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Synthesis, characterization and analytical applications of a new composite cation exchange material poly-o-toluidine stannic molybdate for the separation of toxic metal ions

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ABSTRACT

A new composite cation exchange material poly-o-toluidine stannic molybdate was synthesized by the incorporation of an organic polymer poly-o-toluidine into the matrices of inorganic precipitate of stannic molybdate. The experimental parameters such as concentration, mixing ratio and pH were established for the synthesis of the material. The material was found to be granular and can be conveniently used in column operations. The newly synthesized composite material exhibits improved thermal stability, ion exchange capacity and selectivity for toxic heavy metal ions. The material is characterized using various analytical techniques like FTIR, TGA, DTA, XRD, SEM, TEM and elemental analysis. The X-ray diffraction study showed semicrystalline nature of the material. The pH titration studies revealed monofunctional weak acid behavior of the exchanger. The elution behavior of the exchanger was also examined. The distribution coefficient studies of metal ions on the material were performed in different solvent systems and the material was found to be selective for Hg^{2+} and Pb^{2+} ions. On the basis of distribution coefficient values, some analytically important binary separations of metal ions viz. Al^{3+}–Hg^{2+}, Cu^{2+}–Hg^{2+}, Cu^{2+}–Th^{4+}, Zn^{2+}–Hg^{2+}, Bi^{3+}–Hg^{2+}, Cd^{2+}–Pb^{2+} were achieved on poly-o-toluidine stannic molybdate columns. Hg^{2+} and Pb^{2+} ions were also selectively separated from synthetic mixtures of metal ions. In order to demonstrate the practical utility of the material, quantitative separations of Hg^{2+} from thermal power plant effluents and of Pb^{2+} from lead storage battery industry wastes have been achieved.

1. Introduction

The increasing level of heavy metals in the environment represents a serious threat to human health, living resources and ecological systems. These metals when present beyond the certain concentration are not only toxic but also can lead to serious health problems [1]. So every care should be taken to treat wastewaters before flowing into public sewage, rivers and on land to prevent environmental pollution. Various methods have been developed for the removal of these metals from aqueous systems such as solvent extraction, adsorption, preconcentration, reverse osmosis and ion exchange. Ion exchange is one of the important and cost effective treatments. Conventional ion exchange resins although possess excellent ion exchange properties for the separation and removal of heavy toxic metal ions and are in frequent use in solving problems of diverse nature. But they suffer from two main limitations. Firstly they decompose at elevated temperatures. Secondly they do not withstand in the presence of high ionizing radiations [2]. It is for these drawbacks, researchers prompted to exploit new inorganic materials as ion exchangers which can cope with the above mentioned difficulties. One of the astonishing features of inorganic ion exchangers is that they can be obtained with cavities of specific size. It is for these reasons they often show selectivity towards a particular metal ion or anion or organic molecule. But they also suffer from two main limitations. They undergo hydrolysis when used in aqueous systems and they are obtained usually in non-granular form and thus not suitable for column operations. In order to overcome the above mentioned shortcomings encountered with organic resins and inorganic ion exchangers, attempts have been made to develop organic–inorganic composite ion exchangers by incorporating organic species in the matrix of inorganic exchangers [3–9]. These composite materials exhibit properties entirely different from properties of parent components. These composite materials have improved mechanical strength, greater thermal and chemical stability, high selectivity for hazardous metal ions, enhanced ion exchange capacity, electrochemical properties, optical and magnetic behavior and they can be synthesized in granular form suitable for column operations [3,6,10–12]. In designing composite materials, scientists and engineers have ingeniously combined various metals, ceramics, and polymers to produce a new

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generation of extra ordinary materials that encompass a wide variety of applicants. Most composites have been created to improve combination of mechanical characteristics such as stiffness, toughness and high temperature strength [10–12]. The present work described the synthesis, characterization and analytical applications of a new, thermally stable composite cation exchange material poly-o-toluidine stannic molybdate. The material showed the high selectivity for Pb^{2+} and Hg^{2+} metal ions. These toxic metals are potential pollutants in the environment. Poly-o-toluidine stannic molybdate was successfully used for the quantitative separations of Pb^{2+} and Hg^{2+} ions from the synthetic mixture as well as real sample of Pb^{2+} and Hg^{2+} metal ions. The results of the analysis were found to be satisfactory.

2. Experimental

2.1. Reagents and instruments

The main reagents used for the synthesis were ortho-toluidine, stannic chloride pentahydrate, sodium molybdate and potassium persulphate (Loba Cheme Pvt., Ltd. (India). All other chemicals and reagents used were of analytical grade.

A single electrode pH meter (Toshniwal, India), FTIR spectrophotometer (Perkin-Elmer Spectrum-BX, USA), an automatic thermal analyzer (V2.2A Du Pont 9900), a PW 1148/89 based X-ray diffractometer (Phillips, Holland), an electron microscope (LEO 435 VP, Australia) with attached imaging device, a UV–Vis spectrophotometer (Elico EI 301E, India) an elemental analyzer—Elementary Vario EL III, Carlo-Erba, model 1108, and an automatic temperature controlled water bath incubator shaker Elcon (India) were used.

2.2. Preparation of reagents

The solutions of 0.1 M stannic chloride pentahydrate, 0.1 and 0.2 M sodium molybdate were prepared in demineralized water (DMW). Solutions of 20% (v/v) of double distilled o-toluidine and 0.1 M ammonium persulphate were prepared in 1.0 M HCl.

2.3. Preparation of poly-o-toluidine stannic molybdate

Poly-o-toluidine gels were prepared by mixing 20% o-toluidine and 0.1 M ammonium persulphate with continuous stirring by a magnetic stirrer. Green colored poly-o-toluidine gels were obtained by keeping the solution below 10 °C for an hour. The precipitate of stannic(IV) molybdate was prepared at room temperature (25 ± 2 °C) by adding an aqueous solution of sodium molybdate solution gradually to an aqueous solution of stannic chloride pentahydrate. The white inorganic precipitates were obtained and the pH (1.5) was adjusted by adding 1 M nitric acid or 1 M ammonia solutions. The gels of poly-o-toluidine were then added to the white inorganic precipitate of stannic(IV) molybdate and mixed thoroughly with constant stirring. The resultant green color gels so obtained were kept for 24 h at room temperature (25 ± 2 °C) for digestion. The supernatant liquid was filtered off by suction. The gel was washed with demineralized water (DMW) till the filtrate was neutral. The product was dried in an oven at 50 °C. The dried material was broken into small granules on immersion in DMW. The granules were converted into H^+ form by placing in 1 M HNO_3 solution for 24 h. The excess acid from the material was removed after several washings with DMW and finally dried at 50 ± 2 °C. The particles of size 50–100 μm of the material were obtained by sieving. In this way a number of samples of poly-o-toluidine stannic molybdate were prepared in different experimental conditions. It was decided to study sample S-4 in detail on the basis of highest ion exchange capacity for Na^+ ions.

2.4. Column ion-exchange capacity and thermal effect on ion exchange capacity

To determine the ion-exchange capacity, column process was used [2–6]. 1.0 g dry cation-exchanger in H^+ form was packed in a column (1.0 cm internal diameter) fitted with glass wool at the bottom. Metal nitrates as eluents were used to elute the H^+ ions completely from the cation-exchanger column. The effluent was titrated against a standard solution of 0.1 M NaOH.

To determine the effect of heating temperature on ion exchange capacity of the material, 1.0 g sample of the poly-o-toluidine stannic molybdate in H^+ form was heated at different temperatures in a muffle furnace for 1 h and Na^+ ion exchange capacity was determined after cooling them to room temperature by standard column process as described above.

2.5. Regeneration of the ion exchange material

When the exchanger exhausted, it was regenerated by keeping it overnight in 0.1 M HNO_3. It was washed with demineralized water till neutral and the ion exchange capacity was determined by the same procedure as described above.

2.6. pH titration

0.5 g of composite cation exchanger (H^+ form) was placed in each 250 mL conical flask, followed by the addition of 0.1 M solutions of alkali or alkaline earth metal chlorides and their hydroxides in different volume ratios [12]. The total volume was kept 50 mL to maintain the ionic strength constant. The pH of each solution was determined after equilibration and plotted against milli-equivalents of OH ions added.

2.7. Elution behavior

1.0 M $NaNO_3$ solution was passed through a column containing 1.0 g exchanger maintaining a flow rate 0.50 mL min^{-1}. The effluent was collected in 10 mL fractions and the amount of H^+ ions released in each fraction was determined titrimetrically using standard sodium hydroxide solution.

2.8. Instrumental characterization

Simultaneous thermogravimetric analysis–differential thermal analysis (TGA–DTA) studies of the sample were carried out at a heating rate of 10 °C min^{-1} up to 800 °C in the air atmosphere.

For FTIR analysis, 10 mg (dry mass) of the exchanger in H^+ form was thoroughly mixed with 100 mg (dry mass)of KBr and grinded to a fine powder. A transparent disc was made by applying a pressure of 80 psi (1 psi = 6894.76 pa) in a moisture free atmosphere. The FTIR absorption spectrum was recorded between 450 and 4000 cm^{-1}

For X-ray diffraction analysis, manganese filtered CuKα radiation wavelength (l50.1542 nm) at 298 K was used. The instrument was equipped with graphite monochromator and operating at 40 kV and 30 mA.

Scanning electron micrographs were recorded for poly-o-toluidine, stannic molybdate and poly-o-toluidine stannic molybdate using a scanning electron microscope at 20.0 KV magnification.

TEM studies were carried out to know the particle size of poly-o-toluidine stannic molybdate composite cation exchange material.

2.9. Chemical composition

A 250 mg of poly-o-toluidine stannic molybdate was dissolved in 25 mL hot concentrated hydrochloric acid. The solution was cooled and diluted to 100 mL with demineralized water. The metal contents in the solution phase were determined spectrophotometrically [13,14]. Carbon, hydrogen and nitrogen contents of the material were determined by elemental analysis. The percent composition of the material was: Sn, 21.24; Mo, 34.15; C, 12.816; H, 1.844; N, 4.143 and O, 26.50.

2.10. Sorption behavior of poly-o-toluidine stannic molybdate towards metal ions

The distribution coefficient (K_d) for various metal ions were determined in different solvent systems. Poly-o-toluidine stannic molybdate (0.3 g) in H^+ form was placed into a 100 mL conical flask containing 30 mL solution of 0.0033 M of concerned metal ions. The mixture was continuously shaken for 5 h at 40 ± 2 °C in a shaker incubator. The amount of metal ion left in the solution was determined by EDTA titration. Distribution coefficient values were calculated using the following relationship

$$K_d = \frac{\text{milli equivalent of metal ions/g of ion-exchanger}}{\text{milli equivalent of metal ions/mL of solution}} \text{mL g}^{-1}$$

$$K_d = \frac{I - F}{F} \times \frac{V}{M} \quad \text{mL g}^{-1}$$

where I is the initial amount of the metal ion in the solution phase and F is the final amount of the metal ion in the solution phase.

When the metal ions (M^{2+} and M^{3+}) was treated with poly-o-toluidine stannicmolybdate (H^+ form), the following reactions took place.

$$2\bar{R}H^+ + M^{2+} \rightarrow \bar{R}_2M^{2+} + 2H^+$$

$$3\bar{R}H^+ + M^{3+} \rightarrow \bar{R}_3M^{3+} + 3H^+$$

where, $\bar{R}H^+$ is poly-o-toluidine stannicmolybdate, M^{2+} and M^{3+} are bivalent and trivalent metal ions respectively.

2.11. Quantitative separation of metal ions in binary synthetic mixtures

Quantitative binary separations of some metal ions of analytical interest were achieved on poly-o-toluidine stannicmolybdate. 2.0 g of exchanger in H^+ form was packed in a glass column (internal diameter = 1.0 cm) with a glass wool support at the end. The column was washed thoroughly with DMW. 2.0 mL binary mixture of the metal ions to be separated was poured on to the column and allow to flow at a rate of 0.3–0.5 mL min^{-1} till the solution level was just above the surface of the material. The column was then rinsed with DMW. Individual metal ions were eluted using appropriate eluting reagents. The flow rate of the eluent was maintained (0.3–0.5 mL min$^{-1)}$ throughout the elution process. The effluent was collected in 10 mL fractions and was titrated against the standard solution of 0.01 M di-sodium salt of EDTA.

2.12. Selective separation of Pb^{2+} and Hg^{2+} ions from the synthetic mixtures on poly-o-toluidine stannic molybdate columns

For the selective separation of Pb^{2+}, different sets of the synthetic mixtures containing Pb^{2+}, Cu^{2+}, Cd^{2+}, Ni^{2+}, Al^{3+} and Zn^{2+} were taken in which the amount of the Pb^{2+} was varied keeping the amount of other metal ions constant. For selective separation of Hg^{2+}, different sets of Hg^{2+}, Cu^{2+}, Cd^{2+}, Ni^{2+}, Al^{3+} and Zn^{2+} were taken and the amount of the Hg^{2+} was varied keeping the amount of other metal ions constant. The subsequent procedure remained the same as described earlier.

2.13. Separation of Pb^{2+} and Hg^{2+} from industrial effluents using poly-o-toluidine stannic molybdate columns

2.13.1. Sample preparation

Industrial wastes were collected from industrial area of Aligarh City, India. Pb^{2+} sample was taken from battery manufacturing units and Hg^{2+} from thermal power plant. Samples were treated with a few mL of concentrated nitric acid and stirred thoroughly until clear solutions were obtained. The excess acid was evaporated to small volume. It was then diluted with 0.01 M nitric acid solution to 50 mL. The metal ion contents were determined using atomic absorption spectrophotometer. Pb^{2+} and Hg^{2+} were found to be 15.7 μg mL^{-1} and 9.6 μg mL^{-1}, respectively

2.13.2. Procedure for separation

Different volumes of stock solutions ranging from 0.5 to 5.0 mL were poured into a glass column (internal diameter = 1.0 cm) packed with poly-o-toluidine stannic molybdate with a glass wool support at the base. The solution was allowed to flow through the column at a rate of 0.5 mL min^{-1}. Pb^{2+} and Hg^{2+} ions were then eluted with suitable eluents. The elution process was continued till the effluent showed the absence of lead ions and mercury ions. Mercury and lead ions content in respective effluents were then determined by atomic absorption spectrophotometer.

3. Results and discussion

In this study a number of samples of organic–inorganic composite ion exchange material poly-o-toluidine stannic molybdate were prepared by the sol–gel mixing of organic polymer poly-o-toluidine with the inorganic precipitate of stannic molybdate (Table 1). It is evident from Table 1 that sample S-4 possessed greater Na^+ ion exchange capacity (1.68 meq g^{-1}), better yield and high thermal stability than other samples. Sample S-4 showed good reproducible behavior as evident from the fact that the material obtained from various batches did not show any appreciable deviation in their percentage of yield and ion exchange capacities (Table 2). So, sample S-4 was selected for detailed studies. The improvement in ion exchange capacity of this organic–inorganic

Table 1

Conditions of synthesis and ion exchange capacity of poly-o-toluidine stannic molybdate composite cation exchanger.

Sample code	Conditions of synthesis			Mixing volume ratios (v/v)		Drying temperature (°C)	Weight (g)	IEC (meq g^{-1})
	SC (M)	SM (M)	pH of inorganic precipitates	0.1 M $(NH_4)_2S_2O_8$ in 1.0 M HCl	20% o-toluidine in 1.0 M HCl			
S-1	0.1	0.1	1.0	1	1	50 ± 2	3.21	1.21
S-2	0.1	0.1	1.5	1	1	50 ± 2	2.24	0.85
S-3	0.1	0.2	1.5	1	1	50 ± 2	1.14	1.09
S-4[a]	0.1	0.2	1.5	1	1	50 ± 2	8.052	1.68
S-5	0.1	0.2	1.5	1	1	50 ± 2	6.41	1.15
S-6	0.1	0.1	0.5	1	1	50 ± 2	No ppt.	–

SC: stannic chloride; SM: sodium molybdate, total volume of the mixture solution of SC and SM was kept 200 mL; IEC: ion exchange capacity.

[a] Selected for detailed studies.

Table 2
Reproducibility data for the synthesis, ion exchange capacity and yield of poly-o-toluidine stannic molybdate (sample S-4).

Sample no.	pH of the mother liquor	Mixing ratio (v/v) POT:STM	Stirring time (h) after mixing	Drying temperature (°C)	IEC for Na^+ (meq g^{-1})	Yield (g)
1	1.5	1:1	1	50 ± 2	1.68	8.0
2	1.5	1:1	1	50 ± 2	1.67	8.1
3	1.5	1:1	1	50 ± 2	1.68	8.2
4	1.5	1:1	1	50 ± 2	1.68	8.0
5	1.5	1:1	1	50 ± 2	1.69	8.3

POT: poly-o-toluidine; STM: stannic molybdate.

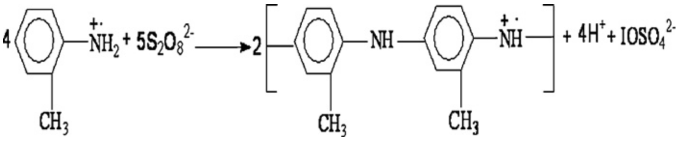

Fig. 1. Preparation of poly-o-toluidine gel.

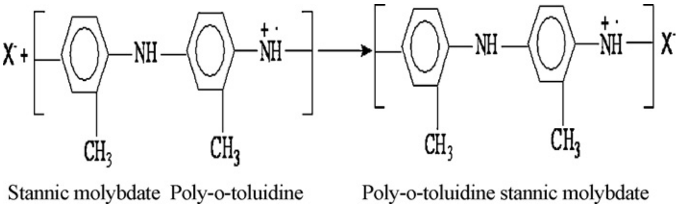

Fig. 2. The binding of poly-o-toluidine into the matrix of stannic molybdate.

composite cation exchanger in comparison to its inorganic counterpart (stannic molybdate [13]) may be due to binding of organic polymer (poly-o-toluidine) with inorganic moiety. Due to the coordination type interactions, all polymer based ion exchanger which have one or more multiple donor atoms offer good ion exchange capacity and extremely high selectivity for toxic metal ions [15].

Poly-o-toluidine gel was prepared by oxidative coupling using $K_2S_2O_8$ in acidic aqueous medium (Fig. 1). The binding of poly-o-toluidine into the matrix of stannic molybdate is given in Fig. 2. Ion exchange capacities for mono and bivalent metal ions have been studied (Table 3). The affinity sequence for alkali and alkaline earth metal ions metal ions were $K^+ > Na^+ > Li^+$ and $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$, respectively. This sequence is in accordance with the hydrated ionic radii. The ion exchange capacity should increase with decreasing hydrated radii and increases with electrode potential [14]. The ions with smaller hydrated ionic radii easily enter the pores of exchanger, resulting in higher adsorption [16]. It was observed that on heating the material at different temperatures, the physical appearance and ion exchange capacity of the dried sample material (S-4) were changed as the temperature increased as shown in Table 4. If we compare the ion exchange capacity after drying the material at 200 °C, Poly-o-toluidine stannic molybdate retained 70% of the initial ion exchange capacity while in case of other materials namely stannic borato molybdate [17], stannic molybdate [13], stannic arsenophosphate [18], showed substantial loss in the ion exchange capacity. However,

Table 3
Ion exchange capacity of poly-o-toluidine stannic molybdate for monovalent and bivalent metal ions.

Metal ions	pH of the metal ion solution	Ionic radii (Å) [16]	Hydrated radii (Å) [16]	Ion exchange capacity (meq g^{-1})
Li^+	3.30	0.68	10.0	1.02
Na^+	6.70	0.97	7.90	1.68
K^+	6.80	1.33	5.30	1.84
Mg^{2+}	6.50	0.78	10.80	1.45
Ca^{2+}	6.50	1.06	9.60	1.83
Sr^{2+}	6.30	1.27	9.40	2.03
Ba^{2+}	6.30	1.43	8.80	2.23

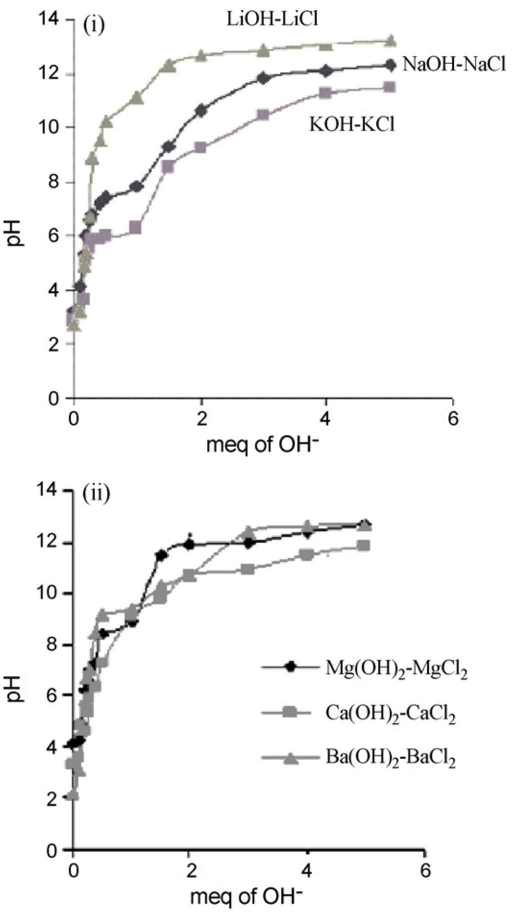

Fig. 3. (i) and (ii) pH titration curves of poly-o-toluidine stannic molybdate.

Table 4
Effect of drying temperature on the ion exchange capacity of poly-o-toluidine stannic molybdate.

Temperature (°C)	Appearance of beads after drying	Ion exchange capacity (meq g^{-1}) for Na^+ ions	Retention of ion exchange capacity (%)	Weight loss (%)
50	Green	1.68	100	0
100	Black	1.62	100	5
200	Black	1.18	70	11
300	Dark brown	0.80	48	12
400	Grey	0.25	15	24

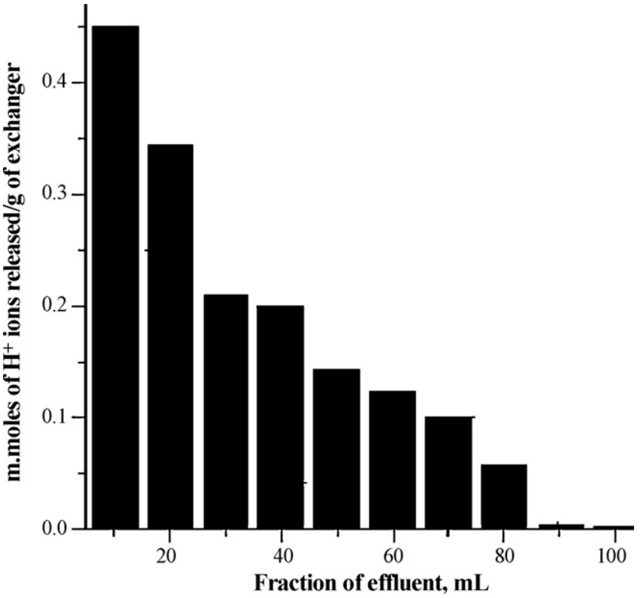

Fig. 4. Elution behavior of H^+ ions of poly-o-toluidine stannic molybdate.

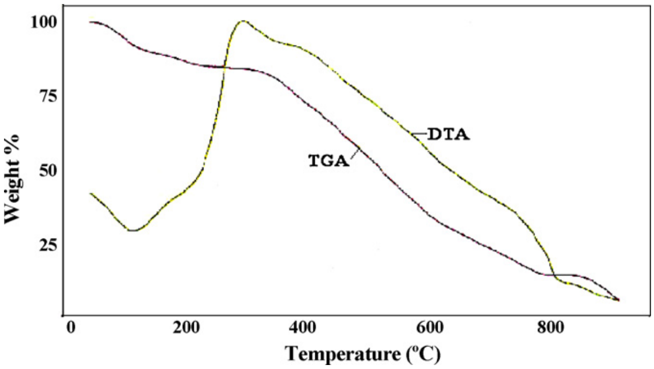

Fig. 5. TGA and DTA curves of poly-o-toluidine stannic molybdate.

this material retained a reasonable ion exchange capacity even up to 300 °C. The reusability of poly-o-toluidine stannicmolybdate was also investigated after regenerating this ion exchange material four times. It was observed that the ion exchange capacity decreased about 20% of its original ion exchange capacity. It indicated that this ion exchange material has a good reusability.

The pH titrations were performed for LiOH–LiCl, NaOH–NaCl, KOH–KCl, $Mg(OH)_2$–$MgCl_2$, $Ca(OH)_2$–$CaCl_2$ and $Ba(OH)_2$–$BaCl_2$ systems (Fig. 3 (i) and (ii)). The pH titration curves showed one inflection point which indicated the monofunctional weak acid behavior of poly-o-toluidine stannic molybdate. It appears to be a strong cation exchanger as indicated by a low pH (2.8) of the solution when no OH^- ions were added to the systems. On the other hand, the weak acidic groups are undissociated and thus inactive at low pH. With the addition of hydroxides, the solution is progressively neutralized and at the same time the ion-exchange is driven to completion. Thus, the pH titration curve of this composite cation-exchanger showed a gradual rise in pH at the early stage of titration and a steep rise at the point of complete neutralization of the cation-exchanger.

The rate of exchange and efficiency of poly-o-toluidine stannic molybdate was determined by elution behavior (Fig. 4) which showed the exchange was quite fast and almost all the H^+ ions were eluted in first 80 mL of eluent.

The TGA–DTA curves (Fig. 5) of the material showed a gradual weight loss of 10.8% up to 200 °C which was due to the loss of external water molecules (n) from the exchanger [19]. The decrease in weight observed between 210 °C and 400 °C may be caused by the elimination of interstitial water molecules [19]. Further weight loss between 450 and 650 °C may be assigned to the removal of water molecules formed by condensation of –OH groups and decomposition of the organic part of the material. Continuous weight loss

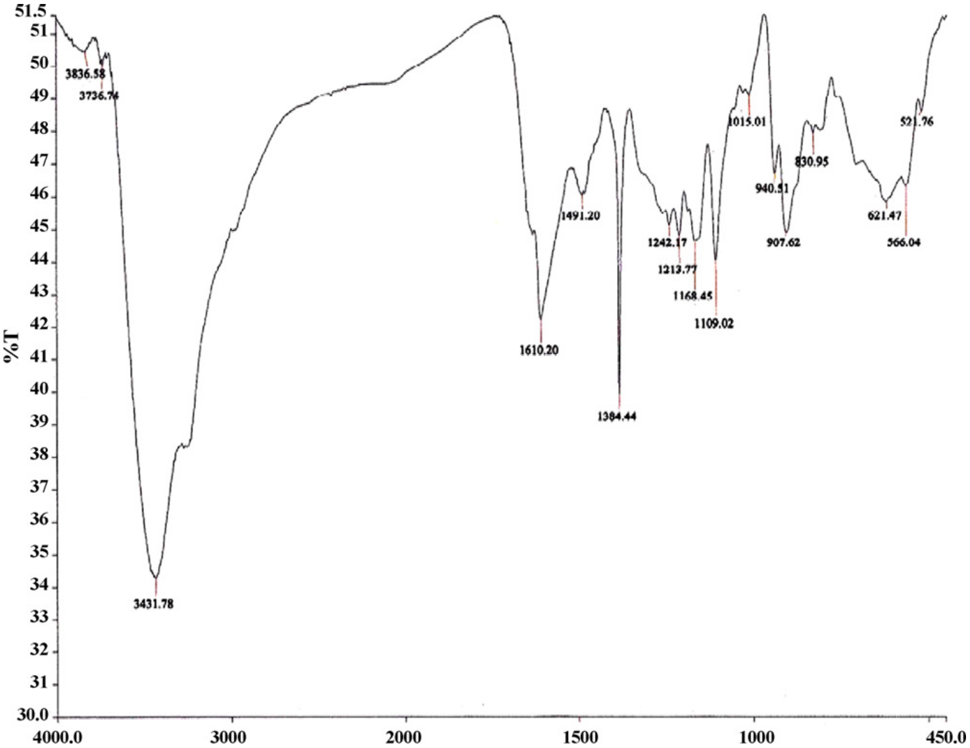

Fig. 6. FTIR spectrum of poly-o-toluidine stannic molybdate.

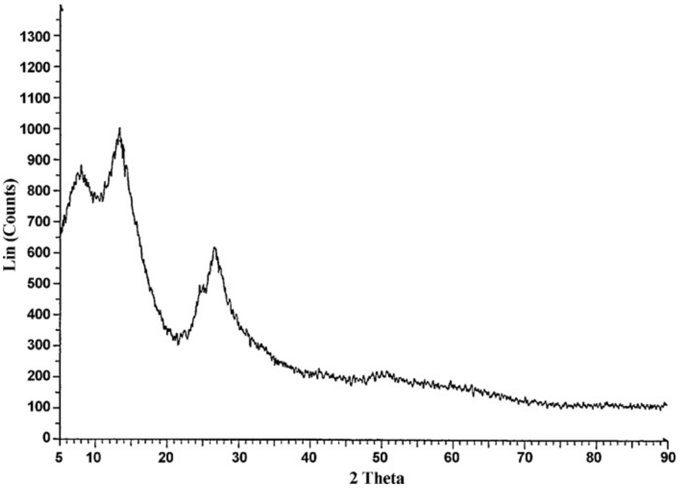

Fig. 7. X-ray diffraction (powder) pattern of poly-o-toluidine stannic molybdate at different 2θ values.

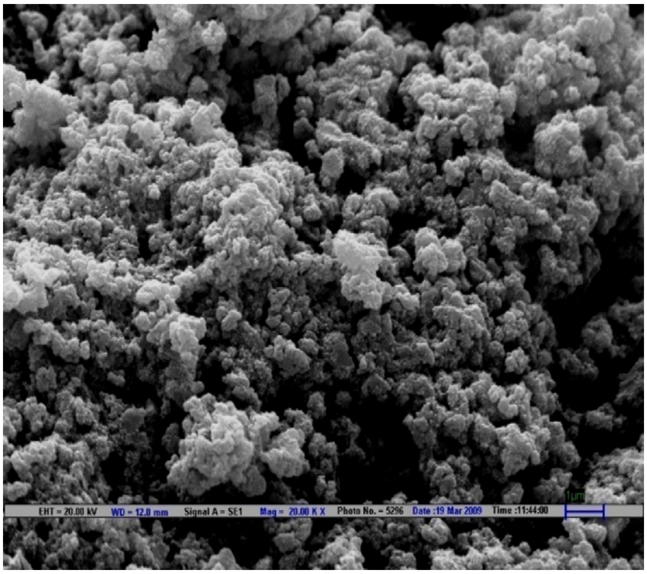

Fig. 8. SEM image of poly-o-toluidine stannic molybdate.

after 650 °C indicated the start of formation of corresponding oxides of metals. These results were also supported by DTA curve. The DTA curve showed two endothermic peaks one with a maximum at 150 °C due to dehydration reaction [20] and another at 800 °C due to decomposition of the compound. Another exothermic broad peak with a maximum at 300 °C indicated the crystallization of the material.

The FTIR spectrum of poly-o-toluidine stannic molybdate (Fig. 6) indicated the presence of band between 3000–3431 cm^{-1} which is the characteristic of free N–H stretching vibrations and suggested the presence of secondary amino group [21]. A sharp peak at 1610 cm^{-1} corresponded to water of crystallization [22]. The peak at 1124 cm^{-1} showed the presence of Sn–O–H and the peak at 907 cm^{-1} represented the presence of molybdate [23]. An assembly of peaks in the region 500–650 cm^{-1} was due to the metal–oxygen stretching vibrations.

X-ray diffraction pattern of poly-o-toluidine stannicmolybdate showed low intense peaks at different 2θ values. The analysis of these small signal peaks supported its semicrystalline nature (Fig. 7).

Scanning electron microscope (SEM) photograph of poly-o-toluidine stannicmolybdate (Fig. 8) showed the fibrous type morphology.

The TEM studies of poly-o-toluidine stannic molybdate (Fig. 9) showed particles size in the range of 10, 16 and 20 nm. Thus, we can say that the material is nano-composite cation exchange material.

The molar ratio, Sn:Mo:C:H:N:O, in poly-o-toluidine Sn(IV) molybdate was estimated to be 1:2.00:6.00:10.35:1.66:9.33; which suggests the formula of the material as

$$(-C_6H_3CH_3NH-)-(SnO_2)(H_2MoO_4)_2\cdot nH_2O$$

where 'nH_2O' is number of external water molecules per mole of the material.

In order to explore the potentiality of poly-o-stannic molybdate in the separation of metal ions, sorption studies of metal ions were performed in different solvent systems viz. demineralized water (DMW), 0.1 M nitric acid, 0.1 M acetic acid, 0.1 M dimethyl sulphoxide and 0.1 M N,N-dimethyl formamide. It is apparent from data in Table 5 that the material is selective for Hg^{2+} and Pb^{2+}. These two metal ions have high K_d values in all solvent systems. The low K_d values for all metal ions in nitric acid medium than acetic acid is due to the presence of high concentration of H^+ ions which reverses the process of adsorption and the process of regeneration predominates over the process of removal. The difference in the K_d values of metal ions indicated the separation possibilities of certain metal ions of analytical interests. The separation capability of the material has been demonstrated by achieving some analytically difficult binary separations (Table 7) viz. Al^{3+}–Hg^{2+}, Cu^{2+}–Hg^{2+},

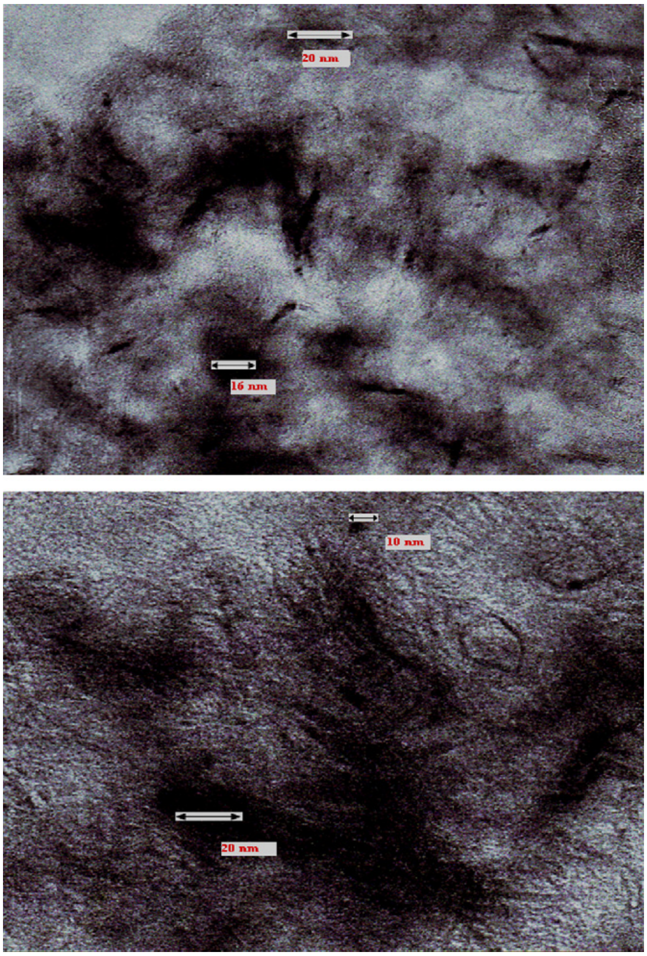

Fig. 9. Transmission electron microphotographs of poly-o-toluidine stannic molybdate showing different particle sizes.

Table 5
Distribution coefficients of metal ions on poly-o-toluidine stannic molybdate in various solvent systems.

Metal ions	DMW	0.1 M HNO_3	0.1 M acetic acid	0.1 M dimethyl sulphoxide	0.1 M N,N-dimethyl formamide
Mg^{2+}	230	155	300	224	197
Ca^{2+}	212	200	270	209	209
Sr^{2+}	193	125	285	184	132
Ba^{2+}	608	220	245	267	288
Pb^{2+}	**1880**	**1800**	**2550**	**1675**	**1221**
Hg^{2+}	**2520**	**1400**	**1480**	**2550**	**1757**
Zn^{2+}	194	70	486	135	89
Cd^{2+}	296	122	334	200	114
Cu^{2+}	230	110	220	210	92
Al^{3+}	106	260	550	93	142
Ni^{2+}	243	250	525	230	116
Fe^{3+}	990	541	920	850	218
Bi^{3+}	196	223	264	360	245
Th^{4+}	860	285	400	728	625

Table 6
Quantitative separations of metal ions in binary mixtures on poly-o-toluidine stannic molybdate columns.

Separation achieved	Amount of meal ion loaded (mg)	Amount of metal ion found (mg)	Recovery (%)	Standard deviation[a]	Volume of eluent (mL)	Eluent used
Al^{3+}	1.35	1.20	88.9	1.83	60	0.1 M DMSO
Hg^{2+}	10.02	9.99	99.7	1.65	90	0.1 M HNO_3
Cu^{2+}	3.18	3.16	99.3	1.45	70	0.1 M N,NDMF
Th^{4+}	11.60	11.00	94.82	1.64	100	0.1 M HNO_3
Cu^{2+}	3.18	3.16	99.3	1.56	70	0.1 M N,NDMF
Hg^{2+}	10.02	10.00	99.8	1.66	100	0.1 M HNO_3
Cd^{2+}	5.62	5.59	99.4	1.74	90	0.1 M N,NDMF
Pb^{2+}	10.36	10.34	99.8	1.68	100	0.1 M N,NDMF

[a] Average of three replicate determinations.

Table 7
Selective separations of Pb^{2+} ion from synthetic mixtures containing Pb^{2+}, Zn^{2+}(2.15 mg), Cd^{2+}(3.70 mg), Cu^{2+} (2.97 mg), Al^{3+} (0.89 mg) and Ni^{2+} (1.93 mg) on columns of poly-o-toluidine stannic molybdate.

Sample no.	Amount of Pb^{2+} loaded (mg)	Amount of Pb^{2+} found (mg)	Recovery (%)	Standard deviation[a]	Eluent used	Volume of eluent (mL)
1	6.83	6.70	99.6	1.62	(0.1 M) N,N-dimethyl formamide	70
2	13.66	13.56	99.5	1.64		90
3	20.49	19.49	98.9	1.64		110

[a] Average of three replicate determinations.

Table 8
Selective separation of Hg^{2+} ions from synthetic mixture containing Hg^{2+}, Zn^{2+} (2.09 mg), Cd^{2+} (3.70 mg), Cu^{2+} (2.97 mg), Al^{3+} (0.89 mg) and Ni^{2+}(1.93 mg) ions on poly-o-toluidine stannic molybdate columns.

Amount of Hg^{2+} loaded (mg)	Amount of Hg^{2+} found (mg)	Recovery (%)	Standard deviation[a]	Eluent used	Volume of eluent (mL)
6.61	6.51	98.5	1.63	0.1 M HNO_3	80
13.22	12.99	98.0	1.66	0.1 M HNO_3	100
19.83	19.69	99.0	1.66	0.1 M HNO_3	110

[a] Average of three replicate determinations.

Cu^{2+}–Th^{4+} and Cd^{2+}–Pb^{2+} of metal ions on the columns of this material. The sequential elution of ions through column depends upon the metal–ligand stability. The weakly retained metal ions eluted first and strongly retained at last. The separations are quite sharp and recovery was quantitative and reproducible. Pb^{2+} and Hg^{2+} ions were also selectively separated from synthetic mixtures of metal ions respectively (Tables 7 and 8). In order to demonstrate the practical utility of the material, quantitative separations of Hg^{2+} from thermal power plant effluents and of Pb^{2+} from lead storage battery industry wastes have been achieved respectively (Tables 9 and 10). The specificity of the material towards lead and mercury is the promising feature of the material, as mercury and lead are the most potent pollutants in the environment that leads to many disorders in the body. A striking feature of these separations was that the

Table 9
Quantitative removal of Hg^{2+} ions from thermal power plant effluent using columns of poly-o-toluidine stannic molybdate.

Metal ion	Volume of sample (mL)	Amount of Hg^{2+} loaded (μg)	Amount of Hg^{2+} found (μg)	Recovery (%)	Standard deviation[a]	Eluent used
Hg^{2+}	1.0	9.60	9.10	94.7	1.82	0.1 M HNO_3
Hg^{2+}	2.0	19.20	19.00	98.9	1.82	
Hg^{2+}	3.0	28.80	28.50	98.9	1.76	
Hg^{2+}	4.0	38.40	38.20	99.4	1.72	
Hg^{2+}	5.0	48.00	47.80	99.5	1.88	

[a] Average of three replicate determinations.

Table 10
Quantitative removal of Pb^{2+} ions from effluents discharged from battery manufacturing unit using poly-o-toluidine stannic molybdate columns.

Metal ion	Volume of sample (mL)	Amount of Pb^{2+} loaded (μg)	Amount of Pb^{2+} found (μg)	Standard deviation[a]	Eluent used
Pb^{2+}	0.5	7.85	7.65	1.54	(0.1 M) N,N-dimethyl formamide
Pb^{2+}	1.0	15.70	15.40	1.64	
Pb^{2+}	1.5	23.55	23.45	1.52	
Pb^{2+}	2.0	31.40	31.40	1.58	
Pb^{2+}	2.5	39.25	38.95	1.52	

[a] Average of three replicate determinations.

metal ions could be recovered at more than 88% (with less than 1.83% SD) as evident from Tables 6 to 10.

4. Conclusion

Poly-o-toluidine stannic molybdate was prepared as a new and novel semicrystalline polymeric–inorganic composite cation exchanger. The material possesses high ion exchange capacity, improved thermal stability and selectivity for mercury and lead ions. It is a promising and useful material where an effective method is needed for the removal and isolation of toxic metal ions from industrial effluents and other water bodies. Removal of Hg^{2+} and Pb^{2+} ions in effluents from thermal power plants and battery manufacturing unit have been practically demonstrated using this material.

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