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PYRIDINE BASED THORIUM(IV) PHOSPHATE HYBRID FIBROUS ION EXCHANGER

Synthesis, characterization and thermal behaviour

K. G. Varshney[1], *A. Agrawal*[2] *and S. C. Mojumdar*[3,4*]

[1]Manav Rachna College of Engineering, Sector 43, Aravalli Hills, Delhi-Surajkund Road, Faridabad 121004, India
[2]Department of Applied Chemistry, Aligarh Muslim University, Aligarh 202002, India
[3]Department of Chemical Engineering, University of Waterloo, 200 University Ave. West, Waterloo, ON, N2L 3G1, Canada
[4]University of New Brunswick, Saint John, NB, E2L 4L5, Canada

Pyridine based thorium(IV) phosphate (PyThP) has been synthesized by drop-wise addition of the thorium(IV) nitrate with constant stirring into a mixture of pyridine and phosphoric acid. This material has been characterized using X-ray, IR spectra, TG, DTG and SEM studies in addition to its ion exchange capacity, elution and pH titrations. The material has been found amorphous and fibrous in nature on the basis of X-ray diffraction and SEM studies. TG has revealed the changes incurred in the material on thermal treatment and IR spectral studies have shown the presence of various groups in its structure.

Keywords: *DTG, fibrous ion exchangers, IR spectroscopy, SEM, TG, X-ray*

Introduction

Hybrid ion exchangers have gained prominence in analytical chemistry in the recent past [1–10] because of their good mechanical stability and enhanced ion exchange characteristics. It may be due to the presence of organic species in the inorganic ion exchange matrix. Many of such materials, particularly those based on cerium(IV) [11] and thorium(IV) [12] possess fibrous nature, as confirmed by their SEM studies. Fibrous ion exchangers are of great use in industrial and environmental applications because of the versatility in their applications such as in the making of cloths, conveyor belts, nets, etc. They can be used to prepare inorganic ion exchange papers or thin layers suitable for chromatographic cation separations and as ion exchange membranes without a binder [13, 14] with good electrochemical behaviour [15].

Many authors have investigated organic and inorganic materials on account of their chemical, biological and environmental significance and their thermal, spectral, microscopic and many other properties have been examined [16–43]. The present work summarizes our study on pyridine based thorium(IV) phosphate as a new cation exchanger, which is in continuation of our earlier efforts to synthesise new and novel ion exchange materials based on polymeric species and explore its environmental applications [6–10].

Experimental

Materials

Reagents and chemicals

Thorium nitrate $Th(NO_3)_4·5H_2O$ and pyridine (C_5H_5N) were obtained from Central Drug House (India) while phosphoric acid (H_3PO_4) was a Qualigens (India) product. All other reagents and chemicals were of Analytical Reagent Grade.

Preparation of the reagent solutions

Thorium(IV) nitrate was dissolved in 1 M HNO_3 while pyridine and orthophosphoric acid solutions were prepared in demineralized water (DMW).

Synthesis of pyridine based thorium(IV) phosphate (PyThP)

A number of samples of PyThP (Table 1) were prepared by adding one volume of 0.1 M $Th(NO_3)_4·5H_2O$ solution in two volumes of (1:1) mixture of 2 M H_3PO_4 and pyridine (varying%) with constant stirring using magnetic stirrer at a 90±5°C. The resulting slurry obtained under these conditions was stirred for 4 h at this temperature, filtered off and then washed with dematerialized water (pH~7) which was free from sulphate ions. Finally, the slurry was dried at room temperature, resulting in a shiny fibrous sheet, which was cut into small pieces and converted into H^+ form by treating

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* Author for correspondence: smojumda@engmail.uwaterloo.ca, scmojumdar@yahoo.com

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Springer, Dordrecht, The Netherlands

Table 1 Synthesis of various samples of pyridine based thorium(IV) phosphate

Sample no.	Pyridine added/%	Na^+-ion exchange capacity/ meq(dry g)$^{-1}$
PyTh P-1	0	0.80
PyTh P-2	1	1.00
PyTh P-3	3	1.33
PyTh P-4	5	1.57
PyTh P-5	7	1.93
PyTh P-6	9	2.10
PyTh P-7	11	1.55
PyTh P-8	13	1.27

with 1 M HNO_3 for 24 h with occasional shaking and intermittent replacement of the supernatant liquid with 1 M HNO_3. The material thus obtained was washed with demineralized water to remove the excess of acid before drying finally, at 45°C and sieved to obtain particles of 50–70 mesh size. The maximum ion exchange capacity was observed in a sample obtained by adding 1 volume of 9% pyridine to a 1:1 v/v mixture of 2 M H_3PO_4 and 0.1 M $Th(NO_3)_4 \cdot 5H_2O$. The sample PyThP-6 was selected for further studies.

Methods

Ion exchange capacity (i.e.c.), concentration and elution behaviour

The i.e.c. for different metal ions was determined by the column process as described earlier [1]. The i.e.c. in meq/dry g is (in the parenthesis) Li^+(1.77), Na^+(2.10), K^+(2.35), Mg^{2+}(3.47), Ca^{2+}(3.83), Sr^{2+}(4.19), Ba^{2+}(4.33).

The concentration and elution behaviour were also studied by the method described earlier [1]. The concentration behaviour indicates that 1 M is the optimum concentration of $NaNO_3$ needed to elute out the H^+-ions from a 1 g column. 110 mL of 1 M $NaNO_3$ were required for a complete elution of the hydrogen ions.

pH titrations

pH titrations were performed by the Top and Pepper's [44] method.

Thermal studies

One gram samples of the material were heated at different temperatures for 1 h each in a muffle furnace, and their i.e.c. were determined by the column process after cooling them to the room temperature. Table 2 summarizes the results of this study.

TG-DTG studies

Simultaneous thermogravimetric analysis-derivative thermogravimetric analysis was carried out using PerkinElmer Pyris Diamond model. Figure 1 shows TG-DTG curve.

Instrumentation

X-ray diffraction studies were carried out on a Bruker analytical X-ray diffractometer model D8 advance, while pH measurements were performed using an Elico Model L1-10 pH meter. IR studies were carried out using the KBr disc method on a Perkin Elmer FTIR spectrometer RX-I and SEM studies were carried out on a LEO 435 VP scanning electron microscope. A PerkinElmer Instrument, Pyris Diamond model was used for TG-DTG studies, and a Heraeus Carlo Erba – 1108 analyzer was used for elemental analysis.

Results and discussion

This study highlights certain interesting features of pyridine based thorium(IV) phosphate as a new hybrid fibrous ion exchanger obtained in the form of sheet. The SEM image (Fig. 2) at a magnification of 1000x, reveals that their particle size is 10 μm.

The most important feature of this material (PyThP-6) is its improved i.e.c. (~2.0 meq/dry g) compared to the i.e.c. of generally shown by the

Table 2 Thermal stability of pyridine based thorium(IV) phosphate after heating to various temperatures for 1 h

Sample no.	Drying temp./°C	Ion exchange capacity/ meq/(dry g)$^{-1}$	Change in colour	Retention of i.e.c./%
1	45	2.10	White	100
2	100	1.46	White	69.5
3	200	0.95	Light brown	45.2
4	400	0.45	Grey	21.4
5	600	0.07	Light grey	3.33

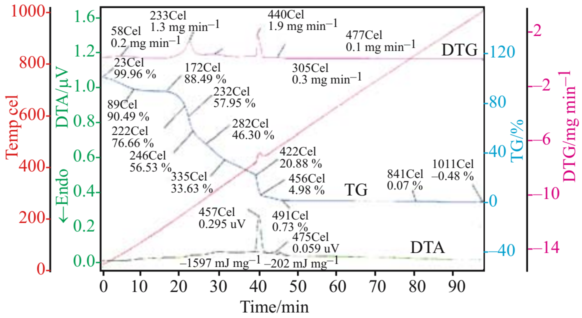

Fig. 1 TG-DTG-DTA curves of pyridine based thorium(IV) phosphate

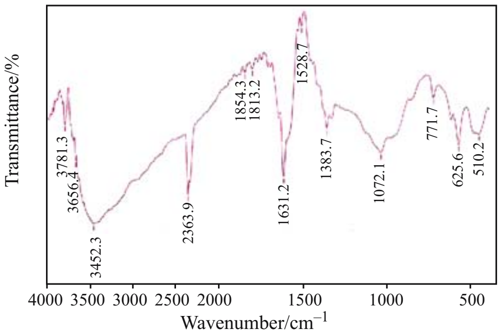

Fig. 3 IR spectrum of pyridine based thorium(IV) phosphate

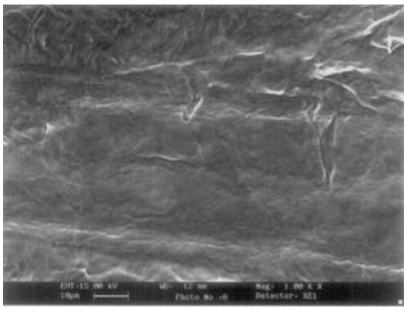

Fig. 2 SEM image of pyridine based thorium(IV) phosphate

inorganic ion exchangers. The ion exchange capacity of alkali metals and alkaline earths show the following trends: $Li^+ < Na^+ < K^+$ and $Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$. It is in the decreasing order of the hydrated ionic radii of these metal ions.

The pH titration curves, obtained under equilibrium conditions for LiOH/LiCl, NaOH/NaCl and KOH/KCl systems indicate a monofunctional exchange process, which may be due to the fact that the first ionization of phosphoric acid and arsenic acid is much faster as compared to the second and third. The pKa values of H_3PO_4 are 2.12, 7.21 and 12.30 which are comparable to the three pKa values of arsenic acid (2.25, 6.77 and 11.60).

Thermal studies (Table 2 and Fig. 1) of this material indicate retention of 69% of its i.e.c. upon heating up to 100°C. Even on heating up to 400°C, the material shows an appreciable i.e.c. of about 21%.

The TG curve (Fig. 1) shows 10.5% mass loss at 130°C that is due to the removal of external water molecules from the exchanger. Beyond this temperature, the further mass loss up to around 400°C may be attributed to the removal of organic part as well as condensation of material. The retained water molecules are slowly eliminated at 456°C at which the production of ThO_2 [45] starts. Above 456°C, the horizontal portion of the curve indicates the formation of pyrophosphate phase.

The IR spectrum (Fig. 3) of the material confirms the presence of external water molecules in addition to the OH groups, and the presence of internal metal oxides and metal hydroxide in the materials. The metal oxide and metal hydroxide bands are observed at 625.6 and 771.7 cm^{-1}. The bands at 510.2 and 1072.1 cm^{-1} indicate the presence of phosphate groups. The absorption bands at 1631.2 and 3452.3 cm^{-1} correspond to the water of crystallization. The bands at 1383.7 cm^{-1} indicate the C–N stretching. The C=N stretching was observed at 1528.7 cm^{-1} [46].

The X-ray diffraction spectrum of the material shows its amorphous nature.

Conclusions

The pyridine based thorium(IV) phosphate is a new and novel fibrous hybrid material possessing an improved ion exchange capacity compared to the parent material thorium phosphate, prepared under similar conditions. This appears to be a promising ion exchanger with higher thermal stability due to a mutual interaction of inorganic and organic parts, resulting into the chemical bonds formation between the atoms originating from both phases.

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