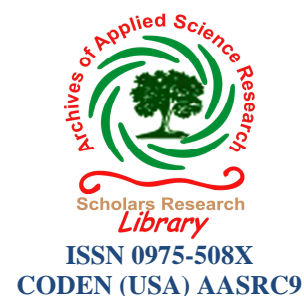




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Studies on novel ion-exchange resin based on styrene-divinylbenzene copolymer and its application for effluent treatment

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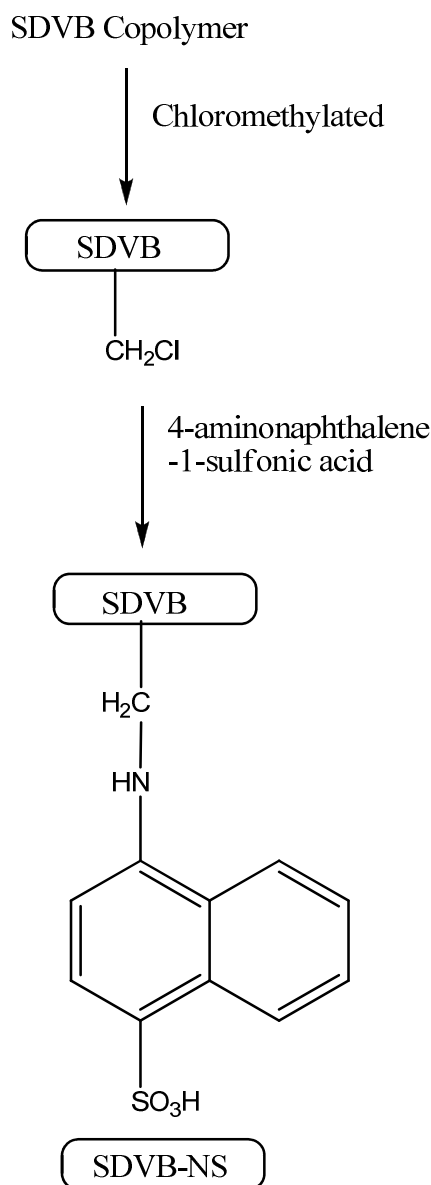
ABSTRACT

The Chloromethylated styrene-divinyl benzene[CM-SDVB] treated with Amino Napthalene Sulphonic acids in THF in concentrated NaOH (pH 9-10) at room temperature for 8 hrs. The resultant polymer designated as styrene-divinylbenzene naphthalene-1-sulfonic acid (SDVB-NS) was characterized by IR spectral studies and thermogravimetry. The SDVB-NS sample was monitored for its ion-exchanging properties. Batch equilibration method has been adopted for such properties. Based on this the SDVB-NS resin was employed for removing the metal ions from effluent coming out of electroplating industry.

Key words: Environmental Analysis, FTIR, Ion Exchange, Batch equilibrium method, Sulfanilic acid, styrene-divinylbenzene.

INTRODUCTION

The effluents from mines and metal industries set up the serious problems in removal of heavy toxic metal ions. The contents of these metals in effluent are almost above the valid limit[1-3]. The contents of this metal can be reduced by treatment of lime, but result is not satisfactory. Thus ion-exchange technique has been proved very useful in this context. The ion exchange resin can be used for metal extraction from ore, analytical reagent, and separation of metal ion and deionization of water[4-10]. Most of commercial ion-exchange resins are sulfonated polystyrene-divinylbenzene copolymer[11-12]. The use of complex ion-formation in ion-exchange resin has been prepared to solve the problem[11,12]. Recently it has been adopted [13,14] and study of the new ion-exchange resin. However the ion-exchange resin based Chloromethylated styrene-divinyl benzene [CM-SDVB] with Napthalene Sulphonic acids has not been received any academic and technical development and its application for effluents coming out from metal industries. The synthetic route is shown below.



MATERIALS AND METHODS

Materials

All the chemicals including SDVB were obtained from local market. The Chloromethylated styrene-divinyl benzene[CM-SDVB] was prepared by reported method[15]. It's chlorine content was found 3.0 mmol./g (10.65%) and 3.0 mmol./g Napthalene Sulphonic acids. All the chemicals used were of either pure or analytical grade.

Synthesis of SDVB- Napthalene Sulphonic acid Resin

To a suspension of CM-SDVB (100g) as per Cl content in THF (100ml) solvent was treated with Napthalene Sulphonic acids (0.3 mole) at room temperature. Then the mixture was refluxed for 5 hrs. The Precipittated SDVB- Napthalene Sulphonic acids were filtered off, wash with water and air- dried.

Measurements

The S content of all SDVB-NS sample were estimated by TF-EA-1101 (Italy). The IR spectra were recorded on Nicolet 760 FTIR Spectrophotometer method[16]. The batch equilibration method was adopted for the ion-exchanging properties[17,18]. The evaluation of the influence of different electrolytes on metal uptake by the polymer, the rate of metal uptake under specified conditions and distribution of various metal ions of different pH values were carried out following the details of the procedures described earlier Table-1.

Effluent samples containing heavy metal ions were collected from industrial situated in Gujarat zone. There samples

contained heavy metal ions along with Mg^{+2} , K^+ , Na^+ , SO_4^{-2} , F^- paper pulp, clay and turbidity. The characteristics of industrial effluents are reported in Table-4.

The procedure adopted to remove heavy metal ions is as follows: 50 ml aliquots of effluents were taken in clean beakers. In each case the pH was adjusted from 6 to 10 with lime 40 mg. **SDVB-** Naphthalene Sulphonic acids was added and solution was stirred with magnetic stirrer for about 10 minutes.

The solution was transferred to 100 ml measuring cylinder and pH was again checked and allowed to stand for four hours. The whole mass was filtered through whatman filter paper No. 40. The whole mass was filtered after necessary treatment were used for estimation of metal ions by atomic absorption [8-21]. Spectrophotometer model AAS 175. Air acetylene mixture was used as fuel. The results are reported in Table-4.

RESULTS AND DISCUSSION

The polymer sample SDVB- Naphthalene Sulphonic acids was in form of dark brown powder and insoluble in common organic solvents. It swells up to some extent in conc. NaOH solution. It did not melt up to 300°C . The S content is 9.6% and consistent with the predicted structure. The IR spectrum comprises the bands due to secondly NH (3400 cm^{-1}), $-\text{CH}_2$ group ($2930, 2850, 1430\text{ cm}^{-1}$) and aromatic ($3030, 1500, 1600\text{ cm}^{-1}$). The TG (thermo gram) of SDVB-NS show a single step degradation. The degradation starts around 260°C , loss rapidly between 300 to 540°C and almost lost 85% at 650°C .

Ion-Exchange properties

The examination of data of ion exchange properties presented in Table-1 reveals that the amount of metal ions taken up by a given amount of the SDVB-NS polymer depends upon the nature and concentration of the electrolyte (ClO_4^- , NO_3^- , Cl^- and SO_4^{-2}) present in the solution. The amounts of metal ions (Fe^{3+} , Cu^{2+} and Ni^{2+}) taken up by the polymer sample increase with the increase in concentration of ions taken up by the polymer sample increase with the increase in concentration of electrolytes like chloride, chlorate and nitrate but decrease with the increase in concentration of the sulfate ions.

Table 1: Evaluation of the influence of different electrolytes in the uptake of several metal ions; ($[\text{Mt}(\text{NO}_3)_2] = 0.1\text{ mole.l}^{-1}$)^a

Metal ions	pH	Electrolyte	Adsorption of mmol. $\cdot 10^1$ of the metal ion on SDVB-NS polymer ^b			
			NaClO_4	NaNO_3	NaCl	Na_2SO_4
Cu^{+2}	4.0	0.01	0.15	0.21	0.12	0.17
		0.1	0.41	0.42	0.46	0.14
		1.0	0.64	0.51	0.56	0.26
Ni^{+2}	5.5	0.01	0.18	0.19	0.18	0.08
		0.1	0.6	0.56	-	0.07
		1.0	0.66	0.72	0.68	0.16
Fe^{+3}	2.75	0.01	0.24	0.18	0.23	0.28
		0.1	0.44	-	0.54	-
		1.0	0.68	0.84	0.76	0.14
UO_2^{+2}	4.0	0.01	0.28	0.27	0.24	0.40
		0.1	0.46	0.40	0.38	0.40
		1.0	0.78	0.88	0.70	0.75
Co^{+2}	5.5	0.01	0.16	0.18	0.14	0.10
		0.1	0.06	0.09	0.08	0.08
		1.0	0.03	0.08	0.06	0.08
Mn^{+2}	5.5	0.01	0.14	0.19	0.18	0.11
		0.1	0.14	0.18	0.18	0.10
		1.0	0.04	0.06	0.05	0.05

a. Volume of electrolyte solution 40 ml, time 24^{th} , volume of metal ion solution 1 ml, Temp. 25°C . Wt. of SDVB-NS polymer 25 mg.

Table-2 Comparison of the rates of metal ion uptake^a

Time (h)	% Attainment of equilibrium state ^b			
	UO_2^{+2}	Cu^{+2}	Fe^{+2}	Ni^{+2}
$\frac{1}{2}$	68	80	70	85
1	75	83	76	86
2	84	86	79	90
3	80	88	94	95
4	90	93	97	96
5	91	94	98	97

a) $[\text{Mt}(\text{NO}_3)_2] = 0.1\text{ mole.l}^{-1}$, volume 1 ml, $[\text{NaNO}_3] = 1\text{ mol.l}^{-1}$, volume 40 ml pH = 3, temp 25°C , wt. of SDVB-NS polymer 25 mg.

b) Related to the amount of metal ions taken up at the state of equilibrium assumed to be established in 24 h and assumed to be 100%.

Rate of metal uptake

The rates of metal absorption by the SDVB-NS sample were measured for UO_2^{+2} , Fe^{3+} , Cu^{2+} and Ni^{2+} ions presence of 1 M NaHCO_3 to know the time required to reach the stage of equilibrium. All experiments were carried out at pH 3. The examination of the results presented in Table-2.

Distribution ratio of metal ions at different pH values

The results described in Table-3 reveals that the amount of metal ions taken up by the sample SDVB-NS at equilibrium increases with the increase in pH. The selectivity of the polymer sample Fe^{3+} ions is higher than that for each of the remaining metal ions. The distribution ratio of Fe^{3+} ion is pH 3. Among the remaining metal ions, Cu^{2+} has a high value of distribution ratio at pH 5 while the other metal ion Ni^{2+} have a low distribution ratio over a pH range from 4 to 6.

Table-3 Distribution ratios, K_D^a

pH	Values for metal ions ^b			
	UO_2^{+2}	Cu^{+2}	Fe^{+3}	Ni^{+2}
1.75	-	-	109	-
2.0	120	-	288	-
2.5	210	-	490	-
3.0	224	118	-	135
4.0	-	222	-	275
5.0	-	224	-	345
6.0	-	-	-	222

The major part of effluents is generated by mineral and metal processing industries. There is a possibility of recycling of water after suitable treatment. These observations have indicated the necessity to derive a more sophisticated method to scavenge the heavy metal ions to a safer limit. The Characteristics of chemical industry situated Gujarat zone and chemical is reported in Table-4. The SDVB-NS resin reduced the heavy metal ions concentration from effluents to the level below the discharge limits as shown in Table-5.

Table 4: Characteristics as effluents contaminated with heavy metal ions obtained from unit of mineral and metal processing industry

Characteristics	Industry situated in Gujarat zone	Characteristics	Industry situated in Gujarat zone
Colour	Reddish brown	Zinc	6.8
pH	5.7	Lead	0.4
Total hardness	940	Cadmium	0.14
Iron	1.08	Magnesium	85.5
Copper	0.72	Calcium	175

Table 5: Removal of Toxic Metal ion from the Effluents from Various Nonferrous Minerals and Processing Industry

Source effluents	Concentrations of various metal ions (ppm)			
	Metal ions	Unsaturated Effluents	After treatment with at 8.0 pH	After treatment with SDVB-NS at 8.0 pH
Industry situated in Gujarat Zone Area	Iron	1.05	Nil	Nil
	Copper	0.74	0.32	Nil
	Zinc	6.5	0.60	0.02
	Lead	0.4	0.12	Nil
	Cadmium	0.16	Nil	Nil
	Magnesium	86.01	88.02	86.5
	Calcium	172.03	171.5	174

"Mg and Ca: metal ions have not been removed from effluents collected from metallurgical industries when the samples of effluents were treated with resin. Because there was incomplete dissociation of salts of bivalent metals Mg and Ca in these effluents. The absorption of ions also depends upon the degree of cross-linking and nature of functional group in resin.

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