

## **Influence of Oxidation on the Metal-Ion Complexation of NOM with Respect to Remediation**

Vercammen, K., Schmitt, D. and Frimmel, F.H.

*Engler-Bunte Institute, Water Chemistry, University of Karlsruhe, Germany*

Natural organic matter (NOM) of a brown water lake was oxidized with UV irradiation to elucidate the influence of oxidation on the metal ion complexation by NOM. UV-Vis fluorescence spectroscopy, as well as size-exclusion chromatography with online detection of UV absorption, fluorescence and metal concentration (ICP-MS) were used to investigate the structural changes caused by oxidation. After oxidation, the fluorescence intensity of NOM increased considerably despite a decrease in the UV absorption. The SEC experiment showed a shift towards smaller molecular sizes after oxidation and a decrease of the NOM complexation in the systems with oxidized NOM. For Pb no such effect could be determined. Experiments performed to study the dissociation kinetics of metal ion-NOM complexes revealed a slower dissociation of Al and Pb complexes with original NOM compared to oxidized NOM. The dissociation rate constants determined from these experiments were used to predict the migration of metal ion-NOM complexes in column experiments. For the divalent metals Pb and Zn, the experimental and modeling results are in good agreement. However, the kinetic transport model underestimated the breakthrough of Al in the presence of oxidized NOM and non-oxidized NOM, respectively.

The stability of the complexes with non-oxidized NOM decreased in the order Al > Zn. After UV-oxidation of NOM, its complexation ability towards metal ions also decreased.

Consequences for the application of NOM in underground barrier systems with respect to metal transport will be discussed. Furthermore, an investigation strategy leading to bench scale experiments to polluted area remediation will be presented.

## **Mediation effects of humic substances in polluted environments: implications for development of remediation technologies**

Perminova, I.V.

*Department of Chemistry, Lomonosov Moscow State University, Moscow, Russia*

Humic substances are multifunctional natural compounds that consist of aromatic backbone highly substituted with functional groups (carboxyl, hydroxyl, carbonyl, and others) and of linked to it polysaccharidic and polypeptidic fragments. Due to such a wide variety of functions, humic compounds can bind both heavy metals and organic ecotoxicants, which affects mobility and bioavailability of the ecotoxicants released into soil and aquatic environments. Complexes of metals with low molecular weight HS – fulvic acids – are highly soluble and mobile, whereas the complexes with humic acids are much less soluble and are easily immobilized in the soil layer (Weber, 1988). The metals bound into humic compounds become non-toxic that causes a net reduction in toxicity in polluted environments in the presence of HS (McCarthy, 1989). In its turn, the transition metal complexes of HS

mediate reductive dehalogenation of chlorinated hydrocarbons (O'Loughlin et al., 2000). The redox-mediating properties of HS are shown to play also an important role in oxidation of organic ecotoxicants under anaerobic conditions where they serve as an electron acceptor (Bradley et al., 1998). The above properties demonstrate a great potential of HS use in the remediation technologies. A spectrum of the mediating effects of HS can be even enhanced if the directed modification is used for obtaining humic derivatives with the wanted properties. So, sulfonation can be used to obtain much more soluble complexes of HS with transition metals, hydroxylation and amination can be used to increase chelating properties of HS, carbonylation – to enhance redox mediating properties, hydrolysis of HS can contribute in hydrophobization of HS and, hence, in increase of their affinity for organic ecotoxicants.

1. Bradley, P.M., Chapelle, F.H., Lovley, D. 1998. *Appl. Environ. Microbiol.* 64, 3102-3105.
2. McCarthy, J.F. 1989. In: *Advances in Chemistry Series No.219. Aquatic Humic Substances: Influence on Fate and Treatment of Pollutants*, eds. I.H. Suffet and P. MacCarthy, American Chemical Society, 263–277.
3. O'Loughlin, E.J., and D.R. Burris. 2000. In Means, J.L. and R.E. Hinchee (Eds.), *Wetlands and Remediation*. Battelle Press, Columbus, OH, 1-8.
4. Weber, J.H. 1988. In: Frimmel, F.H., and Christman, R.F.(Eds.), *Humic Substances and Their Role in the Environment*, Wiley, New York. 165.

### **Neosynthetic zeolites in soil remediation: preliminary study of trace metals sequestration**

Terzano, R.<sup>a</sup>, Spagnuolo, M.<sup>a</sup>, Medici, L.<sup>b</sup>, Bavere, P.<sup>c</sup> and Ruggiero, P.<sup>a</sup>

<sup>a</sup> *Department of Agricultural and Environmental Biology and Chemistry, University of Bari, Italy*

<sup>b</sup> *Institute of Metodologies for Environmental Analyses, Clays Research Section, C.N.R. Tito Scalo (PZ), Italy*

<sup>c</sup> *Department of Crop and Soil Science, Bradfield Hall, Cornell University, Italy*

The use of zeolites to remediate contaminated soils and sediments is a very interesting and widely applied technique to stabilize trace metals *in situ*. To date, due to their important cation exchange capacity, zeolites have being employed to reduce the mobility of trace metals in soils and, consequently, their bioavailability and the migration to other environmental compartments. The aim of this study is to assess the potential capability of zeolites to entrap selected heavy metals within their characteristic spatial structures during their synthesis at condition very close to the ambient. In particular, Zeolite X (zeolite from the series of Faujasite) has been synthesized starting from fly ash obtained from a thermoelectric power station at about pH 13 in four days at 60°C and one month at room temperature.

The synthesis of Zeolite X has been also obtained starting from silica and aluminum salts at pH 13 in solution containing 2500 ppm of Cu(II), Ni(II), Co(II), Cd(II), Pb(II) and Zn(II) in separate experiments. XRD and SEM-EDS analyses confirmed the crystallization of zeolite in the presence of each trace element even though after different incubation times.