

Kinetics and Mechanism for Adsorption of Lead in Aqueous and Industrial Effluent from *Pongamia pinnata* Tree Bark

M.Mamatha¹, H.B.Aravinda², S.Manjappa³, E.T.Puttaiah⁴

¹(Department of Chemical Engineering, Bapuji Institute of Engineering and Technology, Davangere, India)

²(Department of Civil Engineering, Bapuji Institute of Engineering and Technology, Davangere, India)

³(Department of Chemistry, Bapuji Institute of Engineering and Technology, Davangere, India)

⁴(VC, Gulbarga University, Gulbarga, India)

Abstract : Presence of heavy metals in water bodies due to industrialization has led to serious health problems. In the present study, an adsorbent prepared from the raw bark of the *Pongamia pinnata* tree was used for the removal of Lead from aqueous and waste water containing heavy metals. The effectiveness of this adsorbent was studied in batch studies for various size fractions of adsorbent at different pH, concentration of metal ion, amount of adsorbent, contact time, agitation and temperature. The pseudo-first-order, pseudo-second-order and Elovich models were applied to test the kinetic experimental data. Pseudo second order model best fitted the adsorption of Lead ions. The Langmuir and Freundlich adsorption isotherm models were applied for the results. The Langmuir isotherms were best fitted by the equilibrium data. The maximum adsorption was found to be 34.36mg/g in waste water at a temperature of 30^o C.

Keywords - Adsorption, Adsorption isotherms, Heavy metals, Industrial effluents, Lead

I. INTRODUCTION

Rapid growth in the manufacturing sector for the varieties of products and newer processes in the last few decades is the major cause for environmental pollution. Water bodies are polluted to different extent by a number of heavy metals. The heavy metals present in waste water streams are not degradable and at times are taken up by plants.[1] Industrial activities such as electroplating, tanneries, metallurgical, mining, textile, painting, car-radiator manufacturing etc., [2]-[3] generates various heavy metals in the effluent. Stringent regulations are made by various countries for proper disposal of these effluents [4].

Conventional physical, chemical and biological methods such as chemical precipitation [5], electrode deposition [6], membrane separations [7], evaporation, solvent extraction, ion exchange [2], [8], coagulation, cementation, biological treatment, reverse osmosis [9], accumulation by aquatic macrophytes [10] etc are available. As these methods have the problem of precipitate formation during treatment which in turn ends up with disposal problems they are not economically viable. In this regard adsorption is one of the promising methods for removal of heavy metals. Some organic and inorganic materials are used as adsorbents with and without pretreatment such as polymers [11], [12], zeolites [13], [14], lignite [15], waste tires [16], algae [17], crab shells [18], lignin [19], fly ash [20], [21], activated carbon from various agricultural residues [22]-[27], tree barks [8], [28]-[30] for removing various heavy metals from aqueous and waste water.

Level of toxicity affecting living forms depends on type of heavy metal ions such as lead, copper, cobalt, cadmium, chromium, nickel, mercury, arsenic, zinc, manganese etc. Different types of manufacturing processes emit varying levels and types of heavy metals in their effluent. These heavy metals in water exhibit specific damaging effects on flora and fauna if the allowable limits are exceeded [28]. Lead can take part in the biogeochemical cycles and its mobility depends strongly on its chemical form rather than total element concentration [31]. Water bodies are found to be polluted by the presence of heavy metals due to industrial and domestic activities in the surrounding area [32], [33].The present paper highlights the method for removal of lead from aqueous and waste water.

II. MATERIALS AND METHODS

2.1 Adsorbent Preparation

Pongamia pinnata bark was collected in the study area, Davangere, Karnataka, India. The raw bark was Sun dried for 3 days. Then the bark was dried at 80^o C for six hours in hot air oven and cut into 2 to 3 inch pieces. Dried bark was powdered in pulverizer. The powder was washed several times with double distilled water to remove solubles, coloring matter and again dried in hot air oven at 60^o C for 8 hours. The powdered bark was sieved (Indian Standard Sieve) and various fractions of adsorbent was separately stored in air tight containers. The particle diameter of the various sieve fractions are as in TABLE 1.

TABLE 1
Average particle size of adsorbent analyzed by Indian standard sieves

Sl.No.	Sieve Size	Average particle size (µm)
1	2.36mm-1mm	1680
2	1mm-600µ m	800
3	600µm-300µ m	450
4	300 µm-150µ m	225
5	150 µm-75µ m	112.5

2.2 Stock Solution

Analytical grade Lead Sulphate was used to prepare stock solution. Double distilled water was used to prepare stock solution. Solutions of required concentrations were prepared using stock solution. 0.1 N HCl and 0.1N NaOH solutions were used to adjust the pH of the solutions. Industrial effluent (before treatment) from a local industry was collected, filtered using whatmann no.1 filter paper and stored in air tight containers.

2.3 Batch Adsorption Studies

Batch adsorption studies were conducted to determine the equilibrium time required to reach saturation. Adsorption kinetics were carried out using lead Sulphate solutions of 5 to 50 ppm, pH in the range 2 to 9, 2.5 to 10g/L adsorbent of average particle size 225µm, a contact time up to 60 min, constant agitation of 200 rpm and temperature of 30°C. The parameters were varied one at a time and samples collected at predetermined intervals, filtered, centrifuged and analyzed by Atomic Absorption Spectrophotometer (Shimadzu). The amount of lead uptake by the bark was found. All experiments were carried out in duplicate and mean values are presented. The maximum deviation was 5.0 %. The percentage removal of heavy metal from the solution was calculated using (1),

$$\% \text{ Removal} = \frac{C_o - C_i}{C_o} \times 100 \quad (1)$$

Where C_o is initial concentration of heavy metal, C_i is final concentration of heavy metal. The adsorption capacity q_e (mg/g) after reaching equilibrium was calculated using (2).

$$q_e = (C_o - C_e) \frac{V}{W} \quad (2)$$

Where V is the volume (L) of solution and W is the mass (g) of adsorbate used.

III. RESULTS AND DISCUSSION

3.1 Characterization of Adsorbent

A scanning electron microscope (SEM) was used to examine surface of the *Pongamia pinnata* bark. Fig. 1 shows the SEM photograph of the bark. The holes are cave type openings on the surface of the bark and would increase the surface area available for adsorption. TABLE 2 shows the proximate analysis of the *Pongamia pinnata* adsorbent used in the present study.

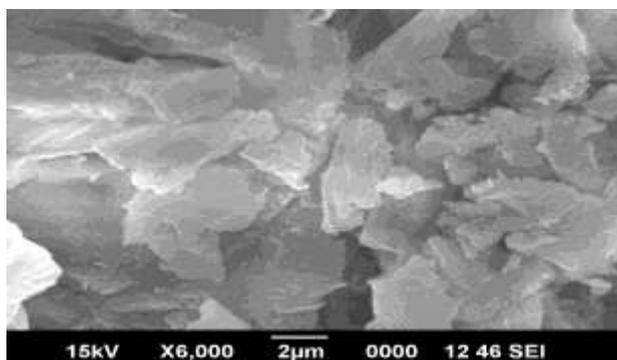


Figure.1 SEM photograph of *Pongamia pinnata* bark

TABLE 2
Proximate Analysis of *Pongamia pinnata* Tree Bark

Sl.No.	Property	Result
1	Bulk density (kg/m ³)	410
2	Moisture content (% Wt.)	8.4
3	Ash content (%Wt.)	14.1
4	Volatile matter (%Wt.)	7.43
5	Fixed Carbon (% Wt.)	83.2
6	Matter soluble in water (%)	1.51
7	Matter soluble in acid (%)	0.56

The spectral analysis of *Pongamia pinnata* tree bark shows the presence of 8 compounds namely, 3-methoxy-(3",4"-dihydro-3"-hydroxy-4"-acetoxy)-2",2"-dimethylpyrano-(7, 8:5",6")-flavone, 3-methoxy-(3",4"-dihydro-4"-hydroxy-3"-acetoxy)-2",2"-dimethylpyrano-(7,8:5",6")-flavone, caryophyllene oxide, obovatachalcone,8-hydroxy-6-methoxy-3-pentyl-1H-isochromen-1-one,6,7,2-dimethylchromono-8, γ , γ , -dimethylallylflavanone,isolonchocarpin, ovaliflavanone A [34].

All the above mentioned compounds can be decomposed through biological degradation by various microorganisms. The decomposition products are either gases or molecules that can be recycled by other microorganisms or plants generating no negative effects on the environment. Thus the bark used for decontaminating industrial effluents can be degraded by natural means [28].

3.2 Effect of pH

The effect of pH on the adsorption of lead is as shown in Fig.2. The pH of solution determines the surface charge of the adsorbent, the degree of ionization and speciation of the adsorbate. Batch equilibrium studies were carried at different pH values in the range of 2 to 9. It was observed from figure that maximum removal of lead ions was in the range of pH 5.0 to 6.0. The removal of metal ions was constant above pH 7. This was due to the formation of metal hydroxides. This show that a strong force of interaction between the lead ions and *Pongamia pinnata* bark that H⁺ ion could influence the absorption capacity. The interaction is more at pH 5.5 due to the competence of acidic H⁺ ion with metal cation for the absorption sites. [24].

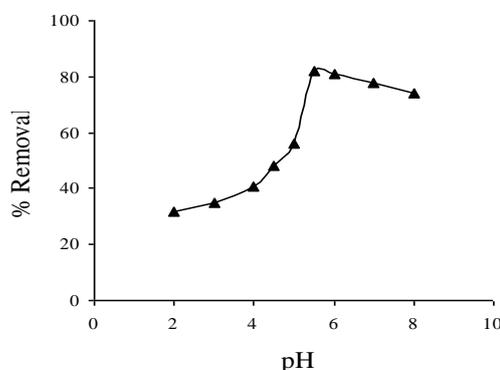


Figure.2 Effect of pH on adsorption. Conditions: Initial adsorbate concentration 10 ppm; adsorbent concentration 10 g/L; contact time 1hr; agitation 200 rpm

3.3 Effect of Initial Metal Ion Concentration

The effect of initial metal ion concentration is as shown in the Fig.3. From the figure it is evident that the metal uptake mechanism is dependent on initial heavy metal concentration. The metal ions are adsorbed onto the active sites of the adsorbent hence as the metal concentration increases the specific sites are saturated and no further adsorption occurs [15]. Batch experiments with varying initial metal ion concentration from 5 ppm to 50 ppm were carried out keeping other parameters constant. It was observed that metal ion uptake was more with a solution of 5 ppm and was observed that increase in metal ion concentration decreased adsorption.

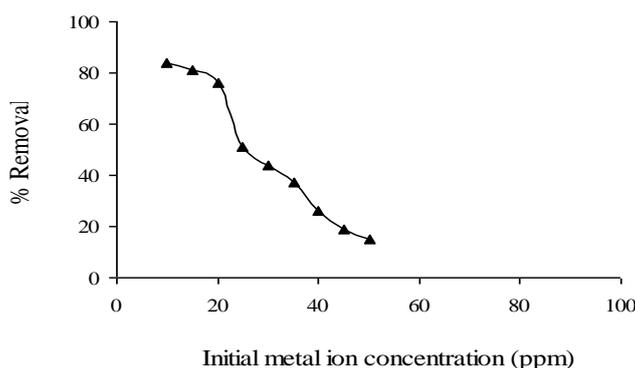


Figure.3 Effect of Initial metal ion concentration on adsorption. Conditions: pH 5.5; adsorbent concentration 10 g/L; contact time 1hr; agitation 200 rpm

3.4 Effect of Adsorbent Concentration

As the number of active sites available for the adsorption of metal ion increases, the adsorption percentage also increases. This occurs as the concentration of adsorbent increases. In the present case, batch study with adsorbent concentration ranging between 2.5g/L to 10g/L keeping all other parameters constant was conducted. The results are as shown in Fig. 4. It shows that 10g/L of adsorbent concentration adsorbs the maximum metal ion in both cases.

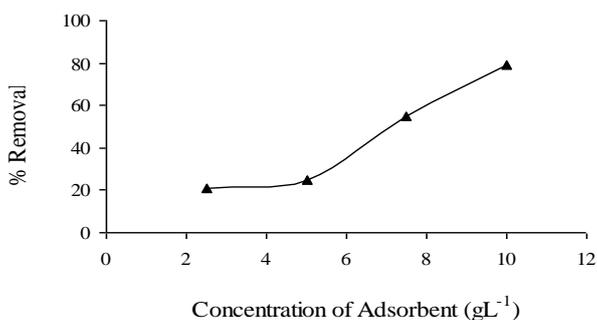


Figure.4 Effect of concentration of adsorbent on adsorption. Conditions: pH 5.5; Initial adsorbate concentration 10 ppm; contact time 1hr; agitation 200 rpm

3.5 Effect of Contact Time

The removal of lead ions from the stock solution increases with time and attains equilibrium value in about 60 to 65 min. Initially within 20 to 40 min the uptake of metal ions from bark is rapid, but gradually decreases with time till it reaches equilibrium. In the beginning the number of active sites available for adsorption is more hence metal uptake increases but later on the available active sites reduce and metal ions need to compete for the vacant sites. Fig.5 shows that at the start of the adsorption the percent removal of metal ions is more and later reaches a constant value where upon no further adsorption was observed.

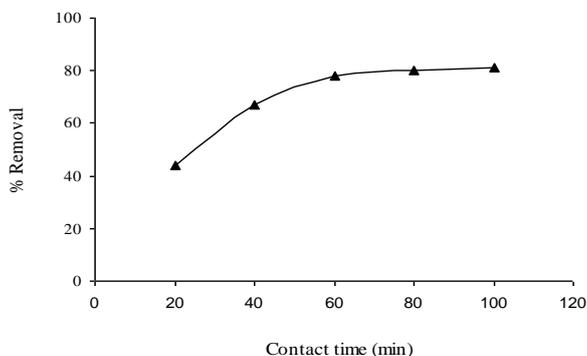


Figure.5 Effect of contact time on adsorption. Conditions: Initial adsorbate concentration 10 ppm; adsorbent concentration 10 g/L; pH 5.5; agitation 200 rpm

3.6 Adsorption Isotherms

From all the batch experiments carried out optimum parameters selected were pH of 5.5, initial metal ion concentration of 10 ppm, adsorbent concentration of 10g/L, contact time of 10 to 60 min, temperature of 30⁰ C and agitation of 200 rpm. The adsorption data was correlated with the Langmuir and the Freundlich isotherm model equations.

The Langmuir isotherm is valid for monolayer adsorption onto a surface with a finite number of identical sites. It is based on assumption of adsorption homogeneity, such as equally available adsorption sites, monolayer surface coverage and no interaction between adsorbed species [8]. According to the Langmuir adsorption isotherm, the adsorption process can be expressed as (3)

$$q_e = \frac{q_m C_e}{K_d + C_e} \tag{3}$$

On rearrangement of (3) to linear form as (4)

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{K_d}{q_m} \tag{4}$$

Where C_e (mg/L) is the equilibrium concentration of lead ions in solution, q_e (mg/g) the adsorption capacity at equilibrium, q_m (mg/g) the maximum adsorption capacity and K_d is the effective dissociation constant. The values of q_m and K_d estimated from the Fig.6 for adsorption of lead were 15.3mg/g and 5.7 respectively. The correlation coefficient of the Langmuir isotherm (R²) was 0.9967.

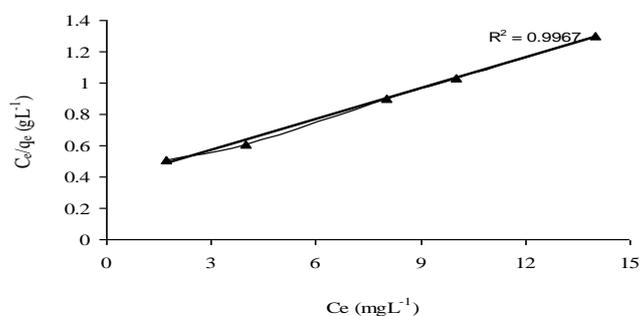


Figure.6 Langmuir adsorption isotherm of lead ion in aqueous solution.

In the Freundlich equation, the empirical relationship whereby it is assumed that the adsorption energy of lead ions binding to a site on an adsorbent depends on the adjacent sites available for adsorption and it is a multilayer adsorption process. The Freundlich isotherm is expressed as (5)

$$q_e = k_f (C_e)^{\frac{1}{n}} \tag{5}$$

On rearrangement to linear form (6)

$$\ln q_e = \ln K_f + \frac{1}{n} C_e \tag{6}$$

Where q_e (mg/g) is the adsorption capacity at equilibrium, C_e (mg/L) the equilibrium concentration of lead ions in solution, K_f and n are the physical constants of the Freundlich adsorption isotherm. The K_f and n values are the indicators of the adsorption capacity and adsorption intensity respectively. The slope and the intercept of the linear Freundlich equation are equal to 1/n and lnK_f respectively as in Fig.7. The constants n and K_f obtained from Fig.7 were 2.04 and 3.07 respectively. The correlation coefficient of the Freundlich isotherm (R²) was 0.9856.

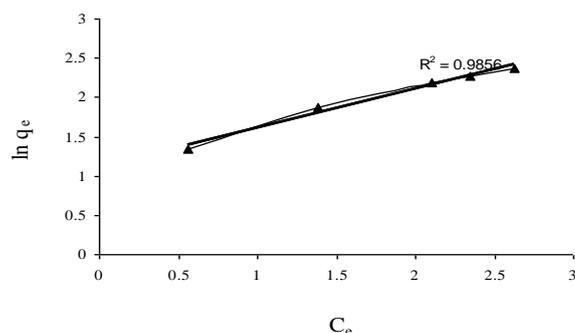


Figure.7 Freundlich adsorption isotherm of lead ion in aqueous solution.

Comparing both of the correlation coefficients obtained, it shows that the Langmuir isotherms suits well for the obtained adsorption data than Freundlich isotherm.

3.7 Adsorption Kinetics

The kinetics involved in the adsorption of lead ions on to *Pongamia pinnata* were studied based on three models namely, the pseudo first order, pseudo second order and Elovich model. For the adsorption of solute from liquid solutions, pseudo first order model is most widely used. This model is as below,

$$\ln(q_e - q_t) = \ln q_e - K_1 t \tag{7}$$

Where q_e is the mass of metal ion adsorbed at equilibrium (mg/g), q_t is the mass of metal adsorbed at time t (mg/g), K_1 is the first order reaction rate constant (min^{-1}). Plot of $\ln(q_e - q_t)$ vs. t indicates the application of the first-order kinetic model as shown in Fig. 8.

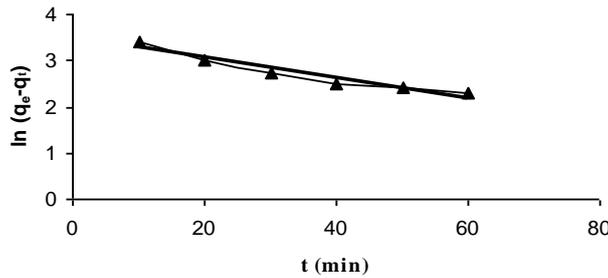


Figure.8 First order kinetic model for lead ion adsorption.

Based on equilibrium adsorption capacity pseudo second order model is as shown in the form

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{8}$$

Where K_2 is the second order reaction rate constant ($\text{g/mg} \cdot \text{min}$). A plot of t/q_t against t is a linear relation for the second order kinetics to be applicable to that model as shown in Fig. 9.

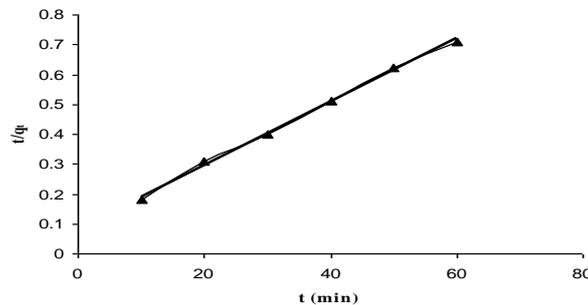


Figure.9 Second order kinetic model for lead ion adsorption.

Elovich model for the adsorption is expressed as

$$q_t = \alpha + \beta \ln t \tag{9}$$

A plot of q_t against $\ln t$ gives a linear relationship for the applicability of the simple Elovich kinetic model as shown in Fig.10.

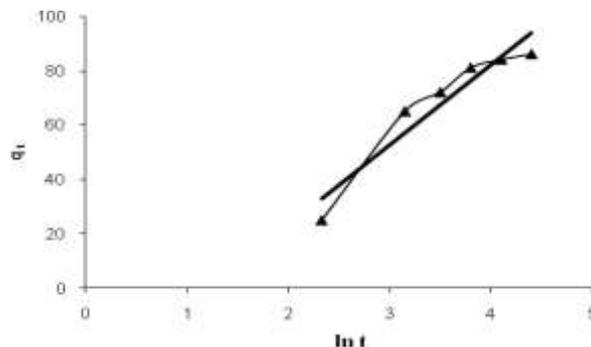


Figure.10 Elovich kinetic model for lead ion adsorption.

Comparing all the above models the parameters obtained are reported in TABLE 3. Based on linear regression ($R^2 > 0.99$) values, the kinetics of lead ion adsorption on *Pongamia pinnata* can be described well by pseudo second order kinetics.

TABLE 3
Parameters of Kinetic models

Metal ion	First order		Second order		Elovich		
	R^2	K_1	R^2	K_2	R^2	α	β
Lead	0.9353	0.02	0.9975	1.31×10^{-3}	0.91	-35.85	29.517

3.8 Mechanism of Adsorption

The mechanism of adsorption of metal ion onto adsorbent follows three steps viz. the movement of metal ion from bulk liquid onto the surface of adsorbent, pore diffusion and intra particle transport. The overall rate of the adsorption is governed by the slowest step of all. For the batch adsorption mode, pore and intra particle diffusion are rate limiting whereas in case of continuous adsorption mode, film diffusion is more likely the rate limiting step. The adsorption rate parameter which controls the batch process for most of the contact time is intra particle diffusion. The possibility of intra particle diffusion resistance affecting adsorption was explored by using the intra particle diffusion model as

$$q_t = k_i t^{1/2} + I \tag{10}$$

Where, k_i is the intra particle diffusion rate constant, a plot of q_t vs. $t_{1/2}$ for lead ions is as shown in Fig. 11. Values of I are as reported in TABLE 4. I values give an idea about the thickness of boundary layer. The larger the intercept the greater is the boundary layer effect.

TABLE 4
Kinetic Parameters and Boundary layer for adsorption

Metal ion.	k_i	I	R^2
Lead	10.69	0.71	0.988

The deviation of straight lines from the origin as shown in the Fig. 11 may be because of the difference between the rate of mass transfer in the initial and final steps of adsorption. Further, such deviation of straight line from the origin indicates that the pore diffusion is not the rate controlling step.

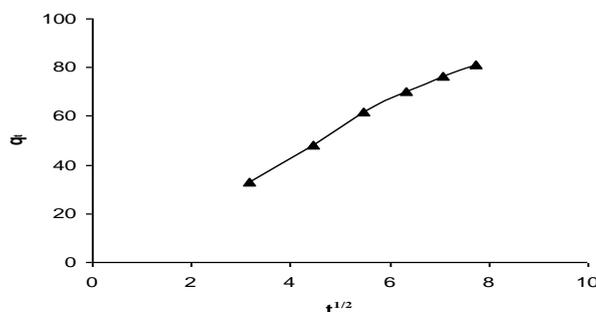


Figure.11 Mechanism of particle diffusion for lead ion adsorption.

From Fig.11, it may be seen that there are two separate regions the first portion is attributed to the bulk diffusion and second portion to the intraparticle diffusion. The values of $k_{i, 1}$ and $k_{i, 2}$ are obtained from slopes of the two straight lines are 12.47 and 7.76 respectively.

3.9 Adsorption of Lead from Industrial Effluent

Raw industrial effluent without treatment was collected from a local wire drawing industry. After filtration, batch experiments were carried out using 100ml of effluent each with 10g/L adsorbent, temperature of 30°C and agitation of 200 rpm. The pH of solution was varied from 2 to 7. Fig.12 shows the effect of pH on the adsorption of lead by *Pongamia pinnata* bark. Maximum removal of lead was observed in the pH range 5 to 6 which was in agreement with the aqueous solution. The maximum adsorption was found to be 34.36mg/g in effluent at a temperature of 30°C. The percentage lead removal was interfered as the effluent consisted of other competing ions such as copper, iron and nickel.

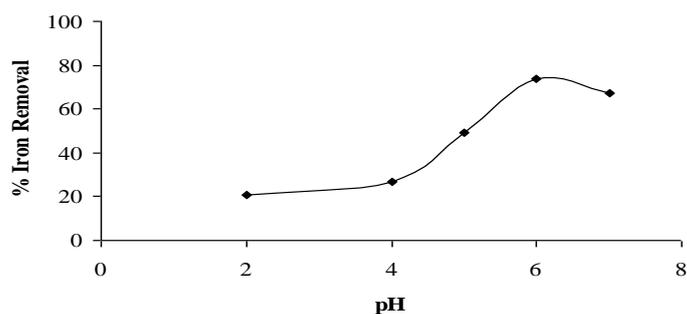


Figure.12 Effect of pH on adsorption of lead from industrial effluent. Conditions: adsorbent concentration 10 g/L; contact time 1 hr; agitation 200 rpm.

IV. CONCLUSION

Pongamia pinnata seeds are widely used for biofuel production, hence in recent years this tree is widely grown in the fields. Thus the availability of the *Pongamia pinnata* tree bark is more. Also the adsorbent preparation does not involve the activation process of the bark hence the preparation is simple and economical. It was concluded from the present study that *Pongamia pinnata* tree bark can be used effectively for the removal of lead from aqueous and industrial effluents. The adsorption data were better fitted by Langmuir model than Freundlich isotherm model. An optimum of 5 to 6 pH, 10g/L of adsorbent, initial metal ion concentration of 10ppm, with a contact time of 60min and agitation 200rpm was chosen from the experiments conducted. Pseudo second order model best fitted the kinetics. In case of industrial effluent, the decrease in the percent removal of lead was due to the interference of other metal ions present. In this regard, *Pongamia pinnata* tree bark can be effectively used as a viable and economic adsorbent for removal of lead from aqueous and industrial effluents.

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