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A Cu(II) ion selective polymer by molecular imprinting method

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ABSTRACT

A molecular imprinted Cu(II) ion selective polymer with high specificity and selectivity was designed by polymerisztion of 4-vinyl pyridine and ethylene glycol dimethacrylate (EGDMA) as functional monomer and crosslinking agent respectively and azo-bis-isobutyronitrile (AIBN) as initiator. The template used here was Cu(II) ion. The characterization is done by FT-IR and UV-vis. and powder-XRD and EPR spectral methods. Non-imprinted polymers were also synthesized.

Keywords: Molecular imprinting, metal ion, polymers, selectivity, specificity

INTRODUCTION

Molecular imprinting is a promising technique for the development of materials with pre-designed recognition sites that are complementary to the template molecules in size, shape and functionary1. Recently, molecular imprinted polymers have aroused extensive attention and been widely applied in many fields, such as solid-phase extraction, chemical sensors, and artificial antibodies owing to their desired selectivity, thermal stability, physical robustness as well as low cost and easy preparation [1]. Herbicides such as determination of phenoxy acetic acid polymers were synthesized and their selectivity studies were reported [2]. Recently theophiline imprinted polymer were synthesized and characterized. The developed system shows high specificity and selectivity [3]. Metal ion imprinted polymers are an important branch of molecular imprinted polymers. It is very important and emphasis on the necessities of novel imprinting methods. In metal ion imprinting metal cations are the template for the imprinting process.

EXPERIMENTAL

Materials and methods

All the polymers involved in the present work were prepared in the laboratory and were characterized. 4-Vinyl pyridine and ethylene glycol dimethacrylate (EGDMA) were purchased from Sigma Aldrich, Bangalore, India. The polymerization initiator 2,2-azo-bis-isobutyronitrile was from Merck, Germany. The metal salts copper(II) acetate, cobalt(II) chloride and nickel(II) chloride were AR grade and purchased from Merck, India. Solvents used were of AR grade and purified by standard methods.

Instrumental

FT-IR spectra were recorded on a Perkin-Elmer Spectrum-400 spectrophotometer. UV measurements were carried out on Shimadzu UV-vis 2400 spectrophotometer. The amount of metal ions was determined by Perkin Elmer A Analyst 300 atomic absorption spectrophotometer.

The Electron Paramagnetic Resonanance (EPR) spectra were recorded on a EPR-Varian E-12 instrument.

Effect of pH on metal ion binding

Another series of experiments was conducted to study the effect of pH. Binding studies are sensitive to variations in pH of the medium. 50 mg of metal ion imprinted polymer and non-imprinted polymers were subjected to rebinding using Cu(II) ion solution at different pH. The amount of Cu(II) ion bound at different pH were calculated.

Selectivity studies

Column experiment: 100 mg of EGDMA-crosslinked Cu(II) ion imprinted or non-imprinted polymers were slurred

with de mineralized water (DMW) and then poured into a pyrex glass column (i.d. 4.0 mm) plucked with small portion of glass wool at the bottom. The coloumn was preconditioned by passing DMW and then metal ion solution. This study was implemented by the mixture of metal ion solutions of Cu(II), (0.001 M; 10 mL) + Co(II), (0.001 M; 10 mL) and Cu(II), (0.001 M; 10 mL) + Ni(II), (0.001 M; 10 mL) was passed through the coloumn at the flow rate of ~ 0.5 mL min^{-1}. The eluted solution was collected and the amount of metal ions bound was determined by Atomic Absorption Spectrophotometric method.

Kinetic studies: 50 mg of the EGDMA-crosslinked Cu(II) ion imprinted polymer was equilibrated with 10 mL of Cu(II) ion solution(8×10^{-2} M) at different temperature range (30-60^{o}C). The amount of metal ions adsorbed was calculated by spectrophotometric method. The effect of temperature on the imprinting processes of the imprinted polymer was observed at different temperatures (30-60^{o}C) and the thermodynamic parameters were determined.

RESULT AND DISCUSSION

Synthesis of EGDMA-crosslinked Cu(II) ion imprinted and non-imprinted polymers

The EGDMA-crosslinked Cu(II) ion imprinted and non-imprinted polymers were prepared by the polymerization of 4-vinyl pyridine and EGDMA with methanol-water mixture as solvent. AIBN was used as the free radical initiator. The template Cu(II) ion was removed from the obtained polymer by dilute acid. After desorption of the metal ion the polymer was washed with distilled water, acetone and alkali. A non-imprinted polymer was also prepared using the same method.

FT-IR spectra

The synthesized polymer was characterized by FT-IR, UV-vis. and powder-XRD techniques.

FT-IR spectra

The imprinted and non-imprinted polymer showed band at 1384 cm^{-1} which corresponds to C-H bend of CH_3 and that at 1454 cm^{-1} is CH_2 bend of EGDMA. The stretching vibrations observed at 1724 cm^{-1} indicates the presence of ester linkage of EGDMA. An intense band at 1600 cm^{-1} is due to the presence of C=N group. On complexation with Cu(II) ion it is shifted to 1569 cm^{-1}. Further, band at 279 cm^{-1} can be attributed to Cu(II)-N stretching vibrations [4].

UV-vis. spectra and Powder-XRD

Electronic spectra provide an accurate and simple method for determining geometry around the transition metal ions [5]. It show that the absorption maxima of EGDMA-crosslinked 4-vinyl pyridine in the region 15,197-16,207 cm^{-1} is assignable to $^{2}T_{2g} \rightarrow {}^{2}Eg$ transition. of EGDMA-crosslinked Cu(II) complex[6]. The powder-XRD data resulted that the crystalline peak gives sharp narrow diffraction pattern [7]. Cu(II) ion complexation shows in an increase in ordered arrangement in the polymer matrix as evidenced by the appearance of sharp peak. Figure 1. shows the amorphous and crystalline nature of imprinted polymers and Cu(II) ion bound imprinted polymers respectively.

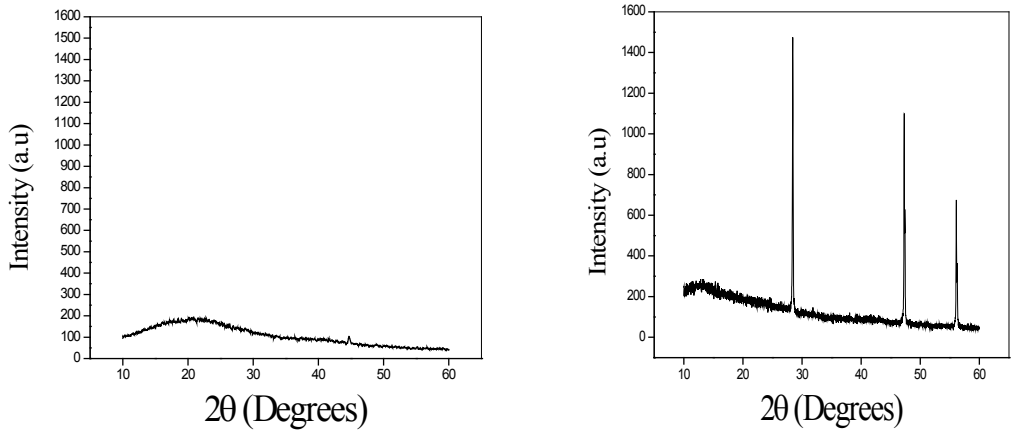

Figure 1. X-ray Diffractograms of EGDMA-crosslinked (a) Cu(II) ion desorbed imprinted polymers and (b) Cu(II) ion complexed polymers.

EPR spectra

The EPR spectral pattern of paramagnetic Cu(II) complexes is influenced by the number of coordinating ligands

as well as the geometry of the complex [8,9]. The EPR spectra of EGDMA-crosslinked Cu(II) ion complexes are compared with the EPR spectra of divinylbencene (DVB), and 1,4-butane diol dimethacrylate (BDDMA-crosslinked Cu(II) ion complexes are given in Figure 2. The EPR parameters of DVB-, EGDMA- and BDDMA-crosslinked Cu(II) ion imprinted polymer complexes were calculated (Table 1). These values indicate tetragonal geometry of Cu(II) complexes. The bonding parameter (α^2 Cu) of Cu(II) complexes indicates the covalency of the ligand group with the coordinating metal ion and it is calculated using the Kivelson and Neimen equation [10]

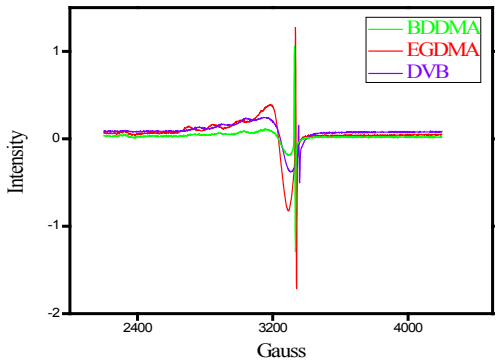

Figure 2. EPR spectra of Cu(II) complexes of DVB-, EGDMA- and BDDMA-crosslinked Cu(II) ion imprinted polymers

Table 1. The EPR parameters of DVB-, EGDMA- and BDDMA-crosslinked Cu(II) ion complexed polymers

Crosslinker	EPR parameters				
	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$	$A_{\perp}$	α^2Cu(II)
DVB	2.224	2.171	150	33.00	0.7554
EGDMA	2.240	2.040	160	56.60	0.7227
BDDMA	2.184	2.081	170	53.33	0.8045

$$\alpha^2 Cu = -(A_{\parallel}/0.036) + (g_{\parallel} - 2.002) + 3/7(g_{\perp} - 2.002) + 0.04$$

Effect of pH

The pH of the medium has a significant effect on metal ion binding [11]. pH dependence on metal ion complexation was investigated towards Cu(II) ions. The metal ion binding was found to increase with increase in pH up to the optimum pH and then decreased.The optimum pH of Cu(II) ion solution was found to be 5.4. The dependence of pH on Cu(II) ion uptake by the imprinted and non-imprinted polymers is given in Figure 3.

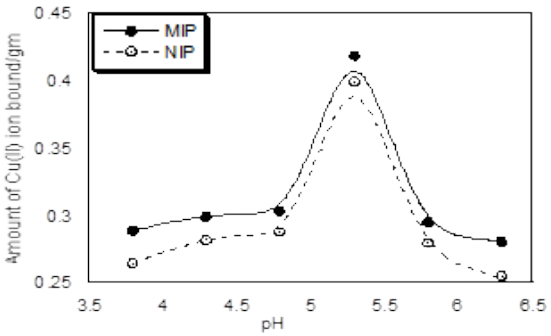

Figure 3. Dependence of pH on Cu(II) ion uptake by 25% EGDMA-crosslinked Cu(II) ion imprinted and non-imprinted polymers

Selectivity studies

The metal ion selectivity studies of EGDMA-crosslinked Cu(II) ion imprinted and non-imprinted polymers was investigated [12]. The results revealed that the Cu(II) ion imprinted system selectively binds Cu(II) ion from a mixture of Cu(II)+Co(II) ion mixture. In the case of Cu(II)+Ni(II) ion mixture, low selectivity values were observed for the Cu(II) ion, there for a complete separation was not possible. Table 2 showed lower selectivity coefficient and higher selectivity of Cu(II)+Co(II) ion mixture than that of Cu(II)+Ni(II) ion mixture.

Table 2. Selectivity coefficients of EGDMA-crosslinked Cu(II) ion imprinted and non-imprinted polymers from Cu(II)+Co(II) and Cu(II)+Ni(II) ion mixture

Mixture of metal ions	Selectivity coefficient (α)	
	MIP	NIP
Cu(II)+Co(II)	0.98	1.23
Cu(II)+Ni(II)	5.68	4.89

Kinetic studies

The effect of temperature on the imprinting processes of EGDMA-crosslinked Cu(II) ion imprinted polymer was observed by kinetic studies. The adsorption studies were conducted at temperatures between 30 and 60°C. The obtained results showed that increase in temperature favors the rebinding process up to 50°C. Adsorption of metal ion increased quantitatively up to a temperature range 40-50°C. Further increase in temperature decreases the metal ion uptake from aqueous solution. From the results the thermodynamic parameters such as free energy change (ΔG^{o}), enthalpy change (ΔH^{o}), entropy change (ΔS^{o}) were determined using the following equations [13]

The thermodynamic parameters of the adsorption process of Cu(II) ions on EGDMA-crosslinked Cu(II) ion imprinted polymer obtained are given in Table 3 and Figure 4.

Table 3. Thermodynamic parameters of the adsorption process of Cu(II) ions on EGDMcrosslinked Cu(II) ion imprinted polymer

Thermodynamic parameters	
ΔH^{o}	2.53 kJ mol^{-1}
ΔS^{o}	3.71 kJ K^{-1} mol^{-1}
ΔG^{o}	4.95 ×10^{-4} kJ mol^{-1}

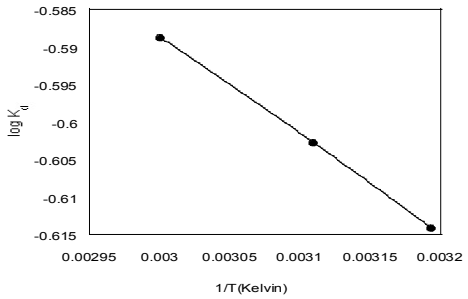

Figure 4. Log K_d vs. 1/T plot for the adsorption of Cu(II) ions onto EGDMA-crosslinked Cu(II)ion imprinted polymer; time of contact 4 h; temperature, 25 ± 2°C.

The experimental data of the adsorption kinetics of EGDMA-crosslinked Cu(II) ion imprinted polymer were applied to the first order kinetics according to the equation $\ln (Qe - Qt) = \ln Qe - K_1 t$

Where Q_e and Q_t are the amount of metal ion adsorbed on adsorbent (mmol/gm) at equilibrium and at time t respectively, and k_1 is the rate constant of first-order adsorption (min^{-1}) [14]. The low correlation coefficient value of 0.95954 indicates that the experimental data does not fit well with the first order kinetics. Then they were subjected to the second order kinetics represented by the equation

$$\frac{t}{Qt} = \frac{1}{(k_2 Qe^2)} + \frac{t}{Qe}$$

Where Q_e and Q_t are the amount of metal ion adsorbed on adsorbent (mmol/gm) at equilibrium and time t respectively, and k_2 is the rate constant of second-order adsorption (gm/mg min^{-1}) . The correlation coefficient in this case was found to be 0.9994. Thus the experimental data is in good agreement with second order kinetics. The kinetic parameters of the adsorption process of Cu(II) ions on EGDMA- crosslinked Cu(II) ion imprinted polymer are given in Table 4.

Table 4. Kinetic parameters of the adsorption process of Cu(II) ions on EGDMA- crosslinked Cu(II) ion imprinted polymer

Kinetic approaches	Rate constant (*k*)	Correlation coefficient (R)
First-order kinetics	k_1 = 1.6326 (×10^{-2} min^{-1})	R_1 = 0.95954
Second-order kinetics	k_2 = 0.1929 [×10^{-3}gm/(mg min^{-1})]	R_2 = 0.99936

CONCLUSION

A Cu(II) ion selective polymer was developed by metal ion imprinting technique. The metal ion imprinted and non-imprinted systems were characterized by FT-IR, UV-vis. and powder X-RD techniques.. When the concentration of Cu(II) ion solution increases the amount of metal ions bound to the polymer increases. The binding of metal ions is pH dependent. The Cu(II) ions are selectively bound from its mixture with Co(II) and Ni(II) ions. Thus the results from the studied system proved the importance of tailoring metal ion imprinted system in the separation of metal ions.

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