Directed Chemical Modification as a Promising Tool for Designing Humic Materials with Tailored Properties

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1. INTRODUCTION

Humification is the second largest process after photosynthesis. Humic materials are typically derived on an industrial scale from peat, sapropel, and coal. Leonardite is the most widely used raw material for production of commercial humic preparations followed by other low-rank coals, peat, and sapropel. Hence, the reserves of inexpensive humics-rich materials are immense; however, these reserves are not currently being tapped for remedial needs.

Two fundamental reasons can be formulated as to why humic substances (HS) are not widely used. First, few natural HS possess the specific reactive properties required for a use in chemical or remedial engineering. Second, humics by definition are polydisperse and heterogeneous, which translates into properties that vary between natural sources and between industrial suppliers. Hence, the structural heterogeneity needs to be reduced or controlled to the extent that reactive properties become predictable; this will facilitate the use of humic materials for practical purposes. From this prospective, chemical modification is proposed as a promising tool for acquiring humic materials with desired properties.

The goals of this study were threefold: first, humic materials were modified to enhance function or property inherent within natural humics (e.g., complexation ability, redox activity; second, humic materials were modified to acquire a novel, tailored property not inherent within natural humics; and, finally, humic materials were modified to change their physical form.

2. MATERIALS AND METHODS

Humic materials: The leonardite humic acid, designated as CHP, was isolated from commercial preparation Powhumus (Humintech Ltd., Germany). Peat HA were isolated from low-moor peat of the lake Sakhtysh (Ivanovo, Russia). Aquatic humic substances were isolated from River Istra using XAD-2 resins.

Modification techniques: Formaldehyde polycondensation with phenols and quinones was used to obtain phenol- and quinonoid-enriched humic materials. Resol-type polycondensation occurring in alkaline milieu was used for phenols, and novolac-type condensation – for quinones as described in (1). Alkoxysilylation of humic materials was carried out using treatment with 3-aminopropyltrimethoxysilane (APTS) in organic solvent (DMF) (2). The alkoxysilylated derivatives were water soluble and capable of immobilization onto hydroxyl-carrying mineral support (e.g., silica). Crosslinking of humic materials was undertaken using curing of phenol- and quinonoid-enriched humic copolymers obtained under resol and novolac conditions. Humic resols were cured by heating at 180 °C, humic novolacs were cured using linking agents - paraform and hexamethylenetetraamine. In addition, epoxy-cycles were introduced into humic backbone and open under heating to produce cross-linked structures.

3. RESULTS AND DISCUSSION

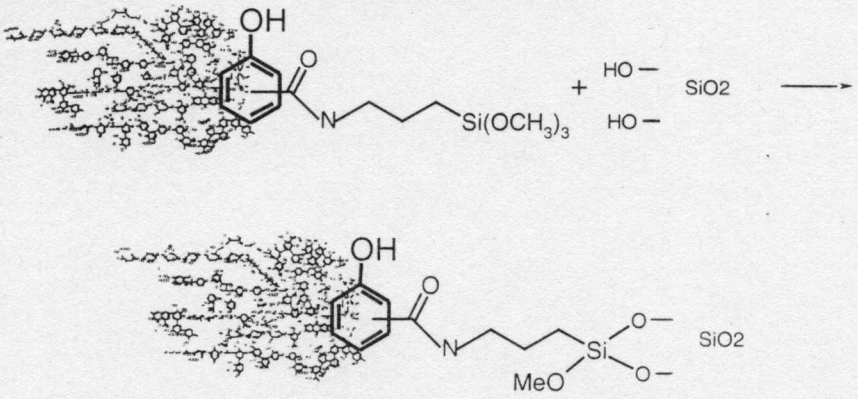
To achieve the goals stated, different modification approaches were undertaken, which are summarized in Figure 1. To introduce new function non-inherent in native humic materials, alkoxysilylation was used. Incorporation of alkoxysilyl-group into humic structure yields humic derivative capable of covalent binding with hydroxyl-carrying surfaces (e.g. silica gel). Of particular importance is, that these derivatives turned out to be water soluble that allows to immobilize them onto mineral surfaces from water solutions. This property can be used for creating reactive barriers for groundwater clean up (2). They can be also used as liquid-phase scavengers (3).

The second approach was based on phenolformaldehyde condensation and was used to enhance redox or complexing properties of humics, was used. This approach allows for incorporation of the desired phenolic- or quinonic fragment with the known redox or complexing properties into the humic backbone.

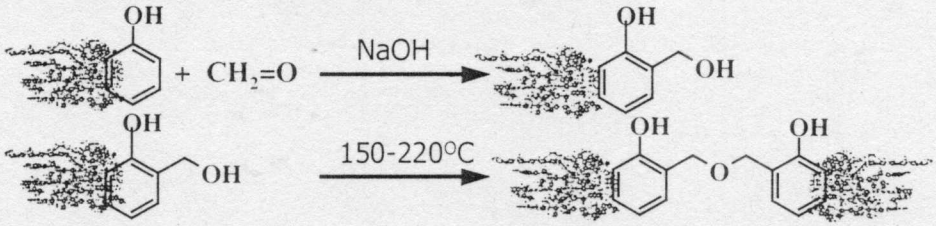
The obtained humic derivatives possess much higher reducing capacity, e.g., they are capable of reducing Np(V) to Np(IV) which is hardly possible with

naturally occurring humics (4). These derivatives can be used for remediation of actinides contaminated sites.

Immobilization of alkoxysilylated derivatives



Phenolformaldehyde polycondensation (RESOL-TYPE)



Crosslinking via introduction and opening of epoxic cycles

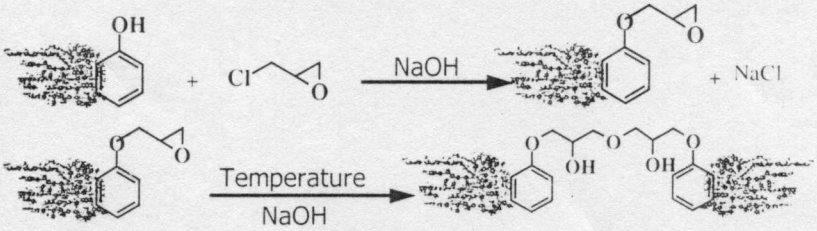


Figure 1: Main types of chemical modification used in this study to prepare humic derivatives with the tailored properties.

The third approach was based on cross-linking reactions aimed to transfer humics into solid form. Curing of phenol-formaldehyde humic copolymers as well as incorporation and subsequent opening of epoxy-cycles was undertaken.

Curing of phenolformaldehyde copolymers allowed to increase size – 25 % of initial polymer acquired molecular weight larger than 300 kD. Incorporation of epoxy-cycles with thermal opening allowed for almost quantitative transfer of initial materials into solid state.

4. CONCLUSIONS

Directed modification was shown to be a promising tool for producing humic materials with tailored properties. A use of widely practiced chemical processes for modification of humics (e.g., phenolformaldehyde condensation) allows an easy scale up of the developed lab techniques to pilot plant and industrial production. This opens broad opportunities for commercial application of HS.

ACKNOWLEDGEMENTS

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