Removal of Lead by Adsorption with Bauxite in a Fluidized -Bed Operation

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Abstract: The objective of the present work is to "Study the Removal of Lead in Water by Adsorption". Bauxite is used as the adsorbent. The various parameters that affect adsorption viz. effect of initial concentration, effect of particle size, effect of adsorbent dose, effect of flow rate etc were studied in fluidized bed operation. The kinetic data were fitted in different models and the isotherm equilibrium data were fitted to Langmuir, Freundlich & Fritz Schulander Models.

Keywords: Adsorption, Fluidized bed, Heavy metal, Kinetic study.

I. INTRODUCTION

Lead is one of the common contaminants of industrial wastewaters. Lead pollution exists in aqueous waste streams of many industries such as manufacture of storage batteries, printing, painting, pigments, and dying, leaded glass. Lead can threaten human life due to its toxicity, accumulation in food chains and persistence in nature. It is a general metabolic poison and enzyme inhibitor and can accumulate in bones, brain, kidney and muscles. Long-term drinking water containing high level of lead can cause serious disorders, such as anemia, kidney disease mental retardation and nervous system damages [1].

Unlike organic compounds, lead is non-biodegradable and accumulates in living organism, therefore, must be removed from water and wastewater. Various methods of lead removal from wastewater have been applied including chemical precipitation, membrane processes, ion-exchange and adsorption. One of the most effective methods for the treatment of heavy metals from aqueous solution has been based on adsorption using low-cost adsorbents.

Adsorption is an efficient method for the removal of tracer components from water. Activated carbon-produced by carbonizing organic materials-is the most widely used adsorbent. Activated carbon has shown good metal ion adsorption capacities [2]. The adsorption process depends on the temperature, nature and concentration of the adsorbate, as well as on the nature of the adsorbent and its aggregation state [3]. The adsorption of lead increases with an increase in pH of the solution from 1 to 4. [4]

Adsorption of Pb(II) ions from aqueous solution onto clinoptilolite to evaluate the effects of contact time, initial concentration and pretreatment of clinoptilolite on the removal of Pb(II) [5]. The performance of a commercially available palm shell based activated carbon to remove lead ions from aqueous solutions by adsorption. Palm shell activated carbon showed high adsorption capacity for lead ions, especially at pH 5 with an ultimate uptake of 95.2 mg/g [6]. The potential of using activated phosphate as a new adsorbent for the removal of Pb from aqueous solutions. The ability of natural zeolite clinoptilolite and bentonite (clay) to remove Pb(II) from aqueous solutions in batch reactors with a maximum contact time of 120 min [7].

II. MATERIAL AND METHODS

A. Selection of adsorbent

The search of new cost adsorbents that have metal binding capacities has investigated and materials locally available in large quantities such as natural materials, agricultural wastes or industrial by products can be utilized as low cost adsorbents.

Bauxite is a product of intense sub aerial weathering who's Fe 23.07, Al 39.85 content is higher and Si 7.59, Mg 0.03, Ca 0.03 content is lower than in merely kaolinised parent rocks. Bauxite is the most important aluminum ore. It consists largely of the minerals gibbsite, boehmite and diaspore together with the iron oxides goethite and hematite, the clay mineral kaolinite and small amounts of anatase. It was first discovered in 1821 by geologist Pierre Berthier.

Lateritic bauxites (silicate bauxites) are distinguished from karst bauxites (carbonate bauxites). The early discovered carbonate bauxites occur predominantly in Europe and Jamaica above carbonate rocks (limestone and dolomite), where they were formed by lateritic weathering and residual accumulation of intercalated clays or of clayey dissolution residues of the limestone. The lateritic bauxites occur in many countries of the tropical belt. They were formed by lateritization of various silicate rocks such as granite, gneiss, basalt, and shale [10]

B. Bauxite processing

Bauxite is strip mined (surface mining) because it is found at the surface, with little or no overburden. Approximately 95% of the world's bauxite production is processed into aluminum. Bauxites are typically classified according to their intended commercial application: metallurgical, abrasive, cement, chemical and refractory. Bauxites are heated in pressure vessels with sodium hydroxide solution at 150-200 ^{o}C through which aluminum is dissolved as aluminate (Bayer process). After separation of ferruginous residue (red mud) by filtering, pure gibbsite is precipitated when the liquor is cooled and seeded with fine grained aluminum hydroxide.

C. Preparation of the adsorbent

Red soil Bauxite consists of Fe and Al oxides were ground to smaller sizes in a jaw crusher and iron mortar and then the crushed material is sieved in a series of mess size to separate different size particles (1.20-2.05 mm). The desired particles are treated with Ferric nitrate. pH of the solution is maintained at 6.0-7.0 by adding NaOH and HCl Now they are allowed to dry in the furnace at a temperature of 80 c. The dried material is washed slowly with water with no coating damage and is air dried for 48 hours. According to XRD analysis the compositions in Bauxite are Al-39.85, Fe-23.07, Si-7.59, Mg-0.03, Ca-0.03.

III. EXPERIMENTAL SETUP FOR KINETICS STUDY

The kinetics studies were carried out in a fluidized bed operation.

TABLE I DIMENSIONS OF THE SETUP

Height of the column	70 cms
Outer diameter	3.175 cms
Inner diameter	2.54 cms
Volume of the tanker	10 Liters
Globe valves	2
Adsorbent	Bauxite

A perforated plate to support the bed of particles

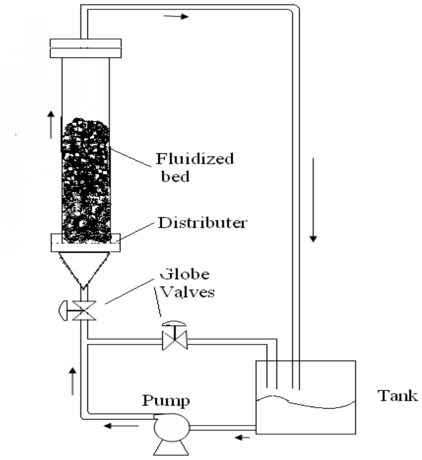

Fig. 1: Solid-Liquid Fluidization

The fluidization takes place in a vertical cylindrical column with a conical bottom through which the fluidized liquid is pumped into the bed of solids supported on distributor which is circular in cross section. The fluidized bed has an inner diameter of 2.54cm and a height of 70cm with a larger cross-sectional area of weir, and it was filled with a fixed amount of bauxite. The experiment was begun with a 5 liters solution containing a fixed concentration of lead solution. The lead solution was pumped into the fluidized bed vertically and fluidized the bauxite bed at a flow rate of 50 mL/s with the temperature kept at room temperature, that is, about 25°C. For measurement of the lead concentration, samples were taken from the effluent of the fluidized bed after a specified period of time [7-8]. The samples were analyzed in Atomic Absorption Spectroscopy (AAS).Different sizes of adsorbent particles are taken [9].

IV. EQUILIBRIUM STUDIES

A. Equilibrium Isotherm

The equilibrium studies were carried out at room temperature. In both the studies eight sets were taken. During each study, four of the eight sets were taken at a time. Two experiments were done for each equilibrium study.

100 ml of the approximately diluted solution prepared from the stock solution was taken in each of eight conical flasks (0.5 ppm to 30 ppm).Same amount of adsorbent were added to the conical flasks and the corks were tightened to prevent leakage of the solution. The conical flasks were then placed in an automatic shaker. The pH of the solution was maintained constant at 7.0 by regularly monitoring the pH. The system was found to be attaining equilibrium after 24 hours of shaking which was tested in the trail run. It was confirmed by measuring the absorbance of the solution in a two hours interval and observed no change in absorbance. Both of the equilibrium studies were carried in identical manner.

B. Kinetics of Adsorption

We have selected the fluidized bed for the study of adsorption kinetics of lead removal by the adsorbent Bauxite. The following kinetic parameter has been investigated.

1. Effect of initial concentration of lead solution
2. Effect of particle size on rate of adsorption
3. Effect of adsorbent dose on rate of adsorption
4. Effect of Flow rate on rate of adsorption.

C. Effect of Initial Concentration

The metal uptake mechanism is particularly dependent on the initial heavy metal concentration: at low concentrations, metals are absorbed by specific sites, while with increasing metal concentrations the specific sites are saturated and the exchange sites are filled .In this study 5000 ml of approximately dilute stock solution was taken in the tank and 50 gm of the adsorbent was added to the Fluidized bed column. The flow rate maintained at constant. The sample collection started after 5 min of time. First three samples were taken at an interval of 15 minutes and latter at an interval of 30 minutes. Sample collections were continued for three hours. The concentration of the lead was determined by using AAS. Three such experiments were carried out with three different initial concentrations (in the range 10 ppm to 40 ppm).

D. Effect of Adsorbent dosage

For this study different amounts of adsorbent (ranging from 100gm to 200 gm) were taken in the Fluidized bed column separately.5000ml of approximately diluted solution was added to the tank. The initial concentration was identical for all the experiments and other parameters like flow rate, pH of the solution, particle size etc, were kept constant. The concentrations of the solution were determined by AAS. Three such experiments were carried out with three different initial concentrations.

E. Effect of particle size

Different particle sizes (2.5mm, 2.0 mm and 1.5 mm) for the experiments and equal amount of adsorbents added to the vessel in separate experiments. Each experiment was conducted with 5000 ml of solution of desired concentration. The flow rate maintained at constant. Sampling was carried out in the same way as earlier. The samples were analyzed by AAS to determine the concentration of the lead in the sample. The smaller the particle size the higher the surface area per unit weight of adsorbent and hence higher percentage of metal removal is expected.

F. Effect of flow rate

100 gms of fixed amount adsorbent was taken in the column and 5000ml of approximately diluted lead solution was added. Three such experiments were carried out with various flow rates (ranging from 50 to 100 ml/sec) keeping all other parameters, amount of adsorbent, pH of the solution, particle size, initial concentration etc. Measurement was carried out in the same manner as stated earlier.

V. **RESULTS AND DISCUSSIONS**

A. Equilibrium studies

The equilibrium bulk concentrations obtained from the equilibrium study have been plotted against the equilibrium surface loading obtained from the differences between the original solute content in the solution and that at the equilibrium and dividing the total amount adsorbed by the amount of adsorbent present. The plot for prepared adsorbent has been shown in the figure 2.The equilibrium data also have been fitted to different isotherms through non linear regression techniques. The adsorption parameters have been presented in the tables 1. The results show that the adsorption equilibrium data for prepared adsorbent is quite satisfactorily fit to the Freundlich isotherm.

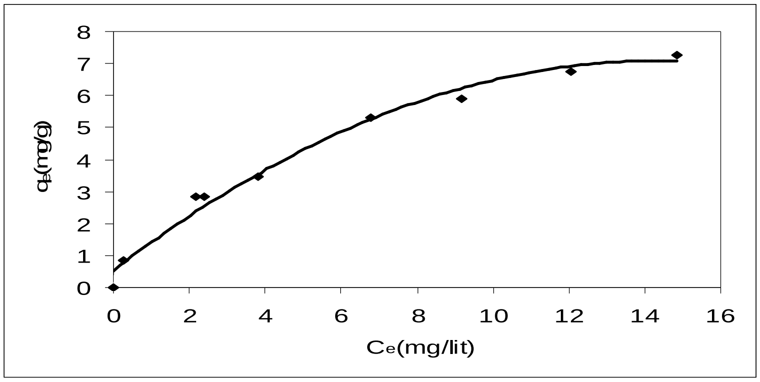

Fig. 2: Equilibrium curve for lead
(C_0 = 1000ppm, T= 303 K, M_a= 2gm, V= 100 ml, pH= 7)

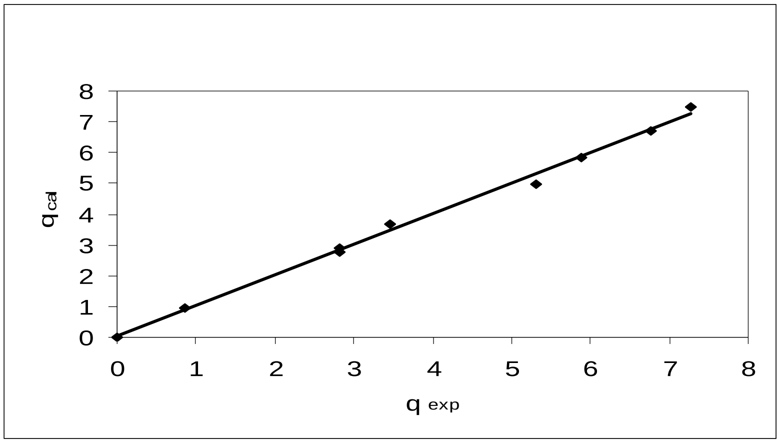

Fig. 3: Comparison of q_{cal} vs. q_{exp} for Freundlich isotherm
(C_0 = 1000ppm, T= 303 K, M_a= 2gm, V= 100 ml, pH= 7)

TABLE II PARAMETER VALUES FROM FITTING THE ADSORPTION EQUILIBRIUM

Isotherm model	**Parameters value**	**Sum of squares error**
Freundlich $q_e = K_f C_e^{1/n}$	K_f=1.8492 n =1.9312	0.2422
Langmuir $q_e = \frac{q_0 . K_l . C_e}{1 + K_l . C_e}$	q_0 = 10.31 K_l = 0.1585	0.4005
Fritz-Schlunder $q_e = \frac{\alpha_1 . C_e^{\beta_1}}{1 + \alpha_2 . C_e^{\beta_2}}$	α_1= 0.2593 β_1= 6.6109 α_2=0.1327 β_2=6.1161	0.9724

B. Kinetic studies

1. **Initial concentration effect**

The result of initial concentration has an effect on the kinetics of adsorption. The procedure of the experiment has been discussed in some detail in the earlier section. The result of the experiment has been shown in the figures 4 and 5, 6. In Fig. 4 the bulk concentrations have been plotted against time and in Fig. 5 reduced bulk concentration, (C/C_0) have been plotted against time. The concentration decay curves, for three different initial concentrations keeping other parameters constant, indicate that initially the rate of disappearance of the adsorbate is high for the solution with higher initial concentration. After a certain period of time the decay curves are found to be almost parallel to each other indicating that the rate of disappearance of adsorbate becomes almost identical and are found to be parallel to each other.

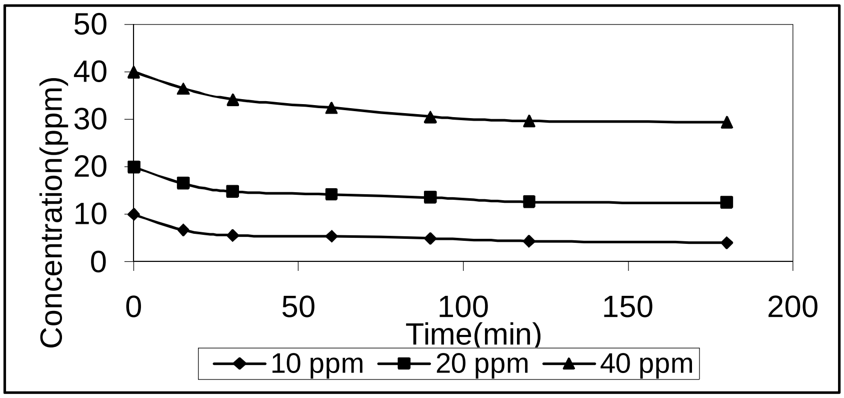

Fig 4: Effect of initial concentration on the adsorption of lead
(M_a= 100gm, V= 5000 ml, pH= 7, T= 303 K, effluent flow rate -50 ml/sec)

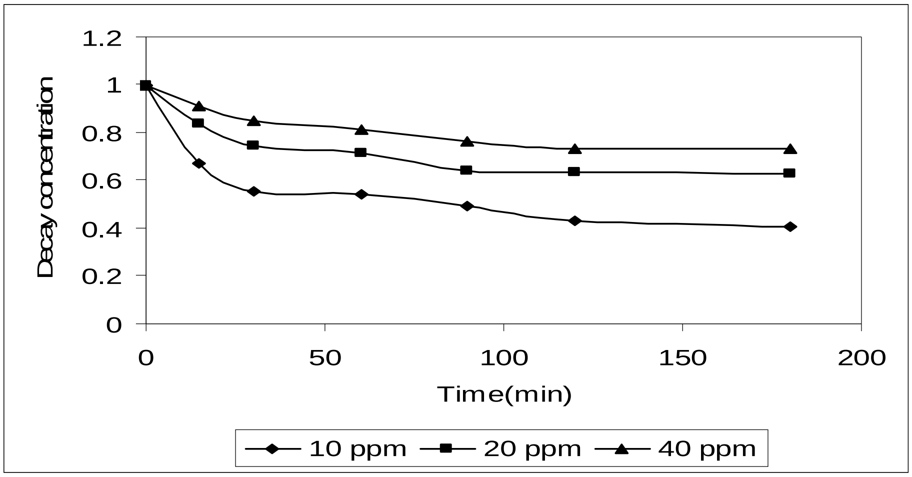

Fig 5: Effect of Decay concentration on the adsorption of lead
(M_a= 100gm, V= 5000 ml, pH= 7, T= 303 K, effluent flow rate -50 ml/sec)

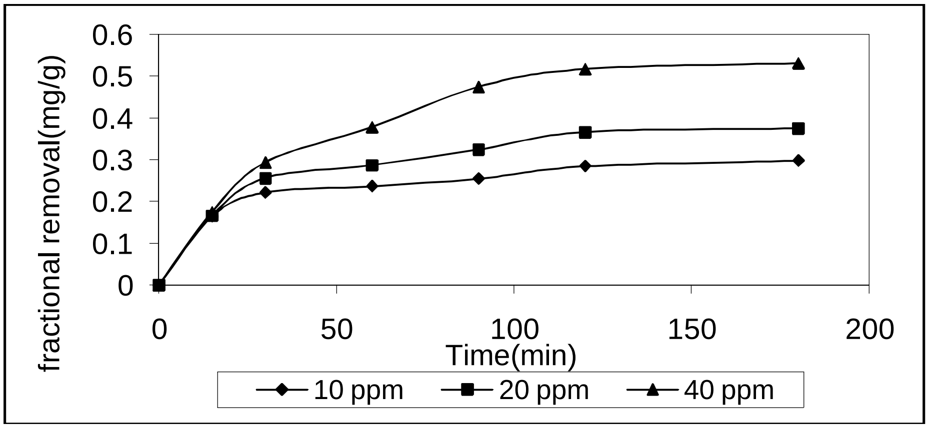

Fig 6: Effect of fractional removal on the adsorption of lead
(M_a= 100gm, V= 5000 ml, pH= 7, T= 303 K, effluent flow rate -50 ml/sec)

2. Effect of adsorbent dose

For this study different amounts of adsorbent (ranging from 100gm to 200 gm) were taken in the Fluidized bed column separately.5000ml of approximately diluted solution was added to the tank. The initial concentration was identical for all the experiments and other parameters like flow rate, pH of the solution, particle size etc, were kept constant. The concentrations of the solution were determined by AAS. Two such experiments were carried out with the same initial concentrations 10 ppm and 5 ppm. From the result it shows that fractional removal of lead increases with increase in adsorbent dose and is found to be almost parallel to each other at 120 min.

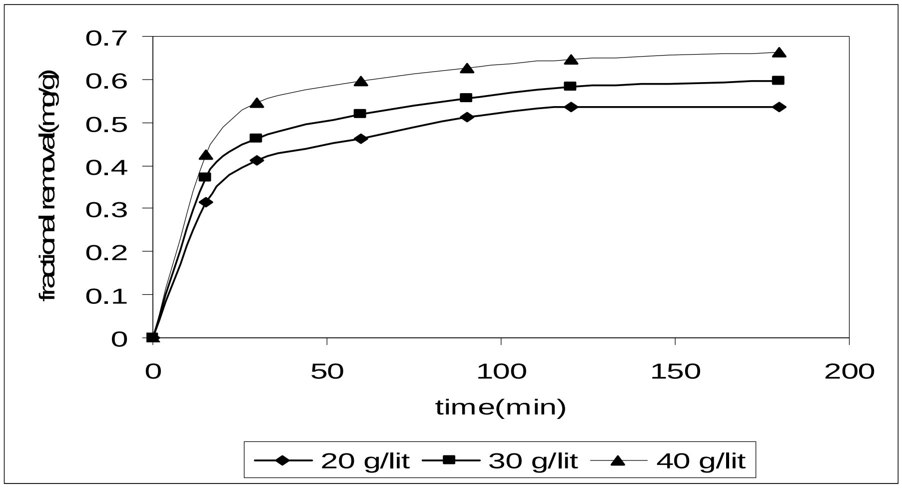

Fig 7: Effect of fractional removal of lead on the adsorbent dose
(C_0=10 ppm, V= 5000 ml, pH=7, T= 303 K, effluent flowrate-50ml/sec)

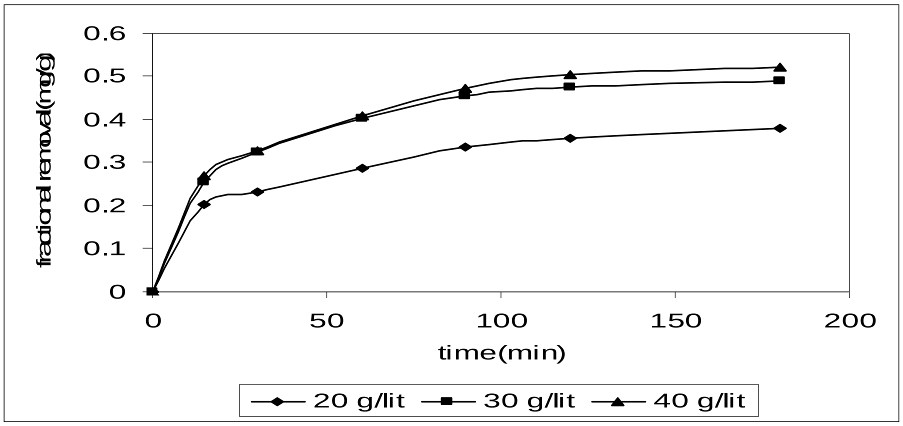

Fig 8: Effect of fractional removal of lead on the adsorbent dose
(C_0=5 ppm, V= 5000 ml, pH=7, T= 303 K, effluent flowrate-50ml/sec)

3. **Effect of particle size**

The adsorption was also found to be dependent on particle size. The results of these experiments are given in figure 9. The concentration decay curves indicates that the mass transfer rate and extent adsorption higher in case of the smaller particles than that in case of bigger size particles.

This is probably due to the fact that smaller particles have more surface area compared to equal amount of the bigger particles. Also the bigger particles have more diffusion resistance to mass transfer than smaller one. Since adsorption is a surface phenomenon, the particles with higher surface area have greater adsorption capacity in comparison to the particles with lower surface area.

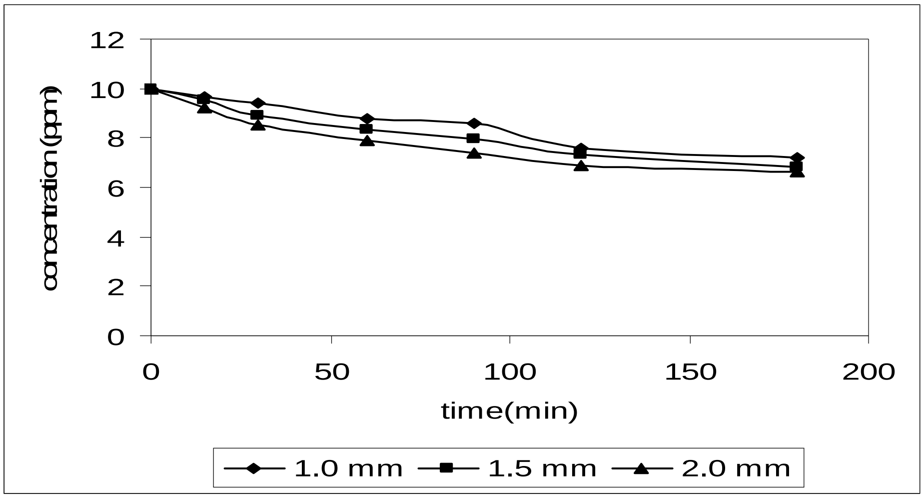

Fig 9: Effect of particle sizes on the adsorption of lead
(M_a= 100gm, V= 5000 ml, pH= 7, T= 303 K, effluent flow rate -50 ml/sec)

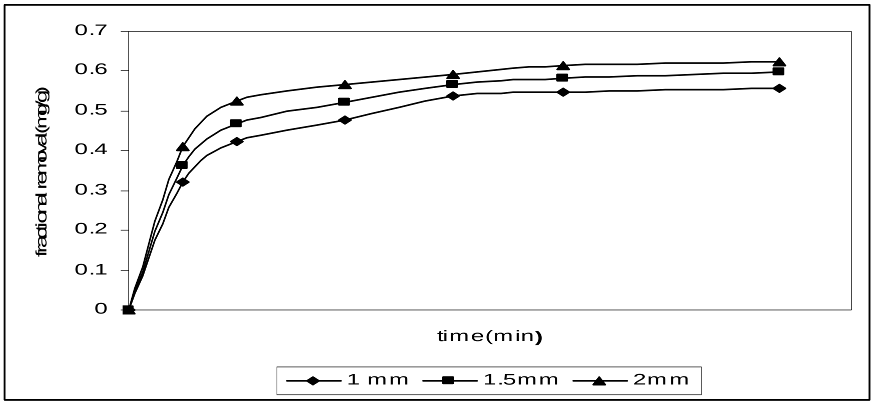

Fig 10: Effect of fractional removal of lead on the adsorbent dose
(C_0=10 ppm, V= 5000 ml, pH=7, T= 303 K, effluent flowrate-50ml/sec)

4. Effect of Flow rate

100 gms of fixed amount adsorbent was taken in the column and 5000ml of approximately diluted lead solution is taken in a tank. Three such experiments were carried out with various flow rates (ranging from 50 to 100 ml/sec) keeping all other parameters, amount of adsorbent, pH of the solution, particle size, initial concentration etc. From the result it shows that as the flow rate increases the contact time between the particles increases so the tendency to adsorb lead also increases. Increase in flow rate increases the removal percent of lead and is found to be almost parallel to each other at time 115 min.

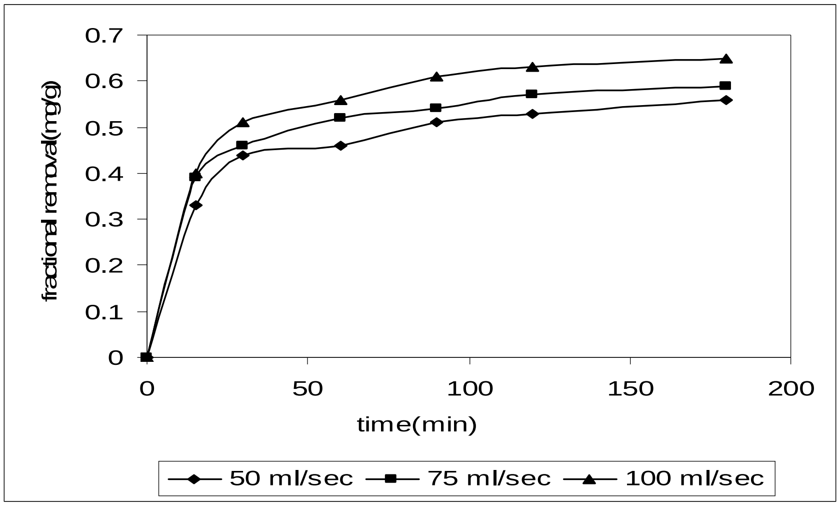

Fig 11: Effect of flow rate on the adsorption of lead
(M_a= 100gm, V= 5000 ml, pH= 7, T= 303 K, effluent flow rate –(50-100) ml/sec)

VI. CONCLUSION

Removal of lead from aqueous solutions is possible using several abundantly available low-cost adsorbents. The present investigation shows that bauxite is an effective adsorbent for the removal and recovery of lead from aqueous solutions. From the kinetics studies it is observed that adsorption of lead is very rapid in the initial stage and decreases while approaching equilibrium. The equilibrium time increases with initial lead concentration. The percentage removal of lead increases with the increase in adsorbent dosage and decrease with increase in initial lead concentration. Smaller particles are much more effective in the removal of adsorbate. Hence percentage lead removal increases with decrease in the particle size.

Experimental results are in good agreement with Freundlich adsorption isotherm model, and have shown a better fitting to the experimental data. Removal percentage of lead using this low cost adsorbent is ranging between 55-62.

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