Removal of lead (II) from aqueous environment by a fibrous ion exchanger: Polycinnamamide thorium (IV) phosphate

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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 polycinnamamide 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 using the material. The removal of lead was 81.2% under optimum conditions. 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.

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1. Introduction

Industrial progress has made life more comfortable but at the same time the natural environment had suffered from the detrimental effects of pollution. Among various pollutants, heavy metal ions are very toxic and carcinogenic in nature [1,2]. The presence of heavy metals in the aquatic environment has been of great concern because of their toxicity at lower concentrations. Some metal ions have cumulative effect capable of being assimilated and stored in the tissues of organism, causing significant adverse physiological effect. Non-biodegradability and persistence of these pollutants in the environment are responsible for health hazards. Among the various heavy metals, lead (II) is a well-known toxic metal, considered as priority pollutant. Adverse effect of lead is well documented. It may cause a range of physiological disorders. 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. Organic lead toxicity affects the central nervous system. Similarly the inorganic form of lead typically affects the peripheral nervous system, hematopoietic, renal, gastrointestinal, cardiovascular and reproductive system [3]. The other hazardous effects of lead are visual disturbances convulsions. Loss of cognitive abilities, antiso-cial behaviors constipation, anemia, tenderness, nausea, vomiting, abdominal pain, gradual paralysis in the muscles and many more. Human pharmacokinetic studies reveal that lead has extremely long terminal elimination half life period in blood of more than 30 days and a similar rate of uptake into tissues. But the major problem is the rate of elimination from bones, estimated to years [4–7]. That is the reason, why children below the age of 7 years are mostly at risk. Drug therapy with chelating agents removes lead primarily from blood and soft tissues and it lowers its concentration in blood consequently deeply stored lead re-equilibrates in circulation. So treating with chelating agents of chronically lead exposed individual is a long time therapy [3]. Therefore, the removal of toxic metal ions especially lead from water prior to supplying water for drinking, bathing, industrial use, etc. is very important and essential.

The removal of toxic metal ions from water is a very difficult task due to high cost of the process. Various methods such as precipitation, ion exchange, solvent extraction, ultra filtration [8] electrodialysis [9] and adsorption, etc. have been used for the removal of lead and other toxic metals from water. Among various processes adsorption is the most commonly and widely used method for the removal of toxic metals. A number of adsorbents have already been used [10–21]. Activated carbon is used more frequently than any other adsorbent for the last three decades [21,22] as it is costly and in recent years the search for low cost adsorbent has grown.

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

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binder [23,24]. Literature survey also reveals that many hybrid types of fibrous ion exchange materials have been synthesized in recent years by the combination of organic polymeric species and inorganic groups [25]. 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. 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-polymers were added to make it stable under the experimental condition. 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 [26–28].

The objective of the present research was to synthesize, characterize and to study the removal efficiency of lead (II) ion using a fibrous ion exchanger, polycinnamamide thorium (IV) phosphate. It has also been found to be highly selective for Pb (II) ion and thus has an industrial importance. So, it was thought worthwhile to study the removal process of Pb (II) using polycinnamamide thorium (IV) phosphate. In the present study detailed removal study was carried out and the equilibrium parameters, thermodynamic parameters and kinetics of the removal process were evaluated. The effects of various parameters such as temperature, adsorbent dose, initial Pb (II) concentration and time were also studied.

2. Experimental

2.1. Reagents and chemicals

Lead nitrate, sodium perchlorate and thorium nitrate used in the present study were of analytical grade and were obtained from Merck. Analytical grade cinnamamide was obtained from Alfa Aesar. Phosphoric acid, methanol and formaldehyde were Qualigens (India) product. Solutions of thorium nitrate were prepared in 1 M HNO$_3$ while those of cinnamamide were prepared in ethanol. The 2 M solutions of orthophosphoric acid were prepared in distilled 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 of 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 polycinnamamide thorium (IV) phosphate

A number of samples were prepared by adding one volume of 0.1 M Th(NO$_3$)$_4$·5H$_2$O solution in two volumes of a (1:1) mixture of 2 M H$_3$PO$_4$ and cinnamamide (0.01–1.0 M) drop wise with constant stirring using a magnetic stirrer at a temperature of 90 ± 2 °C. The resulting slurry was stirred for 10 h at this temperature. Then it was filtered and washed with distilled water (pH ∼ 5). On drying at 20 °C the precipitate resulted into a sheet which was crushed into small pieces of 1–2 mm diameter (approx.) and converted into the H$^+$ form by treating with 1 M HNO$_3$ for 24 h with occa-

sional shaking, and intermittently replacing the supernatant liquid with fresh acid. However the product dried at room temperature was not stable and hence the material was washed with distilled water to remove the excess acid and was finally dried at 20 °C.

2.3. Characterization of polycinnamamide thorium (IV) phosphate

The thermogravimetric analysis and differential scanning calorimetry (TGA/DSC) analysis were 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 were 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 were analyzed by spectrophotometer. 0.5 g of the sample was dissolved in 2 M H$_2$SO$_4$ solution and thorium (IV) was determined by using atomic absorption spectrophotometer. Phosphate was determined spectrophotometrically by the phosphovanado-molybdate method using a UV–vis spectrophotometer as follows: to 10-mL sample solution, taken in a 100-mL volumetric flask, 50 mL of distilled water, 10 mL of ammonium vanadate solution (1.25 g of ammonium vanadate dissolved in 250 mL of distilled water + 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 distilled water) were added. It was then diluted up to the mark before taking its absorbance at 460 nm against a reagent blank prepared in the same manner [29]. 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 were 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 ton. The ion exchange capacity of the material was determined by standard process. 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 [30]. 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 and lead nitrate of various concentrations (0.2–1.4 M) were 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 and lead nitrate solution in different 10 mL portions with a flow rate of 0.5 mL/min in a similar column containing 1 gm of the ion exchanger. To study the thermal stability, 1 g samples of polycinnamamide thorium (IV) phosphate were heated at different temperatures 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. To study chemical stability of polycinnamamide 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 polycinnamamide thorium (IV) phosphate were carried out using standard 10 mg/L, 50 mg/L and 100 mg/L Pb^{2+} solution in the 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 polycinnamamide 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 ($25 \pm 2\,°C$). 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 ten. 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 in a beaker. All the samples and standards were maintained at same temperature to avoid interference due to difference in temperature. pH of the solution was maintained by 0.1 M NaOH and 0.1 M HCl. A number of parameters such as contact time, mass of adsorbent, concentration of adsorbate, and pH affecting the removal of lead ion have been varied widely in order to optimize the adsorption process. In order to study 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 polycinnamamide thorium (IV) phosphate mainly depends on the ease with which lead (II) ions get desorbed from loaded polycinnamamide 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 polycinnamamide 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 HNO_3. It was stirred for 24 h. The residual lead concentration was measured. The study was carried out at room temperature ($25 \pm 2\,°C$).

3. Results and discussion

3.1. Characterization of polycinnamamide thorium (IV) phosphate

The present study is an attempt to explore the synthesis of polycinnamamide thorium (IV) phosphate and its application for the removal of lead from synthetic solution. A number of samples of polycinnamamide thorium (IV) phosphate were prepared by adding different molar solutions of cinnamamide (0.01–1.0 M) and their sodium and lead ion exchange capacities were determined by column process (Table 1). The cation exchange capacity was found to depend on the concentration of cinnamamide. Initially with increase in the concentration of cinnamamide solution used, the ion exchange capacity is also increased. This may be due to the fact that the phenyl group present in the material decreases

Table 1
Synthesis of various samples of polycinnamamide thorium (IV) phosphate.

Sample no.	Cinnamamide solution (M)	Na$^+$ ion exchange capacity (in mequiv/g(dry))	Pb^{2+} ion exchange capacity (in mequiv/g(dry))
PCTP-1	0.01	1.51	2.98
PCTP-2	0.05	1.72	3.55
PCTP-3	0.1	1.90	3.75
PCTP-4	0.2	2.10	4.10
PCTP-5	0.4	1.61	3.51
PCTP-6	0.6	1.45	3.12
PCTP-7	0.8	1.10	2.50
PCTP-8	1.0	0.85	1.51

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

Metal solution	Ion exchange capacity (in mequiv/g (dry))
LiCl	1.36
NaNO$_3$	2.10
KCl	2.20
Mg(NO$_3$)$_2$	2.38
Ca(NO$_3$)$_2$	2.40
Sr(NO$_3$)$_2$	3.01
Pb(NO$_3$)$_2$	4.10
Zn(NO$_3$)$_2$	4.02
Cd(NO$_3$)$_2$	4.15
CuSO$_4\cdot$5H$_2$O	4.08

the electron density near the replaceable H$^+$ ion and substitution of H$^+$ by Pb^{2+} becomes easier. But when, concentration of cinnamamide solution used is increased beyond 0.2 M, the ion exchange capacity decreases. This is probably due to the fact that, when the quantity of polycinnamamide (in the material) is increased to a large extent, the replacement of H$^+$ by Pb^{2+} becomes difficult due to steric hindrance offered by the bulkiness of polycinnamamide. The cation exchange capacity was maximum for 0.2 M solution of cinnamamide. So, the polycinnamamide thorium (IV) phosphate prepared with 0.2 M cinnamamide was used for further studies.

The ion exchange capacity for different cations was measured and was found to show a good affinity for Pb^{2+} ion (Table 2). The material was obtained in the form of sheet with shiny appearance. Scanning electron micrographs of the sample were obtained at 13,000× magnification and are 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 polycinnamamide thorium (IV) phosphate was its drying temperature. The material was obtained in the form of ion exchange paper when dried at a tem-

Fig. 1. SEM micrographs of polycinnamamide thorium (IV) phosphate (magnification, 13,000×).

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

Heating temperature (in °C)	Na$^+$ ion exchange capacity (in meq/g(dry))	Percentage retention of ion exchange capacity	Pb^{2+} ion exchange capacity (in meq/g(dry))	Percentage retention of ion exchange capacity	Colour	Weight of Th and PO$_4^{3-}$ present in 0.5 g of sample (in grams)	
						Th	PO$_4^{3-}$
50	2.10	100	4.10	100	White	0.1064	0.1308
100	1.99	94.76	3.85	93.90	White	0.1102	0.1353
200	1.78	84.76	3.36	81.95	Cream	0.1173	0.1441
400	1.38	65.71	2.37	57.80	Cream	0.1238	0.1522
600	0.94	44.76	1.80	43.90	Light grey	0.1241	0.1525
800	0.12	5.71	0.20	4.87	Light grey	0.1242	0.1526

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

Concentration of eluent (in M)	Pb^{2+} ion exchange capacity (in mequiv/g(dry))	Na$^+$ ion exchange capacity (in mequiv/g(dry))
0.2	1.44	1.23
0.4	2.58	1.39
0.6	2.92	1.48
0.8	3.72	1.88
1.0	4.10	2.10
1.2	4.10	2.10
1.4	4.10	2.10

Table 5
Results of chemical analysis of polycinnamamide thorium (IV) phosphate.

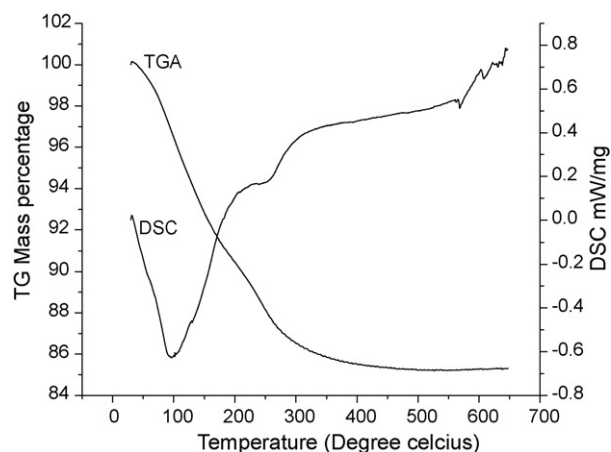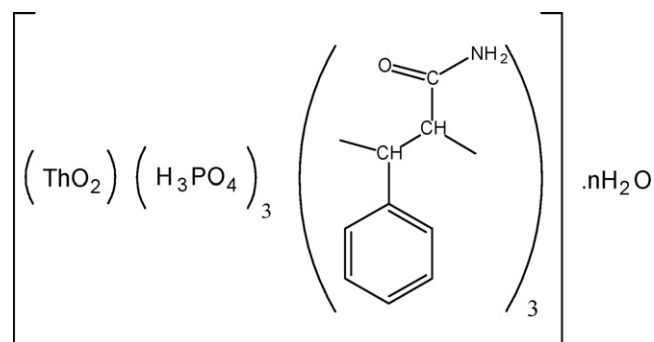| Elements/ions/compounds	Weight in grams	No. of millimoles	Molar ratio
Thorium	0.1059	0.4564	1
Phosphate	0.1301	1.3694	3
Cinnamamide	0.2014	1.3700	3

Fig. 2. Thermogravimetric analysis and differential scanning calorimetry of polycinnamamide thorium (IV) phosphate up to 650 °C.

perature of 20 °C. It was quite stable and retained more than 80% ion exchange capacity even up to 200 °C and retained about 43% ion exchange capacity up to a temperature of 600 °C. 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 is presented in Table 3.

The extent of elution was found to depend on the concentration of eluent (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 millimoles of thorium, phosphate and polycinnamamide were found to be 0.4564, 1.3694 and 1.3700, respectively. The molar ratio of thorium, phosphate and cinnamamide was calculated to be 1:3:3. So, from the above discussion, the tentative empirical formula for the material can be suggested as:

And the molecule is formed by the association of such 'x' units. The size of the molecule depends on the degree of polymerization of cinnamamide. The probable molecular formula is suggested as below.

Table 6
Results of CHN analysis of polycinnamamide thorium (IV) phosphate.

Elements	Percentage (%)
Carbon	29.59
Hydrogen	4.30
Oxygen	32.62
Nitrogen	3.83
Others	29.70
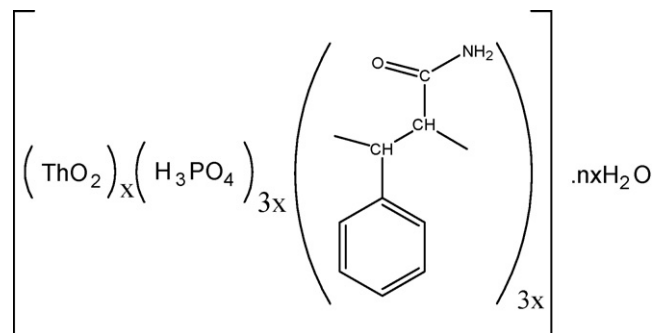
The DSC curve of the material revealed that the process was endothermic up to the temperature of 180.1 °C and then the process becomes exothermic after 180.1 °C (Fig. 2). Initially the process was endothermic may be due to the loss of external water. The TGA
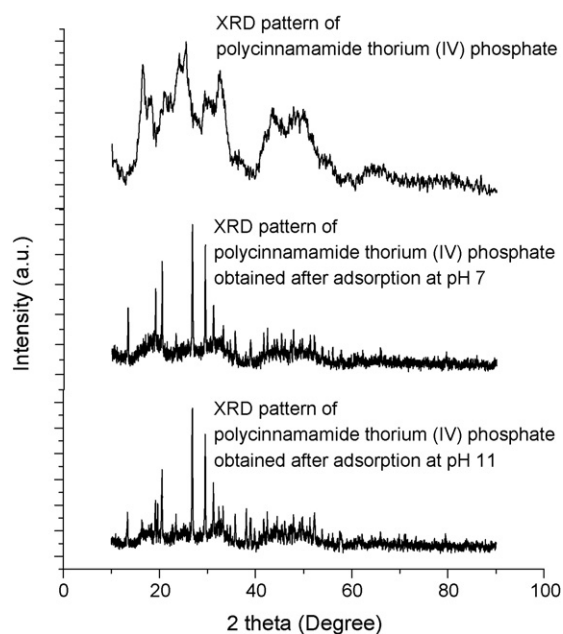
Fig. 3. XRD pattern of polycinnamamide thorium (IV) phosphate and polycinnamamide thorium (IV) phosphate obtained after adsorption at pH 7 and pH 11.

curve shows 8.75% weight loss up to 180.1 °C which may be due to the removal of external water 'n' from the material (Fig. 2). The value of 'n' was found to be 5.3219 using Alberti equation [30,31]:

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

The XRD pattern of the sample is presented in Fig. 3. 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 101.2 m^2/g.

FTIR study of the sample was carried out (Fig. 4) 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 627.48 cm^{-1}. Band at 1074.14 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 544.65 cm^{-1}. The presence band at 3410.37 cm^{-1} is due to the presence of –OH group which indicates the presence of water in crystallization. The absorption band at 1636.16 cm^{-1} is a characteristic of C=O stretching vibrations in amide group [32]. The
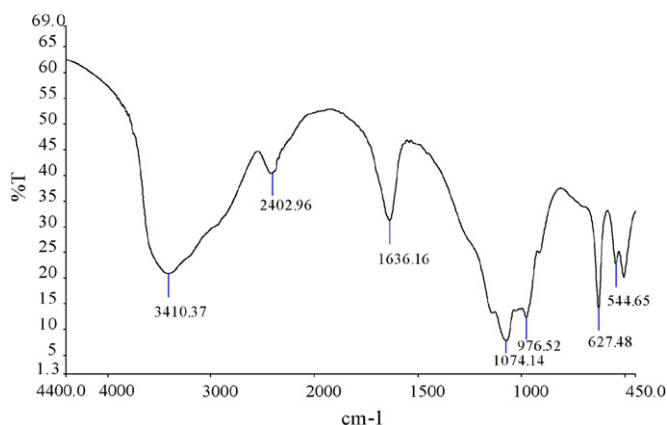
Table 7
Chemical stability of polycinnamamide thorium (IV) phosphate in various acid, alkali and salt solutions.

Solvent (25 mL)	Amount dissolved in mg	
	Thorium	Phosphate
1 M HCl	0.55	0.02
2 M HCl	0.69	0.04
4 M HCl	1.15	0.07
1 M HNO$_3$	0.73	0.03
2 M HNO$_3$	1.11	0.10
4 M HNO$_3$	1.45	0.15
1 M H$_2$SO$_4$	1.33	0.11
2 M H$_2$SO$_4$	Completely	Completely
4 M H$_2$SO$_4$	Completely	Completely
1 M NaOH	0.71	0.04
2 M NaOH	1.09	0.04
4 M NaOH	1.22	0.08
1 M KOH	1.08	0.01
2 M KOH	1.21	0.06
4 M KOH	1.82	0.11
1 M NH$_4$OH	1.11	0.11
2 M NH$_4$OH	1.21	0.16
4 M NH$_4$OH	1.27	0.21
2 M NaNO$_3$	0.01	0.01
2 M KNO$_3$	0.04	0.01

band at 2402.96 cm^{-1} is apparently due to CO_2 background of the measurement system [33]. The band at 976.52 cm^{-1} is due to C–C single bond [34].

In order to know the chemical stability, the material was kept in 25 mL of different mineral acids, bases and salt solutions of different concentrations 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 by batch experiments

3.2.1. Effect of adsorbent dose

The effect of adsorbent dose on the removal of lead was studied at ambient temperature (25 ± 2 °C) and contact 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. 5. It is evident from the figure that the removal of lead increased from 31.1% to 61.8%, 29.6% to 71.8% and 36.8% to 81.2% for 0.1–1.0 g of polycinnamamide thorium (IV) phosphate in 100 mL of synthetic lead solution of initial lead concentration of 10 mg/L, 50 mg/L and 100 mg/L, respectively. However it is observed that after the dosage of 0.5 g, there was no significant change in percentage removal of lead. It may be due to the
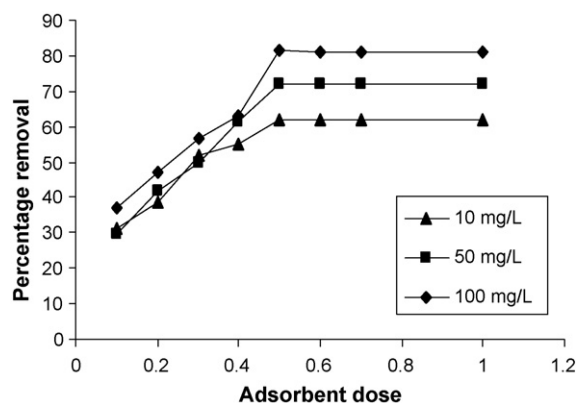

Fig. 4. FTIR spectrum of polycinnamamide thorium (IV) phosphate.

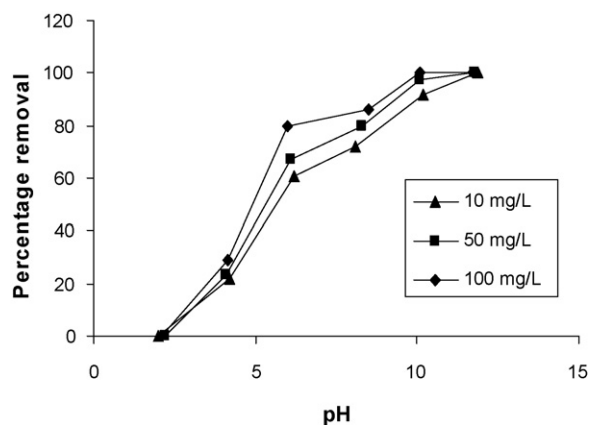**Fig. 5.** Adsorbent dose versus percentage removal of lead with initial concentration of 10 mg/L, 50 mg/L and 100 mg/L.

Fig. 6. Percentage removal of lead of initial concentration of 10 mg/L, 50 mg/L and 100 mg/L versus pH of the synthetic solution.

Fig. 8. Time versus percentage removal of lead with initial concentration of 10 mg/L, 50 mg/L and 100 mg/L.

overlapping of active sites at higher dosage. So, there was not any appreciable increase in the effective surface area resulting due to the conglomeration of exchanger particles [35]. So, 0.5 g/100 mL was considered as optimum dose and was used for further study.

3.2.2. Effect of pH

Percentage removal of lead was studied at ambient temperature ($25 \pm 2\,^\circ$C) and contact time of 30 min for initial lead concentration of 10 mg/L, 50 mg/L and 100 mg/L at different pH. The results are presented in Fig. 6. The pH of the solution after adsorption was measured and was found to decrease slightly. It is evident from the figure that there is practically no removal at pH lower than 2 and almost 99.9% removal was achieved at pH higher than 10. 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 0. This is due to high H$^+$ ion concentration, which reverses the process of removal. 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. 7. At higher pH (i.e. greater than 10) almost complete removal is achieved. This is due to the combined effect of adsorption and precipitation as lead phosphate and lead hydroxide. Fig. 3 represents 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
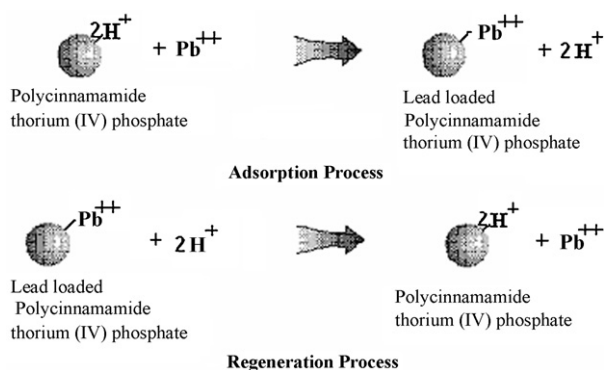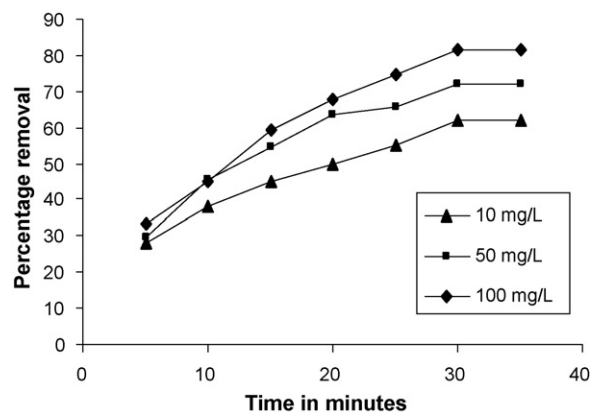
Pb(OH)$_2$ and some of them are converted into lead phosphate and finally get adsorbed over the surface of adsorbent.

3.2.3. Effect of contact time

Adsorption of lead (II) at different contact times was studied for initial lead concentration of 10 mg/L, 50 mg/L and 100 mg/L keeping all other parameters constant. The result is represented in Fig. 8. It is clear from the figure that more than 30% 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 the sorption of lead (II) was studied by Lagergren rate equation [36,37] 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 intervals were almost linear, indicate the validity of Lagergren rate equation of first order kinetics. The adsorption rate constant (K_{ad}), calculated from the slope of the above plot is presented in Table 8.

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 (0.5 g/100 mL). The results are represented as percentage removal of lead versus temperature (Fig. 9). The percentage removal of lead with initial concentration 10 mg/L,

Fig. 7. Adsorption and regeneration process of polycinnamamide thorium (IV) phosphate.

Table 8
Rate constants (K_{ad}) obtained from the graph for different initial concentrations.

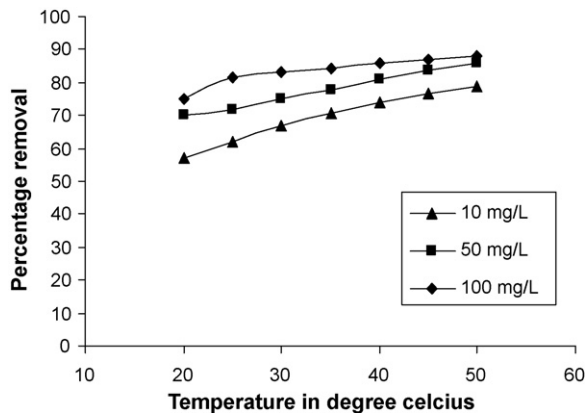| Initial concentration	Slope	Intercept	Rate constant (K_{ad})	Correlation coefficient (R^2)
10	−0.03309	0.01191	0.07622	0.990
50	−0.04347	0.84982	0.10011	0.985
100	−0.04337	1.25610	0.09989	0.977

Fig. 9. Temperature versus percentage removal of lead with initial concentration of 10 mg/L, 50 mg/L and 100 mg/L.

increased from 56.8 to 78.9, the percentage removal of lead of initial concentration 50 mg/L, increased from 70.0 to 85.7 and the percentage removal of lead of initial concentration 100 mg/L, increased from 75.0 to 88.2 for 20–50 °C temperature. The continuous increase in percentage removal with temperature 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 was calculated using the following equations [38–40]:

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

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

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 concentrations of 10 mg/L, 50 mg/L and 100 mg/L was linear.

The K_C value was calculated using the following equation [41–44]:

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

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 slope and intercept of Van't Hoff plots and represented in Table 9. The positive value of entropy (ΔS) indicates the increase in randomness of the ongoing process and hence a good affinity of lead with polycinnamamide 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 temperature. 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.
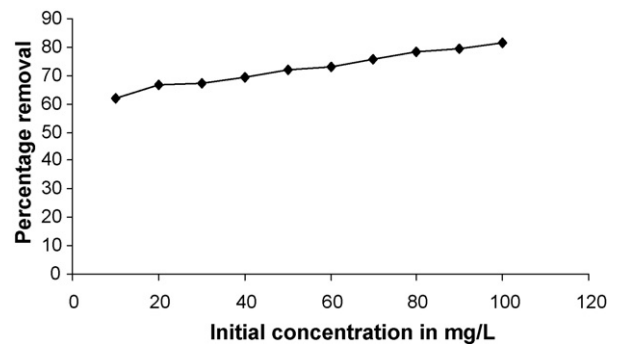

Fig. 10. Initial lead concentration versus percentage removal.

3.2.6. Effect of initial lead concentration

The adsorption of lead onto polycinnamamide thorium (IV) phosphate was studied by varying initial lead concentration using optimum adsorbent dose (0.5 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. 10). The initial lead concentration was increased from 10 mg/L to 100 mg/L and the corresponding removal gradually increased from 61.9% to 81.3%. 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 present in any concentration from water.

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 the following equation [41–43]:

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

where q_0 is the maximum amount of the lead ion per weight of polycinnamamide 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. 11) with $R^2 = 0.991$ indicates the applicability of Langmuir adsorption isotherm. The values of Langmuir parameters, q_0 and b were 8.84918 mg/g and 0.03266 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 [44].

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

where C_o 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 0.75380, 0.37979 and 0.23441, respectively. The values indicated a favorable system.
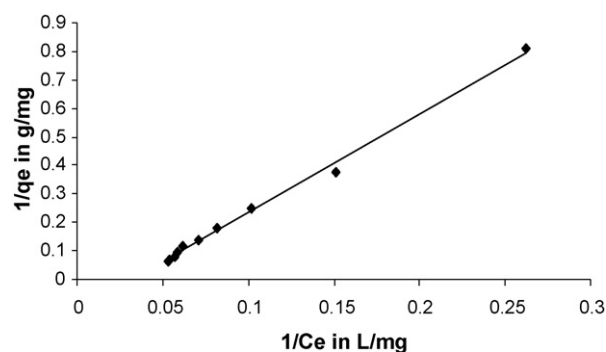
Table 9
Thermodynamic parameters using synthetic lead solution of 10 mg/L, 50 mg/L and 100 mg/L.

Initial lead concentration (mg/L)	ΔH (kJ/mol)	ΔS (kJ/mol)	ΔG (kJ/mol)							R^2
			20 °C	25 °C	30 °C	35 °C	40 °C	45 °C	50 °C	
10	27.617	0.104	−0.987	−1.560	−2.133	−2.706	−3.280	−3.853	−4.426	0.995
50	25.848	0.102	−1.231	−1.797	−2.364	−2.930	−3.496	−4.062	−4.628	0.985
100	21.594	0.091	−1.789	−2.294	−2.798	−3.303	−3.808	−4.313	−4.817	0.944

Fig. 11. Langmuir adsorption isotherm, $1/C_e$ versus $1/q_e$.
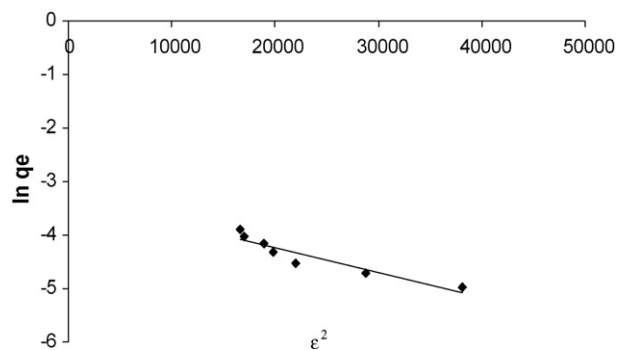
Fig. 12. D–R adsorption isotherm, $\ln q_e$ versus ε^2.

Fig. 13. Percentage removal versus initial cation concentration of solution with initial lead concentration of 10 mg/L, 50 mg/L and 100 mg/L.

It is known that the Langmuir and Freundlich adsorption isotherm constants do not give any idea about the adsorption mechanism. In order to understand the adsorption type, equilibrium data were tested with Dubinin–Radushkevich isotherm [44,45].

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. 12 shows the plot of $\ln q_e$ against ε^2, which was almost linear with correlation coefficient, $R^2 = 0.88055$. 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 1.1×10^{-4} mol^2 kJ^{-2} and that of q_m was 0.013345 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 mol of ion is transferred to the surface of the solid from infinity in solution. The value of E was found to be 67.47683 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 th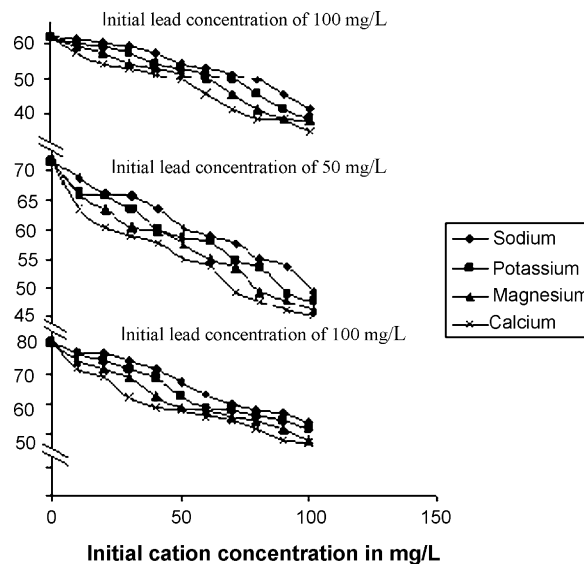e adsorption is physical in nature and if it is in between 8 kJ mol^{-1} and 16 kJ mol^{-1}, then the adsorption is due to exchange of ions [44]. The value in the present study was found to be little greater than 16 kJ mol^{-1}. This may be due to different chemical processes (such as the formation of lead phosphate and lead hydroxide) accompanying the ion exchange process.

3.2.8. Effect of competitive ions

Drinking water and wastewater contain 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 in 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. 13. It was clear from the figure that the presence of these cations reduced the adsorption of lead appreciably with increase in initial concentration of different 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 10. Desorption of the adsorbed lead in neutral distilled water resulted about 4.11%, 4.33% and 4.50% for initial concentration of 10 mg/L, 50 mg/L and 100 mg/L, respectively. 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.

Table 10
Percentage desorption and regeneration of lead of different concentrations by polycinnamamide 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	61.8	61.6	31.0	3.77	2.54	99.67	50.16	6.10	4.11
50	71.8	71.7	36.1	4.48	3.11	99.86	50.27	6.23	4.33
100	81.2	81.0	41.2	5.12	3.66	99.75	50.73	6.30	4.50

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

Polycinnamamide thorium (IV) phosphate, a fibrous ion exchanger has been synthesized from cinnamamide, thorium nitrate and phosphoric acid by co-precipitation method. Synthesis was ascertained by adopting various characterization methods like SEM, XRD, FTIR, and TGA–DSC. Polycinnamamide thorium (IV) phosphate exhibited much greater specific surface area. The adsorption of lead from aqueous solution by polycinnamamide 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 81% and 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 within 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 polycinnamamide thorium (IV) phosphate along with any other adsorbent to meet permissible limit of lead in water.

Acknowledgements

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