Magnetic, redox and structural properties of Mn-O-Ca cluster, synthesized by the green microalga *Chlorella sorokiniana*

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Metabolism of metals in microalgae, as well as their adaptation to metal excess, are of significant environmental importance. We have found previously that the green microalga *Chlorella sorokiniana* accumulates environmental Mn excess in the form of a multivalent Mn-O-Ca cluster with structure that is very similar of oxygen-evolving complex (OEC) in photosystem II[1]. The application of microalgae in the 'green' synthesis of catalytic metal clusters is very important, since the use of toxic chemicals for traditional synthesis could be avoided. The aim of this study was to investigate the magnetic, redox and structural properties of this cluster. The magnetic properties of the cluster, were tested using Low-T-EPR spectroscopy and SQUID magnetometry. Based on the analysis of the EPR spectra, it was concluded that the spin of Mn in the cluster is >1/2. In addition, the spin of Mn is not an integer since parallel mode EPR did not deliver any detectable spectrum. The paramagnetic nature of the Mn-O-Ca cluster was confirmed by the SQUID instrument. Effective magnetic moment calculated per ion Mn was ~5 BM (Mn ratio in biomass was 12,1%). For the investigation of redox and structural properties, an extract of cluster from microalga was used. Cluster extraction involved the application of a series of solvents - phenol in Tris-Cl buffer, chloroform, methanol, 0,17% sodium hypochlorite[2]. Cyclic and differential voltagrams were recorded in the range from -1,5 to 2 mV[3]. The analysis revealed the presence of different oxidation states of Mn (+2, +3, +4). The peak potentials resembled the potentials in OEC model compounds[2].The redox similarities between the Mn-O-Ca cluster in microalgae and OEC imply that cluster may be have a similar catalytic activity. More detailed analysis of activity and structure of Mn-O-Ca cluster is warranted.

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References

1. S. Vojvodić, et al. Mechanisms of detoxification of high copper concentrations by the microalga *Chlorella sorokiniana*. Biochemical Journal 2020; 477:3729-41.
2. M. Villalobos, B. Toner, J. Bargar, G. Sposito. Characterization of the manganese oxide produced by *Pseudomonas putida* strain MnB1. Pergamon 2003; 67:2649-62.
3. C. Zhang, C. Chen, H. Dong, J. Ren Shen, H. Dau, J. Zhao. A synthetic Mn4Ca-cluster mimicking the oxygen-evolving center of photosynthesis. Inorganic Chemistry 2015; 348: 691-3.