Removal of Heavy Metal by using AFC Polymer

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***Abstract*- Presence of lead, a heavy metal in the environment has been a serious concern especially with rapid industrialization which has created new uses for lead. The acute toxicity of lead to aquatic life and humans and the stringent effluent standard to be met by industries as specified by regulatory organizations has necessitated the development of innovative, effective and economical methods for treating lead. An adsorption process using aniline-formaldehyde condensate coated silica gel is an attractive option for the removal of lead from wastewater. In this study batch kinetic and isotherm studies were carried out on a laboratory scale to evaluate the adsorption capacity of aniline-formaldehyde condensate coated silica gel. Effects of pH, initial Pb^{+2} concentrations, dosage of adsorbent and temperature on Pb^{+2} removals was studied. Desorption studies were also conducted using mineral acids to evaluate desorption of Pb^{+2} from the adsorbent. The column analysis was also done to study the effect of bed depth and flow rates on adsorption of Pb^{+2} onto AFC coated silica gel in continuous mode.**

Also in the present study, aniline- formaldehyde condensate was coated on several other base materials such as sand and waste biomaterials such as eggshell, tealeaves and flyash etc. Effects of pH, contact time etc. on Pb^{+2} removals by the above adsorbents were also studied. The kinetics of adsorption of Pb^{+2} ions on aniline-formaldehyde condensate coated silica gel can be adequately described by the Lagergren second order reaction rate model.The batch isotherm studies showed that the adsorption data can be described by the Langmuir and Freundlich model. However, the Langmuir model was found to describe the adsorption data better than the Freundlich model. By ignition of lead bounded waste biomaterials, 90% Pb^{+2} were able to be recovered back in solution.

Keywords: Lead; support material; aniline formaldehyde condensate; complexation; adsorption capacity

Keywords: Advance oxidation processes, photocatalysis, TiO_2, Acid Orange 7

I. INTRODUCTION

The presence of heavy metal ions such as Cu^{2+}, Cr^{6+}, Hg^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, etc. in the environment is of major concern due to their toxicity to many life forms. Various industrial processes result in the release of heavy metals in the natural water systems. This has lead to increasing concern about the effects of toxic metal as environmental contaminants. Unlike organic pollutants, the majority of which are susceptible to biological degradation, metal ions do not degrade into any harmless end products (Gupta *et al.,* 2001).

A number of technologies for treating contaminated effluents have been developed over the years. The most important of these techniques include chemical precipitation, filtration, ion-exchange, reverse osmosis and membrane systems. However, all these techniques have their inherent advantages and limitations in application .

Functionalized polymers with amine as functional group have affinity for metal ions. In the present study, a functionalized polymer namely aniline-formaldehyde condensate (AFC) coated on silica gel, eggshell, sand, tealeaves and flyash separately as support material was synthesized. Main objective of the present study is to investigate the effect of various support material on metal removal capacity of AFC polymer. Studies were conducted using lead (Pb^{+2}) as the model ion and the effect of various parameters affecting adsorption like contact time, initial metal ion concentration and pH has been investigated in batch mode.

A. Methods available for removal of heavy metals

Factors to be considered in the choice of a method to be adopted for the treatment of heavy metal-bearing wastewater should include: high removal efficiency, economic feasibility in terms of materials, equipment and energy, applicability to small, intermediate and large scales, low productivity of highly enriched spent materials and capability of reducing heavy metal ion concentration to levels below established regulatory standards.

The technologies available for the removal of heavy metals from the wastewater include chemical precipitation, ion exchange, reverse osmosis, electrodialysis, adsorption, chemical oxidation or reduction, chemical treatment etc. A brief presentation of each method is given below.

Reverse Osmosis, Electrodialysis, Ion exchange, Chemical Precipitation , Adsorption

B. Types of adsorbents

The principal types of adsorbents include activated carbon, synthetic polymers, silica-based adsorbents, plant biomass etc.

Activated carbon has undoubtedly been the most popular and widely used adsorbent throughout the world. In spite of its prolific use, activated carbon remains an expensive material since higher the quality of activated carbon, the greater its cost.

Norton et al. (2004) used dewatered waste activated sludge from a sewage treatment plant for the biosorption of zinc from aqueous solutions. The adsorption capacity was determined to be 0.564 mmol/g of biosolids.

Olive mill residue was used as adsorbent for removal of Cu^{+2} ion (Pagnanelli et al., 2002). The results revealed that copper was maximally adsorbed in the range of 5.0 to 13.5 mg/g under different operating conditions.The simultaneous biosorption capacity of copper, cadmium and zinc on dried activated sludge (Hammaini et al., 2003) were 0.32 mmol/g for metal system such as Cu-Cd; 0.29 mmol/g for Cu-Zn and 0.32 mmol/g for Cd-Zn. The results showed that the biomass had a net preference for copper followed by cadmium and zinc. Keskinkan et al. (2003) studied the adsorption characteristics of copper, zinc and lead on submerged aquatic plant *Myriophyllum spicatum.* The adsorption capacities were 46.69 mg/g for lead, 15.59 mg/g for zinc and 10.37 mg/g for copper. Crab shell particles were used for removal of lead (Lee et al., 1998). The removal efficiency of lead was dependent on contact time, initial solution pH, crab shell dose, ionic strength, co-ion concentration and settling time. Approximately 99% of the lead was removed within 2 hours after contact with crab shell particles. The removal efficiency was slightly affected by initial solution pH over 3.11.

Ajmal et al. (2000) carried out an adsorption study on *Citrus reticulata*, an agricultural waste originated from the fruit peel of orange, for the removal of Ni^{2+} from electroplating wastewater. It was reported that maximum removal of Ni^{2+} occurred at pH of 6.0 and that the adsorption followed

C. *Adsorption equilibrium and isotherms*

Adsorption occurs when an adsorbent comes in contact with a liquid containing the adsorbate and adsorption sites on the adsorbent become filled. Equilibrium occurs when the adsorption sites are filled. Equilibrium is a phenomenon when the rate of adsorption and rate of desorption are equal (Cooney, 1999).

The relationship between the amount of adsorbate adsorbed onto the adsorbent surface and the equilibrium concentration of the adsorbate in solvent at equilibrium at a constant temperature may be estimated by various adsorption isotherm models. The most common isotherms used in wastewater treatment are Langmuir and Freundlich isotherms.

The basic assumptions of Langmuir isotherms are

- Metal ions are chemically adsorbed at a fixed number of well-defined sites;
- Each site can hold only one ion;
- All sites are energetically equivalent;
- There is no interaction between the ions
- It is single or monolayer

Langmuir adsorption isotherm is expressed as (Voice and Weber, 1983)

$$q_e = \frac{b q_m C_e}{1 + b C_e} \quad (1)$$

Where, q_m, b are empirical constants
C_e = equilibrium concentration of adsorbate in solution after adsorption (mg/L) and

q_e= mg adsorbate/g adsorbent at equilibrium.

The parameter q_m (mg/g) represents the concentration of the adsorbate on the surface when one complete monomolecular layer of coverage is achieved and b (l/mg) is the second parameter.

The constants in Langmuir model can be determined by plotting C_e/q_e versus C_e and making use of equation (1) rewritten as

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (2)$$

The constants can be determined from the slope and the intercept.

Another common isotherm, Freundlich isotherm presents an empirical adsorption isotherm for non-ideal system. The Freundlich model is by far the most utilized isotherm model in wastewater treatment. It has been reported that data for the adsorption involving adsorbates within a liquid phase is best fitted using the Freundlich model (Cooney, 1999). The Two-Parameter Freundlich model relates the sorbed phase concentration to an equilibrium concentration of the adsorbate according to the following equation (Voice and Weber, 1983)

$$q_e = K_f C_e^{1/n} \quad (3)$$

where q_e= mg adsorbate/g of adsorbent at equilibrium and C_e=equilibrium concentration of adsorbate in solution after adsorption mg/L

K_f and n are empirical constants, which depend on several environmental factors.

Taking log on both sides of (3)

$$\mathrm{Log}(q_e) = \log(K_f) + 1/n \log(C_e) \quad (4)$$

II. SCOPE OF THE WORK AND OBJECTIVE

Heavy metals appear in the environment through various anthropogenic activities like copper and cadmium from electro plating industry, chromium from tanning industry, wood preservative, textile industry, mercury from caustic soda and chlorine industries, arsenic from fertilizers etc. Heavy metals are toxic and harmful even at low concentrations and limits have been placed on their concentration in potable water supplies and effluent discharges by various agencies throughout the world. Considering the merits and limitations of various techniques reported in literatures, adsorption is considered an efficient technique for the removal of metal ions. With proper control of the process, it is possible to meet the discharge limits and no harmful by-products are generated like ion exchange and reverse osmosis. Further, when metal ion recovery is possible with reuse of sorbents, adsorption becomes highly cost effective. Literature review highlighted the effectiveness of various functionalized polymers for removals of heavy metal ions form wastewater. Functionalized polymers with amine (NH_2) (derivative of ammonia) as functional group are known to have affinity for metal ions. Nitrogen atom in amine, can make bond with positive charge due to presence of electron in *sp3* orbital of nitrogen. Polyacrylonitrile fibers, polyacrylamides and polyethyleneimine are various functionalized polymers with amine groups, which were successful in removing several heavy metal ions from wastewater. However, the synthesis procedures of many functionalized polymers like polyethylemine, polyvinylpyridine are complex. Also, synthesis of many functionalized polymers involved high cost. Therefore there exists a need for synthesis of low cost functionalized polymer with affinity for metal ions.

Very recently, a functionalized polymer, named aniline formaldehyde condensate (AFC) containing significant number of amine groups (NH_2) was successfully used for removal of copper and chromium from aqueous solution (Kumar, 2005; Kumar 2007). This polymer can be easily synthesized by polymerization of aniline in presence of formaldehyde in acidic medium (Liu and Freund, 1997). Amine group present in the AFC polymer probably replaced one or more of water molecules from metal molecules and formed coordination bonds with metal ions. Upon addition of acid the amine groups got prorogated and released metal ions. Interaction of aniline formaldehyde condensate (AFC) with metal ion in neutral medium and the process of desorption of metal ion are shown in Figures 1(b) and 1(c)respectively.

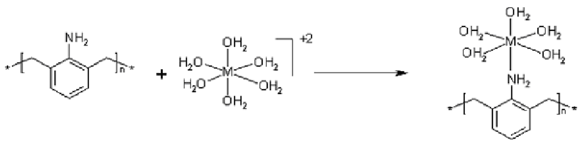

Fig 1(A): Schematic of metal ion and aniline-formaldehyde resin interaction

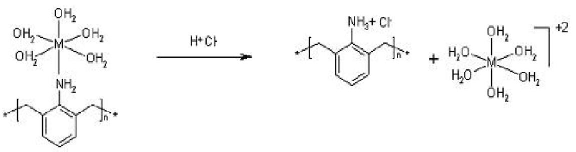

Fig 1(B) Desorption of metal ions from aniline-formaldehyde resin in acidic solution

This AFC polymer is of resinous form. In order to improve the rigidity of the polymer and to facilitate separation of metal ion after metal-polymer interaction, addition of support material in polymer matrix was necessary. Previous work was conducted using silica gel as the support material (Kumar, 2005). Silica gel is a nontoxic, nonflammable and chemically inert material. It is resistant to temperature and organic solvent. However, silica gel is expensive. If silica gel can be replaced by low cost base materials like sawdust, baggase etc. overall treatment cost may decrease significantly. Lead (Pb^{+2}) is selected as the model metal ion and objective of the present study is to investigate the effect of silica gel on efficiency of aniline formaldehyde condensate (AFC) polymer for removal of heavy metal. Detail methodology of the work is listed below:

To investigate the effectiveness of AFC coated silica gel in the removal of lead under varying experimental conditions:

- To determine appropriate kinetic model and isotherm.
- Desorption of lead ion after adsorption.
- Use of alternative low cost materials as support of the AFC.

III. MATERIALS AND METHODS

A. Materials and Reagents

Analytical grade aniline ($C_6H_5NH_2$) purchased from Merck was purified by general distillation method. Aniline was soaked with KOH pellets for overnight before distillation. Silica gel (60–120 mesh size), methanol, formaldehyde (37%) and concentrated HCl were purchased from S.D. Fine Chem and were used as received. AR grade concentrated H_2SO_4 and NaOH were obtained from S.D. Fine Chem and SRL respectively and used to adjust pH values of samples. Lead nitrate [$Pb(NO_3)_2$] was purchased from Oster. All the solutions were prepared using deionized water prepared in the laboratory by Reverse Osmosis process.

B. Synthesis of Adsorbent

Synthesis of Aniline Formaldehyde Condensate

Aniline formaldehyde condensate was synthesized by reacting formaldehyde with aniline as per Liu and Freund (1997) as shown in the Figure 2(a). 10 mL of 37% formaldehyde was added to a mixture of 18.4 mL aniline and 6 mL of HCl. The solution was then heated in a water bath at 80-85^{0}C for 2 hours. The mixture was then neutralized by 8 mL of 30% NaOH and the temperature was decreased to 60^{0}C. After one hour it was removed from the water bath and kept overnight at room temperature.

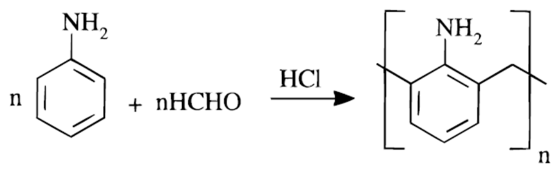

Fig. 2.(a): Synthesis of aniline formaldehyde resin

Coating of silica gel with AFC

Aniline formaldehyde condensate (AFC) obtained was in resinous form. In order to make a granular adsorbent addition of support material was necessary (Kumar, 2005; Kumar 2007). Previous work was conducted using silica as support material for removal of copper and hexavalent chromium (Kumar, 2005 and Kumar et al., 2007). In order to compare and standardize the work with lead ion silica was selected as the support material for present work. AFC resin was dissolved in 25 mL methanol (CH_3OH) and then it was heated in a bath at 60-65^{0}C until all the resin was dissolved. It was observed that maximum 25 g of silica could be mixed in methanol-resin solution. Then the methanol-resin silica mixture was mixed manually for 10-15 minutes.

C. Experimental Methods

Lead nitrate [$Pb(NO_3)_2$] was used as source of lead (Pb^{2+}) in the present work. Stock lead solution was prepared by dissolving 0.7992 gm of lead nitrate in 500 mL distilled water. Lead solution of desired concentration was prepared by diluting stock solution. All experiments with lead were conducted in batch mode in one litre glass beaker containing one litre aqueous solution of lead. Reaction pH was adjusted and maintained constant at desired level with 0.1 N H_2SO_4 /0.1 N NaOH. All experiments were conducted at room temperature (18-22^{0}C) without any temperature control. pH was monitored continuously during the reaction by a combined glass electrode (calibrated with buffers of 4.0 and 7.0) immersed in the aqueous solution. Reaction started after addition of weighted quantity of adsorbent in lead solution. Mixing was done uniformly with the help of a magnetic stirrer. At regular time intervals, effluents were collected from the top of the beaker through a pipette and stored in specimen tubes. The aqueous phase was separated from the adsorbent by filtration.

Experiments were conducted with following variables:

- Effect of pH: Solution pH was varied from 3.0-6.0 using lead concentration of 50 mg/L. Reaction was conducted with AFC silica gel and also without any adsorbent.
- Initial concentration of lead ion: Initial concentration of lead ion was varied from 10-200 mg/L at constant reaction pH of 6.0 using AFC coated silica gel dose of 2 g/L.
- Dose of AFC coated silica gel: Dose of AFC silica gel was varied from 0.5 - 50 g/L at six initial concentrations of Pb^{+2} ions: 25, 50, 75, 100, 150 and 200 mg/L.
- Effect of temperature: The temperature of lead solution was varied from 20 to 40^{0}C and the effect of temperature on lead removal was studied.
- Desorption study: Recovery of lead ions from the functionalized polymer coated silica gel adsorbent.

IV. RESULT AND DISCUSSION

In the present work removal of heavy metal was studied by a functionalized polymer, named aniline-formaldehyde condensate. Pb^{+2} was selected as the metal for this study and studies were conducted in batch as well as continuous mode with polymer coated on silica gel. In batch mode studies were conducted to know the effects of various parameters like pH, initial Pb^{+2} concentration, dose of adsorbent, temperature etc. Continuous mode studies were conducted using a laboratory scale column. Also studies were conducted to know desorption of Pb^{+2} ions from the AFC coated polymer. Efforts were also made to investigate lead removal by AFC polymer coated on various low cost materials.

Table 1: EDX analysis of sand and AFC coated sand before and after Pb^{+2} adsorption

Element	Sand		AFC coated sand before adsorption		AFC coated sand after adsorption	
	Weight (%)	Atomic (%)	Weight (%)	Atomic (%)	Weight (%)	Atomic (%)
C	--		49.09	60.23	79.36	87.10
O	48.23	62.45	32.07	29.54	8.77	7.22
Na	2.55	2.29	2.44	1.57	1.08	0.62
Al	7.39	5.67	3.26	1.78	2.59	1.26
Si	35.76	26.37	13.14	6.89	6.62	2.58
K	6.07	3.22	--	--	1.10	0.99
Pb	--	--	--	--	0.48	0.23

V. SUMMARY AND CONCLUSIONS

Laboratory scale study was conducted in batch and continuous mode to evaluate the potential of AFC polymer for the removal of lead ions from aqueous solution. The summary of experimental observations is given below:

1. Reaction pH was the most critical parameter, which controlled Pb^{+2} removal by aniline-formaldehyde condensate coated silica gel. Removal of Pb^{+2} ions increased with increase in solution pH due to less competition with H^+ ion.
2. The optimum pH for lead adsorption onto AFC coated silica gel was 6.0 with 79% removal and 19 m/g of lead uptake. In control experiment at pH 6.0, lead removal was 10%.
3. The kinetic studies indicated that the equilibrium time required for the adsorption of Pb^{+2} ions from aqueous solution by aniline-formaldehyde condensate coated silica gel was 2 hours.
4. Removal of Pb^{+2} decreased with increase in initial concentration of lead ion (98% and 44% at Pb^{+2} concentrations of 10 mg/L and 200 mg/L respectively). However the uptake of lead ion by aniline-formaldehyde condensate coated silica gel increased with increase in initial concentration of lead. Lead uptake of 40.25 mg/g was achieved at initial concentration of Pb^{+2} of 200 mg/L.
5. Removal of Pb^{+2} ions by aniline-formaldehyde condensate coated silica gel followed second order kinetics. The second order rate constant decreased with increase in the initial Pb^{+2} concentrations.
6. The Langmuir and Freundlich isotherm models can be used to represent the adsorption data. However, the Langmuir model represented the adsorption process better then the Freundlich model.

The Pb^{+2} adsorption yield increased with the increasing temperature. Hence the adsorption process was endothermic.

VI. REFERENCES

[1] Gupta, K.V., Gupta, M. and Sharma, S. (2001) "Process development for the removal of lead and chromium from aqueous solutions using red mud-an aluminium industry waste", Water Res., 35, 1125–1134.
[2] Norton, L., Baskaran, K. and McKenzie, T. (2004) "Biosorption of zinc from aqueous solutions using biosolids", Adv. Environ. Res., 8, 629-635.
[3] Pagnanelli F., T. and Veglio, F. (2002) "Olive mill solid residues as heavy metal sorbent material, a preliminary study", Waste Managem., 22, 901-907.
[4] Hammaini et al., (2003) "Simultaneous uptake of metals by activated sludge", Minerals Engg., 16, 723-729.
[5] Keskinkan, O., Goksu, M.Z.L., Yuceer, A., Basibuyuk, M. and Forster, C.F. (2003) "Heavy metal adsorption characteristics of a submerged aquatic plant *(Myriophyllum spicatum*)", Process Biochem., 39, 179-183.
[6] Lee, M., Lee, S., Shin, H. and Yang, J. (1998) "Characteristics of lead removal by particles crab shell", Process Biochem., 33, 749-753.
[7] Ajmal, M., Rao, R.A.K., Ahmad, R. and Ahmad, J. (2000) "Adsorption studies on Citrus reticulata (fruit peel of orange): removal and recovery of Ni(II) from electroplating wastewater", J. Hazard. Mater. B 79, 117–131.
[8] Cooney, D O., (1999) Adsorption Design for Wastewater Treatment. Lewis Publishers, CRC Press LLC, Boca Raton, Florida.
[9] Kumar, G.P. (2005) "Removal of heavy metals from wastewater by functionalized polymer coated silica gel", M. Tech thsis, Department of Civil Engineering, I.I.T. Guwahati, India.
[10] Kumar, P.A., Ray, M. and Chakraborty, S. (2007) "Hexavalent chromium removal from wastewater using aniline formaldehyde condensate coated silica gel", J. Hazard. Mater., 143, 24-32
[11] Liu, G. and Freund, M.S. (1997) "New Approach for the Controlled Cross-Linking of Polyaniline: Synthesis and Characterization", Macromol., 30, 5660-5665.