Synthesis of Functionalized Phenolformaldehyde Polymer Resins by the Reaction of 2,4-Dihydroxyacetophenone Formaldehyde Resin with Various Amines and Their Metal Ion Uptake Properties

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ABSTRACT: A series of functionalized phenolformaldehyde polymer resins have been synthesized by the reaction of 2,4-dihydroxyacetophenone-formaldehyde resin with the amines, such as ethanolamine, aminophenol, ethylenediamine, and propylenediamine in dichloromethane. The Schiffbase polymers were characterized by IR and ^{1}H-NMR spectroscopic techniques. Thermal stabilities of the polymers were determined by TG and DTA studies. Heavy and toxic metal ions viz., Pb(II), Hg(II), Cd(II), and Cr(VI) have been removed using these polymer resins. Metal uptake efficiency, reusability, effect of pH, effect of time, and effect of initial concentration on the metal uptake were also studied. Amount of metal removed by the resin was determined using atomic absorption spectrophotometry. The retention properties were also tested under competitive conditions and were found to be depend strongly on the pH. Elution of metal ions were investigated in acid media. The uptake behaviour of the resins was approximately described by Freundlich's equation. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 1501–1509, 2004

Key words: synthesis; selectivity

INTRODUCTION

The continuous increase of world needs for most of the known metals, the decrease in grade of available ores, and strict environmental regulations, make it interesting to find effective and efficient methods for processing waste solutions containing metal ions, even at very low concentrations. Adsorption techniques employing activated carbon,[1] starch xanthate,[2] fly ash,[3] and surpentine minerals[4] have been used for the treatment of industrial waste water. Alkaline precipitation[5] and ion exchange[6] methods have also been used for the removal of toxic metals. Although many of these methods have been developed and successfully used, their application can cause problems. Some problems can be connected with heterogeneous reactions and interphase transfer. Other problems can arise if aqueous solutions are preferred for the subsequent procedures rather than organic solvents or solid concentrates. In such cases additional procedures are needed, for example, back extraction, desorption, dissolution of solid concentrates, etc., which complicate the analysis and can result in contamination of the sample from the reagent added. Insoluble polymeric supports are widely investigated and applied for metal recovery from dilute solutions,[7–15] in which various chelating groups have been incorporated and are attached to the polymer matrix. Syntheses of such functionalized polymers have been accomplished using either polymerization or simple functionalization principles. The former involves the polymerization of monomers containing the desired ligands. The main advantages of these polymeric resins are high chemical and mechanical stability. In continuation[16–19] of our research, herein we report the synthesis of a set of selective phenolformaldehyde functionalized resins and the removal of toxic/heavy metal ions. In view of analytical potentialities of 2,4-Dihydroxyacetophenone derivatives,[20,21] it is considered worthwhile to synthesize a functionalized polymer containing this moiety.

EXPERIMENTAL

Materials and methods

2,4-Dihydroxyacetophenone was prepared according to the literature procedure.[22] It was recrystallized from distilled water. Thirty-seven percent formalin (Merck) and oxalic acid (Merck) were used without further purification. Ethanolamine, 2-aminophenol, ethylenediamine, and propylenediamine (Merck) were purified before use. Stock solutions of Pb(II), Hg(II), Cd(II), and Cr(VI) were prepared from AR grade lead

nitrate, mercuric chloride, cadmium nitrate, and po-
tassium dichromate salts.

Physical measurements

Elemental analyses were performed microanalytically
by CDRI, Lucknow. IR spectra were recorded with
KBr pellets, using a Beckmann IR-20 spectrophotom-
eter. NMR spectral analyses were carried out in di-
methylsulfoxide-d_6 using a Bruker DSX 500 MHz in-
strument. NETZSCH, Geratebau, GmbH thermal ana-
lysing system (TAS) was used to evaluate the thermal
stability, decomposition temperature, and kinetic pa-
rameters at heating rate of 10°C min^{-1}. Metal uptake
by the resin was determined using a UNICAM UK
Model 839 Atomic Absorption Spectrophotometer [for
Pb(II), Cd(II)] and [Cr(VI)] and a Shimadzu UV-160 A
spectrophotometer [for Hg(II)].

Synthesis of 2,4-dihydroxyacetophenone formaldehyde resin (DAPF)

A mixture (1 : 1.1) 2,4-dihydroxyacetophenone and
formalin solution, 3% (w/w) oxalic acid were taken in
a reaction tube, sealed, and placed in an oil bath at
100°C for 24 h. The tube was then cooled to room
temperature, desealed, and water was removed by
decantation. The solid remaining in the tube was dis-
solved in dimethylformamide and the solution was
added dropwise to a large excess of 10% aqueous
sodium chloride solution, with constant stirring. The
resin that separated out was collected by filtration,
washed several times with distilled water, until free
from chloride ions. The resin was dried at 60°C for
about 1 h.

Synthesis of chelating resins

2,4-Dihydroxyacetophenone formaldehyde resin
(0.0184 mol, 3 g) is condensed with ethanolamine
(0.0184 mol, 1.3 mL), aminophenol (0.0184 mol, 2 g),
ethylenediamine (0.0092 mol, 0.616 mL), and pro-
pylenediamine (0.0092 mol, 0.75 mL) in dichlorometh-
ane (20 mL) by stirring on a magnetic stirrer for about
2 h to get 2,4-dihydroxyacetophenone formaldehyde
resin–ethanolamine (DAPF-ea), 2,4-dihydroxyaceto-
phenone formaldehyde resin–aminophenol (DAPF-ap),
2,4-dihydroxyacetophenone formaldehyde resin–ethyl-
enediamine (DAPF-en), and 2,4-dihydroxyacetophenone
formaldehyde resin–propylenediamine (DAPF-pn), re-
spectively.

Recommended procedure for the removal of metal ions

The effect of pH on metal ion uptake was studied by
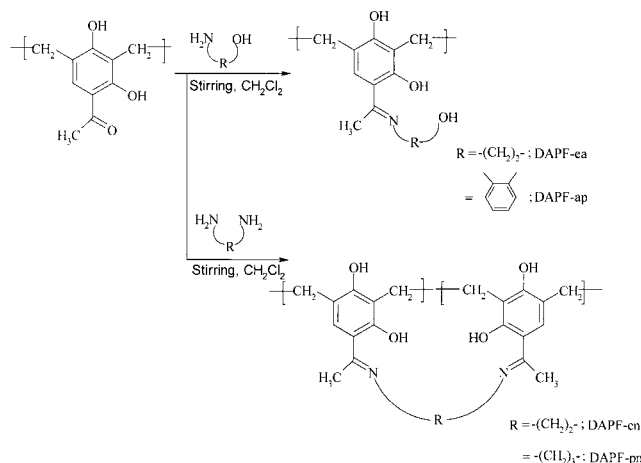stirring 2.5 mL of 1×10^{-2} M metal [Pb(II), Hg(II),

Figure 1 Scheme for the synthesis of chelating polymer resins.

Cd(II) or Cr(VI)] solution, 7.5 mL buffer (pH 2–10)
solution and resin 0.2 g in a 100-mL beaker for 1 h. The
effect of time was studied by repeating the above
procedure at pH 10 at different time intervals (15, 30,
45, 60, and 120 min). The selectivity of the metal ion
was determined by stirring an aliquot containing 0.1
M Pb(II) (0.5 mL), Hg(II) (0.5 mL), Cd(II) (1 mL), and
Cr(VI) (2 mL) in a 100-mL beaker along with 1 g of the
resin and 7.5 mL of buffer (pH 10) solution. The max-
imum uptake capacities of each polymer resin was
determined by reacting 50, 100, 150, 200, 250, and 300
ppm of metal solutions with, polymeric resin under
suitable pH conditions [pH 10 for Pb(II) and Hg(II)
and pH 6 for Cd(II) and Cr(VI)] for about 1 h. In all
cases the metallated resin was filtered and washed
thoroughly with distilled water. The filtrate was col-
lected quantitatively. The amount of metal ion present
in the filtrate was estimated using atomic absorption
spectroscopy and spectrophotometric methods using
1,10-phenanthroline.[23] The amount of metal ion was
deduced from the predetermined calibration curve.

RESULTS AND DISCUSSION

The preparative scheme for functionalised polymer
resins containing NO$_2$ and N$_2$O$_2$ donor atoms is given
in Figure 1. The reaction was carried out in dichlo-
romethane. The 2,4-Dihydroxy phenolformaldehyde
resin is colorless while the functionalized resins have
yellow and pale yellow colors. The color of these
newly formed resins remains unchanged even after
several washings with CH$_2$Cl$_2$. Analytical data and
yields of the resins are given. DAPF: 92% yield. Anal.
calcd: C, 65.85%; H, 4.88%. Found: C, 65.41%, H, 4.9%.
DAPF-ea: 83% yield. Anal. calcd: C, 63.76%; H, 6.28%.
Found: C, 63.3%; H, 6.3%. DAPF-ap: 85% yield. Anal.
calcd: C, 70.58%; H, 5.09%. Found: C, 70.2%; H, 5.1%.
DAPF-en: 75% yield. Anal. calcd: C, 68.18%; H, 5.68%.

TABLE I
^{1}H-NMR Spectral Data of the Resins

Resin	δ (ppm)	Multiplicity	Number of protons	Assignment
DAPF-ea	1.98	Singlet	2H	(—CH$_2$—) of the resin
	2.15	Singlet	3H	(—CH$_3$) methyl
	3.3	Triplet	2H	N—CH$_2$— of ethanolamine
	3.7	Triplet	2H	O—CH$_2$— of ethanolamine
	7.45	Singlet	1H	Aromatic
	12.55	Singlet	1H	Phenolic (—OH), *ortho* to —CH$_2$— group of the resin
	13.05	Singlet	1H	Phenolic (—OH), *ortho* to condensed ethanolamine
DAPF-ap	1.98	Singlet	2H	(—CH$_2$—) of the resin
	2.15	Singlet	3H	(—CH$_3$) methyl
	6.1 to 7.8	Multiplet	5H	Aromatic
	12.3	Singlet	1H	Phenolic (—OH), *ortho* to —CH$_2$— group of the resin
	13.2	Singlet	1H	Phenolic (—OH), *ortho* to condensed aminophenol
DAPF-en	1.9	Singlet	2H	(—CH$_2$—) of the resin
	2.15	Singlet	3H	(—CH$_3$) methyl
	3.7	Triplet	2H	(—CH$_2$—) of the condensed ethylene diamine
	7.4	Singlet	1H	Aromatic
	13.1	Singlet	1H	Phenolic (—OH), *ortho* to —CH$_2$— group of the resin
	13.3	Singlet	1H	Phenolic (—OH), *ortho* to condensed diamine
DAPF-pn	1.95	Singlet	2H	(—CH$_2$—) of the resin
	2.15	Singlet	3H	(—CH$_3$) methyl
	2.7	Quintet	2H	(—CH$_2$) of propylene diamine
	3.6	Triplet	2H	(—CH$_2$—) of propylene diamine
	7.5	Singlet	1H	Aromatic
	13.1	Singlet	1H	Phenolic (—OH), *ortho* to —CH$_2$— group of the resin
	13.3	Singlet	1H	Phenolic (—OH), *ortho* to condensed propylene diamine

Found: C, 67.3%; H, 5.7%. DAPF-pn: 73% yield. Anal. calcd: C, 68.85%; H, 6.01%. Found: C, 67.8%; H, 6.1%. The data suggest that yields of the resins are sufficiently high. The yields of DAPF-ea and DAPF-ap are found to be better than DAPF-en and DAPF-pn. This is because of stereochemical factors. The analytical data are in good agreement with the calculated values.

The resins are insoluble in common organic solvents and soluble in dimethylformamide and dimethylsulfoxide. ^{1}H-NMR spectra of the resins were recorded in DMSO-d$_6$. The multiplicity pattern of the resins are given in Table I. The spectral data support the synthesis of resins.Infrared spectra of the resins were recorded in the range 4000–400 cm^{-1} using KBr discs. A comparison of IR spectra of the DAPF with the other four functionalized resins, shows the absence of νC=O (1665 cm^{-1}) and the presence of νC=N (azomethine) 1608, 1621, 1614, and 1608 cm^{-1}, respectively, for DAPF-ea, DAPF-ap, DAPF-en, and DAPF-pn. IR; DAPF: ν 3400(O—H), 2885(C—H), 1665 (C=O) cm^{-1}. DAPF-ea: ν 3395(O—H), 2887 (C—H), 1608 (C=N) cm^{-1}. DAPF-ap: ν 3320 (O—H), 2726 (C—H), 1621 (C=N) cm^{-1}. DAPF-en: ν 3380 (O—H), 2609 (C—H), 1614 (C=N) cm^{-1}. DAPF-pn: ν 3394 (O—H), 2856 (C—H), 1608 (C=N) cm^{-1} The lower OH stretching frequencies of all the resins (3400–3320 cm^{-1}) are due to hydrogen bonding in polymeric association. Thus the above data support the formation of functionalized polymers.

Thermogravimetric analyses

Thermograms of the functionalized polymers are shown in Figure 2. A mathematical interpretation of thermogravimetric curves enables one to determine kinetic parameters of pyrolysis reactions. Horowitz and Metzer[24] have demonstrated the method of calculation of energy of activation of polymeric substances. The equation used for the calculation of energy of activation (*E*) was,

$$\ln\ln\left(\frac{W_o}{W_t}\right) = \frac{E\theta}{RT_s^2} \qquad (1)$$

where $\theta = T - Ts$; W_o is the initial weight; Wt is the weight at any time t; Ts is the peak temperature; and T is the temperature at particular weight loss. A plot of ln ln $(W_o)/(W_t)$ vs. θ gives an excellent approximation to a straight line. The slope is related to the activation energy. i.e.,

$$\text{Slope} = \frac{E}{RT_s^2} \cdots \qquad (2)$$

Representative plots are shown in Figure 3. The calculated values for the activation energy of decomposition are listed in Table II. The activation energy associated with each stage of decomposition was also evaluated by the well-known Broido method.[25] The
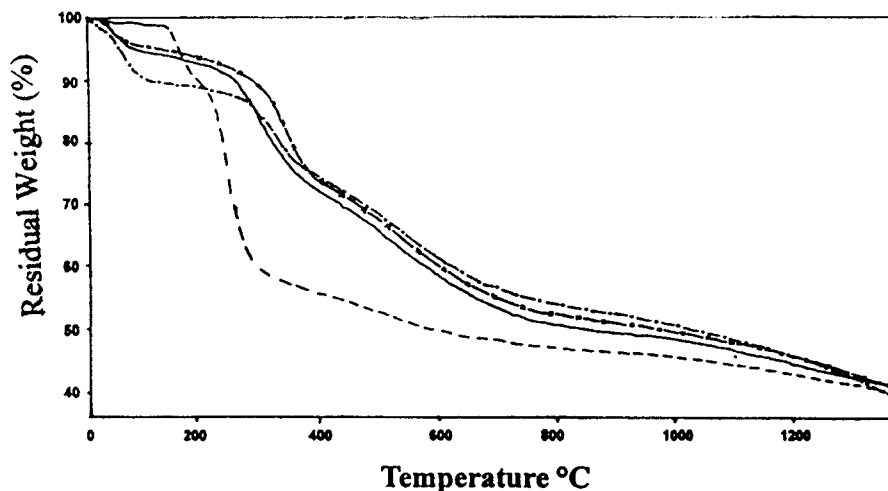
Figure 2 Representative TGA plots of (—) DAPF-ea, (---) DAPF-ap, (-•-) DAPF-en and (-x-) DAPF-pn.

equation used for the calculation of activation energy (E) was,

$$\ln\ln\left(\frac{l}{Y''}\right) = \left(\frac{-E}{R}\right)\frac{1}{T} + \text{Constant}\ldots \quad (3)$$

$$\text{where } Y'' = \frac{W_t - W_\infty}{W_o - W_\infty}$$

that is, Y'' is the fraction of the number of initial molecules not yet decomposed; Wt the weight at any time t; W_∞ the weight at infinite time (= zero); W_o the initial weight. A plot of $\ln \ln (1/Y'')$ vs. $1/T$ gives an excellent approximation to a straight line over a range of $0.999 > Y'' > 0.001$. The slope is related to the activation energy. Representative plots are shown in Figure 4. The calculated values for the activation energy of decomposition are listed in Table II.

Differential thermal analyses

The DTA plots of the polymers are given in Figure 5. The Kissinger[26] method was used for the determina-
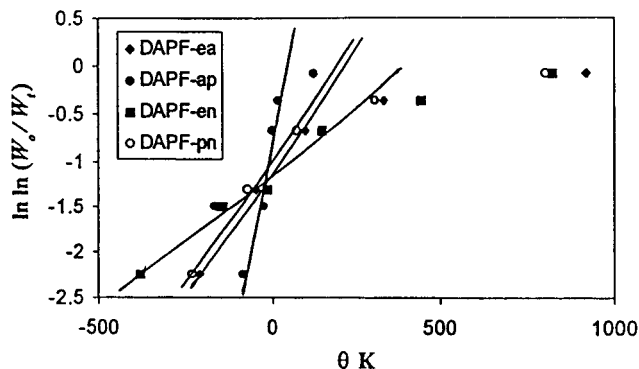

Figure 3 Representative Horowitz and Metzer plots.

tion of activation energy. The equation used for the calculation of activation energy (E) was,

$$\frac{d\left(\ln\dfrac{\phi}{T_m^2}\right)}{d\left(\dfrac{1}{T}\right)} = -\frac{E}{R}\ldots \quad (4)$$

where ϕ is a constant rate of temperature rise; T_m is the temperature at which the peak differential thermal analyses deflection occurs; T is the temperature. The plot of

$$\left(\ln\frac{\phi}{T_m^2}\right)$$

against the reciprocal of the absolute temperature ($1/T$) gives the energy of activation (E) of the decomposition using the equation,

$$\text{Slope} = -\frac{E}{R}\ldots \quad (5)$$

Representative plots are shown in Figure 6. The calculated values for the activation energy of decomposition are 13.86, 9.98, 14.55, and 9.98 kJmol^{-1} for DAPF-ea , DAPF-ap, DAPF-en, and DAPF-pn, respectively. It has been found that all the polymer resins are stable and show maximum peak differential thermal analyses deflection in the temperature range of 350–580°C.

APPLICATIONS

Effect of pH on uptake of metal ion

The effect of pH on metal ion uptake was studied at different pHs by following the recommended proce-

TABLE II
Activation Energy of Decomposition for Various Phenolformaldehyde Supported Chelating Resins

Resin	Peak temperature T_s°C	Decomposition temperature range (°C)	% Weight loss	Method	Activation energy $(kJmol^{-1})$
DAPF-ea	275	100–400	28	HM	15.73
				BR	29.13
	650	400–750	20	HM	15.73
				BR	29.13
	1000	800–1200	6	HM	6.00
				BR	10.40
DAPF-ap	200	100–415	62	HM	31.00
				BR	72.82
	884	415–1200	17	HM	5.30
				BR	7.00
DAPF-en	180	75–240	14	HM	7.11
				BR	18.21
	475	240–667	31	HM	10.84
				BR	29.13
	973	773–1200	17	HM	6.45
				BR	15.61
DAPF-pn	300	105–400	26	HM	16.54
				BR	16.18
	550	400–700	21	HM	14.08
				BR	31.21
	950	700–1200	9	HM	3.20
				BR	16.18

HM Horwitz & Metger
BR Broido

dure. Figure 7 indicates that the uptake of metal ion by resins depends on pH. The overall uptake of metal ions by the resin from pH 2 to pH 10 is in the order Pb(II) > Hg(II) > Cr(IV) > Cd(II). The uptake of Pb(II) and Hg(II) increases with an increase in pH and reaches a plateau value around pH 10. In the case of Cd(II) and Cr(VI), the uptake increases with pH and reaches a plateau value around pH 6 and decreases with an increase in pH. As uptake of metal ions [Pb(II) and Hg(II)] from basic medium is either high or appreciable, a buffer solution of pH 10 is selected for further studies. In the case of Cd(II) and Cr(VI), the uptake was maximum at pH 6. Therefore, a buffer solution of pH 6 is recommended for further studies.
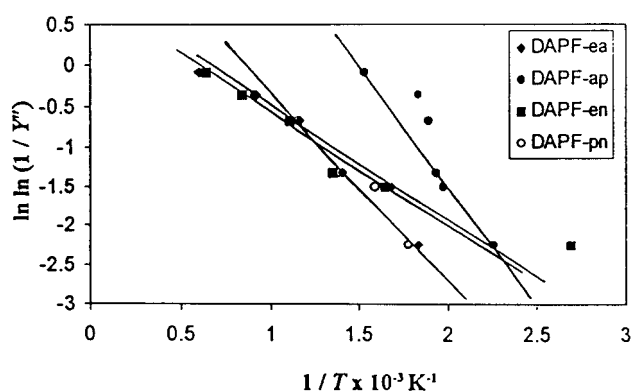

Figure 4 Representative Broido plots.

Effect of time on metal chelation

The effect of time on metal ion uptake was studied at recommended pH by following the procedure described before. From Figure 8 it is evident that 1-h time is sufficient for maximum and constant uptake of the metal ion.

Selectivity studies

The selectivity studies were carried out by following the recommended procedure. In this case, 100 ppm of each metal ion in the solution were allowed to react with the polymer at pH 10. The overall competitive conditions are in good agreement with the results obtained in the noncompetitive conditions. As shown in Figure 9, the metal ion uptake increases from DAPF-ea to DAPF-pn. The high uptake capacity of metal ion by DAPF-pn is probably due to the formation of stable metal chelates. Thus, DAPF-pn is more selective for the removal of Pb(II), Hg(II), Cd(II), and Cr(VI) than the other resins. Thus, the order of selectivity is DAPF-pn > DAPF-en > DAPF-ap > DAPA-ea. The affinity of given polymer for metal ion is in the order Pb(II) > Hg(II) > Cr(VI) > Cd(II).

Effect of initial concentration of metal ions

An important variable in the uptake of heavy metal ions is its (metal ion) concentration. Figure 10 shows
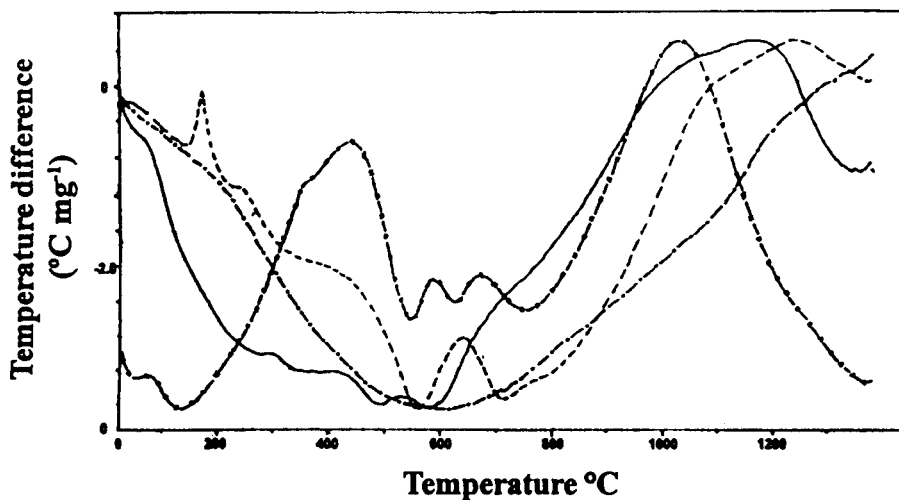
Figure 5 Representative DTA plots of (—) DAPF-ea, (---) DAPF-ap, (-•-) DAPF-en and (-x-) DAPF-pn.

the uptake capacities of the DAPF-ea, DAPF-ap, DAPF-en, and DAPF-pn, for the ions from the single metal aqueous solutions under study. The amount of metal ion uptake was increased with an increase in initial metal ion concentration, and reached a plateau value at higher concentration. The maximum uptake

capacities for DAPF-ea, DAPF-ap, DAPF-en, and DAPF-pn are 10.57, 10.47, 12.45, and 12.87 mg/g of Pb(II); 8.04, 8.42, 8.72, and 11.67 mg/g of Hg(II); 2.24, 2.43, 3.01, and 2.69 mg/g of Cd(II); 3.75, 3.70, 3.69, and 3.53 mg/g of Cr(VI), respectively. The affinity order of
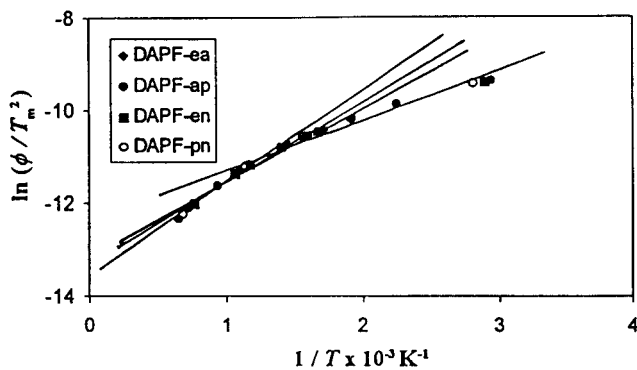
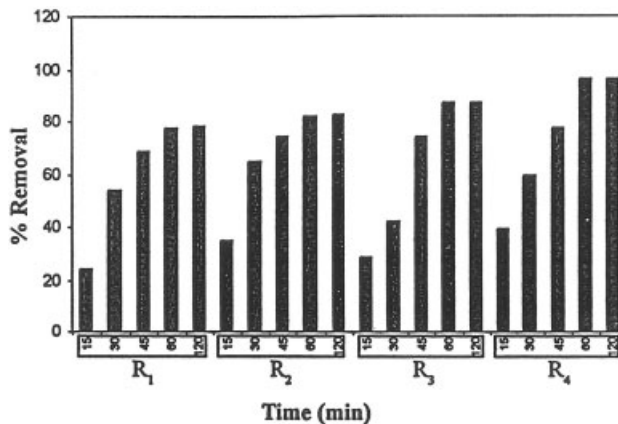

Figure 6 Representative Kissinger plots.

Figure 8 Effect of time on the uptake of Hg(II) by R_1 [DAPF-ea]; R_2 [DAPF-ap]; R_3 [DAPF-en]; R_4[DAPF-pn].
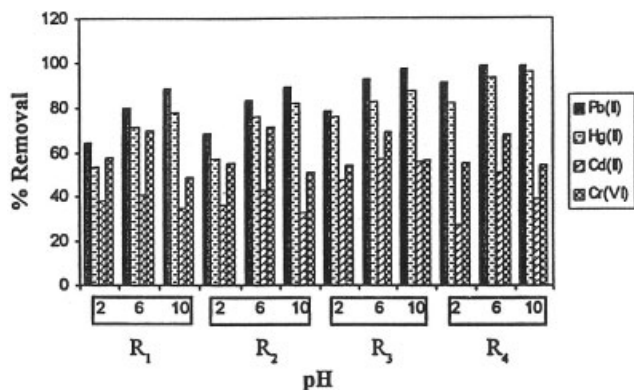

Figure 7 Effect of pH on the uptake of metal ions by R_1 [DAPF-ea]; R_2 [DAPF-ap]; R_3 [DAPF-en]; R_4 [DAPF-pn].
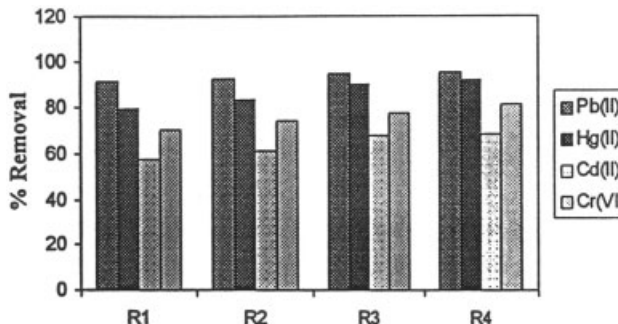

Figure 9 Selectivity on the uptake of metal ions by R_1 [DAPF-ea]; R_2 [DAPF-ap]; R_3 [DAPF-en]; R_4 [DAPF-pn].
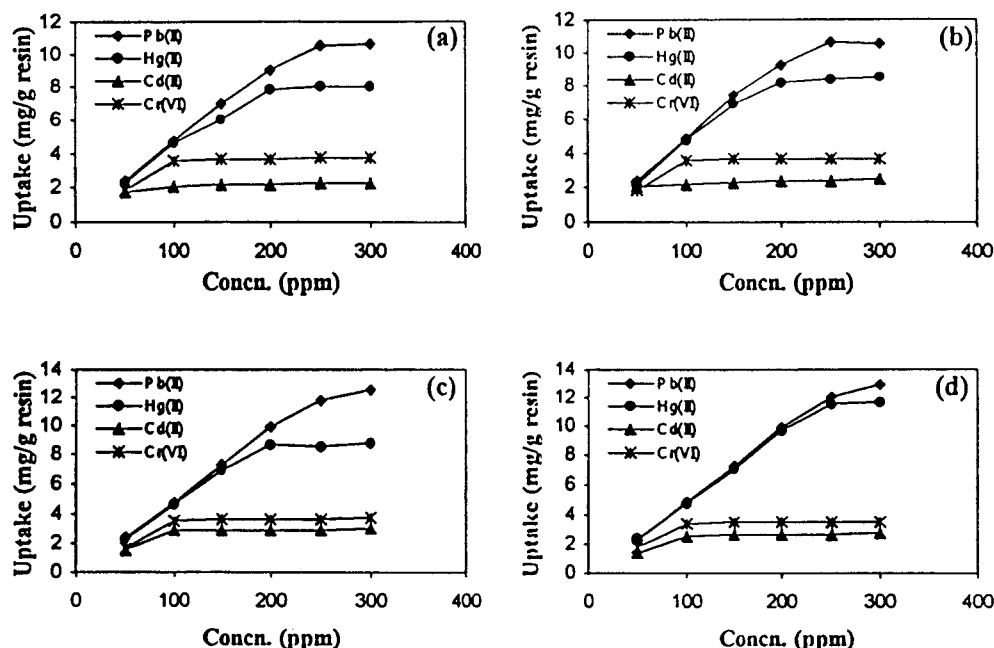
Figure 10 Effect of initial concentration on the uptake of metal ions by (a) [DAPF-ea]; (b) [DAPF-ap]; (c) [DAPF-en]; (d) [DAPF-pn].

the resins is Pb(II) > Hg(II) > Cr(VI) > Cd(II). Different functionalised polymers with wide range uptake capacities for heavy metal ions have been reported. Kimiaki et al.[27] removed 10.3 mg Pb(II)/g resin using a chloromethylated polystyrene containing a —P(OEt)$_2$ group. Denzili et al.[28] showed the uptake of 4.2 mg Cd(II)/g with procion Red MX-3B-immobilized poly (hydroxy-ethylmethacrylate ethylene glycol dimethacrylate). Zhengyu et al.[29] found that the Hg(II) equilibrium uptake capacity of HCHO–thiourea–urea copolymer, HCHO–PhOH–urea copolymer and benzoic acid- modified HCHO– thiourea copolymer was 31.5, 30.2, and 28.8 mg/g of resin, respectively. Chattopadhyay et al.[30] used a chelating resin containing an imidazolylazo group for the removal of Pb(II), Ag(II), and Hg(II). Thus, metal uptake capacities of present polymers are quite comparable to those employed earlier.

The uptake of metal ions by the resin increases with an increase in initial concentration, and reaches a saturation point at higher concentration. This behavior of the polymers was approximately described by Freundlich's equation

$$Y = KC^{1/n}$$

$$\log_{10}Y = \log_{10}K + 1/n\log_{10}C$$

where Y is the grams of metal ion adsorbed per gram of polymer; C is the initial concentration (mol per liter); n and K are empirical constants.

The plot of $\log_{10} Y$ vs. $\log_{10} C$ gave a straight line. The slope is equal to $1/n$ and the intercept equal to $\log_{10} K$. The K and n values for the adsorption of metal ions on various resins are presented in Table III. Thus, the table suggest that the higher the $1/n$ and K values, the maximum will be the adsorption, and vice versa.

Effect of recyclability on adsorption of metal ions

The most important advantage of the functionalized polymer is its reuse after a particular process. The

TABLE III
The Values of Emperical Constants for the Adsorption of Heavy Metal Ions on Various Chelating Resins Obtained from Freundlich's Equation

Resin	1/n				K			
	Pb(II)	Hg(II)	Cd(II)	Cr(VI)	Pb(II)	Hg(II)	Cd(II)	Cr(VI)
DAPF-ea	0.857	0.750	0.182	0.167	3.162	1.259	0.008	0.010
DAPF-ap	0.938	0.900	0.111	0.091	6.310	3.981	0.005	0.007
DAPF-en	1.000	1.000	0.158	0.094	12.589	10.00	0.004	0.006
DAPF-pn	0.900	0.833	0.090	0.091	3.981	2.818	0.005	0.005

TABLE IV
Recyclability of the Resins on the Uptake of Metal Ions at Recommen ded pH from 207.2 ppm of Pb(II), 200.6 ppm of Hg(II), 112.4 ppm of Cd(II), and 52.0 ppm of Cr(VI) Solutions

| Resin | Cycle. No. | Pb(II) | | Hg(II) | | Cd(II) | | Cr(VI) | |
		Metal uptake (ppm)	% Desorption	Metal uptake (ppm)	% Desorption	Metal uptake (ppm)	% Desorption	Metal uptake (ppm)	% Desorption
DAPF-ea	1	182.7	94.9	156.3	98.3	45.6	96.6	45.9	96.2
	2	180.5	96.1	156.2	97.6	45.2	97.2	44.8	97.8
	3	179.4	98.8	154.3	98.2	44.5	96.9	44.2	96.3
	4	178.3	98.2	155.2	96.5	44.1	98.4	43.5	98.4
DAPF-ap	1	185.1	96.7	164.6	95.9	48.5	98.6	45.4	98.2
	2	184.4	97.3	162.3	97.3	46.5	97.8	44.8	97.9
	3	184.1	98.6	161.4	96.8	45.8	97.3	44.2	97.8
	4	183.3	96.4	160.2	98.9	45.3	96.1	43.6	96.3
DAPF-en	1	200.8	94.5	174.6	97.7	64.0	98.7	45.9	98.5
	2	200.2	98.5	174.0	96.9	63.5	97.5	45.2	97.1
	3	198.4	99.4	173.4	98.2	63.1	98.6	43.5	98.7
	4	196.3	96.3	173.2	95.5	62.8	98.4	43.1	98.4
DAPF-pn	1	204.7	97.6	192.6	97.4	57.4	97.3	45.2	97.6
	2	203.4	96.5	190.9	97.3	56.6	96.2	44.4	96.8
	3	202.2	96.8	190.2	96.6	58.1	96.6	44.1	96.2
	4	201.6	98.2	189.4	98.2	55.5	98.4	43.7	98.5

polymer used can be brought into its original state by desorbing the metal ions from metallated resins using 6 M HCl in tetrahydrofuran. The metal free polymers can be reused after neutralization. In acidic medium the metallated polymers are protonated and releases the metal ion into solution. For every cycle the metal ion uptake and % desorption was studied. The data are given in Table IV. The metal ion uptake was found to be almost the same even after four cycles using different polymers.

Industrial applications

The resins have been successfully employed for the removal of heavy metal ions from industrial waste water. The industrial waste water was collected from Karnataka pollution control board, Bangalore. The data are given in Table V.

TABLE V
Removal of Heavy Metal Ions from Industrial Waste Water[a]

| Resin | Heavy metal ion removed[b] | | | |
	Hg(II)	Cd(II)	Cr(VI)	Ni(II)
DAPF-ea	0.290	0.625	1.135	0.410
DAPF-ap	0.310	0.705	1.170	0.180
DAPF-en	0.355	0.810	1.225	0.640
DAPF-pn	0.420	0.780	1.310	0.680

[a] Certified composition of the sample (in ppm) 12.33 Hg; 22.8 Cd; 30.9 Cr; 18.6 Ni.
[b] mg of metal per gram resin.

CONCLUSION

Functionalized polymers have been synthesized by employing a condensation polymerization technique and subsequent modifications. These polymers have been characterized, based on elemental analyses, infrared, and ^{1}H-NMR spectra. Thermal and kinetic data suggest that the resins are highly stable, and may be used for the removal of metal ions at room temperature. The metal uptake efficiency increases with pH and reaches a plateau value around pH 10 [for Pb(II) and Hg(II)]. However, the uptake efficiency reaches a plateau value around pH 6 (for Cd(II) and Cr(VI)) and decreases with an increase in pH. The favorable characteristic of present polymers is the time required for the maximum and constant uptake of metal ion from aqueous media. Just 1-h time is sufficient for the removal of metal ion in the present methods. As observed in Figure 10, the uptake was increased with concentration and reached a plateau value. This is because at higher concentrations no more free sites will be available on chelating polymeric surface either for adsorption or for chelation. The metal ion selectivity of present functionalized polymers is found to be in the order Pb(II) > Hg(II) > Cr(VI) > Cd(II). The metal ion uptake efficiency of the polymers is not altered much even after five cycles. The metal ion uptake efficiency of the polymers are in the order, DAPF-pn > DAPF-en > DAPF-ap > DAPF-ea. Thus, the polymer having propylenediamine moiety (DAPF-pn) is found to be more efficient in the removal of heavy and toxic metal ions.

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