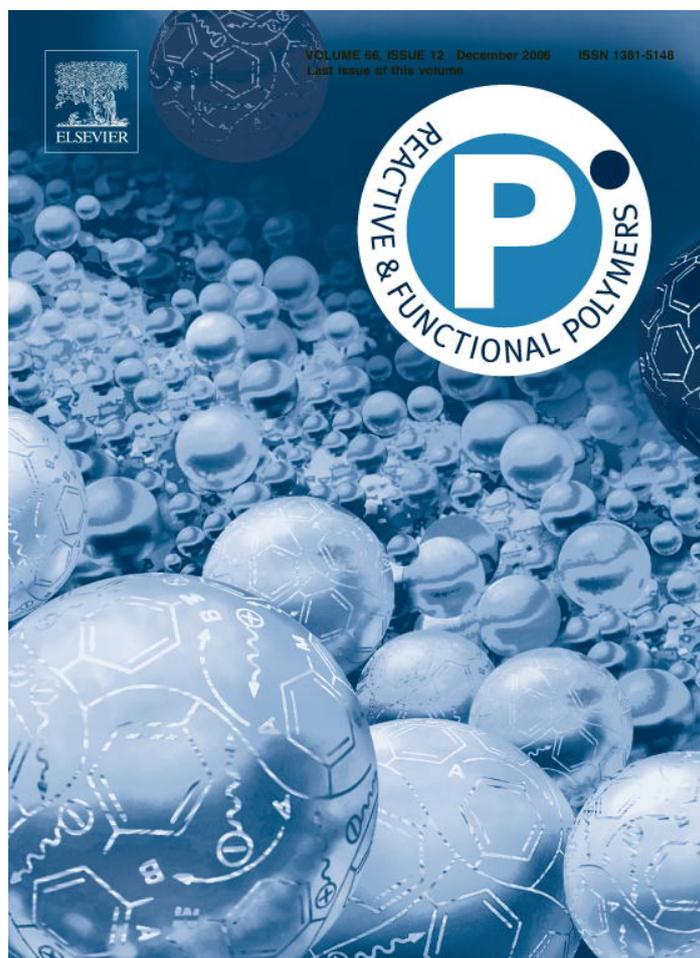


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Complexation and ion removal studies of a polystyrene anchored Schiff base

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Abstract

This paper reports the synthesis of a series of six new polystyrene anchored metal complexes of Co(II), Fe(III), Ni(II), Cu(II), Zn(II), and dioxouanium(VI) using the polystyrene anchored Schiff base of 2-nitrobenzaldehyde and the corresponding metal salts. The metal salts used were anhydrous FeCl_3 , $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, and $\text{UO}_2(\text{CH}_3\text{COO}) \cdot 2\text{H}_2\text{O}$. Physico chemical characterizations have been made from diffuse reflectance and vibrational spectra, elemental analysis, magnetic measurements, and TG studies. The elemental analysis suggest a 1:2 metal:ligand ratio when the complexation has carried out at 70 °C for about 12 h reflux. The ligand is monodentate and coordinates through the azomethine nitrogen. The Fe(III), Co(II), Ni(II), and Cu(II) complexes are all paramagnetic whereas Zn(II) and U(VI) are diamagnetic. Zn(II) is assigned a tetrahedral structure, Cu(II) and Co(II) are assigned a square planar structure and Fe(III), Ni(II), and U(VI) are all assigned an octahedral structure. The polystyrene anchored ligand has been developed as an excellent reagent for the removal of Cu(II). Optimum conditions have been developed for the removal of metal ion from solutions by studying the effect of change of concentration of metal ion, ligand, effect of pH, time of reflux, and interference effect of other ions. It was found that within a span of 20 min it is possible to remove 90% of the metal ion from a 30 ppm metal ion solution in the pH range 4–5.5.

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Keywords: Polymeric Schiff base complex; 2-Nitrobenzaldehyde; Cu(II) removal; Optimum condition

1. Introduction

The study of coordination polymers which was systematically initiated four decades ago is now regarded as one of the developing frontier areas of coordination chemistry. There has been growing emphasis on the studies involving polymer bound

ligands [1,2]. A polymer bound Schiff base manganese complex prepared from polystyrene bound salicylaldehyde and phenylalanine is found to be a good catalyst for the oxidation of cyclohexene, linear aliphatic olefins, and styrene by oxygen [3]. Polystyrene supported *t*-butylhypochlorites have been reported to effect oxidation of alcohols to carbonyl compounds [4]. A photoacoustic study of the thermal diffusivity of some polymer supported halogenobenzimidazole complexes of Co(II) was carried out by Sankara et al. [5]. Due to the macro

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environment created at the coordination center, the polymer bound ligands have considerable difference from the simple ligands. As the application of polymeric complexes is enormous, there exists a continuing interest in the synthesis and characterization of these complexes. The most important advantage of polymer supported strategy is the simplification of product work up, easy separation and isolation. Automation of the process is possible leading to industrial significance. The attachment of macromolecular matrix can also solve the problems of lability, toxicity, or odour, often experienced with low molecular weight reagents. The polymer matrix can be tailor made to provide a specific microenvironment that may be induced some specificity at the reaction site. The practical advantages of attaching insoluble supports are recognized and industrially exploited in waste water treatment of different industries. As the concern on industrial pollution is increasing, the demand for newer method of its control is also increasing. Conventional ion exchange resins are widely used in many commercial applications including the softening or deionizing of water, treatment of industrial waste water and the production and recovery of metals. However these resins have limited use in specialized applications such as the pre-concentration and removal of trace metals for the purpose of analysis, the treatment of industrial waste waters to the parts per billion level, and the removal of radio nuclides from highly acidic waste streams. Hence development of new methods for purification of water from spent process and effluent streams and recovery of valuable metals from industrial waste is of major concern in research field. Insoluble polymeric supports are widely investigated and applied for metal recovery from dilute solution [5–11], in which various chelating groups have been incorporated and are attached to the polymer matrix.

Cross linked polystyrene beads carrying amino methyl phosphoric acid groups [12] and imino diacetic acid groups [13] have been demonstrated to be efficient in the removal of trace quantities of metal ions such as Co(II), Mg(II), Zn(II) etc. Due to chelating effects, these are superior to common ion exchange resins. Organic chelating ligands containing oxime functional group have been extensively used in analytical chemistry for the detection and separation of metals [14–18]. Schiff bases derived from an amine and an aldehyde are an important class of ligands that coordinate to metal ions via azomethine nitrogen and have been

studied extensively [19–21]. Although the Schiff bases are the most versatile and thoroughly studied ligands, only a few Schiff bases have been immobilized to polystyrene matrix and used for metal ion (especially Hg(II), Pb(II), Cd(II), and transition metal ions) removal studies [22,23]. As part of the present investigations, a series of polystyrene bound Schiff base complexes of Fe(III), Co(II), Ni(II), Cu(II), Zn(II), and $UO_2(VI)$ has been synthesized and characterized. A complete analytical study has been carried out to develop the optimum conditions for the removal of Cu(II) using this Schiff base. The presently developed reagent has some clear advantages over the existing ones [24–26].

2. Experimental

2.1. Materials and methods

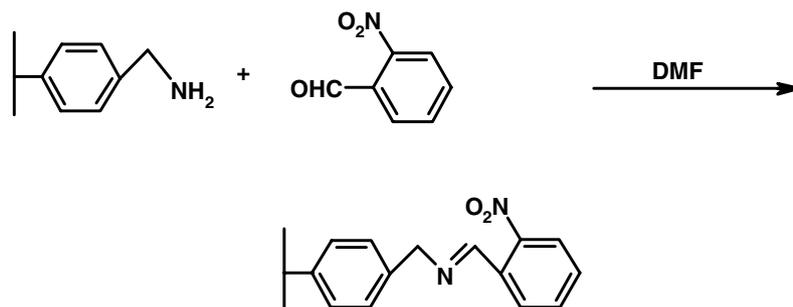
Analytical grade solvents and chemicals were used throughout. Aminomethylated polystyrene (2% cross linked with divinylbenzene) was obtained from Thermax India Ltd., Mumbai. 2-Nitrobenzaldehyde, metal salts (acetates of Ni(II), Cu(II), Zn(II), and U(VI); chlorides of Fe(III) and Co(II)) and the organic solvents such as dimethylformamide (DMF), ethyl alcohol etc., were all products of Merck.

2.2. Synthesis of the polystyrene anchored Schiff base resin (PS-L)

Aminomethylated polystyrene (10 g), preswollen in DMF (20 mL) for 1 h, was refluxed with a DMF solution of 2-nitrobenzaldehyde (10 g in 30 mL) for 4 h. The flesh colored resin was then cooled to room temperature, washed with DMF, water, alcohol, and finally with acetone and then dried in a vacuum desiccator at room temperature. The proposed reaction is given as [Scheme 1](#).

2.3. Syntheses of the polystyrene anchored metal complexes ($M(PS-L)_2 Y \cdot xDMF$) [$M = Co, Cu, Zn, UO_2; x = 1; Y = OAc/Cl^-$]; ($M(PS-L)_2 Y \cdot xDMF$) [$M = Fe, Ni; x = 2/3; Y = Cl_2/OAc^-$]

The procedure adopted for the preparation of complexes is a well established one [28]. The polymeric Schiff base ligand (2 g), preswollen in DMF (20 mL) for 1 h, was refluxed with the metal ion solution (1 g in 20 mL) for 12 h under stirring. The polymer anchored complex formed was then



Scheme 1. 2-Nitrobenzaldehyde Schiff base of amino methylated polystyrene.

suction filtered, washed thoroughly with DMF, water, alcohol and acetone. The complexes were then dried in a vacuum desiccator at room temperature.

2.4. Procedure for the removal of metal ion

2-Nitrobenzaldehyde Schiff base of aminomethylated polystyrene (0.01 g) was swelled in DMF for 1 h. To this suspension Cu(II) solution (30 ppm) was added and refluxed for 20 min. It was then filtered through a Whatman 41 filterpaper and diluted quantitatively to definite volume (50 mL). The amount of metal ion present in the filtrate was estimated by the spectrophotometric method [27]. Optimum conditions for the metal ion removal have been established by repeating the experiment to study the effect of time, pH, metal ion concentration, ligand concentration, and interference action of other ions such as Fe(III), Co(II), Ni(II), Zn(II), UO₂(VI), Na⁺, K⁺, NH₄⁺, Ca²⁺, Cl⁻, Br⁻, NO₃⁻, NO₂⁻ and CH₃COO⁻.

2.5. Apparatus

The elemental analyses were performed on Elementar CHN analyzer (Model VARIO EL III, Germany) and the metal contents were analyzed using

the ICP technique on a Thermo Elemental (Model IRIS INTREPID II XSP DUO, USA). The electronic spectra were recorded on an Ocean Optics UV–VIS spectrophotometer, attached with a CCD detector (Model CHEM 2000, USA). The IR spectra were recorded on Thermo Nicolette FTIR spectrometer (Model Avatar 370, USA). Magnetic susceptibility measurements were done on Vibrating Sample Magnetometer (Model P.A.R. 155, USA). The thermal analyses were carried out on a Perkin Elmer DTA analyzer (Model Diamond, USA).

3. Results and discussion

2-Nitrobenzaldehyde Schiff base of amino methylated polystyrene and its metal complexes were synthesized and characterized by elemental analysis, IR and UV–VIS spectral analysis, magnetic susceptibility measurements and thermal studies. Analytical data of the complexes show 1:2 geometry with respect to metal and ligand and data are presented in Table 1. The complex formation was indicated by a change of color and the complexes are stable at room temperature. All the complexes were found to be insoluble in water and all the common organic solvents including DMF. Due to their insolubility it is not possible to characterize them by X-ray studies.

Table 1
Analytical data of the complexes

Complex and color	Cl found (calc.) %	M found (calc.) %	μ_{eff} BM	Assigned geometry
Fe(PS-L) ₂ Cl ₂ · 2DMF brick-red	8.62 (8.82)	6.63 (6.93)	5.92	Octahedral
Co(PS-L) ₂ Cl · DMF ash	5.33 (5.07)	8.28 (8.42)	2.75	Square planar
Ni(PS-L) ₂ OAc · 3DMF sandalwood	–	6.89 (6.75)	3.34	Octahedral
Cu(PS-L) ₂ OAc · DMF chocolate	–	8.58 (8.73)	1.83	Square planar
Zn(PS-L) ₂ OAc · DMF flesh color	–	8.63 (8.96)	Diamagnetic	Tetrahedral
UO ₂ (PS-L) ₂ OAc · DMF brown	–	25.27 (25.53)	Diamagnetic	Octahedral

3.1. Infra red Spectra

The polymer anchored ligand displayed the characteristic stretching frequencies of the Schiff base at 1655 cm^{-1} (C=N). In the spectra of the complexes this band was shifted to lower frequency by $15\text{--}20\text{ cm}^{-1}$, suggesting nitrogen coordination of the ligand to the metal [19]. The oxygen coordination of the solvent DMF is indicated by the shift of (C=O) band present at 1675 cm^{-1} to lower energy by $20\text{--}55\text{ cm}^{-1}$ [28]. The monodentate nature of the acetate ion is revealed from the energy difference between ν_{sym} (COO) and ν_{asy} (COO) at $1392\text{--}1397\text{ cm}^{-1}$ and $1600\text{--}1608\text{ cm}^{-1}$, respectively [28].

The coordination of nitrogen of the ligand to the metal in the complexes is also confirmed by the presence of new bands at $450\text{--}380\text{ cm}^{-1}$ [29]. ν_{asy} (OUO) band of the uranyl complex occurs at 923 cm^{-1} which fall in the range $870\text{--}960\text{ cm}^{-1}$ normally observed for the majority of uranyl complexes [30].

3.2. Electronic spectra

The structure of the complexes was also confirmed by reflectance electronic spectrum. Three peaks observed at 11780 , 15300 , and 18750 cm^{-1} in the spectra of Fe complex are due to ${}^6\text{A}_{1\text{g}} \rightarrow {}^4\text{T}_{1\text{g}}(\text{G})$, ${}^6\text{A}_{1\text{g}} \rightarrow {}^4\text{T}_{2\text{g}}(\text{G})$, and ${}^6\text{A}_{1\text{g}} \rightarrow {}^4\text{A}_{1\text{g}}(\text{G})$ transition, respectively, suggesting its octahedral nature [31]. The appearance of three bands in the regions 10526 cm^{-1} [${}^3\text{A}_{2\text{g}}(\text{F}) \rightarrow {}^3\text{T}_{2\text{g}}(\text{F})(\nu_1)$], 15670 cm^{-1} [${}^3\text{A}_{2\text{g}}(\text{F}) \rightarrow {}^3\text{T}_{1\text{g}}(\text{F})(\nu_2)$] and 24490 cm^{-1} [${}^3\text{A}_{2\text{g}}(\text{F}) \rightarrow {}^3\text{T}_{1\text{g}}(\text{P})(\nu_3)$] in the electronic spectra of Ni complex suggested its octahedral geometry [32]. The Cu (II) complex register two broad bands at 14708 cm^{-1} and 24857 cm^{-1} . These may be, respectively, due to ${}^2\text{B}_{1\text{g}} \rightarrow {}^2\text{A}_{1\text{g}}$ and ${}^2\text{B}_{1\text{g}} \rightarrow {}^2\text{E}_{\text{g}}$ transitions of square planar Cu(II) complex [33]. The electronic spectra of Co complex exhibited bands at 15200 and 10120 cm^{-1} . The bands were assigned due to $d_{xy} - d_{yz}$ spin allowed transition and ${}^2\text{A}_{1\text{g}} \rightarrow {}^2\text{E}_{\text{g}}$ transition in a square planar field [34]. Reflectance spectrum of the uranyl polychelates exhibit bands at 18181 , 23125 , and 39020 cm^{-1} consistent with the vibronic structure of the triatomic entity of the UO_2 group [35].

3.3. Magnetic susceptibility

The magnetic moment of the iron complex is 5.92 BM which is closer to the spin only value indicating an octahedral structure for the complex [36].

The cobalt complex displayed a magnetic moment of 2.75 BM which corresponds to the low spin square planar geometry of the complex [36]. The effective magnetic moment value of 3.34 BM of the nickel complex indicates the octahedral structure of the complex [36]. The magnetic moment of the copper complex is 1.83 BM which fall in the normal range ($1.75\text{--}2.20\text{ BM}$) expected for magnetically dilute Cu(II) complexes [37]. The Zn(II) and U(VI) complexes are diamagnetic.

3.4. Thermal analysis

The thermal data are also in well agreement with the proposed structures. A weight loss of $10\text{--}7\%$ in the temperature range $140\text{--}300\text{ }^\circ\text{C}$ was observed in the case of Co(II), Cu(II), Zn(II), and U(VI) complexes suggesting the loss of one molecule of coordinated DMF. For Fe(III) and Ni(II) complexes a loss of weight of $18\text{--}25\%$ was observed in the temperature range $150\text{--}280\text{ }^\circ\text{C}$, which shows the coordination of two and three molecules of DMF, respectively.

3.5. Removal of copper (II) using 2-nitro benzaldehyde Schiff base of amino methylated polystyrene

The polymer anchored ligand has been successfully employed for the removal of Cu(II) from solutions and optimum conditions have been developed. The data are given in Table 2.

3.5.1. Effect of time

A known volume of standard Cu(II) solution was refluxed with 2-nitro benzaldehyde Schiff base of amino methylated polystyrene suspended in DMF at different intervals of time. Concentration of the metal ion left was determined spectrophotometrically [27]. From Fig. 1 it is clear that about 90% removal was achieved within 20 min . Hence the time of reflux was fixed as 20 min .

Table 2
Optimum conditions for the removal of Cu(II)

Amount of ligand	0.01 g
Time of reflux	20 min
pH	4–5.5
Percentage removal ^a	90
Metal ion concentration	30 ppm

^a Average of six replicates.

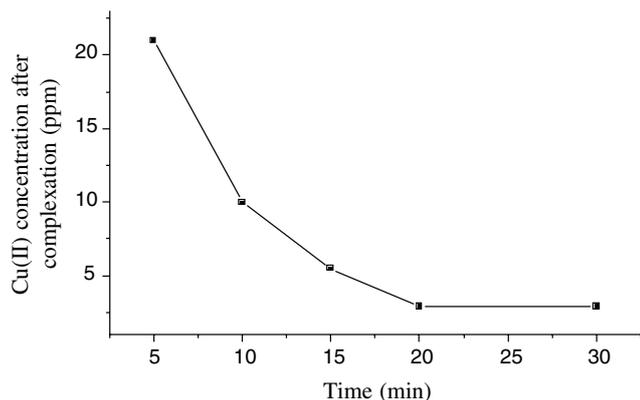


Fig. 1. Effect of time on the removal of Cu(II) using the 2-nitro benzaldehyde Schiff base of amino methylated polystyrene; Cu(II) taken = 30 ppm, mass of ligand = 0.01 g.

3.5.2. Effect of pH

Effect of pH on the removal of Cu(II) was studied by varying the pH of the mixture from 1.5 to 6.0, using buffer solutions, dilute hydrochloric acid and ammonium hydroxide and are shown graphically in Fig. 2. Interestingly, maximum metal ion removal was happened in an acidic pH range of 4–5.5. As the metal precipitates in higher pH, the experiment was limited up to pH 6.

3.5.3. Effect of metal ion concentration

The effect of metal ion concentration was studied in the range 5–70 ppm with a fixed amount of ligand (0.01 g) and from the results (Fig. 3) it is found that at lower concentrations (5–20 ppm) less than 90% removal was achieved. With 30 ppm solution 90% removal was achieved and as the concentration of metal ion increases, the percentage of metal ion

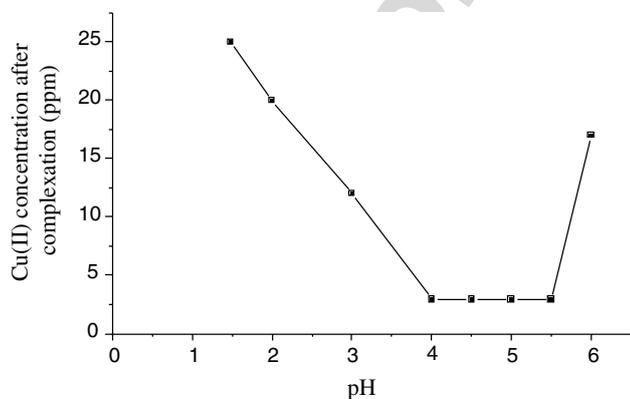


Fig. 2. Effect of pH on the removal of Cu(II) using 2-nitro benzaldehyde Schiff base of amino methylated polystyrene; initial Cu(II) concentration = 30 ppm, mass of ligand = 0.01 g, time = 20 min.

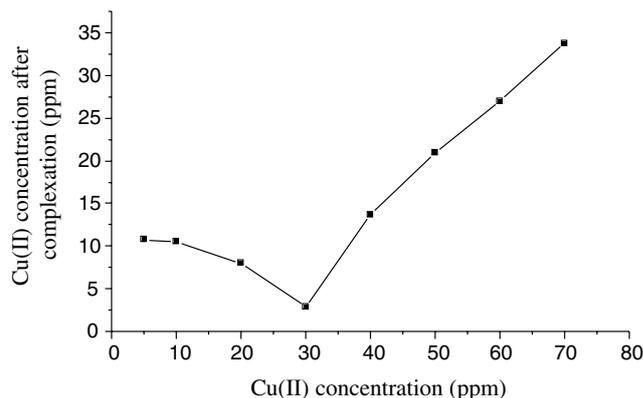


Fig. 3. Effect of metal ion on the removal of Cu(II) using 2-nitro benzaldehyde Schiff base of amino methylated polystyrene; mass of ligand taken = 0.01 g, time 20 min.

removed decreases due to insufficient amount of the ligand. Thus for the studied amount of the ligand, the most effective removal was achieved with a metal ion solution of 30 ppm.

3.5.4. Effect of ligand concentration

The effect of ligand concentration was studied by varying the same from 0.005 to 0.1 g, for a 30 ppm Cu(II) solution. From Fig. 4 it is clear that the percentage of metal ion removed remains the same in the range 0.01–0.1 g. Hence it can be concluded that 0.01 g is the optimum mass of the ligand for achieving a 90% removal from a 30 ppm Cu(II) solution.

3.5.5. Interference due to other ions

A systematic interference study was carried out with foreign ions such as Co(II), Fe(III), Ni(II), Zn(II), UO₂(VI), Na⁺, K⁺, NH₄⁺, Ca²⁺, Cl⁻,

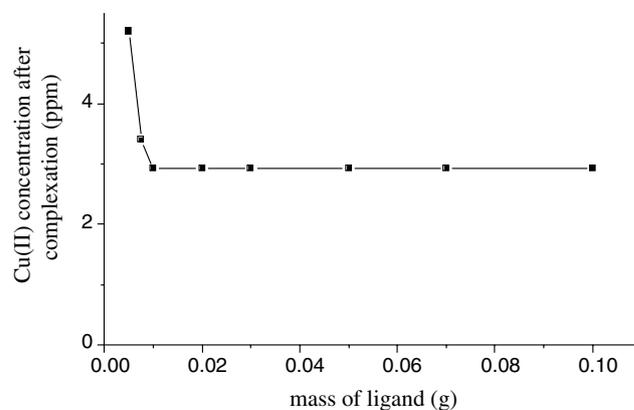


Fig. 4. Effect of ligand on the Cu(II) removal using the 2-nitro benzaldehyde Schiff base of amino methylated polystyrene; Cu(II) taken = 30 ppm, time = 20 min.

Br^- , NO_3^- , NO_2^- , and CH_3COO^- . Cu(II) solution (30 ppm) was mixed with a definite concentration of foreign ion (10–50 ppm). To this mixture DMF suspension of the ligand (0.01 g) was added and the removal experiment was repeated. The experiment was repeated with different concentrations of foreign ion keeping all other factors the same. It was found that most of the ions studied have no interfering action in the removal of Cu(II). However, Fe(III) and Co(II) interfered severely and in fact, Fe(III) interfered even in the presence of ascorbic acid (10 ppm) used as a masking agent.

3.5.6. Resin regeneration

The polystyrene anchored Schiff base can be regenerated by simple acid treatment by the use of HCl (10% v/v).

4. Conclusion

2-Nitrobenzaldehyde Schiff base of aminomethylated polystyrene has been synthesized and a series of six metal complexes were prepared. These complexes have been characterized and were assigned a 1:2 metal:ligand ratio. The ligand could be successfully employed for the metal ion removal study of Cu(II). For a 30 ppm metal ion solution, 90% removal has been achieved by 0.01 g of the ligand. No control of the pH is required for this metal ion removal. Though the method requires heating up to 20 min, it is advantageous in the fact that, the method is simple, the polymer can be regenerated and the amount of polymer required is very little. The only limitation to this method is that Fe(III) and Co(II) interfered in the removal of Cu(II) using the 2-nitrobenzaldehyde Schiff base of amino methylated polystyrene.

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