SORPTION OF ORGANIC DYE METHYLENE BLUE TO HUMIC SUBSTANCES

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Abstract

Humic substances represent a wide range of organic compounds generated by gradual decomposition of plant residues and dead organisms in our ecosystems. They are among the most widespread compounds in the world that contain a huge amount of carbon in its structure. Is contains a lot of functional groups and mainly carboxyl -COOH group. We decided to use humic acid methylation to investigate the effect of the carboxyl group on our experiments.

Humic substances are able to bind various pollutants from Industrial production, agriculture and other human activities (like heavy metals, pesticides, herbicides, dyes, etc.). The interaction possibilities can be different: ion exchange, hydrogen bridge formation, coulombic interactions, hydrogen bridges, van der Waals interactions, hydrophobic interactions, absorption, etc.

The purpose of this work is to measure the decrease of selected initial concentrations of the selected organic dye probe (methylene blue) with a sample of lignitic humic acid and a methylated sample of that humic acid. The obtained humic acid sample will undergo a desorption experiment under the same time conditions. The output of the work will also monitor the ratio between the amount of adsorbed and desorbed methylene blue.

The results can provide more details about the stability dye-humic complexes and the mobility of dye in systems containing humic substances.

Keywords: Humic substances, humic acid, methylation, methylated humic acid, adsorption, desorption

1. INTRODUCTION

As was mentioned, humic acid represents a huge group of carbon contained compounds, which can be find all over the world (water, soil, air). Their structure isn't universal, but it changing with a place of finding and with an origin of the sample. Generally it is a supramolecular structure which contains a huge amount of carbon in its structure. It contains as well wide range of functional groups (carboxyl, phenolic, alcohol, ether, nitrogen, etc.) [1].

In nature humic acids are able to bind various substances from soil - we call this effect soil self-cleaning. It can interact with some herbicides, pesticides, heavy metals, organic dyes, medicines, etc. An adsorption experiments to humic acids can be found in some previous work. The adsorption of methylene blue dye on the pillared clay with immobilized humic acid is 2.6 times more effective, then the pillared clay without humic acid. The maximum dye adsorption on pillared clay with immobilized humic acid was observed at a pH of 5.0-7.0 (it was 95.2 - 99.2 %) [2].

The removal of methylene blue from aqueous solution by peat (with humic substances) was analyzed. Various initial concentrations of methylene blue and temperature were monitored. The absolute amount of adsorbed methylene blue increased with a higher initial dye concentration and rising temperature. It was described as endothermic reaction in which the methylene blue diffuses into the pores after saturation of the outer bonding sites [3].

Humic acid-coated Fe3O4 nanoparticles as magnetic adsorbents were use. Nanoparticles possessed much higher adsorbed amount of humic acid than Fe3O4 nanoparticles and humic acid powder. The time when 50 %

of the methylene blue was adsorbed was 7 min and maximum adsorbed amount of methylene blue was 0.291 mmol/g. [4]

We decided to use humic acid methylation to investigate the effect of the carboxyl group on our experiments. By methylation, the carboxyl groups are blocked and interactions with pollutants are avoided at these active sites. Then it is possible to distinguish them from the other comparisons with humic acids without modification. Diffusions experiments with humic, methylated humic acid and methylene blue with methylene blue bring us inspiration. [5], [6], [7], [8].

For comparison of successful adsorption we done desorption experiments as well.

2. EXPERIMENTAL PART

Our humic acids sample was prepared by extraction from finely granulated South Moravian lignite (Mikulčice, Czech Republic). 60 g of lignite was mixed with 1 dm^3 of concentrated 0.1 M HCl, the suspension was left for 1 hour on the shaker. The decalcified lignite was washed with sufficient distilled water to remove chloride ions. Prepared suspension of lignite was transferred to a plastic container with extraction agent (0.1M sodium hydroxide and 0.1M anhydrous pyrophosphate). The bottle with the extraction agent was left on the shaker for 12 hours.

The suspension was centrifuged and the supernatant (solution of humic acid) was filtered, this filtrate was acidified with hydrochloric acid up to a pH = 2. After two hours, all humic acid had been precipitated, then centrifuged from solution. Solid part (humic acids) were placed into dialysis membrane (MWCO: 3,500; Spectra/Por®, Spectrum laboratories, Inc.) and were immersed in distilled water. The distilled water was regularly replaced with a test for the presence of chloride ions (with $AgNO_3$), after 10 time change it was lyophilized (Virtis benchtop K (Bio Trade s.r.o).

Half of the sample of prepared humic acid was subjected to selective methylation. For 1 g of humic acids were added with 4 cm^3 of chloroform and 2 cm^3 of methanol. Subsequently, 4 cm^3 of a 2M solution of trimethylsilyl diazomethane in hexane (TMS-DM) was added. The mixture was stirred for 2 hours on a mixer in the hood. An additional 0.75 cm^3 TMS-N21 was added after. It was necessary to evaporate the unreacted reagent, the samples were dried overnight in the digester at room temperature.

From the modified acids obtained, it was necessary to evaporate the unreacted reagent. The samples were dried overnight in the digester at room temperature. The picture of obtain humic acid and methylated humic acid can be seen at **Figure 1**.

Figure 1 Picture of color differences (left - humic acid, right - methylated humic acid)

Extracted humic acid and selectively methyleneic acid was subjected to analysis of the FTIR Nicolet iS50 spectrophotometer using the ATR method to determine the spectrum of humic acids and to verify the successful methylation of the prepared sample of methylated humic acids.

For adsorb experiments we used 100 mg of humic acid (HK) and methylated humic acid (mHK), each dissolved in 20 mL of methylene blue of different concentration. The overview of inicial methylen bule concentrations

used for is shown in **Table 1**. The diferences in absorbance were meassured on spektrofotomeher UV-VIS HITACHI U-3900H, up to 288 hours.

Table 1 Initial methylene blue dye concentration used for adsorption experiments

100 mg humic acid with methylen blue	0.1 g/L	0.075 g/L	0.05 g/L	0.025 g/L	0.01 g/L
100 mg methylate humic acid with methylen blue	0.1 g/L	0.075 g/L	0.05 g/L	0.025 g/L	0.01 g/L

After 288 hours, the experiment was stopped. The solid fraction of humic acid/methylated humic acid with adsorbed methylene blue was centrifuged and dryed on the petri dish at room temperature. Then we done desorption expetiments. 10 of obtained samples were desolved each in 10 mL of destilated water. It was observed as well for 288 hours to obtain information about amout of desorbet methylen blue dye. All experiment were realised on laboratory temperature with magnetic stirrer (250 rpm) in vial flask. Picure of dryed samples after adsorption, can be seen on **Figure 2**.

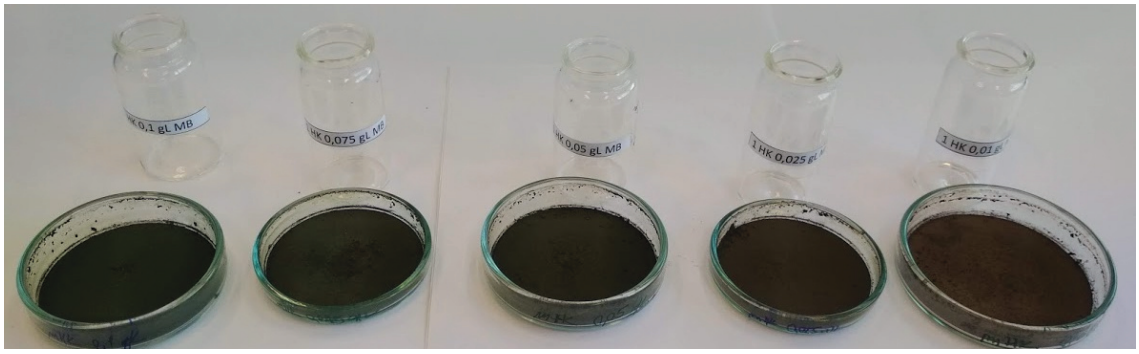

Figure 2 Prepared samples of humic acids after adsorption of methylene blue

3. RESULTS AND DISSCUSION

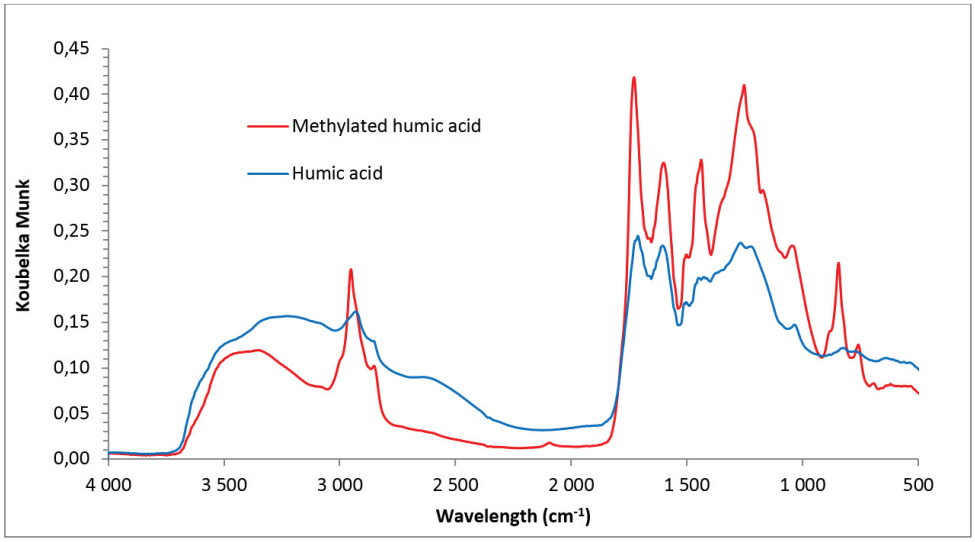

Figure 3 FTIR spectrum -humid acids (blue curve), methylated humic acid (red curve)

Due to FT-IR spectroscopy was confirmed successful methylation of prepared methylated humic acid. On the FT-IR spectra (**Figure 3**) it can be seen, the methylation of functional groups resulted in changes of FT-IR spectra characteristic for esters. The intensity of the broad peak at around 3500 cm^{-1} was decreased by

methylation and the shallow band at 2580 cm^{-1} was completely absent. The absorption band corresponding to C=O stretching was shifted to higher wavenumbers after methylation (from ~1720 cm^{-1} to ~1735 cm^{-1}) and its intensity was increased. The observed changes in spectra caused by methylation corresponded with results published previously. [9], [10].

Adsorption experiments with humic acid was observed via measuring of absorption of methylene blue at peak 665 nm. As can be seen on **Figure 3**, the initial concentration of methylene decreased from 0.002 g of methylene blue (initial concentration) up to 0.001992 g of methylene blue in adsorption to humic acid during 288 hours. Same tendency was observed for all adsorption experiments with humic acid only with different initial concentrations, which are mentioned in **Table 2**.

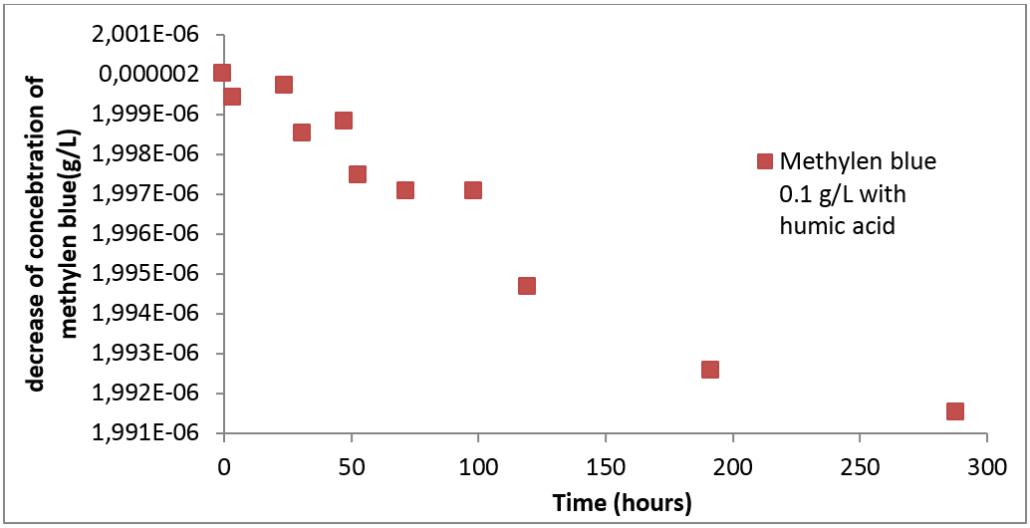

Figure 4 Decreasing of initial concentration of methylene blue with 100 mg of humic acid

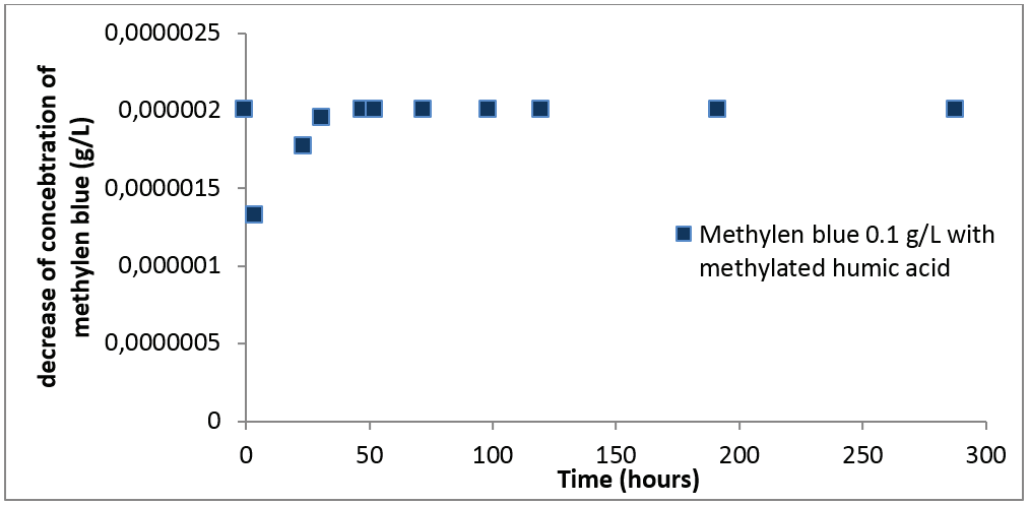

Figure 5 Decreasing of initial concentration of methylene blue with 100 mg with methylated humic acid

Adsorption experiments with selectively methylated humic acid were observed as well. The initial concentration of methylene blue dye had decreased in first 40 hours, but then it increased almost up to the initial concentration of the methylene blue dye. This tendency can be seen on **Figure 5** for initial concentration 0.1 g/L.

As was expected, a lignitc humic acids were able to adsorbed methylene blue dye. The highest adsorption we obtained with initial concentration 0.01 g/L of methylene blue - in this case the concentration of adsorbed dye

rise up to 7.3 %. In case of methylated humic acid, we obtain very low decrement of adsorption, it was able to bind only 0.3 % of dye in case of initial concentration 0.025 and 0.001 g/L. All results can be seen on **Table 2**.

Table 2 Values of adsorbed methylene blue dye into humic acid and methylated humic acids in %

Initial concentration of methylene blue	0.1 g/L	0.075 g/L	0.05 g/L	0.025 g/L	0.01 g/L
Adsorption info 100 mg of humic acid	0.4 %	0.76 %	0.74 %	1.9 %	7.3 %
Adsorption info 100 mg of methylated humic acid	0.1 %	0.1 %	0.1 %	0.3 %	0.3 %

Desorption experiments have provided information on how stable is the adsorption of methylene blue into humic acid and methylated humic acid as well. For 288 hours, we observed concentration of the dye in vial flasks via spectrophotometry. From obtained results is clear that methylene blue dye adsorbed in the first part of experiment partly desorbed. For initial concentration of 0.05 g/L, desorption reached the value 54 % for humic acid and 66.9 % for selectively methylated humic acid. All values are mentioned in the **Table 3.**

Table 3 Table with values of the amount of desorbed methylene blue dye from humic acid in %

Initial concentration of methylene blue	0.1 g/L	0.075 g/L	0.05 g/L	0.025 g/L	0.01 g/L
Desorption from humic acids	34.2 %	31.1 %	54.0 %	46.9 %	24.45 %
Desorption from methylated humic acids	18.4 %	50.0 %	28.6 %	66.7 %	60.0 %

4. CONCLUSION

We prepared sample of humic acid from lignite. Half of prepared humic acid were selectively methylated to block carboxyl groups in its structure. Visually there was a color different of samples and as well due to FT-IR spectroscopy was confirmed successful methylation.

Then we continued with adsorption experiments - humic acid was able to bind up to 7.3 % of dye, methylated humic acid was able to bind maximally 0.3 % of dye. From results is clear that carboxyl groups are mainly responsible for binding with a dye. Because different of binding was big.

Desorption experiment had shown that binding into its structure is week. In case of humic acids it desorbed up to 54 % for concentration 0.01 g/L of dye and in case of methylated humic acid it was 66.7 % for initial concentration 0.025 g/L.

All this experiment bring us interesting data. For future experiment we would like to repeat experiments with same dye and run experiment for longer time. Then retaliate experiment with another type of dye.

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