

The influence of mechanochemical modification on prevention of toxic ability of humic acids towards phenanthrene in aquatic environment

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Abstract. The aim of the research work is to quantify interaction between phenanthrene with modified humic acids in aquatic environment. The changes in the structure and properties of humic acids after modifications were studied with ¹H NMR spectroscopy and potentiometric titration methods. Our research demonstrates that the application of thiourea as a modified agent increases the binding capacity of humic acids towards phenanthrene.

1. Introduction

Polycyclic aromatic hydrocarbons (PAH) – are organic compounds, consisting of three or more condensed aromatic rings and have particular interests regarding their toxic and cancerogenic properties [1]. Typical representative of PAH is phenanthrene, anthropogenic sources among which are coal tar, oil and products of its processing, cigarettes smoke, etc. Extended exposure to phenanthrene leads to the decrease of the amounts of hemoglobin in the blood and causes leucocytosis [2]. Up-to-date methods to purify water from phenanthrene and its various oxidation compounds are used (water oxidation with ozone, hydrogen peroxide and UV exposure). These methods are not environmentally friendly and costly [3]. Therefore, the effort is going towards finding new methods, which are based on organic compounds, like humic acids (HA).

Humic acids are natural compounds having a detoxifying ability towards organic pollutants. Authors of the research paper [4] for the first time proved the relationship between aromaticity of humic acids and their detoxifying ability towards PAH. Prior research showed that mechanoactivation modifies the content and properties of humic acids, increasing their detoxifying abilities [5, 6].

Therefore, the main purpose of our work is the quantification of interaction of phenanthrene with modified humic acids in aquatic environments.

2. Materials and methods

The research was focused on humic acids, which were extracted from initial transitional peat of Tomsk region (HA1), mechanoactivated without any reagents (HA2) and mechanochemically modified in the presence of thiourea (HA3). Peat was treated in a planetary activator mill rotating at 1820 revolution per minute (RPM).



The influence of the modification on composition and acid-base properties of humic acids was determined in Tomsk Regional Center for Collective Use SB RAS using the methods of ^1H NMR spectroscopy.

The amount of basic oxygen-containing functional groups was estimate using the method of potentiometric titration. The experiment was carried out on Multitest IPL - 103 [7-9]. The degree of dissociation and the dissociation constants of each type of functional groups were calculated according to the Henderson-Hasselbalch equation [5].

3. Results and discussion

Table 1 presents the data concerning changes of fragments compositions of humic acids after mechanochemical modifications. According to our results, the above-mentioned humic acids consist of high amounts of aromatic and carbohydrate portions. After the process of modification the slight decline of the H_α and H_β is occurred, which could be associated with breaks within carbons bonds. At the same time, the increase of aromatic fragments in HA3 structure up to 8% was observed (HAr).

Table 1. The fragment structure of modified humic acids according to ^1H NMR spectroscopy.

Sample	Hydrogen content in structural fragments of HAs, %				
	H_{Ar}	$\text{H}_\alpha\text{-C-Ar,}$ $\text{H}_\alpha\text{-C=C-}$	$\text{H}_\beta\text{-C-C=C-}$	$\text{H}_\gamma\text{-C-R}$	$\text{H}_{\text{carbohyd.}}$
HA1	25.20	18.70	15.10	6.10	34.90
HA2	23.93	16.05	14.75	6.88	38.38
HA3	33.55	15.15	12.98	8.36	29.96

As it shown in table 1, applying thiourea as a modifying agent leads to the increase of acid groups amount, which is caused by air oxidation of HA during the mechanochemical modification of peat. In addition, the table shows that the modification of objects structures leads to the increase of the dissociation constants of HA fragments functional groups, thus weakening their acidic properties and increasing their hydrophobicity in aqueous solutions.

Figure 1 shows the dependence of pH from dissociation of functional groups of HA fragments, exposed to different conditions of modification. The data shows, that modification increases the dissociation of functional groups at the aromatic ring for ArOH and decreases for ArCOOH and CnCOOH comparing to the initial HAs. Thus, aptitude of functional groups of these modified HA is reduced compared to the initial sample.

For the quantity analysis of interaction of phenanthrene with modified humic acids in aquatic environment the methods of molecular spectrophotometry were used. The experiment was conducted to compare the absorbance of the standard and sample solution.

For this purpose, a series of standard solutions of hydro-alcoholic phenanthrene within the concentration range - $\text{C}_0(\text{fen})$ from 0.5×10^{-4} up to 4×10^{-4} g/L were prepared. All measurements were performed on a spectrophotometer Agilent Cary Win. The absorbance of these solutions was measured in the wavelength range from 190 to 400 nm and a thickness of cuvette 1 mm. The results of absorbance dependency of standard solutions of phenanthrene represented from the wavelength are presented in figure 2.

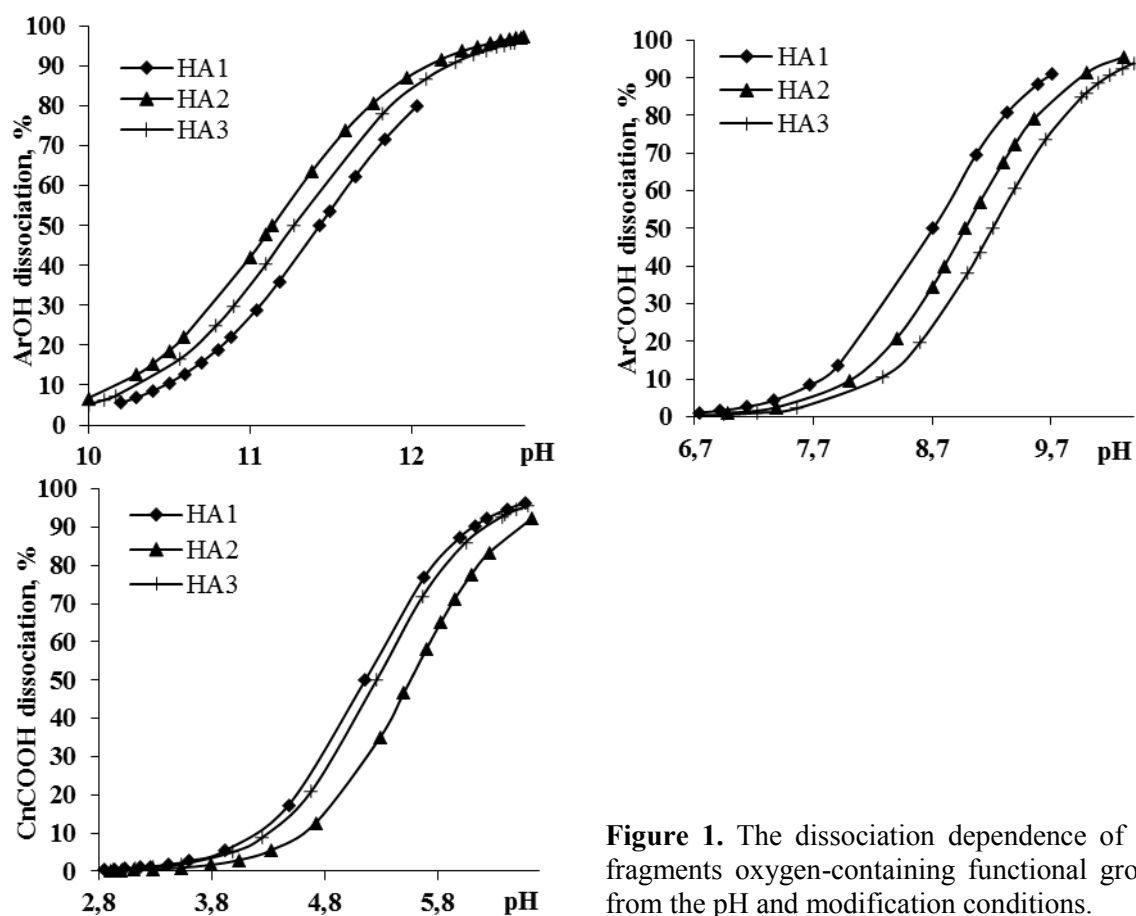


Figure 1. The dissociation dependence of HA fragments oxygen-containing functional groups from the pH and modification conditions.

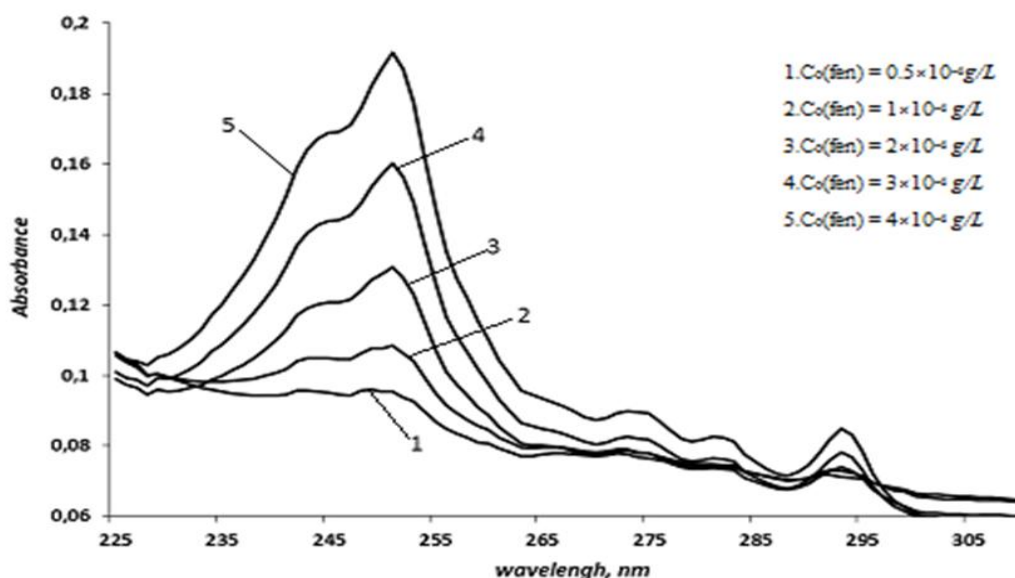


Figure 2. The dependence of the absorbance of the standard solutions of phenanthrene from the wavelength.

To the test solution with a known concentration of phenanthrene the different samples of humic acids with concentration of 0.01 g/L were added, and the absorbance was measured at the same

wavelength. Mathematical treatment of the obtained spectra, comprising the steps of smoothing and consideration of baseline were carried out with the program Assayer.

Table 2 represents the concentration of phenanthrene, absorbed by the molecules. Thereafter, the concentration of phenanthrene, absorbed by the molecules of the modified humic acids is determined by the following equation:

$$C_{abs}(\text{fen}) = 100 \cdot \left[1 - \frac{A_x}{A_0} \right],$$

where A_0 – the optical density of the standard solution of hydro-alcoholic phenanthrene at a wavelength 250 nm, A_x – the optical density of the standard solution of hydro-alcoholic phenanthrene by adding of HA at a wavelength 250 nm.

Table 2. The results of calculation of the absorbed concentration of phenanthrene by humic acids.

$C_0(\text{fen}) \times 10^4, \text{g/L}$	$C_{abs}(\text{fen}), \%$		
	HA1	HA2	HA3
0.5	42.85±5.23*	66.65±4.62	86.67±5.53
1	40.91±5.15	57.89±3.12	61.04±4.05
2	27.50±4.23	30.00±2.82	39.24±3.87
3	21.21±3.70	28.12±1.90	38.28±3.57
4	17.99±1.53	20.69±0.43	26.70±2.35
5	11.76±1.23	19.10±1.52	18.40±2.25
10	9.92±1.45	10.64±0.40	13.85±1.74

* – confidence interval, m = 3, P = 0.95.

The data in the table shows that the application of mechanochemical modification increases the humic acids binding ability towards phenanthrene in the row HA3>HA2>HA1. The application of thiourea as a modifying agent provides the greatest absorption of phenanthrene in $C_0 = 0.5 \times 10^{-4} \text{ g/L}$ with sample HA3 up to 86.66% compared with HA1 (42.85%). With the increase of phenanthrene concentration the residua ratio of toxic substance in the solution increases, which points to the limited absorption capacity of humic acids.

4. Conclusion

The modification of the structure of peat humic acids in the presence of thiourea and mechanochemical action provides an increase in the hydrophobicity of macromolecules structure, increasing the number and availability of aromatic fragments involved in interaction with various PAHs. Phenanthrene as an example we modeled the system and quantified the interaction of the initial and modified HAs with PAH. It was established that modified HA3 bind up to 86.66% of phenanthrene. At the same time, the limited absorbed concentration of toxic PAH by macromolecules HA3 increased up to 40% compared with the initial sample HA1.

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