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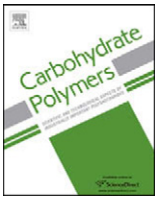

Metal uptake by chitosan derivatives and structure studies of the polymer metal complexes

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ABSTRACT

Two modified chitosan polymers were obtained by reaction of chitosan with cinnamoyl chloride and cinnamoyl isothiocyanate to produce two new derivatives. The new modified polymers were characterized by elemental and spectral analysis to confirm their structures. Their metal up take capacity was investigated both under competitive and noncompetitive conditions. At pH 5.6, the (ChitoCin and ChitoThioCin) polymers exhibit higher capacity for Cu(II) (0.461–0.572 mmol/g) than the other metal ions used. Where the capacities of the other metal ions are: Fe(III) (0.235–0.341 mmol/g), Cr(III) (0.078–0.099 mmol/g), Co(II) (0.046–0.057 mmol/g) and Ni(II) (0.041–0.053 mmol/g). These results show that the capacity of ChitoThioCin polymer is higher than that of ChitoCin for each metal ion. However, at lower pH the capacities (for Cr(III) pH < 1.8 and Fe(III) pH < 3.1) are higher than other metal ions under investigation. It has been found that the absorption follows the Langmuir isotherm better than that of the Freundlich isotherm. The metal complexes with several metal cations were isolated and their structures with the new chitosan polymers were found to be octahedral and schematic representations of the complexes were given.

1. Introduction

Chitin, the second most abundant natural polymer after cellulose, can be extracted from fungi, insect, lobster, shrimp and krill. Crabs obtained from seafood processing waste are an important commercial source (Volesky, 2001). About 5000–8000 tons of crab shell material is disposed off by the seafood industry annually. Chitosan is derived from chitin, by a deacetylation with strong alkali. Chitosan is actually a copolymer of glucosamine and *N*-acetyl glucosamine (Rojas et al., 2005). It is composed of β-(1 → 4)-2-amino-2-deoxy-D-glucopyranose (glucosamine units) and β-(1 → 4)-2-acetamido-2-deoxy-D-glucopyranose (acetyl glucosamine units) (Hamdine, Heuzey, & Bégin, 2005). Chitosan has many properties that have generated interest in its use such as biodegradability, biocompatibility its nontoxic nature and metal uptake capacity (Varma, Deshpande, & Kennedy, 2004). Chitosan based films have proven to be very effective in food preservation. The presence of amino group in C_2 position of chitosan provides major functionality towards biotechnological needs, particularly, in food applications. Chitosan based polymeric materials can be formed into fibers, films, gels, sponges, beads or even nanoparticles (Dutta, Tripathi, Mehrotra, & Dutta, 2009). Elsabee, Abdou, Nagy, and Eweis (2008) have prepared a multilayered structure of chitosan/pectin onto polypropylene films which were used to keep fresh vegetables for 15 days in perfect conditions. In another work phenylthiourea derivative of chitosan was shown to have very strong antimicrobial efficacy as much as 60 times more than the original chitosan (Eweis, Elkholy, & Elsabee, 2006). Chitosan can also impart antimicrobial character onto fabrics like Jute for example especially if it was complexed with metal cations (Higazy, Hashem, ElShafei, Shaker, & Hady, 2010). Chitosan can form complexes with other polyelectrolytes to form gels with high efficiency for metal uptake from aqueous solutions (Cao, Tan, Che, & Xin, 2010). The adsorption properties of *N*-succinyl-chitosan and cross-linked *N*-succinyl-chitosan resin with Pb(II) as template ions was investigated by Suna and Wang (2006). Recently, there has been a growing interest in the chemical modification of chitosan in order to improve its solubility and widen its applications. Examples of the distinct applications, with particular emphasis on tissue engineering, drug delivery and environmental applications, were reviewed by Alves and Mano (2008).

Other chitosan derivatives have been described and were used for metal uptake such as phthalaldehyde (Muzzarelli, Tanfani, Mariotti, & Emanuelli, 1982), salicylaldehyde (Hall & Yalpani, 1980), and glyoxylic acid (Muzzarelli, Tanfani, Emanuelli, & Mariotti, 1982) which were reductively alkylated to chitosan. Holme and Hall (1991) created a novel chitosan derivative by incorporating a hydrophilic spacer arm between the chitosan backbone and

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the desired chelating group. Yalpani and Hall (1984) coupled free sugars to chitosan to give acyclic hydrophilic branches providing an ideal route to such a spacer group. Iminodiacetic acid, which is essentially one half of the well-known chelate ethylenediamine tetraacetic acid (EDTA), was chosen as an appropriate chelating functionality. The Cu(II) binding capacity of the derivative was higher than native chitosan. The use of chitosan for heavy metal-ion retention and parameters that are involved in the behavior were reported by Muzzarelli (1973, 1977). Chitosan phosphate and dithiocarbamate were synthesized by López de Alba, Pachec, Urbina, and Alvarado (1987) to retain uranium (VI). Lasko, Pesic, and Oliver (1993) prepared derivatives from the mercapto succinic acid, pyridoxal hydrocloride and succinamide and compared with chitosan against Cu(II), Cd(II), Fe(II) and Pb(II) ions. Chiessi, Paradossi, Venanzi, and Pispisa (1993) prepared and studied the association complexes between iron(III) or copper(II) ions and deoxylactit-1-yl (1), 2-substituted pentanedioic acid (2), or 2-substituted propanoic acid derivatives of chitosan. Also a chitosan-polyethylene imine copolymer was prepared to trap different ions (Kawamura, Mitsuhashi, Tanibe, & Yoshida, 1993). Guibal prepared a graft copolymer with oxo-2-glutaric acid to chelate uranium and vanadium (Guibal, Saucedo, Jansson-Charrier, Delandhe, & Le Cloirec, 1994) and a derivative with thiourea to trap platinum (Guibal, Vincent, & Navarro, 2000). Ishii, Minegishi, Lavitpichayawong, and Mitachi (1995), and Mitani and Ishii (1997) prepared different chitosan conjugates-aminoacids coupled by the ester bond with the carboxylic groups of the glyoxylic acid previously substituted over the chitosan and were used in the metal-ion retention. The sorption behavior of some radio active metal ions was investigated using chitosan thiourea derivatives (Metwally, Elkholy, Salem, & Elsabee, 2009).

The binding of metal cations to chitosan occurs between the free electron pairs of the nitrogen in the amine group and the void orbitals of the metal. Chitosan was found to be a good candidate for binding cadmium at neutral pH. When the pH was reduced to 4, Cd^{2+} was released and chitosan was regenerated by alkali solution.

Chitosan metal-ion complex can be described as two or more amino groups bind to the same metal ion; which is known as the bridge model. According to the bridge model, intra- or intermolecular complexation may occur between the metal-ion and amine groups from the same or different chains. Some other experiments suggest that only one amino group is involved in the binding and the metal ion is bound to the amino group like a pendant; called the pendant model (Vold, Varum, Guibal, & Smidsrød, 2003). The present work describes the preparation of two novel chitosan derivatives and characterization of their metal up take behavior under different conditions. The metal complexes of the polymers were isolated and characterized by spectroscopic techniques and magnetic measurements. All complexes exhibit octahedral geometry.

2. Experimental

2.1. Materials

Chitosan was obtained by deacetylation of chitin as cited in Abdou, Nagy, and Elsabee (2008) and Acosta, Jiménez, Borau, and Heras (1993). Chitin was extracted from shrimp shells Macrobrachium Rosenbergii (Fresh water shrimp) obtained from El-Oboor fish market in Cairo, Egypt. Cobalt(II) nitrate ($Co(NO_3)_2{\cdot}6H_2O$), nickel(II) nitrate ($Ni(NO_3)_2{\cdot}6H_2O$), copper(II) nitrate ($Cu(NO_3)_3{\cdot}3H_2O$), chromium(III) nitrate ($Cr(NO_3)_3{\cdot}9H_2O$), iron(III) nitrate, ($Fe(NO_3)_3{\cdot}9H_2O$) were Merck. Ammonium thiocyanate, cinnamoyl chloride, acetic acid, oxalic acid, sulfuric acid, potassium permanganate, sodium hydroxide and hydrochloric acid were Merck or BDH chemicals. Organic solvents (acetonitrile, absolute ethanol, ethanol 95%, methanol and DMSO) were reagent grade chemicals. The degree of deacetylation of chitosan was determined by potentiometric titration (Abdou et al., 2008) and elemental analysis (Jiang, Chen, & Zhong, 2003).

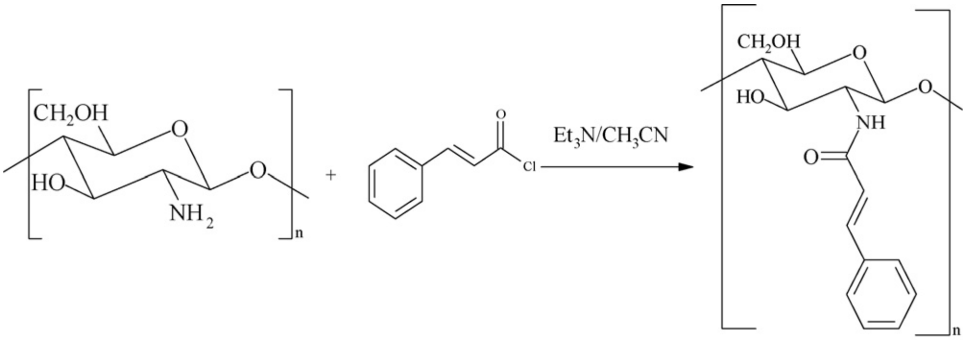
2.2. Synthesis of the chitosan derivatives

2.2.1. Reaction of chitosan with cinnamoyl chloride (ChitoCin polymer)

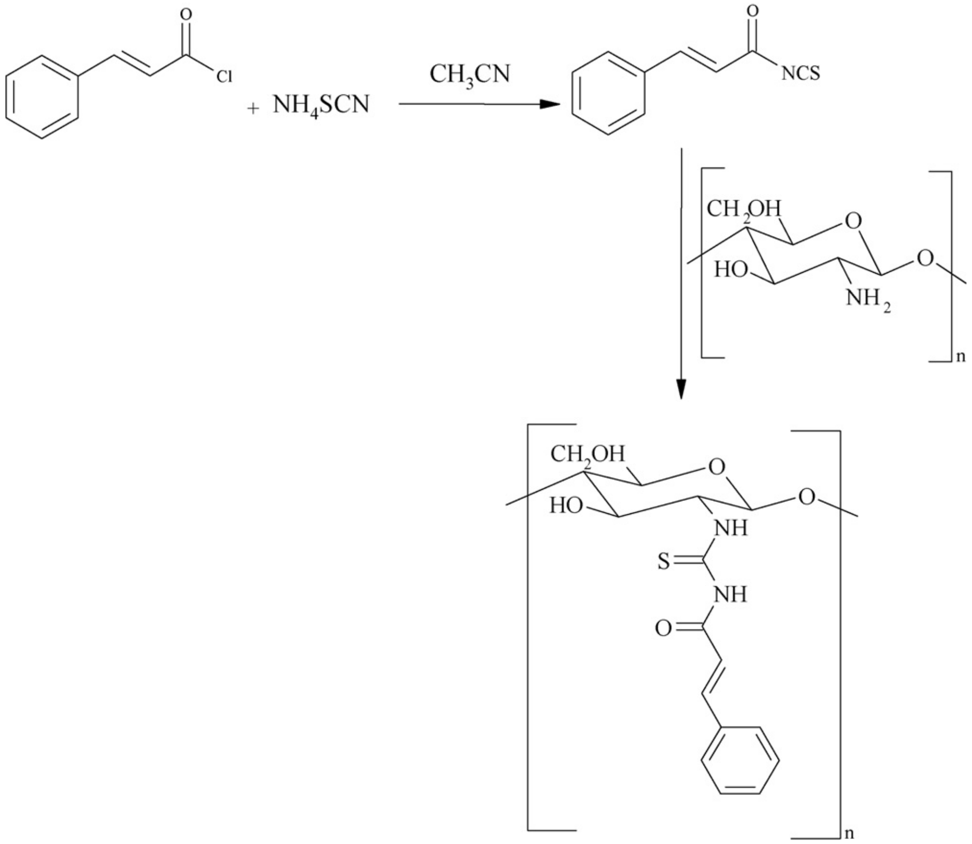
A solution of cinnamoyl chloride (1.666 g, 10.0 mmol) in 50 ml acetonitrile was added drop wise to a suspension of chitosan (1.610 g, 10.0 mmol) in 50 ml acetonitrile, then triethylamine (1.004 g, 10.0 mmol) diluted with 20 ml distilled water was added to the solution and the reaction mixture was stirred for 48 h. The reaction mixture was filtered. A light yellow product was purified in Soxhlet with acetonitrile for 8 h; the isolated polymer was left in air for dryness and kept in a desiccator until used. The yield was 1.974 g (68.31%) and its melting point was above 300 °C. Scheme 1 represents the formation of the (ChitoCin polymer). Elemental analysis; calculated and found%, C 61.85 (61.36), H 5.88 (5.13) and N 4.81 (5.06).

2.2.2. Reaction of chitosan with cinnamoyl chloride and ammonium thiocyanate (ChitoThioCin polymer)

A solution of cinnamoyl chloride (1.666 g, 10.0 mmol) in 50 ml acetonitrile was added drop wise to a solution of ammonium thiocyanate (0.760 g, 10.0 mmol) in 50 ml acetonitrile, kept in an ice bath with stirring for 1 h. The formed white precipitate of ammonium chloride was removed by filtration. Chitosan (1.610 g, 10.0 mmol) in 50 ml acetonitrile was added to the filtrate and stirred for 48 h. The reaction mixture was filtered. A yellow product was washed in Soxhlet by acetonitrile for 3 h; then the isolated polymer was left in air for dryness and kept in a desiccator until used. The yield was 2.413 g (68.94%) and its melting point was



Scheme 1. Synthesis of the (ChitoCin) polymer.



Scheme 2. Synthesis of the (ChitoThioCin) polymer.

above 300 °C. Scheme 2 represents the formation of the (ChitoThioCin polymer). Elemental analysis; calculated and found%: C 54.85 (54.51), H 5.18 (5.49), N 8.00 (7.95) and S 9.15 (9.45).

2.3. Synthesis of the metal complexes

The metal salts were dissolved in methanol and added gradually to a methanolic solution of CC or CCS polymer with the molar ratio 1:1. The reactions were refluxed for 2–4 h where the solid complex polymers were precipitated on hot. The products were filtered, washed with methanol and then air-dried.

The following detailed preparations are given as examples and the others were obtained similarly.

2.3.1. Synthesis of the Fe(III) complex from ChitoCin polymer ligand

A solution of cinnamoyl chitosan (CC) (1.30 g; 4.46 mmol) in 50 ml methanol was added to a solution of $Fe(NO_3)_3 \cdot 9H_2O$ (1.80 g, 4.45 mmol) in 50 ml hot methanol. The reaction was refluxed for 3 h. The yellow precipitate was formed while hot. The solution was left to cool and the solid product was filtered, washed with methanol and diethyl ether, and then air-dried. The yield was (1.35 g; 58.3%), its melting point was >300 °C. The solid complex was kept in a desiccator.

2.3.2. Synthesis of the Co(II) complex from ChitoThioCin polymer ligand

A solution of ChitoThioCin polymer ligand (1.20 g; 3.43 mmol) in 50 ml methanol was added gradually to a solution of $Co(NO_3)_2.6H_2O$ (0.99 g, 3.40 mmol) in 50 ml hot methanol. The reaction was refluxed for 2 h. The reddish yellow precipitate was formed while hot. The solid product was filtered on cold, washed with methanol and diethyl ether and then air-dried. The yield was (0.99 g; 45.4%), its melting point was above 300 °C.

2.4. Used techniques

2.4.1. FT-IR spectra

The FT-IR spectra (4000–400 cm^{-1}) of the compounds were recorded as KBr discs using FT-IR (Shimadzu) spectrophotometer model 4000 at the Micro analytical center, Cairo University, Giza, Egypt. Absorption frequencies are given in wave numbers (cm^{-1}).

2.4.2. Electronic spectra

The electronic spectra of the compounds were obtained using the JASCO V550 spectrophotometer with 1 cm quartz cell.

2.4.3. Elemental analysis

Carbon, hydrogen, nitrogen and sulfur contents were performed by elemental analyzer, at the Micro-analytical Centre, Cairo University, Giza, Egypt.

Analysis of metal ions after the dissolution of the solid complex in hot concentrated nitric acid, HNO_3, then diluting with distilled water and filtering to remove the precipitated polymer ligand. The solution was neutralized with ammonia solution and the metal ions were then titrated with EDTA (Vogel, 1978; West, 1969).

2.4.4. ^{1}H NMR spectra

The ^{1}H NMR measurements were carried out on a *Varian Gemini-200*. Deuterated dimethyl sulfoxide (DMSO-d_6) was used as a solvent. The chemical shifts (δ) were measured with respect to tetra methyl silane (TMS), which used as internal standard.

2.4.5. ESR spectra

ESR spectra of compounds were recorded on a Bruker model EMX, X-band spectrometer (9.78 GHz) with 100 kHz modulation frequency.

2.4.6. Magnetic measurements

Magnetic susceptibilities of the complexes were measured by the Gouy method at room temperature using a magnetic susceptibility balance (Johnson Matthey, Alfa product, Model No. (MKI)). Effective magnetic moments were calculated from the expression $\mu_{\text{eff}} = 2.828\ (\chi_M T)^{1/2}$ B.M., where χ_M is the molar susceptibility corrected using Pascal's constants for the diamagnetism of all atoms in the compounds and T is the absolute temperature (Mabbs & Machin, 1973).

3. Results and discussion

ChitoCin and ChitoThioCin ligands were obtained and their structures were confirmed by elemental analysis as well as FT-IR spectroscopy. Table 1 depicts the vibrational frequencies and their assignments which were compared with other standard chitosan derivatives.

The ^{1}H NMR spectra of the partially dissolved polymer ligands in dimethylsulphoxide, DMSO-d_6, show signals at 2.13 and 0.92 ppm that are assigned to the protons of the CH_2 groups for the ChitoCin and ChitoThioCin polymers, respectively. The signals at 3.40 and 3.29 ppm for ChitoCin polymer and 3.39 and 3.28 ppm for ChitoThioCin polymer are assigned to the protons of CH groups (Pretsch & Seibl, 1983; Silverstein, Webster, & Kiemle, 2005) which are due to the CH protons in different chemical environments. The two signals at 10.02 and 10.06 ppm for ChitoCin polymer is due to the OH protons, which are due to two different chemical environments. ^{1}H NMR spectra of the two polymers did not show the proton signals of the NH, where their values are expected in a higher chemical shift than 10 ppm, this may be due to the low solubility of the two polymers in the solvent.

Absorption spectral data of the two polymer ligands were recorded as Nujol mulls in the solid state. The electronic spectra of the polymers exhibited four absorption bands at (210, 290, 374 and 410 nm) for ChitoCin polymer ligand and (235, 310, 358 and 432 nm) for ChitoThioCin polymer ligand. The first two bands for both polymers correspond to the $^1L_a \rightarrow {}^1A_1$ and $^1L_b \rightarrow {}^1A_1$ transitions of the phenyl ring. The third band corresponds to the $\pi \rightarrow \pi^*$ transition, and the last band corresponds to the $n \rightarrow \pi^*$ transition due to the lone pairs of the oxygen, nitrogen and/or sulfur atoms, which overlapped with the intermolecular charge transfer (CT) from the phenyl ring (Silverstein et al., 2005; Abo-Hussen & Emara, 2004).

Table 1
Vibrational frequencies (cm^{-1}) of the chitosan, ChitoCin polymer and ChitoThioCin polymer and their tentative assignments.

Chitosan	ChitoCin polymer	ChitoThioCin polymer	Tentative assignments
3425 s, 3282 s	–	–	$\nu(NH_2)$
3257 m	3263 m	3250 s	$\nu(OH)$
–	3153 m	3100 m	$\nu(NH)$
–	–	–	$\nu(NH_4)$
–	3062 m	3050 m	ν(Ar–CH)
2932 m, 2879 m	2926 m	2922 m	ν(aliph–CH)
–	–	2065 vs	$\nu(NC{=}S)$
–	1634 vs	1654 vs	$\nu(C{=}O)$
–	1623 s, 1605 m	1625 s, 1543 m	$\nu(C{=}C)$
1646 m	–	–	δ(Amide II)
1580 s	1525	1520 m	$\delta(NH)$
–	–	1421 w	δ(N–C–S)
1460 m	1421	–	δ(aliph–CH)
1407	1383	–	δ(CC–H)
–	–	1344 m	$\nu(C{=}S)$
1162 m, 1029 m	1154 vs	1156 m, 1069 m	ν(C–O)
568 m	476 vs	661 w	δ(N–C–O)
–	–	563 w	δ(N–C–S)

ν, stretching; δ, bending; s, strong; m, medium; w, weak; vs, very strong; sh, shoulder.

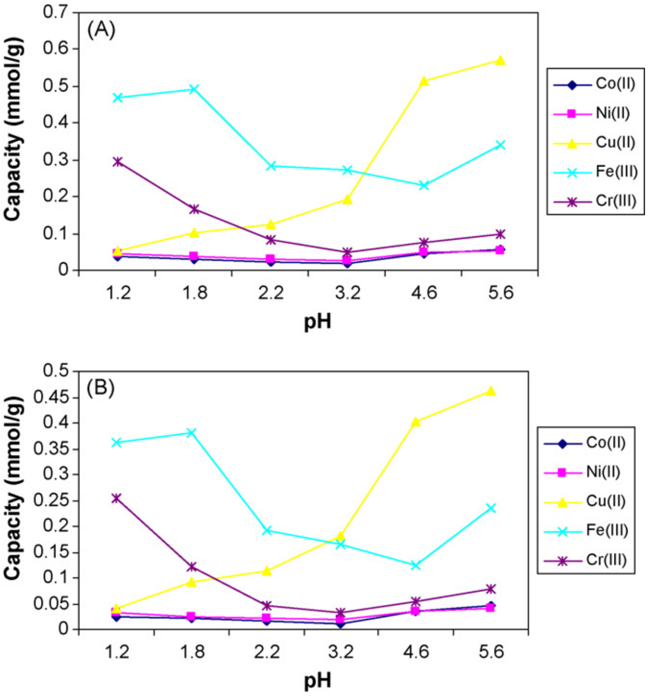


Fig. 1. Capacity (mmol/g) of ChitoCin for a number of divalent and trivalent metal ions under non competitive conditions as a function of pH (A) ChitoCin and (B) ChitoThioCin.

3.1. Metal uptake by (ChitoCin) and (ChitoThioCin) polymers

3.1.1. Batch metal uptake capacity

The metal-ion capacities of the (ChitoCin and ChitoThioCin) polymers were determined under non-competitive conditions as a function of the pH of the buffered solutions of a number of divalent and trivalent metal nitrates. The uptake results indicated that ChitoCin and ChitoThioCin show similar behavior for the uptake of all metal ions under investigation as given in Figs. 1 and 2. The behavior of the two polymers shows that the metal-ion uptake increases rapidly with increasing the pH values in case of Co(II), Ni(II) and Cu(II) ions, while the uptake Cr(III) and Fe(III) ions begins high at lower pH values then decreases gradually with increasing the pH, after that, it increases at higher pH values as shown in Fig. 1.

Around pH 5.6, the (ChitoCin and ChitoThioCin) polymers exhibit higher capacity for Cu(II) (0.461–0.572 mmol/g) than the other metal ions used. Where the capacities of the other metal ions are: Fe(III) (0.235–0.341 mmol/g), Cr(III) (0.078–0.099 mmol/g), Co(II) (0.046–0.057 mmol/g) and Ni(II) (0.041–0.053 mmol/g). These results show that the capacities of ChitoThioCin polymer is higher than that of ChitoCin for each metal ion, also the non-competitive metal uptake experiments appear to be in accordance with the Irving–Williams series (Irving & Williams, 1953).

At low pH values the capacities (for Cr(III) pH < 1.8 and Fe(III) pH < 3.1) are higher than other metal ions under investigation. For Cr(III) the maximum uptake is 0.255 mmol/g for ChitoCin and 0.294 mmol/g for ChitoThioCin at pH 1.2, while the maximum uptake for Fe(III) is 0.382 mmol/g for ChitoCin and 0.492 mmol/g for ChitoThioCin at pH 1.8. The increased uptake of Cr(III) and Fe(III) ions at low pH values is probably due to the relative high stability of

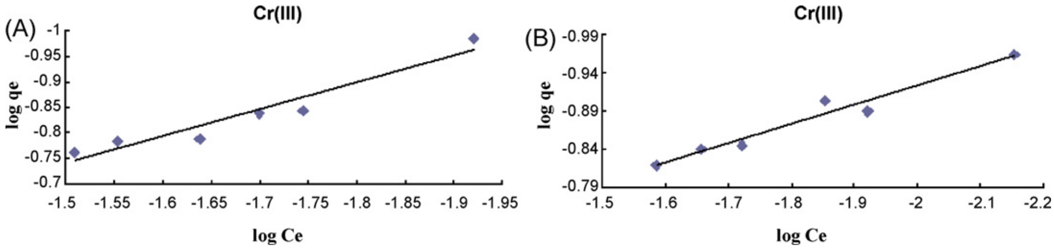


Fig. 2. Freundlich isotherms for the adsorption of Cr (III) onto (A) ChitoCin (B) onto ChitoThioCin.

anionic chloro-complexes at lower pH where the higher hydrogen ion concentration increases and also due to a coordinating effect of the high chloride ion concentration introduced by the buffer. The chloride ions favor the formation of anionic chlorometallates which can be taken up by the polymers through anion exchange.

3.1.2. Metal-ion capacities of polymers under competitive conditions

The results of metal-ion capacities of polymers (ChitoCin and ChitoThioCin) under competitive conditions for a number of divalent [Co(II), Ni(II) and Cu(II)] and trivalent [Cr(III) and Fe(III)] metal ions are shown in Tables 2 and 3. From the obtained data it is found that the order of the overall uptake capacities of the polymers under competitive conditions is Cu(II) > Fe(III) > Co(II) > Cr(III) > Ni(II). These results show that the capacities of ChitoThioCin polymer under competitive conditions are higher than that of ChitoCin for all metal ions under investigation. The (ChitoCin and ChitoThioCin) polymers were highly selective for Cu(II) over the other metal ions in all the mixtures. The high values of metal uptake capacities for Cu(II) found in these experiments most probably indicates the formation of 1:1 Cu(II):ligand complex. The rigidity of the complex matrix (Van Berkel, Driessen, Kodhaas, Reedijk, & Sherrington, 1995) makes it likely that 1:1 metal:ligand complexes are formed.

3.2. Freundlich and Langmuir isotherms for the adsorption of some metal ions under investigation

Freundlich and Langmuir isotherms for the adsorption of Cr(III), Fe(III) and Cu(II) ions from aqueous nitrate solutions were carried out for the two polymeric chitosan adsorbents (ChitoCin and ChitoThioCin). The medium here is acidic due to the use of nitrate salts which render the medium quite acidic (pH ~ 1–2).

Freundlich isotherm could be written as (Eq. (1)) (Ravindran, Steven, Badriyha, & Pribazari, 1999):

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{1}$$

where q_e is the amount of the metal ions adsorbed per unit weight of the sorbent (mg/g), C_e is the equilibrium concentration of the solute in the bulk solution (mg/l), K_F is a constant points toward the relative sorption capacity of the sorbent (mg/g) and $1/n$ is a constant related to the intensity of the sorption processes. The straight lines obtained from the Freundlich isotherm plots of the studied ions indicate that the sorption of Cr(III), Fe(III) and Cu(II) ions fits this pattern. Slopes of the Freundlich plots for ChitoCin equal to 0.5298, 0.6177 and 0.2163 for Cr(III), Fe(III) and Cu(II) ions, respectively, while in case of ChitoThioCin polymer, equal to 0.2538, 0.4978 and 0.1964 for Cr(III), Fe(III) and Cu(II) ions; respectively. The slope

Table 2
Metal-ion capacities of ChitoCin polymer under competitive conditions.

Metal-ions mixtures	Metal-ion capacities (mmol/g) of ChitoCin polymer				
	Co(II)	Ni(II)	Cu(II)	Fe(III)	Cr(III)
(I) Two metal-ions mixtures					
Cu, Ni		0.0045	0.018		
Cu, Cr			0.016		0.0093
Cu, Co	0.0075		0.0155		
Cu, Fe			0.0145	0.0111	
Ni, Cr		0.0072			0.0103
Ni, Fe		0.0065		0.0123	
Ni, Co	0.0105	0.0072			
Cr, Fe				0.0141	0.0065
Cr, Co	0.0113				0.0093
Co, Fe	0.0105			0.014	
(II) Three metal-ions mixtures					
Cu, Co, Cr	0.0075		0.0142		0.0063
Cu, Co, Fe	0.0085		0.0145	0.0091	
Cu, Cr, Fe	S		0.0151	0.0085	0.0065
Cu, Ni, Co	0.0085	0.005	0.0155		
Cu, Ni, Cr		0.0055	0.0165		0.0075
Cu, Ni, Fe		0.0045	0.0142	0.0095	
Ni, Co, Cr	0.0083	0.0055			0.0073
Ni, Co, Fe	0.0085	0.0043		0.0131	
Ni, Cr, Fe		0.0045		0.0095	0.0065
Co, Cr, Fe	0.0113			0.0131	0.0093
(III) Four metal-ions mixtures					
Cu, Co, Cr, Fe	0.0075		0.0115	0.0075	0.0055
Cu, Ni, Cr, Fe		0.0035	0.0123	0.0081	0.0055
Cu, Ni, Co, Fe	0.0061	0.0025	0.0115	0.009	
Cu, Ni, Co, Cr	0.0072	0.0042	0.0125		0.0062
Ni, Co, Cr, Fe	0.0065	0.0031		0.0081	0.0051

Table 3
Metal-ion capacities of ChitoThioCin polymer under competitive conditions.

Metal-ions mixtures	Metal-ion capacities (mmol/g) of ChitoThioCin polymer				
	Co(II)	Ni(II)	Cu(II)	Fe(III)	Cr(III)
(I) Two metal-ions mixtures					
Cu, Ni		0.0072	0.0192		
Cu, Cr			0.0181		0.0081
Cu, Co	0.0085		0.0174		
Cu, Fe			0.0156	0.0123	
Ni, Cr		0.0092			0.0115
Ni, Fe		0.0058		0.0131	
Ni, Co	0.0119	0.0081			
Cr, Fe				0.0173	0.0074
Cr, Co	0.0116				0.0082
Co, Fe	0.011			0.0152	
(II) Three metal-ions mixtures					
Cu, Co, Cr	0.0084		0.0171		0.0072
Cu, Co, Fe	0.0109		0.0151	0.0123	
Cu, Cr, Fe			0.016	0.0095	0.0069
Cu, Ni, Co	0.0097	0.0065	0.0169		
Cu, Ni, Cr		0.0075	0.0164		0.0084
Cu, Ni, Fe		0.0061	0.0175	0.0112	
Ni, Co, Cr	0.0102	0.0068			0.0081
Ni, Co, Fe	0.0107	0.0049		0.0153	
Ni, Cr, Fe		0.0053		0.0135	0.0078
Co, Cr, Fe	0.0132			0.0154	0.0098
(III) Four metal-ions mixture					
Cu, Co, Cr, Fe	0.0097		0.0138	0.0099	0.0074
Cu, Ni, Cr, Fe		0.0057	0.0148	0.0101	0.0077
Cu, Ni, Co, Fe	0.0083	0.0052	0.0132	0.0112	
Cu, Ni, Co, Cr	0.0092	0.0067	0.0143		0.0086
Ni, Co, Cr, Fe	0.0087	0.0056		0.0102	0.0071

value (<1) indicates that the sorption of these ions onto the ChitoCin or ChitoThioCin polymers is a concentration-dependent process (Sheha & Metwally, 2007). This may be attributed to the fact that with progressive surface coverage of the adsorbent, the attractive forces between the metal-ion species such as van der Waals forces, increases more rapidly than the repulsive forces, exemplified by short-range electronic or long-range Coulombic dipole repulsion, and consequently, the metal ions manifest a stronger tendency to bind to the polymer surface (Ravindran et al., 1999).

The data obtained from the Freundlich isotherm suggest that the sorption processes could not be restricted for a specific class of sites and assume surface heterogeneity. Table 4 illustrates the Freundlich parameters calculated for the sorption of Cr(III), Fe(III) and Cu(II) ions and the correlation coefficient values (R^2).

Langmuir isotherm could be written as (Eq. (2)) (Metwally et al., 2009):

$$\frac{C_e}{q_e} = \frac{1}{Q^\circ b} + \left(\frac{1}{Q^\circ}\right) C_e \qquad (2)$$

where q_e is the amount of the metal ions adsorbed per unit weight of the sorbent (mg/g), C_e is the equilibrium concentration of the solute in the bulk solution (mg/l), Q^o is the monolayer adsorption capacity (mg/g) and b is a constant related to the free energy of adsorption (i.e., $b \alpha e^{-\Delta G/RT}$). The obtained data are presented in Fig. 2 and the corresponding Langmuir parameters for the adsorption of the studied ions are listed in Table 4. The order of the monolayer adsorption capacity Q^o for the sorption of studied metal ions was: Fe(III) > Cu(II) > Cr(III) (for both ChitoCin and ChitoThioCin polymers). Since the overall rate constant K_a equals to the product of Langmuir parameters ($b \times Q^o$) (Ravindran et al., 1999). From the obtained data, it is found that the order of the overall rate constant K_a (for ChitoCin) was: Fe(III) > Cr(III) > Cu(II), while for ChitoThioCin was: Fe(III) > Cu(II) > Cr(III). This result is in accordance with the previous data obtained at low pH where Fe(III) was the highest adsorbed metal ion. From Table 4 it seems that the adsorption mechanism fits the Langmuir isotherm better than the Freundlich one. As representative examples of the Freundlich and Langmuir isotherms Cr (III) adsorption onto ChitoCin and ChitoThioCin polymers is given in Figs. 2 and 3, respectively.

3.3. Complexes of the ChitoCin and ChitoThioCin polymer ligands

The ChitoCin and ChitoThioCin polymer ligands reacted with Cu(II), Ni(II), Co(II), Fe(III) and Cr(III) ions to yield the corresponding metal complexes. Table 5 lists the physical and analytical data of the ChitoCin and ChitoThioCin polymer ligands and their transition

Table 4
Freundlich and Langmuir parameters data for the sorption of Cu(II), Cr(III) and Fe(III) from aqueous nitrate solutions by the adsorbents (ChitoCin and ChitoThioCin polymers).

Isotherm		Cu(II)		Cr(III)		Fe(III)	
Type	Parameters	ChitoCin	ChitoThioCin	ChitoCin	ChitoThioCin	ChitoCin	ChitoThioCin
Freundlich	K_F (mg/g)	47.28	45.70	54.96	34.31	72.47	58.82
	$1/n$	0.2163	0.1964	0.5298	0.2538	0.6177	0.4978
	R^2	0.9793	0.9534	0.9628	0.9808	0.9623	0.9718
Langmuir	Q^o	19.54	18.25	14.89	10.79	28.67	20.86
	B	0.5509	0.4098	1.0128	0.4735	2.3609	1.4436
	K_a	10.767	7.480	15.076	5.111	67.682	30.117
	R^2	0.9985	0.9962	0.9758	0.9886	0.9559	0.9731

Table 5
Analytical and physical data for the ChitoCin and ChitoThioCin polymers and their metal complexes.

Reactions of the ligand and metal salts		Molecular formula (molecular weight)	Wt. of the ligand g	Wt. of the metal salt g	Yield	Color	Elemental analyses; calc. (found)				
					g (%)		C (%)	H (%)	N (%)	S (%)	M (%)
(1)	$[Co(ChitoCin)(NO_3)(H_2O)_3]\cdot CH_3OH$	$C_{16}H_{26}N_2O_{12}Co$ 497.317	1.455	1.455	1.354 (58.3)	Brown	38.64 (38.41)	5.27 (4.92)	5.63 (5.27)	–	11.85 (11.66)
(2)	$[Ni(ChitoCin)(NO_3)(H_2O)_3]\cdot H_2O$	$C_{15}H_{24}N_2O_{12}Ni$ 483.051	1.455	1.454	1.531 (58.2)	Yellow	37.30 (37.60)	5.01 (4.64)	5.80 (5.65)	–	12.15 (12.43)
(3)	$[Cu(ChitoCin)(NO_3)(H_2O)_3]\cdot CH_3OH$	$C_{16}H_{26}N_2O_{12}Cu$ 501.500	1.455	1.208	1.316 (59.1)	Green	38.29 (38.74)	5.18 (4.95)	5.58 (5.90)	–	12.66 (12.72)
(4)	$[Fe(ChitoCin)(NO_3)_2(H_2O)_3]\cdot 2H_2O$	$C_{15}H_{26}N_3O_{16}Fe$ 560.223	1.455	2.020	1.354 (58.3)	Brown orange	32.16 (32.42)	4.68 (4.51)	7.50 (7.31)	–	9.97 (9.98)
(5)	$[Cr(ChitoCin)(NO_3)_2(H_2O)_3]\cdot 2H_2O$	$C_{15}H_{26}N_3O_{16}Cr$ 556.00	1.455	2.000	1.531 (58.2)	Pale brown	32.38 (32.12)	4.68 (4.30)	7.55 (7.51)	–	9.35 (9.23)
(6)	$[Co(ChitoThioCin)(NO_3)(H_2O)_2]$	$C_{16}H_{21}N_3O_{10}SCo$ 506.351	1.750	1.455	0.997 (45.4)	Pale brown	37.95 (38.24)	4.18 (4.30)	8.30 (8.69)	6.33 (6.20)	11.64 (11.66)
(7)	$[Ni(ChitoThioCin)(NO_3)(H_2O)_2]$	$C_{16}H_{21}N_3O_{10}SNi$ 506.112	1.750	1.454	1.399 (38.3)	Brown	37.97 (38.01)	4.18 (4.22)	8.30 (8.89)	6.34 (6.02)	11.60 (11.30)
(8)	$[Cu(ChitoThioCin)(NO_3)(H_2O)_2]$	$C_{16}H_{21}N_3O_{10}SCu$ 510.964	1.750	1.208	1.90 (53.4)	Dark green	37.61 (37.72)	4.14 (4.27)	8.22 (8.08)	6.28 (6.14)	12.44 (12.12)
(9)	$[Fe(ChitoThioCin)(NO_3)_2(H_2O)_2]\cdot 2H_2O$	$C_{16}H_{25}N_4O_{15}SFe$ 601.000	1.750	1.455	0.997 (45.4)	Red	31.95 (31.72)	4.16 (4.23)	9.32 (9.45)	5.32 (5.09)	9.32 (9.24)
(10)	$[Cr(ChitoThioCin)(NO_3)_2(H_2O)_2]\cdot 2^1/_2H_2O$	$C_{16}H_{26}N_4O_{15.5}SCr$ 606.450	1.750	1.454	1.399 (38.3)	Brown orange	31.66 (32.33)	4.29 (4.60)	9.23 (9.90)	5.28 (5.19)	8.57 (9.13)

All reactions were heated to reflux for 2–4 h. The melting point of all compounds was higher than 300 °C. The weights of all reactants were 5 mmol.

Table 6
Characteristic of vibrational frequencies (cm^{-1}) of the ChitoCin, ChitoThioCin polymers and their metal complexes and their assignments.

Ligand/complexes		ν(OH) polymer, H_2O, and/or CH_3OH	ν(NH)	ν(C=N)	ν(N–C=S)	ν(C=O)	ν(C–O)	δ(H_2O)	ν(C–S)	ν(M–N)	Other bands
	ChitoCin	–	3153 m	–	2053 m	1701 s, 1684 s	1154 m	–	–	–	1261 vs, ν(C=S)
	ChitoThioCin	–	3100 m	–	2053 m	1701 s, 1684 s	1156 m, 1069 m	–	–	–	1261 vs, ν(C=S)
(1)	$[Co(ChitoCin)(NO_3)(H_2O)_3]\cdot CH_3OH$	3490 br, m	–	1613	1661 w	–	1154 m, 1054 m	1606 s	–	444 w	1542, 1325, and 811
(2)	$[Ni(ChitoCin)(NO_3)(H_2O)_3]\cdot H_2O$	3426 br, m	–	1565	–	–	1154 m, 1059 m	1605 vs	–	455 w	1548, 1332, and 810
(3)	$[Cu(ChitoCin)(NO_3)(H_2O)_3]\cdot CH_3OH$	3400 sh, m	–	1600	1667 m	–	1154 m, 1062 m	1613 s	–	432 w	1547, 1328, and 814
(4)	$[Fe(ChitoCin)(NO_3)_2(H_2O)_3]\cdot 2H_2O$	3405 m, sh	–	1587	–	–	1154 m, 1058 m	1605 s	–	–	1434 sh, s 1354 vs 837 m; Unidentate NO_3^-
(5)	$[Cr(ChitoCin)(NO_3)_2(H_2O)_3]\cdot 2H_2O$	3491 m	–	1593	–	–	1154 m, 1056 m	1605 vs	–	448 w	1431 s, 1351 vs, 831 m; Unidentate NO_3^-
(6)	$[Co(ChitoThioCin)(NO_3)(H_2O)_2]$	3490 br, m	3182 m	–	1661 w	1661 w	1154 m, 1055 m	1606 s	699 m	444 w	1545, 1328, and 817
(7)	$[Ni(ChitoThioCin)(NO_3)(H_2O)_2]$	3426 br, m	3163 m	–	–	–	1158 m, 1061 m	1605 vs	697 m	455 w	1545, 1325, and 809
(8)	$[Cu(ChitoThioCin)(NO_3)(H_2O)_2]$	3400 sh, m	3190 s	–	1667 m	1667 m	1155 m, 1069 m	1613 s	706 m	432 w	1541, 1328, and 814
(9)	$[Fe(ChitoThioCin)(NO_3)_2(H_2O)_2]\cdot 2H_2O$	3405 m, sh	3184 m	–	–	–	1154 m, 1053 m	1605 s	688 m	–	1427 sh, s 1358 vs 841 m; Unidentate NO_3^-
(10)	$[Cr(ChitoThioCin)(NO_3)_2(H_2O)_2]\cdot 2^1/_2H_2O$	3491 m	3170 m	–	–	–	1152 m, 1063 m	1605 vs	711 m	448 w	1435 s, 1362 vs, 839 m; Unidentate NO_3^-

s, strong; m, medium; s, strong; vs, very strong, sh, shoulder, br, broad.

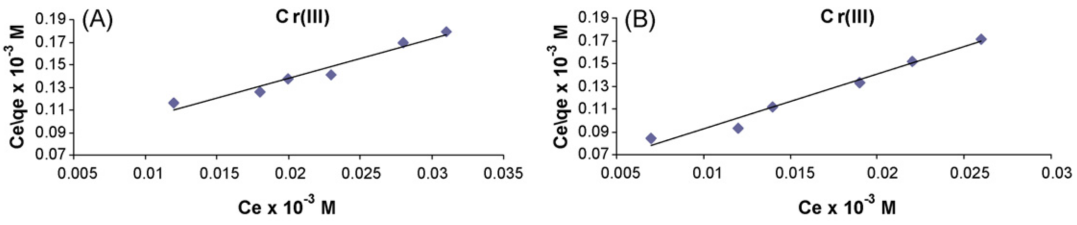


Fig. 3. Langmuir isotherms for the adsorption of Cr(III) onto (A) ChitoCin and (B) onto ChitoThioCin at range from 10^{-5} to 10^{-2} M concentration.

metal complexes. These complexes were investigated by elemental analyses, FT-IR, UV–vis, ESR spectroscopy and magnetic measurements. All the complexes are insoluble in most common solvents and it was not possible to perform molar conductivity measurements.

3.3.1. Infrared spectra of the metal complexes

The tentative assignments for the ChitoCin and ChitoThioCin polymer ligands and their transition metal complexes are listed in Table 6. There are 7 features that characterize these spectra. The first feature is about the stretching frequencies ν(C=O), of the (C=O) group in the free ChitoCin polymer ligand which was observed at 1634 cm^{-1}. This band disappeared in all the metal complexes. This disappearance may be due to the fact that, this group undergoes keto-enol tautomerism and is involved in the coordination of the metal ion as (C–O) group appearing at (1054–1066 cm^{-1}) for ChitoCin complexes (Nakamoto, 1997).

This trend was not the case for ν(C=O), of the (C=O) group in the ChitoThioCin metal complexes, where this band was shifted to lower frequency (1642–1632 cm^{-1}) compared to the ν(C=O) of the free ChitoThioCin polymer ligand at (1654 cm^{-1}). This means that the C=O group still exist as it is, and is involved in the coordination of the ChitoThioCin polymer ligand with the metal ions.

The second feature is the disappearance of the ν(C=S) of the (–C=S) group in the all ChitoThioCin complexes compared to the ν(C=S) in the free ChitoThioCin polymer ligand which lie at 1344 cm^{-1}. This may be due to the fact that, this group is not involved in the coordination of the metal ion as C=S and should be converted to (C–S) at (688–711 cm^{-1}) for ChitoThioCin complexes, as a result of the thion-thiol tautomerism (see Metwally et al., 2009).

The third feature is the disappearance of the stretching frequency of the ν(C–N) in the ChitoCin polymer ligand complexes, and appearance of new bands in the range (1613–1565 cm^{-1}) which is attributed to the stretching frequency of the azomethine group, ν(–C=N), supporting again the formation of the enol form in all metal complexes of the ChitoCin polymer ligand.

The fourth feature is the stretching frequency of the, ν(NH). In case of the ChitoCin complexes, this band disappeared since (–NH–CO–) group was converted from keto to the enol form (–N=C–(OH)). In case of the ChitoThioCin complexes the ν(NH) band was observed in the range (3190–3165 cm^{-1}) compared to its stretching frequency of the free ChitoThioCin ligand which appeared at 3100 cm^{-1}.

The fifth feature is due to weak bands at the range (470–425 cm^{-1}) for ChitoCin and ChitoThioCin complexes, which could be assigned to the stretching frequencies of the ν(M–N) bands. It is expected that the ν(M–O) and ν(M–S) vibrations to be observed below 400 cm^{-1}which are out of the range of the used instrument.

The sixth feature in the coordination behavior of the nitrate, NO_3^-, groups. The NO_3^- ion is coordinated to the metal ion as bidentate for the metal complexes of Co(II) ((1) and (6)), Ni(II) ((2) and (7)) and Cu(II) ((3) and (8)) complexes of both the ChitoCin and ChitoThioCin polymer ligands. The bidentate nitrate group expected to possess three non-degenerated modes of the vibrations (ν, ν_a and ν_s) which appeared at the ranges (1541–1548), (1325–1332), and (809–817) cm^{-1}, for ChitoCin and ChitoThioCin complexes. On the other hand, the unidentate nitrate group is expected to possess three non-degenerated modes of the vibrations (ν_s, $\nu_{s'}$ and ν_{as}) which appeared in the ranges (1427–1434 cm^{-1}), (1351–1361 cm^{-1}) and (831–841 cm^{-1}) for both Fe(III) ((4) and (9)) and Cr(III) ((5) and (10)) ChitoCin and ChitoThioCin complexes, respectively.

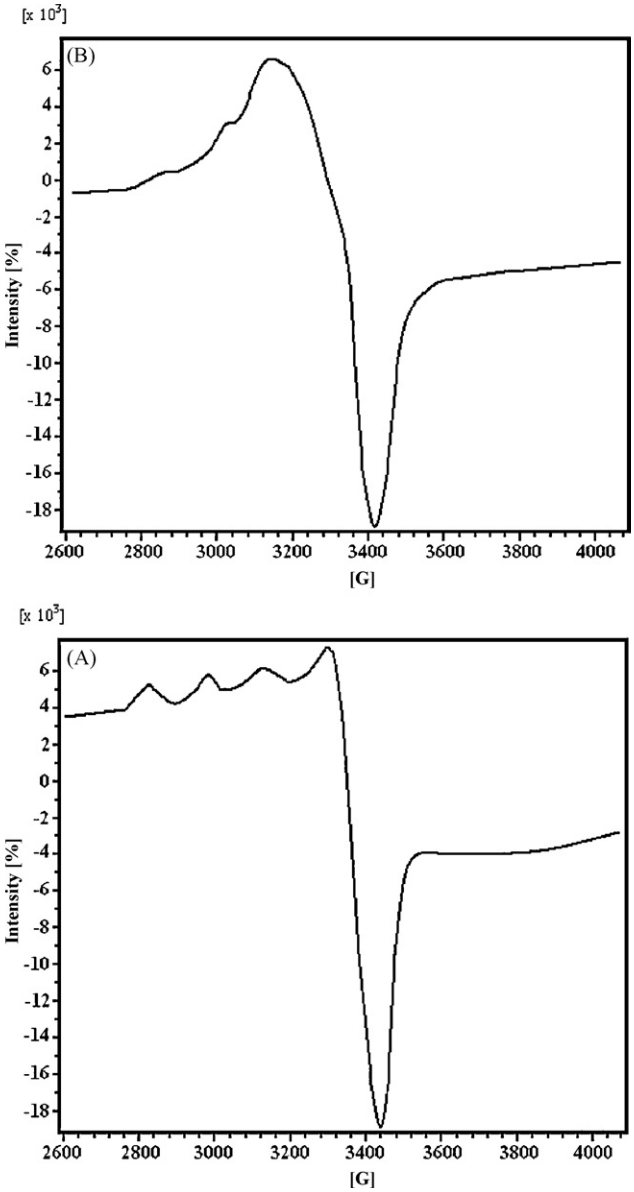


Fig. 4. X-Band ESR spectra of: (A) [Cu(ChitoThioCin)(NO_3)(H_2O)$_2$] (8) and (B) Cu(ChitoCin)(NO_3)(H_2O)$_3$](3).

The last feature in the IR spectra is due to broad bands in the range (3400–3491 cm^{-1}) for the ChitoCin and ChitoThioCin complexes, which can be assigned to the stretching frequencies of the ν(OH) of the OH groups in the polymer, water or methanol molecules associated with the complexes which are also confirmed by the elemental analysis (Khalil & Emara, 2002).

3.3.2. Electronic and ESR spectra, magnetic moment measurements of the metal complexes

The metal complexes of the ChitoCin and ChitoThioCin, polymer ligands are insoluble in most common solvents. The electronic spectra were recorded in the solid state using Nujol mulls method. It is possible to draw up the electronic transitions and predict the geometry with the aid of magnetic moments of the metal ions.

In the ChitoCin polymer metal complexes, the absorption bands of the phenyl groups, and the double bonds appeared, in four regions, at 217–225, 310–323, 355–372 and 400–407 nm. These values are lower than the corresponding absorption bands for the ChitoCin ligand itself which are observed at 230, 324, 374 and 410 nm. The same trend can be observed for the second series of metal complexes of the ChitoThioCin polymer ligand. The values are in the range 219–230, 322–328, 351–375 and 417–430 nm which are lower than the corresponding absorption bands for the ChitoThioCin ligand, appearing at 232, 330, 378 and 432 nm. This may be due to the coordination of the nitrogen, oxygen and sulphur atoms of the two polymer ligands to the metal ions.

The electronic spectra in (Nujol mull) showed that the brown and pale brown Co (II) (1) and (6) complexes have octahedral structure. The transition can be interpreted by using Tanabe-Sugano diagram. In Co(II) octahedral complex, the spectra usually consist of three bands. The first band, is due to $^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$ transition, this band was not observed due to the fact that it occurs in the near infrared region, and out of the range of the used instrument. The second band which is due to $^4A_{2g}(F) \leftarrow {}^4T_{1g}(F)$ transition is observed at 738 and 723 nm, for complexes (1) and (6) respectively. The third band due to $^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$ transition is expected at 688 and 687 nm, for complexes (1) and (6) respectively. The magnetic properties provide a complementary means of distinguishing the stereo-chemistry of the complexes. The measured value of the magnetic moment, μ_{eff}, was 4.95 and 5.13 B.M.; which lie in the range (4.80–5.20 B.M.) of the octahedral compounds (Lever, 1997).

The electronic spectra of the yellow and brown Ni(II) ((2) and (7)) complexes showed several bands. Generally, three spin-allowed transitions are expected. The $^3T_{2g}(F) \leftarrow {}^3A_{2g}(F)$ transition was observed at 742 and 749 nm for (2) and (7) complexes; respectively. The $^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$ transition was not observed which was expected in the near infrared and it is out of the range of the used instrument. The third band is due to $^3T_{1g}(P) \leftarrow {}^3A_{2g}(F)$ transition is observed at 469 and 495 nm for complexes (2) and (7), respectively. This transition may be overlapped by the ligand $n \rightarrow \pi^*$ transition which appeared at 411 and 417 nm for ChitoCin and ChitoThioCin polymer ligand, respectively. The measured values of the magnetic moments, μ_{eff}, were 2.92 and 2.91 B.M, for complexes (2) and (7), respectively, which lie in the range (2.9–3.3 B.M.) of the octahedral compounds.

The electronic spectra of the green and dark green Cu(II) ((3) and (8)) complexes exhibited one band due to $^3T_{2g}(G) \leftarrow E_g$ transition, which was observed at 739 and 702 nm for (3) and (8) complexes; respectively. The measured values of the magnetic moment, μ_{eff}, were 1.85 and 1.91 B.M., which lie at the higher end of the range (2.00–1.73 B.M.), which confirm the distorted octahedral structure (Broussignac, 1968).

X-Band ESR spectra of the Cu(II) ((3) and (8)) complexes, were recorded in the solid state at 25 °C and is shown in Fig. 4. The spectra exhibit two bands with $g_1 = 2.07567$ and $g_2 = 2.09139$ for complex (3) and $g_1 = 2.06052$ and $g_2 = 2.09891$ for complex (8). The shape of the spectra are consistent with the distorted octahedral geometry around the Cu(II) environment in the complexes (Ruf, Noll, Grone, Yee, & Piepont, 1996; Speie, Csihony, Whalen, & Piepont, 1996).

The electronic spectra of the brown and brown orange and red Fe(III) (4) and (9) complexes show several bands which were observed at 729, 621, 484 for complex (4) and one band at 495 nm for complex (9). It was not possible to identify the type of the d–d transitions, due to the strong charge transfer (CT) band tailing from UV-region to the visible region. Generally, from the elemental and the infrared spectra which give a significant proof for the nitrate anion to act as a unidentate ligand. It is expected that the Fe(III) complexes have octahedral arrangement. Magnetic moment, μ_{eff}, of Fe(III) metal ion present in the complexes (4) and (9) were measured and gave 4.89 and 4.92 B.M.; respectively. These values are close but lower than the magnetic moment of the high-spin octahedral, $t_{2g}{}^3e_g{}^2$, which lies in the range 5.92 B.M. On the other hand, the experimental value 4.89 or 4.92 B.M. are too far from the low spin octahedral ($t^5{}_{2g}e_g{}^o$), magnetic moment which lies in the range 2.3 B.M. (Cotton & WilKinson, 1986). Generally a tentative interpretation expect that the structures of Fe(III) (4) and (9) complexes to have high-spin octahedral geometry.

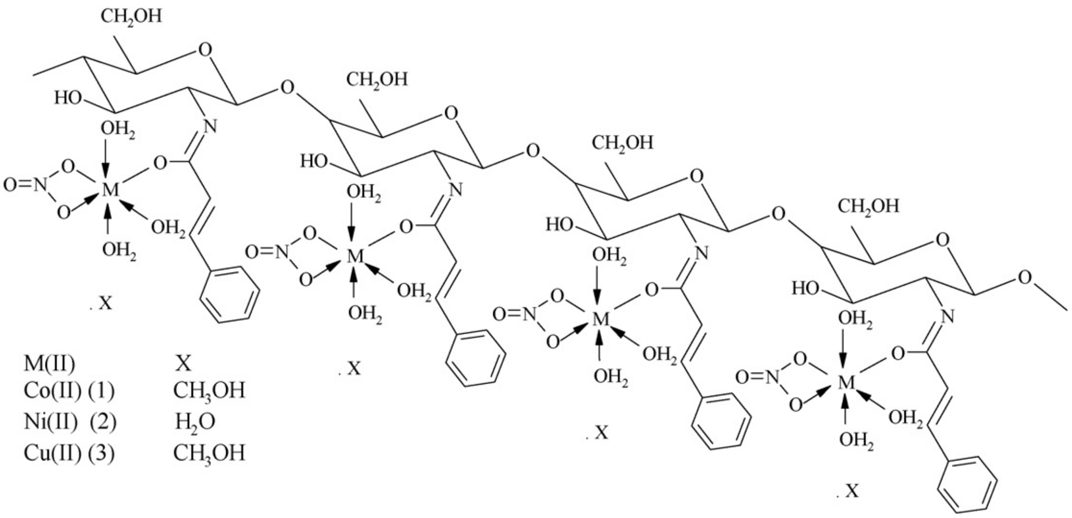


Fig. 5. Suggested structures of the metal complexes of the ChitoCin polymer ligand.

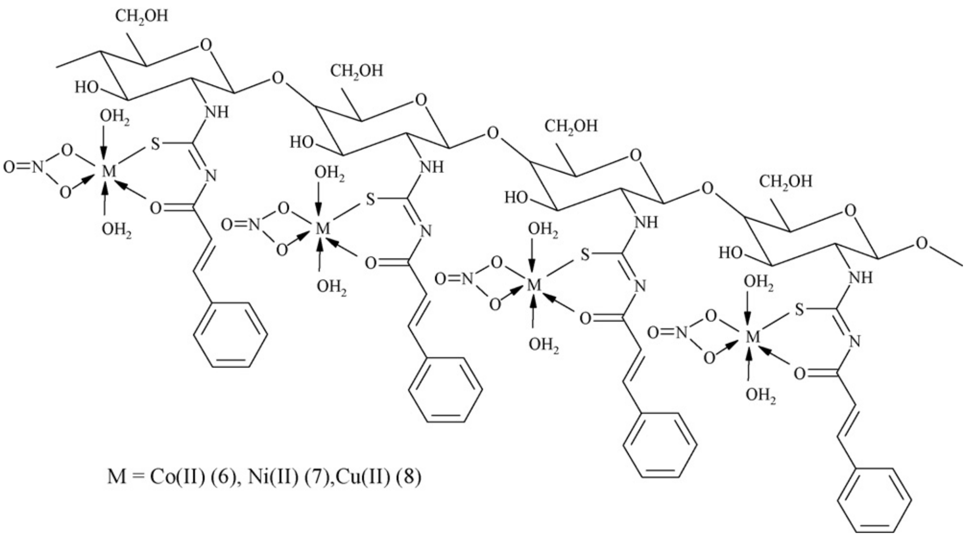


Fig. 6. Suggested structures of the metal complexes of the ChitoThioCin polymer ligand.

The electronic spectra of the pale brown and brown orange Cr(III) ((5) and (10)) complexes show two bands which are observed at 736 and 672 nm for complex (5) and 748 and 665 nm for complex (10).

The first band which is due to $^4T_{2g}(F) \leftarrow {}^4A_{2g}(F)$ was observed at 672 and 665 nm for complex (5) and (10); respectively. The second band which is due to $^4T_{1g}(F) \leftarrow {}^4A_{2g}(F)$ transition was observed at 736 and 748 nm for complexes (5) and (10); respectively. The magnetic moment, μ_{eff}, of the metal ion present in the complex for Cr(III) is expected to be very close to the spin-only value for three unpaired electrons (3.87 B.M.) and (3.89 B.M.) for (5) and (10) complexes; respectively, and also because of the absence of any orbital contribution. From the electronic spectral data and magnetic moment values, it is expected that Cr(III) complexes are octahedral (Cotton & Wilkinson, 1986).

From the interpretation of elemental analysis and infrared, electronic spectra, and ESR and magnetic moments, it is possible to draw up the tentative structures of the transition metal complexes. Figs. 5 and 6 depict the representative structures of the metal complexes.

4. Conclusion

Two new chitosan derivatives have been prepared from the reaction of cinnamoyl chloride (ChitoCin) and cinnamoyl isothiocyanate (ChitoThioCin) with chitosan. The modified chitosan was characterized by elemental analysis to confirm their structures. The metal uptake capacity of the two polymers was measured at different pH values as well as under competitive and non-competitive conditions. It is found that the order of the overall rate constant K_a (for) ChitoCin was: Fe(III) > Cr(III) > Cu(II), while for ChitoThioCin it was: Fe(III) > Cu(II) > Cr(III). Two absorption isotherms were examined for the absorption of metal cations with the two modified chitosan and it was found that the adsorption mechanism fits the Langmuir isotherm better than the Freundlich one. These metal complexes were investigated by elemental analyses, FT-IR, UV–vis, ESR spectroscopy and magnetic measurements. From the UV spectral and magnetic measurements, it was concluded that the complexes are characterized by octahedral geometry. ESR spectra of the Cu(II) complexes for both chitosan derivatives exhibit two bands with $g_1 = 2.07567$ and $g_2 = 2.09139$ for complex (ChitoCin) and $g_1 = 2.06052$ and $g_2 = 2.09891$ for complex (ChitoThioCin). The shape of the spectra are consistent with the distorted octahedral geometry around the Cu(II) environment in the complexes.

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