ADSORPTION OF LEAD IONS FROM AQUEOUS SOLUTION BY FUNCTIONALIZED POLYMER ANILINE FORMALDEHYDE CONDENSATE COATED ON SILICA GEL AS SUPPORT MATERIAL

Jonali Saikia*

Department of Civil Engineering, Indian Institute of Technology Guwahati, India.

***Corresponding Author: Jonali Saikia**

Department of Civil Engineering, Indian Institute of Technology Guwahati, India.

ABSTRACT

Heavy metals are accumulated in the environment as an adverse outcome of several natural as well as diverse anthropogenic activities. They are non-biodegradable and persistent environmental contaminants and their entry into food chains can cause serious health impairments; once their accumulated concentrations in humans exceed maximum permissible limits. Conventional treatment techniques like chemical precipitation, ion exchange, reverse osmosis, membrane technology etc. are widely used for treatment of industrial wastewater containing toxic heavy metals. Some of these techniques are quite expensive and have major disadvantages like partial metal removal, generation of large quantity of sludge containing high concentrations of toxic heavy metals etc. Adsorption is one of the promising technologies which can efficiently remove toxic heavy metals from industrial effluents. This study was done for investigating the lead adsorption capacity of Aniline Formaldehyde Condensate, a resinous functionalized polymer which was later on coated on silica gel as support material. Batch experiments were conducted considering important parameters affecting adsorption process like solution pH, adsorption time, initial Pb^{+2} ion concentrations and dosage of adsorbent. Optimum pH for lead adsorption by AFC silica gel was 6.0, with the maximum lead removal of 80% and corresponding metal uptake of 19.34 mg/g. With the increase in initial Pb^{+2} concentrations from 10 mg/L to 50 mg/L, there was a decreasing trend of lead removal capacities from 98% to 77%, however; corresponding lead uptake followed an increasing trend from 5.56 mg/g to 15.04 mg/g. Langmuir model better describes the adsorption process with Langmuir monolayer uptake of 8.87 mg/g. During desorption study, maximum desorption was achieved using 6N HNO_3 (49.37%), which was successively followed by 6N HCl (44.95%) and 6N H_2SO_4 (44%), similarly; with 0.2 N EDTA, 38.58% recovery of the metal was possible.

KEYWORDS: Adsorption, desorption, first order, second order kinetics, Langmuir, Freundlich isotherms.

1. INTRODUCTION

The element with atomic weights 63 and 200, having specific gravity exceeding 4.0 are considered as heavy metals (Freeman, 1998). Some of the heavy metals like cobalt, copper, iron, manganese, molybdenum, vanadium, strontium, and zinc are essential for living organism in very minute amount. On the other hand, there are some non-essential heavy metals like cadmium, chromium, mercury, lead, arsenic, and antimony, which are highly toxic to the living organisms (USEPA, 1996). In contrast to biologically degradable organic pollutants, heavy metals never degrade into any harmless end products (Gupta *et al.,* 2001). Hence, the presence of heavy metal in natural or industrial wastewaters is one of the most serious global environmental problems (Axtell *et. al.,* 2003, Amarasinghe *et al.,* 2007). So, in order to protect the environment from possible contamination by industrial effluents, it is very essential to remove the heavy metals before discharging such effluents into natural water bodies.

Various natural as well as anthropogenic activities result in continuous release of ubiquitous toxic heavy metal lead into the environment. Industries like acid battery manufacturing, metal plating and finishing, painting etc. generate huge volume of toxic effluents containing lead. Some industrial effluents may contain as high as 200-500 mg/L of Pb^{+2} concentrations, which is significantly higher than the WHO drinking water quality standard of 50 μgL^{-1}, as such the Pb^{+2} concentrations of such effluents must be reduced to 0.05–0.10 mg/L before releasing to sewerage systems or water ways (Ucun *et al.,* 2003; Vilar *et al.,* 2005; Özacar *et al.,* 2008).

Exposure to lead in drinking water above WHO drinking water quality standard of 50μgL^{-1}, poses several adverse effects on human health. Skerfying *et al.,* 1998; Soylac *et*

al., 2002, reported that lead acts as an enzyme inhibitor in human body by replacing zinc which is another essential element from heme enzymes. So, in order to protect the environment from adverse effects of lead, it is mandatory to remove the same from industrial effluents before discharging into receiving water bodies.

Some conventional techniques like chemical precipitation, ion-exchange, reverse osmosis, membrane filtration etc. are available for removal of lead from the contaminated industrial effluents; all these conventional techniques have their own merits and limitations. In case of chemical precipitation, huge volume of sludge with toxic compounds is generated, which is the major limitation of the process (Ahalya *et al.,* 2003). Ion exchange treatment requires resin regeneration and subsequent disposal of substantial volume of used reagent solutions thereby making the method quite expensive.

Adsorption is a promising technique which is widely used for removing heavy metals from the industrial wastewater. The merits of the adsorption process include high efficiency of removal of even very low levels of heavy metals, lower operating cost and generation of minimum volume of either chemical or biological sludge as well as efficient regeneration of the used adsorbent.

Bachale et al., 2016[a] employed several functionalized polymers based on amines derivatives such as ethylenediamine, polyacrylamides, poly-4-vinylpyridine, polyethyleneimine and aniline formaldehyde condensate for adsorption of metal ions. Kumar *et al.,* 2007[a]; Kumar *et al.* 2007[b] also used aniline formaldehyde condensate (AFC) which was coated on silica gel as support material for efficient removal of copper and chromium from wastewater. AFC polymer is characterized by the presence of significant number of amine groups (NH_2). Liu and Freund, 1997; synthesized the above polymer by the polymerization reaction between aniline and formaldehyde in Hydrocholoric acid medium. AFC polymer thus synthesized was of resinous nature, hence; for preparing a granular adsorbent, addition of support material in polymer matrix was essential. In this study, Silica gel was selected as the support material for the AFC polymer. Previous work was conducted using silica as supporting material for removal of copper and hexavalent chromium (Kumar *et al.,* 2007[a] and Kumar *et al.,* 2007[b]). In order to compare and standardize the work with lead ion, silica was selected as the support material for present work. Studies were conducted using lead (Pb^{+2}) as the model ion and batch experiments were conducted varying various parameters affecting adsorption process like solution pH, initial Pb^{+2} concentrations and dosage of the adsorbent. Attention was also focused to determine the appropriate kinetic model. Emphasis was also given to determine the Langmuir and Freundlich isotherm constants. Desorption study was also conducted after adsorption experiments

for the recovery of adsorbed Pb^{+2} ions as well as regeneration of the used adsorbent after adsorption.

2. MATERIALS AND METHODS

2.1 Materials
Aniline ($C_6H_5NH_2$) procured from Merck was purified through general distillation method to remove the impurities. Prior to distillation, Aniline was soaked with KOH pellets for overnight. Silica gel of 60–120 mesh size, methanol (CH_3OH), formaldehyde (37% HCHO) and HCl were procured from Merck. H_2SO_4 of AR grade and NaOH for adjusting sample pH were obtained from SRL. AR grade $Pb(NO_3)_2$ used for preparing stock solution of lead was procured from Merck.

2.2 Synthesis of Aniline Formaldehyde Condensate
AFC polymer was synthesized by the polymerization reaction between formaldehyde (HCHO) and aniline ($C_6H_5NH_2$) in acidic medium (HCl), as suggested by Liu and Freund (1997) (Fig 1(a)). A mixture of 18.4 mL aniline and 6 mL of HCl was taken in a reaction vessel, and 10 ml of formaldehyde (37%) solution was added slowly to the above mixture with precautions, since the resulting reaction was exothermic in nature. The mixture was then heated with proper mixing for 2h, using a water bath where temperature was adjusted to 80-85[0]C. Since, the above mixture was acidic in nature; it was neutralized by adding 8 mL of NaOH solution of 30% strength and subsequently heated for 1 h using water bath maintained at 60[0]C. The resin, thus prepared was thoroughly washed with warm water and washed water was decanted and the prepared resin was dried in a desiccator for a night to remove the moisture.

2.3 Coating of AFC on silica gel
The AFC polymer prepared as mentioned above was in resinous form. Resin was completely dissolved in Methanol (CH_3OH) by heating in a water bath maintained at 60-65[O]C. In order to synthesize a granular adsorbent, silica gel was used as a support material. The mixture of methanol-resin silica was thoroughly mixed manually and air dried over filter papers for duration of 6h. The air-dried mixture was further crushed manually and strained using an ordinary strainer and the granular adsorbent thus obtained was subsequently used for adsorption of Pb^{+2}.

2.4 Experimental design
2.4.1 Adsorption experiments
$Pb(NO_3)_2$ was used as the parent salt for preparing stock solution of lead of 1000 mg/L. Dilute solutions of lead of desired concentrations were prepared by proportionately diluting the stock lead solution with distilled water. All the experiments were conducted in batch mode; in a 1L glass beaker containing lead solution of desired concentrations. As per requirement, either 0.1 N H_2SO_4 or 0.1 N NaOH solution was used for adjusting and maintaining desired pH of the lead solutions while conducting the batch experiments. Solution pH was continuously monitored during each of the reactions by a

combined glass electrode of a pH meter (Make: Systronics; Model: 361) immersed in the aqueous lead 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 predetermined intervals of time, samples were collected with the help of a pipette, filtered out and the filtered samples were stored in specimen tubes prior to analysis. Experiments were conducted with the following variables.

(i) **Effect of solution pH:** Batch experiments were conducted with standard Pb^{+2} solution of 50 mg/L, using 2g/L AFC silica gel as the adsorbent, varying solution pH in the range of 3.0-6.0.

(ii) **Initial concentration of Pb^{+2} ions:** Another set of experiments were conducted in batch mode, varying initial concentration of Pb^{+2} ions in the range of 10-50 mg/L; using 2g/L of AFC silica gel as the adsorbent, at constant pH of 6.0 which was found to be optimum for lead adoption by AFC silica gel.

(iii) **Dosage of AFC coated silica gel:** The dosage of the adsorbent was varied within the range of 0.5- 50 g/L. With each of the above dosage, experiments were conducted using initial concentrations of Pb^{+2} ions as 25, 50, 75, 100, 150 and 200 mg/L. Initially solution pH was adjusted to 6.0 (optimum value) and thereafter all the experiments with varying dosage of adsorbent were conducted without pH control.

(iv) **Isotherm study:** Experimental study was further conducted to see the effect of increase of initial concentration of Pb^{+2} ions on uptake of lead using a fixed adsorbent dosage. The initial Pb^{+2} concentrations selected were 5, 10, 20, 40, 60, 80, 120, 150, 250, 350 and 450 mg/L and in each case, an adsorbent dosage of 2g/L was used.

2.4.2. Desorption experiments

Results of batch experiments revealed that Pb^{+2} adsorption by AFC silica gel was governed by pH of the solution i.e., presence of H^+ ion inhibited the Pb^{+2} removal, so the presence of H^+ should favor desorption of Pb^{+2} from adsorbent to aqueous phase. In the literature use of various mineral acids for desorption of metal ions from the loaded adsorbent are reported (Zhang *et al.,* 1998; Ajmal *et al.,* 2000; Martinez et al. 2006). In the present study, desorption of Pb^{+2} from metal-laden adsorbent was carried out using three mineral acids viz. HCl, H_2SO_4 and HNO_3 of strength 6 N, 2N, 1N and 0.5 N. Also study was conducted using EDTA of strength 0.2N, 0.1N and 0.05N. Lead loaded adsorbent was collected from batch experiments (initial Pb^{+2} 50 mg/L, reaction pH 6, with AFC silica gel dosage of 10 g/L). The desorption experiments were conducted by adding metal loaded adsorbent in 50 mL of either acid or EDTA solution in batch mode. All experiments on desorption were conducted for 1 h.

2.5. Analytical procedure

The supernatant was analyzed for Pb^{+2} concentrations by Atomic Absorption Spectrophotometer (Make: Varian, the Netherlands; Model: model 55B) with an air-acetylene oxidizing flame and a Hollow Cathode lead lamp (at a wavelength 283.3 nm) as the light source. Scanning electron microscopic (Make: Carl Zeiss, Germany; Model: LEO. 1430 VP) study was conducted for visualizing the surface morphology of plain silica gel and corresponding changes in surface morphology of AFC coated on silica gel adsorbent prior to and post Pb^{+2} adsorption. Energy Dispersive X-ray (EDX) analysis was also simultaneously conducted along with SEM analysis to further confirm the presence of lead atom on the AFC silica gel adsorbent post adsorption.

3. RESULTS AND DISCUSSION

3.1. Effect of reaction pH

pH of aqueous solution is an important parameter which governs the adsorption of metal by any adsorbent. So, in order to study the effect of pH on Pb^{+2} adsorption by AFC coated silica gel, pH of the aqueous solution of lead was varied from 3.0-6.0. Practically it was observed that at solution pH > 6.0, precipitation of lead ions occurred and so experiments were conducted up to a maximum pH of 6.0 in order to avoid lead precipitation. Uptake of lead (mg/g) is defined by the ratio of the difference between initial Pb^{+2} ion concentration (mg/L) in aqueous phase, and the Pb^{+2} ion concentration in aqueous phase at equilibrium (mg/L) to the AFC silica gel dosage (g/L).

Results of batch experiments indicated that minimum lead removal of 4% was achieved at solution pH of 3.0. The lead removal (%) follows an increasing trend with increase in solution pH; lead removal (%) was increased to 60.6% when solution pH was raised to 5.0, which further increased to 80% when solution pH was raised to 6.0. Similarly, uptake of lead by AFC coated silica gel follows a similar increasing trend with the rise in solution pH, as is evident from significant increase in lead uptake value from 0.95 mg/g at solution pH of 3.0 to 8.90 mg/g at solution pH of 4.0, which was further increased to 19.34 mg/g, with the increase in solution pH to 6.0.

3.1.1: Kinetic Studies

In order to in investigate the controlling mechanism behind adsorption of Pb^{+2} by AFC coated silica gel, the batch experimental data on variation of pH in the range of 3.0-6.0 were analyzed using two kinetic models, i.e. Lagergren first order kinetic model (Eq.(1(a)) and second order kinetic model (Eq.(2a)) as suggested by Ho and McKay, 2000; Ho, 2006.

$$q_{t=}q_e(1 - e^{-k_1 t}) \tag{1a}$$

$$q_t = q_e \frac{q_e k_2 t}{1 + q_e k_2 t} \tag{2a}$$

The linearized forms of these equations are given by 1(b) and 2(b)

$$log(q_e - q_t) = log q_e - \frac{k_1}{2.303}t \qquad (1b)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \qquad (2b)$$

Where q_t (mg/g) denotes metal uptake at any time t and q_e (mg/g) denotes metal uptake at equilibrium, k_1 (min^{-1}) and k_2 (g/mg.min) denote kinetic rate constants corresponding to Lagergren first order, and the second order kinetic models viz.
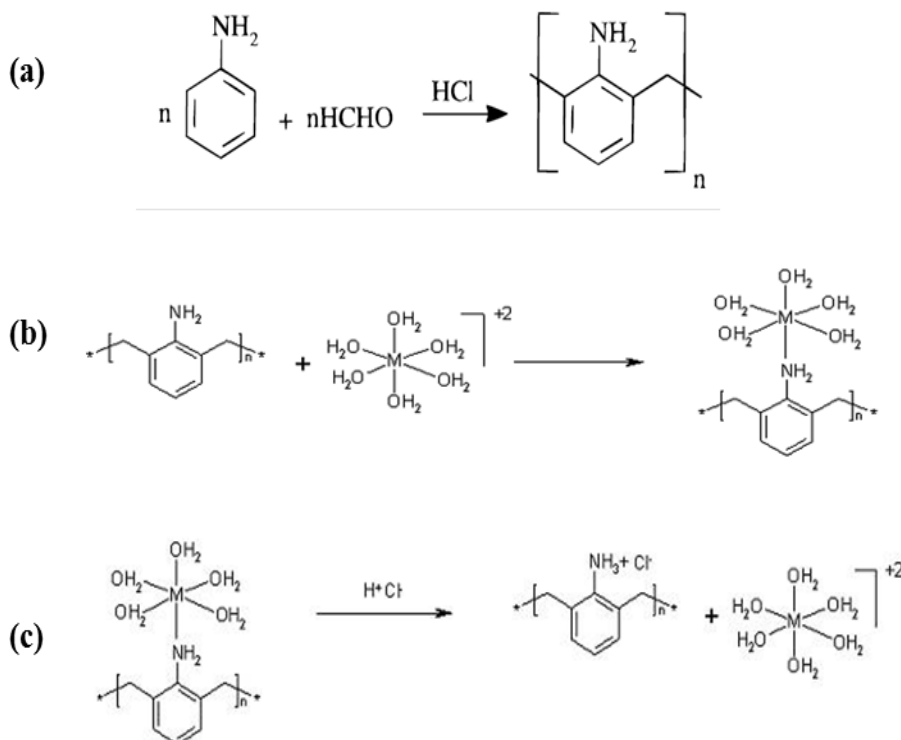

Fig 1: (a) Synthesis of aniline formaldehyde condensate (AFC) (b) Schematic of metal ion and aniline-formaldehyde resin interaction (c) Desorption of metal ions from aniline-formaldehyde resin in acidic solution.
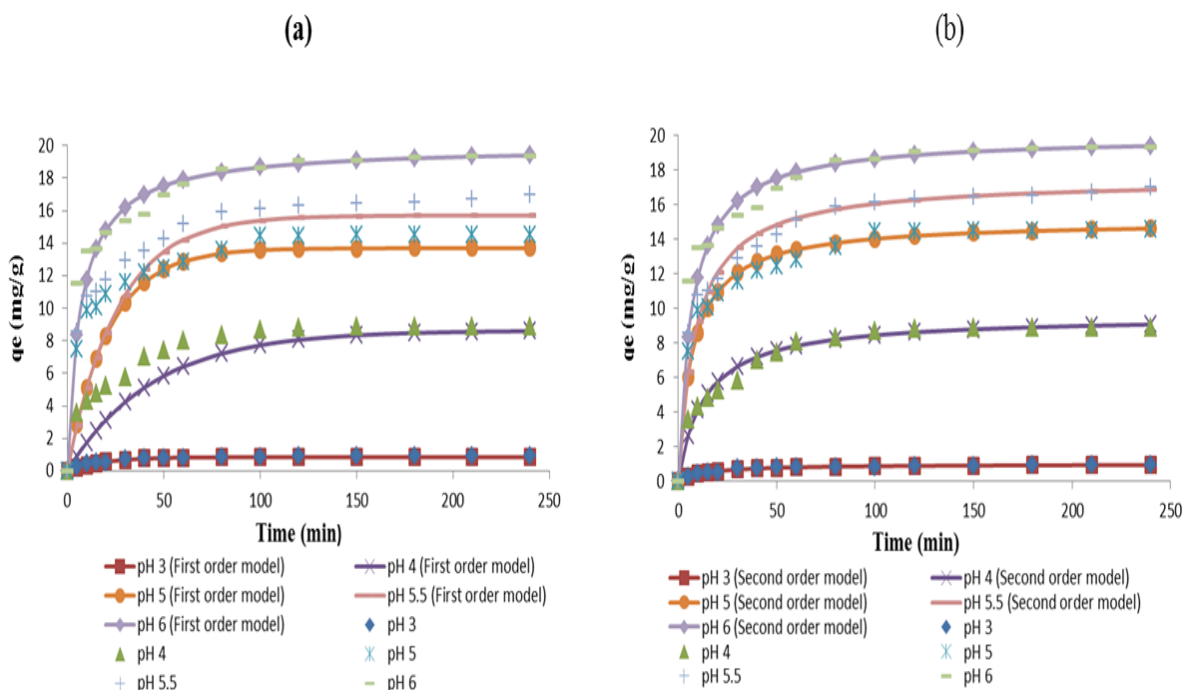

Fig. 2: Kinetics of lead uptake by AFC coated silica gel by (a) first order model of Lagergren (b) second order model of Lagergren.
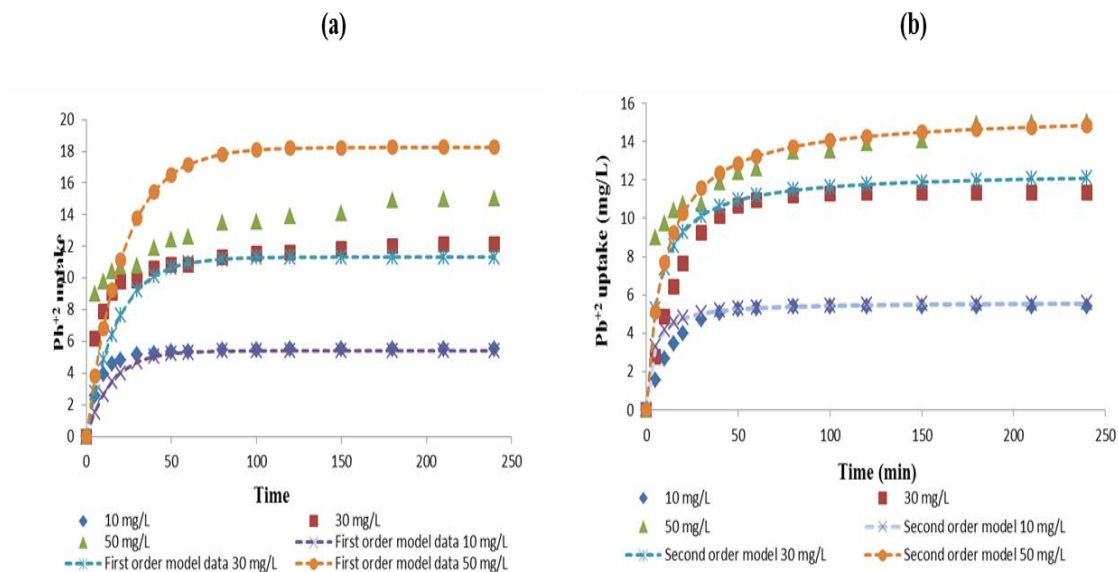
(a)   (b)

Fig. 3: Comparison of Pb^{+2} uptake by experimental and (a) first order model data (b) second order model data at various Pb^{+2} concentrations (pH 6.0; dose: 2g/L AFC coated silica gel).
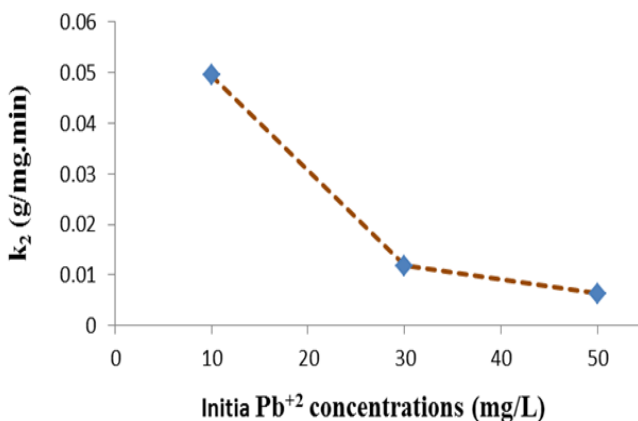

Fig. 4: Effect of initial Pb^{+2} concentrations on second order rate constant (k$_2$).

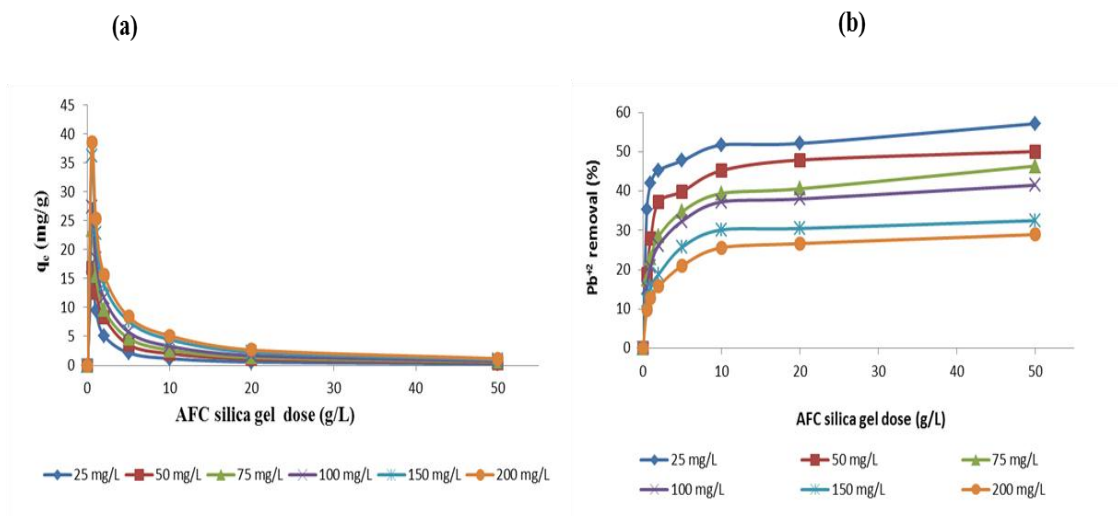(a)   (b)

Fig. 5(a): Effect of AFC coated silica gel dose on(a) (a) lead uptake at various Pb^{+2} concentrations at pH 6.0 (b) lead removal at various Pb^{+2} concentrations at pH 6.0 (Adsorption time 4; Initial Pb^{+2} 25-200 mg/L).

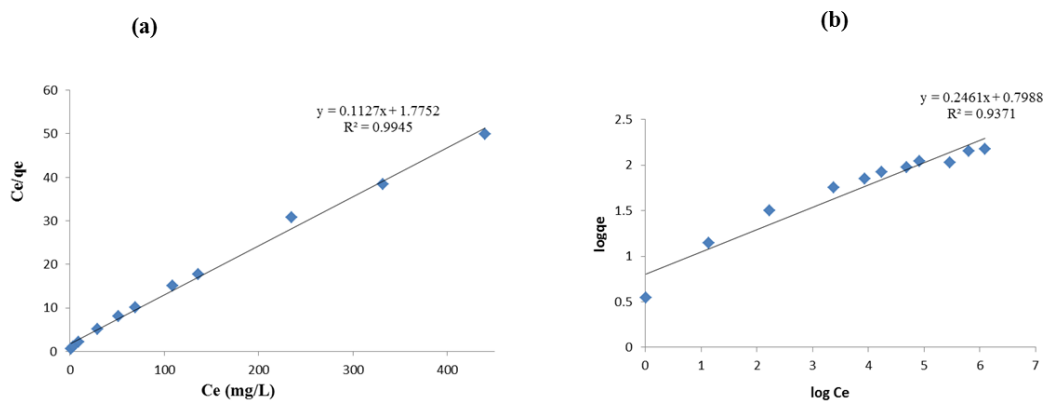(a)   (b)

Fig. 6(a): Langmuir plot for adsorption of Pb^{+2} by AFC coated silica gel (b) Freundlich plot for adsorption of Pb^{+2} by AFC coated silica gel (Adsorbent dose: 2g/L, contact time 4 h; pH 6.0).
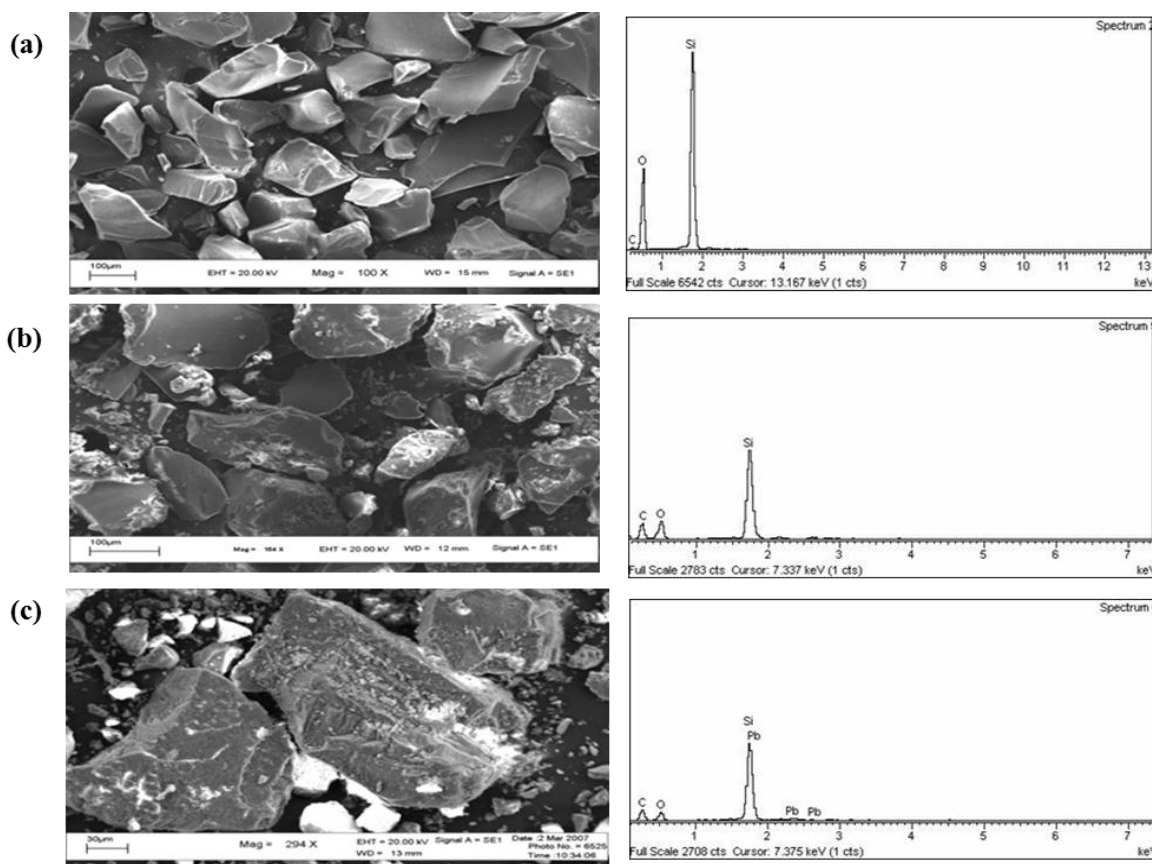

(a)

(b)

(c)

Fig. 7: SEM image and EDX spectra of (a) plain silica gel (b) AFC coated silica gel before Pb^{+2} adsorption (c) AFC coated silica gel after Pb^{+2} adsorption.

Table 1: First order and second order parameters and correlation coefficients at varying pH calculated from the experimental data using AFC coated silica gel.

Solution pH	First order model					Second order model			
	$q_e(exp)$	$q_e(cal)$	Rate constant $k_1 (min)^{-1}$	R^2	χ^2	q_e (cal)	Rate constant k_2 (g/mg.min)	R^2	χ^2
3.0	0.95	0.86	0.055	0.98	0.0780	0.99	0.073	0.99	0.0213
4.0	8.89	8.63	0.023	0.98	17.744	9.57	0.008	0.99	0.576
5.0	14.55	13.68	0.047	0.91	14.873	15.08	0.009	0.99	0.680
5.5	16.99	15.71	0.039	0.94	22.843	17.48	0.006	0.99	1.160
6.0	19.34	18.27	0.047	0.91	25.829	19.96	0.007	0.99	1.654

Initial Pb^{+2} concentration 50 mg/L; adsorbent dose: 2 g/L.

Table 2: Desorption of lead ion from AFC coated silica gel after desorption reaction with HNO₃/HCL/ H₂SO₄/EDTA in 1h.

Strength of mineral acid	HNO₃ Recovery (%)	HCl Recovery (%)	H₂SO₄ Recovery (%)
0.5N	41.21	39.58	39.05
1N	41.79	42.26	40.95
2N	44.89	44.10	43.11
6N	49.37	44.95	44.00
Strength of EDTA	Recovery (%)	--	--
0.05N	32.68	--	--
0.1N	34.53	--	--
0.2N	38.58	--	--

Table 3: Comparison lead removal efficiencies (along with lead uptake) of AFC coated silica gel at various pH levels with experimental data of control experiments (without any adsorbent)

Reaction pH	AFC coated silica gel Pb⁺² removal (%)	Pb⁺² uptake (mg/g)	Control[1] Pb⁺² removal (%)
3.0	4.04	0.95	4.3
4.0	35.05	8.89	6.0
5.0	60.60	14.55	6.2
5.5	75.53	16.99	9.2
6.0	80.23	19.34	10.0

Initial Pb⁺²: 50 mg/L, Adsorbent dose: 2 g/L; Reaction time: 4 hours [1]Control is without adsorbent

Table 4: First order and second order parameters and correlation coefficients calculated from the experimental data of various Pb⁺² concentrations using AFC coated silica gel.

Initial Pb⁺² (mg/L)	First order model					Second order model			
	$q_{e(exp)}$	$q_e(cal)$	Rate constant k_1 (min)⁻¹	R^2	χ^2	q_e (cal)	Rate constant k_2 (g/mg.min)	R^2	χ^2
10	5.56	1.497	0.027	0.90	47.697	5.656	0.0495	0.99	0.155
30	12.155	5.430	0.022	0.93	69.876	12.438	0.0118	0.99	0.287
50	15.04	8.455	0.021	0.91	62.007	15.479	0.0063	0.99	2.463

Solution pH 6.0; adsorbent dose: 2 g/L.

Table 5: Langmuir and Freundlich isotherm parameters for adsorption of Pb⁺² onto AFC coated silica gel.

Langmuir isotherm				Freundlich isotherm		
q_m (mg/g)	b (L/mg)	R^2	R_L	K_f (L/g)	1/n	R^2
8.87	0.063	0.994	0.033	2.222	0.246	0.937

Table 6: Maximum adsorption capacities for lead adsorption to different adsorbents.

Adsorbent material	Adsorption capacity (mg/g)	Adsorption equilibrium parameter b (L/mg)	pH	Reference
Sawdust of *Pinus sylvestris*	22.22	0.052	5.5	Costodes *et al.*,2003
Siderite	10.32	0.418	2.97	Erdem & Ozverdi, 2005
Activated phosphate	155.04	0.0453	3- 4.0	Mouflih *et al.*,2005
Calcined phosphate	89.29	0.284	5.0	Aklil *et al.*,2004
Azadirachta indica	300.1	0.591	7.0	Bhattacharyya & Sharma, 2004
Grape stalk waste	0.241	82.84	5.5	Martinez *et al.*, 2006
AFC coated silica gel	8.87	0.063	6.0	Present work

Table 1 shows the kinetic parameters like theoretical Pb⁺² uptake, rate constants k_1 and k_2 calculated using linearized forms of Lagergren first order and second order kinetic models along with correlation coefficient (R^2) values, for adsorption of Pb⁺² by AFC silica gel in the pH range of 3.0-6.0. In order to suggest the appropriate kinetic model, Correlation coefficients (R^2) values obtained corresponding to first order kinetic model (> 0.91) and second order kinetic model (>0.99) were compared. Higher R^2 values corresponding to Lagergren second order kinetic model suggests that Pb⁺²

adsorption can be better simulated by second order kinetic model of Lagergren.

Ho *et al.,* 2005, suggested Chi-square test as defined by equation 2(c) for identifying the appropriate kinetic model for adsorption.

$$\chi^2 = \sum \frac{(q_t - q_{tm})^2}{q_{tm}} \qquad (2c)$$

Where, q_t (mg/g) denotes the metal uptake at any time t using experimental data and q_{tm} (mg/g) denotes the uptake of metal at equilibrium, calculated from kinetic models. For Pb^{+2} adsorption by AFC silica gel, lesser χ^2 values were obtained corresponding to second order kinetic model, suggesting adsorption process can be better simulated by second order kinetic model.

The kinetic curves (Fig (2a) and 2(b)) obtained, during adsorption of Pb^{+2} by AFC coated silica gel, in the pH range 3-6.0 revealed two phases of adsorption, rapid adsorption occurred within first 30 minutes of contact time in the initial phase followed by progressive adsorption with much slower uptake of lead in the second phase. Weng *et al.,* 2007, reported that the rapid adsorption could be attributed to a surface reaction process, whereas the progressive decrease of adsorption sites results in a slower adsorption reaction.

3.2 Desorption of lead ion
Desorption study was conducted on recovery of lead ions from the lead laden adsorbent using three minerals acids viz. HCl, HNO_3 and H_2SO_4 each of strength 0.5N, 1N, 2N and 6N as well as EDTA solution of strength 0.05N, 01N and 0.2N. Recovery of Pb^{+2} (%) by the above four selected eluents are presented in the Table 2. It is observed that for the three types of mineral acid desobents, Pb^{+2} recovery percentage increases as the strength of the mineral acid is increased. Desorption was maximum (49.4%) with 6N HNO_3, followed by 6N HCl (44.9%). With 6N H_2SO_4, 44% desorption of Pb^{+2} ion was achieved. Similarly, with 0.2 N EDTA maximum desorption of 38.6% was achieved. Zhang *et al.,* (1998) used non-living *R nigricans* as an adsorbent for lead removal; and reported that more than 80% of adsorbed lead was recovered from the metal loaded adsorbent using HCl and HNO_3 as desorbents. Similarly, Bhattacharyya and Sharma (2004) reported about 80% recovery of adsorbed lead from the adsorbent *Azadirachta indica* (Neem) leaf powder using distilled water and dilute nitric acid. Martinez *et al.,* (2006) reported complete desorption of adsorbed Pb^{+2} from grape stalk waste using HCl (0.01 M) or EDTA (0.001M) solutions after three contacts.

3.3 Mechanism of lead removal
In order to have an insight on the mechanism of Pb^{+2} removal by AFC coated on silica gel, in aqueous environment, two sets of batch experiments were conducted varying the pH of the solution from 3.0-6.0, with 50 mg/L of Pb^{+2} as the initial concentration. First

set of experiments were conducted without any adsorbent (control experiment) followed by similar batch experiments using 2g/L AFC silica gel as the adsorbent. Adsorption experiments were followed by desorption experiments in batch mode, to explore the mechanism of Pb^{+2} removal by AFC silica gel and possible recovery of Pb^{+2} from metal-bound adsorbent.

Table 3 shows the comparison between the lead removal efficiencies of AFC silica gel; with the experimental outcome of control set of experiments (without any adsorbent); when pH of the solution was varied from 3.0-6.0. It was observed that significantly higher lead removal efficiencies were achieved using AFC silica gel as the adsorbent; than the control experiments (without adsorbent). This implies that even though removal of lead by the above adsorbent was favored at higher solution pH (5.0-6.0), precipitation was less important during removal of lead ion up to pH of 6.0. Adsorption/complexation by NH_2 group present in aniline-formaldehyde resin was major lead removal mechanisms. Kumar *et al.,* 2007[a] already reported that the lone pair of electrons present in sp^3 hybridized amine nitrogen of AFC polymer probably forms coordination bonds with metal ions thus replacing one or more of water molecules from metal molecules (Fig 1(b)). At relatively higher pH of 5.0-6.0, Pb^{+2} ions competed with H^+ ions for the active sites of the AFC coated silica gel, resulting in higher Pb^{+2} removal capacity, however; with decrease in solution pH, reverse trend is followed and H^+ replaced Pb^{+2} ions bound to the adsorbent, thus, reducing the lead removal capacity of AFC coated silica gel. Upon addition of acid the amine groups got protonated and released metal ions. Fig 1(b) and 1(c) shows the interaction of aniline formaldehyde condensate (AFC) with a metal ion in neutral medium and the process of desorption of metal ion in acidic medium.

3.4 Effect of initial concentration of lead ion
The effect of initial Pb^{+2} concentration on Pb^{+2} adsorption by AFC coated on silica gel was investigated by conducting batch adsorption experiments at optimum pH of 6.0, varying the initial Pb^{+2} concentration in the range of 10-50 mg/L, using a constant adsorbent dosage of 2g/L. The kinetic curves (Fig 2) revealed that equilibrium was achieved within 50 minutes of contact time when the initial Pb^{+2} ion concentration was10 mg/L, which was increased to 100 minutes, as the initial Pb^{+2} ion concentrations was increased to 50 mg/L.

The results of the batch experiments revealed that Pb^{2+} removal (%) by AFC coated silica gel follows a decreasing trend when the initial concentrations of Pb^{+2} ions were increased from 10 mg/L to 50 mg/L. With 2g/L AFC silica gel dosage lead removal (%) was decreased significantly from 98% to 77%, as the initial concentrations of Pb^{+2} ions were increased form 10 mg/L to 50 mg/L. It suggests that the percentage removal decreases with increase in the concentration of lead in aqueous solution due to reduced active sites on the

adsorption surface (Bachale *et al.*, 2016[b]), however, the uptake of lead increases with the increase in initial Pb^{+2} ion concentrations.

Lead uptake was increased significantly from 5.56 mg/g to 15.04 mg/g, when the initial concentrations of Pb^{+2} ions were increased form 10 mg/L to 50 mg/L.

3.4.1: Kinetic Studies
For investigating the nature of kinetics involved during adsorption of Pb^{+2} by AFC silica gel, the batch experimental data on variation of initial concentrations of Pb^{+2} in the range 10-50 mg/L, were analyzed using linearized forms of Lagergren first order kinetic model (Eq.(1(a)) and second order kinetic model (Eq.(2a)) as suggested by Ho and McKay, 2000; Ho, 2006.

Table 4 shows the corresponding kinetic parameters like theoretical Pb^{+2} uptake, rate constants k_1 and k_2 calculated using linearized forms of Lagergren first order and second order kinetic models along with correlation coefficient (R^2) values. For both first order and second order kinetic models, R^2 values were almost similar and well above 0.90, however higher R^2 values (>0.99) corresponding to second order kinetic model, suggests that adsorption of Pb^{+2} by AFC silica gel can be better simulated by Lagergren second order kinetic model.

The experimental data were further analyzed with Chi-square test as suggested by Ho *et al.*, 2005, for confirming the appropriate kinetic model; however, lesser χ^2 value between the experimental and the model predicted q_t values supported that adsorption of Pb^{+2} by AFC coated on silica gel can be better simulated by second order kinetic model. The kinetic curves (Fig 2(b)) revealed that the experimental Pb^{+2} uptake values are more consistent with the Lagergren second order kinetic model predicted Pb^{+2} uptake values, suggesting that the adsorption process of lead by AFC silica gel is dominated by chemisorption which involves either sharing or exchange of electrons between the adsorbent and the adsorbate (AM EI-Wakil *et al.*, 2014).

Fig (4) shows the variation of second order rate constant (k_2) with the corresponding increase in initial Pb^{+2} ion concentrations (10-50 mg/L). The graph revealed a reducing trend of k_2 with increase in initial concentrations of Pb^{+2} ions, k_2 value was declined from 0.0495 to 0.0063 g/mg.min, with the increase in initial Pb^{+2} ion concentrations from 10 mg/L to 50 mg/L. Amarasinghe and Williams (2007), also reported similar reducing trend of k_2 values with increase in initial Pb^{+2} concentrations using tea waste as the adsorbent. They reported that the k_2 value was declined from 0.0586 to 0.0091 g/mg.min, with the increase in initial Pb^{+2} ion concentrations from 50 mg/L to 200 mg/L.

3.5 Effect of Adsorbent dosage
The effect of AFC silica gel dosage on Pb^{+2} uptake was studied by varying the dosage of the adsorbent in the range of 0.5 g/L - 50 g/L, and with each dosage, experiments were conducted separately taking initial concentrations of Pb^{+2} ions as 25, 50, 75, 100, 150 and 200 mg/L. Initially solution pH was adjusted to optimum value of 6, thereafter left uncontrolled for 4 h.

Fig 5(a) and 5(b) shows the variation of Pb^{+2} uptake and removal (%) of Pb^{+2} with adsorbent dosage for various initial Pb^{+2} concentrations using AFC coated silica gel as the adsorbent. It was observed that for each of the selected initial Pb^{+2} concentrations, lead removal (%) shows an increasing trend with the adsorbent dosages. With the increase in adsorbent dosage, the available surface area of the adsorbent was also increased, resulting in higher lead removal (%) at a higher dosage. On the contrary, fig 5(a) revealed a decreasing trend of uptake of Pb^{+2} with increase in adsorbent dosage. Amarasinghe and Williams, 2007; reported that at higher adsorbent dosage; the solution ion concentration drops to a lower value and the system reaches equilibrium at lower values of adsorption capacity indicating the adsorption sites remain unsaturated.

3.6 Adsorption isotherms
In order to reveal the mechanism of adsorption of Pb^{+2} by AFC coated on silica gel, the results of batch adsorption experiments obtained were analyzed using Langmuir Isotherm and the Freundlich isotherm models. The linearized form of Langmuir isotherm is

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \qquad (3a)$$

Where b denotes Langmuir equilibrium constant (L/mg) and q_m (mg/g) denotes maximum Langmuir monolayer adsorption capacity.

Hall *et al.*, 1966), suggested a dimensionless constant separation factor R_L, defined by equation 3(b) for expressing essential characteristics of Langmuir isotherm.

$$R_L = \frac{1}{1 + bC_0} \qquad (3b)$$

Where, C_0 is the maximum initial metal ion concentration in liquid phase. R_L indicates the isotherm type (a) reversible if (R_L=0) (b) Favourable if (0<R_L<1), (c) Linear if (R_L=1) (d) unfavorable if (R_L>1) (Pavan *et al.*, 2008).

Freundlich isotherm best describing adsorption on heterogeneous surface with possibility for more than one monomolecular layer of adsorptive coverage is purely empirical based. The linearized form of Freundlich isotherm is.

$$logq_e = logK_f + \frac{1}{n} \; logC_e \qquad (3c)$$

Where K_f denotes adosrption capacity and n denotes adsorption intensity factor.

Fig fig 6(a) and fig 6(b) shows the Langmuir and Freundlich isotherm plots obtained for Pb^{+2} adsorption by AFC coated on silica gel at optimum pH of 6.0. Table 5 shows the corresponding Langmuir and Freundlich parameters calculated using equations 3(a) and 3(c).

Higher Correlation coefficient value ($R^2 > 0.99$) for Langmuir isotherm as compared to that of Freunlich isotherm model ($R^2 = 0.937$) suggests that the experimental data can be better simulated by Langmuir isotherm model, implying strong surface interaction between Pb^{+2} ions and the AFC silica gel adsorbent during adsorption. Also, R_L value of 0.033 fulfilling the criterion ($0<R_L<1$), further suggests that the lead adsorption by AFC silica gel is favorable. Maximum Langmuir monolayer capacity (q_m) for the AFC silica gel was 8.87 mg/g and the adsorption equilibrium parameter (b), which quantifies the affinity between AFC coated silica gel adsorbent and the adsorbate (Pb^{+2}) was 0.063 L/mg. The maximum Langmuir monolayer capacit (q_m), along with adsorption equilibrium parameter (b) of AFC silica gel obtained in the present study was compared with the corresponding values obtained using some unconventional adsorbents as reported by various researchers (Table 6).

Langmuir monolayer capacity (q_m) obtained in the present work using AFC silica gel as the adsorbent is comparatively lower than the (q_m) values obtained for the other unconventional adsorbents except for Grape stalk waste (0.241 mg/g) as reported by Martinez *et al.,* 2006. King *et al.,* 2008 reported that uptake of metal by the various adsorbents is dependent on the molecular structure, available surface areas and the functional groups present on the adsorbent. The present study focused on adsorption of Pb^{+2} by AFC silica gel; can be considered as favorable as indicated by Freundlich's intensity factor n value of 4.06, fulfilling the criterion $1 < n < 10$. Freundlich's uptake factor, K_f, representing adsorption capacity was 2.22 L/g for the above adsorbent.

3.7. Surface characteristics of the adsorbent
The surface morphology and internal structure of plain silica gel, AFC coated silica gel and AFC silica gel post Pb^{+2}adsorption was visualized using Scanning Electron Microscopic (SEM) technique. Irregular sharp edges dominated the uncoated silica particles (Fig. 7(a), while AFC coated silica gel particles (Fig. 7(b) have less sharp edges, which may be due to coating effect. EDX spectra

indicated presence of carbon, oxygen, sodium, aluminum, and silicon atoms on AFC coated silica gel Fig. (7(b), while presence of lead peak confirmed the adsorption of lead ions by the above adsorbent (Fig. 7(c).

SUMMARY AND CONCLUSIONS

The present study investigated the Pb^{+2} adsorption by AFC silica gel, considering various factors affecting adsorption like pH, initial concentration of metal ion, adsorbent dosage etc. Also desorption study was conducted with emphasis on metal recovery after adsorption. Easy synthesis as well as the low cost of the polymer makes the adsorption process economical. Another advantage of the process is the higher rate of desorption of lead ion. Thus, AFC coated on silica gel can be employed as an efficient adsorbent for removing lead from industrial wastewater.

REFERENCES
1. Ahalya N, Ramachandra TV, Kanamadi RD *Review Paper*, Biosorption of Heavy Metals, Research Journal of Chemistry and Environment, 2003; 7(4): 71-78.
2. Ajmal, M., Rao, R.A.K., Ahmad, R. and Ahmad, J. Adsorption studies on Citrus reticulata (fruit peel of orange): removal and recovery of Ni(II) from electroplating wastewater. J. Hazard. Mater. B, 2000; 79: 117–131.
3. Aklil, A. Mouflih, M. and Sebti, S. Removal of heavy metal ions from water by using calcined phosphate as a new adsorbent. J. Hazard. Mater. A, 2004; 112: 183 –190.
4. Amarasinghe, B.M. W.P.K and Williams, R.A. Tea waste as a low cost adsorbent for removal of Cu and Pb from wastewater, Chem. Eng. Jr., 2007; 132: 299-309.
5. Axtell N. R., Sternberg S. P. K., Laussen K. C. Lead and nickel removal using microspora and lemna minor. Bioresour. Technol, 2003; 89: 41-48.
6. Bachale S., Sharma S., Sharma A. and Verma S. Removal of lead (II) from aqueous solution using low cost adsorbent: A review. International Journal of Applied Research, 2016; 2(7): 523-527.
7. Bachale S., Sharma S., Sharma A. and Verma S. Removal of lead (II) from aqueous solution using Polypyrrole adsorbent. International Journal of Chemical Studies, 2016; 4(4): 135-138.
8. Bhattacharyya K.G. & Sharma A. Adsorption of Pb (II) from aqueous solution by *Azadirachta indica* (Neem) leaf powder, J. Hazar. Mater, 2004; B113, 97-109.
9. Costodes, V.C., Fauduet H., Porte, C. and Delacroix, A. Removal of Cd(II) and Pb(II) ions, from aqueous solutions, by adsorption onto sawdust of Pinus sylvestris, J. Hazar. Mater., B, 2003; 105: 121-142.
10. AM El-Wakil, El-Maaty WM Abu and FS Awad Removal of Lead from Aqueous Solution on Activated Carbon and Modified Activated Carbon Prepared from Dried Water Hyacinth Plant, J Anal

Bioanal Tech, 2014; 5(2). DOI: 10.4172/2155-9872.1000187.

11. Erdem, M. and Ozverdi, A. Lead adsorption from aqueous solution by siderite, Sep. Purif. Technol., 2005; 42: 259–264.

12. Freeman, H. M. Standard Handbook of Hazardous Waste Treatment and Disposal (Second Edition), McGraw – Hill, 1998.

13. G. Liu & M.S. Freund New Approach for the controlled cross-Linking of polyaniline: synthesis and characterization, Macromolecules, 1997; 30: 5660-5665.

14. Gupta, K.V., Gupta, M. and Sharma, S. Process development for the removal of lead and chromium from aqueous solutions using red mud-an aluminium industry waste, Water Res., 2001; 35: 1125–1134.

15. Hall, R. K., Eagleton, L. C., Acrivos, A. and Vermeulen, T. Pore and solid diffusion kinetics in fixed bed adsorption under constant pattern conditions. Ind. Eng. Chem. Fundamentals, 1966; 5: 212-223.

16. Ho, Y.S., Chiu W. and Wang C Regression analysis for the sorption isotherms of basic dyes on sugarcane dust, Bioresour. Technol, 2005; 96: 1285-1291.

17. Ho, Y.S. Second order kinetic model for the sorption of cadmium onto tree fern: a comparison of linear and non-linear methods, Water Res., 2006; 40: 119–125.

18. Ho, Y.S. and McKay, G. The kinetics of sorption of divalent metal ions onto sphagnum moss peat, Water Res., 2000; 34: 735–742.

19. King P., Rakesh N, Beena Lahiri S, Prasanna Y. K , Prasad V.S.R.K. Biosorption of Zinc onto Syzgium cumini L.: Equilibrium and kinetic studies. Chem Eng J., 2008; 144: 181-187.

20. Kumar, G.P., Kumar, P.A., Chakraborty, S. and Ray, M. Uptake and desorption of copper ion using functionalized polymer coated silica gel in aqueous environment, Sep. Purif. Technol., 2007; 57: 47-56.

21. Kumar, P.A., Ray, M. and Chakraborty, S. Hexavalent chromium removal from wastewater using aniline formaldehyde condensate coated silica gel, J. Hazard. Materials, 2007; 143: 24-32.

22. Martinez, M., Miralles, N., Hidalgo, S., Fiol, N., Villaescusa, I. and Poch, J. Removal of lead (II) and cadmium (II) from aqueous solutions using grape stalk waste, J. Hazar. Mater., 2006; B133: 203-211.

23. Mouflih, M., Aklil, A. and Sebti, S. Removal of lead from aqueous solution by activated phosphate", J. Hazard. Mater., 2005; B 119: 183-188.

24. Özacar M, Şengil İA, Türkmenler H. Equilibrium and kinetic data, and adsorption mechanism for adsorption of lead onto valonia tannin resin. Chem Eng J., 2008; 143(1): 32-42.

25. Pavan FA, Mazzocato AC, Gushikem Y Removal of methylene blue dye from aqueous solutions by adsorption using yellow passion fruit peel as adsorbent. Bioresour Technol, 2008; 99: 3162-3165.

26. Skerfving S., Gehardsson L., Schütz A., Strömberg U. Lead-biological monitoring of exposure and effects. J. Trace Elem. Exp. Med, 1998; 11: 289-301.

27. Soylac M., Elci L., Akkaya Y., Dogan M. On-line preconcentrayionsystem for determination of lead in water and sediment samples by flow injection-flame atomic absorptionspectrometry. Anal. Lett., 2002; 35: 487-499.

28. Ucun H, Bayhana YK, Kaya Y, Cakici A, Algur OF. Biosorption of lead (II) from aqueous solution by cone biomass of Pinus sylvestris. Desalin, 2003; 154(3): 233-8.

29. US EPA (U.S. Environmental Protection agency) Clean up the Nations Waste Sites: Markets and Technology Trends, Washington D.C., 1996.

30. Vilar V. J., Botelho CM, Boaventura R.A. Influence of pH, ionic strength and temperature on lead biosorption by Gelidium and agar extraction algal waste. Process Biochem, 2005; 40(10): 3267-75.

31. Weng C.H., Tsai C.Z., Chu S.H., Sharma Y.C. Adsorption characteristics of copper (II) onto spent activated clay, Sep. Purif. Technol, 2007; 54: 187-197.

32. Zhang, L.I, Zhao, L.I, Yu, Y. and Chen, C. Removal of lead from aqueous solution by non-living Rhizopus Nigricans, Water Res., 1998; 32: 1437-1444.