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Lead Selective Zirconium(IV) Sulphosalicylomolybdate as Three Component Ion Exchanger

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A three component inorganic ion exchanger zirconium(IV) sulphosalicylomolybdate has been prepared under varying conditions. Characterization of the exchanger was done by determining ion exchange capacity, distribution coefficient for various metal ions, chemical analysis, pH titration, IR Spectra and thermal analysis. The distribution coefficients (K_d) of 10 metal ions were determined. On the basis of difference in distribution coefficients, some analytically important binary (Cd^{2+}/ Pb^{2+}, Zn^{2+}/Pb^{2+}, Ca^{2+}/Pb^{2+}, Th^{4+}/Pb^{2+}, Cd^{2+}/Cu^{2+}, Zn^{2+}/Cu^{2+} and Th^{4+}/Cu^{2+}) and ternary ($Th^{4+}/Ni^{2+}/Pb^{2+}$, $Th^{4+}/Co^{2+}/Pb^{2+}$, $Th^{4+}/Cd^{2+}/Pb^{2+}$) separations of metal ions have been achieved. The significance of the exchanger is revealed by the important separations carried out from wastewater collected from spinning and weaving mills near Kannur.

Key Words: Lead, Zirconium(IV) Sulphosalicylomolybdate, Ion exchange.

INTRODUCTION

Studies on synthetic inorganic ion exchangers are gaining relevance due to their specific selectivity and high thermal stability[1-5]. Two component inorganic ion exchangers have been much studied as compared to three component ion exchangers. Some of the well studied three component systems include iron(III) antimonosilicate[6] selective for Cd^{2+} and Mo^{6+}, zirconium succinophosphate[7] selective for Th^{4+}, zirconium phosphomolybdate[8] selective for Bi^{3+}, iron(III) tungstophosphate[9] selective for Hg^{2+} and zirconium iodooxalate[10] selective for Ca^{2+}. Other three component exchangers include antimony(III) tungstovanadate[11], zirconium antimonophosphate[12], zirconium arsenovanadate[13], zirconium tungstophosphate[14], zirconium iodomolybdate[15], zirconium selenophosphate[16], tin(IV) selenophosphate[17], zirconium triethylammoniumphosphate[18] and zirconium sulphosalicylophosphate[19]. The present work explains the synthesis, characterization, ion exchange properties and analytical applications of a new phase of mixed materials based on zirconium molybdate and zirconium(IV) sulphosalicylate[20]. Some analytically important binary and ternary separations were carried out using the exchanger.

EXPERIMENTAL

Zirconyl oxychloride, sodium molybdate, sulphosalicylic acid and all other reagents were of analytical grade. Double distilled water was used through out the work.

The instruments used are Systronic digital pH meter MK-IV for pH measurements, FTIR model Shimadzu 820PC for IR studies, Dupot 900 and 950 thermal analyzer, a glass column (30 × 1.1 cm) for column operations and an electric shaking machine for shaking.

Zirconium(IV) sulphosalicylomolybdate was prepared by adding a mixture of sulphosalicylic acid and sodium molybdate to $ZrOCl_2 \cdot H_2O$ solution. The preparation was done by taking different molar ratios of the reagents (Table-1). The gel thus obtained was allowed to settle at room temperature for 24 h, filtered, washed with demineralized water (DMW) and finally ground, sieved to 60-100 mesh and was converted to H^+ form by treatment with 1 M HNO_3. The one with the highest ion exchange capacity was selected for further studies.

The ion exchange capacity of the exchanger sample was determined using column method. 1 g of the exchanger in the H^+ form was taken in a glass column, the H^+ ions were eluted by percolating 250 mL of an electrolyte solution. The flow rate was maintained at 0.5 mL/min. The effluent was collected and titrated with standard NaOH solution.

For chemical analysis, the well-powdered exchanger (0.5 g) was fused with 1:1 mixture of K_2CO_3 and Na_2CO_3. The fused mixture was extracted with hot DMW. The undissolved portion was ignited and weighed[21] as ZrO_2. The molybdenum present was precipitated as lead molybdate, filtered and determined gravimetrically[22]. The filtrate was analyzed for sulphosalicylic acid spectrophotometrically using iron(III) nitrate[23].

To determine chemical stability, 200 mg of the exchanger was shaken with 20 mL of various solutions at 30 ± 2ºC for 6 h. The amount of zirconium, molybdenum and sulphosalicylic acid released into the solutions were determined spectrophotometrically with alizarin red[24], dithiol[23] and iron(III) nitrate[23], respectively.

pH titrations were performed by batch process using the method of Topp and Pepper[25], using NaOH-NaCl system. 0.1 g of the exchanger in the H^+ form were placed in different conical flasks and an equimolar solution of alkali metal chloride and its hydroxide in different volume ratios were added, the final volume being 10 mL to maintain the ionic strength constant. The pH of the solutions were recorded after every 24 h until equilibrium was attained for which approximately 5 d were needed. At equilibrium, pH was plotted against milli equivalents of OH^- ions added.

FTIR Spectrum of the sample was obtained using KBr disc method. Thermogram of the sample was recorded at a heating rate of 10ºC/min.

The distribution coefficients of the ion exchanger for various metal ions were determined by batch process. Samples of the exchanger (0.1 g) were shaken with 0.005 M solutions (20 mL) of the metal ion and kept for 24 h to ensure maximum uptake. The supernatant solution was then titrated against EDTA solution. The distribution coefficient (mL/g) was determined as $K_d = (I-F)/F \times V/W$, where I and F are initial and final volumes of EDTA used for titrations, V is the volume of metal ion solution used and W is the weight of the ion exchanger taken.

For separation studies, 5 g of the exchanger were taken in a glass column (30 × 1.1 cm). The rate of flow in all separations was maintained at 0.5 mL/min. Separations were carried out for the metal ions for which the separation factor was greater than 5.

We have collected few samples of wastewater effluents from spinning and weaving industry in Kannur district. The wastewater samples were pretreated by filtration for removal of any solid material and then neutralized with acid and alkali. The colour producing substances were removed by adsorption using charcoal. The treated water was chemically treated for the detection and separation of heavy elements.

100 mL each of the wastewater samples thus treated was passed through the exchanger column, where the cations present were exchanged on the column. The adsorbed cations were regenerated by treatment with suitable eluents (0.1 M HNO_3 + 0.1 M NH_4NO_3 for Cu and 0.5 M HNO_3 for Pb) passed through the columns.

RESULTS AND DISCUSSION

Details of the synthesis and ion exchange capacity of the exchanger zirconium(IV) sulphosalicylomolybdate is as given in Table-1. The exchanger that exhibited higher ion exchange capacity was used for detailed studies. The exchanger was obtained as bright yellow crystalline solid and is found to be stable in water, alcohol, acetic acid, 1 M H_2SO_4, 1 M HNO_2 and in aqueous solutions of LiCl, NaCl, KCl, $MgCl_2$ and $BaCl_2$.

TABLE-1
PREPARATION OF THE EXCHANGER

Zirconyl oxychloride (250 mL)	Sodium molybdate (250 mL)	Sulphosalicylic acid (250 mL)	Capacity (meq/g)
0.10 M	0.10 M	0.05 M	0.926
0.10 M	0.10 M	0.10 M	0.832
0.10 M	0.10 M	0.20 M	1.458
0.05 M	0.10 M	0.10 M	0.732
0.05 M	0.05 M	0.10 M	0.874
0.05 M	0.10 M	0.05 M	0.690

From the data of chemical analysis, the molar ratio of Zr^{4+}:$C_7H_5O_3SO_3$: MoO_4^{2-} is found to be 2:1:1.

The pH titration curve (Fig. 1) shows first dissociation in acidic medium and second dissociation in basic medium, which indicates that the exchanger in the acid form behaves as a diprotic acid.

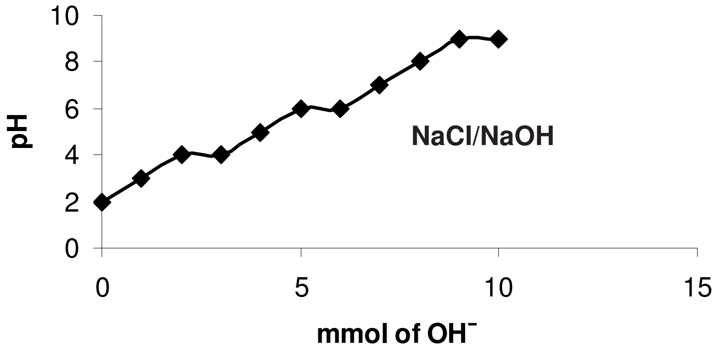

Fig. 1. pH titration curve

The FTIR Spectrum of the exchanger shows peaks at 3500-3000 cm^{-1} (may be due to OH stretching vibrations), 1650 cm^{-1} (due to C=O stretching vibration of carboxylic acid group), 1400 cm^{-1} (characteristic of benzene ring), 1200-950 cm^{-1} (seems to be due to sulphonate and molybdate groups). The peaks at 500 and 600 cm^{-1} may be due to polymerization through (M-O) linkage.

In the thermogram (Fig. 2) of the exchanger, the sharp loss in weight (17.58 %) up to 151.5ºC can be attributed to the loss of external water molecule. The weight loss in the region 151-366ºC may be due to the removal of water molecule as a result of condensation of OH group and is accompanied by the loss of sulphosalicylic acid by vapourization. Weight loss between 366 and 509ºC may be due to loss of water molecules by the condensation of other types of OH groups and the weight loss between 509 and 654ºC may be due to the loss of molybdenum.

The DTA curve of the exchanger shows an endothermic peak (79.9ºC) which may be attributed to the loss of water. The exothermic peak (623.5ºC) may be due to the loss of molybdenum.

On the basis of chemical composition, pH titration, TGA and IR studies, the following formula may be assigned to the exchanger

$$Zr_2(C_7H_5O_3SO_3)(MoO_4)(OH)_5 \cdot nH_2O$$

The number of water molecules were calculated by the method of Alberti *et al.*[26]. If all the water molecules are lost at 151ºC, the weight loss is 17.58 %.

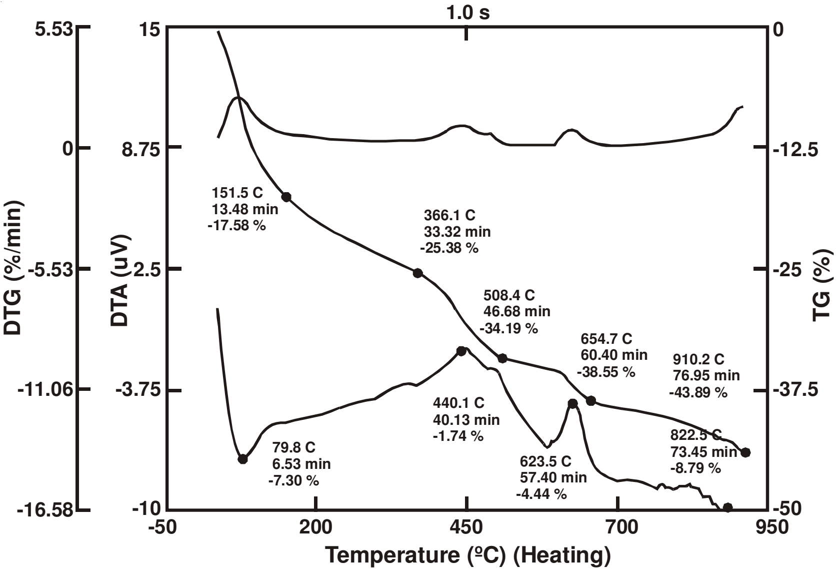

Fig. 2. Thermogram

$$18n + X(M + 18n)/100$$

where X is the weight loss and (M + 18n) is the molecular weight of the material.

The number of external water molecules per molecule of the exchanger was found to be 7.64. The formula therefore can be written as $Zr_2(C_7H_5O_3SO_3)(MoO_4)(OH)_5\cdot 8H_2O$.

The distribution studies shows that lead can be specifically absorbed by the exchanger. The exchanger found to show no affinity for calcium, zinc and thorium. Thus the exchanger may be used for the separation of lead, calcium, thorium and zinc from other metals.

On the basis of the distribution coefficients of the exchanger for various metal ions (Table-2), the quantitative separation in their synthetic mixtures, which were carried out successfully, are summarized in Table-3. Binary separations achieved were Cd^{2+}/ Pb^{2+}, Zn^{2+}/Pb^{2+}, Ca^{2+}/Pb^{2+}, Th^{2+}/Pb^{2+}, Cd^{2+}/Cu^{2+}, Zn^{2+}/Cu^{2+} and Th^{4+}/Cu^{2+}. Ternary separations carried out on the exchanger were $Th^{4+}/Ni^{2+}/Pb^{2+}$, $Th^{4+}/Co^{2+}/Pb^{2+}$, $Th^{4+}/Cd^{2+}/Pb^{2+}$. The recovery ranged from 98-100 % with a variation of ± 1 % for repetitive determinations.

The amount of copper and lead recovered from the wastewater (Table-4) shows that this exchanger may be suitably used for wastewater treatment.

TABLE-2
DISTRIBUTION COEFFICIENTS

Metal ion	K_d
Mg^{2+}	11.45
Ca^{2+}	No sorption
Co^{2+}	14.00
Ni^{2+}	15.60
Cu^{2+}	43.40
Zn^{2+}	No sorption
Cd^{2+}	9.20
Hg^{2+}	5.30
Pb^{2+}	123.80
Th^{4+}	No sorption

TABLE-3
BINARY SEPARATION OF METAL IONS

Metal ion	Eluent	Amount (mg)		Error (%)
		Loaded	Recovered	
Cd^{2+}	0.1 M NH_4NO_3	9.00	8.94	0.66
Pb^{2+}	0.1 M HNO_3	3.80	3.80	0.00
Zn^{2+}	DMW	3.40	3.40	0.00
Pb^{2+}	0.1 M HNO_3	3.80	3.78	0.53
Ca^{2+}	DMW	2.00	2.00	0.00
Pb^{2+}	0.1 M HNO_3	3.80	3.80	0.00
Th^{4+}	DMW	6.90	6.90	0.00
Pb^{2+}	0.1 M HNO_3	3.80	3.76	1.05
Cd^{2+}	DMW	9.00	8.92	0.88
Cu^{2+}	0.1 M HNO_3	3.10	3.10	0.00
Zn^{2+}	DMW	3.40	3.40	0.00
Cu^{2+}	0.1 M HNO_3	3.10	3.08	0.65
Th^{4+}	DMW	6.90	6.90	0.00
Cu^{2+}	0.1 M HNO_3	3.10	3.10	0.97
Ternary separation of metal ions				
Th^{4+}	DMW	3.40	3.40	0.00
Ni^{2+}	0.1 M NH_4NO_3	2.90	2.88	0.69
Pb^{2+}	0.1 M HNO_3	3.80	3.78	0.53
Th^{4+}	DMW	6.90	6.90	0.00
Co^{2+}	0.1 M NH_4NO_3	5.00	4.95	1.00
Pb^{2+}	0.1 M HNO_3	3.80	3.76	0.79
Th^{4+}	DMW	2.00	2.00	0.00
Cd^{2+}	0.1 M NH_4NO_3	9.00	9.02	-0.22
Pb^{2+}	0.1 M HNO_3	3.10	3.10	0.00

TABLE-4
SEPARATION OF METAL IONS FROM WASTEWATER

Sample	Amount recovered (mg)	
	Cu	Pb
A	7.50	12.00
B	6.00	10.00
C	15.00	10.00
D	12.00	8.00
E	10.00	12.00

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