



ISSN: 0975-766X
CODEN: IJPTFI
Research Article

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SYNTHESIS, CHARACTERIZATION AND APPLICATIONS OF POLYMER-METAL CHELATES DERIVED FROM POLY (4-ACRYLOXYBENZALDEHYDE)-DIVINYLBENZENE ISONICOTINOYL HYDRAZONE RESINS

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Received on 05-10-2013

Accepted on 22-10-2013

Abstract

4-acryloxybenzaldehyde was prepared and subjected to suspension polymerization with divinylbenzene as a cross-linking agent. The resulting network polymer was ligated with isonicotinoyl hydrazone. The functional polymer was treated with transition metal ions, Cu(II) and Ni(II). The copolymer and its metal chelates were characterized by elemental analysis, IR, ¹H-NMR, solid state ¹³C cross-polarization magic-angle spinning (CP/MAS) NMR, electron paramagnetic resonance (EPR), thermogravimetric and scanning electron microscopy (SEM) studies. The maximum uptake of the metal ions was determined. Metal uptake efficiency and reusability of the ligated polymer resin were also studied.

Keywords: 4-Acryloxy benzaldehyde; Divinyl benzene; Functionalized polymers; Polymer-metal chelates; Chemical modification;

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 catalyze 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]. Besides hydrazones also find their application in analytical chemistry. They act as multidentate ligands with metals forming colored chelates. These chelates are then used in selective and sensitive determination of metal ions [15-18]. With a view to the complexing abilities of hydrazone derivatives and in continuation of our earlier work [19], the acryloxybenzaldehyde (ABA) cross-linked with divinylbenzene (DVB) was selected. The isonicotinoyl hydrazone (INH) derivative of the cross-linked copolymer acts as insoluble polymeric ligand towards Cu(II) and Ni(II) ions. We report herein the preparation, characterization and applications of isonicotinoyl hydrazone derivative of poly ABA-DVB copolymer towards Cu(II) and Ni(II) ions.

Materials and Methods

Physicochemical 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. ^1H 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 IISc, 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 303K. Particle size distribution is taken using a Malvern particle analyzer and scanning electron microscopy (SEM) was carried out using a JEOL-JSM 840 model. The copolymer was coated with gold. The pH measurements were made with ELICO digital pH meter having a glass electrode model LI 127.

Standard solutions were prepared by taking requisite amounts in 50 ml distilled water and standardized by the known methods [20].

Preparation of monomer: To a solution of 4-hydroxybenzaldehyde (0.2 mol) in 2-butanone, triethylamine (TEA) (0.2 mol) was added and stirred at 0-5°C. Thermometer, mechanical stirrer and dropping funnel were 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-hydroxybenzaldehyde liberates hydrochloride, which was adsorbed by TEA, which ultimately results into the quaternary salt (TEA hydrochloride). This quaternary salt was filtered and washed with ether and the filtrate collected. The filtrate which contains the monomer was washed with aqueous 5% NaOH followed by water. Then the filtrate was extracted with ether and the solvent evaporated to get the monomer. The formation of ABA is confirmed by IR and ¹H NMR. The spectral data is consistent with the structure of monomer. m.p. 46-48°C. The structure of the compound is confirmed by IR and ¹H-NMR spectral studies.

IR (cm⁻¹, KBr): 3050 (Ar C-H stretching), 1750 (ester carbonyl), 1600 (C=C skeletal vibration), 1660 (carbonyl group), 1156 (C-O stretching in esters).

¹H NMR (δ ppm): 5.96, 6.68 (2H, CH₂=CH-), 6.36 (1H, CH₂=CH-), 7.30-8.00 (4H, Ar-H), 10.0 (aldehydic proton).

Polymerization of monomer

Bead polymerization of the monomer (30g) 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 (5.2g) was added as the cross-linking agent. The beads formed were filtered, washed with petroleum ether, butan-2-one, acetone and dichloromethane to remove the unreacted monomer. Finally the beads were washed with water to remove PVA. The product was dried in a vacuum oven at 30°C. Yield 75%. It is characterized by elemental analysis and IR spectral data.

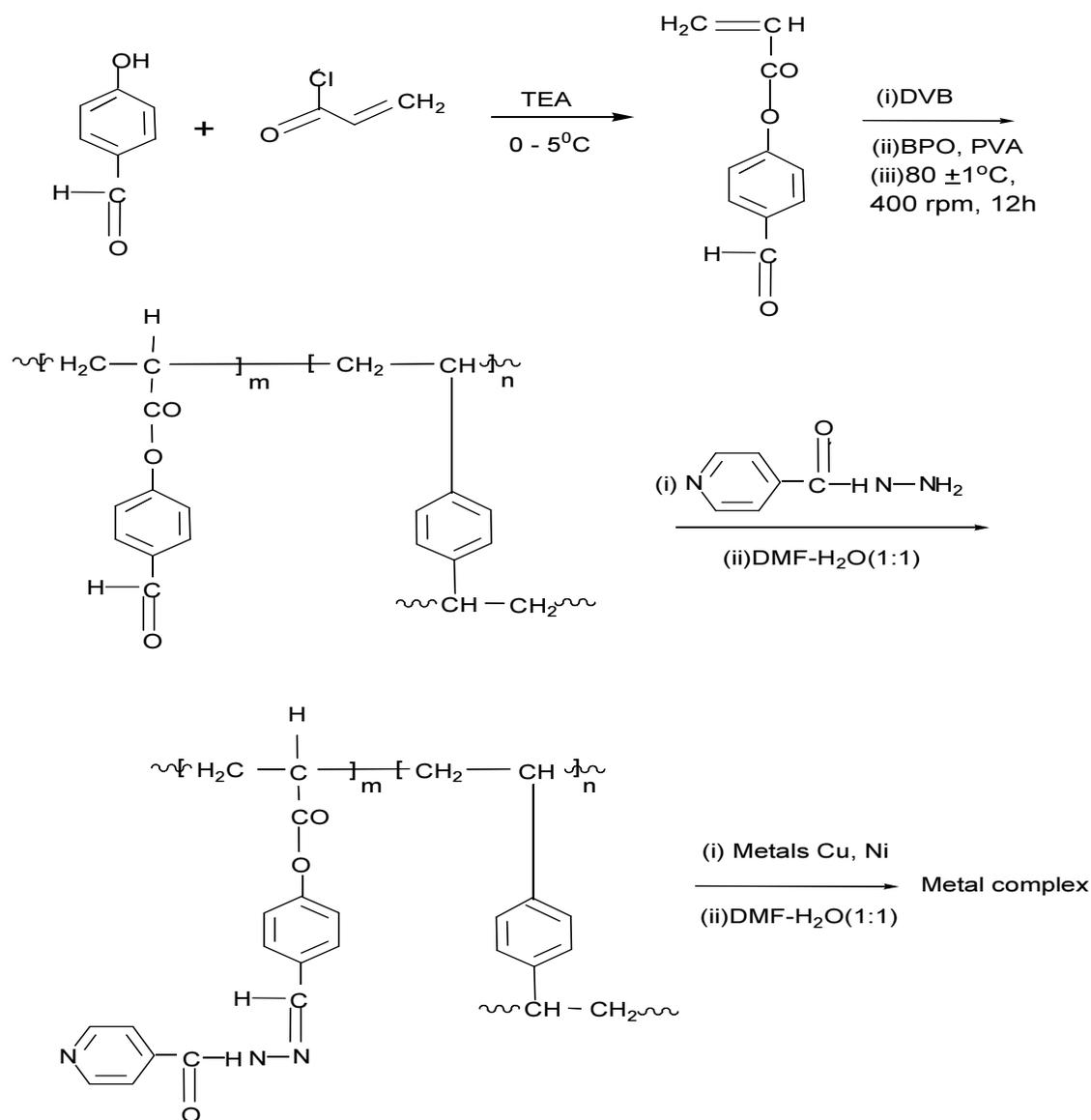
Functionalization of polymer

Functionalization of poly (ABA)-DVB was achieved by incorporating INH moiety through a post-polymerization reaction. Cross-linked polymer (5 g.) and INH (10 g.) in dimethylformamide-water (DMF-H₂O) mixture (1:1) were placed in a 500 ml round-bottomed flask and refluxed for 8 h. The contents were filtered; the functionalized beads

were collected, washed with DMF and water. The functionalized resin was identified by elemental analysis and IR spectrum.

Preparation of metal chelates

5g. of metal salts ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ or $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), 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 greenish yellow (nickel) and green (copper) metallated polymers were washed in hot water ethyl acetate, acetone and dried in a vacuum oven at 60°C . The synthetic steps are shown in Scheme 1.



Scheme 1

Physical properties

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

Chemical analysis

The metal contents in the polymer-metal complexes were estimated titrimetrically [Cu(II)] and gravimetrically [Ni(II)], after acid treatment of the complexes [20].

Results and discussion

Elemental analysis

Elemental analysis data is presented in Table 1. The data show that the conversion of aldehydic carbonyl groups to hydrazone function was 49% by weight (only the surface aldehyde groups were converted to isonicotinoyl hydrazone). The remaining aldehyde groups, deeply buried in the polymer chains were unaffected. Metallation was 36% and 33% respectively for Cu(II) and Ni(II) complexes.

Table-1: Elemental analysis of ABA–DVB copolymer, isonicotinoyl hydrazone functionalized polymer and its metal chelates.

Element	Found %			
	ABA-DVB	ABA-DVD-INH	ABA-DVD-INH-Cu(II)	ABA-DVB-INH-Ni(II)
C	69.71	66.70	64.23	64.58
H	6.43	6.21	6.08	6.11
N	-	6.43	2.38	3.59
Metal	-	-	2.10	2.63
		49*		
* indicates the percentage of conversion				

IR spectral studies

The IR spectrum of ABA-DVB copolymers shows absorption band at 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 1605 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 sharp absorption at 1143 cm^{-1} . The aldehydic carbonyl functionality is identified by a sharp absorption around 1680 cm^{-1} [21-23]. The formation of hydrazone is confirmed by a set of distinct vibrations at 3429 and 1650 cm^{-1} which are due to -NH and C=N stretching respectively. The disappearance of the band at 1680 cm^{-1} indicates the removal of carbonyl function of aldehydic units. The IR spectrum of functionalized copolymer shows intense band at 1690 cm^{-1} due to C=O stretching in hydrazone and its downward shift in Cu(II) complex suggest coordination of metal ion through oxygen

atoms. There is a downward shift of C=N vibration of azomethine from 1650 cm^{-1} to 1595 cm^{-1} which indicates the coordination of azomethine nitrogen atom. The Ni(II) complex shows absorption at 1605 cm^{-1} , which are lowered from 1650 cm^{-1} (C=N str.), in functionalized resin. It is therefore inferred that the ligands coordinate in bidentate fashion. Thus, in each complex the metal atom binds to the ligand through azomethine nitrogen and hydrazone carbonyl oxygen atoms.

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 is compared with its soluble homopolymer analogue. Proton decoupled spectra of homopolymer is taken in CDCl_3 solution. The ^{13}C NMR spectra of ABA homopolymer and ^{13}C CP-MAS of cross-linked copolymers are shown in Fig. 1 and Fig. 2 respectively. The backbone ^1C and ^2C carbons of homopolymer appeared as clear distinct lines at 45.89 and 37.36 ppm respectively. In the case of cross linked copolymer, the intense peak at 41.34 is attributed to the backbone carbons. Because of the residual broadening, the peaks due to methylene and methine carbons are not clearly resolved.

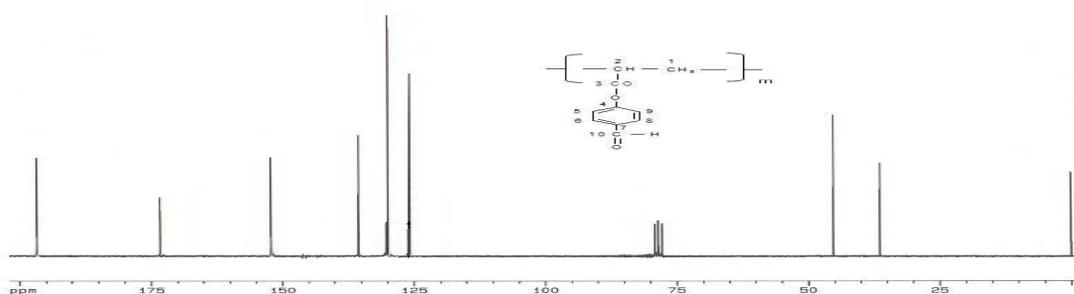


Fig. 1 ^{13}C NMR spectrum of 4-acryloxybenzaldehyde (ABA) homopolymer in CDCl_3 solution.

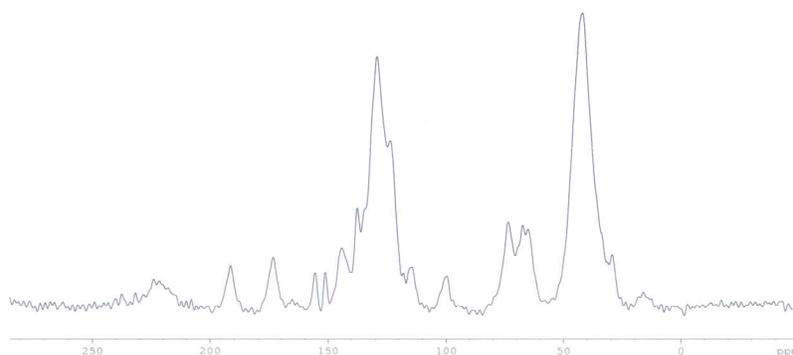


Fig. 2 Solid state ^{13}C CP-MAS NMR spectrum of ABA-DVB copolymer.

The aldehydic carbonyl of ABA appeared at 197.51 ppm as sharp intense line in homopolymer, whereas in cross-linked polymer it appeared at 191.24 ppm as a medium intense peak. The phenyl ester carbonyl [27] gave sharp line at 173.51 ppm in homopolymer and as a sharp peak in cross-linked system at 173.18 ppm. The ^{13}C of phenyl ring appeared at 152.49 ppm. The ^{13}C and ^{12}C , ^{13}C and ^{14}C aromatic carbons of homopolymer gave sharp lines at 135.51 and 130.06 ppm. The line observed at 126.42 ppm is attributed to ^{13}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 128.59 ppm with a shoulder at 122.62 ppm. The ^{13}C CP-MAS NMR spectrum of isonicotinoyl hydrazone derivative of ABA-DVB copolymer shows an intense peak at 41.32 which is attributed to the backbone carbons. The aromatic carbons of solid sample gave only a sharp intense line at 128.72 ppm with a shoulder at 122.86 ppm. The phenyl ester carbonyl gave medium intense peak at 173.08 ppm. The disappearance of peak at 191.24 ppm indicates the absence of aldehydic carbon atom of benzaldehyde unit. This clearly explains the formation of isonicotinoyl hydrazone derivative. Due to residual broadening, a clear separation of the signals is not observed in the spectrum.

EPR spectroscopy

The 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 303K. 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 2.17 and 2.05, thereby indicating covalent character for the metal-ligand bond in the complex. The EPR signal corresponding to Ni (II) complexes are not observed at room temperature.

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 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 metal complexes presently investigated.

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. The thermograms of the copolymer and its functionalized resins are run in air atmosphere. The degradation of ABA–DVB copolymer occurred in two stages. The first stage decomposition is observed from 218-415°C and the weight loss found is 66%. The second stage degradation of the copolymer resin is in the temperature range of 415-635°C. The weight loss involved in this stage is 33.6%.

Table-2: TG data of ABA-DVB copolymer isonicotinoyl hydrazone functionalized copolymer and its metal chelates.

S. No.	System	Weight loss (%) at temperature (°C)									
		IDT's	250	300	350	400	450	500	550	600	650
1	ABA-DVB copolymer	155	11	28	47	58	81.5	95	97	98	-
2	ABA-DVB-BH copolymer	235	5	15	44	62.5	69	89	95.5	97	-
3	ABA-DVB-INH-Cu(II) chelate	171	6.5	13	49	65.4	71.1	85.8	88.7	89.8	95
4	ABA-DVB-INH-Ni(II) chelate	221	5.7	11	27.5	78	84	89.5	92	94	96

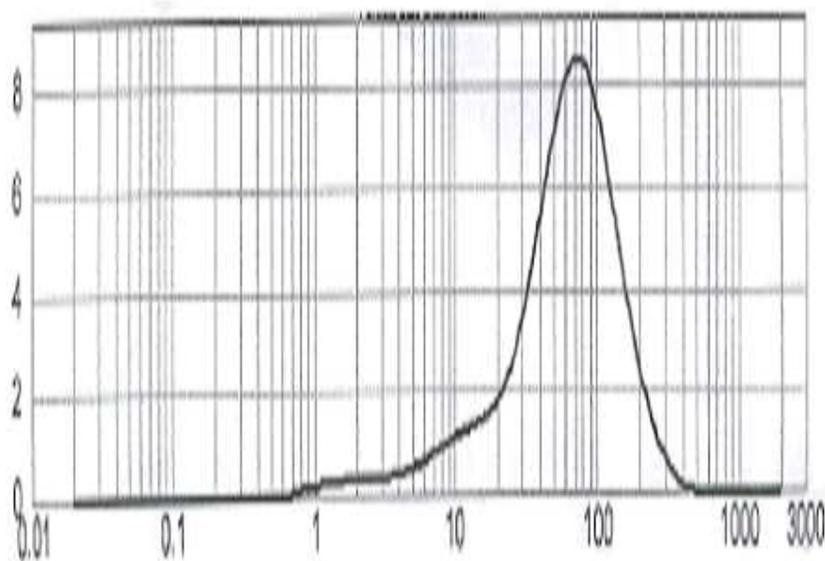
The INH derivative also decomposed in a two-stage process. The first stage of decomposition commenced at 235°C and was completed at 410°C. The initial weight loss of 62.5%. The second stage of decomposition is in the temperature range 410-600°C, with a weight loss of 34.5%.

The initial decomposition temperatures of Cu(II) and Ni(II) metal chelates 171 and 221°C respectively. The complexes decomposed mainly in two stages. The first stage decomposition is an elimination of benzaldehyde and bezaldehyde isonicotinoyl hydrazone units. 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.

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 ABA–DVB copolymer is determined by

Malvern particle size analyzer. . The average particle size of the system is 77.6 μ m and the distribution curve is relatively broad. The particle size distribution curve is shown in Fig. 3.



X-axis is Particle size(μ m)
Y-axis is Volume(%)

Fig. 3: Particle size distribution of ABA-DVB copolymer beads.

Scanning electron microscopy

SEM is the technique employed for studying the shape, size and morphological features of the polymers in beaded form [35-37]. Functionalized resin appears smoother [cf. Fig. 4] than that of the metal anchored resins [cf. Fig. 5]. The rough appearance of the resin surface is as a result of the doping of the metal ions. The copolymer beads were spherical and of various sizes. The beaded nature of the polymer confirms the success of suspension polymerization.

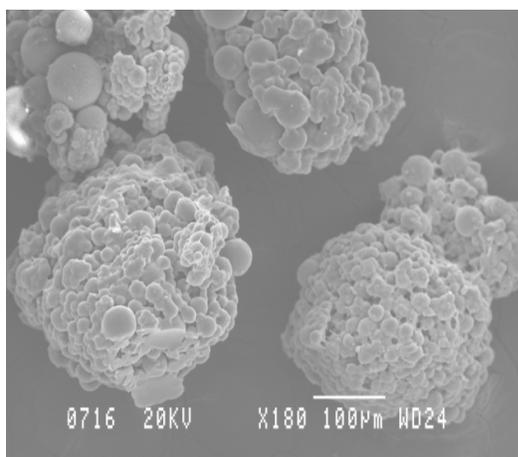


Fig 4 SEM photograph of ABA-DVB-INH

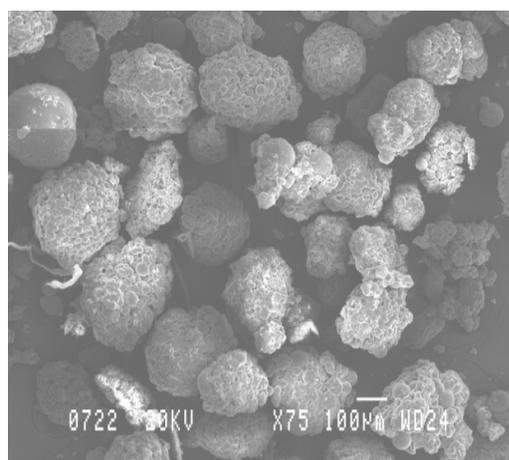


Fig 5 SEM photograph of ABA-DVB-INH- Cu(II) chelate

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] to prevent their 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 Ni (II) ions, batch studies were carried out [39]. The time dependence of the complexation of Cu (II) and Ni (II) by the functionalized ABA-DVB resin was followed by the change in the concentrations of the metal-salts solutions at regular intervals. The data is presented in the form of Fig. 6.

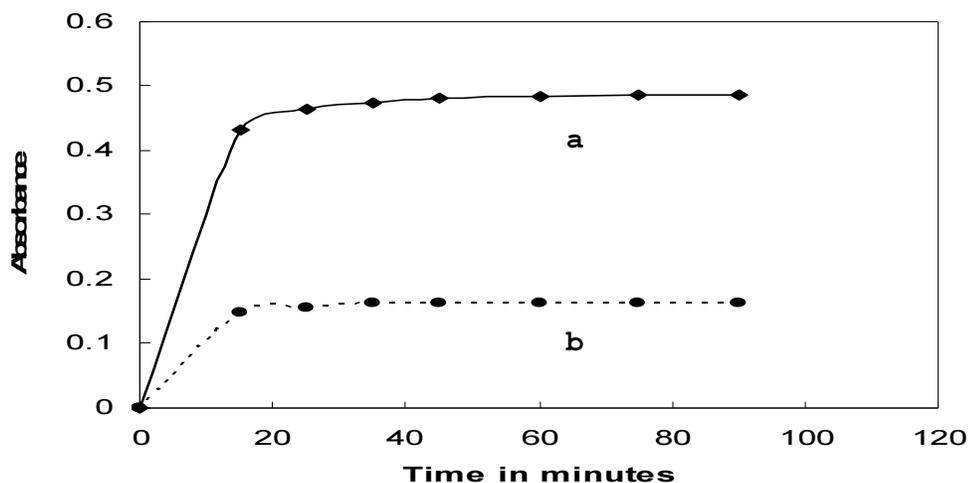


Fig. 6 Effect of time on the uptake of (a)Cu(II) and (b) Ni(II) by ABA-DVB-INHresin.

The complexation of Cu(II) and Ni(II) was completed in 55 and 35 min for functionalized resin.

Effect of pH on uptake of metal ion: To various buffer solutions (pH 3-10), metal ion [Cu(II), Ni(II) (0.1) bulk concentration], functionalized ABA-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 Fig. 7. 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.

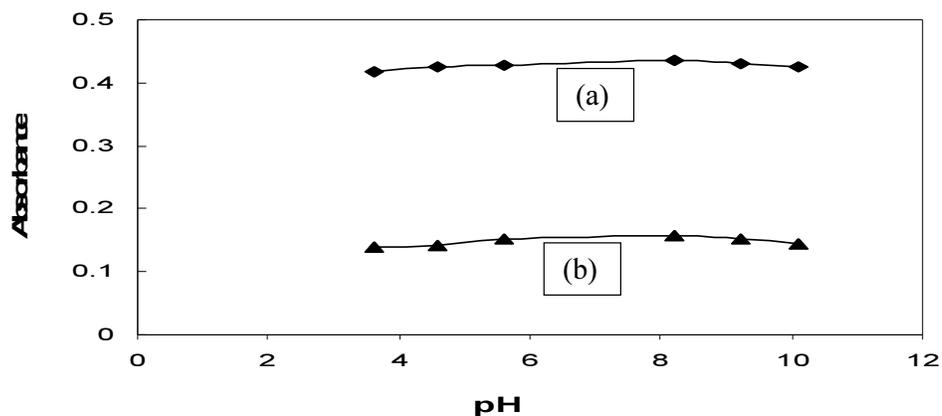


Fig. 7 Effect of pH on the uptake of (a) Cu (II) and (b) Ni (II) by ABA-DVB-INH resin

Reusability of complexed ABA-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 Ni (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 defunctionalize on acid treatment, it could be subjected to functionalization again.

Conclusions

IR spectral studies showed that the azomethine nitrogen and isonicotinoyl carbonyl group and chloride anions were involved in coordination to the metal ions such as Cu (II) and Ni (II). Elemental analysis confirmed that the percentage of functionalization was 49%, while the metallation was 36% and 33% for Cu (II) and Ni (II) complexes, respectively. The EPR spectra of the Cu (II) complex showed that this is covalent in nature. The thermal dissociation patterns show that the copolymer, functionalized resin and metal chelates decompose in two stages and are consistent with the structural features of the copolymer resins. SEM photographs indicate the success of suspension polymerization. A bead structure was observed for the polymers. The time taken for complexation of Cu (II) and Ni (II) was 55 and 35 min. respectively for the functionalized resin. 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.

Acknowledgements

The authors thank the University Grants Commission, New Delhi for financial support in the form of a Major Research Project. The authors also thank University Grants Commission, New Delhi and Department of Science & Technolohg, New Delhi for funding the department through SAP and FIST programmes respectively. The authors also thank the Regional Sophisticated Instrumentation centres of IISC, Bangalore and ICT, Hyderabad and Central University, Hyderabad, India for providing the analytical data.

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