ENHANCED DETOXIFYING ABILITY OF HYDROQUINONES-ENRICHED HUMIC DERIVATIVES WITH RESPECT TO COPPER

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I. INTRODUCTION

Humic substances (HS) are widely known to play a mitigating role in polluted terrestrial and aquatic environments (Schnitzer and Khan, 1972). The main mechanism of detoxifying ability of HS in relation to heavy metals is formation of non-bioavailable complexes. Hence, to enhance detoxifying capacity of HS, chemical modification can be a promising tool, in particular, if it is aimed at enrichment of the structure of HS with chelating fragments. To validate this approach, the quantitative studies on detoxifying ability of the modified HS in relation to heavy metals are in need. The objective of this study was to estimate detoxifying ability of humic derivatives enriched with hydroquinoic moieties with respect to copper(II).

II. MATERIALS AND METHODS

Three HA preparations were used: CHP - leonardite humic acid, CHP-PC - preparation obtained by polycondensation of CHP with catechol; CHP-HQ - preparation obtained by polycondensation of CHP with hydroquinone. The total and carboxylic acidity of the preparations was determined using standard barita and calcium acetate techniques, respectively (Swift, 1996). An amount of phenolic groups (Ar-OH) was calculated by subtracting carboxylic acidity from the total acidity value The acidity values obtained for the preparations under study are shown in Table 1.

Table 1 – Content of acidic groups in humic preparations (mmol/g).

HS sample	Total acidity (mmol/g)	COOH (mmol/g)	Ar-OH (mmol/g)
CHP	4.85	3.81	1.04
CHP-PC	7.44	3.48	3.96
CHP-HQ	7.39	3.34	4.05

As it is seen from Table 1, the content of Ar-OH groups in chemically modified preparations is substantially higher than in the initial one. Ash content in all preparation was not more than 9 %.

Bioassays. In bioassays was used $CuSO_4$*$5H_2O$. Toxicity of copper was estimated using seedling technique. Wheat (*Triticum aestivum* L. cv. Moskovskaya-39) was used as a biotarget. The length of wheat roots was used as a test response. Wheat seeds were placed in water solutions containing 1 mg/L Cu^{2+} and 5, 10, 50, 100 or 500 mg/L HA. As controls, solutions of HA without Cu^{2+}, solution of 1 mg/L Cu^{2+} and distilled water were used. pH 6.4 was maintained in all the experiments. Seeds were grown for 72 hours at 25 C.

III. RESULTS AND DISCUSSIONS

The results of bioassays are shown in Figure 1. As can be seen, there was no growth simulation effect of HA preparations observed in all the variants without copper. At the high HA concentration of 500 mg/L, both initial coal HA - CHP and its hydroquinoic derivative (CHP-HQ) significantly inhibited the root growth: from 11 to 19 %.

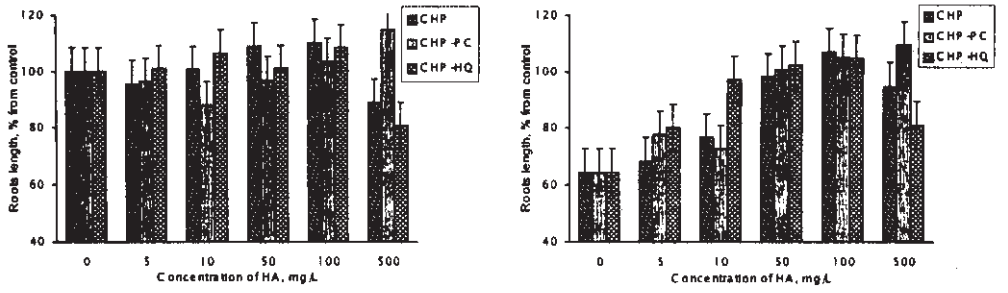

Figure 1 – Influence of different concentrations of HA on roots length without copper (a) and in its presence (b).

There was substantial detoxifying action of all the HA preparations observed in the presence of copper. Of importance is that the both modified preparations significantly decreased toxicity of copper even at the minimal concentration of 5mg/L, whereas for non-modified CHP significant detoxification activity was displayed only at 10 mg/L. Starting with concentration of 10 mg/L, the preparation CHP-HQ provided a complete detoxification of copper. For the other preparations, the complete detoxification was observed starting with the concentration of 50 mg/L. However, the presence of CHP and CHP-HQ at the concentration of 500 mg/L inhibited the growth of seedling roots as in the control experiments. This effect can be referred to the inhibiting activity of the high concentrations of these preparations on root growth.

From the obtained results, the detoxification coefficients (D) were calculated as described in (Perminova et al. 2001). D was calculated as follows:

$$D = \left(1 - \frac{R_d - R_{d+t}}{R_d} \Big/ \frac{R_0 - R_t}{R_0}\right)$$

where: R_0 - roots length of control; R_d - roots length in presence of HA; R_t - roots length in presence of copper; R_{d+t} - roots length in presence of copper and HA.

The detoxification curves - dependence of D on HA concentration - are shown in Figure 2.

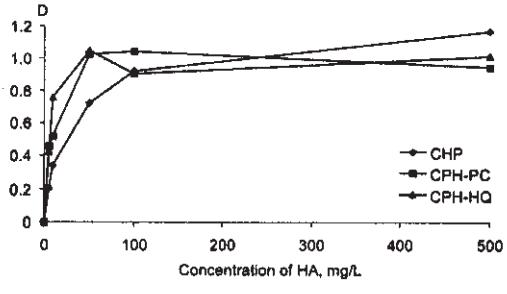

FIGURE 2 – Detoxification curves for leonardite HA and its hydroquinones-enriched derivatives.

On the basis of the D values, the toxicological constants of copper binding to HA normalized to the organic carbon content in HA preparation (K_{oc}^{lox}) were calculated as described previously (Perminova et al., 2001). The values of K_{oc}^{lox} were obtained by approximating the following expression:

$$D = \frac{K_{OC}^{tox} \times C_{HA}}{1 + K_{OC}^{tox} \times C_{HA}}$$

where: C_{HA} is a concentration of HA.

The determined values of K_{oc}^{tox} for CHP, CHP-PC and CHP-HQ were 60000, 140000 and 220000 L/kg C, respectively. Hence, the HA preparations under study can be put into the following ascending order according to their detoxifying ability with respect to copper:

CHP < CHP-PC < CHP-HQ. Of particular importance is that the above sequence follows an increase in quantity of Ar-OH group in preparations (table 1). The obtained results demonstrate that detoxification ability of HA preparations with respect to copper is determined by their complexing properties which are, in turn, determined by the content of chelating fragments in the structure of HS. In general, the conclusion can be made that the hydroquinones-enriched humic preparations possess higher detoxifying ability with respect to copper. Hence, chemical modification can be a promising tool for preparing humic detoxicants of high efficacy and selectivity.

IV. CONCLUSIONS

The hydroquinones-enriched humic derivatives obtained from leonardite humic acid using chemical modification technique displayed higher detoxifying efficacy with respect to copper compare to the initial HA. The detoxifying ability increased along with an increase in phenolic acidity indicating the leading role of incorporated hydroquinoic fragments in copper detoxification. The selected type of chemical modification - enrichment of HS with hydroquinoic moieties - has been proven to be a promising direction for obtaining highly effective humic detoxicants with respect to heavy metals.

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