**XAS investigation of Fe ions in chitosan complexes**


Institute of Physics, Polish Academy of Sciences, Al. Lotnikow 32/46, 02 668 Warsaw, Poland

NIQFAR CCS, Universidade do Vale do Itajaí, CEP 88302-202, Itajaí, SC, Brasil

Chitin is obtained in large quantities from crustacean shells (waste products of seafood processing industries). Chitosan is N-deacetylated product of chitin. Both materials are important natural polymers. They easily biodegraded, are biocompatible and bioactive and possess attractive physical and mechanical properties. From the application point of view a very important aspect is their ability to bind metal ions, including heavy and toxic metals [1]. Consequently, chitosan and its many derivatives have a variety of current and potential applications e.g. in biomedical products, cosmetics, food processing and removal of metallic impurities in wastewaters. One of the prospective types of materials for biomedical application are transition metal – chitosan complexes [2]. Recently, the iron contains biopolymers have been examined as possible useful drug carriers and controlled release beads for various model drugs [3]. The different methods are used to increase the sorbent functionality of chitosan. The crosslinking of polymer chains after complexation with metals ions seems to be a prospective method and is frequently used. Moreover, at the low temperatures the iron crosslinked chitosan (CH-Fe-CL) exhibits magnetic ordering [4]. From the magnetic studies it was suggested that Fe-chitosan are composed of randomly dispersed polymer chains and can be classified as a topologically disordered material in which the distribution of Fe-Fe bond orientations is random. It has already been found that Fe ions can either be penta- or hexa-coordinted and that there are two different Fe sites and more than one polymer chain is involved in formation of these complexes [4]. In spite of wide interest in this class of materials, there is not much reported about x-ray studies of atomic structures of the crosslinked chitosans and many basic questions concerning atomic structure wait for answer.

The X-ray absorption spectroscopy is a very suitable tool for examination of the local atomic order around the Fe ions and we report the preliminary results from measurements of Fe K-edges in two different Fe-chitosan complexes. The measurements were performed at the A1 station HasyLab, Hamburg in fluorescence mode at liquid nitrogen temperature.

Two iron chitosan samples were investigated: (1) the Fe crosslinked chitosan CH-Fe-CL with the iron content of 118 mg/g and (2) N-carboxymethylchitosan complexes with Fe ions (N-CMC-Fe) at the concentration of 7 mg/g. The quantity of iron adsorbed in the samples was and determined by colorimetric methods using 1.10-phenantroline and Shimadzu UV 1601 spectrophotometer.

The Fe XANES for investigated samples and reference Fe, FeO and Fe$_2$O$_3$ samples are presented in Fig. 1. The ionic state of Fe is well defined for reference sample (neutral, +2 and +3, respectively). From the comparison with references one can conclude that the Fe ionic state in investigated samples is close to +3 but slightly differ from pure ionic bond existing in Fe oxide. This support suggestion resulting from magnetic investigation [4] where the reduction of the effective Fe magnetic moment was observed, that the covalence effects are important in this class of materials. Moreover, the observed shift of Fe edge confirmed, that Fe atoms do not segregate in polymer matrix forming metallic clusters. The shape of Fe XANES and radial distribution of atoms around Fe (Fig. 2) is different for two investigated samples therefore the local atomic order in the samples is different. To get more information about atomic neighbours of Fe in these materials the detailed EXAFS analysis with consideration of several models is progressing.
Figure 1: Fe XANES for investigated samples and reference Fe, FeO and Fe$_2$O$_3$ samples

Figure 2: Radial atoms distribution function around Fe

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References