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Research Article

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Studies on Efficacy of Ion Exchangers on the Removal of Metal ions and Hazardous Dyes from Aqueous Solution

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ABSTRACT

A heteropoly acid salts of Tin(IV) molybdosilicate inorganic ion exchanger has been synthesized by co-precipitation method and well characterized by different instrumental techniques. The ion exchanger shows high ion exchange capacity and chemical stability in various solvent systems. Cationic and bifunctional nature of the exchanger was obtained from pH titration studies. Distribution coefficient of different studies of different metal ions on the exchanger shows that the material is highly selective for Hg(II) and Pb(II) ions. Analytical applicability of the exchanger has been demonstrated by achieving some binary separation of metal ions, quantitative separation of Hg(II) and Pb(II) from industrial waste water. Also, sorptive removal of hazardous dyes methylene blue and crystal violet from aqueous solution were achieved using the ion exchanger.

Keywords: Cation exchanger; Heavy metal removal; Dye removal; Waste water treatment; Heteropoly acid salts

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INTRODUCTION

Analytical techniques such as chemical precipitation, ion exchange, adsorption, membrane filtration, coagulation, flocculation, flotation and electro chemical methods are used recently for the treatment of waste water. Nowadays most of the water resources are highly contaminated with inorganic and organic pollutants such as heavy metal ions and hazardous dyes. Literature survey reveals that sorption using ion exchange materials is an efficient and economic process for the remediation of waste water contaminated with toxic heavy metal pollutants [1-6]. Synthetic inorganic ion exchangers are superior to organic resins because of its high temperature and radiation stability. Inorganic ion exchange material belonging to the class of heteropoly acid salts are gaining importance in catalysis, separation of ions, kidney dialysis and ion selective electrodes etc. [7]. Also, they exhibit good ion exchange properties and selectivity for particular heavy metal ions. Hence, the present work describe the preparation of Tin(IV) molybdosilicate ion exchanger and investigation of applicability of the exchanger for the selective removal of heavy metal ions from industrial as well as synthetic waste water. Also, removal studies of hazardous organic dyes carried out were also explained.

EXPERIMENTAL SECTION

Reagents and Chemicals

Analytical reagent grade Stannic Chloride (LobaChemie), Ammonium molybdate (Loba chemie) and Sodium Silicate (LobaChemie) were used for the synthesis of the inorganic ion exchangers. All other reagents and chemicals used were of analytical grade.

Instrumentation

ELICO LI613 pH meter was used for pH measurement studies. FT-IR Spectrometer model Thermo-Nicolet Avtar 370 was used for IR studies, X-ray Diffractometer Bruker AXS D8 Advance was used for X-ray diffraction studies with Cu Kα radiations, TG Perkin Elmer Diamond TG Analysis System for thermogravimetric/ derivative thermogravimetric analysis were used at a rate of 10°C in nitrogen atmosphere.

Jeol Model JSM-6390LV for SEM analysis and Jeol Model-Jed-2300 instruments were used for Energy Dispersive Spectrometric analysis. A glass column apparatus was used for column operations. Magnetic stirrer (Remi Equipments) was used for stirring purposes.

Synthesis of Tin(IV) Molybdosilicate (SnMoSi) Exchanger

Gels of SnMoSi ion exchanger was prepared by mixing boiling aqueous solutions of Ammonium molybdate and Sodium silicate upon vigorous stirring. Acidic pH was maintained by adding 1.0 M HNO_3 drop wise; the gelatinous precipitate locally formed disappears upon vigorous stirring. After boiling for a few minutes, the clear solution obtained was precipitated by the addition of an aqueous solution of Stannic chloride. A white gelatinous precipitate of SnMoSi was formed. Stirring was maintained using a magnetic stirrer at room temperature (25+2°C) for 3 h. The white gel obtained was left for 24 h at room temperature for digestion. The excess reagents were removed by filtration through filter paper. After washing with DMW the white precipitate obtained was dried. Convert the dried exchanger into H^+ form by immersing in 1.0 M HNO_3 solution with intermittent replacing of acid at an interval of 2 h.

Characterization of the Exchanger

Ion exchange capacity:

The IEC of the material was determined by the column method. For this, 1.0 g of the exchanger (H^+ form) was packed in a glass column of 1.1 cm diameter. The H^+ ions present in the exhabger were eluted by using 100 mL of 1.0 M Sodium chloride solution. The effluent was collected at the bottom and titrated against standard Sodium hydroxide solution. The ion exchange capacity in meq/g was calculated using the formula (eqn.1):

$$IEC = \frac{av}{w} \quad (1)$$

Where 'a' is the molarity, 'v' is the volume of alkali used during titration and 'w' is the weight of the exchanger taken in g [8].

pH titration:

Method of Topp and Pepper [9] was used for pH titration studies using NaOH/NaCl, KOH/KCl systems. 500 mg of exchanger was equilibrated with varying amounts of metal chloride and metal hydroxide solutions. pH of each solution was measured after attainment of equilibrium and plotted against milliequivalents of OH^- ions added.

Chemical stability:

The chemical stability of the exchanger was evaluated in various concentrations mineral acids like HCl, HNO_3 and H_2SO_4, bases like NaOH and KOH and organic solvents like acetic acid, acetone, ethanol and diethyl ether. For this 500 mg of the exchanger was kept separately in 50 mL of different solvents at room temperature for 24 h. The change in colour and weight of the exchanger were noted.

Distribution coefficient studies (K_d):

Distribution studies were carried out for different heavy metal ions in demineralised water by batch method. The distributions of ions on the exchanger before and after equilibrium were determined volumetrically using EDTA as the titrant. The K_d values were calculated using the formula (eqn.2);

$$K_d = \frac{(I-F)}{F} \times \frac{V}{W} \quad (2)$$

Where, 'I' is the initial volume of EDTA used, 'F' is the final volume of EDTA used, 'v' is the volume of the metal ion solution and 'w' is the weight of the exchanger in g.

Analytical Applications

Quantitative separation of metal ions in binary synthetic mixtures:

Quantitative binary separation of metal ions of analytical importance was achieved on the column of SnMoSi ion exchanger. The column on which the separations were to be carried out was filled uniformly with the exchanger in the H^+ form. Initially, distilled water was added to pack the granules so that no air bubbles get stuck. Binary mixture of the metal ions to be separated was poured on to the column and allow to flow at a rate of 0.3-0.5 mL min^{-1}. The above process was repeated to ensure maximum sorption. Individual metal ions were eluted using suitable eluting reagents. The flow rate of the eluent was maintained at a rate of 0.3 - 0.5 mL min^{-1} throughout the elution process. The effluent was collected and was titrated against the standard solution of di-sodium salt of EDTA.

Quantitative separation of metal ions from industrial waste water:

Different waste water samples were collected from the outlet of textile and wood industries. The samples were first filtered to remove suspended particle and then neutralised. The waste water solution was decolourised using normal charcoal. The samples thus obtained were analysed to detect heavy metal present in it. The granular ion exchanger having greater selectivity towards heavy metals were packed in a column, 100 mL of the waste water sample was passed through the column at a flow rate of 0.3-0.5 mL/min. Finally the ions were separated using suitable eluting agents and determined quantitatively.

Dye sorption studies:

20 mL of solution of methylene blue (MB) and crystal violet (CV) (40 ppm) dyes were equilibrated with 200 mg of SnMoSi exchanger for 24 h. The dye solutions were then filtered and centrifuged to remove the exchanger prior to analysis. The concentration of the dyes was analyzed by monitoring the absorbance of the dyes before and after attainment of equilibrium with the SnMoSi exchanger using UV–Vis DR Spectrophotometer. The percentage of removal of dye was calculated using the following formula (eqn.3):

$$\text{Removal (\%)} = \frac{Ci - Ce}{Ci} \text{X } 100 \quad (3)$$

Where, C_i is the initial concentration of dyes and C_e is the equilibrium dye concentration in mg/L.

RESULTS AND DISCUSSION

Different samples of Tin(IV) molybdosilicate ion exchanger were synthesized by varying mixing volume ratio of precourses. All the exchanger samples appeared as white granular solid, ion exchange capacities of all the samples were determined. Among these SnMoSi-3 having maximum ion exchange capacity, 0.97 meq/g was selected for detailed studies **(**Table 1). The exchanger SnMoSi was found to be quite stable in lower concentrations of mineral acids such as 1.0 M HNO_3, 1.0 M H_2SO_4 and 1.0 M HCl, 10% solutions of bases and organic solvents such as ethanol, acetone, carbon tetrachloride etc. indicating practical applicability of the SnMoSi exchanger in these solvents.

Table 1: Synthesis and properties of various samples of SnMoSi

Sample	Molar conc. (M) Sn^{4+} MoO_4^{2-} SiO_4^{2-}	Mixing volume ratio	pH	Color and appearance	Ion exchange capacity for Na^+ (meq/g)
SnMoSi -1	0.05 0.05 0.05	02:01:02	1	White granular solids	0.24
SnMoSi -2	0.05 0.05 0.05	01:01:01	1		0.91
SnMoSi -3	0.05 0.05 0.05	01:02:01	1		0.97
SnMoSi -4	0.05 0.05 0.05	02:01:01	0.5		0.43
SnMoSi -5	0.05 0.05 0.05	01:01:02	1		0.68
SnMoSi -6	0.05 0.05 0.05	01:02:02	1		0.54
SnMoSi -7	0.05 0.05 0.05	02:02:01	0.5		0.81

Heating of SnMoSi at different temperatures for 3 h, the ion exchange capacity and physical appearance of the dried sample were changed with increase of temperature (Table 2). The material was found to be thermally quite stable up to 500°C without any appreciable change in its color and appearance. Also the effect of size and charge on ion exchange capacity was studied for alkali and alkaline earth metal ions (Table 3) and the order was found to be $Li^+ < Na^+ < K^+$; $Mg^{2+} < Ca^{2+} < Ba^{2+}$, this sequence is in agreement with hydrated ionic radii [10] i.e., hydrated ionic radii and extent of hydration are inversely relative to atomic radius of the metal ion. Moving down the group IEC increases with decrease in hydrated ionic radii. This may be due to the ions with smaller hydrated ionic radii easily enters the pores of exchanger, resulting in higher sorption.

Table 2: Effect of temperature on IEC

Temperature (°C)	Duration of heating (hrs)	Na^+ IEC
50	3	0.93
100	3	0.89
200	3	0.84
300	3	0.76
400	3	0.72
500	3	0.7

Table 3: Effect of hydrated ionic radii and charge on IEC

Metal ion	Hydrated ionic radii (A°)	IEC (meq/g)
Li^+	3.4	0.93
Na^+	2.76	0.97
K^+	2.32	1.19
Mg^{2+}	7	1.21
Ca^{2+}	6.3	1.32
Ba^{2+}	5.9	1.63

FTIR spectrum of SnMoSi exchanger (Figure 1a) shows a broad band at region of 3385 cm^{-1} and a sharp peak at 1630 cm^{-1}, justifying the presence of –OH stretching and bending modes. A sharp peak observed at 1107 cm^{-1} is attributed to silicate ion and number of peaks observed between 560-800 cm^{-1} region was due to metal oxygen bond and the band at 940 cm^{-1} show the presence of molybdate ion. The sharp band 1380 cm^{-1} is attributed to the presence presence δ (Si-OH) indicates the presence of structural hydroxyl protons in SnMoSi. TG-DTG curves show that thermal decomposition of SnMoSi (Figure 1b) exchanger occurs mainly in two stages. In the first stage of decomposition (50-150°C) 18% weight loss was observed and is due to dehydration, whereas a continuous loss of around 32% observed during second stage was ascribed to decomposition and conversion of SnMoSi exchanger into oxide form. The scanning electron microscope image of SnMoSi (Figure 1c) explains that the particles were broad in size range, having an irregular shape and no sign of crystalline structure. It also reveals granular nature of the exchanger. XRD pattern of SnMoSi exchanger (Figure 1d) shows polycrystalline nature. The diffraction studies reveal that pattern of SnMoSi shows dominated peaks at 2θ values of 26°, 33°, 52° and 63° with small intensities. The mean crystallite sizes of the materials were estimated from the peak width (FWHM) using Scherrer's equation and was 4.12 nm indicating that particles were in nano dimension.

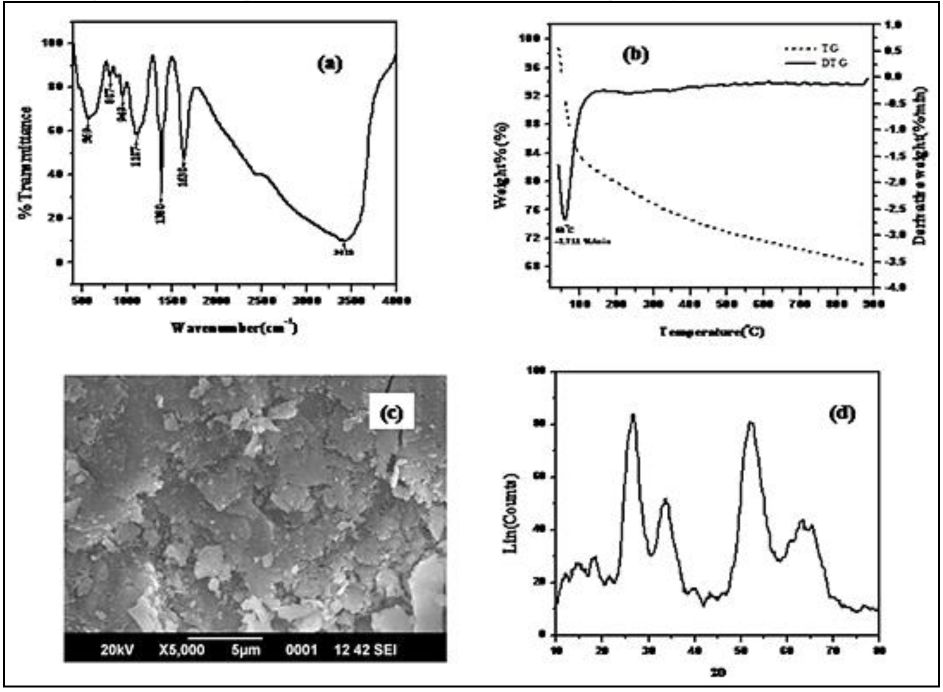

Figure 1: a) FTIR; b) TG-DTG; c) SEM; d) XRD of SnMoSi

pH titration curve drawn for NaCl/NaOH, KCl/KOH systems (Figure 2a) shows bifunctional behaviour of the exchanger, indicating the presence of only one ionizable group. Strong cationic nature of exchangers was confirmed by a low pH (~ 2-3) of the solution without the addition of –OH- ions. The ion exchange capacity obtained from the pH titration curve is in agreement with that obtained by the column method. EDX spectra (Figure 2b) indicate the presence of Sn, Mo, Si and O elements in SnMoSi exchanger without any other impurity elements. Based on the chemical composition, TGA data and IR studies, a tentative mixed oxide formula suggested and was $[(SnO_2).(H_2MoO_4).(SiO_4)].nH_2O$. The number of water molecules (n) was determined using Alberti-Torroca formula (eqn.4),

$$18n = \frac{x(M + 18n)}{100} \quad (4)$$

Where x is the percentage of water content and (M+18n) is the molar mass of the material. The number of water molecules calculated was 4; this includes that due to condensation of structural hydroxyl groups.

In order to explore the potentiality of the exchanger in the separation of metal ions, distribution studies of various metal ions carried out. This indicates that the material was highly selective towards lead and mercury ions (Table 4). The decreasing order of K_d values in demineralised water is given as; $Pb^{2+} > Hg^{2+} > Th^{4+} > Al^{3+} > Co^{2+} > Mg^{2+} > Bi^{3+} > Mn^{2+} > Ni^{2+} > Cd^{2+} > Ca^{2+} > Zn^{2+} > Cu^{2+}$. Study shows that the exchanger SnMoSi can be very well utilized for the separation of lead and mercury from waste effluents. The studies on effect of electrolyte concentrations on distribution coefficients showed that the value decreases with increase in electrolyte concentrations.

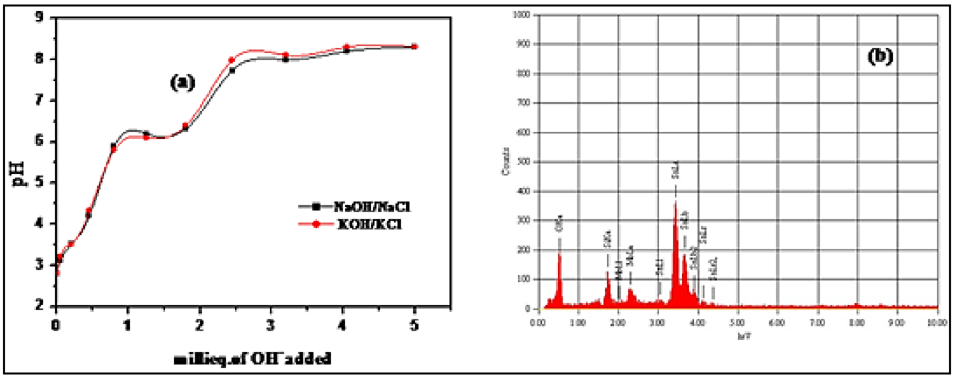

Figure 2: a) pH titration curve; b) EDX of SnMoSi

Separation capability of the exchanger SnMoSi has been demonstrated by achieving some analytically important binary separation of metal ions such as Pb(II)-Cd(II), Pb(II)-Zn(II) etc. **(**Table 5**)**. The separation was based on sequential elution of ions through the column of the exchanger depending on the eluent stability. The weakly retained metal ions get eluted first, followed by stronger one. Also it is observed that separations are quite sharp and reproducible with more than 85% efficiency.

Table 4: Distribution coefficients in water and other electrolytes for SnMoSi

Cations	**DMW**	**Distribution coefficients (K_d)**					
		HNO_3			**NH_4NO_3**		
		0.001 M	**0.01 M**	**0.1 M**	**0.001 M**	**0.01 M**	**0.1 M**
Bi^{3+}	38.6	23.6	10.54	NS	25.7	12.3	4.67
Th^{4+}	120.92	103.6	87.4	65.8	111.6	103.2	94.3
Cd^{2+}	27.76	16.7	8.43	6.21	18.56	12.4	7.43
Pb^{2+}	512.36	338.01	158.3	117.6	421.9	243.7	197.3
Co^{2+}	53.88	40.34	31.5	20.4	47.3	35.2	22.7
Zn^{2+}	15.36	9.43	NS	NS	10.54	2.87	NS
Mg^{2+}	48.04	30.03	22.6	11.9	35.3	25.5	12.5
Mn^{2+}	39.24	28.71	20.33	15.23	31.45	24.76	16.31
Cu^{2+}	NS	NS	NS	NS	NS	NS	NS
Ni^{2+}	38.88	30.43	21.9	17.51	33.43	26.81	20.43
Al^{3+}	111.44	87.54	65.09	50.02	91.22	73.45	64.7
Hg^{2+}	286.6	218.2	178.61	127.76	234.7	194.3	130
Ca^{2+}	20.36	12.41	NS	NS	14.8	5.21	NS
NS:No Observable Sorption							

Table 5: Binary separations of metal ions on SnMoSi

Separations achieved	**$\alpha = K_{d1}/K_{d2}$**	**Eluent**	**Metal ion (mg)**		**Efficiency**
			Loaded	**Eluted**	**(%)**
Pb^{2+} - Cd^{2+}	18.45	0.01 M NH_4NO_3	1.39	1.31	94.24
		1.0 M HNO_3+0.1 M NH_4NO_3	5.18	4.95	95.55
Pb^{2+} - Zn^{2+}	33.35	0.01M NH_4NO_3	1.38	1.08	95.65
		1.0 M HNO_3+0.4 M NH_4NO_3	3.28	2.94	89.63
Hg^{2+} - Cd^{2+}	10.32	0. 1 M NH_4NO_3	1.22	1.12	91.81
		1.0 M HNO_3+0.1 M NH_4NO_3	5.18	4.94	95.37
Pb^{2+} - Mn^{2+}	13.43	0. 01 M NH_4NO_3	1.39	1.27	91.69
		0.5 M HNO_3+0.1 M NH_4NO_3	1.82	1.73	95.08
Pb^{2+} - Ni^{2+}	14.54	0.01 M NH_4NO_3	1.39	1.34	96.66
		0.5 M HNO_3+0.4 M NH_4NO_3	4.32	4.3	99.59
Hg^{2+} - Ca^{2+}	10.65	0.1 M NH_4NO_3	1.22	1.15	94.25
		1.0 M HNO_3+0.2 M NH_4NO_3	1.08	0.94	87.03

Practical utility of the SnMoSi exchanger was demonstrated by achieving quantitative separations of Pb^{2+} from textile industry and Hg^{2+} from wood industry effluents The eluent used for Hg(II) and Pb(II) were 0.1 M NH_4NO_3 and 0.01 M NH_4NO_3. Finally the metal ions were eluted out using respective eluents and then determined titrimetrically with EDTA solution. Around 1.0 mg/100 mL of Pb(II) and Hg(II) ions were removed from the industrial effluents using the exchanger SnMoSi (Table 6).

Table 6: Quantitative removal of Pb^{2+} from textile industry effluents and Hg^{2+} from wood industry effluents

Sample	Metal Ion	Eluent used	In mg/100 mL
Textile industry wastewater (I)	Pb^{2+}	0.01 M NH_4NO_3	1.38
Textile industry wastewater(II)	Pb^{2+}	0.01 M NH_4NO_3	1.4
Wood industry wastewater (I)	Hg^{2+}	0.1 M NH_4NO_3	1.75
Wood industry wastewater (II)	Hg^{2+}	0.1 M NH_4NO_3	1.65

Removal of methylene blue (MB) and crystal violet (CV) dyes from aqueous solution were successfully carried out using SnMoSi exchanger and Figures 3a and 3b depicts the absorption spectrum of MB and CV dye solution before and after treatment with SnMoSi exchanger. Drastic decrease in the intensity of absorption maxima after treatment of the dye solution with the SnMoSi exchanger confirms the removal efficiency of the exchanger towards these dyes. Almost 99% of the MB and CV were removed within 90 min and 120 min of equilibrium time and thus the SnMoSi can be employed as effective and fast material for the treatment of waste water containing dyes.

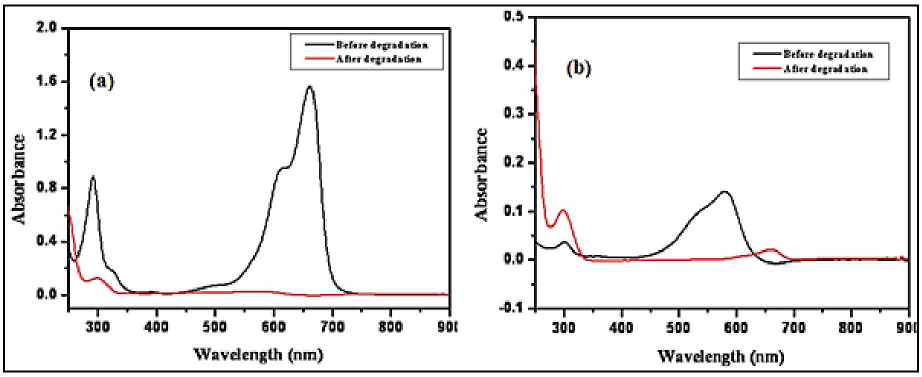

Figure 3: Absorption spectrum of: a) MB; b) CV before and after treatment with SnMoSi exchanger

CONCLUSION

Structural and morphological characterization study reveals that synthesized SnMoSi exchanger were exists in polycrystalline form with nano size. It exhibits very good ion exchange capacity and shows cationic nature. Also shows chemical resistivity to most of the chemicals it is treated with. Very high sorptivity of metal ions and hazardous dyes make SnMoSi exchanger as an excellent material for the removal of these pollutants from industrial effluents.

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