Desalination and Water Treatment
www.deswater.com
16 (2010) 29–38
April

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doi: 10.5004/dwt.2010.1045

Preparation and characterization of a new inorganic cation-exchanger: Zirconium (IV) iodosilicate: Analytical applications for metal content determination in pharmaceutical sample and synthetic mixture

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Received 18 December 2008; Accepted 25 November 2009

ABSTRACT

A new inorganic cation exchanger zirconium(IV) iodosilicate was synthesized and characterized on the basis of X-ray, TGA-DTA, FTIR and SEM studies. This cation-exchanger was found to have a good ion-exchange capacity (0.85 meq g^{-1} for Na^+), high thermal and chemical stability. The chemical composition reveals that Zr:I:Si is in the molar ratio 1:1.57: 1. The chemical stability data shows that material is quite stable in common mineral acids, bases and organic solvents of analytical interest upto 2.0 M. Thermal analysis shows that exchanger retain 80% of ion-exchange capacity upto 400°C. Effect of time and temperature on the sorption of metal ions on this material was explored. The sorption behavior of metal ions was studied in acetic acid, formic acid, DMSO, DMF and succinic acid. Some important and analytically difficult quantitative binary separations viz. Cd(II)-Ba(II), Cd(II)-Ni(II), Cd(II)-Cu(II), Cd(II)-Fe(III) etc. were achieved. The practical applicability of the cation-exchanger was demonstrated in the separation of Zn(II)-Fe(III) from a synthetic mixture as well as from real sample of pharmaceutical formulation.

Keywords: Synthesis; Inorganic ion-exchanger; Zirconium(IV) iodosilicate; Characterization; Analytical application; Pharmaceutical formulation

1. Introduction

The growing concern over the increase level of the toxic metal ions beyond the permissible limit has exaggerated the synthesis of new inorganic ion-exchanger. The interest in these materials is due to their thermal and chemical stability and their specific behavior towards certain ionic species. They have been widely used for the removal of heavy metal ions from wastewater streams coming out of different industries. These heavy toxic metal ions [1–18] if present beyond the certain concentration are not only toxic but also can lead to serious health problems. So every care should be taken to treat these wastewaters before flowing into public sewage, rivers and on land to prevent environmental pollution. In this regard effective sorbents with strong affinity towards certain toxic metal ions should be explored. Among them the polyacids of tetravalent metal ions have been mostly studied because of their excellent ion-exchange characteristics. Among the various inorganic ion exchangers, metal soluble acid salts of tetravalent metal ions (Zr^{4+}, Ti^{4+}, Sn^{4+}) occupied a pivotal position. Zirconium based ion-exchangers have received much attention because of their excellent ion-exchange behavior and some important chemical

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applications in ion-exchange chromatography, membrane science and solid-state electrochemistry. The literature reveals that several three-component Zr(IV) based ion exchangers reported in the literature are zirconium(IV) iodovanadate [19], zirconium(IV) tungestomolybdate [20], zirconium(IV) iodophosphate [21], zirconium(IV) antimoarsenate [22], zirconium(IV) selenioodate [23] zirconium(IV) antimonophospahte [24], zirconium(IV) molybdoarsenate [25], zirconium(IV) selenophosphate [26], zirconium(IV) arsenatovanadate, zirconium(IV) arsenophosphate, and zirconium(IV) selenophosphate.

The present paper describes the detailed study of synthesis, characterization and analytical applications of cation exchanger Zirconium(IV) iodosilicate. The analytical utility of the material was demonstrated by carrying out binary separations in both synthetic and real samples.

2. Experimental details

2.1. Reagents

Zirconiumoxychloride (AR grade, Riedl-del Haen, Germany), sodium metasilicate (AR grade, CDH, India) and potassium iodate (AR grade, CDH, India). All other reagents used were also of analytical reagent grade.

2.2. Apparatus

(Spectronic 20-D Spectrophotometer, USA) for spectrophotometeric determinations, (Elico pH meter, 335, India) for pH measurements, (Perkin Elmer, 1730, USA) for FTIR studies, (Philips X Pert) for X-ray diffraction, Shaker cum incubator (MSW-275, India) for shaking, Muffle Furnace (NSW, India) for heating and (NETZSCH TG.209 F1) for thermal analysis were used.

2.3. Synthesis

In order to get a stable and reproducible product with good ion-exchange properties, a number of samples of zirconium(IV) iodosilicate were synthesized by adding a mixture of 0.1 M potassium iodate and 0.1 M sodium metasilicate into a 0.1 M zirconium oxychloride solution with continuous shaking of the mixture. The pH variation was adjusted by 1 M nitric acid or 1 M ammonia solutions to maintain the desired pH 1. The gelatinous precipitate so formed, was allowed to stand for 24 h in the mother liquor for digestion. The supernatant liquid was removed and the precipitate was washed with demineralized water several times, filtered by suction. The product was completely dried at 40 ± 2°C in an oven. The dried product was then cracked into small granules by putting in deminaralized water to obtain particles of size 50–100 µm. The granules were treated with 1 MHNO_3 for 24 h to ensure complete conversion to H^+ form at room temperature. The material was finally washed with deminaralized water (DMW) to remove any excess of acid. On the basis of high ion-exchange capacity sample ZIS-6 was selected for detailed studies.

2.4. Ion-exchange capacity

The ion-exchange capacity which is generally taken as a measure of the hydrogen ion liberation by neutral salt was determined as usual by the column technique. 1.0 g of dry exchanger in H^+ form was loaded in a column (i.d 1.0 cm) with glass wool support at the base. Metal nitrate solutions (0.1 M) were used to elute H^+ ions completely from the exchanger column at a flow rate of 0.5 mL min^{-1}. The liberated H^+ ions were determined titrimetrically using standard sodium hydroxide solution.

2.5. pH titration

Topp and Pepper [27] method was used for pH titration studies using NaCl-NaOH, KCl-KOH systems. Ion exchanger in H^+ form (1.0 g) was treated with 50 mL of the appropriate mixed solution. The pH of the solution was recorded after shaking for 5 h in a temperature-controlled shaker at 25±2ºC.

2.6. Chemical stability

0.5 g of the material (ZIS-6) was equilibrated with 50 mL solution of analytical interest at room temperature (25±2ºC) and kept for 24 h with intermittent shaking. Zirconium, iodate and silicate released in the solution were determined by standard spectrophotometeric methods [28–30].

2.7. Chemical composition

The composition of the sample was determined by treating the sample with 15 mL concentrated HCl and evaporated to remove excess acid. The aliquot was filtered by using whattman filter paper number 1, and the clear filtrate obtained, was diluted to 100 mL with demineralized water. The amount of zirconium, iodate and silicate were determined by standard spectrophotometeric methods.

2.8. Effect of eluent concentration on ion-exchange capacity and elution behavior

Fixed volume (250 mL) of sodium nitrate solution of varying concentrations was passed through the column containing fixed quantity of ion exchange material (1.0 g). The amount of H^+ ions released was determined titrimetrically using standard procedures.

To see the effect of elution behavior, 1.0 M $NaNO_3$ solution was passed through a column containing 1.0 g exchanger maintaining a flow rate 0.50 mL min^{-1}. The effluent was collected in 10 mL fractions and the amount of H^+ ions released in each fraction was determined titrimetrically using standard procedures as described above.

2.9. IR analysis

IR absorption spectrum of the material in H^+ form was recorded between 400 and 4000 cm^{-1} by KBr disc method.

2.10. X-ray studies

The X-ray diffraction pattern of the material zirconium(IV) iodosilicate in H^+ form was recorded.

2.11. Thermal stability

The effect of drying temperature of the material on the ion-exchange capacity was studied by heating the zirconium(IV) iodosilicate, in the range 100–600ºC for 1 h separately. The ion-exchange capacity for each heated sample was determined by usual column process.

2.12. Scanning electron microscopy

Electron micrographs were recorded for zirconium (IV) iodosilicate by using scanning electron microscope operating at 15.0 kV at 5000 X magnification.

2.13. Sorption studies

Distribution coefficient (K_d)values of various metal ions were determined in several solvent systems to get an idea of partition behavior of the exchanger towards the separation of metal ions of analytical interest. 0.30 g exchanger in H^+ form was treated with 30 mL solution of metal ions in required solvent medium in an Erlenmeyer flask. The mixture was shaken for 5 h at 25±2°C in a temperature controller shaker cum incubator. The uptake of the metal ion was determined as a difference in the initial and final concentrations of the metal ion in solution using 0.01M EDTA as a titrant. The K_d values may be expressed as follows:

$$K_d = \frac{\text{milli equivalent of metalions gm of ion-exchanger}}{\text{milli equivalent of metalions mL of solution}} \text{mL g}^{-1} \tag{1}$$

$$K_d = \frac{I-F}{F} \times \frac{V}{M} \text{ mL g}^{-1}$$

where I is the initial amount of the metal ion in the solution phase, F is final amount of metal ion in the solution phase after treatment with the exchanger, V is the volume of the solution (mL) and M is the amount of ion exchanger taken (g).

2.14. Quantitative separation of metal ions in binary synthetic mixtures

Quantitative binary separations of some metal ions of analytical interest were achieved on zirconium (IV) iodosilicate. 2.0 g of exchanger in H^+ form was packed in a glass column (i.d 1.0 cm) with a glass wool support at the end. The column was washed thoroughly with DMW 2.0 mL binary mixture of the metal ions to be separated was poured on to the column and allowed to flow at a rate of 0.25 mL min^{-1}. The column was then rinsed with DMW. Individual metal ions were eluted using appropriate eluting reagents. The flow rate of the eluent was maintained 0.5 mL min^{-1} throughout the elution process. The effluent was collected in 10 mL fractions and was titrated against the standard solution of 0.01M di-sodium salt of EDTA.

2.15. Selective separation of Fe^{3+} from the synthetic mixture of Fe^{3+}, Ca^{2+}, Pb^{2+}, Cd^{2+} and Mn^{2+}

For selective separation different sets of the synthetic mixture were taken in which the amount of the Fe^{3+} was varied keepin g the amount of other metal ions constant. The subsequent procedure remains the same as described earlier for quantitative separation.

2.16. Quantitative separation of Zn^{2+} and Fe^{3+} in a pharmaceutical sample viz. Astyfer-Z

The pharmaceutical sample Astyfer-Z containing Zn^{2+} and Fe^{3+} ionswas dissolved in about 5.0 mL of aqua regia. The mixture was heated to evaporate excess of acid. The aliquot was filtered by using whattman filter paper number 1, and the clear filtrate obtained, was diluted to 50 mL with demineralized water and used as stock solution. Different amounts of stock solutions were poured into a glass column containing 1.0 g zirconium (IV) iodosilicate with a glass wool support at the base. The solution was left to flow down the column with a flow rate of 0.25 mL min^{-1}. The effluent was recycled through the column to ensure the complete adsorption of metal contents. Zn^{2+} was eluted with 0.1 m DMSO and Fe^{3+} with 0.1 M succinic acid.

Table 1
Synthesis and properties of different samples of zirconium (IV) iodosilicate.

Sample no	Condition of synthesis						Ion-exchange capacity (meq g^{-1}) for Na$^+$ ions
	A Mol L^{-1}	B Mol L^{-1}	C Mol L^{-1}	Mixing ratio (V/V/V)	pH	Temperature (°C)	
ZIS-1	0.1	0.1	0.1	1.0/1.0/1.0	1.0	25±2	0.29
ZIS-2	0.1	0.1	0.1	1.0/1.0/1.0	1.2	25±2	0.27
ZIS-3	0.1	0.1	0.1	1.0/1.0/1.0	1.5	25±2	0.17
ZIS-4	0.1	0.1	0.1	2.0/1.0/1.0	1.0	25±2	0.25
ZIS-5	0.1	0.1	0.1	1.0/2.0/1.0	1.0	25±2	0.55
ZIS-6*	0.1	0.1	0.1	1.0/2.0/2.0	1.0	25±2	0.85
ZIS-7	0.25	0.25	0.25	1.0/2.0/2.0	1.0	25±2	0.84

(A) Zirconium oxychloride, (B) Potassium iodate, (C) Sodium Meta silicate.
*Selected for detailed studies.

3. Results and discussion

Zirconium (IV) iodosilicate a new tri-component cation exchanger was synthesized, characterized and its analytical application was explored. Samples of the exchanger were synthesized in different conditions in order to obtain the sample with good ion-exchange capacity, high chemical stability and reproducibility as compared to others (Table 1). The effect of mixing ratio of reagents and pH on the synthesis were studied. It has been observed that the variation in pH and the mixing ratio of reagents affects both ion exchange capacity and physical appearance of the sample. Increasing the ratio of the anionic part in the reaction mixture enhances the ion-exchange capacity whereas an increase in cationic part has no effect. The most favorable pH for the synthesis of the material was 1.0. Ion-exchange capacity of alkali and alkaline earth metal ions were shown in Table 2. It was evident from the table that ion exchange capacity for alkali metal ions were K$^+$ > Na$^+$ > Li$^+$ and for alkaline earth metal ions were Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}. This sequence was in accordance with the hydrated ionic radii [31,32]. The ion-exchange capacity should increase with decreasing hydrated radii and increases with electrode potential. The ions with smaller hydrated radii easily enter the pores of exchanger, resulting in higher adsorption [33]. It was also observed that the material possessed high thermal stability as the sample maintained about 73% of the initial mass by heating up to 1000°C. However, in terms of ion exchange capacity, this hybrid material was found stable up to 50°C and it retained about 44% of the initial ion exchange capacity by heating up to 600°C.

The pH titration curves (Fig. 1.) of the material showed one inflection point which indicated the monofunctional behavior of zirconium(IV) iodosilicate with a theoretical ion-exchange capacity of 1.12 meq/g.

Table 2
Ion–exchange capacity of various exchanging ions on zirconium(IV) iodosilicate.

Exchanging Ions	Ionic radii (Å)	Hydrated radii (Å)	IEC (meq dry g^{-1}) exchanger
Li$^+$	0.68	10.0	0.70
Na$^+$	0.97	7.90	0.85
K$^+$	1.33	5.30	1.0
Mg^{2+}	0.78	10.80	0.80
Ca^{2+}	1.06	9.60	0.85
Sr^{2+}	1.27	9.40	0.90
Ba^{2+}	1.43	8.80	1.12

IEC—Ion exchange capacity.

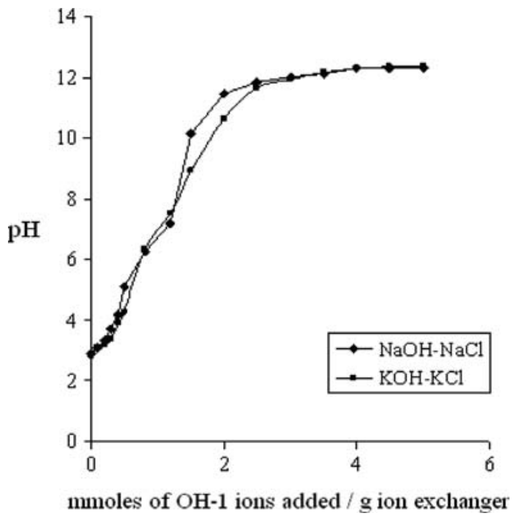

Fig. 1. pH titration curves of zirconium(IV) iodosilicate.

Table 3
Chemical stability of zirconium(IV) iodosilicate in some common solvents.

Solvent	Zirconium released (mg/25 mL)	Iodate released (mg/25 mL)	Silicate released (mg/25 mL)
0.1 M HCl	0.16	0.15	0.10
1 M HCl	0.26	0.20	0.25
0.1 M HNO_3	0.03	0.08	0.12
1 M HNO_3	0.10	0.14	0.14
0.1 M H_2SO_4	0.10	0.15	0.12
1 M H_2SO_4	0.15	0.20	0.19
0.1 M Succinic acid	0.07	0.09	0.15
0.1 M DMSO	0.08	0.12	0.09
0.1 M formic acid	0.12	0.14	0.12

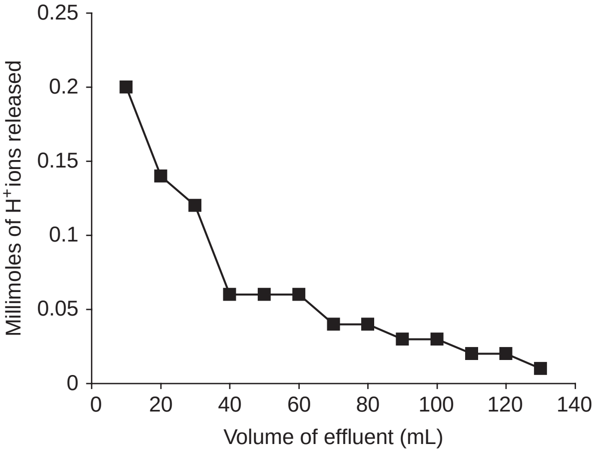

Fig. 2. Elution behavior of zirconium(IV) iodosilicate.

Chemical stability in common solvents is shown in Table 3. The results reveal that zirconium(IV) iodosilicate is fairly stable in common mineral acids, bases and organic solvents upto 2.0 M.

The molar composition of Zr(IV) iodosilicate was found as Zr:I:Si:: 1:1.57:1, which shows that the anionic part is higher than cationic one. On the basis of this molar composition, a tentative formula for Zr(IV) iodosilicate may be written as $(ZrO)_2(OH)_4$ $(HIO_3)_3$ $(H_2SiO_3)_3$ .nH2O. The formula showed that H^+ ions attached to iodate and silicate groups are responsible for the exchange characteristic of the material as it was observed earlier from Table 1 that anionic part contributed towards ion-exchange capacity for this cation-exchanger.

The rate of exchange and efficiency of the zirconium(IV) iodosilicate column was determined by elution behavior (Fig. 2) which shows the exchange is quite fast and almost all the H^+ ions are eluted in first 100 mL of eluent.

The FTIR Spectrum (Fig. 3) of zirconium(IV) iodosilicate revealed the presence of external water molecules in addition to metal oxygen and metal hydroxyl stretching bands. The broad band at 3366.52 cm^{-1} may be due to the presence of external water molecules. A strong and sharp peak with a maximum at 1626.87 cm^{-1} can be attributed to H–O–H bending [31]. The peak at 1384 cm^{-1} may be due to the deformation vibration of metal hydroxyl groups and interstial water molecules [34]. The spectrum shows strong bands at 1096.40 and 807.08 cm^{-1} respectively, which indicates the presence of silicate and iodate groups. The weak band at 471.22 is due to metal oxide bond.

Table 4
Effect of temperature on the ion-exchange capacity of zirconium(IV) iodosilicate on heating time for 1 h.

Temperature (°C)	% Weight loss	Color	% Retention of IEC
50	0.0	White	100
100	2.0	White	96
200	5.0	Dirty white	91
300	12.0	Brownish	82
400	14.0	Brownish	80
500	55.0	Dark brown	47
600	66.0	Dark brown	44

X ray diffraction result (Fig. 4) of the material shows the amorphous nature of the sample.

The Thermogravimetric (TGA-DTA) curve (Fig. 5) shows a continuous weight loss of 10% upto 200ºC which is due to elimination of external water molecules. The derivative curve exhibits three peaks with maxima at 93ºC, 458ºC and 531ºC. The first derivative peak corresponds to weight loss of 10%, further the abrupt weight loss of 40% from 422 to 531ºC owing to volatilization of

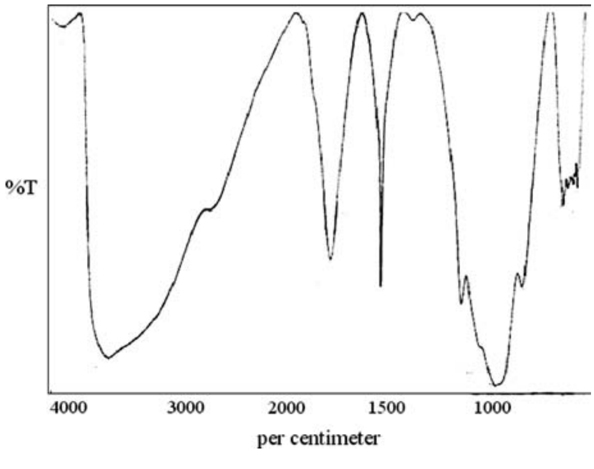

Fig. 3. FTIR Spectrum of zirconium (IV) iodosilicate.

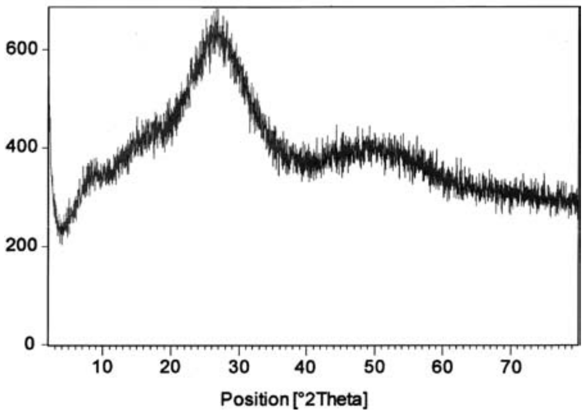

Fig. 4. X-ray diffraction pattern of spectrum of zirconium(IV) iodosilicate.

Fig. 6. Scanning Electron Micrograph of zirconium(IV) iodosilicate at 1000 X magnification.

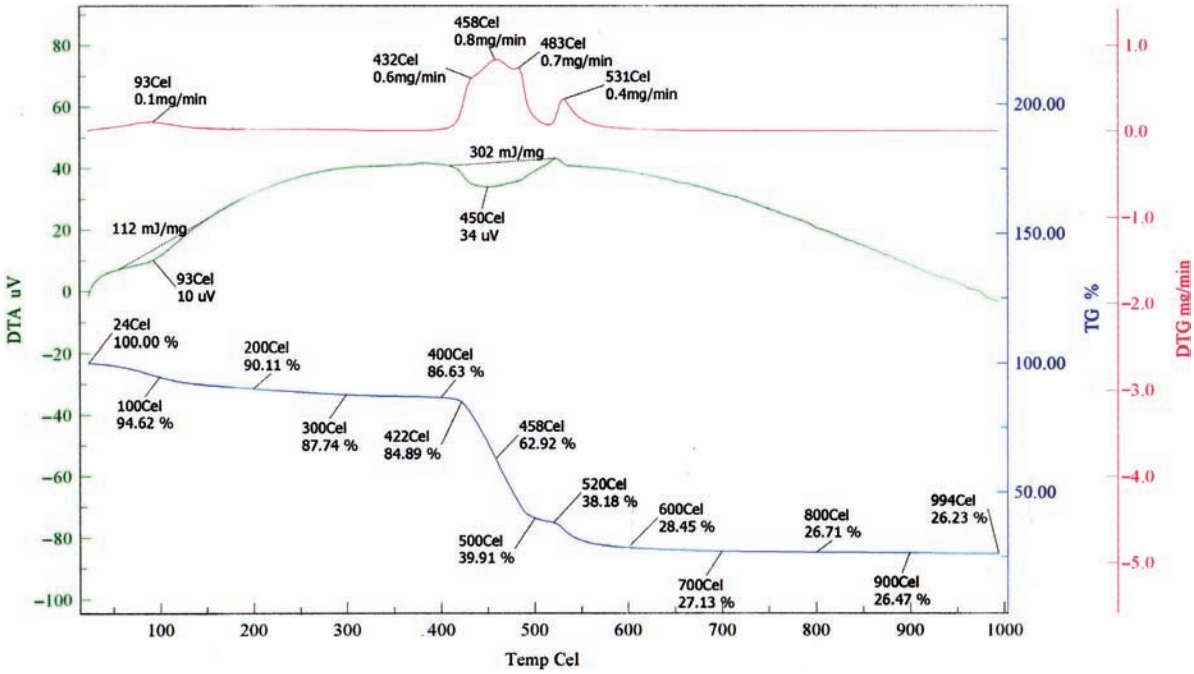

Fig. 5. Simultaneous DTA-TGA curves of zirconium (IV) iodosilicate.

IO_{3-} groups. Lastly an abrupt weight loss in the region of 500–800ºC may be due to decomposition and subsequent structural transformation of the material with the evolution of gaseous products.

The Scanning Electron Micrograph (Fig. 6.) of zirconium(IV) iodosilicate shows a regular uniform morphology. The presence of uniform morphology also indicates the absence of impure phases.

In order to explore the potentiality of the new inorganic cation-exchange material in the separation of metal ions, distribution studies for different metal ions were performed in various solvent systems. It can be inferred from the results (Table 5) that the metal ions show decrease in K_d value with the increase in dielectric constant of solvents studied except Fe^{3+} and Ba^{2+} which shows the higher sorption in the case of DMSO. Further Fe^{3+} ion sho ws relatively higher sorption in all the solvents as compared to other metal ions. The higher K_d values were observed in formic acid and DMSO for Hg^{2+}, Ba^{2+}, Cu^{2+}, Al^{3+} and Ni^{2+} ions. The separation capability of zirconium(IV) iodosilicate has been demonstrated by achieving some binary separations (Table 6) of analytical interest such as Cd^{2+}-Ba^{2+}, Cd^{2+}-Al^{3+}, Cd^{2+}-Ni^{2+}, Cd^{2+}-Fe^{3+}, Cd^{2+}-Cu^{2+}, Cd^{2+}-Hg^{2+}, Mn^{2+}-Fe^{2+} and

Table 5
Distribution coefficients of different metal ions on zirconium(IV) iodosilicate in different solvent systems.

Metal ion	DMW	Formic acid 0.1 M	DMSO 0.1 M	DMF 0.1 M	Acetic acid 0.1M	Succinic acid 0.1 M
Mg^{2+}	404.76	377.39	300.00	287.15	83.33	175.67
Ca^{2+}	505.71	280.53	265.36	119.24	94.39	90.00
Sr^{2+}	494.28	377.39	292.00	186.91	166.95	159.45
Hg^{2+}	1029.41	1006.00	**1006.0**	210.00	143.90	135.00
Cd^{2+}	482.85	281.00	**25.16**	110.52	190.47	187.22
Ba^{2+}	600.00	698.00	**840.00**	226.66	216.47	198.00
Pb^{2+}	433.00	388.00	317.00	288.98	250.00	110.00
Zn^{2+}	400.00	384.00	321.73	104.00	86.66	69.11
Mn^{2+}	562.50	197.39	186.56	100.00	90.47	90.00
Cu^{2+}	484.21	479.00	**456.75**	281.0	100.00	98.00
Al^{3+}	576.12	553.16	**540.00**	292.81	164.00	160.57
Ni^{2+}	687.87	610.90	**580.00**	319.00	140.00	133.00
Fe^{3+}	935.29	1164.00	**2572.0**	842.00	471.00	272.00
Co^{2+}	316.00	219.20	210.00	174.50	119.25	95.00
La^{3+}	425.00	270.30	234.00	208.75	145.90	125.00

Table 6
Quantitative separations of metal ions of a binary mixture using zirconium(IV) iodosilicate column.

Separation achieved	Amount loaded[a] (mg)	Amount Found[a] (mg)	% Recovery	Eluent used	Volume of Eluent (mL)
Ce^{3+}	11.24	11.12	98.93	0.1 M DMSO	100
Fe^{3+}	13.73	13.24	96.43	0.1 M Succinic acid	80
Ce^{3+}	11.24	10.84	96.44	0.1 M DMSO	100
Pb^{2+}	2.69	2.63	97.76	0.1 M Succinic acid	100
Cd^{2+}	11.24	10.95	97.41	0.1 M DMSO	90
Ni^{2+}	5.48	5.83	99.48	0.1 M Succinic acid	80
Cd^{3+}	11.24	11.07	98.48	0.1 M DMSO	90
Fe^{3+}	5.58	5.13	91.93	0.1 M Succinic acid	70
Cd^{2+}	11.24	10.56	93.95	0.1 M DMSO	70
Pb^{2+}	6.35	6.32	99.52	0.1 M Succinic acid	80
Th^{4+}	11.24	10.56	93.95	0.1 M DMSO	90
Pb^{2+}	20.05	19.55	97.50	0.1 M Succinic acid	70
Mn^{2+}	5.49	5.38	97.99	0.1 M DMSO	50
Fe^{3+}	5.58	5.55	99.46	0.1 M Succinic acid	80
Zn^{2+}	6.53	6.43	98.46	0.1 M DMSO	80
Fe^{3+}	5.58	5.50	98.56	0.1 M Succinic acid	110

[a] Average of three replicate determinations.

Table 7
Selective separation of Fe^{3+} ion from the synthetic mixture of Fe^{3+},Ca^{2+},Cd^{2+}, Mn^{2+}, Pb^{2+} on zirconium(IV) iodosilicate columns.

S. No	Amount of Fe^{3+} loaded[a] (mg)	Amount of Fe^{3+} recovered[a] (mg)	% Recovery	Eluent used	Eluent volume (mL)
1	2.23	2.20	98.60	0.1 M succinic acid	70.0
2	4.46	4.38	98.00	0.1 M succinic acid	90
3	6.69	6.65	99.40	0.1 M succinic acid	120

[a] Average of three replicate determinations.

Table 8
Quantitative separation of Fe^{3+} and Zn^{2+} in commercially available pharmaceutical sample (Astefer-Z) on zirconium(IV) iodosilicate columns.

Binary mixtures	Amount loaded[a] (mg)	Amount Recovered[a] (mg)	% Recovery	Eluent used	Eluent volume (mL)
Zn^{2+}	0.40	0.38	95.00	0.1 DMSO	40
Fe^{3+}	0.98	0.95	96.90	0.1 M succinic acid	50
Zn^{2+}	0.80	0.75	93.75	0.1 DMSO	50
Fe^{3+}	1.96	1.90	96.90	0.1 M succinic acid	60
Zn^{2+}	1.20	1.10	91.60	0.1 DMSO	70
Fe^{3+}	2.94	2.85	96.90	0.1 M succinic acid	80

[a] Average of three replicate determinations.

Ca^{2+}-Fe^{2+}. The elution profiles for binary separations are shown in Fig. 7. The practical utility of the material was established by carrying out the selective separation of Fe3+ ions from synthetic mixture (Fe^{3+}, Ca^{2+}, Pb^{2+}, Cd^{2+} and Mn^{2+}) given in Table 7. The practical utility of these separations was also demonstrated by separating metal ions quantitatively from a commercially available pharmaceutical preparation Astyfer-Z (Table 8).

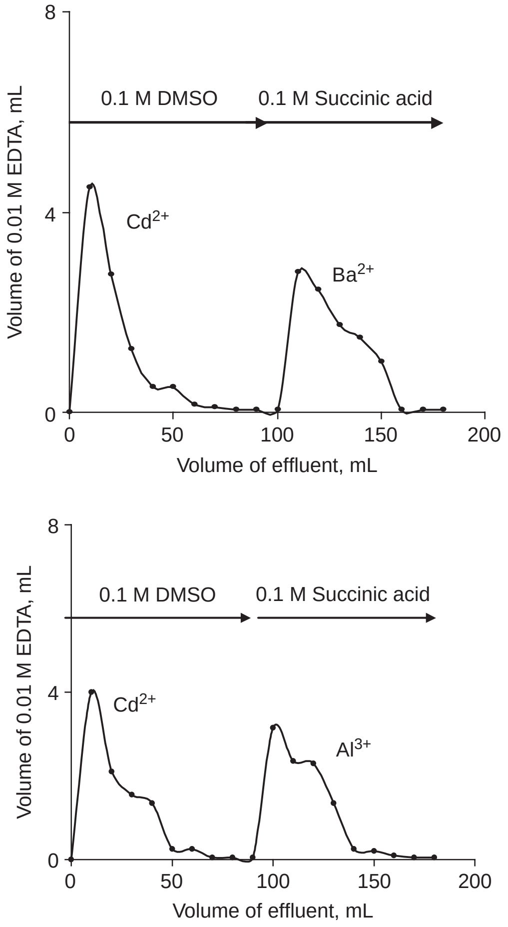

Fig. 7 (I, II)

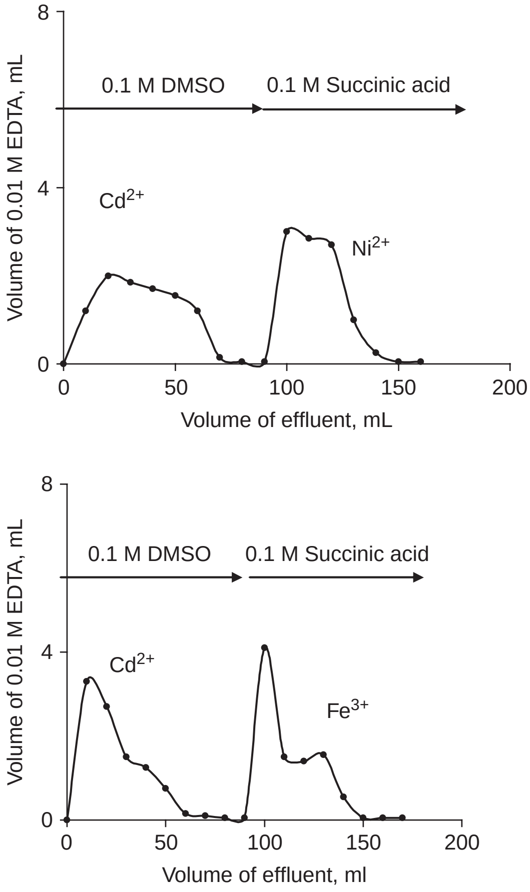

Fig. 7 (III, IV)

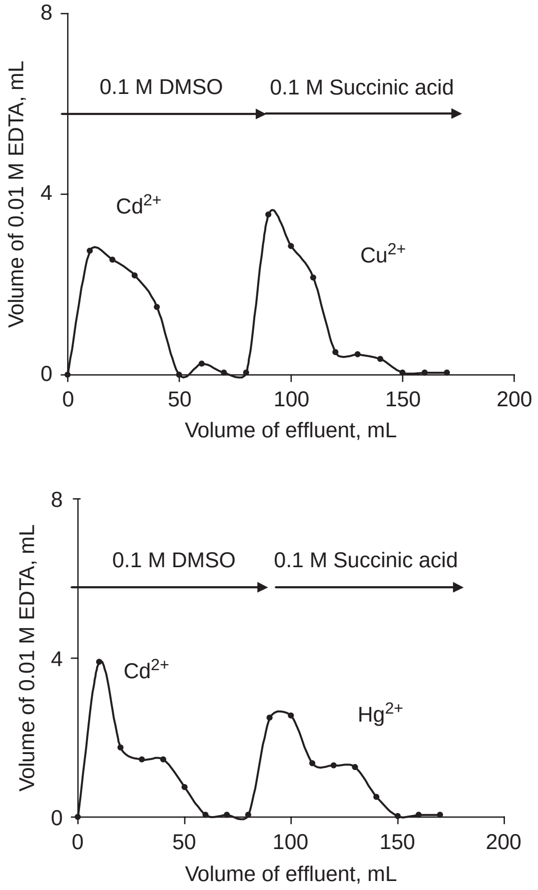

Fig. 7 (V, VI)

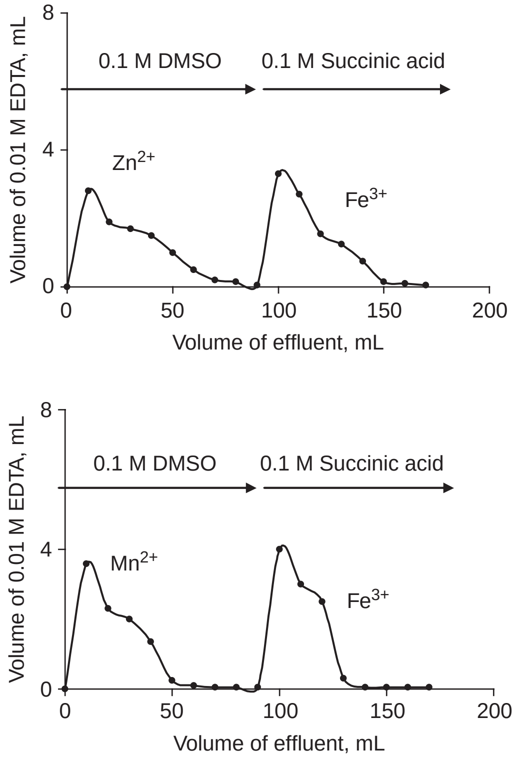

Fig. 7 (VII, VIII)

Fig. 7. (I–VIII) Elution curves for binary separations of metal ions on zirconium(IV) iodosilicate columns.

Acknowledgement

The authors are thankful to Chairman, Department of Chemistry, A. M.U. Aligarh for providing all necessary facilities.

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