



# Chitosan-based ion-imprinted cryo-composites with excellent selectivity for copper ions



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## ABSTRACT

An original strategy is proposed here to design chitosan-based ion-imprinted cryo-composites (II-CCs) with pre-organized recognition sites and tailored porous structure by combining ion-imprinting and ice-templating techniques. The cryo-composites showed a tube-like porous morphology with interconnected parallel micro-channels, the distance between the channel walls being around 15  $\mu\text{m}$ . Both the entrapment of a natural zeolite and the presence of carboxylate groups, generated by partial hydrolysis of amide moieties, led to II-CCs with controlled swelling ratios (25–40 g/g, depending on pH) and enhanced overall chelating efficiency (260 mg  $\text{Cu}^{2+}$ /g composite). To point out the importance of introducing  $\text{Cu}^{2+}$  recognition sites, sorption experiments using mixtures of  $\text{Cu}^{2+}$  and other competing ions ( $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$  or/and  $\text{Pb}^{2+}$ ) were also carried out. The higher values of selectivity coefficients obtained for the II-CCs compared to those of non-imprinted ones highlight the remarkable potential of our sorbents for decontamination of wastewaters and recycling of  $\text{Cu}^{2+}$  ions.

## 1. Introduction

Amongst all pollutants, metal ions are considered as the most problematic ones because of their high persistence into the ecosystem, bioaccumulation and high toxicity. Even though some metal ions are essential in various life processes playing an irreplaceable role in many metabolic cycles, they can irreversibly harm the body when are present in excessive amounts (Hu, 2002). Consequently, intense efforts have been undertaken to minimize the harmful impact of metal ions. Thus, national and international regulations on the disposal and recovery of toxic or valuable metal ions have led to the development of various water treatment technologies, including solvent extraction, chemical precipitation, ion exchange, electrochemical treatment, and membrane filtration technologies (Fu & Wang, 2011). However, these techniques have several limitations, failing to keep up with either the uncontrollable discharge levels of metal ions or the economic and environmental issues, especially when dilute effluents must be decontaminated (Weber, 1985). Adsorption is another process that proved to be suitable for the removal of metal ions from dilute aqueous systems, its significant advantages being the low-cost, availability of sorbents, ease of operation, and effectiveness (Dinu & Dragan, 2008; Fu & Wang, 2011; Mihai, Bunia, Doroftei, Varganici, & Simionescu, 2015). Even so, all the approaches mentioned above are non-selective by their nature. In this context, it is essential to improve the selectivity towards certain metal ions, because of many competitive metal ions present in the

contaminated waters that could also compete for the active sites of sorbents. Recently, ion-imprinted polymers (IIPs) have received an increased attention due to their higher selectivity coefficients compared to non-imprinted ones (Branger, Meouche, & Margaillan, 2013; Jalilzadeh & Senel, 2016; Jalilzadeh, Uzun, Senel, & Denizli, 2016; Wang & Li, 2015a; Wang & Li, 2015b). Selective binding sites for certain metal ions are typically created by elution of target ions, which have been formerly chelated as template ions. For example, IIPs based on 2-hydroxyethyl methacrylate were synthesized using histidine (Jalilzadeh & Senel, 2016), N-methacryloyl-L-aspartic acid or N-methacryloyl-L-cysteine (Jalilzadeh, Uzun, Senel, & Denizli, 2016) as complexing/chelating agents for  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  ions, respectively. Besides the synthetic IIPs, polymers coming from natural resources showed also a high potential and proved to be very promising for engineering IIPs with distinct and valuable features. In particular, polysaccharides with their prominent representative – chitosan (CS), are well-known for their sorption properties, being able to remove metal ions from dilute solutions either by electrostatic interactions or chelation (Dragan, Apopei-Loghin, & Cocarta, 2014; Feng, Wang, Zhang, & Shi, 2013; Guibal, 2004; Wan Ngah & Fatinathan, 2010; Zeng, Chen, Yuan, Guo, & Yu, 2014; Zhu, Bai, Luo, Wang, & Zhai, 2017). Their sorption performance is controlled by the environment particularities and biopolymer properties. However, these factors could limit the accessibility and availability of reactive groups to water and metal ions; moreover, the reduced porosity of polysaccharides slows down the

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mass transfer of metal ions throughout the sorbent. The typical drawback of the most of the reported sorbents is the inherent lack of selectivity when species with similar molecular weights or ionic volumes are separated (Branger, Meouche, & Margailan, 2013). Hence, there still is plenty of room for further improvements by developing new generations of sorbents with enhanced properties in selective metal ion separation and sorption. In this context, we introduce here an original approach for preparation of advanced cryogel composites (cryo-composites) by simultaneous  $\text{Cu}^{2+}$  imprinting and cross-linking polymerization under unidirectional freezing (UF) conditions. The ice-templating approach was chosen as a green and versatile method for preparation of our cryo-composites, since the polymerization reactions are conducted in aqueous solution (Lozinsky, 2014; Savina, Ingavle, Cundy, & Mikhalovsky, 2016). In the UF technique, inorganic dispersions, polymer solutions or their aqueous mixtures are commonly unidirectional frozen in liquid nitrogen (LN) or ethylene glycol, as freezing agents (Aranaz, Gutiérrez, Ferrer, & del Monte, 2014; Dinu, Pradny, Dragan, & Michalek, 2013a; Gutiérrez, Ferrer, & del Monte, 2008; Zhang et al., 2015). Using this pathway, the ice crystals grow in an unidirectional manner, and thus, cryogels with aligned honeycomb or lamellar micro-channeled structures containing poly(L-lactic acid) (Kim, Taki, Nagamine, & Ohshima, 2009), chitosan (Aranaz et al., 2014; Dinu et al., 2013a) poly(ethylene glycol) (Wu, Zhao, Sun, & Zhou, 2012), or poly(hydroxyethyl methacrylate) (Dinu, Pradny, Dragan, & Michalek, 2013b) have been designed so far. Moreover, UF allows the control over freezing conditions, including both the freezing rate and the direction of sample immersion into the freezing agent, leading to oriented porous structures capable to support the fast access of  $\text{Cu}^{2+}$  ions to an increased number of binding sites. Therefore,  $\text{Cu}^{2+}$ -imprinted 3D interpenetrating polymer networks (IPNs) were prepared by simultaneous *in situ* cross-linking of  $\text{Cu}^{2+}$ -chitosan complexes by glutaraldehyde (GA) and polymerization of acrylamide (AAM) in the presence of N,N'-methylenebisacrylamide (BAAM), using UF methodology. In our previous reports, we have designed non-imprinted IPNs with high swelling degrees (Dragan, Perju, & Dinu, 2012), but their gel structure collapsed during  $\text{Cu}^{2+}$  chelation (Dragan & Dinu, 2013), and finally, fell apart after the first sorption/desorption cycle. Consequently, to overcome this weakness, we decided in this study to disperse a natural zeolite into the initial polymer/monomer mixture, generating ion-imprinted cryo-composites (II-CCs) endowed with high chemical stability and tuned swelling properties. The selective sorption of  $\text{Cu}^{2+}$  ions from their mixtures with other species having various ionic radii ( $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ , or/and  $\text{Pb}^{2+}$  ions) was evaluated.

## 2. Experimental section

### 2.1. Materials

Chitosan (CS), with a viscometric average molecular weight of 330 kDa, and 85% deacetylated units, N,N'-methylenebisacrylamide (BAAM, 99%), ammonium persulfate (APS,  $\geq 99.99\%$ ), N,N,N',N'-tetramethylethylenediamine (TEMED, 99%), ethylenediaminetetraacetic acid disodium salt dihydrate (EDTA,  $\geq 98.5\%$ ), glutaraldehyde (GA) as aqueous solution with a concentration of 25%,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (99%),  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  ( $\geq 97\%$ ),  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (99%),  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  (99.5%) and  $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$  ( $\geq 99.99\%$ ) were purchased from Sigma-Aldrich. Acrylamide (AAM) was purchased from Fluka. The natural zeolite comes from the volcanic tuffs cropped out in Macias area (Cluj County, Romania) and contains 60–70% clinoptilolite (CPL).

### 2.2. Synthesis of cryo-composites

Generally, the preparation of NI-CCs and II-CCs was performed by free radical cross-linking copolymerization of AAM in aqueous medium, in the presence of CS and CPL, using the UF approach. GA was added as cross-linker for CS, while BAAM as cross-linker for AAM. The initial

concentration of CS ( $C_{CS}$ ), the initial concentration of AAM ( $C_{AAM}$ ), and the cross-linker ratios were systematically varied in order to optimize the reaction conditions for preparation of cryo-composites. The  $C_{AAM}$ ,  $C_{CS}$ , GA concentration, and BAAM/AAM as molar ratio were varied in the range of 5–25 wt.%, 1–2.45 wt.%, 0.625 wt.%–7.5 wt.%, and 1/40–1/80, respectively. The weight ratio between CS and CPL particles was kept constant at 4:1. The redox initiator system was based on APS and TEMED, and their concentrations were kept constant during all experiments. An aqueous solution of acetic acid with a concentration of 2% (v/v) was used for preparation of CS solutions with desired concentrations. Stock solutions of APS and TEMED were prepared by dissolving either 0.2 g of APS or 0.625 mL of TEMED in 25 mL of MilliQ water. Stock solutions of BAAM were prepared by dissolving the desired amount of BAAM, calculated for a certain monomer/cross-linker ratio, in 10 mL of MilliQ water, under stirring at 30 °C, and then stored for 24 h before use for composite synthesis.

#### 2.2.1. Preparation of NI-CCs

10 g of CS solution (3 wt.%) were mixed for 1 h with 2 mL of MilliQ water containing 74 mg of dispersed CPL, and then 0.64 mL of GA solution (2.5 wt.%) was added dropwise, under vigorous stirring, at a rate of 10  $\mu\text{L}/\text{min}$ . The resulted mixture was cooled down to 0 °C on an ice-bath and kept under stirring for 30 min. Simultaneously, 0.722 g of AAM was dissolved in 2 mL of MilliQ water and then stock solutions of BAAM (1 mL), and TEMED (1 mL) were added. The resulted mixture was also cooled down to 0 °C on an ice-water bath for 30 min. After that, the second mixture was added dropwise onto the CS/CPL/GA mixture, under vigorous stirring. The dispersion containing CS, CPL, GA, AAM, BAAM, and TEMED, with the pH adjusted to 5.5 by adding 0.36 mL NaOH solution (0.5 M), was purged with nitrogen gas for 20 min. Finally, the APS stock solution (1 mL) was added over, and the whole mixture was further stirred for about 1 min. Aliquots from this mixture ( $V_{total} = 18 \text{ mL}$ ) were transferred into 5 mL syringes, sealed with Parafilm, and then the bottom of the filled syringes was maintained close to the surface of liquid nitrogen (LN),  $-196 \text{ }^\circ\text{C}$ , used as freezing agent, in order to control the growth direction of ice crystals (UF). After the complete freezing of reaction mixture (about 7 min), the syringes were transferred into a CC1-K6 Huber Cryostat at  $-18 \text{ }^\circ\text{C}$  for 24 h. The syringes were then taken out and kept at room temperature (RT) for 1 h, and then the gels were pushed out of syringes and cut as discs of 3 mm height. To remove the unreacted compounds, the discs were first immersed into 100 mL of MilliQ water. The washing solution was exchanged every 2 h within the first 12 h and every 6 h for the next 60 h. Thereafter, the swollen cryo-composites were frozen in LN and freeze-dried in a Martin Christ, ALPHA 1–2LD apparatus for 48 h, at  $-57 \text{ }^\circ\text{C}$  and 0.045 mbars.

#### 2.2.2. Preparation of II-CCs

10 mL of 2 wt.% acetic acid solution were added over the mixture of desired amount of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and 0.3 g of CS, to produce a dispersed phase. This mixture was rigorously stirred for 24 h in order to ensure the chelation of  $\text{Cu}^{2+}$  ions by functional groups of CS. After that, 74 mg of CPL dispersed in 2 mL of MilliQ water were added over the  $\text{Cu}^{2+}/\text{CS}$  mixture and kept under stirring for 1 h, followed by the dropwise addition of 0.64 mL of GA solution (2.5 wt.%) under vigorous stirring, at a rate of 10  $\mu\text{L}/\text{min}$ . The whole mixture was cooled down to 0 °C on an ice-bath and kept under stirring for 30 min. The addition of AAM, BAAM, and the redox initiator system was performed in the same manner to that described already for NI-CCs. The freezing conditions (LN as freezing agent and a temperature of  $-18 \text{ }^\circ\text{C}$  for 24 h to ensure the complete gelation) were similar to those used for NI-CC preparation. The syringes were taken out from the cryostat, maintained at RT for 1 h, and then the gels were carefully taken out, cut as discs of 3 mm height, and immersed in 100 mL EDTA ( $0.05 \text{ mol L}^{-1}$ ) to wash out the imprinted  $\text{Cu}^{2+}$  ions. The desorbed II-CCs were gradually washed with water/ethanol mixtures (50/50 for 1 h, and 80/20 for 2 h), and finally

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