International Journal of Research in Advent Technology, Vol.7, No.3, March 2019
E-ISSN: 2321-9637
Available online at www.ijrat.org

Biosorption of Pb^{++} ions from waste waters using the waste leaves of *Cedrus deodara*

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Abstract-The introduction of heavy metals in the fresh or saline water has become one of the serious problems. Through different food chains, they can deposit in the tissues of human and cause the serious health problems. Lead is one of the hazardous metals and causes harmful effects to human and other living organisms, even at very low concentrations. In the present study, the biosorption of Pb^{++} ions has been carried out under batch operations on to the waste leaves of *Cedrus deodara*. The active or organic groups onto the surface of biosorbent were identified by FTIR characterizations. The maximum biosorption is recorded 47.80 %, 30 % and 88.24 % at the contact time 70 minutes, 1 g dosage of biosorbent and higher pH 6. The equilibrium data of biosorption have been tested with Langmuir and Freundlich isotherm models. The biosorption capacity of biomass was found to be 11.494 mg/g, evaluated from Langmuir isotherm model. The rate of biosorption and other parameters were evaluated by pseudo-first order and pseudo-second order models. The experimental data best fitted to pseudo- second order kinetic model with the regression value, R^2 = 0.992 and the rate constant evaluated 4.310 g mol^{-1} min^{-1}.

Keywords: Lead, Biosorption, Batch operations, Isotherms, Kinetics.

1. INTRODUCTIONS

The water pollution due to heavy metals has now become one of the challenging issues in the world and the exposure of heavy metals into aquatic bodies increased very dramatically due the evolution and development of different industries in the world since last two or three decades. The Heavy metals are basically defined as metals with relatively high densities, atomic weights, or atomic numbers. Biologically, these metals are necessary for the different physiological activities in all the organisms under the concerned limits and beyond the limits they are definitely harmful and cause life threatening problems to human and other organisms [1-2]. Through different food chains, heavy metals can accumulate in the tissues and organs of human. Some of heavy metals are very harmful to all living organisms even at very low concentrations. The conventional methods included precipitation, reverse osmosis; membrane driven operations, electrowinning, carbon adsorption etc are suffering from poor performance, high investments, and take longer time, sludge generating and low applicability for large scale operations [3]. Biosorption is a better alternative over such methods and the efficiency of biosorption is based on the choice of suitable biosorbents. Biosorption is defined as the uptake of heavy metal ions from contaminated water by using a waste biomass. The performance of biosorption can be enhanced by applying the optimized conditions in the batch systems. Such optimized conditions are higher dosage of biomass, higher acidic pH, lower metal ion concentrations and moderate temperatures [4]. The choice of biosorbents is very important step in the process of biosorption and the high metal uptake capacity and abundant availability of the biomasses can make biosorption more convenient. The plant and animal based biomasses has frequently been used as biosorbents such as waste leaves, barks, roots, peels, agriculture wastes, tea waste, algal and fungal biomasses, and dead animal parts etc [5,6]. Lead (Pb) is a very common heavy metal and releases into environment through anthropogenic activities such as leaded gasoline, smelting, combustion, battery recycling, lead containing pipes etc. It shows many harmful effects to human in reproductive, nervous and urinary systems and also carcinogenic. Lead retards the rate of photosynthesis and growth of plants [4]. The plant *Cedrus deodara* is a common evergreen and abundant gymnosperm and is found in Uttarakhand, Himanchal Pradesh, Jammu and Kashmir and the hills of north east Himalayas. The niddle like leaves have been collected from the hills of Uttarakhand, India.

2. MATERIAL AND METHODS

After collection of waste leaves, the leaves were washed 2 to 3 times with double distilled water and dried for 24 hours in the laboratory. The moisture of the leaves was removed by the drying of leaves in the tray dryer for 3 hours at 65-70 ^{0}C under controlled conditions. Finally, the dry leaves have been grinded into particle size 120 microns and preserved in the sealed bottles. About 0.1 g leaf powder was used for the FTIR characterizations. The synthetic waste water was prepared by the dissolution of $Pb(NO_3)_2$ in the double distilled water. The pH of the stock solution was maintained 4 because the acidic range favors the solubility of metal ions. The stock solution containing 1000 mg/L of lead ions was diluted in different working solutions having the concentrations 10, 20, 30, 40 and 50 mg/L. The pH of working solutions was adjusted 1, 2, 3, 4, 5 and 6 by using 0.1 N HCl or 0.1 N NaOH. A different amount of biomass i.e. 0.1 to 1.0 g used for the batch operations. A requisite amount of biomass was treated with 100 ml of working solution containing a desired concentration of Pb^{++} ions at an rpm 170. The concentration of metal ions in the solution was identified by Atomic Absorption Spectroscopy (Thermo Scientific: iCE 3000 Series). The biosorption efficiency is calculated by using the following formula:

Biosorption efficiency = $C_1 – C_2/ C_1$ *100

Where C_1 and C_2 are the initial and final concentrations of the contaminated waste water.

3. RESULTS AND DISCUSSION

3.1 FTIR Characterizations

Fourier transform infrared spectroscopy (FTIR) is depending on the interference of radiation and the spectrum is observed through the technique of interference. The FTIR spectrum of untreated leaf powder of *Cedrus deodara* in the range of 4000 to 450 cm^{-1} is given in the Fig:1. The FTIR study confirms the presence of some important organic groups on the surface of adsorbent. These groups involve in the complexation with metal ions. The peaks have obtained at 3380 cm^{-1}, 2921 cm^{-1}, 2851 cm^{-1}, 1735 cm^{-1}, 1622 cm^{-1}, 1543 cm^{-1}, 1516 cm^{-1} 1317 cm^{-1}, 1248 cm^{-1}, 1106 cm^{-1}, 1061 cm^{-1} and 763 cm^{-1}. Such peaks are due to the presence of –OH, –NH, C–H, $-CH_2$, C=O, C=C, $–CH_3$, C–N, C-O, C-N etc on the surface of leaf powder.

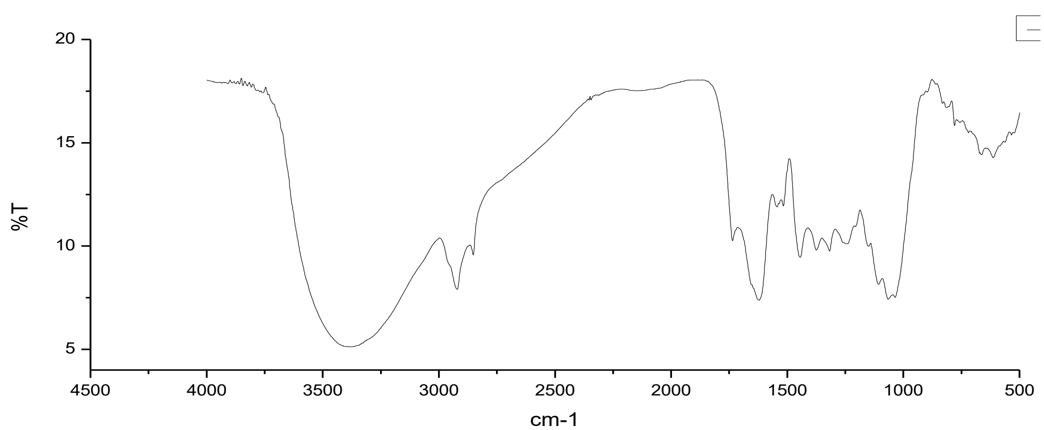

Fig. 1 FTIR Characterization of *Cedrus deodara* leaf powder

3.2 Effect of pH and contact time

The most important factor of biosorption is pH of the solutions. At lower pH, the active or binding groups on the biosorbent undergo protolysis and get positively charged [4]. Hence, repulsion occurs between such groups and metal ions that causes less biosorption but about all the active sites are purely available for the complexation with metal ions and causes high removal efficiency at higher pH. The biosorption efficiency of lead is recorded 8.01 % at pH 3. It slowly increases to 26.10 % at pH 4. After that it increases 76.28 % at pH 5 and the maximum percentage biosorption 88.24 % is achieved at the pH 6 (Fig: 2A). The applied batch operations show that a minimum time is required for the better interaction of metal ions and leaf powder. In general, the biosorption increases with the increase of contact time and becomes constant or slowly increases after a certain time [5]. The removal efficiency for Pb^{++} ions was observed 20.10 % at initial contact time 10 minutes. It increases very regularly to 35.0 % at contact time 50 minutes. The maximum biosorption efficiency is recorded 47.80 % at contact time 70 minutes, concentration 10 mg/L and pH 4 (Fig: 2B).

3.3 Effect of amount of biosorbent and temperature

The biosorption of metal ions usually increases with the increase of the amount of biomass due to the larger surface area at same particle size [6]. The number of binding groups for complexation increases with the dosage of biosorbents. The biosorption is found only 9.81 % at 0.2 gm of biosorbent and increases to 19.09 % at 0.7 gm. After that, it increases to 25.40 % at biosorbent dose 0.9 gm. The percentage removal of lead is recorded 30 % at the highest amount of biomass i.e.1.0 gm (Fig: 3A). The experimental results show that the removal efficiency of lead (II) ion on to the leaf powder increases with the rise of temperature. It is due the factor that the adsorbate particles escaped from the outer surface to inner surface of the biosorbent as the temperature increased. After a certain temperature, the removal becomes constant or decreased; actually it happens due to the further dissolution of adsorbed metal ions in the waste water [7]. The biosorption efficiency 29.28 %, recorded at 10^0C and increases very regularly to 45.91 % at 60^0C. The maximum percentage biosorption was found 47.39 % at 70^0C (Fig: 3B).

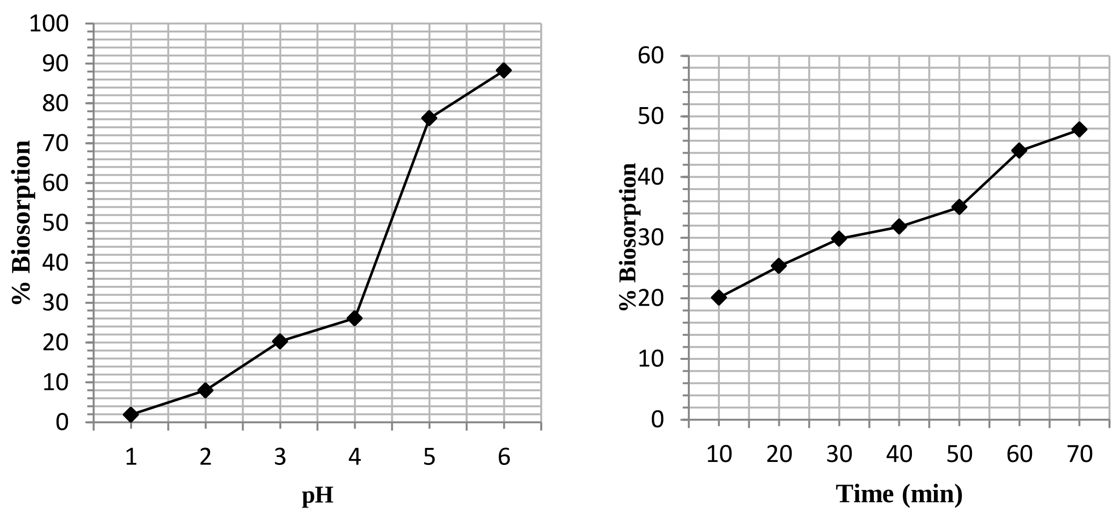

Fig. 2 (A) Effect of pH (B) Effect of contact time

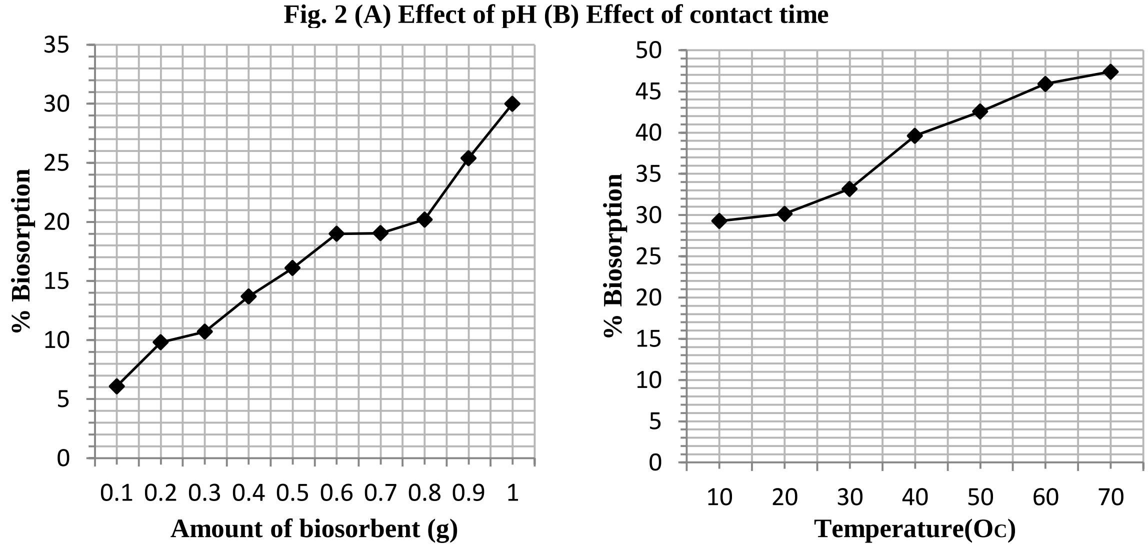

Fig. 3 (A) Effect of dosage (B) Effect of temperature

3.4 Effect of concentration

The biosorption of metal ions is also based on the concentrations of aqueous solution. The percentage removal of metal ions is usually decreased with the increase of concentrations but the amount of sorbate ions increased (Fig: 4); this may due to the motive power of concentration differences as the initial metal ion concentration [4-7]. The biosorption 25.30 % was found at 10 mg/L and that decreases to 13.98 %. The maximum amount of lead sorbate was found to be 6.99 mg/g at 50 mg/L after contact time 25 minutes and at pH 4.

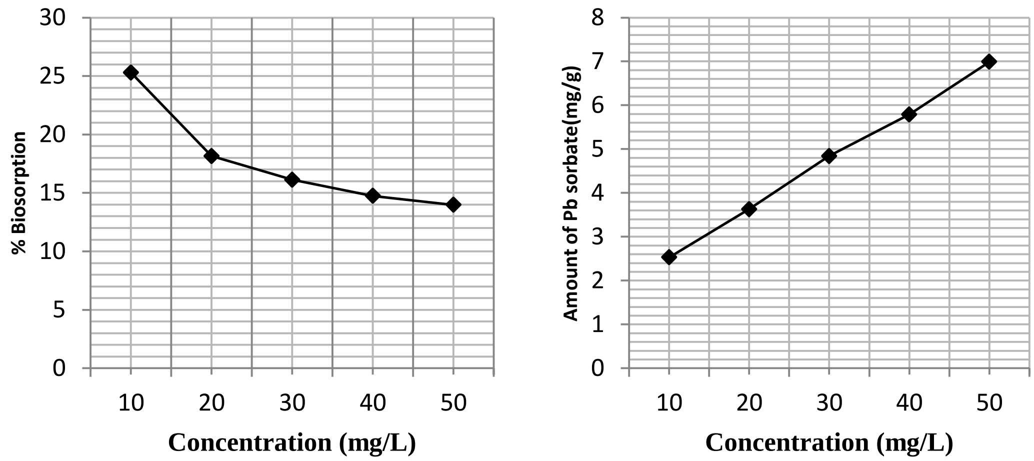

Fig. 4 Effect of concentrations

3.5 Kinetics of biosorption

The kinetics of biosorption gives a better explanation of rate of biosorption in the applied batch operations and designation of optimized batch conditions for the maximum removal of metal ions from waste water. The two common kinetic models i.e. Lagergren's pseudo first order and pseudo second order were applied [8,9]. The Lagergren's pseudo-first-order is mathematically defined as:

$$\ln (q - q_t) = \ln q - k_1 t$$

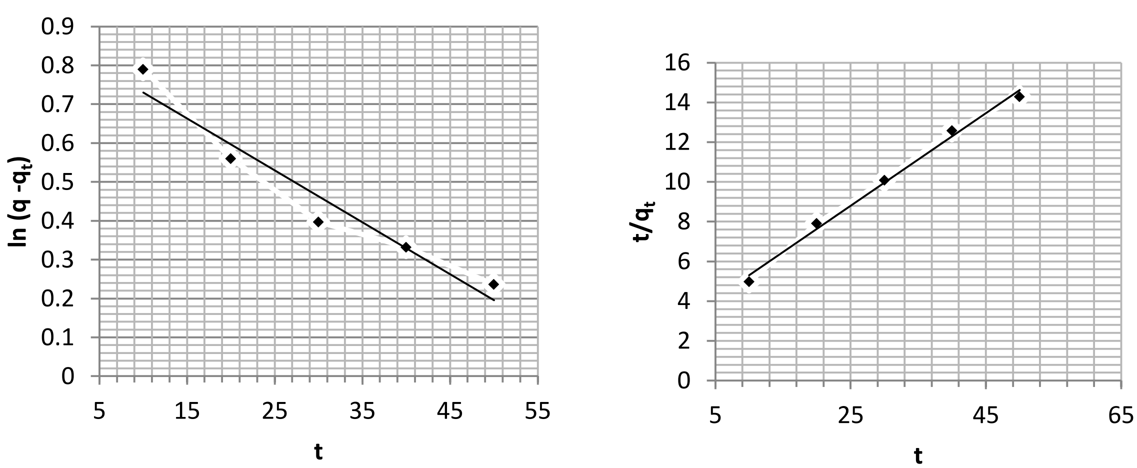

Fig. 5 (A) Pseudo first order (B) Pseudo second order kinetic models

Where q and q_t are the amount of lead uptake by the leaf powder at equilibrium and at a time t in mg g^{-1} and k_1 is the rate constant for first order kinetics in min^{-1}. The value of rate constant is obtained from plot ln ($q-q_t$) vs t. The value of k_1 is calculated 0.013 min^{-1}. The value of regression (R^2) is found 0.929 and that indicates a better applicability of pseudo first order kinetic model for lead biosorption onto the biomass. Pseudo-second-order explains the dependency of biosorption rate on the square root of unoccupied binding sites. A simplest mathematical form of the pseudo second order model is given as below:

$$t/q_t = (1/k_2 q^2) + (1/q)t$$

Where k_2 is the pseudo second order rate constant (g/mol/min) and q and q_t are the amount of metal sorbed on the surface of adsorbent in mg g^{-1} at a specific time t. These all second order kinetic parameters have been calculated from the graph t/q_t vs t. The rate constant k_2 is found 4.310 g/mol/min and high value of R^2 (0.992) indicates pseudo second order model is better applicable than pseudo first order.

3.6 Biosorption isotherms: The biosorption capacity and suitability of biosorption in applied batch operation can be checked by using different isotherm models. These isotherm models are characterized by some parameters which gives important information of metal sorption. The equilibrium data of adsorption were checked by Langmuir and Freundlich models. Langmuir isotherm model [7] is used for the evaluation of biosorption capacity of biosorbents and related to the interaction of metal ions with the homogeneous binding sites inside the biosorbents. Mathematically, the linear form of the model is written as:

$$C_2/q_e = 1/K_l X + 1/K_l * C_2$$

Where, C_2 and q_e are related to equilibrium concentration of contaminated water and amount of metal sorbate on the surface of biosorbents (mg/g). The constant K_l and X are the biosorption capacity (mg/g) and biosorption equilibrium constant (L/mg). The values of K_1 and X are found 11.494 mg/g and 0.0318 L/mg from the graph C_2/q_e vs C_2; the regression value (R^2) is found 0.920. A characteristic dimensionless parameter is R_L can be defined mathematically as:

$$R_L=1/1+XC_1$$

Where, X and C_1 are Langmuir equilibrium constant and the initial metal ion concentration (mg/L). The value of R_L is found less than one at all concentrations. It indicates better applicability of monolayer adsorption.

The Freundlich isotherm [10] is concerned with the binding sites on the heterogeneous surface of biosorbent have different energy variations. The Freundlich model can be given as:

$$\log q_e = \log K_f + 1/n \log C_2$$

Where q_e and C_2 are the amount of lead (II) ions adsorbed (mg/g) and the equilibrium concentration of solution (mg/L). The Freundlich constants K_f and n are the adsorption capacity and intensity of biosorption, respectively. The values of K_f and 1/n are evaluated from the slope and intercepts of the plot log q_e versus log C_2 and found 0.769 mg/g and 0.174. Here, the value of 1/n is less than one and that indicates favorable biosorption process. A high value of correlation coefficient (R^2) 0.989 indicates Freundlich isotherm model is more favorable than Langmuir model.

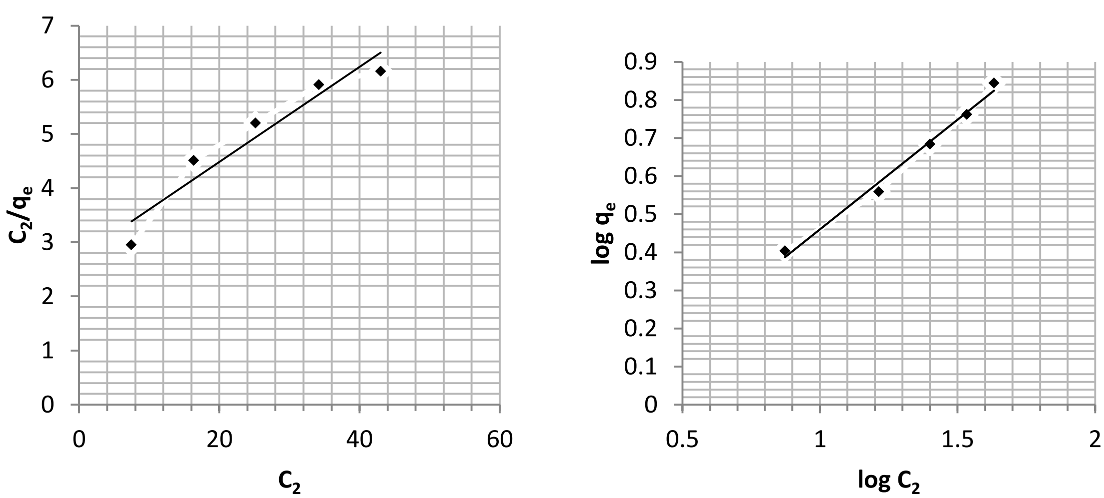

Fig. 6 (A) Langmuir isotherm model (B) Freundlich isotherm model

4. CONCLUSIONS

The present work has explored the potential use of waste leaves for the removal of lead from waste water. The batch adsorption data were fitted to kinetic and isotherm models and their paramenters evaluated. All these parameters indicated the suitability of lead adsorption on the waste leaf powdre of *Cedrus deodara.*

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