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PYRIDINE BASED CERIUM(IV) PHOSPHATE HYBRID FIBROUS ION EXCHANGER

Synthesis, characterization and thermal behaviour

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A new phase of the hybrid fibrous ion exchanger, pyridine based cerium(IV) phosphate (PyCeP), has been synthesized in the form of a sheet like paper by mixing ceric sulphate, phosphoric acid and pyridine in a particular ratio to get the material of the optimum ion exchange characteristics. This material has been characterized with the help of ion exchange capacity, elution and concentration and pH titrations behaviour in addition to some physicochemical studies like X-ray diffraction, IR, TG, DTG and SEM studies. The SEM study confirms the fibrous nature of the material while amorphous nature is revealed by its X- ray spectrum.

Keywords: *cerium, DTG, ion exchanger, IR, phosphate, pyridine, SEM, TG, XRD*

Introduction

Fibrous ion exchangers exhibit a high efficiency in the process of sorption from gaseous and liquid media [1–5]. Hence they have drawn the attention of researchers, particularly the environmentalists. Their main advantage has been the capability of being produced in various forms, such as staples, cloth, and non-woven materials and therefore is opening up new possibilities in technological processes. The ion exchangers based on cerium(IV) [6] and thorium(IV) [7] have been found to possess fibrous nature, as confirmed by their SEM studies. They can be used to prepare inorganic ion exchange papers or thin membranes without binder [8, 9] possessing good electrochemical behaviour [10] and suitable for chromatographic cation separations. We are engaged in these laboratories in synthesis of new and novel hybrid fibrous ion exchangers [11–20] by combining organic polymeric species like polystyrene, polyacrylonitrile, polyacrylamide, pectin, cellulose acetate with polybasic inorganic acid salts. The materials possess promising ion exchange characteristics and better stability than their inorganic counterparts. Earlier [21] we have synthesized pyridine based thorium(IV) phosphate as a hybrid fibrous ion exchanger, which has shown high selectivity for Pb(II) ions. In continuation of such a study the present paper summarizes the synthesis and characterization of cerium(IV) phosphate (PyCeP) ion exchanger as a hybrid fibrous material showing selectivity for Hg(II) ions.

Experimental

Materials

Reagents and chemicals

Ceric sulphate [$Ce(SO_4)_2{\cdot}4H_2O$] 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

0.05 M ceric sulphate was dissolved in 0.5 M H_2SO_4 while pyridine and orthophosphoric acid solutions were prepared in demineralized water (DMW).

Synthesis of pyridine based cerium(IV) phosphate (PyCeP)

A number of samples of PyCeP were prepared by adding one volume of 0.1 M $Ce(SO_4)_2{\cdot}4H_2O$ solution in two volumes of (1:1) mixture of 6 M H_3PO_4 and pyridine (varying %age), drop-wise with constant stirring using magnetic stirrer at a temperature of 70±5°C The resulting slurry obtained under these conditions was stirred for 4 h at this temperature, filtered and then washed free of sulphate ions with demineralized water (pH ~7). 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 with 1 M HNO_3 for 24 h with occa-

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sional shaking and intermittently replacing the supernatant liquid with 1 M HNO_3. The material thus obtained was then washed with demineralized water to remove the excess acid before drying finally at 45°C and sieved to obtain particles of 50–70 mesh size. The maximum ion exchange capacity was observed of a sample obtained by adding 1 volume of 5% pyridine to a 1:1 v/v mixture of 6 M H_3PO_4 and 0.05 M $Ce(SO_4)_2 \cdot 4H_2O$. This sample (PyCeP-4) was, therefore, selected for further studies. Table 1 shows the synthesis of various samples.

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 [11], the results are summarized below. The i.e.c. is shown in the parenthesis in meq/dry g. Li^+(1.63), Na^+(2.10), K^+(2.15), Mg^{2+}(3.36), Ca^{2+}(3.77), Sr^{2+}(3.90), Ba^{2+}(4.15).

The concentration and elution behaviour were also studied by the method described earlier [11]. The concentration behaviour indicates that 120 mL of 1 M $NaNO_3$ were needed to elute out almost completely the H^+ ions from 1 g column.

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

Sample No.	Pyridine added/%	Na^+-ion exchange capacity/meq(dry g)$^{-1}$
PyCeP-1	0	1.40
PyCeP-2	1	1.57
PyCeP-3	3	1.85
PyCeP-4	5	2.00
PyCeP-5	7	1.92
PyCeP-6	9	1.55
PyCeP-7	11	1.50
PyCeP-8	13	1.32

pH titrations

These titrations were performed by the Top and Pepper's [22] 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

Thermogravimetric analysis–differential thermogravimetric analysis was carried out by PerkinElmer Pyris Diamond model. Figure 2 shows the TG-DTG/DTA curves.

Instrumentation

pH measurements were performed using an Elico Model L1-10 pH meter, while X-ray diffraction studies were carried out on a Bruker analytical X-ray diffractometer model D8 advance. IR studies were performed using the KBr disc method on a PerkinElmer FTIR spectrometer RX-I and SEM studies were done with LEO 435 VP scanning electron microscope. A Universal V1 9D TA instrument was used for TG-DTG/DTA analysis. Elemental analysis was carried out on a Heraeus Carlo Erba-1108 analyzer.

Results and discussion

Inclusion of pyridine in the structure of an inorganic ion exchanger has been found to produce enhanced ion exchange properties of cerium(IV) phosphate [6]. The present study is continuation of such a study. We have explored in this paper the possibility of synthesizing pyridine based cerium(IV) phosphate as a new hybrid fibrous ion exchanger (PyCeP), which possesses a higher i.e.c. (2.0 meq/dry g) than the

Table 2 Thermal stability of pyridine based cerium(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	2.00	Yellowish	100
2	100	1.63	Yellowish	81.5
3	200	1.27	Grayish yellow	63.5
4	400	0.74	Grayish	37.0
5	600	0.09	Grayish	4.5

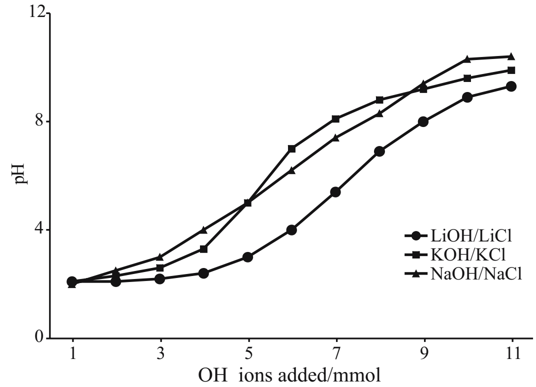

Fig. 1 Equilibrium pH titration curves of pyridine based cerium(IV) phosphate

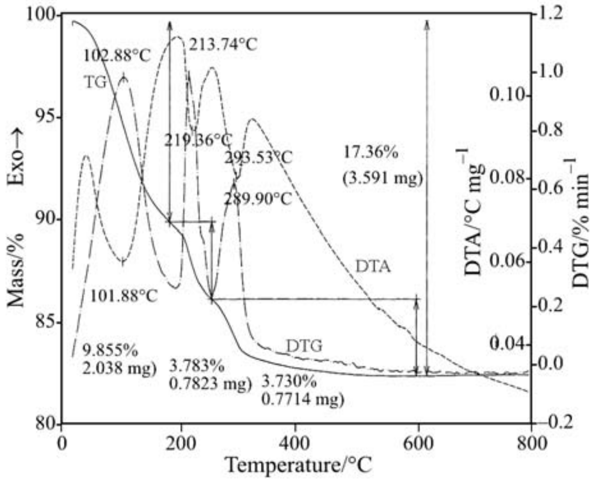

Fig. 2 TG-DTG/DTA curve of pyridine based cerium(IV) phosphate

fibrous cerium(IV) phosphate (1.4 meq/dry g) itself as shown in Table 1. It may be due to the enhanced interlayer distances in the material as a result of intercalation of a polar pyridine molecule into the layers of cerium(IV) phosphate matrix. The material is obtained in the form of a filter paper sheet, opening the possibilities of its use as a binder free membrane. The SEM of the material (Fig. 3) at a magnification of 1000×, reveals their particle size as 10 μm and fibrous nature. These ion exchange papers compare favorably with those of cerium(IV) based materials with regard to their stability with strong reducing agent. This property plays a vital role in chromatographic separations where reducing agents are often used as eluents or spot test reagents.

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, as usual. The pH titration curves (Fig. 1) 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 is much faster as compared to the second and third. The first, second and third pKa values of H_3PO_4 are 2.12, 7.21 and 12.30, respectively.

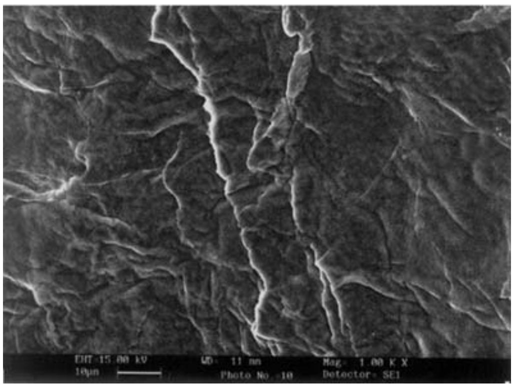

Fig. 3 Scanning electron micrograph of pyridine based cerium(IV) phosphate

Thermal studies (Table 2) of this material indicate that on heating up to 100°C, it shows retention of 81.5% of its i.e.c. Even heating up to 400°C, material shows an appreciable retention i.e.c. (37%) proving that the material has an appreciable thermal stability.

The TG curve (Fig. 2) shows 9.8% mass loss up to 102°C, which is due to the removal of external water molecules from the exchanger. On further heating up to 260°C, a mass loss of 3.8% correspond to the removal of strongly coordinated water molecules along with the elimination of organic from the framework of the material. Beyond this temperature condensation might have also started, which is reflected in DTA curve of the material, having an endo effect at 293°C. The condensation process continues up to 400°C, where the mass becomes almost constant. It also involves the formation of CeO_2 at 450°C [23]. Finally a mass loss between 600 and 800°C, represents a kinetic un-stability of the decomposition products.

Thermal effects are due to both removal of the part of pyridine and removal of strongly coordinated water molecules. In this temperature region, the statistically relevant decrease of the percentage retention of i.e.c. occurs (Table 2). Thus, the data suggests that decrease of i.e.c. of material tested is interrelated with the volatilization of both (pyridine and coordinated water molecules) from the structure of this type of ion exchanger.

The IR studies (Fig. 4) confirm the presence of metal oxygen and metal hydroxide bonds in addition to the external water molecules and phosphate groups in the material. Bands at 536.0 and 1098.4 cm^{-1} are

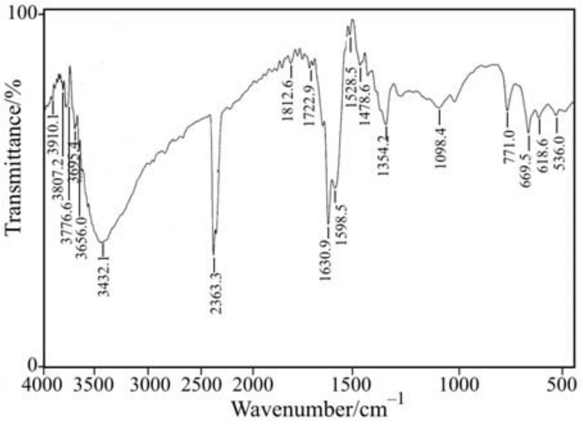

Fig. 4 Infrared spectrum of pyridine based cerium(IV) phosphate

due to the phosphate groups. The metal oxygen and metal hydroxide bands are observed at 618.0, 771.0 and 669.5 cm^{-1} while bands at 1598.5 and 1630.9 cm^{-1} represent the external water molecules in addition to its usual range at 3432.1 cm^{-1}. The bands at 1354.2 cm^{-1} indicate the C–N stretching. The C=N stretching was observed at 1478.6 and 1528.5 cm^{-1}. The X-ray diffraction pattern of the material shows its amorphous nature.

Conclusions

The addition of pyridine to cerium(IV) phosphate enhances the ion exchange capacity of parent material cerium(IV) phosphate, prepared under similar conditions. This appears to be a promising ion exchanger with good thermal stability due to a mutual interaction of inorganic and organic parts, resulting into the chemical bonds formation between the atoms originated from both phases.

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References

1 M. P. Zverew, Chemosorptive Fibres, Khimiya, Moscow 1981, p. 191.
2 L. A. Volf, Fibres of Specific Properties, Khimiya, Moscow 1980, p. 240.
3 I. N. Ermolenbo, E. D. Bugalov, I. P. Lyublinder and S. R. Dogetev, Nanka'I Tebhniba, Minsk 1975, p. 215.
4 L. A.Volf, Chem. Ind. (Bulgaria), 3 (1983) 134.
5 T. Miyamatsu, Sen' Gabbaishi, 39 (1983) 53.
6 G. Alberti, U. Costantino, F. Di Greogorio, P. Galli and E. Torracca, J. Inorg. Nucl. Chem., 30 (1968) 295.
7 G. Alberti and U. Costantino, J. Chromatogr., 50 (1970) 482.
8 G. Alberti, M.A. Masuci and E. Torraca, J. Chromatogr., 30 (1967) 379.
9 A. K. De and K. Chowdhury, Sep. Sci., 10 (1975) 39.
10 G. Alberti and R. Passino (Eds), Pontificiae Academiae Scientiarum, Scripta Varia, 629 (1976).
11 K. G. Varshney, N. Tayal and U. Gupta, Colloids Surf. A Physicochem. Eng. Asp., 145 (1998) 71.
12 K. G. Varshney, N. Tayal, A. A. Khan and R. Niwas, Colloids Surf. A Physicochem. Eng. Asp., 181 (2001) 123.
13 K. G. Varshney and N. Tayal, Langmuir, 17 (2001) 2589.
14 K. G. Varshney, P. Gupta and N. Tayal, Indian J. Chem., 42 A (2003) 89.
15 K. G. Varshney, Solid State Phenomena, 90 (2003) 445.
16 K. G. Varshney, N. Tayal, P. Gupta, A. Agrawal and M. Drabik, Ind. J. Chem., 43 A (2004) 2589.
17 K. G. Varshney, A. Agrawal and S. C. Mojumdar, J. Therm. Anal. Cal., 81 (2005) 183.
18 S.C. Mojumdar, K. G. Varshney, P. Gupta and A. Agrawal, Res. J. Chem. Env., 10 (2006) 85.
19 K. G. Varshney, M. Drabik and A. Agrawal, Indian J. Chem., 45 (A) (2006) 2045.
20 S. C. Mojumdar, K. G. Varshney and A. Agrawal, Res. J. Chem. Env., 10 (2006) 89.
21 K. G. Varshney, A. Agrawal and S. C. Mojumdar, J. Therm. Anal. Cal., 90 (2007) .
22 N. E. Topp and K. W. Pepper, J. Chem. Soc., (1949) 3299.
23 C. Duval, 'Inorganic Thermogravimetric Analysis', Elsevier, Amsterdam 1953, p. 492.

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