Synthesis and Characterization of Cerium(IV) Arsenomolybdate Cationic Exchanger

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In present work, three component inorganic ion exchanger of an H⁺ form of cerium(IV) arsenomolybdate has been synthesized by mixing solution of ceric ammonium nitrate (0.1 M) with sodium arsenate solution (0.1 M) and sodium molybdate solution (0.1 M) in different volume ratios to get different samples. One of the samples was selected on the basis of high ion-exchange capacity as determined by column method. The ion-exchange capacity of the material for Na⁺ has been found to be 0.98 meq/g of the exchanger. The material has been characterized on the basis of pH titration, thermal and chemical stabilities, FTIR, TGA, X-ray and SEM studies. The scanning electron microscopy of the material shows a regular diamond shape morphology. Chemical stability of the exchanger was checked in various acidic and basic media. Binary separations of some important metal ion pairs were achieved.

Keywords: Cerium(IV) arsenomolybdate, Cation-exchanger, Distribution coefficient, Binary separation.

INTRODUCTION

Some trace metals are toxic and their presence in water adds to the accumulation in living organism, causing health problems in human beings, plants and animals [1]. Therefore, it is necessary to remove such metals by using some separation techniques [2]. In an ion-exchange process, the exchange of the ion takes place stoichiometrically between the stationary and mobile phase. The ion-exchange phenomenon was recognized by two Thomson [3] and Ways [4,5] in the soil by the name at base-exchange. An ion exchanger is usually water insoluble solid substance which can take up ions of positive or negative charge from an electrolyte solution in an equivalent amount. There are several requirements for a suitable ion-exchanger which are closely interacted. Inorganic ion exchangers [6-8] have drawn considerable attention owing to their high thermal and chemical stability [9]. Many natural and synthetic substances are capable of ion-exchange for technical purposes. However, only those substances which have adequate mechanical and chemical properties are suitable. Three most important groups are detailed within the order of their development: inorganic, natural organic base and synthetic ion-exchangers. Amongst these, the aluminosilicates, both natural and synthetic are suitable for many purposes. Zeolites are naturally occurring cation exchangers. The synthetic ion exchangers fill increasingly the requirements both of laboratories and technology

[10]. Similarly a large number of three component ion exchangers like stannic(IV) silicomolybdate [11], zirconium(IV) selenomolybdate, titanium(IV) tungstoarsenate [12] and zirconium(IV) iodotungstate [13] have been reported.

In the present work, the new cerium(IV) arsenomolybdate which is durable, low in cost and high in ion-exchange capacity, was prepared. The material has been characterized on the basis of pH titration, TGA, FTIR, X-ray and SEM studies. These materials have been demonstrated by achieving some analytical separations, the providing ion-exchange material useful in environmental analysis.

EXPERIMENTAL

Ammonium hexanitratocerate (IV), sodium arsenate and sodium molybdate were obtained from S.D. Fine Chem. Ltd. (India). All other chemicals and reagents were also of analytical grade. pH measurements were performed using an Toshniwal research pH meter (Model pH-110). Samson S-300D electronic balance was used for weighing. Thermal studies were carried out by using Tancos electric muffle furnace. For drying the samples NSW India's oven was used. XRD and FTIR Model 'Philips analytical X-ray B.V. Diffractometer' and Cary Agilent 630 FTIR was used. TGA was obtained with the help of Perkin Elmer (Pyris Diamond) in alumina pan with a current of nitrogen.

TABLE-1
 SYNTHESIS OF CERIUM(IV) ARSENO MOLYBDATE (CAM)

S. No.	Molar concentration (M)			Mixing ratios	pH	Yield (g)	Colour	Ion exchange capacity (meq/g)
	Ce ⁴⁺	AsO ₃ ²⁻	MoO ₄ ²⁻					
CAM1	0.1	0.1	0.1	1:1:1	1	1.02	Yellowish gelatinous	0.57
CAM2	0.1	0.1	0.1	2:1:2	1	2.32	Yellowish gelatinous	0.41
CAM3	0.1	0.1	0.1	2:1:1	1	2.01	Yellowish gelatinous	0.23
CAM4	0.1	0.1	0.1	1:2:1	1	3.00	Yellowish gelatinous	0.46
CAM5	0.1	0.1	0.1	2:2:1	1	4.00	Light yellow	0.62
CAM6	0.1	0.1	0.1	1:3:1	1	6.01	Light yellow	0.98
CAM7	0.1	0.1	0.1	3:3:2	1	3.02	Light yellow	0.68

Synthesis: The seven different samples of cerium(IV) arsenomolybdate (CAM) were prepared by adding mixture of 0.1 M ammonium hexanitratocerate(IV) solution and 0.1 M sodium molybdate solution, 0.1 M sodium arsenate solution with continuous stirring in various mixing volume ratios, pH of the resulting gel was maintained at 1.0 and allowed to stand for 24 h in the mother liquor at room temperature and then filtered. The excess acid was removed by washing with demineralized water and dried at 40 ± 1 °C in an oven. The dried products were then cracked into small granules by putting them in demineralized water. The granules so obtained were converted into H⁺ form by keeping it in molar HNO₃ for 24 h. The products thus obtained were washed with demineralized water several times and finally dried at 40 ± 1 °C in an oven. The results are summarized in Table-1.

Characterization

Ion-exchange capacity: The ion exchange capacity of all the samples was determined by column method. The samples in H⁺ form were packed in seven glass columns and washed with demineralized water. 250 mL molar NaNO₃ solution was passed through the each column maintaining the flow rate 0.5 mL min⁻¹. The hydrogen ions in the effluents were determined by titrating against standard NaOH solutions in each case. The ion-exchange capacity of the material for mono and bivalent metal ions was determined as shown in Table-2.

 TABLE-2
 ION EXCHANGE CAPACITY OF CAM EXCHANGER FOR DIFFERENT CATIONS

Cation	Salt used	Concentration of salt used (M)	IEC (meq/g)	Hydrated ionic radii (Å)
Li ⁺	LiCl	0.1	0.76	10.0
Na ⁺	NaCl	0.1	0.98	7.90
K ⁺	KBr	0.1	1.16	5.30
Mg ²⁺	MgCl ₂	0.1	1.32	10.80
Ca ²⁺	CaCl ₂	0.1	1.09	9.60
Ba ²⁺	BaCl ₂	0.1	1.28	8.80

pH titration: The pH titration of the material was performed by the method of Toppe and Pepper [13]. The pH titration was carried out using NaCl-NaOH system. 0.50 g of exchanger in H⁺ form was placed in each of the several 250 mL conical flasks followed by the addition of equimolar solution at alkali metal chloride and their hydroxide in different volume ratios with final volume being 50 mL to maintain the ionic strength constant [14]. The pH of all the solutions was recorded after 24 h then equilibrium was attained. The pH of the solution

was recorded after equilibrium and the pH titration curve was plotted against the milliequivalents of OH⁻ ions added as shown in Fig. 1.

Fig. 1. pH titration curve of cerium(IV) arsenomolybdate

Thermal stability: The ion-exchanger (0.50 g) was heated at different temperatures for 1 h in a muffle furnace. After cooling them to room temperature the effect of heating on weight and ion-exchange capacity of the ion-exchanger was examined. The colour of the sample is also found to be affected with the increase in temperature [15]. The results are summarized in Table-3.

 TABLE-3
 THERMAL STABILITY OF EXCHANGER AFTER HEATING TO VARIOUS TEMPERATURE FOR 1 h

Drying temp. (°C)	Weight of ion exchanger before heating (g)	Change in colour	Weight loss (%)	IEC (meq/g)
100	0.50	Light yellow	2	0.89
200	0.50	Yellow	4	0.77
300	0.50	Dark yellow	6	0.70
400	0.50	Pale brown	8	0.63
500	0.50	Brown	10	0.58
600	0.50	Dark brown	12	0.50
700	0.50	Chocolate brown	16	0.43
800	0.50	Black	18	0.31
900	0.50	Dark black	20	0.24

Chemical stability: Chemical stability of the ion-exchanger was determined by dissolving 0.50 g, of the exchanger in 25 mL of different [16], mineral acids such as HCl, HNO₃ and H₂SO₄ bases NaOH and KOH and organic solvent such as formic acid of different concentration, with intermittent shaking and

TABLE-4
CHEMICAL STABILITY OF EXCHANGER IN DIFFERENT SOLVENTS

Solution	Before treatment (mg)	After treatment (mg)	Time (h)	Weight loss (%)	Ion exchange capacity
1 M HCl	500	495	24	1	0.98
2 M HCl	500	485	24	3	0.89
3 M HCl	500	475	24	5	0.75
1 M HNO ₃	500	500	24	0	0.98
2 M HNO ₃	500	500	24	0	0.97
3 M HNO ₃	500	495	24	1	0.85
1 M H ₂ SO ₄	500	490	24	2	0.80
2 M H ₂ SO ₄	500	470	24	6	0.72
3 M H ₂ SO ₄	500	450	24	10	0.68
2 M NaOH	500	420	24	16	0.45
2 M KOH	500	400	24	20	0.40
1 M HCOOH	500	500	24	0	0.72
2 M HCOOH	500	495	24	1	0.67
6 M H ₂ SO ₄	500	0	24	100	–
6 M NaOH	500	0	24	100	–

kept them as such for 24 h at room temperature and then filtered and finally dried at 40 ± 1 °C in an oven and cooled at room temperature. Know the weight loss of the material was observed and ion-exchanger capacities were determined by column method as represented in Table-4.

Distribution studies: 0.50 g portion of the dry exchanger in H⁺ form were equilibrated with 25 mL of different metal ion solutions in the required medium and kept for 24 h with intermittent shaking [17]. The metal ion concentration in each case before and after equilibrium was done by titrating against EDTA solution with the help of appropriate indicators.

K_d values as summarized in Table-5. Distribution coefficient were calculated the following equations:

$$K_d = \frac{I - F}{F} \times \frac{V}{M}$$

where, I is the initial volume of the EDTA solutions and F is the final volume of the EDTA solution used, V is volume of the solution taken and M is the mass of the exchanger.

TABLE-5
DISTRIBUTION COEFFICIENT OF
METAL IONS FOR EXCHANGER

Cation	Form	K _d (mL/g)
Ca ²⁺	Carbonate	10.02
Mg ²⁺	Acetate	15.11
Zn ²⁺	Acetate	3.18
Cu ²⁺	Acetate	5.84
Co ²⁺	Acetate	6.08
Ni ²⁺	Sulphate	18.90
Pb ²⁺	Nitrate	45.08
Bi ³⁺	Nitrate	9.06
Mn ²⁺	Sulphate	3.45
Cd ²⁺	Chloride	14.69

SEM and IR studies: SEM was obtained for cerium(IV) arsenomolybdate by the Instrumentation Centre, IIT Roorkee. Photograph are shown in Fig. 2. FTIR spectrum of the material was obtained KBr disc method. The absorption spectrum was recorded between 3800 and 800 cm⁻¹ (Fig. 3).

X-ray studies: The X-ray diffraction analysis of the material which was obtained by name of the instrument. Philips Analytical X-ray diffractometer available at Instrumentation

Fig. 2. SEM photograph of cerium(IV) arsenomolybdate

Fig. 3. IR spectrum of cerium(IV) arsenomolybdate

Centre, IIT Roorkee. Nature of the particle shows a semi-crystalline nature with intermittent peaks of weak intensities (Fig. 4).

TGA curve: Thermo gravimetric analysis of the exchanger in H⁺ form was carried out at a heating rate of 10 °C/min in Nitrogen atmosphere from room temperature 30 ± 2 °C to mention of total temperature of given graph 1000 °C. The results are shown in Fig. 5.

Separations: For binary separations [18], 0.50 g of the ion-exchanger in H⁺ form was taken in a glass column. The

Fig. 4. XRD of cerium(IV) arsenomolybdate

Fig. 5. TGA curve of cerium(IV) arsenomolybdate

column was washed thoroughly with demineralized water and mixture of metal ion solution to be separated was then poured into the column and maintaining a flow rate 5-6 drops/min and recycled at least three times. The separation was achieved by passing a suitable eluents. The flow rate of the effluent was maintained at 0.5 mL/min throughout the elution process.

The effluent was determined titrimetrically against EDTA solution.

Binary separation of those metal ions can be achieved for which the separation factor is greater than 3:

$$\text{Separation factor } (\alpha_B^A) = \frac{K_d \text{ values of metal ions A}}{K_d \text{ values of metal ions B}}$$

The separation factors are the guiding measures for the separation.

RESULTS AND DISCUSSION

Cerium(IV) arsenomolybdate of the different samples have been synthesized (Table-1) with the highest ion exchange capacity of 0.98 meq/g was selected for present study. The ion exchange capacity for alkali and alkaline earth metal ions are shown in Table-2. The sequence shown by the material is as follows: $K^+ > Mg^{2+} > Ca^{2+} > Ba^{2+} > Na^+$. The sequence is in accordance with the hydrated ionic radii of the exchanging ions.

The pH titration curve of cerium(IV) arsenomolybdate perform NaCl-NaOH system (Fig. 1). The ion-exchange capacity was found to be 1.20 meq/g. The curve revealed that the material behaves as strong cation. Exchanger as indicated by a low pH (2.54) of the solution when no OH^- ions were added to the system.

The effect of heating on ion exchange capacity of the synthesized cation exchanger for Na^+ ions was studied. Data show that the ion exchange capacity decreases with increase of temperature. The results are given in Table-3. Chemical stability studies concluded that the material is fairly stable in lower concentration of HCl, HNO_3 , H_2SO_4 and NaOH and KOH. The material was found to be quite stable in organic acid like formic acid. It was found to be completely dissolved in 6 M H_2SO_4 and 6 M NaOH solutions.

The distribution studies of metal ions in aqueous media are shown in Table-5, selectivity of the exchanger was found to be Pb^{2+} , Ni^{2+} and Mg^{2+} for which the K_d values are 45.08 $mL\ g^{-1}$, 18.90 $mL\ g^{-1}$ and 15.11 $mL\ g^{-1}$, respectively.

X-ray diffraction pattern of the exchanger in H^+ form reveals the semi-crystalline nature with some sharp peaks.

Newly synthesized cerium(IV) arsenomolybdate shows a regular uniform morphology, also indicate semi-crystalline nature (Fig. 2). IR spectrum of the material show a strong and broad band in the region 3800-800 cm^{-1} which is corresponding to symmetric and asymmetric OH stretching and the band at 3364.51 cm^{-1} is due to H-O-H bending.

TABLE-6
BINARY SEPARATION ACHIEVED WITH THE HELP OF CAM EXCHANGER

Metal ion pair	Amount loaded (μg)	Amount loaded (μg)	Metal ion eluted (%)	Error (%)	Total elution volume (mL)	Eluent used
Pb^{2+}	1590	1580	99.73	+0.27	40	0.1 M HNO_3
Cd^{2+}	682	654	104.28	-0.28	50	0.02 M HNO_3
Pb^{2+}	1590	1590	100	0.00	40	0.1 M HNO_3
Mg^{2+}	1507	1508	99.93	+0.01	70	0.4 M HNO_3
Pb^{2+}	1590	1475	107.79	-1.15	40	0.1 M HNO_3
Cu^{2+}	1059	1032	102.61	-3.27	60	0.5 M HNO_3
Pb^{2+}	1590	876	181.50	-7.14	40	0.1 M HNO_3
Co^{2+}	792	839	94.39	+1.53	60	0.1 M HNO_3 + 0.5 M NH_4OH

Thermogravimetric curve of cerium(IV) arsenomolybdate shows continuous loss in weight up to 1000 °C which indicate 6.6, 11, 13 and 15 % weight lose with in the temperature range of 100-400 °C corresponding to the loss of water molecules.

Binary separation of Pb(II)-Cd(II), Pb(II)-Mg(II), Pb(II)-Cu(II) and Pb(II)-Co(II) were achieved on a column of these ion exchanger by using suitable eluents selected after studying the electrolyte effect on distribution coefficients. Binary separation of Pb-Cd, amounts found of lead and cadmium shows that almost all the lead metal ions one eluted while 104.28 % cadmium ions are eluted showing the percentage error of -0.28 % (Table-6).

In Pb-Mg separation, the difference between loaded amounts and amounts found show that magnesium 99.93 % eluted with +0.01 % error and lead is eluted to 100 % with 0.00 % error. In case of Pb-Cu combination, lead can be removed 107.79 % with -1.15 % error (Table-6).

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