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Research article

Evaluation studies for the eradication of lead ions from aqueous system using *Salvadora persica* as a potential biosorbent material

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HIGHLIGHTS

- Evaluation studies for the eradication of lead ions
- Use of *Salvadora persica* as a potential biosorbent material

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ABSTRACT

Biosorption characteristics of an environmentally benign material (*Salvadora persica*) was investigated for the removal of Pb(II) ions from the aqueous solution. Various parameters like, the effect of sorbent dosages, contact time, pH and temperature on biosorption process were examined in a batch process. The maximum biosorption of Pb(II) ions occurred at 0.50 g of biosorbent at pH 6.0 for the contact time of 80 min. Langmuir, Freundlich and Dubinin-Redushekvich isotherms were applied. Langmuir adsorption isotherm was the best fitted among all the isotherms studied. The biosorption of Pb(II) ions followed the pseudo second order kinetic model. Thermodynamic parameters such as Gibbs free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o) were also evaluated. From thermodynamic study it is obvious that biosorption process is feasible, spontaneous and exothermic

Key words: Biosorption, Kinetics, Lead removal, *Salvadora persica*

1. Introduction

Industrial and rural wastes containing heavy metals are the major sources of water pollution which ultimately affect the human health by entering into the food chain (Laxen, 1983). The toxicity of heavy metals to water organisms has been a matter of awareness to biologists for many years. Heavy metals have been excessively added to the environment due to the rapid industrialization. Toxic metals such as Cd, Zn, Cr, Pb, Cu and others, find their ways to the industries such as metal machining, nickel batteries, pigments, electrolysis, electroplating and so on (Low and Lee, 1991). The recent expansion of industrial activities, including mining, smelting, and synthetic compounds creation have led to an exponential increase in the amounts of heavy metals released into the environment (Matheickal and Yu, 1999; McConnell and Edwards, 2008). These metals are non-biodegradable with the tendency of bioaccumulation in the living systems (Horsfall and Spiff 2004; Witek-Krowiak *et al.*, 2011; Wahid *et al.*, 2013). Heavy metals when present in high concentrations are familiar to be very toxic to all the living organisms (Giller *et al.*, 1998). Recovery of heavy metals from industrial waste streams has become very important in the recent times, as society realizes the environmental impacts of these persistent and toxic contaminants as well as the necessity for recycling and conservation of essential metals (Hashim and Chu, 2004). Although these are naturally present in the rocks, soils and water, but the environmental contamination via anthropogenic sources, due to increased industrialization has resulted in serious problems in the food chain. It consequently damaged the health of all organisms including the mankind (Jamal *et al.*, 2006). Therefore, there is a need to remove these heavy metals by an economical and environment friendly process (Barsha Dash, 2009).

The commonly used procedures for removing metal ions from aqueous streams include chemical precipitation, lime coagulation, ion exchange, reverse osmosis and solvent extraction (Rich and Cherry 1987). But these processes have some disadvantages like cost, sludge production, clogging, and time consumption. Therefore, the search for new cost-effective technologies for the removal of heavy metals from wastewaters has been directed towards biosorption, which is known for the last few decades. Some waste materials from the food industry have shown their capabilities to act as biosorbents for heavy metals (Volesky, 1986; Bailey *et al.*, 1999; Cheremisinoff, 2002; Velásquez and Dussan, 2009). Biosorbents due to their natural abundance, low cost and eco-friendly nature are the ideal materials to work as alternatives for the previously established heavy metal mitigation techniques (Kratochivl *et al.*, 1998).

Salvadora persica is a species of *Salvadora* (Hassan Suliman Halawany, 2012) which is a small tree or shrub with a crooked trunk, seldom more than one foot in diameter. The root bark of the tree is similar to sand, and the inner surfaces are an even lighter shade of brown (Reddy *et al.*, 2008; Kumar *et al.*, 2012). The infrared and atomic emission spectroscopic techniques were used in the study of the organic and inorganic structures and composition of *Salvadora* sticks. The results showed that the organic part of the sticks of *Salvadora persica* consists mainly of cellulose, hemicelluloses and lignin. The lignin content in the pulp is higher than its content in the outer layers (Khatak *et al.*, 2010).

Lead can contaminate the environment by anthropogenic sources as well as natural geochemical processes. It can accumulate along the food chain and is not amenable to biological degradation in humans and is extremely toxic and causes many diseases (Jain *et al.*, 1989; Toxicological profiles 1999; Dursun, *et al.*, 2003). Its excessive concentration exhibits noxious effects on plants as well (Kastori *et al.*, 1992; Opeolu *et al.*,2010). Therefore, in the present study, *Salvadora persica* as a novel sorbent was used for the removal of Pb(II) ions from wastewater. It was expected that the negatively charged polymeric species present in this plant can work as absorption sites for the removal of Pb(II) cations from aqueous solutions. Graphical concept for mitigation of lead ions from aqueous media using *Salvadora persica* as biosorbent material is shown in Figure 1.

2. Materials and methods

2.1 Preparation of *Salvadora persica* samples

The branches of *Salvadora persica* plant were collected and thoroughly washed with tap water in order to get rid of any impurity. Finally, the samples were rinsed with double distilled water (DDW), peeled off and dried in sunlight to remove the water contents. The dried material was grinded to make fine powder and passed through 80 µm sieve for uniform particle size.

2.2 Chemicals and standard solutions

Hydrochloric acid (HCl) and sodium hydroxide (NaOH) of analytical grade were purchased from Sigma-Aldrich for pH adjustments. The standard solutions of Pb(II) ions were prepared by dissolving the desired

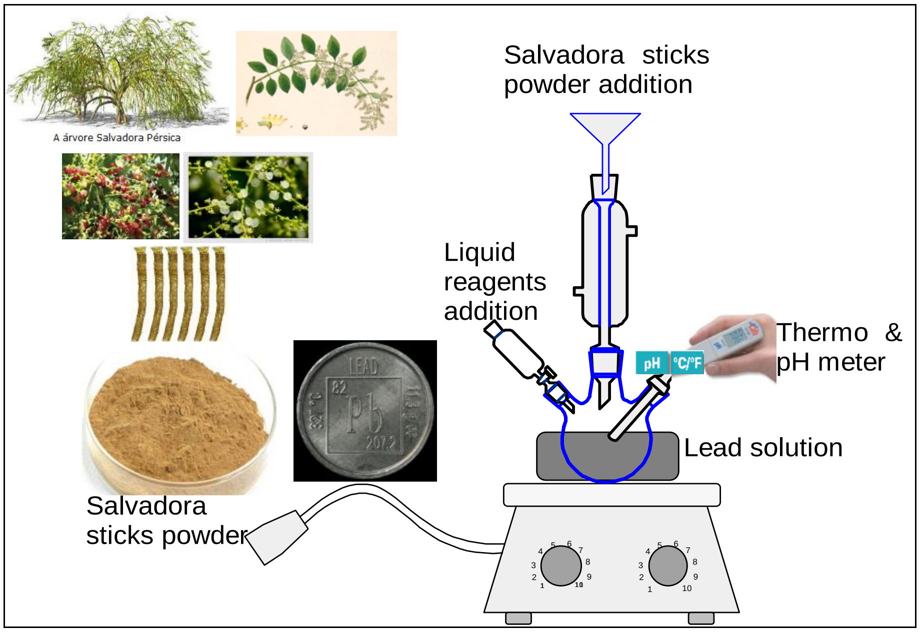

Figure 1: Graphical concept for mitigation of lead ions from aqueous media using *Salvadora persica* as biosorbent material.

2.2 Chemicals and standard solutions

Hydrochloric acid (HCl) and sodium hydroxide (NaOH) of analytical grade were purchased from Sigma-Aldrich for pH adjustments. The standard solutions of Pb(II) ions were prepared by dissolving the desired amounts of $Pb(NO_3)_2$ (Sigma-Aldrich) in DDW. The residual concentration of metal ions was measured by atomic absorption spectrophotometer (A Analyst 700 Perkin Elmer) using an air/acetylene flame. All the experiments were carried out in triplicate and the mean of the quantitative results was used for further calculations. For the calculation of mean value, the percent relative standard deviation was calculated and if the value of standard deviation for a sample was greater than 5%, the data was discarded.

2.3 Effect of Adsorbent dose

Six conical flasks were taken and 50 ml of 50 mg/L of Pb(II) ions solution was added in each of them. The adsorbent dose was ranged from 0.1 to 0.6 g with an increment of 0.1 g from flask 1-6. The mixtures were shaken for 30 min at 125 rpm. The samples were filtered and concentration of residual lead was measured.

2.4 Optimization of pH

The batch experiment was carried out by contacting 0.5 g of *Salvadora persica* with 50 ml of 50 mg/L of metal solution in 250 ml conical flask at pH value, ranging from 2 to 10. The pH of the solutions was adjusted either by HCl or NaOH, employing Metrohm 780 advanced pH meter. The mixture was shaken at 125 RPM for 30 min at room temperature, filtered and analyzed for lead contents.

2.5 Optimization of contact time and temperature

The time optimization was done by conducting the batch biosorption experiments with an initial metal ions concentration of 50 mg/L and 2.0 g/L biosorbent dosage, at different time periods ranging from 10-120 min with 10 min interval for each measurement. The effect of temperature was measured by performing experiments at 10, 20, 30, 40, 50 and 60 ^{o}C (30 min stirring at 125 rpm) at pre-optimized sorbent dose, pH, and time.

2.6 Isotherm and kinetic models

The data obtained from the studies was fitted by employing Langmuir, Freundlich and Dubinin-Redushekvich adsorption isotherms. Different kinetic models like Pseudo first order, Pseudo second order and Intra-particle diffusion were used for comparison with the experimental data. The thermodynamic parameters like Gibbs free energy, enthalpy and entropy were also calculated to observe the feasibility and spontaneity of the biosorption reaction.

3. Results and discussion

3.1 Effect of biosorbent dosages on Pb(II) sorption

The effect of various *Salvadora persica* dosages on the sorption of Pb(II) ions was studied and the results are shown in Figure 2. The results indicate that the minimum adsorption was 90.24% at 0.10 g dose of the adsorbent, while the maximum adsorption value was 97.07% at 0.50 g of *Salvadora persica*. It was noted that the adsorption increased with the increase in the adsorbent amount, until equilibrium was attained at the 0.50 g of sorbent. This was due to the reason that initially there were many free sites available on the surface of the cellularic material. Such behaviour was expected since the metal uptake capacity of the adsorbent increases with the increase in dose rate (Raju *et al.*, 2012).

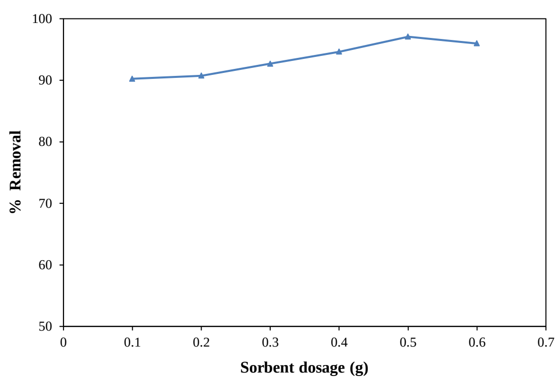

Figure 2: Variations in removal efficiencies (%) of Pb(II) ions at different Salvadora persica dosages

3.2 Effect of pH

The effect of pH was studied over the range from 2 to 10 and is shown in Figure 3. The results revealed that the maximum uptake of Pb(II) occurred at pH 6 and its removal efficiency was 98.54%. The above and below this pH value, the adsorption capacity decreased quite significantly. At the low pH value (2 to 4), the removal of Pb(II) ions was inhibited, possibly due to the competition between hydrogen and metal ions on the sorption sites, with an apparent dominance of hydrogen ions. But, as the pH was increased above 4, the active sites having negative charge density exposed on the adsorbate surface, causing more electrostatic attractions to the metal cations, therefore, higher biosorption onto the adsorbate surface occurred. The decrease in Pb(II) ions removal above pH 6 was due to the precipitation of Pb(II) ions as hydroxides (Awwad and Salem, 2012).

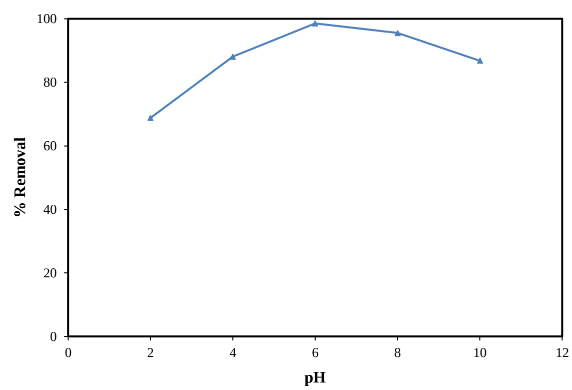

Figure 3: % age removal of Pb(II) ions at different pH values during biosorption process

3.3 Effect of time and temperature on Pb(II) sorption

The effect of contact time and temperature on adsorption of Pb(II) ions were studied and the results are shown in Figure 4. The Figure 4A indicates that minimum removal efficiency was 92.12% after 10 min, while the maximum removal was attained at a contact time of 80 min which was 98.30% and remained constant till 120 min. It was important to note that the removal rate of sorbate was very rapid initially, but it gradually decreased with time until it reached the equilibrium. This phenomenon was attributed to the fact that a large number of vacant surface sites are available for adsorption at the early stages, and after a lapse of time, the remaining vacant surface sites were difficult to be occupied due

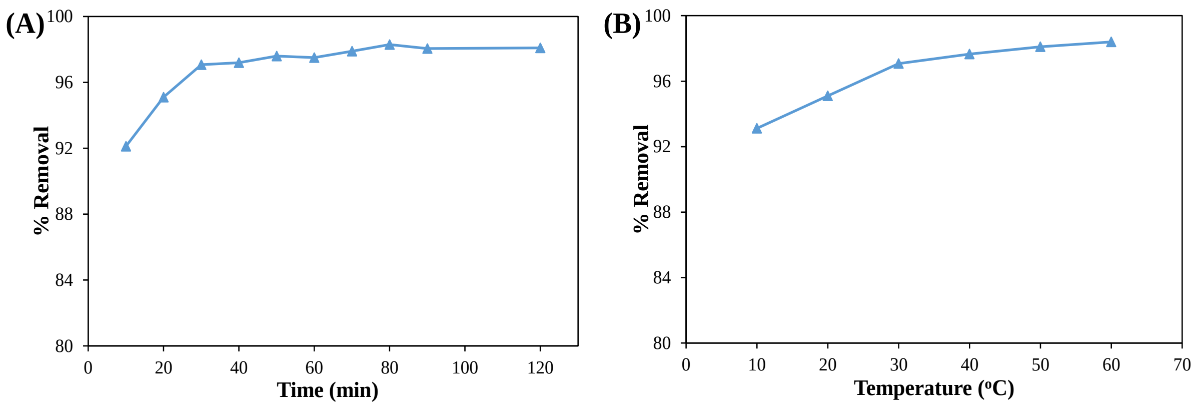

Figure 4: Effects of (A) contact time (min) and (B) temperature (°C) on biosorption of Pb(II) ions

to repulsive forces between the solute molecules on the solid and bulk phases. Initial removal occurred immediately as soon as metal ions and adsorbate came into contact but after that when some of the easily available active sites were occupied, the metal needed more time to find out the sites for binding (Kord-Mostafapour *et al.*, 2012).

Figure 4B shows that as the temperature was increased, the removal efficiency of biosorbent powder for Pb(II) ions also increased. The maximum adsorption of Pb(II) ions was obtained at 60°C. The increase in removal efficiency with an increase in temperature was due to the fact that kinetic energies of the metal ions increased with an increase in temperature. The higher kinetic energy increased their chances of collisions with sorbate molecules which eventually enhanced the metal-sorbate interactions.

3.4 Adsorption isotherms

Three adsorption isotherms namely Langmuir, Freundlich and Dubinin-Redushekvich were applied to the data obtained during the sorption studies and results are shown in Figure 5. The Figure 5A indicates that the value of correlation coefficient (R^2) was 0.8909 for Langmuir expression. While R^2 values for Freundlich and Dubinin-Redushekvich isotherms were 0.527 and 0.6934, respectively, (Figure 4B & 4C). It is evident that the Langmuir adsorption isotherm was the best fitted among the employed isotherm models. The Langmuir adsorption isotherm follows the assumption that sorption takes place at specific homogeneous sites within the sorbent molecules (Sari and Tuzen, 2009). While, the Freundlich and Dubinin-Redushekvich adsorption isotherms give information for the adsorption on a heterogeneous surface and the adsorption mechanism based on Gaussian energy distribution of heterogeneous system, respectively. The obeying of Langmuir isotherm in this study revealed that the surface of *Salvadora persica* was homogenous, which was further highlighted from the very low R^2 values of other two isotherms which showed the lack of heterogeneous regions in the investigated material

3.5 Application of the Kinetic models for Pb(II) sorption

Kinetics of biosorption is one of the most promising characteristics to understand the rate determination of biosorption reactions. In this regard, the pseudo-first-order, pseudo-second-order and Intra-particle diffusion kinetic models were applied to the experimental data obtained in the present studies (Figure 6). Lagergren first-order equation given below is the most popular kinetic equation for the rapid initial phase.

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad \text{-----------------}(1)$$

where q_t is the amount of adsorption time t (min) (mg g^{-1}); k_1 the rate constant of the equation (l/min); q_e is the amount of adsorption equilibrium (mg g^{-1}). The adsorption rate constant, k_1, was determined by plotting of ln ($q_e - qt$) against t. The pseudo second-

order model predicts the behaviour over the whole time adsorption similar to the adsorption mechanism used for the determination of rate-controlling step of

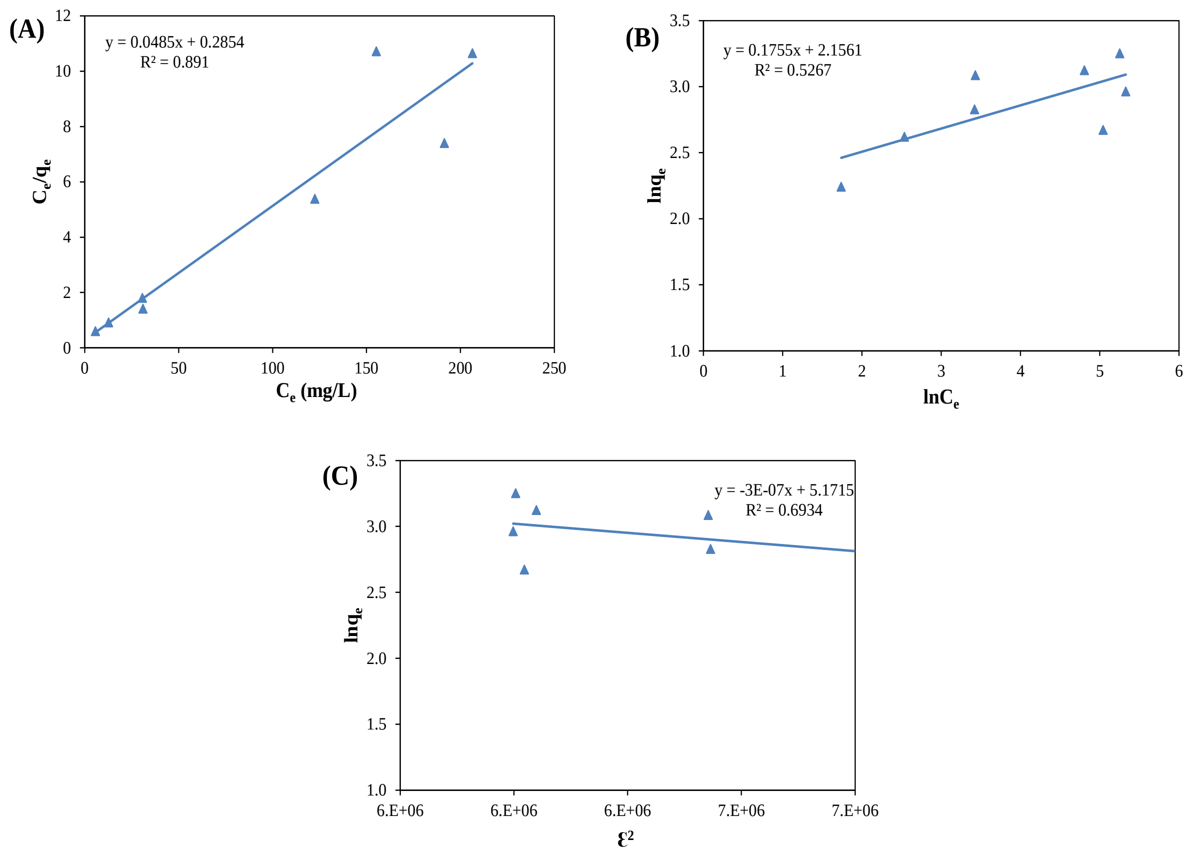

Figure 5: Correlation coefficient (R^2) values of, (A) Langmuir, (B) Freundlich and (C) Dubinin-Redushekvich adsorption isotherms for biosorption of Pb(II) ions on *Salvadora persica*

sorption reaction. The pseudo second-order rate equation is expressed as:

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

The Intra-particle diffusion model can be represented by the equation

$$q_t = k_{iD} t^{0.5} + C \text{ --------------------------- (3)}$$

Where k_i is the intra-particle diffusion rate constant (mg g^{-1} $min^{-0.5}$) and the intercept C, obtained by extrapolation of the linear portion of the plot of q_t versus $t^{0.5}$ (Ofomaja, 2010).

The plotted data indicated that the R^2 values for pseudo-first-order, pseudo-second-order and Intra-particle diffusion kinetic models were 0.1906, 0.9999 and 0.3498, respectively. The results clearly showed that the pseudo second order kinetic model was best fitted among the all other employed kinetic methods. It is thus evident that biosorption of Pb(II) on *Salvadora persica* is pseudo-second order reaction and the removal of metallic cations from aqueous solution took place by physicochemical interactions.

3.6 Thermodynamic studies of Pb(II) sorption on *Solvadora persica*

The adsorption standard free energy changes (ΔG^o) was calculated by using the following equation.

$$\Delta G^o = -RT\ln K_D \text{ ------------------------------- (4)}$$

Where *R* is the universal gas constant and *T* is the temperature in kelvin (Li *et al.*, 2005).

Table 1: Calculated thermodynamic parameters

ΔS° (kJ^{-1}/mol)	ΔH° (kJ/mol)
91.96947	-21471

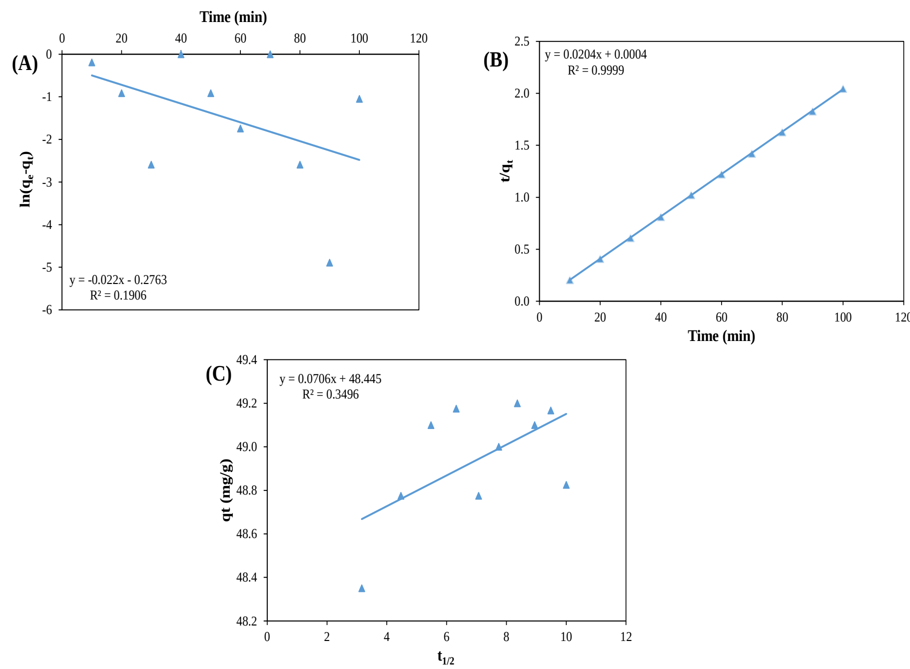

Figure 6: Correlation coefficient (R^2) of (A) Pseudo first order, (B) Pseudo second order and (C) Intraparticle Diffusion kinetic models for biosorption of Pb(II) ions on *Salvadora persica*

The thermodynamic parameters such as Enthalpy ΔH° and Entropy ΔS° were studied for *Salvadora Persica* as shown in Table 1. The negative value of ΔH° showed that adsorption is exothermic.

The negative value of ΔG showed that process is spontaneous. The positive value of ΔS° indicates the increasing randomness at the solid/liquid interface for the sorption of Pb(II) ions onto the *Salvadora persica*.

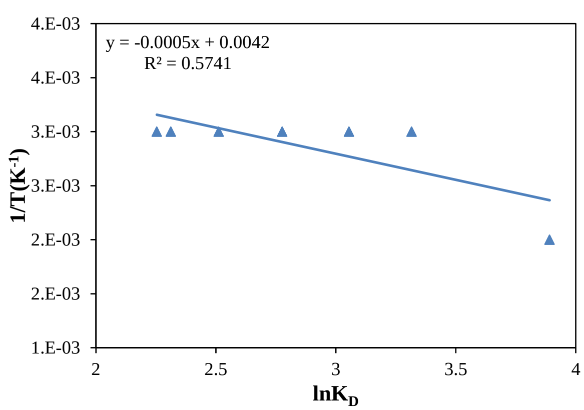

Figure 6: Thermodynamic studies for biosorption of Pb(II) ions on *Salvadora persica*

4. Conclusion

In this study, the highest percentage removal of lead ions was obtained at the biosorbent dosage of 0.5 g at pH 6. The optimum time and temperature for sorption of Pb(II) ions was 30 min and 30 °C, respectively. Langmuir adsorption isotherm was best fitted to the isothermal data of *Salvadora persica* which showed that the sorption on sorbent surface is homogeneous. *Salvadora persica* followed the pseudo second order kinetic model which indicated the removal of Pb(II) ions through physicochemical interactions. Thermodynamics studies revealed that biosorption process was spontaneous and exothermic in nature. Therefore, it is concluded that *Salvadora persica* is an efficient and environmental friendly biosorbent material for the removal of Pb(II) ions

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