Synthesis, Characterization and Ion Exchange Properties of a three Component Cation Exchanger [Stannic(IV) iodosilicate]: Separation of Cd(II) from Mg(II), Ni(II) and Zn(II)

SUBHASH CHAND*, SEEMA, CHANDRA VIJAY CHAHAL and ARTI

Department of Chemistry, Meerut College, Meerut (India).
*Corresponding author: E-mail: subhash.nirban@gmail.com, chahalmonu83@gmail.com

ABSTRACT

A new three component cation exchanger [Stannic(IV) iodosilicate] has been prepared by adding a mixture of 0.1M potassium iodate and 0.1M sodium metasilicate to 0.1M stannic chloride and maintained pH 1. The ion exchange capacity of the exchanger has been determined (0.66 meq/g) for Na^+ ions. The IEC for various other metal ions has also been determined. The cation exchanger is found to have high thermal and chemical stability. The synthesized cation exchanger is also characterized by IR, TGA, SEM and XRD studies.

The distribution behaviour of the exchanger for Mg(II), Ni(II), Zn(II), Cu(II), Mn(II), Co(II), Pb(II), Bi(III), Cd(II) and Ca(II) metal ions has been studied. On the basis of the differences in distribution coefficients, three binary separations (Mg^{2+}-Cd^{2+}, Ni^{2+}-Cd^{2+}, Zn^{2+}-Cd^{2+}) of metal ion pairs have been achieved.

Key words: Inorganic cation exchanger, Stannic(IV) iodosilicate, Ion exchange capacity, Distribution studies, Binary separation.

INTRODUCTION

Ion exchange is a reversible chemical reaction where an ion from a solution is exchanged for a similarly charged ion attached to an immobile solid particle

$$Ca^{2+} + Na_2 - X \; Ca \rightleftharpoons X + 2Na^+$$

We can also say that Ion exchange is an exchange of Ions between two electrolytes or between an electrolyte solution and a complex. In most cases the term is used to denote the processes of purification, separation and decontamination of aqueous and other ion containing solutions with solid ion exchangers.

Typical ion exchangers are ion exchange resins (gel polymer), zeolites, clay and soil humus. Ion exchangers are either cation exchangers that exchange positively charged ions (cations) or anion

exchangers that exchange negatively charged ions (anions). Ion exchangers have binding preferences for certain ions or classes of ions depending on their chemical structure. This can be dependent on the size of the ions, their charge or their structure.

When an ion exchanger is brought in to contact with an electrolyte solution by shaking a given quantity of exchanger with the solution, exchange of ions take place until equilibrium is attained. At equilibrium the solution generally contains the same ionic species as it originally did, although the concentration of these species has changed and additional ions previously attached to the exchanger. The same ionic species as in the solution are found in the ion exchanger but the concentrations differ from those in the solution[1].

At first ion exchangers were mostly used for water softening but they soon became widely employed in many other fields. They assumed great importance in chemical research, in analysis, in preparative work as well as in technology. The appearance of ion exchangers had a great impact on analytical chemistry[2].

In the last forty years there has been a great upsurge in the researchers on synthetic inorganic ion exchangers. The main emphasis has been given to the development of new materials possessing chemical stability and selectivity for certain metal ions important from analytical and environmental point of view[3].

Tin(IV) based ion exchangers have received attention because of their excellent ion exchange behaviour. Some two component ion exchangers i.e. Stannic tungstate[4], Stannic phosphate[5], Stannic molybdate[6], Stannic oxide[7] and Tin antimonate[8] have been synthesized. Other three component ion exchangers Stannic vanadophosphate[9], Stannic tungstosilicate[10], Stannic molybdophosphate[11], Tin(IV) antimono arsenate[12], Tin(IV) molybdosilicate[13], Tin(IV) tungstophosphate[14], Tin(IV) pyrophosphate[15], Tin(IV) selenophosphate[16], Tin(IV) iodophosphate[17], Tin(IV) tungstoselenate[18], Tin(IV) arsenosilicate[19], Tin(IV) selenoarsenate[20], Tin(IV) vanadotungstate[21], Tin(IV) vanadoarsenate[22], Tin(IV) molybdoarsenate[23] and Tin(IV) tungstosilicate[24] have also been synthesized.

The present work has been undertaken in an attempt to synthesized a three component ion exchanger (Stannic iodosilicate). Separation of Cd(II) from various metal ions has been achieved.

EXPERIMENTAL

Reagents and chemicals

Stannic(IV) chloride($SnCl_4.5H_2O$) and potassium iodate(KIO_3) were obtained from CDH (India) while sodium metasilicate($Na_2SiO_3.5H_2O$) was a Qualigens (India) product. Chlorides and Nitrates of metal ions from CDH (India) used were of analytical grade.

Instruments / apparatus used

pH measurements were performed using Toshniwal Research pH Meter. Tanco's Electric Rotary Shaker was used for shaking. X-ray diffraction studies were made on a Philips Analytical X-ray Diffractometer. Thermonicolet IR Spectrophotometer for FTIR was available at IIT Roorkee. For TGA a Perkin Elmer Instrument was used. Scanning Electron Micrographs were also obtained from IIT Roorkee. All the glass wares used during the work were made of Borosil.

Preparation of ion exchange material

Stannic iodosilicate was prepared by adding mixture of 0.1M aqueous solutions of sodium metasilicate and potassium iodate in a 0.1M aqueous solution of stannic chloride with constant stirring using a magnetic stirrer in ten different volume ratios. The desired pH was adjusted by adding dilute hydrochloric acid. The precipitates of all the ten samples were aged in the mother liquors for twenty four hours at room temperature.

Decant the supernatant liquid from all the samples and filtered the precipitates of all the ten samples. The excess of acid from the samples was removed by washing with distilled water. When precipitates became neutral then dried them at 40 ± 1^0C in an oven. The dried ten samples were cracked into small granules by putting them into hot distilled water, again dried the samples and convert them into H^+ from by shaking them with M HNO_3 solutions at room temperature. The material was finally washed with distilled water to remove the excess acid.

After washing the materials were finally dried at 40±1⁰C.

Ion Exchange Capacity

The IEC of the material was determined by the column process (table-2). 500mg of the dry exchanger (H^+ form) was packed into a column in each case having a glass wool support at the base. First distilled water was passed through the column to remove any excess of acid remained sticking on the particles. M $NaNO_3$ solution was passed through the column and maintained the flow rate at 9-10 drops/min. The effluent was carefully collected in to a flask and titrated against a standard NaOH solution to determine the ion exchange capacity of all the ten samples.

pH titration

pH titration was performed by the batch process. Topp and Pepper method was used for pH studies in LiCl-LiOH, NaCl-NaOH, KCl-KOH, $CaCl_2$-$Ca(OH)_2$, $MgCl_2$-$Mg(OH)_2$ and $BaCl_2$-$Ba(OH)_2$ system[25]. For pH titration 500mg of exchanger was shaked with 50ml of the solution concerned.

IEC for various cations

Ion exchange capacity of the synthesized bulk sample was also determined by column process. The ion exchanger in H^+ form was placed in a glass wool supported column. Different salt solutions of 0.1M concentrations were used as eluents. Hydrogen ions eluted from the column were determined titrimetrically. IEC of the exchanger was determined for some monovalent and divalent cations.

Thermal stability

Ion exchanger samples were dried at different temperatures from 100⁰C to 700⁰C in a muffle furnace. For each 100⁰C rise in temperature, loss in weight and IEC were determined. To find the thermal stability seven equal parts of 500mg each of the dry exchanger were heated in crucible for one hour at various temperatures in the muffle furnace. After cooling the exchanger at room temperature, the ion exchange capacity for sodium ion was determined by column process using standard NaOH solution.

Chemical stability

The chemical stability of Stannic iodosilicate was examined in solutions of several mineral acids such as HCl, HNO_3 and H_2SO_4 and bases NaOH and KOH of different strength. Chemical stability was also checked in organic acid such as acetic acid and formic acid. A 0.5g of the exchanger was equilibrated with 25ml of the solvent of interest and kept for 24 hours at room temperature. The material is found to be quite stable in lower concentration of the mineral acids. The remaining amount of exchanger was filtered and washed with distilled water. After drying the remaining exchanger, ion exchange capacity was determined using standard NaOH solution (column process).

Distribution studies

The distribution coefficient (K_d) values for metal ions Mg^{2+}, Ni^{2+}, Zn^{2+}, Cu^{2+}, Mn^{2+}, Co^{2+}, Pb^{2+}, Bi^{3+}, Cd^{2+}, Ca^{2+} were determined in distilled water. 500mg portion of the dry exchanger (Stannic iodosilicate) in H^+ form were taken in beaker with 25ml of different metal ion solutions and shake the solution for six hours with the help of rotary shaker. Put the solution as such for twenty four hours. The amount of metal ions present in the solution before and after equilibrium were determined by titrating it against EDTA using standard procedures[26].

The K_d values, as summarized in table 7 were obtained using the formula:

$$K_d = \frac{I\text{-}F}{F} \cdot \frac{V}{M}\,(ml/g)$$

XRD

The X-ray diffraction analysis of Stannic iodosilicate was obtained from Instrumentation Centre, IIT Roorkee

SEM images

Scanning electron micrographs were also obtained from IIT Roorkee. The SEM Images have been captured at different magnifications

IR analysis

FTIR spectrum of Stannic iodosilicate was obtained from Instrumentation Centre. KBr Disc method was used for the spectrum. The spectrum obtained was recorded between $4000cm^{-1}$ and $400cm^{-1}$ (fig-4)

Thermogravimetric analysis

TGA of the exchanger in H⁺ form was carried out at a heating rate of 10⁰C/min. The exchanger was heated from 50⁰C to 750⁰C in air atmosphere. TGA curve is shown in fig-5

Separation of metal ions achieved

In order to explore the separation ability of the exchanger several binary separations were tried using a column with a glass wool support at the base. 500mg of Stannic iodosilicate was packed in to the column. The column was washed throughly with distilled water and then the mixture of metal ion solution to be separated was loaded on it. The solution was allowed to move through the column at very slow rate(1ml/min). The solution passed through the column repeatedly three times. The absorbed metal ions were then eluted with suitable eluents. The effluents were collected into the beakers and metal ions in the effluent were determined titrimetrically using EDTA solution.

RESULTS AND DISCUSSION

Stannic iodosilicate was synthesized in ten different samples by the mixing the reactant solutions in different volume ratios(table-1). The different samples were named as SIS-I, SIS-II, SIS-

Table 1: Conditions for synthesis of different samples of Stannic iodosilicate

S. No.	Sample No.	Concentration(M)			Mixing Ratio V/V/V	pH	Appearance of precipitate
		SC	PI	SMS			
1	SIS-I	0.1	0.1	0.1	1:1:1	1	White
2	SIS-II	0.1	0.1	0.1	2:1:1	1	Creamy White
3	SIS-III	0.1	0.1	0.1	1:2:1	1	White
4	SIS-IV	0.1	0.1	0.1	1:1:2	1	White
5	SIS-V	0.1	0.1	0.1	2:2:1	1	White
6	SIS-VI	0.1	0.1	0.1	2:1:2	1	White
7	SIS-VII	0.1	0.1	0.1	1:2:2	1	White
8	SIS-VIII	0.1	0.1	0.1	3:1:1	1	Creamy White
9	SIS-IX	0.1	0.1	0.1	1:3:3	1	White
10	SIS-X	0.1	0.1	0.1	3:1:3	1	White

SC – Stannic chloride, PI- Potassium iodate, SMS- Sodium metasilicate

Table 2: IEC of ten samples of Stannic iodosilicate

Sample No.	Colour of beads before generation	Colour of beads after generation	IEC (meq/g)
SIS-I	White	White	.521
SIS-II	Creamy White	White	.407
SIS-III	White	White	.264
SIS-IV	White	White	.430
SIS-V	White	White	.393
SIS-VI	White	White	.580
SIS-VII	White	White	.309
SIS-VIII	Creamy White	Creamy White	.490
SIS-IX	White	White	.437
SIS-X	White	White	.660

Sample no. SIS-X was selected for further study and synthesized in bulk due to its highest IEC.

III, SIS-IV, SIS-V, SIS-VI, SIS-VII, SIS-VIII, SIS-IX, SIS-X. The ion exchange capacity of various samples of Stannic iodosilicate is given in table-2. The ion exchange capacity seems to be much higher for sample SIS-X as compared to other samples. Therefore the sample SIS-X was selected for bulk synthesis. The volume ratio for bulk synthesis of SIS-X was 3:1:3. The bulk synthesis was done in the similar way as described in synthesis part and the exchanger was represented as SIS-X-B.

Table 3:

| Sample No.	NaCl-NaOH		Weight of ion exchanger	pH
	NaCl (ml)	NaOH (ml)		
SIS-X-B	50	0	500 mg	3.01
SIS-X-B	45	5	500 mg	8.30
SIS-X-B	40	10	500 mg	9.51
SIS-X-B	35	15	500 mg	10.04
SIS-X-B	30	20	500 mg	10.49
SIS-X-B	25	25	500 mg	10.75
SIS-X-B	20	30	500 mg	10.94
SIS-X-B	15	35	500 mg	11.06
SIS-X-B	10	40	500 mg	11.26
SIS-X-B	05	45	500 mg	11.74
SIS-X-B	0	50	500 mg	11.84

Table 4: IEC of Stannic iodosilicate for mono and divalent cations

S. No.	Cation	Solution Concentration	Salt Used	Hydrated Radii	IEC
1	K^+	0.1M	KBr	5.30	.692
2	Na^+	0.1M	$NaNO_3$	7.90	.66
3	Li^+	0.1M	LiCl	10.0	.536
4	Ba^{2+}	0.1M	$BaCl_2$	8.80	.417
5	Mg^{2+}	0.1M	$MgCl_2$	10.80	.348
6	Ca^{2+}	0.1M	$CaCl_2$	9.60	.37

Table 5: Thermal effect on Stannic iodosilicate

S. No.	Sample No.	Temp (^{0}C)	Weight before heating(g)	Weight after heating(g)	Colour after heating	IEC
1	SIS-X-B	100	0.50	0.47	Creamy white	0.58
2	SIS-X-B	200	0.50	0.45	Yellow	0.49
3	SIS-X-B	300	0.50	0.43	Dark Yellow	0.44
4	SIS-X-B	400	0.50	0.42	Brown	0.41
5	SIS-X-B	500	0.50	0.41	Black	0.36
6	SIS-X-B	600	0.50	0.41	Black	0.35
7	SIS-X-B	700	0.50	0.40	Black	0.29

Nabi et al observed that the effective charge on the cation also plays role in ion exchange capacity of the exchanger i.e., ion exchange capacity decreases with increasing charge of the ion[27]. Hydrated ionic radii are in the reverse order of their ionic sizes for a series of metal ions in a group. The effect of size and charge of the exchanging ingoing ion on the IEC of the material was studied for alkali and alkaline earth metals, the sequence shown by SIS-X-B is as follows.

$$Li^+ < Na^+ < K^+ \quad ; \quad Mg^{2+} < Ca^{2+} < Ba^{2+}$$
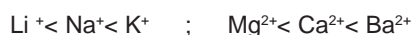
The calculated IEC was summarized in table-4.

Fig-1 represents the pH titration curve for monovalent system, namely NaCl-NaOH. Eleven equal portions of the exchanger were treated with NaCl-NaOH system and pH was noted.

The first sample gave the pH of 3.01 and found that increase in volume of NaOH, increases the pH. The rapid change in pH due to change in medium from acidic to basic. The pH of all eleven samples is given in table-3. The IEC was calculated with the pH titration curve which is nearly same. Thermal study results showed that the ion exchange capacity of SIS-X-B was also affected with temperature change. As the drying temperature of

Table 6: Chemical stability of Stannic iodosilicate in different solutions

Solution	Weight before treatment (g)	Weight after treatment (g)	IEC
DMW	0.50	0.50	0.66
1N HNO$_3$	0.50	0.46	0.421
2N HNO$_3$	0.50	0.42	0.372
1N HCl	0.50	0.44	0.414
2N HCl	0.50	0.39	0.336
1N H$_2$SO$_4$	0.50	0.47	0.447
2N H$_2$SO$_4$	0.50	0.44	0.369
2N HCOOH	0.50	0.46	0.47
2N CH$_3$COOH	0.50	0.45	0.448
2N KOH	0.50	Dissolved	-
2N NaOH	0.50	Dissolved	-

Table 7: Distribution coefficient for different metal ions

Metal ion	Taken as	K_d (ml/g)
Mg(II)	Acetate	2.50
Ni(II)	Ammonium sulphate	16.083
Zn(II)	Acetate	12.154
Cu(II)	Acetate	8.726
Mn(II)	Acetate	6.59
Co(II)	Acetate	43.50
Pb(II)	Nitrate	18.579
Bi(III)	Nitrate	13.846
Cd(II)	Chloride	48.256
Ca(II)	Carbonate	1.66

the material increases, ion exchange capacity decreases due to loss in weight of the exchanger. The weight loss and IEC are given in table-5.

The chemical stability data given in table-6 revealed that Stannic iodosilicate is fairly stable in higher concentration of organic acids (HCOOH, CH$_3$COOH) and is quite stable in mineral acids. The exchanger is completely dissolved in basic media (2M NaOH, 2M KOH).

The distribution behavior of metal ions show the high selectivity of the exchanger for Cd(II), indicating its importance in environmental studies.
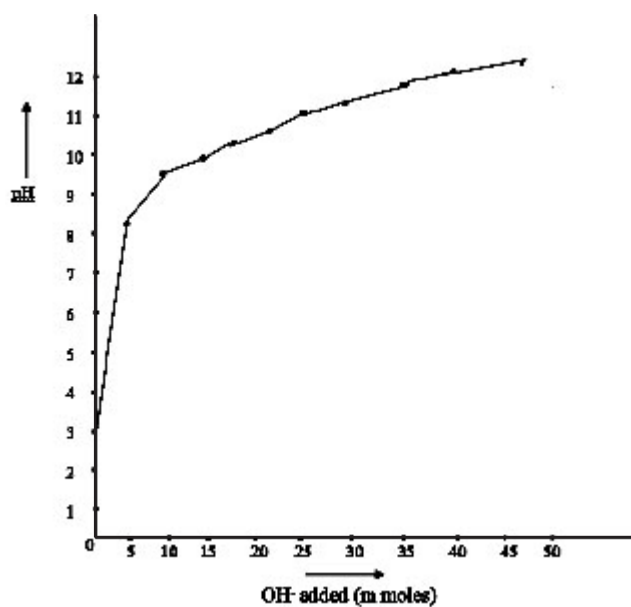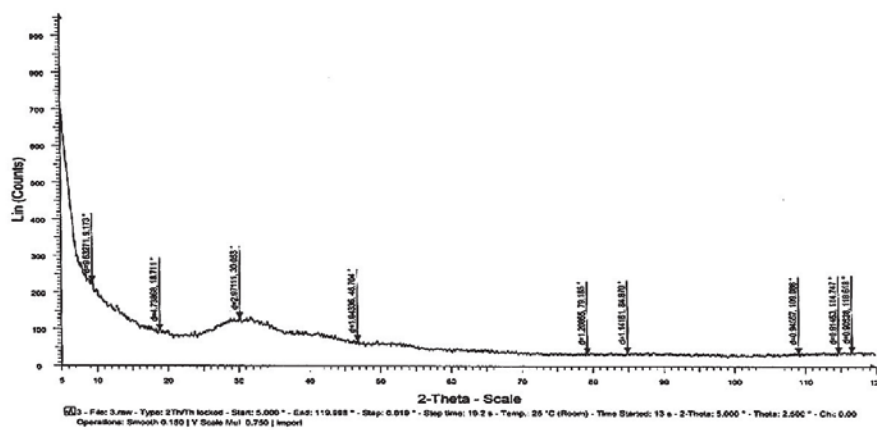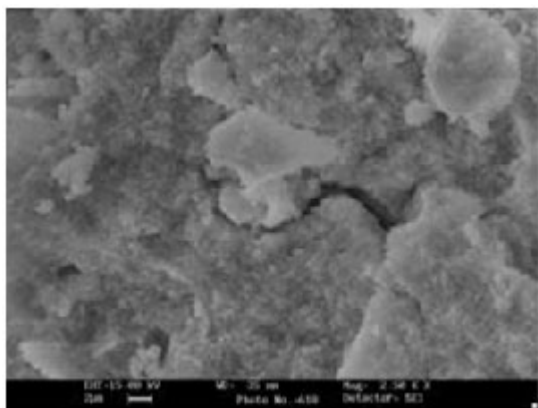
Fig. 1:

Fig. 2:

Fig. 3(a):

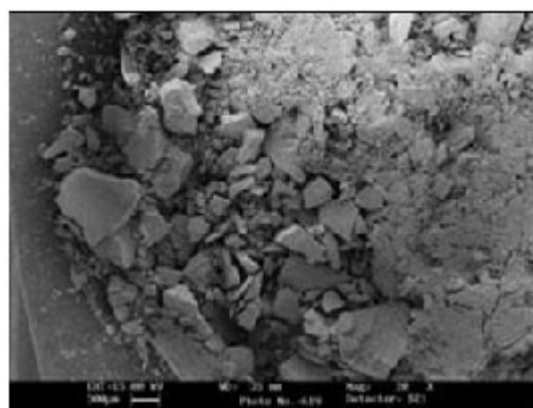**Fig. 3(b):**

The increasing sequence of affinity of the exchanger for the different metal ions is given below: $Ca^{2+} < Mg^{2+} \qquad < Mn^{2+} < Cu^{2+} < Zn^{2+} < Bi^{3+} < Ni^{2+} < Pb^{2+} < Co^{2+} < Cd^{2+}$

The K_d values for different metal ions are given in table-7. The X-ray diffraction pattern (fig-2) of the material exhibits several peaks of weak intensities indicating its amorphous nature. The amorphous nature of the exchanger was also confirmed by scanning electron microscopy. SEM image of newly synthesized SIS-X-B shows irregular shapes.

Infrared spectrum shows a broad peak at $3432cm^{-1}$ which is due to hydroxostretching vibrations[28]. Another strong peak with a maximum of $1633cm^{-1}$ due to H-O-H bending[29]. The spectrum of the exchanger showed two peaks at $1074cm^{-1}$ and $960cm^{-1}$ which indicate the presence of silicate and iodate groups respectively. The metal oxygen bond (Sn-O) peak was observed at $546cm^{-1}$.

Thermogravimetric analysis of Stannic iodosilicate showed that the exchanger is quite stable. Weight loss of the ion exchanger heated at various temperatures was recorded (fig-5). There
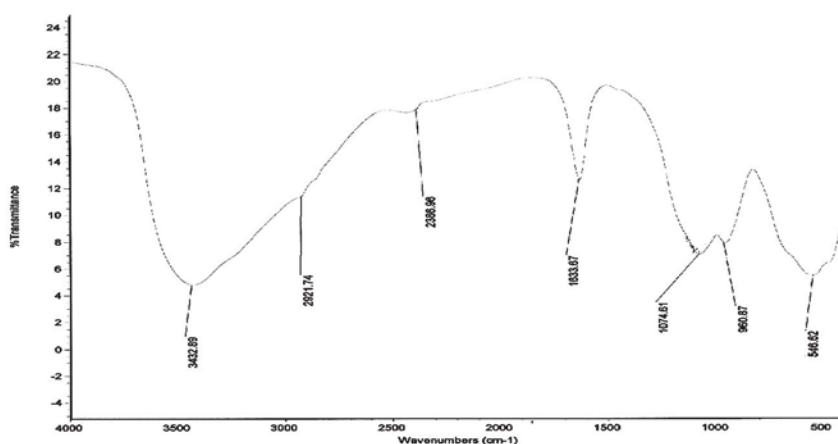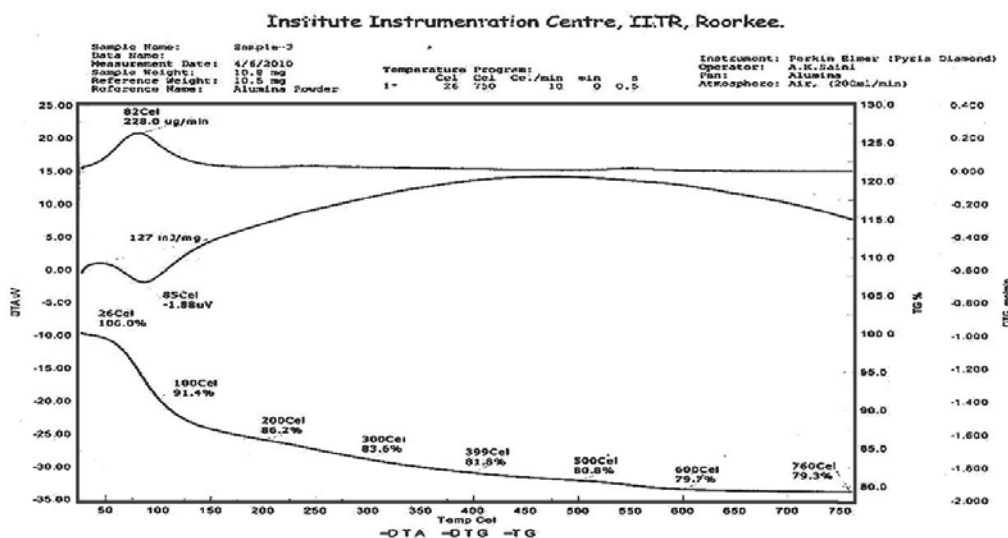

Fig. 4:

Fig. 5:

Table 8:

Sample No.	Separation	Metal ions in μg		% Error	Eluent used
		Loaded	Found		
1	Cd-Mg	4107	4106	-0.03	0.4M NH_4NO_3
		86	85.14	-1.08	0.25M HNO_3
2	Cd-Ni	4107	4098	-0.22	0.1M HNO_3 in 0.5M NH_4OH
		1069	1063	-0.5	0.001M HNO_3
3	Cd-Zn	4107	4105	-0.05	1M HNO_3
		1092	1090	-0.2	0.01M $HClO_4$

is a sharp decline in weight of the compound when temperature arises from 25^0C to 200^0C due to loss of coordinated water molecules. Further decline in weight was observed from 200^0C to 400^0C (86.2%-81.8%) and after the temperature of 400^0C, the loss in weight of exchanger was less. The further loss in weight was due to the loss of different components of the exchanger.

Separations of metal ions were achieved on the basis of K_d values. The distribution studies showed that the material was found to possess exceptional high K_d value for Cd(II) and hence

considered to be highly selective for Cd(II). Cd(II) has been considered as a major polluting material in water, indicating its importance in environmental pollution control.

For Binary separation of metal ions, the separation factor was calculated. The separations of three metal ion pairs were achieved for which the value of separation factor was greater than three. Binary separations of Cd(II)-Zn(II), Cd(II)-Ni(II) and Cd(II)-Mg(II) were achieved quantitatively from the column of Stannic iodosilicate.

REFERENCES

1. Ion Exchange Separations in Analytical Chemistry, Olof Samuelson, John Wiley & Sons, 58 (1963).

2. Ion Exchange, Jacob A. Marinsky, Marcel Dekker, Inc., New York, **1**: 3 (1966).

3. Synthetic ion exchange materials and their analytical applications, K.G. Varshney

4. M. Qureshi and K.G. Varshney, Journal of Inorganic and Nuclear Chemistry, **30**(11): 3081 (1968).

5. Y. Inoue, *J. of Inorganic and Nuclear Chemistry,* **26**(12): 2241 (1964).

6. M. Qureshi and J.P. Rawat, *J. of Inorganic and Nuclear Chemistry*, **30**(1): 305 (1968).

7. El-Said I. Shabana, Nasr Z. Misak, *Solid State Ionics*, **44**(1-2): 41 (1990).

8. K.G. Varshney, N. Tayal, A.A. Khan & R. Niwas, *Colloids and Surface* (A), **181**: 123

9. M. Qureshi and R.C. Kaushik, *Analytical Chemistry*, **49**(1): 165 (1977).

10. S.D. Sharma, S. Mishra and A. Agarwal, *Indian J. Chem.*, **33**A: 696 (1994).

11. M.G. Marageh, S. W. Husain, A. R. Khanchi, Applied Radiation and Isotopes, **50**: 459 (1999)

12. Susheel K. Mittal, Prit pal Singh, *Reactive and Functional polymers*, **40**(3): 231 (1999).

13. M. Qureshi, A.P. Gupta, S. Nasir, A. Rizvi, N.A. Shakeel, Reactive Polymers, Ion Exchanger, Sorbents, **3**(1): 23 (1984).

14. A.P. Gupta, M.Qureshi, Y.Sharma, *J. Ind. Chem. Soc.*, **63**(2): 206 (1986).

15. X. Ming, L. Xu, L. Liu, C. Jenchen, *Zhengguoxitu*, **3**(3): 82 (1985).

16. S.A. Nabi, Z.M. Siddiqui, R.A.K. Rao, *Bull,*

(2001).

Chem. Soc. Jpn., **58**(80): 2380 (1985).

17. S.A. Nabi, W.A. Siddiqui, *J. Liq. Chromatogr.,* **8**(6): 1159 (1985)

18. S.A. Nabi, Z.M. Siddiqui, *Bull. Chem. Soc. Jpn.*, **58**(2): 1159 (1985).

19. K.G. Varshney, A.A. Khan, A. Maheshwari, S. Anwar, U. Sharma, *Ind. J. Technol.*, **22**(3): 99 (1984).

20. S.A. Nabi, R.A.K. Rao, A.H. Siddiqui, Fresenius, Z. *Anal. Chem.*, **311**(5): 503 (1982).

21. M. Qureshi, R.C. Kaushik, *Sep. Sci. Technol.*, **17**(5): 739 (1982).

22. P.S. Thind, J.P. Rawat*, Chem. Anal.* [Warsar] **24**(1): 65 (1978).

23. M. Qureshi, R. Kumar, R.C. Kaushik, *Sep. Sci. Technol.*, **13**(20): 195 (1978).

24. S. Chand, Seema, Teena, Manju, I.T.A.S., **2**(1): 181 (2010).

25. N.E. Topp, K.W. Pepper, *J. Chem. Soc.,* 3299 (1949).

26. I.M. Kolthoff and P.J. Elving, *Treatise on Analytical Chemistry*, **3**: 2 (1961).

27. S.A. Nabi, N. Rahman, W.U. Farooqui and S. Usmani, *Indian J. Chem.*, **34**A: 317 (1995).

28. AP. Gupta, G.L.Verma and Saiqa Ikram, *React. & Fun. Polymers*, **43**: 33 (2000).

29. W.A. Siddiqui, S.A. Khan, *Bull. Mater. Sci*, **30**(1): 43 (2007)