Removal of metal ions bearing industrial effluents by H-acid containing ion exchange resin

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ABSTRACT

The new polyamine (PA) have been synthesized by condensation reaction of 1,4-bis(chloromethyl) benzene and 4,4'methylenedianiline. Further the PA was treated with 2,4,6-Trichloro-1,3,5-triazine at 0^oC gives the intermediate product, which was further reacted with H-acid in THF solution The synthesized polymer designated as polyamine-s-triazine-H-acid (PATH) was characterized by elemental analysis, IR spectral studies, and thermogravimetry analysis. Batch equilibration method has been adopted to monitor the ion-exchanging properties of resultant PATH compound. Furthermore, the PATH resin was employed for removing the metal ions from effluent. The contents of this metal can be reduced by treatment of lime, but result is not satisfactory, while the PATH resin found affective towards the removal of metal ions such as Fe, Cu, Zn, Pb, and Cd from industrial effluents.

Keywords: Polyamines, H-acid, 2,4,6-Trichloro-1,3,5-triazine, Ion-exchange properties, Batch equilibrium method
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INTRODUCTION

Heavy toxic metal pollution has become a major problem today for mines and metal industries. The contents of these metals in effluent are almost above the valid limit [1-3]. The removal of heavy metals is of special interest due to their uprising and resolution in the environment. In recent years, various methods for heavy metal removal from industrial effluents have been extensively studied [4-6]. The ion exchange technique i.e. batch equilibrium method has been proved very useful in this context [7,8]. The method is technically simple and allow to efficient removal of metals from solutions. This method includes many examples for selective removal of heavy metal ions from water and industrial waste waters by means various modern types of ion exchangers [9-11]. The ion exchange resin can also be used for metal extraction from ore, effluents, analytical reagent, and separation of metal ion and deionization of water [12-19]. The present author [20] has prepared and studies the new ion-exchange resin and its properties. In continuation to this work [20] the present paper includes the synthesis and characterization of new ion-exchange resin. Further its ion-exchanging properties and applications for effluents coming out from metal industries were also studied.

EXPERIMENTAL SECTION

1,4-bis(chloromethyl) benzene, 4,4'methylenedianiline, triazine derivative, THF etc were purchased from local market. All the chemicals used were of either pure or analytical grade.

The elemental analysis of PATH sample was estimated by TF-EA-1101 (Italy). The IR spectra were recorded on Nicolet 760 FTIR Spectrophotometer. H acid groups of PATH were determined by known method [21]. The batch equilibration method was adopted for the ion exchanging properties [7,8]. The evaluation of the influence of different electrolytes on metal uptake by the polymer, the rate of metal uptake under specified conditions and

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distribution of various metal ions of different pH values were carried out [7,8]. Effluent sample containing heavy metal ions was collected from Industry situated near Bhopal. This sample contained heavy metal ions along with Mg^{+2}, K^+, Na^+, NC^-, SO_4^{-2}, F^-, paper pulp, clay and turbidity. The characteristics of Industry situated near Bhopal and chemical is reported in **Table-5**.

Scheme-1
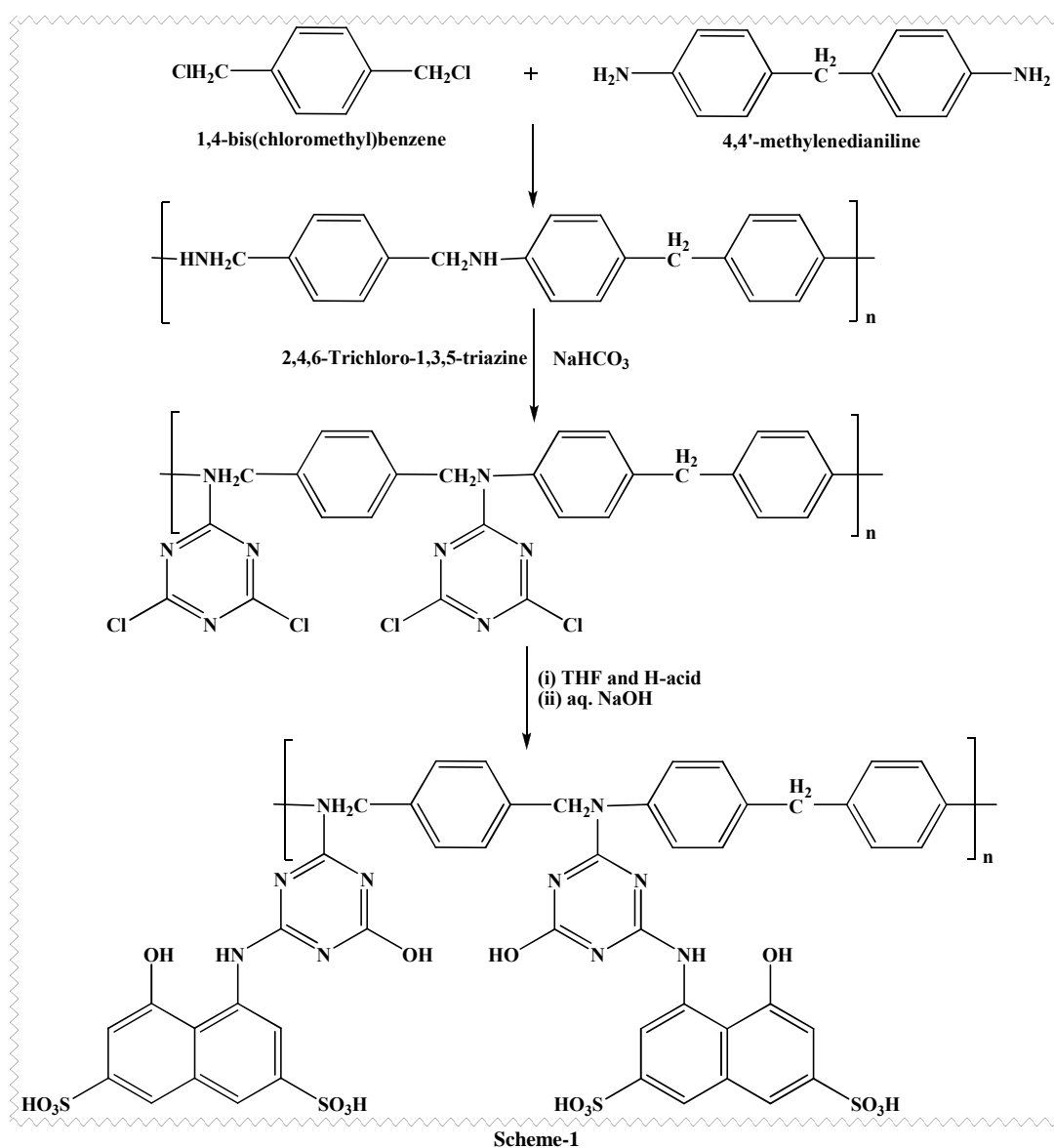
Synthesis of polyamines (PA)
The polyamine based on 1,4-bis(chloromethyl) benzene and 4,4'methylenedianiline was condensed by reported method [22]. The procedure is as follow.

A stoichoimetric mixture of 1,4-bis(chloromethyl) benzene and 4,4'methylenedianiline followed by $NaHCO_3$ in acetone was refluxed for 3 hrs. The resultant polymeric product was washed and air dried and grind in to fine powder.

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. 0.1 mole 2,4,6-Trichloro-1,3,5-triazine was added to this solution and pH was brought and maintain to 7-8 by adding $NaHCO_3$. The whole mixture was then stirred for half an hour. The product was filtered, dried and was directly used for further reaction.

Synthesis of PAT-H- acid (PATH)
To a mixture of PAT product (0.01 mole) and H-acid (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 82%. Melting point of PATH was above 350°C and its insoluble in water and common organic solvents. The IR and Elemental analysis along with some physical properties are given in **Table 1**, while the synthetic route is shown in scheme 1.

Table 1: Analysis of ion exchange resin PATH

Molecular Formula: $C_{47}H_{38}N_{10}O_{16}S_4$	Elemental Analysis	%C	%H	%N	%S
Molecular Weight: 1126 gm/mole	Calculated	50.13	3.31	12.44	11.39
Repeating Unit: 4 SO_3H group/Unit	Found	50.1	3.2	12.4	11.3
Infrared Spectral Features around cm^{-1}	Thermo gravimetric Analysis				
3514 -OH	Temp °C		% Wt. Loss		
3385 -NH	300		8		
3030, 1500, 1600 Aromatic stretching	400		19		
2932, 2854, 1431 methylated group	500		52		
865 s-triazine	600		76		
	670		88		

Procedure for Removal of heavy metal ion:
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. 2,4,6-Trichloro-1,3,5-triazine of PATH 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 4 hours. The whole mixture was filtered through whatman filter paper No. 40. Further the mixture was filtered after necessary treatment was used for estimation of metal ions by atomic absorption [23-25]. Spectrophotometer model AAS 175. Air acetylene mixture was used as fuel.

RESULTS AND DISCUSSION

The polymer sample PATH 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 350°C. The elemental contents in **Table-1** are consisting with the predicted structure. The SO_3H content of PATH is also agreed with the structure, which suggests four SO_3H group per repeating unit. The IR spectrum comprises the bands due to secondly NH (3385 cm^{-1}), -OH group (3514 cm^{-1}), methylated group (2932, 2854, 1431 cm^{-1}), aromatic (3030, 1500, 1600 cm^{-1}) and s-triazine (865 cm^{-1}), which confirmed the structure of PATH. The TGA of PATH contains single step degradation. The degradation starts from 275°C, loss rapidly between 300 to 500 °C and almost lost 88% up to 670°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 PATH 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 taken up by the polymer sample increase with the increase in concentration of the sulfate 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 PATH sample were measured for Fe^{3+}, UO_2^{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 **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 hour for the purpose. In the experiments with solution containing UO_2^{2+} and Fe^{3+} ions, more than 66% 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 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] (mole .l^{-1})	Adsorption of m mol. .10^1 of the metal ion on PATH polymer ^{b}.			
			NaClO$_4$	NaNO$_3$	NaCl	Na$_2$SO$_4$
Cu^{2+}	5.5	0.01	0.17	0.12	0.20	0.39
		0.05	0.27	0.14	0.22	0.36
		0.1	0.28	0.22	0.23	0.35
		0.5	0.36	0.25	0.27	0.33
		1.0	0.58	0.30	0.34	0.27
Fe^{3+}	2.75	0.01	0.14	0.17	0.01	0.28
		0.05	0.30	0.22	0.03	0.12
		0.1	0.32	0.23	0.08	0.11
		0.5	0.36	0.25	0.12	0.07
		1.0	0.46	0.32	0.32	0.06
UO$_2$$^{2+}$	4.0	0.01	0.23	0.22	0.20	0.36
		0.05	0.28	0.24	0.23	0.33
		0.1	0.32	0.33	0.28	0.31
		0.5	0.37	0.61	0.30	0.27
		1.0	0.68	0.65	0.59	0.24
Co^{2+}	5.5	0.01	0.23	0.22	0.17	0.11
		0.05	0.23	0.20	0.15	0.09
		0.1	0.10	0.19	0.12	0.07
		0.5	0.05	0.11	0.10	0.06
		1.0	0.03	0.06	0.06	0.02
Mn^{2+}	5.5	0.01	0.22	0.27	0.24	0.18
		0.05	0.19	0.24	0.23	0.14
		0.1	0.14	0.23	0.23	0.05
		0.5	0.12	0.21	0.20	0.02
		1.0	0.09	0.10	0.14	0.01
Zn^{2+}	5.5	0.01	0.19	0.11	0.15	0.19
		0.05	0.18	0.10	0.13	0.11
		0.1	0.14	0.08	0.08	0.10
		0.5	0.07	0.08	0.02	0.05
		1.0	0.05	0.05	0.01	0.02

Table 3: Comparison of the rates of metal (Mt) ion uptake

Time (h)	Attainment of equilibrium state^b			
	Fe^{3+}	UO$_2$$^{2+}$	Cu^{2+}	Mn^{2+}
0.5x	76.3	45.4	41.3	26.5
1	84.1	66.2	56.7	50.4
2	91.6	84.5	66.1	67.2
3	95.3	92.8	79.8	80.8
4	98.2	97.2	87.2	86.5
5	---	---	94.8	90.1
6	---	---	95.9	91.2
7	---	---	96.1	91.8

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 PATH at equilibrium increases with the increase in pH. The selectivity of the polymer sample UO$_2$$^{2+}$ and Fe^{3+} ions are higher than that for each of the remaining metal ions. The distribution ratio from Fe^{3+} ions is lower than that for UO$_2$$^{2+}$ by about 2400 units at pH 2.5. The lower values of the distribution ratio for Fe^{3+} ions requires its attachment with proper sites on three different polymer chains and that of the UO$_2$^{2}+ ion requires such an attachment with sites on tow polymer chains. Among the remaining metal ions, Cu^{2+} has a high value of distribution ratio at pH 6 while the other three mental ions Co^{2+}, Zn^{2+} and Mn^{2+} have a low distribution ratio over a pH range from 4 to 6.

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

P^H	Distribution ratio of metal ions					
	Cu^{2+}	Fe^{3+}	UO$_2$$^{2+}$	Co^{2+}	Mn^{2+}	Zn^{2+}
1.5	---	168	558	---	---	---
1.75	---	212	671	---	---	---
2.0	---	584	712	---	---	---
2.5	---	1230	3630	---	---	---
3.0	166	---	---	---	---	---
4.0	320	---	---	7	335	103
5.0	751	---	---	108	436	180
6.0	3652	---	---	445	505	336

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 tolerance limit of heavy metals for discharge of effluents into natural stream are different for different metals (e.g. for India Cu-3 ppm, Cd-2.0 ppm, Pb-0.1 ppm Zn-5.0 ppm and Fe-3.0 ppm) the PATH 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 5: Characteristics as effluents contaminated with heavy metal ions obtained from unit of mineral and metal processing industry

Characteristics	Effluents of Industry situated near Bhopal
Colour	Reddish Brown
pH	5.8
Total hardness	958
Iron	1.70
Copper	1.19
Zinc	8.70
Lead	0.88
Cadmium	0.27
Magnesium	112.54
Calcium	218.57

Table:6 Removal of Toxic Metal ion from the Effluents from various Nonferrous Minerals and Processing Industry

Source of effluents	Concentrations of various metal ions (ppm)			
	Metal ions	**Untreated effluents**	**After treatment with lime at 8.0 pH**	**After treatment with PATH at 8.0 pH**
Industry Situated Near Bhopal	**Iron**	1.70	0.28	Nil
	Copper	1.19	0.50	Nil
	Zinc	8.70	0.81	Nil
	Lead	0.88	0.17	Nil
	Cadmium	0.27	Nil	Nil
	Magnesium	112.54	112.05	111.79
	Calcium	218.57	218.50	214.25

As shown in **Table-6** "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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