



Research Article

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Design of copper ion imprinted polymers based on crosslinked 4-vinylpyridine

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ABSTRACT

Copper ion imprinted polymers were synthesized for selective removal of Cu(II) ions from water. The polymers were prepared using template metal ion Cu(II), EGDMA and TTEGDA as crosslinkers using AIBN as initiator. The non-imprinted polymers were also prepared without use of the copper ion. To determine the selectivity of ion imprinted polymers, competitive sorption studies were carried out and proved that ion imprinted polymers (IIP) showed good selectivity for the target metal ion and can be applied for the selective removal of copper ions from aqueous medium.

Keywords: molecular imprinting; crosslinking; templates; swelling; selectivity

INTRODUCTION

The metal ion imprinted polymers are very useful in the selective separation of a specific metal ion from mixture of metal ions, whether the ion is valuable or toxic in the industrial process[1-3]. The synthesis of the metal ion imprinted polymers is usually conducted by cross-linking the monomers with functional groups specifically recognizable to the target (template) metal ion present[4-6]. During this formation, the functional monomers are polymerised in the presence of a template, which is subsequently removed by washing and/or extraction after the polymerisation. Thus, the rebinding template could be recognised by the polymer. MIPs are now well known as synthetic polymeric receptors or robust artificial antibodies and have attracted considerable attention from the scientific and industrial communities owing to their inherent simplicity, reusability, robust polymer network and cost-effectiveness[7-9].

In the present work new type of copper ion imprinted polymers are prepared using different crosslinking agents of varying hydrophilicity. The rigidity and selectivity of the imprinted polymer is mainly influenced by the nature and amount of crosslinking agent used in the synthesis of the imprinted polymers. The imprinted polymer should be rather rigid to preserve the structure of the cavity after splitting of the template. On the other hand flexibility of the polymer facilitates a fast equilibrium between the release and uptake of the template in the cavity. The specific binding of the imprinted polymer is as a result of the rigidity of the polymer backbone to keep the cavities of the original metal ion without any deformation.

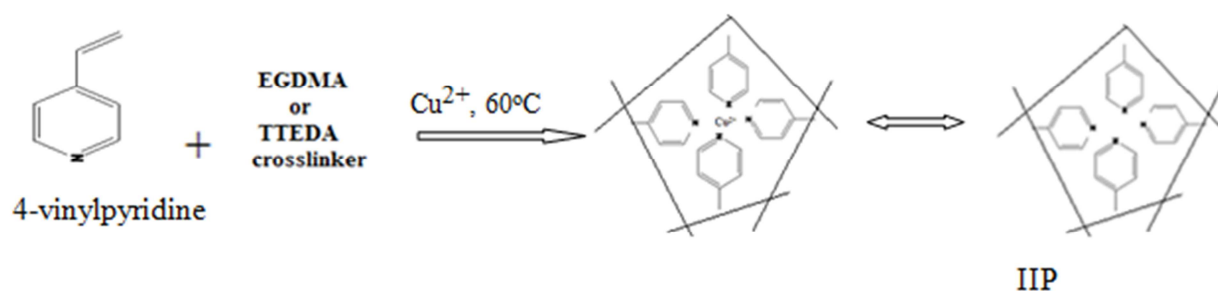
EXPERIMENTAL SECTION

4-vinylpyridine (4-VP) was obtained from Sigma-Aldrich (USA). Ethylene glycol dimethacrylate (EGDMA) and Tetra Ethylene Glycol Diacrylate(TTEGDA) was purchased from Sigma-Aldrich (Germany), 2,2'-azobisisobutyronitrile (AIBN), from Merck (Germany), EGDMA, were purified by distillation under reduced pressure. All solvents were of HPLC grade and used as such. Fourier transform infrared (FTIR) spectra of the metal ion imprinted, non-imprinted, and the copper ion bound polymers were recorded between 4000-800 cm⁻¹, using a Perkin Elmer 400 FTIR spectrophotometer. UV-vis. spectrophotometric measurements were carried out using Shimadzu 2400 UV-vis. spectrophotometer. SEM-EDAX was taken on JEOL-JSM-840A Scanning Electron

Microscope in nitrogen atmosphere. The amount of metal ion adsorbed was determined before and after binding, using Perkin Elmer Atomic Absorption Analyzer 300.

Synthesis of EGDMA- and TTEGDA-crosslinked Cu(II) ion imprinted and non-imprinted 4-vinylpyridine based polymers

In the present study ion imprinted and non-imprinted polymers were synthesized using copper ion as template, EGDMA and TTEGDA as crosslinkers (60 and 80%), 4-vinylpyridine as the functional monomer using AIBN as free radical initiator. The polymerization was carried out at 60°C in methanol-water mixture. The resultant bulk polymer was filtered, washed with ethanol, distilled water and dried in an oven. The non-imprinted polymers were prepared without the template Cu(II) ion.



Scheme 1 Synthesis of crosslinked polymers based on 4-vinyl pyridine

RESULTS AND DISCUSSION

Characterization

The EGDMA- and TTEGDA-crosslinked imprinted and non-imprinted polymers were characterized by FT-IR, UV-vis., SEM, SEM-EDAX and powder XRD techniques.

(i) FT-IR spectra

In copper ion imprinted poly(4-vinylpyridine) an intense band obtained at 1599 cm⁻¹ is due to the presence of C=N group. On metal ion complexation this band is shifted to 1552 cm⁻¹. Further the appearance of a band at 247 cm⁻¹ can be assigned to M-N stretching. In the EGDMA-crosslinked polymers the imprinted and non-imprinted polymers showed band at 1382cm⁻¹ corresponding to C-H bend of CH₃ and the one at 1454 cm⁻¹ is the CH₂ bend of EGDMA. The stretching vibrations observed at 1724 cm⁻¹ indicates the presence of ester linkage of EGDMA. A band at 1600 cm⁻¹ is due to the presence of C=N group. This band is shifted to lower wavelength region ~1568 cm⁻¹ on complexation with Cu(II) ions. This shows the involvement of C=N group of vinylpyridine with Cu(II) ions. The band corresponding to 279 cm⁻¹ can be attributed to Cu(II)-N stretching vibrations. In the case of TTEGDA-crosslinked polymers, band at 1638 cm⁻¹ which corresponds to C=N group is shifted to 1629 cm⁻¹, on copper ion binding.

(ii) UV-vis. spectra

The electronic spectral data of imprinted, non-imprinted and metal bound polymers were carried out using UV-vis. spectrophotometer. The absorption maxima of EGDMA- and TTEGDA-crosslinked Cu(II) ion imprinted polymers are observed at 15,105 - 14,727 cm⁻¹ and from 15,174 to 14,947 cm⁻¹ respectively which are assignable to 2T_{2g} → 2E_g transition (Fig.1). Due to Jahn-Teller distortion, d⁹ configuration of the Cu(II) ion complexes of EGDMA- and TTEGDA-crosslinked system resulted in a tetragonal structure[10].

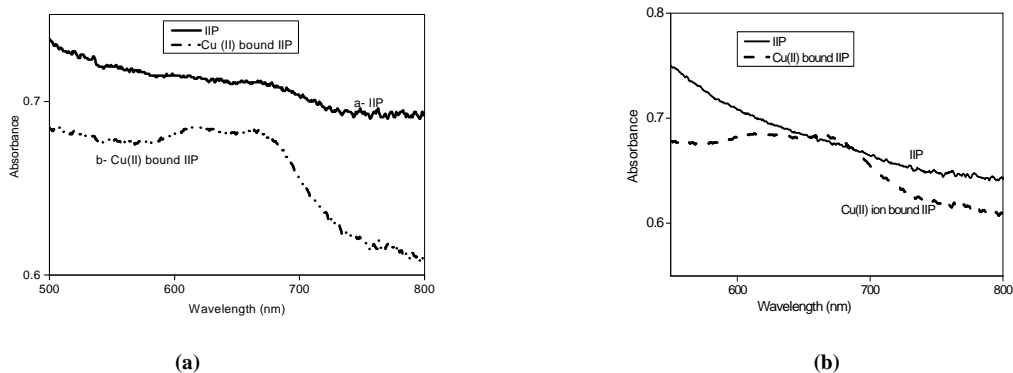


Fig .1 UV-vis. spectra of (a) EGDMA- and (b) TTEGDA-crosslinked Cu(II) ion bound and unbound polymers

(iii) SEM-EDAX

The chemical composition of the polymer was confirmed by SEM-EDAX (Fig.2). The presence and complete removal of copper in Cu(II) ion bound and unbound polymers were confirmed by SEM-EDAX.

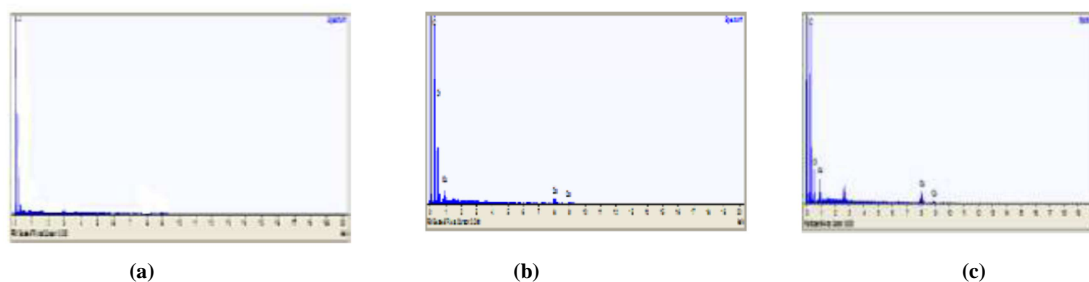


Fig.2 SEM-EDAX of EGDMA- and TTEGDA-crosslinked Cu(II) ion (a) desorbed, and (b) & (c) bound polymers

(iv) X-ray diffraction pattern

X-ray diffraction is one of the most important characterization tools used in solid state chemistry and materials science. The data obtained from XRD curve can be applied for the characterization of polymers. XRD curve of copper ion bound polymers are given in (Fig.3). The crystalline natures of copper ion bound polymers are denoted by sharp peaks in XRD pattern. The XRD pattern of TTEGDA-crosslinked Cu(II) ion bound polymers showed characteristic peaks at 43.6° and that of EGDMA-crosslinked polymers showed peak at 2 theta value 43.7° corresponding to (111) plane of face centered lattice plane (JCPDS, Copper file No. 04-0836.).

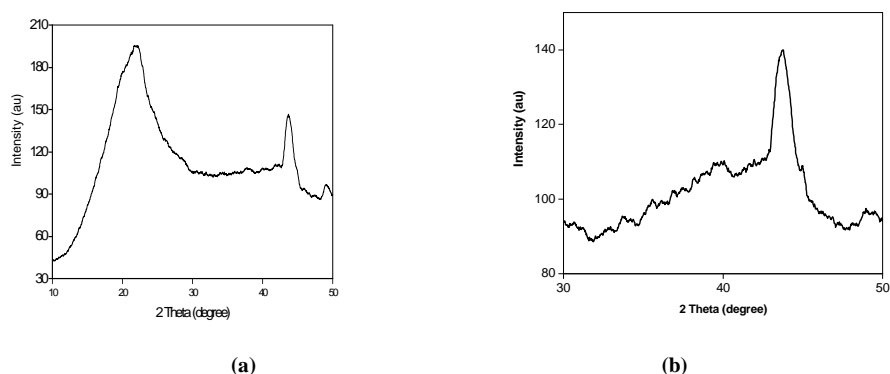


Fig. 3 XRD patterns of (a) EGDMA- and (b) TTEGDA- crosslinked Cu(II) ion bound polymers

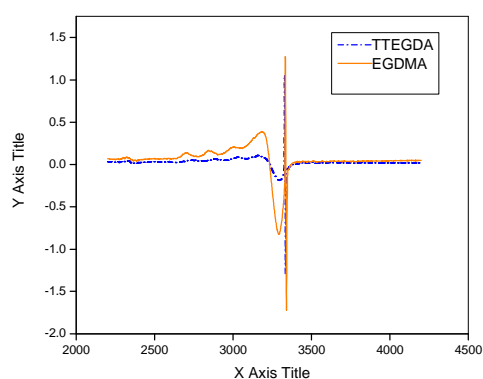
(v) EPR - spectra

Fig. 4 EPR spectra of (a) EGDMA- and (b) TTEGDA- crosslinked Cu(II) ion bound polymers

EPR Spectra of EGDMA and TTEGDA crosslinked copper ion bound polymers are given in (Fig. 4.) and parameters are given table. These values are in agreement with the distorted tetrahedral geometry. The value of g_{\parallel} suggests the covalent nature of Cu-O bond. The bonding parameter (α^2_{Cu}), which is a measure of in plane sigma bonding of the Cu-O bond, was indicating the covalent nature of the complex.

Table .1 EPR parameters of values of EGDMA- and TTEGDA- crosslinked Cu(II) ion bound polymers

Cross linked Polymer	g_{\parallel}	g_{\perp}	A_{\parallel}	A_{\perp}	α^2Cu
EGDMA	2.25	2.03	160	57	0.73
TTEGDA	2.22	2.21	155	34	0.76

Swelling studies

Swelling studies of imprinted and non-imprinted polymers of varying extent of crosslinking were carried out by immersing the polymers in water for 24 h. The EWC values of imprinted and non-imprinted polymers are given in Table .2. TTEGDA-crosslinked polymers have high swelling capacity compared to EGDMA-crosslinked polymers. This is due to the high flexibility of TTEGDA crosslinking agent. In general EWC(%) of the imprinted polymer is higher than that of the non-imprinted polymer. The copper ion bound polymers showed low EWC values compared to unbound polymers. This is due to additional crosslinking on Cu(II) ion complexation resulting in the contraction of the polymer chains which results in decrease in swelling.

Table. 2 EWC(%) values of Cu(II) ion imprinted, non-imprinted, and Cu(II) ion bound polymers

Polymer used	TTEGDA-crosslinked	EGDMA-crosslinked
IIP	99	98
NIP	95	93
Cu(II) ion bound IIP	96	94
Cu(II) ion bound NIP	92	89

Optimization of conditions of metal ion binding

The conditions of Cu(II) ion rebinding were optimized by studying the Cu(II) ion rebinding of both TTEGDA- and EGDMA-crosslinked (60 and 80%) polymers with varying time, concentration and pH.

(i) Metal ion binding studies

The metal ion binding studies of EGDMA- and TTEGDA-crosslinked Cu(II) ion imprinted and non-imprinted polymers were carried out towards Cu(II), Co(II) and Ni(II) ions of varying concentration. In all cases Cu(II) ion imprinted polymer rebind Cu(II) ions specifically than Co(II) and Ni(II) ions and the binding increases with increase in concentration. TTEGDA-crosslinked polymers showed high binding capacity compared to EGDMA-crosslinked polymers due to hydrophilic nature and also metal ion binding decreases with increase in crosslink density (Fig.5).

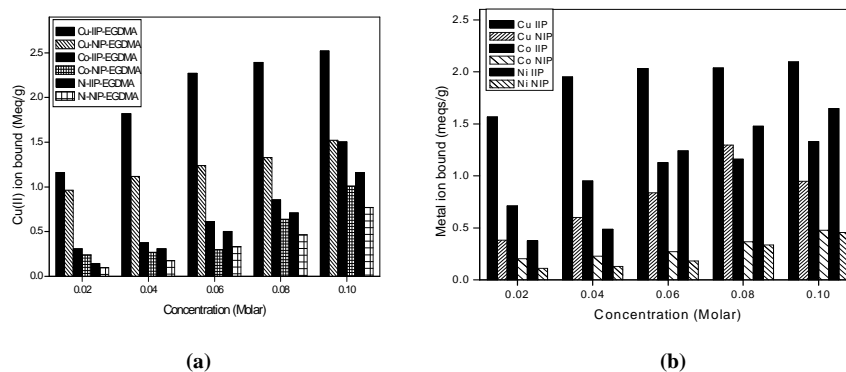


Fig. 5 Effect of concentration of metal ion solution on its binding by 60% (a) EGDMA - and (b) TTEGDA-crosslinked Cu(II) ion imprinted and non-imprinted polymers

(ii) Time dependence on Cu(II) ion binding

The dependence of time on metal ion binding of the polymers was investigated by batch equilibration method (Fig.6). The imprinted polymer possesses shape and complimentary binding sites which took more time to attain saturation. This is because the template molecule has to penetrate through the highly crosslinked polymer networks to access imprinted cavities for rebinding. In non-imprinted polymers there is no such specific arrangement of binding sites so the binding of the template is fast. The IIP acquired saturation within 120 min for TTEGDA- and 135 min for EGDMA-crosslinked ion imprinted polymers whereas NIP required 110 min.

(iii) pH dependence on Cu(II) ion binding

The pH of the medium has a significant effect on metal ion binding. The metal ion binding of TTEGDA- and EGDMA-crosslinked Cu(II) ion imprinted and non-imprinted polymers were investigated by varying pH from 3-6. In the entire cases copper ion binding increased with increase in pH, reached an optimum value and decreased. At

lower pH value protonation of the polymer took place leading to lower metal ion uptake (Fig.7 a,b). The optimum pH for Cu(II) ion binding was found to be 5.5 in the case of both EGDMA and TTEGDA crosslinked polymers

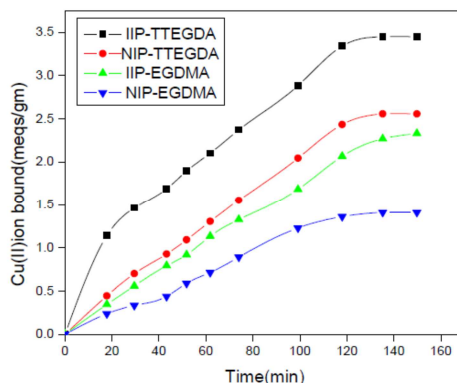


Fig. 6 Effect of time on Cu(II) ion uptake by 60% EGDMA- and TTEGDA- crosslinked Cu(II) ion imprinted and non-imprinted polymers

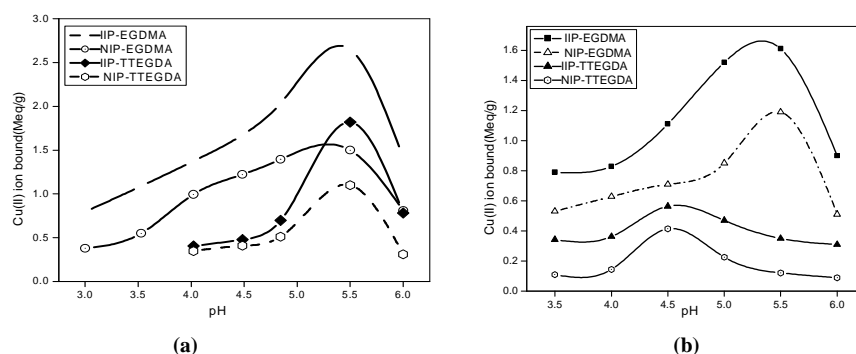


Fig. 7 Effect of pH on copper ion binding by (a) 60%, (b) 80% EGDMA- and TTEGDA- crosslinked Cu(II) ion imprinted and non-imprinted polymers

Sorption studies

The effect of concentration of metal ion solution on sorption rate and capacity were studied. Definite amount of imprinted and non-imprinted polymers were added to 10 ml of metal ion solution. The solutions were shaken in closed flasks. At regular intervals of time metal ion bound was determined by AAS. The sorption characteristics were assessed by plotting both Langmuir and Freundlich isotherms. The results obtained are given in Fig.8 which describes that Langmuir type sorption took place in both EGDMA- and TTEGDA-crosslinked polymers.

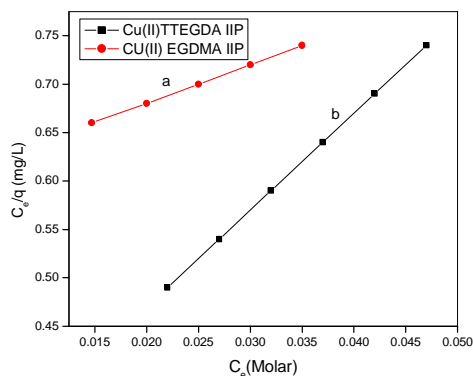


Fig. 8 Langmuir isotherm for 60% (a) EGDMA - and, (b) TTEGDA-crosslinked Cu(II) ion imprinted polymers

Selectivity studies

Selectivity studies were carried out using 60% EGDMA- and TTEGDA- crosslinked polymers. In the case of EGDMA-crosslinked polymers maximum selectivity is obtained in copper-cobalt mixture compared to copper-nickel mixture. Compared to TTEGDA-crosslinked polymer EGDMA-crosslinked system showed effective separation (Fig.9). This is due to the fact that functional host molecules on the imprinted polymer surface are immobilized with strict configuration suitable for Cu(II) ions, and that the ionic recognition is influenced by the nature of metal ion, ionic radius and charge.

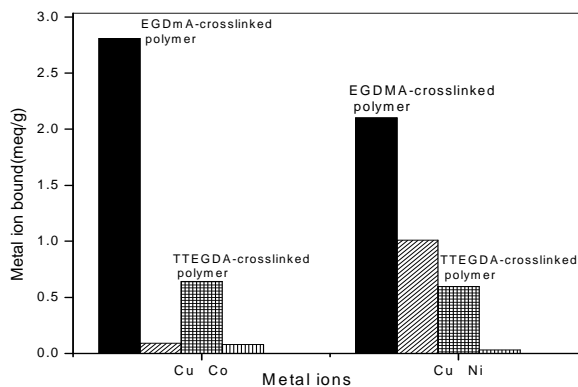


Fig.9 Selectivity studies of copper ion imprinted polymers based on 4-vinyl pyridine

Analysis of waste water

The synthesized copper ion imprinted polymers based on crosslinked poly (4-vinylpyridine) were applied for the selective separation of copper ions from water samples collected from Vembanadu lake, by column method and analyzed by AAS. The obtained values described that the developed copper ion imprinted polymers are effective sorbents for removal of copper ions from water samples. The results are listed in Table 3.

Table. 3 Analysis of waste water

Polymer used	Cu(II) ion found in lake water (mg/L)	Removed (mg/L)	Recovery (%)
EGDMA-crosslinked	0.66	0.640	98
TTEGDA-crosslinked	0.66	0.631	97

CONCLUSION

Ion imprinting technology leads to highly stable synthetic polymers possessing selective molecular recognition properties. The present paper report the possibilities of developing Cu(II) ion selective polymers by ion imprinting approach. The synthesized Cu(II) ion imprinted polymer possess high sorption capacity. Swelling of imprinted polymer is higher than that of non-imprinted system and decreased on complexation. The sorption of Cu(II) ions increased with increase in pH and a saturation value was obtained at pH 5.5. Copper ion imprinted polymer exhibited high selectivity towards Cu(II) ions from its mixture with Co(II), Cu(II) and Ni(II) ions than non-imprinted polymer. The prepared polymer was stable and showed good selectivity and fast rebinding capacity towards Cu(II) ion compared with other sorbents. On the basis of all the above experimental results it can be concluded that, the developed Cu(II) ion imprinted polymer has very good application prospects in the separation of Cu(II) ions from mixture of metal ions and it was proved successfully that it is a good sorbent for copper ion from waste water samples.

In general ion imprinted polymers showed memory for the desorbed metal ion. This kind of recognition property is obtained by keeping the geometry of the desorbed metal ion as such during the rebinding process which in turn depends on the stability of the polymer matrix. The stability of the polymer matrix is depended on the nature of the monomers and extent of crosslinking agent. The memory of the metal ion desorbed system could be exploited for the specific and selective sorption of desorbed metal ions from a mixture of metal ions. Thus the developed ion imprinted interpenetrating polymer networks can be used as an effective biosorbent for removing metal ions from aqueous environment.

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