

## Humic Substances and Their Silanol Derivatives in Remediation Technologies

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Good quality of soil and groundwater is one of the most important assets throughout the World. There are various methods for their remediation, among which one of the most promising is creation of the permeable reactive barriers (PRB). Recently, another alternative approach is emerged based on a use of engineered nanoparticles (ENPs) for groundwater remediation. Nano-zerovalent iron (nZVI) is one of the most promising nanomaterials. However, vague understanding of potential harm ENPs may cause to humans and biotic receptors hinders application of ENPs in remediation technologies. Here, we propose to use natural surfactants – humic substances (HS) which are ubiquitous throughout the environment, firstly, for in situ installation of PRBs, and, secondly, for designing innovative hybrid nanomaterials composed of highly reactive nZVI particles embedded within biocompatible matrices of HS.

To reach these goals, humic materials were, firstly, modified to enhance their surface active properties with respect to mineral matrices, secondly, the obtained humic derivatives were immobilized onto mineral support to obtain humic nanocoating for remediation technologies; thirdly, humic materials were used to embed nanoparticles of ZVI. To introduce new function in native humic materials, treatment with aminoorganosilane was used. Leonardite humic acid (CHS) and peat humic acid (PHA) were used for the experiments. 3-amino-propyltriethoxy-silane (APTES) was used for treatment of humics. The reaction was run at different APTES-to-HS ratios. Sorption performance was assessed silica gel. The amount of sorbed silylated HS was up to 220 mg of HS per g of silica gel.

To prove the feasibility of silanol derivatives of HS as agents for remediation technologies for the installation PRB, studies were performed to evaluate their sorption capacity with respect to the azodye Direct Brown, used for dyeing fabrics in the textile industry. Sorption of azo dye on pure silica gel and on silace gel modified by silanol derivatives of HS were studied by technique of isotherms. To 50 mg of pure silica or modified silica gel was added 10 ml of azo dye in the range of 5-200 mg / l and stirred on a rotary mixer for 24 hours. As a result, it was shown that the modified silica absorb better than the original silica azo dye. So, for the original silica sorption maximum was 1.1 mg, while for silica modified by silanol derivatives of HS sorption maximum was from 2.5 to 5.9 mg of azo dye 1 g of silica gel, respectively .

The experiments on stabilization of nZVI were run using nZVI particles obtained by reduction of FeSO<sub>4</sub> with NaBH<sub>4</sub> under argon gas. After purification with ethanol and distilled water, nZVI in 5% ethanol was mixed with 1% solution of CHS in water. As result, nZVI suspension in HS was obtained which was stable over one day at the exposure to atmospheric air. According to the data of Moessbauer spectroscopy, the content of ZVI after 1 day exposure accounted for 20% of the initial iron content in the solution. This shows a good promise for developing humics-based technologies for stabilization of nZVI by HS.

Thus, we have proven the possibility of using HS and their silanol derivatives in different remediation technologies including sorption PRBs (on the example of azodyes). We have also shown that the efficiency of sorption system can be drastically improved through inserting reactive NPs such as nZVI into the PRB. It is assumed that humic film would fix and stabilize nZVI and thereby increasing the efficiency of the entire system.

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