

Synthesis of Alkoxysilylated Humic Derivatives with Different Modification Rate Capable of Self-Adhering to Mineral Surfaces

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1. INTRODUCTION

The effective method to purify ground water is installation of Permeable Reactive Barrier (PRB). A PRB is a subsurface wall of reactive permeable media emplaced across the flow path of a contaminant plume. The plume is allowed to migrate passively through the PRB and in the process contaminants are precipitated, sorbed, or degraded. A typical PRB is costly to install but economical to maintain. Much of the installation cost is related to the excavation of aquifer material that is then replaced with reactive porous media; furthermore, these systems are typically over-designed to address uncertainties in groundwater flow and to accommodate an anticipated loss of treatment efficiency with time. Humic-based materials show considerable promise as refractory and inexpensive reactive components for PRB. Due to a wide variety of functions, humic substances (HS) can bind both heavy metals and organic contaminants. The contaminants bound into humic complexes become non-toxic that causes a net reduction in toxicity of polluted environments. The humic-coatings immobilized on the surface of granular support could provide a very promising medium for sequestering contaminants dissolved in the ground water. However, the naturally occurring HS do not produce covalent bonding with granular aquifer support.

The goal of this work was to prepare the water-soluble derivatives of HS that have been specifically modified to adhere to the mineral matrices which would facilitate in-situ installation of humic barrier. A new approach was used for this purpose. It is aimed at modification of carboxyl groups available within HS with 3-amino-propyltrimethoxy-silane (APTS). To keep intact the intrinsic reactivity of HS with respect to metals, the derivatives with different modification rates of carboxyl groups were obtained. Their capability to adhere to the surface of silica gel was investigated.

2. MATERIALS AND METHODS

Leonardite humic acids – the main commercial source of humic acids - were used for all modifications. They were isolated from the commercial potassium humate (Powhumus, Humintech Ltd., Germany) and designated CHP. 3-amino-propyltrimethoxy-silane (APTS) was used for treatment of CHP. The choice of APTS was provided by the presence of reactive amino groups in its structure which can yield amide bonds upon reaction with carboxyl and carbonyl groups (1, 2).

A weight of HA (1 g) was stirred with dry dimethyl formamide (DMF) and the calculated amounts of silylation agent (APTS) were added to this mixture under continued stirring to yield the derivatives with 5, 10, 20, 50, 100 and 200% modification degree. The necessary amounts of APTS were calculated based on the content of carboxyl groups in the CHP, which accounted for 3.5 mmol/g. Given the molecular weight of APTS of 180 g/mol, to obtain the derivatives with different modification degree, 0.05, 0.1, 0.2, 0.5, 1.0, 2.0 g APTS per one gram of CHP were used. The reaction was carried out at 120°C for 20 hours. Then, DMF was evaporated and the derivative was dried in vacuum under heating at 40°C. The obtained derivatives were designated as CHP-APTS-X, where X – is a modification rate.

The sorption of modified HS on mineral support was studied using silica gel as example of mineral support. For this purpose, the solutions of obtained derivatives in water at concentration of 5 g/l were prepared and aliquots of 10 mL were added to 0.1 g of silica gel. A decrease in derivative concentration in solution was measured using UV-vis spectrophotometry. The carboxylic acidity was determined using calcium acetate method.

3. RESULTS AND DISCUSSION

The obtained derivatives were characterized using elemental analysis, titrimetric techniques, SEC, ^{13}C NMR and FTIR spectroscopy. FTIR spectra of the obtained derivatives are shown in Fig. 1. They were normalized to the intensity of $-\text{CH}_2-$ peaks (2920 cm^{-1}) to provide for better comparison. It can be seen that along with an increase in the modification degree, the intensity of COOH-peaks (1720 cm^{-1}) decreased, whereas the intensity of amide bonds (1690 cm^{-1}) increased. This shows that the developed approach allows to incorporate into the HA structure controllable amount of the alkoxy-silyl groups.

The content of COOH groups in the original and modified HS are presented in Fig. 2. The content of COOH groups is a particularly important parameter for APTS-modified humic materials as it provides a direct estimate for the amount of residual carboxyl groups

non-reacted with APTS. Hence, it can be used to calculate the modification degree as a ratio of the carboxyl-group reacted with APTS to the total amount of carboxyl groups.

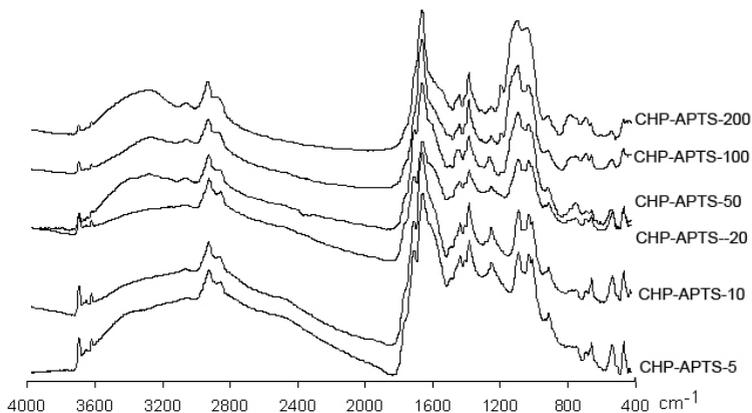


Figure 1. FTIR spectra of APTS modified CHP with different modification grade.

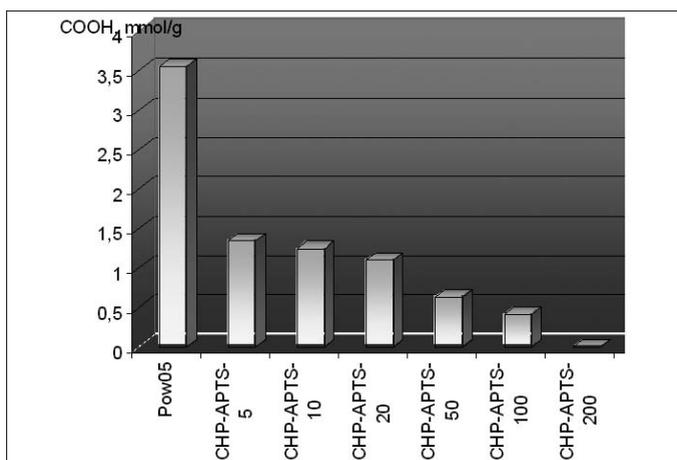


Figure 2. The concentration of COOH groups in original and modified HA.

The sorption of the obtained derivatives onto silica containing minerals was studied using batch experiments. It was shown that the sorption on silica gel depended on the modification rate of CHP-APTS. The amount of immobilized CHP (mg) on 1 g of SiO₂ is shown in Fig. 3. It can be seen that the sorption affinity of the derivatives increased drastically starting with the modification degree of 20% and reached its maximum value at the modification degree of 100%.

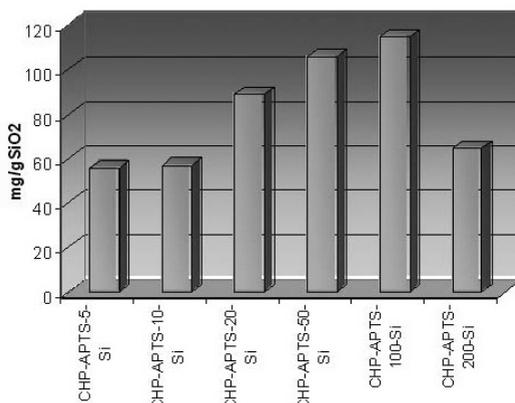


Figure 3. The amount of immobilized CHP (mg) on 1 g of SiO₂.

4. CONCLUSIONS

The dependence of adhering ability of the alkoxy-silyl-derivatives of HS on the modification degree of carboxyl-groups was demonstrated. The maximum sorption affinity was observed for the derivatives with 100% modification, whereas starting with 20% modification the remarkable increase in adhering ability was observed as compared to the parent HS. The conclusion was made that 20%-modification degree can be considered as an optimum modification rate which provides for a reasonable adhering ability and is much closer to the parent HS by the properties as compared to 100% modified HS.

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