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XAFS DETERMINATION OF LOCAL ATOMIC ARRANGEMENT OF IRON IN Fe-CHITOSAN COMPLEXES

M.T. Klepka*, K. Lawniczak-Jablonska, and I.N. Demchenko

Institute of Physics, Polish Academy of Sciences, Al. Lotnikow 32/46, PL-02668 Warsaw, Poland

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**) e-mail: mklepka@ifpan.edu.pl*

The widespread study of metallo-organic chelating compounds is inspired by perspectives of biomedical, ecological and industrial applications. One type of metallo-organic materials are transition metal - chitosan complexes [1]. Presented studies were focused on iron-chitosan complexes. Most new materials used in biomedicine is based on natural materials, mainly polymers, because of their biocompatibility, bioactivity and easy biodegradation. One of them is chitosan, N-deacetylated product of chitin which is obtained in large quantities from crustacean shells (waste products of seafood processing industries). Both materials are significant natural polymers. Chitosans exhibit attractive for nowadays technology physical and mechanical properties. From the application point of view a very important aspect is their ability to chelate metal ions, including heavy and toxic ones [1]. Chitosans have better ability to chelate transition metal ions than other polymers. This skill is correlated with free amino ($-\text{NH}_2$) groups [2] (Fig. 1) or other as *e.g.* carboxyl ($-\text{COOH}$) in case of carboxylmethyl chitosan [3] (Fig. 2).

Chitosan, since its discovery in 1859, was widely studied and found adaptation in many applications *e.g.* in water treatment, food processing or as a dietary supplement. Nowadays, the iron containing biopolymers have been examined as possible drug carriers and controlled release beads for various models of drugs. To achieve this goal a lot of attempts were undertaken to increase the sorbent functionality of the chitosan. The prospective method for this seems to be the crosslinking of polymer chains with metal ions (Ch-Fe-CL) or the insertion of carboxylic functional group in chitosan (N-CM-Ch-Fe).

In spite of wide interest of chitosan with 3d metals there is a lack of information about metal coordination, especially in case of Fe-chitosan complexes. Knowing the usefulness of XAFS (EXAFS and XANES) for studies of non-crystalline materials, we have applied this technique for investigation of local atomic order around Fe atoms in different chitosan complexes. Measurements of Fe K-edges were performed in HASYLAB at station A1 in fluorescence mode of detection at liquid nitrogen temperature.

At the beginning, Fe valence was investigated and was qualitatively estimated using XANES. Set of reference iron oxides were measured and energy position of first derivative was compared with Ch-Fe-CL and N-CM-Ch-Fe.

In both chitosans dominant part of iron atoms exists as Fe^{3+} ions (Fig. 3).

Investigation of the first coordination sphere in Ch-Fe-CL using EXAFS indicated that two Fe positions are equally possible, consist of two subshells and correspond to (i) three oxygen and two nitrogen atoms; (ii) two oxygen and three nitrogen atoms. Furthermore, one Fe atom at distance of around 3 Å and at least three more at distance of around 3.5 Å were identified in the second coordination sphere. Third coordination sphere consists of six oxygen or nitrogen atoms. Knowing that the amine group should come from the single chitosan monomer, at least two or three monomers (or even polymers) should be bonded to each Fe atom and each of this polymer has in turn built-in another Fe atom.

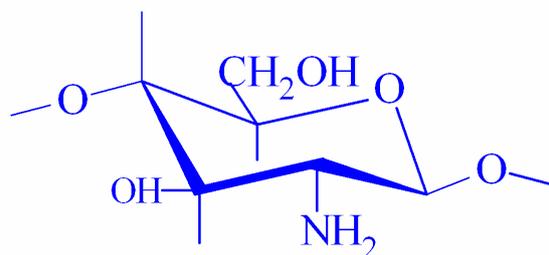


Figure 1. Monomer of chitosan structure.

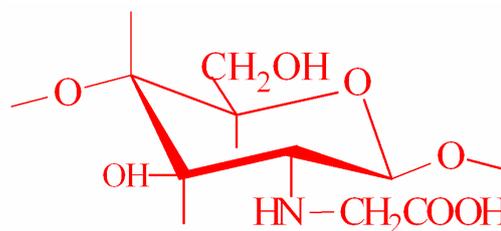


Figure 2. Monomer of N-carboxylmethyl chitosan structure.

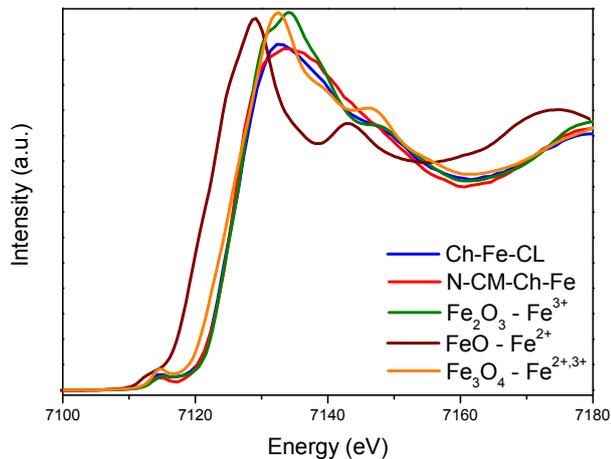


Figure 3. Experimental XANES spectra of Fe-chitosans and reference oxides.

In the case of N-CM-Ch-Fe only one Fe coordination was identified with two subshells consist of three oxygen and two nitrogen atoms. Other Fe atoms were identified neither in first nor in second coordination sphere, but third coordination sphere indicated the presence of Fe atoms. In the second coordination sphere three carbon and two oxygen atoms were identified. This provides the evidence that carboxyl group is an active one and Fe atoms showed a high ability to be chelated by polymers with this group. The detected two nitrogen atoms came from two monomers (or separated polymers), only 20% of monomers contain the carboxyl group, and the additional monomer (at least one) should have $-\text{COOH}$ group.

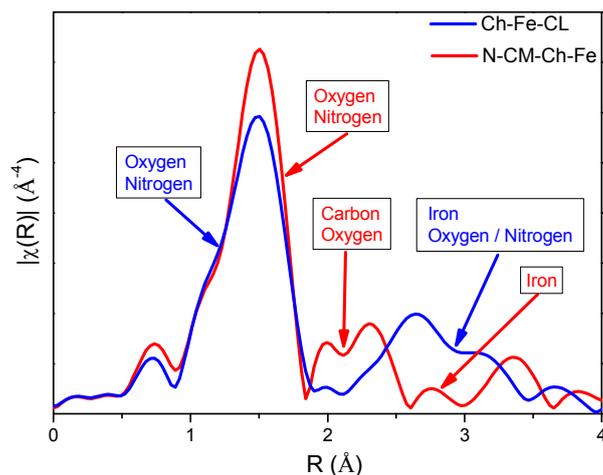


Figure 4. Comparison of Fourier transformed experimental EXAFS spectra for Ch-Fe-CL (blue line) and N-CM-Ch-Fe (red line).

A similarity of first coordination sphere and the differences between further coordination spheres for both chitosans are clearly visible in R space (Fig. 4).

The XANES analysis confirmed that in the considered Fe-chitosans the dominant part of the iron atoms exists as Fe^{3+} ions, which share three electrons in covalence bonding with at least two polymers or monomers. The EXAFS analysis indicated that Fe in both chitosans is penta-coordinated and local atomic structure up to third coordinataion sphere was determined. Obtained results are in agreement with recent magnetic and Mössbauer studies on these chitosans [4].

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