Melamine–formaldehyde–NTA chelating gel resin: Synthesis, characterization and application for copper(II) ion removal from synthetic wastewater

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Abstract

A new chelating resin was synthesised by anchoring nitrilotriacetic acid (NTA) to melamine during the melamine–formaldehyde gelling reaction in the presence of water, using acetone and guaiacol as a porogen mixture. This technique gives a porous chelating gel resin capable of removing heavy metals from wastewater. FT-IR, XRD, elemental analysis, surface area and water regain measurements were conducted for characterization of the new chelating gel resin. A comprehensive adsorption study (kinetics isotherm, and thermodynamics) of Cu(II) removal from synthetic acidic aqueous solutions by adsorption on this resin was conducted regarding the effects of time, temperature, initial pH and copper(II) initial concentration.

1. Introduction

Water contamination by heavy metals is of great importance from a health point of view because of its high toxicity and susceptible carcinogenic effect. The threat to mankind comes from the accumulation of such non-biodegradable ions in water and soil polluted by contaminants from mining and industry. Adsorption of Cu(II) was used in this study as it is usually found in wastewaters from a number of sources: mining, plating baths, coal burning, wire manufacturing, steel manufacturing, fertilizer, pigments, printing circuits and paints. The process of heavy metals remediation is continually evolving and includes the preparation of new materials and the improvement of removal techniques.

Chelating resins are promising substances for the removal of heavy metals from wastewaters because of their multi-adsorbing functions: ion exchange, physical adsorption and chelation [1]. Reports of different types of chelating resins include polyethy-lene polyamine, polythioether, dithiocarboxylic acid, mercapto, mercatoamine, thiourea and heterocycle [2]. Many different kinds of functionalities have been studied for their potential to remove metal ions from wastewater such as, iminoacetic acid, Schiff bases, hydroxamic acid, amidoxime, thiol, thizole and amine [3]. The chelating mechanism depends on coordination of the metal ion to active chelating sites present within the resin. These active sites characterized by functional groups which are capable of coordination: these would include donor atoms such as O, N, S and P [4,5].

It is necessary for the resin to have a high surface area to accommodate as many metal ions as possible, good porosity to facilitate the transportation of ions inside the pores (kinetics) and a suitable hydrophilic character (solution-flow driving force).

Recently, the synthesis of melamine–formaldehyde (MF) by the sol–gel condensation method has attracted attention because of the highly porous organic and carbon aerogels that may be produced. Indeed, carbon aerogels have many applications in different fields such as gas adsorption, separation of heavy metals, purification of drinking water, electronic capacitors and fuel cell electrodes [6]. Although MF and modified-MF organic resins have potential use as metal adsorbents, few publications can be found about this application. For example, the terpolymer

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resin (salicylic acid–melamine–formaldehyde) was synthesised and its ion-exchange properties towards Cu(II), Ni(II), Co(II), Zn(II), Cd(II), Pb(II) and Fe(III) was examined. This terpolymer showed high selectivity for Cu(II), Ni(II) and Fe(III) [7]. Resins having an amide group as a chelating-function group or anchoring bond are common. For example, the adsorption behaviour of Pb(II), Zn(II) and Cu(II) on cross-linked pectic and alginic acids, and their amide derivatives was tested [8]. Poly(amide-ester)s from 2,6-pyridine dicarboxylic acid and ethanolamine derivatives were synthesised. Their adsorption behaviour towards heavy metals was studied and high selectivity of such polycondensate towards Au(III) was found [9].

The aim of our research is to investigate the feasibility of employing MF gel resin (benefiting from its high porosity) as a medium for heavy metal adsorption from wastewaters by activating it with organic chelating agents. In this paper, the synthesis of melamine–formaldehyde hydrogel modified with nitrilotriacetic acid (NTA), a well-known strong chelating agent, was conducted to produce a chelating gel resin with suitable porosity and surface area. We believe that NTA is anchored directly by carboxylic groups forming amide bonds with some of the amine groups belonging to the melamine molecule in the resin network structure during the course of the main melamine–formaldehyde gel reaction [10]. A solvent mixture, as a porogen, was used instead of fumed silica to simplify the synthesis procedure and lower the cost.

2. Theory

2.1. Resin charactrization

The water regain factor represents the percentage of water intrinsically held by the resin. To calculate this factor, the following equation was employed:

$$W\% = \frac{W_w - W_d}{W_w} \times 100 \tag{1}$$

where W_w and W_d are the wet and dry weights of the resin, respectively.

The surface area of the resin was calculated using the following equation:

$$A_s = \frac{G N_{Av} \varnothing 10^{-20}}{M M_w} \tag{2}$$

where A_s is the gel resin surface area in m^2/g, G the amount of methylene blue adsorbed (g), N_{Av} the Avogadro's number $(6.02 \times 10^{23}\ \text{mol}^{-1})$, $\varnothing$ the methylene blue molecular cross-section (197.2 Å^2), M_W the molecular weight of methylene blue (373.9 g mol^{-1}) and M is the mass of adsorbent (g).

The IR spectra of MF and MF–NTA resins were measured in the range 400–4000 cm^{-1} to detect any difference in structure and to investigate the anchoring of NTA through the amide bond. CHNO elemental analysis was conducted for resin samples to confirm the IR result and to investigate the percentage of NTA anchoring in the MF–NTA structure. The X-ray diffraction (XRD) patterns of the MF and MF–NTA gel resins were

recorded to reveal their morphology type. The range of diffraction angles (2θ) was 6–40°.

2.2. Cu(II) adsorption

The kinetics study is essential to determine the rate of adsorption. In our study we used two classic models: Lagergren (pseudo first-order) [11–15] and reversible first-order equations [13,15–17]. The latter model is always applied for the adsorption of ions on a heterogeneous surface [16–18]. The integrated form of the Lagergren pseudo first-order equation was used to determine the adsorption rate constant. It is expressed as follows:

$$\log(q_e - q) = \log q_e - k_{ad}\frac{t}{2.303} \tag{3}$$

where q_e and q are the solute amounts adsorbed by the gel resin (mg/g) at equilibrium and time t, respectively. The term k_{ad} is the adsorption rate constant (min^{-1}). The reversible first-order equation has the following linear form:

$$\ln(1 - U_t) = \ln\left(1 - \frac{x}{X_e}\right) = -kt \tag{4}$$

where $U_t = x/X_e$ (x is the related concentration of solute adsorbed on resin at certain time and X_e is the concentration of solute at equilibrium). The term k is the overall adsorption rate constant and equals the sum of k_1 and k_2 where k_1 and k_2 are the forward (adsorption) and backward (desorption) rate constants, respectively. To calculate these parameters, another auxiliary equation was used [17]:

$$K_c = \frac{X_e}{C_i - X_e} = \frac{k_1}{k_2} \tag{5}$$

where K_c is the equilibrium constant and C_i is the initial ion concentration.

For thermodynamic studies, the adsorption equilibrium stability constants ($K_c = k_1/k_2$) derived from the reversible first-order equation was considered. According to literature [18], $K_c = C_s/C_e$, where C_s and C_e are the adsorbed and equilibrium concentrations (mg/l), respectively. We preferred to use the former definition as it is more precise. The Gibbs free energy of the adsorption process (ΔG^{ads}) was calculated using the Van't Hoff equation:

$$\Delta G^{ads} = -RT \ln K_c \tag{6}$$

The enthalpy (ΔH^{ads}) and entropy of adsorption (ΔS^{ads}) were calculated from the slope and intercept of the plot of $\ln K_c$ versus $1/T$:

$$\ln K_c = \frac{\Delta S^{ads}}{R} - \frac{\Delta H^{ads}}{RT} \tag{7}$$

The adsorption isotherm illustrates the type of interaction between the solute and the adsorbent. At equilibrium the capacity and affinity of the adsorption process can be determined. The Freundlich and Langmuir adsorption models were used in this study [19,20]. Linearised forms of these models were applied

to adsorption equilibrium data from the experiments. For the Freundlich model, the linear equation has the following form:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \qquad (8)$$

where q_e is the adsorbed amount at equilibrium and C_e is the concentration at equilibrium. The terms K_F and n are Freundlich parameters which are related to the adsorption capacity and intensity, respectively. The Freundlich model assumes a heterogeneous surface where the adsorption sites have a range of energies. For the Langmuir model, the linearised equation has the following known form:

$$\frac{1}{q_e} = \frac{1}{Q_o} + \frac{1}{bQ_oC_e} \qquad (9)$$

where q_e and C_e have the same meaning as for the Freundlich model. The term Q_o is adsorption capacity (mg/g) and term b is related to and energy of adsorption (l/mg). the Langmuir model is based on monolayer adsorption onto sites of equal energy. A related dimensionless factor (R_L) is calculated to indicate whether adsorption is favourable ($0 < R_L < 1$) or not [16,17]. R_L has the following expression:

$$R_L = \frac{1}{1 + bC_i} \qquad (10)$$

The distribution ratio of Cu(II) ion between the gel resin and aqueous phase (D) was calculated at the different pH values under study. The distribution ratio provides information about the activity of the resin towards the Cu(II) ion at different temperatures for different pH values. It is defined as follows:

$$D = \frac{Q_{resin}}{Q_{solution}} \qquad (11)$$

where Q_{resin} is mass (mg) of metal ion adsorbed by 1 g of the resin and $Q_{solution}$ is the mass (mg) of metal present in 1 ml of solution.

3. Experimental

3.1. Materials and instruments

The following analytical grade chemicals were used in this work: $CuCl_2\cdot2H_2O$ (May & Baker Ltd., Dagenham, England), melamine 99% (Aldrich), formaldehyde 38% (BDH), guaiacol (Sigma), acetone (BDH) and NTA (Sigma). Deionised water was used for resin synthesis and the preparation of Cu(II) ion solutions.

The following instruments were used in this study: Perkin–Elmer atomic absorption spectrometer (3100), Shimadzo spectrophotometer (UV-120-02), Hanna instrument pH-meter (H18519), Perkin–Elmer FT-IR spectrometer and Siemens diffractometer (D500).

3.2. Preparation of the MF–NTA resin

Melamine (1.26 g) and NTA (0.64 g) were mixed in 5 ml hot water (pH 1.1) to form dense slurry. Acetone and guaiacol (5 ml

each) were added to this mixture. Finally formaldehyde (2 ml) was added to the mixture and the vial was tightly closed. The vial was agitated until a homogenous suspension was formed and this was then placed in a preheated oven at 150 °C. Shortly before the formation of the solid gel, two distinct phases were observed. The upper one consisted mainly of acetone and guaiacol, and the lower transparent phase of liquid gel phase which converted to solid by the end of reaction (typically 50–55 min). The white gel resin formed was left for an extra 30 min for more cure and NTA anchoring at 100 °C. The solid gel resin was removed from the vial and left on a bench for further curing for about 20 h. During this time most of the acetone was evaporated and most of the guaiacol was exuded. The gel resin sample was ground and washed twice, in each with 200 ml of hot water (95 °C) for 1 h to remove the residual acetone and guaiacol. After washing, the gel resin grains were left to cool for 30 min then washed again five times with deionised water. The excess water was removed by centrifugation. Gel resin grains were then sieved and each fraction was kept in a tightly closed vial.

3.3. Gel resin characterization

3.3.1. Water regain

The gel resin was soaked in deionised water for 48 h to ensure water content equilibrium. The excess water was removed by centrifugation for 30 min at 1000 rpm and then weighed. The same sample was dried at 50 °C for 72 h and reweighed.

3.3.2. Surface area

The surface area of the gel resin was measured by methylene blue adsorption as this material is known to be adsorbed as a monolayer only on solid sorbents [21]. A standard solution of this material was prepared (0.0178 g/l). A calibration curve for methylene blue was drawn ($\lambda = 660$ nm) by measuring diluents from standard stock. To calculate the surface area, 0.1 g of MF–NTA gel resin was treated with 25 ml of methylene blue of concentration 0.0178 g/l. The treatment lasted until there was no further decrease in absorbance. The amount of methylene blue adsorbed was calculated based on concentration difference between the initial and equilibrium values, which were measured by spectrophotometry.

3.3.3. IR, elemental analysis and XRD measurements

The resin samples were dried before IR and CHNO analysis. For XRD, the samples were in the wet form.

3.4. Cu(II) adsorption characterization

3.4.1. Cu(II) solution preparation

A solution of 1000 ppm of Cu(II) ion was prepared by dissolving 2.7143 g of $CuCl_2\cdot2H_2O$ in 1000 ml of deionised water. Other working solutions were prepared from this stock solution by appropriate dilution.

3.4.2. Batch adsorption experiments

All of the following adsorption experiments were conducted by a batch method where a certain volume of Cu(II) solution of

specified initial concentration was treated by a measured weight of adsorbing gel resin. The samples were agitated at a fixed rate of 150 rpm. The experiments were repeated for three temperatures (15, 25 and 35 °C). The grain size of gel resin was also fixed (0.755–1 mm). The use of a smaller grain size would give a higher adsorption rate, but we chose a larger grain size to illustrate the worst-case scenario — if the larger size gives good results, the resin is likely to be promising in practical applications.

The effect of initial pH and kinetic studies were examined in one experiment. A solution of 100 ppm was used. We placed 30 ml volumes of this solution in four separate 250 ml conical flasks. These were adjusted to pH values of 3, 4, 5 and 6. The pH values were adjusted using HCl and NaOH (0.1 and 0.01 M) before adding the MF–NTA gel resin. Then, 0.3 g of the gel resin, corresponding to 0.105 g of dry resin, was added into each flask, which was agitated at the specified temperature. We use the term "gel resin" to specify that the resin include the regaining water. Liquor samples of 1.5 ml were withdrawn from each flask with a micropipette every 10 min for a total period of 1 h. This amount did not affect the adsorption process. The residual concentrations were then measured by atomic absorption.

We studied the adsorption isotherm at a single pH value of 5. We chose a pH of 5 since this is representative of many typical wastewaters. Also, metal ions start to precipitate as hydroxides at a pH of 6 which can give deceiving results. A pH of 2 (or 3) causes hydrolysis of the amide bond and this will decrease the adsorption activity of the resin. The experiments were carried out at temperatures of 15, 25 and 35 °C. For each isotherm, six initial concentrations of Cu(II) ion were used: 50, 60, 70, 80, 90 and 100 ppm. The volume was constant (30 ml in 250 ml conical flask) and the gel resin dosage was 0.3 g. The experiments were conducted by batch agitation at 150 rpm. Liquor samples were withdrawn in the same manner as described above.

For the thermodynamic study, the adsorption equilibrium was investigated for temperatures of 15, 20, 25, 30 and 35 °C. To ensure consistency, each experiment was carried out three times and averages values were taken.

Experiments were conducted with no adsorbent to reveal the effect of glass walls on adsorption which was found negligible.

3.4.3. Regeneration of MF–NTA gel resin

According to the literatures [22,23], the use of mineral acids to elute adsorbed metal ions is avoided because of the hydrolyse tendency of amide group. In some investigations, HCl was used for elution with no mention regarding hydrolysis of amide moieties [24]. In another paper, hot acetic acid was used to elute the metal [25]. We used hot EDTA solution (0.01 M) several times to elute Cu(II) from the gel resin. EDTA has a higher formation stability constant with Cu(II) than that of NTA.

4. Results and discussion

4.1. General

The grains of MF–NTA gel resin are white in colour and insoluble in water, acetone and ethanol. Diluted acids and alkalis do not affect the grains, but concentrated acids may cause hydrolysis of amide groups. It was noticed that the colour of the resin changed from its original white one to a deep pale blue upon Cu(II) adsorption for all samples. This is the same colour for the Cu(II)–NTA complex in aqueous solution. This suggests that the chelating mechanism strongly contributes to the adsorption process. The coordination of Cu(II) to the chelating agent is the same regardless of whether the agent is free (in solution) or anchored to the resin surface [26]. Mass balance calculations revealed that most of the NTA sites react with the Cu(II) ions to form the chelates. This reveals the ease with which the Cu(II) ion is able to access most of the resin porosity and react with the NTA active sites. Also, the study revealed that the ion-exchange mechanism takes place in the removal process especially at higher temperatures. The gel resin was effectively regenerated by washing several times with EDTA solution. This work shows the practical applicability of such a gel resin for the removal Cu(II) from wastewater.

4.2. Water regain and surface area

The water regain for the gelled resin was found to be 36.11 mmol g^{-1} ($W\% = 65$). This relatively high value indicates the surface heterogeneity and hydrophilic character of the gel resin which facilitates the adsorption of metal ions. The surface area of the gel resin was calculated from Eq. (2) to be 163 m^2 g^{-1}.

4.3. Resin structure through IR spectra, elemental analysis and XRD analysis

The IR spectrum of MF–NTA was compared with that of MF resin. Fig. 1 shows the spectra of MF resin and MF–NTA. Several important differences between the spectra were observed. The MF–NTA C=O stretch of the formed amide group appears at 1636 cm^{-1}, the C–N stretch at 1261 cm^{-1}, the N–H out-of-plane bend at 699 cm^{-1}, the In-plane O–H bend of carboxylic group at 1395 cm^{-1}, the C–O stretch of carboxylic group at 1202 cm^{-1} and the out-of-plane O–H bend at 900 cm^{-1}. For the MF resin, the secondary amine C–N stretch appears at 1149 cm^{-1} — this is not found in MF–NTA spectrum. The IR spectra suggest the formation of an amide bond between carboxylic groups of NTA with a primary amine group present in the melamine molecule. Elemental analysis showed an increase of carbon and oxygen contents in the resin at the expense of nitrogen as only one nitrogen atom is present in the NTA molecule (see Table 1). From calculations, 15–25% of melamine molecules were anchored by NTA — that is, about 60% of NTA was anchored to the structure (NTA:melamine = 1:3 ratio). Experiments demonstrated that an excess of NTA produces more amide bonds at the expense of dimethylene ether and diaminomethylene bridges. This causes the resin to lose its mechanical strength. Also, the treatment

Table 1
Elemental analysis of MF and MF–NTA resins

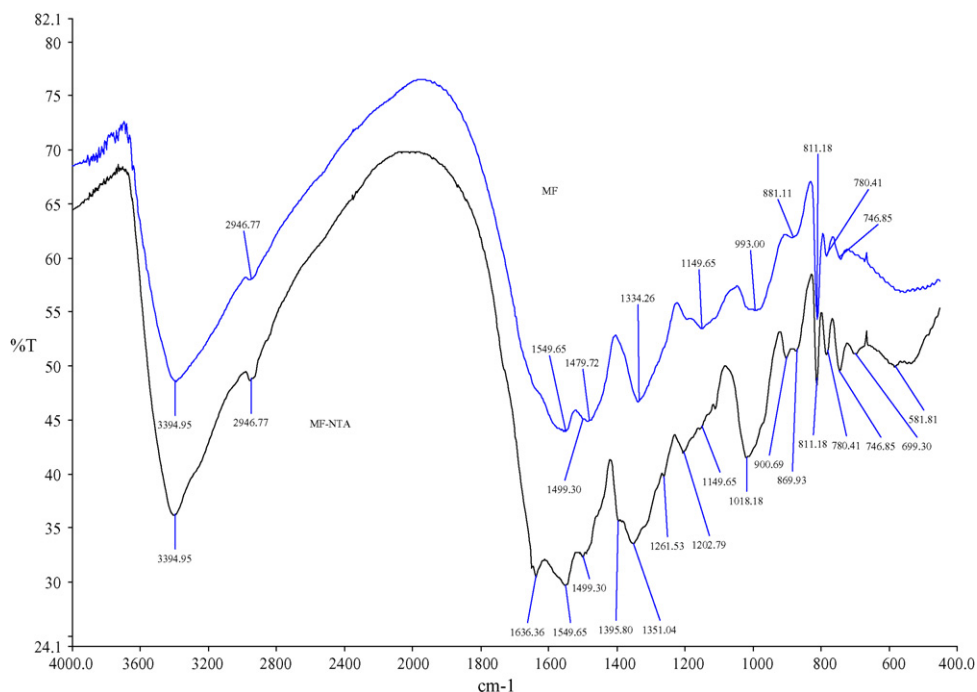| Resin	C	H	N	O
MF	35.14	5.12	42.72	17.02
MF–NTA	40.34	5.34	33.28	21.04

Fig. 1. IR spectra of MF and MF–NTA resins.

of MF–NTA resin with concentrated HCl causes hydrolysis of amide bonds with a consequent reduction in activity. Fig. 2 shows a possible structure for the MF–NTA resin. XRD patterns of MF and MF–NTA gel resin were recorded: the lack of any peak would suggest that the structure is amorphous.

4.4. pH effect and Kinetics of adsorption

The effect of initial pH on adsorption rate is shown in Figs. 3–5 for temperatures of 15, 25 and 35 °C, respectively. The curves are continuous and smooth suggesting a stable and uniform adsorption process. The acidic solutions showed good adsorption behaviour. For example at pH of 5, the removal percentage was 81, 77 and 84% at temperatures 15, 25 and 35 °C, respectively. The removal percentage decreases with increasing acidity and this may contribute to an increase of H^+ ions. It was noticed that all solutions showed a decrease in pH by the end of the experiments. This decrease in pH was mainly due to ion-exchange contribution in the adsorption process. Preliminary experiments showed a higher removal percentage of the Cu(II) ion above a pH of 6, probably due to hydroxide precipitation in the process. This explains why we preferred to avoid working with pH values above 6.

Half-load time ($t_{1/2}$) for all experiments was below 10 min. The experimental data gave a good fit to both the Lagergren and reversible first-order equations. The parameters of these equations are shown in Tables 2 and 3. The Lagergren capacity at equilibrium (q_e) was calculated considering dry resin.

For all temperatures under consideration, there was a good correlation between k_{ad} and k. Also, the values of k_2 is significantly lower than k_1 which means that equilibrium is shifted towards adsorption under the initial concentration studied. The reversibility of the reaction points to the possibility of regeneration of the gel resin. The rate constant values of k_{ad} and k_1 are encouraging to use this resin for practical applications.

Table 2
Lagergren adsorption parameters

T (°C)	Parameter	pH			
		3	4	5	6
15	k_{ad} (min^{-1})	0.070	0.080	0.087	0.083
	q_e (mg/g)	18.26	21.77	20.14	18.93
	R^2	0.9854	0.9750	0.9938	0.9844
25	k_{ad} (min^{-1})	0.058	0.067	0.067	0.071
	q_e (mg/g)	14.95	17.80	17.27	17.78
	R^2	0.9620	0.9828	0.9776	0.9790
35	k_{ad} (min^{-1})	0.079	0.070	0.072	0.077
	q_e (mg/g)	19.22	17.66	18.08	18.94
	R^2	0.9755	0.9812	0.9730	0.9609

Table 3
Reversible first-order rate constants

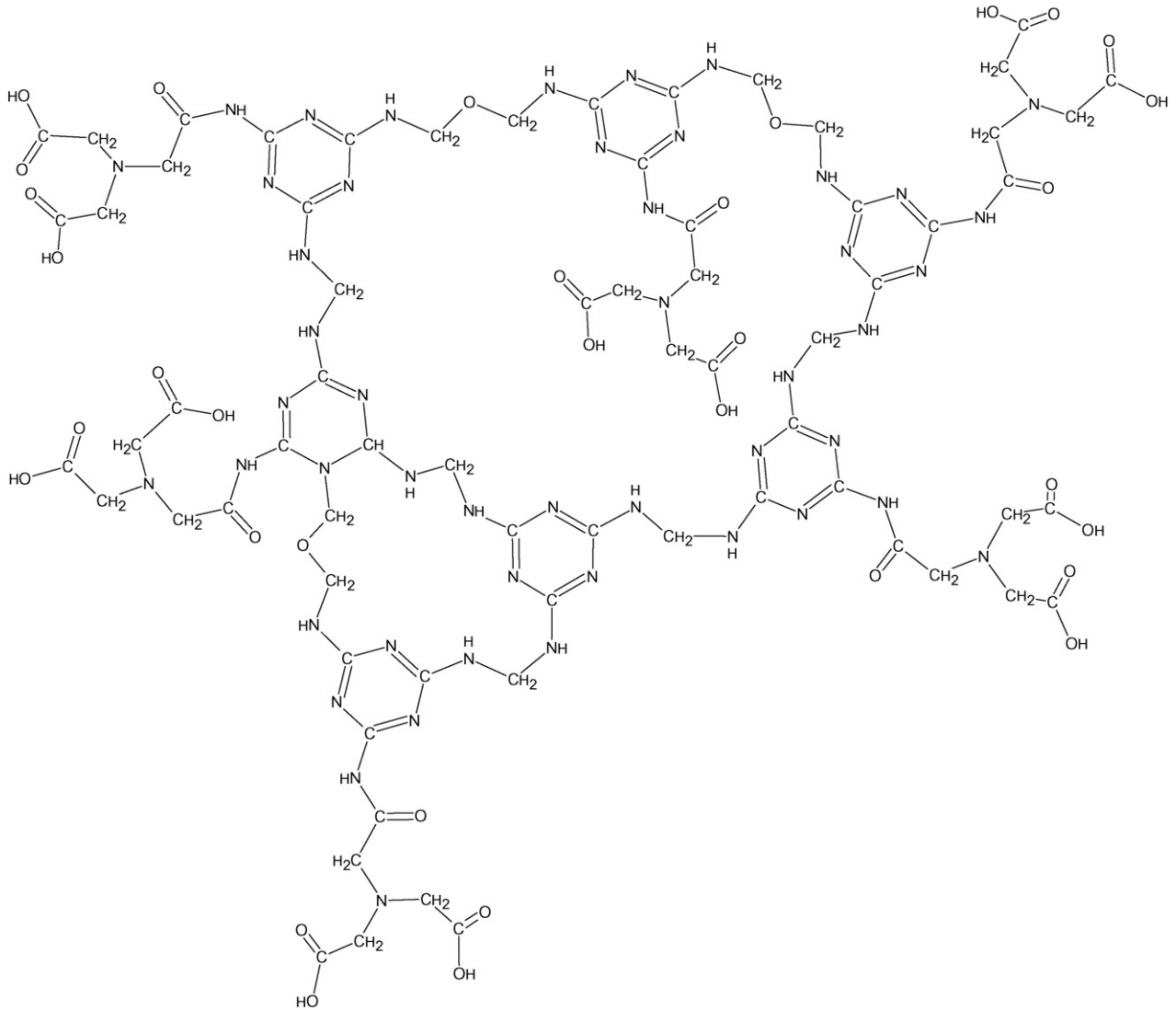| T (°C)	pH	k (min^{-1})	k_1 (min^{-1})	k_2 (min^{-1})
15	3	0.0807	0.0629	0.0178
	4	0.0811	0.0649	0.0162
	5	0.0868	0.0703	0.0165
	6	0.0833	0.0700	0.0133
25	3	0.058	0.0406	0.0174
	4	0.067	0.0502	0.0168
	5	0.067	0.0516	0.0154
	6	0.070	0.0574	0.0126
35	3	0.0792	0.0602	0.0190
	4	0.0702	0.0562	0.0140
	5	0.0719	0.0604	0.0115
	6	0.0769	0.0699	0.0077

Fig. 2. A possible structure of MF–NTA resin.

4.5. Adsorption isotherm

Fitting the experimental data using the Langmuir and Freundlich isotherms show that both models represent satis-factorily the adsorption process (high correlation coefficients) although it seems that the Freundlich isotherm gives a better fit. Tables 4 and 5 show the respective parameters. The Langmuir capacity (Q_o) and Freundlich capacity term (K_F) were calculated considering dry resin.
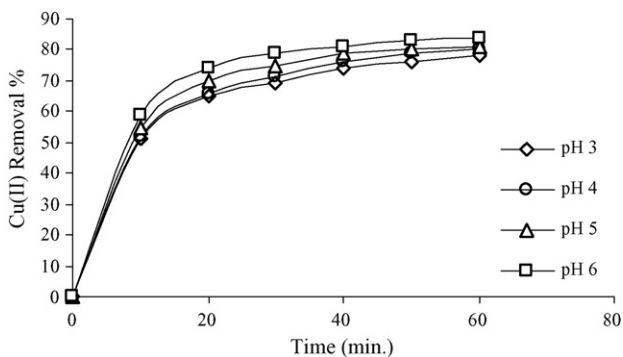

Fig. 3. Cu(II) removal rate. $T = 15\,^{\circ}$C, 150 rpm, initial concentration 100 ppm, volume 30 ml, gel adsorbent 0.3 g. pH values of 3, 4, 5 and 6.
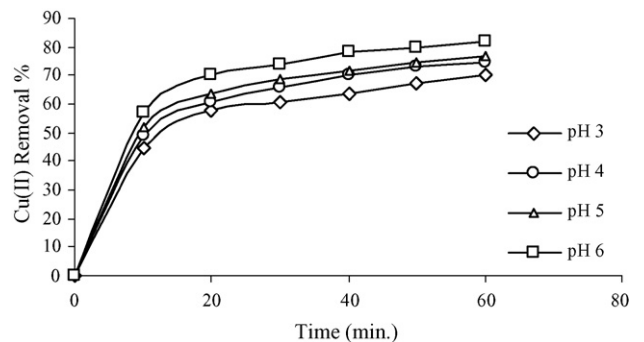

Fig. 4. Cu(II) removal rate. $T = 25\,^{\circ}$C, 150 rpm, initial concentration 100 ppm, volume 30 ml, gel adsorbent 0.3 g. pH values of 3, 4, 5 and 6.

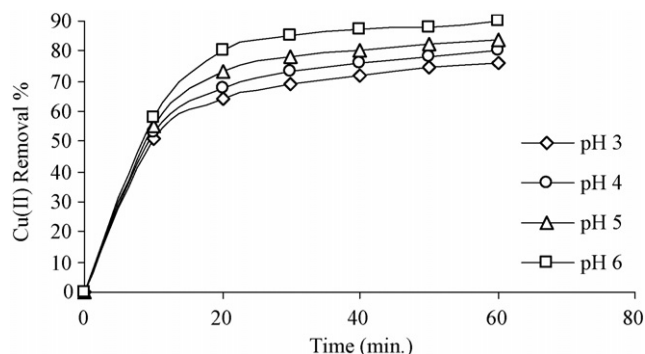Fig. 5. Cu(II) removal rate. $T = 35\,°C$, 150 rpm, initial concentration 100 ppm, volume 30 ml, gel adsorbent 0.3 g. pH values of 3, 4, 5 and 6.

The Langmuir model shows that the gel resin has maximum adsorption capacity (Q_o) between 18.6 and 29.7 mg/g depending on temperature, and the adsorption is favourable ($1 > R_L > 0$) [17]. The parameter b is higher for temperatures of 15 and 35 °C than that for 25 °C. This suggests higher chemical adsorption at temperature boundaries [27]. Similarly, the Freundlich parameter (K_F) is higher for temperatures of 15 and 35 °C representing higher capacities. The effect of pH on ion distribution factor (D) is shown in Table 6.

Table 7 shows the adsorption capacity of MF–NTA compared with capacities of other different types of sorbents studied recently [28–33]. The MF–NTA resin shows moderate capacity compared with these materials.

4.6. Thermodynamic study

The adsorption stability constants (K_c) at different pH values are higher for temperatures of 15 and 35 °C than that for 25 °C. This means that different mechanisms are involved in the

Table 4
Langmuir parameters

T (°C)	Q_o (mg/g)	b	R_L	R^2
15	23.1	0.027	0.27	0.9826
25	18.6	0.025	0.29	0.9296
35	29.7	0.029	0.34	0.9599

Table 5
Freundlich parameters

T (°C)	K_F	n	R^2
15	0.168	0.60	0.9835
25	0.096	0.57	0.9562
35	0.373	0.66	0.9715

Table 6
Effect of pH on D at different temperature

pH	3	4	5	6
D ($T = 15\,°C$)	1013	1143	1218	1500
D ($T = 25\,°C$)	667	857	957	1300
D ($T = 35\,°C$)	905	1143	1500	2571

Table 7
Comparison of Cu(II) capacities between MF–NTA and recent materials found in literature

Material	Q_o (mg/g)	Ref.
Spirogyra (biomass)	133.3	[28]
Raw kaolinite	10.78	[29]
AMA	7.09	[30]
PMA	8.55	[30]
Chitosan–cellulose beads	53.2	[31]
P(HEMA-*co*-MAH)	122.7	[32]
Polydithiocarbamate (synthetic resin)	35	[33]
MF–NTA	29.7	Present study

adsorption process and the contribution of each mechanism is temperature-dependent. So we divided the whole temperature range into two parts: 15–25 and 25–35 °C. We cannot specify 25 °C to be the exact mid point for adsorption behaviour, but it is likely to be close. Figs. 6 and 7 show plots of Van't Hoff (ln K_c versus $1/T$). For range 15–25 °C, the enthalpy (ΔH^{ads}) is negative which means an exothermic adsorption process and it is likely that the chelation mechanism dominates in this range (Table 8) [34]. The entropy (ΔS^{ads}) is negative corresponding to a decrease in degree of freedom of the system as the Cu(II) ions are restricted by complex formation. For the range 25–35 °C, the enthalpy (ΔH^{ads}) is positive which means an endothermic adsorption process and here the ion-exchange mechanism is likely to dominate (Table 8) [35–38]. The decrease in pH (more H⁺ ions) upon equilibrium is higher for a temperature of 35 °C which also indicates the ion-exchange mechanism in this range (Table 9). Furthermore, weak-acid ion-exchange
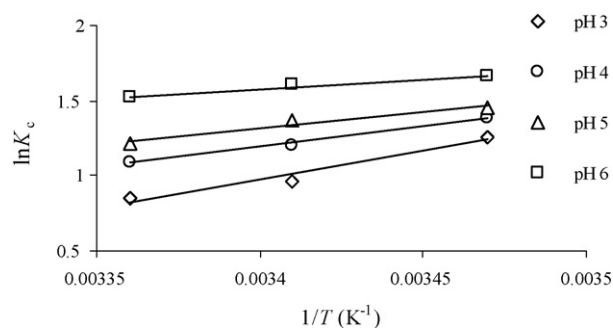

Fig. 6. Van't Hoff plot for Cu(II) adsorption on MF–NTA gel resin for pH values of 3, 4, 5 and 6. Temperature range (15–25 °C).

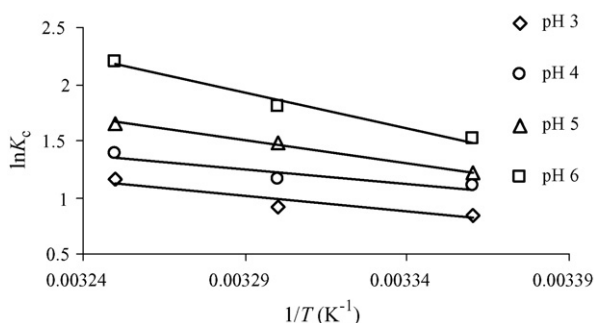Fig. 7. Van't Hoff plot for Cu(II) adsorption on MF–NTA gel resin for pH values of 3, 4, 5 and 6. Temperature range (25–35 °C).

Table 8
Change in thermodynamic parameters: ΔH^{ads} and ΔS^{ads}

pH	15–25 °C		25–35 °C	
	ΔS^{ads} (J/mol K^{-1})	ΔH^{ads} (kJ/mol)	ΔS^{ads} (J/mol K^{-1})	ΔH^{ads} (kJ/mol)
3	−99.7	−31.714	+83.1	+22.696
4	−65.9	−22.288	+82.4	+21.875
5	−50.0	−17.923	+124.8	+34.127
6	−23.5	−10.775	+186.0	+51.686

Table 9
Final pH values at equilibrium

T (°C)	Initial pH			
	3	4	5	6
15	3.36	3.34	3.31	3.31
25	3.13	3.10	3.06	3.06
35	3.08	3.04	3.00	2.98

Table 10
Change in free energy, ΔG^{ads} (kJ/mol)

T (°C)	pH 3	pH 4	pH 5	pH 6
15	−3.022	−3.323	−3.471	−3.977
25	−2.099	−2.712	−2.996	−3.757
35	−2.953	−3.559	−4.247	−5.649

behaviour can be considered specifically as carboxylic groups are the ion-exchange groups present. The entropy (ΔS^{ads}) is positive corresponding to an increase in degree of freedom of the system due to release of two hydrogen ions for each Cu(II) ion. Generally, the free energy (ΔG^{ads}) is negative confirming the spontaneous nature of this adsorption process and the absolute value increases with pH and temperature (Table 10).

5. Conclusions

The study shows that NTA can be anchored to the MF matrix by an amide bond to form MF–NTA chelating resin. The produced gel resin is hydrophilic and has a surface area of 163 m^2 g^{-1}. The pendent chelating sites (NTA moieties) have the capability to bind heavy metals present in wastewater. The MF–NTA resin showed good removal behaviour towards Cu(II) ions. Two adsorption mechanisms are concluded from the results of the adsorption process: chelating adsorption (dominates over the range 15–25 °C) and ion exchange (dominates over the range 25–35 °C). Thermodynamics shows that adsorption occurs spontaneously. The rate of Cu(II) removal under specified condition (pH 3–6, temperature 15–35 °C) is within minutes ($t_{1/2} \approx 10$ min). The kinetic models, reversible first- and pseudo first-order, give good fit to the experimental results. The rate constants of these models suggest the high rate of adsorption and the ease of regenerating the resin. The Freundlich model gives a better fit to adsorption isotherm results than the Langmuir model which indicates more heterogeneity of the resin surface. The adsorption capacity is relatively high (23.1, 18.6 and 29.7 mg/g at temperatures 15, 25 and 35 °C, respectively).

The resin containing the heavy metal ions can be regenerated by using EDTA solution. This regenerated resin can then be used in further adsorption process.

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