

Determination of the mechanism of interaction of humic acids of peats with a strong electron acceptor - bromanil

Maria MikhailovnaGertsen^{(a)*}, Elena DmitrievnaDmitrieva^(a)

^(a)Laboratory of Chemistry, Tula State University, Tula, Russian Federation pr. Lenina, 92, 300600

* Corresponding author:

mani.leontyeva@gmail.com

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Abstract

The binding capacity of humic acids of peats in the relation to bromanil is determined. It is shown that the percentage of binding of bromanil with humic acids and hyatomelanic acids has the similar values and does not exceed 18%, which indicates a minimal contribution of donor-acceptor interaction in the process of binding polyaromatic hydrocarbons with humic acids. It has been proved that the leading role in the binding of humic acids with polyaromatic hydrocarbons belongs to intermolecular hydrophobic interactions, which leads to the formation of supramolecular structures between the aromatic "core" of humic acids and polyaromatic hydrocarbons.

Keywords: humic acids, hyatomelanic acids, polyaromatic hydrocarbons, bromanil.

1. Introduction

Regardless of the source of humic acids (HAs) origin distinguishing feature of their chemical structure is the presence of the aromatic carbon skeleton, substituted alkyl, carboxyl, hydroxyl, methoxyl group and the peripheral part, enriched with polysaccharide and polypeptide fragments [1]. Humic acids interact by donor-acceptor mechanism due to the presence of a significant amount of carboxyl and hydroxyl groups, which are the predominant substances in the aromatic ring of humic acids, and hydrophobic fragments in the macromolecule can provide hydrophobic binding [2]. In accordance with [3], donor-acceptor and hydrophobic binding determines the high affinity of humic acids to polyaromatic hydrocarbons (PAHs) and other organic toxicants, which are the dangerous class of pollutants, thereby helping to solve one of the main environmental problem [4,5]. Generally the soil is the receiver of any technogenic and natural pollutants, where they decay and constantly penetrate into plants and the environment or constitute a repository in which some pollutants can exist for many years after penetration into the soil [6]. Identification of the mechanism of the interaction of humic acids with a strong electron acceptor - bromanil is the relevant objective, as it allows us to propose a method of binding humic acids with polyaromatic hydrocarbons of various structures, as representatives of the heavy fraction of oil. The purpose of this work is to identify the binding capacity of humic acids of peats with a strong electron acceptor - bromanil and to establish the mechanism of the interaction of humic acids with polyaromatic hydrocarbons.

2. Materials and methods

Humic acids was isolated from peats of various origin: reed fen peat (RFP), sphagnum high-moor peat (SHP), black alder fen peat (BFP), sphagnum transition peat (STP) [7-8] that were chosen as the objects of this research. Humic acids were isolated from peats of various origin of the Tula region by the traditional method of water-alkaline extraction: 0.1N NaOH solution was poured into the peat/alkali ratio - 1/6 to the peat sample, boiled for 2 hours with constant stirring and left for a day. A 10% solution of HCl was added to the solution of the resulting humates to pH = 2-3. The precipitated humic acids were centrifuging for 20 minutes at 4000 rpm, thoroughly washed with distilled water until pH = 7. Purification of humic acids was carried out by dialysis. Dialysis was carried out in the membrane bags with a pore size of 12-14 kDa. Dialysis duration was 24 hours. The obtained humic acids were dried in a drying cabinet at $t = 40^{\circ}\text{C}$ [9]. Himatomelanic acids (HMAs) were isolated from humic acids of peats by the hot ethanol extraction. A weighed portion of humic acids weighing 1 g was poured with 200 ml of ethanol and boiled under reflux for 4 hours. The extract obtained was filtered. The precipitate is a fraction that is insoluble in ethanol — post-light substances. The concentrated ethanol extract was subjected to distillation. After that, it was dried for a day at normal temperature to obtain solid hymatomelanic acids [10]. Synthesis of bromanil was carried out as follows: 10 g of hydroquinone (1 mol) was dissolved by heating in 100 ml of glacial acetic acid and 10 g of bromine (4 mol, 12.54 ml) were added with stirring. After adding all the bromine, the mixture was left for 24 hours. Then a small amount of concentrated HNO_3 was added to the mixture and heated on a water bath for a short period of time to complete the synthesized and oxidized. The mixture was cooled, then poured into water. The precipitated bromanil is filtered, washed with water and dried in air, purified by recrystallization from glacial acetic acid. To study the interaction of humic acids with bromanil, an aqueous solution of bromanil was prepared by solubilization. The portion of the bromanil was dissolved in acetone, an aliquot part was taken so that the concentration of the resulting solution did not exceed the level of the aqueous solubility of the bromanil. The concentration of the working solution is $1 \cdot 10^{-5}$ M.

Solutions of humic acids and hymatomelanic acids were prepared by dissolving the suspensions in 0.1 M NaOH, followed by dilution with distilled water. Electronic spectra were recorded in the wavelength range of 190–450 nm [11].

3. Results and discussion

The complexity of the structure and composition of humic acids of peats determines the complex nature of the interaction of various structural fragments that are part of humic acids with PAHs. Aromatic structures that are part of humic acids of peats can act as electron density acceptors when interacting with the conjugated system of PAH molecules. When a PAH molecule interacts with the HAs macromolecule, a complex is formed, the bond in which is due to the intermolecular π - π -electron interaction of the PAH aromatic system and the aromatic fragment of the HAs to form a charge transfer complex (CTC) [12]. To confirm the hypothesis of the contribution of donor - acceptor interaction in the process of binding humicacids with polyaromatic hydrocarbons, experiments were conducted to study the interaction of a strong acceptor of bromanil with HAs in an aqueous medium. For this, the optical density of the solution of pure bromanil was measured in the presence of humic acids. The concentration of bromanil was $3 \cdot 10^{-5}$ M, corresponding to its water solubility. UV - absorption spectra of a bromanil solution in the presence of humic acids at the concentration of $4 \cdot 10^{-5}$ g/l. The scheme of formation of a complex with charge transfer is presented in Fig. 1.

Figure 1. Bullpen between a fragment of humic acids and bromanil

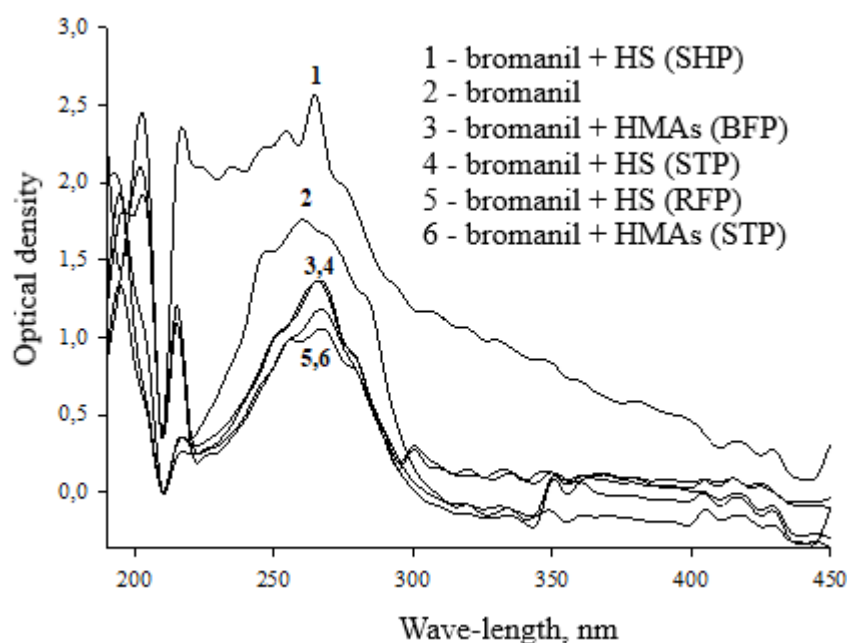


Figure 2. UV-absorption spectra of solutions

In the presence of humic acids (Fig. 2), the absorption maximum of bromanil by 10 nm toward the long-wavelength region is observed. The decrease in the intensity of the peak in the absorption maximum at 260 nm is associated with the formation of a CTC between HAs and bromanil, which leads to a regular decrease in the concentration of bromanil in the solution with time. To quantify the degree of donor - acceptor interaction between HAs and bromanil, the concentration of bound bromanil was calculated by the formula (1):

$$C_b = \frac{A_b}{A_0 - A_b} \times \frac{1}{[HAs]} \quad (1)$$

where C_b is the concentration of bound bromanil; A_b is the optical density of bromanil at the absorption maximum in the presence of humic acids; A_0 is the optical density of pure bromanil at the absorption maximum; $[HAs]$ is the concentration of humic acids ($4 \cdot 10^{-5}$ g / l). The values obtained are presented in the table.

Table 1. Binding ability of humic acids of peats in the relation to bromanil

Preparations	Concentration of the bound bromanil $C_b \cdot 10^{-3}$, mol / dm ³	Bromanil Binding Percentage, %
HAs (SHP)	0,44	14,65±0,02
HAs (STP)	0,54	17,83±0,03
HAs (RFP)	0,36	11,87±0,01
HAs (BFP)	0,33	11,00±0,03
HMAs (STP)	0,30	10,28±0,06
HMAs (BFP)	0,31	10,52±0,05

The percentage of binding of bromanil with humic acids of peast and HMAs has similar values and does not exceed 18%, which indicates a minimal contribution of donor-acceptor interaction in the process of binding polyaromatic hydrocarbons to humic acids. Thus, the leading role in the binding of humic acids to polyaromatic hydrocarbons

belongs to intermolecular hydrophobic interactions, leading to the formation of supramolecular structures between the aromatic "core" of humic acids and polyaromatic hydrocarbons (Fig.3).

Figure 3. The interaction of the fragment of humic acids with naphthalene

The interaction of humic acids with naphthalene is carried out, as we assumed above, due to the penetration of PAH molecules into the cavities and voids of humic acids macromolecules, which are bound exclusively by hydrophobic binding. The interactions of low-aromatic humatomelanic acids with polyaromatic hydrocarbons are carried out between parallel-arranged aromatic structures and condensed PAH rings due to van der Waals forces, which combine several types of intermolecular interactions, namely, π - π -Stacking interaction. To a lesser extent, polyaromatic hydrocarbons interact with aliphatic fragments - the molecular periphery of humic acids. The increase in the proportion of such components in the composition of humic acids and MMC leads to a significant decrease in the binding constant for PAH. The binding is most likely due to Van der Waals forces, in a "plane-to-plane" manner, due to dispersion London forces and hydrophobic effects.

4. Conclusion

To a lesser extent, polyaromatic hydrocarbons interact with aliphatic fragments - the molecular periphery of humic acids. The increase in the proportion of such components in the composition of humic acids and MMC leads to a significant decrease in the binding constant for PAH. The binding is most likely due to Van der Waals forces, in a "plane-to-plane" manner, due to dispersion London forces and hydrophobic effects.

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