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Interaction of Cu(II) on N-(2-pyridylmethyl) and N-(4-pyridylmethyl) chitosan

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Chitosan functionalized with 2-pyridinecarboxaldehyde and 4-pyridinecarboxaldehyde were used to study the equilibrium constants of adsorption copper(II) in aqueous solutions. The degree of substitution of NH_2 groups of the chitosan was 0.85. The adsorption parameters K (adsorption constants Langmuir) and $\{R_T\}$ (maximum value of adsorbed copper(II) ions) were calculated using Langmuir's equations by non-linear regression methods. The K_L (equilibrium adsorption constant) and $\{R_T\}$ values for N-(2-pyridyl-methyl)chitosan systems were higher than those for N-(4-pyridyl-methyl)chitosan. The difference is related to the nitrogen position at the pyridine ring, since the degree of substitution is the same in the two polymers. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Over the last few years, a large number of chelating resins derived from chitosan have been synthesized for selective separation of heavy metal ions[1-3].

Chitosan is a natural polysaccharide which is obtained by chitin hydrolysis in an alkaline medium. Usually, the disacetylation is carried out in sodium hydroxide or potassium hydroxide at high temperatures under heterogeneous conditions[4,5]. This disacetylation is incomplete, though a copolymer is created by a mixture of $\beta(1 \rightarrow 4)$-2-acetamido-2-desoxy-D-glucose (a) and $\beta(1 \rightarrow 4)$-2-amino-2-desoxy-D-glucose (b) (*Figure 1*), and the *a* ratio between the monomeric units depends on the conditions under which the preparation is set up.

The presence of amine groups on the polymeric chain possibly masks a great number of chemical modifications, especially Schiff's reaction with aldehydes and ketones[6,7]. The modification on the polymer's surface through chemical bonding with organic molecules has been used to investigate the interactions that take place on the solid–liquid interface. These modified polymers have been shown to be very important in analytical applications, especially in different chromatographic procedures[8-12], as well as in biological systems when complexes supported on polymer have demonstrated similarities to mimic the activity of metalloenzymes[13].

In this work we determined the selective capacity of chelating resins, such as N-(4-pyridylmethyl)chitosan (4PMC) and N-(2-pyridylmethyl) chitosan (2PMC), to form complexes with copper(II) ions.

These new functional groups on chitosan may have the capacity to promote a better interaction between polymer

and metallic ions by the formation of a complex, thus the capacity of adsorption could be increasing. In this present study, chitosan was functionalized with 2-pyridinecarboxaldehyde (1) and 4-pyridinecarboxaldehyde (2) (*Figure 2*). These modifications were used to adsorb Cu(II) in aqueous solutions to verify the influence of the nitrogen position in the adsorption process.

EXPERIMENTAL

Chitosan with degree substitution of group amino 0.76 was obtained through basic hydrolysis of chitin according to the methods in the literature[4,5]. 2-pyridinecarboxaldehyde, 4-pyridinecarboxaldehyde and sodium cyanoborohydride were obtained from Aldrich. The other analytical grade reagents were obtained from Merck.

The chitosan derivatives were synthesized through Schiff's reaction by a modified conventional method[1-3]. An ethanolic solution of chitosan (CTS) (1 mmol glucosamine residue) was continuously stirred and refluxed with 4-pyridinecarboxaldehyde (4 mmol) or 2-pyridinecarboxaldehyde (4 mmol) for 24 h. The formation of the Schiff base is observed by colour change in chitosan, yellow for N-(4-pyridyl-methyl) chitosan and purple for N-(2-pyridyl-methyl) chitosan. The functionalized polymer was soluble in dilute aqueous acetic acid.

The polymers were purified in Soxhlet with ethanol and acetone for removal of excess aldehyde. Afterwards, the imine groups were reduced with cyanoborohydride for 24 h. The solids were washed with water to remove the excess cyanoborohydride, filtered and dried at 60°C for 4 h. The IR spectra were obtained in KBr disk on a IR-FT, Bomem

MB-100 spectrophotometer. The polymer samples were solubilized in CD_3COOD/D_2O (3% w/w) and spectra of n.m.r. ^1H and ^{13}C were obtained in 200 MHz on a Bomem 200 spectrophotometer.
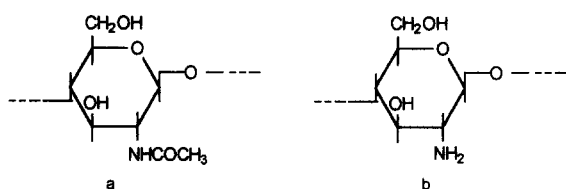

Figure 1 Structure of chitosan: (A) $\beta(1 \rightarrow 4)$-2-acetamido-2-desoxy-D-glucose and (B) $\beta(1 \rightarrow 4)$- 2-amino-2-desoxy-D-glucose

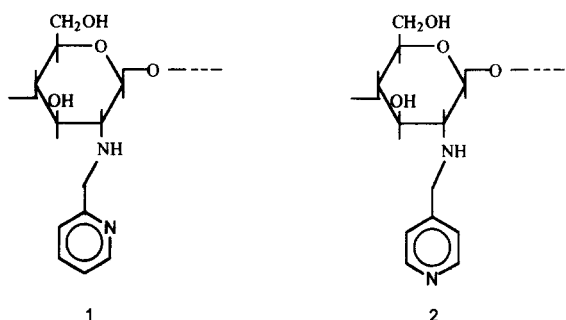**Figure 2** Structure of 2PMC (A) and 4PMC (B)

Adsorption of metal ions to polymers

Solutions of metal ions in the concentration range 1–5 mmol dm^{-3} containing *Tris* buffer (pH 7.6) were shaken for 60 min. With 100 mg of each polymer in a reaction flask maintained at 25.0 ± 0.5°C. The copper filtered-off and the quantity adsorbed (in polymer) were determined by subtracting the concentration in the supernatant solution from the initial concentration. The colour of polymer complexed with metal is greenish blue, characteristic of the copper(II) complex.

The concentration of metal ions was determined using a Hitachi model Z-8000 polarized Zeeman atomic adsorption spectrophotometer.

The pH value at equilibrium was measured using a Micronal model B-340 pH meter.

RESULTS AND DISCUSSION

The degree of chitosan substitution was determined from the elemental data analysis of chitosan, 2PMC and 4PMC,

Table 1 Elemental analysis of polymer[a]

Polymers	%C	%H	%N
Chitosan	41.13	7.31	7.35
2PMC	48.59 (48.89)	5.80 (6.02)	9.25 (9.25)
4PMC	48.45 (48.24)	5.74 (5.88)	9.08 (9.08)

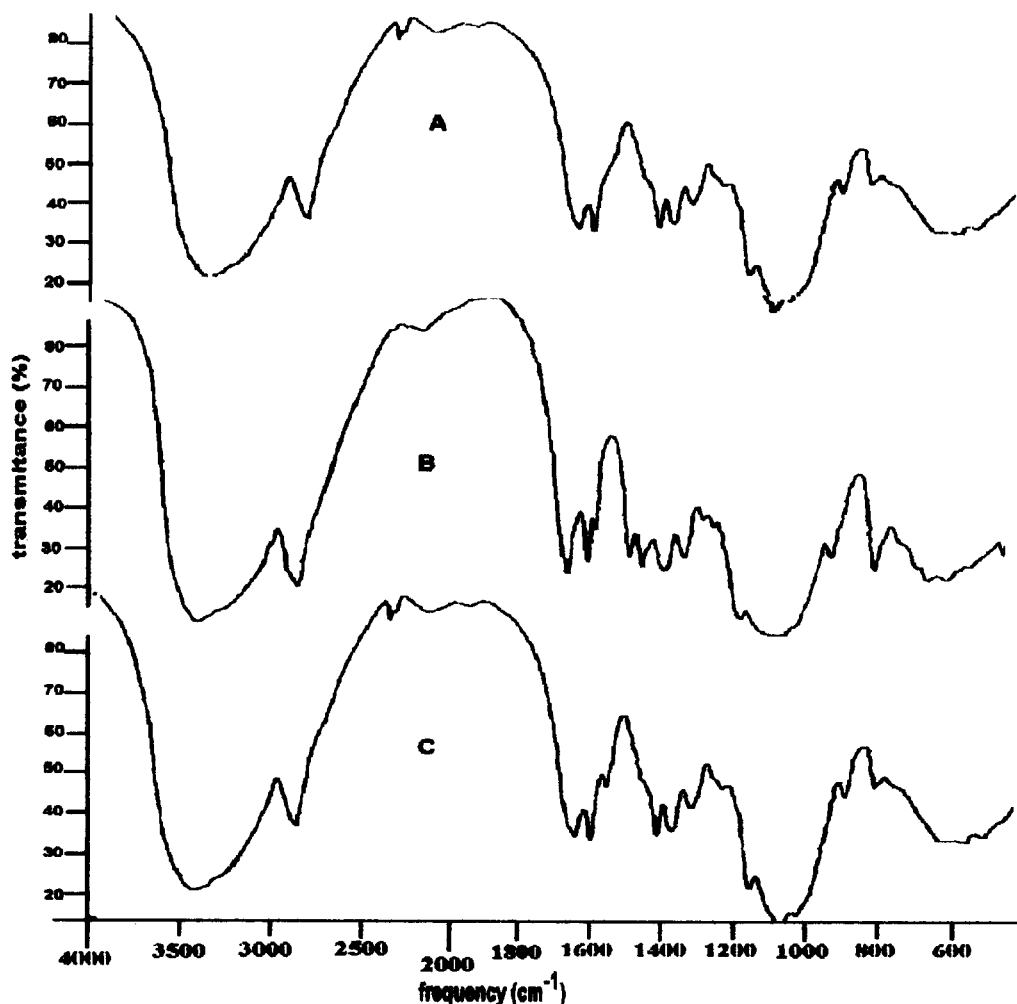[a]Values calculated for of Loewenschuss and Schumuckle methods[15]

Figure 3 Infrared spectra of QTS (A), 2PMC (B) and 4PMC (C)

shown in *Table 1*. They were calculated according to the Loewenschuss and Schumuckler[15] method.

The reaction of chitosan with 2PMC and 4PMC produced a 0.85 substitution in NH_2 groups of the chitosan. The amount of H_2O in chitosan after the change is about 6%.

The i.r. spectrum of CTS, 2PMC and 4PMC is shown in *Figure 3*. One may see that even in 2PMC and PMC spectra, QTS bands are more predominant. The substitution is observerd by the appearance of a band at 1550–1572 cm^{-1} which is characteristic of the pyridinic ring being absent in the spectrum of CTS[16].

The n.m.r. H^1 spectrum of CTS, 2PMC and 4PMC (*Figure 4*) shows peaks between 2.5 and 3.5 ppm attributed to protons of the glycosidic ring, peaks between 7.5 and 8.5 ppm attributed to protons of pyrinic ring, and peaks near 6 ppm attributed to proton of imine[16].

The n.m.r. ^{13}C of CTS, 2PMC and 4PMC is shown (*Figure 5*) to be constituted basically for six peaks between 25 and 110 ppm which are attributed to carbon of the glycoside ring, a peak between 125 and 145 ppm attributed to the carbon pyridinic ring and a peak at 165 ppm attributed to carbon of the iminic bond[17,18].

Table 2 Differents forms of linearization of Langmuir[18] isotherm

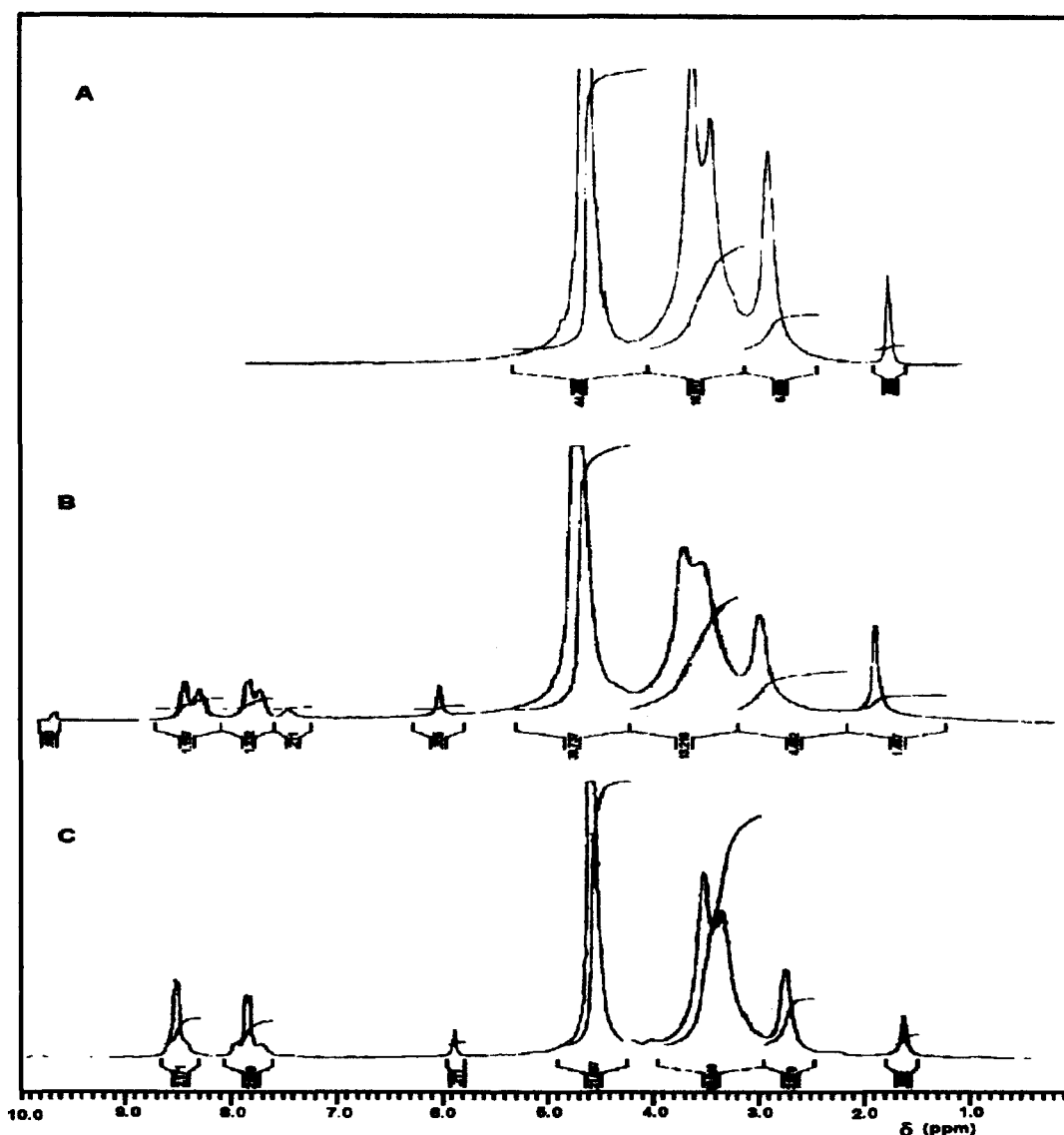| Transformation non-linear and linear	Plot	Parameters
(1) $\{RMe\} = \{R_T\}K[Me]/(1 + K[Me])$	$\{RMe\}$ *versus* [Me]	K and $\{R_T\}$
(2) $[Me]/\{RMe\} = 1/K\{R_T\} + [Me]/\{R_T\}$	$[Me]/\{RMe\}$ *versus* [Me]	$K = $ coef. ang./interc. $\{R_T\} = 1$/coef. angular
(3) $1/\{RMe\} = 1/\{R_T\} + (1/(R_T.K))(1/[Me])$	$1/\{RMe\}$ *versus* (1/[Me])	$K = $ interc./coef. ang. $\{R_T\} = 1$/interc.
(4) $\{RMe\} = \{R_T\} - (1/K)(\{RMe\}/[Me])$	$\{RMe\}$ *versus* $\{RMe\}/$[Me]	$K = -1$/coef. ang. $\{R_T\} = $ interc.
(5) $(\{RMe\}/[Me] = K\{R_T\} - K\{RMe\}$	$\{RMe\}/$[Me] *versus* $\{RMe\}$	$K = -$ coef. ang $\{R_T\} = -$ interc./coef. ang.

Figure 4 N.m.r. ^{1}H spectra of QTS (A), 2PMC (B) and 4PMC (C). Solvent: CD_3COOD/ D_2O

Adsorption isotherm

4PMC and 2PMC have the capacity to adsorb ions in solution. The relationships between the adsorbed amount and adsorbate concentration in solution are usually described by Langmuir's isotherm[19,20]. Langmuir's equation is useful for a monolayer adsorption, containing a defined number of identical sites.

The model masks the assumption that there is regular energy of adsorption on the surface, and there is not a change in the adsorbate on the surface.

The isotherm can be written as follows

$$\{RMe\} = \frac{K\{R_T\}[Me]}{1 + K[Me]} \tag{1}$$

Table 3 Value of adsorptions parameters calculated for methods of non-linear and linear regression

2PMC	r^a	K (dm^{-3} mmol^{-1})	$\{R_T\}$ (mmol g^{-1})	K_L (dm^3 g^{-1})
(1)	0.998	2.16 ± 0.17	1.63 ± 0.05	3.25 ± 0.27
(2)	0.998	2.22 ± 0.11	1.62 ± 0.04	3.60 ± 0.20
(3)	0.996	2.26 ± 0.15	1.59 ± 0.06	3.59 ± 0.27
(4)	−0.983	2.23 ± 0.17	1.61 ± 0.06	3.59 ± 0.30
(5)	−0.985	2.16 ± 0.16	1.63 ± 0.13	3.52 ± 0.38
4PMC	r	K (dm^{-3} mmol^{-1})	$\{R_T\}$ (mmol g^{-1})	K_L (dm^3 g^{-1})
(1)	0.998	0.87 ± 0.09	0.71 ± 0.04	0.62 ± 0.07
(2)	0.994	0.93 ± 0.07	0.69 ± 0.03	0.64 ± 0.06
(3)	0.980	1.24 ± 0.18	0.62 ± 0.08	0.77 ± 0.15
(4)	−0.975	1.05 ± 0.10	0.65 ± 0.03	0.68 ± 0.07
(5)	−0.974	0.99 ± 0.09	0.68 ± 0.11	0.67 ± 0.12

(Refer to the equations in *Table 2*)
^{a}Non-linear and linear correlation coeficient
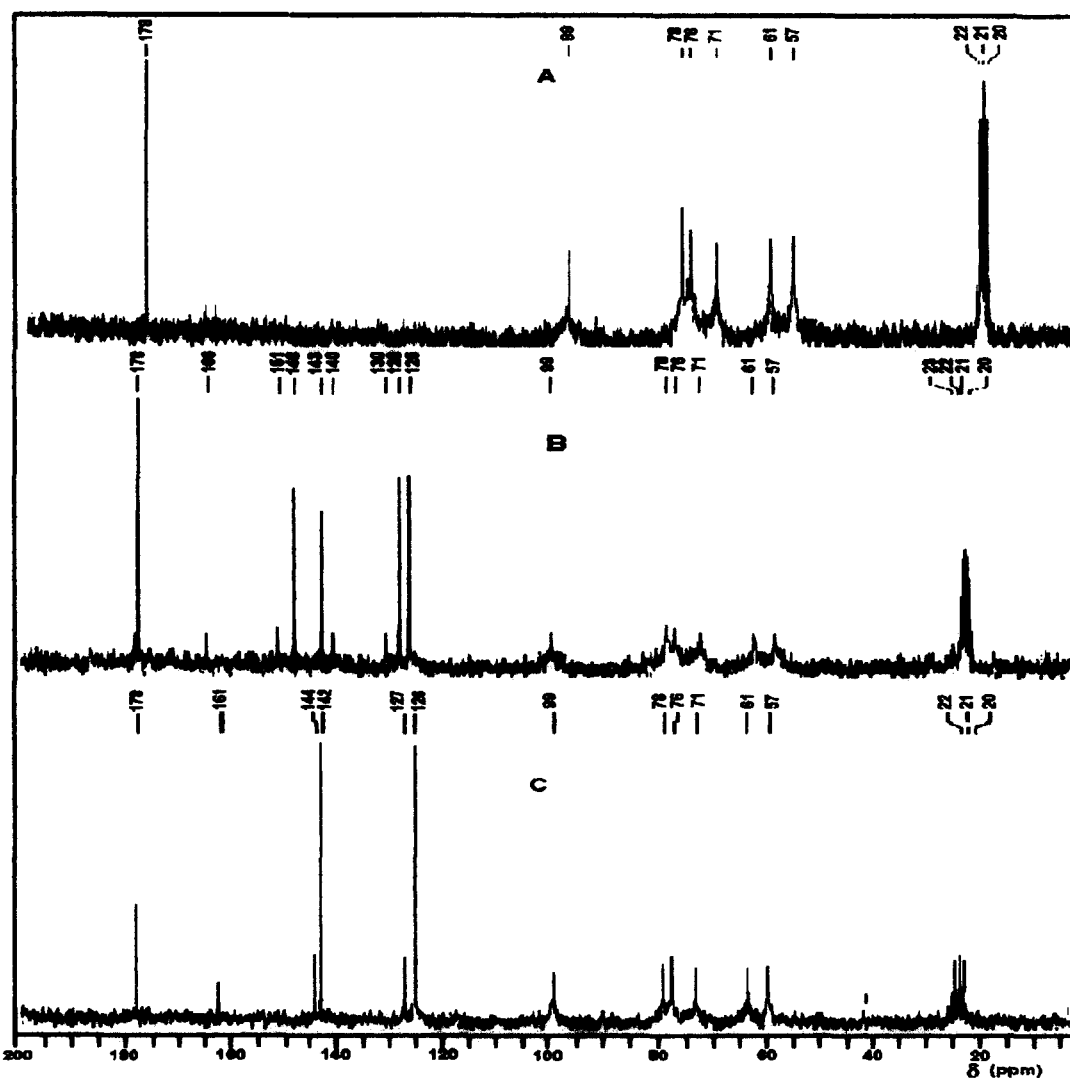$K_e\{R_T\}$ from equation (1), K_L from equation (2)

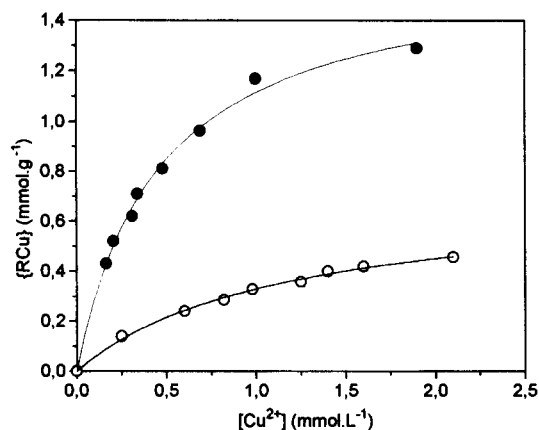**Figure 5** N.m.r. ^{13}C spectra of QTS (A), 2PMC (B) and 4PMC (C). Solvent: CD$_3$COOD/ D$_2$O

Figure 6 Adsorption isotherm of copper(II) for 2PMC and 4PMC, $T =$ 25.0 ± 0.5 pH 7.6 and shaken time 60 min: •, 2PMC; ∘ , 4PMC

Figure 7 Improved structure of complex copper(II)—2PMC (1), and copper(II)—4PMC (2)

In equation (1), the symbols in braces stand for the solid phase: consequently {RMe} is the amount of solute (in mmol) by unit of adsorbent mass (in grams), {R_T} is the maximum value of adsorbed metal ions (mmol) by adsorbent (g), K (dm^{-3} mmol) is the Langmuir constant of adsorption, and [Me] is the concentrations of metal ions (mmol dm^{-3}) in equilibrium. *Figure 6* shows the adsorption isotherm for the two cases studied.

The Langmuir isotherm equation is most frequently used because of its ability of to fit the experimental data of adsorption and its capacity to estimate the adsorption parameters. The equation can be converted into its linear form, and its two parameters are determined by plotting the data. The Langmuir isotherm can be converted into a linear form in several different ways[21], as shown in *Table 2.Table 3* reports the estimation of parameters, adsorption by methods of non-linear and linear regression. The equilibrium adsorption Langmuir constant, K_L, was calculated from equation (2). In equation (2), {R_T} is the maximum value of adsorbed metal ions (mmol) by adsorbent (g), K_L (dm^3 g^{-1})[22].

$$K_L = K\{R_T\} \qquad (2)$$

The calculated values of K and {R_T} for the 2PMC system agree well, using either the linear or the non-linear regression method. For the 4PMC system, the parameter values show a deviation when using the linear and non-linear regression methods. The {R_T} value showed a slight deviation of 3–13% and K produced a 7–42% deviation. The conversion of Langmuir's equation into its linear form ignores the error distribution in the estimation of the isotherm parameters, therefore resulting, in some cases, in different parameters, depending on the way it is converted. An alternative that corrects these problems is to use the non-linear regression method to determine the {R_T} and K values, resulting in the estimation of parameters of adsorption without deviation or tendency, and with a normal distribution of errors and variance constant[20,21].

The highest value of copper(II) adsorption was determined using the non-linear regression method, and it was found to be (1.63 ± 0.05) mmol g^{-1} for the 2PMC and (0.71 ± 0.04) mmol g^{-1} for the 4PMC.

These results were compared with those for chitosan crosslinking [23,24] and show that the pyridine group preserve adsortion domains of modified chitosan.

The adsorption constant of 2PMC is about 2.5-fold higher than that of 4PMC. The difference is related to the nitrogen position at the pyridinic ring since the degree of substitution is the same in the two polymers. The structures are shown in
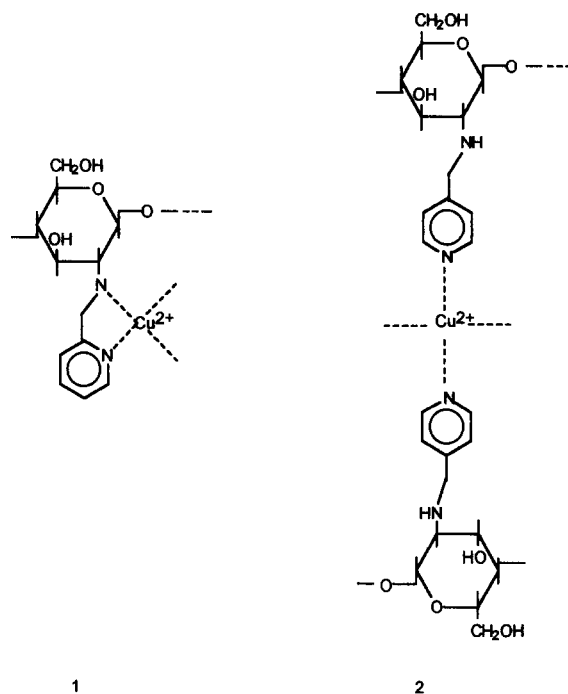
Figure 7. The 2PMC is a N,N-bidentate ligand, while the 4PMC is a monodentate one. The presence of bidentate ligand in 2PMC makes the complex formed between copper(II) and the polymer more stable owing to the chelate effect, when compared with the complex formed between the copper(II) and 4PMC.

Studies were made by Park *et al.*[25] using chitosan and copper(II), proving the possibility of intra- and intermolecular complexation between metal and the NH$_2$ polymer groups. The intramolecular complexation would involve amine groups in the same chain, while the intermolecular complexation would involve amine groups in different chains.

The chelating resins derived from poly(4-vinylpyridine) form stable intermolecular chelates with several metallic ions, and its constant formation is higher than those similar to the monomer. This increase is attributed to the polymer effect[26].

An intermolecular binding would be better for the 4PMC, and for 2PMC the formation of a complex involving both nitrogen at the same monomeric unity occur, owing to their position in the ring. It must be realized in this analysis that the substitution of D-glucosamine with the pyridinic ring might not be able to form inter- and intramolecular binding with 2PMC and intramolecular binding with 4PMC owing to the steric impediment.

The adsorption constant behaviour of the complexes formed between the polymer and the copper(II) are in agreement with the stability constant values, in solution, between copper(II) and the corresponding monomer. The complex formed with copper(II) and 2(methylamino-methyl)pyridine (ML/M.L) has $K = 9.07$ ($K =$ logarithm of equilibrium constant), while the other, one copper(II) and 4-methylpyridine (ML$_2$/M.L^2), has $K = 5.19$[27].

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