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

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ABSTRACT

The polyamine (PA) was prepared by condensation of Xylidine dichloride and ethylene diamine. The PA was then treated with cyanuric chloride at 0°C-5°C and the pH is adjusted to 7.8 with $NaHCO_3$. The resultant polyamine cynurate (PAC) was than condensed with 4-amino-1-naphthalene sulfonic acid in conc. NaOH (pH 9-10) at room temperature for 2 hrs. The resultant polymer is designated as 4,4'-((6-((4-ethylbenzyl)(2-(methylamino)ethyl)amino) -1,3,5-triazine-2,4-diyl)bis(azanediyl))bis(naphthalene-1-sulfonic acid) was characterized by elemental analysis, IR spectral studies, and Thermogravimetry.

Key words: Polyamines, Sulfonic acid, ion-exchange properties, Batch equilibrium method, Thermogravimetry.

INTRODUCTION

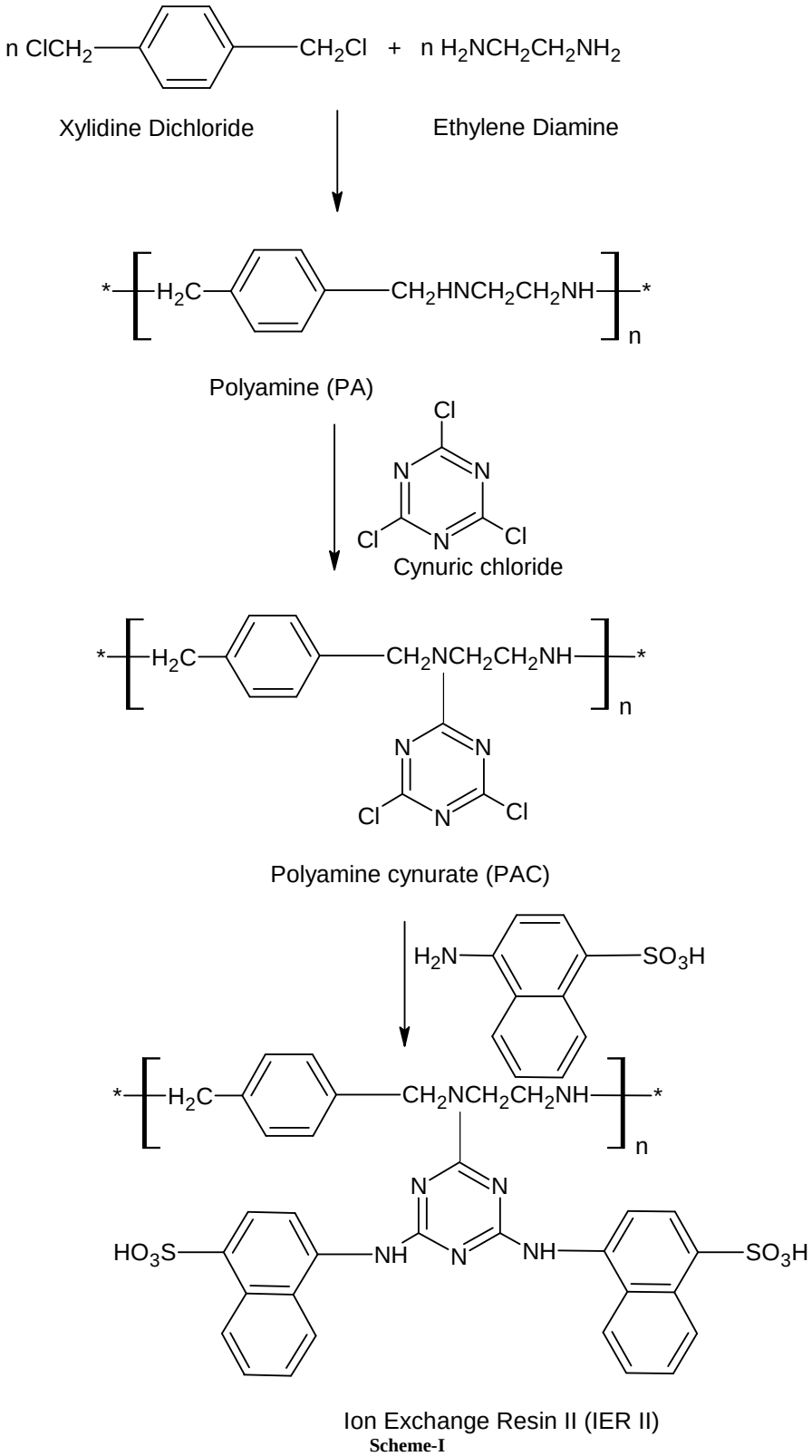
The effluents from mines and metal industries set up the serious problems in removal of heavy toxic metal ions. The contents of these metals in effluent are almost above the valid limit [1-3]. The contents of this metal can be reduced by treatment of lime, but result is not satisfactorily. Thus ion-exchange 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 polystyrenedivinylbenzene copolymer [11-12]. The use of complex ion-formation in ion-exchange resin has been prepared to solve the problem [11-12].The present paper comprises the synthesis of novel ion-exchange resin 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 xylidine dichloride and Ethylenediamine was performed by reported method [13]. The procedure is as follow.

A stoichiometric mixture of xylidine dichloride, Ethylenediamine and $NaHCO_3$ in acetone was refluxed for 12 hrs. The resultant polymeric product was washed and air-dried and grind in to fine powder.


n ClCH2
CH2Cl
+ n H2NCH2CH2NH2
Xylidine Dichloride
Ethylene Diamine
H2C
CH2HNCH2CH2NH
n
Polyamine (PA)
Cl
N
Cl
Cynuric chloride
CH2NCH2CH2NH
Polyamine cynurate (PAC)
H2N
SO3H
HO3S
NH
Ion Exchange Resin II (IER II)

Scheme-I

Synthesis of Cyanurate polyamine (PAC)
PA (0.1 mole) was transferred in to round bottom flask containing 100 ml dioxane maintained at 0°C to 5ºC by external cooling and stirred. 7.2 gm 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 Ion Exchange Resin-II (IER-II)
0.2 Mole (49.4 gm) of 4-amino-1-naphthalene sulfonic acid was added to 0.1 moles of cyanurated polyamines i.e. PAC and pH was brought to 9-10 by adding concentrated solution of NaOH. The temperature of this mixture was raised to 25^0-30^0C and stirred vigorously for two hours. The derivatized ion exchange resin [IER-II] thus formed was filtered, washed with distilled water and finally dried at 110^0C. The yield of novel ion exchange resin [IER-II] was about 72%.

MEASUREMENTS
The elemental analyses of IER-II sample were estimated by TF-EA-1101 (Italy). The IR spectra were recorded on Nicolet 760 FTIR Spectrophotometer. 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 elemental contents in Table-1 are constituent with the predicted structure. The SO_3H content of IER-II are also agreed with the structure. The IR spectrum comprises the bands due to N-CH_2, group of polyamine (3280 cm^{-1}), aromatic (3032, 3067 cm^{-1}). The band around 1262, 1320, 3385 and 3416 cm^{-1} due to especially NH-Aryl- in polyamines chain. The TGA of IER-II contains single step degradation. The degradation starts from 250°, loss rapidly between 300 to 350 and almost lost 77% at 400°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 IER-II depends upon the nature and concentration of the electrolyte present in the solution. In presence of perchlorate, chloride and nitrate ions, the amount of Fe^{+3}, Cu^{+2} and UO_2^{+2} ions taken up by the polymer sample decrease with decrease in concentration of the electrolyte, while in presence of sulfate ion the amount of Fe^{+3}, Cu^{+2} and UO_2^{+2} ions taken up by the polymer sample increase with decrease in concentration of the electrolyte.

Rate of Metal Uptake
The distribution of each of six metal ions Cu^{+2}, Fe^{+3}, Co^{+2}, Mn^{+2}, Zn^{+2} and UO_2^{+2} between the polymer phase and aqueous phase was estimated at room temperature and in presence of 1M $NaNO_3$ solution 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 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 h for the purpose. In the experiments with solution 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 $UO_2^{2+} > Fe^{3+} > Cu^{2+} > Mn^{2+}$. 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-I (IER-II)

Elemental Analysis: $C_{19}H_{21}N_7O_6S_2$ **(507)**

	C%	H%	N%	S%
Calculated :	49.5	4.1	17.5	11.5
Found :	49.4	4.0	17.5	11.5

IR features: 3280 (N-CH_2-), 3032 and 3067 cm^{-1} (aromatic), 1262, 1320, 3385, 3416 (NH-Aryl), 2945 cm^{-1} (-CH_2-)

TGA

Temp°C	250	300	350	400
% Wt.Loss	5	19.4	50	77

Table. 2: Evaluation of the influence of different electrolytes in the uptake of several metal ions

Metal Ion	pH	Electrolyte	Adsorption of mmol. · 10^{-1} of the metal ion on IER-II			
			$NaClO_4$	$NaNO_3$	NaCl	Na_2SO_4
Fe^{3+}	2.75	1	0.35	0.25	0.27	0.04
		0.5	0.32	0.20	0.16	0.05
		0.1	0.27	0.18	0.06	0.08
		0.05	0.24	0.17	0.04	0.10
		0.01	0.11	0.13	0.02	0.24
Cu^{2+}	5.5	1	0.53	0.29	0.34	0.26
		0.5	0.35	0.25	0.24	0.27
		0.1	0.25	0.18	0.21	0.31
		0.05	0.19	0.15	0.18	0.34
		0.01	0.16	0.12	0.17	0.36
UO_2^{2+}	4.0	1	0.55	0.50	0.28	0.22
		0.5	0.34	0.42	0.23	0.23
		0.1	0.26	0.26	0.20	0.24
		0.05	0.23	0.21	0.19	0.28
		0.01	0.15	0.18	0.16	0.32
CO^{2+}	5.5	1	0.06	0.10	0.06	0.065
		0.5	0.07	0.115	0.11	0.08
		0.1	0.115	0.10	0.13	0.09
		0.05	0.10	0.11	0.15	0.10
		0.01	0.11	0.11	0.16	0.12
Mn^{2+}	5.5	1	0.10	0.16	0.13	0.01
		0.5	0.11	0.20	0.17	0.035
		0.1	0.16	0.22	0.22	0.06
		0.05	0.18	0.23	0.24	0.10
		0.01	0.22	0.26	0.25	0.14
Zn^{2+}	5.5	1	0.09	0.09	0.03	0.02
		0.5	0.10	0.10	0.07	0.06
		0.1	0.13	0.11	0.11	0.10
		0.05	0.14	0.12	0.17	0.14
		0.01	0.16	0.13	0.18	0.17

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

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

pH	% Attainment of Equilibrium stage			
	Fe^{+3}	UO_2^{+2}	Cu^{+2}	Mn^{+2}
0.5	67.6	36.36	38.15	19.0
1	72.3	68.6	53.85	45.1
2	92.0	91.3	67.3	65.0
3	95.0	97.0	75.35	77.0
4	97.0	97.0	83.63	82.0
5	98.0	98.0	91.0	91.1
6	-	-	95.0	94.0

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 IER-I 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%.

CONCLUSION

In present communication we prepare novel ion-exchange resin based on ethylene diamine. The novel ion-exchange resin containing a well known metal complexing agent and cyanurate polyamine.The Ion Exchange Resin-II (IER-II) sample was showed good chelating and ion-exchanging properties.

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REFERENCES

[1] R.E.Wing, W.in. Doane, and C.R Runell, *J.Appl. Polym. Sci*, **1995**, 19, 847.
[2] A.K.D Metra and A. Karchadhanvi, *Ind. J. Chem*, **2000**, 39 B, 311.
[3] L.F.Martin, Industrial water Purification Noyes Data corporation Park Ridge New Jercy, **1974**
[4] L.S.M Bento,Proc. *Sugar process. Res. Conf*, **1990**, 99-115.
[5] M. Shimatani and co. workers to snow brand milk products co, U.S.Pat. 5,084, 285, Jan.28, **1992**,
[6] O.L. Sprockel and J.C.Price, *Drug Dev. Ind. Pharm*.**1990**, 16 ,2, 361-376.
[7] Smith, L.A,.chemical research & Licensing Co, U.S.Pat, 4, 978, 807, Dec.18, **1990**,
[8] F.E. Ahmed, B.D.Young, and A.W.Bryson, *Hydrometallurgy*, **1992**, 30, 1-3, 257-275.
[9] J.A.Ritter and J.P.Bibler, *water Sci. Techno*.**1992**, 25(3), 65-172.
[10] CEP, C.R., 70-77, Aug.**1979**
[11] G.F.D'Alelio, U.S.Pat 2, 366, 007, Dec.26, **1945**, General Electric co
[12] G.F.D'Alelio , U.S.Pat. 2,596, 417, Apr.22, **1952**, General Electric co
[13] Tsuchida, E., Sanada, k., Moribe, k., and Shinohara, I. *Markromol.Chem*.**1972**, 151, 207, 33.
[14] Snell, F.D., and Biffeu, F.M., Commerical Methods of Analysis Tarapovevjla Sars & Co. Bombay, **1972**
[15] Greger, H.P., Tieter, M., Citaval L., and Becker E.I., *Ind. Elng. Chem*., **1952**, 44, 2834.
[16] Decoeso, R.C., Donarma, L.G. and Tanic, E.A. *Anal. Chem*., **1962**, 34, 845