

DESIGN OF HUMIC MATERIALS OF A DESIRED REMEDIAL ACTION

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I. INTRODUCTION

Due to a wide variety of functions, humic substances (HS) can bind both heavy metals and organic ecotoxicants. The ecotoxicants bound into humic complexes become non-toxic that causes a net reduction in toxicity in polluted environments. In addition, HS are shown to play an important role in redox transformations of both organic xenobiotics, heavy metals, and radionuclides. Despite the above properties, HS have not been widely used in remediation technologies. The fundamental reason is the extreme structural heterogeneity, which translates into chemical properties that are difficult to control. The tools to reduce structural heterogeneity are needed to ensure control over reactive properties of HS and, hence, to facilitate a use of humic materials in remedial practice. The objective of this research was to develop and test the strategy for preparing "designer" humics – the humics possessing the desired reactive properties (complexing ability, redox activity, etc.) and physical form (soluble, colloidal, solid). The techniques of chemical modification and cross-linking were used for this purpose.

The techniques of sulfonation and hydroxylation were used to achieve the desirable reactive properties of HS. The sulfonation was to produce derivatives that form much more soluble complexes with transition metals. Hydroxylation, in particular, quinones-enrichment, was to increase the binding, detoxifying and redox-mediating properties of HS toward heavy metals and radionuclides. Two different strategies were formulated and tested to obtain hydroxylated and quinone-moieties enriched humics. The first one implied a direct chemical modification of humics - conversion of phenols into quinones - using appropriate oxidants (e.g., Fenton, Fremy's salt, etc.). The second one was based on polycondensation approach when natural humics and the quinones desired served as counterparts. Of importance is that the latter approach allows both functionalization and cross-linking of humics, - this makes it particularly promising.

II. MATERIALS AND METHODS

The leonardite humic acid, designated as CHP, was isolated from the commercial preparation Powhumus (Humintech Ltd., Germany) and used for both sulfonation and hydroxylation studies. Peat HA, designated as PHA-Sk3, was isolated from low-moor peat of the lake Sakhtysh (Ivanovo, Russia) and used for sulfonation studies.

Sulfonation was conducted using sulfuric acid and chlorosulfonic acid as sulfonating agents.

Hydroxylation was conducted using a number of existing techniques including the Fenton reaction (oxidation with $H_2O_2 + Fe(II)$) the Elbs reaction (oxidation with $K_2S_2O_8$), the Teuber reaction (oxidation with potassium nitrosodisulfonate – Fremy's salt) ((Hudlický, 1990). The reagents were chosen because oxidation reactions can be carried out in alkaline medium when HA are dissolved. To conduct hydroxylation, a weight of leonardite HA was dissolved in alkaline solution and hydroxylating agent was added. After reaction, the obtained derivative was precipitated by acidification of the reaction mixture and desalted using dialysis. The oxidized derivatives were then reduced using sodium sulfite as a reductant to transfer quinone moieties into hydroquinone ones.

Phenolformaldehyde (PF) condensation was conducted using CHP as one phenolic counterpart and either hydroquinone (HQ) or catechol (CC) as another phenolic counterpart. Conditions of PF condensation were as described for novolac-type resins (Lee et al., 2003). Copolymerization of p-benzoquinone (PBQ) and HA was performed at pH~8 (Preston et al., 1982). The co-polymers were prepared using ratios of 100, 250 and 500 mg of monomer per 1 g of HA.

The solubility and stability of the metal complexes of the sulfonated derivatives was estimated using the corresponding interactions with Fe(III) and Hg(II). Reducing performance of the hydroxylated and quinonoids-enriched derivatives was determined as described in (Matthiessen 1995) using Fe(III)/Fe(II) reduction as an indicator reaction. The detoxifying performance of the obtained derivatives was estimated using seedlings technique and Cu(II) as a model contaminant.

III. RESULTS AND DISCUSSIONS

The sulfonated derivatives were analysed for the content of elements including sulfur, for the content of strong acidic groups (Swift, 1996) and for the complexing characteristics in relation to Fe(III) and Hg(II): content of strong binding sites (BS) and stability constants of Fe(III)- and Hg(II)-complexes of HS derivatives. The obtained characteristics are summarized in Table 1. As follows from the obtained values of C/S ration and strong acidity, much higher efficiency of sulfonation was achieved using chlorosulfonic acid (CIS-derivatives) as a sulfonating agent compared to sulfuric acid (S-derivatives). The CIS- derivatives had 50 % more of strongly acidic sites as before sulfonation. The proportional increase was observed for the amount of strong metal-binding sites. A slight decrease in the stability constants of the sulfonated derivatives was observed both for Fe(III) and Hg(II) complexes.

Table 1 – Compositional and complexing characteristics of the sulfonated humic derivatives.

Sample	Atomic ratio, C/S	Strong acidity, meq/g	Fe(III)-BS mmol/g	*Log K, Fe(III), L/mol	Hg(II)-BS, mmol/g	Log K, Hg(II), L/mol
CHP	256	2.9±0.5	2.2	12.0	2.2	13.1
CHP-S	296	3.3±0.2	2.8	11.3		
CHP-CIS	30	4.5±0.1	3.4	11.5	4.5	12.4
PHA-Sk3	265	3.3±0.1	0.9	12.4		
PHA-Sk3-S	210	2.1±0.1	1.5	12.2		
PHA-Sk3-CIS	43	3.7±0.2	1.9	11.4		

*calculated on the basis of molar concentration of the strong binding sites given in the table.

The results on the composition and redox properties of the hydroxylated derivatives using oxidation and polycondensation techniques are given in Table 2.

As it can be seen, the quinones-enriched derivatives obtained using polycondensation technique have substantially higher content of the target functions – phenolic hydroxyls - compared to those obtained by the subsequent oxidation-reduction approach. Of particular importance is that the former derivatives have much higher reducing capacity in relation to Fe(III) compared to that of the oxidized-reduced derivatives.

The studies on detoxifying ability of the sulfonated derivatives in relation to Cu and Hg have shown that it has slightly decreased in relation to Cu, but did not change toward Hg. The studies on detoxifying abilities in relation to Cu(II) for hydroxylated derivatives have revealed that much higher performance of the polycondensation derivatives was observed compared to the oxidized-reduced ones. Among the polycondensation derivatives, the highest detoxifying ability was observed for CHP-BQ100 and CHP-CC250. In general, detoxifying ability of hydroquinonic derivatives was lower compared to that of catecholonic derivatives. The obtained results confirm that the main mechanism of detoxifying action of HS in relation to Cu(II) is a formation of non-bioavailable chelates. Catechol-enriched HS derivatives have much higher content of chelating moieties compared to the hydroquinonic-moieties enriched derivatives.

The consistency of the above changes in properties of the humic derivatives with the changes in their structure allows us to conclude on the feasibility of the proposed approach - to use chemical modification for preparing humic materials of the desired properties.

IV. CONCLUSIONS

The conducted research has demonstrated that the most promising way for obtaining humic derivatives of the desired remedial action is incorporation of specific reactive moieties into the humic

backbone using polycondensation approach. The big advantage of the polycondensation approach over the direct introduction of the target functional groups into the humic backbone is a possibility to introduce a whole number of specifically arranged reactive centers using a very limited amount of substitution sites. Realization of the both approaches for obtaining quinonoide-enriched humic derivatives have revealed much higher reducing and detoxifying ability of polycondensation derivatives compared to the directly oxidized-reduced ones. The performance of the above derivatives was evaluated using Fe(III)/Fe(II) as a redox couple, and Cu(II) as a toxicant. The proposed strategy opens a way to much broader application of humic materials in remediation technologies.

Table 2 – Compositional and redox characteristics of the hydroxylated CHP derivatives obtained using subsequent oxidation-reduction and polycondensation techniques.

HS sample	Atomic ratio		Acidity, mmol/g			Reducing capacity, meq/g
	H/C	O/C	Total Acidity	COOH	Ar-OH	
CHP	0.85	0.38	4.85	3.81	1.0	0.58
POLY-HQ	1.33	0.31	6.19	0.20	6.0	2.20
CHP-HQ100	1.18	0.26	6.83	3.53	3.3	1.02
CHP-HQ250	1.15	0.34	7.39	3.34	4.0	2.67
CHP-HQ500	1.20	0.38	7.03	2.94	4.1	3.80
POLY-CC	0.84	0.30	9.75	0.97	8.8	2.04
CHP-CC100	0.76	0.43	7.06	3.81	3.3	2.06
CHP-CC250	0.80	0.40	7.44	3.48	4.0	2.83
CHP-CC500	0.81	0.41	7.64	3.40	4.3	2.77
POLY-BQ	0.87	0.46	7.49	2.63	4.9	3.73
CHP-BQ100	1.05	0.37	6.68	4.82	1.9	1.06
CHP-BQ250	0.71	0.37	7.46	4.77	2.7	0.99
CHP-BQ500	1.01	0.34	7.74	3.71	4.0	1.89
CHP-RFr	0.81	0.42	5.45	4.46	1.0	0.70
CHP-REI	0.89	0.38	5.82	4.59	1.2	0.56
CHP-RFe	0.85	0.38	5.84	4.08	1.8	0.74

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References

- Hudlický, M., 1990. Oxidation in Organic Chemistry. ACS Series:163-168.
- Lee, Y.-K.; Kim, D.-J.; Kim, H.-J.; Hwang, T.-S.; Rafailovich, M.; Sokolov, J., 2003. Activation energy and curing behavior of resol- and novolac-type phenolic resins by differential scanning calorimetry and thermogravimetric analysis. *J. Appl. Polym. Sci.* 89: 2589–2596.
- Matthiessen, A., 1995. Determining the redox capacity of humic substances as a function of pH. *Vom Wasser* 84: 229–235.
- Preston, C.M.; Rauthan, B.S.; Rodger, C.; Ripmeester, J.A., 1982. A hydrogen-1, carbon-13 and nitrogen-15 NMR study of p-benzoquinone polymers incorporating amino nitrogen compounds ("synthetic humic acids"). *Soil Sci.* 134: 277-293.
- Swift, R.S., 1996. Organic matter characterization. In: *Methods of Soil Analysis. Part 3. Chemical methods*: 1036-1041.