Preparation and Characterization of Silanized Silica Gel-Supported Poly(acrylic acid) Network Polymer and Study of Its Analytical Application as Selective Extractor for Lead Ion

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ABSTRACT: A novel silanized silica gel (SSG)-supported poly(acrylic acid) network polymer (ion exchanger) has been synthesized and characterized for the study of its analytical applications. The chemical nature of the ion exchanger has been elucidated with the help of FTIR, NMR, TGA, DSC, and SEM. The immobilization of the polymer network on SSG has been studied. The optimum pH range for quantitative extraction of lead was found to be 4.5–6.0. The effects of pH and stripping agent on extraction and elution of Pb(II), respectively, have been investigated. Ion exchange and break through capacity of the exchanger have been determined at room temperature. Pb(II) has been extracted quantitatively from various environmental samples. A plausible mechanism for lead ion exchange has been suggested. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 475–480, 2008

Key words: silanized silica gel; crosslinked poly(acrylic acid); extraction; lead ion

INTRODUCTION

Recently, the solid phase extraction (SPE) technique[1] has been found wide application because the technique is very fast, simple, and cost effective. SPE is based on the utilization of a solid supporting phase, which is coated or immobilized with different materials such as polyelectrolyte, high molecular mass carboxylic acid, chelating agent, surfactant, and quaternary ammonium salt. Silica gel acts as successful support because it does not swell or strain, has good mechanical strength, and can undergo heat treatment.[1] Quite a good number of literatures appear to deal with silica supported polymer for selective separation of metal ions.[2] The easy, rapid, cost effective, and quantitative extraction of lead(II) from various ores, alloys, and wastewater is a well-defined problem to the analytical chemists.[3] There are many removal methods available for lead such as solvent extraction,[4] ion-exchange,[5] adsorption,[6] etc. Ion adsorption onto solid polymer surface is now considered one of the most promising techniques for concentration, removal, and recovery of metal ions from wide variety of sources.[7] The selectivity of these materials toward metal ion can be controlled[7] by the immobilized functional group, pH of the medium, presence of masking agent, and temperature. In the present decade, several researchers are engaged in synthesizing suitable polymers having selective lead ion binding capacity.[8,9] The crosslinked poly(acrylic acid) (X-PAA) is widely used in the retention and recovery of heavy metal ions.[10,11] However, X-PAA, coated on silanized silica gel (SSG) has not yet been reported.

The present article involves the preparation and characterization of SSG-supported PAA network polymer and study of its analytical application as selective extractor for lead ions from aqueous solutions. A new preconcentration procedure for lead(II) ion by the network polymer has been developed.

EXPERIMENTAL

Chemicals and reagents

Acrylic acid (AA) (Qualigens, Mumbai, India), sodium lauryl sulfate (NaLS) (Glaxo, Mumbai, India), *N,N*-methylene bis acrylamide (MBA) (Fluka, Buchs, Switzerland), ammonium per sulfate (APS) (S.d. fine Chem., Boisar, India), lead nitrate (Merck, Mumbai, India), silica gel (Mesh 120) (Qualigens, Mumbai, India), hexamine (S.d. fine Chem., Boisar, India), dimethyl dichlorosilane (Merck, Mumbai, India), and
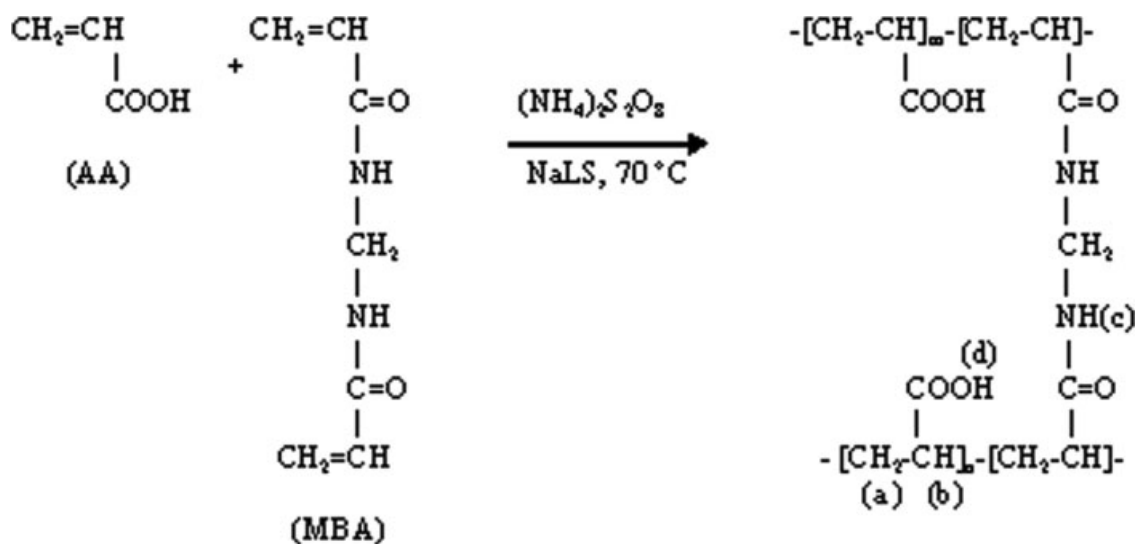
Scheme 1 Synthesis of crosslinked PAA.

methanol (Bengal Chemicals, Mumbai, India) were used as received.

Equipments

Fourier transform infrared (FTIR) spectra of the polymer were recorded on Shimadzu FTIR (Model No. 8400S) using KBr pellets. The NMR spectra of the sample (in $CDCl_3$ solution) were recorded using DRX-300 spectrometer operating at a proton frequency of 300 MHz. Thermal analysis was conducted using a Stantum Redcraft Thermal Analyzer (STA-780) in air at a rate of 10°C/min. The amount of metal ion in the solution was measured by atomic absorption spectrophotometer (AAS, Shimadzu, AA 6300) with fixed wavelength (217 nm), L 233 lamp (12 mA), slit width (0.7 nm), acetylene flow (2.0 L/ min), and burner H (7 mm), and complexometrically. An Elico LI 120 pH meter, thermostat and chromatographic column (i.d. = 0.8 cm) were used.

Preparation of X-PAA

The Polymerization was carried out in a three-necked round-bottom flask that was kept in a constant temperature (70°C) water bath. Acrylic acid (1 mL), distilled water (10 mL), and sodium lauryl sulfate (1 g) were taken in a flask and mixed well by a magnetic stirrer. Pure nitrogen gas was passed through the solution for half an hour to create inert atmosphere. MBA (0.5 g) and ammonium persulfate (1 g) were then added and stirred. After 2 h, the precipitated white polymer was separated through filtration, washed several times with distilled water, and dried under vacuum until constant weight.

Silanization of silica gel and immobilization of the polymer (X-PAA)

Silica gel (25 g) was rendered hydrophobic by exposing it to the vapor of dimethyl dichlorosilane (2.5 mL) in nitrogen atmosphere to prepare SSG.[12] SSG was then washed with methanol and dried. The chemically treated gel was then impregnated with the 20 mL 18% (w/v) solution of synthesized X-PAA in benzene and dried in a rotary vacuum evaporator to achieve uniform coating. Ion exchanger bed was prepared by usual method.[12]

General extraction procedure

The prepared ion exchanger was loaded in the chromatographic column (i.d 0.8 cm) to achieve a bed height of 8 cm, and then it was washed with 2M HCl to remove excess organic solvent. An aliquot of metal ions in acetate buffer was passed through the column (preadjusted pH 5.5) at a flow rate of 1.0 mL/min. After extraction (retention) of metal ions, it
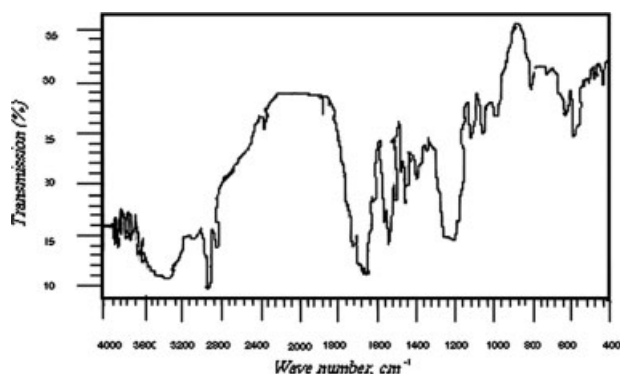

Figure 1 FTIR spectrum of the crosslinked polymer.

TABLE I
Assignment of IR Peaks

Peak position (cm^{-1})	Nature of peak (intensity)	Peak assignment
1200–1240	Medium	C—C long skeleton, C—O stretching.[14,15]
1640	Sharp, Strong	Carbonyl stretching of a secondary amide.[14,15]
1700	Sharp, Strong	Carbonyl stretching of carboxylic acid.[14,15]
2880	Sharp, Strong	C—H stretching of an alkane.[14]
2900	Sharp, Strong	Hydrogen bonded OH group of carboxylic acid.[15]
3360	Broad, Medium	N—H stretching of an amide.[15]

was eluted (striped) with suitable eluent (stripping agent). The amount of metal ion in each fraction of effluent was determined complexometrically.[13]

RESULTS AND DISCUSSION

Chemical nature of the ion exchanger

The FTIR spectrum of the synthesized polymer (Scheme 1) is shown in Figure 1. The spectrum shows several characteristic peaks. The peak position and their assignment[14,15] are shown in Table I. The peak assignment indicates that the synthesized polymer contains both amide (1640 cm^{-1}) and carboxylic acid group (1700 cm^{-1}). These are the characteristic spectral feature of bisacrylamide X-PAA.[16,17] The peak at 3600 cm^{-1} indicates clearly the presence of moisture in the sample.

The presence of crosslinking in the polymer was also verified by the solubility and hardness test. PAA, [—CH$_2$—CH (COOH)—]$_n$ is highly soluble in aqueous medium. However, the synthesized polymer is completely insoluble in water. The insolubility in water may be attributed to the presence of crosslinking in the PAA. The hardness of the polymer is increased with the increase of crosslinker (MBA).

The bonding of the polymer was further verified by NMR spectroscopy. The proton NMR spectrum of the polymer is shown in Figure 2. The spectrum shows sharp peaks at 1.25, 2.55, 6.11, and 11.4 ppm that are probably corresponding to a, b, c, and d proton[14,15] of the proposed structure (Scheme 1).
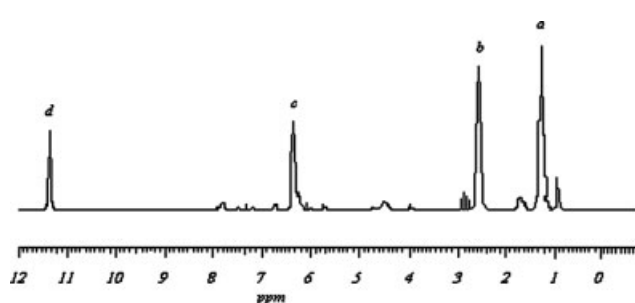
Thus NMR spectrum confirms the crosslinking of PAA. The peaks in the region 3.5–4.5 ppm indicate the presence of moisture in the sample.

The TGA (Thermogravimetric analysis) and DSC (Differential thermal analysis) curves of the prepared polymer are given in Figure 3. The TGA curve shows mainly three steps weight loss. First step (25–100°C, ≈10%), second step (100–375°C, ≈50%), and third step (375–450°C, ≈20%) are probably due to loss of absorbed moisture, decomposition of PAA, and degradation of crosslinker. DSC curve supports the three stages degradation by exhibiting three endothermic peaks at 65, 242, and 403°C, respectively.

The SEM photograph of the polymer coated SSG is shown in Figure 4. The photograph confirms that the material is porous in nature and coated with the polymer. As evident from thermogravimetric analysis,[18] about 140 mg of the polymer (X-PAA) was immobilized on the surface of 1 g SSG (percentage of grafting[10] = 14). The value indicates that the present immobilization technique is more effective than the system reported earlier[18] (96 mg/g) without using dimethyl dichloro silane. SSG contains 2.94% (w/w) chlorine (as evident from chemical analysis[13]). In the silanization process, dimethyl dichloro silane is attached with silica gel through the formation of highly stable Si—O—Si linkage and elimination of hydrogen chloride (Scheme 2). The SSG immobilizes X-PAA through weak hydrophobic attraction. The
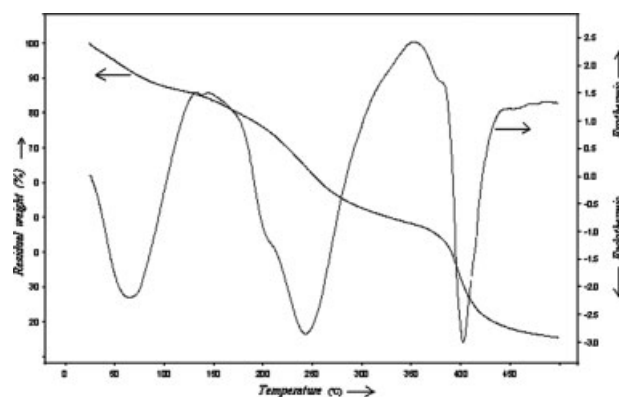
Figure 2 Proton NMR spectrum of the crosslinked polymer.

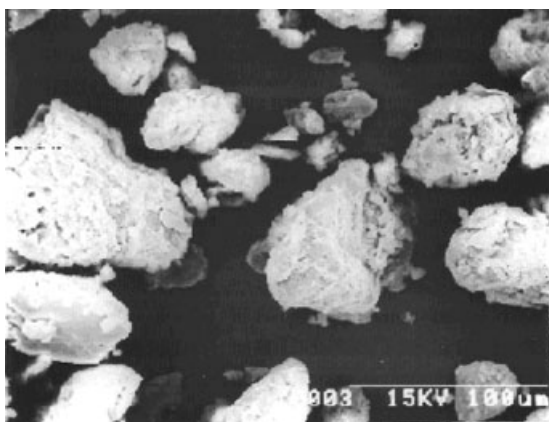**Figure 3** TGA diagram of the crosslinked polymer.

Figure 4 SEM photograph of the ion exchanger.

weak interaction is revealed from the fact that the bound polymer is easily separated from the grafted product while it is leached with organic solvent such as benzene. Thus dimethyl dichloro silane probably acts as coupling agent, which couples water insoluble polymer onto SSG (hydrophobic) surface through hydrophobic interaction (represented by dotted line) (Scheme 2).

Physicochemical characteristics of the ion-exchanger

The exchange capacity of the prepared exchanger was determined[12] at 25°C and found to be 2.52 mequiv. H^+/g. The value is superior to the literature[12] values (1.90–1.96 mequiv. H^+/g) of commercially available resins SRS100 and VERSATIC10. The break-through capacity of the prepared exchanger was 33.63 mg of Pb(II) per gram of dry exchanger (polymer coated silica) (i.e., 240 mg of Pb(II) per gram of polymer itself) at pH 5 and flow rate of 1 mL/min. The lead uptake capacity of the polymer is fairly higher than reported values[18,19] (24, 44.2, 134.5, and 147.9 mg/g for resins of polyethylenimine, carboxylic, sulfonic, and phosphoric acids, respectively). At the flow rate of 1 mL/min, only 6.4% of the available carboxylic acid (1.5×10^{21} per g of resin) was used to bind lead ($PbAc^+$). Break-through capacity was increased with the decrease of
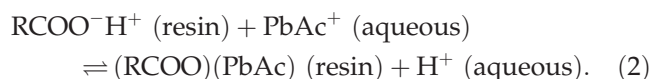
flow rate. The density and crosslink density (ratio of molar mass of the repeating unit, M_o to average molar mass between consecutive crosslink, M_c; M_o/M_c) of the material was 1.2 g/cm^3 and 0.72, respectively. The density and crosslink density were measured by a pykometer and swelling studies.[17] The specific surface area of the exchanger was found to be 54 m^2/g and it was determined by methylene blue method.[20]

## Effect of pH on Pb(II) extraction and extraction mechanism

The extraction of Pb(II) was studied within the pH range 2.5–7.5 (Fig. 5) using 0.1M acetate buffer. However, the quantitative extraction of Pb(II) was found at pH 4.5–6.0. The complete retention of Pb(II) in the resin bed was found even at a flow rate of 1.0 mL/min (manually controlled). Common anions such as Cl^-, ClO_4^-, and NO_3^- did not interfere in extraction. In acetate buffer medium (pH = 4.5–6.0), the lead ion remains in equilibrium[21] [eq. (1)] as:

$$PbAc_2 = PbAc^+ + Ac^-. \qquad (1)$$

Having suitable size and positive charge, the ionic species ($PbAc^+$) goes to the exchange site as per following suggested path [eq. (2)]:

$$RCOO^-H^+ \text{ (resin)} + PbAc^+ \text{ (aqueous)}$$
$$\rightleftharpoons (RCOO)(PbAc) \text{ (resin)} + H^+ \text{ (aqueous)}. \quad (2)$$

The absence of sharp peak at 1700 cm^{-1} and appearance of a new peak at 1595 cm^{-1} in the FTIR spectrum of lead adsorbed exchanger (spectrum is not shown) clearly indicates the presence of carboxylate anion[14] in the metal loaded sample. At low pH (<4.5), the equilibrium [eq. (2)] shifts toward left. As a result, quantitative extraction of Pb^{2+} did not take place in this condition. The metal ion passed through with the mobile phase as soluble lead acetate at pH ≤ 3. Although at high pH (>6), the lead ion undergoes hydrolysis and did not participate in the exchange process [eq. (2)].
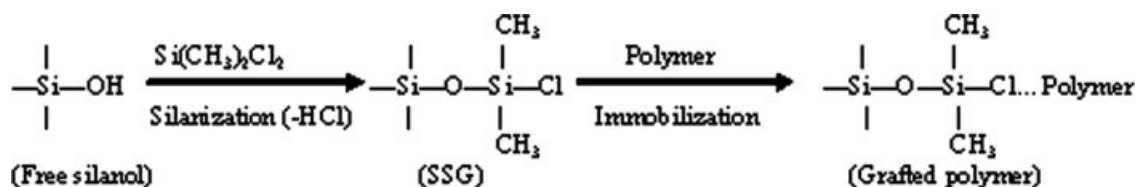
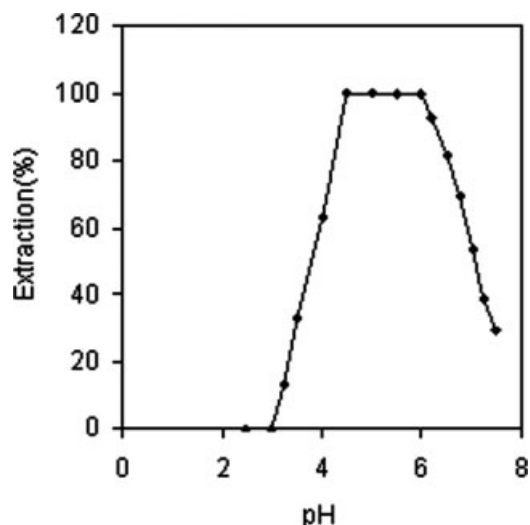**Scheme 2** Immobilization of crosslinked PAA onto silanized silica gel.

Figure 5 Extraction (%) versus pH plot of Pb(II) at room temperature.

Elution of Pb(II) in noncompetitive and competitive conditions

The systematic studies on stripping (Table II) gave the quantitative ($\geq$99%) elution of Pb(II) with HNO$_3$ ($\geq$0.005M), HCl ($\geq$0.005M), and CH$_3$COOH($\geq$0.1M). No elution of Pb(II) was observed with H$_2$SO$_4$ due to formation of insoluble lead sulfate. The 0.01M HNO$_3$ was found to be the best stripping agent (eluent) because it requires the least volume of nitric acid compared to the same concentration of hydrochloric and acetic acids, and it was used throughout the experiments. The elution process follows the reverse reaction of extraction [eq. (2)]. Efficiency of organic acid (acetic acid) is less than that of the inorganic acids (HNO$_3$ and HCl) because of its lower degree of dissociation. Lead comes out from resin bed mainly as soluble nitrate and chloro-complex while one elutes with nitric acid and hydrochloric acid, respectively.[22] Hence, higher amount (mole) of HCl is required to elute each mole lead in comparison to HNO$_3$. In the present study, 0.005M strong acids (HCl and HNO$_3$) elute more than 99% resin bound lead. However, Gardea and coworkers[19] reported that at least 0.1M HCl was required to stripe 67.8, 77.3, and 95.7% lead from resins of sulfonic, phosphonic, and carboxylic acids, respectively. Thus stripping of lead is easier in the developed resin. Nickel(II), copper(II), cobalt(II), cadmium(II), zinc(II), and tin(II) are the diverse metal ions commonly found along with lead(II) in many real samples (such as ores, alloys, and electroplating waste). In contrast to Pb(II), Ni(II), Co(II), Cu(II), Zn(II), Sn(II), and Cd(II)were eluted quantitatively with 0.002, 0.003, 0.005, 0.02, 0.05, and 0.1M H$_2$SO$_4$, respectively, in noncompetitive conditions. The observed trend in eluting strength of sulfuric acid indicates that the stronger the interaction between metal ion and exchanger the higher the acid concentration required for quantitative elution of that metal ion.

The elution of Pb(II) in the competitive condition is shown in the form of elution profile of Ni(II), Cu(II), Cd(II), and Pb(II) (Fig. 6). All the metal ions were extracted quantitatively at pH 5.5 from a multicomponent synthetic mixture. After extraction Ni(II), Cu(II), and Cd(II) were first eluted with 0.002, 0.005, and 0.1M H$_2$SO$_4$, respectively, maintaining the sequence. Then the remaining Pb(II) was eluted with 0.01M HNO$_3$. Thus it was possible to separate Pb(II) from multicomponent synthetic mixture by using selective stripping (eluting) agents.

Preconcentration and recovery of lead ion

The results of preconcentration process are shown in Table III. The 165 mL multicomponent synthetic mixture containing lead(II) was passed through the resin bed at the flow rate of 1.0 mL/min and pH 5.5. After selective extraction, Pb(II) was eluted from the resin bed with minimum volume of 0.1M HNO$_3$. In this process, the recovery and preconcentration factor were found to be 99.23% and 13.65, respectively.

Extraction of lead(II) from environmental samples

To evaluate the accuracy and applicability of the proposed method for the analysis of real environmental

TABLE II
Elution Behavior of Lead(II) in Different Eluents with Different Concentrations

Eluents	Concentration (M)	V_{max} (mL)[a]	V_t (mL)[b]	Recovery (%)[c]
HNO$_3$	0.005	40	60	99.2
	0.01	20	50	99.3
	0.05	15	25	99.3
	0.10	06	12	99.5
HCl	0.005	30	70	99.1
	0.01	25	55	99.2
	0.05	15	30	99.3
	0.10	10	15	99.5
CH$_3$COOH	0.01	–	100	–
	0.05	80	120	85.7
	0.10	40	70	99.1
	0.25	35	60	99.5
	0.5	10	30	99.5
H$_2$SO$_4$	2.0	–	100	–
	3.0	–	100	–
KNO$_3$	0.05	–	100	–
		–	100	–
H$_2$O	–	–	–	–

Pb(II) taken = 2.17 mg; column = 0.8 cm $\times$ 8 cm; flow rate = 1.0 mL/min.
[a] Volume of effluent (mL) having maximum concentration of the lead ion.
[b] Total volume of effluent (mL).
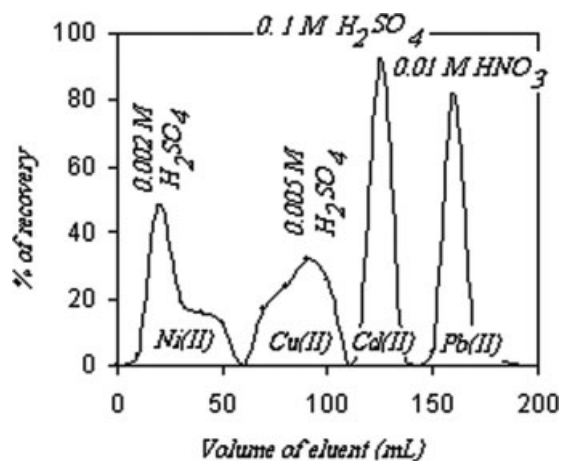[c] Metal ion eluted/Metal ion loaded $\times$ 100.

Figure 6 Elution profile of metal ions (Ni(II), Cu(II), Cd(II), and Pb(II)) [Flow rate = 1.0 mL/min, pH = 5.5, Column = 0.8 cm × 8 cm].

samples, it was applied to the determination of lead in tap, well and electroplating waste samples. The 100 mL aqueous solution of samples having known concentration of Pb(II) ion (pH adjusted to 5.5) was passed through the column at the flow rate of 1.0 mL/min. The extracted lead ion was eluted with minimum volume of $0.1M$ HNO_3 and subjected to the determination of lead content by AAS (Table IV). Data indicates that the proposed method is highly sensitive and a preconcentration procedure is applicable to determine lead up to ppb levels and can be used for the abatement of lead in environmental samples.

CONCLUSIONS

The present study shows that the synthesized exchanger acts as cation exchanger with high exchange and break through capacity, and chemical stability. Exchanger bed could be used more than 40 cycles with little loss of exchange capacity. The developed technique could be applied for the selective extraction of lead(II) from environmental samples. The proposed method is highly efficient, cost effective, simple, and rapid, and it needs only 2.5 h

TABLE III
Preconcentration and Recovery of Lead Ions

Vol. of lead ion solution passed (mL)	165
Initial concentration of lead ion (mg/mL), C_i	0.197
Vol. of $0.1M$ HNO_3 (mL) for elution	12
Concentration of lead ion in the effluent (mg/mL), C_f	2.69
Recovery (%)	99.23
Preconcentration factor (C_f/C_i)	13.65

Flow rate = 1.0 mL/min; pH = 5.5; Column = 0.8 cm × 8 cm.

TABLE IV
Determination of Lead(II) Ion in Environmental Samples

Environmental samples	Pb(II) added (μg/L)	Pb(II) ion found by AAS (μg/L)	Recovery (%)
Tap water	0	7.5 ± 0.5	–
	10	17.7 ± 0.9	101
	50	56.2 ± 1.6	97
Well water	0	3.5 ± 0.3	–
	10	13.2 ± 0.7	98
	50	53.3 ± 1.2	99
Electroplating waste	0	11.2 ± 0.6	–
	10	21.4 ± 0.9	101
	50	60.0 ± 1.8	98

for complete extraction of lead(II). Dimethyl dichlorosilane immobilizes the polymer onto silica gel surface efficiently.

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