

# SYNTHESIS AND CHARACTERIZATION OF HUMIC DERIVATIVES ENRICHED WITH HYDROQUINOIC AND CATECHOLIC MOIETIES

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## I. INTRODUCTION

Chemical modification is a promising tool for preparing humic materials of the desired properties (Almendros, Dorado, 1999). In the context of remediation technologies, to the most important properties of humic substances (HS) belong complexing and redox ones provided by the presence of carboxyl and hydroxyl groups in humic backbone. Hydroquinone-quinone transfers determine redox reactions of HS, whereas salicylic and catecholic moieties are responsible for chelating interactions of HS with heavy metals. Hence, the enhanced redox and chelating activity could be expected from HS enriched with hydroquinone or catecholic moieties. The objective of this study was to develop and optimize the techniques of enrichment of HS with hydroquinone and catecholic moieties.

Two different approaches were used for this purpose. The first one was aimed at conversion of the available in the structure of HS phenolic fragments into quinones. The second approach implied incorporation of the hydroquinone and catecholic fragments into the structure of humics using polycondensation technique.

## II. MATERIAL AND METHODS

Leonardite humic acids obtained by desalting of the commercial potassium humate Powhumus (Humintech Ltd., Germany) was used for all the modifications.

### Modification techniques

For hydroxylation of humic substances the number of existing techniques for hydroxylation of phenols was chosen (Hudlický, 1990) including the Fenton reaction (oxidation with  $H_2O_2 + Fe(II)$ ) the Elbs reaction (oxidation with  $K_2S_2O_8$ ) and the Teuber reaction (oxidation with potassium nitrosodisulfonate – Fremy's salt). These reagents were chosen because oxidation reactions can be carried out in alkaline medium when humic acids are dissolved.

A weight of leonardite HA was dissolved in alkaline solution. Hydroxylating agent was added to the obtained solution of HA. 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.

Methods of phenolformaldehyde(PF) condensations of hydroquinone(HQ) and catechol(CC) as well as reaction of p-benzoquinone(pbq) polymerization with introduction of humic acids in reaction system were applied to obtain co-polymers.

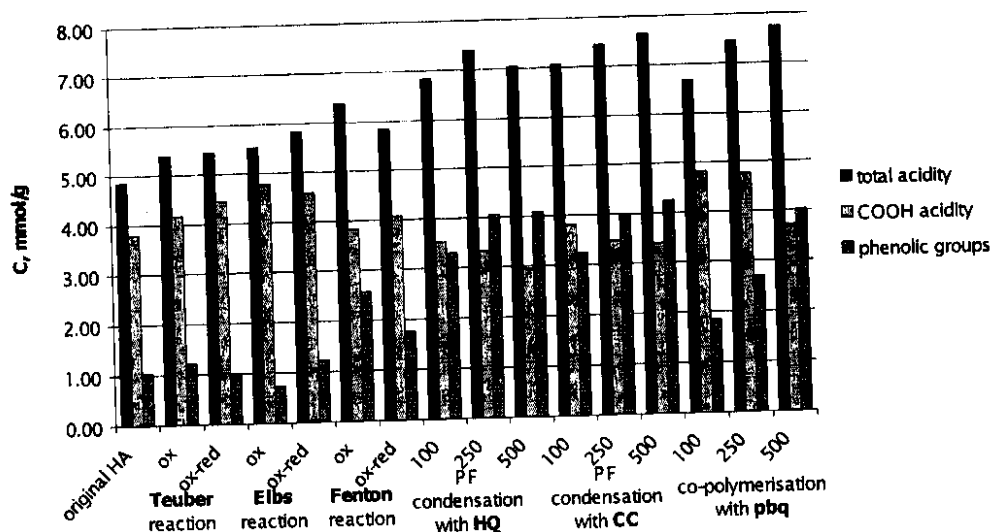
Conditions of PF condensations corresponded to the ones of preparation of novolac-type resins (Lee et al., 2003). Co-polymerization of p-benzoquinone and HA was performed at pH=8 (Preston et al., 1982). The co-polymers were prepared using ratios of 100, 250 and 500 mg of monomer per 1 g of HA.

### Characterization techniques

Total acidity of the humic derivatives was determined using barite technique, carboxylic acidity – using calcium acetate technique as described elsewhere (Swift, 1996).

## III. RESULTS AND DISCUSSIONS

Results of determination of the total and carboxylic acidity of the synthesized derivatives are shown in fig.1. An amount of phenolic hydroxyls was determined by subtracting carboxylic acidity from the total acidity value.



**Figure 1** – Acidic functional group concentration in original and modified HA ox – oxidized, ox-red – oxidized then reduced, number – amount of mg of monomer per 1 g HA.

As it can be seen from the given results, the most pronounced increase in the content of phenolic hydroxyls proportional to the content of hydroquinone and catechol moieties, was observed for the derivatives obtained with a use of polymerization and polycondensation techniques. At the same time, direct hydroxylation of humic acid did not lead to an increase in the amount of the phenolic hydroxyls, but slightly increased carboxylic acidity of the preparations. This can be caused by the oxidative cleavage of aromatic rings during hydroxylation.

#### **IV. CONCLUSIONS**

Among the two approaches undertaken to obtain hydroquinone-enriched humic derivatives, polycondensation turned out to be much more promising tool compared to the direct oxidation of phenolic units into quinone ones. The large substitution degree of an aromatic ring in the humic backbone can be the reason of low efficacy of direct hydroxylation reactions.

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