

# Reduction of Heavy Metal Concentration from Wastewater using *Atriplex Farinosa* Leaves: Isotherms and Kinetics

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**Abstract-** Liquid waste-wastewater- is essentially the water supply of the community after it has been used in a variety of applications. In recent years, heavy metal concentrations, besides other pollutants, have increased to reach dangerous levels for living environment in many regions. Among the heavy metals lead has the most damaging effects on human health. It can enter a human body through uptake of food (65%), water (20%) and air (15%). In this background certain low cost and easily available biosorbent was used and reported in this study. The scope of the present study is to remove Lead from its aqueous solution using *Atriplex Farinosa* Leaves as biosorbent. The results showed that the biosorption capacity of *Atriplex Farinosa* Leaves biosorbent was more for Lead removal. The Langmuir, Freundlich, Tempkin and Dubinin-Radushkevich (D-R) models were used to describe the biosorption equilibrium of Lead *Atriplex Farinosa* Leaves biosorbent and the biosorption followed the Langmuir isotherm. The kinetic models showed that the pseudo-second order rate expression was found to represent well with the biosorption data for the biosorbent.

**Keywords:** *Atriplex Farinosa*, Central composite design, Lead, Isotherms, Kinetics, FTIR.

## 1. INTRODUCTION

The presence of toxic and polluting heavy metals in wastewaters from industrial effluents, water supplies and mine waters and their removal has received much attention in recent years. The amount of heavy metals that industrial wastewaters often contain is considerable and would endanger public health and the environment if discharged without adequate treatment [1].

Heavy metals are elements such as Pb (Lead), Zn (Zinc), Cu (Copper), Cd (Cadmium), Ni (Nickel), Ag (Silver), Cr (III) (Chromium), Hg (Mercury), Fe (Iron), Co (Cobalt), As (Arsenic) [2] which are usually associated with toxicity and natural components of the Earth's crust. Industrial processes have greatly enhanced the mobilization of heavy metals. Excess heavy metals are introduced into aquatic ecosystems as by-products of industrial processes and acid-mine drainage residues. They are highly toxic as ions or in compound forms: they are soluble in water and may be rapidly absorbed into living organisms [3]. After absorption, these metals can bind to vital cellular components, such as structural proteins, enzymes and nucleic acids, and interfere with their functioning. Due to the stringent environmental laws or increased awareness of people about environmental aspects, treatment of the effluent streams has got exceptionally great importance now a day.

Lead is rarely found as the free metal in nature, but it is present in several minerals, principally in galena (PbS) the main source for lead production. It is also found as anglesite (PbSO<sub>4</sub>) and cerrusite (PbSO<sub>3</sub>). Lead is one of the most commonly used non-ferrous metals. It has many applications; its largest use is in making storage batteries, most of which are recycled. As a result of its resistance to corrosion and its malleability, it finds use in building constructions, storage tank lining and corrosive liquid containers. Lead is present in exhaust gases mainly as lead halides and oxides, but incomplete combustion results in about 10% of alkyl lead compounds also being present. Other source of lead emissions are copper and nickel smelters, iron and steel production. Estimates vary as to the importance of vehicle emissions as the source of the lead contamination [4].

Therefore, there is a huge demand for innovative and affordable methods to remove heavy metals from industrial effluents and wastewater. Chemical and electrochemical precipitation, cationic and anionic ion-exchange resins, membrane filtration, and sorption have historically been the most frequently used techniques for removing heavy metals from wastewaters [5]. While some procedures, like reverse osmosis and ion-exchange, are expensive, others, like precipitation processes, have issues with the disposal of metal-containing sludge.

The objective of the present study is to explore the feasibility of biosorption technique for lead biosorption from aqueous solutions using low cost, non-conventional, easily and abundantly available plant biomass based material *Atriplex Farinosa* Leaves powder. From the survey of the literature, no information is available for the biosorptive removal of lead by using the above mentioned biosorbent. So the above biosorbent was chosen for the present study as they are abundantly available in nature for the removal of lead batch process. The functional groups on the surface of the biosorbents that contributes to the biosorption are characterized using Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD) analyses. Four biosorption isotherm models like Langmuir, Freundlich, Tempkin and Dubinin-Radushkevich (D-R) are used to study the fit of the experimental equilibrium data obtained in the study. The pseudo first order, pseudo second order and Elovich models are tested with experimental data for their validity. The thermodynamics of the biosorption process is also investigated and the changes in Gibbs free energy, enthalpy and the entropy are determined. Influence of various physio-chemical parameters on metal removal efficiency is explained in terms of models obtained from Response Surface Methodology (RSM). Optimization of

important process parameters like temperature, solution pH, biosorbent dosage and initial metal concentration for the efficient removal of Lead from aqueous solution was determined by RSM. This study is intended to establish an efficient, effective, ecofriendly and economically viable process for the removal of metals from wastewater effluent.

## 2. MATERIALS AND METHODS

### 2.1 Biosorbent

*Olea Europaea* is a deciduous tree that grows up to 8m tall, it is monoecious, with a single trunk and rounded crown. *S. africana* has smooth and flaking bark that is grey or pinkish brown. The leaves alternate, crowded at the ends of branches, orbicular, 8–15 cm long x 8–15 cm across. Leaves are 3-5 lobed and covered in stellate hairs. *Sterculia africana* sheds its leaves during the dry season and comes into flower before the leaves reappear at the start of the monsoon. It was also a treatment to treat head lice. It is an important fodder and the wood was used to make fishing platforms.



Fig 2.1: Biosorbent Preparation from *Atriplex Farinosa* Leaves.

### 2.2 Chemical

NaOH and HCl were the additional chemicals used in the current study. Solutions' pH can be changed using 0.1 N HCl and 0.1 N NaOH. All compounds were employed as analytical reagents (AR).

Stock solutions of lead concentration 1000 mg/L were prepared by dissolving 1.6 g of  $Pb(NO_3)_2$  and 4.4 g of  $Zn(SO_4) \cdot 7H_2O$  in 1000 ml of distilled water. The solution was prepared using standard flasks. The range of concentration of the prepared metal solutions varied between 20 and 100 mg/L. The solutions were prepared by diluting the lead stock solution, which were obtained by dissolving in deionized water.

$$\text{Pb (or) Zn equivalent to 1g} = \frac{\text{Molecular wt. of } Pb(NO_3)_2 \text{ (or) } Zn(SO_4) \cdot 7H_2O}{Pb \text{ (or) Zn equivalent wt} \times \text{Purity.}}$$

### 2.3 Apparatus

The total metal concentration in solution was analyzed with Atomic Absorption Spectrophotometer (GBC Avanta Ver 1.32, Australia) at a wavelength of 217 nm for lead metal.

A pH meter from Systronics and an electronic balance from Shimadzu were used to determine the pH of the adsorbate and the weight of the adsorbent.

### 2.4 Batch Biosorption Experiments

#### 2.4.1 Biosorption isotherm models:

Biosorption isotherm helps in determining the properties of the biosorbents such as pore volume, pore size or energy distribution and specific surface area. The isotherm curve can also be utilized to obtain information concerning the desorption mechanism strictly connected with interaction between the biosorbent and adsorbate molecules. Therefore, the efficiency of an industrial biosorbent can be assessed through this curve. The correct interpretation of experimental biosorption isotherm can be realized in terms of some mathematical equations called biosorption isotherm model equations. Such equations are derived assuming an ideal physical model for the biosorption system. The model assumptions are usually a result of experimental observations. The experimental results allow for the formulation of a hypothesis about the character of the biosorption process. This hypothesis can be tested experimentally and if found suitable, could be developed into a theory, i.e., a suitable biosorption isotherm equation. The resulting biosorption isotherm offers valuable data for evaluating performance. They first aid in determining whether a certain biosorbent can achieve the desired purity level. This is important when multiple impurities are present and one or more impurities are poorly adsorbed. Secondly, the isotherm allows calculation of uptake ( $q_e$ ) at equilibrium, which has a major impact on the process economy. It can also be used to predict the relative performance of different types of biosorbents.

Biosorption isotherm studies were conducted by contacting 0.1 g of *Atriplex Farinosa* Leaves powder with 30 ml of Lead metal solutions of different concentrations in the range of 20 – 100 mg/L, at a temperature of 303 K and optimum pH of metals. These solutions were agitated at 180 rpm for equilibrium time and then analyzed for equilibrium concentration of metal in solutions. This entire procedure was repeated for different temperatures of 303, 308, 313 and 318 K. The same procedure was repeated with 0.1 g of *Ficus Hippida* leaves powder under similar conditions at different temperatures ranging from 303 – 318 K.

Prior to 1914 only a few theoretical interpretations of biosorption isotherms were in use. But thereafter, several isotherm equations were put out by various researchers. Among those used often are:

- Langmuir isotherm
- Freundlich isotherm
- Tempkin isotherm
- Dubinin - Radushkevich isotherm

### 2.4.1.1 Langmuir isotherm

The Langmuir biosorption isotherm [7] was based on the following assumptions:

- Fixed number of biosorption sites: at equilibrium, at any temperature, a fraction of the biosorbent surface sites ( $\theta$ ) is occupied by adsorbed molecules and the rest ( $1-\theta$ ) is free.
- All sorption processes are homogeneous.
- There is only one sorbate
- One sorbate molecule reacts with only one active site.
- No interaction between the sorbate species.
- A monolayer surface phase is formed.

The equation proposed by Langmuir was universally applicable to chemisorption with some restrictions involving physical biosorption. This equation is applicable to the physical or chemical biosorption on solid surface with one type of biosorption active center. As long as its restrictions and limitations are clearly recognized, the Langmuir equation can be used for describing equilibrium conditions for sorption behavior in different sorbate-sorbent systems or for varied conditions within any given system. The Langmuir equation is given by:

$$q = \frac{q_{\max} K_{aeq}}{1 + K_{aeq}} \quad (2.1)$$

The constant of Langmuir  $b$  (L/mg) is correlated with the biosorption of energy and  $Q_{\max}$  denotes monolayer biosorption capacity of the biosorbent (mg/g). The Langmuir model was linearized as needed to fit the experimental results.

$$\frac{1}{q} = \frac{1}{q_{\max}} + \frac{1}{K_a q_{\max} C_{eq}} \quad (2.2)$$

### 2.4.1.2 Freundlich isotherm

Freundlich biosorption isotherm was proposed by Boedecker in 1895 as an empirical equation. Later Freundlich [8] made some useful modifications as a result of which, it assumed great importance. The Freundlich biosorption equation can be written as:

$$q = KC_{eq}^{\frac{1}{n}} \quad (2.3)$$

Taking the logarithm of both sides,

$$\ln q = \ln K + \frac{1}{n} \ln C_{eq} \quad (2.4)$$

Where "q" denotes the equilibrium biosorption capacity (mg/g), "C<sub>eq</sub>" is the equilibrium concentration of the adsorbate in solution, "K" denotes the biosorption process constant, and "n" denotes the intensity of the biosorption process.

### 2.4.1.3 Tempkin isotherm

Tempkin and Pyzhev proposed that the heat of biosorption of all the molecules in the layer would decrease linearly with coverage because of the indirect adsorbate/biosorbent interaction. [9]. The Tempkin isotherm's linear form can be expressed as:

$$q = \frac{RT}{b} \ln(A_T C_{eq}) \quad (2.5)$$

Where  $A_T$  (L/mg) and  $b_T$  are Tempkin isotherm constants, 'T' is absolute temperature in Kelvin and 'R' is the universal gas constant (J/mol.K).  $C_{eq}$  is the equilibrium concentration of the adsorbate.

### 2.4.1.4 Dubinin-Radushkevich isotherm

The Dubinin-Radushkevich (D-R) [10] model was also applied to estimate the porosity apparent free energy and the characteristics of biosorption. The D-R isotherm does not assume a homogeneous surface or constant biosorption potential. The D-R model has commonly been applied in the following Eq. (2.6) and its linear form can be shown in Eq. (2.7):

$$q_e = Q_m \exp(-K\epsilon^2) \quad (2.6)$$

$$\ln q_e = \ln Q_m - K\epsilon^2 \quad (2.7)$$

Where  $K$  is a constant related to the biosorption energy,  $Q_m$  the theoretical saturation capacity,  $\epsilon$  the Polanyi potential, calculated from Eq. (2.8).

$$\epsilon = RT (1 + 1/C_e) \quad (2.8)$$

The slope of the plot of  $\ln q_e$  versus  $\epsilon^2$  gives  $K$  ( $\text{mol}^2 (\text{kJ}^2)^{-1}$ ) and the intercept yields the biosorption capacity,  $Q_m$  ( $\text{mg g}^{-1}$ ). The mean free energy of biosorption ( $E$ ), defined as the free energy change when one mole of ion is transferred from infinity in solution to the surface of the solid, was calculated from the  $K$  value using the following equation 2.9:

$$E = 1/\sqrt{2K} \quad (2.9)$$

## 2.4.2 Biosorption kinetic models

The investigation of biosorption kinetics in wastewater is crucial because it sheds light on the reaction routes and its mechanism. Forecasting the time at which the adsorbate is removed from aqueous solution is essential for building a good sorption treatment facility. Any biosorption process is typically regulated by three diffusive transport channels for the adsorbate:

- From the fluid in its bulk to the film covering the biosorbent.
- The biosorbent surface to the film.
- The metal ions are then bound to the active sites after moving from the surface to the interior sites.

However, in kinetic modeling, all three of these stages are combined, and it is predicated that the biosorption is driven by the discrepancy between the average solid phase concentration and equilibrium concentration. Additionally, it is demonstrated from

the experimental data that external borders barely have any impact at the optimal agitation speed. Thus, the kinetic model's application is only dependent on the solution's initial and ultimate concentrations at various time points. It is incorrect to apply simple kinetic model such as first and second order rate equations to a sorption process with solid surface, which is rarely homogenous. Secondly, the effects of transport and chemical reaction are often experimentally inseparable.

Kinetic experiments were performed by contacting 0.1 g of *Atriplex Farinosa Leaves* powder and 0.1 g of *Ficus Hispida* leaves powder with 30 ml of different concentrations (20 – 100 mg/L) of Lead metal solutions at constant agitation speed, optimum temperature and pH for the contact time of 1 min. At the end of predefined time of 1 min, metal solutions were centrifuged and supernatants were analyzed for unadsorbed metal concentrations. The above procedure was repeated under similar experimental conditions for different time periods in the range of 1 – 90 min.

To explain the mechanism of a solute sorption from aqueous solution onto a biosorbent, a number of kinetic models have been put forth:

- Pseudo first order/Lagergren kinetic model
- Pseudo second order kinetic model
- Elovich model

#### 2.4.2.1 Lagergren or Pseudo first order kinetic model

Based on the solid biosorption capacity, the pseudo first order or Lagergren kinetic rate equation for the sorption of liquid solid system was developed. It is one of the most widely used sorption rate equations for sorption of a solute from a liquid solution [11]. According to the authors, the overall biosorption rate is directly proportional to the driving force, i.e., the difference between initial and equilibrium concentrations of the adsorbate ( $q_e - q_t$ ). Therefore, the pseudo first order kinetic equation can be expressed as:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (2.10)$$

Where  $q_e$  and  $q_t$  are the sorption capacities at equilibrium and at time  $t$ , respectively (mg/g) and  $k_1$  is the rate constant of pseudo first-order sorption ( $\text{min}^{-1}$ ). After integration and applying boundary conditions,  $q_t = 0$  at  $t = 0$  to  $q_t = q_t$  at  $t = t$ ; the integrated form of Eq. (3.10) becomes:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \quad (2.11)$$

' $k_1$ ' can be calculated from the slope of the linear plot between  $\log(q_e - q_t)$  vs ' $t$ ' for different adsorbate concentrations.

#### 2.4.2.2 The pseudo-second-order equation

If the rate of sorption is a second-order mechanism, the pseudo-second-order chemisorption kinetic rate equation is expressed as [12]:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \quad (2.12)$$

Where  $q_e$  and  $q_t$  are the sorption capacity at equilibrium and at time  $t$ , respectively (mg/g) and  $k$  is the rate constant of pseudo-second-order sorption ( $\text{g}/(\text{mg min})$ ). For the boundary conditions  $q_t = 0$  at  $t = 0$  to  $q_t = q_t$  at  $t = t$ ; the integrated form of Eq. (2.12) becomes:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e} t \quad (2.13)$$

where  $t$  is the contact time (min),  $q_e$  (mg/g) and  $q_t$  (mg/g) are the amount of the solute adsorbed at equilibrium and at any time,  $t$ . Eq. (2.13) does not have the problem of assigning as effective  $q_e$ . If pseudo-second-order kinetics is applicable, the plot of  $t/q_t$  against  $t$  of Eq. (2.13) should give a linear relationship, from which  $q_e$  and  $k$  can be determined from the slope and intercept of the plot and there is no need to know any parameter beforehand.

#### 2.4.2.3 Elovich model

The Elovich model gives the information about the type of adsorption mechanism. The model is used to describe second order kinetics of chemisorption and it is based on the assumption that the adsorption surface is energetically heterogeneous. It is expressed as:

$$q = \frac{\ln(\alpha\beta)}{\beta} + \frac{1}{\beta} \ln t \quad (2.14)$$

Where,  $\alpha$  is the initial adsorption rate constant (mg/g.min) and  $\beta$  is related to extent of surface coverage and activation energy of chemisorption (g/mg).

The experimental data obtained in this study were tested to fit this model for assessing the adsorption mechanism.

### 3. RESULTS & DISCUSSION

#### 3.1 Contact time effect:

Using *Atriplex Farinosa Leaves* as a biosorbent, the effect of contact time on the biosorption of Lead from aqueous solution was investigated at various initial metal concentrations (20-100 mg/L), constant temperature 303 K, constant agitation speed of 180

rpm, and solution pH of 5 for Lead. In Figs. 3.1.1 and 3.1.2, the impact of contact time on the percentage biosorption and metal uptake is depicted. As contact time increased from 1 to 5 minutes, the percentage of biosorption and metal uptake of Lead onto *Atriplex Farinosa* Leaves biosorbent increased sharply. As contact time increased from 5 minutes to 20 minutes, they increased gradually before reaching a plateau after reaching equilibrium at 20 minutes. It demonstrates that the biosorption process is fairly quick, and the quick biosorption rate denotes the biosorbent's greater affinity for the metal ions. The early period's higher biosorption rate was caused by an increase in the number of empty sites that were available, as well as by a rise in the concentration gradient between adsorbate in solution and adsorbate on the biosorbent surface.

This was due to the variations in the chemical structures and interaction between functional groups of the biosorbent and metal molecule [17-18]. Similar trends were reported in the literature for the removal of Lead using coffee grounds and vegetable biomass [19], activated phosphate [20], rice husk ash [21], coconut shell [22], using carbon nanotubes [23], *reynoutria Japonica* [24], *Medicago Sativa* [25] and thermophilic bacteria [26].

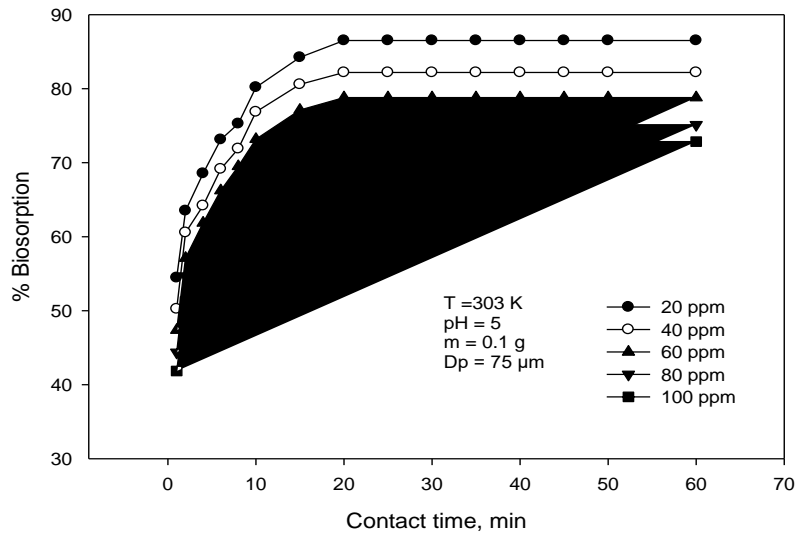


Figure.3.1.1 Contact time effect of on % biosorption of Lead by *Atriplex Farinosa LeavesL.*

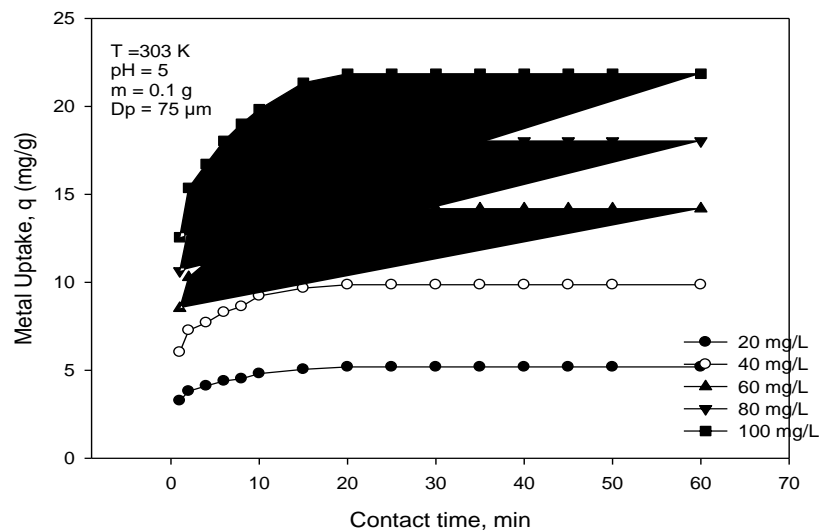


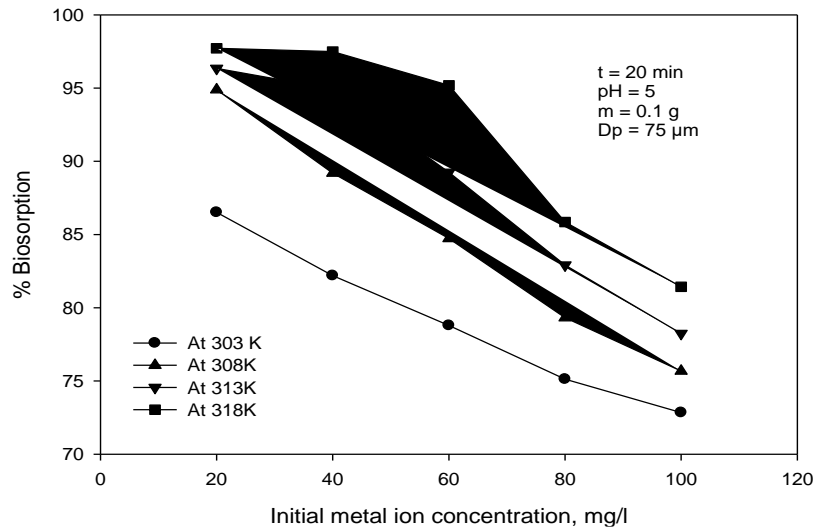
Figure.3.1.2. Effect of contact time on metal uptake of *Atriplex Farinosa LeavesL.* biosorbent for Lead removal.

**3.2 Effect of initial concentration of metal:**

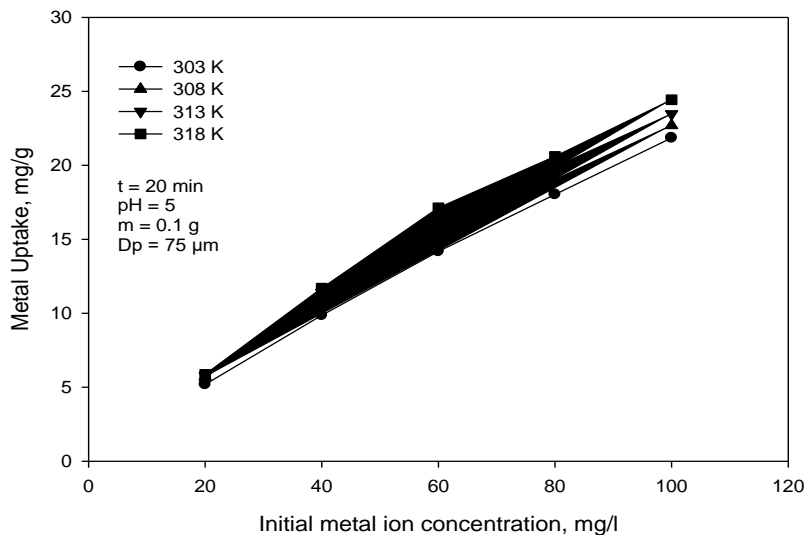
The experiments were conducted for Lead solution pH of 5, temperature range of 303 – 318 K, and constant agitation speed of 180 rpm to study the influence of initial metal concentration (20-100 mg/L) on biosorption of Lead metal from aqueous solution and the results are shown in Figs. 3.2.1 and 3.2.2. The percentage of biosorption decreased and metal uptake increased with an increase in initial concentration of metal from 20 to 100 mg/L at all the temperatures.

The percentage biosorption of Lead decreased from 86.51 to 72.84 % and the metal uptake increased from 5.19 to 21.85 mg/g with an increase in initial concentration of Lead from 20 mg/L to 100 mg/L at the temperature of 303 K.

Due to the fact that the majority of the metal molecules in solution could be adsorbed on the biosorbent's accessible active sites, the percentage of biosorption was found to be higher at low concentrations. The increasing quantity of metal molecules in solution at higher concentrations might be too much for the solid's vacant active sites to handle. This results in the biosorbent surface's active sites becoming saturated, which lowers the biosorption rate. [27].



**Figure.3.2.1.** Effect of initial metal ion concentration on % biosorption of Lead by *Atriplex Farinosa LeavesL.* biosorbent at different temperatures.



**Figure.3.2.2.** Effect of initial metal ion concentration on Lead uptake by *Atriplex Farinosa LeavesL.* biosorbent at different temperatures.

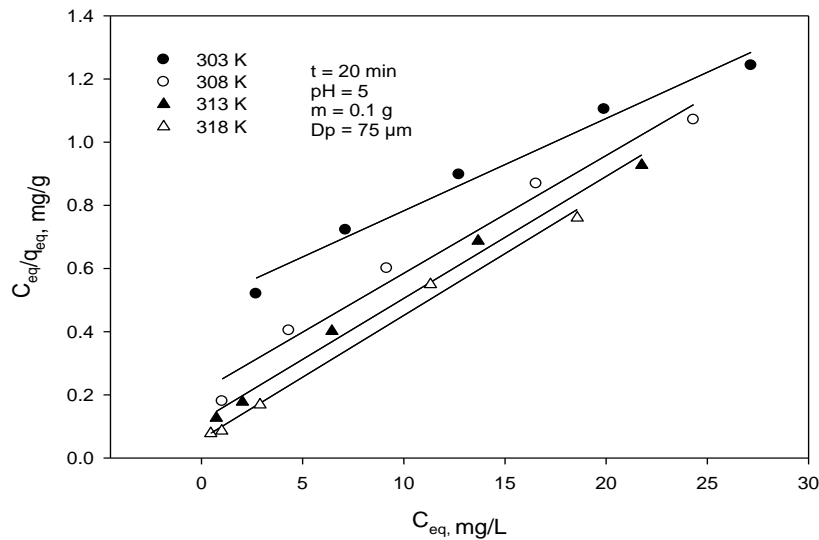
**3.3 Equilibrium Isotherm Studies:**

By varying the Lead metal concentrations in the range of 20 – 100 mg/L at temperature of 303 – 318 K, solution pH of 5 for Lead with biosorbent particle size of 74 μm, the experimental results were tested with different isotherm models like Langmuir, Freundlich, Tempkin and Dubinin – Radushkevich.

**3.3.1. Langmuir model**

According to the experimental data for the biosorption of lead against *Atriplex Farinosa LeavesL.* at different temperatures presented in Figs. 3.3.1, the biosorption obeys the Langmuir model as indicated by the linear plot of specific sorption ( $C_e/q_e$ ) against the equilibrium concentration ( $C_e$ ). Over the whole concentration range the plots were found to be linear and the high values of determination coefficient ( $R^2$ ) suggest the applicability of Langmuir isotherm model to the experimental data. The applicability of Langmuir isotherm model indicates the homogeneity with finite number of active sites on *Atriplex Farinosa Leaves* biosorbent surface. It also suggests the possibility of uniform monolayer coverage of biosorbent surface with metal molecules. The Langmuir isotherm constants,  $q_{max}$  and  $K_a$  were calculated from the slope and intercept of the linear plots. These values increased from 0.059 to 0.645 L/mg for Lead with an increase in solution temperature from 303 to 318 K. This indicates the bonding strength increased with an increase in solution temperature for both the metals.

The maximum biosorption capacity,  $q_{max}$  (mg/g), represents a practical limiting biosorption capacity when the surface is fully covered with metal ions, particularly in cases where the biosorbent does not reach its full saturation in experiments and assists in the comparison of biosorption performance. The maximum biosorption capacity of the biosorbent ( $q_{max}$ ) at different temperatures was determined from the slopes of linear plots and all calculated values are shown in Tables – 3.1.1 for Lead.

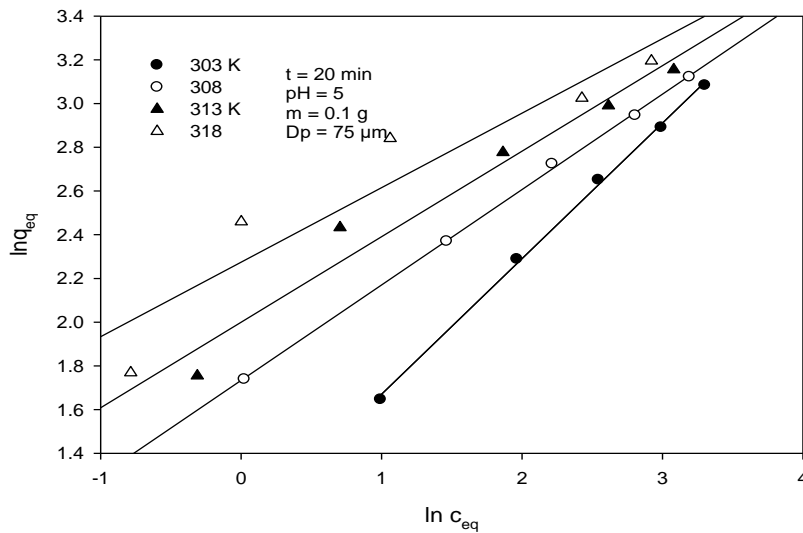


**Figure.3.3.1** Langmuir isotherm for Lead by *Atriplex Farinosa LeavesL.* biosorbent at different temperatures.

**3.3.2 Freundlich model**

The charts at all temperatures were linear, and the high  $R^2$  values indicated that the model had good applicability. The Freundlich isotherm accurately describes the data over the concentration range (20-100 mg l<sup>-1</sup>), according to analysis of the data. The slope and intercept of the plots were used to calculate the values of  $K_F$  and  $n$ . The Freundlich constant and linear correlation coefficient are shown in Table 4.1.2.

High values of Freundlich constant related to biosorption capacity ( $K_f$ ) obtained indicate the fast uptake capacity of *Grewia Orbicula* leaves biosorbent. However, these values of  $K_f$  increased with an increase in temperature indicate the endothermic nature of biosorption process. The values of Freundlich constant ‘ $n$ ’ greater than 1 indicated that the biosorption process was favourable and it might be due to chemical interactions between adsorbate and adsorbent. Similar trends were obtained for the removal of Lead using rice husk; Peat.

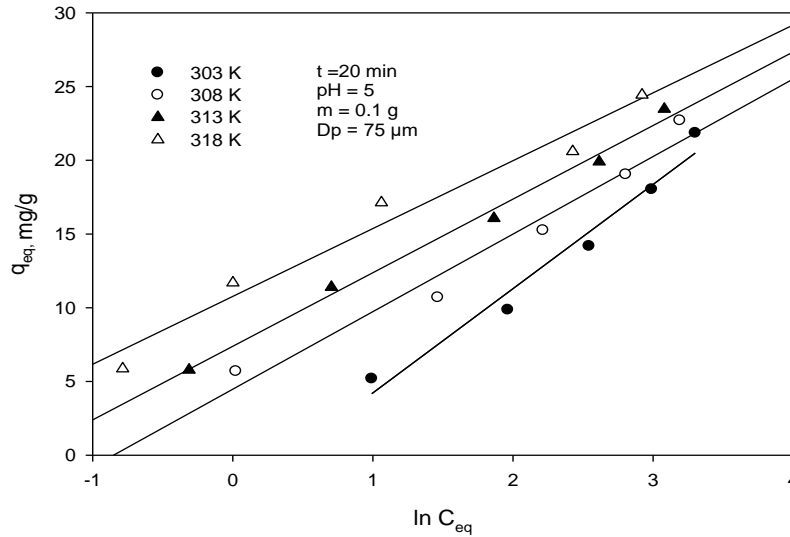


**Figure.3.3.2** Freundlich isotherm for Lead by *Atriplex Farinosa LeavesL.* biosorbent at different temperatures.

**3.3.3 Model of Tempkin**

Tempkin and Pyzhev investigated the effects of heat of biosorption and the adsorbate-adsorbent interaction on biosorption isotherms, and they hypothesized that as a result of these interactions, the energy of biosorption for all molecules falls linearly with coverage.

High correlation coefficient,  $R^2$ , values suggest that the biosorption process could be due to heterogeneous surface coverage. This is in good agreement with the results already mentioned in the Freundlich isotherm studies. However, relatively lower correlation coefficients,  $R^2$ , values compared to Freundlich isotherm model indicate the non applicability of Tempkin model. Similar trends were observed for the removal of Lead using Papaya wood [28].

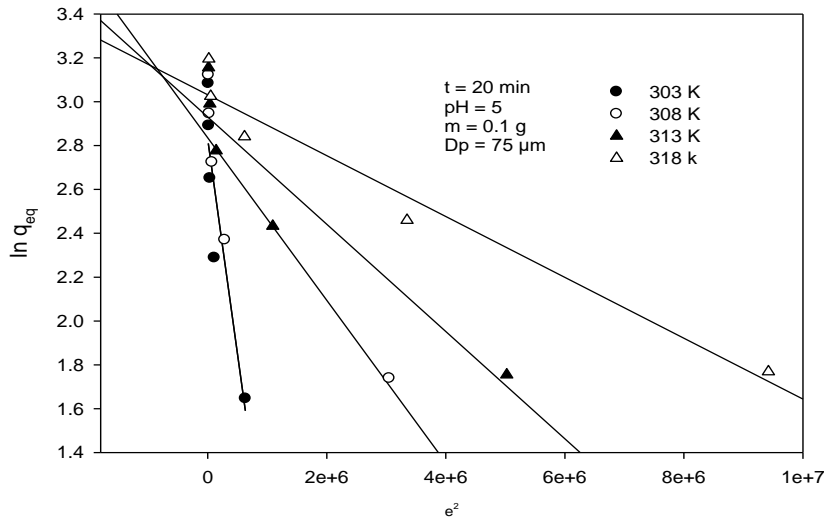


**Figure.3.3.3** Tempkin isotherm for Lead by *Atriplex Farinosa LeavesL.* biosorbent at different temperatures.

**3.3.4 Dubinin- Radushkevich (D-R) model**

The D-R isotherm is used to identify the physisorption and chemisorption behaviours based on E value. The adsorption behaviour is physisorption if E values are in the range of 1-8 kJ/mol, chemisorption if E values are in the range of 8-16 kJ/mol.

The model was tested and the results are shown in Fig.3.3.4. Low values of correlation coefficients show the non applicability of the model to the experimental results. The calculated adsorption energy (E) values were in the range of 10.14 to 12.05 kJ/mol, for the biosorption of Lead. The values of E are above the physisorption range and fall in the ion-exchange range 8-16 kJ/mol, which indicates the ion-exchange mechanism.



**Figure.3.3.4** Dubinin-Radushkevich isotherm for Lead by *Atriplex Farinosa LeavesL.* biosorbent at different temperatures.

The equilibrium data were tested by all the four isotherm models. Based on the high correlation coefficient ( $R^2$ ) values presented in Table 3.1.1 the best isotherm was determined. From these values, it was observed that Langmuir Isotherm with correlation coefficient of 0.9982 fitted well followed by Freundlich, Tempkin and D-R isotherms with a correlation coefficient of 0.9886, 0.9696 and 0.843, respectively at a solution temperature of 303 K. At remaining temperatures also the same type of trends were observed for both the metals.



Table.3.1.1. Bisorption isotherm constants for Lead removal using *Atriplex Farinosa Leaves* biosorbent.

Langmuir isotherm			Freundlich isotherm			Tempkin isotherm			Dubinin Radushkevich isotherm		
$q_{max}$ (mg/g)	$K_a$ (L/mg)	$R^2$	n	$K_f$ (mg/g)	$R^2$	b	$A_T$ (L/mg)	$R^2$	K (mol <sup>2</sup> /KJ <sup>2</sup> )	$q_{max}$ (mg/g)	$R^2$
34.22624	0.059567	0.99826137	1.611715	2.856086	0.9886526	356.31	0.66813	0.9696411	0.004854503	16.88103	0.8434
26.81993	0.175936	0.99633218	2.290641	5.66294	0.9923582	486.97	2.34367	0.9653460	0.009185547	17.037	0.8029
25.90047	0.323689	0.99014855	2.554458	7.385549	0.9629190	521.43	4.39197	0.9926285	0.006061203	18.73523	0.8969
25.57032	0.645995	0.99199519	2.932213	9.721638	0.9882098	574.60	10.385	0.9695977	0.003440397	20.73113	0.9593

Table.3.1.2. Kinetic model parameters for Lead removal using *Atriplex Farinosa Leaves* biosorbent.

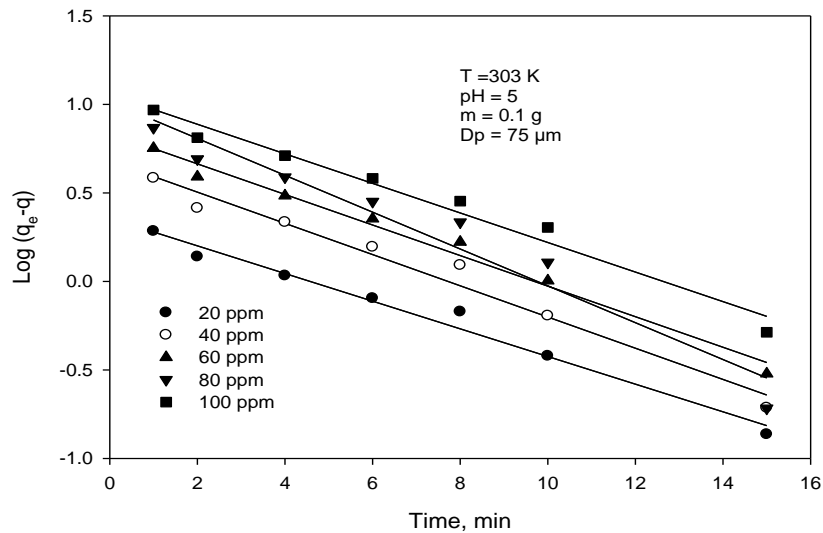
Initial concentration (mg/l)	Pseudo- first order			Pseudo- second order			Elovich		
	$q_e$ (mg/g)	$k_1$ (L/min)	$R^2$	$q_e$ (mg/g)	$k_2$ (L/mg.min)	$R^2$	$\beta$ (g/mg)	$\alpha$ (mg/g.min)	$R^2$
2.273916	0.17983	0.98211	5.294806	0.217696	0.99977	2.0921	726.313	0.9267	
4.795833	0.203023	0.97475	10.06066	0.115581	0.99976	1.0705	1070.26	0.9143	
6.8688	0.198832	0.98388	14.46996	0.079414	0.99978	0.7294	1273.96	0.9150	
10.37993	0.239748	0.94591	18.39108	0.063537	0.99976	0.5675	1480.13	0.9067	
11.3353	0.192209	0.97443	22.35795	0.044923	0.99971	0.4388	1612.15	0.9231	

### 3.4. Kinetics of biosorption

The prediction of biosorption rate gives important information for designing batch biosorption systems. Information on the kinetics of solute uptake is required for selecting optimum operating conditions for full-scale batch process. The kinetics of the biosorption data was analysed using three kinetic models, pseudo-first-order, pseudo-second-order and Elovich. These models correlate solute uptake, which are important in predicting the reactor volume.

#### 3.4.1. The pseudo-first-order equation

Experiments were conducted with different concentrations of Lead with pH of 5 and 6, temperature 303 K and constant agitation speed of 180 rpm to identify the mechanism of Lead removal using *Atriplex Farinosa Leaves* biosorbent. The results obtained are shown in Figs. 3.4.1 for Lead. From this figure it was found that, the first order was not fitted well for the entire range of concentrations studied for metal. The values of  $k_1$  and  $R^2$  are tabulated in Table. 3.1.2 for Lead. The low values of  $R^2$  suggest that, this model was not suitable for this biosorption process. Similar results were observed for the removal of Lead by using coconut shell, Terminalia Catappa leaves.

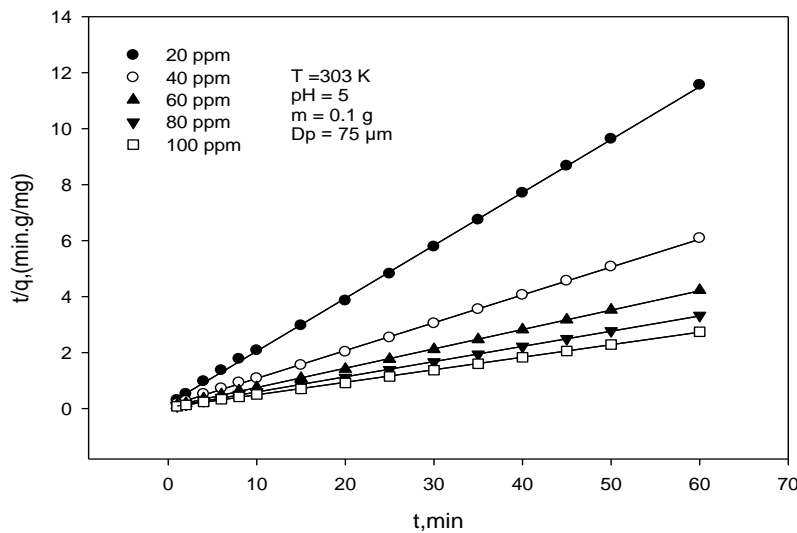


**Figure.3.4.1** Pseudo-first order plot for the biosorption of Lead by *Atriplex Farinosa Leaves L.* for different concentrations of metal.

**3.4.2. The pseudo-second-order equation**

The suitability of pseudo-second order kinetic model for the biosorption of Lead metal using *Atriplex Farinosa Leaves* biosorbent was evaluated. It is revealed from the Fig. 3.4.2 that the equilibrium data was well fitted over the entire range of concentrations. The values of constants and biosorption capacity were calculated and tabulated in the Table. 3.1.2. From the data, it is evident that high values of  $R^2$  suggest the applicability of pseudo-second order model to the experimental data.

The applicability of second order indicates the presence of both physisorption and chemisorption. However, chemisorption mechanism might be responsible for rate control of the overall biosorption process under the study. The uptake of metals may be due to valence forces and exchange of electrons between *Atriplex Farinosa Leaves* biosorbent surface and metal molecules. These surface exchange reactions take place until all active sites on the biosorbent surface are completely occupied with metal molecules and then metal molecules diffuse into the internal pores of the biosorbent. It also implies that, the biosorption rates were very fast and equilibrium times were short.



**Figure.3.4.2** Pseudo-second order plot for the biosorption of Lead by *Atriplex Farinosa Leaves L.* for different concentrations of metal.

**3.4.3. Elovich model:**

Elovich kinetic model was tested using the experimental data. The plots are shown in Fig. 3.4.3. The results are given in Table – 3.1.2. From the plots it is revealed that it is not applicable for both the metals. To determine the exact kinetic model that represent the experimental data, pseudo-first order, pseudo second order and Elovich models were tested and found that the pseudo second order kinetic model was fitted well for both the metals.

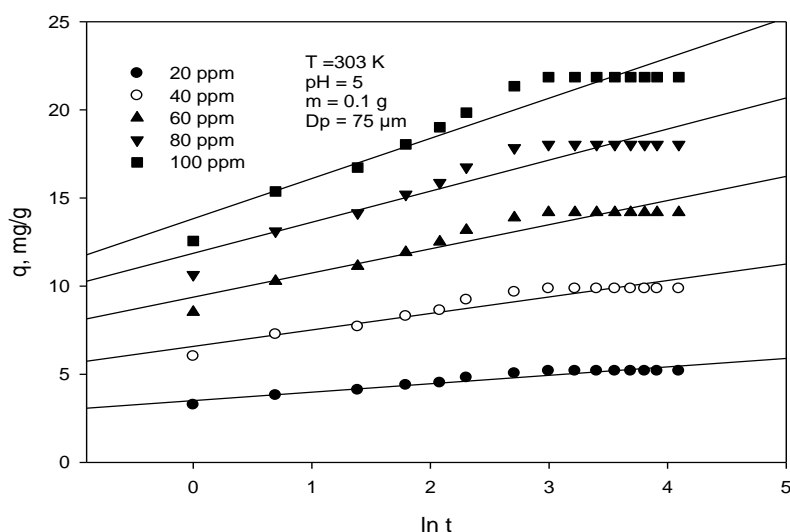


Figure.3.4.3 Elovich Kinetic model for biosorption of Lead onto *Atriplex Farinosa LeavesL.* biosorbent.

#### 4. CONCLUSION

The data obtained from the biosorption studies showed that a contact time of 20 min was sufficient for the maximum removal of Lead from aqueous solution using *Atriplex Farinosa Leaves* biosorbent. The experimental data of biosorption of metal onto both the biosorbent were fitted well with the Langmuir isotherm model. The isotherm reveals that the biosorption of the metals onto both the biosorbent was favourable. E values obtained from D-R isotherm indicated that the biosorption of Lead metal onto the biosorbents were just above the physisorption range and fall in the chemisorption range. Kinetic analyses showed that chemisorption was likely involved since the biosorption of the metal onto the biosorbent was highly rapid and tended to follow the pseudo-second order kinetic model over the whole contact duration for the range of concentrations examined.

Thermodynamic experiments showed that lead biosorption onto *Atriplex Farinosa Leaves* biosorbent was endothermic, spontaneous, and practicable. Following are the recommended metal values for utilizing *Atriplex Farinosa Leaves* as a biosorbent. For Lead, a maximum removal efficiency of 83.77% was estimated to be achieved at 312.23 K, a pH of 4.72 in the solution, an initial metal concentration of 58.5 mg/L, and a biosorbent dosage of 0.27 g. Based on the results, it can be concluded that the *Atriplex Farinosa Leaves* are an effective and alternative biosorbent for the removal of Lead from an aqueous solution because of their high biosorption capacity, cost effectiveness and abundant availability.

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