

BINDING OF LEAD TO HUMIC ACID RELATED TO ITS CARBOXYL AND PHENOL GROUPS CONTENTS

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Humic acids (HA) are heterogeneous, polydisperse mixtures of natural organic polyelectrolytes, containing a large number of different functional groups. Even though, it is known that humic carboxyl and phenol groups play a prominent role in the complexing of metal ions, no reports have appeared on derivatization of those groups in order to estimate their effect on lead binding. This can be achieved by selective blocking of HA carboxyl and phenol groups which would prevent their contribution to the complexation reaction. In this paper, obtained derivatized HAs, with blocked carboxyl and phenol groups, are used in comparison to underivatized HA, for investigation of the influence of the functional groups on the HA complexation properties.

HAs were obtained following the procedure suggested by the International Humic Substances Society (IHSS) (Sparks *et al.*, 1996) from a well-humified organic horizon of old beech-forest soil (10 cm depth), in autumn 2003, using standard grinding equipment. Selective blocking of carboxyl functional groups was achieved by esterification performed by methanol-thionyl chloride procedure suggested by Hosangadi and Dave (1996). To a solution of 500 mg of HA in 20 ml of methanol, was added 5 ml of thionyl chloride. The reaction mixture was then heated, centrifuged and washed with distilled water until free of chlorides. The obtained esterified humic derivative (EHA) was dried in a rotary evaporator and in a vacuum desiccator over P₂O₅. Selective blocking of phenol functional groups was achieved by acetylation performed by adding of 15 ml of acetic anhydride and 3 drops of conc. H₂SO₄ to 600 mg of dried HA. The mixture was heated on a boiling water bath for 4 hours. The content was poured into ice-water. The crystalline solid acetylated humic derivative (AHA) was filtered off and washed thoroughly with cold, distilled water until it was free of acid and then dried over P₂O₅ in a vacuum desiccator. Selective blocking of the functional groups was confirmed by FT-IR spectra of underivatized and derivatized HAs.

The stability constants of metal-humate complexes through ion-exchange method were determined as described by Schnitzer and Skinner (1966). The logarithm of the stability constant of the complex ($\log K$) was evaluated from the following relationship:

$$\log\left(\frac{D_0}{D} - 1\right) = \log K + n \log[L]$$

where D_0 is distribution constant of the Pb^{2+} in absence of HA; D is distribution constant of Pb^{2+} in presence of HA; K is stability constant of Pb^{2+} -humic complex; n is number of moles of HA which combine with one mole of Pb^{2+} ; $[L]$ is concentration of HA in mole per litre. D_0 was determined from the expression:

$$D_0 = \frac{\alpha_0 \cdot V}{(100 - \alpha_0) \cdot m_{\text{resin}}}$$

where α_0 is percent of total metal bound to exchange resin (Dowex AG 50W-X8); $100 - \alpha_0$ is percent of total metal remaining in solution; V is volume of solution; m_{resin} is weight of exchange resin. D is measured in the same manner as D_0 in presence of different HA concentrations. n is obtained from the slope of the plot of $\log [(D_0/D)-1]$ versus $\log [L]$, while the corresponding $\log K$ value is obtained from the intercept. Obtained results are shown in Table.

Table. Stability constants and n values of Pb^{2+} -humic complexes at pH 6.50.

	HA	EHA	AHA
log K	5.85	4.15	3.75
x	1.21	0.94	0.79

Obtained $\log K$ values show the following sequence: $\text{HA} > \text{EHA} > \text{AHA}$. Thus, the most stable complex is formed between Pb^{2+} and underivatized HA, indicating that both carboxyl and phenol groups are involved in complexation of lead. The complex stability is decreased in case of blocked carboxyl groups, due to relation: $\log K_{\text{EHA}} < \log K_{\text{HA}}$, while stability is even more decreased in case of blocked phenol groups, due to relation: $\log K_{\text{AHA}} \ll \log K_{\text{HA}}$. Those results suggest that beside dominant way of metal-humic interaction which involves both carboxyl and phenol groups and the interaction way which involves only carboxyl groups, it is possible that even interaction involving only phenol groups can be considered to happen. In that case even more stable complex is formed than complex when only carboxyl groups are involved.

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