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Synthesis, characterization and analytical applications of N-dodecyl pyridinium chloride-cerium (IV) phosphate fibrous ion exchanger: selective for Hg(II) and its binary separations

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ABSTRACT

An intercalated hybrid fibrous ion exchanger has been synthesized by incorporating N-dodecyl pyridinium chloride with the inorganic cation exchanger, cerium (IV) phosphate. The synthesized, N-dodecyl pyridinium chloride-cerium (IV) phosphate (DPC-CeP) cation exchanger was characterized using X-ray diffraction studies, SEM, thermogravimeric (and differential thermogravimetric) analysis and elemental analysis. The ion-exchange characteristics (ion-exchange capacity, elution and concentration behaviour) and thermal stability were also determined by usual chemical method. The adsorption studies for alkaline earths and heavy metal ions on the synthesized material were also performed in different acidic media. DPC-CeP has been found to be selective for Hg(II) ions. Hence, some binary separations of Hg(II) ions from the mixture containing other metal ions have been carried out on its column, exploring the potential role of the synthesized material in environmental studies and water treatment.

Keywords: Intercalated fibrous ion exchanger; Cerium (IV) phosphate; N-dodecyl pyridinium chloride; Adsorption; Hg-selective; Environmental studies

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1. Introduction

Hybrid fibrous ion-exchange materials [1–3] have received attention owing to its exhibition of outstanding chemical, mechanical and thermal stability, as well as selectivity towards metal ions. The amalgamation of organic species and inorganic ion-exchange material overcome the shortcomings of organic and inorganic ion exchangers. The earlier studies have demonstrated that the introduction of organic species into an inorganic ion-exchange material enhances reproducibility in ion-exchange behaviour and chemical stability to some extent [4,5]. These hybrid ion-exchange materials have the added advantages of both of organic and inorganic ion exchangers. They have shown good chemical stability conversant to the organic resins and good thermal stability, a well-known characteristic of inorganic ion exchanger. These materials are capable of controlling the environmental pollution as they exhibit good efficiency in

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the process of sorption from gaseous and liquid media. A large number of such materials have been synthesized by incorporating organic monomers/polymers into inorganic ion exchangers and have shown the promising ion-exchange characteristics [6–8].

Surfactant reduces the interfacial tensions [9] between the solid and liquid phases and plays significant role in adsorption of metal ion on the solid surfaces. This property of surfactants has led to the studies related to their use in the synthesis of ion-exchange materials and for the removal of metal ions through their adsorption. The previous studies have shown [7,10–18] the ability of surfactant to increase the ion-exchange capacities, fast ion-exchange process and enhancement in the selectivity and adsorption characteristics of ion exchangers for various metal ions. The addition of TX-100 [13]; sodium dodecyl sulphate [14]; sodium dodecyl benzene sulphonate [15] and sodium bis(2-ethylhexyl) sulphosuccinate [17] to the cerium (IV) phosphate not only increased the cation-exchange capacity, but also increased the thermal and mechanical stability. The metal adsorbing tendency of the surfactant-based cation exchangers was also found to be dependent on the nature of surfactant (e.g. SDS and SDBS removed Pb^{2+} ions, TX-100; Hg^{2+} and AOT; Cu^{2+}, Pb^{2+}, Cd^{2+}, Zn^{2+}, Hg^{2+}). Thus, the change in surfactant changes the mechanical and thermal stability of the fibrous material and also their ion-exchange capacity and metal ion selectivity. Therefore, in an attempt to obtain material with better ion-exchange characteristics and adsorption ability, N-dodecyl pyridinium chloride-cerium (IV) phosphate (DPC-CeP) was synthesized and studied. The following paper discusses the synthesis of DPC-CeP, its characterization and ion-exchange behaviour. The synthesized material has been found to be selective for Hg(II) ions. Mercury is among the most toxic heavy metals which enter the environment through various industries like paper and pulp industry, chlor-alkali plants, molding processes, paints and pharmaceuticals. The environment pollution by Hg (II) ions is serious because it is capable of entering blood streams, the digestive systems or lungs. Vapours of Hg or its ions are toxic. Some mercury compounds are highly volatile or are insoluble in water and cause the potential hazards for the human. Traces of mercury have been identified as deleterious to aquatic ecosystem and human health. The synthesized material can be used for the separation of Hg(II) ions from the other ions.

2. Experimental

2.1. Reagents and chemicals

Ceric sulphate ($Ce(SO_4)_2.4H_2O$) was obtained from CDH (India) while N-dodecyl pyridinium chloride and phosphoric acid (H_3PO_4) were obtained from Merck-Schuchardt (Germany) and Qualigens (India), respectively. All other reagents and chemicals used during the experiments were of Anal R grade.

2.2. Instruments/apparatus used

The X-ray diffraction (XRD) patterns were recorded on a Philips Analytical X-ray B. V. diffractometer type PW 170 BV equipped with CuKα ($\lambda = 1.54056$ Å) radiation source operated in the $\theta/2\theta$ mode in the 10–90° (2θ) range with the step-scan of $2\theta = 0.001°$. For thermogravimeric (and differential thermogravimetric) analysis (TGA/DTA)/DTG studies, Perkin Elmer Pyris Diamond model was used. Elemental analysis (C, H, N) was performed by Heraeus Carlo Erba-1,108 analyzer while Cerium and phosphorus determination was carried out by Inductively coupled plasma atom emission spectrometer model No. 8440. LEO 435 VP scanning electron microscope was used for scanning electron microscopy (SEM) study.

2.3. Preparation of the reagent solutions

Solution of ceric sulphate was prepared in 0.50 M H_2SO_4. The solutions of N-dodecyl pyridinium chloride and phosphoric acid (6.0 M) were prepared in demineralized water.

2.4. Synthesis of the ion-exchange material

Various samples of DPC-CeP were prepared by adding one volume of 0.05 M ceric sulphate solution to two volumes of a (1:1) mixture of 6.0 M H_3PO_4 and DPC solutions drop-wise with constant stirring using a magnetic stirrer at temperature 60 ± 5˚C. The resulting slurry was stirred for 3½ h at this temperature, filtered and then washed with demineralized water till pH of the washings reached ~4. The obtained material was dried at room temperature and gave sheet-like product. The sheet was cut into small pieces and kept in 1.0 M HNO_3 solution for 24 h to charge them into H^+-form. After converting the material into H^+-form, it was washed with demineralized water. The material was then dried at 45˚C and sieved to obtain particles of size 50–70 mesh. Table 1 provides the values of the

Table 1
Samples of DPC-CeP, their compositions and ion exchange capacity

Sample no.	Concentration of DPC used	Na^+-ion exchange capacity (meq/dry g)
Sample-1	0	1.30
Sample-2	0.00001 M	2.50
Sample-3	0.0001 M	3.15
Sample-4	0.001 M	2.75

ion-exchange capacity obtained for the different samples prepared by adding different amounts of DPC. Sample-3 possessed the highest values of ion exchange-capacity, and therefore, was selected for further studies.

Cerium (IV) phosphate was synthesized under the similar conditions, by adding one volume of 0.05 M ceric sulphate solution to one volume of 6.0 M H_3PO_4 drop-wise with constant stirring using a magnetic stirrer at 60 ± 5˚C. The resulting slurry was treated further as described above to obtain 50–70 mesh-sized particles.

2.5. Determination of ion-exchange capacity (IEC)

The ion-exchange capacity of the samples was determined using the column process by taking 1.0 g of the material (in H^+-form) in a glass burette of internal diameter ~1 cm, fitted with glass wool at its bottom. 250 mL of 1.0 M $NaNO_3$ solution was used as eluant, maintaining a very slow flow rate (~0.5 mL min^{-1}). The effluent was titrated against a standardized alkali solution to determine the total amount of released H^+-ions.

2.6. Concentration behaviour

The extent of elution of H^+ ions was found to depend upon the concentration of the eluent used. Hence, a fixed volume (250 mL) of the $NaNO_3$ solution of varying concentrations was passed through the column containing 1.0 g of the ion exchanger. The effluent was collected and titrated against standardized alkali solution for the H^+-ions eluted out.

2.7. Elution behaviour

A similar column (as above) containing 1.0 g cation exchanger was eluted with 1.0 M $NaNO_3$ solution in different 10 mL fractions with a flow rate as described as above.

2.8. Thermal stability

Several 1.0 g samples of the materials (CeP and DPC-CeP) were taken and kept in a muffle furnace to heat them at different temperatures namely; 45, 100, 200, 300 and 400˚C for 1 h. The samples were then cooled to room temperature and their ion-exchange capacity was determined by the usual column process.

2.9. Adsorption studies

200 mg of the cation exchanger in H^+ -form was added to a mixture containing 18 mL of the acid solution and 2 mL of the metal ion solution. The mixture was kept for 24 h, with shaking intermittently to achieve equilibrium. The amounts of the metal ions in the solution before and after achieving the equilibrium were determined by the EDTA titrations and the distribution coefficients (K_d) were calculated using the following Eq. (1):

$$K_d = \frac{I - F}{F}\frac{V}{M}\left(\mathrm{mL\,g^{-1}}\right) \quad (1)$$

where I and F are the initial and final amount of the metal ions in the solution phase, V is the volume (mL) of the solution and M is the amount (g) of the cation exchanger taken.

2.10. Binary separations achieved

Several binary separations of the metal ions were carried out using a column with internal diameter ~0.6 cm containing 2.0 g of the ion-exchange material. The column was washed thoroughly with demineralized water and the mixture to be separated was loaded onto it, maintaining a flow rate of ~2–3 drops min^{-1}. The separation was achieved by passing a suitable solvent through the column as eluant and the metal ions in the effluent were determined quantitatively by EDTA titrations.

3. Results and discussion

In the preliminary experiment, it was observed that the addition of DPC increased the ion-exchange capacity of cerium (IV) phosphate for the exchange of Na^+ ions. The values of ion-exchange capacity for cerium (IV) phosphate were 1.3 meq/dry g, but, when 1.0×10^{-4} moles of DPC was added to it, the ion-exchange capacity value increased to 3.15 meq/dry g (Table 1). Table 2 summarizes the ion-exchange capacity of the various reported hybrid fibrous ion-exchange materials including the surfactant-based cation exchangers. The addition of surfactants increases the porosity in the material and also reduces the interfacial tensions between the liquid and solid phases. The newly synthesized DPC-CeP possesses higher ion-exchange capacity as indicated by the values given in the table. This observed increase in the values of ion-exchange capacity is may be contributed by many factors including the increase in the interlayer distance between the layers of cerium (IV) phosphate by the surfactant molecules. The increase in distance among the layers of the fibrous material increases the porosity in the material and exposes more surface area for the interaction with the mobile phase, thereby, increases the number of ion-exchange sites. Additionally, the surfactant molecules reduce the surface tension and increases the wetting and spreading tendency of the liquid phase with the stationary phase DPC-CeP. The liquid phase wets the material and penetrates into the fine pores of the ion-exchange material. Thus, the surfactant molecules facilitate better opportunity for the exchange of ions between the liquid phase and solid phase. As a result, the exchanging rate of ions becomes fast and the value of ion-exchange rate is increased. The order of the ion-exchange capacity of DPC-CeP followed

Table 3
Ion Exchange capacity of DPC-CeP for different metal ions

Metal ion solutions	Ion exchange capacity (meq/dry g)
LiCl	2.75
$NaNO_3$	3.00
KCl	3.15
$MgCl_2$	2.55
$Ca(NO_3)_2$	3.20
$SrCl_2$	3.35
$BaCl_2$	3.45

Fig. 1. SEM image of DPC-CeP.

Table 2
Ion exchange capacity of DPC-CeP and other hybrid fibrous materials

S. no.	Name of the materials	Ion exchange capacity (meq/dry g)	Reference No.
1.	N-dodecyl pyridinium chloride Ce(IV) phosphate	3.15	Present work
2.	Acrylonitrile Ce(IV) phosphate	2.86	[2]
3.	Acryl amide Ce(IV) phosphate	2.60	[3]
4.	Acryl amide Th(IV) phosphate	2.0	[4]
5.	Pectin Ce(IV) phosphate	1.78	[5]
6.	Pectin Th(IV) phosphate	2.15	[5]
7.	Cellulose acetate Th(IV) phosphate	1.70	[6]
8.	*n*-Butyl acetate Ce(IV) phosphate	2.25	[7]
9.	TX-100-SnP	2.75	[12]
10.	TX-100-CeP	3.00	[13]
11.	SDS-CeP	2.92	[14]
12.	SDBS-CeP	2.17	[15]
13.	AOT-SnP	2.40	[16]
14.	AOT-CeP	3.02	[17]
15.	SDBS-SnP	2.20	[18]

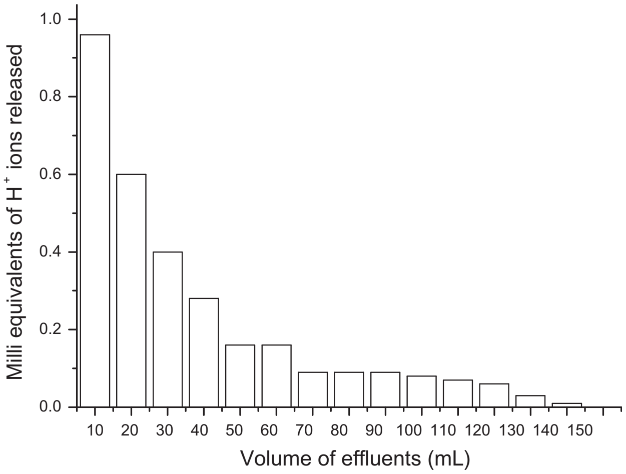

Fig. 2. Histograms showing the elution behaviour of DPC-CeP.

Table 4
Variation of ion exchange capacity of DPC-CeP with eluant concentrations

Concentration of $NaNO_3$ (M)	Ion exchange capacity (meq/dry g)
0.2	0.95
0.4	1.25
0.6	1.95
0.8	2.75
1.0	3.15
1.2	2.90

$Li^+ < Na^+ < K^+$ for the alkali metals and $Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$ for the alkaline earth metals (Table 3). This order is in accordance with the decreasing order of the hydrated ionic radii of these metal ions. The material can also be obtained in the form of fibrous sheet. SEM study demonstrates the fibrous nature of the material, as presented in Fig. 1.

The elution behaviour reveals that the ion-exchange process is quite fast and almost all the H^+ ions are eluted out in the first 150 mL of the effluent from a column containing 1.0 g of the ion exchanger (Fig. 2). Similarly, the optimum concentration of the eluant was found to be 1.0 M (Table 4) for the complete removal of H^+ ions from the above column.

The study on thermal stability reveals some interesting results. The DPC-CeP appears to be thermally more stable than cerium (IV) phosphate (CeP). Compare with CeP, the stability of DPC-CeP is higher on heating it up to 100˚C in which DPC-CeP retains 93.6% of its initial value of ion-exchange capacity. The material retains 58.7% of its ion-exchange capacity on heating up to 200˚C (Table 5) contrary to the CeP which retains 61.8% and only 13.1% of its initial values of ion-exchange capacity on heating to 100 and 200˚C, respectively (Table 5).

The thermograms shown in Fig. 3 reveal two-step mass losses. The losses in 5.55 and 3.94% of the original mass occur on heating up to 147˚C with an endo effect at 68˚C. The loss in mass is associated with the removal of external water molecules as well as with the partial removal of DPC. Further losses of 5.12 and 5.41% (of its initial mass) occur at 323˚C (with endo effects at 157˚C) and at 312˚C representing the removal of the remaining part of DPC. At this temperature, condensation might have also started with the removal of strongly co-ordinated water molecules. Beyond 323˚C, the weight remains almost constant on heating up to 789˚C with the formation of CeO_2 at 450˚C [19]. The studies on the variation in ion-exchange capacity on heating to different temperatures (up to 100˚C) shows little influence on the removal of external water molecules and also on the values of ion-exchange capacity (Table 5). A decrease in ion-exchange capacity between 200 and 300˚C may be due

Table 5
Thermal stability of CeP and DPC-CeP after heating to different temperatures for 1 h

	Na^+-ion exchange capacity (meq/dry g)		Physical appearance		% Retention of ion exchange capacity	
Drying temperature (˚C)	CeP	DPC-CeP	CeP	DPC-CeP	CeP	DPC-CeP
45	1.30	3.15	Yellow	Yellow	100	100
100	0.84	2.95	Bright yellow	Yellow	61.8	93.6
200	0.17	1.85		Bright yellow	13.1	58.7
300	0.07	1.50	Light yellow		5.15	47.6
400	0.03	0.75	Cream yellow	Bright yellow	2.20	23.8
			Cream	Light yellow		

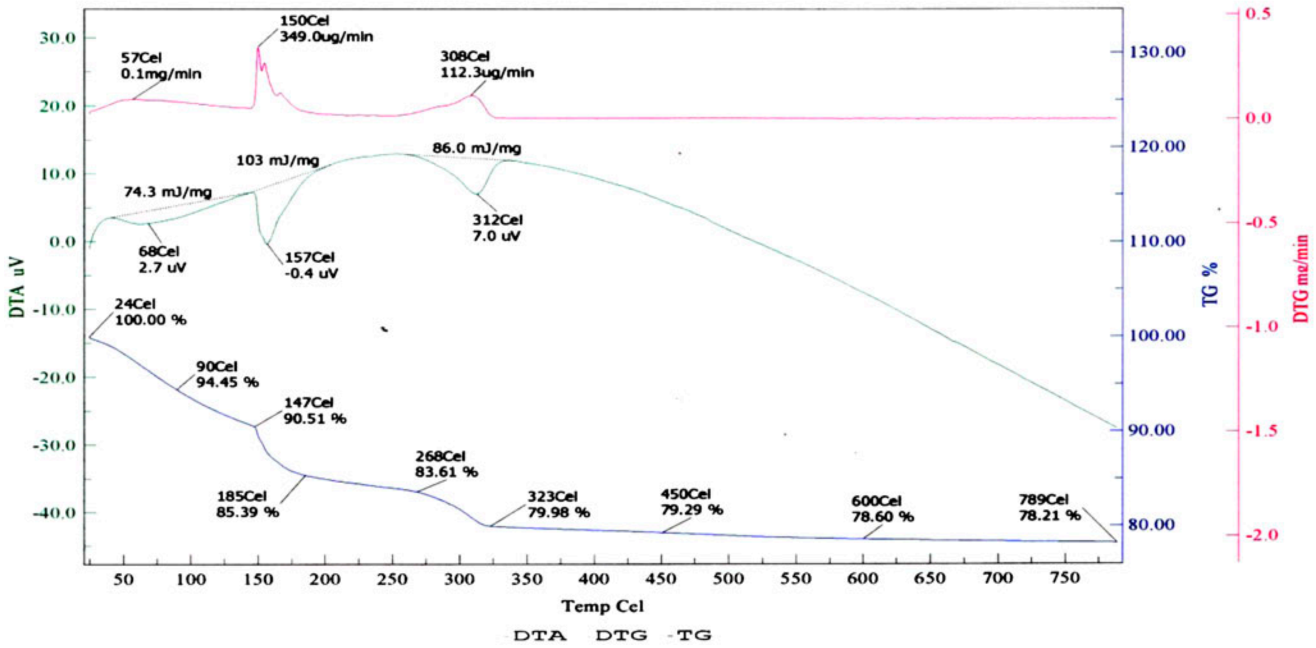

Fig. 3. TGA/DTA curves of DPC-CeP.

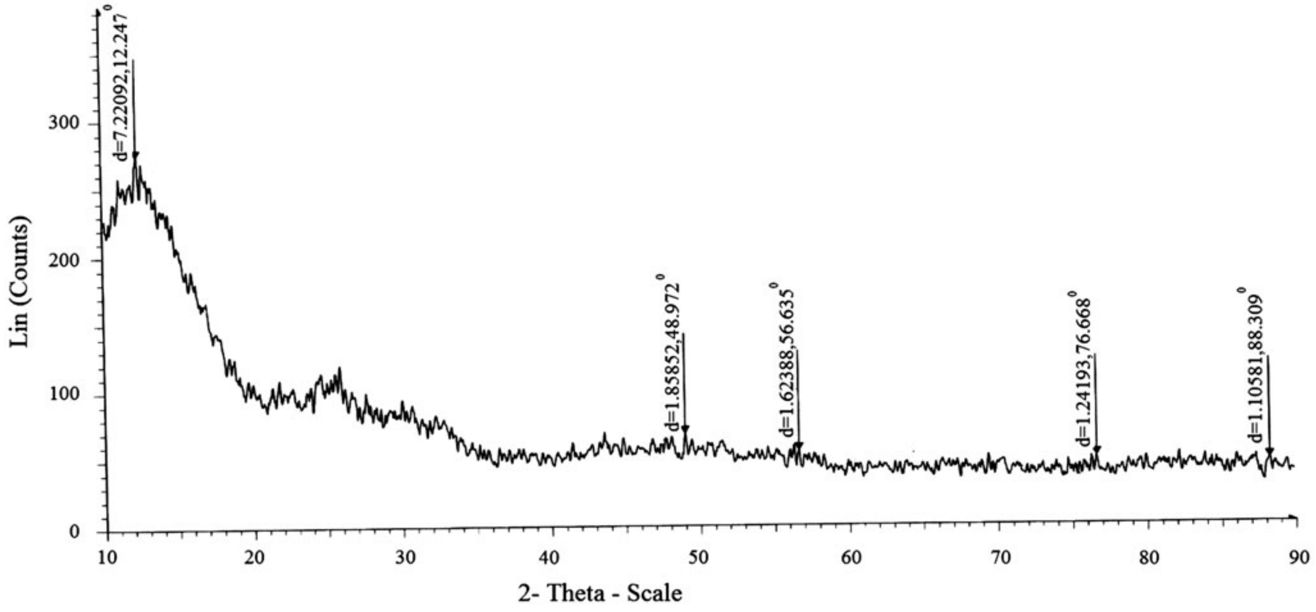

Fig. 4. X-ray diffraction patterns of DPC-CeP.

to the removal of DPC and strongly co-ordinated water molecules. Beyond 300°C, a sharp decrease in ion-exchange capacity is observed which may occur due to both, the formation CeO_2 and disruption of intercalated fibrous structure [19]. The electron diffraction studies were carried out on a limited amount of synthesized materials. The diffraction patterns obtained on the materials are displayed in Fig. 4 did not give any well-defined peak within the studied range of 2θ values from 10° to 90°. Thus, the XRD patterns indicate that the material is not crystalline; rather it is in the amorphous form (Joint Committee

Table 6
K_d values of some metal ions on DPC-CeP in DMW and acid media

		HCl			HNO_3			$HClO_4$		
Metal ions	DMW	0.01 M	0.1 M	1.0 M	0.01 M	0.1 M	1.0 M	0.01 M	0.1 M	1.0 M
Mg(II)	683.33	571.43	487.50	422.22	571.43	487.50	370.00	487.50	422.22	370.00
Ca(II)	542.86	542.86	462.50	400.00	462.50	400.00	309.09	462.50	350.00	275.00
Sr(II)	800.00	542.86	462.50	400.00	650.00	462.50	350.00	650.00	462.50	275.00
Ba(II)	975.00	760.00	616.67	514.29	975.00	760.00	616.67	760.00	514.29	437.50
Fe(III)	1000.0	780.00	528.57	450.00	633.33	528.57	388.89	450.00	388.89	300.00
Mn(II)	820.00	666.67	557.14	475.00	666.67	475.00	411.11	820.00	475.00	411.11
Ni(II)	1050.0	557.14	475.00	411.11	475.00	411.11	360.00	666.67	557.14	318.18
Co(II)	975.00	760.00	514.29	437.50	616.67	514.29	377.78	616.67	437.50	377.78
Cu(II)	1075.0	683.33	571.43	487.50	487.50	422.22	370.00	840.00	683.33	487.50
Cd(II)	2200.0	2200.0	1433.3	1050.0	1433.3	820.00	666.67	1050.0	820.00	666.67
Hg(II)	TA	4600.0	2250.0	1466.7	1466.7	1075.0	683.33	1075.0	1075.0	571.43
Pb(II)	1400.0	800.0	542.86	462.50	650.00	350.00	275.00	462.50	309.09	246.15

Table 7
Binary separations of metal ions achieved on DPC-CeP columns

S. no.	Separation		Amount loaded (μ g)		Amount found (μ g)		Error (%)		Eluant used	Volume of eluant used (ml)
	M_1	M_2	M_1	M_2	M_1	M_2	M_1	M_2		
1.	Pb(II)	Hg(II)	33,152	32094.4	32415.3	31411.5	−2.2	−2.1	Pb: 1.0 M HCl	50
									Hg: 1.0 M NH_4Cl + 1.0 M HCl	60
2.	Ni(II)	Hg(II)	9390.9	32094.4	9390.9	31411.5	0	−2.1	Ni: 0.1 M $HClO_4$	50
									Hg: 1.0 M NH_4Cl + 1.0 M HCl	40
3.	Ca(II)	Hg(II)	6412.48	32094.4	6269.98	30728.7	−2.2	−4.2	Ca: 0.1 M HNO_3	40
									Hg: 1.0 M NH_4Cl + 1.0 M HCl	50

on Powder Diffraction Studies File No. 4-0783). The elemental analysis of the sample of DPC-CeP gave the composition of different constituents as 0.3% carbon; 0.23% hydrogen; 0.12% nitrogen; 32.59% cerium; 24.11% phosphorus and remaining 42.65% oxygen.

The adsorption studies on the synthesized material for some alkaline earth metal ions and heavy metal ions have been performed in the different acidic media (Table 6). The presence of N-dodecyl pyridinium chloride in the matrix of cerium (IV) phosphate increased the values of ion-exchange capacity and also increased the adsorption ability for some heavy metal ions. The adsorption behaviour of DPC-CeP shows that the material is highly selective for Hg(II) ions, which is one of the polluting ionic species. Its high selectivity towards Hg(II) ions provides an opportunity in analytical and environmental chemistry for the separation and removal of Hg(II) ions from the wastewater or from the mixture of other ions. The potential use of DPC-CeP in environmental studies has been demonstrated by achieving some binary separations of Hg(II) ions from the mixture containing Mg(II)-Hg(II) ions, Ca(II)-Hg(II) ions, Sr (II)-Hg(II) ions and Pb(II)-Hg(II) ions using the columns containing DPC-CeP. The results of separations are summarized in Table 7.

4. Conclusions

The cation exchanger, DPC-CeP, synthesized by incorporating DPC into the matrix of cerium (IV) phosphate. It was characterized by physical and chemical methods. The ion-exchange capacity of DPC-CeP is increased to 3.15 meq/g for Na^+ ions, compared with 1.30 meq/g for CeP. DPC-CeP is thermally more stable than cerium (IV) phosphate. The ion-exchange capacity decreased with the rise in temperature, but was found still having higher ion-exchange capacity than CeP. It possesses higher adsorption ability for heavy metal ions. DPC-CeP is selective for Hg(II) ions and the experiment demonstrated that the material can be used for binary separations of Hg(II) ions from the mixtures containing Mg(II)-Hg(II) ions, Ca(II)-Hg (II) ions, Sr (II)-Hg(II) ions and Pb(II)-Hg(II) ions. DPC-CeP has potential to be developed into filtering fibres and membranes. The high selectivity of the DPC-CeP towards Hg(II) ions can be exploited for its potential use in environmental pollution control during water treatment.

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