



Interaction of humic acids with heavy metals - a theoretical study

Elizaveta S. Konkova (1,2), Oleg N. Shishilov (1), Alexandra S. Konkova (2), Sergey A. Gromov (2,3)

(1) Russian Technological University – MIREA, Institute of Fine Chemical Technologies, Vernadskogo avenue 86, Moscow, 119571, Russia (e-mail: e.konkova.igce@gmail.com), (2) Yu.A. Izrael Institute of Global Climate and Ecology, Moscow, Russia, (3) Institute of Geography, Russian Academy of Sciences, Moscow, Russia

A complexation with humic acids is one of highly likely pathways for binding of heavy metals (HM) in the natural environment that can prevent their further spread over the surroundings. HM can be accumulated and stored in the form of complexes with humic substances (HS) for a long time. Sulfur containing groups of HS are active sites for complexing with HM list. Sulfur content is larger in organic surface layers of wetland soils compared to, for example, neighboring well-aerated soils due to enrichment of marsh soil organic matter by S [1]. Understanding general features of these processes will help a lot with estimation of HM balance and elaboration of their geological cycles. Main purpose of our study was to reveal possible binding sites for HM in humic acid molecules and evaluate a storage capacity of HM by humic substances. Because real humic acids are very complicated polymeric compounds with irregular structure and variable composition we decided to start with theoretical DFT study of HM complexes with model humic acid.

Four heavy metals were chosen for the study: mercury, cadmium, copper and lead. Mercury and cadmium are among the most toxic metals while while copper and lead were chosen because of the existence of significant local emission sources of them in Russia. Two most suitable models of humic molecule structure were modified at the preliminary stage of investigation basing on literature information about functional groups contents, namely, the Stevenson's and Kleinhempel's humic models supplemented with additional S-containing groups (SH and SO₃) [2,3,4]. All calculations were performed in the frame of scalar-relativistic approximation of DFT method using the Priroda program [5]. Applying PBE exchange-correlation functional and basic set SBK it was shown that SH-groups are most likely binding sites for Hg, Cd and Pb as it could be expected. In case of Cu the amine groups are very competitive and preferable in some cases as well as O-containing chelating groups, e.g. carboxylates. Further we are planning to check and clarify these results using humic acid samples from several regions of Russia as a next step of the project.

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