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Synthesis, characterization and applications of polymer-metal chelates derived from poly[((4-acryloxy acetophenone)-divinylbenzene)] benzoyl hydrazone resins

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Abstract. 4-Acryloxy acetophenone was prepared and subjected to suspension polymerization with divinylbenzene as a cross-linking agent. The resulting network polymer was ligated with benzoyl hydrazone. The functional polymer was treated with metal ions [Cu(II), Fe(II)]. The polymer-metal complexes obtained were characterized by elemental analysis, IR, 1H-NMR, solid state ^{13}C cross-polarization magic-angle spinning (CP/MAS) NMR, electron paramagnetic resonance (EPR), thermogravimetric and scanning electron microscopy (SEM) studies. The maximum uptake efficiency for the metal ions was determined. The reusability of the polymer ligand was tested and it was shown that even after four cycles, the efficiency of the uptake was not altered.

Keywords. 4-Acryloxy acetophenone; divinyl benzene; functionalized polymers; polymer-metal complexes; chemical modification; suspension polymerization; cross-linkage agent; network polymer.

1. Introduction

The interaction between metal ions and polymerized ligands may lead to the formation of coordination polymers in which the chelated metal ions are bounded by ligand molecules.[1,2] Anchoring reagents to insoluble supports has come to be known as solid phase synthesis based on the pioneering efforts of Merrifield[3] in polypeptide synthesis. Rapid developments now not only make polypeptide synthesis on polymer supports, but immobilized photosensitizers and immobilized transition metal complexes are also frequently reported.[4] Polymer-metal complexes have been of interest to many chemists, because not only they are excellent models for metalloenzymes, but they have also led to developments in metal ion separation and recovery of metal ions. Increasing environmental concerns in waste-water treatment has led to the use of organic ligands anchored to solid supports in order to remove and recover important metal ions from aqueous solutions.[5–7] Copolymers of activated meth(acrylates) have been utilized to synthesize macromolecular drug carriers.[8] Wang *et al.*[9] have indicated that the polymeric support and the polymeric end groups affect the catalytic activity and selectivity of these complexes in hydrogenation reaction. The complexes obtained from maleic acid-styrene, acrylic acid-vinyl pyrrolidone copolymers and nickel(II), platinum(II) and palladium(II) metal ions were found to be useful catalysts for the hydrogenation of 2-chloro-4-nitrotoluene,[10] while copper(II) chelates synthesized from chloromethylated polystyrene were reported[11] to catalyse Diels–Alder cyclization reactions. A survey of the literature reveals that hydrazones derived from low molecular weight aromatic ketones like acetophenone and benzophenone draw the attention of synthetic chemists due to their varied biological activities.[12–14] Hydrazones also find their application in analytical chemistry. They act as multidentate ligands with metals forming coloured chelates. These chelates are then used in selective and sensitive determination of metal ions.[15–19] With a view to the complexing abilities of hydrazone derivatives and in a program to develop selective resins, acetophenone hydrazone incorporated into the polymer, the 4-acryloxyacetophenone (AAP) cross-linked with divinylbenzene (DVB) was selected. The benzoyl hydrazine (BH) derivative of the cross-linked copolymer acts as insoluble polymeric ligand towards Cu(II) and Fe(II) ions. We report here the preparation, characterization and applications of hydrazone derivatives of poly[((AAP)-DVB)] towards Cu(II) and Fe(II) ions. The metal uptake efficiency and reusability of the resin are studied.

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2. Experimental

2.1 *Physico-chemical measurements*

Elemental analysis of the cross-linked copolymers and their metal complexes were carried out on Thermo Finningan FLASH EA 1112 CHNS analyzer. The IR spectra were recorded on Perkin-Elmer IR spectrophotometer model 983 G using KBr pellets. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra of the samples were run on a dpx 200 MHz in $CDCl_3$ with tetramethylsilane (TMS) as internal standard. ^{13}C cross-polarization magic-angle spinning (CP/MAS) NMR spectra were recorded on a Bruker-dsx-300 MHz CP/MAS at Indian Institute of Science, Bangalore. A Perkin Elmer model 3700 with TGA-7 computer and a Mettler TA 3000 system were used to evaluate the thermal stability and decomposition temperature of the copolymers and their metal complexes. EPR spectra of the copolymer metal complexes were recorded on varion E-4X band spectrophotometer at 303 K. Particle size distribution of copolymer beads were studied with Malvern particle size analyzer by laser diffraction method. The sample was dispersed in paraffin oil. Scanning electron microscopy (SEM) was carried out using a JEOL-JSM 840 model. The copolymer was coated with gold. An ELICO UV-VIS SL 164 double beam spectrophotometer is used for absorbance measurements. The pH measurements were made with ELICO digital pH meter having a glass electrode model LI 127.

Standard salt solutions were prepared by taking requisite amounts in 50 ml double distilled water and standardized by the known methods.[20] Buffer solutions of pH range 3–6 were prepared from 1 M acetic acid and 1 M sodium acetate solution. Buffer solutions of pH range 8–10 were prepared from 1 M ammonium hydroxide and 1 M ammonium chloride.

2.2 *Preparation of monomer*

To a solution of 4-hydroxyacetophenone (0.2 mol) in 2–butanone, triethylamine (TEA) (0.2 mol) was added and stirred at 0–5°C. Thermometer and mechanical stirrer and dropping funnel are arranged. To this mixture, acryloyl chloride (0.2 mol) in ether was added in a period of 60 min. The condensation of acryloyl chloride with 4-hydroxyacetophenone liberates hydrochloride, which is adsorbed by TEA, which ultimately results into the quaternary salt (TEA hydrochloride). This quaternary salt is filtered and washed with ether and the filtrate collected. The filtrate which contains the monomer is washed with aqueous 5% NaOH followed by water. Then the filtrate is extracted with ether and the solvent evaporated to get the monomer. The formation of AAP is confirmed by IR and ^{1}H NMR. The spectral data is consistent with the structure of monomer. m.p. 52–54°C. IR (cm^{-1}, KBr): 3022 (Ar C–H stretching), 2934 (methylene C–H stretching), 1745 (ester carbonyl), 1654 (C=O stretching in keto carbonyl) 1602 (C=C skeletal vibration), 1165 (C–O stretching in ester) ^{1}H NMR (δ ppm): 2.4 (3H, s, CH3-), 5.2–6.5 (3H, CH2=CH protons), 6.8 and 7.8 (4H, Ar-H).

2.3 *Polymerization of monomer*

Bead polymerization of the monomer (30 g) was carried out at 80±1°C using polyvinyl alcohol (PVA) as the stabilizer and BPO as catalyst in a four-necked reaction kettle fitted with a water condenser, a synchronized mechanical stirrer, a dropping funnel and a nitrogen inlet. A controlled stirring rate of 400 rpm was maintained for 12 h DVB (5.2 g) was added as the cross-linking agent. The beads formed were filtered, washed with petroleum ether, 2-butanone, acetone, dichloromethane to remove the unreacted monomer and finally with water to remove PVA. The product was dried in a vacuum oven at 30°C and obtained an yield of 68%.

2.4 *Functionalization of polymer*

Functionalization of poly[((AAP)-DVB)] was achieved by incorporating benzoyl hydrazine (BH) moiety through a post-polymerization reaction in a state of dispersion. Cross-linked polymer (5 g) and BH (10 g) in dimethylformamide-water (DMF-H_2O) mixture (1:1) were placed in a 500 ml round-bottomed flask and refluxed for 12 h. The contents were filtered and the functionalized beads were collected, washed with DMF, ethyl acetate and water (scheme 1).

2.5 *Preparation of metal complexes*

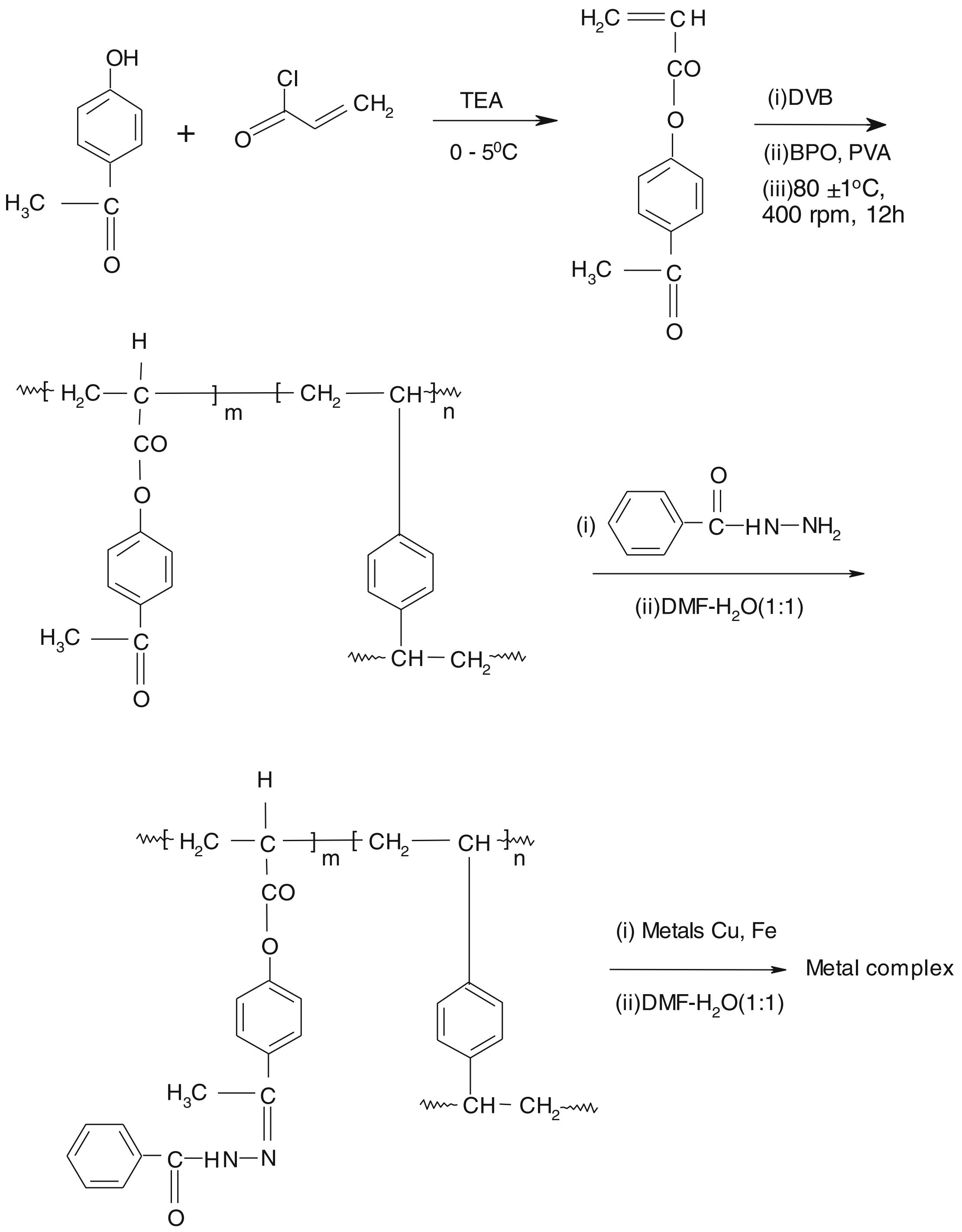
5 g of metal salts ($CuCl_2$. $2H_2O$ or $(NH_4)_2Fe(SO_4)$ $2.6H_2O$, respectively, in a DMF-H_2O (1:1) were treated with 5 g of a functionalized polymer and refluxed for 10 h in double-distilled water at a pH of 6.9 ± 0.1. The reaction mixture was filtered and the resulting green [Cu(II)] and brown [Fe(II)] metallated polymers were washed in hot water, ethyl acetate, acetone and dried in a vacuum oven at 60°C.

2.6 *Physical properties*

Both the polymer metal complexes are insoluble in common organic solvents and non-hygroscopic in nature.

2.7 *Chemical analysis*

The metal contents in the polymer-metal complexes were estimated titrimetrically after acid treatment of the complexes.[20]



Scheme 1. Synthesis of title compounds.

Table 1. Elemental analysis of poly[((AAP)-DVB)], poly[((AAP)-DVB)]-BH functionalized polymer and metal chelates.

	Found %			
Element	Poly[((AAP)-DVB)]	Poly[((AAP)-DVB)]-BH	Poly[((AAP)-DVB)]-BH -Cu(II)	Poly[((AAP)-DVB)]-BH -Fe(II)
C	68.95	71.62	69.37	67.26
H	6.27	6.73	6.52	6.37
N	–	4.58	1.64	1.73
Metal	–	–	1.75	1.58
		52*		

*indicates the percentage of conversion

3. Results and discussion

3.1 *Elemental analysis*

Elemental analysis data is presented in table 1. The data show that the conversion of keto carbonyl groups to hydrazone function was 52% by weight (only the surface keto groups were converted to benzoyl hydrazone). The remaining keto groups, deeply buried in the polymer chains were unaffected. Metallation was 28 and 30%, respectively for Cu(II) and Fe(II) complexes.

3.2 *IR spectral studies*

The IR spectrum of poly[((AAP)-DVB)] copolymer shows absorption band at around 2929 cm^{-1}, which has been identified as -CH backbone methylene stretching vibrations. The ester carbonyl is identified through the appearance of a strong absorption band at 1732 cm^{-1}. A strong absorption around 1600 cm^{-1} is due to C=C stretching vibration of the phenyl rings. The (C–O–C) stretching vibrations in compound are confirmed by a band at 1170 cm^{-1}. The keto carbonyl functionality is identified by a sharp absorption band around 1651 cm^{-1}.[21–23] The formation of hydrazone is confirmed by a set of distinct vibrations at 3350 and 1632 cm^{-1} which are due to –NH, and C=N stretching, respectively. The disappearance of the band at 1651 cm^{-1} indicates the removal of carbonyl function of ketone units. The appearance of a new absorption band at 1685 cm^{-1} is due to C=O group of benzoyl hydrazine moiety with a shoulder at 1660 cm^{-1}. The shoulder that appears at 1660 cm^{-1} is due to the inner keto groups present in poly[((AAP)-DVB)] copolymer. The FTIR spectra of poly[((AAP)-DVB)] copolymer and its benzoyl hydrazine functionalized resins are shown in figure 1. The Cu(II) complex shows peak at 1602 cm^{-1}, which are lowered from 1632 cm^{-1} (C=N str.), in functionalized resin. Amide group vibrations increase in frequency from 1505 to 1520 cm^{-1}. These changes in amide group vibrations suggest amide oxygen coordination in keto form. The band observed at around 590 cm^{-1} is assigned to $\nu_{\text{Cu-N}}$ vibrations. It is therefore inferred that the ligands coordinate in bidentate fashion. The IR spectrum of functionalized copolymer shows intense band at 1651 cm^{-1} due to C=O stretching in hydrazone and its downward shift in Fe(II) complex suggest coordination of metal ion through oxygen atoms. There is a downward shift of C=N vibration of azomethine from 1632 to 1610 cm^{-1} which indicates the coordination of azomethine nitrogen atom. Thus, in each complex the metal atom binds to the ligand through azomethine nitrogen and hydrazone carbonyl oxygen atoms.

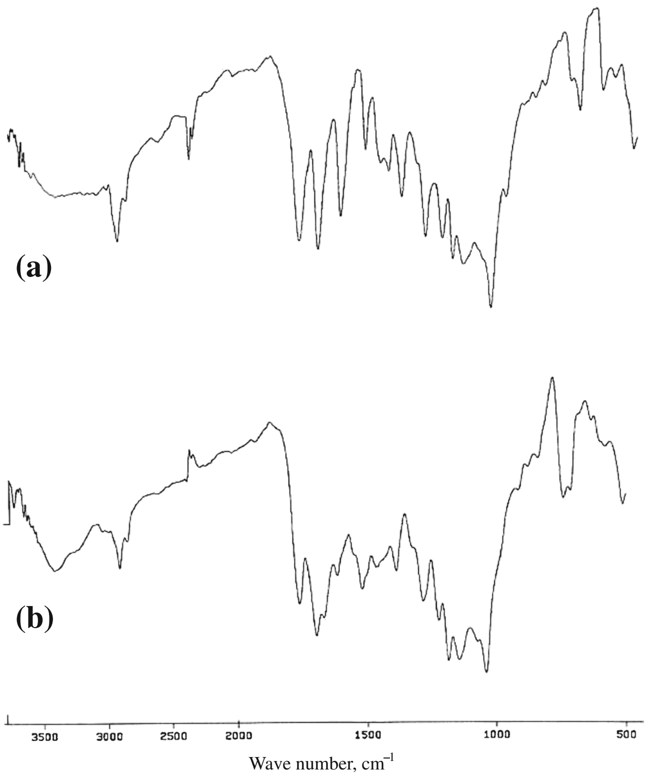


Figure 1. FTIR spectra of (**a**) poly[((AAP)-DVB)]; (**b**) poly[((AAP)-DVB)]-BH resins.

3.3 *Solid State ^{13}C CP–MAS NMR spectroscopy*

In the present investigation in addition to elemental analysis and FT IR spectroscopy, ^{13}C CP–MAS NMR[24–26] is used for identifying the polymer units. The sample is spun at two different spins and by comparing the two spectra, the spinning side bands are eliminated. The ^{13}C CP–MAS of cross-linked copolymer has been compared with its soluble homopolymer analogue. Proton decoupled spectra of homopolymer is taken in $CDCl_3$ solution. The ^{13}C NMR spectra of AAP homopolymer and ^{13}C CP–MAS of cross-linked copolymers are shown in figures 2 and 3a, respectively. The backbone ^{1}C and ^{2}C carbons of homopolymer appeared as clear distinct lines at 46.15 and 37.93 ppm, respectively. In the case of cross linked copolymer, the intense peak at 41.17 is attributed to the backbone carbons. Because of the residual broadening, the peaks due to methylene and methyl carbons are not clearly resolved. The ketonic carbonyl of AAP appeared at 198.71 ppm as sharp intense line in homopolymer, whereas in cross-linked polymer it appeared at 196.72 ppm as a medium intense peak. The phenyl ester carbonyl[27] gave sharp line at 175.21 ppm in homopolymer and as a sharp peak in cross-linked system at 172.59 ppm. The ^{4}C of phenyl ring appeared at 154.68 ppm. The ^{5}C and ^{9}C, ^{6}C and ^{8}C aromatic carbons of homopolymer gave sharp lines at 134.64 and 129.92 ppm. The line observed at 135.54 ppm is attributed to ^{7}C of aromatic ring. In the case of ^{13}C CP–MAS NMR, because of residual broadening the clear splitting of aromatic signals are not observed. The aromatic carbons of solid sample gave only a sharp intense line at 129.29 ppm with a shoulder at 122.45 ppm. The ^{13}C CP-MAS NMR spectrum of benzoyl hydrazone derivative of poly[((AAP)-DVB)] [cf. figure 3b] shows an intense peak at 41.44 is attributed to the backbone carbons. The aromatic carbons of solid sample gave only a sharp intense line at 128.25 ppm with a shoulder at 122.86 ppm. The phenyl ester carbonyl gave medium intense peak at 173.62 ppm. The disappearance of peak at 196.72 ppm indicates the absence of ketonic carbon atom of acetophenone unit. This clearly explains the formation of benzoyl hydrazone derivative. Due to residual broadening, a clear separation of the signals is not observed in the spectrum.

3.4 *EPR spectroscopy*

EPR parameters gave a measure of the nature of the complexation with the metal ion. Anisotropic spectra are obtained for polychelates in crystalline state at 303 K. The $g_{\parallel}$ and $g_{\perp}$ are computed from the spectra using DPPH free radical as g marker. For the covalent complexes, g is less than 2.3 and for ionic environment it is normally 2.3 or larger.[28] The values $g_{\parallel}$ and $g_{\perp}$ for Cu(II) complex was 2.20 and 2.04, thereby indicating covalent character for the metal–ligand bond in the complex. The EPR signal corresponding to Fe(II) complex is not observed.

A survey of the literature reveals that Cu(II) and NI(II) metal complexes of poly(salicylaldehyde acrylate)-divinylbenzene semicarbazone resin[29] exhibit paramagnetic property. The nature of metal–ligand bond was reported to be covalent in these complexes. Similarly, Ni(II) complex of poly(2-hydroxy-4-methacryloyloxy acetophenone-formaldehyde) was

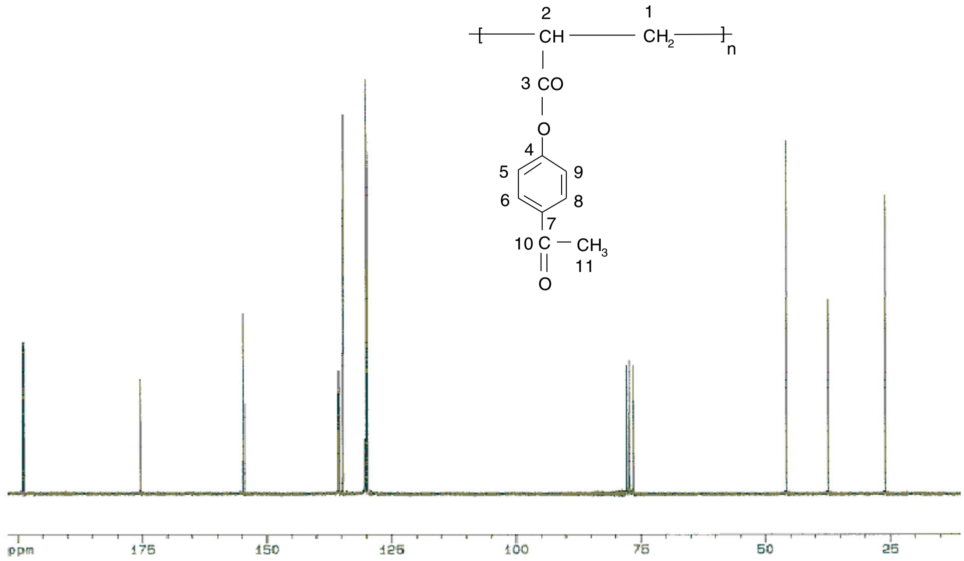


Figure 2. ^{13}C NMR spectrum of poly(4-acryloxy acetophenone) [homopolymer].

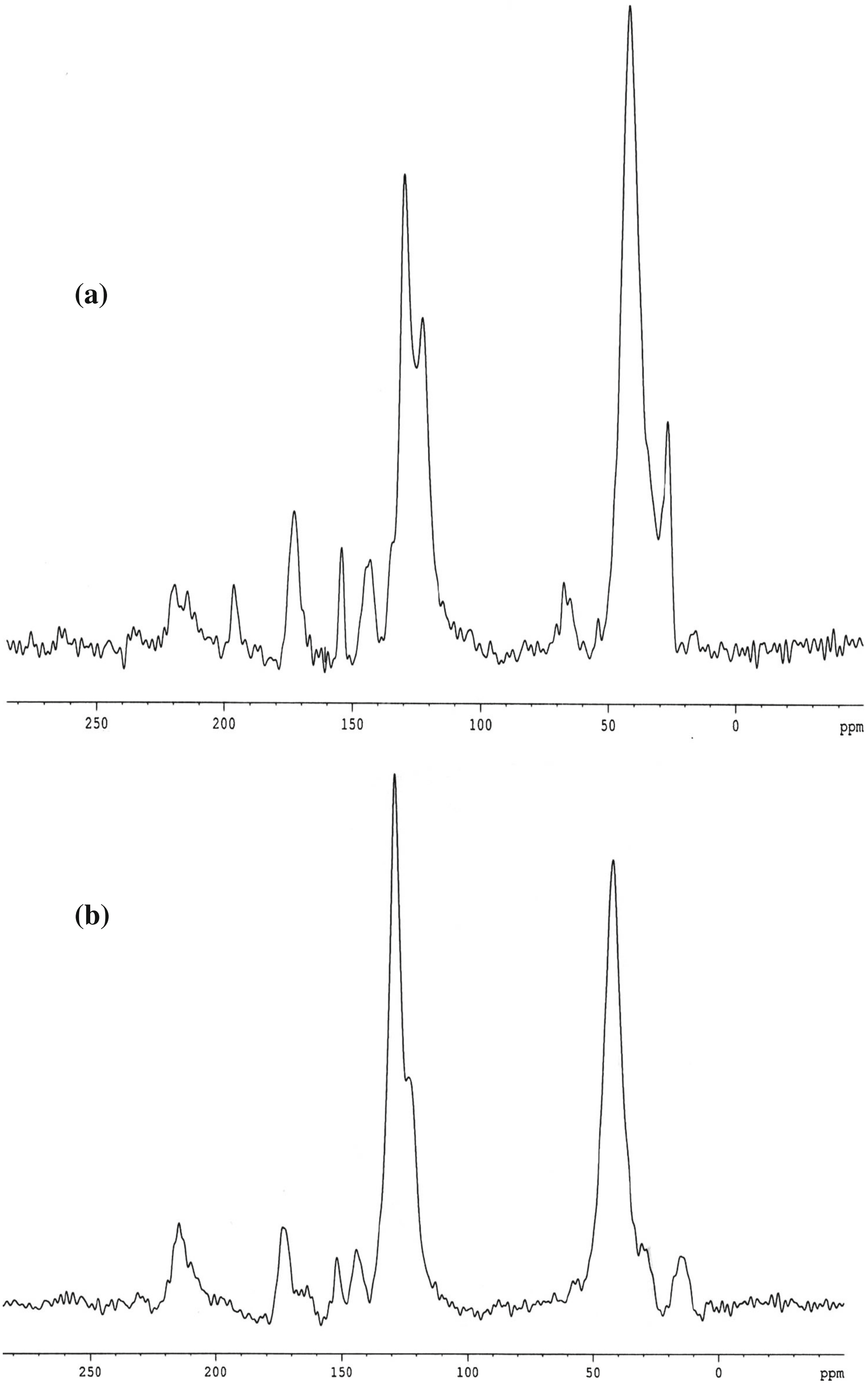


Figure 3. ^{13}C CP–MAS of (**a**) poly[((AAP)-DVB)]; (**b**) poly[((AAP)-DVB)]-BH resins.

also reported[30] to exhibit paramagnetic behaviour with a distorted octahedral geometry.[31] Hence, based on the covalent nature of the metal–ligand bond observed in the present studies and also based on the reports made in the literature,[29–31] octahedral geometry is suggested for the complexes.

3.5 *Thermogravimetric analysis*

In order to study the thermal stability and decomposition pattern of cross-linked copolymers, dynamic thermogravimetric analysis is under taken[32] and the data presented in the table 2 and thermograms are shown

Table 2. TG data of poly[((AAP)-DVB)], poly[((AAP)-DVB)]-BH functionalized polymer and metal chelates.

		Weight loss (%) at temperature (°C)										
Sl. no.	System	IDT's	250	300	350	400	450	500	550	600	650	700
1	Poly[((AAP)-DVB)]	176	7.8	12.5	27	50	61.7	80.8	90	91.8	96	–
2	Poly[((AAP)-DVB)]-BH	220	6.4	15	25.5	45	55.7	80	89	91.5	94	–
3	Poly[((AAP)-DVB)]-BH-Cu(II) chelate	290	4.7	9	29.5	71.4	78	82	84	91	94	96
4	Poly[((AAP)-DVB)]-BH-Fe(II) chelate	295	5.4	10.4	27.5	76	80	89.5	92	95	97	98

in figure 4. The thermograms of the copolymer and its functionalized resins are run in air atmosphere. The degradation of poly[((AAP)-DVB)] occurred in two stages. The first stage decomposition is observed from 176 to 444°C and the weight loss found was 60%. The second stage degradation of the copolymer resin was in the temperature range of 444–604°C. The weight loss involved in this stage was 27.7%.

The BH derivative also decomposed in a two-stage process. The first stage of decomposition commenced at 220 °C and was completed at 430°C. The initial weight loss is 53%. The second stage of decomposition was in the temperature range 430 and 594°C and the weight loss was 45.6%.

The thermal degradation data of BH functionalized poly[((AAP)-DVB)] Cu(II) and Fe(II) metal complexes is presented in table 2. The initial decomposition data of Cu(II) and Fe(II) complexes are 290 and 295°C, respectively. The degradation occurs mainly in two stages and decomposition is fast up to 400°C. The first stage of decomposition is due to the rupture of weak linkages and volatilization of low molecular weight fragments. The second slow decomposition of chelates at higher temperatures may be due to the breakage of main chain accompanied by the volatilization of the cleaved products.

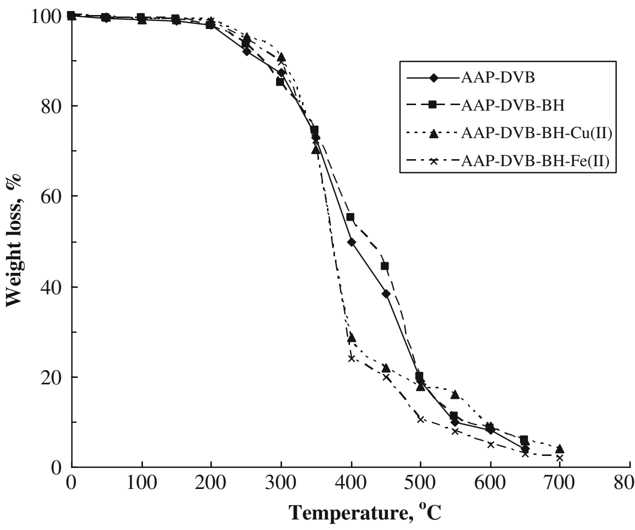


Figure 4. Thermogravimetric curves.

3.6 *Particle size analysis*

The success and reproducibility of the suspension polymerization is determined by measuring the average particle size of the beads formed.[33,34] The particle size distribution of the AAP–DVB copolymer is determined by Malvern particle size analyzer. The different classes of the particle sizes and percentage bands of the particles are presented in table 3. The average particle size of the system is 86.12 μm and the distribution curve is relatively broad. The particle size distribution curve is shown in figure 5.

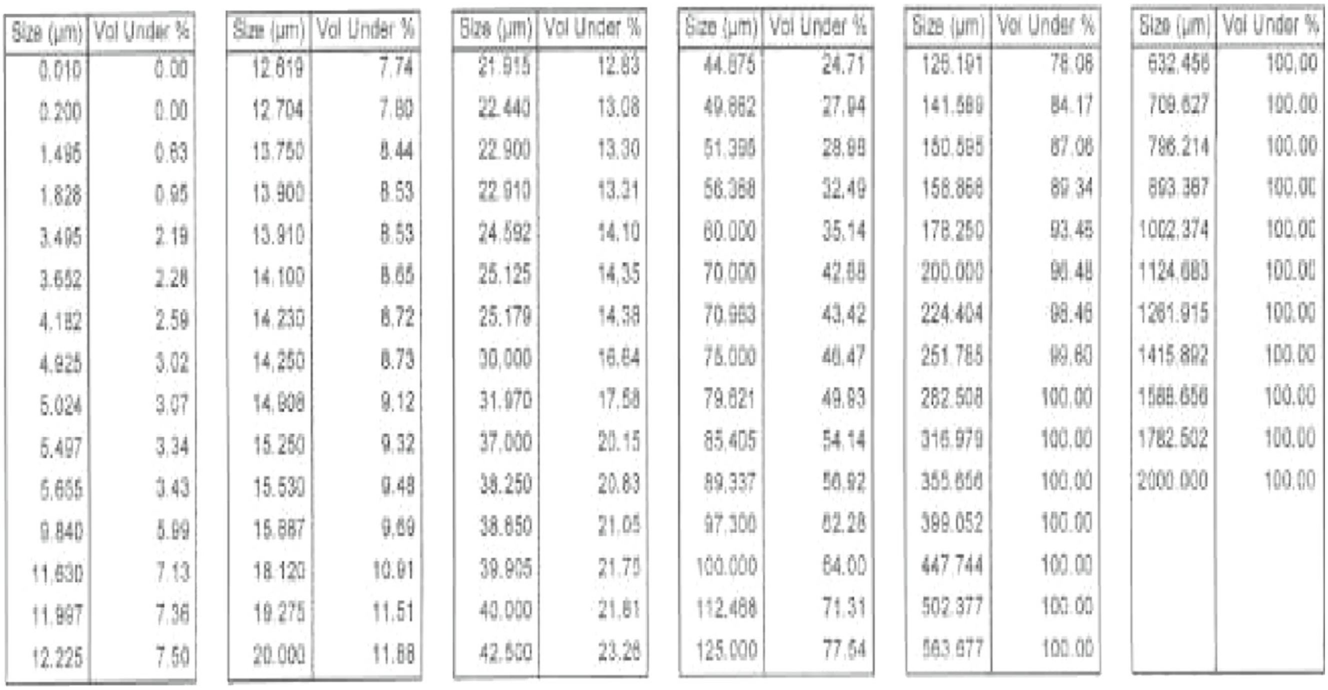
3.7 *Scanning electron microscopy*

SEM is the technique employed for studying the shape, size and morphological features of the polymers in beaded form.[35–37] The SEM photographs are presented in figure 6. The SEM photographs of BH functionalized AAP-DVB Cu(II) and Fe(II) metal complexes are shown in figures 6c and d. Functionalized resin appears smoother [cf. figure 6b] than that of the metal anchored resins. The rough appearance of the resin surface in due to the result of the doping of the metal ions. The copolymer beads [cf. figure 6a] were spherical and of various sizes. The beaded nature of the polymer confirms the success of suspension polymerization.

3.8 *Applications*

The time course of resin–metal interaction is of considerable importance if the resin is to be used in a dynamic system such as a packed column or a flowing system. If complexation is not sufficiently rapid for certain metal ions, then their retention on a column will be low owing to the short contact time between the resin and solution. Thus, absorption of resin should be examined over an extensive period. Slow exchange rates of many chelating resin have been reported[38,39] to prevent their

Table 3. Particle size analysis of poly[((AAP)-DVB)] copolymer.



Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %
0.010	0.00	12.619	7.74	21.915	12.83	44.875	24.71	126.191	78.06	632.456	100.00
0.200	0.00	12.704	7.80	22.440	13.08	49.862	27.94	141.589	84.17	709.627	100.00
1.496	0.63	13.750	8.44	22.900	13.30	51.396	28.89	150.595	87.06	796.214	100.00
1.828	0.95	13.900	8.53	22.910	13.31	56.368	32.49	158.866	89.34	893.367	100.00
3.495	2.19	13.910	8.53	24.592	14.10	60.000	35.14	178.250	93.45	1002.374	100.00
3.652	2.28	14.100	8.65	25.125	14.35	70.000	42.88	200.000	96.48	1124.683	100.00
4.182	2.59	14.230	8.72	25.179	14.38	70.963	43.42	224.404	98.46	1261.915	100.00
4.925	3.02	14.250	8.73	30.000	16.64	75.000	46.47	251.785	99.60	1415.892	100.00
5.024	3.07	14.908	9.12	31.970	17.58	79.621	49.93	282.508	100.00	1588.656	100.00
5.497	3.34	15.250	9.32	37.000	20.15	85.405	54.14	316.979	100.00	1782.502	100.00
5.655	3.43	15.530	9.48	38.250	20.83	89.337	56.92	355.656	100.00	2000.000	100.00
9.840	5.99	15.887	9.69	38.650	21.05	97.300	62.28	399.052	100.00		
11.630	7.13	18.120	10.91	39.905	21.75	100.000	64.00	447.744	100.00		
11.997	7.36	19.275	11.51	40.000	21.81	112.468	71.31	502.377	100.00		
12.225	7.50	20.000	11.88	42.500	23.28	125.000	77.64	563.677	100.00		

commercial use. The rate of complexation depends on the chemical nature of the metal ion and the ligand, as well as the structure of the polymer matrix. The steric constraints in a dense macromolecular matrix lower the reactivity of ligand function.

In order to optimize the time required for complexation towards Cu(II) and Fe(II) ions, batch studies were carried out.[40] The time dependence of the complexation of Cu(II) and Fe(II) by the functionalized AAP-DVB resin was followed by the change in the concentrations of the metal-salts solutions at regular intervals. The data is presented in the figure 7.

Experiments show that the resin is capable of binding with metal ions such as Cu^{2+}, Fe^{2+}, Ni^{2+} and Co^{2+}

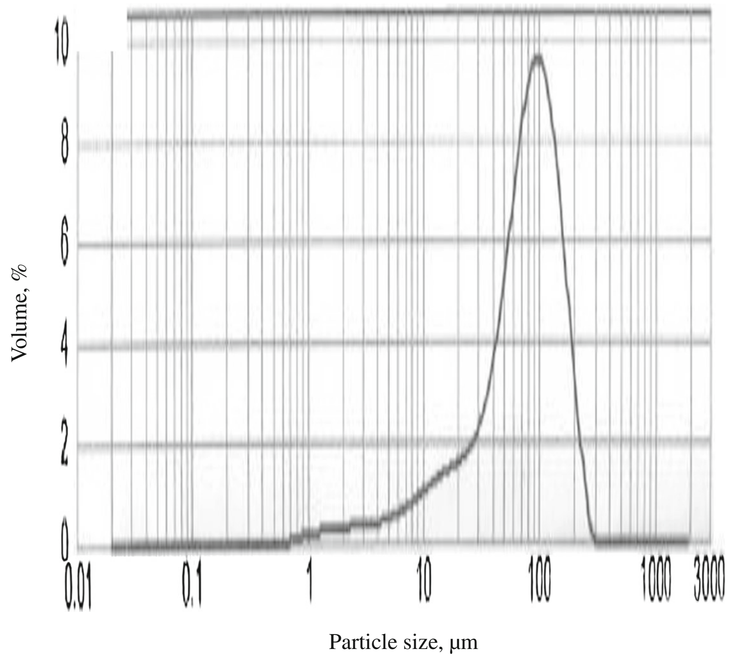


Figure 5. Particle size distribution of poly[((AAP)-DVB)] copolymer beads.

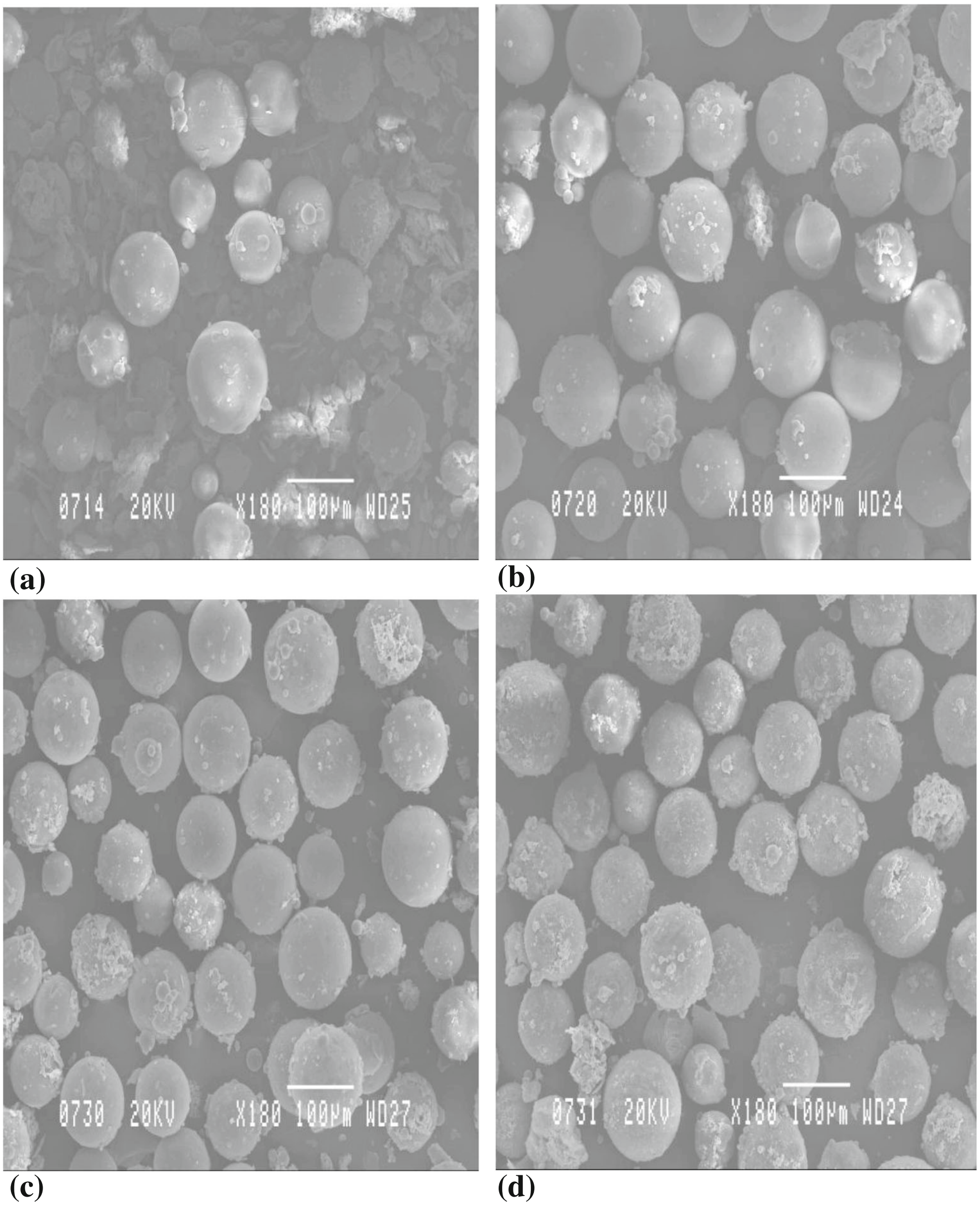


Figure 6. SEM photographs of (**a**) poly[((AAP)-DVB)], (**b**) poly[((AAP)-DVB)]-BH functionalized resin, (**c**) poly[((AAP)-DVB)]-BH Cu(II) complex and (**d**) poly[((AAP)-DVB)]-BH Fe(II) complex.

ions. The complexation of Cu(II) and Fe(II) was completed in 50 and 60 min for functionalized resin. The resin is also capable of binding with Ni^{2+} and Co^{2+} ions but with a lesser % uptake. The time taken for the maximum uptake of Ni^{2+} and Co^{2+} ions is found to be 30 and 40 min, respectively. The percentage of metal ion taken up is found to be 11 and 14%, respectively for Ni^{2+} and Co^{2+} ions. But in the present study the studies are restricted to Cu^{2+} and Fe^{2+} ions only that have greater % of uptake by the functionalized resin. Chelation of Cu(II) and Fe(II) is possible in the presence of other common ions present in waste water.

3.9 *Effect of pH on uptake of metal ion*

To various buffer solutions (pH 3–10), metal ion [Cu(II), Fe(II) (0.1) bulk concentration], functionalized AAP-DVB resin (5 g) was added and maintained under shaking for 90 min. The metallated beads were filtered and thoroughly washed. The bound metal ion was released by acid treatment and the metal content determined titrimetrically is presented in figure 8. From the plots, it can be concluded that the change in pH has relatively little effect on the uptake of metal ions by the functionalized resin. The reason for this is that the

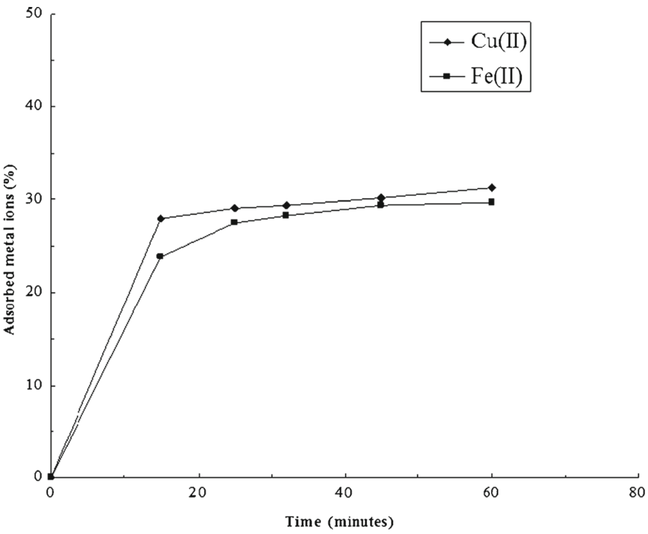


Figure 7. Cu(II) and Fe(II) uptake by the functionalized poly[((AAP)-DVB)] average of three determinations.

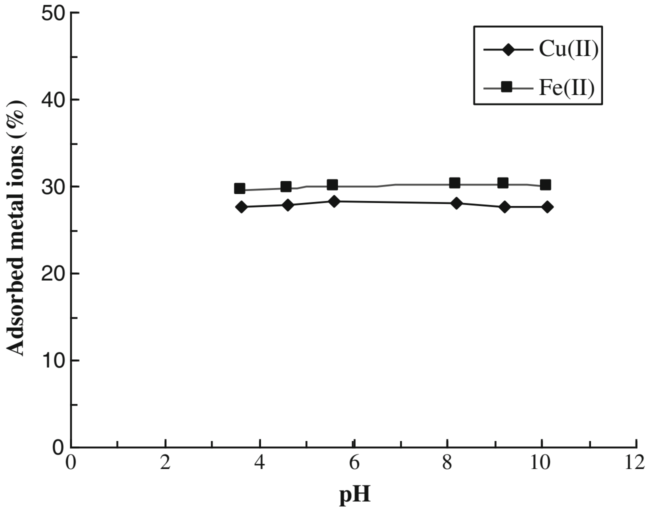


Figure 8. Effect of pH on adsorption of metal ions Cu(II) and Fe(II) average of three determinations.

chelation of atoms mainly depends on the structural features of the ligand and may be influenced by the pH of the medium. Hydrazones can exit either in keto form or in an enol form. In acid solution the nitrogen atom of hydrazone in keto form, may be protonated which may affect the formation of complex, as the same nitrogen atom is involved in chelation with metal ion. In alkaline solutions the enol form may be in anionic form and coordinate with the metal ion. But in the present study, the pH of the solution has negligible effect as the hydrazone moiety is in a polymer matrix and change in the structural features of the hydrazone based on the changes in the pH has little effect on complexation. Hence, the effect of change in the hydrogen ion concentration or hydroxyl ion concentration has only little effect and does not influence the extent of chelation much.

The uptake of metal ions by the present resin is compared with that of the poly(4-acryloxybenzophenone thiosemicarbazone)-divinylbenzene resins that were reported in the literature.[41] The comparative results are presented in table 4.

The results show that the time taken for the maximum uptake of metal ions by the present resins are much lower than that of poly(4-acryloxybenzophenone thiosemicarbazone)-divinylbenzene resins.

In the case of poly(4-acryloxybenzophenone thiosemicarbazone)-divinylbenzene resins, the uptake of Cu^{2+} and Fe^{2+} ions was pH dependent and the percent metal ion uptake increases with a rise in pH of the solution from 7 to 11. At pH 7 the amount of metal ion uptake was 12 and 11%, respectively for Cu^{2+} and Fe^{2+} ions and at pH 10 the amount of metal ion uptake was 74 and 46%, respectively for Cu^{2+} and Fe^{2+} ions. The percent metal ion uptake by poly (4-acryloxybenzophenone thiosemicarbazone)-divinylbenzene resins and the present resins are presented in table 4.

Table 4. Percentage metal ion uptaken and time taken for maximum uptake of metal ions.

	Poly(4-acryloxybenzophenone thiosemicarbazone)-divinylbenzene resins					Poly[(4-acryloxy acetophenone)-divinylbenzene] benzoyl hydrazone resins			
	Time taken for maximum uptake of metal ion, minutes		% metal ion uptake			Time taken for maximum uptake of metal ion, minutes		% metal ion uptake	
pH	Cu^{2+}	Fe^{2+}	Cu^{2+}	Fe^{2+}	pH	Cu^{2+}	Fe^{2+}	Cu^{2+}	Fe^{2+}
–	–	–	–	–	3.6	50	60	27.6	29.6
–	–	–	–	–	4.6			27.8	29.8
–	–	–	–	–	5.6			28.2	29.9
7	60	90	12	11	–			–	–
8			19	19	8.2			28.1	30.2
9			69	43	9.2			27.7	30.2
10			74	46	10.1			27.7	30.1
11			–	48	–	–	–	–	–

It is observed that the uptake of metal ions by the present resins is independent of pH as compared with poly(4-acryloxybenzophenone thiosemicarbazone)-divinylbenzene resins. Further, the percent metal ion uptake by the present resins at pH 8.2 is greater when compared to poly(4-acryloxybenzophenone thiosemicarbazone)-divinylbenzene resins. Whereas at pH 9 and 10 the percent metal ion uptake by poly (4-acryloxybenzophenone thiosemicarbazone)-divinylbenzene resins was greater than the present resins.

3.10 *Reusability of complexed AAP-DVB functionalized resin*

The most important advantage of chelating resin is their possible reuse after a particular process. The resin, once used, can be returned to its original form by desorbing the complexed metal ions with hydrochloric acid. The metal-free resin can be reused after washing with water several times. The recycling of the purified resin with the addition of Cu(II) and Fe(II) solution results in the intake of almost the same amount of respective metal ions as initially adsorbed. The process was repeated four times. The retention of the initial capacity, even after four cycles of repeated operations, suggests that the resin can be used several times without any reduction in capacity. Here, it is noteworthy that if the resin defunctionalized on acid treatment, it could be subjected to functionalization again. The BH modified polymer is insoluble in hydrochloric acid. During treatment with acid the BH moiety may detach from the polymer. But the poly[((AAP)-DVB)] is insoluble in HCl. It can be separated by decantation of acid solution and can be refunctionalized with BH after a thorough wash with water. The metal ion can be recovered by concentrating the acid solution.

4. Conclusions

Suspension polymerization of AAP using BPO as catalyst and DVB as a cross-linking agent was carried out. The BH ligand was attached to the carbonyl functional group and the resulting ligated polymer used to prepare polymer-metal complexes. IR spectral studies showed that the azomethine nitrogen and benzoyl carbonyl group and chloride/sulphate anions were involved in coordination to the metal ions such as Cu(II) and Fe(II). Elemental analysis confirmed that the percentage of functionalization was 51%, while the metallation was 28% and 30% for Cu(II) and Fe(II) complexes, respectively. The EPR spectra of the Cu(II) complex showed that the bonds are covalent in nature. Thermal studies were carried out and the thermal dissociation patterns discussed. SEM photographs indicate the success of suspension polymerization. A bead structure was observed for the polymers. The maximum uptake efficiency for the metal ions was determined. The reusability of the polymer ligand was tested and it was shown that even after four cycles, the efficiency of the uptake was not altered.

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