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Synthesis and physicochemical characterization of excellent thermally stable and mercury selective organic–inorganic composite cation exchanger polyvinyl alcohol thorium(IV) phosphate

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ABSTRACT

A Hg(II) ions selective composite cation exchanger polyvinyl alcohol Th(IV) phosphate was synthesized by sol–gel method and characterized by various techniques such as FTIR, X-ray diffraction, thermogravimetric analysis/differential thermal analysis/differential thermogravimetry, SEM and TEM to confirm its nature, thermal stability, surface morphology, and particle size. The enhanced ion-exchange capacity of hybrid exchanger than that of the inorganic exchanger was due to assimilation of organic polymer polyvinyl alcohol by Th(IV) phosphate gel. Elution behavior was estimated to ascertain the viability of this cation exchanger for column operation. The distribution studies revealed that composite cation exchanger is selectivity for Hg(II) ions. These properties of composite cation exchanger make it useful for future applications toward removal of mercury from variety of polluted water bodies as well as industrial effluent treatment plants.

Keywords: Sol–gel synthesis; Physicochemical characterization; Thermal stability; Ion-exchange behavior; Polyvinyl alcohol Th(IV) phosphate

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1. Introduction

Removal of mercury is of particular interest because it has been found as one of the most toxic heavy metal and widely spread in air, water, and land through natural and anthropogenic sources and has harmful effects on human as well as aquatic creatures [1]. The increasing concentration of mercury in the human body badly affecting the activity of antioxidant enzymes, such as glutathione peroxidase and glutathione reductase as well as the enzymes of the thioredoxin system, thioredoxin, and thioredoxin reductase [2]. Excessive dose can lead to permanent damage to the brain as well as kidneys. An inorganic mercuric compound precipitates proteins of the mucous membrane causing abdominal cramps, cognitive disorders, gastric mucus, heart diseases, and neurological problems [3,4]. Organic mercurials are highly toxic in nature and Hg(II) ions have high affinity towardlipidic substances and can also affect the fetal tissues. Methyl mercury is a lethal neurotoxin accumulates in human body by food chain [5]. Due to the health and environmental hazards associated with mercury compounds, various guidelines and protocols were practiced by environmental

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protection agencies (EPAs) in many countries [6] as well as World Health Organization (WHO) has set various protocols and permissible value for inorganic mercury in drinking water as 6 μg l^{-1} [7].

Therefore, development of a simple, economical, and practical method is highly demanded for environmental protection, food and beverage industries, and clinical diagnostics. Precipitation, adsorption, filtration, coagulation, extraction, ion exchange, flotation, and membrane separation are the techniques available for heavy metal removal [8–17]. Among different methods for Hg(II) ions removal, ion exchange was found as one of the most versatile and effective treatment methods. Inamuddin et al. prepared mercury selective composite cation exchanger Nylon-6,6 Zr(IV) phosphate by sol gel approach and separation of some heavy metals ions was achieved on composite cation exchanger column [18]. Khan and Inamuddin synthesized polyaniline Sn (IV) phosphate composite cation exchanger using sol–gel method and utilized for preparation of Hg(II) ions selective membrane electrode [19].

The inorganic ion exchangers and organic resins previously employed have now been replaced by organic–inorganic composite ion exchangers as new class of ion exchangers which not only revolutionized heavy metal removal process but also established itself as a major tool in sustainable development technology for environment protection [20,21]. In this study, an "organic-inorganic" composite cation-exchange material, polyvinyl alcohol Th(IV) phosphate was prepared under varying conditions and characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), thermogravimetric analysis/differential thermal analysis/differential thermogravimetry (TGA/DTA/DTG), scanning electron microscopy (SEM), transmission electron microscopy (TEM) to validate the various physiochemical properties and structure of the material. The newly synthesized material being Hg(II) ions selective can be useful for removal of mercury from polluted water bodies.

2. Experimental

2.1. Reagents and instruments

The main reagents used for the synthesis were thorium nitrate pentahydrate, $Th(NO_3)_4{\cdot}5H_2O$, polyvinyl alcohol (PVA), (Central Drug House, India), orthophosphoric acid, H_3PO_4, (Fischer Scientific, India), and nitric acid, HNO_3, (E-Merck,India). All other reagents and chemicals used were of analytical reagent grade and used as received.

An FTIR spectrophotometer (Interspec-20, Spectro lab UK), X-ray diffractometer (Miniflex-II, Japan), scanning electron microscope (SEM) (JEOL, JSM 6510-LV, Japan), transmission electron microscope (TEM) (Philips, CM-200, UK), digital muffle furnace (Macro scientific, MSW-251, India), TGA/DTA Recorder (Exstar TG/DTA-6300), an air oven (Universal oven, Mammart type, Jindal Scientific Instrumentation, India), digital electronic balance (Wensar, MAB-220, India), magnetic stirrer (Labman LMMS-1L4P), and a water bath incubator shaker (Narang Scientific Works, NSW-133, India) for all equilibrium studies having a temperature variation of ± 0. 5˚C were used.

2.2. Preparation of organic–inorganic composite cation-exchange material

2.2.1. Preparation of reagent solutions

0.1 M thorium nitrate $Th(NO_3)_4{\cdot}5H_2O$ and 2 M orthophosphoric acid (H_3PO_4) solutions were prepared in demineralized water (DMW).

Table 1
Conditions of preparation of various samples of Th(IV) phosphate and polyvinyl alcohol Th(IV) phosphate composite cation exchange material

	Mixing volume ratios (V/V)					
Sample	0.1 M $Th(NO_3)_4{\cdot}5H_2O$	2 M H_3PO_4	PVA (g)	Digestion time (h)	Appearance of beads after drying	Na^+ ion exchange capacity (meq g^{-1} dry exchanger)
S-1	1	1	–	24	Bright white	0.76
S-2	1	2	–	24	Bright white	0.72
S-3	1	3	–	24	Bright white	0.84
S-4	1	4	–	24	Bright white	0.74
S-5	1	5	–	24	Bright white	0.70
S-6	1	3	0.5	24	Bright white	1.36
S-7	1	3	1.0	24	Bright white	0.96
S-8	1	3	1.5	24	Bright white	0.94
S-9	1	3	2.0	24	Bright white	0.90

2.2.2. Preparation of inorganic exchanger

A variety of samples of inorganic ion exchanger Th (IV) phosphate were prepared by adding aqueous solutions of 0.1 M $Th(NO_3)_4 \cdot 5H_2O$ into 2 M H_3PO_4; in different mixing volume ratios at room temperature (25 ± 2˚C). The obtained gels were digested for 24 h at room temperature. The supernatant liquid was decanted and the gels were washed with DMW till neutral pH. After washing till neutral, the gels were dried in an electric oven maintained at 45 ± 0.5˚C. The dried product was cracked into small granules (~125 μm) and ion exchanger was kept in 1 M HNO_3 for 24 h with occasional shaking intermittently replacing the supernatant liquid with fresh 1 M HNO_3. The excess acid was removed after several washings with DMW and material was dried at 45 ± 0.5˚C. For the determination of IEC, one gram of the dry cation exchanger in the H^+ form was taken into a glass column having an internal diameter (~i.d.) 1 cm and fitted with glass wool support at the bottom. 1.0 M sodium nitrate ($NaNO_3$) as eluent was used to elute the H^+ ions completely from cation exchanger column, maintaining a very slow flow rate (~0.5 ml min^{-1}). The effluent was titrated against a standard 0.1 M NaOH solution using phenolphthalein indicator. The ion exchange capacity was calculated by using the following expression:

$$\text{Ion exchange capacity} = \frac{V \times N}{W} (\text{meq g}^{-1} \text{ dry exchanger}) \tag{1}$$

where V is the volume of NaOH consumed (ml), N is the normality of NaOH, and W is the weight of the dry cation exchanger (g).

A number of samples of “Th(IV) phosphate” cation-exchanger were prepared (Table 1) and on the basis of Na^+ ion-exchange capacity sample S-3 was selected for the preparation of composite cation exchanger.

2.2.3. Preparation of polyvinyl alcohol Th(IV) phosphate hybrid cation exchanger

A variety of samples of organic–inorganic composite cation-exchange materials were prepared by mixing different masses of PVA dissolved in DMW into the inorganic precipitates of Th(IV) phosphate using magnetic stirrer having higher IEC 0.84 meq g^{-1} dry exchanger (S-3). These slurries were kept for 24 h at room temperature (25 ± 2˚C) for digestion. The supernatant liquid was replaced and the excess acid was removed by several washings with DMW and the materials were dried in an air oven over at 45˚C. The dried products were converted to H^+ form and the ion exchange capacity was determined according to the method discussed above.

2.3. X-ray diffraction (XRD) study

XRD patterns of the Th(IV) phosphate inorganic exchanger and polyvinyl alcohol Th(IV) phosphate composite cation exchange material were recorded by a X-ray diffractometer (Phillips, Holland, PW 1,148/89 with Cu Kα radiations).

2.4. Fourier transform infrared (FTIR) spectroscopic study

Fourier transform infrared (FTIR) spectroscopic spectrums of inorganic exchanger Th(IV) phosphate and polyvinyl alcohol Th(IV) phosphate composite material in the range 450–4,000 cm^{-1} were recorded on Fourier transform infrared spectrophotometer Perkin Elmer-Spectrum, BX USA.

2.5. Thermogravimetric analysis (TGA)/differential thermal analysis (DTA)/differential thermogravimetric (DTG) studies

The thermal degradation process of polyvinyl alcohol Th(IV) phosphate composite was investigated using TGA/DTA/DTG thermogravimetric analyzer (EXSTAR TG/DTA-6300), under nitrogen atmosphere using a heating rate of 20˚C min^{-1} from 28 to 1,396˚C.

2.6. Scanning electron microscopic (SEM) studies

Scanning electron microscopic images of Th(IV) phosphate and PVA Th(IV) phosphate composite cation exchanger were taken by JEOL, JSM, 6510-LV, (Japan).

2.7. Transmission electron microscopic (TEM) studies

Transmission electron microphotographs of inorganic ion exchanger Th(IV) phosphate and hybrid cation exchanger PVA Th(IV) phosphate were taken by a transmission electron microscope Phillips CM-200, UK.

2.8. IEC for alkali and alkaline earth metals

One gram of the oven-dried cation exchanger, sample (S-6) in the H^+ form was taken into a glass column having an internal diameter (i.d.) ~1 cm and fitted with glass wool support at the bottom. 1.0 M solutions of alkali and alkaline earth metal nitrates were used as effluents to elute the H^+ ions completely from the polyvinyl alcohol Th(IV) phosphate composite cation-exchange column, maintaining a very slow flow rate (~0.5 ml min^{-1}). The effluent was titrated against a standard 0.1 M NaOH solution using phenolphthalein indicator.

2.9. Thermal effect on IEC

In order to study the effect of heating temperature on the IEC, samples (1 g) of the organic–inorganic composite cation-exchange material (S-6) in the H^+ form were heated at various temperatures in a muffle furnace for 1 h and the Na^+ ion-exchange capacity was determined by column process after cooling them at room temperature.

2.10. Effect of effluent concentration

To find out the optimal concentration of the effluent for complete elution of H^+ ions, a fixed volume (250 ml) of $NaNO_3$ solution of different concentrations ranging from 0.20 to 2.0 M were passed through a column containing one gram of the cation-exchange material (S-6) in the H^+ form with a flow rate of ~0.5 ml min^{-1}. The effluent was titrated against a standard alkali solution of 0.1 M NaOH for the H^+ ions eluted out.

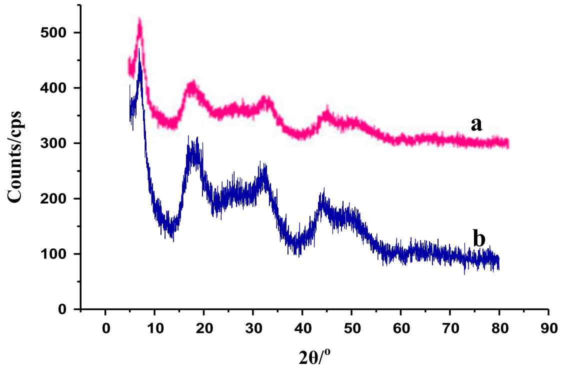

Fig. 1. Powder XRD pattern of chemically prepared inorganic ion exchanger Th(IV) phosphate (a) and polyvinyl alcohol Th(IV) phosphate composite cation exchanger (b).

2.11. Elution behavior

To find out the efficiency of column containing one gram of the cation exchanger (S-6) in H^+ form, it was eluted with 1 M $NaNO_3$ solution in different 10.0 ml fractions with minimum flow rate as described above. Each fractions of 10.0 ml effluent was titrated against a standard alkali solution for the H^+ ions eluted out.

2.12. Selective sorption (K_d values) studies

The distribution coefficient (K_d) values of various metal ions on polyvinyl alcohol Th(IV) phosphate was

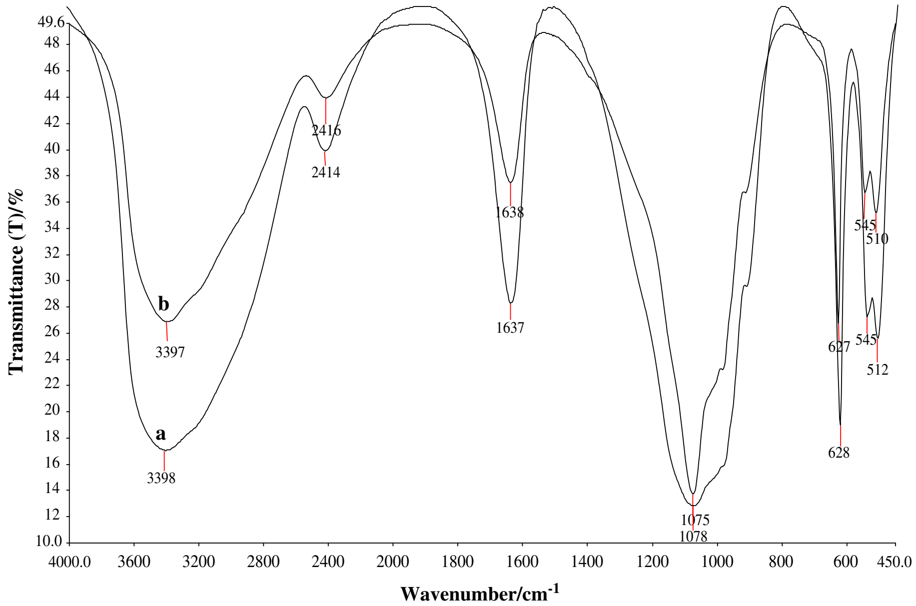

Fig. 2. FTIR spectra of inorganic ion exchanger Th(IV) phosphate (a) and polyvinyl alcohol Th(IV) phosphate composite cation exchanger (b).

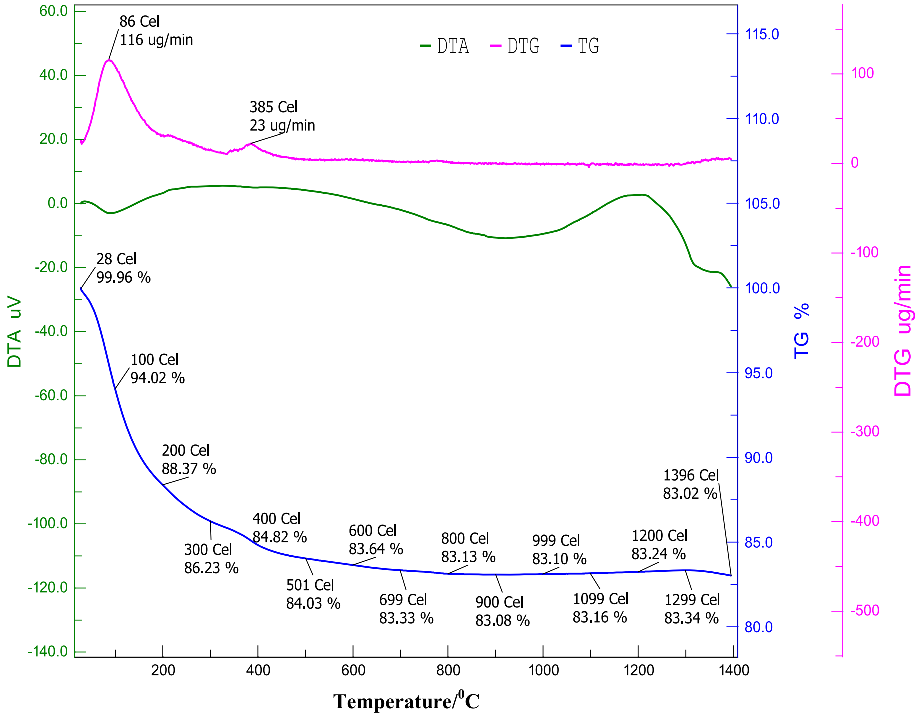

Fig. 3. Simultaneous TGA/DTA/DTG curves of polyvinyl alcohol Th(IV) phosphate composite cation exchanger.

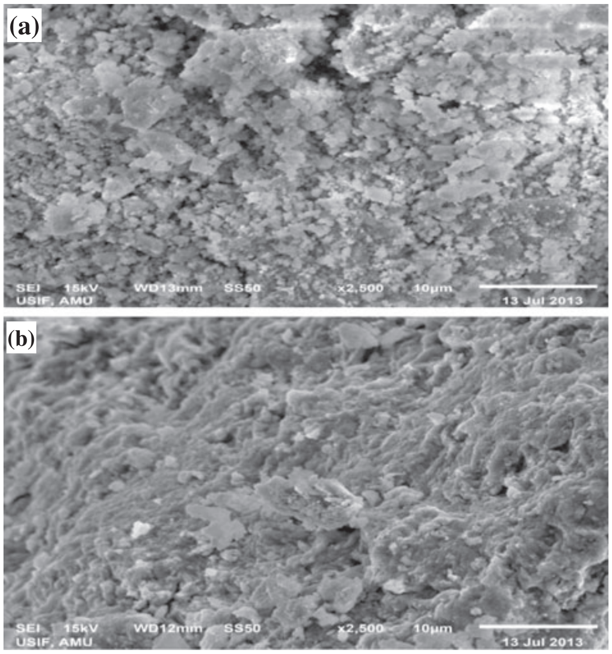

Fig. 4. Scanning electron microphotographs (SEM) of chemically prepared Th(IV) phosphate (a) and polyvinyl alcohol Th(IV) phosphate composite cation exchanger (b) at the magnification of 2,500×.

calculated by a batch method in various solvent systems. Two-hundred milligrams of composite ion exchanger beads in the H^+ form was taken in Erlenmeyer flasks and treated with 20 ml of different metal nitrate solutions in the required medium. The mixture was kept for 24 h with continuous shaking for 6 h in a temperature controlled shaker incubator at 25 ± 2˚C to attain equilibrium. The metal ions present in the solution before and after equilibrium were determined by titrating against the standard 0.005 M solution of ethylene diamine tetra acetic acid, di sodium salt (EDTA) [22]. The distribution coefficient (K_d) values were calculated using the formula given below:

$$K_d = \frac{I - F}{F} \times \frac{V}{M} (\text{ml g}^{-1}) \tag{2}$$

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

2.13. Separation factor

The separation factor may be defined as the relative tendency of two ions to be adsorbed in an exchanger from solutions of equal concentration. It is a

Table 2
Elemental composition of chemically prepared PVA Th(IV) phosphate composite cation exchanger

PVA Th(IV) phosphate			
S. No.	Elements	Weight%	Atomic%
1	Th	41.75	4.97
2	O	40.83	70.54
3	P	11.06	9.87
4	C	6.35	14.61

measure of chromatographic separation and is also expressed as the ratio of the distribution coefficients of the metal ions to be separated as:

$$\text{Separation factor } (\alpha_B^A) = \frac{K_d(A)}{K_d(B)} \quad (3)$$

where $K_d(A)$ and $K_d(B)$ are the distribution coefficients for the two competing species A and B in the ion-exchange system.

2.14. Quantitative binary separation of heavy metal ions

Quantitative binary separations of some heavy metal ions were performed on the PVA Th(IV) phosphate column. One gram of the composite cation exchanger in a glass column was utilized for column separations in the H^+ form. The mixture of two heavy metal ions with an initial concentration of 0.01 M each was loaded on the glass column and allowed for 1 h to absorb the heavy metal ions on the exchanger and passed slowly on to the column with a flow rate of 2–3 drops min^{-1}. The mixture was recycled two or three times in order to ensure complete adsorption on composite ion exchanger beads. The separation was achieved by passing a suitable solvent having flow rate of 1 mL min^{-1} through the column as the effluent. The quantity of metal ions before and after separation was determined by ethylene diamine tetra acetic acid, di sodium salt (EDTA) titration [22].

3. Results and discussion

In this study, various samples of polyvinyl alcohol Th(IV) phosphate were prepared by sol–gel route under different conditions of mixing ratios of fixed concentrations of reactants. It was found that mixing ratios of reactants have small influence on IEC of above said composite ion exchanger. It was observed that the IEC of inorganic ion exchanger increases by increasing anionic part having fixed cationic part up to the mixing ratios of 1:3, however further increase in the ratio of anionic part IEC decreases. Slurry of inorganic ion exchanger having maximum IEC (0.84 meq g^{-1} dry exchanger) was selected for the preparation of composite ion-exchange material. Different masses of polyvinyl alcohol dissolved in DMW were added into various inorganic ion exchanger slurries and it was observed that the IEC was decreased due to obstruction of exchange sites as amount of polyvinyl alcohol increased (Table 1). The composite material possessed IEC of 1.36 meq g^{-1} dry exchanger which is higher than that of inorganic counterpart Th (IV) phosphate (0.84 meq g^{-1} dry exchanger). The improvement in the IEC may be due to the binding of organic polymer polyvinyl alcohol with inorganic counterpart leading to the formation of granular

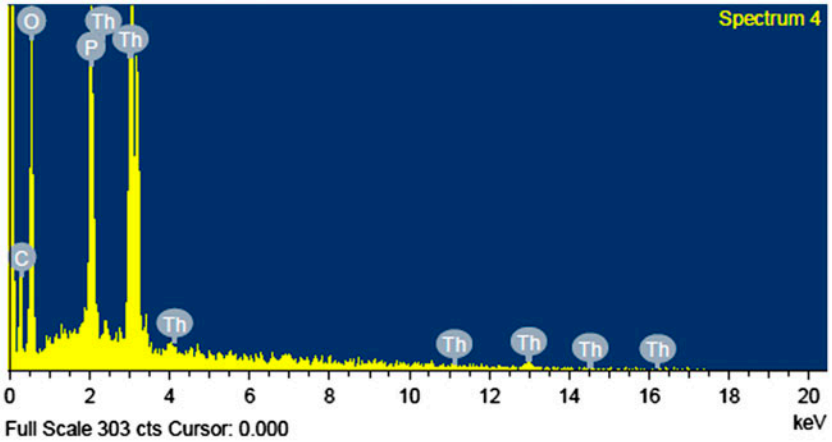

Fig. 5. Typical EDX spectrum of chemically prepared PVA Th(IV) phosphate composite cation exchanger recorded during scanning electron microscopy (SEM) analysis.

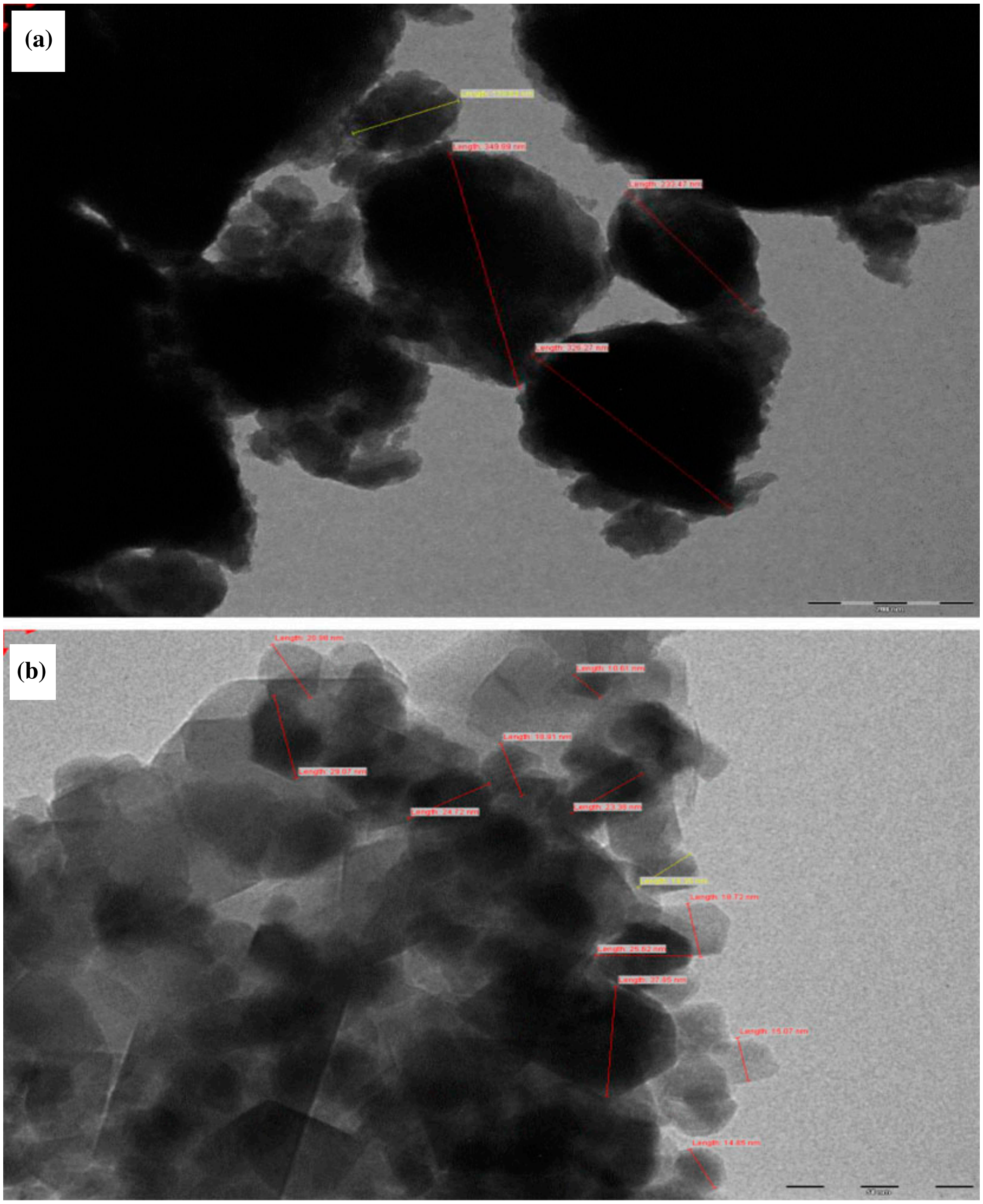

Fig. 6. Transmission electron microphotographs (TEM) of chemically prepared Th(IV) phosphate (a) and polyvinyl alcohol Th(IV) phosphate composite cation exchangers (b).

material suitable for column operation. The material was found reproducible in behavior which is evident from the fact that the material obtained for different batches did not show any appreciable deviation in IEC, color, yield, and other ion-exchange parameters. The XRD patterns of Th(IV) phosphate (S-3) and polyvinyl alcohol Th(IV) phosphate (S-6) showed very small peaks of 2θ values (Fig. 1) which indicated the amorphous nature of inorganic as well as composite cation exchange materials. The FTIR spectrum of this composite cation exchanger PVA Th(IV) phosphate (Fig. 2) confirms C–H stretching (2,416 cm^{-1}) [23], bending vibration of water (1,638 cm^{-1}), ionic phosphate (1,075 cm^{-1}) [24], presence of metal oxygen bond (627 cm^{-1}) [25], while a broad absorption band around 3,397 cm^{-1} confirms the presence of –OH

Table 3
Ion-exchange capacity of various exchanging ions on polyvinyl alcohol Th(IV) phosphate composite cation exchanger

Exchanging ions	Ionic radii (Å)	Hydrated ionic radii (Å)	Ion-exchange capacity (meq g^{-1} dry exchanger)
Li^+	0.68	3.40	1.20
Na^+	0.97	2.70	1.36
K^+	1.33	2.32	1.39
Mg^{2+}	0.78	7.00	0.36
Ca^{2+}	1.06	6.30	0.44
Sr^{2+}	1.27	–	0.52
Ba^{2+}	1.43	5.90	0.60

Table 4
Effect of eluent of temperature on ion-exchange capacity (I.E.C.) of polyvinyl alcohol Th(IV) phosphate composite cation exchanger (heating time for 1 h)

Heating temperature (°C)	Appearance of beads after heating	Weight loss (%)	Na^+ ion exchange capacity (meq g^{-1} dry exchanger)	% Retention of IEC
50	Bright white	4.13	1.30	100
100	Bright white	5.21	1.28	98.4
150	Bright white	7.54	1.28	98.4
200	Bright white	10.8	1.26	96.9
250	Dull white	12.4	1.22	93.8
300	Dull white	13.7	1.18	90.7
350	Dull white	14.2	1.14	87.6
400	Dull white	14.8	1.12	86.1
450	Dull black	15.7	1.08	83.1
500	Dull black	16.3	1.00	76.9
550	Dull black	16.5	0.90	69.2
600	Dull black	16.8	0.50	38.4
650	Dark black	17.2	0.24	18.4
700	Dark black	17.4	0.14	10.7
750	Dark black	17.8	0.06	4.6
800	Dark black	18.4	0.04	3.1

Table 5
Effect of eluent concentration on ion-exchange capacity of polyvinyl alcohol Th(IV) phosphate composite cation exchanger EC

$NaNO_3$ (M)	Na^+ ion-exchange capacity (meq g^{-1} dry exchanger)
0.2	0.60
0.4	0.70
0.6	0.76
0.8	0.80
1.0	1.36
1.2	1.36
1.4	1.36
1.6	1.36
1.8	1.36
2.0	1.36

stretching of water molecules [26]. Broadness of peaks in the region of 3,600–3,200 cm^{-1} and 1,200–1,000 cm^{-1} is due to presence of inter and intra molecular hydrogen bonding [27]. A close similarities between FTIR spectrum of Th(IV) phosphate and polyvinyl alcohol Th(IV) phosphate is due to the appreciable binding between inorganic precipitate and organic polymer polyvinyl alcohol. The thermogram of polyvinyl alcohol Th(IV) phosphate composite cation exchanger (Fig. 3) exhibited excellent thermal stability. When composite is heated up to 100°C only 5.94% weight loss was observed which is assigned due to the removal of external water molecules from the surface of composite material. The sharp endothermic peak appeared in DTA curve at 100°C also confirms this transition. A slightly slow 5.65% weight loss is observed on further heating up to 200°C due to

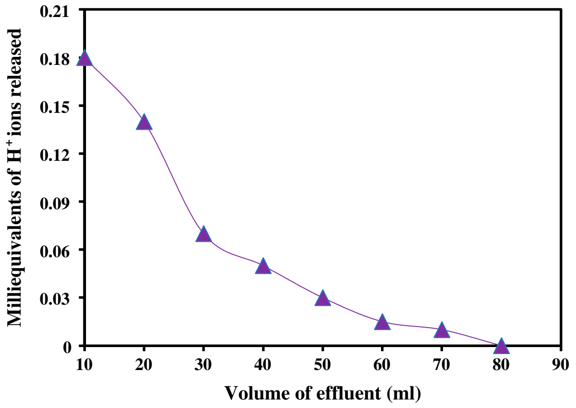

Fig. 7. Elution behavior of polyvinyl alcohol Th(IV) phosphate composite cation exchanger.

removal of strongly coordinated water molecule from the hybrid ion exchanger [28]. An increase in temperature up to 300˚C followed 2.14% weight loss which indicates conversion of phosphate group into pyrophosphate accompanied by condensation process [29]. A loss in mass of 2.59% was observed while heating is continues up to 600˚C which is due to the decomposition of organic polymer. Above 600˚C, curve becomes almost constant which is indication of formation of anhydrous oxide. SEM photographs (Fig. 4) showed the difference in surface morphology of inorganic ion exchanger Th(IV) phosphate and organic–inorganic composite ion exchanger polyvinyl alcohol Th(IV) phosphate. The difference in surface morphology confirms the formation of composite cation exchange material. The elemental composition determined by the energy dispersive X-ray (EDX) analysis is given in Table 2. The presence of chemical constituents (C, O, Th, P) in the EDX spectrum confirms the formation of PVA Th(IV) phosphate composite cation exchanger (Fig. 5). Transmission electron microscope (TEM) photographs (Fig. 6) showed the difference in particle size of inorganic ion exchanger Th(IV) phosphate and organic–inorganic composite cation exchanger polyvinyl alcohol Th(IV) phosphate. The particle size for Th(IV) phosphate was found to be in the range of 135.82–349.89 nm while after binding of organic polymer polyvinyl alcohol with Th(IV) phosphate particle size of polyvinyl alcohol Th(IV) phosphate composite cation exchanger was found to be in the range of 10.61–37.85 nm.

The charge and size of exchanging ions have fundamental role on the IEC of ion exchanger. The study of size and charge of effluent showed that IEC of this composite cation exchanger for the alkali and alkaline earth metals increases with the decrease in

Table 6

K_d values of some metal ions on polyvinyl alcohol Th(IV) phosphate composite cation exchanger in different solvent systems

Metal ions	Solvents												
		HNO_3			HCl			$HClO_4$			0.1 M CH_3COOH + 0.1 M CH_3COONa (V/V)		0.1 M HNO_3 + 0.1 M NH_4NO_3 (V/V)
	DMW	0.01 M	0.1 M	1 M	0.01 M	0.1 M	1 M	0.01 M	0.1 M	1 M	(1:2)	(2:1)	(1:1)
	K_d values												
Cd^{2+}	433	380	210	156	394	267	178	353	277	136	186	410	116
Hg^{2+}	521	430	275	220	485	374	368	450	396	268	384	487	345
Cu^{2+}	378	300	247	190	360	313	134	350	215	84	178	360	112
Ni^{2+}	416	225	180	150	160	124	121	283	240	214	109	196	104
Zn^{2+}	371	280	213	134	286	254	86	317	200	168	156	364	118
Fe^{3+}	224	186	135	98	200	150	90	200	154	134	194	380	134
Mg^{2+}	330	218	165	140	120	118	98	167	122	–	150	248	–
Ca^{2+}	210	140	86	96	73	68	–	125	94	56	110	150	70

Table 7
Separation factor of heavy metal ions on PVA Th(IV) phosphate composite cation exchanger

	Solvents		
Separation factor	1 M HCl	0.1 M HNO_3 + 0.1 M NH_4NO_3 (1:1)	0.1 M CH_3COOH + 0.1 M CH_3COONa (1:2)
$\propto_{Cd}^{Hg}$	2.06	2.97	2.06
$\propto_{Cu}^{Hg}$	2.74	3.08	2.15
$\propto_{Ni}^{Hg}$	3.04	3.31	3.52
$\propto_{Zn}^{Hg}$	4.27	2.92	2.46

Table 8
Some binary separation of heavy metal ions achieved on PVA Th(IV) phosphate composite cation exchanger column

Separation achieved	Amount loaded (μg)	Amount found (μg)	Error (%)	Effluent used	Volume of effluent (ml)
Hg(II)	5,139.30	5,139.30	0.00	1 M HNO_3	70
Cd(II)	4,627.05	4,645.07	+0.38	0.1 M HNO_3 + 0.1 M NH_4NO_3 (1:1)	60
Hg(II)	5,139.30	5,156.45	+0.33	1 M HNO_3	70
Ni(II)	4,362.24	4,387.29	+0.57	0.1 M HNO_3 + 0.1 M NH_4NO_3 (1:1)	50
Hg(II)	5,139.30	5,139.30	0.00	1 M HNO_3	60
Cu(II)	3,624.00	3,578.08	−1.26	1M $HClO_4$	60
Hg(II)	5,139.30	5,121.24	−0.35	1M HNO_3	70
Zn(II)	4,462.00	4,389.32	−1.62	1M HCl	60

hydrated ionic radii [30,31] of eluent as shown in Table 3. Thermal stability experiment shows that the physical appearance, mass loss, and IEC of the composite cation exchanger material PVA Th(IV) phosphate (S-6) was changed significantly with increase in the heating temperature. The results showed that the composite cation exchanger is thermally stable as the sample maintained about 76.9% of initial IEC and 83.7% of mass by heating up to 500°C as shown in Table 4. The rate of elution is always dependent upon the concentration of effluent used for a particular application. In the present study, $NaNO_3$ is used as effluent to elute replaceable H^+ ions and found that 1.0 M $NaNO_3$ is found optimum for the maximum release of H^+ ions [32,33] from one gram of composite cation exchanger as shown in Table 5. The elution behavior study was used to determine the elution efficiency of cation-exchange column containing one gram of cation exchanger. The result showed that the elution of replaceable ions is quite fast as all the exchangeable ions are eluted out by 80 ml of effluent (1 M $NaNO_3$) with 2–3 drops min^{-1} as shown in Fig. 7.

The distribution studies were performed for 8 metal ions in 13 solvent systems (Table 6). The result indicates that the material is highly selective for Hg(II) ions, which is a toxic environmental pollutant whereas selectivity coefficient (K_d) values were found dependent on the concentration of electrolyte. To study the separation capability of composite cation exchanger PVA Th(IV) phosphate separation factor of different heavy metal ion pairs was obtained (Table 7). Separation factor indicated that the separation of heavy metal ions is feasible. On the basis of separation factor some important binary separation of heavy metal ion pairs such as Hg(II)–Cd(II), Hg(II)–Ni(II), Hg(II)–Cu(II) and Hg(II)–Zn(II) were carried out (Table 8) and was observed that elution of heavy metal ions depends upon the metal-eluting ligand stability as Hg(II) ions remains in column for a longer time than that of other heavy metal ions. The separations were fairly sharp and recovery of Hg(II) ions was quantitative and reproducible.

4. Conclusion

The organic–inorganic composite cation exchanger polyvinyl alcohol Th(IV) phosphate was synthesized by sol–gel technique. The cation exchanger showed good IEC, fast elution efficiency, excellent thermal stability, and selectivity for a toxic heavy metal Hg(II) ions. The composite cation exchanger is fairly useful material and may be utilized to remove Hg(II) ions from various polluted water bodies.

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Nomenclature

$Th(NO_3)_4·5H_2O$	—	thorium nitrate pentahydrate
H_3PO_4	—	orthophosphoric acid
K_d	—	distribution coefficient
I	—	initial amount of the metal ion in the solution phase
F	—	final amount of the metal ion in the solution phase
V	—	volume of the solution (ml)
M	—	amount of exchanger (g)

Abbreviations

PVA	—	polyvinyl alcohol
EDTA	—	ethylene diamine tetra acetic acid, di sodium salt
i.d.	—	internal diameter
DMW	—	demineralized water
TGA	—	thermogravimetric analysis
DTA	—	differential thermal analysis
DTG	—	differential thermogravimetry
XRD	—	X-ray diffraction
FTIR	—	Fourier transform infrared spectroscopy
SEM	—	scanning electron microscopy
TEM	—	transmission electron microscopy

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