Synthesis, characterization and ion-exchanging properties of novel ion-exchange resin

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ABSTRACT

The polyamine (PA) was prepared by condensation of 1,4-bischloromethyl benzene and banzidine. The PA was then treated with cyanuric chloride at 0°C followed by reaction with sulfanilic acid in THF in conc. NaOH (PH 9-10) at room temperature for 8 hrs. The resultant polymer designated as polyamine-s-triazine-disulfanilic acid (PATDS) was characterized by elemental analysis, IR spectral studies, and thermogravimetry. The PATDS sample blend with zeolites at various proportions and blends were monitored for its ion-exchanging properties. Batch equilibration method has been adopted, for such properties.

Key words: Polyamines, s-triazine, Sulfanilic acid, ion-exchange properties, Batch equilibrium method, thermogravimetry.

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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 satisfactorily. Thus ion-exchange technique has been proved very useful in this context. The ion-exchange resin can be use 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].The aim of the present work to prepare and study the novel ion-exchange resin blend with zeolites. Hence the present paper comprises the synthesis of novel ion-exchange resin blend with zeolites and its ion-exchanging properties. The synthetic route is shown in scheme 1.

MATERIALS AND METHODS

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

Synthesis of polyamines (PA)
The synthesis of polyamine based a 1,4-dichloro methyl benzene and 1,2-ethanediamine was performed by reported method [13]. The procedure is as follow.

A stoichiometric mixture of 1,4-dichlormethyl benzene, ethanediamine and NaHCO$_3$ in acetone was refluxed for 3 hrs. The resultant polymeric product was washed and air-dried and grind in to fine powder.
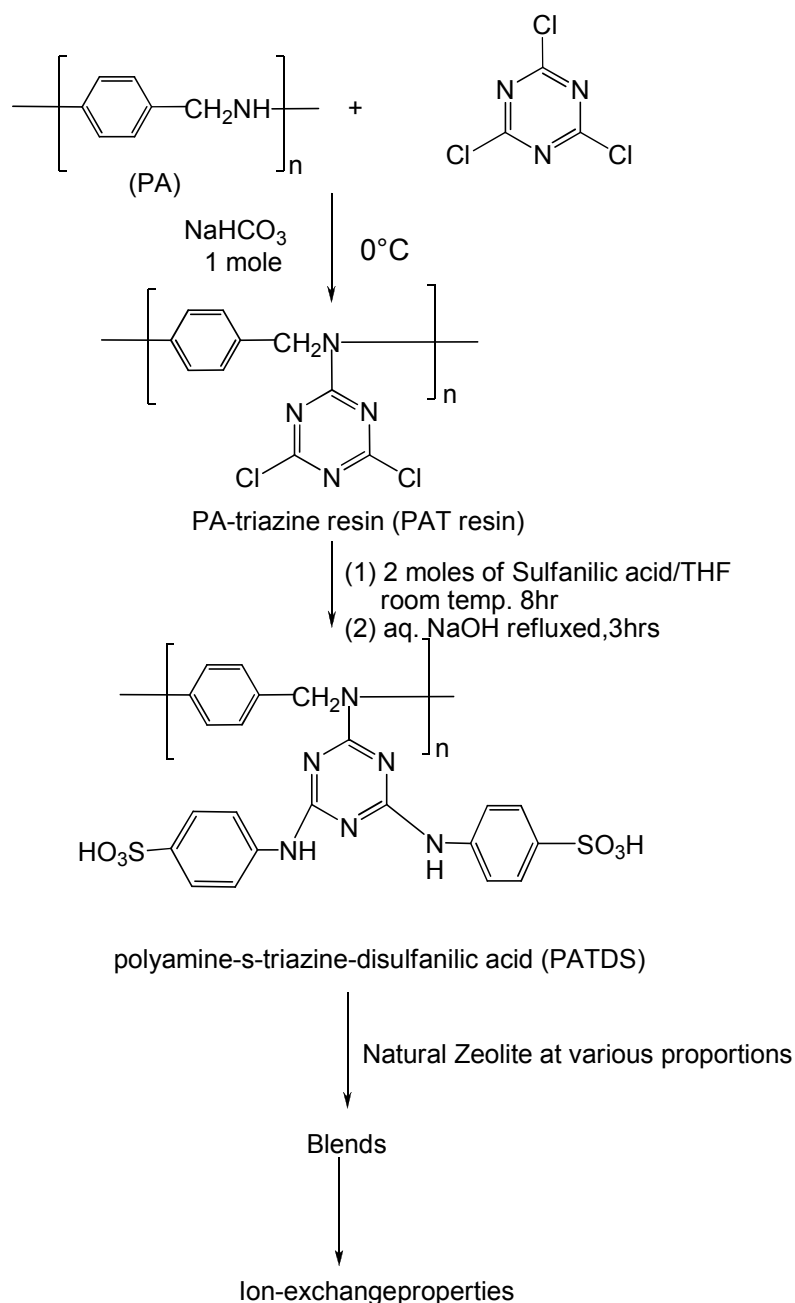
Scheme-1

Synthesis of PA-triazine resin (PAT resin)

PA (0.1 mole) was transferred in to 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 half and hour. The product was filtered and was directly used for further reaction.

Synthesis of PAT-Disulfanilic acid (PATDS)

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 of the mixture was heated upto 60°C gently for 5 minute and it was stirred at room temperature for 8 hrs. The resulted gel type material was filtered, washed by water and air-dried. It was powdered to 100 mesh size. Yield was 88%. It did not melt up to 300°C and insoluble in water and common organic solvents. PATDS blend with natural zeolites at various proportions.

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MEASUREMENTS

The elemental analyses of all PATDS sample were estimated by TF-EA-1101 (Italy). The IR spectra were recorded on Nicolet 760 FTIR Spectrophotometer. Sulfanilic acid groups of PATDS were determined by 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 of different PH values were carried out following the details of the procedures described earlier[15-16].

RESULTS AND DISCUSSION

The polymer sample PATDS was in form of dark brown powder and insoluble in common organic solvents. It swell up to some extent in conc. NaOH solution. It did not melt up to 300ºC. The elemental contents in Table-1 are constituent with the predicted structure. The SO_3H content of PATDS are also agreed with the structure. The IR spectrum comprises the bands due to secondly 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 single step degradation. The degradation starts from 280°C, loss rapidly between 300 to 500 and almost lost 85% 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 Cd^{2+} 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 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+}, Cd^{2+} , Cu^{2+} and Mn^{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 Tab.3 Shows that Cd^{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 h for the purpose. In the experiments with solution containing Cd^{2+} and Fe^{3+} ions, more than 70% of equilibrium was established in the first h. This reveals that the rate of uptake of metal ions follows the order Cd^{2+}, $Fe^{3+} > Cu^{2+} > Mn^{2+}$. 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 no reported.

Table-1: Analysis of ion exchange resin PATS

Elemental Analysis: $C_{22}H_{18}N_6O_6S_2$ (526)

	C%	H%	N%	S%
Calculated :	50.19	3.42	15.96	12.16
Found :	50.1	3.4	15.9	12.1

SO$_3$H groups: 2 per repeat unit.

IR features: 3400 (-NH-), 1604, 1500, 3050 cm^{-1} (aromatic), 1520, 1260, 860 (S-triazine), 2930, 2850, 1430 cm^{-1} (-CH$_2$-)

TGA

Temp ºC	300	400	500	600	700
% Wt. Loss	9	17	47	72	85

Table. 2: Evaluation of the influence of different electrolytes in the uptake of several metal ions;
([Mt (NO$_3$)$_2$] = 0.1 mole · l $^{-1}$)^a

Metal ions	PH	[Electrolyte]	Adsorption of mmol. · 10^1 of the metal ion on PATS polymer[b].			
		(mole · l $^{-1}$)	NaClO$_4$	NaNO$_3$	NaCl	Na$_2$SO$_4$
Cu^{2+}	5.5	0.01	0.18	0.12	0.18	0.35
		0.05	0.25	0.14	0.19	0.33
		0.1	0.24	0.19	0.20	0.32
		0.5	0.32	0.22	0.24	0.30
		1.0	0.52	0.26	0.30	0.27
Fe^{3+}	2.75	0.01	0.15	0.16	0.02	0.26
		0.05	0.29	0.22	0.07	0.12
		0.1	0.31	0.22	0.10	0.09
		1.0	0.42	0.30	0.31	0.09
Cd^{2+}	4.0	0.01	0.21	0.22	0.21	0.32
		0.05	0.24	0.21	0.22	0.33
		0.1	0.21	0.26	0.25	0.33
		0.5	0.32	0.50	0.28	0.23
		1.0	0.62	0.56	0.32	0.21
Co^{2+}	5.5	0.01	0.20	0.20	0.14	0.12
		0.05	0.20	0.18	0.13	0.11
		0.1	0.11	0.18	0.13	0.09
		0.5	0.07	0.12	0.12	0.07
		1.0	0.05	0.07	0.07	0.04
Mn^{2+}	5.5	0.01	0.22	0.24	0.20	0.18
		0.05	0.18	0.22	0.22	0.15
		0.1	0.16	0.21	0.22	0.07
		0.5	0.14	0.21	0.21	0.02
		1.0	0.11	0.11	0.15	--------
Zn^{2+}	5.5	0.01	0.18	0.12	0.15	0.17
		0.05	0.19	0.12	0.16	0.13
		0.1	0.15	0.11	0.11	0.12
		0.5	0.10	0.08	0.05	0.08
		1.0	0.08	0.08	0.02	0.02

a. Volume of electrolyte solution 40 ml, time 24h, volume of metal ion solution 1ml, temp. 25 ºC
b. Wt. of PATDS polymer 25 mg.

Table-3: Comparison of the rates of metal (Mt) ion uptake[a]

Time (hrs)	Attainment of equilibrium state [b].			
	Fe^{3+}	Cd^{2+}	Cu^{2+}	Mn^{2+}
0.5	65.8	33.7	39.2	21.0
1	74.7	67.0	55.1	48.1
2	90.6	86.2	68.3	64.3
3	93.1	94.1	77.8	76.9
4	93.1	94.7	84.5	83.9
5	97.1	95.1	92.2	87.8
6	---	---	94.1	91.6
7	---	---	98.0	96.5

a. [Mt (NO$_3$)$_2$] = 0.1 mole · l $^{-1}$, volume 1 ml, [NaNO$_3$]=1 mol ·l $^{-1}$, volume 40 ml, pH = 3, temp 25º C, wt of PATDS 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%.

Table-4: Distribution rations, D, of different metal ions as a function of the pH

pH	Distribution ration of metal ions					
	Cu^{2+}	Fe^{3+}	Cd^{2+}	Co^{2+}	Mn^{2+}	Zn^{2+}
1.5	-----	-----	285	----	----	-----
1.75	-----	145	445	----	----	-----
2.0	-----	180	530	---	----	----
2.5	----	465	615	---	----	----
3.0	145	995	2815	----	155	----
4.0	255	---	----	25	265	95
5.0	590	----	----	105	345	150
6.0	2835	---	----	360	415	290

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 PATDS at equilibrium increases with the increase in pH. The selectivity of the polymer sample Cd^{2+} and Fe^{3+} ions are higher than that for each of the remaining metal ions. The distribution ratio for Fe^{3+} ions is lower than that for Cd^{2+} by about 1800 units at pH 3. The lower values of the distribution ratio for Fe^{3+} ionCd UO$_2$$^{2+}$ ion requires such an

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attachment with sites on two polymer chains . Among the remaining metal ions, Cu^{2+} has a high value of distribution ration at pH 6 while the other three mental ions Co^{2+} , Zn^{2+} , and Mn^{2+} have a low distribution ration over a pH range from 4 to 6. Further work in the direction of wide range at such polymers and their ion exchanging properties are under progress.

Acknowledgement

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