



Chemical character of humic acids isolated from raised bog

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Summary

Humic acids (HA) extracted from *Eriophorum-Sphagnum* peat of the raised bog were investigated. Peat is used for balneological treatments. HA are characterised by small value of surface area, total pore volume and pore diameter calculated by BET adsorption isotherm. The ion exchange capacity depends mainly on the HA present in the peat. The sorption capacity of peat includes the sorption capacity of HA and other compounds of organic matter. The object of this paper was to investigate chemical properties of *Eriophorum-Sphagnum* HA isolated from raised bog peat and used in balneology.

Key index words: exchange capability, humic acids, sorption capacity, textural parameters

Introduction

The physiological activity of peats is observed in peat-bath therapy of humans and in promotion of growth in some plants (Peña-Méndez, 2005; Szajdak and Maryganova, 2007, 2008). Balneological peat as an ecologically clean and natural substance is more human friendly than synthetic compounds. Poland has a long-term tradition of using the balneological peat (Latour and Ponikowska, 1995; Latour, 2002). Balneological peat has a physical effect through its temperature, and a biochemical effect through biologically active substances (Lukanov *et al.*, 2002). It is mainly used for rheumatic diseases that are also quite common in Poland. The investigations revealed that some extracts from peats, including the fractions of biochemically active humic, fulvic and hymatomelanolic acids, may be used successfully against stress and skin diseases etc. (Beer *et al.*, 2000, 2003). They also have relaxing effects and are efficient in cosmetic, sauna, and spa procedures. Some studies have shown that naturally occurring HA prolong the clotting time of blood in vitro and in vivo. This anticoagulation effect is partially based on the inhibition of activated factor II (F IIa=thrombin), and activated factor X (F Xa), and activated factor VII (F VIIa) (Klöcking *et al.*, 1999, 2004).

Material and methods

Samples of peats were collected from raised bog located near Kołobrzeg, North part of Poland (Table 1). The humification degree (according to Minkina and Valigin, 1939) and botanical composition of peat samples was determined microscopically (Maciak and Liwski, 1996). Isolation of HA was achieved using standard IHSS procedure (Swift, 1996), other chemical parameters were determined using the procedures of Rowell (1994). HA obtained from Fluka was used as standard in the investigations. The soil profile

represents *Eriophorum-Sphagnum* peat (2 m depth) with 50% of decomposition. Some physicochemical characteristics of this soil are given in Table 1. Soil was sampled from 10 sites. Samples were air dried and crushed to pass a 1 mm-mesh sieve. These 10 sub-samples were mixed for the reason of preparing a 'mean sample', which used for the determination of pH (in 1M KCl), content of HA, ash, water, and SiO₂.

Measurements of surface area and porosity

Textural parameters of HA were evaluated from low-temperature (77K) nitrogen adsorption-desorption isotherms. The isotherms of nitrogen-adsorption-desorption on peat HA and the standard of HA are shown in Figure 1, and specific surface and the parameters characterising porous structure of HA are given in Table 2.

Sorption capacity determination

The determination of total sorption capacity of cations by peat was studied according to the procedure described by Hładoń (1980) using buffered 1.0 mol l⁻¹ ammonium acetate solution as an adsorbate. Adsorbed ions were determined as NH₃ by distillation technique. Results of sorption capacity determination are listed in Table 2.

Determination of ion exchange capability

The peat was dried to a constant weight, or 1.0 g of HA was placed in an Erlenmeyer flask of 250 ml in capacity followed by addition of 50.0 ml of 1.0 mol l⁻¹ of sodium chloride solution and vigorous shaking of obtained suspension for 15 min. Then, the suspension was filtered through a sintered glass crucible G-4. The amount of hydrochloric acid formed as a result of the ion exchange was determined in the filtrate by titration. Results are given in Table 3.

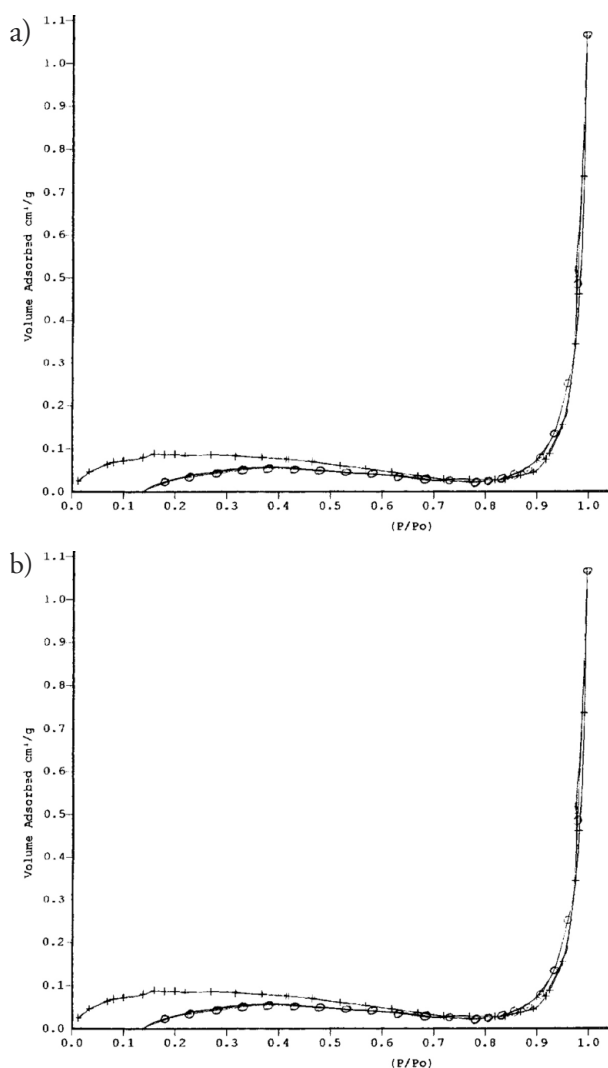


Figure 1. The adsorption isotherm :a) HA isolated from peat; b) Standard of HA

Results and discussion

The examined peat type with pH (in 1 N KCl) 4.0 belongs to very acidic peat types (Table 1). However the content of HA and ash was 47.9 % and 5.2%, respectively. The investigated peat revealed high content of water (90.1%) and low quantities of SiO₂ (0.1%). These properties are typical for raised bog (Szajdak, 2002).

The adsorption and desorption of the compounds in peat are described in terms of equilibrium transfer processes between the compounds in the bulk solution exterior to the

peat particles and the intraparticle liquid phase. Under the condition studied, the processes are controlled either by diffusion rate through the surface film or by diffusion through the interstices of the particles. Properties of pore surfaces control adsorption and transport of water and chemicals in soils. The results on gas adsorption in peat can be compressed into parameters characterizing (i) area available to a particular adsorbate, and (ii) surface roughness or irregularity. Specific surface area is known to be characteristic of the ability of peat to retain and transport nutrients and water. It was revealed that specific surface area of soils correlates with sorptive capacity and ion-exchange capacity, retention and release of chemicals, swelling, water retention, and dry – aggregate stability (Hajnos *et al.*, 2000).

The textural studies were established for the evaluation of the sorption properties of HA. The shape of isotherms of low-temperature adsorption and desorption of nitrogen are sigmoidal, representing BET adsorption isotherm type II, (Fig. 1). It suggests that the nitrogen adsorption is reversible. Thus this indicates that the particles of nonpolar adsorbents are bonded mainly by the adsorbent-adsorbate dispersion interaction. The strength of the interaction of this type is rather low, representing of van der Waal’s forces.

It was shown that the surface area and total pore volume of the HA extracted from peat are smaller than in standard HA, 22% and 19%, respectively, although pore diameter calculated by BET isotherm for HA isolated from peat was 9% bigger than in the standard of HA. The value of the pore diameters of HA both from standard and extracted from peat indicates that they are mesopores (Table 2).

As follows from the textural parameters of the HA, adsorption does not play a significant role in their sorption properties. Due to small specific surface of HA, they have low absorption capacity.

The colloidal fraction, which consists of the humified organic matter of peat, is recognised as the active component in soils, responsible for the sorption capacity. The relative contribution of soil organic matter to cation exchange capacity is largely determined by the amount of soil organic matter, the amount and mineralogy of clay, and the soil pH. For peat soils low in clay, soil organic matter can be responsible for essentially all of soils’s cation exchange capacity (Weil and Magdoff, 2004).

The investigations revealed that the functional groups of the HA significantly participate in the ion exchange interactions. Total sorption volume of HA and ion-exchange capacity was higher than in peat 120 % and 202%, respec-

Table 1. Chemical composition of investigated peat

Depth of sampling m	Peat species, decomposition degree, %	pH in 1N KCl	Content of humic acids [%]	Ash content [%]	Water content [%]	SiO ₂ [%]
0-2	Eriophorum-Sphagnum 50	4.0	47.9	5.2	90.1	0.10



Table 2. The specific surface and porous structure of the HA

Parameter	Standard	HA isolated from peat
Specific surface $S_o(m^2 g^{-1})$	0.50	0.41
Total pore volume ($cm^3 g^{-1}$)	0,00082	0,00069
Pore diameter calculated by BET (Å)	65.0	71.0

Table 3. Total sorption volume and ion-exchange capacity

Sample	Total sorption volume $mmol g^{-1}$	Ion-exchange capacity $mmol g^{-1}$
Peat	0.27	1.78
Humic acids	0.39	3.60

tively. These results suggest that the ion-exchange properties of the peat are almost exclusively determined by those of the HA (Table 3). The investigations revealed that sorption capacity seems to be the main factor responsible for the sorption ability of peat and of the HA. However the study showed that the sorption capacity of the HA is higher than peat. It indicates that other humic substances than HA may adsorb cations.

Conclusions

1. *Eriophorum-Sphagnum* HA has a characteristically low specific surface value, total pore volume and pore diameter calculated by BET adsorption isotherm.
2. Ion exchange capacity is mainly depended of the HA presented in *Eriophorum-Sphagnum* peat.
3. The sorption capacity of peat includes the sorption capacity of HA and other compounds of organic matter.

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