

Synthesis, Characterization, and Metal-Ion Uptake Studies of Chelating Resins Derived from Formaldehyde-Condensed Azodyes of Aniline and 4,4'-Diaminodiphenylmethane Coupled with Phenol/Resorcinol

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ABSTRACT: The diazonium salts of aniline and 4,4'-diaminodiphenylmethane coupled with phenol and resorcinol were condensed with formaldehyde in alkaline media to yield polymeric resins. These polymers were found to readily react with metal ions like Cu^{2+} and UO_2^{2+} , forming polychelates. The azodyes, resins, and polychelates were characterized by several instrumental techniques such as elemental analysis, FTIR, $^1\text{H-NMR}$, GPC, XRD, TG-DTG, and DSC studies. The chelating capacity of the resins toward Cu^{2+} and UO_2^{2+} ions was studied by spectrophotometry. The extent of metal loading of the resins was studied by varying the time of contact, metal-ion concentration, and pH of the reaction medium. The alkali and alkaline earth metal ions had little effect on the metal-ion uptake behavior of the resins. The resin derived from the azodye of 4,4'-diaminodiphenylmethane was found to be more efficient in removing the metal ions from solution than were the resins from aniline. The optimum conditions for effective separation of Cu^{2+} from UO_2^{2+} were determined. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 3128–3141, 2000

Key words: azodyes; polycondensation; metal ion uptake; separation of metal ions

INTRODUCTION

Azo compounds have been widely used as analytical reagents owing to their specific complexing behavior.¹ Mahapatra et al.² studied the poly-metallic complex compounds of multidentate azodye ligands. Saxena et al.³ synthesized a chelating resin by linking Alizarin Red-S with a com-

mercially available styrene-divinylbenzene copolymer, AmberliteXAD-2, through an azo group and used the resin for the preconcentration of Pb^{2+} , Cd^{2+} , Zn^{2+} , and Ni^{2+} . Pramauro et al.⁴ studied the chelating aggregates of a host micelle and a derivative of 1-(2-pyridylazo)-2-naphthol as a suitable material for preconcentration and separation of transition-metal ions. The polystyrene resins functionalized with azobenzyl phosphinic acid ligands were studied by Ueda et al.⁵ The resins were used for the preconcentration, separation, and determination of micro- or milligram quantities of lead, uranium, and copper. Phenol-formaldehyde resins with chelating functions have been extensively studied for their metal-adsorption behavior. A resin synthesized by condensation of phenol-formaldehyde-piperazine was reported to be selective for Cu^{2+} .⁶ Bayer⁷

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studied the Schiff base of glyoxal-*o*-aminophenol and then polymerized it and observed that the resulting polymer had high affinity toward Cu^{2+} , Ni^{+2} , and UO_2^{2+} .

A literature survey reveals that no attempt has been made so far to synthesize chelating resins by condensing azodyes with formaldehyde. The present communication dealt with the synthesis and characterization of formaldehyde-condensed azodye resins of aniline with phenol and resorcinol (AN-PHE-HCHO, AN-RES-HCHO) and 4,4'-diaminodiphenylmethane (DDM) with phenol (DDM-PHE-HCHO) and studied their metal-ion uptake behavior toward Cu^{2+} and UO_2^{2+} . The optimum conditions were determined for an effective separation of Cu^{2+} and UO_2^{2+} .

A broad spectrum of metal ions frequently used for uptake studies such as Cu^{II} , Fe^{III} , Ni^{II} , Co^{II} , Zn^{II} , Pb^{II} , Mo^{VI} , U^{VI} , Mn^{II} , and Cr^{III} , for example, vary considerably in their adsorption characteristics, which is attributed to several factors such as the acidity of the metal ions, the chelating behavior of the resins, and the pH of the reaction medium. The rate at which the metal ions are adsorbed is also often seen to obey Irving-William's order. It was therefore thought pertinent to choose a simple binary mixture, such as Cu^{2+} and UO_2^{2+} , for the present study, the metal ions varying considerably in their reactivity with the resins. In addition, the three resins employed for the purpose are structurally different. Their different adsorption behavior in varying experimental conditions would provide the optimum parameters for the effective separation of the metal ions in the binary mixture.

EXPERIMENTAL

Reagents

The starting materials such as DDM (Merck, Darmstadt, Germany), resorcinol, and the sulfate and nitrate salts of Cu^{2+} and UO_2^{2+} (Merck/BDH, Mumbai, India, AnalaR grade) were used as received. The phenol, aniline, and solvents used for different experiments were distilled prior to use.

Synthesis of the Resins

The azodyes AN-PHE, AN-RES, and DDM-PHE were prepared by coupling the diazonium salts of the amines with phenol/resorcinol following a standard procedure.⁸ The dyes were suspended

over 30 mL of water at 40°C with a few drops of dil NaOH. A formaldehyde solution (37% v/v) was added in a 1 : 2 molar ratio and the mixture was refluxed in an oil bath at 120–130°C for 2–3 h. The insoluble resin was filtered off, washed repeatedly in demineralized water, and dried at 70°C. The dried resin was powdered and suspended over water at pH 3 for 24 h. It was filtered off, washed with a large excess of water, and dried at 70°C.

Synthesis of the Polychelates

To 100 mg of the dried resin (100 mesh, ASTM) suspended over methanol, 10 mL of a metal salt solution in water (0.15M) was added. The mixture was stirred for 2 h at 40°C. The solid was filtered off, washed in distilled water followed by petroleum ether, and dried at 70°C.

Metal-ion Uptake

The resins were treated with aqueous solutions of Cu^{2+} and UO_2^{2+} of known concentration. The pH of the solutions was adjusted to the desired value using either 0.1M HCl or 0.1M NaOH. A suspension of the resin on the metal solution of a known volume and concentration was agitated for a definite time period at 30°C. The resin was filtered off and washed in demineralized water. The filtrate along with the washings was collected and quantitative determination of metal ion was done spectrophotometrically following the neocuproin method for Cu^{2+} and the oxine method for UO_2^{2+} .⁹ The percentage of metal loading was calculated using the following equation:

$$\text{Metal uptake (\%)} = \frac{W_i - W_f}{W_i} \times 100 \quad (1)$$

where W_i is the micrograms of the metal ion in the solution initially present, and W_f , the micrograms of the metal ion left in the solution after adsorption.

Measurements

The intrinsic viscosity of the resins dissolved in tetrahydrofuran (THF) was determined by viscometry using an Ubbelohde suspended level viscometer. The molecular weight of the resins was determined by gel permeation chromatography (Waters) calibrated by narrow standard polystyrene. The elemental analysis was carried out in a Carlo Erba 1108 elemental analyzer. The FTIR

Table I Physical Data

Compound	Color	N %		Solubility in Different Solvents ^a						
		Found	Calcd	H ₂ O	CH ₃ OH	C ₂ H ₅ OH	CHCl ₃	CCl ₄	THF	DMSO
AN-PHE	Brick red	13.96	14.14	—	+	+	+	+	+	+
AN-PHE-HCHO	Brown	11.66	12.5	—	—	±	+	+	+	+
AN-PHE-HCHO-Cu(II)	Gray	3.67	—	—	—	—	+	+	+	+
AN-PHE-HCHO-UO ₂ ²⁺	Red	8.78	—	—	—	—	+	+	+	+
AN-RES	Brick red	13.1	13.08	—	+	+	+	+	+	+
AN-RES-HCHO	Brown	12.17	11.66	—	—	±	+	+	+	+
AN-RES-HCHO-Cu(II)	Gray	1.9	—	—	—	—	+	+	+	+
AN-RES-HCHO-UO ₂ ²⁺	Red	7.66	—	—	—	—	+	+	+	+
DDM-PHE	Brick red	13.73	13.71	—	+	+	+	+	+	+
DDM-PHE-HCHO	Dark brown	12.19	12.15	—	—	—	—	—	—	±
DDM-PHE-HCHO-Cu(II)	Gray	6.58	6.54	—	—	—	—	—	—	—
DDM-PHE-HCHO-UO ₂ ²⁺	Gray	6.67	6.25	—	—	—	—	—	—	—

^a (+) soluble; (±) partially soluble; (—) insoluble.

spectra were recorded in a Bruker IFS 66V spectrophotometer in the range 4000–400 cm⁻¹ in the KBr phase. The ¹H-NMR spectra were run using deuterated dimethyl sulfoxide (DMSO-*d*₆) as the solvent in a 300-MHz FT NMR (Bruker DRX-300) instrument. The TG-DTG (DuPont 951) and DSC (DuPont 9900) scans of the materials were run up to 600/700°C at a heating rate of 10°C/min in a nitrogen atmosphere. The wide-angle X-ray diffractograms (2θ range 4–35°, scanning rate 0.05°/1.25 min) of the resins and the polychelates were obtained from a PW 1820 diffractometer. The estimation of the metal-ion concentration in dilute aqueous solutions was made using a Systronics digital spectrophotometer.

RESULTS AND DISCUSSION

Solubility, Intrinsic Viscosity, and Molecular Weight

The freshly prepared powdered resin (5 mg) was suspended over 5 mL of the chosen solvent and the solubility was checked after 24 h. It was found that the resins AN-PHE-HCHO and AN-RES-HCHO were insoluble in water and methanol, partially soluble in ethanol, but fairly soluble in CHCl₃, CCl₄, THF, dimethylformamide (DMF), and DMSO (Table I). The corresponding Cu²⁺ and UO₂²⁺ polychelates were found to be insoluble in water, methanol, and ethanol and soluble in other solvents. The resin DDM-PHE-HCHO was soluble in DMSO and partially soluble in other sol-

vents and insoluble in water. The intrinsic viscosity of the resins determined from the Huggins plot of log[η]_{sp}/C versus C, where [η]_{sp} is the specific viscosity, and C, the concentration of the resin solution in DMSO in g/dL. The intrinsic viscosity of the resins, [η]_{int}, was found to be low (AN-PHE-HCHO, 0.112 dL/g; AN-RES-HCHO, 0.06 dL/g). Several authors have made a similar observation.¹⁰ The GPC data providing average molecular weights and polydispersity (AN-PHE-HCHO: *M*_n = 197, *M*_w = 2217, *M*_z = 5660, and *M*_{z+1} = 10149, polydispersity = 11.23; AN-RES-HCHO: *M*_n = 237, *M*_w = 1930, *M*_z = 3530, and *M*_{z+1} = 4912, polydispersity = 8.15) indicated a broad molecular weight distribution, the resins varying in their degree of condensation and crosslinking. The resin DDM-PHE-HCHO was not completely soluble in THF and, hence, its molecular weight could not be determined.

FTIR Spectra

The FTIR spectra of the azodye DDM-PHE, its resin, and Cu²⁺ and UO₂²⁺ polychelate of the resin are presented in Figure 1. The Ph—O stretch for the azodye at 1268 cm⁻¹ was registered at 1239 cm⁻¹ in the resin. On complexation with Cu²⁺, this absorption further shifted to 1226 cm⁻¹. The N=N and the C=C ring vibrations in the polychelate DDM-PHE-HCHO-Cu²⁺ did not shift from their respective positions in the resin. A number of additional peaks were observed at

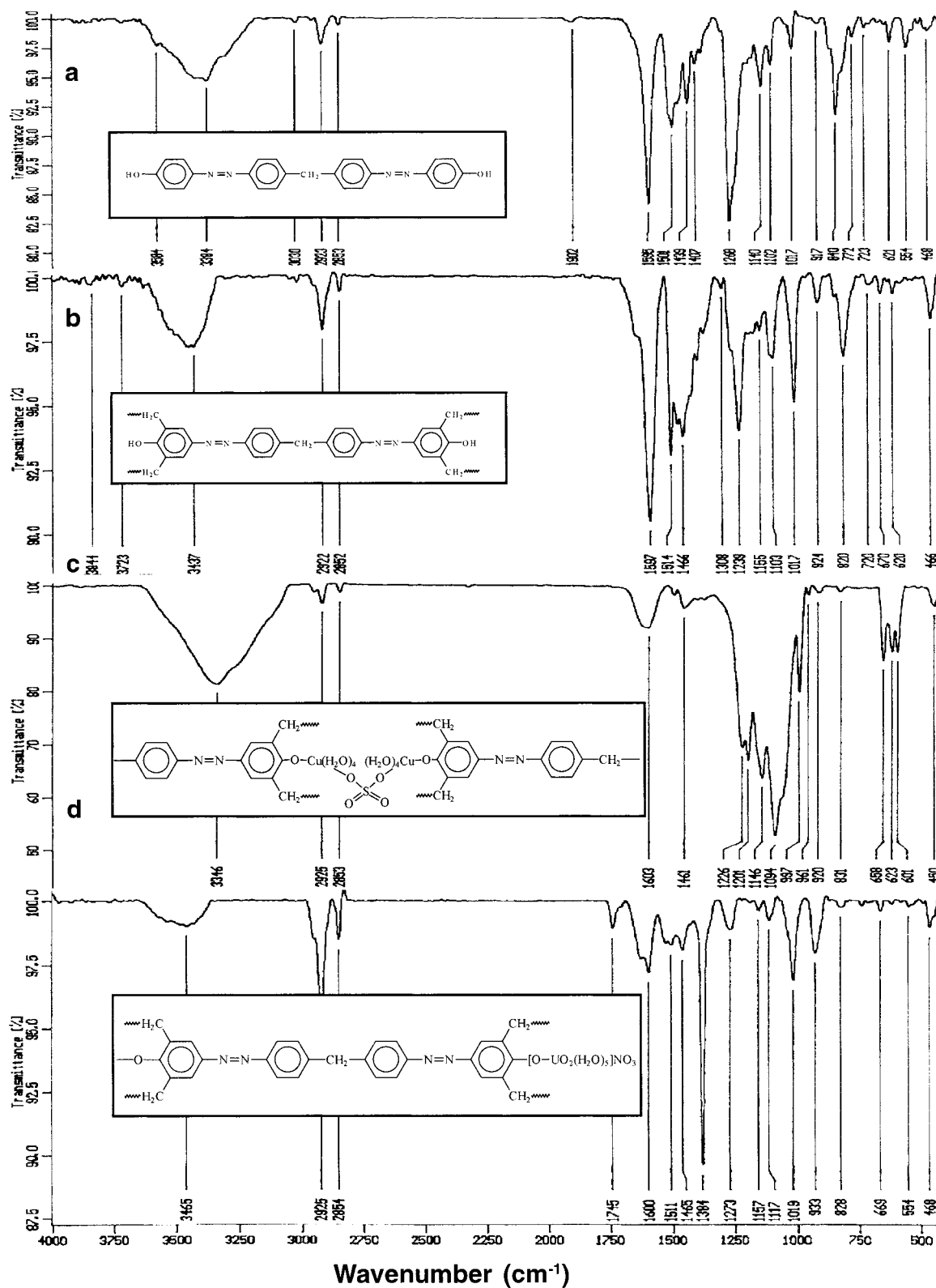


Figure 1 FTIR spectra of (a) DDM-PHE, (b) DDM-PHE-HCHO, (c) DDM-PHE-HCHO- Cu^{2+} , and (d) DDM-PHE-HCHO- UO_2^{2+} .

1146, 1094, 997, and 658 cm^{-1} . Absorption in these positions is characteristic of a bridging sulfato group. Nakamoto et al.¹¹ studied the bridged sulfato complexes of Co(II) and reported similar observations. The SO_4^{2-} ion (from CuSO_4) used to synthesize the polychelate functions as a bridging group between the resin molecules. Absorptions at 658 , 623 , and 601 cm^{-1} were assigned to the $\text{Cu}^{2+}\text{—O}$ stretch. Several workers have made extensive band assignments for metal chelate compounds and have observed metal–ligand stretching vibrations in this range.¹²

Complexation with UO_2^{2+} did not shift the $\text{N}=\text{N}$ and the $\text{C}=\text{C}$ ring vibrations and Ph—O absorption was not observed. A sharp absorption at 1384 cm^{-1} was assigned to a free NO_3^- , the nitrate group [from $\text{UO}_2(\text{NO}_3)_2$] used to synthesize the polychelate remaining in the complex matrix as a counteranion.¹¹ The $\text{UO}_2^{2+}\text{—O}$ stretch was not observed.

For the resin AN–PHE–HCHO, the formation of Cu^{2+} polychelate led to a shift of Ph—O vibrations from 1240 cm^{-1} in the resin to 1233 cm^{-1} in the polychelate. Coordination of the phenolic oxygen to the metal ion also resulted in an aromatic $\text{C}=\text{C}$ stretch shifting from 1660 , 1608 cm^{-1} in the resin to 1648 , 1589 cm^{-1} in the polychelate.^{10,13,14} Appearance of a new absorption at 614 cm^{-1} was ascribed to the $\text{Cu}^{2+}\text{—O}$ stretching vibration. The $\text{UO}_2^{2+}\text{—O}$ absorption was not registered. In the case of AN–RES–HCHO, the M—O bond for the Cu^{2+} complex appeared at 665 , 649 , and 615 cm^{-1} , and for the UO_2^{2+} complex, at 632 cm^{-1} . For both AN–PHE–HCHO and AN–RES–HCHO, Cu^{2+} polychelates registered sulfate groups as bridging functions, and UO_2^{2+} polychelates had nitrate as counteranions, as was seen in the case of the DDM–PHE–HCHO resin.

$^1\text{H-NMR}$ Spectra

The $^1\text{H-NMR}$ (300 MHz) spectra of the azodyes and their corresponding resins are presented in Figure 2. The azo dye AN–PHE registered the aromatic protons in the range $6.114\text{--}7.816\text{ ppm}$. Two doublets, one upfield (6.96 , 6.931 , $J = 8.4\text{ Hz}$) and the other downfield (7.788 , 7.816 ppm , $J = 8.4\text{ Hz}$) were observed. The area of the doublet appearing downfield was twice that of the one appearing upfield. The upfield doublet was assigned to the two protons *ortho* to the phenolic —OH group. The downfield doublet was assigned to the four protons *ortho* to $\text{N}=\text{N}$. Such a well-resolved spectral pattern of the azo dye was lost

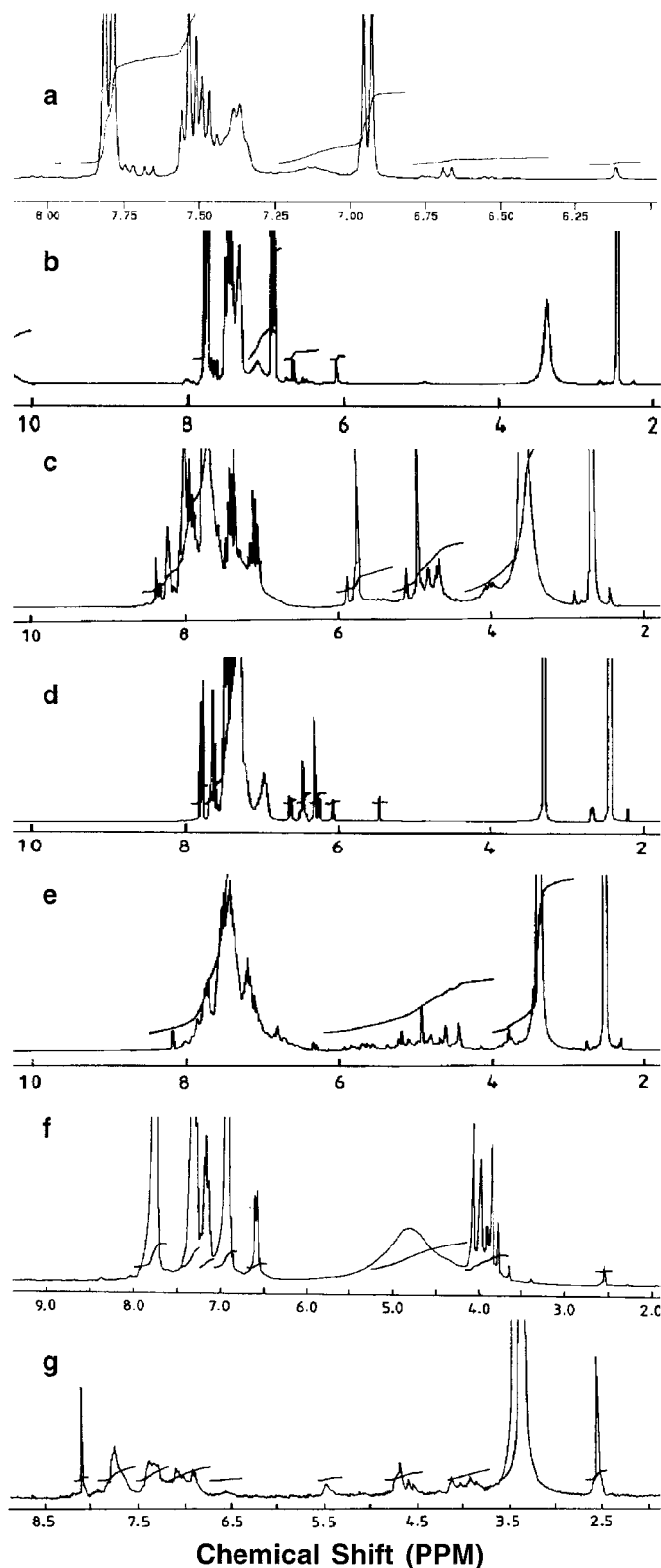


Figure 2 $^1\text{H-NMR}$ spectra of (a) AN–PHE (aromatic protons), (b) AN–PHE, (c) AN–PHE–HCHO, (d) AN–RES, (e) AN–RES–HCHO, (f) DDM–PHE, and (g) DDM–PHE–HCHO.

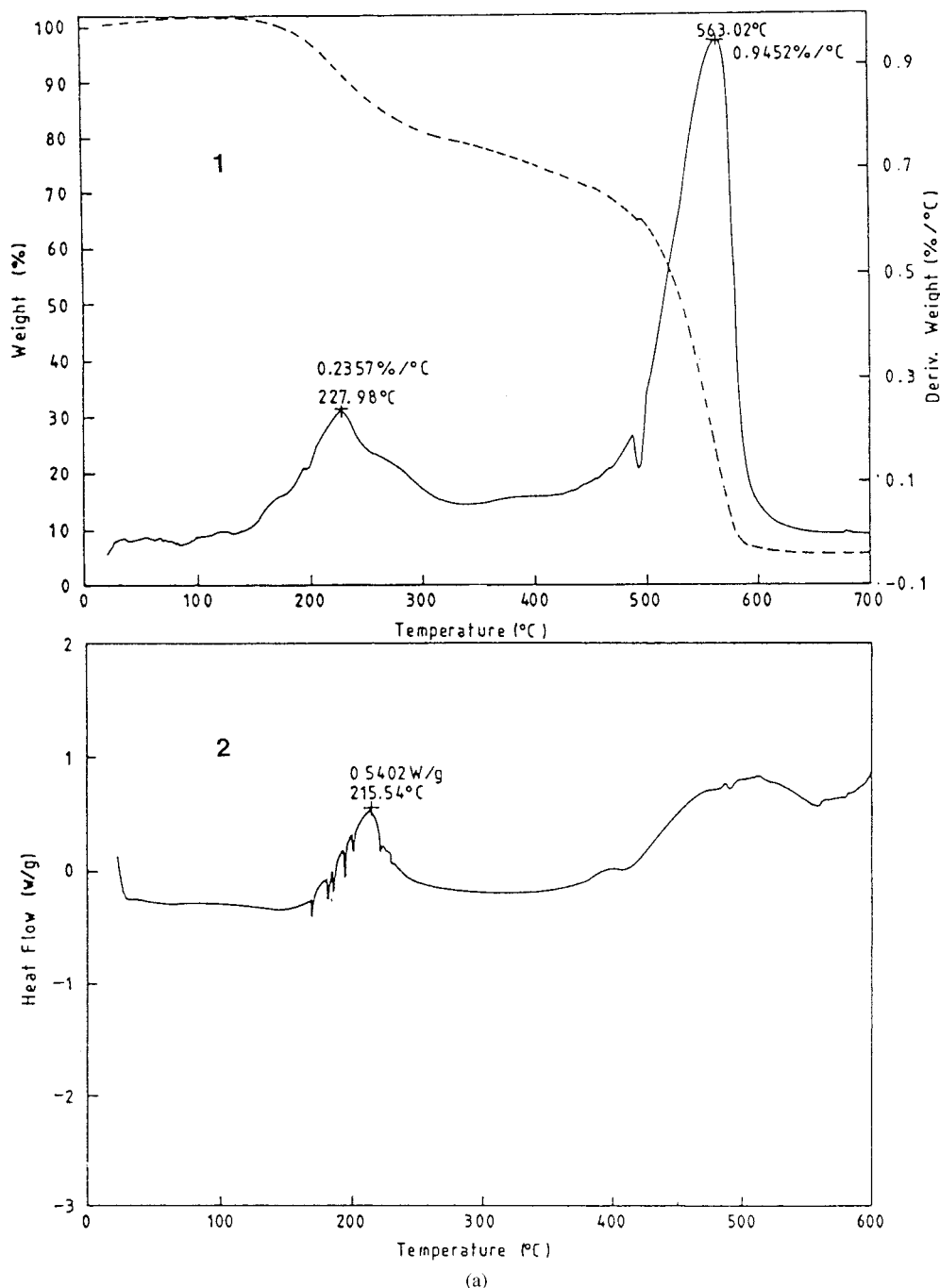


Figure 3 (a) (1) TG-DTG and (2) DSC traces of AN-PHE-HCHO. (b) (1) TG-DTG and (2) DSC traces of AN-PHE-HCHO-UO₂²⁺.

upon condensation with HCHO and the aromatic protons appeared as a complex set of multiplets. Evidence for polycondensation was demonstrated by the peaks in the range 4.49–4.95 ppm, which was assigned to the —CH₂— group appearing as bridging functions.¹⁵

For the AN-RES-HCHO and DDM-PHE-HCHO resins, the observations were similar. The

aromatic protons appeared as a complex multiplet and additional peaks appeared in the range 4.5–5 ppm. The DDM moiety itself in DDM-PHE had a methylene group, which was seen in the range 3.63–4.06 ppm. In the resin DDM-PHE-HCHO, additional peaks in the region 4.5–4.7 ppm were ascribed to bridging methylene groups generated upon polycondensation.

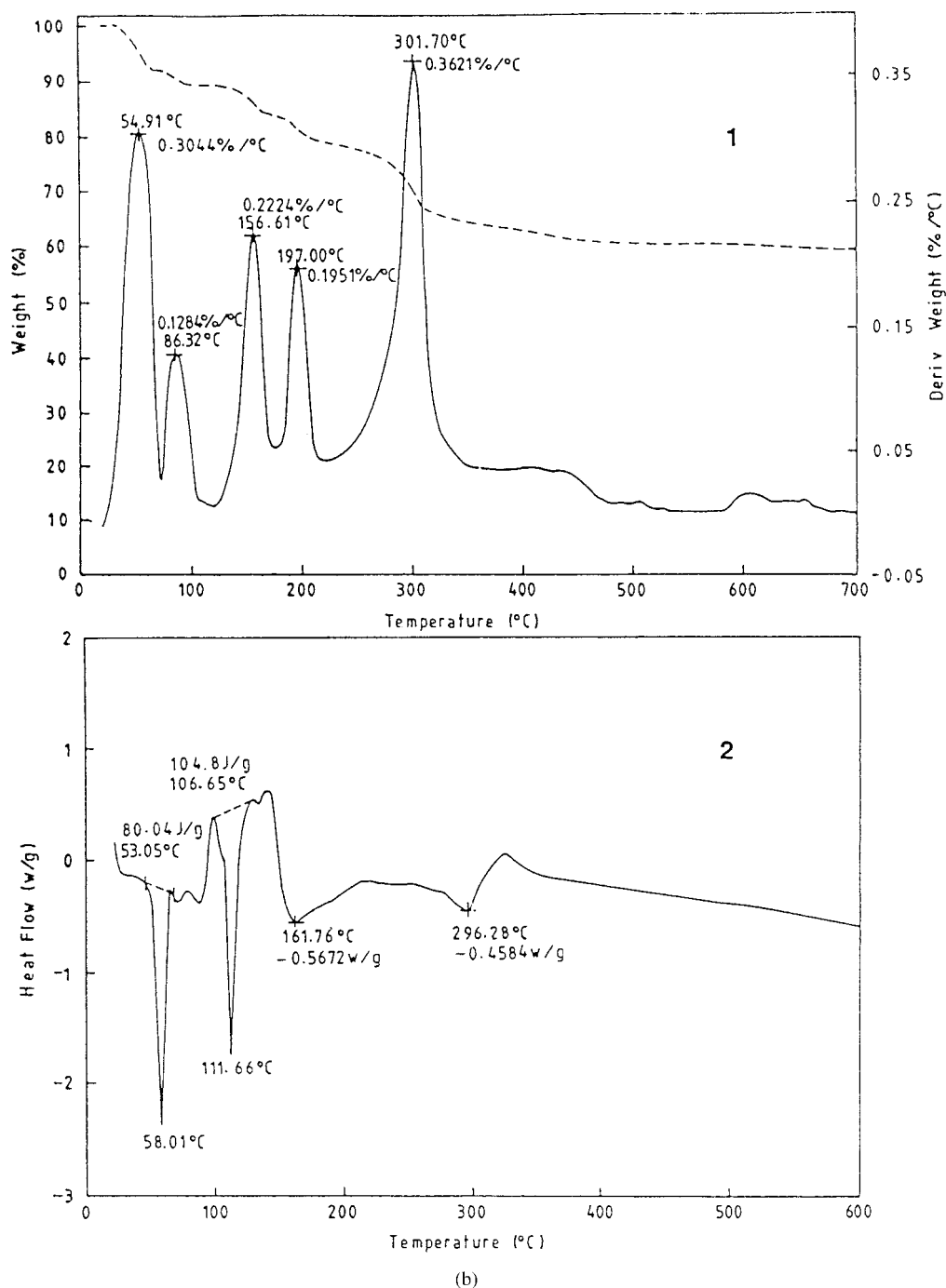


Figure 3 (Continued from the previous page)

TGA and DSC Studies

The TGA-DTG and DSC traces of the resins and the UO_2^{2+} polychelates showed complementary features (Fig. 3). The resin AN-PHE-HCHO did not lose weight until 170°C, and until 200°C, the weight loss was only 2.65%. Beyond 200°C, the

resin lost weight in two distinct stages, the rate of weight loss in the second decomposition stage (470–590°C, 0.9452%/°C at 563.02°C) being much faster than in the first (190–290°C, 0.2357%/°C at 227.98°C). The DSC scan of this resin registered an exotherm in the range 190–290°C with a max-

Table II TG Data

Sample	% Weight Loss in the Temperature Range (°C)				Y_c (%) ^a
	Up to 130	130–200	200–400	400–700	
AN-PHE-HCHO	0.01	2.65	22.73	68.994	5.616
AN-PHE-HCHO- UO_2^{2+}	11.15	8.22	18.22	3.19	59.22
AN-RES-HCHO	0.01	12.71	28.21	54.09	4.978
AN-RES-HCHO- UO_2^{2+}	4.8	3.85	41.26	9.29	40.8

^a Char yield at 700°C.

imum at 215.54°C. Hence, this exotherm was ascribed to thermal curing manifested by loss of H_2O molecules. Curing is known to be associated with phenol-formaldehyde-type resins.¹⁶ The resin did not register a glass transition or a melting temperature.

The polychelate AN-PHE-HCHO- UO_2^{2+} lost weight in a number of steps. It lost 8.26% within 70°C and 11.2% in the range 70–200°C. This was ascribed to desorption of methanol, the solvent medium for the polychelate synthesis, and coordinated or lattice water, respectively. These losses were also exhibited in the form of two endotherms appearing within 150°C (58.01°C, ΔH 80.04 J/g; 111.66°C, ΔH 104.8 J/g). The increase

in crystallinity of the polychelate over that of the resin was manifested by a well-defined melting temperature of the polychelate at 161.76°C. The char yield of the polychelate was 59.22% at 700°C as against 5.616% in case of the resin ascribed mostly to metal oxides (Table II). The AN-RES-HCHO resin and its polychelate AN-RES-HCHO- UO_2^{2+} showed nearly identical features.

It could be seen that the polychelates began to lose weight much before their corresponding resins did, which indicated that the incorporation of the metal ion into the resin matrix led to a decrease in thermal stability, contrary to the observation of other workers.¹⁷ The easy loss of poorly held solvent molecules bonded to polar functions

Table III Kinetic Parameters

Sample	Temperature Range (°C)	T_{\max} (K)	Methods ^a	E (kCal)	A (s^{-1})	ΔS ($\text{cal K}^{-1} \text{mol}^{-1}$)
AN-PHE-HCHO	130–610	—	CR	23.243	2.9×10^5	–35.452
	150–280	500.98	VK	26.511	3.3×10^9	–16.012
	150–280	500.98	BR	25.985	1.9×10^9	–17.103
	470–610	836.02	VK	11.78	1.55	–59.707
	470–610	836.02	BR	12.746	2.64	–58.654
AN-PHE-HCHO- UO_2^{2+}	130–610	—	CR	5.904	11.7	–54.941
	80–210	327.19	VK	0.898	1.7×10^{-3}	–71.341
	80–210	327.19	BR	1.893	9.4×10^{-3}	–67.979
	220–350	574.7	VK	2.039	4.05×10^{-3}	–70.784
	220–350	574.7	BR	2.991	8.8×10^{-3}	–69.238
AN-RES-HCHO	130–610	—	CR	11.373	7.27×10^2	–47.465
	130–260	441.62	VK	25.844	7.9×10^9	–14.008
	130–260	441.62	BR	27.815	8.5×10^{10}	–9.302
	490–620	826.02	VK	11.998	2.86	–58.509
	490–620	826.02	BR	11.561	1.63	–59.589
AN-RES-HCHO- UO_2^{2+}	130–610	—	CR	13.758	9.23×10^2	–46.527
	330–470	653.82	VK	3.014	7.45×10^{-3}	–69.829
	330–470	653.82	BR	4.314	2×10^{-2}	–67.822

^a CR: Coats-Redfern; VK: Van Krevelen; BR: Broido.

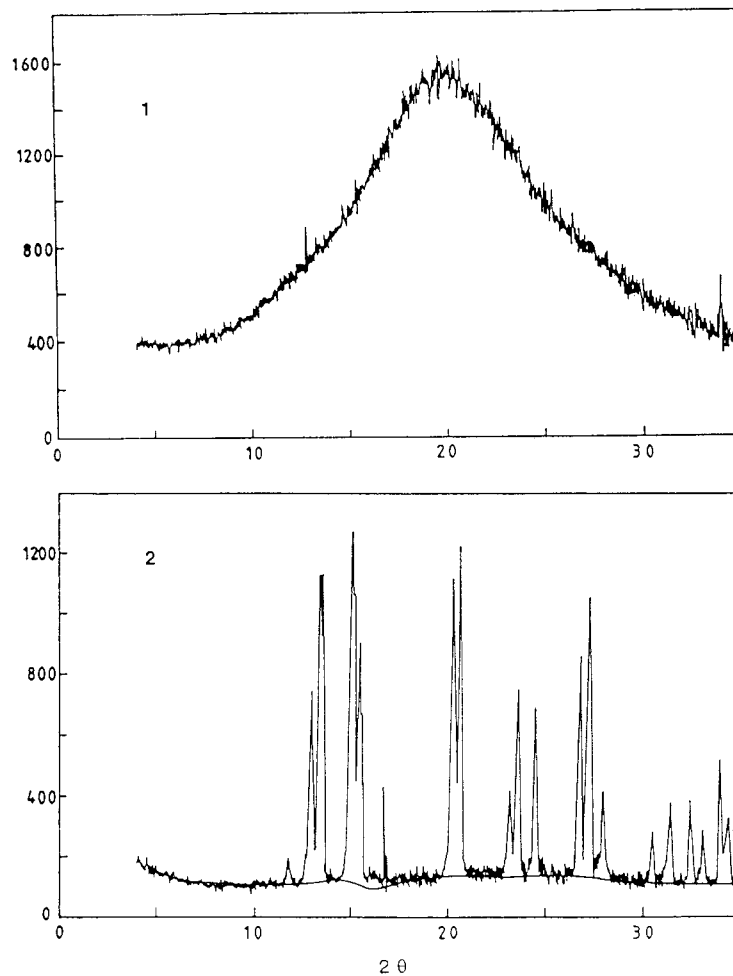


Figure 4 XRD of (1) AN-PHE-HCHO and (2) AN-PHE-HCHO- UO_2^{2+} .

Table IV Effect of Contact Time

Resin	M^{n+}	$[M^{n+}]$ ($\mu\text{g}/10\text{ mL}$)	Metal Ion Adsorbed in μg per 100 mg of Resin at Different Time Intervals (h) ^a				
			0.167	0.5	1	6	24
AN-PHE-HCHO	Cu(II)	200	50	52.5	62.5	75	170
AN-RES-HCHO	Cu(II)	200	58.4	61.3	81	120	175
DDM-PHE-HCHO	Cu(II)	200	120	200	200	200	200
DDM-PHE-HCHO	Cu(II)	2000	490	537	658	1184.6	1717.6
AN-PHE-HCHO	UO_2^{2+}	200	35	45	47.5	51.6	75
AN-RES-HCHO	UO_2^{2+}	200	40.3	50.9	55.8	59	80.62
DDM-PHE-HCHO	UO_2^{2+}	200	35.3	56.8	78.3	122.5	151.2
DDM-PHE-HCHO	UO_2^{2+}	2000	102	216.2	435	510	638

^a Resin quantity: 100 mg; sorbent size: 100 mesh; temperature 30°C; pH: natural.

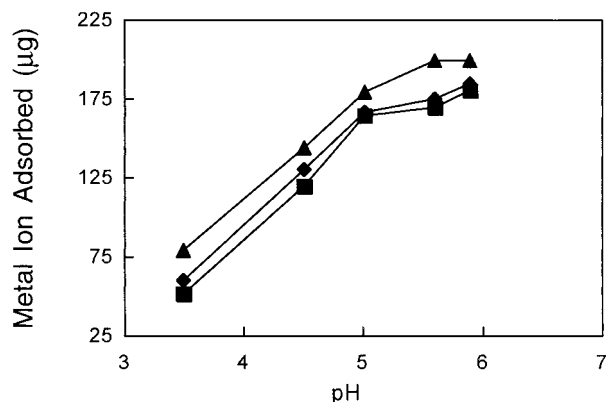


Figure 5 Effect of pH on the adsorption of Cu(II) by (■) AN-PHE-HCHO, (◆) AN-RES-HCHO, and (▲) DDM-PHE-HCHO. Resin quantity: 100 mg; size: 100 mesh; [Cu(II)]: $20 \mu\text{g mL}^{-1}$; temperature: 30°C ; contact time: 24 h.

in the polymer matrix and/or anchored to the metal ion is ascribed to decreased thermal stability. The metal ion in the polychelate was also stated to catalyze the thermal decomposition of the resin network.¹⁸

Evaluation of Kinetic Parameters

To ascertain the relative thermal stability of the resins and the polychelates, kinetic parameters such as activation energy, frequency factor, and entropy changes associated with the thermal decomposition were evaluated by using several models such as Coats-Redfern, Van Krevelen, and Broido, fitting in different mechanisms into each model.¹⁹ The results are furnished in Table

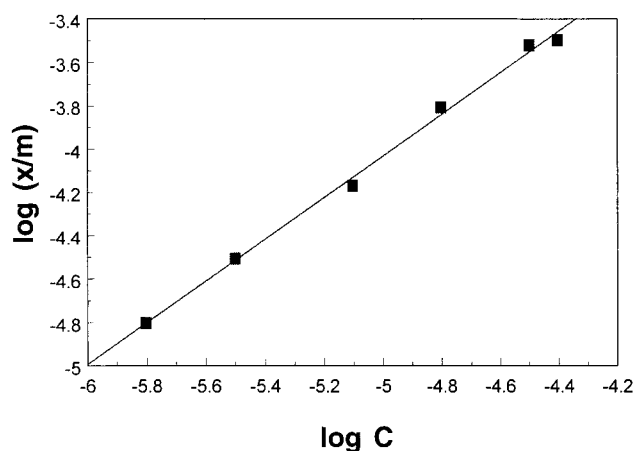


Figure 7 Determination of k_{ad} and n from Freundlich adsorption isotherm for adsorption of Cu(II) by DDM-PHE-HCHO.

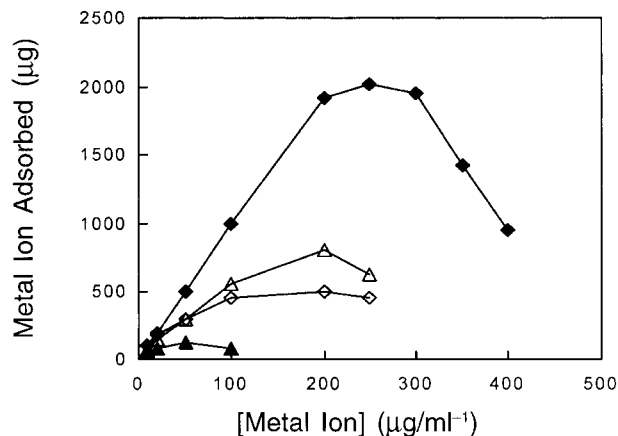


Figure 6 Effect of metal-ion concentration: Metal ion adsorbed (μg) per 100 mg of resin at varying metal-ion concentration. Resin: AN-PHE-HCHO, (◇) Cu(II), (▲) UO_2^{2+} ; DDM-PHE-HCHO, (◆) Cu(II), (△) UO_2^{2+} .

III. In case of the polychelates, activation energies for thermal decompositions are much lower than are those of the corresponding resins. Hence, it is concluded that the polychelates are less stable than are the resins.

XRD Study

The XRD patterns of the resin AN-PHE-HCHO and the polychelate AN-PHE-HCHO- UO_2^{2+} are presented in Figure 4. The resin exhibited no peaks in the 2θ range of 4 – 35° . The polychelate exhibited one strong peak at 15° and a number of additional reflection planes of medium intensity at 13.47 , 15.49 , 20.21 , and 27.188° . This was as-

Regression Output:

Constant ($\log k_{\text{ad}}$)	0.7769
Std Err of Y Est	0.0362
R Squared	0.9963
No. of Observations	6
Degrees of Freedom	4
X Coefficient(s)(1/n)	0.9616
Std Err of Coef.	0.0291

Table V Effect of Resin Quantity

Resin	[M ⁿ⁺] (μg per 10 mL)	Resin Quantity (mg)	μgm of Metal Ion Adsorbed ^a	
			Cu(II)	UO ₂ ²⁺
AN-PHE-HCHO	200	50	120	50
		100	180.5	81.8
		200	200	102
		400	200	115
		500	200	125
AN-RES-HCHO	200	50	135	57
		100	184.9	85.6
		200	200	111.6
		400	200	122.4
		500	200	137.8
DDM-PHE-HCHO	2000	50	1400	377
		100	1916.6	638
		200	2000	1016.6
		400	2000	1190
		500	2000	1232

^a Sorbent size: 100 mesh; temperature 30°C; contact time: 24 h; pH: 4.9 for UO₂²⁺, 5.89 for [Cu(II)] of 20 $\mu\text{g mL}^{-1}$, and 5.3 for [Cu(II)] of 200 $\mu\text{g mL}^{-1}$.

cribed to a significant increase in the crystallinity of the resin consequent upon coordination to the metal ion.²⁰

Metal-ion Uptake Studies

Effect of Contact Time

The Cu⁺² and UO₂²⁺ solutions (10 mL, 20 $\mu\text{g mL}^{-1}$) were treated with the resins (100 mg, 100

mesh) at the natural pH of the salt solutions. The time of contact was varied between 10 min and 3 days. The results are furnished in Table IV. The equilibrium time for the adsorption of the Cu⁺² exceeded 6 h for the AN-PHE-HCHO and AN-RES-HCHO resins, whereas for the resin DDM-PHE-HCHO, the equilibrium was attained within 30 min. The adsorption of UO₂²⁺ by DDM-PHE-HCHO was much slower than was that of Cu⁺². Nearly 100% of the Cu⁺² ion was removed within 30 min, whereas after 24 h of contact time, 75.6% UO₂²⁺ could be adsorbed. When the initial concentration of the metal ions was increased to 200 $\mu\text{g mL}^{-1}$, the rate of adsorption was slowed considerably. After 24 h of contact time, a maximum of 85% Cu⁺² and 30% of UO₂²⁺ could be loaded onto the resin. Several authors^{21,22} noted higher adsorption for Cu⁺² over other metal ions. It is known that the insoluble chelating resins take up transition-metal ions in high yields from aqueous media, but they often adsorb metal ions very slowly due to the lower activity of the ligands placed inside the resin. The metal complexing capacity of the resins depends not only on the nature of the ligand groups but also their accessibility toward the metal ions. Steric hindrance by the resin matrix and its hydrophobic nature is known to limit the chelating reaction.²³

Effect of pH

The effect of the pH of the metal-ion solution on the adsorption behavior of the resins was investigated (Fig. 5) in the pH range 3.42–5.89 for Cu⁺² and 2.67–4.9 for UO₂²⁺ at a contact time of

Table VI Effect of Alkali and Alkaline Earth Metal Ions

Resin	[Cu(II)] ($\mu\text{g mL}^{-1}$)	Added Salt	% Metal-ion Uptake at Different Concentrations of the Added Salt ($\mu\text{g mL}^{-1}$) ^a					
			0	20	50	100	200	500
AN-PHE-HCHO	20	Na ⁺	90.25	91	88.16	87.11	—	—
		K ⁺	90.25	90.66	91.5	91	—	—
		Mg ²⁺	90.25	90.5	89.25	90.2	—	—
AN-RES-HCHO	20	Na ⁺	92.45	92.83	91.21	91.15	—	—
		K ⁺	92.45	92.35	89.15	89.2	—	—
		Mg ²⁺	92.45	92.8	90.52	90.13	—	—
DDM-PHE-HCHO	200	Na ⁺	95.83	95.2	94.8	93.5	90.5	89.45
		K ⁺	95.83	95.5	95.6	94.45	89.31	89.9
		Mg ²⁺	95.83	95.7	94.9	94.5	87.8	85.6

^a Common anion: SO₄²⁻; sorbent size: 100 mesh; temperature: 30°C; contact time: 24 h; pH: natural.

Table VII Separation of Cu(II) from UO_2^{2+} with Increasing UO_2^{2+} Concentration

Resin	[Cu(II)] ($\mu\text{g mL}^{-1}$)	[UO_2^{2+}] ($\mu\text{g mL}^{-1}$)	Metal-ion Uptake (%) ^a	
			Cu(II)	UO_2^{2+}
AN-PHE-HCHO	20	5	60.16	0
	20	10	60.66	5
	20	20	60.5	15.5
	20	40	60.25	20.48
AN-RES-HCHO	20	5	65.31	1.57
	20	10	65.2	7.5
	20	20	65.21	17.25
	20	40	65.3	25.9
DDM-PHE-HCHO	200	50	68.89	0
	200	100	68.53	3.95
	200	200	69.89	8.22
	200	400	67.57	13

^a Resin quantity: 100 mg; sorbent size: 100 mesh; pH: 4.5; temperature: 30°C; contact time: 24 h.

24 h and at 30°C. Further increase in pH resulted in the precipitation of the metal ions as hydroxides. The AN-PHE-HCHO and AN-RES-HCHO resins were able to remove over 90% of Cu^{+2} from the salt solution (20 $\mu\text{g mL}^{-1}$) at an optimum pH of 5.89, whereas 40% of UO_2^{2+} could be removed at the optimum pH of 4.9. The DDM-PHE-HCHO

resin, on the other hand, removed almost the entire amount of Cu^{+2} at pH 5.89. Increasing the metal-ion concentration sharply decreased the rate of adsorption of metal ions by AN-PHE-HCHO and AN-RES-HCHO. The DDM-PHE-HCHO resin, however, could remove nearly 96% of Cu^{+2} at pH 5.89 even when the metal-ion concentration was increased 10-fold (200 $\mu\text{g mL}^{-1}$). Dev and Rao²⁴ observed that in the case of Cu^{+2} the increase in pH resulted in an increase in metal-ion uptake by the resin. Rivas et al.²⁵ observed a maximum capacity for Cu^{+2} and UO_2^{2+} at pH 4 and 2, respectively.

Effect of Metal-ion Concentration

The effect of the variation of the metal-ion concentration on the Cu^{+2} - and UO_2^{2+} -ion uptake behavior of the resin was studied in the range 10–400 $\mu\text{g mL}^{-1}$ (Fig. 6). For the AN-PHE-HCHO and AN-RES-HCHO resins, it was observed that with increase in the metal-ion concentration, the quantity of the metal ion adsorbed increased steadily until 200 $\mu\text{g mL}^{-1}$ and, thereafter, a decreasing trend was noticed. The resin DDM-PHE-HCHO was effective up to a metal-ion concentration of 250 $\mu\text{g mL}^{-1}$, beyond which the adsorption efficiency of the resin decreased.

Table VIII Effect of pH on the Separation of Cu(II) from UO_2^{2+}

Resin	pH	Cu(II) ^a			UO_2^{2+} ^a		
		[Cu(II)] ($\mu\text{g mL}^{-1}$)	Uptake (%)	K_d ^b (mL g^{-1})	[UO_2^{2+}] ($\mu\text{g mL}^{-1}$)	Uptake (%)	K_d (mL g^{-1})
AN-PHE-HCHO	2.6	20	10.5	11.73	20	0	0
	3.03	20	11.25	12.67	20	0	0
	3.53	20	26.57	36.18	20	0	0
	4.5	20	60.5	153.16	20	15.5	18.34
	4.9	20	63	170.27	20	16.2	19.33
AN-RES-HCHO	2.6	20	13.7	15.87	20	0	0
	3.03	20	15.3	18.06	20	0	0
	3.53	20	30.8	44.5	20	0	0
	4.5	20	65.21	187.43	20	17.25	20.84
	4.9	20	67.52	207.88	20	17.3	20.91
DDM-PHE-HCHO	2.6	200	12.85	14.74	200	0	0
	3.03	200	22.53	29.08	200	0	0
	3.53	200	54.8	121.23	200	0	0
	4.5	200	69.89	232.11	200	8.22	8.95
	4.9	200	85.98	613.26	200	10.81	12.12

^a Resin quantity: 100 mg; sorbent size: 100 mesh; temperature: 30°C; contact time: 24 h.

^b Distribution coefficient, K_d (mL/g) = mmol of metal on the sorbent/mmol of metal in solution \times mL of solution/g of resin.

Both the AN-PHE-HCHO and AN-RES-HCHO resins removed the UO_2^{2+} ion effectively from an optimal metal-ion concentration of $50 \mu\text{g mL}^{-1}$, beyond which the adsorption rate decreased. The resin DDM-PHE-HCHO, on the other hand, was effective up to a metal-ion concentration of $200 \mu\text{g mL}^{-1}$. The adsorption coefficients, k_{ad} , of the resins for each metal ion was computed from the Freundlich adsorption isotherm (Fig. 7):

$$\log(x/m) = \log k_{\text{ad}} + 1/n \log C \quad (2)$$

where C is the initial concentration of the metal ion in millimoles; m , the weight of the resin in grams; x , the quantity of the metal ion adsorbed by the resin in millimoles; and n , a constant. The results for Cu^{2+} adsorption for the resin AN-PHE-HCHO are $k_{\text{ad}} = 2.806 \times 10^{-2}$, $n = 1.816$; the resin AN-RES-HCHO, $k_{\text{ad}} = 5.54 \times 10^{-2}$, $n = 1.659$; and the resin DDM-PHE-HCHO, $k_{\text{ad}} = 5.982$, $n = 1.039$. The results for UO_2^{2+} adsorption by DDM-PHE-HCHO are $k_{\text{ad}} = 0.4012$ and $n = 1.258$. The low k_{ad} value for AN-PHE-HCHO and AN-RES-HCHO indicated a slower rate of attainment of equilibrium as compared to DDM-PHE-HCHO, for which the k_{ad} value was many times higher, indicating that the equilibrium was attained relatively faster.

Effect of Resin Quantity

To determine the quantity of the resin required to completely remove metal ions from a stock solution of a known concentration, the resin quantity was progressively increased. It was observed that 200 mg of the AN-PHE-HCHO or AN-RES-HCHO resin is required to completely remove the metal ions from a 10 mL Cu^{2+} solution of $20 \mu\text{g mL}^{-1}$. The same quantity of the DDM-PHE-HCHO resin could remove all the metal ions present in a 10 mL solution containing $200 \mu\text{g mL}^{-1}$ Cu^{2+} (Table V). Feng et al.²⁶ observed that with increasing resin quantity the percentage of metal uptake increased, leading to the complete removal of the metal ion.

Effect of Alkali and Alkaline Earth Metal Ion

The effect of the cations Na^+ , K^+ , and Mg^{2+} (common anion: SO_4^{2-}) on the adsorption behavior of the resins was studied. The concentrations of the added cations were varied in the range 20 – $500 \mu\text{g mL}^{-1}$ and the concentration of the metal-salt so-

lutions was kept fixed at $20 \mu\text{g mL}^{-1}$. It was observed that the added cations did not significantly affect the percentage of Cu^{2+} uptake (Table VI). Thus, the resins could be used to remove Cu^{2+} ions from saline and nonsaline water rich in these ions. Dev and Rao²⁴ noticed a similar trend in case of chelating resins functionalized with the *N*-(hydroxyethyl)ethylenediamine ligand.

Separation of Cu^{2+} from UO_2^{2+}

Based on the sorption behavior of the resins at different pH, the separation of Cu^{2+} and UO_2^{2+} in a binary mixture was attempted. For this study, two sets of experiments were carried out. In the first experiment, 10 mL of a solution containing a $20 \mu\text{g mL}^{-1}$ of Cu^{2+} and varying amounts of UO_2^{2+} (5 – $40 \mu\text{g mL}^{-1}$) was treated with 100 mg of the resin at pH 4.5 and the extent of adsorption of each metal ion was determined after 24 h of contact time. It was observed that at this pH the resins preferably adsorbed Cu^{2+} (Table VII).

In the second set of experiments, a 10 mL solution containing equal amounts (20 or $200 \mu\text{g mL}^{-1}$) of both Cu^{2+} and UO_2^{2+} was treated with 100 mg of the resins and the pH was varied in the range 2.6 – 4.9 . All the resins showed high affinity for Cu^{2+} , and within the pH range 2.6 – 3.5 , the resins did not adsorb any detectable amount of UO_2^{2+} (Table VIII), thus providing the optimum condition for an effective separation of Cu^{2+} and UO_2^{2+} . Mendez and Pillai²⁷ reported a resin that is highly selective for Cu^{2+} over UO_2^{2+} and VO^{2+} above pH 3.

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