1c/P007 - Kinetics of chromium (VI) reduction by iron (II) – speciation effects

Buerge I.J. and S.J. Hug, Swiss Federal Institute for Environmental Science and Technology (EAWAG), Duebendorf, Switzerland. Cr(VI) is a priority pollutant of some soils and natural waters in industrial areas. Reduction of Cr(VI) by Fe(II) to essentially non-toxic Cr(III) is a frequently discussed and partly employed remediation strategy. The kinetics and reaction pathways are strongly influenced by pH, organic ligands, and mineral surfaces and can basically be described by -d[Cr(VI)]/dt=Sk[Fe(II)L][Cr(VI)], where L stands for OH-, organic ligands, and surface groups. Fe(III)-stabilising ligands such as OH-, bi- and multidentate carboxylates, and phenolates accelerate the reaction, whereas Fe(II)-stabilising ligands like phenanthroline essentially stop the reaction. The rate coefficients increase with decreasing reduction potentials of FeL. The relationship of log k vs EH (Fe(III)L) is quite linear and can partly be described by Marcus theory. Solid phases accelerate Cr(VI) reduction by Fe(II) in the order a-FeOOH ‰ g-FeOOH >> montmorillonite > kaolinite ‰ SiO2 >> Al2O3. The reaction is mainly driven by the high reactivity of adsorbed Fe(II). Whereas adsorbed Cr(VI) is reducible by dissolved Fe(II), the sparingly soluble BaCrO4 is largely protected from reduction. Understanding the kinetics of formation and the properties of the Cr(III) products is important with respect to their mobility and possible reoxidation by Mn(III/IV) minerals. In initially homogeneous solution finely dispersed colloids (Cr(III)/Fe(III) (hydr)oxides) are formed. In the presence of mineral particles, solid phases grow preferentially on these pre-existing surfaces. With organic ligands present, soluble Cr(III) complexes are formed, which are more mobile and possibly more amenable to unwanted reoxidation to Cr(VI).

1c/P008 - Degradable fluorescent whitening agents? Scientific contributions to overcome a prejudice

Richner P., J. Kaschig, J.B. Kramer, Ciba Specialty Chemicals Inc. Fluorescent whitening agents (FWAs) in detergents are regarded as non-degradable or at least not readily degradable because the customary biodegradability tests fail to show a clear-cut decrease in concentration of DOC (dissolved organic carbon). Research permitting a definitive assessment of their fate in the environment from the standpoint of environmental sciences was therefore desirable. While the most important FWAs in quantitative terms are the diaminostilbene (DAS) derivatives, the DSBP FWAs come into their own to meet special technical requirements. These FWAs belong to a different class, the 4,4'-distyrylbiphenyl derivatives, which has been the focus of in-depth studies. Part of the FWA finds its way into surface water. On exposure to sunlight, FWAs in an aquatic environment are converted within minutes to photoisomers. The marked ability of the mixture of DSBP isomers to absorb light results in exceptionally efficient direct photodegradation of this class of FWA. The light-induced reactions proceed at a fast enough rate to cause significant degradation of DSBP in lakes and rivers. Field studies in Switzerland on lake Greifen and on the river Glatt substantiate the scale and rate of these reactions. Photodegradation finally yields in two products namely benzaldehyde-2-sulpho acid salt and diphenyl-4,4'-dialdehyde. Both photodegradation products are shown to be readily biodegradable in OECD test 301F. DSBP-type fluorescent whitening agents thus break down by a mechanism, which combines abiotic and biological degradability and end up as biodegradation products. They are the only FWAs to date that are eliminated on the criterion of a decrease in DOC. These results (together with the environmental risk assessment and Life Cycle Assessment) shows that FWAs based on DSBP are ingredients, which contribute to further improvements of the environmental impact of detergents.

1c/P009 - Development of quantitative relationships between structure, reactivity and detoxifying ability of humic substances to organic xenobiotics

Perminova I.V., A.V. Kudryavtsev, N.A. Kulikova, N.Yu. Yashchenko, V.S. Petrosyan, Dept. of Chemistry, Lomonosov Moscow State University, Moscow, Russia. Humic substances impact greatly chemical and toxicological behaviour of organic xenobiotics released into soil and water ecosystems. To predict the resulting changes in speciation and toxicity of ecotoxicants in the different humicscontaining environments, quantitative relationships between structure, reactivity and detoxifying ability of humic substances are to be established. In this work QSAR approach was applied to creation of the corresponding relationships. A set of humic substances used included the samples isolated from coal, peat, soil and water. As organic xenobiotics were used PAHs (anthracene, fluoranthene and pyrene) and a sym-triasinic herbicide - atrazine. The structure of humic substances was characterised by the fragmental composition determined from the data of 13C NMR spectroscopy. Reactivity to PAHs and atrazine was estimated by determination of the constants of corresponding interactions. Detoxifying ability of humics in relation to PAHs and atrazine was assessed with a use of toxicological experiments. Different methods of regression analysis (partial least square method, principal component analysis etc.) were applied to establish quantitative relationships between structure, reactivity and detoxifying ability of humics. The obtained models are described; their advantages and disadvantages are discussed.

1c/P010 - Reductive dehalogenation of polyhalogenated alkanes by surface bound Fe(II) in aquifer material

Elsner M., Th.B Hofstetter, S.B. Haderlein, R.P. Schwarzenbach. Swiss Federal Institute for Environmental Sciences (EAWAG) and Swiss Federal Institute of Technology Zurich (ETHZ), Dübendorf, Switzerland. Polyhalogenated alkanes (PHAs) are widespread groundwater contaminants. While they are persistent under toxic conditions, they can be degraded both in biotic as well as in abiotic reduction processes under anoxic conditions. In iron reducing aquifers certain PHAs are reduced in abiotic reactions, in which surface bound Fe(II) species play an important role. The objective of this work is to characterise the reactivity of these surface bound Fe(II) species in a natural aquifer matrix for different classes of organic pollutants. The experiments were conducted in aquifer columns containing sediment from a riverbank, which were operated under iron reducing conditions. In these systems various nitroaromatic compounds (NACs) were reduced at the same reaction rate, irrespective of their one-electron potentials. In competition experiments with two NACs at a time, however, the reaction of the compound with the lower potential was inhibited until the transformation of the second NAC had been completed. Earlier work had shown that the reactivity of these systems was due to a