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NITROGEN ADSORPTION STUDY OF THE SURFACE PROPERTIES OF THE SECONDARY TRANSFORMED PEAT-MOORSH SOILS*

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A b s t r a c t. The influence of moorshing processes of peat soils on nitrogen adsorption and on specific surface area was investigated. Soil samples for study were taken from differently moorshified peat-moorsh soils, characterizing by W_1 index ranged from 0.44 to 0.82. The samples represented two kinds of moorsh formations, i.e., peaty moorsh (Z_1) and propert moorsh (Z_3). Nitrogen adsorption measurements at 77 K were used for determining the surface area and pore volume. The Brunauer-Emmett-Teller (BET) method was used as the standard procedure for determination of the surface area. The adsorption and desorption isotherms of N_2 on peat-muck soils at 77 K exhibited similar shape and all belonged to the type II, according to BET classification. The adsorption increased in the series of the soil samples Nos 11<1<13<12 and 10<5<6<8 for the peaty moorsh (Z_1) and for the proper moorsh (Z_3), respectively. The above series agreed with the changes of the index of the secondary transformation, W_1, except for the samples Nos 12 and 5. The nitrogen-BET specific surface area of soil samples ranged from 2.45 to 4.90 m^2 g^{-1}, and no direct relation between the surface area and the index of the secondary transformation, W_1, was found. When soil samples are first grouped into the classes Z_1 and Z_3, and then, for each group, arranged according to the value of the index W_1, the relationship between W_1 and the specific surface area became more visible. Generally, for the proper moorsh (Z_3), an increase of the nitrogen-BET surface area and a decrease of the pore volume were correlated with the increase of the W_1 index (except for the samples Nos 8 and 5). In the case of the peaty moorsh (Z_1) a decrease of the nitrogen-BET surface area and an increase of the pore volume were connected with the increase of the W_1 index, (except for the samples Nos 12 and 13).

K e y w o r d s: peat-moorsh soils, nitrogen adsorption, surface properties

INTRODUCTION

Peat is an inexpensive, naturally occurring, plant derived organic sediment. The natural abundance and low cost of peat make it a favourable medium for the use in ground and wastewater remediation [5-7] or for the amelioration [14,22].

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A peat was used as a model for soil organic matter which is recognized as the predominant, high surface area sorbent for sorption of nonionic organic contaminants from water [3,12,15].

Nitrogen adsorption measurements at 77 K are widely used for determining the surface area and the pore size distribution of different solid materials. The measurement of adsorption at the gas-solid interface is also an essential part of the most fundamental and applied research on the nature and behaviour of solid surfaces. The Brunauer-Emmett-Teller (BET) gas adsorption theory has become the most widely used standard procedure for determination of the surface area of finely divided and porous materials [13,19,28].

The peat-moorsh soils contain high amount of different organic compounds [31] which strongly influence their properties, especially the specific surface area [2-4,8,21,27,29,32]. The aim of this work was to estimate the effect of the mucking processes occuring in peat soils on nitrogen adsorption and on specific surface area.

MATERIALS AND METHODS

The soil materials represent different kinds of moorsh formation, as the peaty moorsh (Z_1) and proper moorsh (Z_3) according to Okruszko [17,18], or peat weakly secondary transformed (W_1=0.41-0.50), medium secondary transformed (W_1=0.51-0.60), strongly secondary transformed (W_1=0.61-0.70), very strongly secondary transformed (W_1=0.71-0.80) and completely degraded (W_1>0.80), according to the index of the secondary transformation, W_1, [9-11]. The peat soil samples have been taken from the Polesie Lubelskie Region and from the Biebrza River Valley from a depth 0-10 cm, or 5-20 cm in the case of strongly moorshified peat soils. The material was carefully mixed, and after removing the plant roots was sieved with a sieve of mesh size 1 mm. The selected properties of peaty-moorsh soils are collected in Table 1.

The adsorption - desorption isotherms of nitrogen gas at liquid nitrogen temperature, 77 K, were obtained with Sorptomatic 1999 (Fisons) apparatus. Before adsorption measurements, the peat samples were dried at 105 ^{o}C and outgassed overnight at 105 ^{o}C under a vacuum.

The surface area particular peat-moorsh soil samples was evaluated from the adsorption-desorption isotherms using the BET equation. It is now generally accepted to use the BET method to determine the specific surface area from physical adsorption data [13,19]. The first step in BET method is determination of the monolayer capacity (N_m) from the BET plot. The monolayer capacity is defined as the quantity of the adsorbate that can be accommodated in a completely filled, single layer of molecules (the monolayer) on the surface of the solid. The specific surface

Table 1. Some selected properties of investigated peat-moorsh soil samples

No. of soil	W_1	Z^*	Ash content	Bulk density	Total porosity	pH		Total amino acids**	***C_{org}	Humic acids***	Fulvic acids***
			% d.m.	g cm^{-3}	vol. %	H_2O	KCl	g kg^{-1}	% d.m.	% C_{org}	% Corg
12	0.44	Z_1	22.69	0.21	88.5	5.13	4.54	5.21	34.77	38.66	8.84
11	0.48	Z_1	20.54	0.28	84.7	4.72	4.23	7.57	36.03	39.83	8.71
1	0.55	Z_1	17.56	0.25	84.6	5.48	5.18	8.13	38.52	23.72	8.09
10	0.60	Z_3	2.24	0.34	81.4	5.44	4.97	8.27	37.81	42.16	10.18
13	0.61	Z_1	15.14	0.24	85.2	5.84	5.33	8.45	39.37	25.89	11.49
6	0.65	Z_3	20.52	0.32	82.5	5.38	4.93	9.78	40.35	35.22	8.06
8	0.71	Z_3	22.77	0.30	83.6	6.15	5.75	11.3	37.13	36.22	11.67
5	0.82	Z_3	22.27	0.39	78.7	5.54	5.00	18.5	39.78	37.87	7.93

Explanations: Z^* - kind of moorsh according to Okruszko; W_1 - the index of the secondary transformation, according to Gawlik; C_{org} -organic carbon; ** - adapted from Szajdak *et al.* [31]; *** - Bambalov and Belenkaya method [1], adapted from Lishtvan *et al.* [16].

area (S_N) is directly proportional to the monolayer capacity, and is calculated from the dependence: $S_N=N_mL\omega$, where L is the Avogadro number and ω is the molecule cross-sectional area (ω=16.210^{-20} m^2 for nitrogen molecule).

RESULTS AND DISCUSSION

The adsorption and desorption isotherms of N_2 on peat-moorsh soils at 77 K are shown in Fig. 1. All curves have similar shape and belong to the type II, according to the BET classification. Characteristic feature of the type II isotherms is the hysteresis loop, associated with the capillary condensation, taking place in mesopores. The hysteresis loops shown here are of the type H_3, i.e., they do not exhibit any limiting adsorption at high p/p_o and can be attributed to slit-shaped pores [28]. The adsorption increases in the order of the soil samples Nos 11<1<13<12 and 10<5<6<8 for the peaty moorsh (Z_1) and for the proper moorsh (Z_3), respectively (cf. Fig. 1). Except for the samples Nos 12 and 5, which are characterised by the lowest and the highest values of W_1, the above series agree with the changes of the index of the secondary transformation, W_1. The samples Nos 12 and 5 are weakly secondary transformed peat (the sample No. 12) and completely degraded peat (the sample No. 5).

Table 2 collects the parameters of BET equation, evaluated from the experimental data in the range of the relative pressures $0<p/p_o<0.35$; the total amount of the adsorbed nitrogen and the results of the specific surface area.

Many attempts have been made to calculate the mesopore size distribution from physisorption isotherms [13,23,28]. The total pore volume is often derived from the total amount of adsorbed N_2 at a relative pressure close to unity, by assuming

T a b l e 2. The parameters of the BET equation in range $0<p/p_o<.35$, the total amount of the adsorbed nitrogen, pore volume and the specific surface area for the investigated peat-moorsh soils

No. of soil	W_1	Z^*	N_m $cm^3\ g^{-1}$	C_{BET}	S_{n2} $m^2\ g^{-1}$	N_2-tot. $cm^3\ g^{-1}$	*Specific pore volume $cm^3\ g^{-1}$	Micropore volume $cm^3\ g^{-1}$
12	0.44	Z_1	1.01	5.88	4.38	17.53	7.24E-03	1.26E-03
11	0.48	Z_1	0.80	4.22	3.50	11.00	4.09E-03	6.55E-04
1	0.55	Z_1	0.75	5.51	3.25	13.17	4.81E-03	9.21E-04
10	0.60	Z_3	0.56	7.60	2.45	25.71	6.03E-03	8.24E-04
13	0.61	Z_1	0.85	5.24	3.68	17.39	5.22E-03	1.01E-03
6	0.65	Z_3	0.67	6.40	2.29	10.62	4.61E-03	7.46E-04
8	0.71	Z_3	1.12	3.44	4.90	9.38	5.82E-03	1.07E-03
5	0.82	Z_3	0.62	7.11	2.69	11.26	3.90E-03	7.40E-04

Explanations: see Table 1; N_m - monolayer capacity; N_2-tot. - total nitrogen adsorbed at $p/p_o=0.98$; * - at $p/p_o=0.98$.

that the pores are than filled with liquid adsorbate. The macropore volume is often obtained from the Dubinin-Radushkevich (DR) equation, applied to adsorption isothermal data over a limited range of the relative pressures, p/p_o (below the onset of capillary condensation). The estimated volumes of meso- and micropore are also shown in Table 2. The specific pore volume for investigated peat-muck soils increases in the order: 5<11<6<1<13<8<10<12 and some, an unequivocal relationship between the pore volume and the secondary transformation index has been found. The micropore volume for soil samples increases in the series: 11<5<6<10<1<13<8<12. Generally, both pore volumes for samples Z_1 increase with the W_1 index increase, except for the sample No. 12. In the case of the samples Z_3, the specific pore volume and the micropore volume increase if the W_1 index decreases, except for the sample No. 8.

Nitrogen surface areas were determined by BET analysis of the adsorption data. In all cases, the correlation coefficient for the fit of the BET equation to adsorption data was higher than 0.997. The results of the BET monolayer adsorption capacities (N_m) and the parameters C of the BET equation are given in Table 2. The nitrogen-BET specific surface areas for peat-moorsh soil samples ranged from 2.45 to 4.90 $m^2\ g^{-1}$ (cf. Table 2). These values are higher than those reported by other authors [4,21,24,25]. The N_2-surface area of the studied samples increases in the following way: 10<5<6<1<11<13<12<8. The samples Nos 10, 5 and 6 (Fig. 2) exhibit the lowest values of the surface area. Unfortunately, no streight dependence between the surface area and the W_1 index of the secondary transformation has been found.

However, when the soil samples are first grouped according to the kind of moorsh formation, i.e., into groups Z_1 and Z_3, and then ordered according to increasing value of the W_1, a dependence of W_1 and the specific surface area becomes

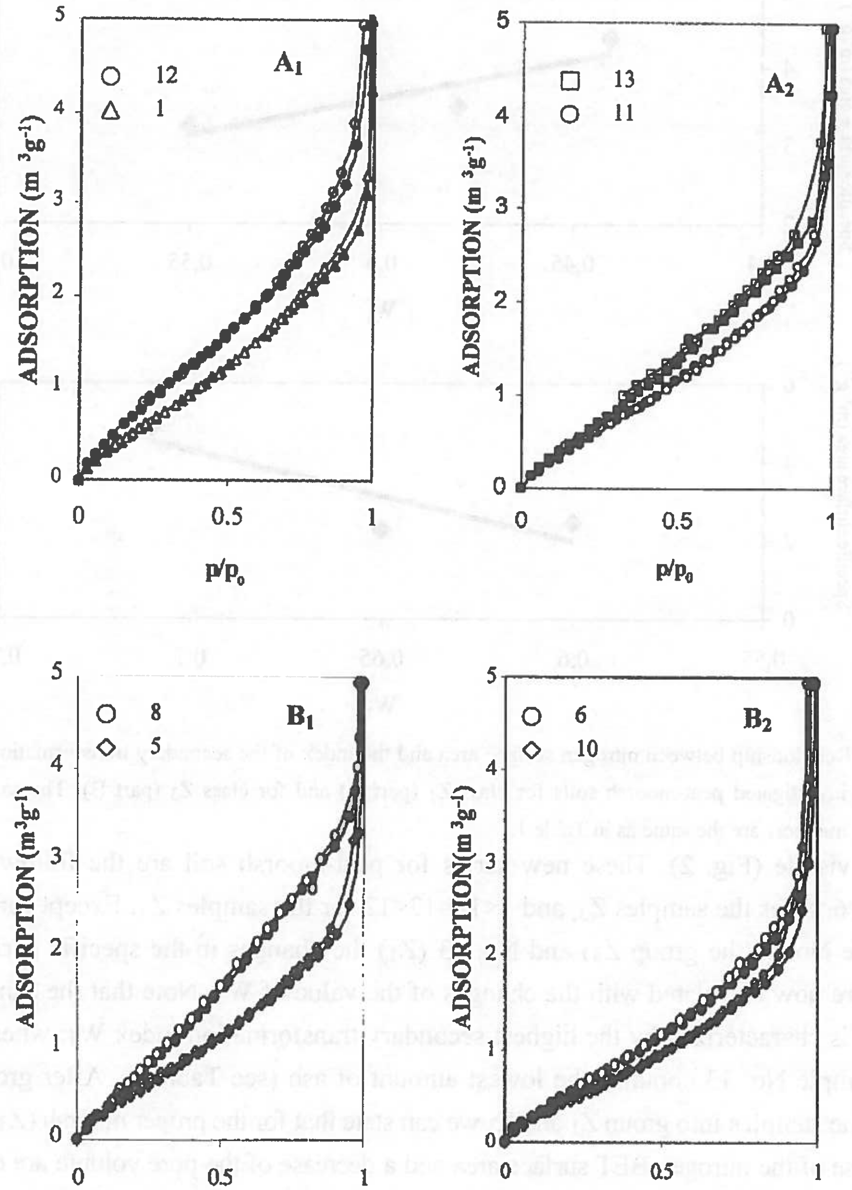

Fig. 1. Nitrogen adsorption-desorption isotherms for investigated peat-moorsh soils for class Z_1 (part A_1 and A_2) and Z_3 (part B_1 and B_2); white symbols - adsorption branch and black symbols - desorption branch The sample numbers are the same as in Table 1.

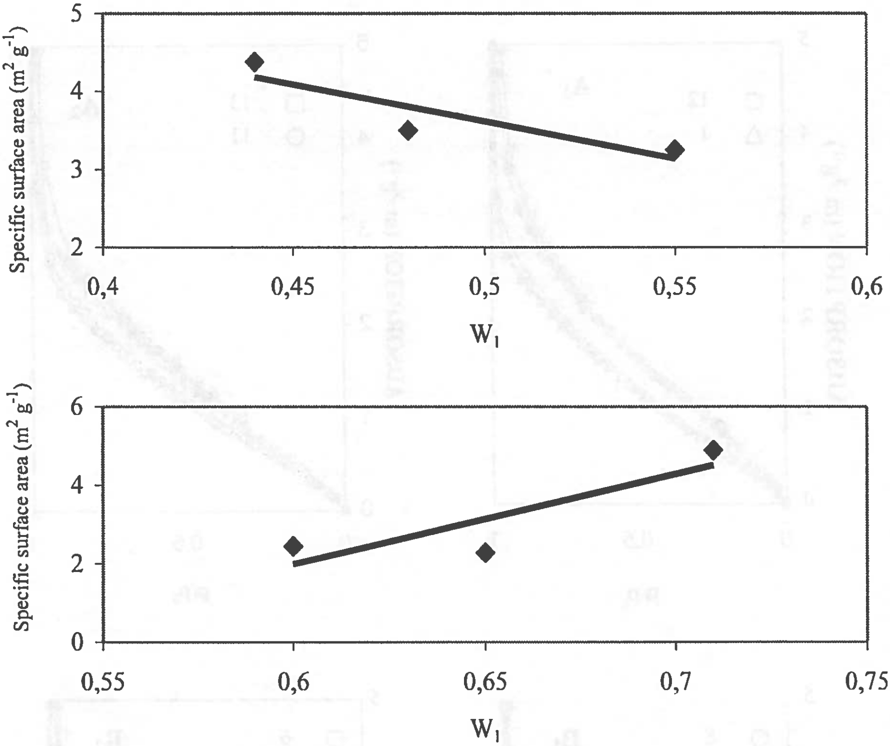

Fig. 2. Relationship between nitrogen surface area and the index of the secondary transformation for investigated peat-moorsh soils for class Z_1 (part A) and for class Z_3 (part B). The sample numbers are the same as in Table 1.

more visible (Fig. 2). These new series for peat-moorsh soil are the following: 10<5<6<8 for the samples Z_3, and 1<11<13<12 for the samples Z_1. Except for the sample No. 5 (the group Z_3) and No. 13 (Z_1) the changes in the specific surface area are now correlated with the changes of the value of W_1. Note that the sample No. 5 is characterized by the highest secondary transformation index W_1, whereas the sample No. 13 contains the lowest amount of ash (see Table 1). After grouping the samples into group Z_1 and Z_3 we can state that for the proper moorsh (Z_3) an increase of the nitrogen-BET surface area and a decrease of the pore volume are connected with the increase of the W_1 index, except for the samples Nos 8 and 5. In the case of the peaty-moorsh (Z_1) a decrease of the nitrogen-BET surface area and an increase of the pore volume are connected with the increase of the W_1 index, except for the samples Nos 12 and 13. The samples denoted 8, 5 and 12, 13, belonging to Z_3 and Z_1 class, exhibit significant difference in their properties (see Tables 1 and 2).

Obviously, adsorption of nitrogen and surface area depend on the nature of the peat soils. Different kinds of functional groups have been identified in natural organic matter coming from different sources. The most important are the carboxylic-, phenoloc-, hydroxylic groups [20,26,31,33]. Nitrogen and sulphur-containing functional groups, such as amino-, imino- and sulphonic acid groups may also be present in smaller quantities [30,31]. The basic components of organic matter are the humic-, fulvic acids and the humin. These compounds possesse functional groups, which form polar and nonpolar adsorption centres that can be involved in chemical bonding. The fulvic and humic acids contain in average 13.4 % carboxyl C, 14.3 % aromatic C, 23.0 % aliphatic C, 49.3 % C-O and C-N-C of the constituents groups, respectively [20]. In the adsorption process of nitrogen the adsorption centres play a smaller role than the porous structure because nitrogen is an inert adsorbate. Chiou *et al.* [4] used the standard BET method to measure the surface areas of high organic content soils and humic acids extracted from soil and discussed the mechanical uptake of organic compounds by soil organic matter in terms of the surface areas as determined by N_2-BET and ethylene glycol retention methods. For surface area determined by N_2-BET method Chiou *et al.* [4] used the term "free surface area". The free surface area corresponds to the interfacial area of a solid, which exists before the adsorption and unequivocally measured by an adsorbate that does not change the structure of the solid.

CONCLUSION

All adsorption isotherms were similar shape and belong to the type II, according to the BET classification. Their hysteresis loops are of the type H_3. The adsorption isotherms increase in the series 11<1<13<12 and 10<5<6<8 for the peaty moorsh (Z_1) and the proper moorsh (Z_3), respectively. Generally, these series agree with the index of the secondary transformation, W_1, except for the samples Nos 12 and 5. The nitrogen-BET specific surface areas for peat-moorsh soil samples range from 2.45 to 4.90 $m^2 g^{-1}$. Any directly relationship between surface area and W_1 index of secondary transformation has been found. If the soil samples are grouped according to the kind of morsh formation Z_1 and Z_3, and then within the group with increasing value of the W_1 index, a dependence between W_1 and specific surface area is better visible. For the proper moorsh (Z_3) an increase in the nitrogen-BET surface area and a decrease in the pore volume are connected with the increase of the W_1 index, except for the samples Nos 8 and 5. In the case of the peaty moorsh (Z_1) a decrease of the nitrogen-BET surface area and an increase of the pore volu-me are connected with the increase of the W_1 index, except for the samples Nos 12 and 13. The samples Nos 8, 5 and 12, 13 belonging, respectively to Z_3 and Z_1 classes, exhibit significant difference in their properties. Both classifications of the secondary transformation of the peat-moorsh soils, i.e., Z_1-Z_2-Z_3 according to Okruszko and W_1 index according to Gawlik, should be used simultaneously.

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