Research Article

Tin(IV) sulphosalicylate composite ion exchange material in environmental remediation and the effect of vanadate and tungstate ion in the matrix of tin(IV) sulphosalicylate

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Abstract
A new composite ion exchange material tin(IV) sulphosalicylate was synthesized, and compared its properties with tin(IV) vanadosulphosalicylate and tin(IV) tungstosulphosalicylate. These materials exhibit good ion exchange capacity, higher stability, reproducibility and selectivity for heavy metals. It was characterized on the basis of FTIR, XRD, TGA and SEM. The distribution coefficient of different metal ions on the composites is in the different order. These materials were found to be selective for Pb(II) and Cd(II) ions. On the basis of difference in K_d values some important binary separations of metal ions were achieved. Separations of heavy metal ions from synthetic mixtures were achieved with these materials.

Introduction

There have attained a great deal of attention in organic-inorganic mixed materials where integration of properties of the organic and inorganic components leading to the formation of new materials with a single molecular scale having composite properties. The intrinsic multifunctional character of these materials makes them potentially useful in multiple fields [1]. Thus efforts have been made to synthesize such hybrid ion exchangers with good ion exchange properties, high stability, reproducibility, and selectivity for heavy toxic metal ions as discussed by S A Nabi et al. [2]. The improved properties of organic–inorganic composite cation exchangers make them more useful for the remediation of waste water [3, 4].

Presence of heavy elements such as lead, cadmium, mercury, nickel, etc in drinking water show potential toxicity and adverse health effects to living organism if it exceeds an acceptable limit. The industrial effluents discharged into the water bodies contain these types of heavy metals ions which cause serious health problems like damages to brain, kidney and reproductive systems of human beings. Composite ion exchangers have been found useful for the removing toxic heavy metals from water bodies with definite advantages. The present paper reports the synthesis, comparison of properties of composite ion exchange materials, tin(IV) sulphosalicylate, tin(IV) vanadosulphosalicylate and tin(IV) tungstosulphosalicylate and uses in the environmental remediation.

Experimental
Materials and reagents

Stannic chloride (E.Merck), sodium molybdate (E.Merck), sodium vanadate and 5-sulphosalicylic acid (Loba Chem) were used for the synthesis of the exchangers. All other reagents and chemicals used were of analytical grade.

A glass column was used for column operations. FT-IR Spectrometer model Thermo-Nicolet Avtar 370 for IR studies, X-ray Diffractometer Bruker AXS D8 Advance for X-ray diffraction studies, JEOL Model JSM - 6390LV for scanning electron microscopic analysis, TG Perkin Elmer Diamond TG Analysis System for thermogravimetric analysis were used. UV-Visible spectrophotometer model JASCO V660 was used for spectrophotometric measurements.

Synthesis

1) Tin(IV) sulphosalicylate

0.1 M stannic chloride solution was added into the solution of 0.05 M 5-sulphosalicylic acid with constant stirring at room temperature and the pH was maintained at 1.0 using solutions of 1.0 M NaOH/1.0 M HNO$_3$. The resulting light clay coloured gel was kept for 24 hrs at room temperature. It was then filtered, washed with deionized water and dried. The exchanger was then converted into the H$^+$ form as usual.

2) Tin(IV) vanadosulphosalicylate (SnVS)

0.1 M solution of stannic chloride was added into the mixture of 0.05 M 5-sulphosalicylic acid and 0.05 M sodium vanadate with constant stirring at room temperature and pH was adjusted at 1.0 using solutions of 1.0 M NaOH/1.0 M HNO$_3$ and kept for 24 hrs. Brownish orange colour solid obtained was then filtered, washed with deionized water and dried. The remaining procedure for getting H$^+$ form of the exchanger was same as above.

3) Tin(IV) tungstosulphosalicylate (SnWS)

Stannic chloride (0.1 M) solution was added into the mixture of 0.05 M 5-sulphosalicylic acid and 0.05 M sodium tungstate with constant stirring at room temperature and pH was adjusted at 1.0 using solutions of 1.0 M NaOH/1.0 M HNO$_3$ and kept for 24 hrs. The resulting light green colour solid was then filtered, washed with deionized water and dried. The exchanger was then converted into the H$^+$ form as usual.

The ion exchange capacity of the material was determined by column method [5] and the effect of temperature on ion exchange capacity was studied [6]. The chemical resistivity of the sample was assessed in mineral acids like HCl, HNO$_3$ and H$_2$SO$_4$, bases like NaOH and KOH and organic solvents like acetic acid, acetone, ethanol and diethyl ether. For this, 0.5 g of the sample was soaked in 50 mL of different solvents, kept for 24 hrs and changes in colour, nature and weight of the sample were noted. The effect of size and charge of exchanging ion on IEC was also studied [6]. pH titration curve of the materials were found out using Topp and Pepper method [7].

Selectivity studies were carried out for various metal ions in demineralized water by batch process [5]. Quantitative separations of some important metal ions were achieved on ion exchangers' columns. 1.0 g of exchanger in H$^+$ form was packed in a glass column (0.5 cm, internal diameter) with a glass wool support at the bottom. The column was washed thoroughly with demineralized water and the mixture of two metal ions (each with initial concentration of 0.1 molL^{-1}) was loaded onto it and allowed to pass through the column at a flow rate 5–20 drops min^{-1} until the level was just above the surface of the material. The process was repeated twice or thrice in order to ensure the complete sorption of metal ions on the bead. The separation of metal ion was achieved by collecting the effluent in 10 ml fraction and titrated against the standard solution of disodium salt of EDTA (0.01 mol L^{-1}).

Results and Discussion

The SnS (light clay colour), SnVS (brownish orange colour) and SnWS (light green colour) ion exchange materials obtained have sodium ion exchange capacity of 0.92 meqg^{-1}, 0.87 meqg^{-1} and 0.97 meqg^{-1} respectively. The ion exchange capacity of SnS decreased by adding vanadate, the anionic part while by adding tungstate, the anionic part, ion exchange capacity of SnS increased. The variation in the IEC shows the anionic part role for changing the properties of SnS. The material was found reproducible in behavior as the material obtained from different batches did not show any appreciable deviation in ion exchange capacity, color, and yield. Elemental composition for the materials by energy dispersive x-ray spectroscopic analysis (EDS) and CHN analysis is shown in **Table 1**. EDS spectra are shown in **Figure 1**. These composite exchangers are stable in mineral acids such as 1.0 M HNO$_3$, 1.0 M H$_2$SO$_4$ and1.0 M HCl, 0.01 M solutions of bases and organic solvents such as ethanol, acetone, carbon tetrachloride etc.

FT-IR spectrum of SnS, SnVS and SnWS (**Figure 2**) shows a broad band in the region ~3428 cm^{-1}, ~3416 cm^{-1} and ~ 3418 cm^{-1} respectively which is attributed to symmetric and asymmetric –OH stretching vibrations of structural hydroxyl group [8]. The band at ~1631 cm^{-1}, ~1622cm^{-1} and 1622 cm^{-1} of SnS, SnVS and SnWS may be due to the deformation vibration of free water molecules. Bands at about 582 cm^{-1}, 571 cm^{-1} and 561 cm^{-1} for SnS, SnVS and

SnWS respectively indicate the presence of Sn-O bond. The band at 1171 cm^{-1} for SnS, 1161 cm^{-1} for SnVS and SnWS is assigned to the SO_3 asymmetric stretching vibrations of sulphosalicylic acid salts [9]. The FT-IR spectra of the materials show the slight peak maxima shift for all vibration frequencies which suggest the some effect of anionic part in SnS.

Table 1 Elemental analysis in weight percentage of materials by EDS and CHN analysis.

Materials	Sn	C	S	H	O	V	W
SnS	30.18	20.14	9.26	1.77	38.65	-	-
SnVS	22.72	15.42	7.13	1.51	43.47	9.75	-
SnWS	32.13	11.32	4.71	1.12	25.04	-	25.68
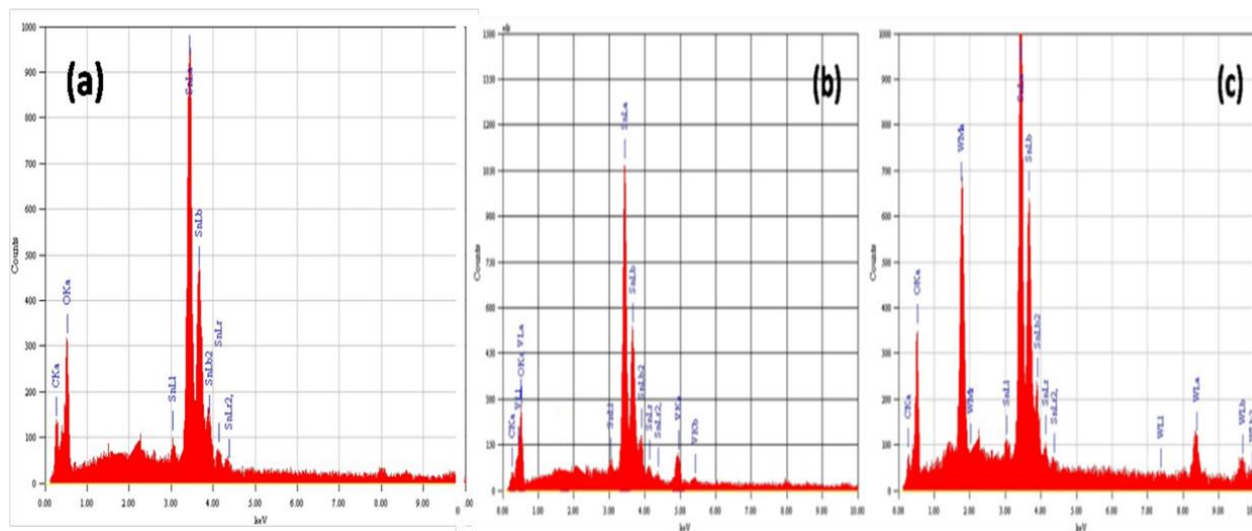
Figure 1 EDS of (a) SnS, (b) SnVS and (c) SnWS.
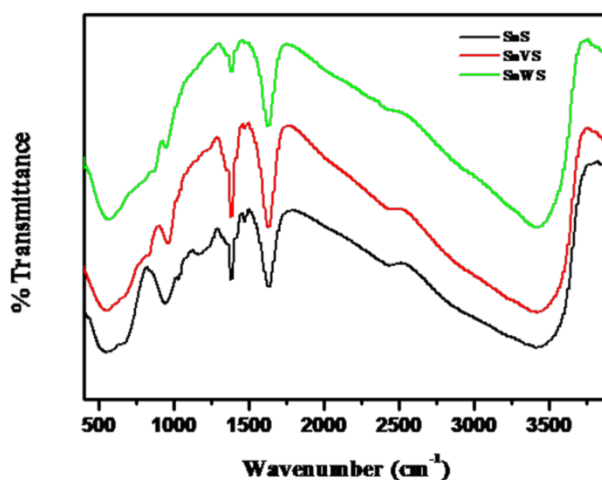
Figure 2 FT-IR spectra of the composite ion exchange materials.

XRD pattern of the materials is shown in the **Figure 3**. No prominent peaks corresponding to the 2θ values indicate the amorphous nature of the materials [10]. TG analysis (**Figure 4**) of SnS shows 10% weight loss up to 100 °C due to the evaporation of external water molecules and condensation of structural hydroxyl groups [11,12] and that of SnVS and SnWS shows 6% weight loss up to 150 °C due to the elimination of strongly coordinated and interstitial water molecules. Very slow weight loss was observed between 200 and 600 °C, due to the decomposition of organic part of the materials. Nearly horizontal segment in TGA curve starting from 600 to 700 °C indicated the transformation of composite ion exchangers to oxide form [13].
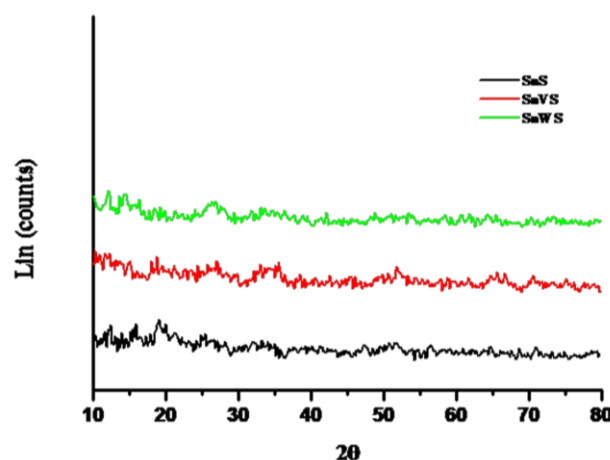
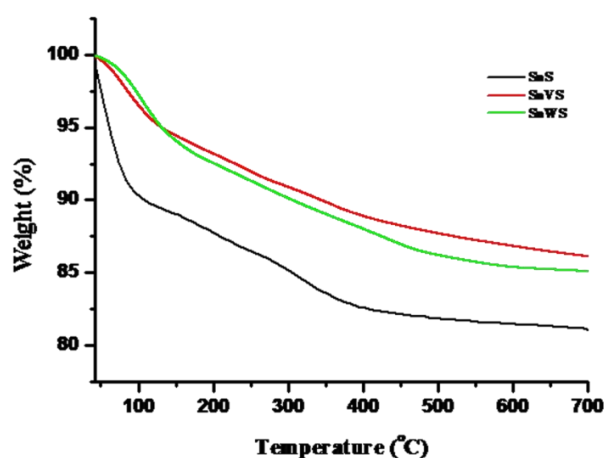**Figure 3** XRD of composite ion exchange materials.

Figure 4 TGA of composite ion exchange materials.

Based on chemical composition from EDS and TGA data the tentative mixed oxide formula suggested for the material SnS is $(SnO_2)(C_7H_5O_3SO_3)(OH)_2.nH_2O$ and for SnVS is $Sn_2(V_2O_5)(C_7H_5O_3SO_3)(OH)_3.nH_2O$. The tentative mixed oxide formula suggested for SnWS is $Sn_2(WO_3)(C_7H_5O_3SO_3)(OH)_3.nH_2O$. The number of water molecules in SnS, SnVS and SnWS is ~2.5, ~2 and ~2.5 respectively which was determined by Alberti-Torroca formula [14].

Scanning electron microscope (SEM) photographs showed the difference in surface morphology of the composite materials (**Figure 5**). It was observed that after binding of anionic part into SnS, its morphology has been changed. SEM images confirmed the rough surface and irregular structure of all the three composite ion exchange materials which is due to the agglomeration of particles.
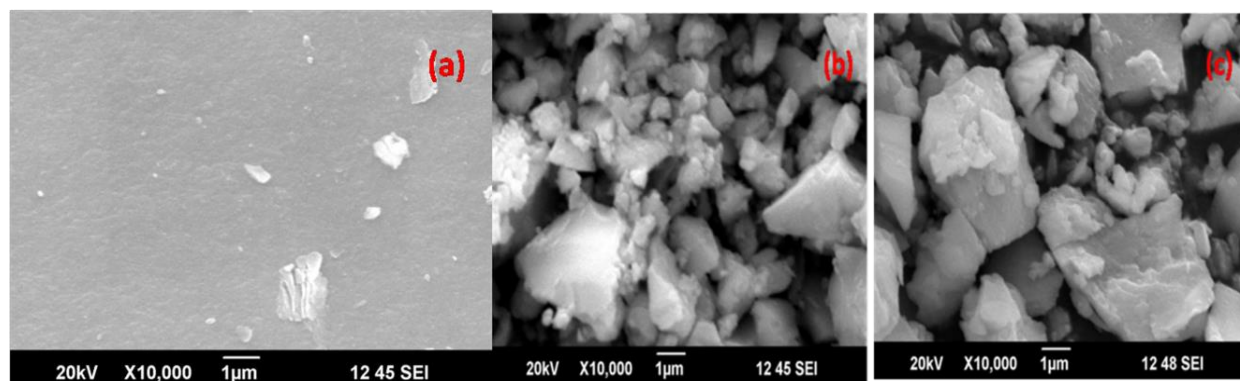

Figure 5 SEM images of (a) SnS, (b) SnVS and (c) SnWS.

UV-Vis DRS measurement can be used as a distinctive technique for knowing the surface coordination and the interaction of metal ions on ion exchange material. UV-Visible diffuse reflectance spectra of SnS (**Figure 6**) show that absorption lies in the UV-Visible region. The reflectance spectra show a strong decrease after 320 nm. This decrease is related to optical transitions occurring in the optical band gap. UV-Visible diffuse reflectance spectra show that the absorption edge is different for SnVS (440 nm) and SnWS (330 nm). The spectra of SnVS show unusual absorbing ability for visible light compared with SnS and SnWS which can be observed in the color of the samples (browinish orange colour).
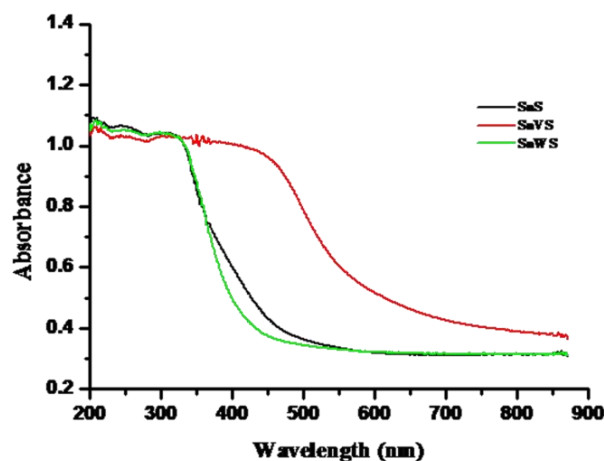
Figure 6 UV-Visible diffuse reflectance spectra of composite ion exchange materials.

The temperature effect on ion exchange capacity of composite ion exchange materials is shown in **Figure 7**. The physical appearance and ion exchange capacity is changed with the increase in the temperature. It may be due the decomposition of the organic part of the composite material with increase in temperature. Ion exchange capacity of SnS is retained its IEC ~72% up to 300°C which ascertained the high thermal stability of the material. The ion exchange capacity of SnVS and SnWS decreases slightly with temperature and the samples retained prominent capacity (~ 40%) up to 300°C. This indicates that the presence of anionic parts tungstate and vandate decrease SnS thermal stability with respect to its ion exchange capacity.
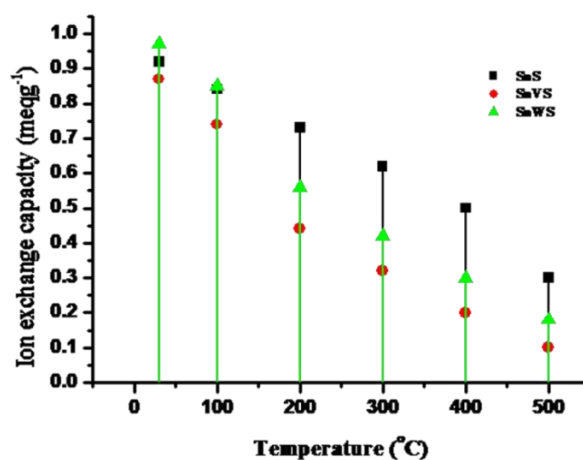
Figure 7 Effect of temperature on IEC of composite ion exchange materials.

The charge and size of exchanging ions also play a significant role in the ion exchange capacity of ion exchangers. The effect of size and charge on ion exchange capacity (**Table 2**) was studied for alkali and alkaline earth metal ions and the affinity order was found to be same for the composite exchangers SnS and SnWS i.e. Li(I) < Na(I) < K(I) and Mg(II) < Ca(II) < Ba(II) confirming that ion exchange varied with the hydrated ionic radii of the ions. But

in the case of SnVS the affinity order does not follow the theoretical sequence. This may be due to the decisive role of the solubility products of the corresponding vanadates of the metal ion in the adsorption process [5, 15].

Table 2 Effect of hydrated ionic radii and charge on IEC

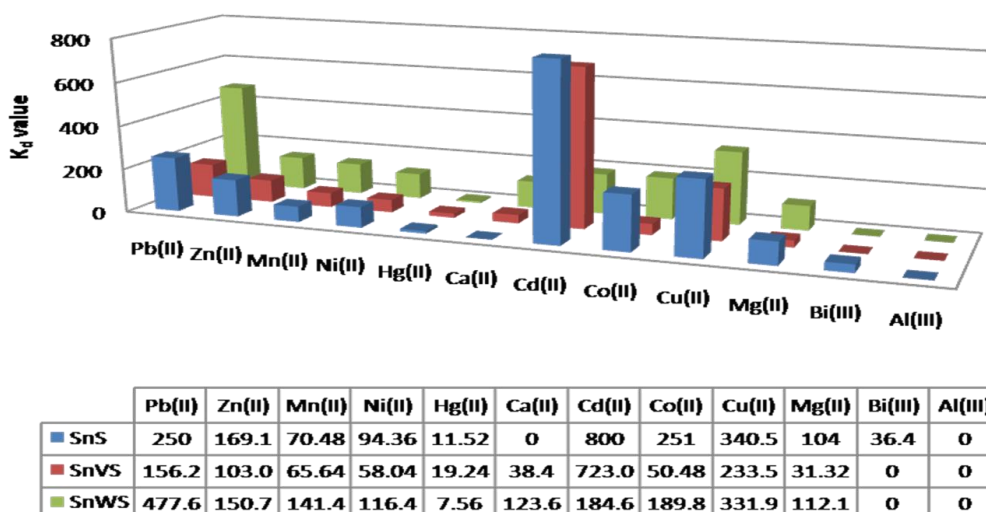| Materials	Metal ion	Hydrated ionic radii (A°)	IEC (meqg^{-1})
SnS	Li(I)	3.40	1.15
	Na(I)	2.76	0.92
	K(I)	2.32	0.84
	Mg(II)	7.00	0.68
	Ca(II)	6.30	0.54
	Ba(II)	5.90	0.37
SnVS	Li(I)	3.40	0.72
	Na(I)	2.76	0.87
	K(I)	2.32	0.95
	Mg(II)	7.00	1.06
	Ca(II)	6.30	0.91
	Ba(II)	5.90	0.46
SnWS	Li(I)	3.40	0.86
	Na(I)	2.76	0.97
	K(I)	2.32	1.13
	Mg(II)	7.00	0.94
	Ca(II)	6.30	1.41
	Ba(II)	5.90	1.81

The pH titration curve (**Figure 8a**) obtained under equilibrium condition exhibited only one inflation point for SnS, which specified the monofunctional strong cationic nature of the ion exchanger. Strong cationic nature of SnS was supported by low pH value of the mixture when no OH− ions are added to the system. pH titration curve of exchangers SnVS and SnWS shows bi-functional nature (Figure 8b and 8c).
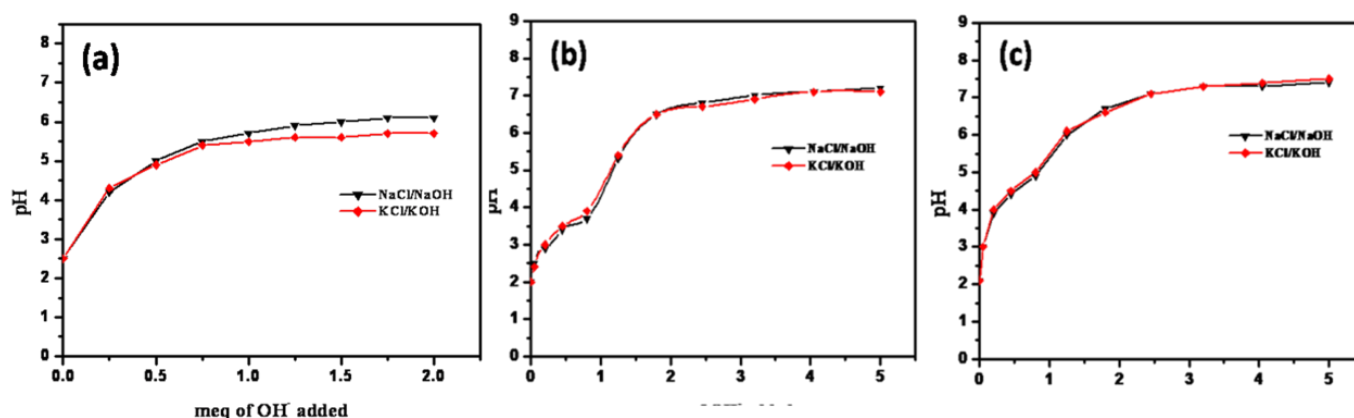
Figure 8 pH titration curves of (a) SnS, (b) SnVS and (c) SnWS.

Distribution studies of twelve metal ions on the composite exchangers in dimineralized water were studied. The results confirmed the high affinity of SnS for Cd(II) and Cu(II) ions as compared to other metal ions. Therefore, SnS ion exchanger may be used for detection and separation of cadmium and copper ions from the industrial wastewater. The distribution coefficient values indicated the sequence of selectivity for different metal ions onto SnS ion exchanger as Cd(II) > Cu(II) > Co(II) > Pb(II) > Zn(II) > Bi(III) > Ni(II) > Mn(II) > Mg(II) > Hg(II) (**Figure 9**). The results shows that SnVS is highly selective for Cd(II) and Cu(II) ions. But in the case of SnWS, selectivity is more towards Pb(II) and Cu(II) ions. The order of selectivity for other metal ions on each exchanger is also different (Figure 9).

	Pb(II)	Zn(II)	Mn(II)	Ni(II)	Hg(II)	Ca(II)	Cd(II)	Co(II)	Cu(II)	Mg(II)	Bi(III)	Al(III)
SnS	250	169.1	70.48	94.36	11.52	0	800	251	340.5	104	36.4	0
SnVS	156.2	103.0	65.64	58.04	19.24	38.4	723.0	50.48	233.5	31.32	0	0
SnWS	477.6	150.7	141.4	116.4	7.56	123.6	184.6	189.8	331.9	112.1	0	0

Figure 9 Distribution studies of metal ions on composite ion exchange materials.

To study the separation capability of the composite ion exchanger materials separation factor of different heavy metal ion pairs were obtained (**Table 3**). Separation factors indicated that separation of heavy metal ions is feasible. On the basis of separation factor binary separation of some heavy metal ions were carried out. The eluents for the separations were selected by studying the effect of electrolyte concentration on distribution coefficients. It is evident from the elution results that the sequential elution of the metal ions occurred from the column of the materials which depends upon the stability of the metal eluting ligand [16].

Table 3 Binary separation of metal ions on SnS, SnVS and SnWS.

Material	Separation achieved	Separation factor	Eluent	Metal ion (mg)		% Efficiency
				Loaded	Eluted	
SnS	Mn(II)		$0.1\ M\ HNO_3$	1.53	1.51	98.69
	Cd(II)	11.35	$0.5\ M\ HNO_3 + 0.4\ M\ NH_4NO_3$	2.80	2.75	98.21
	Mg(II)		$0.01\ M\ HNO_3$	2.80	2.72	97.14
	Cd(II)	21.98	$0.5\ M\ HNO_3 + 0.4\ M\ NH_4NO_3$	2.80	2.69	96.07
	Hg(II)		$0.01\ M\ HNO_3$	2.35	2.32	98.72
	Cd(II)	69.44	$0.5\ M\ HNO_3 + 0.4\ M\ NH_4NO_3$	2.80	2.70	96.43
SnVS	Co(II)	14.32	$0.1\ M\ HNO_3$	1.92	1.90	98.96
	Cd(II)		$0.4\ M\ HNO_3 + 0.4\ M\ NH_4NO_3$	2.80	2.75	98.21
	Mg(II)	23.09	$0.01\ M\ HNO_3$	2.80	2.72	97.14
	Cd(II)		$0.4\ M\ HNO_3 + 0.4\ M\ NH_4NO_3$	2.80	2.72	97.14
	Hg(II)	37.58	$0.01\ M\ HNO_3$	2.35	2.34	99.57
	Cd(II)		$0.4\ M\ HNO_3 + 0.4\ M\ NH_4NO_3$	2.80	2.78	99.29
SnWS	Hg(II)	24.42	$0.01M\ NH_4NO_3$	1.92	1.90	98.96
	Cd(II)		$0.2\ M\ HNO_3 + 0.2\ M\ NH_4NO_3$	2.80	2.75	98.21
	Hg(II)	43.91	$0.01\ M\ HNO_3$	2.35	2.34	99.57
	Cu(II)		$0.3\ M\ HNO_3 + 0.3\ M\ NH_4NO_3$	2.80	2.75	98.21
	Hg(II)	63.17	$0.2\ M\ NH_4NO_3$	2.35	2.34	99.57
	Pb(II)		$0.4\ M\ HNO_3 + 0.4\ M\ NH_4NO_3$	2.80	2.78	99.29

The results show that heavy metal Cd(II) can be successfully separated on a column of the ion exchanger SnS and SnVS by making use of the high separation factor of these ions on the exchanger. The successful separations achieved show the practical utility of the material. On the basis of separation factor binary separation of some heavy metal ion were carried out on the exchanger SnWS. It is found that elution of heavy metal ions depends upon the metal-eluting ligand stability as Pb(II) remains in column for a longer time than that of other heavy metal ions. Other heavy metal

ions Cu(II) and Cd(II) can be successfully separated on a column of the ion exchanger SnWS. The results confirmed that the separations of metal ions are quite sharp, and the recovery is quantitative and reproducible.

Conclusion

In the present study, tin(IV) tungstosulphosalicylate composite cation exchanger synthesized showed appreciably enhanced ion exchange capacity as compared to tin(IV) sulphosalicylate and tin(IV) vanadosulphosalicylate. The composite cation exchangers showed granulometric and reproducible behavior, and thermal stability. The distribution behavior study of SnS and SnVS confirmed their selectivity for Cd(II). The promising feature of the composite ion exchange material, SnWS is its selectivity for the Pb(II) most toxic metal ion present in the environment. The enhanced properties of this composite ion exchangers may significantly contribute towards the practical applicability in the treatment of industrial discharge.

Acknowledgement

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