COMPOSITE MICROSPHERES BASED ON CHITOSAN AND POLY(VINYL AMINE) AND THEIR SORPTION CAPACITY FOR Cu^{2+}

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In this study, new composites, based on chitosan (CS) and poly(vinyl amine) (PVAm), were obtained. The composites have been prepared as beads by ionic/covalent cross-linking. Two strategies were used for the covalent cross-linking: post cross-linking, where the cross-linking agent was added after the bead formation and *in situ* cross-linking, where the covalent cross-linking was performed in tandem with the ionotrop gelation. The influence of the cross-linking strategy on the swelling ratio, *SR*, has been first evaluated, and it was observed that the beads prepared by the second strategy had a higher *SR* than those prepared by the first strategy. An enhancement of the sorption capacity of CS/PVAm composites for Cu^{2+} ions was found, when the beads were cross-linked *in situ*. The reusability of the composite beads has been also tested and it was found that the sorption capacity for Cu^{2+} increased in the 2nd cycle of sorption.

Keywords: chitosan, poly(vinyl amine), composite, copper

INTRODUCTION

The large quantities of heavy metal ions discharged from mines and industries like paints, pigments, metal fabrication, fertilizers and textiles have become a significant environmental problem.[1] These ions are a hazard to public health and the environment when discharged inappropriately.[2] Conventional removal methods, such as chemical precipitation, filtration and reverse osmosis, are inefficient in removing trace levels of heavy metals from polluted aqueous solutions.[3] Notably, adsorption on activated carbon is recognized as an effective method for the removal of pollutants from wastewaters. However, since this process is expensive, low cost biosorbents have received increased attention, as they can significantly reduce the cost of the process.[4-6]

CS is the only polycation coming from renewable resources, well known for its chelating properties against heavy metals, and it is composed from β-(1→4)-2-amino-2-deoxy-D-glucopyranose and β-(1→4)-2-acetamido-2-deoxy-D-glucopyranose units randomly distributed along the polymer chain (Figure 1).

Due to the presence of amino and hydroxyl groups, which can serve as active sites, in its structure, CS can be used as a sorbent for the removal of different polluting agents, dyes or heavy metal ions. However, CS is very sensitive to pH as it can either form a 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, ethylene glycol diglycidyl ether and isocyanates, have been used.[7,8] Chitosan derivatives have been extensively investigated as adsorbents.[9,10]

Recently, CS composites have been developed to adsorb heavy metals and dyes from wastewater.[11] Different kinds of substances have been used to form composites with chitosan, such as clinoptilolite,[6,12,13] montmorillonite,[14] polyurethane,[15] activated clay,[16] bentonite,[17] poly(vinyl alcohol), poly(vinyl chloride),[18] poly(ethylene imine)[1] and kaolinite.[18]

One way to modulate CS sorption capacities would consist in obtaining new composites with a

synthetic polycation having reactive primary amine groups. The purpose of this study was to prepare new composites, based on CS and

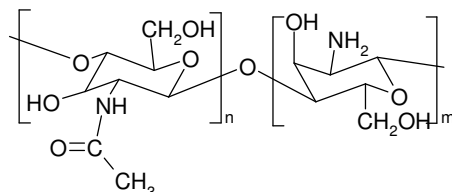poly(vinyl amine) (PVAm), a synthetic polycation less investigated for the composite preparation.

Figure 1: Chemical structure of chitosan

EXPERIMENTAL

Materials

Chitosan (CS) powder was provided by Sigma Aldrich. The degree of acetylation (DA) of CS was evaluated to be 85%. The average molar mass of CS was determined by viscometry. The intrinsic viscosity of CS solved in a mixture of 0.3 M acetic acid and 0.2 M sodium acetate (1:1, v/v) was measured with an Ubbelohde viscometer at 25 ± 0.1 °C. The viscometric average molar mass (M_v) of CS was estimated using Equation 1:[19]

$$[\eta] = 1.38 \ x \ 10^{-4} \ M_v^{0.85} \qquad (1)$$

The M_v of CS used in this study was determined to be 467 kDa.

PVAm as aqueous solution with a concentration 18 wt%, with a molar mass of 340 kDa, and a degree of hydrolysis of 95 wt%, was received from BASF (Ludwigshafen, Germany). $CuSO_4 \cdot 5H_2O$, 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 any further purification.

Synthesis of CS/PVAm composite beads

Post cross-linking strategy

A dilute solution of PVAm was obtained by mixing 2.3 g aqueous solution of PVAm, with a concentration of 18 wt%, with 7.7 mL distilled water for 15 min. The dilute solution of PVAm was mixed with 20 g of CS solution, with a concentration of 3 wt%, for 15 min under vigorous stirring. After 15 minutes, the mixture was dropped by a syringe into 90 mL aqueous solution of sodium tripolyphosphate (TPP) with a concentration of 0.1 M, under mild magnetic stirring. The formed microspheres were kept in this solution for 3 h, at room temperature. Then, the composite beads were separated from the TPP solution, washed three times with distilled water and transferred into a mixture of 30 mL water of pH 11, 30 mL ethanol, 2 mL epichlorohydrin (ECH), the final pH being adjusted to 11 with NaOH 6%. The composites were kept in this mixture for 24 h, at room temperature. Then, the microspheres were intensively washed with distilled water in order to remove the excess of small ions.

In situ *cross-linking*

For *in situ* cross-linking, the synthesis strategy was different. 2 mL ECH was added in two parts, as follows: 1) 1 mL ECH was added dropwise into 20 g of CS solution, with a concentration of 3 wt%, and 2) 1 mL ECH was mixed with a solution of PVAm obtained from 2.3 g PVAm with a concentration of 18 wt% and 7.7 mL distilled water, both solution mixtures being kept under stirring until the complete inclusion of ECH. Next, the two solutions were mixed together and the mixture pH was adjusted from 4 to 5 with 2 M NaOH. The polycation mixture was added by a syringe into 90 mL aqueous solution of TPP with a concentration of 0.1 M, under mild magnetic stirring. The formed microspheres were kept in TPP for 3 h, at room temperature. After that, the composite beads were separated from the TPP solution, washed three times with distilled water, and put in an aqueous solution of pH 11, for 24 h, at room temperature. Finally, they were intensively washed with distilled water in order to remove the excess of small ions with methanol for dehydration, and then dried at room temperature for ~24 h, and under vacuum at 40 °C, for 48 h.

Characterization of CS/PVAm composites

FTIR spectra were recorded with a Bruker Vertex FT-IR spectrometer, with a resolution of 2 cm^{-1}, in the range of 4000-400 cm^{-1} by the KBr pellet technique. Infrared analysis was performed for all sorbents, before and after being regenerated with HCl 0.1 M.

The swelling behavior of the composites was gravimetrically evaluated by suspending 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 wet beads were then weighed and the water uptake was calculated with Equation (2):

$$SR = \left[\frac{W_w - W_d}{W_d} \right], g/g \qquad (2)$$

where: W_w is the mass of the wet sample, and W_d is the mass of the dry sample.

Adsorption studies

The study of the Cu^{2+} retention properties of the composite beads was carried out using a batch equilibrium procedure. Thus, approximately 0.1 g of dried microspheres were placed in flasks and left for 24 h in 10 mL of distilled water. After 24 h, the water was removed and the samples were soaked in an aqueous solution of $CuSO_4$, having a concentration of 0.07 mol/L, for different periods of time, the equilibrium pH of $CuSO_4$ solutions being 4.5. Then, the beads were filtered off and the residual concentration of Cu^{2+} remaining in the filtrate was measured by UV-Vis spectroscopy at 808 nm, on a SPECORD M42 Carl Zeiss Jena, Germany. The adsorption capacity of the sorbent was calculated with Equation (3):

$$q = \frac{(C_i - C_t) \times A_M \times 10}{m}, mg/g \qquad (3)$$

where C_i and C_t are the concentrations of the Cu^{2+} in aqueous solution (mg/L) before and after the interaction with the chelating sorbent, respectively, A_M is the atomic mass of copper and m is the amount of the dry sorbent (g).

The release of Cu^{2+} from the composites and cross-linked CS microspheres was performed with 0.1 M HCl, 10 mL solution for 0.1 g of sorbent. The regeneration of the sorbents was performed with 0.1 M NaOH, followed by washing to neutral pH.

RESULTS AND DISCUSSION
Composite preparation and characterization

Figure 2 represents the schematic diagram of the composite synthesis.

The CS/PVAm composites have been prepared as beads by an ionic/covalent cross-linking. Ionotrop gelation was performed in TPP, and covalent cross-linking by ECH. Two strategies were used for the covalent cross-linking of microspheres: post cross-linking, when the cross-linking with ECH was performed after the bead formation in TPP, and *in situ* cross-linking, when the covalent cross-linking was performed in tandem with the ionotrop gelation. Cross-linked CS microspheres without PVAm were also prepared, for comparison.
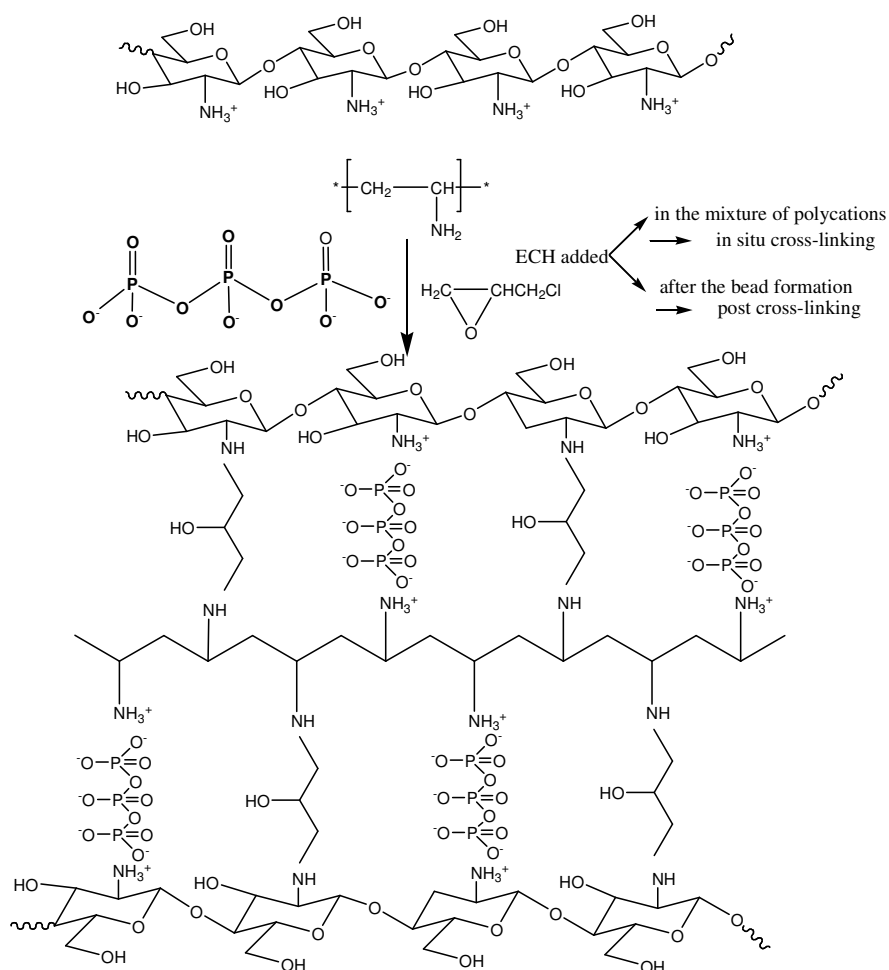

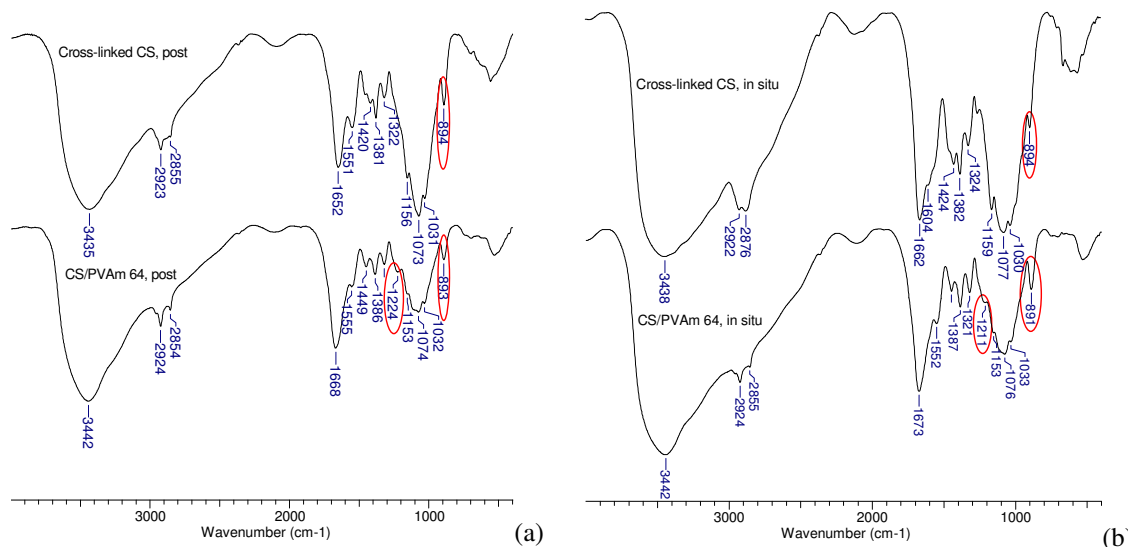Figure 2: Schematic representation of CS/PVAm composite synthesis

Figure 3: FTIR spectra for post cross-linked CS and CS/PVAm composite, (a) and *in situ* cross-linked CS and CS/PVAm composite (b)

The FTIR spectra of CS/PVAm composites do not show any important differences in the structure, compared with those of the cross-linked CS, because PVAm has a simple structure without any important bands in the FTIR spectrum.

Figure 3 shows the FTIR spectra for the cross-linked CS and CS/PVAm composites. The main peaks visible in the FTIR spectra are located at: 3442 cm^{-1} attributed to –OH and –NH stretching vibration, 2924 and 2854 cm^{-1} attributed to CH and CH$_2$ stretching vibrations, 1668 cm^{-1} assigned to C=O bond in acetamide groups (amide I band), 1551 cm^{-1} assigned to amide II band, 1449 cm^{-1} assigned to the CH$_2$ groups in PVAm, 1386 cm^{-1} assigned to the –CH symmetric bending vibration in –CHOH unit, 1320 and 1153 cm^{-1} characteristic of the N-acetylglucosamine unit, 1074 and 1032 cm^{-1} assigned to –CO stretching vibrations in –COH. The peaks at 1224 and 893/894 cm^{-1} (Figure 3a), and at 1211 and 891/894 cm^{-1} (Figure 3b) correspond to P=O stretching and deformation from TPP. Although

the peak at around 894 cm^{-1} appears in both FTIR spectra for cross-linked CS and CS/PVAm composites, the peaks at 1224 cm^{-1} (Figure 3a) and 1211 cm^{-1} (Figure 3b) appear only in the composite spectra, which shows that PVAm retain more TPP ions than CS alone. The results obtained for the swelling behavior of the CS and CS/PVAm composites were plotted in Figure 4. As can be observed, the swelling ratio, *SR*, of the CS beads is lower than the *SR* of the CS/PVAm composites, meaning that the CS beads are better cross-linked compared with the composite microspheres. The influence of the cross-linking strategy on the *SR* has been also evaluated, a strong influence of this parameter on the *SR* being observed, the beads prepared by the *in situ* cross-linking strategy having a higher *SR* than those prepared by the post cross-linking strategy. This means the beads formed by the post cross-linking strategy have a higher cross-linking density.
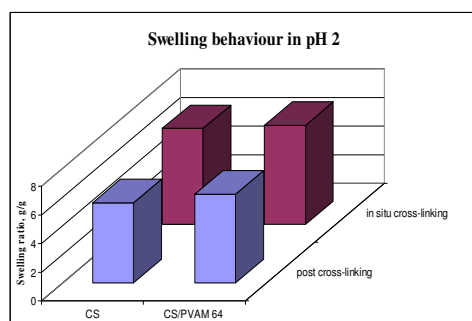

Figure 4: Influence of cross-linking strategy on the swelling behavior of cross-linked CS and CS/PVAm composite beads
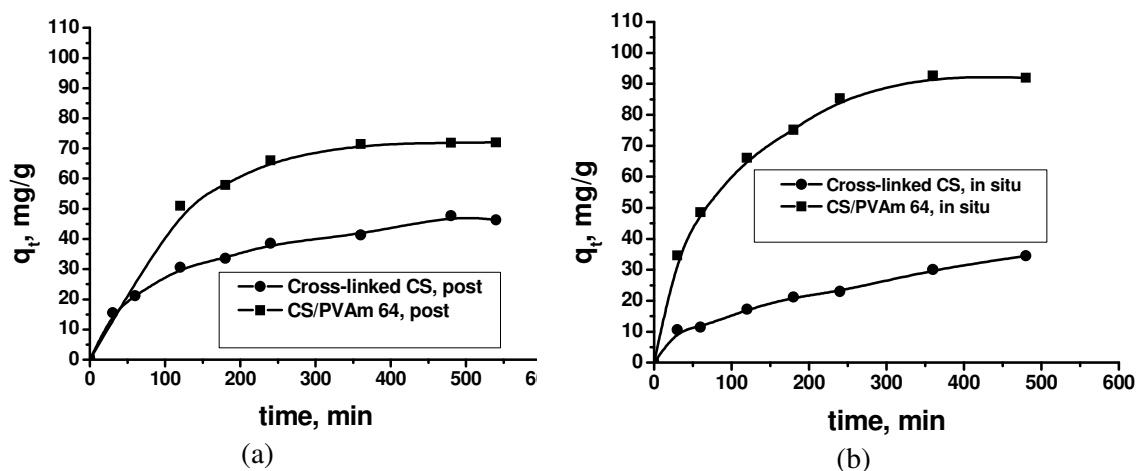
Figure 5: Sorption kinetics of post cross-linked CS and CS/PVAm composite beads (a), and *in situ* cross-linked CS and CS/PVAm composite beads (b)

Adsorbtion studies of Cu^{2+}

Figure 5 shows the sorption kinetics of Cu^{2+} by the cross-linked CS and CS/PVAm composite beads obtained using the two cross-linking strategies, post cross-linking (Figure 5a) and *in situ* cross-linking (Figure 5b). It can be noticed that, for both cross-linking strategies, the CS/PVAm composites present a higher sorption capacity compared with the sorption capacity of CS alone. It can also be noticed that the composites obtained by post cross-linking strategy have a lower sorption capacity compared with the sorption capacity of the composites obtained by *in situ* cross-linking. This is because the post cross-linked composites have a higher cross-linking degree compared to the *in situ* cross-linked composites.
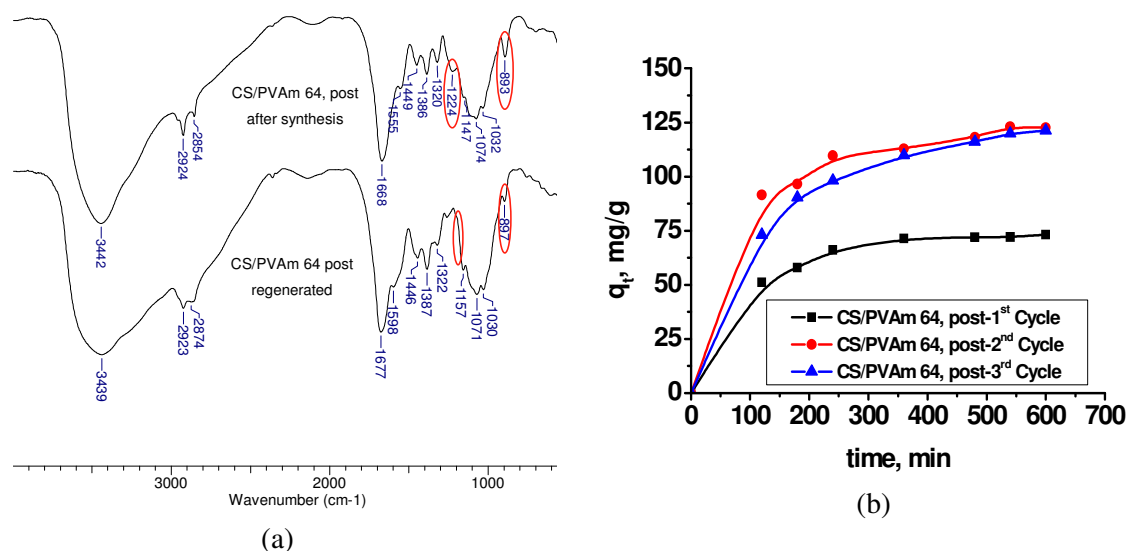

Figure 6: (a) FTIR spectra of post cross-linked CS/PVAm composites after synthesis and regeneration; (b) reusability of the composite, 1st, 2nd and 3rd cycles of sorption
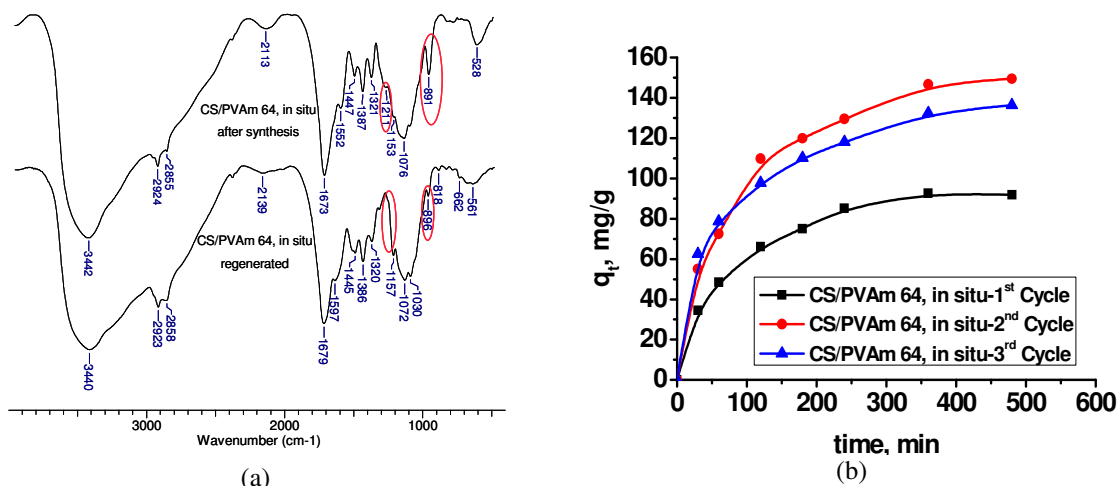
| (a) | (b) |

Figure 7: (a) FTIR spectra of *in situ* cross-linked CS/PVAm composites after synthesis and regeneration; (b) reusability of the composite, 1st, 2nd and 3rd cycles of sorption

The reusability of the composites was also tested. Figure 6b shows that the equilibrium sorption capacity of the post cross-linked composite increases from 73.15 mg/g, in the fist cycle, to 122.56 mg/g, in the second cycle. After composite synthesis, the excess of TPP ions was not completely removed, these ions blocking the metal binding sites. After regeneration, most of the TPP ions were removed, leaving behind available metal binding sites. The equilibrium sorption capacity found for the 3rd cycle of sorption was comparable with that found for the 2nd cycle. From the FTIR spectra of the initial and regenerated composites (Figure 6a), it can be noticed that the band located at 1224 cm^{-1}, corresponding to P=O stretching, is absent in the FTIR spectra of the regenerated composite, and the band located at 893 cm^{-1}, corresponding to P=O deformation, is less intense.

As Figure 7 shows, the situation is similar in the case of *in situ* cross-linked composites. The equilibrium sorption capacity increases from 91.93 mg/g, in the 1st cycle, to 149.56 mg/g in the 2nd cycle (Figure 7b). The difference between the sorption capacity found in the 3rd and 2nd cycle is not so significant, compared with the difference between the 1st and 2nd cycle. From Figure 7a, it can also be noticed that the band from 1211 cm^{-1}, corresponding to P=O stretching, disappears from the regenerated composite FTIR spectra, and the band located at 891 cm^{-1}, corresponding to P=O deformation, decreased in intensity.

CONCLUSION

Novel composites based on CS and a synthetic polycation, PVAm, with enhanced sorption capacity for Cu^{2+} have been reported in this study. The composites were obtained by an ionic/covalent cross-linking, two strategies being used for the covalent cross-linking. In the post cross-linking strategy, the covalent cross-linker, ECH, was added after bead formation, and in the *in situ* cross-linking strategy, ECH was added to the reaction mixture. The composites characteristics were compared with those of the cross-linked CS without PVAm. It was found that the sorption capacity of the composites was higher than that of the CS alone. The cross-linking strategy also affected the sorption capacity, the *in situ* cross-linked composites having a higher sorption capacity compared with the post cross-linked ones. The reusability of the composites was tested and it was found that, in the second cycle of sorption, the composites were able to retain a higher amount of Cu^{2+} ions, because a higher number of amine groups were available for chelation.

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