{1}{q_{eq}} t \quad (7)$$

A plot of t / q_t vs t should give a linear relationship for the applicability of the second order kinetics. The rate constant (k₂) and adsorption at equilibrium (q_{eq}) can be obtained from the intercept and slope respectively.

2.8. Adsorption Isotherms

The adsorption isotherm model was used to characterize the interaction of Pb(II) ions with the fungal biomass. The Langmuir model is based on the assumption that maximum adsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface, the energy of

adsorption is constant and there is no migration of adsorbate molecules in the surface plane (Kapoor *et al.* 1999 and Bayramoglu *et al.* 2002). The Langmuir model is described by the following equation

$$q_{eq} = q_m \frac{q_m C}{k_d + C} \quad (8)$$

where C and q also show the residual metal concentration and the amount of metal adsorbed on the adsorbent at equilibrium respectively. The $k_d = k_2/k_1$ is the Langmuir constant of the system. The semi – reciprocal plot of C/q vs C was employed to generate the intercept k_d / q and the slope $1/q$

The Freundlich equation is the empirical relationship whereby it is assumed that the adsorption energy of a metal binding to a site on an adsorbent depends on whether or not the adjacent sites are occupied (Bayramoglu *et al.* 2002 and Aksu *et al.* 1999). The Freundlich model is described by,

$$q_{eq} = K_F C_e^{1/n} \quad (9)$$

q_e – Metal uptake at equilibrium concentration mg/g ; C_e – Equilibrium metal ion concentration, mg/g; K_F – Freundlich’s constant of adsorption capacity ; n – Freundlich’s constant of adsorption intensity. The K_F was estimated from the y – intercept and n was calculated from the slope.

2.9. Thermodynamics of Biosorption of Pb(II) ions

In the present study, the biosorption experiments were carried out in the temperature (30, 35, 40, 45 & 50°C). The values of the thermodynamic parameters such as ΔG° , ΔH° and ΔS° , describing Pb(II) ions uptake by dry and immobilized cells of *Rhizopus arrhizus* were calculated using the thermodynamic equations (Fraiji *et al.* 1992). The biosorption process can be regarded as a heterogeneous and reversible process at equilibrium. The apparent equilibrium constant for the process has been shown to be

$$K_c = \frac{K_{ad}}{C_e} \quad (10)$$

The change in Gibbs free energy of the biosorption process is thus given as

$$\Delta G^\circ = -Rt \ln K_c \quad (11)$$

Where ΔG° is the standard Gibbs free energy change for the biosorption (J/mol), R the universal gas constant (8.314 J/mol.K) while T is the temperature (K). The effect of temperature on the biosorption of Pb(II) ions by *Rhizopus arrhizus* is shown from thermodynamics,

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (12)$$

or

$$\Delta G^\circ = -\Delta S^\circ (T) + \Delta H^\circ \quad (13)$$

A plot of T against ΔG° gives a straight line with slope – ΔS° and an intercept of ΔH° was obtained.

2.10. Statistical Analysis

All data represent the mean of three independent experiments. Standard deviation and error bars are indicated whenever necessary. All statistical analysis and plots were performed using Sigma Plot for Windows version 10 software (Systat Software, Inc).

III. RESULTS AND DISCUSSION

3.1. Biosorption Rate of Pb (II) ions

The equilibrium biosorption rate of Pb(II) ions on the dry and immobilized fungal biomass from aqueous medium was investigated in batch systems. The biosorption time of Pb(II) ions on the dry and immobilized *Rhizopus arrhizus* from solution containing 500 mg/L of Pb(II) ions is given in Fig - 1. The saturation level occurred after 48 h for dry and immobilized fungal biomass were found to be 479 and 496 mg/ L of Pb(II) ions respectively. After 48 h the concentration of adsorbed metal ions by *Rhizopus arrhizus* was not significant. In biosorption process, there are several parameters that determine the biosorption rate, including structural properties of biosorbent such as protein, carbohydrate composition and surface charge density, topography and surface area (Kacer *et al.* 2002). The biosorption of Cu (II), Pb (II) and Cd (II) by marine algae *Ecklonia maxima* and the biosorption equilibrium were established at 60 min (Feng *et al.* 2004). Ni biosorption by free and immobilized algal cells and the biosorption equilibrium were reached at 120 min (Abu Al – Rub *et al.* 2004). The biosorption equilibrium time of Cr (IV) on the dead and immobilized biomass of *R. arrhizus* was 2 h (Prakasham *et al.* 1999).

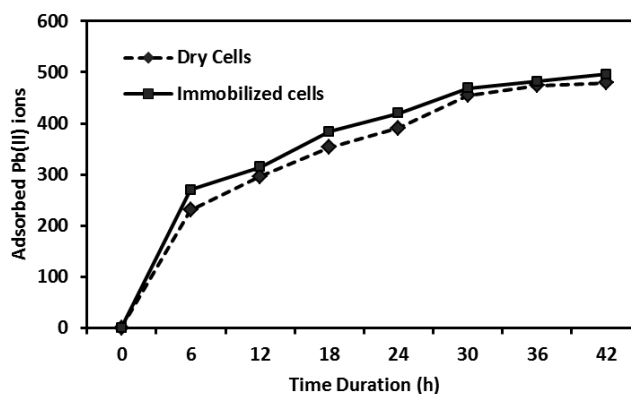


Fig. 1. Biosorption rates of Pb(II) ions on the dry and immobilized *Rhizopus arrhizus*. Biosorption conditions: initial concentration of Pb(II) ions – 500 mg / L; pH – 4, temperature - 35°C.

3.2. Effect of pH on Biosorption of Pb(II) ions

Biosorption of Pb(II) ions by dry and immobilized *Rhizopus arrhizus* increased when the medium pH was increased (Fig – 2). As seen from the figure the amount of biosorbed Pb(II) ions on dry and immobilized fungal biomass were 474 mg/L and 492 mg/L of Pb(II) ions respectively. In this study the equilibrium biosorption of Pb(II) ions for both the fungal biomass preparations were similar in pH – 5. The metal biosorption hence depends on the protonation or deprotonation of these carboxyl groups, which have pKa between 3 and 4 (Fourest & Volesky 1997).

The maximum biosorption of Pb(II) ions on the biomass of *Candida albicans* was observed at pH 5.0. The highest metal uptake values obtained for Pb(II) was 186.10 ± 0.9 mg/g. The lowest metal uptake value was determined at pH 2.0 for Pb(II) (178.92 ± 1.01 mg/g) (Baysal *et al.* 2009).

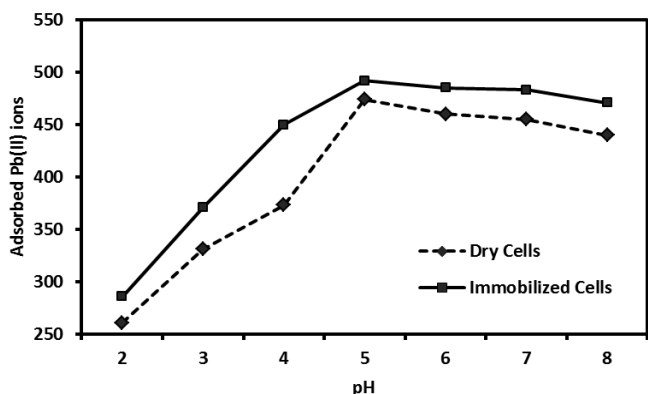


Fig. 2. Effect of pH on the biosorption capacities of the dry and immobilized *Rhizopus arrhizus* for Pb(II) ions. Biosorption conditions: initial concentration of Pb(II) ions – 500 mg / L, biomass – 0.1g, temperature - 35° C.

In the present study the adsorbed Pb(II) ions by free and immobilized *C. glutamicum* were found to be low at pH – 2. It was suggested that at lower pH value the surface of the adsorbent is surrounded by hydronium ions (H^+) thereby preventing the metal ions from approaching the binding sites of the sorbent (Wong *et al.* 2003). This means that at higher H^+ concentration, the surface of biosorbent become positively charged such that the attraction between the biomass and the metal cations reduced (Saeed *et al.* 2004).

3.3. Effect of Initial Pb(II) ions Concentration on Biosorption

The Pb(II) ions biosorption capacities of the tested adsorbents (dry and immobilized cells) were presented as a function of the initial concentration of metal ions (50 – 1500 mg/L). Biosorption capacities of all the tested biosorbents increased with increasing initial concentration of Pb(II) ions in the medium and reached a saturated value at 1500 mg L⁻¹ of Pb(II) ions. As seen from the Fig – 3 the amount of biosorbed Pb(II) ions on the dry and immobilized *Rhizopus arrhizus* biomass were 1004 and 1369 mg g⁻¹ respectively. The biosorption capacity of dead *Fusarium flocciferum* was 19.2 mg Cd (II) g⁻¹ dry biomass (Delgado *et al.* 1998). The biosorption capacity of the NaOH pretreated *A. niger* was 7.24 mg of Pb(II) ions, 3.43 mg for Cd(II) ions and 2.66 mg for Cu(II) ions per gram dry biomass (Kapoor *et al.* 1999).

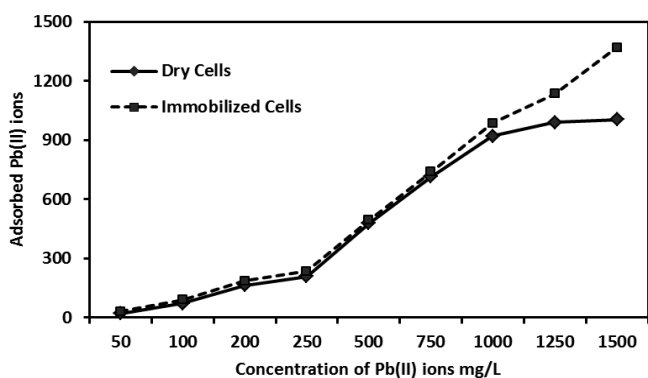


Fig. 3. Biosorption capacities of the dry and immobilized *Rhizopus arrhizus* for Pb(II) ions. Biosorption conditions: initial concentration of Pb(II) ions – 500 mg / L, biomass – 0.1g, pH – 5, temperature - 35° C.

3.4. Biosorption Kinetic Modeling

In order to investigate the mechanism of biosorption of Pb(II) ion and its potential rate controlling step kinetic models have been used to test the experimental data. The rapid kinetics have significant practical importance, as it will facilitate smaller reactor volumes ensuring high efficiency and economy (the first and second order equations), can be used in this case assuming the measured concentrations are equal to cell surface concentrations. The experimental biosorption capacities and the theoretical values for dry and immobilized *Rhizopus arrhizus* biomass were compared by the first and second order rate equations (Table I). The theoretical q_{eq} values estimated from the first order kinetics model gave significantly different values when compared to experimental values and the correlation coefficients were also found to be slightly lower for dry and immobilized *Rhizopus arrhizus* biomass. The correlation coefficients for the linear plots of t / qt against t for the second order equation were greater than 0.950 of 48 h for dry and immobilized *Rhizopus arrhizus* biomass. The theoretical q_{eq} values were very close to the experimental q_{eq} values in the case of pseudo second order kinetics. These results suggest that the second – order mechanism for dry and immobilized *Rhizopus arrhizus* biomass was predominant and the chemisorptions may be the rate limiting step that controls the biosorption process (Allen *et al.* 2005). Therefore these results showed that the biosorption systems are best described in pseudo second order kinetic model than the first order kinetic model. The adsorption of Pb(II) from aqueous solution on *C. albicans* obeys pseudo second-order kinetic model. A similar phenomenon was observed in the adsorption of Pb(II) on *Pleurotus ostreatus* (Xiangliang *et al.* 2005) and Pb(II) on *Sargassum* sp. (Martins *et al.* 2006). Kinetic analysis of Pb²⁺, Cd²⁺, Ni²⁺ and Zn²⁺ biosorption by *Mucor rouxii* represented the pseudo second-order rate equation which described the biosorption kinetic was better than the Lagergren model (Yan & Viraraghavan 2003).

3.5. Langmuir and Freundlich Adsorption Isotherms

The two most commonly used adsorption isotherms for biosorption studies (the Langmuir and Freundlich isotherms) were investigated. The Langmuir constants (q_m and k_d) along with correlation coefficients (R^2) have been calculated from the plots for biosorption of Pb(II) ions on the biosorbents and the results are given in Table II. The maximum capacity q_m determined from the Langmuir isotherm defines the total capacity of the biosorbents for Pb(II) ions. The order of maximum capacity (q_m) for the biosorbents for lead removal were found to be immobilized > dry fungal biomass (Table II). It is clear that increase of q_m value was due to an increase in the adsorptive sites on the biosorbents. The living organisms induce the production of metallothioneins which are protein that contain large amounts of cysteine and bind heavy metal ions in order to respond to the effects of heavy metals (Hafez *et al.* 1997). The Langmuir constant (k_d) estimated from the intercept which measure the stability of the complex formed between metal ions and adsorptive surface layer of the biosorbents under specified experimental conditions. The

presence of small k_d value indicated that the metal ions had high binding affinity for the biosorbent and the k_d values are presented in Table II. The k_d values for the adsorption of Pb(II) ions were 6.49 and 2.05 for dry and immobilized *Rhizopus arrhizus* respectively. The k_d value was low for immobilized bacterial biomass and it indicates that the high binding affinity between the biosorbents and heavy metal ions.

The Freundlich constants k_F and n showed easy separation of metal ions from aqueous medium and indicate favorable adsorption (Cetinkaya *et al.* 1999). The intercept k_F value is an indication of the adsorption capacity of the adsorbents; the

slope $1/n$ indicates the effect of concentration on the adsorption capacity of dry and immobilized *Rhizopus arrhizus* in the aqueous solution (Table II). The n values showed easy uptake of Pb(II) ions from aqueous medium with a high adsorption capacity as seen from Table II. In these systems, the metal removal process is based on solid – liquid contacting and separation process. Such preparations offer advantages in terms of mechanical strength and durability, handling and ease scale up. In the present investigation it is clear that Freundlich model fits well than Langmuir isotherm model.

TABLE I. The Pseudo first and second order kinetics constant for biosorption of Pb(II) ions on *Rhizopus arrhizus*.

Biosorbents	Experimental q_{ex} (mg / g)	Pseudo First Order			Pseudo Second Order		
		q_e (mg / g)	$k_1 \times 10^{-2}$ (1 / min)	R^2	Q_e (mg / g)	$k_2 \times 10^{-4}$ (1 / min)	R^2
DryCells	479	152	2.056	0.8989	470	2.185	0.9527
Immobilized Cells	496	169	1.77	0.8595	495	1.748	0.9690

TABLE II. Langmuir and Freundlich Isotherm model constant and correlation coefficient for biosorption of Pb(II) ion on *Rhizopus arrhizus*.

Biosorbents	Experimental q_{eqex} (mg / g)	Langmuir Constant			Freundlich Constant		
		q_m (mg / g)	$k_d \times 10^{-3}$ (M)	R^2	k_F	N	R^2
Dry Cells	1004	1007	6.49	0.9543	0.26	0.89	0.9768
Immobilized Cells	1369	1369	2.05	0.9759	0.13	0.92	0.9930

TABLE III. Free energy values obtained from the biosorption of Pb(II) ions using *Rhizopus arrhizus* at different temperatures.

Kelvin (K)	Dry Cells			Immobilized Cell		
	ΔG° (J/mol/K)	ΔH° (J/mol/K)	ΔS° (J/mol/K)	ΔG° (J/mol/K)	ΔH° (J/mol/K)	ΔS° (J/mol/K)
303	-1076	0.012	3.551	-789	0.009	2.604
308	-1094			-802		
313	-1111			-815		
318	-1129			-828		
323	-1147			-841		

3.6. Thermodynamics of Biosorption of Pb(II) ions

The thermodynamic of biosorption of Pb(II) ions by dry and immobilized *Rhizopus arrhizus* is shown in Table III. Table III shows the slope is 0.012 J/mol/K while the intercept is 3.551 J/mol/K for dry *Rhizopus arrhizus*. Therefore, the values of the entropy and enthalpy for dry *Rhizopus arrhizus* was 0.012 J/mol/K and 3.551 J/mol/, respectively. Table III also shows the slope is 0.009 J/mol/K while the intercept is 2.604 J/mol/K for immobilized *Rhizopus arrhizus*. Therefore, the values of the entropy and enthalpy for immobilized *Rhizopus arrhizus* was 0.009 J/mol/K and 2.604 J/mol/, respectively. From the data in Table III it can infer that the positive values of ΔH° indicate the endothermic nature of the sorption of Pb (II) ions on dry and immobilized *Rhizopus arrhizus*. The negative values of ΔG° indicate the feasibility of the process and indicate spontaneous nature of the sorption. However the negative value of ΔG° decreased with an increase in temperature, indicating that the spontaneous nature of sorption of Pb (II) ions is inversely proportional to the temperature. The positive values of ΔS° show the increased randomness at the solid / solution interface during the sorption also reflects the affinity of the sorbent for Pb (II) ions.

IV. CONCLUSIONS

Rhizopus arrhizus have been successfully used as the biosorbing agent for removal of Pb(II) ion from aqueous solution. The biosorption of Pb(II) ion depends on the experimental conditions particularly medium pH, temperature and concentration of metal ion in the medium. The results from this study show that pH, temperature and Pb(II) ion concentration highly affect the overall metal uptake capacity of biosorbent. The biosorption rate of Pb(II) ions on the biosorbent seems to follow the second – order kinetics. The Freundlich and Langmuir adsorption models were employed for the mathematical description of biosorption equilibrium data. The calculated isotherm constants were used to compare the biosorptive capacity at different experimental data for the removal of Pb(II) ion. The results of this investigation demonstrate that the Freundlich model fits a little better than the Langmuir model from the adsorption equilibrium data in the examined concentration range. The large negative value of change in free energy obtained for the biosorption of Pb(II) ions by dry and immobilized *Rhizopus arrhizus* shows spontaneity of the biosorption process at that temperature.

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