

## Removal of copper ions from aqueous solution by adsorption on ionic hybrids based on chitosan and clinoptilolite

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### ABSTRACT

Ionic hybrids based on chitosan and clinoptilolite with sorption capacity for copper(II) ions higher than that of cross-linked chitosan are presented in the paper. Hybrids based on chitosan and clinoptilolite were characterized by swelling degree in water as a function of pH, and by the sorption and desorption of copper(II).

**Keywords:** chitosan, clinoptilolite, ionic hybrid, copper(II), sorption/desorption

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### INTRODUCTION

Water contamination with heavy metals generates environmental problems because of their high toxicity and non-biodegradability, which causes a high persistence. They are known to bring about several health problems like nervous system damage, and even cancer. Among the conventional methods of heavy metal removal such as precipitation, electrolytic concentration, membrane filtration, ion exchange and adsorption, the adsorption process is especially used in the water treatment.<sup>1-3</sup> Nowadays, a strong interest in finding low cost and naturally occurring adsorbents such as zeolites as an alternative to the existing adsorbents can be observed.<sup>4-13</sup> Among the natural zeolites, clinoptilolite has attracted a strong interest last decades as cation exchanger with a high selectivity for ammonium, clinoptilolite bearing materials being primarily used to remove ammonium from municipal wastewaters.<sup>5,6</sup> Clinoptilolite is a hydrated alumina-silicate member of the heulandite group<sup>5,7</sup> occurring in the zeolitic volcanic tuff, being widespread in many countries in the world. Clinoptilolite is characterized by infinite three-dimensional frameworks of aluminium, silicon

and oxygen.<sup>5</sup> Its adsorption capacity for heavy metal cations,<sup>8-12</sup> and organic pollutants<sup>6,13,14</sup> has been also demonstrated. However, the cation exchange capacity (CEC) of natural clinoptilolite is relatively low, and therefore some surface modifications have been performed to increase the CEC and the adsorption capacity for organic pollutants.<sup>12,13</sup> By modification of clinoptilolite with cationic surfactants, the anion exchange capacity has been considerably increased, making them ideal candidates as environmental remediation materials, the removal not only of simple and complex anions but also of organic compounds like anionic dyes being possible.<sup>15-19</sup> In addition, clinoptilolite highly dispersed in polymer matrices improves/enhances mechanical, thermal or adsorption properties of the corresponding composites.<sup>20-22</sup> A less investigated direction of application is that of hybrid materials with chelating/ion exchange properties. Our goal was to prepare hybrid chelating resins by embedding clinoptilolite microparticles as guest in a matrix of chitosan as host, chitosan being widely used as a chelating natural polymer in the environmental remediation.<sup>23-26</sup> The clinoptilolite based hybrid chelating material (HCPL) as microspheres were

characterized by swelling in water as a function of pH, and by the adsorption capacity of copper(II), compared with cross-linked chitosan.

## EXPERIMENTAL

### Materials

The natural clinoptilolite sample used in this study comes from volcanic tuffs cropping out in Macicas area (Cluj county, Romania) and has the following ideal composition:  $\text{NaKC}_{0.5}\text{A}_{5.4}\text{Si}_{30.6}\text{O}_{72} \cdot 20\text{H}_2\text{O}$  ( $\text{Si}/\text{Al} = 5.7$ ).<sup>5</sup> According to Bedelean et al., specific area of clinoptilolite from Macicas area is  $21.42 \text{ m}^2/\text{g}$ .<sup>5</sup> The clinoptilolite sample was ground and sieved through a range of sieves, and only the particles that passed through a 0.05 mm and remained on 0.032 mm sieves were used for this study. The selected fraction was washed three times with distilled water, to remove any soluble salts, and dried at  $40^\circ\text{C}$  in the oven under vacuum, 24 h. Chitosan with a molar mass of 334 kg/mol and deacetylation degree of 82%, purchased from Fluka, was used without further purification. Chitosan was characterized by FT-IR analysis, for the determination of deacetylation degree (according to ref. 27), and by viscometry, for molar mass calculation (according to ref. 28).

### Methods

The chitosan solutions, with a concentration of 3 g/L, were obtained by dissolving the chitosan powder in 1 vol.-% acetic acid solution and intensive stirring for at least 48 h. The required amount of clinoptilolite powder was mixed with distilled water, the volume of water being  $\frac{1}{2}$  volume of chitosan solution used for the synthesis of the hybrid, and kept under vigorous magnetic stirring for 1 h at least. Two volumes of chitosan solution were mixed with one volume of water containing the dispersed clinoptilolite, and after a vigorous magnetic stirring, the epichlorohydrin (ECH) as cross-linker was added step-by-step. The mixing went on until the ECH was completely included in the reaction mixture. The mixture thus prepared was added by a syringe into an aqueous solution of sodium tripolyphosphate with a concentration of 0.1 M, under mild stirring. The hybrid microspheres were kept under stirring 5 h at  $37^\circ\text{C}$  and then were separated from the dispersion medium and intensively washed with distilled water to remove the excess of small ions. For characterization in dried state, the hybrid microspheres were filtered off, dried at room

temperature for 24 h and under vacuum at  $40^\circ\text{C}$ , for 48 h.

X-ray diffraction analysis was performed on a WAXD - D8 ADVANCE diffractometer, Bruker, Germany, with scanning scope of  $0-40^\circ$  ( $2\theta$ ), scanning speed of  $0.5^\circ/\text{min}$ , using  $\text{CuK}\alpha$  radiation, at room temperature. The ESEM studies were performed on samples fixed by means of colloidal silver on copper supports. The samples were covered with a thin layer of gold by sputtering (EMITECH K550X). The coated surface was examined by using the Environmental Scanning Electron Microscope type Quatro 200, operating at 15 kV with secondary electrons, in high vacuum mode.

Study of the metal ion retention properties of the hybrids was carried out using a batch equilibrium procedure. Thus, 0.25 g of dry HCPL was placed in a flask and contacted with 25 mL of the aqueous solution of  $\text{CuSO}_4$ , for 24 h. The regeneration of the samples loaded with  $\text{Cu(II)}$  was performed with 0.1 M HCl solution.

## RESULTS AND DISCUSSION

Powder X-ray diffractogram of the natural clinoptilolite sample is presented in Figure 1.

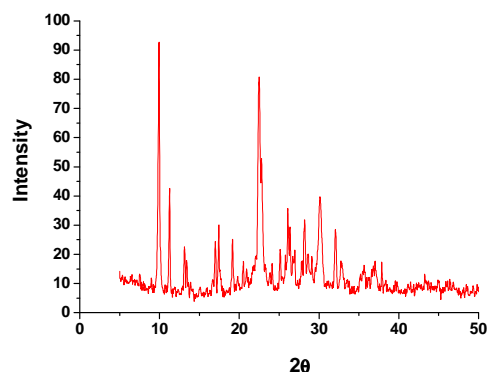


Figure 1 Powder X-ray diffractogram of natural clinoptilolite

The X-ray diffractogram in Figure 1 shows characteristic peaks for clinoptilolite.<sup>5,7</sup> Figure 2 shows the ESEM image of the clinoptilolite microparticles selected for this study.

Two HCPL samples with a low content (HCPL1.10) and a high content (HCPL1.2) of clinoptilolite were compared with chitosan without zeolite (HCPL0) (Table 1).

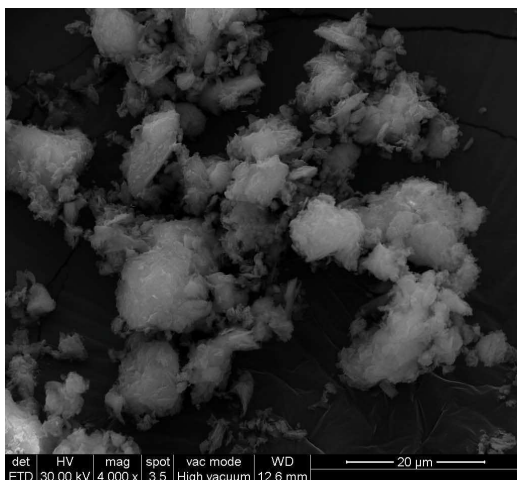


Figure 2 ESEM image of natural clinoptilolite

The water uptake values ( $Q_w$ ), collected in Table 1, show the decrease of  $Q_w$  at both pH = 5.5 and 2, the influence of clinoptilolite content being evident at pH 2.

**Table I** Water uptake ( $Q_w$ ) of the hybrids as a function of pH

Sample	CPL <sup>a)</sup> / Chitosan	$Q_w$ <sup>b)</sup> , [g/g]	
		pH = 5.5	pH = 2
HCPL0	0	2.831	3.396
HCPL1.10	1:10	1.708	2.628
HCPL1.2	1:2	1.701	2.387

<sup>a)</sup> clinoptilolite

It was very interesting to see how the presence of clinoptilolite influenced the adsorption capacity of the hybrid for metal cations compared with cross-linked chitosan. Therefore, the adsorption of Cu(II) after a contact time of 24 h, for all the hybrids was compared in Figure 3. As can be observed, the presence of clinoptilolite significantly increased the adsorption capacity for Cu(II) of the hybrids HCPL1.10 and HCPL1.2 compared with the sample without zeolite (HCPL0). The difference between the two hybrids is a slight increase of the adsorption capacity with the increase of clinoptilolite content.

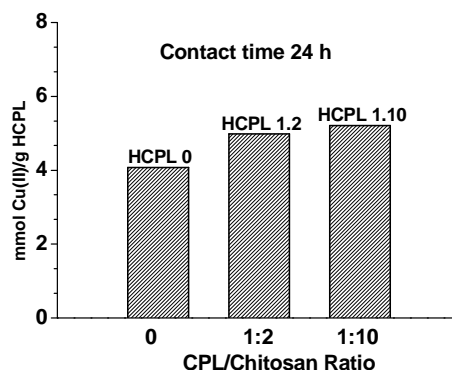


Figure 3 Adsorption capacity of the hybrids HCPL for Cu(II) as a function of the ratio between clinoptilolite (CPL) and chitosan

The optical microscope images of the hybrid HCPL 1:10 after the adsorption of Cu(II) and after the desorption of Cu(II) ions with HCl 0.1 M are presented in Figure 4 left and right, respectively.



Figure 4 The hybrid microspheres (HCPL1.10) after the adsorption of Cu(II) (left) and after metal desorption (right); microparticle size is around 800  $\mu$ m, by ESEM

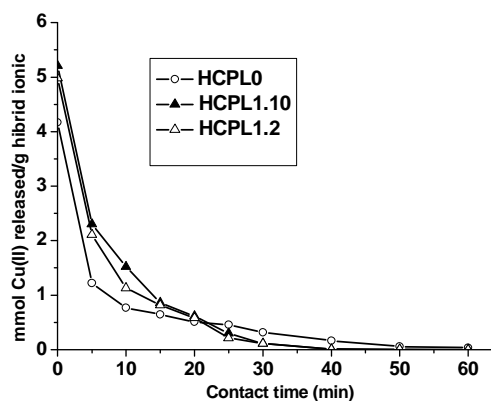


Figure 5 The desorption of Cu(II) from the hybrids with HCl 0.1 M as a function of contact time

Another important characteristic of chelating resins is the rate of desorption of the metal adsorbed. Figure 5 shows that both hybrids have a faster desorption of Cu(II), approximately 30 min. compared with cross-linked chitosan microspheres (HCPL0), when the desorption was ready in 60 min.

### CONCLUSIONS

By the results presented here we showed that the ionic organic/inorganic hybrids prepared from chitosan and clinoptilolite from Macicas-Romania, cross-linked with ECH, have promising adsorption capacity for Cu(II) ions, which were higher compared with cross-linked chitosan.

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