# Synthesis of Alkoxysilylated Humic Derivatives Capable of Self-Adhering to Mineral Surfaces

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## 1. INTRODUCTION

One of the most effective methods for purifying of ground water is Permeable Reactive Barrier (PRB) installation. 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 in polluted environments.

The obtaining of soluble HS that have been specifically modified to adhere irreversibly to the surfaces of the mineral media will make possible to create PRB in situ.

A new approach was used for this purpose. It is aimed at modification of Humic acids with different functional organosilanes. As the result new trialkoxysilyl-humic derivatives were obtained.

## 2. MATERIALS AND METHODS

Leonardite humic acids, designated as CHP, were obtained by desalting of the commercial potassium humate Powhumus (Humintech Ltd., Germany) and used for modification with 3-amino-propyltrimesthoxy-silane (APTS). For the same modification were used peat HA, designated as PHA and river HA, obtained from Istra river, designated as AHF. The element and functional composition are presented in Table 1. Total acidity of humic derivatives was determined using barita technique as described elsewhere (1).

Table 1: Element and functional composition of starting humic acids.

| HA | C [%] | H [%] | N [%] | COOH [mmol/g] | OH [mmol/g] |
|---|---|---|---|---|---|
| CHP | 59.0 | 4.31 | 1.24 | 3.5 | 2.1 |
| PHA | 53.2 | 4.77 | 3.4 | 4.2 | 1.5 |
| AHF | 50.8 | 4.45 | 2.44 | 5.4 | 1.1 |

For silylation of humic acids was used 3-amino-propyltrimethoxy-silane (APTS). APTS was chosen because of its functional amino groups, which can react with carboxyl and carbonyl groups of humic acids (3, 4).

A weight of HA was mixed in dry DMFA. Silylation agent (APTS) was added to the obtained mixture. The reaction was undertaken at 120 °C for 20 hours. After reaction, DMFA was evaporated under high vacuum. The obtained derivative was dried in vacuum under heating at 40 °C. Obtained derivatives were designated as CHP-APTS, PHA-APTS and AHF-APTS.

The irreversible sorption of modified humic substances on mineral support was shown on the example of silica gel.

For this purpose, solutions of obtained derivatives 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 dHA derivatives concentration in solution was measured using UV-vis spectrophotometry (2).

## 3. RESULTS AND DISCUSSION

The obtained derivatives were characterized using elemental analysis, titrimetric techniques, SEC, $^{13}$C-NMR and FTIR spectroscopy.

FTIR specters of obtained derivatives are shown in Figure1 (a) - CHP-APTS, (b) - PHA-APTS, (c) - AHF-APTS.

Absorption bands of C=C groups (1610 cm$^{-1}$) in IR spectra indicate presence of aromatic moieties in HA. Band at 1710 cm$^{-1}$ is assigned to C=O bond of COOH and CO groups. Band at 1250 cm$^{-1}$ is assigned to C-O bond in phenol and COOH groups, and band at 1050-1150 cm$^{-1}$- to C-O in alcohol groups. The listed bands indicate presence of different oxygen-containing functional groups in parent HS material. Peak assignments made for FTIR spectra of modified humic materials (HA-APTS) are listed below: 1090-1020 cm$^{-1}$ – Si-O-C groups, 2940-2845 cm$^{-1}$ – (-$CH_2$)-groups, 1690 cm$^{-1}$–Shiff bases, 3360-3180 cm$^{-1}$ and 1400 cm$^{-1}$ – amide bond (2).

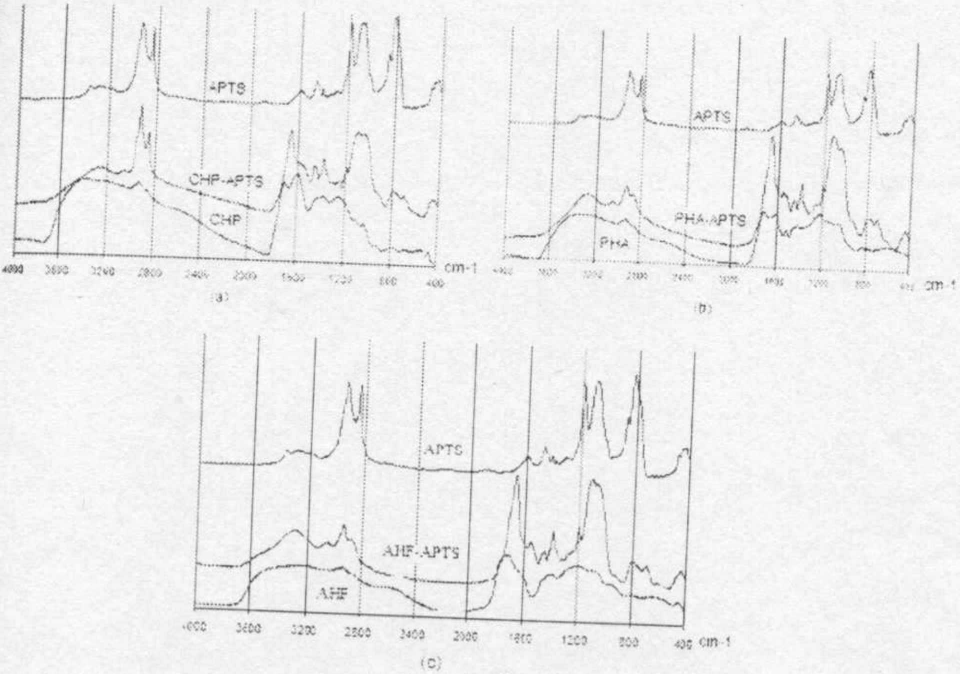


Figure 1: FTIR spectrums of new humic derivatives and parent materials. (a) – CHP-APTS, (b) – PHA-APTS.

So, amino groups of APTS react with both carboxyl and carbonyl groups of humic acids, forming amide bonds and Shiff bases.

The concentration of COOH groups in original and modified HA is presented in Figure 2. For studying of the sorption ability of the obtained substances on silica containing minerals, the experiment under dynamic conditions was brought up. Through two columns with silica gel, solutions of parent HA and modified derivatives were passed. The photos of these columns are presented on Figure 3. Parent HA could not sorb on silica gel, while modified HA fully sorbed on it.

The studies of sorption ability of the obtained derivatives in relation to silica gel shown, that amount of humic acids immobilized on 1 g $SiO_2$ was 100 mg. It was proved that the sorption of alcoxysilyl humic derivatives on silica gel is irreversible (2).

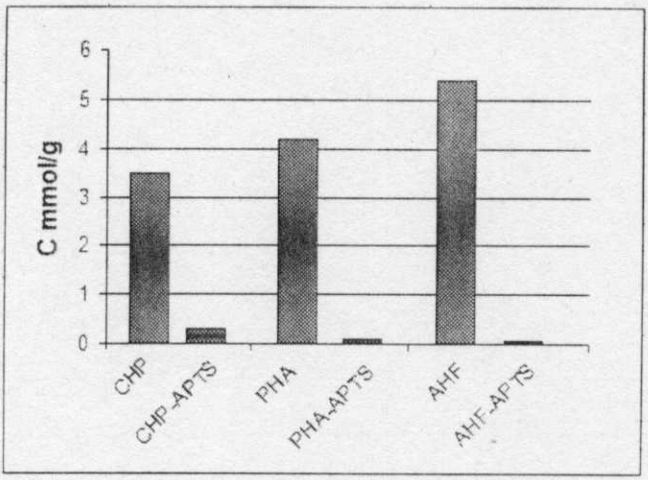
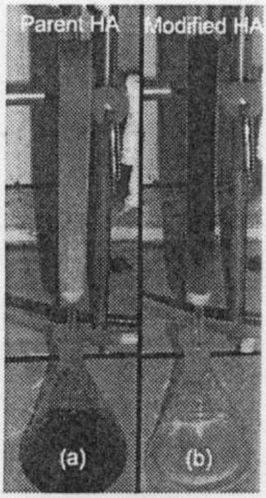


Figure 2: The concentration of COOH groups in original and modified HA (2).

Figure 3: Sorption of parent (a) and modified (b) HA on silica gel (below).



## 4. CONCLUSIONS

The method of modification of humic acids with 3-amino-propyltrimethoxy-silane was suggested. The irreversible sorption of humic derivatives on mineral support was proved. The suggested approach allows to obtain silica-humic sorbents, containing 100 mg of humic acids on 1 g of silica gel (2).

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## REFERENCES

(1) Swift, R. S.: Organic matter characterization in Methods of soil analysis. Part 3. Chemical methods, pp. 1036-1041 (1996).

(2) Perminova I.V. et al.: Humic derivatives, methods of preparation and use. Patent pending, PCT application № /RU2006/000102.

(3) Prado, A. G. S., Sales, J. A. A., Airoldi, C.: The increased thermal stability associated with humic acid anchored onto silica gel. Journal of therm. Anal. And Calorim. V. 70, 191-197 (2002).

(4) Koopal, L. K., Yang, Y., Minnaard., A. J.: Chemical immobilization of humic acid on silica. Coll.and Surf. V. 141, 385-395 (1998).