Characterization of 17α-ethinylestradiol adsorption on DOM using high performance liquid chromatography and fluorescent spectroscopy

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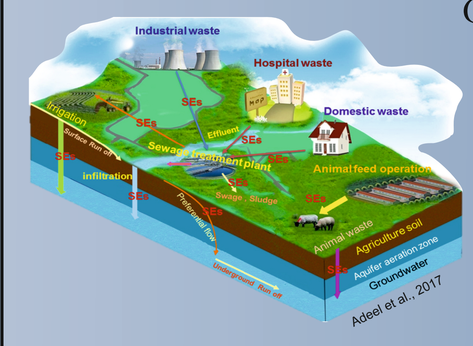
SHORT SUMMARY

1. Estrogenic Endocrine Disrupting Chemicals(EDCs) are becoming one of the major problem in water protection. In this research we choose to study the adsorption processes of EE2 (17-ethinylestradiol) on dissolved FA (fulvic acid) molecules.
2. For adsorbent we use Suwanne River FA standards (from International Humic Substances Society) and a Danube River FA sample (preparation based on Dittmar et al., 2014). An increasing amount of EE2 solution was added to the organic stock solutions, and after dialysis the amount of non-adsorbed EE2 were measured.
3. To measure the EE2 concentrations we used HPLC and calculated the relative adsorption capacity, and the Kd values. To investigate changes in the FA molecules optical properties we took EEM (emission excitation matrix) spectra, and calculated the coble peaks and fluorescent indices.
4. We found, that the fulvic acid adsorbent, which contain more carboxyl groups, have a slightly higher adsorption capacity. Although dissolved fulvic acid molecules have evincible adsorption capacity, its magnitude is negligible compared to solid phase adsorbents. We also found some difference in the optical properties of the FA adsorbents.

1. INTRODUCTION

With the rapid development of the chemical industry along with the pharmaceutics endocrine disruptor chemicals (EDCs) such as estrogens have been released into the aquatic systems in large quantities. Although estrogen compounds has typically low solubility in water (25 mg/l) only a trace amount can cause disturbance in endocrine processes of the wildlife and even human life.



Classical sewage treatment processes are based on physical, biological and chemical processes. These treatments cannot effectively clean the water from these molecules, so the conjugated estrogens enters the environment. Mainly into water bodies. The main problem is, that little is known about the processes that can cause mobility of these substances.

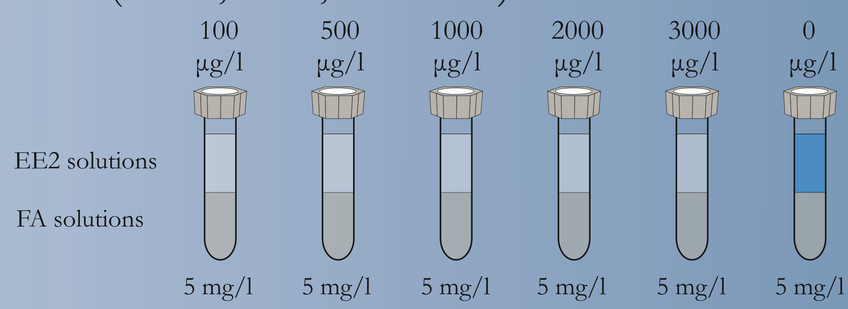
Effectively 3 processes can be used to remove EE2 from water: 1) biotic or abiotic **degradation** 2) **volatilization** into gas phases 3) **adsorption** onto molecules or solid phases. In an aqueous system, besides biotic degradation, adsorption occurs mainly (Feng et al., 2010). In water bodies probably the most effective adsorbents for EDCs are the dissolved organic molecules (DOM).

DOM is a complex of chemically unspecified compounds that are either locally produced or originated from soil. It can be separated into two fractions based on their solubility at a given pH: 1) Humic acid (HA) fraction that precipitated in strongly acidic medium, and 2) Fulvic acid fraction that remained dissolved in both acidic and alkali medium.

2. METHOD

In this research we choose to study the adsorption processes of EE2 (17-ethinylestradiol) on dissolved FA (fulvic acid) molecules.

EE2 was added in different concentrations to each of the dissolved adsorbent (FA III, FA II, DANUBE).



The solutions were shaken for 3 hours.

After that the samples were dialyzed for 72 hours against distilled water in a 1 kDa molecular weight cut off dialysis tube (Bedard et al., 2014).

Blind samples were also prepared to determine whether the organic material passed through the dialysis membrane

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3. MEASUREMENTS

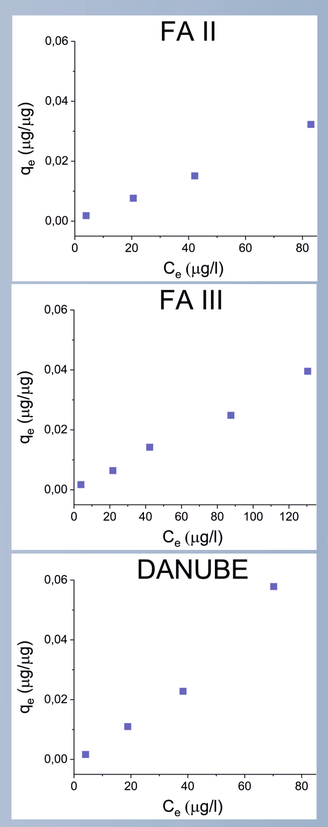
The EE2 concentrations in the dialysis waters were measured by HPLC (fluorescent detector and C18 column).
We calculated the $\mathbf{K_d}$ values (partition coefficient) and the **n, and** $\mathbf{K_F}$ values (relative adsorption capacity) from the Freundlich isotherm.

$$K_{d\ solid} = \frac{C_s}{C_{aq}} \qquad q_e = K_F \cdot c_e^n$$

The changes in the FA fractions were analyzed with fluorescent spectroscopy.
We calculated the HIX, BIX, FI values, and determine the Coble peaks using R-statistics.

$$BIX = \frac{I_{380}}{I_{430}} \quad \lambda_{exc}310 \qquad FI = \frac{I_{450}}{I_{500}} \quad \lambda_{exc}370 \qquad HIX = \frac{\int_{435}^{480} I}{\int_{300}^{345} I} \quad \lambda_{exc}254$$

4. RESULTS and CONCLUSIONS



	k_d	K_F	n (Freundlich)	O/C ratio
FA II	0.0003-0.0008	0.0006 ± 0.0001	1.06 ± 0.04	0.82
FA III	0.0002-0.0004	0.0003 ± 0.0001	0.97 ± 0.06	0.78
DANUBE	0.0004-0.0008	0.0005 ± 0.0002	1.04 ± 0.1	n/a

As the isotherms show there are no significant differences between the 3 fulvic acids adsorption properties.

However, in the case of FA II and DANUBE fulvic acid the K_d values are slightly higher than in FA III. Also the O/C ratio of the FA II is higher than the FA III.

The higher O/C ratio indicates that the molecules are more oxidized, therefore contains more carboxyl groups. The EE2 molecules can attached to the carboxyl groups by hydrogen bond.

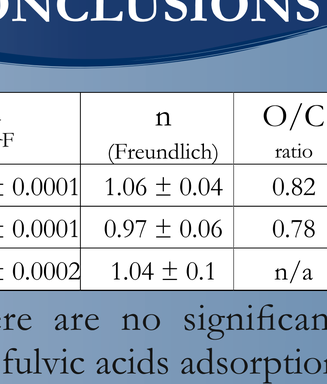
Although dissolved fulvic acid molecules have evincible adsorption capacity, its magnitude is negligible compared to solid phase adsorbents.

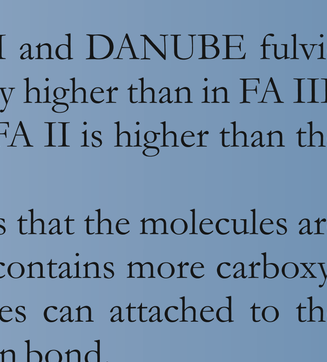
We found strong relationship between the coble peak „b" and „t" (Protein-like organic molecules) and the EE2 concentration in the **dialysis water**.

There are no other differences in the optical properties due to the EE2 concentration in either dialysis water or samples (tube water).

We found correlation between the HIX indices and the EE2 concentrations. The values of the HIX indices are decreasing with the increasing of adsorbed EE2 concentration in the **tube water**.

This can be explained by the fact that the intensity ratio of the peaks "a" and "b" varies with the amount of adsorbed EE2.





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