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Effects of selected chemical and physicochemical properties of humic acids from peat soils on their interaction mechanisms with copper ions at various pHs

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ABSTRACT

The main aims of this study were to investigate the interactions of copper ions (Cu(II)) at pH 5 and 7 with humic acids (HAs) isolated from four peat soils at different humification stages, as well as to determine the physico-chemical properties of HAs that may have an influence on the above interactions. For this purpose, a number of parameters were determined for the qualitative and quantitative analysis of peat soils, HAs, and HA-Cu(II) interactions. Processes in the HA-Cu(II) systems were studied using fluorescence spectroscopy (for chemical complexation) and atomic absorption spectrometry with carbon measurements (for coagulation processes). The influence of HA properties on their interactions with Cu(II) ions was evaluated using matrices of correlation coefficients between some HA properties and parameters describing the HA-Cu(II) interactions. Results showed that the complexation capacity was higher at pH 7 than at pH 5. The coagulation mechanism at pH 7 appeared to be based on the precipitation of Cu(II)-humates following the neutralization of HA functional groups by Cu(II) ions, while coagulation at pH 5 appeared to be controlled by the ionic strength. The complexation capacity increased significantly with increasing content of carboxylic and phenolic groups, O/H atomic ratio, degree of internal oxidation and surface negative charge of HAs. The binding of Cu(II) ions was stronger for HAs characterized by a higher aromaticity and humification degree (expressed respectively as absorbance at 280 nm and E4/E6 ratio). The stability constants were higher at pH 7 than at pH 5 and in most cases they did not correlate significantly with HA properties.

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1. Introduction

Humic acids (HAs) are among the most important components of soil in terms of determining its agricultural and environmental properties (Senesi and Loffredo, 1999). In particular, HAs show a high sorption capacity for several cations relevant to agriculture and the environment (Senesi, 1992; Senesi and Loffredo, 2008). Thus, HAs are among the main factors responsible for the concentration, form, mobility and toxicity of metal cations in soils. However, HAs possess a limited sorption capacity, i.e., an excessive dose of metal sorbed on HAs can cause the saturation of HA negative surface charges thus causing their coagulation. As a consequence, the risk arises of metal accumulation in soil precipitated as HA insoluble salts, which may lead to soil pollution and/or micronutrient deficiency for plants.

Copper (Cu) is one of the micronutrients necessary for plant growth, but in too high amounts it becomes a toxic metal. The presence of this metal is especially important in organic soils, where the amount of

HAs is high. Thus together with the low pH typical of these soils, the HA content and state can markedly influence the behavior of Cu (Boguta and Sokołowska, 2013a, 2013b). Furthermore, the ascertained significant variability of physicochemical properties of organic soils is known to affect the properties of their HAs (Boguta and Sokołowska, 2014), which, in turn, is expected to affect the mechanisms of interaction between HAs and Cu(II) ions.

Although the interactions between soil HAs and Cu(II) ions have been studied in the past (Fuentes et al., 2013; Garcia-Mina, 2006; Jerzykiewicz et al., 2002; Senesi, 1992), there are still several contradictory opinions concerning the interaction mechanisms and the influence of HA properties on these interactions. In general, it has been reported that the carboxylic groups of humic acids are mainly responsible for the binding processes with metal ions (Jeong et al., 2007; Rahman et al., 2010). However, other results also indicate both the carboxylic and phenolic functional groups of humic acids are capable of forming complexes (Christl and Kretzschmar, 2007; Christl, 2012; Erdogan et al., 2007; Pehlivan and Arslan, 2006); as well as the possibility of binding metal ions to HA particles by other donor atoms, e.g., nitrogen (Jimoh, 2011; Silva and Oliveira, 2002). Few researchers have studied copper

ion interactions taking into account the complex physicochemical nature of HAs, i.e., their variable composition of carbon, oxygen, hydrogen, nitrogen and other elements as well as their varying degree of structural transformation (i.e., their humification degree, aliphatic and aromatic structures, large variety of functional groups etc.). Moreover, most of the previous studies were based rather on the assumption of only a theoretical, model 1:1 ratio between metal ions and functional groups of humic acids (the simplest model; see Stevenson, 1994; Tipping, 2002). It should also be stressed that there is not much information in the literature about attempts of relating the mechanisms between humic acids and metals to the simple parameters describing humic acids only. Knowledge of such correlations would be helpful to establish a reasonable dosage of copper in soils rich in organic matter.

Taking into account the above arguments, the main aims of this paper are to study the interactions of selected HAs isolated from peat soils at different humification stages with Cu(II) ions at various concentrations (typical in the environment) at pH 5 and 7, and to discover the physicochemical properties of HAs that may have a statistically significant influence on the mechanisms of HA-Cu(II) interactions. A wide range of metal concentrations was chosen, which afforded a comprehensive approach to the problem of the various copper interactions with humic acids, starting from soluble complex formation to the processes of coagulation and flocculation.

2. Materials and methods

2.1. Soils

Four peaty-muck soils (S1 to S4) were collected from various locations at Polesie Lubelskie and the valley of the Biebrza River (East Poland). According to the Okruszko classification (Okruszko, 1976), sample S1 is a peaty muck (Z_1) and the other three soils (S2, S3, S4) are proper mucks (Z_3). Soil S1 at the early mucking stage (MtI) was sampled at depth of 5–10 cm and soils S2, S3 and S4 at a medium mucking stage (MtII) at a depth of 5–20 cm. As the mucking processes of these soils took place in the same climatic zone and under similar humidity and land-forming conditions, the studied samples can be assumed to be distinguished mostly by secondary transformations (Szajdak and Styla, 2010). These can be evaluated by the water absorption index (W_1) determined according to the method of Gawlik (1992), and the stage of the humification processes evaluated by the Springer humification number (H_z). Determination of the H_z index is based on spectrophotometric measurement of humic substance content in an extract obtained after boiling a soil sample in a mixture of 0.5% sodium hydroxide with 0.5% sodium oxalate; absorbance of the extract is recorded at 530 nm, then the H_z degree is calculated using calibration based on HAs standards (Schlichting et al., 1995).

Soil samples were analyzed for a number of properties including: pH, measured in H_2O and 1 M KCl water solution using a digital pH-meter (Radiometer, Copenhagen); total porosity, measured by mercury porosimetry (Autopore IV 9500); bulk density, determined by the pycnometric method; and ash content, calculated by weighing the residue after combustion at 550 °C in a muffle furnace (FCF 12 SP, Czylok). Hydrophobic/hydrophilic properties were evaluated by measuring the contact angles (Θ) (Dang-Vu et al., 2009) using a goniometer apparatus (DSA1, Kruss). The total soil carbon (TC) and organic carbon (TOC) were determined using a C/N analyzer (TOC MULTI N/C 2000, HT 1300, Analytik Jena).

2.2. Humic acids

The extraction of humic acids (HAs) from soil samples was carried out according to a slight modification of the procedure recommended by the International Humic Substances Society (Swift, 1996). Briefly, each air-dried and 2-mm-sieved soil sample was equilibrated at pH 1.0 with 0.1 M HCl at a ratio of 10 cm³ HCl/1 g soil. The suspension

was shaken for 1 h and then the supernatant was separated from the residue by centrifugation at 8000 g for 20 min and discarded. The soil residue was then extracted overnight with 0.1 M NaOH under an N_2 atmosphere and mechanical stirring at a soil:extractant ratio of 1:10. The supernatant was then separated from the residue by centrifugation at 8000 g for 20 min and acidified to pH 1.0 with 6 M HCl. After 12 h the precipitated HAs were centrifuged at 8000 g for 20 min and redissolved by adding a minimum volume of 0.1 M KOH under N_2. Solid KCl was added to attain a concentration of 0.3 M, and then the suspension was centrifuged at 8000 g for 20 min to remove the suspended solids. The HAs were reprecipitated at pH 1.0 by adding 6 M HCl and the suspension was centrifuged at 8000 g for 20 min after 12 h. The HAs were then purified with a 0.1 M HCl/0.3 M HF solution by mechanical shaking overnight. The procedure was repeated until the ash content was set below 1%. The HAs were then washed with distilled water until a negative Cl⁻ test was obtained, and finally lyophilised.

The ash content was determined as the residue obtained after heating a HA sample for 4 h at 550 °C. The elemental (C, H, N) composition was measured by a Perkin-Elmer CHN 2400 analyzer. The oxygen content was calculated by difference: O% = 100% − (H% + C% + N%). The atomic ratios H/C, O/H, O/C, C/N were calculated, as well as the degree of internal oxidation, by Zdanow's formula: $\omega = [(2O + 3N) - H] / C$ (Dębska et al., 2012). Carboxylic groups (COOH), and the sum of carboxylic and phenolic hydroxyl groups (COOH + OH) were determined according to Dragunowa and Kucharenko (Kononowa, 1968). The E_4/E_6 ratio was calculated as the ratio of absorbances at 465 and 665 nm of HA solutions (40 mg dm⁻¹, pH = 8) (Chen et al., 1977). The Kumada parameter (Δlogk) was calculated as the difference of the decimal logarithm of absorbances at 400 and 600 nm: $\Delta logk = logA_{400} - logA_{600}$ (Kumada, 1987). Absorbance at λ = 280 nm was measured according to Traina et al. (1990). The surface charges at pH 5 and 7 (Q5 and Q7) were calculated on the basis of potentiometric titration curves recorded by an automatic titrator (Titrino 702 SM, Metrohm AG) (Matyka-Sarzyńska et al., 2000).

2.3. Interactions of humic acids with copper(II) ions

For complexation studies, three-dimensional fluorescence spectra in the form of excitation-emission matrices (EEM) were recorded for HA solutions to which Cu(II) ions were added at concentrations ranging from 0 to 10 mg dm⁻³ and adjusted to pH 5 and pH 7 with HCl or NaOH solutions. A PerkinElmer (Norwalk, CT) LS 55 luminescence spectrometer was used, setting emission and excitation slits at a 5 nm bandwidth and selecting a scan speed of 1200 nm min⁻¹ for the emission monochromator. The wavelength emission was scanned from 300 to 600 nm, while the excitation wavelength was increased sequentially by 5 nm steps from 250 to 500 nm. The excitation/emission matrices (EEM plots) were generated as contour maps from fluorescence data using the Surfer 8.01 software (Golden Software Inc., Golden, CO) and fluorescence spectra were electronically corrected for instrumental response. The sensitivity and stability of the instrument were previously measured using the Raman band intensity. Two fluorescence peaks (designed as α and β), which changed markedly as a function of Cu(II) concentration, were selected to determine the complexing capacity of HAs and the stability constants of HA-Cu(II) complexes by using the single-site fluorescence quenching model proposed by Ryan and Weber (1982). The relative fluorescence intensity (FI) values (arbitrary units) were also calculated for the two main peaks α and β recorded in EEM spectra of HAs and HA-Cu(II) complexes.

In order to analyze the stability of HA-Cu(II) systems, coagulation studies were conducted in a range of Cu(II) ion concentrations from 0 to 40 mg dm⁻³ at a constant HA concentration. A series of HA solutions containing increasing amounts of Cu(II) ions at pH 5 and 7 were stirred for 24 h. The solutions were then centrifuged at 8000 g for 20 min, and analyzed for their Cu and C contents by atomic absorption spectrometry (AAS, contrAA 300, Analytik, Jena) and C analyzer (Multi NC2000,