

Sulphur Containing Derivatives of Humic Substances and Their Use for Remediation of Contaminated Environments

Māris Kļaviņš¹, Diāna Dūdare², Andris Zicmanis³, ¹⁻³*Faculty of Chemistry, University of Latvia*

Abstract – Derivatives of humic substances containing sulpho-, and thiol groups were synthesized and their properties were analyzed for their elemental composition; functional group content changes in spectral characteristics. The derivatives of humic substances showed significant differences in the number and in the ability to interact with the metal ions, which were reflected in their complexation properties towards metal ions. FTIR spectra gave evidence of the presence of metal ions, strongly bound and protected in inner sphere complexes. The obtained derivatives of humic substances can be used for remediation of environments contaminated with heavy metal ions.

Keywords – Derivatives of humic substances, synthesis, environment remediation, heavy metals

I. INTRODUCTION

Humic substances (HS) are high molecular weight refractory polycationites formed during decay of living organic matter and through biosynthesis of low molecular weight organic substances (metabolites or decay products of living organisms) [1]. Humic substances are usually viewed as refractory and inert, but they do have numerous functional groups which influence their behaviour in the environment. Humic substances do contain carboxyl groups, phenolic and carbohydrate hydroxyl groups, amino groups, quinonic groups and reactive positions in aromatic structures [2]. Presence of many functional groups in the structure of humic substances determines their ability to interact with metal ions by forming stable complexes and influencing metal ions speciation in the environment and mobility, behaviour and speciation forms in the environment [3]. Considering the complex forming properties of humic substances, they are suggested for use in remediation of environments contaminated with metals [4, 5]. Considering presence and high concentrations of many functional groups in the structure of humic substances their derivatization can be done, unless use of many derivatization reagents is of limited use, considering low solubility and presence of labile structures in their molecules. On the other hand, main complex forming groups in the structure of humic substances (-COOH, -OH and other) are relatively inert [6, 7]. Derivatization of humic substances is prospective for obtaining derivatives of humic substances for studies of their structures, as well as to obtain derivatives with modified properties and with prospective areas of use, considering that large-scale production of humic substances is being started. Several studies have been done to obtain derivatives of HS for their structural studies [6 – 8]. At the same time the actual

number of methods suggested for derivatization of humic substances is highly limited and their derivatization in general has been used mostly for their structural analysis.

The aim of the present study is to develop approaches for synthesis of sulpho- and thiol groups containing derivatives of humic substances with increased complex forming ability in respect to metal ions.

II. MATERIALS AND METHODS

A. Materials

Analytical quality reagents (Merck Co., Sigma – Aldrich Co., Fluka Chemie AG) were used without purification. For preparation of solutions, high purity water Millipore Elix 3 (Millipore Co.) 10 – 15 MΩ was used throughout the study.

B. Studied humic acids (HA) and their characterization

Humic acids were isolated from a raised bog peat (Dzelves Bog, location depth 150 – 200 cm, age ~ 2000 ¹⁴C years, peat decomposition degree 10 %, humic acid/fulvic acid ratio: 6.8), purified as suggested previously [9, 10]. Peat HA properties: C 45.53 %; H 5.60 %; N 0.47 %; S 0.81 %; ash 1.29 %. Other determined parameters: concentration of carboxylic groups 4.2 mmol/g; total acidity 9.31 mmol/g; phenolic hydroxyl groups 5.11 mmol/g.

Elemental composition. Carbon, hydrogen, nitrogen and sulphur concentrations in the humic acid samples (elemental analysis of C, H, N, S) were determined by combustion-gas chromatography technique, using an Elemental Analyzer Model EA-1108 (Carlo Erba Instruments). Ash content was measured after heating 50 mg of each humic acid sample at 750 °C for 8 h. Elemental composition was corrected considering the ash content, and the oxygen amount was calculated as a difference.

Total acidity. An automatic titrator TitroLine easy (Schott-Geräte GmbH) was used for measuring total acidity of HA and their modification products. To estimate the total acidity [10], 20 mg of humic acid or its modification product, were dispersed in 10 ml of 0.1 M Ba(OH)₂ solution, then shaken overnight under N₂ atmosphere, filtered and washed with water. The filtrate with the washing solution was potentiometrically titrated with 0.1 M HCl down to pH 8.4 under N₂ flow.

Hydrophobicity of humic substances. Hydrophobicity of humic substances was characterized by their distribution between the water and polyethylene glycol (PEG) phases (PEG 20000, Fluka) [11] as the distribution coefficient $K_{\text{PEG/W}}$ (analogous to the octanol/water distribution coefficient K_{ow}).

Infrared spectra. Fourier transform infra-red (FTIR) spectra were recorded in the 4000 to 500 cm^{-1} wave number range by using Perkin Elmer 400 IR spectrophotometer, in KBr pellets obtained by pressing mixtures of 1 mg samples and 400 mg KBr with the precautions taken to avoid moisture uptake.

C. Modification of humic acids

Synthesis of derivatives of humic acids modified with thiol groups (III)

To the solution of 10 g of humic acids in 100 ml of 5 % NaOH 9.3 g (0.1 mol) of 2,3-epoxy-1-chloropropane were added and the suspension was stirred at 20 °C for 6 h. The weight of 4.8 g (0.02 mol) of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ was added to the reaction mixture and additionally stirred at 60 °C for 8 h. The reaction mixture was acidified with 6 N HCl to pH 1. The precipitated thiol derivatives of humic acids were filtered off, the precipitates re-dissolved into 0.1 N HCl and precipitated with 6 N HCl. Precipitates were washed with water, acetone and were dried. The weight of 8.6 g of humic acids modified with sulpho groups was obtained with the following elemental composition: C - 46.67 %; H - 5.33 %; N - 0.37 %; S - 3.67 %.

Synthesis of derivatives of humic acids modified with sulphoalkyl groups

The amount of 10.41 g (0.1 mol) of NaHSO_3 was added to the dispersion of 10 g of humic acid in 50 ml of formalin and then dropwise 10 % NaOH to achieve pH 10 – 12.

The reaction mixture was stirred at 80 °C for 6 h and afterwards acidified with 6 N HCl to pH 1 after the filtration process. The precipitated sulphoalkyl humic acids were filtered off and washed with water, acetone and dried. The weight of 8.6 g of humic acids modified with sulpho groups was obtained with the following elemental composition: C 42.91 %; H 5.21 %; N 0.26 %; S 4.76 %.

Synthesis of sulphopropyl humic acid (III)

The weight of 10 g of humic acids was added into the solution of 100 ml of dimethylformamide 1,3-propanesultone (Table 1) and was stirred at 70 °C for 8 h. The reaction product was poured into 1 l of acetone, the precipitated modified humic acids were filtered off, washed with water, acetone and dried. Reaction conditions and properties of obtained products are summed up in the Table 1.

D. Humic acids-metal complexation.

Study of the interaction between metal ions and humic acids by using ion selective electrode

Metal-humic binding was analyzed with Consort Cu^{2+} ion selective electrode (ISE) (pHoenix Electrode Co.). ISE was filled with 10 % KNO_3 solution and conditioned with 5 M NaNO_3 . The calibration curve in the 6.3×10^{-4} to 3.17×10^2 M Cu^{2+} concentration range was determined. 10 ml aliquots of HA solution (10 mg/l) were mixed with 40 ml aliquots $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ solution with the final Cu^{2+} concentration 100 mg/l and held for 24 h. In the filtered solutions the unbound Cu^{2+} concentration was measured with ISE (all measurements were done in triplicate).

Conditional stability constants were determined for complexation reactions, which can be written as an equation (Scatchard equation):

$$K_o = \frac{\text{CuHA}}{[\text{Cu}] \cdot (\text{HA} - \text{CuHA})} \quad (1)$$

where: Cu – total number of moles of Cu^{2+} ;

HA – the total number of moles of humic acid in solution;

CuHA – number of moles, which are linked in complexes.

E. Copper speciation analysis in contaminated soils

The investigated soil was calcareous soil artificially contaminated with copper at a final concentration 100 mg/kg. Selective fractionation includes, as described in the literature [15], the extraction of easily available copper fraction (extraction for 1 h with 8 ml of magnesium chloride solution (1 M MgCl_2 pH 7.0), carbonate bound metal fraction (extraction with 1 M CH_3COONa adjusted to pH 5.0 with acetic acid), metal bound to iron/manganese oxides, oxohydroxides (extracted with 0.04 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 25% (v/v) acetic acid) and metal bound to organic matter (extracted with 0.02 M HNO_3 and 30% H_2O_2 adjusted to pH 2 at 85 °C for 2 h with occasional agitation).

III. RESULTS AND DISCUSSION

All known structural models of humic substances suggest presence of reactive structures in their molecules (Fig. 1) and thus also the ability to obtain derivatives of humic substances with highly modified properties. In order to increase complex forming capacities of humic substances we have suggested the modification of HS with strong complex forming groups – sulphur containing groups (sulpho- and thiol groups), to increase ability of obtained modified humic substances to bind metal ions.

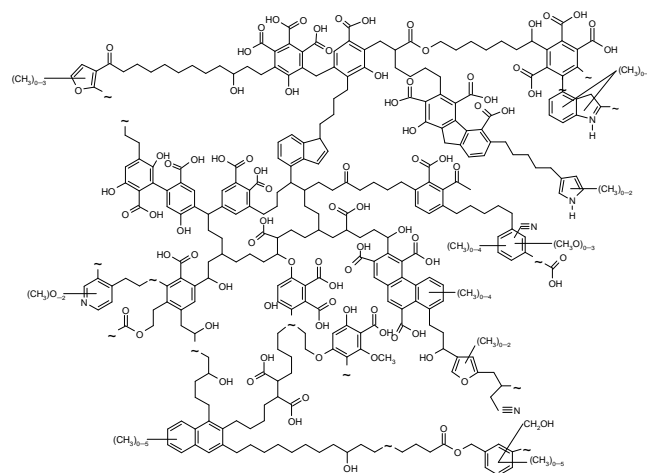


Fig. 1. Possible structures of soil humic substances (according to Schulten and Schnitzer 1993).

The suggested derivatization approaches (Fig. 2) are based on reactions of hydroxyl groups in the structures of humic substances either with 1,3-propanesultone to obtain sulphopropyl humic acid (III), or humic acids modified with sulphoalkyl group (VIII) or using etherification with 2,3-epoxy-1-chloropropane and following thiolysis of epoxy group to obtain humic acid modified with thiol groups (VI).

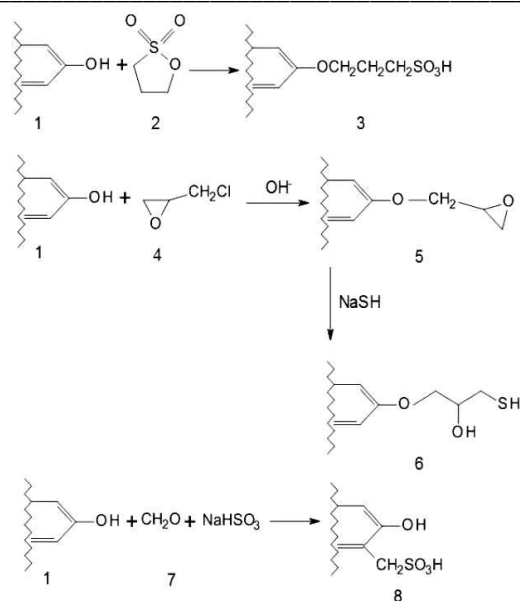


Fig. 2. Modification methods of humic substances with sulpho (III and VIII) and thiol (VI) groups.

Selection of experimental conditions is based on lignin/tannin modification reactions, considering experience of humic acid modification conditions in previous studies [6, 7, 13, 14]. Selected derivatization conditions allow to obtain sulphopropyl humic acid (III) with a differing derivatization degree (Table 1).

TABLE 1
CONDITIONS* OF SYNTHESIS AND YIELDS OF
SULPHOPROPYLDERIVATIVES OF HS

Amount of 1,3-propanesultone	T °C	T hrs	S, %
0.1 mol	80	8	8.34
0.2 mol	80	8	8.66
0.1 mol	20	25	8.55
0.05 mol	80	8	8.15
0.01 mol	80	8	3.42
0.05 mol	40	8	2.18
0.05 mol	20	8	1.38
0.05 mol	80	4	1.22

*Conditions of the synthesis in details are described in Materials and Methods

Yields of humic acids modified with sulfoalkyl group (VIII) or thiol groups are less variable and rather limited by experimental conditions, but also allow to obtain correspondingly substituted substances. During derivatization process the molecular mass of humic substances is reduced. On the one hand, it can be explained by destruction of humic macromolecules during derivatization process, but at the same time disintegration of hydrogen bonds of HA subunits allow to use obtained derivatives for structural studies of HA.

The obtained sulphur containing derivatives of humic substances are characterized by determining weight gain during synthesis, as well as by elemental analysis, FTIR spectra.

In FTIR spectra sorption maximum characterizing for C-S (780 cm^{-1}), S-S (466 cm^{-1}), organic sulphates (1388 cm^{-1}) and other bonds can be seen (Fig. 3).

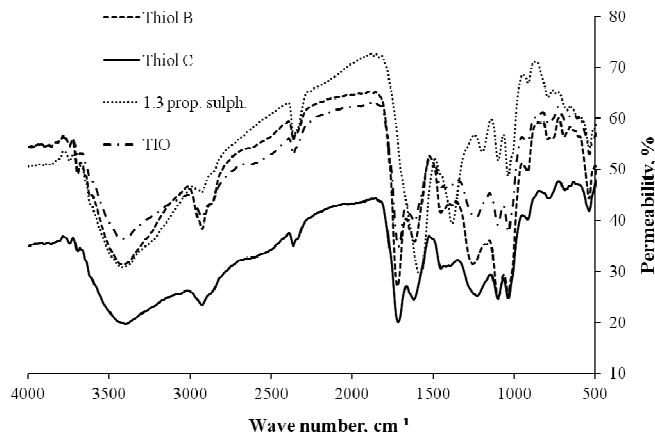


Fig. 3. FTIR spectra of obtained sulphur containing derivatives of humic substances.

Derivatization of humic substances with sulpho groups significantly influences their hydrophobicity as evidenced by the changes in their polyethyleneglycol-water distribution coefficient (Table 2).

TABLE 2
CHARACTERISTICS OF HUMIC ACIDS MODIFIED WITH
SULPHUR CONTAINING FUNCTIONAL GROUPS

	Peat HA (I)	Sulpho-propyl-humic acid (III)	Humic acid modified with sulfoalkyl group (VIII)	Humic acid modified with thiol groups (VI)
Total acidity, mEq/g	8.4	12.3	10.8	8.2
$K_{\text{PEG/W}}$	17.6	21.4	24.6	18.5
M_w , kDa	22.5	18.4	12.5	15.6
logK	4.89	nd	4.8	4.97

Humic acids modified with sulpho (III and VIII) and thiol (VI) groups have higher metal binding capacities and the formed complexes are more stable than with humic acids. Thus the obtained derivatives are prospective for use in contaminated environment remediation. To test this, a well-known sequential extraction approach suggested by Tessier and others [15] were used. According to sequential extraction approach total metal amount in contaminated soil is divided as easily extractable metals (environmentally most dangerous fraction as far as metals present in this fraction are accessible to soil biota and plants), metals bound to carbonates, iron and manganese oxides, organic matter and refractory fraction. The aim of remediation, therefore, could be reduction of most easily available metal fraction.

The speciation analysis of copper present in contaminated soil after treatment with peat humic acids and modified humic acids (Fig. 4) demonstrates significant reduction of easily available copper forms in contaminated soils. Thus, humic acids modified with sulpho (III and VIII) and thiol (VI) groups are prospective agents for contaminated soil treatment. It could be expected that after mineralization of humic acids presence of sulpho- and thiol groups in humic acids could

form stable sulphates or sulphides thus increasing stabilization effect of metal.

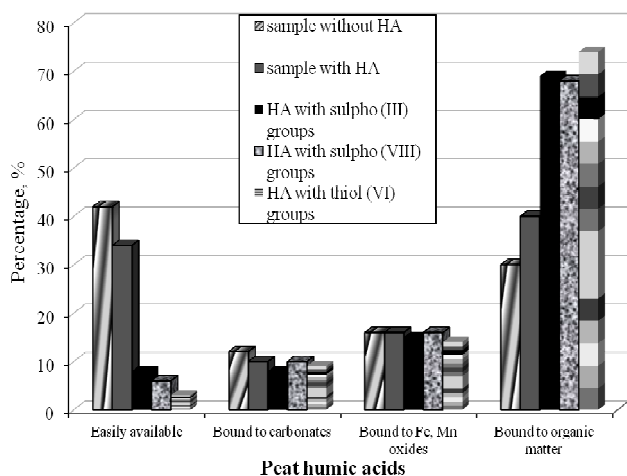


Fig. 4. Copper speciation analysis of contaminated soils treated with peat humic acid and humic acids modified with sulpho (III and VIII) and thiol (VI) groups

IV. CONCLUSIONS

Considering large scale production of humic substances, obtaining of derivatives of humic substances, including HS with modified properties, are perspective and sustainable areas of use.

The derivatives of humic substances showed significant differences in the number and in ability to interact with the metal ions, which was reflected in their complexation properties towards metal ions.

The obtained derivatives of humic substances can be used for remediation of environmental contaminated with heavy metal ions. Modified humic acids with sulpho (III and VIII) and thiol (VI) groups have higher metal binding capacities and the formed complexes are more stable, therefore the obtained derivatives are prospective for remediation of contaminated environment.

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Maris Klavins, Dr. hab. chem., Professor at the University of Latvia, Faculty of Geography and Earth Sciences, Department of Environmental Sciences. M. Klavins obtained his scientific degree in chemistry of biologically active compounds at the Moscow State University in 1986 but a habilitation degree at the University of Latvia in 1994. He is a member of the Academy of Sciences of Latvia, coordinator of International Humic Substances Research Society (IHSS). Research interests are related to studies of natural organic matter, wetlands and bogs and environmental pollution problems.

Address: University of Latvia, Raiņa bulv. 19, LV-1586, Riga, Latvia
E-mail: maris.klavins@lu.lv



Diana Dudare, M. Sc., doctoral student at the University of Latvia, Faculty of Geography and Earth Sciences, Department of Environmental Sciences. She is interested in research of peat humic substances, their interaction with metals, depending on their structure and properties.
E-mail: dianadudare@inbox.lv



Andris Zicmanis, Dr. hab. chem., Professor at the University of Latvia, Faculty of Chemistry. A. Zicmanis obtained his first scientific degree in organic chemistry at the Riga Polytechnic Institute in 1969 and his second scientific degree at the Moscow Institute of Fine Chemical Technology in 1989 (later equalized to a habilitation degree at the Latvian Academy of Science in 1992). He is a member of the Academy of Sciences of Latvia. Research interests are related with various methods of organic synthesis, including polymer-bound reagents and catalysts, and ionic liquids in organic synthesis.

Address: University of Latvia, Raiņa bulv. 19, LV-1586, Riga, Latvia
E-mail: andris.zicmanis@lu.lv

Māris Kļaviņš, Diāna Dūdare, Andris Zicmanis. Humusvielu sēru saturošie atvasinājumi un to izmantošana piesārņotu teritoriju sanācijā

Humusvielu atvasinājumu iegūšana ir perspektīva un ilgtspējīga joma, ņemot vērā humusvielu lielos apjomus apkārtējā vidē. Daudzu funkcionālo grupu klātbūtnē humusvielu struktūrā nosaka to spēju mijiedarboties ar metālu joniem, veidojot stabilus kompleksus un ietekmējot metālu jonu atrašanās vidē un to mobilitāti. Ņemot vērā humusvielu kompleksveidošanās raksturu, tās var tikt izmantotas piesārņotu teritoriju

rekultivācijai. Pētījuma mērķis ir izstrādāt pieejas humusvielu sēru un tiolgrupu saturošo atvasinājumu sintēzē ar paaugstinātu kompleksveidošanās spēju attiecībā uz metālu joniem. Pētījumā tika izmantota humusvielu atvasinājumu sintēžu metode, spektrālās analīzes metode (Furjē transformācijas infrasarkanā starojuma spektrometrija), potenciometrijas metode, kā arī veikta pētīto humusvielu fizikāli ķīmisko īpašību izpēte.

Pētījumā tika sintezēti humusvielu sēru un tiolgrupu saturošie atvasinājumi un analizētas īpašības pēc to elementsastāva, kā arī tika raksturotas funkcionālo grupu satura izmaiņas pēc to spektrālajām īpašībām. Iegūtie humusvielu atvasinājumi parāda spēju saistīties ar metālu joniem, atkarībā no to kompleksveidošanās īpašībām. FTIR spektru analīze parāda metālu jonu saistīšanos humusvielu molekulas iekšējās sfēras kompleksos. Modificētajām humīnskābēm ar sēra (III un VIII) un tiola grupām (VI) piemīt lielāka metālu saistīšanās spēja, kur izveidojušies kompleksi ir stabilāki, tāpēc pētījumā iegūtos humusvielu atvasinājumus var izmantot piesārņotu teritoriju sanācijā. Apstrādājot piesārņotas augsnes ar kūdras humusvielām un modificētajām humusvielām, vara koncentrācijas noteiktās tā formās būtiski samazinās, tādējādi modificētās humusvielas ar sēra (III un VIII) un tiola grupām (VI) var tikt pielietotas piesārņotu augšņu rekultivācijā.

Марис Клявиньш, Диана Дударе, Андрис Цицманис. Гуминовые вещества, содержащие производные серы, и их использование в санации загрязненных территорий

Получение производных гумусовых веществ (ГВ) перспективно и плодотворно, учитывая высокое содержание ГВ в окружающей среде. Присутствие многих функциональных групп в структуре ГВ определяет их способность взаимодействовать с ионами металлов, образуя устойчивые комплексы и тем самым влиять на содержание и подвижность ионов тяжелых металлов в среде. Учитывая эту комплексообразующую способность гумусовых веществ, можно использовать их в рекультивации загрязненных территорий. Целью этого исследования является разработка синтеза ГВ производных серы и тиол групп с высокой комплексообразующей способностью по отношению к ионам металлов. В исследование был использован метод синтеза производных ГВ, спектральный анализ (спектроскопия Инфракрасного излучения Трансформации Фурье), потенциметрический метод, а также были установлены физико-химические свойства изучаемых ГВ.

В процессе исследования синтезированы ГВ, содержащие производные серы и тиол групп, проанализированы особенности их элементного состава, а также описаны изменения функциональных групп по их спектральным характеристикам. Полученные производные гумусовых веществ показали способность связываться с ионами металлов в зависимости от их комплексообразующих свойств. ИК-анализ Фурье показал связывание иона металла внутренней сферой комплекса молекулы ГВ. Модифицированным гуминовым кислотам с серой (III и VIII) и тиол группами (VI) присуще высокая способность связывания металлов, образующиеся комплексы стабильные, поэтому полученные производные ГВ можно использовать для санации загрязненных территорий. Обработывая загрязнённые почвы ГВ торфа и модифицированными ГВ, концентрации определенных форм меди значительно уменьшаются, поэтому ГВ модифицированные группами серы и тиола могут быть использованы в рекультивации почв.