

Dedicated to the memory of
Professor Eugen Segal (1933-2013)

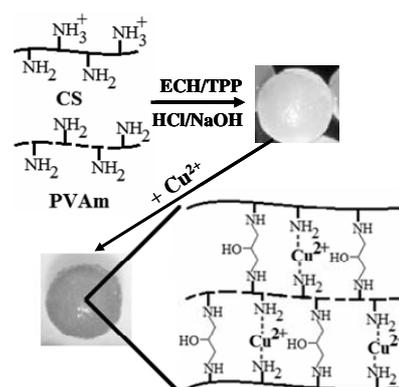
COMPOSITE MICROSPHERES BASED ON CHITOSAN AND POLY(VINYL AMINE)

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Three composites, based on chitosan (CS) and poly(vinyl amine) (PVAm) with a weight ratio of 90:10, were prepared as beads by an ionic/covalent cross-linking. Ionotropic gelation was performed in triphosphosphate (TPP), and chemical cross-linking in epichlorohydrin (ECH). The composite overall code is C91 followed by letters A, B, and C. The ECH:NH₂ molar ratio was 2:1 in the composites C91.A and C91.B, and the polymer concentration was 3.3 wt.%, and 2 wt.%, respectively. In the composite C91.C, the ECH:NH₂ molar ratio was 1.5:1 and the polymer concentration 2 wt.%. The influence of pH, contact time, and the initial concentration of Cu²⁺ on the composites sorption capacity was studied. The sorption of Cu²⁺ ions was well described by pseudo-second order kinetic model, suggesting chemisorption as the rate determining step. Based on Langmuir isotherm model, the maximum adsorption capacity of C91.A, C91.B and C91.C for Cu²⁺ ions was 178.73, 189.13 and 182.08 mg Cu²⁺/g beads, respectively.



INTRODUCTION

Copper is an essential trace element required for the development and survival of a wide variety of organisms, from bacteria to mammals because Cu ions can adopt distinct redox states.¹ In order to obtain a normal immune response it is necessary a strict control of trace copper intake. Copper deficiency is associated with anemia and a decrease in serum ceruloplasmin activity. However, large doses of Cu²⁺ can produce liver or kidney failure, several neurological defects and, in extreme cases, even death.² Therefore, a strict control of Cu²⁺ concentration in wastewaters is a stringent issue. Conventional processes for the

removal of heavy metal ions from industrial effluents consist of precipitation, ion exchange, solvent extraction and adsorption. Adsorption processes use activated carbon and synthetic polymers but, in last decades, an increasing interest has been focused on natural sorbents.³ Natural sorbents consist of biomass,⁴ agriculture waste,⁵ and biopolymers such as chitosan (CS).⁶⁻⁸

CS, the only polycation coming from renewable resources, is composed of β -(1-4) linked-2-amino-2-deoxy-D-glucopyranose and β -(1-4)-2-acetamido-2-deoxy-D-glucopyranose units randomly distributed along the polymer chain. CS properties like biodegradability, biocompatibility, antibacterial activity, recommend it for various biomedical

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applications.^{9,10} Moreover, due to the numerous free amino and hydroxyl groups, CS is very efficient for metal binding through different mechanisms.¹¹⁻¹⁴ However, CS is very sensitive to pH as it can either form gel or dissolve, depending on the pH values. To improve CS stability in acidic solutions and its mechanical strength, different cross-linking agents, such as glyoxal, formaldehyde, glutaraldehyde, epichlorohydrin, ethyleneglycol diglycidyl ether and isocyanates, have been used. Chitosan derivatives have been extensively investigated as adsorbents.¹⁵

Various CS composites have been developed to adsorb heavy metals and dyes from wastewater.¹⁴ Different kinds of substances have been used to form composites with CS such as clinoptilolite,^{7,12,13} montmorillonite,¹⁶ bentonite, poly(ethylene imine),¹⁷ kaolinite.¹⁸

Three composites based on CS and poly(vinyl amine) (PVAm) were synthesized in this work and their sorption capacity for Cu^{2+} ions was tested. The composites were characterized by Fourier transform infrared spectroscopy (FTIR) and equilibrium swelling ratio. The sorption capacity for Cu^{2+} , as a function of pH, contact time, and Cu^{2+} initial concentration was investigated.

RESULTS AND DISCUSSION

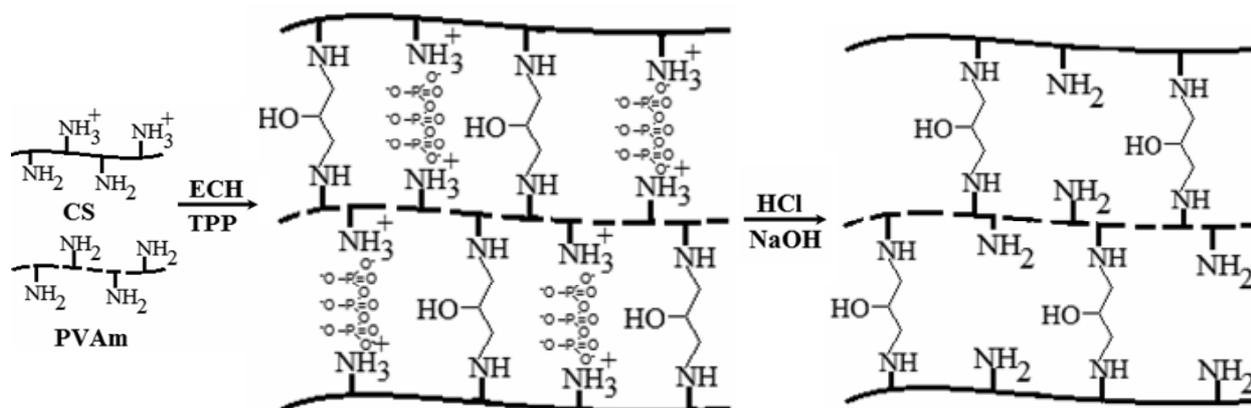
1. Composite preparation and characterization

A schematic description of the composite synthesis is presented in Scheme 1.

The composites have been prepared as beads by an ionic/covalent cross-linking. Ionotrop gelation was performed in tripolyphosphate (TPP), and the covalent cross-linking by epichlorohydrin (ECH). The sample code, synthesis conditions and swelling ratios (SR_{eq}) were summarized in Table 1.

As Table 1 shows, the values of SR_{eq} at pH 2 were influenced by the feed composition. For the same molar ratio ECH: NH_2 (2:1) SR_{eq} increased from 13.05 g/g (C91.A) to 22.56 g/g (C91.B), when the polymer concentration decreased from 3.3 to 2. When the cross-linking ratio decreased from 2:1 to 1.5:1, SR_{eq} increased to 44.74 g/g (C91.C).

Fig. 1 shows the FTIR spectrum of the composite C91.A before and after regeneration.



Scheme 1 – Synthesis of CS/PVAm composites.

Table 1

Sample code, feed composition and swelling ratios at pH 2 of the CS/PVAm composites

Sample	Mass ratio CS:PVAm (%)	Polymer concentration (%)	Molar ratio ECH: NH_2	SR_{eq} (g/g)
C91-A	90:10	3.3	2:1	13.05
C91-B	90:10	2	2:1	22.56
C91-C	90:10	2	1.5:1	44.74

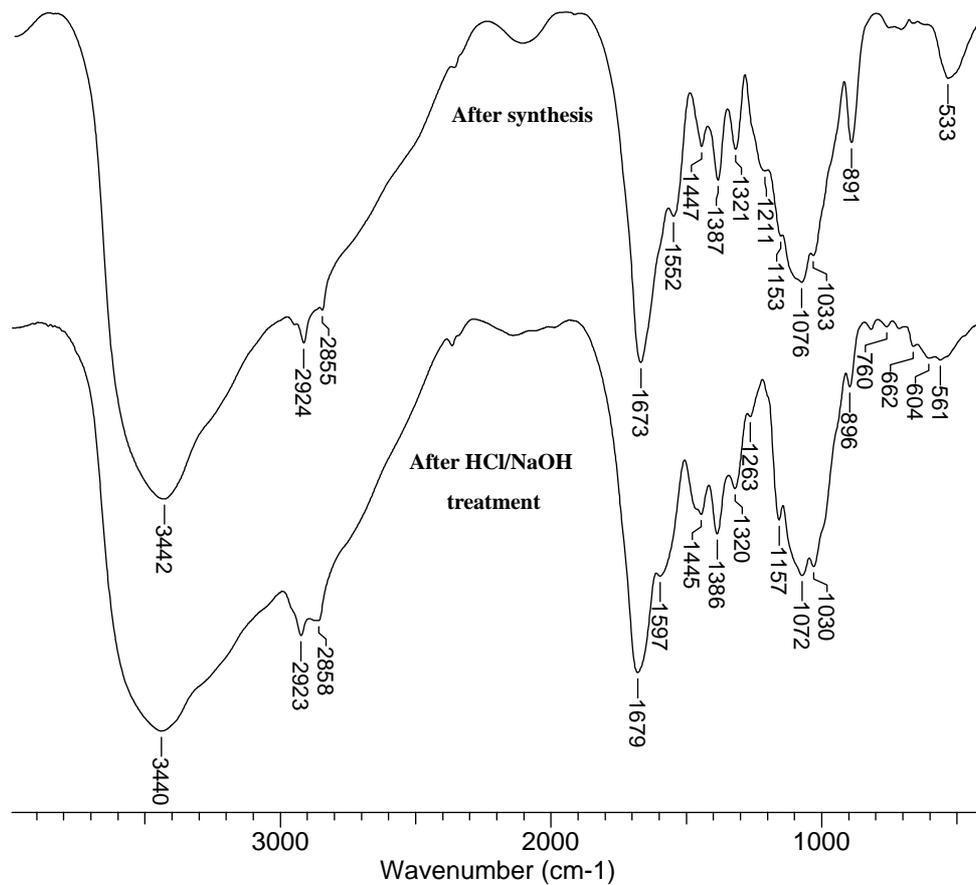


Fig. 1 – FTIR spectra for C91.A composite before and after regeneration.

After the synthesis, the following bands are present in the composite spectrum: the peak at 3442 cm^{-1} , which corresponds to -OH and -NH stretching vibrations; absorption bands at 2924 cm^{-1} and 2855 cm^{-1} assigned to asymmetric and symmetric vibration of -CH₂ groups; a strong band at 1673 cm^{-1} attributed to C=O bond (amide I) with a shoulder at 1552 cm^{-1} attributed to the NH vibration in NH₂ groups (amide II); the peaks located at 1447 cm^{-1} , 1387 cm^{-1} , and 1321 cm^{-1} are attributed to the C-N stretching vibration (amide III); the peaks at 1153 cm^{-1} , 1076 cm^{-1} and 1033 cm^{-1} are assigned to C-O stretching vibrations in -COH, and to the stretching vibration of C-O-C bridge in the N-acetylglucosamine unit. The peaks from 1211 and 891 cm^{-1} correspond to P=O stretching and deformation from triphosphate anions. It can be observed that the peak from 1211 cm^{-1} disappeared and the peak from 891 cm^{-1} decreased in intensity and was shifted at 896 cm^{-1} after the composite regeneration, and this shows that the TPP anions were removed from the system.

2. Adsorption of Cu²⁺ onto composites

Fig. 2 shows the effect of the pH of Cu²⁺ solution on the sorption capacity of C91 composites.

From Fig. 2, it can be observed that, for all composites, the sorbed amount of Cu²⁺, q_e , increased when pH of Cu²⁺ solution was raised from 2 to 4.5, and at pH higher than 4.5 the q_e started to decrease, the optimum sorption pH being located at 4.5. In the acidic range, most of the amino groups from the composite are ionized as NH₃⁺, and thus the electrostatic repulsion between Cu²⁺ and NH₃⁺ prevent the adsorption of the metal ions onto the composite, while at pH values higher than 4.5 the sorption capacity decreased because a small amount of Cu²⁺ started to deposit as Cu(OH)₂.

The influence of the contact time on the sorption capacity of the C91 composites is presented in Fig. 3.

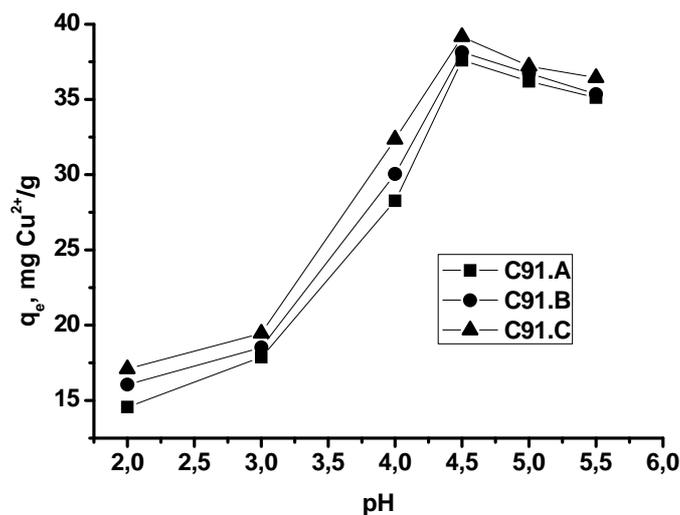


Fig. 2 – Cu^{2+} retention on C91 composites as a function of pH; temperature 25°C , contact time 24 h, and initial concentration of Cu^{2+} 0.007 mol/L.

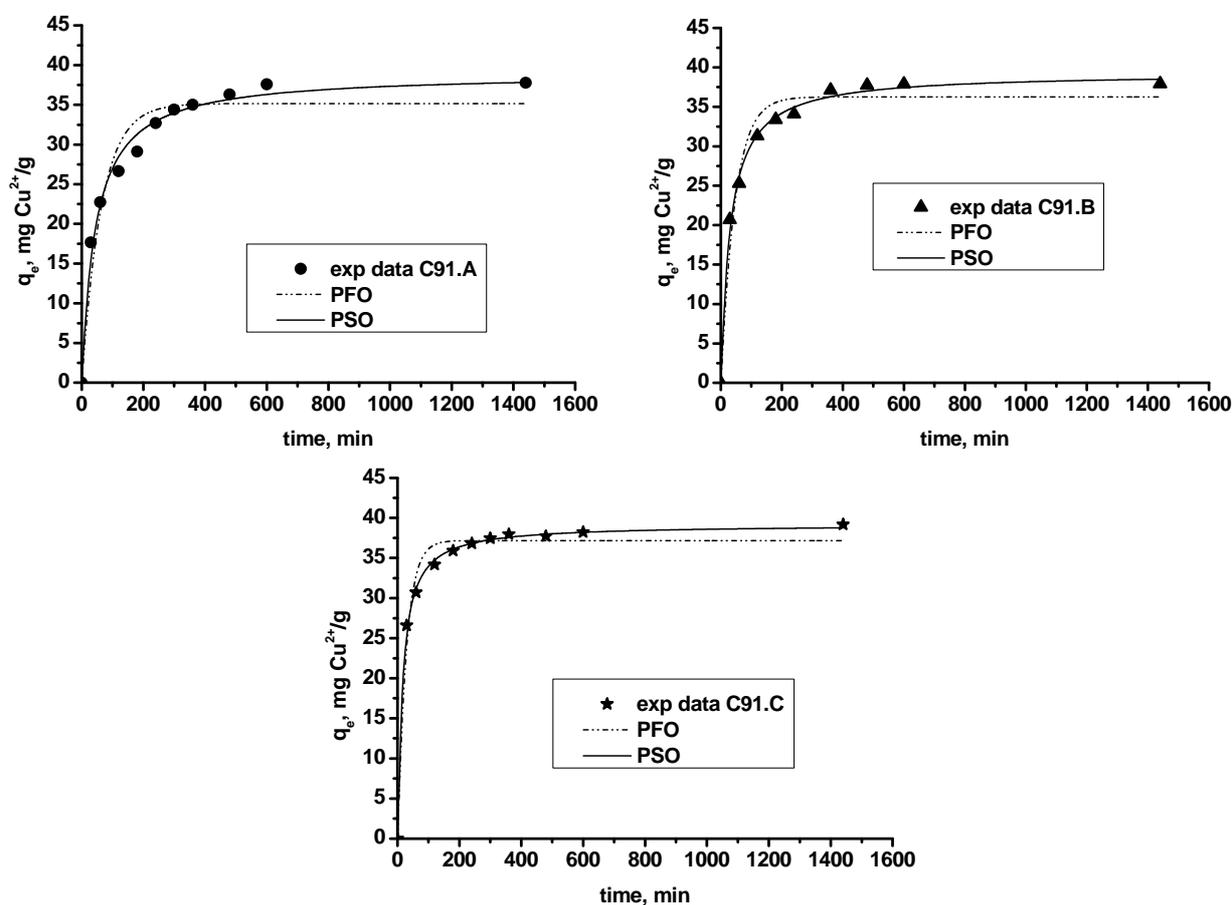


Fig. 3 – Sorption kinetics of Cu^{2+} onto the C91 composites; temperature 25°C , sorbent dose 0.1 g, pH 4.5, and initial concentration of Cu^{2+} 0.007 mol/L.

Two kinetic models were fitted on the experimental data, pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetic models. Recent work showed that the non-linear regression method is more accurate in the determination of the kinetic

parameters, the calculation errors are reduced compared with the linear fitting.¹⁹ Therefore, the non-linear regression of the two kinetic models was applied in this work. The Lagergren rate equation, also known as the pseudo-first-order

(PFO) kinetic model, considers the adsorption rate proportional with the difference between the equilibrium adsorption capacity and the adsorbed amount.²⁰ The nonlinear form of PFO kinetic model is expressed by Equation (1):

$$q_t = q_e(1 - e^{-k_t t}) \quad (1)$$

where: q_e and q_t are the amounts of metal ion sorbed at equilibrium (mg/g) and at time t , respectively, and k_t is the rate constant of the PFO kinetic model (min^{-1}).

The pseudo-second-order (PSO) kinetic model is based on the assumption that the rate-determining step may be a chemical sorption involving valence forces through sharing or exchange electrons between adsorbent and sorbate.²¹ The nonlinear form of PSO kinetic model is expressed by Equation (2):

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (2)$$

where: q_e and q_t have the same meaning as in Equation (1), and k_2 is the rate constant of PSO kinetic model ($\text{g mg}^{-1} \text{min}^{-1}$).

The kinetic parameters obtained after fitting the two kinetic models on the experimental data are presented in Table 2. From Table 2 it can be observed that the experimental data were well described by PSO kinetic model, the equilibrium adsorption capacity, $q_{e,calc}$, being close to the experimental values, $q_{e,exp}$. Also the application of PSO kinetic model to the experimental data gave high correlation coefficients ($R^2 > 0.98$) and low Chi-square test (χ^2) values. Hence, it can be concluded that chemisorption is the main mechanism of sorption. It can also be observed that the values of k_2 are influenced by the synthesis conditions. For the same ECH:NH₂ molar ratio of 2:1, k_2 value increased from 0.000581 g/mg min, for the composite having the polymer concentration of 3.3 wt.%, to 0.000851 g/mg min, for the composite having the polymer concentration of 2 wt.%. In the case of the composites with the same polymer concentration, 2wt.%, the value of k_2 increased with the decrease of ECH:NH₂ molar ratio. The increase of k_2 value with the decrease of the polymer concentration and of the cross-linking degree could indicate a higher diffusion rate of Cu²⁺ ions.

In the adsorption process of a solute from solution onto a solid surface, the solute adsorbed on the solid surface is in a dynamic equilibrium

with the solute remained in the solution. A plot of the solute concentration adsorbed on the solid surface (mg/g) as a function of the solute concentration in the solution at equilibrium (mg/L), at constant temperature, gives an adsorption isotherm, which can be described by some adsorption models.⁷ Fig. 4 shows that the retention capacity of C91 composites for Cu²⁺ ions increases with the increase of the equilibrium metal concentration.

In the present study, three isotherm equations were tested: Langmuir (Equation 3), Freundlich (Equation 4) and Dubinin–Radushkevich (Equation 5).

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (3)$$

$$q_e = K_F C_e^N \quad (4)$$

$$q_e = q_{DR} \exp\{-\beta[RT \ln(1 + \frac{1}{C_e})]^2\} \quad (5)$$

where: q_e is the amount of metal ions adsorbed in mg/g, C_e is the concentration (mg/L) of Cu²⁺ in the solution at equilibrium, K_L , the Langmuir constant, represents the adsorption equilibrium constant, q_m is the maximum adsorption capacity (mg/g), K_F is the Freundlich constant, which predicts the quantity of Cu²⁺ ions per gram of sorbent at the unit equilibrium concentration, N is a measure of the nature and strength of the adsorption process and of the distribution of active sites. In Equation (5), q_{DR} is the maximum adsorption capacity of the metal ion (mg/g), and β is the D-R isotherm constant (mol^2/kJ^2). The constant β is used to obtain the E value, which is the mean free energy when one mole of ion is transferred from infinity in solution to the surface of a solid and can be computed using Equation (6).²²

$$E = \frac{1}{\sqrt{2\beta}} \quad (6)$$

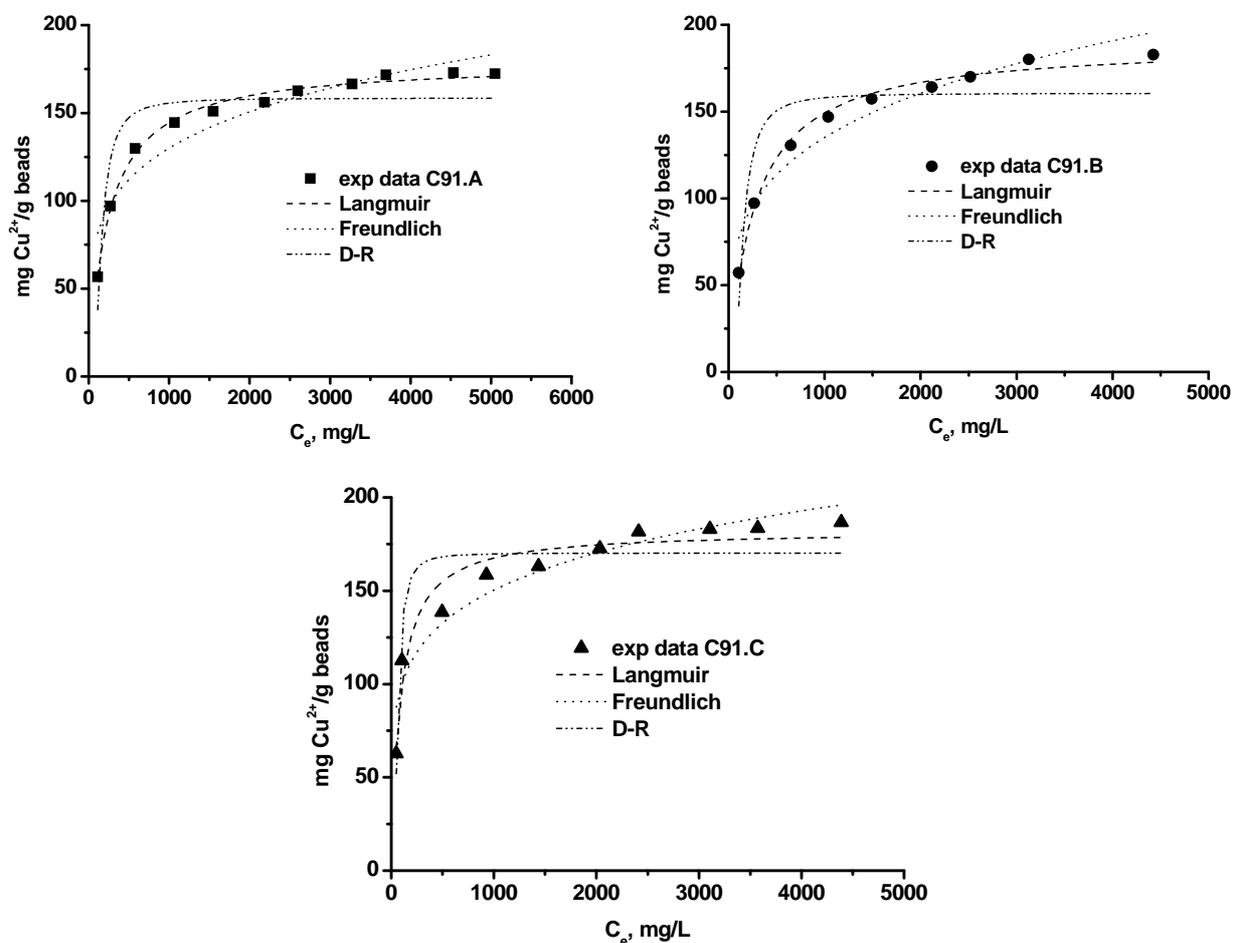
The E value is used to establish the type of adsorption process under consideration. If this value is bigger than 8 kJ/mol, the adsorption process can be assumed to involve chemical sorption. On the other hand, if E values are below 8 kJ/mol, the adsorption process is of a physical nature.

The isotherm parameters corresponding to the adsorption models were calculated and listed in Table 3.

Table 2

Kinetic model parameters for the adsorption of Cu^{2+} onto CS/PVAm composite beads

Parameter	C91.A	C91.B	C91.C
$q_{e,exp}$ (mg/g)	37.77	37.93	39.17
PFO kinetic model			
$q_{e,calc}$ (mg/g)	35.15	36.26	37.16
k_1 (min^{-1})	0.0158	0.02194	0.03638
R^2	0.9446	0.9669	0.98
χ^2	7.14	4.27	2.53
PSO kinetic model			
$q_{e,calc}$ (mg/g)	38.98	39.31	39.17
k_2 (g/mg min)	0.000581	0.000851	0.00167
R^2	0.9877	0.996	0.9987
χ^2	1.577	0.5587	0.1607

Fig. 4 – Equilibrium adsorption isotherms of Cu^{2+} onto the C91 composites fitted by three isotherm models.

As Table 3 shows, the Langmuir model quite well fitted the experimental data obtained for the adsorption of Cu^{2+} onto C91 composites, with a maximum sorption capacity, q_m , of 178.73 mg/g, 189.13 mg/g, and 182.08 mg/g for C91.A, C91.B, and C91.C, respectively.

The essential characteristics and the feasibility of the Langmuir model were expressed in terms of a dimensionless constant, commonly known as

separation factor (R_L), which is expressed by the following equation:^{22,23}

$$R_L = \frac{1}{1 + K_L C_i} \quad (7)$$

where K_L (L/mg) refers to the Langmuir constant and C_i is the maximum initial concentration of adsorbate (mg/L). The R_L values indicate the

adsorption is unfavorable ($R_L > 1$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$).²³ The R_L values calculated for all three composites are 0.0364 for C91.A, 0.0408 for C91.B and 0.0137 for C91.C. These values are situated between 0 and 1, indicating a favorable sorption process.

In Table 3 there are also listed the values of mean free energy of sorption per mole of the sorbate (E), calculated from Dubinin–

Radushkevich equation. In all cases E value is bigger than 8 kJ/mol (13.11 kJ/mol for C91.A, 13.76 kJ/mol for C91.B and 31.94 kJ/mol for C91.C) supporting thus the chemisorption as the controlling mechanism of sorption.

To get further information about the sorption mechanism of Cu^{2+} , the FTIR spectra of the composite beads loaded with Cu^{2+} are presented in Fig. 5A.

Table 3

Adsorption isotherm parameters of Langmuir, Freundlich and Dubinin–Radushkevich models for the adsorption of Cu^{2+} ions on C91 composites

Parameter	C91.A	C91.B	C91.C
Langmuir			
q_m (mg/g)	178.73	189.13	182.08
K_L (L/mg)	0.00422	0.00374	0.01145
R_L	0.0364	0.0408	0.0137
R^2	0.9928	0.989	0.9462
χ^2	9.63	17.65	95.96
Freundlich			
K_F (mg/g)	29.82	24.18	43.48
N	0.213	0.249	0.1795
R^2	0.8982	0.9321	0.9246
χ^2	137.21	118.41	134.13
Dubinin–Radushkevich			
q_{DR} (mg/g)	158.46	160.55	170.07
β (mol^2/kJ^2)	0.00291	0.00264	0.00049
E (kJ/mol)	13.11	13.76	31.94
R^2	0.807	0.753	0.845
χ^2	259.75	430.75	274.99

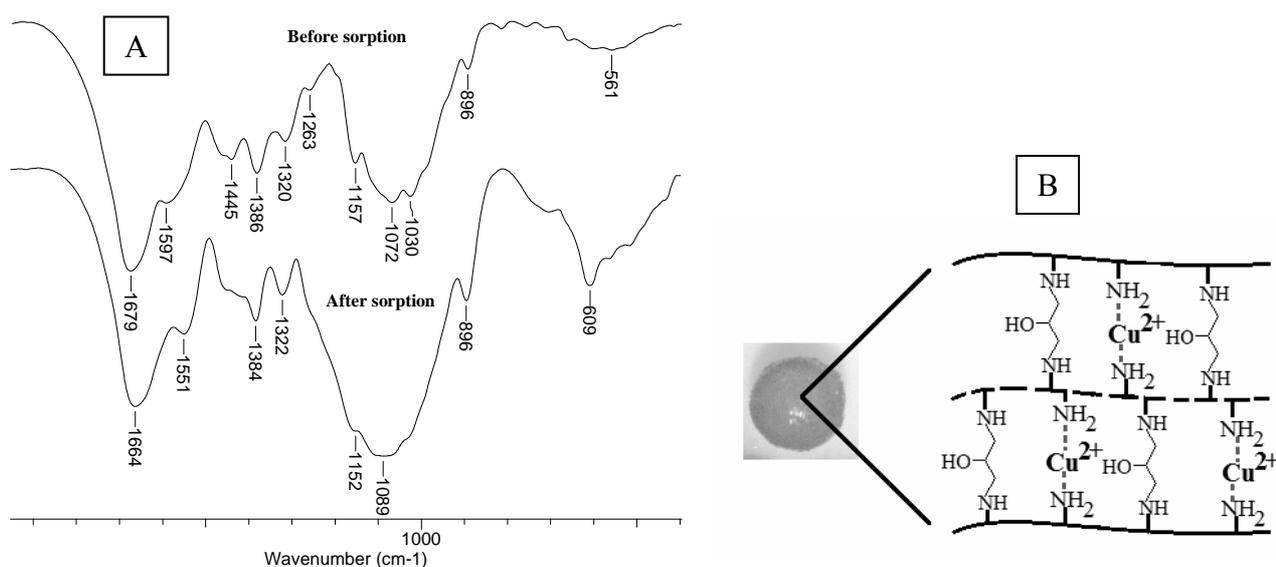


Fig. 5 – FTIR spectra of the composite C91.A before and after sorption (A) and the possible sorption mechanism (B).

Only the region 1700-500 cm^{-1} is presented in Fig. 5A because the region between 3500-2000 cm^{-1} was less affected by the Cu^{2+} uptake. As can be seen, the peak from 1679 cm^{-1} is shifted to 1664 cm^{-1} , the shoulder from 1597 cm^{-1} is shifted to 1551 cm^{-1} after Cu^{2+} sorption. The peak at 1263 cm^{-1} no longer appears in the FTIR spectra of the composite loaded with Cu^{2+} . The peak at 1157 cm^{-1} was reduced to a shoulder and was shifted to 1152 cm^{-1} , the peak at 1072 cm^{-1} shifted to 1089 cm^{-1} , and the peak from 1030 cm^{-1} disappeared. In addition to all these changes a new peak appeared at 609 cm^{-1} , this peak being characteristic for the metal-N binding. All these changes support the participation of N atoms as the main binding sites for metal ions. Based on the information given by the FTIR spectra, a possible sorption mechanism of Cu^{2+} on the C91 composites is presented in Fig. 5B.

EXPERIMENTAL

Materials. CS powder was purchased from Sigma Aldrich. The degree of acetylation (DA) of CS was evaluated to be 85%. The average molar mass of CS, M_w , was determined by viscometry.²⁴ The M_v of CS used in this study was determined to be 467 kDa. PVAm as aqueous solution with a concentration of 18 wt.%, with a molar mass of 340 kDa, and a degree of hydrolysis of 95 wt.%, was received from BASF (Ludwigshafen, Germany). $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, used as metal ion source for the sorption experiments, was purchased from Sigma Aldrich. All the reagents were of analytical grade or highest purity available, and used without further purification.

Preparation of composite beads. The synthesis of the composite as beads consists of the following steps: (1) preparation of the mixture between CS solution with ECH and PVAm solution with ECH, the added ECH being calculated for a certain molar ratio ECH: NH_2 (Table 1), and stirring until the mixture was completely homogenized; (2) formation of beads by dropping the mixture previously prepared into an aqueous solution of 0.05 M TPP, at room temperature, keeping the beads in TPP for 3 h; (3) the beads were separated from TPP and transferred into a mixture containing ethanol and an aqueous solution of pH 11 with a weight ratio of 50:50, the final solution pH being 9. The composite beads were kept in this solution for 24 h. After that, the microspheres were intensively washed with distilled water in order to remove the excess of small ions and then dried at room temperature for ~ 24 h, and under vacuum at 40 °C, for 48 h. In order to remove all TPP ions the composites were treated with 0.1 M HCl for 1 h, rinsed with distilled water and treated with 0.1 M NaOH for 1 h. The process was repeated once again and after that the composite beads were washed to neutral pH.

Methods. The structure of the composites was investigated by FTIR spectroscopy. The dried samples were first frozen in liquid nitrogen, and then broken in a mortar to get the samples as powder. FTIR spectra were recorded with a Bruker Vertex FT-IR 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.

The swelling behavior of the composites was gravimetrically evaluated by immersing the dry microspheres of known weight in water at pH 2, for 48 h. After 48 h, the samples were removed from water and the water excess was quickly removed using filter paper. The swollen beads were then weighed and the water uptake was calculated with Equation (8):

$$SR = \left[\frac{W_w - W_d}{W_d} \right], \text{g/g} \quad (8)$$

where: W_w is the weight for the wet sample, and W_d is the weight for the dry sample. The measurements were performed in two replicates and average data were used for calculation of SR_{eq} .

Batch Sorption Experiments. Batch adsorption studies were used to determine the effect of pH, contact time and initial concentration of Cu^{2+} . The adsorption capacity of the sorbent was calculated with Equation (9):

$$q = \frac{(C_i - C_e) \times V}{m}, \text{mg/g} \quad (9)$$

where: C_i and C_e are the concentrations of the Cu^{2+} in aqueous solution (mg/L) before and after the interaction with chelating sorbent, respectively, V is the volume of Cu^{2+} aqueous solution (L), and m is the amount of the dry sorbent (g).

CONCLUSIONS

In this study were obtained three composites based on CS and a synthetic polycation, PVAm, with enhanced sorption capacity for Cu^{2+} ions. The composites were obtained by an ionic/covalent cross-linking, ECH being used for the covalent cross-linking, and TPP anions for the ionotropic gelation. The composites were characterized by FTIR spectroscopy, and swelling behavior. The influence of pH, contact time and initial Cu^{2+} concentration on the composites sorption capacity was tested. The sorption of Cu^{2+} ions was proved to be dependent on the solution pH, and the optimum pH value for the adsorption was located at 4.5. The PSO kinetic model well fitted the kinetic data and demonstrated that chemisorption was the rate determining step for the sorption of Cu^{2+} . The Langmuir isotherm model well fitted the experimental data with a maximum sorption capacity of 178.73 mg/g, 189.13mg/g, and 182.08 mg/g for C91.A, C91.B, and C91.C, respectively. The values of the mean free energy of adsorption calculated from the Dubinin-Radushkevich isotherm revealed that the adsorption mechanism was predominantly a chemical process.

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