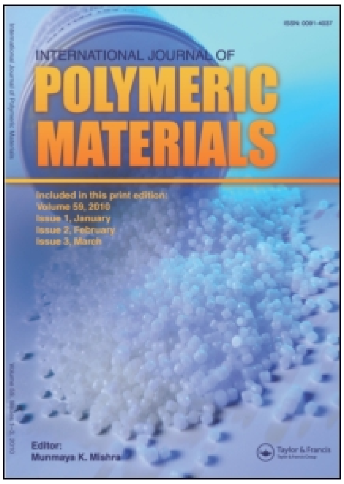

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Synthesis, Characterization and Ion–Exchanging Properties of Novel Ion-Exchange Resin, Part 1

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A polyamine (PA) was prepared by condensation of 1,4-bischloromethyl benzene and 1,2-ehanedeamine. The PA was then treated with cyanuric chloride at 0°C followed by reaction with sulfanilic acid in THF in concentration. NaOH (PH 9–10) at room temperature for 8 h. The resultant polymer, designated as polyamine-s-triazine-sulfanilic acid (PATS), was characterized by elemental analysis, IR spectral studies, and thermogravimetry. The PATS sample was monitored for its ion-exchanging properties by batch equilibrium method.

Keywords: batch equilibrium method, ion-exchange properties, polyamines, s-triazine, sulfanilic acid, thermogravimetry

INTRODUCTION

The effluents from mines and metal industries pose serious problems in removal of heavy toxic metal ions. The contents of these metals in effluent are almost above the valid limit [1–3]; they can be reduced by treatment with lime, but the result is not satisfactory. Thus ion-exchange technique has proved very useful. 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 commercial ion-exchange resins are sulfonated polystyrene-divinylbenzene copolymers [11,12]. The presence of complex ion-formation in ion-exchange resin has been used to solve the problem [11,12]. The aim of the present work is to prepare and study a novel ion-exchange resin.

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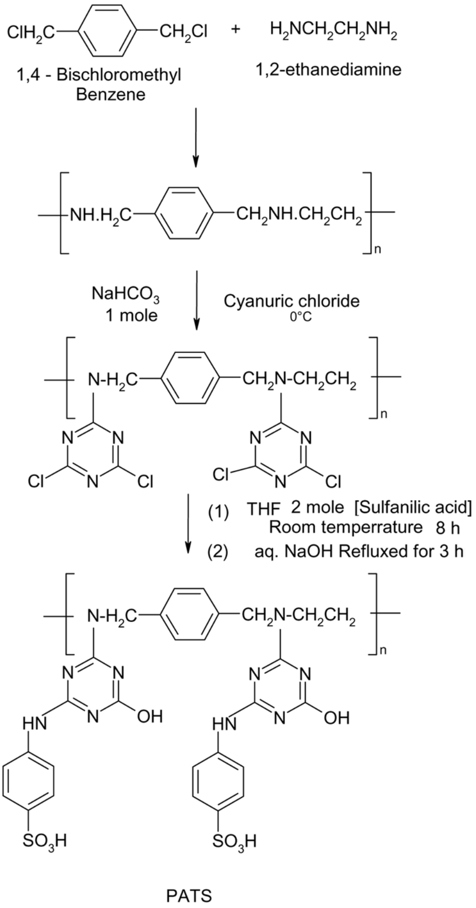
Hence, the present paper comprises the synthesis of novel ion-exchange resin. Hence, the present paper comprises the synthesis of novel ion-exchange resin and its ion-exchanging properties. The synthetic route is shown in Scheme 1 below.

EXPERIMENTAL

Material

All the chemicals used were of either pure or analytical grade.



SCHEME 1 Synthetic route.

Synthesis of Polyamines (PA)

The synthesis of polyamine based or 1,4-dichloro methyl benzene and 1,2-ethanediamine was performed by a reported method [13]. A stoichiometric mixture of 1,4-dichlormethyl benzene, ethanediamine and $NaHCO_3$ in acetone was refluxed for 3 h. The resultant polymeric product was washed and air-dried and ground to fine powder.

Synthesis of PA-Triazine Resin (PAT Resin)

PA (0.1 mole) was placed in, round-bottom flask containing 100 ml THF, maintained at 5°C by external cooling, and stirred. 7.2 gm (0.1 mole) cyanuric chloride was added to this solution and pH was brought to 7–8 by adding $NaHCO_3$. The whole mass was then stirred for 30 min. The product was filtered and was directly used for further reaction.

Synthesis of PAT-Sulfanilic Acid (PATS)

To a mixture of PAT product (0.01 mole) and sulfanilic acid (3.7 g, 0.02 mole) in THF (100 ml), conc. NaOH was added with maintaining pH 9–10. The mixture was heated to 60°C gently for 5 min and was then stirred at room temperature for 8 h. The result and gel type material was filtered, washed by water and air-dried. It was powdered to 100 mesh size. Yield was 90%. It did not melt up to 300°C, and was insoluble in water and common organic solvents.

Measurements

The elemental analyses of all PATS samples were estimated by TF-EA-1101 (Italy). The IR spectra were recorded on Nicolet 760 FTIR Spectrophotometer. Sulfanilic acid groups of PATS were determined by a known method [14]. The batch equilibration method was adopted for the ion-exchanging properties [15,16]. 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 at different pH values were carried out following the details of the procedures mentioned earlier [15,16].

RESULTS AND DISCUSSION

The polymer sample PATS was in the form of a dark brown powder insoluble in common organic solvents. It swelled up to some extent

TABLE 1 Analysis of Ion Exchange Resin PATS

	Elements analysis: $C_{28}H_{26}N_{10}O_8S_2$ (694)			
	C%	H%	N%	S%
Calculated:	48.41	3.74	20.17	9.22
Found:	48.40	3.70	20.10	9.20

SO_3H groups: 2 per repeat unit.

in conc. NaOH solution. It did not melt up to 300°C. The elemental contents in Table 1 are consistent with the predicted structure. The SO_3H content of PATS are also in agreement with the structure. The IR spectrum comprises bands due to second NH ($3400\,cm^{-1}$), methylated group (2930, 2850, $1430\,cm^{-1}$), s-triazine and aromatic (3030, 1500, $1600\,cm^{-1}$). The TGA of PATS contains a single-step degradation. The degradation starts from 280°C, rapidly loss between 300 to 500 and reaches 85% loss at 650°C.

Ion-Exchange Properties

The examination of data presented in Table 2 reveals that the amount of metal ions taken up by a given amount of the PATS polymer depends upon the nature and concentration of the electrolyte present in the solution. The amounts of Fe^{3+}, Cu^{2+} and UO_2^{2+} 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 amounts of the remaining three metal ions, Co^{2+}, Mn^{2+}, and Zn^{2+}, taken by the polymer sample decrease with the increase in concentration of chlorate, chloride, nitrate and sulfate ions.

Rate of Metal Uptake

The rates of metal absorption by the PATS sample were measured for Fe^{3+}, UO_2^{2+}, Cu^{2+} and Mn^{2+} ions in the 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. An examination of the results presented in Table 3 shows that UO_2^{2+} and Fe^{3+} ions required slightly more than three hours for the establishment of equilibrium and Cu^{2+} and Mn^{2+} ions required about five hours for this purpose. In the experiments with solutions containing UO_2^{2+} and Fe^{3+} ions, more than 70% of equilibrium was established in the first hour. This reveals that the rate of uptake of metal ions follows the order UO_2^{2+},

TABLE 2 The Influence of Different Electrolytes on the Uptake of Several Metal Ions: ([Mt $(NO_3)_2$] = 0.1 mole · l^{-1})[a]

			Adsorption of mmol. · 10^1 of the metal ion on PATS polymer[b]			
Metal ions	pH	[Electrolyte] (mole · l^{-1})	$NaClO_4$	$NaNO_3$	NaCl	Na_2SO_4
Cu^{2+}	5.5	0.01	0.17	0.13	0.19	0.34
		0.05	0.24	0.15	0.19	0.32
		0.1	0.23	0.20	0.21	0.31
		0.5	0.31	0.23	0.25	0.29
		1.0	0.51	0.27	0.31	0.26
Fe^{3+}	2.75	0.01	0.14	0.15	0.02	0.26
		0.05	0.28	0.21	0.06	0.10
		0.1	0.30	0.21	0.10	0.08
		1.0	0.40	0.29	0.30	0.08
${UO_2}^{2+}$	4.0	0.01	0.21	0.20	0.20	0.30
		0.05	0.25	0.21	0.21	0.31
		0.1	0.20	0.27	0.24	0.32
		0.5	0.30	0.51	0.27	0.24
		1.0	0.60	0.55	0.31	0.20
Co^{2+}	5.5	0.01	0.21	0.20	0.15	0.11
		0.05	0.21	0.19	0.14	0.10
		0.1	0.10	0.17	0.13	0.08
		0.5	0.08	0.10	0.12	0.06
		1.0	0.06	0.08	0.06	0.04
Mn^{2+}	5.5	0.01	0.20	0.25	0.21	0.17
		0.05	0.17	0.22	0.22	0.14
		0.1	0.15	0.20	0.22	0.08
		0.5	0.13	0.20	0.20	0.03
		1.0	0.10	0.10	0.14	–
Zn^{2+}	5.5	0.01	0.19	0.12	0.15	0.16
		0.05	0.17	0.10	0.15	0.12
		0.1	0.14	0.11	0.10	0.10
		0.5	0.09	0.08	0.06	0.07
		1.0	0.07	0.07	0.02	0.02

[a] Volume of electrolyte solution 40 ml, time 24 h, volume of metal ion solution 1 ml, temperature 25°C.

[b] Weight of PATS polymer 25 mg.

$Fe^{3+} > Cu^{2+} > Mn^{2+}$. The rates of uptake of Zn^{2+} and Co^{2+} ions have been found to be very low at pH 3. Hence the values are not reported.

Distribution Ratio of Metal Ions at Different pH Values

The results described in Table 4 reveal that the amount of metal ions taken up by the polymer sample PATS at equilibrium increases with

TABLE 3 Comparison of the Rates of Metal (Mt) Ion Uptake[a]

	Attainment of equilibrium state[b]			
Time (h)	Fe^{3+}	UO_2^{2+}	Cu^{2+}	Mn^{2+}
0.5	69.9	37.8	41.0	22.1
1	78.9	71.1	56.2	49.1
2	94.8	90.3	69.0	65.1
3	97.0	98.0	79.8	78.0
4	97.0	98.8	86.6	84.8
5	–	–	93.1	89.9
6	–	–	95.0	92.5
7	–	–	99.0	97.6

[a] $[Mt\ (NO_3)_2] = 0.1$ mole · l^{-1}, volume 1 ml, $[NaNO_3] = 1$ mol · l^{-1}, volume 40 ml pH = 3, temperature 25°C, weight of PATS polymer 25 mg.

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

the increase in pH. The selectivity of the polymer sample toward UO_2^{2+} and Fe^{3+} ions are higher than towards each of the remaining metal ions. The distribution ratio for Fe^{3+} ions is lower than that for UO_2^{2+} by about 1800 units at pH 3. The lower values of the distribution ratio for Fe^{3+} ions requires its attachment with proper sites on three different polymer *Loci* and that of the UO_2^{2+} ion requires such an attachment with sites on two polymer *Loci*. Among the remaining metal ions, Cu^{2+} has a high value of distribution ratio at pH 6 while the other three metal ions Co^{2+}, Zn^{2+}, and Mn^{2+} have a low distribution ratio over a pH range from 4 to 6. Further work in the direction of such polymers and their ion exchanging properties is under progress.

TABLE 4 Distribution Ratios, D, of Different Metal Ions as a Function of pH

	Distribution ratio of metal ions					
pH	Cu^{2+}	Fe^{3+}	UO_2^{2+}	Co^{2+}	Mn^{2+}	Zn^{2+}
1.5	–	–	280	–	–	–
1.75	–	140	440	–	–	–
2.0	–	185	535	–	–	–
2.5	–	460	610	–	—	–
3.0	140	990	2820	–	160	–
4.0	260	–	–	20	260	100
5.0	595	–	–	100	350	155
6.0	2830	–	–	365	420	290

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