

# CHITOSAN-MODIFIED NATURAL CLINOPTILOLITE STUDIED BY $^{13}\text{C}$ NMR

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## 1. Introduction

Adsorption is one of the most used methods for removal of pollutants from waste water which requires large amounts of efficient and relatively cheap adsorbents. This can be achieved, e.g., using waste materials or materials available from natural resources. In the last decade there is increasing interest in combined adsorbents based on natural zeolite and biopolymers. Both materials are cheap and generally known for good adsorption properties. Their combination can increase adsorption capacity of the final product as well as to improve its physical properties [1,2].

This paper concerns  $^{13}\text{C}$  NMR study of adsorbent based on natural clinoptilolite whose large deposits are located in Nižný Hrabovec, East Slovakia and chitosan which is polysaccharide prepared by the deacetylation of chitin usually obtained from waste biomass. Chitosan is hydrophilic, biocompatible, biodegradable and bioadhesive polymer with antibacterial properties [3,4]. The chitosan-modified clinoptilolite used in this study was prepared by pelletization of clinoptilolite particles with the chitosan (in the weight ratio of 1:1). The aim of this study was to detect the changes in biopolymer chains conformation due to the interaction with surface of zeolite particle and/or cross-linking of biopolymer chains with or without another additive (TPP).

## 2. Experimental

The  $^{13}\text{C}$  NMR experiments were performed at room temperature on Varian 400 MHz NMR spectrometer using 4 mm rotor and a magic angle spinning (MAS) rate of 6 kHz.  $^{13}\text{C}$

NMR spectra were recorded under cross-polarization (CP) condition with  $90^\circ$  pulse of 2.7  $\mu$ s, the contact time of 1 ms, acquisition time of 10 ms, a high power proton decoupling of 93 kHz, a recycle delay of 5 s, and averaging over 1024 and 2600 scans for chitosan and chitosan-modified clinoptilolite. The preparation of samples of chitosan-modified clinoptilolite consists in the protonation of chitosan in acetic acid solution which was then mixed with clinoptilolite powder in the weight ratio 1:1. The pellets of adsorbent were obtained using tripolyphosphate as cross-linking agent. The NMR experiments were performed on dehydrated sample and sample hydrated for 3 hours in exsiccator with water.

### 3. Results and Discussion

Chitosan is a copolymer of glucosamine (Fig. 1a)) and N-acetyl glucosamine (Fig. 1b)) linked by  $\beta$  1–4 glucosidic bonds, chitosan is obtained by N-deacetylation of chitin [4].

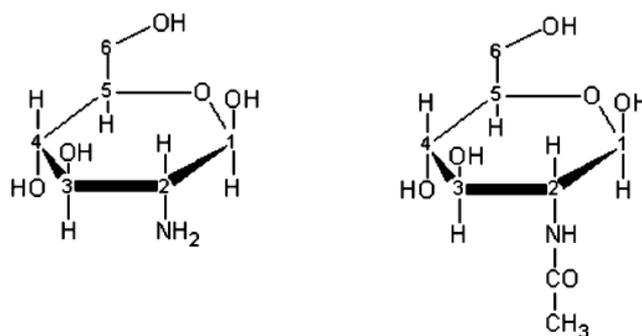


Fig.1: Chitosan monomers – a) glucosamine and b) N-acetyl glucosamine [5].

The structure of chitosan then consists of eight non-equivalent carbons (denoted in Fig. 1 with 1, 2, 3, 4, 5, 6, carbon in carbonyl group C=O and carbon in methyl group CH<sub>3</sub>) which give seven lines in <sup>13</sup>C NMR spectra, due to the fact that the lines of carbons 3 and 5 overlap (Fig. 2a). The assignments of the lines observed in the spectra based on the results reported in [6] are listed in Table 1. From the presence of the lines assigned to carbonyl and methyl carbons we can infer that chitosan contains acetylated monomers. Interesting feature of the spectra recorded for chitosan-modified clinoptilolite is that the lines assigned to methyl and carbonyl carbons are split into two and three lines, respectively (Fig. 2b,c, Table 1). The protonation of chitosan in the process of preparation of chitosan-modified clinoptilolite results in polycationic polymer with -NH<sub>3</sub><sup>+</sup> and -NH<sub>2</sub><sup>+</sup> sites. The chitosan chains can be then via these sites immobilized on the negatively charged zeolite surface and cross-linked when tripolyphosphate (TPP) is added to the solution forming NH<sub>3</sub><sup>+</sup> – TPP – NH<sub>3</sub><sup>+</sup> (-NH<sub>2</sub><sup>+</sup>)

interchain bonds. Rejected calcium ions from zeolite structure preferentially precipitate with phosphate anions and they can form  $\text{Ca}^{2+} - \text{TPP} - \text{Z}^- - \text{NH}_3^+$  ( $-\text{NH}_2^+$ ) bonds. The cross-linking and immobilization of chitosan chains can change geometry in the environment of the carbon 2 and the carbons in methyl and carbonyl groups which can be detected as new lines appearing in  $^{13}\text{C}$  NMR spectra (Fig. 2b,c, Table 1).

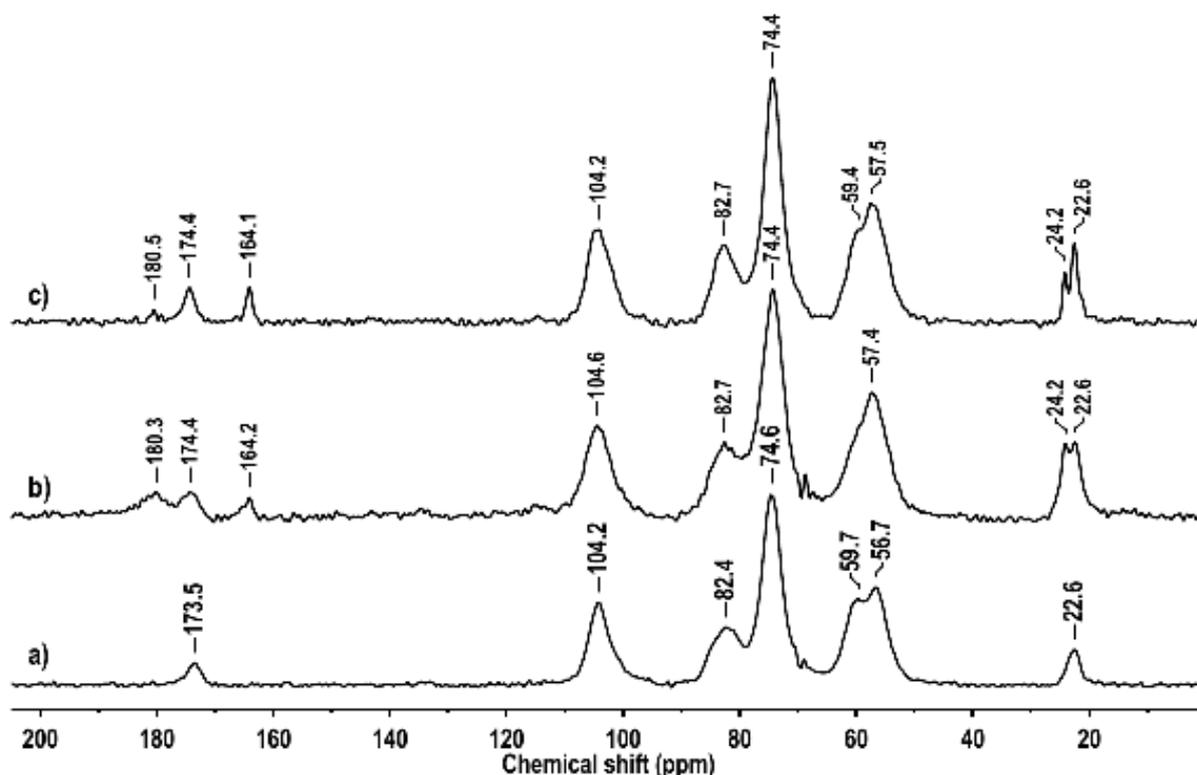


Fig.2:  $^{13}\text{C}$  CP MAS NMR spectra of a) chitosan, b) dehydrated chitosan-modified clinoptilolite and c) hydrated chitosan-modified clinoptilolite.

Tab. 1. Assignment of the lines observed in  $^{13}\text{C}$  CP MAS NMR spectra of a) chitosan and b) dehydrated chitosan-modified clinoptilolite and c) hydrated chitosan-modified clinoptilolite.

	Carbon						
	CH <sub>3</sub>	1	2	3+5	4	6	C=O
Line in Fig. 2a) (ppm)	22.6	104.2	56.7	74.6	82.4	59.7	173.5
Line in Fig. 2b) (ppm)	22.6 24.2	104.6	57.4	74.4	82.7	57.4	164.2 174.4 180.3
Line in Fig. 2c) (ppm)	22.6 24.2	104.2	57.5	74.4	82.7	59.4	164.1 174.4 180.5

#### 4. Conclusions

$^{13}\text{C}$  NMR spectra recorded for chitosan and adsorbent based on chitosan-modified natural clinoptilolite indicate that the preparation method provides adsorbent with chitosan chains immobilized on the zeolite surface and cross-linked via interchain bonds. The  $\text{NH}_3^+$  sites which do not participate in these bonds can serve as potential sites for adsorption of anionic species of water treated, but this possibility will require further study.

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