

The Interaction between Humic Substances and Metals, Depending on Structure and Properties of Humic Substances

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Abstract. It has been widely studied recent as well as historic accumulation of elements in peat profiles depending on intensity of anthropogenic pollution and thereby peat profiles serve as archives for research of environmental change. Peat ability to accumulate major and trace elements depends on the character of element supply, potency of metal ions to bind functionalities in the peat structure, pH reaction, oxygen presence, presence of complexing compounds, inorganic ions and many other factors. It has been hypothesized, that the main factor affecting metal accumulation in peat profile are humic acids (HA). Major and trace element presence in peat are of importance as an indicator of peat genesis and organic matter humification processes and for industrial use of peat. Trace element accumulation in peat profiles has been widely used to reconstruct changes of human pollution and track down sources and characterize intensity of anthropogenic pollution.

Keywords: humic substances, peat, heavy metals, sorption

1. Introduction

Natural organic substances of heterogeneous structure play an important role in the environment, where humic substances (HS) are most prevalent [1]. Humic substances can be found in peat, soil, natural waters, rivers, lakes and marine sediments, lignite, coal, and other natural materials as result of chemical and biological transformation [2]. Formation process of humic substances is related to the humification process, where biomolecules of dead organisms are decaying and transforming. Basic composition of macromolecules of humic substances mainly form condensed aromatic rings, lignin structure elements, alkylaromatic structures, phenols, quinones, which are linked to aliphatic, oxygen, nitrogen or sulfur-containing chemical bonds [3].

It has been shown that humic substances depending on their properties and structural characteristics, has the ability to bind with various metal ions [4]-[6]. Ability to interact with metal ions plays an important role in the environment, which is one of the fundamental research problem of humic substances.

As innovative solutions for the use of peat can be mentioned peat-containing sorbents. Direct chemical modification methods can be used for synthesis of peat-containing sorbents, promoting the use of environmentally friendly solutions and new technological solutions. A variety of iron-containing materials can be used for sorption, iron humates can be synthesized by treatment of humic acids with iron compounds. There are many modification possibilities, as example, saturation of peat humic substances with iron salts, as well iron humate precipitation. Interaction between peat humic substances and pollutants occurs as a result of cation exchange forming chelate complex.

The aim of this study was to analyze peat organic matter diagenesis: changes of properties of humic acids, relations between the humification process, properties of peat, peat HA, their ability to interact with metal ions, as well ability to accumulate metals.

2. Experimental

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2.1. Materials

Analytical quality reagents (Merk Co., Sigma – Aldrich Co., Fluka Chemie AG RdH Laborchemikalien GmbH Co.) were used without further purification. All chemicals used in this study were of analytical quality. For preparation of solutions, high purity water Millipore Elix 3 (Millipore Co.) 10 – 15 MΩcm was used throughout the study.

2.2. Isolation and characterization of humic substances

The analysis was carried out on samples of humic substances preparatively extracted from three ombrotrophic bog peat profiles (Latvia). For isolation of humic substances from bogs, the obtained peat profiles were separated into 10 cm layers, and humic substances were extracted using the procedures recommended by the International Humic Substances Society (IHSS) [7]. Humic substances from waters of the River Daugava (Latvia) were obtained as suggested by Thurman and Malcolm [8]. Commercially obtained TEHUM humic substances (Czech Republic) were used as well.

Elemental analysis (C, H, N, S, O) was carried out using an Elemental Analyzer Model EA – 1108 (Carlo Erba Instruments). Barium hydroxide method [9] was used to estimate the total concentration of carboxylic groups and total acidity.

2.3. Humic substances sorption study

Sorption experiments were carried out using three different origins (peat, aquatic, industrial) of humic substances. Three nanomaterials of colloidal dispersion of 40 % ZnO and nanopowders of Fe₂O₃ and Bi₂O₃ were used. Humic substances from Gagu Bog and TEHUM HS were dissolved in 0.1 M NaOH, but HS from Daugava River were dissolved in 0.1 M Na₂CO₃, afterwards diluted to the necessary concentrations of 30, 20, 10, 5, 1, 0.5 mg/L. In 100 mL glass bottles 5.5 mg of metal oxide (5.5 mL of ZnO stock solution of 10 g/L) was poured with 90 mL of HS solution, adding ionic strength of 10 mL 0.02 M NaCl. Glass bottles were shaken for 1 and 24 hrs at room temperature. Then suspension of HS and nanoparticles was filtered through a double filter paper, poured into in 1-cm plastic cuvette and total dissolved HS analyses of samples were carried out using fluorescence spectrometer (HACH Lange, DR 2800) with a single wavelength (λ) at 450 nm. Measurements of pH values were done before and after poured solutions were shaken.

3. Results and Discussion

3.1. Characterization of major and trace elements

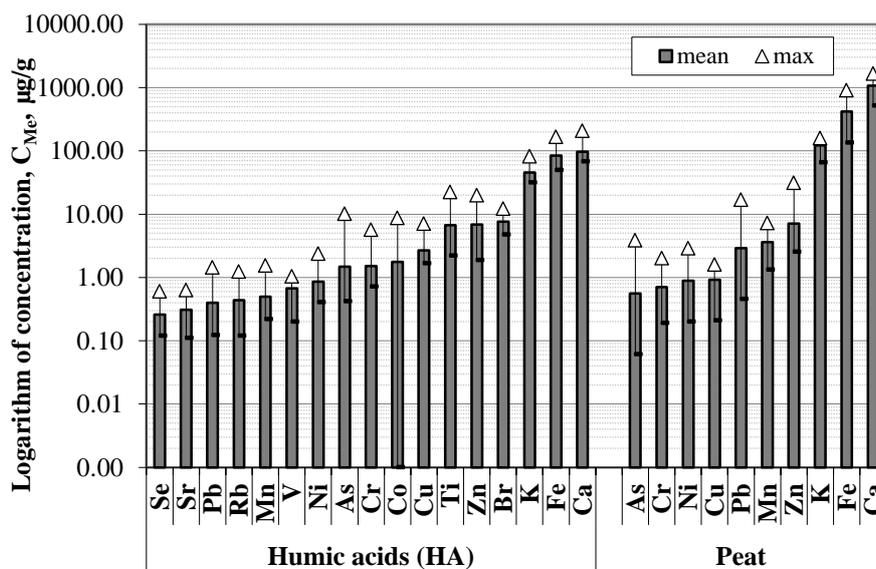


Fig. 1: Content (µg/g) of major and trace elements in peat and in humic acids from Eipurs, Dizpurvs and Dzelve bogs.

It was found that the elemental variability in humic acids of Dzelve, Eipurs and Dizpurvs bogs depend on the peat composition, botanical composition and degree of decomposition, as well as the elemental content in humic acids. The concentrations of 17 elements - Fe, Pb, As, Cu, Ca, Mn, Cr, Ni, K, Zn, Ti, Se, V,

Sr, Co, Rb, Br was determined in humic acids of Dzelve, Eipurs and Dizpurvs bogs (Fig. 1). The prevalence of determined major elements and trace element concentrations have certain distribution pattern in studied bogs, which is unique to high-type bogs. Our study indicates the impact of human-induced pollution on element concentrations in the upper layers of the studied bogs, both in humic substances and in peat (Fig. 1).

Variability analysis of metal content in humic acids of Eipurs and peat bog Dzelve shows that the correlation matrix between metal concentrations in peat bogs and humic substances, was observed in the tightest correlation between iron, zinc, copper and calcium content in peat and humic substances in peat bog Eipurs. The most significant pair correlation in humic acids of Eipurs can be divided into metal pairs copper - chromium and calcium - potassium.

3.2. Complex forming ability of humic acids

Copper stability constants ($\log K=4.06-5.73$) significantly changed within studied bog profiles (Fig. 2), also well correlated with age and decomposition degree of peat layer from which humic acids were isolated, thus stressing the importance of the humification conditions in the bog and, to a lesser extent, of the humic acid precursor living material in the bog botanical composition. Higher complexing stability constants were observed in humic acids of Eipurs bog, due to the active binding with carboxylic groups, as well as a lower amount of aromatic structures.

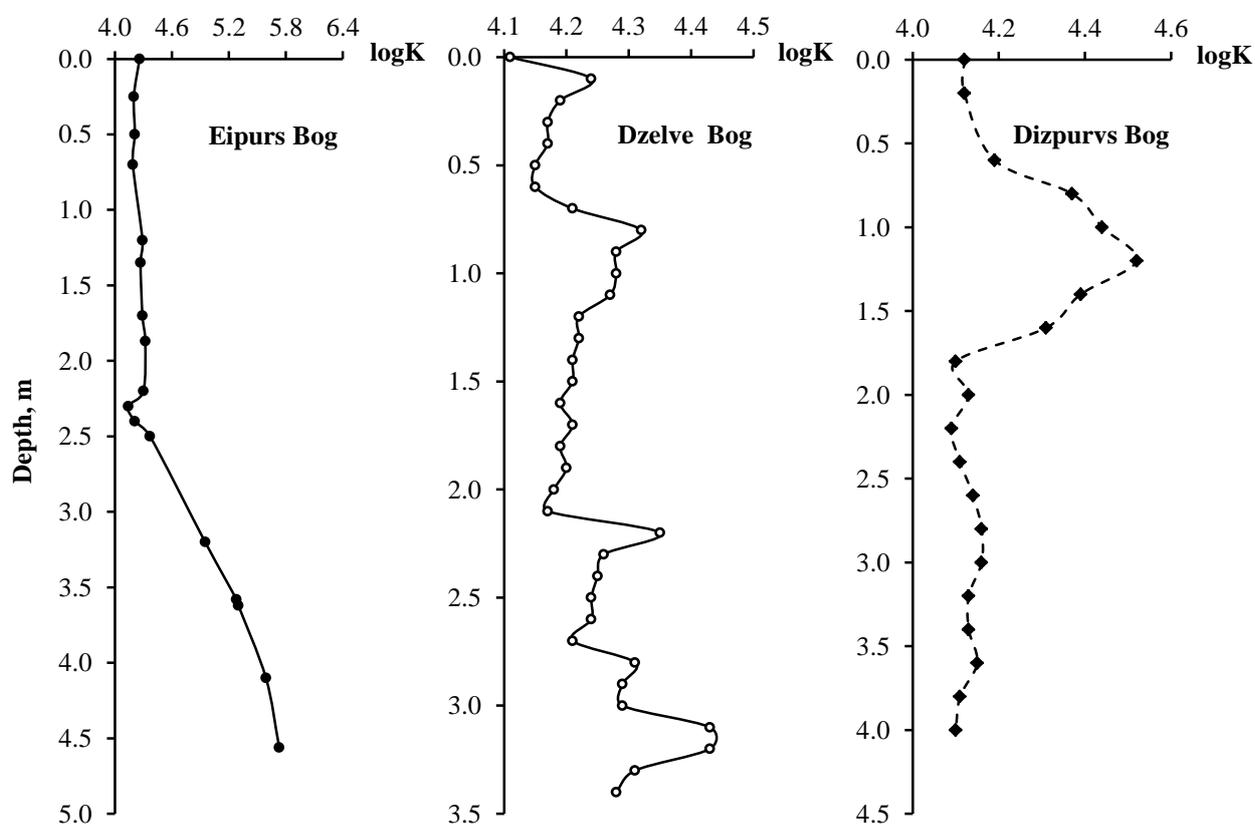


Fig. 2: Copper (Cu^{2+}) complexing stability constants with humic acids of Eipurs, Dzelve and Dizpurvs bogs.

3.3. Sorption studies between HS and metals

Three different origins (peat, aquatic, industrial) of HS samples have been tried out as nano sorbents for the removal of nanoparticles (NPs) of bismuth(III), iron(III) and zinc(II) oxides.

The lowest sorption capacity was noticed with nano-sized Bi oxides (Fig. 3). Utmost sorption capacity at HS concentration of 30 mg/L was determined using peat HS from Gagu Bog (10 mg/g). Either HS isolated from Daugava River and industrial HS showed similar sorption capacity at HS concentration of 30 mg/L, namely, 8.2 and 7.8 mg/g.

Uptake of Fe nanoparticles by varied concentrations of HS solutions is represented in Figure 4. Samples of HS from Gagu Bog and Daugava River indicated similar sorption capacity at HS concentration of 30 mg/L, respectively, 10.7 and 10 mg/g. Lowest sorption capacity was found with industrial HS (7.6 mg/g).

The relatively high sorption on Fe NPs can be related to the neutralization of the positive surface charge of the iron oxide (Fe_2O_3) nanoparticle, because of the sorption of negatively charged HS macromolecules [10].

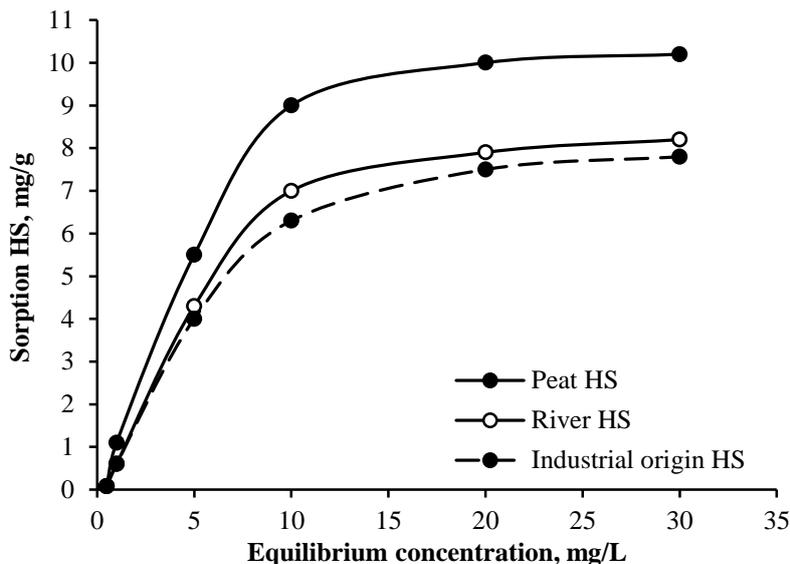


Fig. 3: Sorption isotherms of different origin HS using nanoparticle of bismuth.

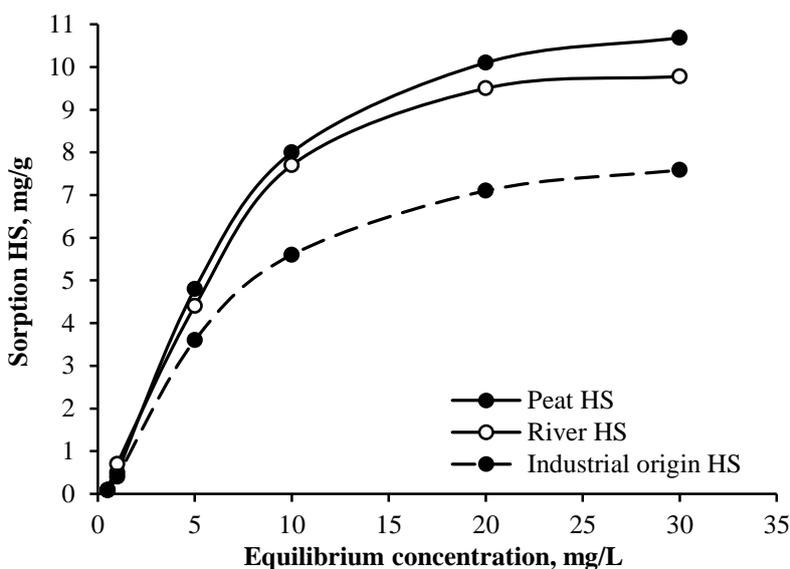


Fig. 4: Sorption isotherms of different origin HS using nanoparticle of iron.

The Zn NPs uptake by studied HS samples in respect to different concentrations of HS solutions is shown in Figure 5. It was found that the difference between sorption capacity of HS can differ by up to 3.5 times when humic substances from different sources were used, suggesting that the sorption capacity strongly depends on the physical and chemical properties of HS.

Peat HS from Gagu Bog (depth of 80-100 cm) showed the highest sorption capacity 14.5 mg/g with nanoparticle of Zn at HS concentration of 30 mg/L. Inferior sorption capacity of 13 mg/g was determined using HS samples isolated from Daugava River and the lowest sorption capacity was observed by industrial origin TEHUM HS (6 mg/g) (Fig. 5).

Ion binding in humic substances is largely dependent on their elemental (carbon, hydrogen, nitrogen) and functional (carboxyl group) composition. The elemental composition of the studied peat HS from Gagu Bog reflects their original material and is characterized by higher values of C (57.75 %), while the content of C in other HS is 51.42 % (Daugava HS) and 50.70 % (TEHUM HS). The values of hydrogen and nitrogen in studied HS vary in similar amplitude. An average concentration of carboxyl group is higher in HS isolated

from the peat, reaching > 4.4 mEq/g, while in the humic substances isolated from Daugava River COOH values reach > 4 mEq/g.

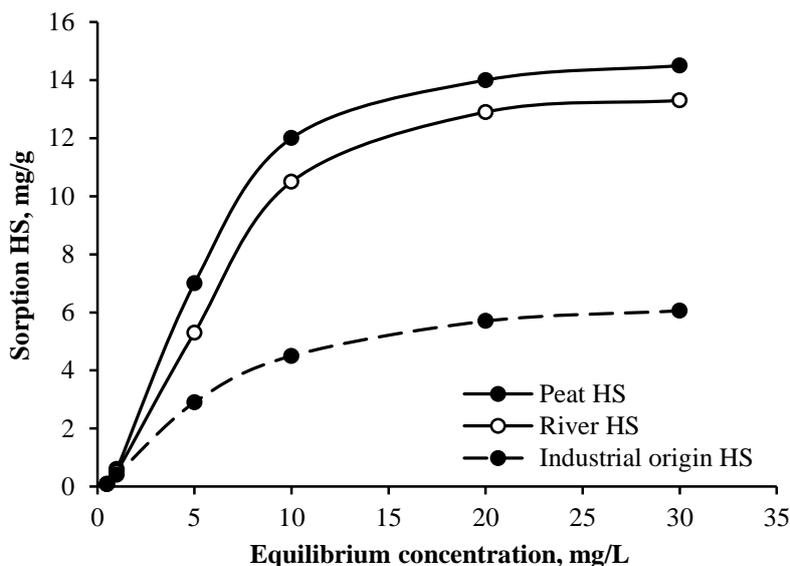


Fig. 5: Sorption isotherms of different origin HS using nanoparticle of zinc.

Notwithstanding, another factor that can affect the sorption process of studied HS with nanoparticles, is various size of NPs. In our study NPs size varies in relatively large amplitude: from 20 - 40 nm (Fe_2O_3), 28 - 56 nm (Bi_2O_3), 40 nm (ZnO). In this aspect, more attention should be paid to physico-chemical characterization of NPs for future study of interaction between NPs and humic substances.

The sorption experiments of different origin HS using nanoparticles indicated that sorption onto peat HS from Gagu Bog is much higher in comparison with HS from other sources. It was found that industrially produced TEHUM HS did not bind so well nanoparticles. The initial pH values significantly vary during sorption process, thence supplementary experiments should be carried out to study the effect of pH on the sorption process, including the study of the sorption kinetics.

4. Conclusions

The main factors affecting the sorption capacity between humic substances and metal ions are physical and chemical properties of HS, elemental (specially, carbon) and functional (carboxyl group) composition, concentration of added HS solution. The results showed that the initial pH values significantly vary during sorption process, but does not affect noticeably the sorption capacity. The obtained results of this study underscore the importance of understanding HS-metal interactions, underlining the importance of humic substances as natural materials in the environment.

The study of the interaction of humic substances of different origin (peat, aquatic, industrial) and three different types of nanomaterials indicates the importance of HS origin towards capacity of nanomaterial sorption, namely, sorption capacity of peat HS from Gagu Bog (Latvia) is much higher in comparison with HS from other sources. The main factors affecting the sorption capacity between humic substances and nanoparticles are physical and chemical properties of HS, elemental and functional composition, concentration of added HS solution. Natural colloids present in the environment in large scale in comparison with NPs, thereby, it is also necessary to understand the behaviour of manufactured nanoparticles. The obtained results of this study underscore the importance of understanding HS-nanoparticle interactions, underlining the important role of humic substances as natural nanomaterials in the environment.

5. Acknowledgments

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