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Studies on polyoxyethylene octyl phenyl ether supported thorium(IV) phosphates: a new cation exchange material

AMITA SOMYA[1,*] and KALPANA MAHERIA[2]
[1]Department of Chemistry, Presidency University, Bengaluru 560 064, India
[2]S.V. National Institute of Technology, Ichchhanath, Surat 395 007, India
*Author for correspondence (amitasomya@presidencyuniversity.in)

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Abstract. A new surfactant supported cation exchanger and adsorbent named, polyoxyethylene octyl phenyl ether supported thorium(IV) phosphate (TX-100ThP) has been reported along with its synthesis, physico-chemical characterization such as scanning electron microscopy, X-ray diffraction, thermogravimetric analysis–differential thermal analysis and Fourier transform infra-red study. Following the characterization, the formed product has been tested for its efficiency in ion exchange chemistry and in analytical chemistry. For the testing, adsorption of alkaline earths—Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} and transition metal ions such as Fe^{3+}, Mn^{2+}, Ni^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Hg^{2+} and Pb^{2+} have been explored in different acidic media and the results revealed the selectivity of synthesized material towards Hg^{2+} ions. On that basis, the material has been used to treat the binary laboratory-made samples, exploring the environmental importance of the cation exchanger in material science.

Keywords. Surfactant; cation exchanger; thorium phosphate; adsorption.

1. Introduction

Organo-inorganic hybrid cation exchangers [1] are of recent origin with the number of ample opportunities for the researchers and analysts owing to their thermal, chemical and mechanical stability in addition to metal ion selectivity. As organic ion exchangers have been quite reproducible and chemically stable, however, they do not show stability towards heat. Moreover, they lose their ion-exchange properties on being exposed to strong radiations. Inorganic ion exchangers are established in analytical chemistry owing to their thermal and radiation resistance and their selective adsorption for different metal ions. However, the main drawback of these materials has been their chemical and mechanical instability. Further, they are not much reproducible in ion-exchange behaviour. The drawbacks and advantages of both the exchangers have paved the way to explore the studies on organo-inorganic or hybrid ion exchangers. Hence, hybrid ion exchangers have attracted the attention of analytical chemists because of their tunable interesting properties those are not seen in pure organic as well as in inorganic ion exchangers. A number of such materials [2–10] was synthesized in laboratories revealing their worth in analytical chemistry by showing promising ion-exchange characteristics.

Surfactants, or surface-active agents are important in tuning the adsorption characteristics of cation exchanger materials [7,11,12] for several metal ions using as media and this ubiquitous property of surface-active agents has tempted to their widespread importance in environmental applications. Encouraged by this, in recent years, some surfactant-based hybrid ion exchangers [13–21] have been synthesized by introducing surfactants in the matrix of inorganic ion exchangers. Insoluble acid salts of tetravalent metal have been found to have layered structure corresponding to intercalating agent. This research study is an attempt to synthesize new cation exchange material, i.e., polyoxyethylene octyl phenyl ether supported thorium(IV) phosphate (TX100-ThP) which is Hg^{2+} selective showing the magnificient ion-exchange capacity (IEC), 3.25 meq g^{-1}.

Mercury is the most widely known toxic and unique global pollutant which can neither be created nor degraded and exists in nature in three forms, namely, elemental, organic and inorganic, with each one having its own impact of toxicity [22], causes a wide range of adverse health effects. Mercury enters the environment through a number of industries such as paper industries, electrical industries, dentistry, paint, pesticides, fertilizers, thermometers, amalgam, pharmaceuticals, cosmetics and some industrial processes such as production of caustic soda, in nuclear reactors, as a preservative of pharmaceutical products and as antifungal agents for food processing and once released it circulates in air, soil and water. Even exposure to vapours of mercury is dangerous to human beings as it enters the blood stream leading to blindness and deafness, kidney damage,

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digestion-related problems, lack of muscle coordination and intellectual disability. Hence, now it is a challenging job to treat waste water containing mercury. In spite of the fact that several research studies have been conducted in removal of mercury from waste water, there is still room for finding new materials that can be used to eliminate mercury. This paper presents a method for the synthesis of a new polyoxyethylene octyl phenyl ether supported ThP, its characterization and exploration of analytical applications by accomplishing binary separation of mercury. This chemical compound has been found to be thermally and mechanically stable. Polyoxyethylene octyl phenyl ether is a non-ionic surfactant commonly known as Triton X-100 and has already proven its explicit characteristic in adsorption of certain metal ions [11,12]. The objective of using polyoxyethylene octyl phenyl ether has been to increase the capacity of ThP substantially by enhancing the interlayer distances in ThP.

2. Materials and methods

2.1 *Materials*

Thorium nitrate [$Th(NO_3)\cdot 5H_2O$] was obtained from Central Drug House (India). Polyoxyethylene octyl phenyl ether and phosphoric acid (H_3PO_4) were purchased from Merck-Schuchardt (Germany) and Qualigens (India), respectively. Other chemicals, used were of analytical grade reagent(s).

2.2 *Instruments used*

Fourier transform infra-red (FTIR) study was performed on Nicolet iS5 FTIR spectrometer, whereas scanning electron microscopy (SEM) study was performed using TESCAN Vega 3 LMU instrument. X-ray diffraction (XRD) study was carried out on a Philips Analytical X-ray B.V. diffractometer type PW 170 B.V. For thermogravimetric–differential thermal analysis, Universal V4.5A TA instrument (TG–DTA Q500 V20.10 build 36) was used with a nitrogen flow of 50 ml min^{-1} and a heating speed of 10°C min^{-1}.

2.3 *Preparation of the reagent solutions*

Thorium nitrate was dissolved in 1 M HNO_3 and the rest of the solutions such as polyoxyethylene octyl phenyl ether and 2 M of H_3PO_4 were prepared in demineralized water (DMW).

2.4 *Methodology*

2.4a *Synthesis of cation exchange material*: Thorium nitrate and polyoxyethylene octyl phenyl ether were mixed vigorously and kept for 3–4 h on a magnetic stirrer at the room temperature, and then 2 M of H_3PO_4 was added with constant stirring at a temperature of 45 ± 5°C. The resulting slurry was constantly stirred at the same temperature using a magnetic stirrer. It was filtered and washed by DMW till pH ∼ 7 after cooling and keeping for 24 h. The material resulted to a sheet which was then, converted into H^+-ionic species by the treatment with nitric acid and was finally washed with demineralized water, dried at 25–30°C and sieved through 50–70 mesh-sized particles for further studies. Three samples of the material were synthesized by varying the concentration of TX-100, i.e., below critical micelle concentration (CMC), at CMC, and above CMC.

ThP was also synthesized by adding 0.1 M of thorium nitrate solution to 2 M of H_3PO_4 in 1:1 ratio with continuous stirring on a magnetic stirrer at the same temperature, i.e., 45 ± 5°C. The produced slurry was treated further by the above said method to get 50–70 mesh-sized particles.

2.4b *Studies on IEC*: For determining IEC, a glass column having an internal diameter ∼1 cm, length ∼75 cm and 50 ml in volume was used after packing its bottom with glass wool and 1 g synthesized exchange material (H^+-ionic form). Eluant of 250 ml of 1 M $NaNO_3$ solution was passed into the packed column with the flow rate of ∼0.5 ml min^{-1}. The capacity of the exchange material was determined [23] by titrating the effluent against a 0.1 M sodium hydroxide solution and calculated using the formula:

$$\text{IEC} = \text{Strength of NaOH} \times \text{Volume of NaOH}/\text{Amount of exchange material.}$$

2.4c *Regeneration study*: A regeneration study was performed by regenerating the ion-exchange material with the treatment of 1 M HNO_3 after each use. IEC was determined as given above and the output between regeneration (OBR) was found to be 13 ml for the same.

2.4d *Elution study*: A glass column (as described above) packed with 1 g of exchanger was used for the elution study. 1 M $NaNO_3$ (i.e., 85 g l^{-1} of $NaNO_3$) solution was eluted from the same column in different 10 ml fractions.

2.4e *Operating temperature range study*: Several 1 g samples of the exchange material were studied at various temperatures starting from 45 to 800°C by keeping them in a muffle furnace at different temperatures for 1 h each and cooled to room temperature. Then, IECs of cooled materials were determined by the said column process.

2.4f *Adsorption studies*: About 0.2 g exchanger was mixed to 2 ml of metal ion solution and 18 ml acid solution. This mixture was held for 24 h to achieve equilibrium. Before and after achieving equilibrium, metal ions concentration was calculated by conducting EDTA complexometric titrations using formula:

$$K_d = \frac{I - F}{F}\frac{V}{M}\left(\text{ml g}^{-1}\right)$$

Table 1. Synthesis of TX-100ThP samples with varying concentrations of polyoxyethylene octyl phenyl ether.

Sample number	Concentration of polyoxyethylene octyl phenyl ether (M)	IEC (meq g^{-1})
1	0	1.10
2	10^{-5}	1.55
3	10^{-4}	3.25
4	10^{-3}	2.55

Table 2. Comparative study on IEC of TX-100ThP with previously synthesized exchange materials.

Sample number	Exchange materials	IEC (meq g^{-1})
1	Triton X-100 Th(IV) phosphate	3.25
2	Acrylonitrile Ce(IV) phosphate [2]	2.86
3	Acryl amide Ce(IV) phosphate [3]	2.60
4	Acryl amide Th(IV) phosphate [4]	2.00
5	Pectin Ce(IV) phosphate [5]	1.78
6	Pectin Th(IV) phosphate [5]	2.15
7	Cellulose acetate Th(IV) phosphate [6]	1.70
8	*n*-Butyl acetate Ce(IV) phosphate [7]	2.25
9	Acrylonitrile Zr(IV) phosphate [8]	2.08
10	Triton X-100 Ce(IV) phosphate [13]	3.00
11	Triton X-100 Sn(IV) phosphate [14]	2.75
12	Sodium dodecyl sulphate Ce(IV) phosphate[15]	2.92
13	*N*-dodecyl pyridinium chloride Ce(IV) phosphate [16]	3.15

where I and F are initial and final amount of metal ions in the solution, V is the total volume of solution in ml and M is the amount of exchange material in *g*.

2.4g *Separation studies*: A handful of binary separations were conducted on some columns having i.d. ~0.6 cm packed with 2 g exchanger. After washing the column thoroughly with demineralized water, the loading of metal ions coupled were separated. The process was repeated 2–3 times in order to get total adsorption of metal ions on exchanger matrics. An appropriate eluent was used to separate metals by passing through the same column and the amount of metal ions in the collected effluent was calculated using EDTA complexometric titrations.

3. Results and discussion

The best sample of the synthesized material was found with the concentration of polyoxyethylene octyl phenyl ether at CMC, hence was selected for further studies as per the maximum IEC, shown in table 1. The prominent characteristic of polyoxyethylene octyl phenyl ether supported ThP was to have tremendously high IEC for Na^{+}-ions (3.25 meq g^{-1}) which is two and half times more than that

Table 3. IEC of TX-100ThP for some metal ions.

Metal ion solutions	IEC (meq g^{-1})
Li(I)	2.75
Na(I)	3.25
K(I)	3.30
Mg(II)	2.45
Ca(II)	3.00
Sr(II)	3.15
Ba(II)	3.20

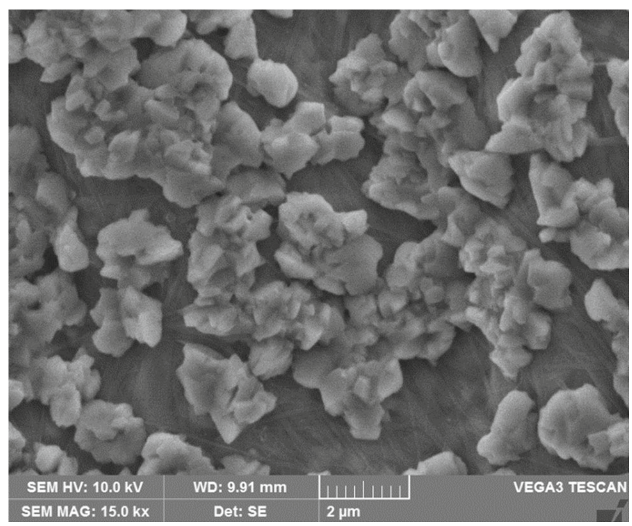

Figure 1. SEM study of TX-100ThP.

Table 4. Regeneration study.

Regeneration number	IEC (meq g^{-1})	% Retention in IEC
0	3.25	100
1	2.90	89.2
2	2.60	80
3	2.55	78.5
4	2.40	73.8
5	2.25	69.2
6	2.00	61.5
7	1.35	41.5
8	0.85	26.1
9	0.15	4.6

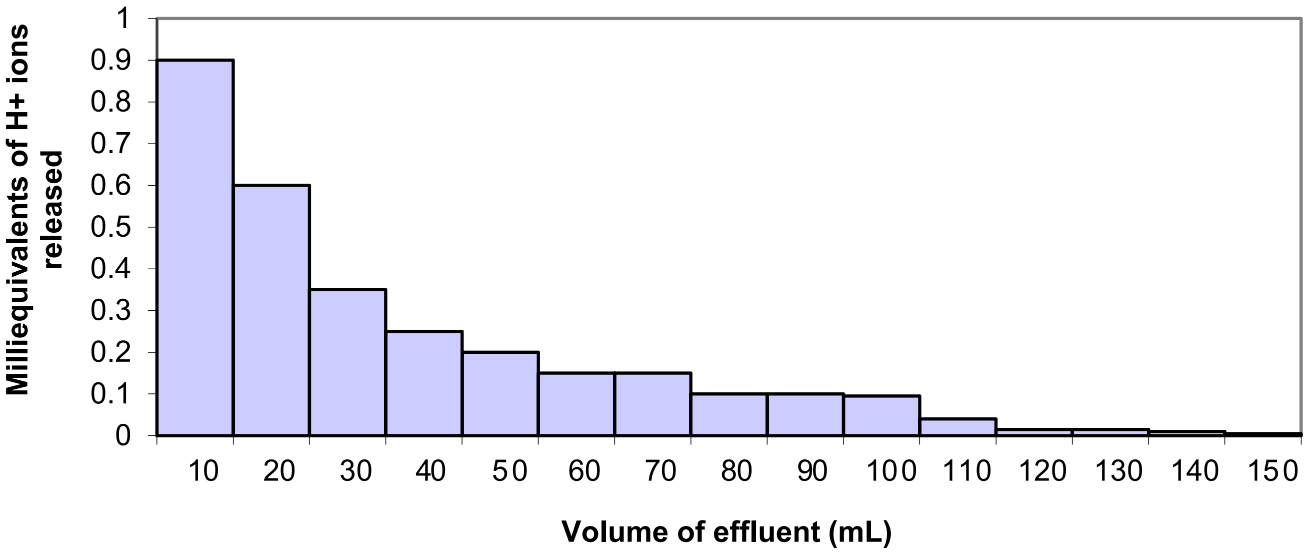

Figure 2. Elution study on TX-100ThP.

Table 5. Eluent concentration study.

Concentration of $NaNO_3$ (M)	IEC (meq g^{-1})
0.2	0.75
0.4	1.60
0.6	1.75
0.8	2.50
1.0	3.25
1.2	3.25

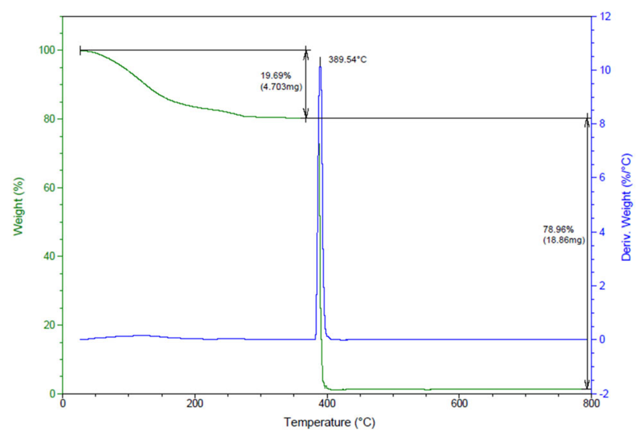

Figure 3. TGA–DTA data of TX-100ThP.

Table 6. Operating temperature range study of ThP.

Temperature (°C)	IEC (meq g^{-1})	Colour	% Retention in IEC
25	1.10	White	100
100	0.94	White	85.5
200	0.57	Off white	51.8
300	0.17	Brownish white	15.4
400	0.03	Brownish black	2.7

Table 7. Operating temperature range study of TX-100ThP.

Temperature (°C)	IEC (meq g^{-1})	Colour	% Retention in IEC
25	3.25	White	100
100	3.10	White	95.4
200	2.75	White	84.6
300	2.15	Cream white	66.2
400	1.85	Yellow white	56.9
500	1.15	Brownish white	35.4
600	0.25	Brown	7.70

of ThP, i.e., 1.3 meq g^{-1}. In fact, it is highest among the other organo-inorganic, hybrid ion-exchange materials, reported earlier (table 2). It may be due to the increased interlayer distances of the layers of ThP owing to its intercalation behaviour resulting in the faster exchange of ions. The exchange capacity of synthesized material for some alkali metals such as lithium(I), sodium(I), potassium(I) and alkaline earths like magnesium(II), calcium(II), strontium(II) and barium(II) reveals their decreasing order of hydrated ionic radii, given in table 3. Furthermore, the material resulted in a fibrous sheet, which is revealed by the SEM study shown in figure 1.

The regeneration study depicts that the synthesized material retains its 89.2% of IEC after first time regeneration which decreases up to 26.1% in the 8th cycle of regeneration before reaching 4.6% at the 9th time, which clearly indicates that material can be reused seven times after regenerating it (table 4).

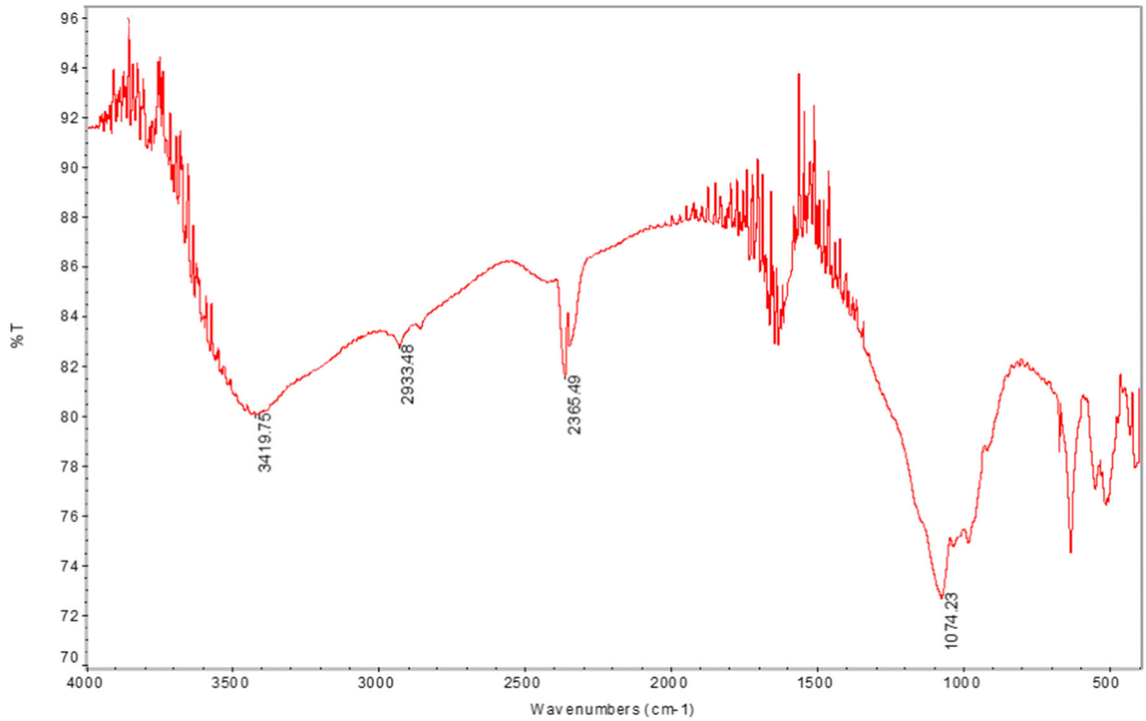

Figure 4. FTIR graph of TX-100ThP.

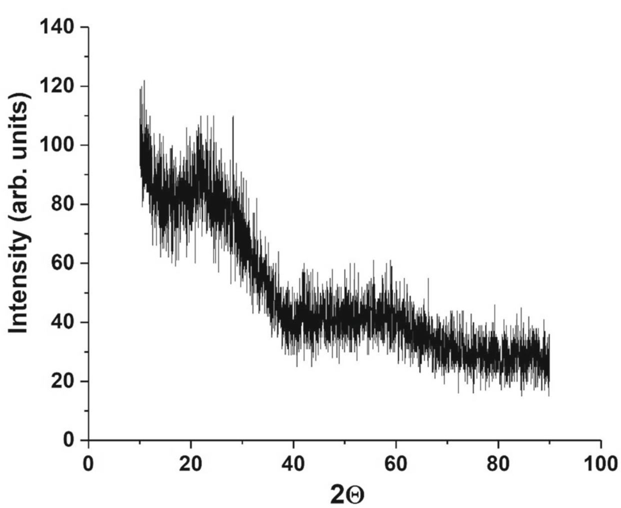

Figure 5. XRD study on TX-100ThP.

The elution study reveals fast exchange of ions and it also exhibits that initial 150 ml of the eluent (i.e., only 12.75 g of $NaNO_3$) was sufficient to elute maximum of H^+ ions from a column of 1 g of exchange material (figure 2) and, the optimum concentration of the eluent ($NaNO_3$) was found to be 1 M (table 5) for the exchange of H^+ ions from the glass column.

The study on operating temperature range shows that the synthesized material is quite stable at various temperatures pointing certain fascinating results. In fact, the said material seems to be more thermally stable than ThP. The TX-100ThP is stable up to 100°C retaining 95.4% of its IEC. On increasing the temperature to 200°C, the retention of IEC is 84.6% (table 7) and at 400°C the retention is 56.9% of IEC whereas ThP loses its IEC retaining only 2.7% of IEC at this temperature (table 6).

The thermogravimetric curves (figure 3) of the material show only one-step mass loss, 19.69% at 400°C with an exo effect at 389.54°C which indicates the removal of additional water molecules, and of polyoxyethylene octyl phenyl ether. The thermo-gram as well as data from thermal analysis (table 7) also reveal the operating temperature range of the material till 400°C. Beyond 400°C, the weight of the material becomes constant continuing up to 800°C with the formation of ThO_2 at 450°C [24]. The thermal studies reveal that there is little effect on the exchange capacity by the removal of external water molecules at 100°C. A change in the exchange capacity up to 400°C might be possibly due to disruption of the organic part, i.e., surfactant polyoxyethylene octyl phenyl ether from the intercalated structure of synthesized exchange material.

The matrix of synthesized ion exchanger consists of ThP which is revealed by FTIR study. This study (figure 4) indicates the peaks at 500 and 1074.23 cm^{-1} representing phosphate groups [25]. The peaks at 600 cm^{-1} reveal the metal-oxide and metal-hydroxide bonding. The peaks at 1650 and 3419.75 cm^{-1} confirm the presence of additional water molecules and –OH groups, respectively, while peaks at 2365 and 2933.45 cm^{-1} show the presence of alkyl groups in synthesized material. The XRD study (figure 5) reveals amorphous solid state of synthesized material.

Table 8. Distribution coefficients for few alkaline earths and transition metal ions on TX-100ThP.

Metal ions	Metal ion concentration used (mg l^{-1})	DMW	HCl			HNO_3			$HClO_4$		
			0.01 M	0.1 M	1 M	0.01 M	0.1 M	1 M	0.01 M	0.1 M	1 M
Mg^{2+}	16,264	571.4	683.3	571.4	422.2	571.4	422.2	327.3	487.5	327.3	261.5
Ca^{2+}	18,890	800.0	542.9	462.5	400.0	650.0	462.5	400.0	442.9	400.0	309.1
Sr^{2+}	21,330	650.0	650.0	400.0	350.0	542.9	400.0	350.0	462.5	400.0	309.1
Ba^{2+}	20,910	616.7	616.7	437.5	3330.0	541.3	377.8	290.9	541.3	330.0	230.8
Fe^{3+}	12,980	633.3	528.6	450.0	300.0	633.3	388.9	340.0	450.0	300.0	266.7
Mn^{2+}	15,830	820.0	666.7	557.1	360.0	557.1	411.1	318.2	557.1	475.0	253.9
Ni^{2+}	23,260	557.1	666.7	475.0	360.0	557.1	411.1	360.0	475.0	411.1	283.3
Co^{2+}	23,280	760.0	760.0	616.7	377.8	616.7	514.3	437.5	616.7	330.0	258.3
Cu^{2+}	19,328	840.0	683.3	571.4	422.2	571.4	487.5	422.2	840.0	487.5	327.3
Cd^{2+}	24,680	666.7	666.7	557.1	475.0	557.1	411.1	360.0	666.7	475.0	318.2
Hg^{2+}	27,410	4600	4600	2250	1467	2250	1467	1075	4600	1467	840.0
Pb^{2+}	26,496	650.0	542.9	462.5	309.1	462.5	350.0	275.0	650.0	462.5	350.0

Table 9. Separation study on the TX-100ThP columns.

Binary metals couple	Metal loaded (μg)	Metal found (μg)	Error (%)	Eluant	Amount of eluent used (ml)
Pb^{2+}–Hg^{2+}					
Pb^{2+}	33,152	31,678.6	−4.4	0.1 M $HClO_4$	50
Hg^{2+}	32,094.4	30,728.7	−4.2	1 M NH_4Cl + 1 M HCl	60
Fe^{3+}–Hg^{2+}					
Fe^{3+}	8935.2	8732.1	−2.3	1 M $HClO_4$	50
Hg^{2+}	32,094.4	30,728.7	−4.2	1 M NH_4Cl + 1 M HCl	50
Ba^{2+}–Hg^{2+}					
Ba^{2+}	21,972.3	21,461.3	−2.3	1 M HNO_3	50
Hg^{2+}	32,094.4	32,094.4	0	1 M NH_4Cl + 1 M HCl	60

The adsorption study of some alkaline earths and transition metals on the matrices of synthesized material have been explored in DMW and varying concentrations of HCl, HNO_3 and $HClO_4$ media (table 8). Polyoxyethylene octyl phenyl ether has not only enhanced the capacity of the material, but also increased the adsorption of metals. Table 8 shows that the specific selectivity of the material was found for Hg^{2+}, one of the most water polluting toxic metal. The high sensitivity of synthesized material for Hg^{2+} depicts an important role of the said material in analytical chemistry. Based on the thermal study and selectivity towards Hg^{2+} ions, the use of the above material can be assumed in thermal power plants and nuclear plants as well where the treatment of Hg^{2+} is essentially required. Therefore, the application of TX-100ThP has been explored by performing few binary separations including Hg^{2+} on TX-100ThP columns. Table 9 depicts these results.

4. Conclusion

The support of non-ionic surfactant, polyoxyethylene octyl phenyl ether and the synthesis of ThP has drastically enhanced the exchange capacity as well as adsorption for certain metals. Further, TX-100ThP is found to be thermally very stable and showed specific selectivity for Hg^{2+} ions. The highest selectivity of the synthesized material for Hg^{2+} exhibits its important role in pollution control of the environment.

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