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Development of composite ion-exchange adsorbent for pollutants removal from environmental wastes

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ABSTRACT

A composite cation exchange material "n-butylacetatezirconium(IV) iodate" was prepared under different experimental conditions. Ion-exchange material synthesized at pH 0.8 shows an ion-exchange capacity of 1.8 meq g−¹ for Na+ ions. The material has been characterized on the basis of X-ray, TGA, FTIR, SEM, AFM and Raman studies. Ion-exchange capacity, pH titration, elution behavior and distribution studies were also carried out to determine the preliminary ion-exchange properties of the material. The effect of temperature on the ion-exchange capacity of the material has also been studied. The sorption behavior towards metal ions was studied in ethyl acetate, DMF, DMSO and H_3PO_4 systems. A few quantitative binary separations of metal ions on the column, packed with this material has been achieved to establish its usefulness as ion-exchanger. The practical utility of n-butylacetatezirconium(IV) iodate cation exchanger has been established to recover toxic metals from environmental wastes.

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1. Introduction

In the field of ion-exchange material, hybrid ion-exchange materials play an important role in many environmental and industrial applications. A number of organic and inorganic ion-exchange materials have been synthesized. However, there are certain drawbacks associated with pure organic and inorganic ion-exchange materials, e.g. low ion-exchange capacity, degradation of ionexchange properties at higher temperature and ionizing radiations. Moreover, in case of inorganic ion-exchanger it is very difficult to obtain granular form of material. Hence, in order to overcome all these barriers, hybrid ion-exchangers with conjugated properties of polymer and intrinsic properties of inorganic exchanger have been introduced. The hybrid ion-exchanger can also be used as a sorbent [\[1\]](#page-7-0) ion-exchanger [\[2–4\], a](#page-7-0)s catalyst [\[5\], i](#page-7-0)on selective electrode [\[6–9\]](#page-7-0) and in the host guest chemistry [\[10,11\]](#page-7-0) for separation of radioactive isotopes and also finds a large number of applications in pollution control and water treatment [\[12,13\]. T](#page-7-0)here is a continuous need to investigate new hybrid ion-exchangers which are capable of removing toxic substances from aqueous effluent [\[14\].](#page-7-0) The composite ion-exchangers are being investigated due to their intercalation properties [\[15–19\]. Z](#page-7-0)irconium based hybrid

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ion-exchanger have drawn much attention because of their better ion-exchange characteristics and other chemical properties, applicability in the field of ion-exchange membrane and solid state electrochemistry. The present paper describes the synthesis and ion-exchange properties of n -butylacetatezirconium(IV) iodate cation exchanger with better chemical and thermal stability.

2. Experimental

2.1. Materials and methods

Zirconium (IV) oxychloride [Loba Cheme Pvt. Ltd.], Potassium iodate [Central Drug House (P) Ltd. n-butylacetate (Merek, Indian limited)] and all other reagents used were of analytical grade.

2.2. Apparatus

Spectronic 20-D (USA) spectrometer, Digital pH meter Elico (EL-10, India), FTIR spectrophotometer from Perkin Elmer (1730, USA), Thermogravimetric Analysis/Differential Thermal Analysis (TGA/DTA) analysis by DTG – 60 H; C305743 00134 (Schimadzu), an X'Pert PRO (PW-3040/60 Netherlands, Holland) for X-ray diffraction, scanning electron microscope (SEM; LEO, 435 VF) of different magnifications. Shaker cum incubator (MSW-275, India), muffle furnace for the study of heating effect.

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A: Zirconium (IV)oxychloride, B: potassium iodate, C: n-butylacetate, IEC: ion-exchange capacity.

2.3. Synthesis of n-butylacetatezirconium(IV) iodate cation exchanger

The n-butylacetatezirconium(IV) iodate cation exchanger was prepared by using the following method. Nine different samples were prepared under varying concentration of reagents mixing volume ratio, concentration, pH and temperature as described in Table 1. The sample S-5 was selected on the basis of highest ion-exchange capacity. The composite material (sample S-5) was prepared by adding a mixture of aqueous solutions of 0.2 M zirconium (IV) oxychloride and 0.4 M potassium iodate into 10% solution of n-butyl acetate at a flow rate of 1 mL min−¹ with continuous stirring. The pH of solution was adjusted by adding the diluted solution of ammonia or nitric acid. The resulting white precipitate, so formed was kept in mother liquor for 24 h. The supernatant liquid was removed and the precipitate was filtered under suction. The excess acid was removed by washing with demineralized water and dried in an oven at 50 ± 2 °C. The dried material was grounded into small granules, sieved and converted into H⁺ form by treating with 1.0 M nitric acid solution for 24 h. The material obtained was washed with demineralized water to remove excess acid and finally dried in an oven at 50 ± 2 °C.

2.4. Ion-exchange capacity

For determination of ion-exchange capacity, one gram of the exchanger in H^+ form was taken into a glass column (i.d. 0.5 cm) plugged with glass wool at the bottom. The length of the bed was approximately 1.5 cm in height. 0.1 M alkaline earth metal nitrate solutions were used to elute H^+ ions from the exchanger. The flow rate of eluent was kept at 0.5 mLmin⁻¹. The H⁺ ions content of the effluent was then determined by titrating against a standard solution of sodium hydroxide.

2.5. pH titration

In order to determine the nature of the ionogenic group of n butylacetatezirconium(IV) iodate cation exchanger, pH titrations study was done by using Topp and Pepper method [\[20\]. 0](#page-7-0).5 g of the exchanger in H⁺ form was taken in each of several 50 mL conical flasks followed by the addition of equimolar solutions of alkali metal chlorides and their corresponding hydroxides as NaCl–NaOH, KCl–KOH systems. The final volume was adjusted to 50 mL to maintain the ionic strength.

2.6. Effect of eluent concentration

A fixed volume (250 mL) of varying concentrations of sodium nitrate solutions were used for complete elution of H⁺ ions from the column containing 0.5 g of the exchanger in H^+ form. The effluent was titrated against the standard sodium hydroxide.

2.7. Elution behavior

0.5 g of exchanger in H^+ form was eluted with 1.0 M NaNO₃ solution. The effluent was collected in 10.0 mL fraction at a flow rate (0.5 mL min−1). Each fraction of 10.0 mL was titrated against a standard solution of sodium hydroxide.

2.8. FTIR studies

The FTIR study of n-butylacetatezirconium(IV) iodate cation exchanger sample was performed by KBr disc method, the exchanger $(H^+$ form) was thoroughly mixed with KBr and finely powdered. A transparent disc was formed by applying a pressure of 80,000 psi in a moisture free atmosphere. IR absorption spectra were recorded in the region 400–4000 cm^{-1} .

2.9. X-ray studies

The X-ray diffraction pattern (XRD) of the composite material was recorded with a analytical diffractometer using Cu K α radiation $(\lambda = 1.5418 \text{ Å})$.

2.10. Thermal stability

The effect of drying temperature on the ion-exchange capacity of the material was studied by heating from 50 to 700 \degree C for 1 h. The ion-exchange capacity for each heated sample was determined as described earlier.

2.11. Thermal analysis

Thermogravimetric analysis was carried out in N_2 gas atmosphere at a rate of 10° C min⁻¹ by increasing the temperature up to 700 °C.

2.12. Scanning electron microscopy

Electron micrographs of n-butylacetatezirconium(IV) iodate cation exchanger were recorded using scanning electron microscope at different magnifications.

2.13. Atomic force microscope

For morphological characterization, scanning probe microscope was used. All measurements were done in ambient environment at the room temperature. The measuring head with the 3 cantilever displacement detection system was installed on the corresponding piezotube scanner. For topography imaging of the synthesized sample placed on a HOPG substrate. The tapping mode AFM was selected using commercial etched silicon tips as AFM probes with typical resonance frequency of ca. 300 Hz.

2.14. Raman studies

Raman spectra of synthesized composite material were recorded on a Raman spectrophotometer. The samples were excited at 488 nm argon laser through a $50 \times (NA = 0.75)$ objective resulting in a spot size of around $2 \mu m$ in diameter. The Raman signal was recorded with the same objective in a backscattering geometry. The polarization of the incident laser was changed using a half wave plate.Distribution (sorption) studies

Distribution coefficient (K_d) of metal ions, e.g. Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺, Pb²⁺, Hg²⁺, Cd²⁺, Zn²⁺, Mn²⁺, Cu²⁺, Fe³⁺, Ni²⁺, Al³⁺, Bi³⁺ and La³⁺ were determined by batch method in different solvents of analytical interest. Distribution coefficients were actually used to access the overall ability of the material to remove the ions of interest under different sets of conditions. Various portions of (300 mg each) exchanger in H^+ form were taken in Erlenmeyer flasks and mixed with 30 mL of different metal nitrate solution in the required medium and subsequently shaken for 6 h in temperature controlled shaker at $25 \pm 2^{\circ}$ C to attain the equilibrium. The amount of metal ion before and after the equilibrium was determined by EDTA titration. The distribution coefficients were calculated using the equation:

$$
K_d = \frac{\text{Amount of metal ion retained in one gram of the exchanger phase (mg g-1)}{\text{Amount of metal ion in unit volume of the supernatant solution (mg mL-1)} }
$$

$$
K_d = \frac{(I - F)/300 \text{ mg}}{F/30 \text{ mL}}
$$

where *I* is volume of EDTA used before treatment of metal ionexchanger.

F is the volume of EDTA consumed by metal ion left in solution phase.

The sorption of metal ions involves the ion-exchange of the H⁺ ions in exchanger phase with that of metal ions in solution phase. For example:

 $2R-H^+ + Pb^{2+}$ Exchanger phase Solution phase \rightleftharpoons R_2 -Pb Exchanger phase $+$ $2H^+$
Solution phase

 $R = n$ -butylacetatezirconium(IV) iodate cation exchanger.

2.16. Quantitative separations of metal ions in synthetic binary mixtures

Quantitative separations of some important metal ions were achieved on n-butylacetatezirconium(IV) iodate cation exchanger column. 1 g of exchanger in H^+ form was packed in a glass column of 0.6 cm internal diameter with a glass wool support at the end. The column was washed thoroughly with demineralized water and the mixtures of two metal ions (each with initial concentration 0.1 M) were loaded on it and allowed to pass through the column at a flow rate of 5–20 drops min^{-1} until the level was just above the surface of the material. The process was repeated two or three times to ensure the complete sorption of metal ions on the bead. The separation of metal ions was achieved by collecting the effluent in 10 mL fractions and titrated against the standard solution of 0.01 M di-sodium salt of EDTA.

3. Results and discussion

In the present study, a number of samples of n butylacetatezirconium(IV) iodate cation exchanger were prepared by sol–gel method by mixing zirconium (IV) iodate and n-butyl acetate. The cation exchanger appears to be promising with respect to better ion-exchange capacity along with thermal and chemical stability. It is evident from [Table 1](#page-1-0) that the mixing ratio and pH affect the physical appearance and ion-exchange capacity of the

Table 2

Ion-exchange capacity of exchanger on different exchanging ions on nbutylacetatezirconium(IV) iodate.

		Exchanging ions Ionic radii (A°) Hydrated ionic radii (A°) IEC (mmol g^{-1})	
Li ⁺	0.68	3.40	0.80
$Na+$	0.97	2.76	0.78
K^+	1.33	2.32	0.50
Mg^{2+} Sr ²⁺	0.78	7.00	0.75
	1.27	6.30	0.70
$Ca2+$	1.43	5.90	0.68
$Ba2+$	1.43	5.90	0.56

IEC: ion-exchange capacity.

composite materials. It is informed in [Table 1](#page-1-0) that the cation exchange characteristics of n-butylacetatezirconium(IV) iodate cation exchanger is due to the presence of ionogenic group of the inorganic part of the material to which counter ions are attached. On the basis of better ion-exchange capacity along with thermal and chemical stability, sample S-5 was selected for further studies.

It has been observed that the size and charge of the exchanging ions affects ion-exchange capacity of the material. It is evident from ion-exchange capacity data (Table 2) that the affinity sequence for alkali metal ions follows the sequence Li^+ > Na⁺ > K⁺ while for alkaline earth metal ions $Mg^{2+} > Sr^{2+} > Ca^{2+} > Ba^{2+}$. This sequence is in accordance with the size of hydrated ionic radii of the metals [\[21–23\].](#page-7-0) The variations of ion-exchange capacity with concentration (Fig. 1) suggest that the ion-exchange capacity of cation exchanger depends upon the concentration of eluent. It increases with the increase in concentration of the eluent. The highest capacity was observed with 1.0 M solution of NaNO₃ after that it became almost constant. The elution behavior of the material confirms that the exchange is quite fast as only 100 mL of 1.0 M NaNO₃ solution is needed for almost complete elution of H^+ ions ([Fig. 2\).](#page-3-0) From this observation it has been found that the efficiency of the column is quite satisfactory.

Ion-exchange capacity of the material is also affected by heating as indicated in [Table 3.](#page-3-0) The ion-exchange capacity decreases with increase in temperature. The material appears to be thermally stable up to $200\degree C$ as it retains significant ion-exchange capacity. The FTIR spectra of n-butylacetatezirconium(IV) iodate cation exchanger ([Fig. 3\)](#page-3-0) showed a strong intensive band at 3409 cm^{-1} and a medium intensity band at 1629 cm⁻¹, which could arise due to the presence of free –OH groups and/or physically bound water [\[24\]. T](#page-7-0)he band at about 1500 cm⁻¹ is actually at 1388 cm⁻¹ and corresponds to the v_{symm} stretching of COO of *n*-butylacetate [\[25\].](#page-7-0)

Fig. 1. Elution behavior of H⁺ ions on n-butylacetatezirconium(IV) iodate cation exchanger.

Fig. 2. Effect of eluent concentration on ion-exchange capacity of nbutylacetatezirconium(IV) iodate cation exchanger.

An assembly of two sharp peaks in the region of 750–705 cm−¹ may be due to the superposition of metal–oxygen stretching vibration. The thermogravimetric curve (Fig. 4) shows a continuous weight loss of mass (about 18%) up to 200 °C, which is due to the removal of external water molecules [\[26\]. G](#page-7-0)radual weight loss of 10% observed between 200 and 450 ◦C was due to loss of interstitial water molecules removed by virtue of the condensation of –OH groups. Further weight loss from 450 to 600 ◦C may be due to complete decomposition of the organic part of the material. Beyond 600 \degree C onwards, a horizontal level indicate that there is no further weight loss as the material is completely converted to metal oxide. Derivative thermogravimetric curve (DTG) which shows two prominent peaks with a maximum at 80 and 500 ◦C corresponding to weight loss incurred during heating. On the basis of pH titration curve ([Fig. 5\)](#page-4-0) it can be concluded that the functional group that is $HIO₃$ attached to the skeleton of the exchanger behave as a monofunctional weak acid.

This exchanger showed a reasonably good chemical stability in different solvent. The material was apparently stable in $HNO₃$, HCl, HCOOH, H_3PO_4 , succinic acid and lactic acid while slightly being soluble in H_2SO_4 , CH₃COOH, DMF and *n*-butanol with higher solubility in ammonium hydroxide solution up to 5 M. The chemical stability of this exchanger may be due to the presence of metal–metal strong bonding.

Scanning electron microscope (SEM) photograph of nbutylacetatezirconium(IV) iodate cation exchanger [\(Fig. 6](#page-4-0)) indicates a plate like morphology of this material. From the detailed analysis of these SEM photographs, the particle size was found to be about $5-10 \,\mu$ m.

The typical X-ray diffraction pattern ([Fig. 7\) s](#page-4-0)hows sharp peaks which correspond to the crystalline nature of the material.

Table 3 Effect of temperature on the ion-exchange capacity of n-butylacetatezirconium(IV) iodate cation exchanger on heating time for 1 h.

Temperature $(^{\circ}C)$	Colour	% Weight loss	% Retention of IEC
50	White	0.0	100
100	White	4.2	88
200	Light pink	9.6	72
300	Light pink	29	56
400	Light pink	68	36
500	Light pink	69	20
700	Light pink	70	13.8

IEC: ion-exchange capacity.

Fig. 3. FTIR spectra of n-butylacetatezirconium(IV) iodate cation exchanger.

[Fig. 8](#page-4-0) shows the tapping mode AFM images of the material from solution to substrate surface. The shining portion corresponds to the light and dark portion in the AFM image. It can be concluded from the figure that molecules of iodate and n-butylacetate were embedded on the surface of zirconium (IV) and clearly reveals the cube like morphology of the composite material [\[27\].](#page-7-0)

Raman spectra of the composite material ([Fig. 9\)](#page-4-0) exhibit two prominent bands. The bands observed corresponding to 438.1680 and 574.85815 cm−¹ are assigned E2-high and E1-LO respectively as has been indicated in the case of n -butylacetatezirconium (IV) iodate cation exchanger [\[28–31\].](#page-7-0)

Fig. 4. TGA curve of n-butylacetatezirconium(IV) iodate cation exchanger.

Fig. 5. pH-titration of n-butylacetatezirconium(IV) iodate cation exchanger with various alkali metal hydroxides.

In order to explore the potentiality of the new composite cation exchange material for the separation of metal ions. Distribution studies for 17 metals ions were performed in different solvent systems ([Table 4\).](#page-6-0) The uptake of metal ions depends on the nature of solvent medium. Therefore the selectivity of metal ions varies from one medium to another. The higher uptake of Hg^{2+} and Zr^{4+} ions in DMSO in comparisons to other metal ions make the material selective for Hg²⁺ and Zr⁴⁺ ions. This is also observed for Pb²⁺ ion in pure water medium. The importance of the material has been demonstrated in the separation of metal ions by achieving some important binary separations such as $Th^{4+}-Zr^{4+}$, La³⁺-Zr⁴⁺, $Cu^{2+}-Hg^{2+}$, Mg²⁺-Al³⁺, Zr⁴⁺-Cu²⁺ and Ca²⁺-Pb²⁺. [Tables 6 and 7](#page-6-0) show the results of selective separation of Pb^{2+} and Zr^{4+} from the synthetic mixtures of other metals. The salient features of these separations are reflected in the chromatograms shown in [Fig. 10](#page-5-0) and the results in [Table 5. I](#page-6-0)t is clear that the separations are quite sharp and recovery is quantitative and reproducible.

Fig. 6. Scanning electron microphographs (SEM) of n-butylacetatezirconium(IV) iodate cation exchanger.

Fig. 7. Powder X-ray diffraction pattern of *n*-butylacetatezirconium(IV) iodate cation exchanger.

Fig. 8. Tapping mode AFM images of n-butylacetatezirconium(IV) iodate cation exchanger.

Fig. 9. Raman spectra of n-butylacetatezirconium(IV) iodate cation exchanger.

Fig. 10. Chromatograms of binary separations of metal ions on n-butylacetatezirconium(IV) iodate cation exchanger column. a = 0.1 M DMSO, b = 0.01 M DMSO, c = 0.1 M H_3PO_4 , d = 0.1 M DMF.

Table 4

Distribution coefficients of different metal ions on n-butylacetatezirconium(IV) iodate cation exchanger in different solvent systems.

Table 5

Quantitative separation of metal ions from a binary mixture using on n-butylacetatezirconium(IV) iodate cation exchanger column at room temperature.

Table 6

Selective separations of Pb²⁺ from a synthetic mixtures containing Ca²⁺, Cd²⁺, Pb²⁺, Mn²⁺, Cu²⁺ and Bi³⁺ on columns of on n-butylacetatezirconium(IV) iodate cation exchanger.

^a Average of five replicate determinations.

Table 7

Selective separations of Zr⁴⁺from a synthetic mixtures containing Zn²⁺, Ca²⁺, Cd²⁺, Mn²⁺, Cu²⁺ Zr⁴⁺ and Bi³⁺ on columns of on n-butylacetatezirconium(IV) iodate cation exchanger.

^a Average of five replicate determinations.

4. Conclusion

n-Butylacetatezirconium(IV) iodate cation exchanger, a crystalline cation exchanger shows selective behavior towards heavy metal ions and can withstand fairly high temperature. Thermally stable, it retains significant ion-exchange capacity up to 200 °C. It can be used for the quantitative separation of binary mixture of metal ions of analytical importance. The material can be explored further for the removal and recovery of important metal ions from industrial effluents. The n-butylacetatezirconium(IV) iodate cation exchanger, thus, exhibits the characteristics of a promising ionexchanger which can be explored for other applications.

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