## Synthesis, Spectral, Thermal, and Chelation Potentials of Polymeric Hydrazone Based on 2,4-Dihydroxy Benzophenone

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**ABSTRACT:** A chelating polymer, poly(2,4-dihydroxy benzophenone hydrazone-formaldehyde) [poly(DHBPH-F)], was synthesized by the polycondensation of 2,4-dihydroxy benzophenone hydrazone with formaldehyde in the presence of oxalic acid as a catalyst. Poly(DHBPH-F) was characterized by Fourier transform infrared and <sup>1</sup>H-NMR spectral data. The molecular weight of the polymer was determined by gel permeation chromatography. Polychelates were obtained when the dimethylformamide solution of the polymer containing a few drops of ammonia was treated with an aqueous solution of metal ions. Elemental analysis of the polychelates indicated that the metal-ligand ratio was 1 : 2. The IR spectra of the polymer-metal complexes suggested that the metals were coordinated through the oxygen of the phenolic-OH group and the nitrogen of the azomethine group. The electron paramagnetic resonance and magnetic moment data

### INTRODUCTION

Recent interest in the design, synthesis, and characterization of Schiff-base hydrazone has attracted our attention in view of its ability to coordinate metal ions, acting as tetradentate ligands in metal chelates involving N<sub>2</sub>O<sub>2</sub> donor atom sets and in wastewater treatment. The adsorption of chelating resins is a common method for the recovery of heavy metals from wastewater. The main advantage of chelating resins compared to classical ion exchangers is their ability to form strong complexes with heavy metals. However, chelating resins are distinguished from ordinary types of ion-exchange resins by being highly selective toward metal ions and by the combination of ion-exchange and complexation chelating functional groups on solid supports for the concentration and separation of trace metal ions.<sup>1</sup> The chelation characteristics of hydrazone ligands are largely dependent on coordination sites, such as O, N, S, and P, in the polymer matrix with different coordinating indicated a square planar configuration for Cu(II) chelate and an octahedral structure for Ni(II) chelate. The thermogravimetric analysis, differential scanning calorimetry, and X-ray diffraction data indicated that the incorporation of the metal ions significantly enhanced the degree of crystallinity. The polymerization initiation, electrical conductivity, and catalytic activity of the polychelates are discussed. Heavy-metal ions [viz., Cu(II) and Ni(II)] were removed with this formaldehyde resin, and the metal-ion uptake efficiency at different pH's, the nature and concentration of the electrolyte, and the reusability of the resin were also studied. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 2146–2152, 2010

**Key words:** radical polymerization; metal–polymer complexes; thermogravimetric analysis (TGA); gel permeation chromatography (GPC)

powers, and this may give rise to varied bonding and different stereochemical patterns in their coordination characteristics. They are also useful for constructing supramolecular structures.<sup>1–3</sup> The incorporation of transition-metal ions into polymeric Schiff-base hydrazone not only affects its physical characteristics, such as its strength, but also its chemical activity.

The condensation products of hydroxyl carbonyl compounds with alkyl diamines provide interesting tetradentate Schiff-base ligands used to make a combinatorial library of ligands.<sup>4,5</sup> However, complexes of chromium, nickel, manganese, and ruthenium with a wide variety of Schiff bases having donor atoms such as N2O2 and N4 around the metal ion have been used as catalysts for carbonylation, hydrogenation, hydroformylation, and epoxidation reactions.<sup>1,6,7</sup> Schiff-base complexes obtained from quinoline are also known for their antibacterial activity, thermal stability, and biological activity, such as photosynthesis and the transport of oxygen in mammalian and other respiratory systems.<sup>8,9</sup> In view of the recent interest in the energetics of metal-ligands and binding in metal chelates involving NO donor ligands,<sup>10,11</sup> we report herein Schiff-base hydrazone complexes derived from hydrazine-bridged tetradentate ligands involving N2O2 donor atoms, their

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synthesis, and the spectral and thermal properties of poly(2,4-dihydroxy benzophenone hydrazone–formaldehyde) [poly(DHBPH–F)] toward Cu(II) and Ni(II) ions. Chelation studies at different pH values and the electrolytes, regeneration, and reusability of the resin are also reported.

#### **EXPERIMENTAL**

#### Materials

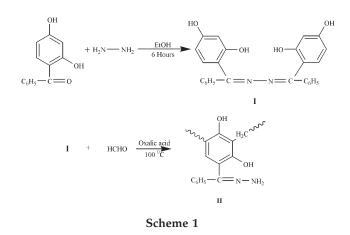
The starting materials, including 2,4-dihydroxy benzophenone, hydrazine monohydrate, formaldehyde, and acetate salts of Cu(II) and Ni(II) (E-Merck, Germany), were used as received. The solvents were dried before use by conventional methods.<sup>12</sup>

#### Ligand synthesis

The hydrazone monomer 2,4-dihydroxy benzophenone hydrazone (DHBPH) was synthesized by condensation between 2,4-dihydroxy benzophenone (10.85 g, 0.05 mol) and hydrazine monohydrate (1.21 mL, 0.025 mol) in ethanol. The mixture was refluxed for 6 h at 85°C, and the reaction mixture was poured into cold water, which resulted in the precipitation of the Schiff base hydrazone, which was filtered and dried under reduced pressure (yield = 71%). For the preparation of the polymer, 2,4, dihydroxybenzophenone hydrazone (2,4DHBH) (5 g, 0.022 mol), formaldehyde (3.6 mL, 0.044 mol), and oxalic acid (0.25 g, 3 wt %) were placed in a round-bottom flask, which was sealed and kept at 100°C for 24 h in an oil bath. The polymeric hydrazone formaldehyde formed in the flask was washed with distilled water and then dissolved in dimethylformamide (DMF), and NaCl (10%) solution was added to reprecipitate the polymer. Then, the polymer was filtered and dried *in vacuo* (yield = 69%). The IR and <sup>1</sup>H-NMR spectrum were consistent with the assigned structure (Scheme 1).

#### Synthesis of the polymer-metal complexes

The polymer–metal complexes were prepared in an alkaline medium by the dissolution of the polymer poly(DHBPH–F) (1.28 g, 0.5 mmol) in DMF. An aqueous solution of Cu(II)/Ni(II) acetate (0.25 mmol) was added dropwise with constant stirring, and the pH of the solution was adjusted to 7 with an ammonia solution. The reaction mixture was digested for 3 h in a water bath at 80°C; the resulting solid was filtered and washed with hot distilled water. The yield of poly(DHBPH–F)–Cu(II) was found to be 68%, and that of poly(DHBPH–F)–Ni(II) was 64%.



#### Instruments

Elemental analyses were carried out on a Coleman C, H, O, N analyzer. The metal-ion content in the polymer-metal complexes was determined by the usual titration procedure after the polymer was decomposed with concentrated sulfuric acid and concentrated nitric acid. The viscosity measurements of poly(DHBPH-F) were made in an Ubbelohde suspended-level viscometer with DMF at 30°C. The number-average molecular weight  $(M_n)$  and weightaverage molecular weight  $(M_w)$  of poly(DHBPH-F) were determined by a gel permeation chromatograph (Waters model 501) calibrated with polystyrene standards with tetrahydrofuran (THF). The IR spectra were recorded on a Bomem MB 104 Fourier transform infrared (FTIR) spectrophotometer in the range 4000–400 cm<sup>-1</sup>. The <sup>1</sup>H-NMR spectrum of poly(DHBPH-F) was recorded on a Hitachi 400 MHz spectrophotometer in CDCl<sub>3</sub> with tetramethylsilane as the internal standard.

The magnetic moments were measured by the Gouy method and corrected for diamagnetism of the compound with Pascal's constant. The electron paramagnetic resonance (EPR) analyses were carried out at room temperature on a Varian spectrophotometer (USA). X-ray diffraction experiments were performed on a Philips PW 1820 diffractometer (England). Thermogravimetric analysis (TGA) was carried out on an SDT Q600 V8.3 Build 101 (Japan); a 2.5-mg sample was used at a heating rate of 20°C/ min in air. The electrical conductivity of the polychelates was measured on pellets 10 mm in diameter and 2 mm thick with a Keithley electrometer.

The hydrolysis of ethyl acetate and the polymerization of acrylonitrile by Cu(II)/Ni(II) chelates at 65 and 70°C, respectively, were carried out in the usual manner.<sup>13</sup> The catalytic oxidation of cyclohexanol to cyclohexanone was carried out in a Schlenk tube under an oxygen atmosphere. Cyclohexanol (2.5 mmol), 2-butanone (6 mL), polymer Cu(II)/ Ni(II) complexes (0.5 mmol on the basis of the metal), and H<sub>2</sub>O<sub>2</sub> (0.5 mmol) were taken and stirred magnetically at 80°C for 6 h. Aliquots (1  $\mu$ L) were withdrawn and analyzed by gas chromatography.

# Metal-ion uptake of poly(DHBPH–F) at different pH values

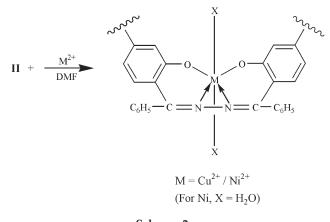
The selective adsorption of transition-metal ions onto the poly(DHBPH–F) was investigated in a batch-wise manner. The polymer (1.28 g, 0.5 mmol) dissolved in DMF (40 mL) was treated with an aqueous solution of Cu(II)/Ni(II) (0.25 mmol). The pH of the solution was adjusted to the desired value with either 0.1 mol of HCl or 0.1 mol of NH<sub>3</sub> solution; this suspension was agitated for 24 h over a magnetic stirrer at 600 rpm. The precipitated complexes were filtered off and washed thoroughly with demineralized water. The filtrate, along with washings, were collected, and a quantitative determination of metal-ion concentration was done by the titrimetric method for Cu(II) and by the dimethyl glyoxime method for Ni(II).<sup>14</sup>

#### Metal-ion uptake of poly(DHBPH–F) in the presence of different electrolytes

The polymer sample (20 mg in 25 mL) dissolved in DMF was added to an electrolytic solution (NaCl/  $Na_2SO_4$ , 25 mL) of a known concentration. The pH of the solution was adjusted with 0.1 mol of HCl or 0.1 mol of NH<sub>3</sub> solution. The solution was stirred for 24 h at ambient temperature. To this solution, 10 mL of a 0.1M solution of metal ion [Cu(II) or Ni(II)] was added, and the pH was adjusted to the required value. The mixture was again stirred at 25°C for 24 h and filtered. The solid was washed, and the metal-ion content was determined by a standard titrimetric method for Cu(II) and by the dimethyl glyoxime method for Ni(II).<sup>14</sup> The amount of metalion uptake by the polymer was calculated from the difference between a blank experiment and the reading in the actual experiments. The experiments were performed in the presence of several electrolytes with Cu(II) and Ni(II) ions.

#### Regeneration of poly(DHBPH-F)

The regeneration of the polymeric resin after chelation with divalent metal ions was examined with 7 mol of HCl (25 mL) to test the resin for divalent metal-ion absorption. The chelated ligands were placed in the desorption medium and stirred for 36 h at room temperature. The desorption ratios for the metal ions released from the polymeric resin into the aqueous phase was calculated from the amount of metal ion initially taken up by the polymer matrix and the final metal-ion concentration released into the desorption medium.



## Scheme 2

#### **RESULTS AND DISCUSSION**

The novel Schiff-base hydrazone polymer poly (DHBPH–F) was prepared from DHBPH and formaldehyde in the presence of oxalic acid as a catalyst with a 65% yield. Polymer–metal complexes were obtained from a DMF solution of polymer and an aqueous solution of the metal ions Cu(II) and Ni(II) in the presence of few drops of ammonia solution (Scheme 2).

The polymer-anchored ligand was yellow in color, whereas the color of the polymer-anchored Cu(II) and Ni(II) were brown and pale yellow, respectively. The polymer was soluble in DMF, CHCl<sub>3</sub>, THF, and dimethyl sulfoxide and insoluble in benzene, toluene, methanol, and water. All of the Cu/Ni polychelates were insoluble in all of the common organic solvents but were sparingly soluble in THF and DMF. The elemental analysis data (Table I) suggested that the metal-to-polymer ratio was 1 : 2, and this was in good agreement with the calculated values. The intrinsic viscosity  $([\eta])$  was obtained by extrapolation of  $\eta_{sp}/C$  to zero concentration. The intrinsic viscosity of poly(DHBPH-F) obtained was 0.436 dL/g.  $M_n$  and  $M_w$  of the poly(DHBPH–F) were determined by gel permeation chromatography with THF  $(M_n = 1.82 \times 10^4, M_w = 3.62 \times 10^4)$ . The polydispersity index  $(M_w/M_n)$  for poly(DHBPH-F) was 1.98.

The FTIR of poly(DHBPH–F) and its polychelates are shown in Figure 1. The absorption band near 3100–3600 cm<sup>-1</sup> corresponded to phenolic —OH. The vibration of the azomethine groups of the free ligand was observed at 1614 cm<sup>-1</sup>. The v(C=N) frequency of the complexes shifted by about 4–16 cm<sup>-1</sup> when compared to the free ligand; this indicated that the nitrogen atom of the azomethine group was coordinated to the metal ion. The sharp ligand band at 1114 cm<sup>-1</sup> was representative of the phenolic C—O vibration. On chelation, a small shift ( $\Delta v = 10$  cm<sup>-1</sup>) toward a higher frequency was observed in both polychelates, which suggested coordination through

Elemental Analysis Data of Poly(DHBPH–F) and Its Metal Complexes											
		Elemental analysis (wt %)									
		Carbon		Hydrogen		Oxygen		Nitrogen		Metal	
Abbreviation	Empirical formula	Calcd <sup>a</sup>	Found	Calcd <sup>a</sup>	Found	Calcd <sup>a</sup>	Found	Calcd <sup>a</sup>	Found	Calcd <sup>a</sup>	Found
Poly(DHBPH–F) Poly(DHBPH–F)–Cu(II) Poly(DHBPH–F)–Ni(II)	$\begin{array}{c} (C_{15}H_{14}O_2N_2)_n \\ (C_{15}H_{13}O_2N_2)_x \cdot Cu(II) \\ (C_{15}H_{13}O_2N_2)_x \cdot Ni(II)(H_2O)_y \end{array}$	70.87 56.78 54.54	70.84 56.79 54.57	5.51 4.10 4.55	5.48 4.13 4.50	11.02 8.83 8.48	11.04 8.79 8.48	12.60 10.10 14.55	12.64 10.08 14.53	 20.19 17.88	 20.21 17.92

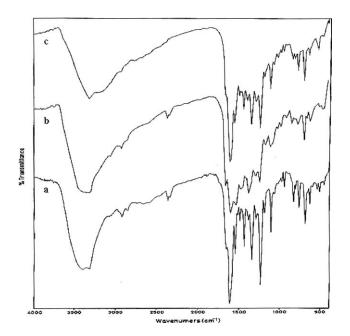
TABLE I Clemental Analysis Data of Poly(DHBPH–F) and Its Metal Complexes

<sup>a</sup> Calculated percentages of C, H, O, N, and metal ions for the polymer–metal complexes on the basis of the value of x = y = 2. For the found values, x = 2.02 and y = 2.01.

the phenolic oxygen.<sup>15</sup> The absorption bands at 510–550 and 450–475 cm<sup>-1</sup> were ascribed to the formation of M–O and M–N bands, respectively,<sup>16</sup> which further supported the coordination of the azomethine nitrogen and the phenolic oxygen.

The <sup>1</sup>H-NMR spectrum (Fig. 2) of poly(DHBPH–F) showed a resonance signal at 8.01 ppm, which may have been due to the phenolic —OH protons. The resonance signal at 7.2 ppm was due to aromatic protons. The resonance signals at 1.25 and 2.8 ppm were due to methylene and methine protons. Because the polychelates were insoluble in common organic solvents, the <sup>1</sup>H-NMR spectra of the polychelates are not reported.

The magnetic susceptibility parameters of polymer–metal complexes give an indication of the geometry of the ligands around the central metal ion. The EPR and magnetic moment data are given in Table II.  $g_{\parallel}$  and  $g_{\perp}$  were computed from the spectra with 1,1-diphenyl-2-picryl hydrazyl (DPPH) free radical as a g marker. The EPR results of the Cu(II) complex revealed  $g_{\parallel} = 2.27$  and  $g_{\perp} = 2.17$ , which were in close

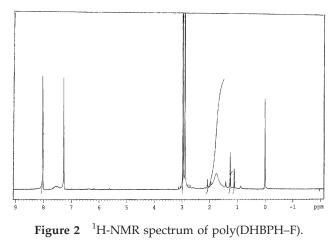


**Figure 1** FTIR spectra of (a) poly(DHBPH–F), (b) poly-(DHBPH–F)–Cu(II), and (c) poly(DHBPH–F)–Ni(II).

agreement with species with two nitrogen and two oxygen donor atoms coordinated to central metal ion having a square planar configuration, whereas the EPR parameters calculated for the Ni(II) complex were  $g_{\parallel} = 2.62$  and  $g_{\perp} = 2.18$ . The *g* values were much consistent with Ni(II) in an octahedral environment. The Cu(II) polychelate had a magnetic moment of 1.73 BM, which fell in the normal range (1.75–2.20 BM) expected for magnetically dilute Cu(II) complexes and which indicated a square planar configuration.<sup>17</sup> The magnetic moment of 3.39 BM and the paramagnetic behavior of the Ni(II) complexes suggested an octahedral geometry.<sup>18</sup>

The X-ray diffractograms of the poly(DHBPH–F) and its polychelates are shown in Figure 3. The X-ray diffraction pattern indicated that poly(DHBPH–F) was amorphous, whereas its polychelates exhibited a number of reflection planes resulting in good crystallinity. The crystallinity of the polychelates may not have been due to ordering in the polymer induced during metal chelate anchoring, more so, because the anchoring of metals to the polymer would imply interchain crosslinking between the polymeric chains as a result of an increase in electron density due to metal-ion uptake, which should have further decreased, rather than increased, any such ordering.

The glass-transition temperatures for the poly (DHBPH–F), poly(DHBPH–F)–Cu(II), and poly(DHBPH–



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TABLE II Magnetic Moment and EPR Spectral Data of the Polymer–Metal Complexes						
	Magnetic	EPR				
Polymer-metal	moment					

complex	(BM)	$g_{\parallel}$	$g_{\perp}$	Geometry
Poly(DHBPH–F)–Cu(II)	1.73	2.27		Square planar
Poly(DHBPH–F)–Ni(II)	3.39	2.62		Octahedral

F)-Ni(II) chelates were found to be 315, 504, and 480°C, respectively. The difference in transition may have been due to the crosslinking induced during complexation. Thermograms of the chelating polymer and its Cu(II) and Ni(II) complexes in the temperature range 30-800°C are shown in Figure 4. The decompositions corresponding to 12, 8, and 6% for the polymer and Ni(II) and Cu(II) polychelates, respectively, observed in the temperature range 50-180°C were attributed to moisture or solvent entrapped in the molecule. The weight loss in the temperature range 190-480°C was probably due to the degradation of the main chain [nearly 71% for the polymer, 62% for Ni(II), and 45% for Cu(II)]. In the case of polychelates, a stable metallic oxide is formed as the final decomposition product.<sup>19</sup> This behavior clearly indicated that the macromolecular imines in this study, which provided N<sub>2</sub>O<sub>2</sub> donor sites, exhibited a greater affinity toward Cu(II) than toward the Ni(II) ion; this coordination prevented the splitting of imine and hydroxyl molecules. Also, the metal ions providing a coordination crosslink between polymer chains increased the thermal stability. The IR, <sup>1</sup>H-NMR, EPR, and magnetic moment studies confirmed that the chelation of the metal ions may have possibly occurred between two groups from different polymeric chains, as shown in Scheme 2.

The electrical conductivities of the Cu(II) and Ni(II) polychelates were  $3.32 \times 10^{-9}$  and  $0.82 \times 10^{-9}$ 

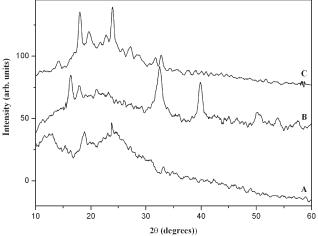


Figure 3 X-ray diffractograms of (A) poly(DHBPH-F), (B) poly(DHBPH-F)-Cu(II), and (C) poly(DHBPH-F)-Ni(II).

The effect of pH on the metal uptake of chelating agents on polymeric materials is a very important parameter. The ionization of the chelating ligand and the stability of the metal-ligand complexes vary

when the pH is changed. The effect of pH on the transition-metal-ion uptake for poly(DHBPH-F) was examined for Cu(II) and Ni(II) ions in aqueous solutions at different pH values with an adsorption time of 24 h. The results of the three experiments of the adsorption of metal ions for changing pH values are shown in Figure 5. Both the Cu(II) and Ni(II) metal ions examined in this study showed the same behavior. M(OH)<sub>2</sub> was precipitated at pH 8 for Cu(II) and Ni(II); this prevented capacity studies beyond neutral pH. It was evident that metal-ion uptake by the resin depended strongly on the pH. In general, metal uptake is seen to significantly increase with increasing pH.<sup>20-22</sup> This was ascribed to the ease of coordination of the phenoxide ion over that of the phenolic -OH group at higher pH and also the enhanced basicity of the C=N nitrogen, which gets protonated in acidic conditions.

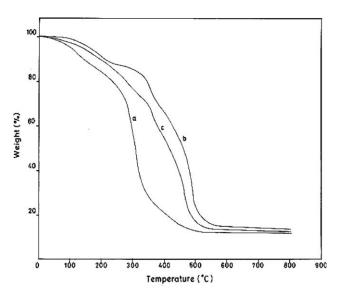
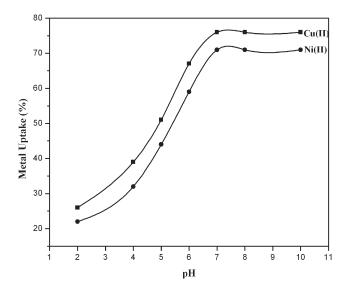


Figure 4 TGA traces of (a) poly(DHBPH-F), (b) poly (DHBPH-F)-Cu(II), and (c) poly(DHBPH-F)-Ni(II).

 $\Omega^{-1}$  cm<sup>-1</sup>, respectively. The data indicate that the polychelates were poor electrical conductors. The Cu(II) complex was found to catalyze the oxidation of cyclohexanol to cyclohexanone (16% yield) in the presence of H<sub>2</sub>O<sub>2</sub>, whereas the Ni (II) complex showed negative results. The ester hydrolysis of ethyl acetate to ethanol and acetic acid yielded around 16%, and polymerization of acrylonitrile with 40% conversion was achieved with the Cu(II)/ Ni(II) polychelates.

## Effect of pH on the metal-ion uptake properties



**Figure 5** Metal-ion uptake behavior of poly(DHBPH–F) at different pH's.

## Influence of electrolytes on the metal-ion uptake properties

Table III reveals that the amount of metal ions taken up from a given amount of a polymer depends on the nature and concentration of the electrolyte present in the solution. In the presence of chloride (NaCl) and sulfate ions (Na<sub>2</sub>SO<sub>4</sub>), the uptake of Cu(II) and Ni(II) ions increased with increasing concentration of the electrolytes. This observation was explained on the basis of the stability constant with these metal ions.<sup>23,24</sup> This observed increase in uptake may have been due to the nature of the ligand group in the repeat unit of the polymer.

#### Polymer regeneration and recyclability

A most important property of chelating polymer resins is their capacity for reuse. Regeneration of the adsorbed metal ions from the poly(DHBPH–F) was studied in a batch-wise system. In the desorption experiment, polymeric resin loaded with metal ions was placed in a desorption medium containing 7 mol of HCl (25 mL), and the amount of metal ions released was determined. The desorption ratios for the metal ions used in this study were calculated with the following equation:<sup>25</sup>

Desorption ratio (%)

 $\frac{\text{Amount of metal ion released}}{\text{Amount of metal ion adsorbed on the polymer}} \times 100\%$ 

More than 96% of the adsorbed metal ions were removed with a 7M HCl solution. We established the reproducibility of the aforementioned results by repeating the sequence four times with the same

Metal ion		Electrolyte	Percentage of the metal ion taken up in the presence of			
	pН	(mol/L)	NaCl	Na <sub>2</sub> SO <sub>4</sub>		
Cu(II)	3	0.01	33	34		
		0.05	37	37		
		0.1	39	38		
	5	0.01	48	47		
		0.05	53	50.5		
		0.1	55	54		
	7	0.01	73	70		
		0.05	75	73		
		0.1	78	76.5		
Ni(II)	3	0.01	22	21		
( )		0.05	24.5	25		
		0.1	27	28.5		
	5	0.01	39	40.5		
		0.05	41.5	42		
		0.1	43.5	44		
	7	0.01	68	69		
		0.05	69.5	71		
		0.1	73	73.5		

TABLE III Percentage Metal Uptake of Poly(DHBPH–F) with

polymeric resin for each of the metal ions. The results for repeated use of the poly(DHBPH–F) resin for the various metal ions are shown in Figure 6. As shown in Figure 6, the uptake efficiency of the resin was not altered much, even after four cycles of adsorption–desorption operations; this revealed good recyclability and stability of the polymer under acidic conditions.

0.75 (i-a) (i-

**Figure 6** Reuse of poly(DHBPH) for Cu(II) and Ni(II) with an initial metal-ion concentration of 100 ppm for the adsorption at pH 5 and 25°C with 0.02 g of polymer at an initial volume of 100 mL.

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#### CONCLUSIONS

A novel functionalized chelating polymer, poly-(DHBPH-F), was synthesized on the basis of the condensation reaction of 2,4-dihydroxy benzophenone and hydrazine monohydrate with formaldehyde in the presence of oxalic acid as a catalyst, and metal complexes were prepared. The chelating polymer and its complexes were characterized by elemental, IR, and <sup>1</sup>H-NMR analyses and assigned a metal-to-ligand ratio of 1 : 2. The thermal stability of the polymeric hydrazone and its polychelates followed the order poly(DHBPH-F)-Cu(II) > poly-(DHBPH-F)-Ni(II) > poly(DHBPH-F). The catalytic activity of the polychelates was explained on the basis of the formation of an intermediate substratepolychelate complex and a subsequent reaction leading to the products.<sup>26</sup> The metal uptake efficiency of the chelating polymer increased with pH and reached a plateau value around pH 7. Finally, we concluded that this polymer, with various divalent metal ions in an aqueous medium at neutral pH and above, could be effectively used for the removal of heavy-metal ions from aqueous solutions and wastewater.

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