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Research Article

SYNTHESIS, CHARACTERIZATION AND ANALYTICAL APPLICATIONS OF A NEW CATION EXCHANGER: CERIUM(IV) IODOVANADOSILICATE

Manju, Teena and *Subhash Chand
Department of Chemistry, Meerut College, Meerut,
U.P. India
**Author for Correspondence: teenaprakash15@gmail.com*

ABSTRACT

A new four component inorganic cation exchanger, Cerium (IV) iodovanadosilicate is synthesized by mixing four solutions each having the concentration of 0.1 M and then adjust pH 1.0. Studies of effect of temperature and effect of different chemicals on ion exchange properties of the exchanger are carried out and pH titration curve is also plotted. Instrumental studies (FTIR, XRD and TGA) of the exchanger are also done. Distribution coefficients for eleven metal ions are determined to find the selectivity of the exchanger towards metal ions. The exchanger was applied for binary separations, quantitative analysis of aluminium and magnesium ions in antacid samples, water softening and removal of transition metal ions.

***Keywords**: Synthetic Inorganic Cation Exchanger[Cerium(IV) iodovanadosilicate(CIVS), Ion Exchange Capacity, Distribution Coefficient, Instrumental Studies, Applications of CIVS*

INTRODUCTION

Ion exchange method may be said to be the exchange of all the exchangeable ions of the same charge for other ions of the same charge with the help of an ion exchanger (Samuelson,1954). Many different natural and synthetic products show ion exchange properties. The most important of these are ion exchange resins, ion exchange coals, mineral ions exchangers and synthetic inorganic ion exchangers (Helfferich, 1962). Ion exchangers can be used in a wide range of applications such as heavy metal separation, catalysis, photocataytic activity, antimicrobial activity etc (Deepak *et al.*, 2014, Koloynska *et al.*, 2017 Arshia *et al.,* 2015). Among these, synthetic inorganic ion exchangers are promising materials as they possess robust properties, good ion exchange characteristics, thermal stability and chemical resistivity. Review of the literature shows that some three component ion exchanger based on cerium are reported. The examples includes Cerium(IV) molybdophosphate (Apsara *et al.*, 2011) and Cerium(IV) phosphosilicate (Preetha *et al.*, 2014). Some of the reported four component ion exchangers are Zirconium(IV) tungstoiodophosphate (Siddiqui *et al.*, 2007), Titanium(IV) tungstovanadophosphate (Naqvi *et al.*, 1971) and Tin(IV) tungstovanadophosphate (Varshney *et al.*, 1979) and Nano-crystalline Titanium(IV) tungstomolybdate (Bezabih *et al.,* 2017). No studies are found on four component cation exchanger based on cerium (IV). The present work, is therefore undertaken to synthesize and study the ion exchange properties of a new material namely Cerium(IV) iodovanadosilicate (CIVS). Ion exchange capacity of the synthesized material is determined by two methods namely column method and pH titration method. Further characterization is also reported in this paper that includes determination of chemical stability, thermal stability and distribution studies. Characterization on the basis of instrumental analysis is also done with the help of FTIR, XRD and TGA techniques. This exchanger is found to possess extensive application in analytical and industrial chemistry. The important applications achieved with the help of CIVS are binary separation, analysis of Mg^{2+} and Al^{3+} in antacid samples, water softening and removal of transition metal ions.

MATERIALS AND METHODS

Reagents and Chemicals

Ceric ammonium nitrate {$(NH_4)_2[Ce(NO_3)_6]$}, potassium iodate (KIO_3) and sodium metasilicate ($Na_2SiO_3.9H_2O$) were obtained from Qualigens (India). Sodium metavanadate ($NaVO_3$) was a E. Merck product. Other reagents used during the experimental work were also of AR grade.

Instruments/Apparatus Used

Samson S-300D Electronic Balance was used for weighing the samples. An Electric Oven (NSW India) was used for drying the samples. Toshniwal Research pH Meter (Model pH-110) was used for pH measurements. Thermal studies were carried out using Tanco's Electric Muffle Furnace whereas equilibrium studies were done with the help of Tanco's Electric Rotary Shaker. X-Ray Diffractogram, FTIR and TGA Curve were obtained from Instrumentation Centre, IIT Roorkee where Philips Analytical X-ray B.V. Diffractometer, Thermonicolet IR Spectrophotometer and Exstar TG/DTA 630 were available.

SYNTHESIS

Twelve samples were prepared by adding 0.1 M ceric ammonium nitrate solution to a mixture of solutions of 0.1 M potassium iodate, 0.1 M sodium metavanadate and 0.1 M sodium metasilicate in different volume ratios with intermittent shaking of the mixture to obtain the precipitates and then maintain the pH of the resultant solutions one by adding conc. nitric acid. The precipitates thus obtained were kept overnight for the growth of the particles size at room temperature. After that supernatant liquid was decanted and the precipitates were washed with distilled water till the precipitates become acid free. Then the precipitates were dried at 40±1°C in an oven. The dried materials were cracked with the help of hot distilled water to get the granules. Finally the granules were charged using molar nitric acid solution. The charged materials were then washed with distilled water till free of adhering acid and then dried at 40±1°C in an oven. Now these granules can be used as an exchanger.

Table 1. Synthesis of Cerium(IV) iodovanadosilicate

Sample No.	**Molar Conc.**				**Mixing Ratio V/V/V/V**	**pH**	**Colour of Granules After Drying (40±1°C)**	**Yield (g)**	**IEC (meq/g)**
	Ce^{4+}	**IO_3^-**	**VO_3^-**	**SiO_3^-**					
CIVS-1	0.1	0.1	0.1	0.1	2:1:1:1	1	Dark Yellow	2.92	0.11
CIVS-2	0.1	0.1	0.1	0.1	1:1:2:1	1	Yellow	3.32	0.15
CIVS-3	0.1	0.1	0.1	0.1	1:1:1:2	1	Yellow	3.64	0.28
CIVS-4	0.1	0.1	0.1	0.1	1:2:1:1	1	Dark Yellow	3.85	0.82
CIVS-5	0.1	0.1	0.1	0.1	1:3:1:1	1	Dark Yellow	3.70	0.65
CIVS-6	0.1	0.1	0.1	0.1	1:1:3:1	1	Yellowish Orange	1.97	0.15
CIVS-7	0.1	0.1	0.1	0.1	1:1:1:3	1	Dark Yellow	3.26	0.06
CIVS-8	0.1	0.1	0.1	0.1	3:1:1:1	1	Mustard Yellow	3.18	0.13
CIVS-9	0.1	0.1	0.1	0.1	1:2:2:1	1	Mustard Yellow	2.11	0.17
CIVS-10	0.1	0.1	0.1	0.1	1:1:2:2	1	Yellowish Orange	2.78	0.06
CIVS-11	0.1	0.1	0.1	0.1	2:1:1:2	1	Yellow	2.01	0.11
CIVS-12	0.1	0.1	0.1	0.1	3:3:1:1	1	Dark Yellow	5.17	0.09

CIVS-4 was selected for bulk synthesis owing to its highest IEC (0.82 meq/g) and for further studies.

CHEMICAL CHARACTERIZATION

Ion Exchange Capacity (IEC)

The IEC of all the above stated twelve samples was determined by column method (Nilchi *et al.*, 1999) in which ion exchanger bed is supported by glass wool at the base of the column. IEC of the aforesaid bulk synthesized material was also determined by the same column method. IEC of CIVS-4 was determined for alkali and alkaline earth metals. For this, 0.1 M solutions of different uni and bivalent metal salts were passed through the column and the H^+ ions so liberated were determined by acid base titration (Qureshi *et al.*, 1972).

Table 2: Ion Exchange Capacity of CIVS-4 for Different Cations (meq/g)

Sl.No.	**Cation**	**Salt Used**	**Concentration of Salt Used**	**IEC (meq/g)**	**Hydrated Ionic Radii (A^0)**
1	Li^+	LiCl	0.1 M	0.65	10.0
2	Na^+	NaCl	0.1 M	0.82	7.90
3	K^+	KBr	0.1 M	0.91	5.30
4	Mg^{2+}	$MgCl_2$	0.1 M	0.44	10.80
5	Ca^{2+}	$CaCl_2$	0.1 M	0.52	9.60
6	Ba^{2+}	$BaCl_2$	0.1 M	0.57	8.80

pH Titration

IEC was also determined by pH titration method. pH titration was performed on CIVS-4 for NaCl-NaOH system by (Topp and Pepper's 1949), method at room temperature. 500 mg of the exchanger was kept in contact with varying volume mixtures of the sodium hydroxide (0.1 M) and sodium chloride (0.1 M) solutions for 24 hours. pH of the supernatant solutions was measured and is plotted against milliequivalents of hydroxide ions. The capacity corresponding inflection point was calculated from the curve (Figure 1).

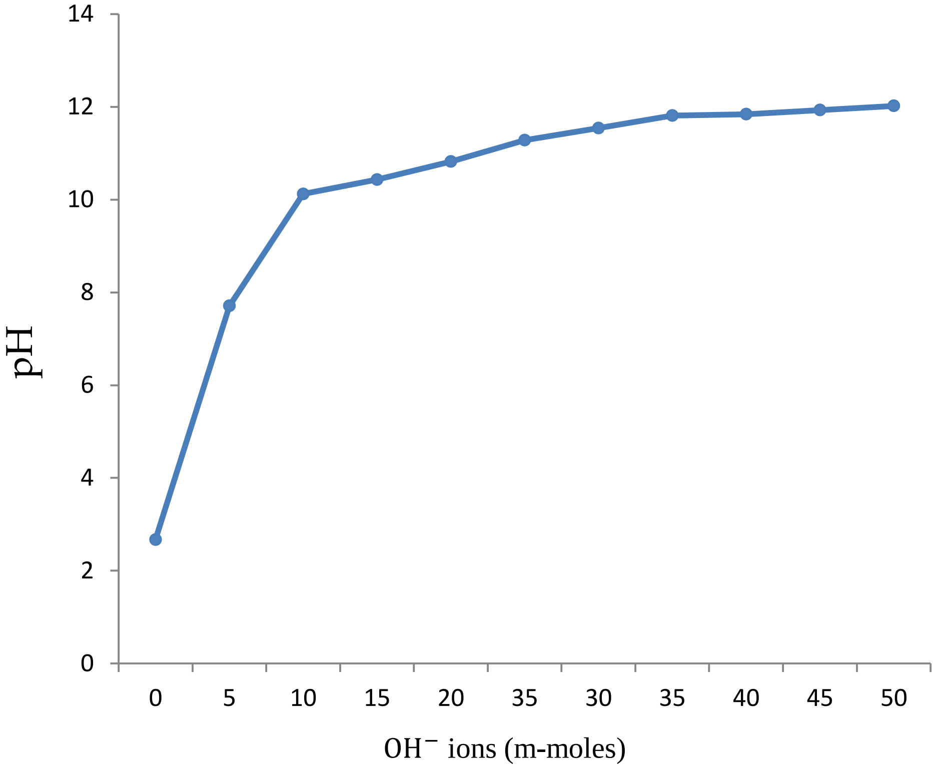

Figure 1: pH Titration Curve of CIVS

Thermal Stability

Eight equal parts of 500 mg each of the exchanger, CIVS-4, were heated at different temperatures from 50°C to 700°C in a muffle furnace for one hour. For each rise in temperature, loss in weight and loss in ion exchange capacity for sodium ions as a function of temperature were determined for the exchanger. The results are summarized in Table 3.

Table 3: Thermal Stability of Cerium(IV) iodovanadosilicate

Sl. No.	**Drying Temperature (°C)**	**Weight of Ion Exchanger After Heating (g)**	**Change in Colour**	**Percentage Retention of Weight**	**IEC (meq/g)**
1	50	0.50	Dark Yellow	100%	0.82
2	100	0.49	Yellow	98%	0.77
3	200	0.46	Pale Yellow	92%	0.69
4	300	0.45	Greenish Yellow	90%	0.52
5	400	0.35	Dirty Green	70%	0.45
6	500	0.33	Brown	66%	0.41
7	600	0.25	Dark Brown	50%	0.15
7	700	0.24	Dark Brown	48%	0.10

Chemical Stability

To observe the extent of dissolution of the exchanger in different mineral acids, organic acids and bases, 500 mg of the materials was equilibrated with 25 ml of solution of interest for 24 hours at room temperature. After chemical treatment, the remaining amount of the exchanger was filtered and washed with distilled water till acid free. Finally, the remaining sample was dried at 40±1°C in an oven and the ion exchange capacity was determined by the usual column operation with the help of standard NaOH solution. The results are given in Table 4.

Table 4: Chemical Stability of Cerium(IV) iodovanadosilicate

Sl.No.	**Solution**	**Percentage Weight Loss**	**Ion Exchange Capacity (meq/g)**
1	1 M HCl	8%	0.78
2	2 M HCl	14%	0.72
3	3 M HCl	28%	0.62
4	1 M HNO_3	12%	0.65
5	2 M HNO_3	26%	0.60
6	3 M HNO_3	36%	0.54
7	1 M H_2SO_4	40%	0.62
8	2 M H_2SO_4	44%	0.53
9	3 M H_2SO_4	60%	0.37
10	1 M HCOOH	4%	0.64
11	2 M HCOOH	6%	0.58

12	1 M CH_3COOH	4%	0.67
13	2 M CH_3COOH	8%	0.65
14	6 M KOH	Completely Dissolved	-
15	5 M NaOH	Completely Dissolved	-

Distribution Behaviour

The distribution coefficients for eleven metal ions in water were determined by batch equilibrium method (Rahangdale *et al.*, 2009) to find the selectivity of the exchanger for metal ions. 500 mg of the exchanger was shaked with 30 ml of metal ion solutions (0.1 M) at room temperature for 6 hours in conical flasks. The mixture was then kept for 24 hours at room temperature. The metal ion concentration, before and after sorption was determined by complexometric titration (Kolthoff, 1961, Vogel, 1968) with EDTA using appropriate indicators. The K_d values were calculated according to the formula-

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

Where I - Volume of 0.1 M EDTA consumed before equilibrium (ml).
F - Volume of 0.1 M EDTA consumed after equilibrium (ml).
V - Volume of metal ion solution taken (ml).
W - Weight of ion exchanger (g).

Table 5: Distribution Coefficient of CIVS-4 for Different Metal Ions

Sl.No.	**Cation**	**Form**	**K_d (ml/g)**
1	Ca^{2+}	Carbonate	4.82
2	Mg^{2+}	Acetate	1.22
3	Zn^{2+}	Acetate	5.02
4	Cu^{2+}	Acetate	23.81
5	Mn^{2+}	Acetate	3.88
6	Co^{2+}	Acetate	27.33
7	Pb^{2+}	Nitrate	2.97
8	Bi^{3+}	Nitrate	36.21
9	Cd^{2+}	Chloride	41.60
10	Ni^{2+}	Ammonium Sulphate	1.02
11	Al^{3+}	Ammonium Sulphate	8.41

PHYSICAL CHARACTERIZATION

Infrared Spectroscopy (IR)

The IR spectrum of the prepared ion exchanger was obtained from Instrumentation Centre, IIT Roorkee. The disc technique using KBr was employed for obtaining the spectrum. The IR spectrum was scanned oven the wavelength range 400 - 4000 cm^{-1}. Figure 2 shows IR spectrum of CIVS-4.

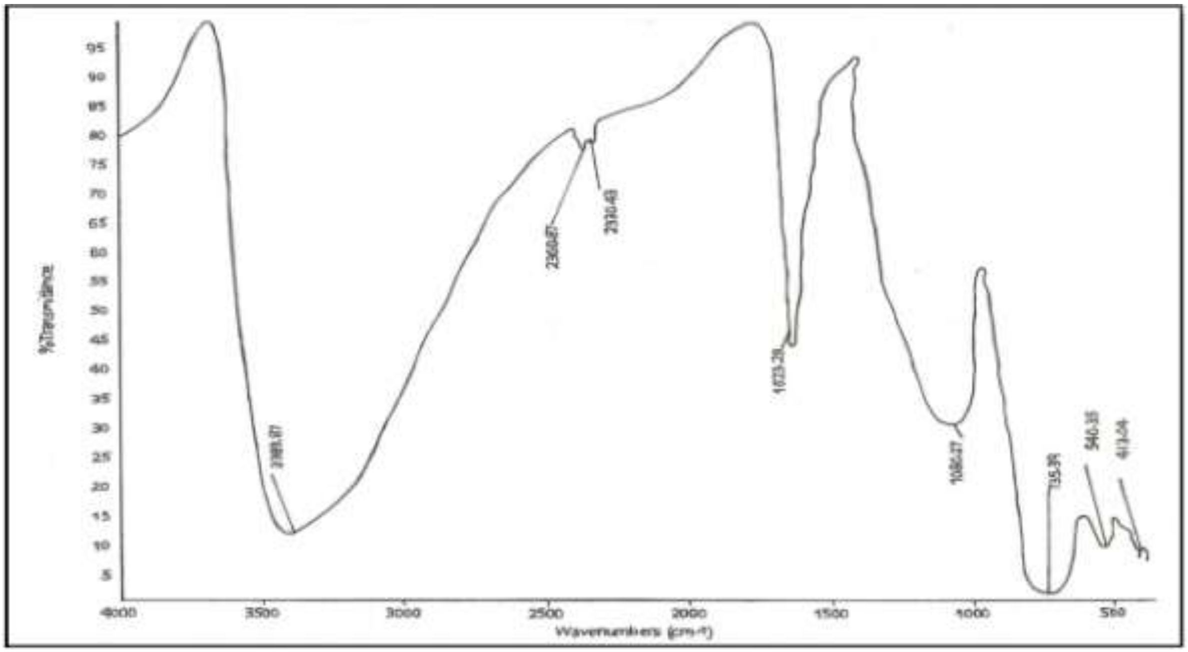

Figure 2: FTIR Spectrum of Cerium(IV) iodovanadosilicate

X-ray Diffraction (XRD) Study

XRD pattern of the exchanger was obtained from Instrumentation Centre, IIT Roorkee where X-ray B.V. Diffractometer with Cu Kα radiation beam was available. The data was collected between 5° to 120°.

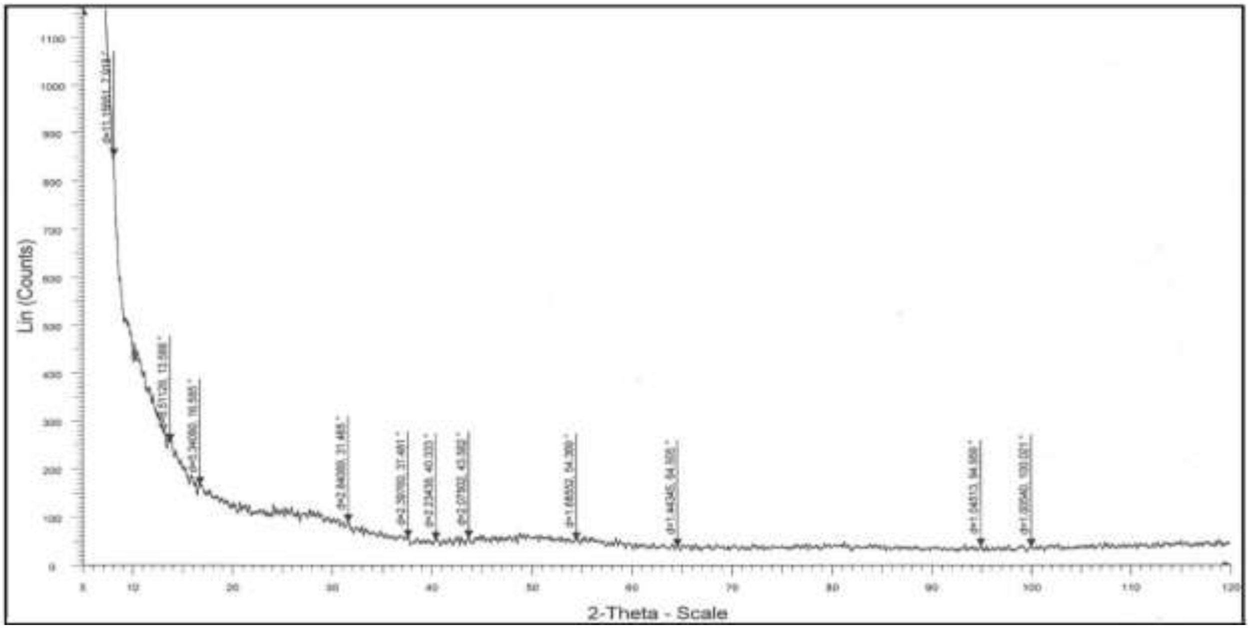

Figure 3: XRD Pattern of Cerium(IV) iodovanadosilicate

ThermogravimetricAnalysis (TGA)

The thermal stability of the synthesized ion exchanger was also evaluated by TGA. The measurements were carried out with a heating of 10°C/min under flow of nitrogen starting from ambient condition up to 1000°C. TGA Curve was also obtained from Instrumentation Centre, IIT Roorkee and is shown in Figure 4.

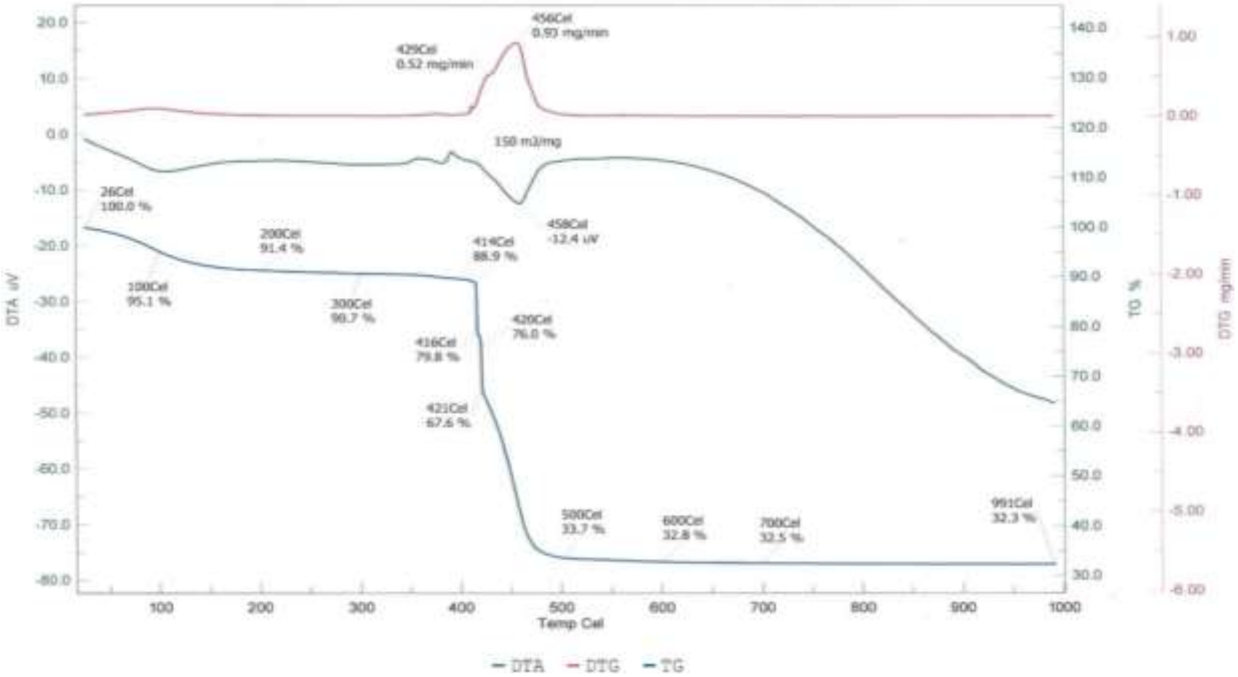

Figure 4: TGA Curve of Cerium(IV) iodovanadosilicate

APPLICATION

Binary Separation

The separation of metal ions was tried for those for which the separation factor was greater than three. Separations of Cd(II) from Pb(II), Zn(II) and Ni(II) were achieved with the help of Cerium(IV) iodovanadosilicate. Along with the above stated metal ion pairs, separation of Co(II)-Zn(II) was also achieved. The eluents used were $HClO_4$, HNO_3, NH_4NO_3 and NH_4OH of different concentrations.

Table 6: Separation Factor of Different Metal Ions for CIVS

Sample No.	**Separation Factor**	$\alpha_B^A = \frac{K_d \textit{ Value of } A}{K_d \textit{ Value of } B}$	**Value of Separation Factor**
1	α_{Pb}^{Cd}	$\frac{41.60}{2.97}$	14.01
2	α_{Zn}^{Cd}	$\frac{41.60}{5.02}$	8.29
3	α_{Ni}^{Cd}	$\frac{41.60}{1.02}$	40.78
4	α_{Zn}^{Co}	$\frac{27.33}{5.02}$	5.44

Table 7: Binary Separation Achieved on Cerium(IV) iodovanadosilicate

Sample No.	Metal Ion Pair	Amount Loaded (µg)	Amount Found (µg)	% of Metal Ion Eluted	% Error	Total Elution Volume	Eluent Used
1	Cd^{2+}	6295	6182	98.20	- 1.80	30 ml	1 M HNO_3
	Pb^{2+}	1450	1450	100	0.00	50 ml	0.1 M $HClO_4$
2	Cd^{2+}	6295	6070	96.43	- 3.57	40 ml	1 M HNO_3
	Zn^{2+}	1570	1504	95.80	- 4.20	40 ml	0.01 M $HClO_4$
3	Cd^{2+}	6295	6295	100	0.00	50 ml	0.1 M HNO_3 +0.5 MNH_4OH
	Ni^{2+}	587	528	89.95	-10.05	40 ml	0.001 M HNO_3
4	Co^{2+}	7660	7543	98.47	-1.53	50 ml	1 M NH_4NO_3
	Zn^{2+}	1570	1374	87.52	-12.48	50 ml	0.2 M $HClO_4$

Analysis of Antacid Samples

Antacids sample solutions were loaded on the column of the exchanger. The absorbed Mg^{2+} and Al^{3+} ions were eluted using 0.1 M NH_4NO_3 and 0.1 M NH_4NO_3+0.1 M HNO_3 respectively and determined by complexometric titrations.

Table 8: Analysis of Antacid Samples

Sample No.	Antacid Sample	Amount Loaded (µg)		Amount Found (µg)		Percentage Error	
		Mg^{2+}	Al^{3+}	Mg^{2+}	Al^{3+}	Mg^{2+}	Al^{3+}
1	Diegene	184.47	828.59	175.46	783.77	-4.88	-5.41
2	Siloxogene	99.71	291.40	97.28	283.29	-2.44	-2.78
3	Diovol	94.85	226.63	92.41	226.63	-2.57	0.00
4	Gelusil	243.20	249.58	237.12	242.82	-2.50	-2.70

Water Softening

Hardness causing metal ions (Ca^{2+} and Mg^{2+}) were also removed with the help of CIVS-4. Definite volume of hard water sample was passed through the column. The loaded ions were eluted using suitable eluting agents. The amount of calcium and magnesium eluted were determined by complexometric titrations using EBT as an indicator and are given in Table 9.

Table 9: Removal of Ca^{2+} and Mg^{2+} With the Help of CIVS

Sample No.	Metal Ion	Amount Loaded (µg)	Amount Found (µg)	% of Metal Ion Eluted	% Error	Total Elution Volume	Eluent Used
1	Ca^{2+}	681	641	94.13	-5.87	50 ml	1.0 M HNO_3
2	Mg^{2+}	413	389	94.19	-5.81	50 ml	0.01 M $HClO_4$

Removal of Transition Metal Ions

The same ion exchanger was also applied in removing the transition metal ions from the different influents following the same method i.e. column method. The qualitative analysis (Svehla, 1989) as well as quantitative determination of metal ions was done before and after treatment with the ion exchanger. The results are summarized in Tables 10 and 11.

Table 10: Qualitative Tests for Transition Metal Ions

Sample No.	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
1	Co^{2+}	Pink	Colourless	Effluent + Sodium hydroxide solution → No precipitate(Co^{2+} absent)
2	Ni^{2+}	Green	Colourless	(a) Effluent + Sodium hydroxide solution→ No precipitate(Ni^{2+} absent) (b) Effluent + Ammonia → No precipitate (Ni^{2+} absent)
3	Cu^{2+}	Blue	Colourless	(a) Effluent + Sodium hydroxide solution→ No precipitate(Cu^{2+} absent) (b) Effluent + Ammonia → No precipitate (Cu^{2+} absent)

Table 11: Removal of Transition Metal Ions With the Help of CIVS

Sample No.	**Metal Ion**	**Amount Loaded (μg)**	**Amount Found (μg)**	**% of Metal Ion Eluted**	**% Error**	**Eluent**	**Volume of Eluent Used**
1	Co^{2+}	7660	7425	96.93	-3.07	1 M NH_4NO_3	60 ml
2	Ni^{2+}	587	564	96.08	-3.92	0.1 M $HClO_4$	50 ml
3	Cu^{2+}	4830	4703	97.36	-2.64	0.2 M HNO_3	50 ml

RESULTS AND DISCUSSION

Different twelve samples of Cerium(IV) iodovanadosilicate have been synthesized under similar condition with varying volume ratios of the solutions. The observations of synthesis of the exchanger samples are given in Table 1. The results show that sample CIVS-4 possessed highest ion exchanger capacity (0.82 meq/g) for Na^+ and therefore it was chosen for detailed studies.

The results of ion exchange capacity for alkali metals and alkaline earth metals are given in Table 2. The concentration of metal salt solutions have little effect on IEC whereas size and charge of the exchanging ion affects the IEC more (Nilchi *et al.*, 2006) CIVS-4 shows higher capacity for alkali metals than alkaline earth metals. The exchanger show maximum IEC for K^+ ions (0.91meq/g). The IEC of CIVS-4 increases with the decrease in hydrated ionic radii of the metal ions.

The pH titration results are plotted in Figure 1, for alkali salt and their hydroxide. The graph indicates that the material behaves as strong cation exchanger as indicated by the low pH (2.67) of the solution when no OH^- ions were added to the system. The IEC of CIVS-4 is 0.85 $meqg^{-1}$ calculated at the inflexion point.

The effect of heating on IEC of CIVS-4 was observed and it was found that it retains about 98% exchange capacity up to 100°C. However the capacity start decreasing when the drying temperature is further increased. But in fact the exchanger shows sufficient IEC (0.41meq/g), even when the drying temperature was raised to 500°C.

The chemical stability data given in Table 4 revealed that CIVS-4 is fairly stable in organic acids (HCOOH and CH_3COOH) and quite stable in mineral acids such as HCl, HNO_3 and H_2SO_4. The maximum stability of CIVS-4 was found in HCl and the exchanger retains about 80% of the IEC in 3 M HCl. The material was found to be dissolved in basic media (5 M NaOH and 6 M KOH).

The distribution coefficients (K_d values) were calculated for eleven metal ions in aqueous medium and are given in Table 5. It reveals that CIVS-4 possess highest selectivity for Cd(II). The increasing sequence of affinity of the exchanger for eleven metal ions is given below-

Ni(II)< Mg(II)<Pb(II) <Mn(II) < Ca(II) < Zn(II) < Al(III) < Cu(II) < Co(II) < Bi(III) < Cd(II)

In FTIR (Figure 2) study, the broad band in the region 3600-3000 cm^{-1} may be assigned to interstitial water molecules and OH groups (Rao, 1963). Another strong and sharp peak with a maximum of 1623 cm^{-1} may be due to H-OH bending. A band at 1080.27 cm^{-1} shows the presence of silicate (Maragheh *et al.*, 1996). The peaks at 725 cm^{-1} and 540 cm^{-1}correspond to vanadate and iodate respectively. In the spectrum, a peak at 413 cm^{-1} is assigned to Ce-O stretching band (Liao *et al.*, 2001).

Absence of sharp peaks in the X-ray diffraction pattern of CIVS-4 (Figure 3) indicates that the material is amorphous in nature.

TGA Curve shows about 8% weight loss upto 200°C. From 200°C to 414°C, there is no appreciable weight loss. Further heating of the material from 414°C to 500°C shows a rapid decline in weight (55%). Therefore, the thermogram of CIVS-4 clearly suggests that the loss in weight upto 200°C is due to

removal of external water molecules. The stability of the exchanger is quite significant in the temperature range 200°C to 414°C (Moosavi *et al.,* 2009). Above 500°C, the weight remains nearly constant.
The extremely high affinity of CIVS-4 for Cd(II) suggests its possible use for cadmium separation from other metal ions. When Cd(II) is eluted by 0.1 M HNO_3 + 0.5 M NH_4OH, 100% of the cadmium was recovered. In binary separations, the recovery ranges from 87.52% to 100%. The quantitative separations of Al^{3+} and Mg^{2+} from antacid samples have been made possible on the column of the exchanger. Water softening results showed nearly same extent of removal of calcium and magnesium ions. Transition metal ions (Co, Ni, and Cu) can be easily removed by using the column of this exchanger.

CONCLUSION

Newly synthesized CIVS is a promising ion exchanger, with good ion exchange capacity. The establish material in analytical chemistry uses for the separation of trace metals like Pb, Cd & Co etc. to remove with help of synthesized cation exchanger.

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