STUDIES ON ION-EXCHANGE RESIN BASED ON [STYRENE - MALEIC ANHYDRIDE] COPOLYMER

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ABSTRACT

Commercial [styrene-maleic anhydride](SMA)-copolymer was treated with aniline at room temperature for 6 hrs. The resultant Phenylamine pendented [styrene maleic–anhydride] copolymer was designated as Phenylamine styrene malimic acid(PSMA). It was characterized by elemental analysis, -COOH group, -OH group, IR spectral features and thermogravimetry. The polymeric metal chelates of PSMA were prepared with various transition metal ions Cu(II), Ni(II), Co(II), Mn(II), and Zn(II). All the polymeric chelates were characterized by metal: ligand (M/L) ratio, spectral charactivities, magnetic moments and thermogravimetry.

The ion-exchange properties of PSMA were evaluated by batch equilibrium method. For this the effect of electrolytes on metal uptake by polymer, rate of metal uptake by polymer and distribution of metal ion on polymer and mother liquor over wide pH range. The study also was extended to the treatment of metal industries effluents. Ultimately the so called resin can be utilized commercially for the treatment of metal pollutant water i.e. it will save environment.

Keywords : Characterization , Environmental Analysis , FTIR , Ion Exchange

Introduction:

The contamination of water resources by industrial effluents is a serious issue. Metal ion toxicity has increased substantially because of the use of metal ions as catalysts in industry and as semiconductors in electric and electronic devices. Mineral processing and metal-finishing produce large amounts of waste effluents containing harmful metals such as chromium, zinc, cadmium, copper, iron and lead. In recent years, the effective treatment of heavy metal ions from an aqueous solution has received much attention because of their toxicities in relatively low concentration and tendency to bioaccumulation.[1,2].Styrene maleic anhydride copolymers (SMACs) were commercially introduced in the production of water- soluble resins, possessing high functionality, low solution viscosity, and water insensitivity upon drying. 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 [3-5]. 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 [6-12]. Most of commercial ion-exchange resins are sulfonated polystyrene-divinylbenzene copolymer [13-14]. Recently the carboxy containing ion exchange resins including SMA copolymer have been studies extensively for their ion exchange properties [14-20]. However the ion-exchange resin based Commercial [styrene-maleic anhydride](SMA)-copolymer was treated with aniline has not been received any academic and technical development. In context to this the present paper comprises the syudy of new ion-exchange resin shown in Scheme-1.
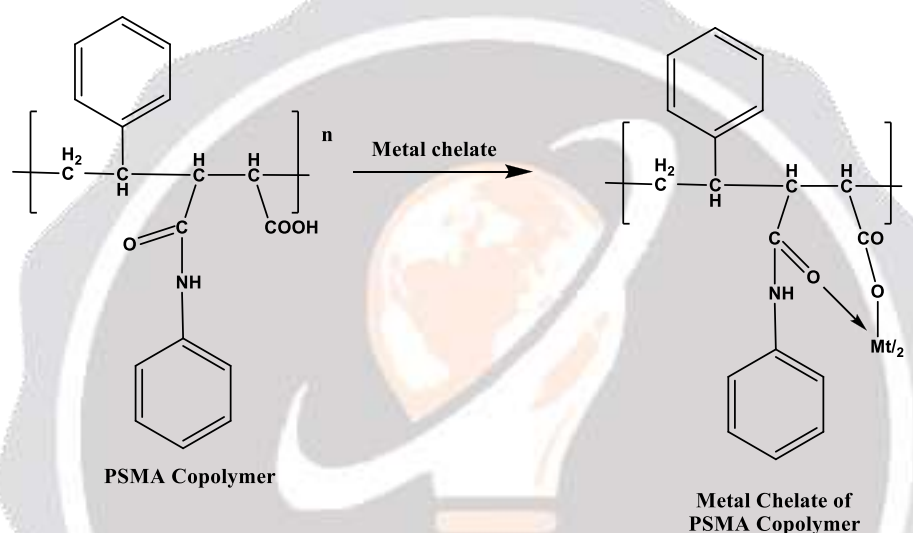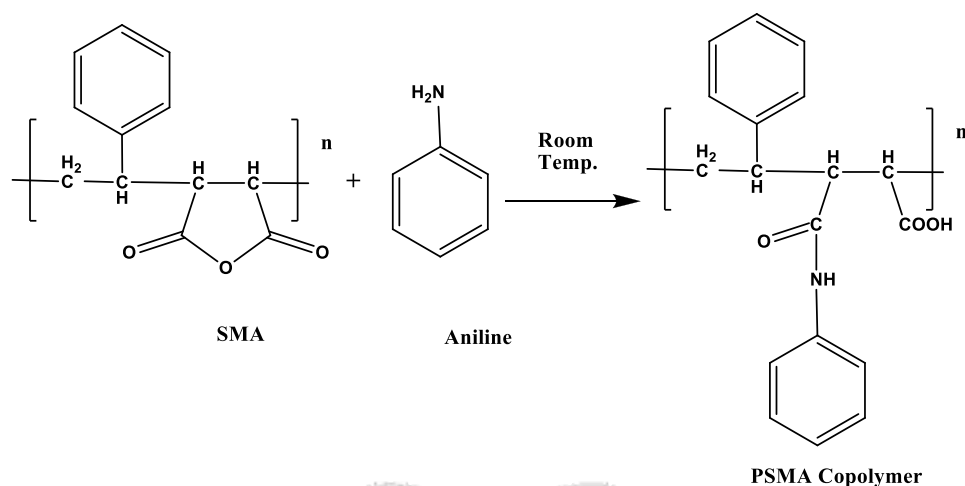
Scheme-1.

EXPERIMENTAL SECTION
Materials
The following chemicals were used Commercial [styrene-maleic anhydride](SMA)-copolymer and aniline All the chemicals used were of either pure or analytical grade.

Synthesis of Phenylamine styrene malimic acid(PSMA) Resin
The synthesis of Phenylamine styrene malimic acid(PSMA)based a commercial [styrene-maleic anhydride](SMA)-copolymer(0.01 mole) was treated with aniline (0.01 mole) at room temperature. The Precipittated PSMA was filtered off, wash with water air- dried. The yield of PSMA was 75%. Elemental Analysis of ion exchange Resin of PSMA in Table-1

Table 1 : Elemental Analysis of ion exchange Resin of PSMA

Empirical Formula	Mol. Cal g/mol	Elemental Analysis (%) Found(Calcd)		
		C	**H**	**N**
$C_{18}H_{17}NO_3$	295	73.15(73.20)	5.75(5.80)	4.70(4.74)

IR-Spectral Feacture (cm⁻): 3030,1520,1640 (Aromatic)

　　　　　　　　　1710(CO), 2890, 2940 (CH_2)

　　　　　　　　　3400(-NH)

Preparation of polymeric metal chelates
PSMA polymer sample (Table-2) was selected for the synthesis of chelates. All the polymeric metal chelates were prepared by mixing aq. solutions of metal nitrate and sodium salt solution of PSMA sample in

stoichometric amounts. A solution of 1.5M NaOH solution (100ml) was added dropwise to a well stirred solution of PSMA resin sample of 29.5 g. 0.1 mole in 1:1 (v/v) ethanol-acetone mixture (700 ml) at room temperature. During neutralization some sticky precipitates appeared, water was added to dissolve these precipitates. The resulting solution was diluted to 1.5 L with water. This stock solution (0.1 M) reagent was used for preparing all polychelates.

To the above mentioned 0.1M solution of sodium salt of PSMA resin (100ml) at room temperature the aq. Solution of metal ion containing adequate amount of metal ion was added with stirring. For the precipitation of Cu(II), Ni(II), Co(II), Mn(II), and Zn(II) chelates the solution used contained slightly more than 0.005 mol of the metal dichelate. The pH of resulting solutions was found to be 4.0 and 5.0 during the formation of Cu(II), Ni(II), Co(II), Mn(II), and Zn(II) polymeric chelates, respectively.   The solid was filtered by decantation, washed with water and then with ethanol and finally air dried. The characteristics of these polymeric chelates are presented in Table-2.

Measurements

The elemental analysis of Phenylamine styrene malimic acid(PSMA) sample were estimated by elemental analyzer TF-EA-1101 (Italy).

The IR spectra of PSMA polymer sample and the polymeric metal chelates were recorded on Nicolet 760D FTIR in KBr with a Spectrophotometer. –COOH, -NH groups of PSMA were determined by known method.

The solid diffusion spectra of polymeric chelates were recorded with Beckman DK-2A spectrophotometer with solid reflectance attachment using MgO as reference material.

Magnetic susceptibilities of the polymeric chelates were estimated at room temperature on Gouy balance using $Hg[Co(NCS)_4]$ as calibrant. Molecular susceptibilities were corrected for diamagnetism of the component atoms by the use of pascal's constant[22].

Thermogravimetry of the PSMA resin and polymeric metal chelates was carried on DuPont 950 TGA analyzer in air at heating rate of $10^0C/min$.

Table-2 : Analysis of polymeric chelates of PSMA copolymer

Polymer/ Polymer chelates	Resultant pH	Colour	MW of Repeat Unit (gm/mol)	Metal		μ_{eff} B.M.
				Calcd. %	Calcd. %	
PSMA	-	Colourless	295	-	-	-
$[PSMA-Cu(II)(H_2O)_2]_n$	4.0	Green	671	9.45	9.40	1.99
$[PSMA-Ni(II)(H_2O)_2]_n$	5.0	Palegreen	666	8.79	8.75	4.02
$[PSMA-Co(II)(H_2O)_2]_n$	5.0	Pink	667	8.83	8.80	2.83
$[PSMA-Mn(II)(H_2O)_2]_n$	5.0	Pink	664	8.28	8.25	4.80
$[PSMA-Zn(II)(H_2O)_2]_n$	5.0	Colourless	672	9.70	9.75	Diamagnetic

Table-3 : TGA Analysis of polymeric chelates of PSMA copolymer

Polymer/Polymer Chelates	Weight loss(%) at various temp.(^0C)					
	200	300	400	500	600	700
PSMA	15	20	22	35.5	48.5	92.90
$[PSMA-Cu(II)(H_2O)_2]_n$	3.6	4.7	12	42.5	53.5	82
$[PSMA-Ni(II)(H_2O)_2]_n$	6.6	8.6	16	25.5	60.1	81

$[PSMA\text{-}Co(II)(H_2O)_2]_n$	7.5	8.4	14.8	25.5	61.1	80
$[PSMA\text{-}Mn(II)(H_2O)_2]_n$	5.4	6.5	9.2	18	40.2	82
$[PSMA\text{-}Zn(II)(H_2O)_2]_n$	2.8	3.2	4.5	15.4	40.1	80

The batch equilibration method was adopted for the ion-exchanging properties [23-24] 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 [23-24]. Effluent sample containing heavy metal ions was collected from chemical industry GIDC Vallbh Vidhyanagar. This sample contained heavy metal ions along with Mg^{+2}, K^+, Na^+, SO_4^{-2}, F^- paper pulp, clay and turbidity. The characteristics of chemical industry GIDC Vallbh Vidhyanagar and chemical is reported in table-5.

RESULTS AND DISCUSSION

The polymer sample PSMA was in form of colourless and insoluble in common organic solvents. It swells up to some extent in conc. NaOH solution. It did not melt up to 100^oC. The elemental contents in Table-3 are constituent with the predicted structure. The IR spectrum comprises the bands due to secondly NH (3400 cm^{-1}), methylated group (2930, 2850, 1430 cm^{-1}) and aromatic (3030, 1500, 1600 cm^{-1}). The TGA of PSMA contains single step degradation. The degradation starts from 200^oC, loss rapidly between 600 to 700 and almost lost 85% at 700^oC.

All the polymeric chelates are insoluble in common organic solvents. Each of them is decomposed by mineral acids affording the parent polymeric ligand. The TGA data reveal that polymeric chelates are apparently un affected when heated up to 300^0C. Examination of the results of metal analysis of the polymeric chelates reveals that the metal to ligands (M:L) ratio is 1:2 for the polychelares of all the divalent metal.

The IR spectra of the polymeric chelates resembled each other in general shape and relative intensity of bands. A comparison of the IR spectrum of polymeric ligand PSMA and that of the polymeric chelates PSMA-Cu(II) reveal that the broad absorption band in the region from 3600-2500 cm^{-1} in the spectrum of the polymeric ligand is much less broad in the spectrum of polymeric chelates. This indicates the absence of internal H-bonding due to chelation.

Magnetic moments of polymeric chelates are given in Table-2. The diffuse electronic spectrum of Cu^{+2} chelates shows two broad bands, 15590 and $22500cm^{-1}$. The first band may be due to a $^2Eg \rightarrow ^2T_2g$ transition, while the second band may be due to charge transfer. The first band shows structures suggesting a distorted octahedral structure for the Cu^{+2} metal chelates. The Co^{+2} metal chelates gives rise to two absorption bands at 21270, 18600 and $11950cm^{-1}$, which can be assigned $^4T_1g(F)\rightarrow^4A_2g$, $^4T_1g(F)\rightarrow^4T_1g(P)$ and $^4T_1g(F)\rightarrow^4T_2g$ transitions, respectively. These absorption bands and the μ_{eff} value indicate octahedral configuration of the Co^{+2} metal chelate [27,28]. The spectrum of Mn^{+2} polymeric chelate comprised three bands at $14800cm^{-1}$, $17620cm^{-1}$ and $22450cm^{-1}$. These bands may be assigned to $^6A_1g\rightarrow^6A_1g(^4Eg)$, $^6A_1g\rightarrow^4T_2g(^4G)$ and $^6A_1g\rightarrow^4T_1g(^4G)$ transitions, respectively. The high intensity of the bands also suggests that they may have some charge transfer character. The magnetic moment is found to be lower than normal range. In the absence of low temperature measurement of magnetic moment, it is difficult to attach any significance to this. As the spectrum of the metal chelates of Ni^{+2} show three distinct bands at 22580 cm^{-1}, 15100 cm^{-1} and 8300 cm^{-1} are assigned as $^3A_2g\rightarrow^3T_1g(P)$, $^3A_2g\rightarrow^3T_1g(F)$ and $^3A_2g\rightarrow^3T_2g$ transition, respectively, suggesting the octahedral environment for Ni^{+2} ion.

Ion-Exchange Properties

The examination of data presented in Table-4 reveals that the amount of metal ions taken up by a given amount of the PSMA polymer depends upon the nature and concentration of the electrolyte present in the solution. The amounts of Cu(II) Ni(II) and Fe(III) ions 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 ions like chloride, chlorate and nitrate but decrease with the increase in concentration of the sulfate ions. The reverse trend is observed [24]. Author also reported that the absorption of the Fe(III) ion by the PSMA resin increase with an increase in the concentration of sulphate ions.

Table 4: Evaluation of the influence of different electrolytes in the uptake of several metal ions; ([Mt $(NO_3)_2$] = 0.1 mole.I^{-1})[a]

Metal ions	pH	Electrolyte	Adsorption of mmol. .101 of the metal ion on PATS polymer b.

			$NaClO_4$	$NaNO_3$	NaCl	Na_2SO_4
Cu^{+2}	4.0	0.01	0.14	0.2	0.1	0.18
		0.1	0.4	0.04	0.45	0.12
		1.0	0.62	0.5	0.55	0.24
Ni^{+2}	5.5	0.01	0.16	0.18	0.18	0.08
		0.1	0.4	0.54	-	0.06
		1.0	0.68	0.74	0.68	0.15
Fe^{+3}	2.75	0.01	0.22	0.16	0.21	0.27
		0.1	0.42	-	0.54	-
		1.0	0.66	0.82	0.75	0.12

a.   Volume of electrolyte solution 40 ml, time 24th , volume of metal ion solution 1 ml, Temp. 25°C.
b.   Wt. of PSMA polymer 25 mg.

Rate of metal uptake

The examination of the results presented in Table-5 reveals that the time required for reaching the state of equilibrium under given experimental conditions depends upon the nature of the metal ion. The time required to attain the state of equilibrium and the amount of the metal ion taken up at the stage of equilibrium increases in the order Cu(II) > Ni(II) >. Fe(III)

Table-5 Comparison of the rates of metal ion uptake[a]

Time (h)	% Attainment of equilibrium state[b]		
	Cu^{+2}	Fe^{+2}	Ni^{+2}
½	80	70	85
1	83	76	86
2	86	79	90
3	88	94	95
4	93	97	96
5	94	98	97

a) [Mt $(NO_3)_2$] = 0.1 mole $\cdot 1^{-1}$, volume 1 ml, [$NaNO_3$] = 1 mol $\cdot 1^{-1}$, volume 40 ml pH = 3, temp 25°C, wt. of PSMA 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%.

Distribution ratio of metal ions at different pH values

Examination of the results described in Table-6 of the effect of pH on the amount of metal ions distributed between two phases indicate that the relative amount of metal ions taken by up the polymeric material increase with an increase in the pH of the medium. The distribution ratio of Cu(II) at 5 pH and of Ni(II) at pH 6 are comparable. Disribution ratio of Fe(III) ions may be due to steric restriction in the accommodation of three units around a single metal ion.

Table-6 Distribution rations, K_D [a]

pH	Values for metal ions[b]		
	Cu^{+2}	Fe^{+3}	Ni^{+2}
1.75	-	108	-
2.0	-	285	-
2.5	-	480	-
3.0	120	-	130
4.0	220	-	280
5.0	-	-	350
6.0	-	-	220

$$K_d = \frac{\{ \text{Wt. (in mg) of metal ions taken up by 1 g of resin} \}}{\{ \text{Wt. (in mg) of metal ions present in 1 mL of resin} \}}$$

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 necessary to derivative more sophisticated method to scavenge the heavy metal ions to a safer limit. The PSMA resin reduced the heavy metal ions concentration from effluents to the level much below the discharge limits as shown in table-6. Hence the polymeric reagents can be considered very effective tertiary treatment reagents.

Table 7: Characteristics as effluents contaminated with heavy metal ions obtained from unit of mineral and metal processing industry

Characteristics	Effluents of chemical industry GIDC Vallbh Vidhyanagar	Characteristics	Chemical Industries Effluents
Colour	Reddish brown	Zinc	6.70
pH	5.5	Lead	0.50
Total hardness	930	Cadmium	0.15
Iron	1.09	Magnesium	85.02
Copper	0.75	Calcium	170.05

Table 8: Removal of Toxic Metal ion from the Effluents fromVarious Nonferrous Minerals and Processing Industry

Source effuents	Concentrations of various metal ions (ppm)			
	Metal ions	Unsaturated Effluents	After treatment with at 8.0 pH	After treatment with PSMA at 8.0pH
Chemical Industries Effluents	Iron	1.09	Nil	Nil
	Copper	0.75	0.30	Nil
	Zinc	6.70	0.61	0.02
	Lead	0.50	0.10	Nil
	Cadmium	0.15	Nil	Nil
	Magnesium	85.02	8820	88.20
	Calcium	170.05	172.1	170

Concusion

SMA polymer reacts with aniline and affords PSMA polymeric ligand. The applicability of the this polymeric ligand was explored by preparing polymeric chelates using different divalent metal ion indicating that the PSMA polymeric ligand has good chelating properties and high thermal stability.

The PSMA copolymer resin was found as effective ion exchanger for various trivalent and divalent metal ions such as Fe^{3+}, Cu^{2+} and Ni^{2+} ions. Since PSMA copolymer contain (-COOH) group and amine, it play a key role in the ion exchange phenomenon, because of it higher tendency of capturing metal ions. Thus PSMA copolymer has immense applications as an ion exchange resin in waste water treatment, metal recovery and for the identification of specific metal ions. Due to considerable differences in the uptake capacities at different pH and media of electrolyte, and the rate of metal ion uptake and distribution ratios at equilibrium, it is possible to separate particular metal ions from ores or other admixtures by this technique.

Acknowledgement

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