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Polyacrylamide thorium (IV) phosphate as an important lead selective fibrous ion exchanger: Synthesis, characterization and removal study

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Abstract

The objective of the present research was to synthesize, characterize and to investigate the removal efficiency of lead (II) ion from synthetic lead solution by a hybrid fibrous ion exchanger. In the present study polyacrylamide thorium (IV) phosphate was synthesized by co-precipitation method and was characterized using SEM, XRD, FTIR and TGA–DSC. To know the practical applicability, a detailed removal study of lead ion was carried out. The removal of lead was 52.9% under neutral condition, and using 0.4 g of adsorbent in 100 mL of lead solution having initial concentration of 100 mg/L. Adsorption kinetic study revealed that the adsorption process followed first order kinetics. Adsorption data were fitted to linearly transformed Langmuir isotherm with R^2 (correlation coefficient) > 0.99. Thermodynamic parameters were also calculated to study the effect of temperature on the removal process. In order to understand the adsorption type, equilibrium data were tested with Dubinin–Radushkevich isotherm. The percentage removal was found to increase gradually with increase in pH and 99% removal was achieved at pH 10. The process was rapid and equilibrium was established within first 30 min.
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Keywords: Lead; Fibrous ion exchanger; Adsorption isotherms; Thermodynamic parameter; Lagergren rate equation

1. Introduction

Among the various methods adopted for removal of different pollutants, ion exchange method has drawn the attention of researchers because it exhibits a high efficiency of sorption from gaseous and liquid media [1]. Usually they consist of a monofilaments having uniform size ranging in diameter from 20 μm to 300 μm. The main advantage for using such materials is that it can be made in various forms as per the requirement like granules, membrane, filters, etc. Although granular ion exchangers ensure very favorable parameters for ion exchange processes, their application in large scale processes is hardly possible because of the high resistance of filtering layers. This difficulty is eliminated when fibrous ion exchange materials are used since the layer resistance is easily predetermined by the density of a fibrous material packing in accordance with

technological requirements. Because of the above reason, these materials are of great importance and will gain momentum in future [2,3].

Many inorganic fibrous materials are found in literatures which were used for various purposes particularly for chromatographic separation of cations and preparation of membranes without binder [4,5]. Literature survey also reveals that many hybrid types of fibrous ion exchange materials have been synthesized in recent year by the combination of organic polymeric species and inorganic groups [6]. These materials have many industrial and environmental applications including the purification of water in the atomic power plants under the condition of high temperature and pressure.

Toxic metals are very often discharged by a number of industrial process which leads to the contamination of fresh water. Domestic and municipal waste water have also contributed towards the contamination of fresh water by lead. Non-biodegradability and persistence of these pollutants in the environment is responsible for health hazards [7,8]. Among the various heavy metals, lead (II) is a well-known toxic metal that

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is considered as priority pollutant and its adverse effects are well documented. It may cause a range of physiological disorders [9,10]. Lead metabolism can also closely mimic that of calcium, particularly at the receptor site of membranes, where it can, in fact replace calcium and thus adversely affect both neuromuscular and synaptic transmissions. This parallelism with calcium metabolism also explains why lead can progressively accumulate in bone during the major part of our lives [11]. May be the most serious effect of a low-level lead exposure is as a potent neurotoxin. This explains why its most profound neurological effects seem to occur at times in the life-cycle when the human central nervous system is at its most vulnerable stage and still in the process of development, i.e. during intra-uterine life and during childhood [12–15].

Removal of lead from waste water using conventional methods such as chemical precipitation, ion exchange, solvent extraction, ultrafiltration [16], electrodialysis [17] and adsorption are used. For the removal of lead, a number of adsorbents such as activated carbon [18], sargassum [19], chitosan [20], metal oxide gel [21], saw dust [22], humas-boehmite complex [23], animal bone powder, ceramics [24], nanosized SnO_2 [25], microporous titanosilicate [26], polymerized banana stem [27], teawaste [28], maize cob [29] and fly ash [30] have been used.

Among several available methods, ion exchange appeared to be interesting. Its application is relatively simple as mild operating conditions are required. Thorium (IV) phosphate, belonging to the group of tetravalent metal acid salts is a good ion exchanger. However it is found to have a poor mechanical strength for which suitable co-polymer like acrylamide was added to make it stable under the experimental condition. So, it was thought worthwhile to synthesis, characterization and to study the removal process of lead (II) using polyacrylamide thorium (IV) phosphate. The present paper has summarized the synthesis, characterization and ion-exchange behavior of polyacrylamide thorium (IV) phosphate.

2. Experimental

2.1. Reagents and chemicals

Acrylamide, lead nitrate, sodium perchlorate and thorium nitrate used in the present study was of analytical grade and was obtained from Merck. Phosphoric acid, methanol and formaldehyde was Qualigens (India) product. Solutions of thorium nitrate were prepared in 1 M HNO_3 while those of acrylamide were prepared in deionized water. The 2 M solutions of orthophosphoric acid were prepared in deionized water. 1000 mg/L stock solution of lead (II) was prepared by dissolving 1.5985 g of $Pb(NO_3)_2$ in 1 L distilled water. The required concentration of lead solution was obtained by serial dilution of 1000 mg/L lead solution. Methanol–formaldehyde reagent was prepared by adding 3 drops 37% formaldehyde to 1 L methanol. Ionic strength adjuster (ISA) was prepared by adding 80.25 g of sodium perchlorate to 100 mL distilled water in a volumetric flask. The measuring cylinder, volumetric flask and conical flask used were of Borosil.

2.2. Synthesis of polyacrylamide thorium (IV) phosphate

A number of samples of polyacrylamide thorium (IV) phosphate were prepared by adding one volume of 0.1 M $Th(NO)_3 \cdot 5H_2O$ solution in two volume of (1:1) of 2 M H_3PO_4 and acrylamide solution (0.1–1.0 M) The resulting slurry obtained was stirred (400 rpm) vigorously over a magnetic stirrer provided with hot water bath at a temperature of 90 ± 2 °C for 10 h. It was then filtered and washed several times with deionized water (pH ∼ 5). On drying at a temperature of 20 ± 2 °C, it resulted into a thin sheet. It was then crushed into small pieces and was treated with 1 M HNO_3 for 24 h with constant stirring to convert it into its H^+ form. The material obtained was washed repeatedly with deionized water to remove excess of acid present and it was finally dried at 20 °C. It was then stored in air tight container and was used for further studies.

2.3. Characterization of polyacrylamide thorium (IV) phosphate

The thermogravimetric analysis and differential scanning calorimetry (TGA/DSC) analysis was carried out using NETZSCH STA 409C. 30 mg of the sample was used and alumina was used as reference. Scanning electron micrographs of the sample was obtained by JEOL JSM-6480LV scanning electron microscope. The sample was coated with platinum for 30 s at a current of 50 mA before the SEM micrograph was obtained.

BET surface area of the sample was measured at liquid nitrogen temperature using BET surface area analyzer (QUANTACHROME Autosorb I). Thorium (IV) and phosphate was analyzed by spectrophotometer. 0.5 g of the sample was dissolved in 2 M H_2SO_4 solution and thorium (IV) was determined by using atomic absorption spectrophotometer. Phosphate was determined spectrophotometrically by the phosphovanadomolybdate method using a UV–vis spectrophotometer as follows: to the 10-mL sample solution, taken in a 100-mL volumetric flask, were added 50 mL of demineralized water (DMW), 10 mL of ammonium vanadate solution (1.25 g of ammonium vanadate dissolved in 250 mL of DMW + 20 mL of concentrated HNO_3, diluted to 500 mL), and 10 mL of ammonium molybdate solution (12.5 g of ammonium molybdate dissolved in 250 mL of DMW). It was then diluted up to the mark before taking its absorbance at 460 nm against a reagent blank prepared in the same manner [31]. Percentage of carbon, hydrogen and nitrogen was analyzed with the help of CHN analyzer (CE-440 Elemental Analyzer). The oxidation and reduction temperature of the instrument was set as per the instruction manual of the instrument. Powder XRD of the sample using Cu Kα radiation was obtained at a scan rate of 1°/min and was analyzed using standard software provided with the instrument. XRD pattern of the material was obtained by using PHILLIPS X'PERT X-ray diffractometer. FTIR of the sample was obtained using PerkinElmer FTIR spectrophotometer SPECTRUM RX-I. FTIR spectrum of the sample was obtained by KBr pellet method. The ratio of the sample to KBr was 1:50 and the pellet was prepared at a pressure of 5 tonnes. The ion exchange capacity of the ion material was determined by stan-

Table 1
Synthesis of various samples of polyacrylamide thorium (IV) phosphate and their sodium and lead ion exchange capacity

Sample no.	Acrylamide solution (M)	Na$^+$ ion exchange capacity using 1 M NaNO$_3$ (mequiv./g(dry))	Pb^{2+} ion exchange capacity using 1 M Pb(NO$_3$)$_2$ (mequiv./g(dry))
PATP-1	0.01	1.40	2.88
PATP-2	0.05	1.60	3.40
PATP-3	0.1	2.11	3.89
PATP-4	0.2	1.82	3.52
PATP-5	0.4	1.71	3.10
PATP-6	0.6	1.50	2.32
PATP-7	0.8	1.00	1.80
PATP-8	1.0	0.80	1.10

dard process (Tables 1 and 2). 1 g of the material in its H$^+$ form was taken in a glass tube of internal diameter of 1 cm with glass wool at its bottom. 250 mL of 1 M solution was used as eluent with a flow rate of 0.5 mL/min by using a peristaltic pump. Nitrate/chloride salt of each cation was used for this purpose. The eluent was titrated against a standard alkali solution to determine the total amount of H$^+$ released which is equivalent to the cation retained by the material [32]. The magnitude of elution depends on the concentration of the eluent. So, to know the magnitude of elution, a constant volume (250 mL) of sodium nitrate of various concentrations (0.2–1.4 M) was allowed to pass through a constant weight of the material (1 g) at a rate of 0.5 mL/min the H$^+$ ion concentration in the eluent was determined by titrating it with a standard alkali solution. To know the minimum volume required for complete elution, an experiment was conducted by passing 1 M sodium nitrate solution in different 10 mL portion with a flow rate of 0.5 mL/min in a similar column containing 1 g of the ion exchanger. To study the thermal stability, 1 g samples of polyacrylamide thorium (IV) phosphate were heated at different temperature in a muffle furnace for 1 h and their ion

exchange capacities were determined by usual column process after cooling them to the room temperature. The result obtained is represented in Table 3. To study chemical stability of polyacrylamide thorium (IV) phosphate, different 500 mg portions of the material were kept in 25 mL of the various mineral acids, bases, and salt solutions of different concentrations for 24 h each, with stirring. The supernatant liquid was analyzed for the thorium (IV) and phosphate contents by the methods mentioned above.

2.4. Batch experiments

The lead sorption experiments from its aqueous solution on polyacrylamide thorium (IV) phosphate were carried out using standard 10 mg/L, 50 mg/L and 100 mg/L Pb^{2+} solution in absence of other competing ions. The adsorption experiments were carried out in 250 mL glass conical flask with stopper by adding 0.1–1.0 g of polyacrylamide thorium (IV) phosphate in 100 mL of synthetic lead (II) solution. Stoppers were provided to avoid change in concentration due to evaporation. All the adsorption experiments were carried out at ambient temperature (25 ± 2 °C). After continuous stirring over a magnetic stirrer at about 400 rpm for a predetermined time interval, the solid was separated by filtration through Whatman-42 filter paper and the remaining Pb^{2+} concentration was determined by lead ion selective electrode (Orion 96-82 Ionplus Sureflow Lead Electrode) and Orion 720 A+ ion analyzer. Two standards were prepared that bracket the expected sample range and which differ in concentration by a factor of 10. Measurement was done by taking 50 mL of each standard and sample into separate 150 mL beaker and 2 mL ionic strength adjuster (ISA) and 50 mL methanol–formaldehyde reagent. All the sample and standards were maintained at same temperature to avoid interference due to difference in temperature. pH of the solution was maintained

Table 2
Ion exchange capacity of polyacrylamide thorium (IV) phosphate for various metal solutions

1 M solutions of different metal salts	Ion exchange capacity (mequiv./g(dry))
LiCl	1.36
NaNO$_3$	2.11
KCl	1.80
Mg(NO$_3$)$_2$	1.88
Ca(NO$_3$)$_2$	2.40
Sr(NO$_3$)$_2$	3.01
Pb(NO$_3$)$_2$	3.89

Table 3
Thermal stability of polyacrylamide thorium (IV) phosphate after heating to various temperatures for 1 h

Heating temperature (°C)	Na$^+$ ion exchange capacity (mequiv./g(dry))	Percentage retention of ion exchange capacity	Pb^{2+} ion exchange capacity (mequiv./g(dry))	Percentage retention of ion exchange capacity	Colour
50	2.11	100	3.89	100	White
100	2.00	94.78	3.62	93.05	White
200	1.89	89.57	3.32	85.34	Cream
400	1.12	53.08	2.12	54.49	Light grey
600	1.00	47.39	1.88	48.32	Light grey
800	0.10	4.73	0.18	4.62	Light grey

by 0.1 M NaOH and 0.1 M HCl. A number of parameters such as contact time, mass of adsorbent concentration of adsorbate, pH, affecting the removal of lead ion have been varied widely in order to optimize the adsorption process. In order to see the effect of other competing cations on lead sorption, standard solutions of sodium, potassium, calcium and magnesium were added separately to synthetic lead solution.

2.5. Desorption and regeneration studies

The reusability of polyacrylamide thorium (IV) phosphate mainly depends on the ease with which lead (II) ions get desorbed from loaded polyacrylamide thorium (IV) phosphate sample. For this 100 mL of 10 mg/L, 50 mg/L and 100 mg/L lead solution was treated with 0.4 g of polyacrylamide thorium (IV) phosphate and was kept under stirring for 24 h. The content of the flask was filtered and separated. The filtered adsorbent was retreated with 100 mL neutral distilled water and distilled water adjusted to different pH with the help of 1 M HNO₃. It was stirred for 24 h. The residual lead concentration was measured. The study was carried out at room temperature ($25 \pm 2\,^\circ$C).

3. Results and discussion

3.1. Characterization of polyacrylamide thorium (IV) phosphate

The present study is an attempt to explore synthesis of polyacrylamide thorium (IV) phosphate and its application for the removal of lead from synthetic solution. A number of samples of polyacrylamide were prepared by adding different molar solution of acrylamide (0.01–1.0 M) and their sodium and lead ion exchange capacity was determined by column process (Table 1). The cation exchange capacity was found to depend on the concentration of acrylamide. The cation exchange capacity was maximum for 0.1 M solution of acrylamide. So, the polyacrylamide thorium (IV) phosphate prepared with 0.1 M acrylamide was used for further studies.
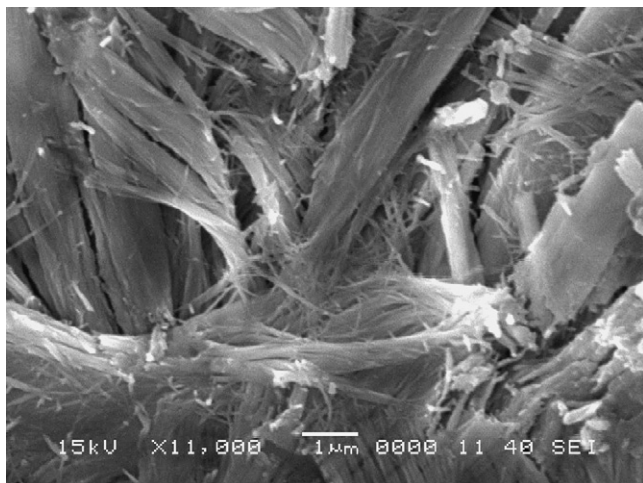

Fig. 1. SEM micrographs of polyacrylamide thorium (IV) phosphate (magnification: 11,000×).

Table 4
Effect of concentration of eluent on ion exchange capacity of lead and sodium

Concentration of eluent (M)	Pb²⁺ ion exchange capacity (mequiv./g(dry))	Na⁺ ion exchange capacity (mequiv./g(dry))
0.2	1.42	1.22
0.4	2.52	1.40
0.6	2.80	1.52
0.8	3.12	1.80
1.0	3.89	2.11
1.2	3.89	2.12
1.4	3.89	2.12

The ion exchange capacity for different cations was measured by column process and 250 mL of 1 M solution of each salt was used as eluent. It was found to shows a good affinity for Pb²⁺ ion (Table 2). The material was obtained in the form of sheet with shiny appearance. Scanning electron micrographs of the sample was obtained at 11,000× magnification and is presented in Fig. 1. It is evident from the SEM micrograph that the material is fibrous in nature.

The important feature in the synthesis of polyacrylamide thorium (IV) phosphate was its drying temperature. The material was obtained in the form of ion exchange paper when dried at a temperature of 20 °C. It was quite stable and retained more than 85% ion exchange capacity even up to 200 °C and retained about 47% ion exchange capacity up to a temperature of 600 °C. It is indicated that with the increase in temperature, the ion exchange capacity of material was found to decrease and hence the experiments were carried out at room temperature. The decrease in ion exchange capacities may be due to the decomposition and loss of structural water molecule. The water molecule may exist in the form of thorium oxide and phosphoric acid and hence provides exchangeable H⁺ ion. The thermal stability of the material was found to be more than normal inorganic ion exchanger, which may be due to its hybrid nature. The sodium and lead ion exchange capacity at different temperatures are presented in Table 3.

The extent of elution was found to depend on the concentration of eluent. Sodium ion and lead ion exchange capacity for different eluent concentration was studied at ambient temperature and is represented in Table 4. The optimum concentration of the eluent for complete elution of H⁺ ion in 250 mL of solution was found to be 1.0 M for both sodium and lead ion. The minimum volume required for complete elution was found to be 130 mL.

On the basis of the chemical analysis (Table 5) and elemental analysis (Table 6) for thorium and phosphate, the number of moles of thorium, phosphate and acrylamide were found to

Table 5
Results of chemical analysis of polyacrylamide thorium (IV) phosphate

Elements/ions/compounds	Weight (g)	Number of moles	Molar ratio
Thorium	0.1099	0.4547×10^{-3}	1
Phosphate	0.1351	1.4221×10^{-3}	3
Acrylamide	0.1145	3.1805×10^{-3}	7

Table 6
Results of CHN analysis of polyacrylamide thorium (IV) phosphate

Elements	Percentage (%)
Carbon	22.90
Hydrogen	3.056
Oxygen	9.782
Nitrogen	8.558
Others	55.705

0.4547×10^{-3}, 1.4221×10^{-3} and 3.1805×10^{-3}, respectively. The molar ratio of thorium, phosphate and acrylamide was calculated to be 1:3:7. So, from above discussion, the tentative empirical formula for the material can be suggested as:

$$[(ThO_2)(H_3PO_4)_3(CH_2=CHCONH_2)_7]\cdot nH_2O$$
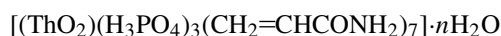
The DSC curve of the material reveled that the process was endothermic up to the temperature 183.7 °C and then the process becomes exothermic (Fig. 2). Initially the process was endothermic may be due to the loss of external water. The TGA curve shows 9.88% weight loss up to 183.7 °C which may be due to removal of external water 'n' from the material (Fig. 3). The value of 'n' was found to be 6.414 using Alberti equation [33,34]

$$18n = \frac{X(M + 18n)}{100} \tag{i}$$

The XRD pattern of the sample is presented in Fig. 4. Broad peaks were obtained instead of sharp peaks indicating the sample was poorly crystalline. XRD was analyzed using standard software but a very low intensity peak of lead phosphate was found. BET surface area was obtained to know the specific surface area and was found to be 91.2 m^2/g.

FTIR study of the sample was carried out (Fig. 5) in order to know the presence of different groups and structures in the material. The metal oxides and hydroxides are indicated by the band at 627.97 cm^{-1}. Band at 1075.63 cm^{-1} is associated with P–O stretching indicating the presence of phosphate group. The presence phosphate groups are further confirmed by the presence of absorption band at 544.98 cm^{-1}. The presence band at 1384.41 cm^{-1} [35] and 3410.37 cm^{-1} is due to presence of –OH group which indicates the presence of water of crystallization. The absorption band at 1637.64 cm^{-1} is a characteristic of C=O stretching vibrations in amide group [36]. The band at
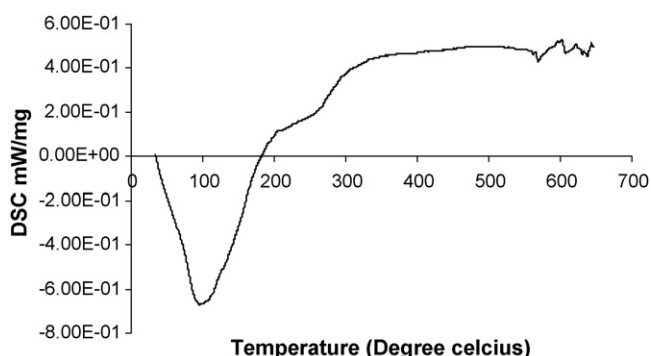
Table 7
Chemical stability of polyacrylamide thorium (IV) phosphate in various acid, alkali and salt solutions

Solvent (25 mL)	Amount dissolved (mg)	
	Thorium	Phosphate
1 M HCl	0.58	0.03
2 M HCl	0.71	0.05
4 M HCl	1.20	0.06
1 M HNO$_3$	0.79	0.04
2 M HNO$_3$	1.10	0.11
4 M HNO$_3$	1.49	0.16
1 M H$_2$SO$_4$	1.38	0.12
2 M H$_2$SO$_4$	Completely	Completely
4 M H$_2$SO$_4$	Completely	Completely
1 M NaOH	0.72	0.03
2 M NaOH	1.10	0.05
4 M NaOH	1.25	0.10
1 M KOH	1.10	0.02
2 M KOH	1.24	0.08
4 M KOH	1.88	0.12
1 M NH$_4$OH	1.12	0.12
2 M NH$_4$OH	1.22	0.18
4 M NH$_4$OH	1.28	0.24
2 M NaNO$_3$	0.02	0.01
2 M KNO$_3$	0.05	0.00

2368 cm^{-1} is apparently due to CO$_2$ background of the measurement system [37].

In order to know the chemical stability, the material was kept in 25 mL of different mineral acids, bases and salt solutions of different concentration for 24 h and the supernatant liquid was analyzed for thorium and phosphate (Table 7). The material was found to exhibit a high chemical stability. It was found that the material was quite stable in most of the mineral acids and salt solutions. It was soluble only in sulphuric acid.

3.2. Removal study of lead (II) ion

All the experiments are at batch conditions.

3.2.1. Effect of adsorbent dose

The effect of adsorbent dose on the removal of lead was studied in neutral condition (pH 7), at ambient temperature (25 ± 2 °C) and at a contact time of 30 min for initial lead con-

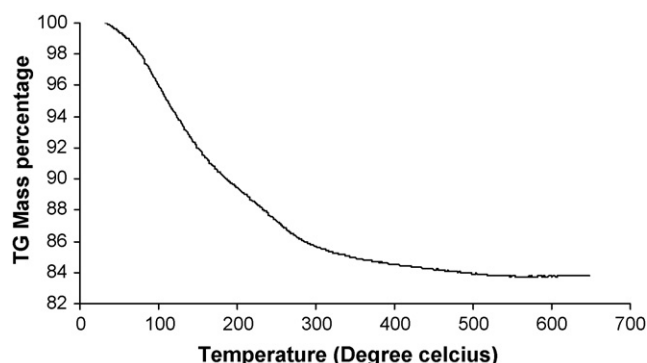Fig. 2. Differential scanning calorimetry of sample up to 650 °C.

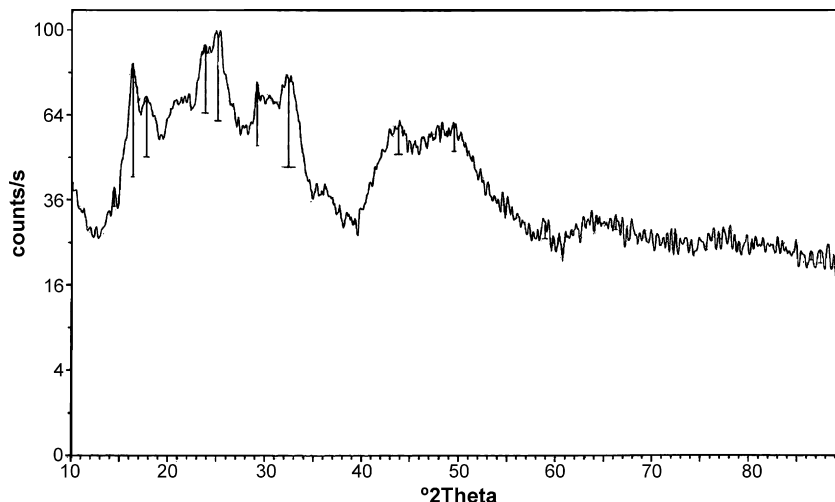Fig. 3. Thermogravimetric analysis of sample up to 650 °C.

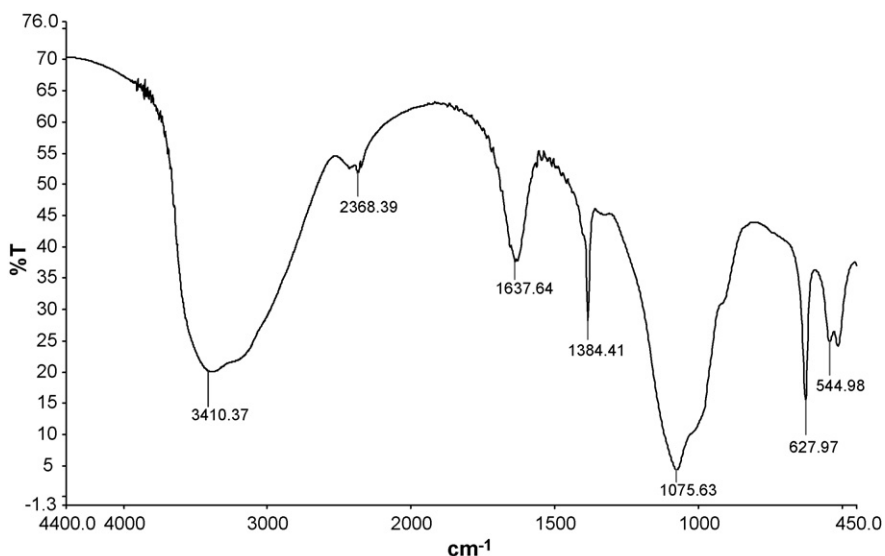Fig. 4. XRD pattern of acryl amide thorium (IV) phosphate.

Fig. 5. FTIR spectrum of acryl amide thorium (IV) phosphate.

centration of 10 mg/L, 50 mg/L and 100 mg/L. The results are presented in Fig. 6. It is evident from the figure that the removal of lead increased from 18.5% to 43.2%, 18.8% to 45.8% and 20.8% to 52.9% for 0.1–1.0 g/100 mL acryl amide thorium (IV) phosphate and initial lead concentration of 10 mg/L, 50 mg/L and 100 mg/L, respectively. The final pH of the solution was measured and found to decrease. The pH of the final solution was found to be 6.58, 6.22 and 6.12 for initial lead concentration of 10 mg/L, 50 mg/L and 100 mg/L, respectively. It is observed that after dosage of 0.4 g/100 mL, there was no significant change in percentage removal of lead. It may be due to the overlapping of active sites at higher dosage. So, there was not any appreciable increase in the effective surface area resulting in the conglomeration of exchanger particles [38]. So, 0.4 mg/100 mL was considered as optimum dose and was used for further study. The maximum removal of lead was found to be less than 55% and hence the removal process cannot bring the concentration of lead to its permissible limit.

3.2.2. Effect of pH

Percentage removal of lead with varying pH was studied in batch experiments using 0.4 g of adsorbent in 100 mL synthetic solution, at ambient temperature ($25 \pm 2\,^{\circ}$C) and at a contact
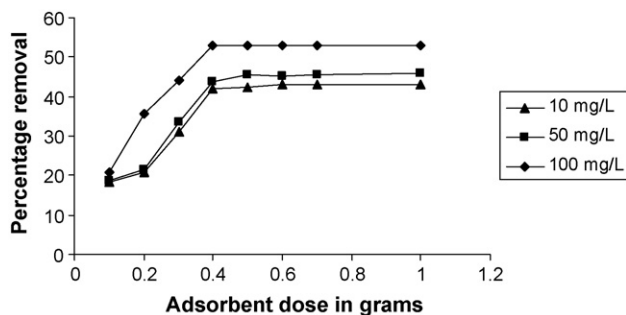

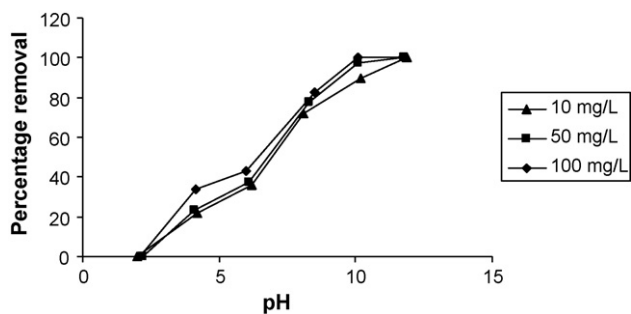Fig. 6. Adsorbent dose vs. percentage removal of lead with initial concentration of 10 mg/L, 50 mg/L and 100 mg/L.

Fig. 7. Percentage removal of lead of initial concentration of 10 mg/L, 50 mg/L and 100 mg/L vs. pH of the synthetic solution.

Table 8
Change in pH during the removal process

Initial concentration of 10 mg/L		Initial concentration of 50 mg/L		Initial concentration of 100 mg/L	
Initial pH	Final pH	Initial pH	Final pH	Initial pH	Final pH
2.0	2.0	2.2	2.2	2.1	2.1
4.2	4.18	4.1	4.0	4.13	4.11
6.2	6.0	6.1	5.9	6.0	5.9
8.1	8.0	8.3	8.1	8.5	8.3
10.2	9.9	10.1	9.8	10.1	9.9
11.9	11.5	11.8	11.4	11.7	11.4

time of 30 min for initial lead concentration of 10 mg/L, 50 mg/L and 100 mg/L. The results are presented in Fig. 7. The pH of the solution after adsorption was measured and was found to decrease slightly (Table 8). It is evident from the graph that there is practically no removal at pH lower than 2 and almost 99.9% removal was achieved at pH higher than 10 for initial lead concentration of 10 mg/L, 50 mg/L and 100 mg/L. There is a gradual increase in percentage removal with increase in pH. At pH 3–7, the removal of lead was very low. This is because at lower pH the removal is only due to ion exchange (adsorption). At pH lower than 2, the removal was almost zero. This is due to high H^+ ion concentration, which reverses the process of adsorption. At lower pH, the process of regeneration predominates over the process of removal. And hence the process of conversion of adsorbent into its H^+ form plays an important role leaving behind lead (II) in the aqueous solution. The process of adsorption and regeneration is demonstrated by Fig. 8. At higher pH (i.e. greater than 10), almost complete removal is achieved. This is due to combined effect of adsorption and precipitation as lead phosphate and lead hydroxide. Figs. 9 and 10 represent the XRD analysis of adsorbents recovered after adsorption at pH 7 and pH 11. The XRD analysis revealed that there were phases of lead phosphate and lead hydroxide at both the pH. But the intensity of the peaks for lead hydroxide was more at pH 11. So, it was concluded that, some of the lead is converted into Pb(OH)$_2$ and some of them are converted into lead phosphate and finally get adsorbed over the surface of adsorbent.
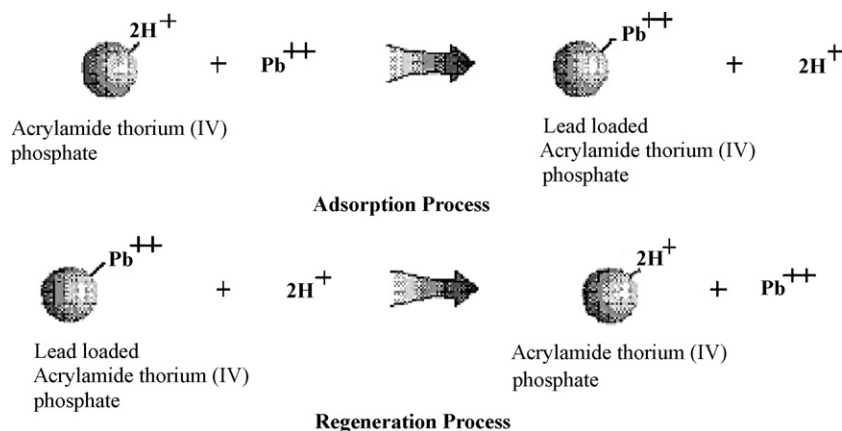
3.2.3. Effect of contact time

Adsorption of lead (II) at different contact time was studied for initial lead concentration of 10 mg/L, 50 mg/L and 100 mg/L at pH 7 keeping all other parameters constant. The result is represented in Fig. 11. It is clear from the figure that more than 25% removal took place within first 5 min and equilibrium was established after 30 min. The change in the rate of removal might be due to the fact that initially all adsorbent sites were vacant and the solute concentration gradient was high. Later, the lead uptake rate by adsorbent was decreased significantly, due to the decrease in number of adsorption sites as well as lead concentration. Decreased removal rate, particularly, towards the end of experiments, indicates the possible monolayer formation of lead ion on the outer surface.

3.2.4. Adsorption kinetics

Adsorption of lead (II) ion was rapid for the first 5 min and its rate slowed down as the equilibrium approached. The rate constant K_{ad} for sorption of lead (II) was studied by Lagergren rate equation [39,40] for initial lead concentration of 10 mg/L, 50 mg/L and 100 mg/L.

$$\log(q_e - q) = \log q_e - K_{ad}\left(\frac{t}{2.303}\right) \qquad (ii)$$

where q_e and q (both in mg/g) are the amounts of lead adsorbed at equilibrium and at time 't', respectively. The plots of $\log(q_e - q)$ versus 't' at different time interval was almost linear, indicates the validity of Lagergren rate equation of first order kinetics

Fig. 8. Adsorption and regeneration process of acryl amide thorium (IV) phosphate.
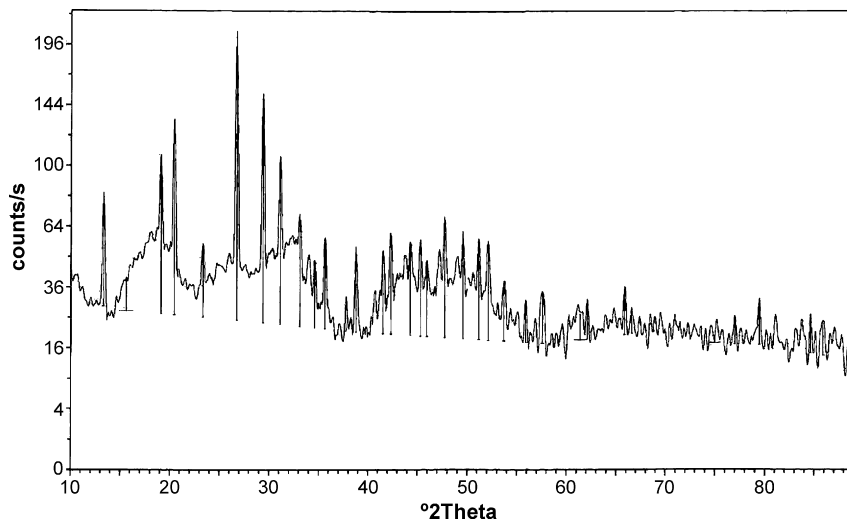
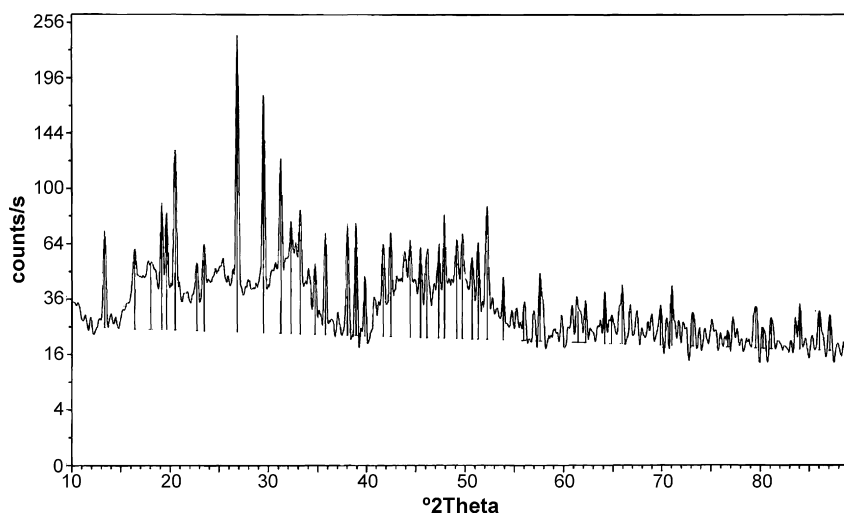Fig. 9. XRD pattern of acryl amide thorium (IV) phosphate obtained after adsorption at pH 7.

Fig. 10. XRD pattern of acryl amide thorium (IV) phosphate obtained after adsorption at pH 11.

(Fig. 12). The adsorption rate constant (K_{ad}), calculated from the slope of the above plot is presented in Table 9.

3.2.5. Effect of temperature

The effect of temperature on the adsorption of lead with initial concentration 10 mg/L, 50 mg/L and 100 mg/L was studied using optimum adsorbent dose (0.4 g/100 mL). The results are represented as percentage removal of lead versus temperature (Fig. 13). The percentage removal of lead with initial concentration 10 mg/L, increased from 38.9 to 68.5, the percentage removal of lead of initial concentration 50 mg/L, increased from 41.0 to 68.6 and the percentage removal of lead of initial con-
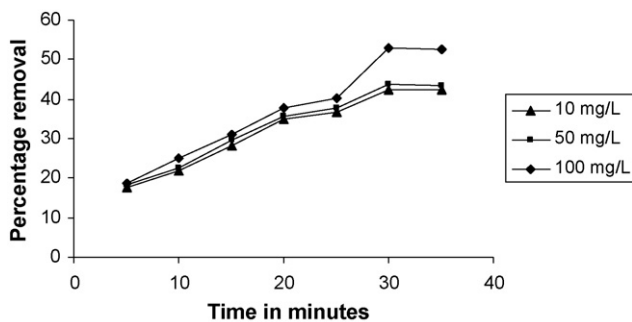

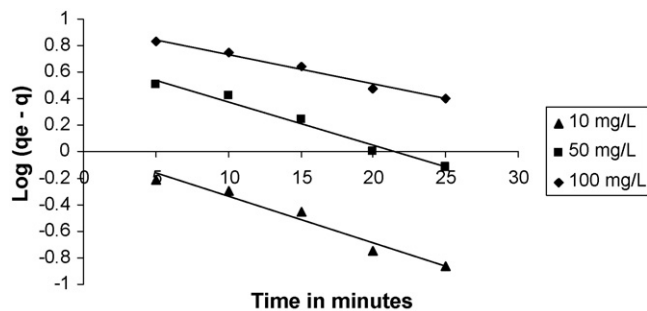Fig. 11. Time vs. percentage removal of lead with initial concentration of 10 mg/L, 50 mg/L and 100 mg/L.

Fig. 12. Adsorption kinetics, time vs. log ($q_e - q$) with initial lead concentration of 10 mg/L, 50 mg/L and 100 mg/L.

Table 9
Rate constants (K_{ad}) obtained from the graph for different initial concentration

Initial concentration (mg/L)	Slope	Intercept	Rate constant (K_{ad})	Correlation coefficient (R^2)
10	−0.03504	0.01373	0.08069	0.962
50	−0.03883	0.74261	0.08943	0.975
100	−0.02257	0.95990	0.05197	0.980

centration 100 mg/L, increased from 42.5 to 70.0 for 20–50 °C temperature. However it can be clearly seen from the figure that, at the temperature of 20 °C the removal was almost 40% and with increase in temperature the percentage removal increased slowly and reached almost 68%. The continuous increase in percentage removal indicated that the adsorption process was endothermic in nature.

This was further supported by calculating thermodynamic parameters. The change in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) of adsorption were calculated using the following equations [41–43]:

$$\log K_C = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \tag{iii}$$

$$\Delta G = \Delta H - T\Delta S \tag{iv}$$

where ΔS and ΔH are the changes in entropy and enthalpy of adsorption, respectively. A plot of $\log K_C$ versus $1/T$ for initial lead concentration of 10 mg/L, 50 mg/L and 100 mg/L was linear (Fig. 14).

The K_C value was calculated using the following equation [44]:

$$K_C = \frac{C_1}{C_2} \tag{v}$$

where C_1 is the amount of lead ion adsorbed per unit mass of adsorbent and C_2 is the concentration of lead in aqueous phase.

Values of ΔH and ΔS were evaluated from the slope and intercept of Van't Hoff plots and represented in Table 10. The positive value of entropy (ΔS) indicates the increase in randomness of the ongoing process and hence a good affinity of lead with acryl amide thorium (IV) phosphate. Negative value of ΔG at each temperature indicates the feasibility and spontaneity of ongoing adsorption. A decrease in values of ΔG with the increase in temperature suggests more adsorption of lead at higher tem-
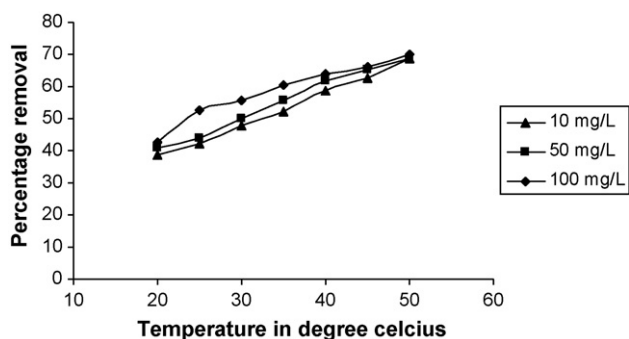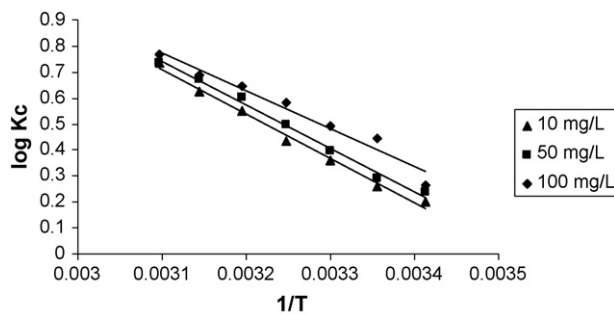

Fig. 14. Van't Hoff plots, $\log K_C$ vs. $1/T$.

perature. The endothermic nature of the process was once again confirmed by the positive value of enthalpy (ΔH). Positive value of enthalpy (ΔH) suggests that entropy is responsible for making the ΔG value negative. So, the adsorption process is spontaneous, since the entropy contribution is much larger than that of enthalpy.

3.2.6. Effect of initial lead concentration

The adsorption of lead onto acryl amide thorium (IV) phosphate was studied by varying initial lead concentration using optimum adsorbent dose (0.4 g/100 mL) at ambient temperature (25 ± 2 °C) for a contact time of 30 min. The results are represented in graphical form as percentage removal versus initial lead concentration (Fig. 15). The initial lead concentration was increased from 10 mg/L to 100 mg/L and the corresponding removal gradually increased from 42.2% to 52.9%. However it is clear from the figure that, there was not any appreciable increase in percentage removal with increase in initial lead concentration. But the increase in percentage removal with initial lead concentration was continuous. From above it is clear that the removal method can be implemented to remove lead from water present in any concentration.

3.2.7. Adsorption isotherm

The adsorption data were fitted to linearly transformed Langmuir isotherm. The linearized Langmuir equation, which is valid for monolayer sorption onto a surface with finite number of identical sites, is given by [38,39] the following equation (vi):

$$\frac{1}{q_e} = \frac{1}{q_0 b C_e} + \frac{1}{q_0} \tag{vi}$$

Fig. 13. Temperature vs. percentage removal of lead with initial concentration of 10 mg/L, 50 mg/L and 100 mg/L.
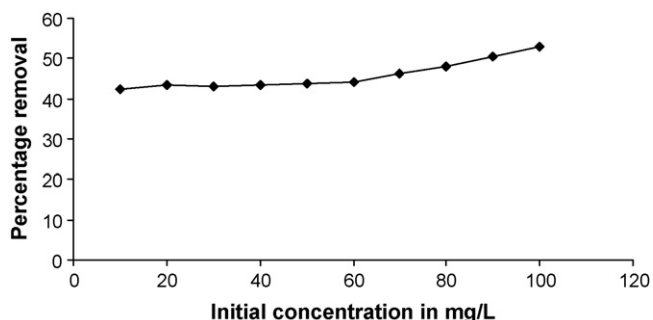

Fig. 15. Initial lead concentration vs. percentage removal.

Table 10
Thermodynamic parameters using synthetic lead solution of 10 mg/L, 50 mg/L and 100 mg/L

Initial lead concentration (mg/L)	ΔH (kJ mol^{-1})	ΔS (kJ/(K mol))	ΔG (kJ mol^{-1})							R^2
			20 °C	25 °C	30 °C	35 °C	40 °C	45 °C	50 °C	
10	32.60527	0.11465	−0.987	−1.560	−2.134	−2.707	−3.280	−3.853	−4.427	0.991
50	31.94398	0.11323	−1.232	−1.798	−2.364	−2.930	−3.496	−4.063	−4.629	0.992
100	27.78521	0.10094	−1.789	−2.294	−2.799	−3.304	−3.808	−4.313	−4.818	0.965

where q_0 is the maximum amount of the lead ion per weight of acryl amide thorium (IV) phosphate to form a complete monolayer on the surface (adsorption capacity), C_e denotes equilibrium adsorbate concentration in solution, q_e is the amount adsorbed per unit mass of adsorbent, and b is the binding energy constant. The linear plot of $1/C_e$ versus $1/q_e$ (Fig. 16) with $R^2 = 0.993$ indicates the applicability of Langmuir adsorption isotherm. The values of Langmuir parameters, q_0 and b are 35.6357 mg/g and 0.00497 L/mg, respectively.

In order to predict the adsorption efficiency of the adsorption process, the dimensionless equilibrium parameter was determined by using the following equation [45]:

$$r = \frac{1}{1 + bC_0} \tag{vii}$$

where C_0 is the initial concentration. Values of $r < 1$ represent favorable adsorption. The r-value for initial concentration of 10 mg/L, 50 mg/L and 100 mg/L was found to be 0.9526, 0.8009 and 0.6680, respectively. The values indicated a favorable system.

It is known that the Langmuir and Freundlich adsorption isotherm constant do not give any idea about the adsorption mechanism. In order to understand the adsorption type, equilibrium data were tested with Dubinin–Radushkevich isotherm [44].

The linearized D. R. equation can be written as

$$\ln q_e = \ln q_m - K\varepsilon^2 \tag{viii}$$

where ε is Polanyi potential, and is equal to $RT \ln(1 + 1/C_e)$, q_e is the amount of lead adsorbed per unit mass of adsorbent, q_m is the theoretical adsorption capacity, C_e is the equilibrium concentration of lead, K is the constant related to adsorption energy, R is the universal gas constant and T is the temperature in Kelvin.
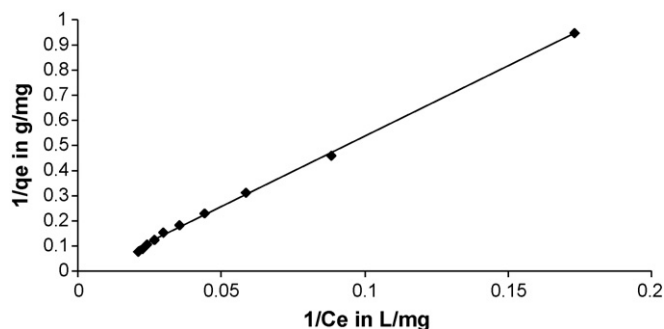
Fig. 17 shows the plot of $\ln q_e$ against ε^2, which was almost linear with correlation coefficient, $R^2 = 0.9631$. D.R. isotherm constants K and q_m were calculated from the slope and intercept of the plot, respectively. The value of K was found to be 2.57×10^{-4} mol^2 kJ^{-2} and that of q_m was 0.00743 g/g.

The mean free energy of adsorption (E) was calculated from the constant K using the relation [46],

$$E = (-2K)^{-1/2} \tag{ix}$$

It is defined as the free energy change when 1 mole of ion is transferred to the surface of the solid from infinity in solution. The value of E was found to be 44.098 kJ mol^{-1}. The value of E is very useful in predicting the type of adsorption and if the value is less than 8 kJ mol^{-1}, then the adsorption is physical in nature and if it is in between 8 kJ mol^{-1} and 16 kJ mol^{-1}, then the adsorption is due to exchange of ions [47]. The value in the present study was found to be little greater than 16 kJ mol^{-1}. This may be due different chemical process (such as formation of lead phosphate and lead hydroxide) accompanying the ion exchange process.

3.2.8. Effect of competitive ions

Drinking water and waste water contains many cations. Therefore, it was thought worthwhile to study the effect of competitive ions like sodium, potassium, calcium and magnesium on the adsorption of lead. Since, these are the ions which are commonly found in drinking water as well as industrial effluent. Varying concentration of these solutions was prepared from their nitrate salts. The initial concentration of lead was fixed at 10 mg/L, 50 mg/L and 100 mg/L while the initial concentration of other cations varied from 10 mg/L to 100 mg/L. The results of these studies are given in Fig. 18. It was clear from the figure that presence of these cations reduced the adsorption of lead appreciably with increase in initial concentration of different
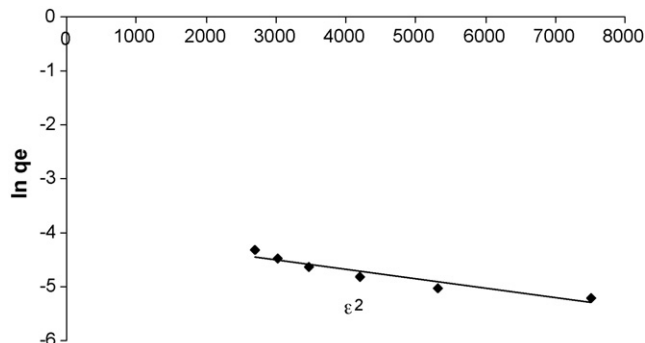

Fig. 16. Langmuir adsorption isotherm, $1/C_e$ vs. $1/q_e$.

Fig. 17. D–R adsorption isotherm, $\ln q_e$ vs. ε^2.

Table 11
Percentage desorption and regeneration of lead of different concentration by acryl amide thorium (IV) phosphate at varying pH

Initial lead concentration (mg/L)	Amount adsorbed (mg/L)	Amount desorbed (mg/L)				Percentage desorption or regeneration			
		pH 2	pH 4	pH 6	Distilled water	pH 2	pH 4	pH 6	Distilled water
10	42.1	42.0	20.9	2.14	1.55	99.76	49.64	5.08	3.68
50	43.6	43.5	20.9	2.27	1.70	99.77	47.93	5.21	3.89
100	52.8	52.6	25.4	2.79	2.22	99.62	48.11	5.28	4.20

cations. The cations reduced the lead adsorption in the order of, calcium > magnesium > potassium > sodium.

3.2.9. Desorption and regeneration studies

In order to know the nature of adsorption, i.e. physical or chemical, desorption study was carried out. The result of the study is presented in Table 11. Desorption of the adsorbed lead in neutral distilled water resulted about 4.2% for initial concentration of 100 mg/L. And for initial concentration less than 100 mg/L, the percentage desorption was less than 4.2%. Thereby indicating the process of adsorption is predominantly chemical or ion-exchange in nature.

At the end of the adsorption process, when the working capacity of an adsorbent is exhausted, it has to be regenerated. Ion exchangers are usually regenerated with acid or alkali solution. Regeneration study at different pH was essential to know the optimum pH at which almost 100% desorption or complete regeneration takes place. In the present study regeneration of cation exchanger was carried out at pH of 2, 4 and 6 with hydrochloric acid and the optimum pH for regeneration was found to be 2.

4. Conclusion

Polyacrylamide thorium (IV) phosphate, a fibrous ion exchanger have been synthesized from acrylamide, thorium nitrate and phosphoric acid by co-precipitation method. Synthesis was ascertained by adopting various characterization methods like SEM, XRD, FTIR, and TGA–DSC. Polyacrylamide thorium (IV) phosphate exhibited much greater specific surface area. The adsorption of lead from aqueous solution by acryl amide thorium (IV) phosphate was found to occur readily. Adsorption of lead was found to follow first order kinetics. The effect of other cations was also studied and was found that the cations reduced the lead adsorption in the order of calcium > magnesium > potassium > sodium. The percentage removal was found to be less than 60% but with increase in pH the percentage removal gradually increased and almost 99% removal was achieved at pH 10. Regeneration study of the ion exchanger was also carried out and was found that the ion exchanger can be easily regenerated with nitric acid at pH less than 2. The removal process cannot bring the concentration of lead to its permissible limit. But it can be used as the primary step for the removal of lead for which further studies are being carried out to couple acryl amide thorium (IV) phosphate along with any other adsorbent to meet permissible limit of lead in water.
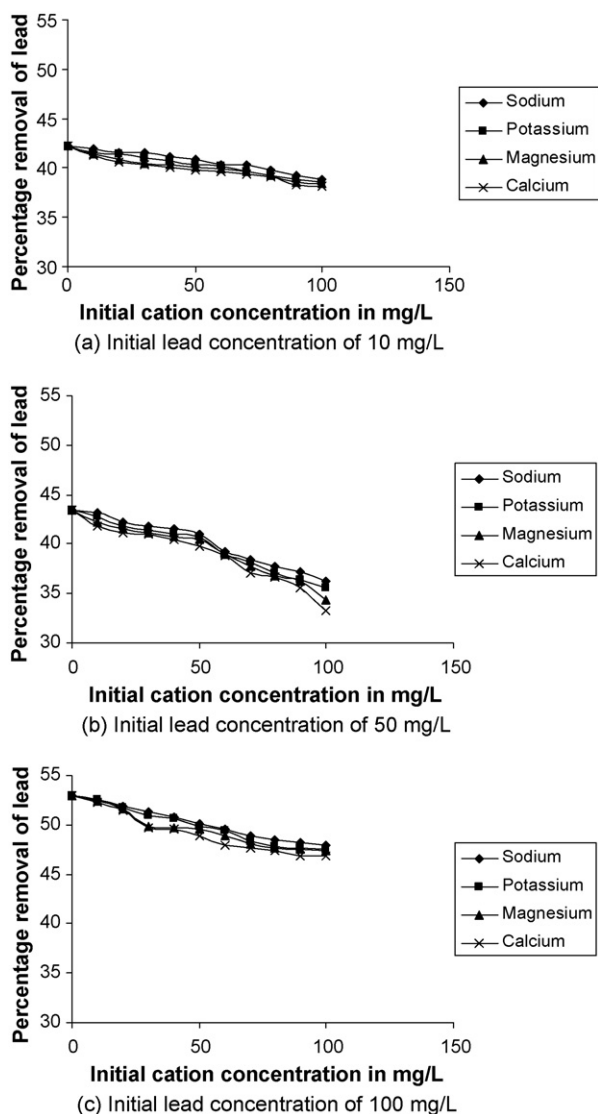
Fig. 18. Percentage removal vs. initial cation concentration of solution with initial lead concentration of 10 mg/L, 50 mg/L and 100 mg/L.

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