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Synthesis and characterization of a new organic–inorganic Pb^{2+} selective composite cation exchanger acrylonitrile stannic(IV) tungstate and its analytical applications

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ABSTRACT

A new polymeric–inorganic cation exchanger acrylonitrile stannic(IV) tungstate composite was synthesized by sol–gel technique by incorporating stannic(IV) tungstate precipitate with acrylonitrile. Composite materials formed by the combination of inorganic ion exchangers of multivalent metal acid salts and organic polymers (acrylonitrile, cellulose acetate, polyaniline, polypyrrole, polythiophene, etc.), providing a new class of 'organic–inorganic' composite exchangers with better mechanical and granulometric properties, good ion exchange capacity, higher stability, reproducibility and selectivity for heavy metals. The physico-chemical characterization was carried out by elemental analysis, TGA, SEM, XRD, FTIR and TEM studies. Ion exchange capacity, pH titrations, elution and distribution behavior were also carried out to understand the ion exchange behavior of the material. The adsorption behavior of heavy metal ions has been reported in nitric acid and two surfactants media by batch processes. The analytical applications of the material have been explored by achieving some analytically important binary separations from aqueous solution on its columns. The practical applicability of acrylonitrile stannic(IV) tungstate was demonstrated in the quantitative separation of $Fe^{3+}$and Zn^{2+} contents of a commercially available pharmaceutical sample namely Fefol-Z.

1. Introduction

The organic–inorganic composite materials have a wide variety of applications [1–8]. Composite materials can be used to modify inorganic materials or to modify organic polymeric materials that display very different properties from their original component [9,10]. These materials formed by mixing of organic polymers and inorganic particles and possess all the good properties of both the constituents. Organic and inorganic ion exchangers have some limitations individually. The main limitation of the organic resin is its poor thermal stability. The mechanical strength and removal capacity of ordinary organic ion exchange resins be likely to decrease under high temperature conditions which are commonly encountered in processing liquid radioactive waste stream [11,12]. Inorganic ion exchangers are not very much reproducible in behavior and fabrication of the inorganic adsorbents into rigid beads type media suitable for column operation is quite difficult [13]. In order to prevail over the above limitations of organic resins and inorganic adsorbents, organic–inorganic composite ion exchangers have been introduced [14–22]. So, efforts have been made to synthesize such composite ion exchangers which have a good ion exchange capacity, high stability, reproducibility and selectivity for heavy toxic metal ions. In the present study, a new organic–inorganic composite ion exchangers polyacylonitrile Sn(IV) tungstate has been prepared that possessed such characteristics and high selectivity for lead, a very toxic element in the environment. The exposure of lead can bring adverse health effects and cause severe poisoning in children. It is one of the most common contaminants comes from the following main industries such as storage batteries, printing, painting, pigments, dying, and leaded glass. Lead will not degrade into non-toxic end-products and will accumulate in living organisms. It is therefore essential to reduce lead to an acceptable low concentration limit from the wastewater. One of the most used methods of lead removal is ion exchange method. So, The utility of polyacrylonitrile Sn(IV) tungstate has been explored for the quantitative and selective separations of Pb^{2+} from the mixtures of metal ions and the separation of Fe^{3+} and Zn^{2+} from commercially available multivitamin formulations namely Fefol-Z by using the packed column of the material.

2. Experimental

2.1. Reagents and instrumentation

The main reagents used for the synthesis of the material were stannic chloride penta-hydrate (BDH, India), sodium tungstate and

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Table 1
Condition of synthesis of different samples of acrylonitrile stannic(IV) tungstate cation exchange material.

Sample no.	Condition of synthesis						Ion-exchange capacity (meq g^{-1}) for Na^+ ions
	Acrylonitrile (%)	Stannic chloride (M)	Tungstate (M)	Mixing ratio (v/v/v)	pH	Temperature (°C)	
S-1	5	0.1	0.1	1:1:1	1.0	25 ± 2	1.20
S-2	5	0.2	0.2	1:1:1	1.0	25 ± 2	1.25
S-3	5	0.2	0.2	1:1:1	0.76	25 ± 2	No ppt
S-4	5	0.2	0.2	1:1:1	1.5	25 ± 2	1.33
S-5	5	0.2	0.2	1:1:2	1.0	25 ± 2	1.65

acrylonitrile (CDH, India) and all other chemicals and reagents used were of analytical reagent grade.

A single electrode pH meter (Toshniwal, India), FTIR spectrophotometer (Perkin-Elmer Spectrum-BX, U.S.A.), 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*

Solutions of stannic chloride and sodium tungstate were prepared in demineralized water (DMW) and acrylonitrile solution was prepared in ethanol.

2.3. *Synthesis of acrylonitrile stannic(IV) tungstate*

In order to get a stable product with good ion exchange properties, a number of samples of acrylonitrile stannic(IV) tungstate were synthesized by mixing an aqueous solution of 0.1 M sodium tungstate into 0.1 M Sn(IV) chloride penta-hydrate solution gradually with continuous shaking of the mixture in varying mixing ratios. The pH variation was adjusted by adding 1 M nitric acid or 1 M ammonia solutions to maintain the desired pH. Acrylonitrile (5%) was added drop wise into the inorganic precipitate of stannic(IV) tungstate and mixed thoroughly with constant stirring for 1 h. The gelatinous precipitate so formed, was allowed to stand for 24 h in the mother liquor for digestion. The supernatant liquid was removed and the precipitates were washed with demineralized water several times to remove excess reagents. The products were dried at 40 ± 2 °C in an oven. The dried products were then kept in demineralized water for cracking and to obtain the particle of the size range ~125 μm. These were converted to H^+ form by placing them in 1 M HNO_3 solution and washed with demineralized water to remove excess acid and finally dried at 40 ± 2 °C. Hence, a number of samples were prepared, and on the basis of ion exchange capacity and percentage yield, sample S-5 was selected for detailed studies (Table 1).

2.4. *Ion exchange capacity*

The ion exchange capacity, which is generally taken as a measure of the hydrogen ion liberated by neutral salt to flow through the composite cation exchanger was determined by standard column process. 1.0 g (dry mass) of the composite ion exchange material in H^+ form was placed in a glass column with a glass wool support at the bottom. It was washed with demineralized water to remove any excess of acid remained sticking on the particles. The hydrogen ions eluted with 0.1 M solution of different alkali and alkaline earth salts. The flow rate was kept 0.5 mL min^{-1}. The collected effluent was titrated against a standard solution of sodium hydroxide using phenolphthalein as an indicator. The hydrogen ions released were then calculated.

2.5. *Thermal effect on ion exchange capacity*

To determine the effect of heating temperature on ion exchange capacity of the material, 1.0 g sample of the acrylonitrile stannic(IV) tungstate (S-5) 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 at room temperature by standard column process as described above.

2.6. *Effect of eluent concentration*

To find out the optimum concentration of the eluent for complete elution of H^+ ions, a fixed volume (250 mL) of $NaNO_3$ solution of different concentrations was passed through the columns, containing 1.0 g of the exchanger in H^+ form with a flow rate of 0.5 mL min^{-1}. The effluents were titrated against a standard solution of 0.1 M NaOH to find the H^+ ions eluted out.

2.7. *Elution behavior*

For this study, $NaNO_3$ solution of optimum concentration was passed for complete elution of H^+ ions through a column containing 1.0 g of the composite cation exchanger (H^+ form) with a flow rate of 0.5 mL min^{-1}. The effluent was collected in 10 mL fractions and each fraction was titrated against a standard alkali solution.

2.8. *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 [23]. 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.

2.9. *Chemical dissolution*

Two hundred milligrams portions of the composite cation exchanger in H^+ form were treated with 25 mL each of different acids such as HCl, HNO_3, H_2SO_4, and different bases such as NaOH, KOH, organic solvents such as dimethyl sulphoxide (DMSO), acetone, *n*-butyl alcohol, and also with double distilled water (DMW) for 24 h with occasional shaking. The supernatant liquid was analyzed for stannic and tungsten by UV–Vis spectrophotometer using suitable reagents [24,25].

2.10. *Characterization*

To determine the chemical composition of acrylonitrile stannic(IV) tungstate, 0.25 g of the sample (S-5) was dissolved in hot concentrated HCl. Carbon, hydrogen and nitrogen contents were analyzed using elemental analyzer and stannic and tungsten by UV–vis spectrophotometer using suitable reagents [24,25].

Table 2
Ion-exchange capacity of various exchanging ions on acrylonitrile stannic(IV) tungstate cation exchange material.

Exchanging ions	Ionic radii (Å)	Hydrated ionic radii (Å)	IEC (meq g^{-1})
Li^+	0.68	10.0	1.32
Na^+	0.97	7.90	1.65
K^+	1.33	5.30	1.73
Mg^{2+}	0.78	10.80	1.66
Ca^{2+}	1.06	9.60	1.72
Sr^{2+}	1.27	9.40	1.80
Ba^{2+}	1.43	8.80	1.92

Thermogravimetric analysis (TGA) study of the sample was carried out at a heating rate of 10 °C min^{-1} up to 1200 °C in the air atmosphere. TGA is a simple analytical technique that measures the weight loss of a material as a function of temperature. As materials are heated, they can loose weight from a simple process such as drying, or from chemical reactions that liberate gasses. Thermogravimetric curves (thermograms) provide information regarding polymerization reactions, the thermal stability of final materials, and direct analysis.

10 mg of the material (H^+ form) was mixed with 100 mg (dry mass) of KBr and ground to a very fine powder. A transparent disc was formed by applying a pressure of 80,000 p.s.i. (1 p.s.i. = 56894.76 Pa). The IR absorption pattern was recorded between 400 and 4000 cm^{-1} using Nicolet Fourier transform spectrometer.

For X-ray diffraction analysis, manganese filtered CuKα radiation wavelength (150.1542 nm) at 298 K was used. The instrument was equipped with graphite monochromator and operating at 40 kV and 30 mA.

Scanning electron micrograph (SEM) was performed on ground materials (as prepared) by an electron microscope at different magnifications. SEM is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography and composition.

TEM studies were carried out to know the particle size of the acrylonitrile stannic(IV) tungstate composite cation exchange material.

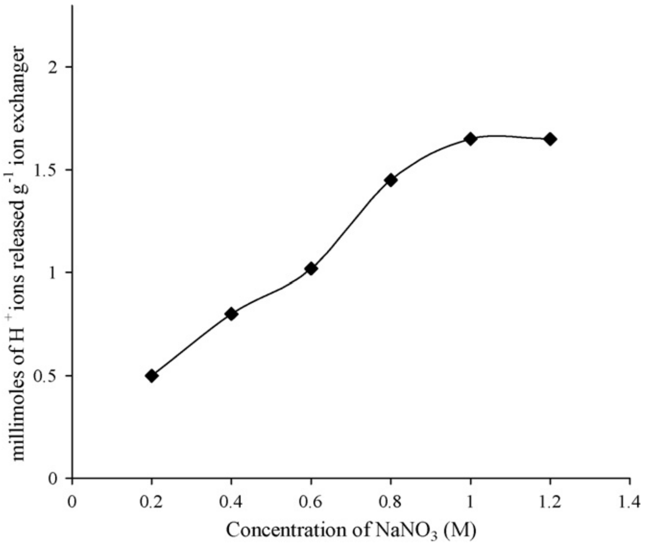

Fig. 1. Effect of eluent concentration on ion exchange capacity of acrylonitrile stannic(IV) tungstate composite cation exchanger.

2.11. Distribution studies

In order to get an idea of partition behavior of the exchanger towards the separation of metal ions of analytical interest, distribution coefficients (K_d) were determined in several solvent systems. A, 0.5 g exchanger in H^+ form was treated with 40 mL solution of metal ions in required solvent medium in a 100 mL Erlenmeyer flask. The mixture was shaken for 6 h at 25 ± 2 °C in a temperature controlled incubator shaker. The amount of metal ions before and after adsorption was determined by titration against a standard solution of 0.01 M di-sodium salt of EDTA. The K_d values may be expressed as follows.

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

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

where I is the initial amount of the metal ion in the solution phase, F the final amount of metal ion in the solution phase after treatment with the exchanger, V the volume of the solution (mL) and M is the amount of ion exchanger taken (g).

Table 3
Effect of temperature on the ion-exchange capacity of acrylonitrile stannic(IV) tungstate cation exchange material on heating time for 1 h.

Temperature °C	Color	IEC	% Retention of IEC
50	White	1.65	100
100	White	1.65	100
200	Slight brown	1.33	80.6
300	Light brown	1.10	66.7
400	Light brown	1.00	60.6
500	Dull white	0.90	54.5
600	Dull white	0.65	39.4
700	Grey color	0.45	27.3

IEC – ion exchange capacity

2.12. Separations

2.12.1. Quantitative separation of metal ions in binary synthetic mixtures

Quantitative separations of some important metal ions of analytical utility were achieved on acrylonitrile stannic(IV) tungstate columns. 1.5 g of exchanger in H^+ form was packed in a glass col-

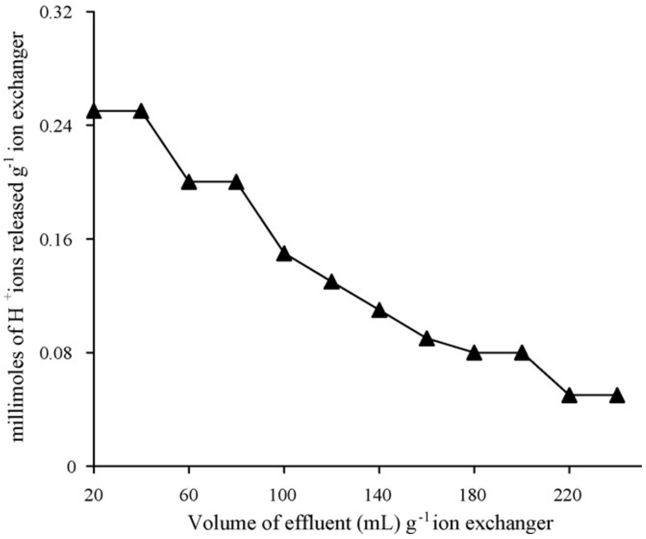

Fig. 2. Elution behavior of acrylonitrile stannic(IV) tungstate composite cation exchanger.

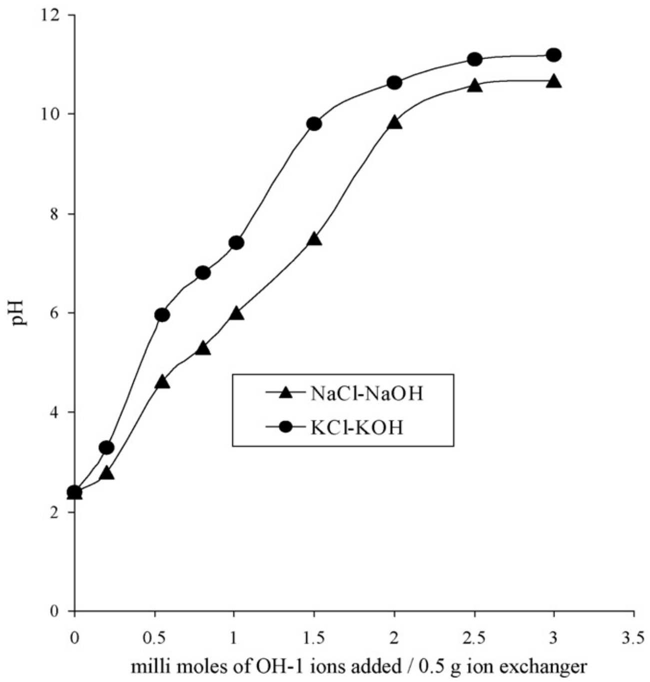

Fig. 3. pH titration curves for acrylonitrile stannic(IV) tungstate composite cation exchanger with alkali and alkaline earth metal hydroxides.

Table 4
The solubility of acrylonitrile stannic(IV) tungstate in various solvent systems.

Solvent (25 mL)	Sn (mg/25 mL)	W (mg/25 mL)
1 M HCl	3.2	1.1
1 M HNO_3	1.4	0.20
1 M H_2SO_4	1.5	0.24
0.1 M NaOH	15.28	12.54
0.1 M KOH	17.40	16.50
DMSO	0.80	0.23
Acetone	0.14	0.50
n-Butanol	0.32	0.19
DMW	0.0	0.0

Table 5
Composition of acrylonitrile stannic(IV) tungstate.

Weight of the exchanger (mg)	Millimoles of the components					Mole ratio
	Sn	W	C	H	N	
250	0.806	3.22	0.697	1.457	0.266	1:4:3

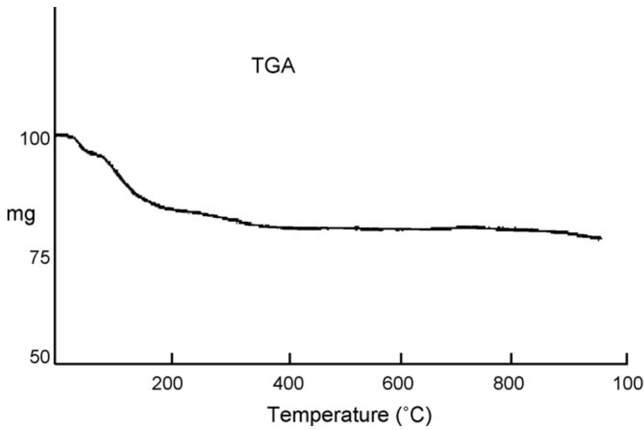

Fig. 4. TGA curve of acrylonitrile stannic(IV) tungstate.

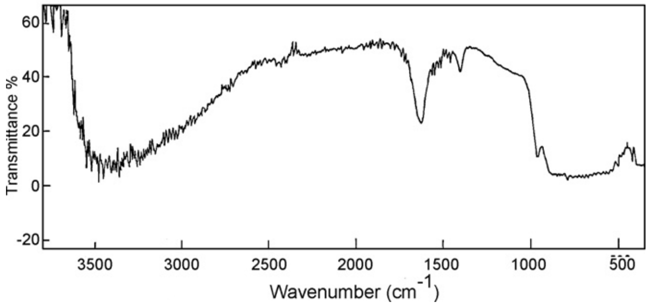

Fig. 5. FTIR spectra of acrylonitrile stannic(IV) tungstate.

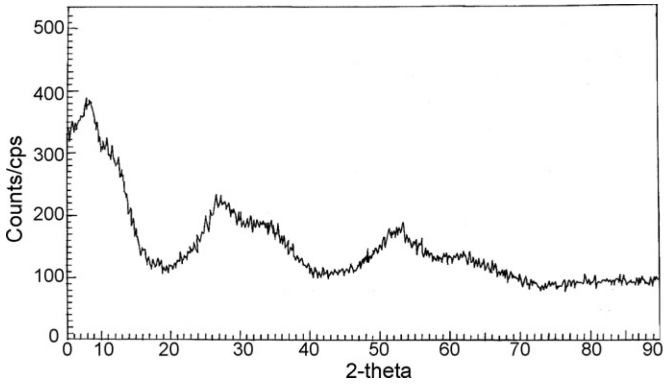

Fig. 6. Powder X-ray diffraction pattern of acrylonitrile stannic(IV) tungstate.

Table 6
Distribution coefficients (K_d) of metal ions on acrylonitrile stannic(IV) tungstate in different solvent systems.

Metal ions	Triton X-100 0.2%	Triton X-100 0.5%	Triton X-100 1.0%	SDS 0.2%	SDS 0.5%	SDS 1%	0.1 M nitric acid	0.001 M nitric acid
Mg^{2+}	330	326	308	233	223	213	280	304
Ca^{2+}	425	336	258	547	500	223	285	308
Sr^{2+}	343	338	272	412	335	312	219	338
Ba^{2+}	592	374	330	1215	1043	220	214	304
Hg^{2+}	1000	838	713	515	433	250	316	1340
Cd^{2+}	800	572	220	345	226	221	316	459
Cu^{2+}	813	650	229	300	326	362	185	556
Ni^{2+}	310	300	283	227	209	174	290	335
Zn^{2+}	335	422	475	296	230	150	220	275
Pb^{2+}	2800	1900	1750	1304	1207	1191	5150	5300
Fe^{3+}	633	340	254	2567	275	248	267	400
Al^{3+}	232	189	186	492	367	103	280	296
Ce^{3+}	278	233	188	513	457	215	223	246
Bi^{3+}	311	191	163	227	234	380	257	360
Th^{4+}	234	232	221	860	167	150	212	433

SDS – sodium lauryl sulphate

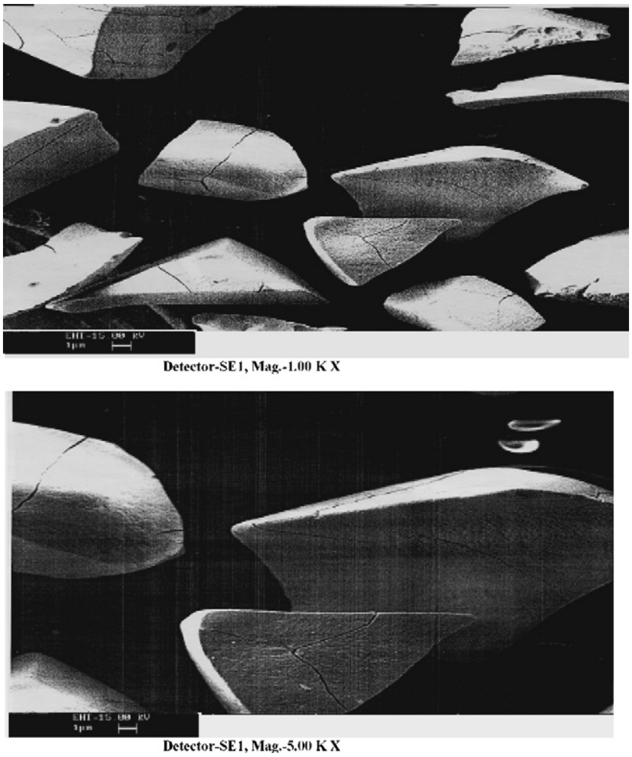

Fig. 7. Scanning electron microphotographs of chemically prepared acrylonitrile stannic(IV) tungstate at different magnifications.

umn of 0.9 cm internal diameter with a glass wool support at the end. The column was washed thoroughly with deminralized water and the mixture of two metal ions having initial concentration 0.1 M of each with different volume ratios, was loaded on it and allowed to pass through the column at a flow rate of 0.20 mL min^{-1} till the solution level was just above the surface of the material. The column was then rinsed with deminralized water so that the metal ions, which were not exchanged, could be removed. Individual metal ions adsorbed on the exchanger, were then eluted using the appropriate eluting reagents. The flow rate of the eluent was maintained 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.

2.12.2. Quantitative separation of Fe^{3+} and Zn^{2+} in commercially available pharmaceutical formulation Fefol-Z

2.12.2.1. Preparation of sample. One tablet of Fefol-Z was treated with 10 mL concentrated HCl and evaporated to remove excess acid. The aliquots were filtered by using whattman filter paper number 1, and the clear filtrates obtained, were diluted to 25 mL with demineralized water.

2.12.2.2. Procedure. Different amounts of stock solution were applied into a glass column containing 1.0 g acrylonitrile stannic(IV) tungstate with a glass wool support at the base. The solution was left to flow down the column with a flow rate of 0.50 mL min^{-1}. The effluent was recycled through the column to ensure the complete adsorption of metal contents. Zn^{2+} and Fe^{3+} were then eluted with 1% SDS. The weakly retained metal ion (Zn^{2+}) eluted first and strongly retained metal ion (Fe^{3+}) at last.

2.12.3. Selective separation of Pb^{2+} from a synthetic mixture of metal ions

For selective separations, mixture of metal ions Pb^{2+}, Zn^{2+}, Fe^{3+}, Cu^{2+}, Cd^{2+}, Ni^{2+} and Al^{3+} was poured onto the top of two columns and was allowed to flow down at a rate of 0.5 mL min^{-1} until the level of the sample solutions was just above the resin surface. It was recycled through the columns to ensure complete adsorption of the metal ions. The mixture of metal ions namely Zn^{2+}, Fe^{3+}, Cu^{2+}, Cd^{2+}, Ni^{2+} and Al^{3+} eluted together first and Pb^{2+} which retained by the exchange material strongly was eluted at last.

3. Results and discussions

In this study, various samples of new composite cation exchanger acrylonitrile stannic(IV) tungstate were prepared by incorporating acrylonitrile into inorganic matrices of stannic(IV) tungstate in different mixing ratios as given in Table 1. This cation exchanger appears to be a promising material with good ion exchange capacity, thermal, mechanical, and chemical stability. The improvement in these characteristics of organic–inorganic composite cation exchanger may be due to the binding of acrylonitrile with inorganic moiety (stannic(IV) tungstate). The material has granulometric property, good reproducible behavior as is evident from the fact that these materials obtained from various batches did not show any considerable deviation in their percentage of yield and ion exchange capacities. Ion exchange capacities for mono and bivalent metal ions have been studied (Table 2). The affinity sequence for alkali metal ions are $K^+ > Na^+ > Li^+$ and for alkaline earth metal ions are $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$. The size and charge of the exchanging ion affects the ion-exchange capacity of acrylonitrile stannic(IV) tungstate. This sequence is in accordance with the size of the hydrated radii of the exchanging ions. Ions with the smaller radii easily enter the pore of the exchanger, resulting in greater absorption [23]. Ion exchange capacity of the material was also affected by heating. On heating at different temperatures for

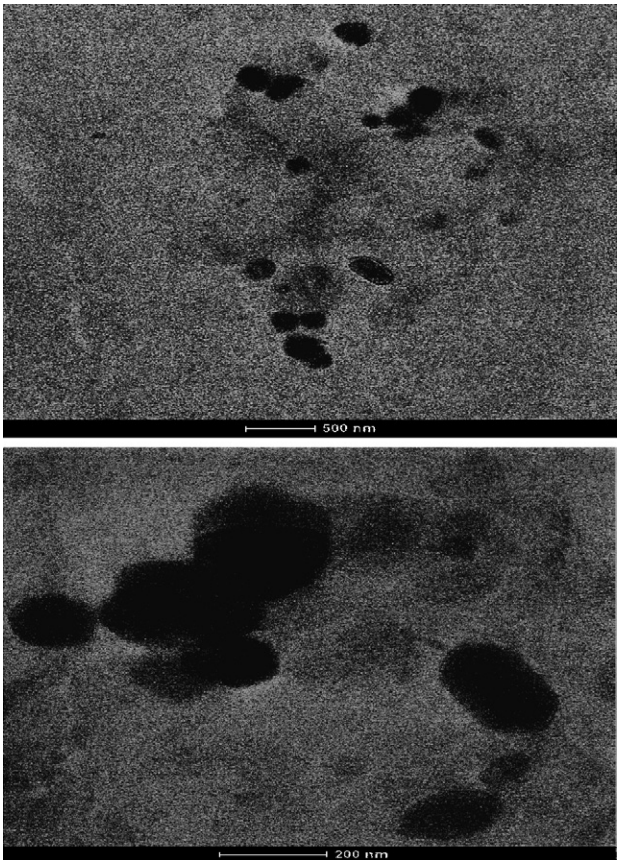

Fig. 8. Transmission electron microphotographs (TEM) of acrylonitrile stannic(IV) tungstate.

Table 7
Quantitative separations of metal ions of a binary mixture using acrylonitrile stannic(IV) tungstate cation exchange material column.

Separation achieved	Amount loaded[a] (mg)	Amount found[a] (mg)	% Recovery	% Error	Eluent used 1% SDS (mL)
Hg^{2+}	4.01	3.91	97.54	−2.46	80
Pb^{2+}	4.14	4.04	97.58	−2.41	90
Zn^{2+}	1.31	1.28	97.70	−2.30	65
Fe^{3+}	1.12	1.00	90.00	1–0.00	60
Cu^{2+}	1.27	1.23	96.85	−3.15	65
Pb^{2+}	4.14	4.04	97.58	−2.41	90
Cd^{2+}	2.25	2.19	97.33	−2.67	70
Pb^{2+}	4.14	4.04	97.58	−2.41	90
Th^{4+}	4.64	4.75	102.50	+2.50	85
Pb^{2+}	4.14	4.04	97.58	−2.41	90
Fe^{3+}	1.12	1.04	92.85	−7.15	60
Pb^{2+}	4.14	4.04	97.58	−2.41	90
Ni^{2+}	1.17	1.14	97.43	−2.57	60
Pb^{2+}	4.14	4.04	97.58	−2.41	90
Mg^{2+}	0.49	0.43	86.78	−13.22	55
Pb^{2+}	4.14	4.04	97.58	−2.41	90

[a] Average of three replicate determinations.

1 h, the mass, physical appearance and ion exchange capacity of acrylonitrile stannic(IV) tungstate (S-5) were changed (Table 3).

One interesting property acrylonitrile stannic(IV) tungstate (S-5) that differentiated it from other exchange materials was that it can withstand temperature as high as 500 °C with a loss of only 45.5% in ion-exchange capacity. Although acrylonitrile cerium (IV) phosphate [20] decomposed beyond 100 °C only. Stannic tungstoselenate, aluminium tungstate, stannic molybdoarsenate, and stannic silicomolybdate [26–29] also experience a drastic loss in ion-exchange capacity on heating in the temperature range of 100–700 °C. It is observed that, for complete elution of H^+ ions, the concentration of the eluent also plays an important role. The optimum concentration of $NaNO_3$ as eluent is 1.0 M for maximum release of H^+ ions from 1.0 g of this composite cation exchange material as shown in Fig. 1. The efficiency of this composite cation exchanger column was determined by the elution behavior which indicated that the exchange is quite fast at the beginning and maximum H^+ ions are eluted out in the first 150 mL by using 1.0 M $NaNO_3$ solution (Fig. 2).

The pH titration curves for acrylonitrile stannic(IV) tungstate (S-5) were obtained under equilibrium conditions with NaOH/NaCl and KOH/KCl systems indicated mono-functional behavior of the material as shown in Fig. 3. It appears to be a strong cation exchanger as indicated by a low pH (2.5) of the solution when no OH ions were added to the system. The rate of H^+–K^+ exchange was faster than those of H^+–Na^+. The theoretical ion exchange capacity for these ions was found to be 2.4 meq g^{-1}.

The solubility experiment (Table 4) showed that the material was quite stable in common mineral acids, organic acids and alkalies. On the basis of chemical composition studies and instrumental analyses, the molar ratio of the elements in the proposed composite cation exchange material was estimated to be Sn:W:CH_2CHCN::1:4:3 (Table 5) which tentatively suggests the following formula of the material: $[(SnO_2)(H_2WO_4)_4(CH_2CHCN)_3]{\cdot}nH_2O$.

Thermogravimetric analysis (TGA) curve (Fig. 4) of the acrylonitrile stannic(IV) tungstate shows 5% weight loss up to 100 °C which may be due to loss of external water molecules (n) from the exchanger [30]. The number of external water molecules (n) per mole of the material as calculated from Alberti's equation [31] is found to be 4.

$$\%\,\text{weight loss} = \frac{18n}{M + 18n} \times 100$$

where ($M + 18n$) is the molecular weight of the material, and n is the number of external water molecule per mole of the material.

Further weight loss approximately 14% between 100 and 250 °C may be due to removal of strongly coordinate water molecules from the frame work of the material. Slow weight loss of mass about 4% between 250 and 360 °C may be due to the slight decomposition of organic part of the material. The thermo-gravimetric analysis of the composite exchanger indicates that the composite cation exchanger is thermally stable because only 23% mass was lost up to 1000 °C.

The infrared spectrum of acrylonitrile stannic(IV) tungstate (Fig. 5) indicated the presence of external water molecules in addition to the metal–oxygen and metal OH stretching band. In the spectrum, a broad band at 3500 cm^{-1} is found which can be attributed to O–H stretching frequency. A sharp peak at 1670 cm^{-1} corresponds to H–O–H bending band, being also representative of the strongly bonded –OH groups in the matrix [32]. The O–H stretching bands merge together and are shifted to lower frequency in the spectrum of the exchanger. This is due to the possibility of H-bonding. A band at about 1400 cm^{-1} can be due to stretching vibration of C–N [33]. A weak absorption band at 2400 cm^{-1} is due to the presence of $R{-}C{\equiv}N$ group [34]. A broad peak in the region between 500 and 800 cm^{-1} was due to metal–oxygen bond [35].

The X-ray diffraction pattern of this material was recorded in powdered sample exhibited (Fig. 6) weak intensities thereby suggested that acrylonitrile stannic(IV) tungstate is amorphous in nature.

The scanning electron micrographs of acrylonitrile stannic(IV) tungstate (Fig. 7) at different magnifications shows a regular uniform diamond morphology. The presence of uniform morphology also indicates the absence of impure phases [36].

The TEM studies of acrylonitrile stannic(IV) tungstate (Fig. 8) shows particles size in the nano-range.

Table 8
Selective separation of Pb^{2+} ion from the synthetic mixture of Pb^{2+}, Zn^{2+}, Fe^{3+}, Cu^{2+}, Cd^{2+}, Ni^{2+} and Al^{3+} on acrylonitrile stannic(IV) tungstate cation exchange material columns.

S. no.	Amount of Pb^{2+} loaded[a] (mg)	Amount of Pb^{2+} recovered[a] (mg)	% Recovery	% Error	Eluent used 1% SDS (mL)
1	2.07	2.00	96.62	3.38	75
2	3.10	3.08	99.35	0.65	80
3	6.20	6.12	98.70	1.30	85

[a] Average of three replicate determinations.

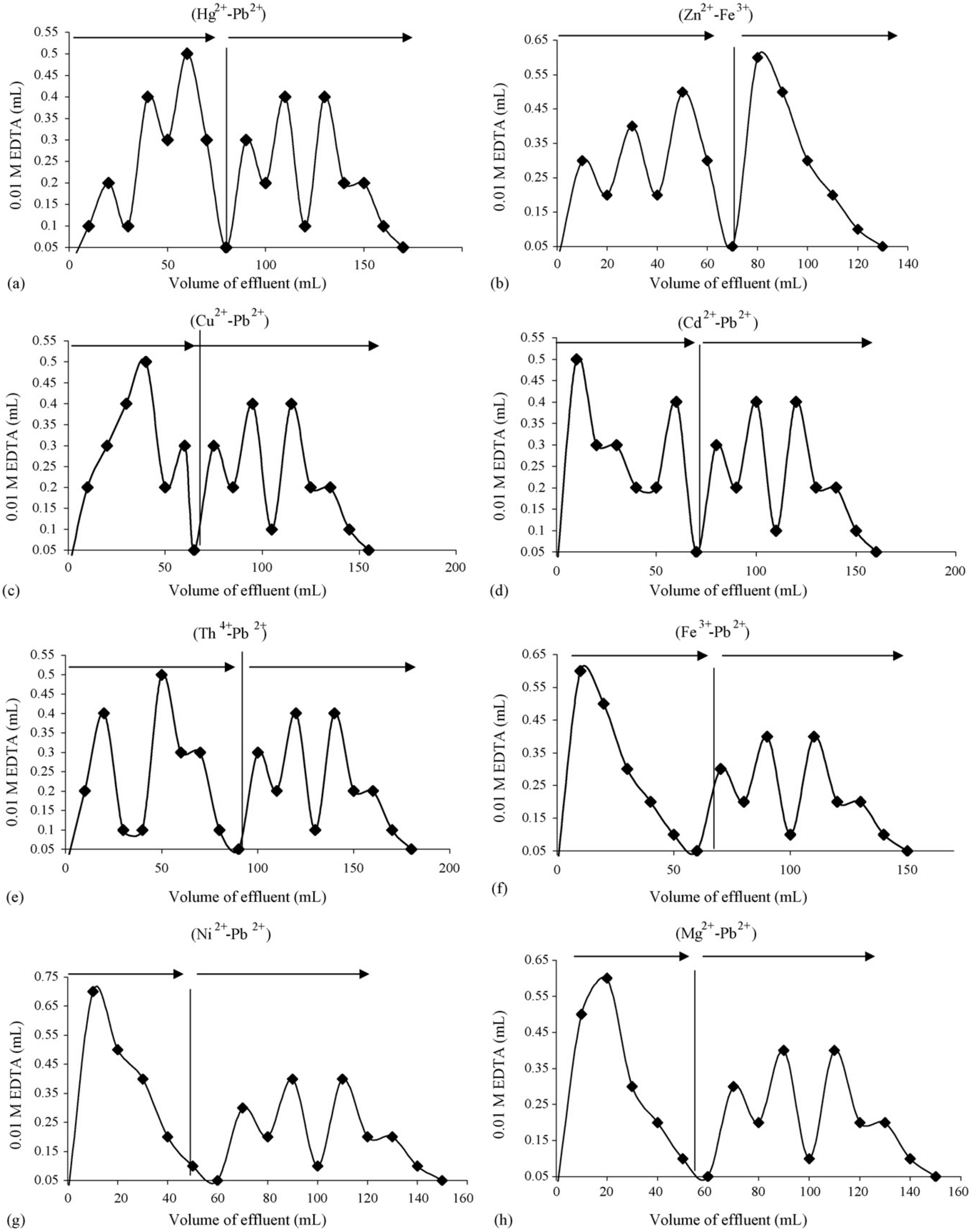

Fig. 9. (a–h) Chromatograms of binary separations of metal ions on aluminium tungstate column eluent used – 1% SDS (for each case).

In order to explore the potentiality of this composite cation exchange material in the separation of metal ions, distribution studies for 15 metal ions were performed in nitric acid and two surfactants namely Triton X-100 and sodium lauryl sulphate (SDS) (Table 6). It was also observed from the distribution studies (K_d values) that Pb^{2+} was highly adsorbed in all solvents which is a major polluting metal in the environment, while remaining metals are poorly adsorbed. The effect of concentration of nitric acid and

Table 9
Quantitative separation of Zn^{2+}, and Fe^{3+} present in multivitamin samples Fefol-Z and Hampher on a column acrylonitrile stannic(IV) tungstate.

Sample	Metal ions	Amount loaded[a] (mg)	Amount found[a] (mg)	% Recovery	% Error	Eluent used 1% SDS (mL)
Fefol-Z	Zn^{2+}	2.19	2.12	96.80	−3.20	60
	Fe^{3+}	2.40	2.30	95.83	−4.17	70
	Zn^{2+}	2.56	2.53	98.83	−1.17	70
	Fe^{3+}	2.80	2.70	96.43	−3.57	80

[a] Average of three replicate determinations.

surfactants (Triton X-100 and SDS) on K_d values of metal ions was also studied. The K_d values decrease in general with an increase in concentration of nitric acid and both ionic (Triton X-100) and neutral (SDS) surfactants. The same order was observed by Siddiqi and Pathania [37]. The reversed order is observed with Zn^{2+} in Triton X-100 and Cu^{2+} and Bi^{3+} in SDS solvent systems. The differential behavior on the uptake of metal ions by the material in these solvents systems indicates the separation possibilities of certain metal ions of analytical interests from a given mixture. The separation capability of the material has been demonstrated by achieving some important binary separations such as Hg^{2+}–Pb^{2+}, Zn^{2+}–Fe^{3+}, Cu^{2+}–Pb^{2+}, Cd^{2+}–Pb^{2+}, Th^{4+}–Pb^{2+}, Fe^{3+}–Pb^{2+}, Ni^{2+}–Pb^{2+} and Mg^{2+}–Pb^{2+}. Table 7 is summarizing the salient features of these separations. 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 order of elution and eluents used for binary separations are also shown in Fig. 9(a)–(h). The separations are quite sharp and recovery was quantitative and reproducible. High K_d values of Pb^{2+} enable their selective separation from the mixture of metal ions viz. Pb^{2+}, Zn^{2+}, Fe^{3+}, Cu^{2+}, Cd^{2+}, Ni^{2+} and Al^{3+} (Table 8). The practical use of acrylonitrile stannic(IV) tungstate is demonstrated further in the analysis of Zn^{2+} and Fe^{3+} in a commercially available pharmaceutical formulation namely Fefol-Z (Table 9). The results of the analysis were found to be satisfactory.

4. Conclusion

In the present study, a new composite cation exchanger acrylonitrile stannic(IV) tungstate has been prepared which have good ion exchange capacity (1.65), chemical and thermal stabilities. TEM photographs show that the particle size in nano range. The differential behavior of the exchanger towards metal ions in different solvent systems showed the separation possibilities of metal ions of analytical interest from a given mixture. It is clear from the results that the quantitative and efficient separations of various metal ions are feasible on acrylonitrile stannic(IV) tungstate column. So this cation exchange material can be conveniently utilized for the removal and isolation of heavy toxic metal ions, released from wastewater stream.

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