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ORIGINAL PAPER

Structural, morphological and magnetic characterization of metal-chitosan/poly (vinyl amine) complexes

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Abstract Cu^{2+} and Ni^{2+} complexes of chitosan/poly(vinyl amine) (CS/PVAm) composites were prepared. The metal-CS/PVAm complexes were characterized by FT-IR spectroscopy, SEM-EDX, X-ray diffraction (XRD), and magnetic moment determination. FT-IR spectra of the metal-CS/PVAm complexes showed the characteristic bands of anhidroglucose unit were affected by the metal complexation, and new bands assigned to Me–N and Me-O bonds were observed. SEM images of the surface of metal-composite complexes show the influence of metal ion on the morphology of the complexes, the strong binding of Cu^{2+} and Ni^{2+}, involving most of the amino groups, leading to a dense surface structure. The chemical composition on the surface of metal-CS/PVAm complexes was determined from EDX measurements. XRD provided information about the amorphous or crystalline nature of the composite and metal-composite complexes. Using magnetic susceptibility method, the oxidation degree of metal ions from the polymer phase, the homogeneous distribution of the ligand groups from the volume of the CS/PVAm beads, and the existence of the antiferromagnetic interactions between the metal ions were determined.

Keywords Chitosan · Poly (vinyl amine) · Composites · Metal complexes · Magnetic properties

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Introduction

A very important property of functional polymers is their ability to complex with a variety of metal ions in solution. Lately, considerable attention has been drawn to the chemistry of the metal complexes of polymers containing chelating functional groups, which usually contain nitrogen, oxygen, phosphorus, and other donor atoms [1]. Metal-polymer complexes present entirely new and improved properties, such as biological and catalytic activity, superconducting behavior and so on [2–8]. Thus, the chelating polymers find applications in collecting transition metal ions as well as alkali and alkaline earth metal ion separation, pre-concentration and recovery of trace metal ions, catalysis, organic synthesis, nuclear chemistry, water and waste water-treatment, pollution control, industrial processes, hydrometallurgy and polymer-drug conjugates [3, 5, 8–12]. Polymers used in the complex formation can be synthetic [1–4, 13–16] or natural polymers, coming from renewable resources [10, 11, 17–22].

The complexation of metal ions with Schiff base ligands is an intense studied field of research in coordination chemistry. The Schiff base polymer complexes have been widely used for industrial purposes and also exhibit a broad range of biological activities including antifungal, antibacterial, antimalarial, anti-inflammatory, antiviral, and antipyretic properties [14–16]. The preparation of some metal-polymer complexes formed between Cu^{2+}, Co^{2+}, and Ni^{2+} ions and chelating resins (CR) bearing iminodiacetate groups has been previously reported by our group. The evaluation of the influence of the counterion in the metal salts, and the influence of the nominal cross-linking degree of CR on the properties of the metal-CR complexes have been investigated [20].

Among the natural polysaccharides, chitosan is widely used due to its ability to strongly complex with heavy metal ions, especially with Hg, Cu, Pb, Zn, Ni, Cr [23]. Metal-chitosan

complexes are known to exhibit antimicrobial and antitumoural activity [19]. Due to the presence of amino groups, chitosan has the particular property to form complexes with metal ions at a nearly neutral pH by chelation [20–23].

The preparation of some CS/PVAm composite beads and the investigation of their ability to bind different heavy metal ions such as Cu^{2+}, Co^{2+}, Ni^{2+}, and Cr^{3+} have been recently presented [24–26]. The present paper is focused on the in detail characterization of the metal-composite complexes formed between Cu^{2+} and Ni^{2+} ions and CS/PVAm composites compared with the metal-cross-linked CS complexes, and to evaluate the influence of the counterion nature in the metal salts on the properties of the metal-polymer complexes. FT-IR spectroscopy, SEM-EDX, X-ray diffraction (XRD), and magnetic moment determination were the main methods used to characterize the metal-polymer complexes.

Experimental

Materials

Low molar mass CS was purchased from Sigma-Aldrich and used as received. The average molar mass, determined by viscometry as previously shown [27], was 467 kDa. Degree of acetylation (DA) of CS was evaluated by infrared spectroscopy using a Vertex 70 Bruker FTIR spectrometer [28]. An average value of DA = 15%, resulted from three measurements, was taken into account. PVAm as aqueous solution with a concentration of 18 wt%, a molar mass of 340 kDa, and a degree of hydrolysis of 95 wt%, was received from BASF (Ludwigshafen, Germany). $CuSO_4 \cdot 5H_2O$, $NiSO_4 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, and $NiCl_2 \cdot 6H_2O$ used as metal ion source for the complex formation, were purchased from Sigma Aldrich. Sodium tripolyphosphate (TPP) (85%) was purchased from Sigma-Aldrich and used as received. Epichlorohydrin (ECH) purchased from Sigma-Aldrich was distilled twice on KOH. All the other reagents (NaOH, methanol) were of analytical grade, and used without further purification.

CS/PVAm ionic composite beads, used in this study, were prepared according to the method previously presented [24–26]. Briefly, CS/PVAm composites were synthetized by a "tandem" ionic/covalent cross-linking. The mass ratio between CS and PVAm was 60 wt.% of CS and 40 wt.% of PVAm, and the molar ratio ECH:NH_2 was 2:1. First, ECH was divided into two portions, one being mixed with a CS solution with a concentration of 3 wt.% (obtained by dissolving the CS powder in 2 vol.% acetic acid), and the second being mixed with a PVAm solution having the concentration of 18 wt.%, after complete homogenization of ECH, the two mixtures were combined. The final mixture was dropped by a syringe into 180 mL 0.05 M TPP, under mild magnetic stirring, at 22 °C, for 3 h. After this, the composite beads were separated from TPP solution, washed three times with distilled water, and transferred into a mixture of 60 mL water of pH 11 and 60 mL ethanol, at 22 °C, for 24 h. Finally, the composite beads were washed with distilled water to remove the excess of small ions, with methanol for dehydration, dried at room temperature for 24 h, and under vacuum at 40 °C, for 48 h. For comparison cross-linked CS beads were synthetized using the same procedure as in the case of CS/PVAm composites.

Methods

Synthesis of the metal – polymer complexes

Metal-CS/PVAm complexes were prepared using a batch equilibrium procedure. Hence, 0.5 g of dried composite beads were placed in a flask and contacted with 500 mL of aqueous solution of 0.05 M aqueous solutions of $CuCl_2 \cdot 2H_2O$, $CuSO_4 \cdot 5H_2O$, $NiCl_2 \cdot 6H_2O$, and $NiSO_4 \cdot 6H_2O$, at room temperature, under mild magnetic stirring (~150 rpm), the contact duration being 24 h, this being enough to achieve equilibrium of sorption [25]. After 24 h the metal-composite complexes were rinsed several times with distilled water, to remove the excess of metal ions, and dried in the air for 24 h, and under vacuum for 48 h. Metal-cross-linked CS complexes were obtained using the same protocol as in the case of metal-CS/PVAm complexes.

The total amount of metal ions (Cu^{2+}/Ni^{2+}) loaded in the beads was determined as previous shown [24–26]. In brief, after 24 h, the beads were filtered off, and the residual concentration of the metal ion remained in the filtrate was measured by UV-Vis spectroscopy (at 808 nm for Cu^{2+} ions, and at 721 nm for Ni^{2+} ions) using a UV–Vis Spectrophotometer (SPECORD200 Carl Zeiss Jena). The amount of the Me^{2+} sorbed at equilibrium, q_e (mg/g), was calculated by eq. (1).

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where: C_0 and C_e are the concentrations of the metal ion in aqueous solution (mg/L), before the interaction with composite beads and at equilibrium, respectively, V is the volume of the aqueous phase (L), and m is the amount of the dried sorbent (g).

Characterization of the metal-polymer complexes

FT-IR characterization

The structure of the metal-polymer complexes was investigated by FT-IR spectroscopy. The dried samples were first frozen in

liquid nitrogen, and then broken in a mortar to get the samples as powder. FT-IR spectra were recorded with a Bruker Vertex FTIR spectrometer, resolution 2 cm^{-1}, in the range of 4000–400 cm^{-1} by KBr pellet technique, the amount of the sample being about 5–8 mg in each pellet.

SEM-EDX study

The surface and internal morphology of the dried metal-polymer complexes was observed using an Environmental Scanning Electron Microscope (ESEM) type Quanta 200, operating at 20 kV with secondary electrons, in low vacuum mode.

Elemental composition of the metal-polymer complexes was determined with Environmental Scanning Electron Microscope (ESEM) type Quanta 200 having coupled an energy dispersive X-ray spectroscopy (EDX). The EDX detector used is the Si detector—EDX silicon-drift detector enables rapid determination of elemental compositions and acquisition of compositional maps. Samples are imaged at 10 mm WD (working distance), which is the stage eucentric position and the collection point of the EDX detector. It is used in conjunction with the LFD detector. LFD: Large Field Detector Accelerating Voltage: 20 kV; Low vacuum mode, uncoated samples.

XRD characterization

X-ray diffraction patterns were recorded using a Diffractometer Bruker D8 ADVANCE, Bragg–Brentano parafocusing goniometer, scans recorded in step mode by using the Ni-filtered Cu Kα radiation (λ = 0.1541 nm). The working conditions were 36 kV and 30 mA tube power. All the diffractograms were collected in the range of 5–40° (2θ) at room temperature. The fine powders were obtained by first freezing the metal composite complexes in liquid nitrogen, and then breaking them in a mortar until the samples as powder were obtained.

Magnetic moment determination

The magnetic susceptibility of the cross-linked CS and CS/PVAm composite charged with Cu^{2+} and Ni^{2+} was investigated by the Gouy method [29], which consists of measuring the mass change of the investigated sample in an inhomogeneous magnetic field. The measurements and calculations were carried out according to the methodology previously described in Ref. [30]. First, the change in mass of the metal-free polymer sample in the magnetic field was determined and the magnetic susceptibility was calculated. The same steps were done with the polymer loaded with metal cations. The measurements were made using a quartz tube that did not contain paramagnetic centers. The characteristic of the tube was determined using $CuSO_4$ as a reference substance. Magnetic susceptibility was calculated with eq. (2):

$$\chi_g^{pm} = \chi_g^m \cdot W + \chi_g^p \cdot (1-W) \quad (2)$$

where: χ_g^{pm} is the magnetic susceptibility of the polymer which hosts the metallic ions per gram, χ_g^m - is the magnetic susceptibility of metal ions in polymer phase per gram, W – is

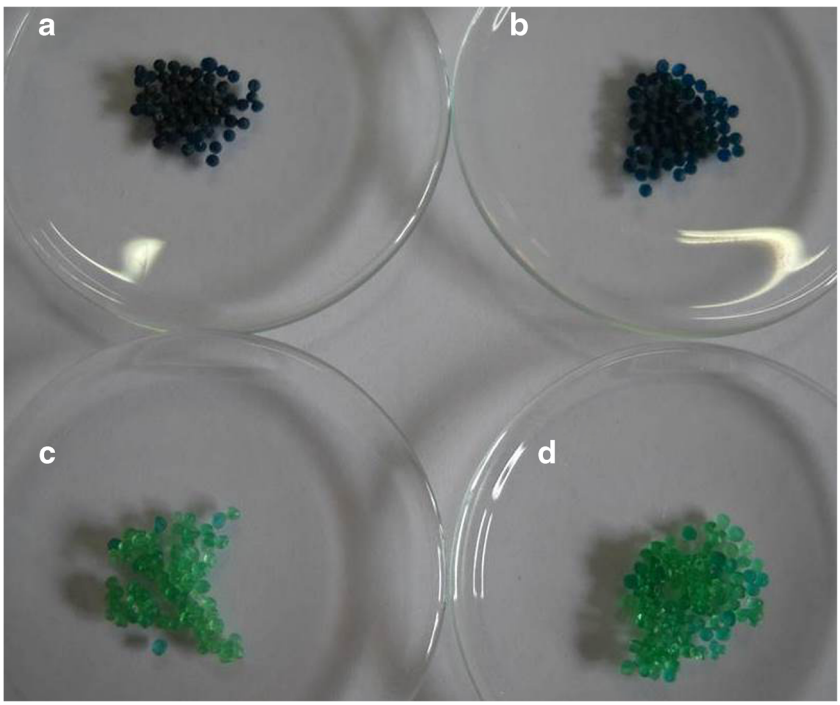


Fig. 1 Optical images of the metal-CS/PVAm composite complexes with metal ions coming from: $CuCl_2$ **a**, $CuSO_4$ **b**, $NiCl_2$ **c**, and $NiSO_4$ **d**; the concentration of metal ion solutions ($CuCl_2$/$CuSO_4$/$NiCl_2$/$NiSO_4$) was 0.05 M

the weight of metal in polymer phase, χ_g^p –is the magnetic susceptibility of polymer without metal per gram.

The magnetic susceptibility of metal ions in polymer phase was calculated with eq. (3):

$$\chi_g^m = \frac{\chi_g^{pm} - \chi_g^p \cdot (1-W)}{W} \quad (3)$$

The molar magnetic susceptibility, χ_M, was given by eq. (4):

$$\chi_M = M \cdot \chi_g^m \quad (4)$$

where M is the molar mass of metal ion.

Based on the χ_M values, the effective magnetic moment of Cu^{2+} and Ni^{2+} ions in the polymer phase was calculated with eq. (5):

$$\mu_{ef} = 2.83\sqrt{\chi_M \cdot T} \quad (5)$$

where T is absolute temperature, K.

Determination of the effective magnetic moment of Cu^{2+} and Ni^{2+} ions in metal-cross-linked CS complexes The cross-linked CS sample having a low content of Cu^{2+} ions was prepared as follows. 1.5813 g of polymer were contacted with 500 mL aqueous solution of $CuCl_2 \cdot 2H_2O$, with a concentration of $5 \cdot 10^{-3}$ M for 24 h, at a temperature of 22 °C. The equilibrium sorption pH was 4. The cross-linked CS sample with a higher content of Cu^{2+} ions was prepared by contacting 1.2175 g of polymer with 500 ml aqueous solution of $CuCl_2 \cdot 2H_2O$, with a concentration of $5 \cdot 10^{-1}$ M for 24 h, at 22 °C and pH 4. The cross-linked CS sample having a low content of Ni^{2+} ions was prepared by contacting 1.5 g of polymer with 500 mL aqueous solution of $NiCl_2 \cdot 6H_2O$ with a concentration of $5 \cdot 10^{-3}$ M for 24 h, at a temperature of 295 K. The equilibrium sorption pH was 5. The cross-linked CS sample with a high content of Ni^{2+} ions was prepared by contacting 1.1 g of polymer with 500 ml aqueous solution of $NiCl_2 \cdot 6H_2O$ with a concentration of 10^{-1} M, at pH 5, for 24 h at 22 °C. The content of Cu^{2+} and Ni^{2+} ions from the polymer phase was titrimetrically determined, after desorption, using Trilon B and Murexid. The metal ions desorption was carried out by contacting the sample with 10 mL of 2 M HCl solution for 24 h.

Determination of the effective magnetic moment of Ni^{2+} and Cu^{2+} ions in metal-CS/PVAm composite complexes The following samples were prepared: for sample No.1: 0.5 g of composite were contacted with 500 mL of $5 \cdot 10^{-3}$ M aqueous solution of $NiCl_2 \cdot 6H_2O$, the equilibrium sorption pH

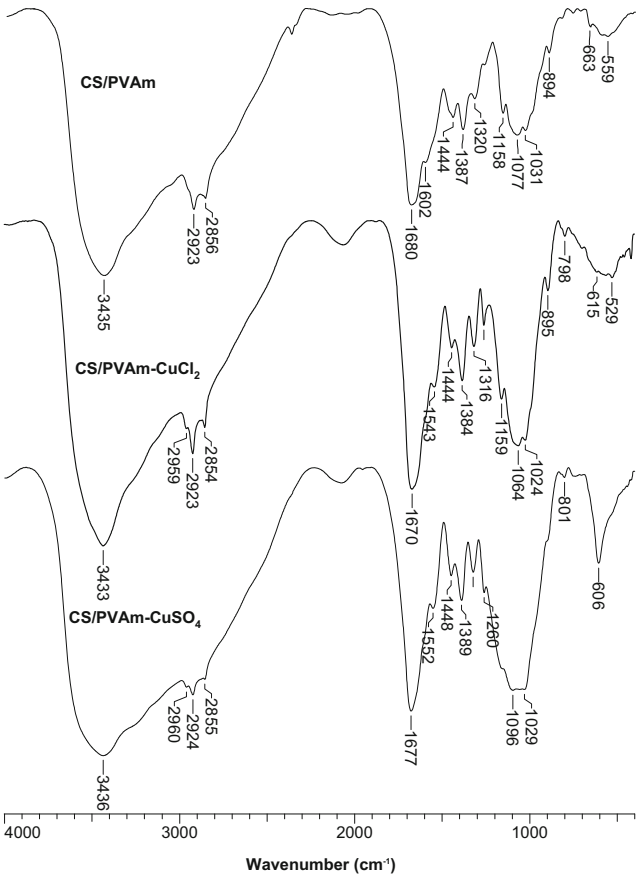


Fig. 2 FT-IR spectra of Cu^{2+}-CS/PVAm complexes

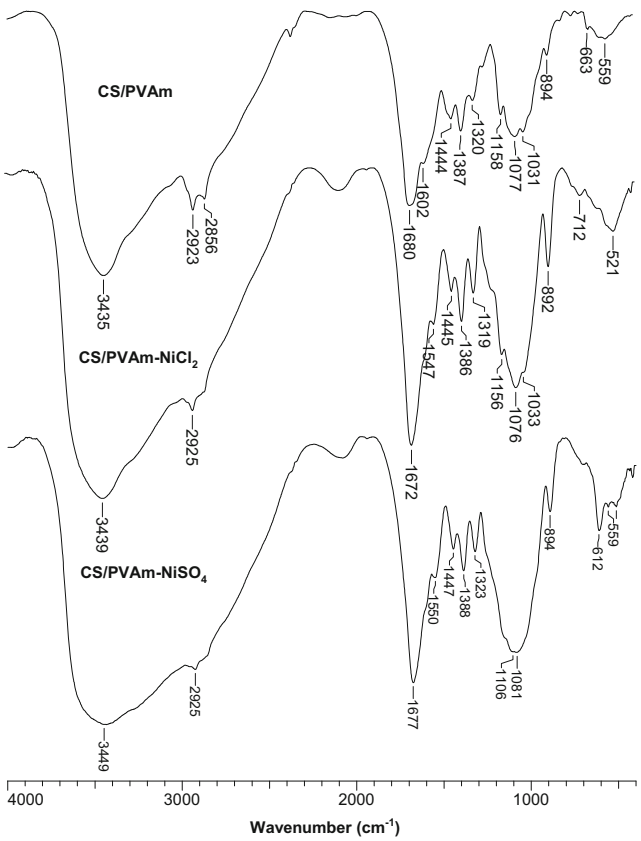


Fig. 3 FT-IR spectra of Ni^{2+}-CS/PVAm complexes

Table 1 Main absorbtion bands of metal-CS/PVAm complexes

Sample	ν band (cm^{-1})				
Bond	CS/PVAm	Cu^{2+}- CS/PVAm		Ni^{2+}- CS/PVAm	
		$CuSO_4$*	$CuCl_2$*	$NiSO_4$*	$NiCl_2$*
C = O, amide I	1680	1677	1670	1677	1672
N-H, amide II	1602	1552	1543	1550	1547
C-O-C bridge	1158	-	1159	-	1156
C-O stretching of C3 of CS (secondary OH)	1077	1096	1064	1106	1076
C-O stretching of C6 of CS (primary OH)	1031	1029	1024	1081	1033

* The concentration of metal ion solutions ($CuCl_2$/$CuSO_4$/$NiCl_2$/$NiSO_4$) was 0.05 M

being 4.4; for sample No.2, 0.5 g of composite were contacted with 500 mL of 10^{-1} M aqueous solution of $NiCl_2$•$6H_2O$, the equilibrium sorption pH being 3.9; for sample No.3, 0.5 g of composite were contacted with 500 mL of $5•10^{-3}$ M aqueous solution of $CuCl_2$•$2H_2O$, the equilibrium sorption pH being 4.8; for sample No.4, 0.5 g of composite were contacted with 500 mL of 10^{-1} M aqueous solution of $CuCl_2$•$2H_2O$, the equilibrium sorption pH being 4.75. The contact time of the composite with the metal ions solution was 24 h, at room temperature. After that, the metal-polymer complexes were transferred to filter paper, washed with distilled water, and dried in the air.

Results and discussion

Optical images of the CS/PVAm composite after the loading with Cu^{2+} ions from $CuCl_2$ and $CuSO_4$ (a and b, respectively) and Ni^{2+} from $NiCl_2$ and $NiSO_4$ (c and d, respectively) are presented in Fig. 1.

Ft-IR

FT-IR spectroscopy has been used for the characterization of metal-polymer complexes, because the frequency at which a characteristic group of a polymer absorbs is modified by complexation with metal ions, the shift or absence of a certain band present in the starting ligand as well as the presence of new bands being usually observed. Therefore, the first information about the structural changes caused by the complexation of CS/PVAm composite with Cu^{2+} and Ni^{2+} were given by FT-IR spectra (Figs. 2 and 3).

The main peaks visible in the FT-IR spectrum of the CS/PVAm composite (Figs. 2 and 3) are as follows: a broad peak at 3435 cm^{-1} assigned to the –OH and –NH stretching vibrations as well as to hydrogen bonds; the peaks from 2923 cm^{-1} and 2856 cm^{-1} which are assigned to the CH and CH_2 symmetric and asymmetric stretching vibrations; the peak from 1680 cm^{-1} assigned to the stretching vibration of C = O in secondary amide bond of the acetamido groups in CS, and the peak from 1602 cm^{-1} attributed to the –NH bending vibration of secondary amide; the peak located at 1444 cm^{-1} is assigned to CH_2 scissoring of the groups in PVAm; the peak from 1387 cm^{-1} is assigned to the secondary -OH, while the peak located at 1320 cm^{-1} was assigned to the C-N stretching vibration. The peak from 1158 cm^{-1} corresponds to the asymmetric stretching of C-O-C bridge in CS. The peak located at 1077 cm^{-1} corresponds to C-O stretching of C3 from CS (secondary OH), and the peak from 1031 cm^{-1} was assigned to the C-O stretching of C6 of CS (primary OH). The structural changes, which occurred after the complexation of the CS/PVAm composite beads with Cu^{2+} and Ni^{2+} are supported by the FT-IR spectra, the main spectral changes being summarized in Table 1.

As can be seen from Figs. 2 and 3, all FTIR spectra of the prepared complexes are defined by the appearance of new peaks in the low-frequency region (620–500 cm^{-1}), peaks that are assigned to the stretching vibrations of Me-O and Me-N bonds. In all cases, the peak from 1602 cm^{-1} corresponding to -NH bending vibrations shifted to lower frequencies, thus

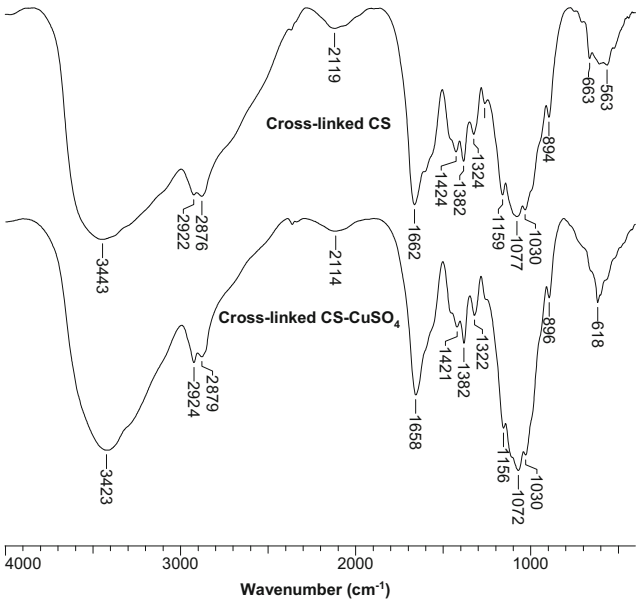


Fig. 4 FT-IR spectra of Cu^{2+}- cross-linked CS complexes

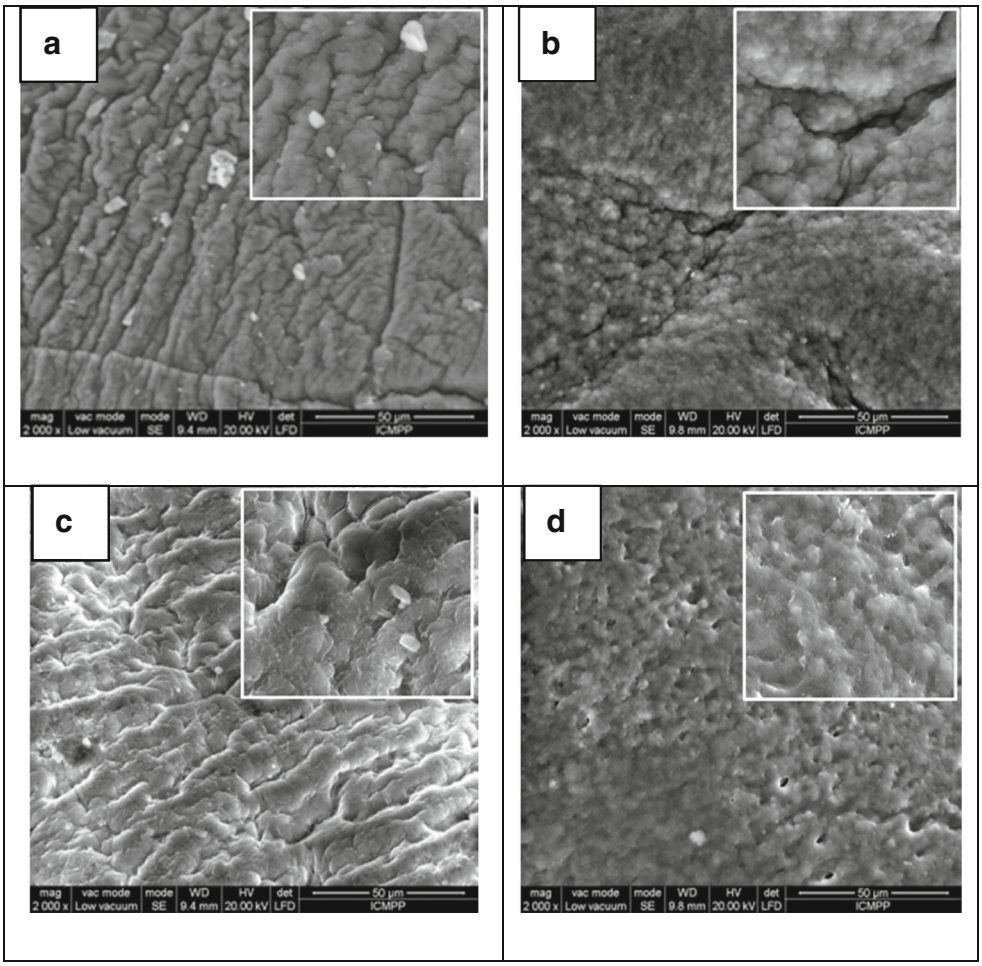


Fig. 5 SEM images of **a** CS/PVAm-$CuCl_2$; **b** CS/PVAm-$NiCl_2$; **c** CS/PVAm-$CuSO_4$; **d** CS/PVAm-$NiSO_4$, the scaling bar and the magnification being: 50 μm and 2000×; the scaling bar and the magnification for the inset are: 20 μm and 5000×

indicating the involvement of the amino groups in the complex formation. Moreover, the influence of the metal source ($CuCl_2$, $CuSO_4$, $NiCl_2$, and $NiSO_4$) can be observed in the FT-IR spectra. Thus, when $CuSO_4$/$NiSO_4$ was used, all the important peaks were affected by metal complexation, this suggesting an effective coordination between CS/PVAm composite and metal ions (Cu^{2+}/Ni^{2+}) via amine and hydroxyl functional groups. Furthermore, the absence of the peak corresponding to C-O-C bridge indicates the depolymerization of CS as a result of the coordinating bond with metal ions [31]. All these results indicate that the complexes are formed in the "bridge model", where the metal ions are bound with several functional groups from CS and PVAm, via inter- and/or intramolecular complexation [32]. When $CuCl_2$/$NiCl_2$ was used, it can be seen that the C-O-C ether bridge was not affected by the metal complexation. This would suggest that the complexes are formed in the "pendant model", in which the metal ions are bound to an amine group in a pendant fashion.

As Fig. 4 shows, only slight changes were visible in the spectrum of cross-linked CS after loading with Cu^{2+} ions. Thus, it can be observed that no important shifts of the peaks located at 1159 cm^{-1}, 1077 cm^{-1} and 1030 cm^{-1} occurred after the binding of Cu^{2+} ions on cross-linked CS beads, the binding of metal ion being supported mainly by the new peak at 618 cm^{-1}. This would suggest that the complexes are formed in the "pendant model", and supports the difference between CS/PVAm composites and cross-linked CS in binding Cu^{2+} ions.

SEM-EDX

The SEM images of the surface of metal-composite complexes presented in Fig. 5 illustrate the influence of metal ion (Cu^{2+} compared to Ni^{2+}) and of the metal source ($CuSO_4$/$NiSO_4$ compared with $CuCl_2$/$NiCl_2$) on the complex composition. As can be seen, the metal-composite complexes present a dense surface structure this supporting a very strong binding of Cu^{2+} and Ni^{2+} involving most of the amino groups; the more compact surface the strongest binding is.

The chemical composition on the surface of metal-composite complexes was evaluated using the semi-quantitative analysis SEM-EDX, the EDX profiles of complexes being presented in Fig. 6. As Fig. 6 shows, the EDX spectra were consistent with the presence of C, N, P and O from the CS/PVAm composite,

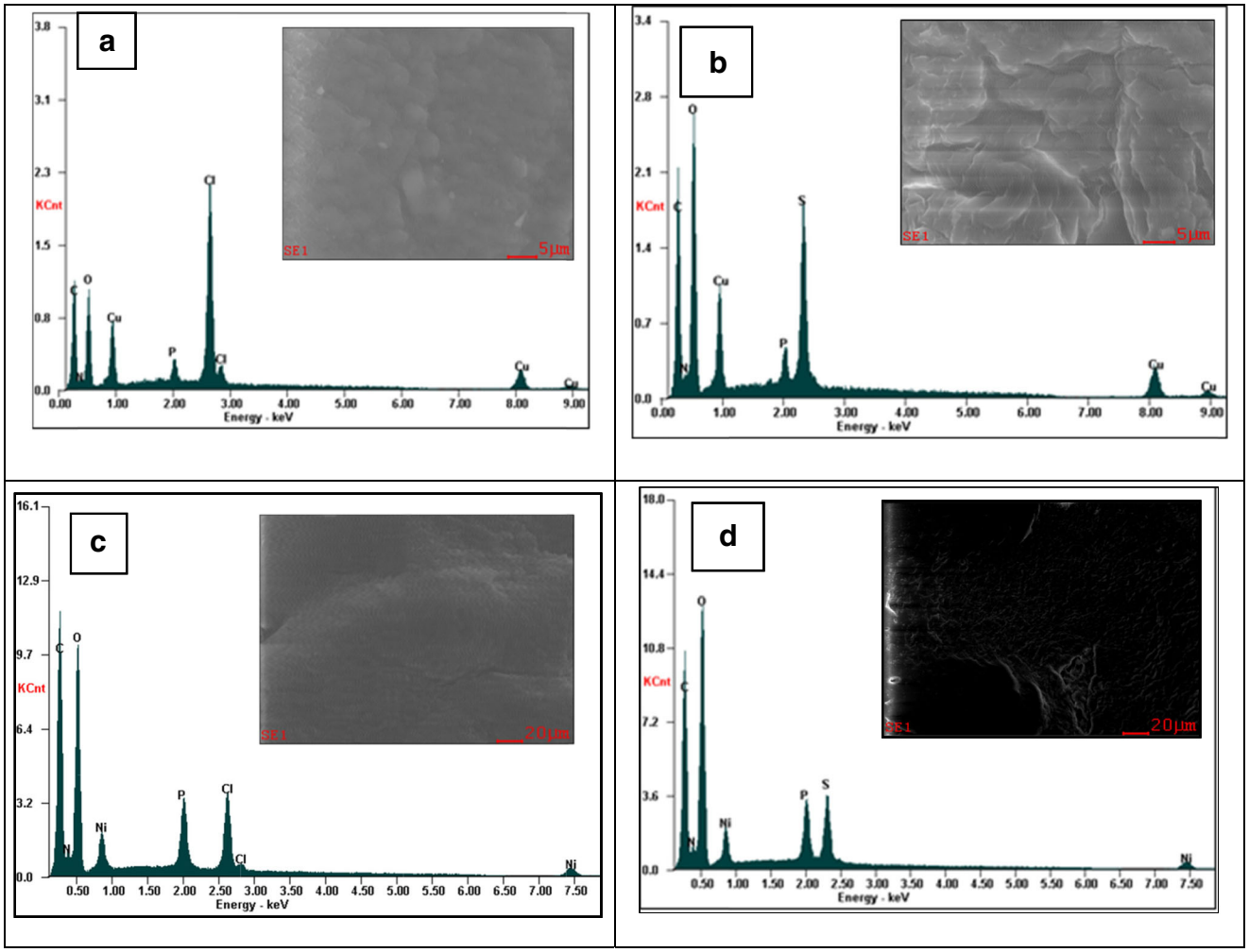


Fig. 6 EDX profiles of metal-composite complexes: **a** CS/PVAm-$CuCl_2$; **b** CS/PVAm-$CuSO_4$; **c** CS/PVAm-$NiCl_2$; and **d** CS/PVAm-$NiSO_4$

and Cu or Ni. Sufficient amounts of Cl or S were also identified on the surface of metal-composite complexes, which are coming from the metal ions source.

The weight percentages of C, N, O, Cl, S, Cu, and Ni from metal-composite complexes are listed in Table 2.

As Table 2 shows, the content of metal cations found on the surface of the composites was influenced by the metal ion and the metal source. Thus, the CS/PVAm-Cu^{2+} complexes presented a much higher content of metal ions compared with CS/PVAm-Ni^{2+}, 7.98 wt.% compared with 1.74 wt.%. In the case of CS/PVAm-Cu^{2+} complexes, the metal source ($CuCl_2$/$CuSO_4$) did not influence the weight percent of Cu^{2+} ions, while in the case of CS/PVAm-Ni^{2+} complexes, the Ni^{2+} wt.% increased from 1.74 ± 0.14 wt.%, when $NiCl_2$ was used, to 2.21 ± 0.3 wt.%, when $NiSO_4$ was used as metal source. The presence of Cl and S atoms (Fig. 5, Table 2) indicates that

Table 2 The chemical composition on the surface of metal-composite complexes determined from EDX measurements

Sample	Semi-quantitative elemental analysis (wt.%)[a]						
	C	N	O	Cl	S	Cu	Ni
CS/PVAm-$CuCl_2$[b]	48.89 ± 0.86	8.03 ± 0.5	23.25 ± 1.65	10.49 ± 0.6	-	7.98 ± 0.37	-
CS/PVAm-$CuSO_4$[b]	41.79 ± 0.96	8.01 ± 0.64	35.65 ± 1.21	-	5.59 ± 0.28	7.88 ± 0.51	-
CS/PVAm-$NiCl_2$[b]	51.69 ± 3.4	10.53 ± 0.51	29.8 ± 4.52	4.52 ± 1.47	-	-	1.74 ± 0.14
CS/PVAm-$NiSO_4$[b]	43.77 ± 0.96	9.28 ± 0.46	39.04 ± 1.36	-	3.09 ± 0.42	-	2.21 ± 0.3

[a] Expressed as mean values of four measurements carried out on each sample ± SD

[b] The concentration of metal ion solutions ($CuCl_2$/$CuSO_4$/$NiCl_2$/$NiSO_4$) was 0.05 M

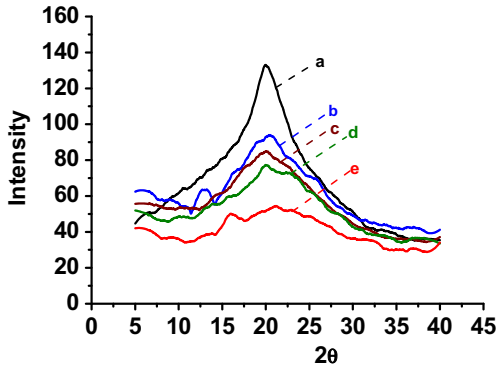


Fig. 7 XRD diffractograms for **a** CS/PVAm; **b** CS/PVAm-$CuSO_4$; **c** CS/PVAm-$NiSO_4$; **d** CS/PVAm-$NiCl_2$; **e** CS/PVAm-$CuCl_2$

the corresponding anions of the metal ions were also adsorbed on the surface of the metal-composite complexes.

The semi-quantitative results obtained by EDX are in good agreement with the quantitative results obtained by the determination of the total amounts of Cu^{2+} and Ni^{2+} hosted by the composite (using eq. 1), the average values being: 234.4 mg/g composite, 226.8 mg/g composite, 75.3 mg/g composite, and 60.2 mg/g composite when the metal source was $CuSO_4$, $CuCl_2$, $NiSO_4$, and $NiCl_2$, respectively.

XRD

X-ray diffraction studies give information about the amorphous or crystalline nature of the composite and the metal-composite complexes. It is well known that even if the polymer support has a crystalline nature, a higher amount of absorbed metal leads to a lower crystallinity degree of the metal-polymer complex [18, 19]. The XRD diffractograms of the composite and metal-composite complexes are presented in Fig. 7.

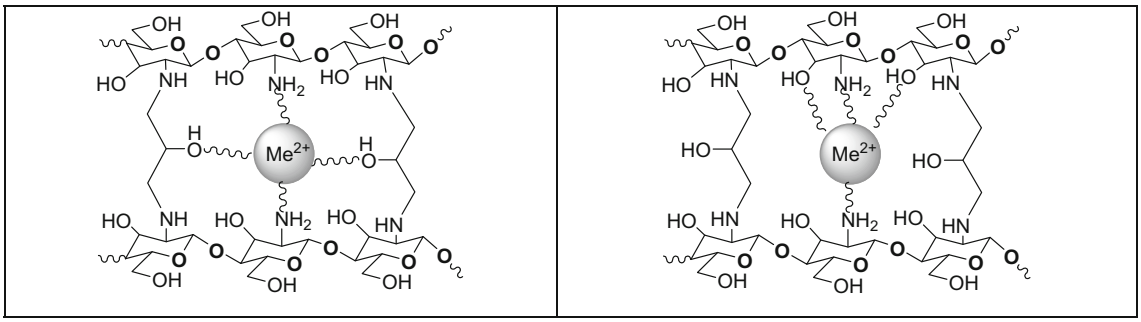
From Fig. 7 it can be seen that CS/PVAm composite shows a peak of crystalline nature at 20.2 °, and the metal-composite complexes are characterized by a broad amorphous peak. As mentioned in literature, the metal complexation leads to significant changes in the composite morphology, indicating a complete disruption of the interpolymer bonds [19]. The influence of the metal source ($CuCl_2$, $CuSO_4$, $NiCl_2$, $NiSO_4$) can also be observed. Thus, in the case of Cu^{2+} the metal-composite complex formed when $CuSO_4$ was used as metal source presents a sharp crystalline peak at 12.9 ° and a broad amorphous peak. When $CuCl_2$ was used as metal source for the metal-composite complex, the crystalinity degree of the complex was smaller. In the case of the Ni^{2+}-composite-complexes, the Ni^{2+} source has a small influence, which can be almost neglected. Also, from Fig. 7 it can be observed that, when $CuSO_4$/$NiSO_4$ where used as metal source, the difference between the crystallinity degree of the two metal-composite complexes could be almost neglected, while when $CuCl_2$/$NiCl_2$ where used as metal source, the Ni^{2+}-composite complex presented a higher crystallinity degree compared with the Cu^{2+}-composite complexes.

Magnetic properties

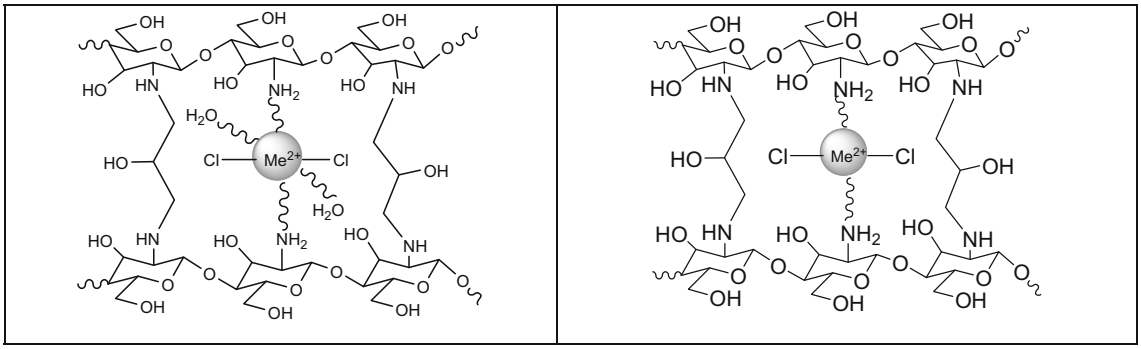
Both CS/PVAm composites and cross-linked CS possess in their structural unit a large number of electron donor atoms (O, N). This fact causes the electronic state of metal ions complexed with ligand groups of the polymer. Using magnetic susceptibility method allows the determination of the oxidation degree of metal ions from the polymer phase, the homogeneous distribution of the ligand groups from the volume of the polymer beads, the existence of the antiferromagnetic interactions between the metal ions caused by the bridges formed between them, and, in many cases, the geometry of the entourage of the central atom. For detecting the existence of non-uniformity in the distribution of the ligand groups in the volume of the polymer beads and the interactions between the metal ions, the magnetic susceptibility of the polymer samples, having low and high content of metal cations, was investigated.

Determination of the effective magnetic moment of Cu^{2+} ions in Cu^{2+}-cross-linked CS complex

The effective magnetic moment of the sample with a reduced content of metal ions (2.63 mg Cu/g or 0.263%) was μ_{ef} = 1.73 μB, while for the sample having a much higher content of metal (20.53 mg Cu/g or 2.053%), the effective



Scheme 1 Binding possibilities of Cu^{2+} on the cross-linked CS

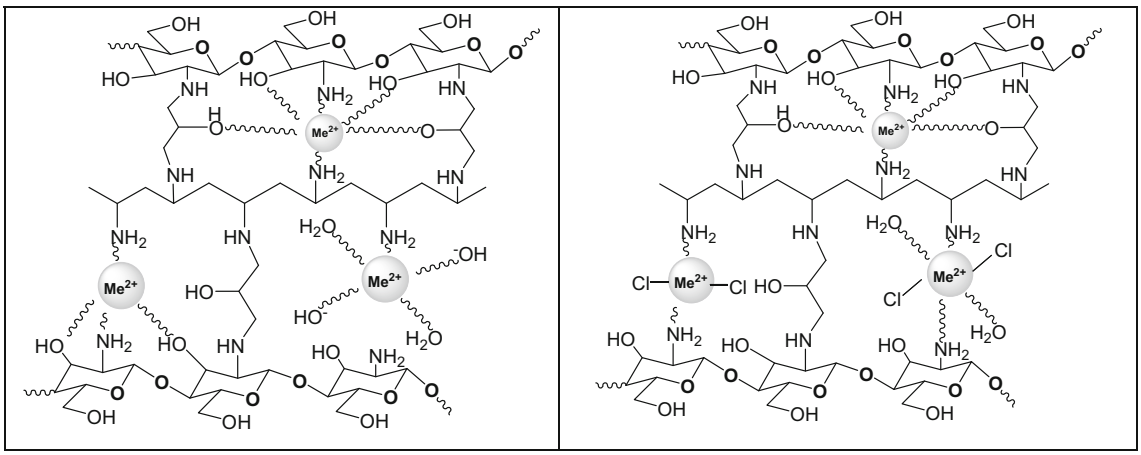


Scheme 2 Binding possibilities of Ni^{2+} on the cross-linked CS

magnetic moment was $\mu_{ef} = 1.76$ μB. These data indicate that the metal from the polymer phase had the d^9 configuration, supporting that the metal cations are in form of Cu^{2+}. Regardless the metal content from the polymer phase (ranging from 2.63 to 20.53 mg Cu^{2+}/g), the samples are diluted magnetic, indicating that no interactions between the Cu^{2+} ions are present. This proved that the metal atoms from the polymer phase are "isolated", and the electron donor atoms do not form bridges between Cu^{2+} ions. It is also possible to assume that the ligand groups were homogeneous distributed throughout the volume of the polymer beads. Two possibilities for binding Cu^{2+} by the cross-linked CS are presented in Scheme 1.

Determination of the effective magnetic moment of Ni^{2+} ions in cross-linked CS

The effective magnetic moment of the sample with a low content of metal ions (13.5 mg Ni/g or 1.35%) was $\mu_{ef} = 4.05$ μB. The second sample presenting a much higher content of metal (54.8 mg Ni/g or 5.48%) had an effective magnetic moment $\mu_{ef} = 3.77$ μB. It is well known that Ni^{2+} cations and the low molar mass ligands form two classes of compounds [29]. One class of compounds is paramagnetic, having a green or blue color, and a tetrahedral or octahedral geometry. The second class of compounds is diamagnetic, having red or yellow color and a square-planar configuration. The theoretical spin magnetic moment of Ni^{2+} ions (d^8 configuration) is 2.83 μB, and the experimentally obtained value ranges from 2.8 to 3.5 μB [29]. The magnetic moment of Ni^{2+} ions (coming from the sulfate solution) from the cross-linked ionic polymers containing amino and alcohol groups (in some polymers), having a metal content of 2.19 to 3.4%, ranges between 2.9–3.4 μB [32], and in some cases, between 1.4–1.8 μB [33]. The values of the magnetic moment, smaller than 2.8 μB, indicate that the complexes are both tetrahedral and octahedral and square-planar. The polymer samples loaded with Ni^{2+} ions prepared in this work are green and, therefore, the ligands form a tetrahedral and/or octahedral entourage. The magnetic moment value of Ni^{2+} ions in the polymer phase was higher than 2.8 μB. Such high values of the magnetic moment were observed for the Ni^{2+} in carboxylic polymers [33–35]. It is assumed that the high values of the effective magnetic moment of Ni^{2+} ions in the polymer phase is conditioned by the partial involvement of the orbital component. Increasing the Ni^{2+} content into the polymer phase from 13.5 to 54.8 mg/g, the magnetic moment decreased from 4.05 to 3.77 μB. Probably, this is due to the fact that the increase of Ni^{2+} content leads to the decrease of the distortion degree of the complexes. This could happen if some of the polymer ligands are replaced by small ligands such as solvent molecules (H_2O) or chloride ions (Scheme 2). As a result of this



Scheme 3 Binding possibilities of Ni^{2+} on the CS/PVAm composites

process, the polymer ligands can restrain a higher amount of Ni^{2+} cations.

Determination of the effective magnetic moment of Ni^{2+} and Cu^{2+} ions in CS/PVAm composite

The content of metal ions in the composite phase was determined like in the case of the cross-linked CS and constituted 40 and 110 mg Ni/g and respectively 28.41 and 122.18 mg Cu/g, , the loading being much higher than in the case of the cross-linked CS. The magnetic properties of the complexes of Ni^{2+} and Cu^{2+} in the composite phase are significantly different from those formed in the cross-linked CS. The effective magnetic moment, μ_{ef}, of Ni^{2+} ions in the composite phase of sample containing 40 mg metal/g, is 3.13 μB, i.e. much lower than that found for the Ni^{2+} ions present in the cross-linked CS (4.05 μB), at the same concentration of the aqueous solution. A magnetic moment of 3.13 μB corresponds to distorted octahedral complexes entourage of metal [33]. When an aqueous solution of 0.1 M $NiCl_2$ was used, the Ni^{2+} cations presented a diamagnetic square planar configuration. The effective magnetic moment, μ_{ef}, of Ni^{2+} ions in this case was zero. This confirmed that increasing the content of Ni^{2+} ions led to a change in the electronic state of the metal ion. A schematic representation of the metal binding in this case is presented in Scheme 3.

It is surprising that Cu^{2+} complexes are diamagnetic, regardless the metal content in the sample. This could be possible only if the Cu^{2+} cations are reduced to Cu^{+}. Using ESR spectroscopy [36], Cu^{2+} ions retained by cross-linked ionic polymers containing amine groups, coordinate with the nitrogen and oxygen atoms, forming $[(R_3N)_4Cu(H_2O)_2]An_2$ compounds, where An is Cl^-, NO_3^-, ClO_4^-. Upon hydration of the polymer sample containing Cu^{2+} ions, takes place transfer of Cl^- anions from the external to internal sphere, that is, there is a hydration isomerism:

$$\left[(R_3N)_4Cu(H_2O)_2\right]Cl_2 \leftrightarrow \left[(R_3N)_4CuH_2OCl\right]Cl{\cdot}H_2O$$

$$\leftrightarrow \left[(R_3N)_4CuCl_2\right]{\cdot}2H_2O$$

Even if we assume that antiferromagnetic interactions occur in the composite phase between Cu^{2+} cations via Cl^- bridges, this would not lead to a reduced effective magnetic moment until zero. So, the most plausible assumption is that the Cu^{2+} cations in the polymer phase are reduced to Cu^{+}.

Conclusions

The CS/PVAm composite beads loaded with Cu^{2+} and Ni^{2+} ions, coming from both chloride and sulfate salts, were characterized using different techniques. The FT-IR spectroscopy confirmed the formation of the complexes between the CS/PVAm composites and the metal cations. Thus, after complexation with Me(II) the bands characteristic to the polysaccharide structure were influenced, and some new bands, assigned to M-O and M-N, also appeared. The FT-IR spectra support the influence of the metal source ($MeCl_2$/$MeSO_4$). Thus, when $CuSO_4$/$NiSO_4$ were used, the band from 1158 cm^{-1} disappeared and the bands from 1077 cm^{-1} and 1031 cm^{-1} were shifted to 1096 cm^{-1}/1106 cm^{-1} and 1039 cm^{-1}/1081 cm^{-1} and also decreased in intensity. When $CuCl_2$/$NiCl_2$ were used, the characteristic bands of anhydroglucose units were not influenced as much as in the case of $CuSO_4$/$NiSO_4$. The SEM images of the surface of metal-CS/PVAm complexes showed the influence of metal ion (Cu^{2+}/Ni^{2+}) and of the metal source ($MeSO_4$/$MeCl_2$). Hence, the strong binding of Cu^{2+}/Ni^{2+} led to a dense surface structure, the surface being more compact in the case of the Cu^{2+} ions indicating a stronger binding of the metal ions. The chemical composition on the surface of metal-composite complexes was evaluated using the semi-quantitative analysis SEM-EDX. The EDX profiles of complexes were consistent with the presence of C, N, P and O from the CS/PVAm composite, and Cu or Ni. Also, sufficient amounts of Cl or S were identified on the surface of metal-composite complexes, which are coming from the metal ions source, indicating that the anions were also adsorbed. X-ray diffraction studies gave information about the amorphous or crystalline nature of the composite and composite-metal complexes. It was observed that the Cu^{2+}-composite complexes presented a higher crystallinity degree compared with Ni^{2+}-composite complexes. The existence of non-uniformity in the distribution of the ligand groups in the volume of the polymer beads and the interactions between the metal ions were determined using the magnetic susceptibility of the cross-linked CS and CS/PVAm composite samples, having low and high content of metal cations. The magnetic properties of the complexes of Ni^{2+} and Cu^{2+} in the composite phase are significantly different from those formed in the cross-linked CS. In the case of Ni^{2+} – CS/PVAm complexes, it was observed that increasing the content of Ni^{2+} ions led to a change in the electronic state of the metal ion. The Cu^{2+} complexes are diamagnetic, regardless the metal content in the sample.

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