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Study of New Synthesized Cerium (IV) Iodoarsenate: An Inorganic Cation-Exchanger and its Applications

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Abstract: Cerium based cation-exchanger is cerium (IV) iodoarsenate has been synthesized as a new inorganic cation-exchanger. The material was synthesized by adding 0.1 M ceric ammonium nitrate solution to a mixture of 0.05 M potassium iodate solution and 0.05 M sodium arsenate solution in different volume ratios to get six samples. One of the sample 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 1.19 meq/g of dry exchanger. The exchanger was characterized using FTIR, X-ray, SEM analysis and TGA curve. The ion-exchange capacity of the material for various alkali and alkaline earth metal ions has been determined. Effect of the temperature on ion-exchange capacity was studies. Distribution behaviour for ten metal ions has been determined by column method. Analytical important binary separation of metal ions has been achieved with the help of synthesized cation-exchanger.

Keywords—Inorganic ion-exchanger; ion-exchange capacity; pH titration; thermal and chemical stabilities; distribution behaviour; separation studies.

I. INTRODUCTION

Water is an important and necessary resource for life support [1]. The analysis of trace elements in natural water, wastewater, biological, Industrial and geological samples in complex mixtures is the challenging problem in analytical chemistry [2]. Trace elements can be removed from wastewater by using one of the methods is ion-exchange. Ion-exchange technology is most versatile technology in the field of separation science. At this time it is a standard analytical tool and is broadly used in inorganic biological and organic separations [3]. Ion-exchange technique may be defined as the reversible interchange of ions between a ion-exchange material (solid phase) and a liquid phase in which there is no permanent change in structure of the ion–exchanger.

Synthetic inorganic ion-exchangers it can be used for research purpose in the last many years [4]. The development of new synthesized exchanger possessing high ion-exchange capacity, high chemical and thermal stability and selectivity for certain metal ions are most important form environmental pollution and analytical separation point of view. In recent years, various zeolite with completely regular crystal have been synthesized for examples zeolites 4A [5] and zeolites [6]. Various two component ion-exchanger have been prepared and studied as shown by the literature [7-11]. Similarly the studies of three and four component ion-exchangers such as cerium(IV) iodotungstate [12], zirconium (IV) iodoxlate [13], zirconium(IV) selenomolybdate [14], iron(III) tungstomolybdate [15] and cerium(IV) zirconium phosphotungstate [16].

The present study deals with the new synthesized inorganic cation-exchanger of a new phase of cerium(IV) iodoarsenate. The ion-exchanger has been characterized was done on the basis of better ion–exchange capacity. The material is good thermal and chemical stabilities. The providing a good material use for wastewater treatment.

II. EXPERIMENTAL

Whole the experimental work depends on the titration i.e. Acid base-titration, oxidation-reduction titration and complexomertic titration. A hit and trial method is used to find a better exchanger by mixing six samples in different volume ratios. Ion-exchange capacity, Kd values and binary separations are found with column method. Simple and complexometric titration is used to estimate the amount of cation present in the solution. The detail of experimental work of the paper is given below:-

A. *Reagents and Chemicals*

Ceric ammonium nitrate, potassium iodate and sodium arsenate were obtained from S.D fine chem. Ltd. (India) and E. merk (India). All other chemicals and reagents used were also of analytical grade.

B. *Instrumentation*

The pH measurement were performed using an Toshniwal Research pH meter (Model pH-110). Tanco's Electric Rotary Shaker was used for shaking the solution to maintains equilibrium studies. Samson S-300D Electronic Balance was used for weighing. NSW India's Oven was used for drying the samples. IR studies were made on a FTIR Cary Aglient 630 (ATR Module). TGA was obtained with the help of Perken Elmer available at IIT Roorkee. Thermal stability measurement were used Tanco's Electronic Muffle Furnace.

C. *Synthesis of Cation-Exchanger*

Different samples of the three component ion-exchanger were prepared by adding 0.05 M potassium iodate solution and 0.05 M sodium arsenate solution to 0.1 M ceric(IV) ammonium nitrate solution in different volume ratios with continuous stirring to obtain a gel then maintained the pH-1, with the help of dil nitric acid and allowed to stand 24 hours at room temperature and filtered. The excess acid was removed with the help of demineralized water and then the product was dried in an oven at 40±1°C temperature. The material was broken in some granules when immersed in hot demineralized water and the obtain granules were converted into H^+ form by treating them with molar nitric acid solution for twenty four hours at room temperature. The charged material was then washed with demineralized water to remove excess acid and finally dried in an oven at 40 ± 1°C. The dried product were used as an inorganic cation-exchanger. The results are summarized in table I.

TABLE I. Synthesis of cerium (IV) iodoarsenate.

Molar Conc. (M)			Mixing Ratios	pH	Appearance of Precipitate	Appearance of Beads After Drying At 40±1°C	IEC (meq/g)
Ce^{4+}	IO_3^-	AsO_3^{2-}					
0.1	0.05	0.05	1:1:1	1	Light Yellow ppt.	Light Yellow ppt.	0.98
0.1	0.05	0.05	1:2:1	1	Light Yellow ppt.	Light Yellow ppt.	0.96
0.1	0.05	0.05	1:2:2	1	Light Yellow ppt.	Light Yellow ppt.	0.92
0.1	0.05	0.05	2:1:1	1	Dark Yellow ppt.	Dark Yellow ppt.	0.82
0.1	0.05	0.05	2:1:2	1	Dark Yellow ppt.	Dark Yellow ppt.	0.80
0.1	0.05	0.05	1:3:2	1	Light Yellow ppt.	Light Yellow ppt.	1.19

III. CHARACTERIZATION

The synthesized material i.e. three component cation-exchanger is characterized on the bases of FTIR, SEM, XRD, TGA etc. Detailed study of these are described as below:-

A. *Ion-Exchange Capacity*

The IEC of the dried material was determined by column process. 0.50 g exchanger in H^+ form was taken in a column with glass wool support at the base [17]. Molar sodium nitrate solution was passed through the column maintaining their flow rate 5-10 drops/min. The effluent was carefully collected in a conical flask and titrated against standard sodium hydroxide solution. To determined the total H^+ ions released. Sample (VI) was selected for further studies, therefore it was synthesized in bulk form [18]. The IEC of the selected sample was also determined for alkali and alkaline earth metal ions. The results are shown in table II.

TABLE II. Ion-exchange capacity of cerium(IV) iodoarsenate for different metal cations.

Cation	Salt Used	Concentration of Salt Used	IEC (meq/g)	Hydrated Ionic Radii (A^0)
Li^+	LiCl	0.1 M	0.94	10.0
Na^+	NaCl	0.1 M	1.19	7.90
K^+	KBr	0.1 M	0.79	5.30
Mg^{2+}	$MgCl_2$	0.1 M	1.56	10.80
Ca^{2+}	$CaCl_2$	0.1 M	0.90	9.60
Ba^{2+}	$BaCl_2$	0.1 M	0.83	8.80

B. *pH Titration*

The pH titration was performed by Topp and Pepper method [19]. The pH titration was carried out using NaCl-NaOH system. The ion-exchange capacity was determined with the help of pH titration curve. Eleven equal portion of 0.50 g each of the exchanger in H^+ form were placed in eleven 250 ml conical flask separately, followed by equimolar sodium chloride solution and sodium hydroxide solution in different volume ratios were added. The final volume of the solution was kept 50 ml to maintain a constant ionic strength. The pH of all the solution were recorded after equilibrium and pH titration curve was plotted against milli-equivalent of hydroxide ions added as shown in Figure 1.

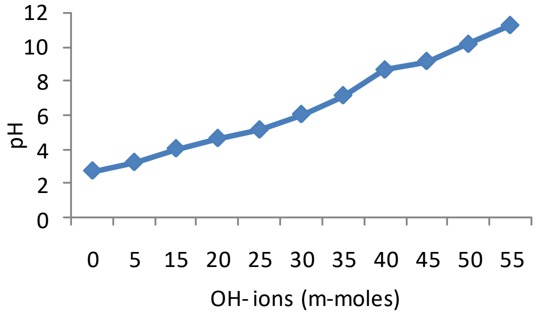

Fig. 1. pH Titration curve of cerium(IV) iodoarsenate.

C. *Chemical Stability*

For the determination of chemical stability of cerium(IV) iodoarsenate against different solvents, fifteen equal amount 0.50 g each of the material were kept separately in 50 ml of various minerals acids, organic acids and bases of different concentration taken in fifteen different containers with intermittent shaking and then kept as such for twenty four hours at room temperature and then filtered and finally dried in an oven 40±1°C. The residues were cooled to room temperature in a dessicator, and the change in colour, weight loss of the sample were observed and then their ion-exchange capacity were determined by using column method. The results are shown in table III.

TABLE III. Chemical stability of cerium(IV) iodoarsenate.

Solution	Percentage Weight loss	Ion-Exchange Capacity
2 M HCl	0	1.19
4 M HCl	1	1.02
6 M HCl	2	1.00
2 M HNO_3	0	1.19
4 M HNO_3	0	1.19
6 M HNO_3	1	1.16
2 M H_2SO_4	4	0.91
4 M H_2SO_4	8	0.71
6 M H_2SO_4	10	0.39
2 M HCOOH	6	0.98
4 M HCOOH	8	0.84
2 M CH_3COOH	0	1.19
4 M CH_3COOH	1	1.01
4 M KOH	Completely Dissolved	-
4 M NaOH	Completely Dissolved	-

D. *Thermal Stability*

Thermal stability of the exchanger in H^+ form was determined by using column method. Nine equal samples of 0.50 g each of the material were it as various temperature for one hour in a muffle furnace. After cooling them to room temperature the effect of heating on weight and ion-exchange capacity of the material was examined [20]. Data shows that the ion-exchange capacity decrease with increase in temperature. The results are shown in table IV.

TABLE IV. Thermal stability of cerium(IV) iodorarsenate.

Drying Temperature (^{0}C)	**Weight of Ion-Exchanger Before Heating (g)**	**Change in Colour**	**IEC (meq/g)**
100 ^{0}C	0.50	Light Yellow	0.99
200 ^{0}C	0.50	Dark Yellow	0.93
300 ^{0}C	0.50	Pale Brown	0.81
400 ^{0}C	0.50	Dark Brown	0.72
500 ^{0}C	0.50	Dark Brown	0.51
600 ^{0}C	0.50	Reddish Brown	0.32
700 ^{0}C	0.50	Duski Black	0.21
800 ^{0}C	0.50	Black	0.10
900 ^{0}C	0.50	Black	0.04

E. Distribution Studies

Distribution Coefficient of different metal ions in demineralized water and various solvents were carried out by determined concentration of metal ions by batch method [21]. In this method, 0.50 g of the dry ion-exchanger in hydrogen form were equilibrated with 0.1 M solution of various metal ions, taken in different containers. The mixture was shaken for twenty four hours to attained equilibrium. The concentration of metal ions present in this solution was determined by titrating it against disodium salt of EDTA using appropriate indicators [22]. Kd values may be expressed as following formula.

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

Where I and F is the volume of EDTA solution used before and after equilibrium respectively, V is the volume of solution taken and M is the weight of dry exchanger. The results are shown table V.

TABLE V. Distribution coefficient studies of cerium(IV) iodoarsenate.

Metal Ions	**Form**	**Kd (mlg^{-1})**
Mg (II)	Acetate	7.19
Ca (II)	Carbonate	8.02
Mn (II)	Acetate	10.11
Zn (II)	Acetate	7.80
Co (II)	Acetate	3.43
Cu (II)	Acetate	20.23
Cd (II)	Chloride	39.01
Ni (II)	Sulphate	18.13
Pb (II)	Nitrate	45.13
Bi (III)	Nitrate	12.0

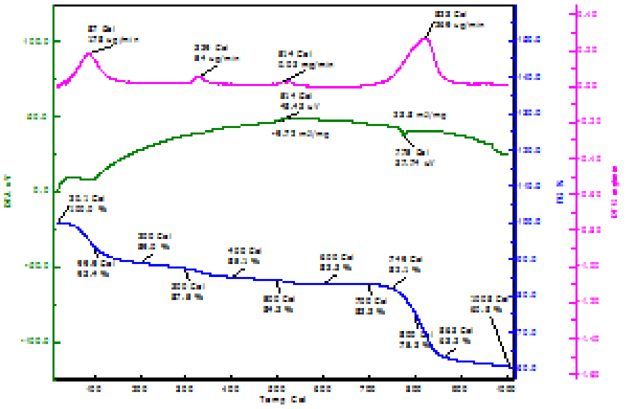

Fig. 2. TGA curve of cerium(IV) iodoarsenate.

F. TGA Curve

The TGA curve of cerium(IV) iodoarsenate is shown in Figure 2. Thermogram curve shows the weight loss at 0^{0}C to 1000^{0}C. Initially the loss in weight is rapid, then the weight loss become slow with increase in temperature and ultimately the weight of the sample become almost constant.

G. IR and SEM Analysis

FTIR analysis of the exchanger in hydrogen form was taken. The material was thoroughly mixed with 1g of KBr and ground to a fine powder. The IR spectrum was recorded between 800 cm $^{-1}$ and 3800 cm^{-1}. The results are shown in Figure 3. The scanning electron microscopy of the exchanger shows a regular shape morphology. SEM photograph are shown in figure 4.

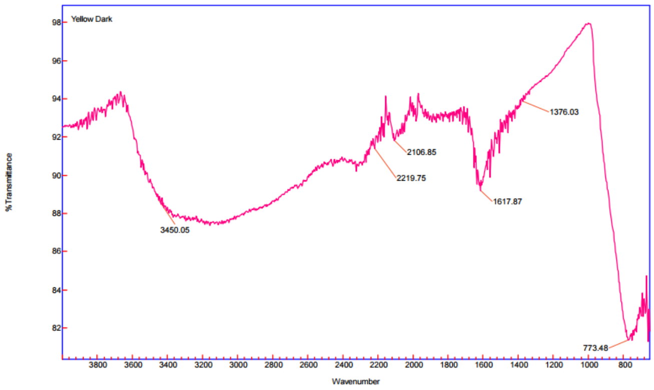

Fig. 3. IR spectrum of cerium(IV) iodoarsenate.

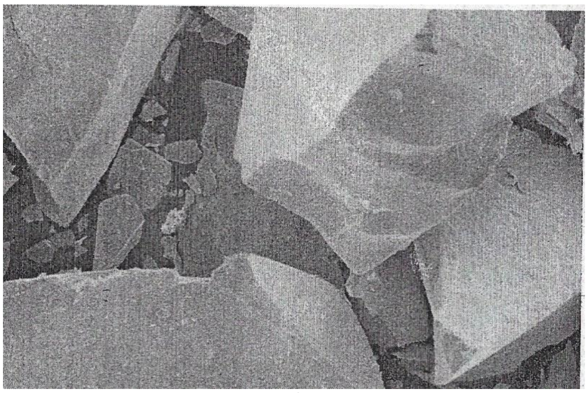

Fig. 4. SEM photograph of cerium(IV) iodoarsenate.

H. XRD

For X-ray analysis of the material in H$^+$ form was obtained with the help of Philips Analytical X-ray B.V. Differactometer was available at instrumentation centre, IIR Roorkee in U.K. The X-ray diffraction pattern of the exchanger do not shows any sharp peaks. It denote semi-crystalline nature.

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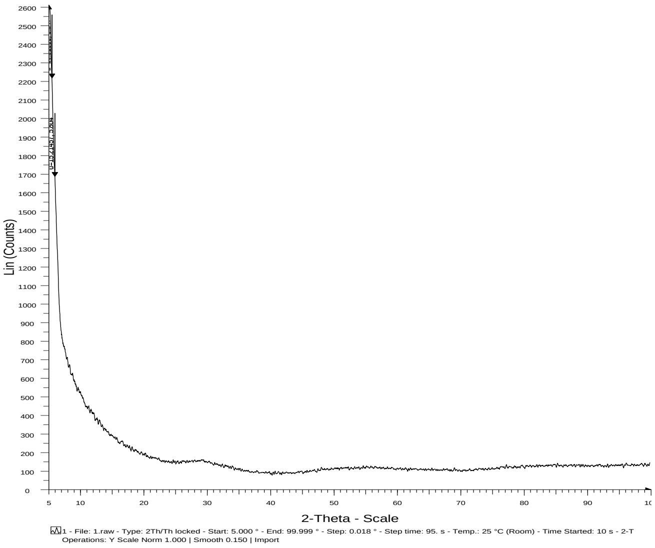

Fig. 5. XRD pattern of cerium(IV) iodoarsenate.

I. Metal Ion Separations

Ion-exchange find various application in analytical chemistry, ion-exchange method is applied in several cases for separation of metal ions. Some important application of ion-exchanger are:-

1. Binary separation of metal ions
2. Removal of coloured metal ions

1. Binary Separations of Metal Ions

Binary separation technique is used extensively for the separation of metal ions from large volumes of natural and wastewater. The total free metal ion content of a water sample is determined by passing the sample through cation- exchanger and titrating the acid liberated with a standard alkali solution .The values of separation factor for different metal ions pairs obtained for cerium(IV) iodoarsenate were greater then three and their values are given in tableVI.

TABLE VI. Separation factor of different metal ions for cerium(IV) iodoarsenate.

Separation Factor	$\alpha_B^A = \frac{Kd\ value\ of\ A}{Kd\ value\ of\ B}$	Value of Separation Factor
α_{Co}^{Pb}	$\frac{45.13}{3.43}$	13.157
α_{Zn}^{Pb}	$\frac{45.13}{7.80}$	5.786
α_{Zn}^{Cd}	$\frac{39.01}{7.80}$	5.002
α_{Mg}^{Cd}	$\frac{39.01}{7.19}$	7.360

For binary separations, 0.50 g of the exchanger in H^+ form was packed in glass column. The column was washed with demineralized water and then metal ion mixture was poured in column separately. The absorbed metal ions were eluted with appropriate eluents one by one. The flow rate of the effluent was maintained at 1ml/min throughout the elution process. The effluents were collected separately conical flask and metal ion concentration were determined (Complexometric Titration) against disodium EDTA salt solution using suitable indicators. The results are summarised in table VII.

TABLE VII. Binary separation achieved with the help of cerium(IV) iodoarsenate.

Metal Ion Pair	Amount Loaded (μg)	Amount Found (μg)	% Metal Ion Eluted	% Error	Total Eution Volume	Eluent Used
Pb (II)	6361	6361	100	0.00	40 ml	0.1 M HNO_3
Co (II)	2946	2809	95.34	-5.66	60 ml	0.2 M $HClO_4$
Pb (II)	6361	6006	94.42	-6.58	40 ml	0.1 M HNO_3
Zn (II)	2354	2356	100.08	+0.08	40 ml	0.2 M $HClO_4$
Cd (II)	2489	2480	100.44	+0.44	50 ml	0.1 M HNO_3
Zn (II)	2354	2300	97.70	-3.38	40 ml	0.5 M NH_4OH
Cd (II)	2478	2361	95.27	-5.73	50 ml	0.1 M HNO_3
Mg (II)	2650	2659	100.03	+0.03	70 ml	0.4 M NH_4NO_3

2. Removal of Coloured Metal Ions

Ni (II), Co (II), Cu (II) can be removed from their aqueous solution with the help of cerium(IV) iodoarsenate. The detection of transition metal ions in their aqueous solution was done qualitatively passing through the column of cation-exchanger.

TABLE VIII. Qualitative tests for transition metal ions for cerium(IV) iodoarsenate.

Metal Ion	Colour of the Salt Solution Before Passing Through Exchanger	Colour of the Salt Solution After Passing Through Exchanger	Detection of Metal Ion in the Effluent
Ni(II)	Green	Colorless	a) Effluent NaOH Solution- No Precipitate Ni(II) absent b) Effluent Ammonia-No Precipitate Ni(II) absent
Co(II)	Pink	Colorless	Effluent + Sodium hydroxide Solution- No Precipitate Co(II) absent
Cu(II)	Blue	Colorless	a) Effluent NaOH Solution- No Precipitate Cu(II) absent b) Effluent Ammonia-No Precipitate Cu(II) absent

For qualitatively determination of coloured metal ions, different definite volumes of the three solutions were loaded on the ion-exchanger in packed in three different columns. The flow rate of 10 drops per minute was maintained. The solutions were passed three times through the ion-exchanger. The effluents of the three columns were collected in three different containers. The presence of the metal ions all the containers was confirmed by performing qualitative analysis as given in table VIII. All the qualitative test found to be negative.

IV. RESULTS AND DISCUSSION

Different samples of cerium(IV) iodoarsenate of the various composition have been synthesized shown in Table I. Sample(VI) was selected as it showed better ion-exchange capacity than others. The ion-exchange capacity was measured with different alkali and alkaline earth metal ions are shown in Table II. The ion-exchange capacity of the dry exchanger in H^+ form for ions following the order of $Na^+ > Li^+ > K^+$ and $Mg^{2+} > Ca^{2+} > Ba^{2+}$ respectively.

The pH titration curve of the prepared material was performed NaCl –NaOH system were carried out under equilibrium conditions. The curve (Figure 1) revealed that the material behave as a strong cation–exchanger. The ion-exchange capacity calculated from the curve at pH -7.0 was 1.50 meq/gm of the exchanger. To examine the effect on IEC of the exchanger is also affected by temperature. The material was heated at different temperature like 100^0C, 200^0C, 300^0C, 400^0C, 500^0C, 600^0C, 700^0C, 800^0C and 900^0C, and IEC for Na^+ ion was found to be 0.99, 0.93, 0.81, 0.72, 0.51, 0.32, 0.21, 0.10, 0.04 be inference from Table IV. The exchanger was found to be fairly stable in HCl and HNO_3 and less stable in H_2SO_4 at high concentration. It was found to be completely dissolve in high concentrated molar solutions of KOH and NaOH.

Distribution behaviour (Table V) of the material several metal ions shows high selectivity of the exchanger of Pb (II) and Cd (II) for which the Kd values were 45.13 $meqg^{-1}$ and 39.01 $meqg^{-1}$ respectively. The infrared spectrum of the material in H^+ form is shown in Figure 3. shows a strong and board band in the region ~ 3800 cm^{-1}, 800 cm^{-1} may be assigned is due to interstitial water molecules and OH group. Another shows a strong and weak band at 1376.03 cm^{-1} and 1617.87 cm^{-1} which indicates the presence of iodate and arsenate respectively. The peak at 773.48 cm^{-1} is associated with metal oxide bond. Thermogravimetric analysis of cerium(IV) iodoarsenate (Figure 2) shows the loss in weight due to water molecule. The graph of shows weight loss of 6.6% at 99.9^0C, 11% at 200^0C, 12.5% at 300^0C, 14.9% at 400^0C, 15.7% at 500^0C. After 600^0C, the weight loss is found to be very small i.e. 16.7% at 600^0C, 16.7% at 700^0C and 17.9% at 749^0C, 36.8% at 863^0C. At 1008^0C a rapid decline in weight, 39.2% is noticed. Since of heating, oxide of cerium are formed .finally the weight become constant and the residue contains the metal oxide only. New synthesized ion-exchanger shows a regular uniform morphology (Figure 4). The X-ray diffraction pattern of the exchanger reveals fact that the material is semi-cystalline nature (Figure 5). The separation of Pb (II)-Co (II), Pb (II)-Zn (II), Cd (II)-Zn (II), Cd (II)-Mg (II), were achieved on column of exchanger. The results are shown in table VII. The eluents used were nitric acid, ammonium nitrate and perchloric acid. This is due to the small separation factor. The recovery ranges from 98-100%. The separation of Cd (II)-Zn (II) mixture is very high in case of the water analysis. Detection of metal ions made it possible to decide the determination process according to qualitative analysis. The results are shown in table VIII.

V. CONCLUSION

The new synthesized ion-exchanger based on cerium(IV). This ion-exchanger is useful in analytical separation technology. Our ion-exchanger Possess selectivity for toxic metals such as Cd, Pb and that are highly toxicity increases in the organism.

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