

Synthesis and Characterization of New Tin(IV) Iodophosphosilicate Cation Exchanger

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The synthesis of four components heterocyclic viz., tin(IV) iodophosphosilicate cation exchanger is reported in this study. Ion exchange capacity for Na⁺ is found to be 1.10 meq/g. This new cation exchanger possesses good stability against temperature upto 600 °C and chemicals of different strengths. Ion exchange capacity is also determined for different transition metal ions and a relationship between ion exchange capacity and hydrated radii is established. The cation exchanger is found to be selective for cadmium ions. Infrared of cation ion-exchanger indicates the presence of all the four expected components. X-ray diffraction and SEM showed that exchanger is in crystalline form.

Keywords: Tin(IV) Iodophosphosilicate, Cation exchanger, Exchange capacity, Cadmium.

INTRODUCTION

Water pollution due to toxic heavy metals has become a serious environmental problem worldwide. With the rapid extension of industrialization (*e.g.* electro plating, ceramic, mining, fertilizer, tanneries, leather, batteries, pesticides, paper), these heavy metals are regularly discharged into the natural water resources and cause various diseases and disorders by damage to the aquatic environment [1]. Unlike organic pollutants, these are not biodegradable and have a tendency to accumulate in living beings which are extremely harmful to human health [2]. Cadmium is an element of recognized environmental toxicity [3], being highly toxic even at low concentrations, damaging organs such as kidneys, liver and lungs. A number of methods including chemical precipitation, coagulation–flocculation, floatation, ion exchange, biosorption and membrane filtration have been employed for the removal and recovery of these toxic metal ions [4-10]. The emulsion liquid membranes and nano-baskets of calixcrown are recently being used for the extraction of alkali metals [11].

However, ion-exchange materials have gained popularity for being more selective and less expensive as compared to other methods [12]. For the separation of metal ions in solution and water purification a large number of organic and inorganic ion-exchange materials have been synthesized. Several works on the synthesis of four components inorganic cation exchanger [12-15] are reported in the literature. The advantage of inorganic exchanger over organic exchanger [16,17] also creates an attraction towards them.

EXPERIMENTAL

All the chemicals and reagents used were of analytical grade (AR), pentahydrate (0.1 M), potassium iodate (0.1 M), orthophosphoric acid (0.1 M), sodium metasilicate (0.1 M), were used as received in the synthesis of exchanger.

X-ray diffraction: X-ray diffraction pattern of the best prepared ion exchange material was recorded by X-ray diffractometer with CuK_α radiation beam ($\lambda = 0.154060$ nm) to determine the structure of the ion exchangers, where the finely powdered samples of the ion exchanger were packed into a flat aluminium holder and the X-ray source was a rotating anode operating at 30kV and 30mA.

Thermogravimetric analysis: The measurements of thermal analysis of the best prepared sample were carried out using thermogravimetric analyzer (Shimadzu TGA-50, Japan) with a heating rate 20 °C/min under flow of nitrogen to avoid thermal oxidation of the powder samples, starting from ambient condition up to 600 °C.

Infrared spectroscopy: The IR spectrum of the best prepared ion exchanger was examined using Fourier transform infrared spectrophotometer (Shimadzu FTIR-8400 S, Japan). The disc technique using KBr as a matrix was found to be suitable. In this concern, the ion exchanger was thoroughly mixed with KBr and the mixture was ground and then pressed with a special press to give a disc of standard diameter.

Scanning electron microscope: The grounded prepared samples were scanned to identify their structure and estimate the particle diameter at different magnifications

using scanning electron microscope (JEOL JSM 6360 LA, Japan).

Synthesis of four-components cation ion-exchanger, i.e., tin(IV) iodophosphosilicate (TIPS): Solutions of each 0.1 M tin(IV) chloride pentahydrate, potassium iodate, sodium metasilicate and orthophosphoric acid were inter-mixed resulting in the formation of white precipitate. Inter-mixing of the solutions was done in ten different volume ratios (Table-1). After intermixing pH adjusted to 1 using 1 M HCl and left the precipitate for 24 h at room temperature. Settled down precipitate were filtered and washed thoroughly with distilled water till the pH of effluent become neutral then kept on the marked watch glasses and dried in an oven at 40 °C temperature for 24 h.

Generation: Granulization [18] was performed by cracking of dry matrices with hot distilled water to increase their surface area and again dried at 40 °C for 24 h. This process was repeated three times. The charged matrix was washed with distilled water till the excess acid present in matrix was removed. Then each charged matrix was dried in different marked watch glasses.

Determination of ion exchange capacity: The ion exchange capacity (IEC) was determined as usual by the column technique [19]. Dry exchanger (0.5 g) in H⁺ form was loaded in a column with glass wool support at the base. Sodium nitrate (1 M) solution was used to elute H⁺ ions completely from the exchanger column at a low rate of 0.5 mL/min. The liberated H⁺ ions were determined titrimetrically using standardized NaOH solution (0.1 M). Weighed 500 mg of each dry sample and placed in seven different columns. NaNO₃ solution (1 M) was prepared and kept in each column and allowed to pass through exchanger. The solution was passed continuously till the pH became the same as pH of NaNO₃ solution. The solution was titrated with standardized NaOH solution and ion exchange capacity was calculated by following expression:

$$\text{IEC} = \frac{\text{Molarity of NaOH} \times \text{Used volume of NaOH}}{\text{Weight of exchanger}}$$

The sample 9 has maximum ion exchange capacity i.e. 1.10 meq/g (Table-1). On the basis on ion exchange capacity, this sample was selected for the bulk synthesis and detailed study was made.

Thermal stability: In order to study the thermal stability of new cation exchanger (TIPS), seven equal portion of cation exchanger were heated at different temperatures ranging from room temperature 25 °C upto 600 °C in a muffle furnace for 60 min separately. Weight loss, change in ion exchange capacity and change in colour of all the samples were recorded as shown in Table-2.

Chemical stability: Chemical stability of the exchanger (TIPS-9) was also studied against different solvents of different concentrations; weight loss and change in ion exchange capacity of the exchanger in twelve solutions of different concentrations were observed (Table-3).

Determination of ion exchange capacity for other metal ions: Ion exchange capacity of the exchanger was also be check for few more alkali and alkaline earth metals ions and a relation between ion exchange capacity and hydrated radii was established (Table-4).

pH titration: Ion exchange capacity of the synthesized cation exchanger in bulk was also determined by pH titration method. In this method, equal eleven portion of the exchanger were placed in eleven solutions of equal volume containing sodium chloride (0.1 M) and sodium hydroxide (0.1 M) solution in eleven different volume ratios as given in Table-5. All the solutions were intermittently shaken and then kept as such for 24 h. pH of each solution was determined. At high pH values (9-12), decrease in removal efficiency achieved by tin(IV) iodophosphosilicate can be described with formation of

TABLE-1
EFFECT OF SYNTHESIS PARAMETERS ON THE ION EXCHANGE CAPACITY (IEC) OF TIN(IV) IODOPHOSPHOSILICATE (TIPS)

Sample No.	SnCl ₄ ·5H ₂ O (0.1 M)	KIO ₃ (0.1 M)	ortho-H ₃ PO ₄ (0.1 M)	Na ₂ SiO ₃ solution (0.1 M)	Weight of ppt (g)	IEC (meq/g)
TIPS 1	50 mL	50 mL	50 mL	50 mL	1.55	0.42
TIPS 2	50 mL	100 mL	50 mL	50 mL	1.60	0.36
TIPS 3	50 mL	50 mL	100 mL	50 mL	1.62	0.57
TIPS 4	50 mL	50 mL	50 mL	100 mL	1.48	0.45
TIPS 5	100 mL	50 mL	50 mL	50 mL	1.75	0.48
TIPS 6	100 mL	100 mL	50 mL	50 mL	2.10	0.62
TIPS 7	100 mL	50 mL	100 mL	50 mL	2.33	0.84
TIPS 8	100 mL	50 mL	50 mL	100 mL	2.04	0.77
TIPS 9	150 mL	100 mL	100 mL	50 mL	3.12	1.10
TIPS 10	150 mL	50 mL	100 mL	100 mL	2.88	0.97

TABLE-2
EFFECT OF TEMPERATURE ON THE ION EXCHANGE CAPACITY OF TIN(IV) IODOPHOSPHOSILICATE ON HEATING TIME FOR 1 h

Temperature (°C)	Weight of exchanger (mg)		Weight loss (mg)	Colour of exchanger		IEC (meq/g)
	Before heating	After heating		Before heating	After heating	
25	500	500	0	White	White	1.10
100	500	490	10	White	Brownish white	1.05
200	500	480	20	White	Brown	0.91
300	500	440	60	White	Brown	0.84
400	500	425	75	White	Yellowish brown	0.70
500	500	405	95	White	Yellowish brown	0.58
600	500	380	120	White	Dark brown	0.56

TABLE-3
SOLUBILITY OF TIN(IV) IODOPHOSPHOSILICATE
(TIPS-9) IN VARIOUS SOLVENTS

Solvents	Time (h)	Weight of exchanger (mg)		IEC (meq/g)
		Before treatment	After treatment	
Distilled water	24	500	500	1.10
NaCl (1 N)	24	500	500	1.10
NaCl (2 N)	24	500	500	1.10
NaNO ₃ (1 N)	24	500	500	1.09
HCl (1 N)	24	500	490	1.02
HCl (2 N)	24	500	480	0.96
HNO ₃ (1 N)	24	500	490	0.82
HNO ₃ (2 N)	24	500	480	0.77
H ₂ SO ₄ (1 N)	24	500	500	0.78
H ₂ SO ₄ (2 N)	24	500	490	0.70
HCOOH (2 N)	24	500	500	0.68
CH ₃ COOH (2 N)	24	500	490	0.90
NaOH (1 N)	24	500	220	0.48
NaOH (2 N)	24	500	–	–
KOH (2 N)	24	500	–	–

(–) indicate completely dissolved

TABLE 4
ION EXCHANGE CAPACITY WITH DIFFERENT METAL IONS

Metal ion	Compound	Hydrated radii (Å)	IEC (meq/g)
Li ⁺	LiCl	10.0	0.56
Na ⁺	NaCl	7.90	1.10
K ⁺	KBr	5.30	1.22
Mg ²⁺	MgCl ₂	10.80	0.48
Ca ²⁺	CaCl ₂	9.60	0.62
Ba ²⁺	BaCl ₂	8.80	0.88

TABLE-5
EFFECT OF pH ON ION EXCHANGE OF Sn⁴⁺ IONS

S. No.	Volume (mL)		Exchanger taken (g) (TIPS-9)	pH
	NaOH (0.1 M)	NaCl (0.1 M)		
1	0	50	0.50	2.10
2	5	45	0.50	7.12
3	10	40	0.50	9.20
4	15	35	0.50	10.08
5	20	30	0.50	11.08
6	25	25	0.50	11.39
7	30	20	0.50	11.70
8	35	15	0.50	11.80
9	40	10	0.50	12.01
10	45	5	0.50	12.12
11	50	0	0.50	12.20

Sn(OH)₄ during reaction of Sn⁴⁺ ions with OH⁻. In this state, hydrolysis accompanied by precipitation of metal hydroxides may occur [20]. However, at low pH values, the decrease in lead ion removal may be returned to the competition of H⁺ ions with Sn⁴⁺ in the ion exchange process onto the prepared cation exchanger.

Distribution studies: Distribution studies of the cationic exchanger with six metal ions were performed by batch process [21]. Complexometric titrations were performed to find the metal ion concentration in their solution before and after treatment with exchanger [22]. The value so obtained was used to calculate K_d values for all the six metals by following expression:

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

where, I = Initial value of EDTA; F = Final value of EDTA; V = Volume taken (mL); W = Weight of exchanger (g).

RESULTS AND DISCUSSION

Different amount of precipitates in different volume ratio were obtained. Sample no. 9 contain maximum amount and ion exchange capacity. Therefore, sample-9 had shown good amount and maximum ion exchange capacity therefore selected for further study.

IR proved the presence of all the expected four components, at 3400 cm⁻¹ -OH stretching of water molecule, 1550-1300 cm⁻¹ indicating the presence of metal oxide, 567 cm⁻¹ for iodate, 1200 cm⁻¹ for phosphate and 1000-600 cm⁻¹ for silicate (Fig. 1). X-ray diffraction pattern of material in H⁺ form reveals the fact that the exchanger is crystalline in nature with sharp peaks with weak intensities (Fig. 2). The SEM images of the exchanger had given in the range of 1.0-100.0 μm (Fig. 3).

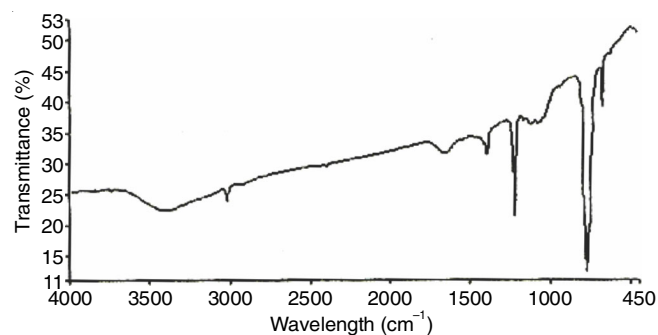


Fig. 1. FTIR of the tin(IV) iodophosphosilicate exchanger

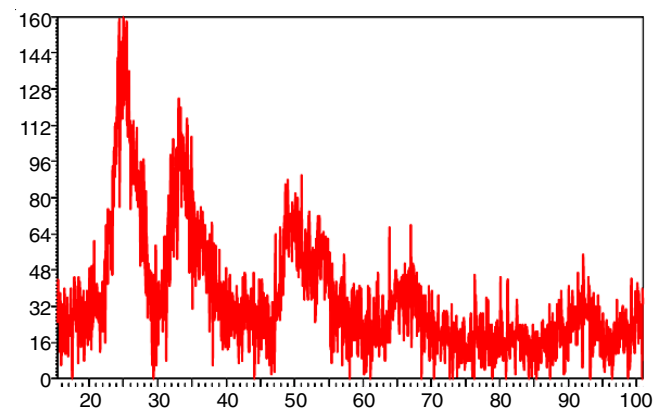


Fig. 2. XRD of tin(IV) iodophosphosilicate exchanger

The relation between ion exchange capacity and hydrated ionic radii exhibits that ion exchange capacity decreases with increase in hydrated radii of the cation. Thermal stability study revealed that the exchanger remain almost its ion exchange capacity up to 100 °C. The exchanger shows ion exchange capacity even at 600 °C. In chemical stability study, it was found that exchanger does not lose ion exchange capacity in distilled water. While in 2 N H₂SO₄ and HCl insignificant loss was noted. The exchanger was completely dissolved in alkaline solutions. Stability against different chemicals was found satisfactory. The K_d values for the metal ions are given

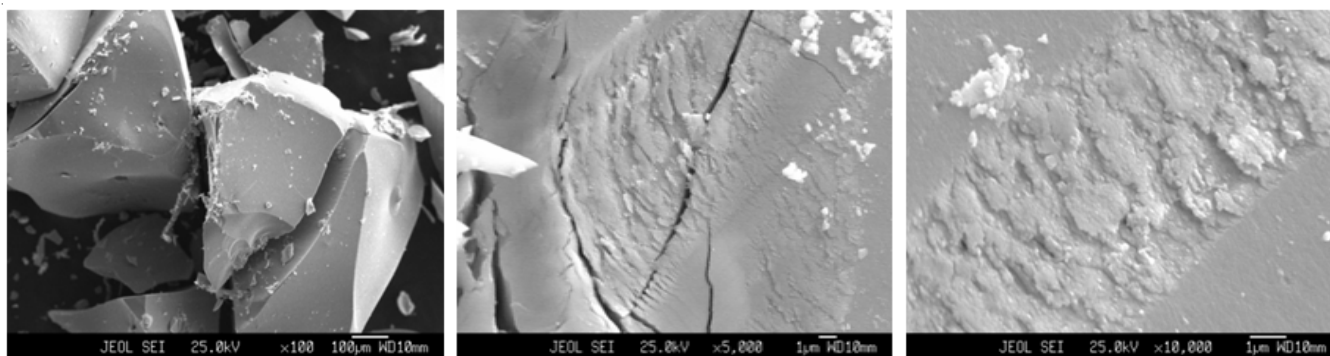


Fig. 3. SEM images of tin(IV) iodophosphosilicate exchanger

in Table-6. Hence, cation exchanger is found to be selective for cadmium ions. The present study limit distribution studies to a certain pH to each metal ion to avoid the hydrolysis metal ions.

TABLE-6
DETERMINATION OF K_d VALUES OF TIN(IV)
IODOPHOSPHOSILICATE CATION EXCHANGER

Metal ion	EDTA volume used (0.1 M)		K_d value (mL/g)
	Before treatment	After treatment	
Th ³⁺	26.6	26.4	0.38
Pb ²⁺	22.4	18.5	10.54
Zn ²⁺	26.6	24.4	4.51
Cd ²⁺	25.4	5.6	176.78
Cu ²⁺	5.2	25.0	3.48
Mg ²⁺	26.1	24.4	0.48

Conclusion

The crystalline cation-exchanger Sn(IV) iodophosphosilicate was found to have good ion-exchange capacity, high chemical and thermal stability and selectivity for metal ions. The differential behaviour of the exchanger towards metal ions in different solvent systems showed the separation possibilities of metal ions of analytical interest from a given mixture. The analytical importance of the material was deduced from K_d values for different metal ions in different solvents.

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