



## Hydration and water holding properties of cross-linked lignite humic acids



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### ABSTRACT

Lignite and lignite humic acids, which are used as soil amendments sometimes, are supposed to improve soil properties such as water holding capacity. The structure of those materials is composed of various organic molecules stabilized mostly by weak interactions. Therefore, excess of water causes only partial swelling, but most of the physical structure is destabilized. This accelerates the desiccation and hampers their application as natural hydrogel-like substances. In order to stabilize the structure of lignite humic acids and improve the water holding capacity, we applied formaldehyde cross-linking procedure based on covalent coupling of aromatic humic acids moieties. By combining the <sup>1</sup>H NMR relaxometry and methods of thermal analysis, the kinetics and degree of hydration, water distribution and moisture uptake were investigated. It was found that cross-linking induced a reduction in moisture sorption capacity at low relative humidity and an increase at higher relative humidity, which was attributed to the separation of functional groups and decreasing of structural compactness after cross-linking. As a result, the cross-linked humic acids, exhibited faster water uptake and approximately three-fold higher water holding capacity in comparison with the parental sample. The distribution of relaxation times of water protons in swollen humic acids revealed the unification of pore size distribution upon cross-linking. Although the improved hydration of cross-linked lignite humic acids already resembles the hydration of some hydrophilic polymers, the water holding capacity is still below the capacity of classical hydrogels. Nevertheless, the low price of lignite, sorption properties and its overall positive affect on soil quality and productivity give a promise in application of this material both in agriculture and remediation technologies.

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### 1. Introduction

Intensive agricultural practices together with needs to meet the increasing global food demands are responsible for the desertification processes occurring in the hottest and Southernmost world countries (Kefi et al., 2007). In order to keep soil fertility, both organic and inorganic fertilization practices are traditionally applied. Nowadays, new organic amendments are under consideration. In fact, they are supposed to increase both soil fertility, soil physicochemical characteristics and carbon sequestration, thereby favoring crop productions and preventing emissions of greenhouse gases to the atmosphere (Lehmann and Joseph, 2009). Last decade, among the most studied organic amendments belong chars (or biochars) (Madari et al., 2012), which are carbon-rich products obtained through carbonization of biomasses as it occurs, for example, during pyrolysis and pyrogasification ((Cimò et al., 2014; Conte et al., 2013b; De Pasquale et al., 2012; Knicker, 2010; Knicker et al., 2013). However, also other “cheap and available” carbon-

containing materials deserve special attention. One of the most prominent is lignite, which unlike charcoal, has lower structural integrity, contains high amounts of volatile components and has relatively low carbon/oxygen ratio. The latter is caused by the presence of original, not coalified wooden rests, high content of mineral inclusions and relatively high content of humic substances (HS) (Honek et al., 2009).

Humic substances are versatile materials caused mainly by their polyfunctionality (Nasir et al., 2011b). The functions include a wide range of interactions (Sutton and Sposito, 2005), biological activity (David et al., 2014; Jindo et al., 2012), water holding capacity (Stevenson, 1994). However, the positive effect of humic substances-based amendments in environmental and agricultural applications can be easily reversed. For example, the *S. cerevisiae* D7 tests showed the positive antimutagenic effect of native sodium and potassium salts. However, a short heating of those samples induced a negative effect (Marova et al., 2011). Thus, the humic acids preparation and modification requires a special attention.

Numerous studies have shown that humic substances are capable of altering both the chemical and the physical speciation of the ecotoxicants and affect their bioavailability and toxicity (Simpson and Hatcher, 2004).

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The potential utilization of humic substances originating either from lignite or from other sources in agriculture, in environmental technologies and industry has been reported several times (Bakajova et al., 2011; Ctvrtnickova et al., 2011; Nasir, 2011; Nasir et al., 2011a; von Wandruszka, 2000). Using nitric acid and/or hydrogen peroxide (Kucerek et al., 2003), air (Kučerík et al., 2008) or air oxidation under elevated temperature (Calemma et al., 1994), in lignite, the content of humic acids can be significantly increased. However, the unpredictable behavior and structural heterogeneity are (among others) factors reducing the wider applications of humic substances. Their chemical modification is one of the possibilities, how to enhance and control their reactivity, thermal and chemical resistance, sorption properties and solubility (Ryabova and Mustafina, 2003). In this case, the procedures known from polymer science are frequently applied. For example, modification of humic acids with formaldehyde decreases the solubility, increases sorption capacity for calcium cations, whereas the average ionization constant remains unchanged. Formaldehyde crosslinking causes also redistribution of the electron density in the condensed HA system, thereby enhancing the acid properties of weak acid groups and thus increasing the static exchange capacity (Ryabova and Mustafina, 2003). Another promising direction for controlled cross-linking of humic substances is curing of humic phenol-formaldehyde segments, which enhances their detoxifying ability towards heavy metals (Kovalenko et al., 2006). Using those reactions, additional phenolic and quinonoid moieties can be incorporated into humic backbone (Perminova et al., 2005).

Because the modification of humic substances represents additional costs, it has to improve the targeted properties significantly. One of the most prominent properties of humic substances is the water retention capacity, which is connected with their partial hydrophilicity and porous character (Jaeger et al., 2010). At low water content, the water molecule bridges (WaMB) connect and stabilize the segments of soil organic matter (Aquino et al., 2011; Schaumann and Bertmer, 2008; Schaumann and LeBoeuf, 2005). Increasing water content improves sorption capacity of organic matter towards the non-polar compounds (Borisover, 2013; Borisover and Graber, 2004), which underlines the importance of non-covalent polar links in stabilization of soil organic matter supramolecular structure. Excess of water content breaks those interactions (Kucerek et al., 2012) thereby decreasing the structural compactness. This might cause problems in humic-substances based amendments due to their fast desiccation and uncontrolled water release. From the polymer chemistry point of view, this situation can be improved by introduction of covalent bindings, i.e. cross-linking connecting loosely bound molecules.

The cross-linking plays very likely also a role in the humification of natural organic matter and the diagenesis of organic geopolymers (Grasset and Ambles, 1998; Grasset et al., 2002; Pignatello, 2012). This structural stabilization may be important to the ecological function of humic substances, but this issue has been poorly investigated yet (Schneckenburger et al., 2012). Therefore, the investigation of properties of cross-linked humic substances is beneficial both for understanding of their function and their application potential.

The objective of this study was to test the chemical and physicochemical properties of pre-oxidized and formaldehyde cross-linked humic acids obtained from South Moravian lignite. Further, the detail study on the water holding capacity, hydration mechanisms and water distribution in parental and cross-linked humic acids is presented. Obtained information has the relevance in fundamental research, because it brings new information about the hydration mechanisms of humic acids as well as in technologies related to their industrial and agricultural applications.

## 2. Materials and methods

### 2.1. Extraction, oxidation and modification of humic acids

South Moravian lignite mined in Mikulcice (mine Mir, near Hodonin, Czech Republic) was used as a source of humic acids. Humic acids were

isolated by alkaline extraction. Air-dried lignite fraction was mixed with the aqueous solution of 0.5 mol L<sup>-1</sup> NaOH and 0.1 mol L<sup>-1</sup> Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> and shaken for 3 hours. The suspension was centrifuged and the supernatant was treated with concentrated HCl to reach pH 1 in order to precipitate the humic acid. HA were then treated overnight with a 0.5% (v/v) HCl-HF solution to remove residual ashes, dialyzed (Spectrapore dialysis tubes, 1000 M<sub>w</sub> cut-off) against distilled water until chloride-free, and freeze-dried.

Oxidation of HA was performed as follows: 3 g of humic acids were mixed with 60 mL of different oxidizing agents (H<sub>2</sub>O<sub>2</sub> or HNO<sub>3</sub>) with corresponding concentrations (1 and 3% and 1 and 5% for hydrogen peroxide and nitric acids, respectively) and intensively stirred for 30 min at room temperature. Furthermore, the mixture was 3 times washed by 100 mL of distilled water in order to remove excess of oxidizing agent, filtered and freeze-dried.

Formaldehyde polycondensation was conducted under the conditions reported by (Ryabova and Mustafina, 2003). 0.3 g of humic acids were dispersed in 200 mL distilled water and the pH was adjusted to 7 by 0.1 mol L<sup>-1</sup> NaOH. Further, the catalytic amount of NaOH (0.2 mL, 1 mol L<sup>-1</sup>) was added followed by 1 g of a 35% aqueous solution of formaldehyde. The mixture was stirred for one hour at 60 °C under reflux. The product was treated with the concentrated HCl until pH about 1 in order to precipitate the humic acids. Those were then dialyzed (Spectra/Por® dialysis tubes, 1000 M<sub>w</sub> cut-off) against distilled water until chloride-free and freeze-dried. The cartoon of the reaction for formaldehyde cross-linking inspired by the works of (Perminova and Hatfield, 2005; Ryabova and Mustafina, 2003) is reported in Fig. 1 and the obtained products are listed in Table 1.

The abbreviation of samples has been chosen in this way: original sample without any treatment is abbreviated "ORIG" and its formaldehyde cross-linked derivative is "ORIG\_FM". The modified samples are marked as "OX", the suffix "P" stands for hydrogen peroxide and "N" for nitric acid. The number indicates the concentration of respective oxidizer and suffix "\_FM" means that the modified HA sample was cross-linked as well.

For analyses carried out in liquid state, humic acids were converted into soluble sodium salts. 50 mg of freeze-dried humic acids were suspended in 50 mL of distilled water. Automatic titrator Titroline alpha plus was employed to stepwise titrate the suspension until the humic acids were dissolved and pH reached 7.4. After that the system was let to equilibrate additional 60 minutes, then filtered and freeze-dried. In this way the sodium humates of original, oxidized and modified samples were obtained.

### 2.2. Chemical and physical characterization of humic acids

#### 2.2.1. Fourier transformed infrared spectrometry

FTIR spectroscopy was used to assess the changes in chemical composition of both modified and cross-linked humic samples with respect to the composition of original sample. Conventional KBr pellet technique was employed. From 0.5 to 1 mg of humic samples, previously dried at 105 °C for 4 hours in the oven, were mixed with KBr (1:200 w/w) in an agate mortar. Obtained mixture was squeezed to form a pellet and measured in the FTIR spectrometer Nicolet iS10. FTIR spectrometer was set to 128 scan and resolution was 4 cm<sup>-1</sup> in air dry atmosphere. All obtained FTIR records were elaborated using Omnic 8.0.342 software. For the comparison of intensities of selected bands, the spectra were normalized to overlay the intensities (baselines) at 4000 and 500 cm<sup>-1</sup>, as indicated in (Ctvrtnickova et al., 2011).

#### 2.2.2. Elemental analysis

Elemental analyses (carbon, hydrogen, nitrogen, and sulfur; the content of oxygen was taken as a difference from 100%) were performed on a Perkin Elmer Series II CHNS/O Analyzer 2400 at Engineering Test Institute Brno. Table 1 shows the results of the organic elements on ash- and

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