EFFECT OF SECONDARY TRANSFORMATION STATE OF PEATY-MOORSH SOILS ON ADSORPTION ISOTHERM OF WATER VAPOUR*

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A b s t r a c t. Water vapour adsorption on peat-moorsh soils in various phases of the moorshing process was investigated. The soil material represented two kinds of moorsh: peaty moorsh (Z_1) and proper moorsh (Z_3) characterizing different classes of peat transformation, i.e., 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). The Brunauer-Emmet and Teller (BET) equation was used to analyse the experimental adsorption results and to calculate the specific surface area from both adsorption and desorption isotherms. Generally, the values of the specific surface area obtained from desorption isotherms were higher than those obtained from sorption curves. The shape of all curves was similar; i.e., all the curves belonged to the same class of isotherms according to the BET classification. The values of the correlation coefficient, R, indicated that the BET equation provided a good fit to the experimental data. For all studied samples the BET specific surface area estimated from the sorption isotherm ranged between 250 and 340 m^2 g^{-1} and between 320-460 m^2 g^{-1}, if the desorption isotherms were used. The average BET specific surface area for the samples of the peaty moorsh (Z_1) and the proper moorsh (Z_3) were similar. The relationship between surface area and water holding capacity index W_1, characterising the state of the secondary transformation was found.

K e y w o r d s: agrophysics, peat-moorsh soils, adsorption of water vapour, specific surface area

INTRODUCTION

The transformation of plant material in hydrogenic sites like marsh or swamps, where anaerobiosis conditions are predominant, lead to formation of peat deposits

in which peat mass of different decomposition degree and properties are accumulated.

After drainage, peat mass undergoes processes of secondary transformation and it is changed into moorsh, which differ from peat in many respects [15,16]. One of these differences concerns water-holding capacity, and since this quantity in the case of moorsh formations is gradually lessen with worsening of soil-water conditions and the passage of time, it was used as the base for a classification of secondary transformed peat formations (moorshes). The classification comprises six classes which are define on index of water retainability defined by symbol W_1 [6-8].

This index ranges from 0.17 to 1.0 and increases with the degree of peat transformation. The first class (W_1=0.36-0.40) represents peat at the initial stage of the secondary transformation, the last class (W_1=0.80) consists of the completely degraded peat. Se-condary transformation process, that occurs in organic materials of drained peat soils causes changes in their properties, and thereby the primary character of the soils formed from these materials is also changed [9,10,23].

Adsorption is a process widely used for characterization of solid surfaces, particularly, for the determination of the specific surface area [12,17]. The moorshing process influences positively, to some extent, the surface area of peat materials [21,23].

In this work we report the studies of water vapour adsorption on peat-moorsh soils in various phases of the moorshing process. The Brunauer-Emmet and Teller (BET) [3] equation is used to analyse the experimental adsorption results and to calculate the specific surface area from both adsorption and desorption isotherms.

MATERIALS AND METHODS

The peat soil samples were taken from Polesie Lubelskie Region and in the Biebrza River Valley. The soil samples were collected of the depth 0-10 cm (weakly moorshed soils) and 5-20 cm (medium and strongly moorshed soils). According to Okruszko [16] the soil material represented two kinds of moorsh: peaty moorsh (Z_1) and proper moorsh (Z_3), which characterized different classes of the peat transformation. There were peat formation 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) [6,9]. Some selected properties of peat-moorsh soils are collected in Table 1.

The surface area of soil samples was evaluated from adsorption-desorption isotherms. It is now generally accepted to use the BET method to derive the specific surface area from physical adsorption data [3,5,17,22]. The first step in the application

T a b l e 1. Some physical and chemical properties of peat-moorsh soil samples

No. of soil	W_1	Kind* of moorsh	Ash content % d.m.	Bulk density g cm^{-3}	Total porosity vol. %	pH		mg 100 g^{-1} of soil			mg 100 g^{-1} of soil	
						H_2O	KCl	P_2O_5	K_2O	Mg	$N-NH_4$	$N-NO_3$
12	0.44	Z_1	22.69	0.21	88.5	5.13	4.54	26.0	16.9	30.0	7.31	23.34
11	0.48	Z_1	20.54	0.28	84.7	4.72	4.23	49.0	9.6	9.0	4.53	29.03
1	0.55	Z_1	17.56	0.25	84.6	5.48	5.18	60.0	19.3	60.0	1.07	37.76
10	0.60	Z_3	21.24	0.34	81.4	5.44	4.97	34.0	15.7	21.0	2.05	18.52
13	0.61	Z_1	15.14	0.24	85.2	5.84	5.33	41.0	8.4	7.0	1.67	14.23
3	0.63	Z_3	37.81	0.46	74.9	5.17	4.63	37.0	13.3	40.0	0.49	19.90
6	0.65	Z_3	20.52	0.32	82.5	5.38	4.93	87.0	10.8	60.0	1.47	22.99
9	0.65	Z_3	18.94	0.31	80.9	5.45	4.97	34.0	9.6	8.0	2.75	17.39
7	0.67	Z_3	16.26	0.28	82.7	4.75	4.23	34.0	28.9	40.0	1.32	23.58
4	0.71	Z_3	15.80	0.31	80.9	5.70	5.32	46.0	15.7	30.0	2.67	24.22
8	0.71	Z_3	22.70	0.30	83.6	6.15	5.75	64.0	10.8	30.0	2.88	19.93
2	0.72	Z_3	18.03	0.36	77.8	4.95	4.49	18.0	15.7	50.0	1.15	21.01
14	0.74	Z_3	21.47	0.29	84.1	5.78	5.33	64.0	12.0	12.0	2.96	13.41
5	0.82	Z_3	22.27	0.39	78.7	5.54	5.00	37.0	9.6	40.0	0.16	13.69

Explanation: W_1 - secondary transformation index; * - Okruszko classification.

of the BET method is to determine the monolayer capacity (N_m) from the BET plot and the second one is to calculate the surface area from the dependence: $S = N_m L \omega$, where L is the Avogadro number and ω is the molecule cross-sectional area ($10.8 \ 10^{-20} \ m^2$ for water molecule).

The adsorption-desorption isotherms of water vapour were measured by gravimetric method using a vacuum chamber. The soil sample of the weight approximately 3 g was put into a glass vessel and placed over sulphuric acid solution. The sample was then equilibrated with water vapour during two days. The amount of adsorbed water vapour was computed as the difference between the weight of the sample with adsorbed water and that of dry sample (dried in an oven at 105 °C). The relative water pressures were obtained from the density of sulphuric acid solutions. The adsorption measurements were repeated three times, keeping the temperature constant, T=20 °C ± 0.5. This procedure is in accordance with the Polish standard PN-Z-19010-1 for the surface area of soil determination.

RESULTS AND DISCUSSION

The term "adsorption" appears to connote the condensation of gasses on the free surfaces, in contradistinction to gaseous absorption process where the molecules of a gas penetrate into the bulk phase of the absorbing solid. The term "sorption" involves both phenomena, adsorption and absorption. The term, adsorption, presently used in the physical chemistry for mineral adsorbents and soils is not

adequate for the organic soils. In this case the term sorption is more realistic. The peat soils undergo swelling and shrinking and a high degree of volume reduction of the peat when dried has been observed [1,2,9].

The water vapour sorption on peat-moorsh soils indicates that the sorption (saturation) and desorption (drying) processes run independently in the full range of the relative water vapour pressures. The sorption-desorption isotherm does not exhibit the hysteresis loop (Table 3). The sorption behaviour of water vapour within a model soil organic mater (SOM), and peat, was studied by Lin [14] and strong asymmetries between sorption and desorption rates for water vapour was observed.

Figures 1 and 2 show experimental sorption and desorption isotherms, respectively. In general, the shape of all curves is similar, i.e., all the curves belong to the same class of isotherms according to the BET classification [22]. However, the detailed course of the curves and the amount of sorbed water in particular, vary from sample to sample, what is obviously results of the different basic properties of the samples (Table 1). Peat is naturally occurring, plant-derived organic sediment. It is rather complex material containing cellulose and lignin as major constituents which, especially lignin, possesses functional groups such as alcohols, ketones and acids that can be involved in chemical bonding. Peat soils at different stages of moorshing contain different amounts of total amino acids. Szajdak *et al.* [24] found a positive relationship between amino acids content in the peat soil and degree of the peat secondary transformation, as defined by the W_1 index. These constituents contain several polar and nonpolar functional groups. The humic acids contain about eight functional groups (OH, COOH), the density of polar groups is 6.4 per 100 A^2, so the hydrophobic sites occupy 40% of the surface, whereas hydrophilic - 60% [18,25]. Fulvic acids are composed of a series of oxidized aromatic rings with extensive sidechains and contain about 9.1 (in meq g^{-1}) COOH and 3.3 (in meq g^{-1}) phenolic OH groups [18]. These groups create primarily hydrogen bonding or van der Waals forces. Several polar functional groups are the sorption sites for water molecules. Because of a high dipol moment and the ability to form hydrogen bounds, water can adsorbs in a highly specific manner forming quite complex adsorbed layer which can exhibit different properties depending on the kind of the surface functional groups binding water molecules.

The experimental data have been approximated by the BET equation. An example of the linear form of the BET equation, i.e., the so-called BET plot, evaluated for selected peat soil samples is shown in Fig. 3. Table 2, however, collects the BET equation parameters. The values of the correlation coefficient, R, indicate that the BET equation provides a good fit to the experimental data. In all cases the values of R vary from 0.996 to 1, if the calculations are performed for the relative pressures below

T a b l e 2. Parameters of the BET equation at its lineal range $0<p/p_0>0.35$

No. of soil	Z	W_1	N_m (mg g^{-1})		BET constant		R	
			ads	des	ads	des	ads	des
12	Z_1	0.44	68.74	89.10	81.30	51.79	0.999	0.997
11	Z_1	0.48	74.54	97.83	73.24	44.83	0.999	0.997
1	Z_1	0.55	84.20	110.29	89.77	68.35	0.999	0.997
10	Z_3	0.60	81.56	105.75	165.01	73.86	0.999	0.997
13	Z_1	0.61	95.57	123.12	87.49	56.00	0.998	0.996
3	Z_3	0.63	69.52	92.85	107.34	55.53	1.000	0.998
6	Z_3	0.65	92.87	123.12	111.43	56.00	0.999	0.996
9	Z_3	0.65	88.10	115.03	135.95	78.00	0.999	0.998
7	Z_3	0.67	85.46	108.92	104.67	72.74	0.999	0.997
4	Z_3	0.71	92.90	123.12	96.20	56.00	0.999	0.996
8	Z_3	0.71	93.93	126.66	103.44	58.55	0.999	0.996
2	Z_3	0.72	85.97	115.50	133.54	57.20	0.999	0.995
14	Z_3	0.74	91.32	123.12	137.00	56.00	0.999	0.996
5	Z_3	0.82	53.33	70.50	99.40	60.68	0.999	0.997

Explanation: see Table 1; N_m - monolayer capacity; R - correlationa coefficient.

T a b l e 3. Specific surface area of the moorsh formations soil and the difference between the amount of the desorbed and sorbed water vapour

No. of soil	Z	W_1	S_{BET} (m^2 g^{-1})		$\Delta=N_{ads}$(mg g^{-1})	
			ads	des	$p/p_o=0.0065$	$p/p_o=0.365$
12	Z_1	0.44	248.4	324.1	0.48	30.75
11	Z_1	0.48	269.4	353.5	1.81	32.62
1	Z_1	0.55	305.2	399.3	6.29	36.47
10	Z_3	0.60	294.7	382.2	2.35	37.20
13	Z_1	0.61	345.4	444.9	2.00	40.41
3	Z_3	0.63	251.2	334.8	5.31	33.87
6	Z_3	0.65	335.6	444.9	3.66	42.02
9	Z_3	0.65	318.3	415.7	4.54	40.79
7	Z_3	0.67	308.8	393.6	4.74	34.93
4	Z_3	0.71	335.7	444.9	7.36	42.56
8	Z_3	0.71	339.5	457.7	3.24	43.19
2	Z_3	0.72	309.6	417.4	6.60	40.85
14	Z_3	0.74	330.0	444.9	0.77	41.42
5	Z_3	0.82	192.7	254.8	3.64	24.26

Explanation: see Table 1; ads - sorption; des - desorption; S_{BET} - specific surface area; Δ - results between the amount of the desorbed and sorbed water vapour; N_{ads} - the amount of the sorbed water vapour; N_{des} - the amount of the desorbed water; p/p_o - relative pressure.

$p/p_o=0.35$. General obtained for experimental sorption (R = 0.999) than for desorption data (R≅0.996-0.998).

The BET constant (C) is often used to calculate the net heat of adsorption, $Q_{BET}=E_1-E_c=RT \ln C$, where E_c is the heat of condensation of adsorbate and E_1 is the heat of adsorption of the first layer [12,17]. For the investigated moorsh formations, the value of the net heat of adsorption or adsorption energy were similar and
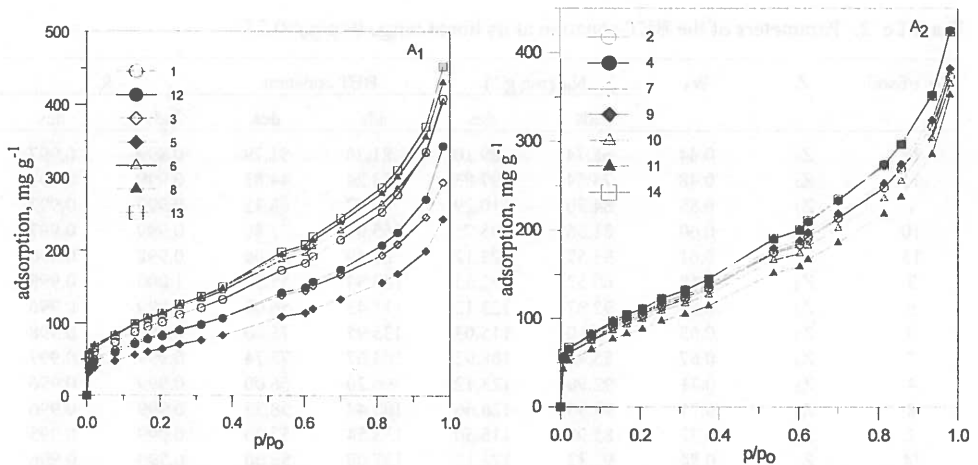
Fig. 1. The sorption isoterms for investigated peat-moorsh soils (part A₁ and A₂). Explanation: see
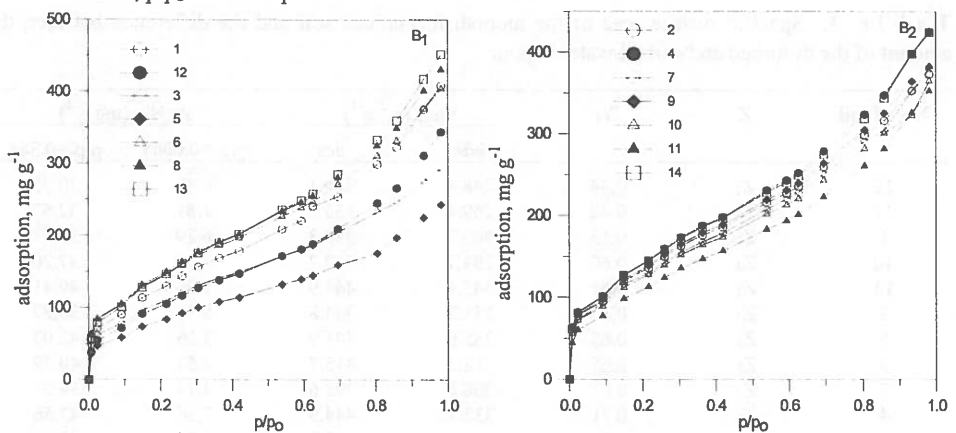Table 1; p/p₀ - relative pressure.

Fig. 2. The desorption isoterms for investigated moorsh formations (part B₁ and B₂). Explanation: see
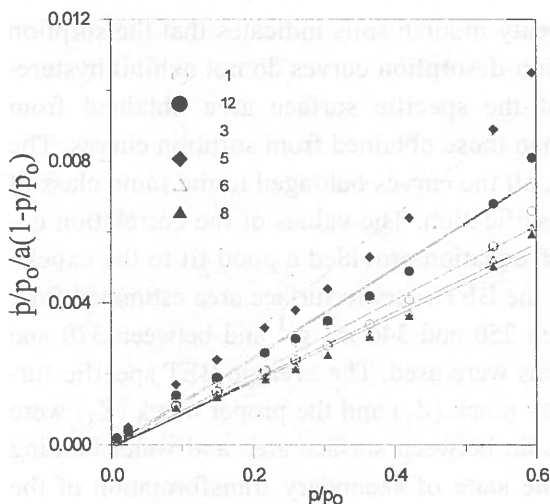Table 1; p/p₀ - relative pressure.

close to about 11.0 kJ mol^{-1} and 9.5 kJ mol^{-1} for sorption and desorption processes,
respectively (Table 4). The net heat of sorption for peaty moorsh (Z_1) and proper
moorsh (Z_3) were the same as given above. Any relationship between water hold-
ing capacity index W_1 and the net heat of sorption was also not found (Table 4).

In Table 3 the values of the specific surface area are collected. Generally, the
va-lues obtained from desorption isoherms were higher than those obtained from
sorption curves. For all studied samples the BET specific surface area estimated
from the sorption isotherm ranged between 250 and 340 m^2 g^{-1} and between 320
and 460 m^2 g^{-1}, if the desorption isotherms were used. For moorsh soil sample,

T a b l e 4. Average surface area and average net heat of sorption for peat-moorsh soil samples

W_1		0.41-0.50		0.51-0.60		0.61-0.70		0.71-0.80	
S_{aver}	ads	258.9	(14.8)	299.9	(7.4)	311.9	(36.8)	328.7	(13.3)
	des	338.8	(20.8)	390.8	(12.1)	406.8	(45.7)	441.2	(17.0)
Q_{aver}	ads	10.59	(0.19)	11.71	(1.05)	11.40	(0.40)	11.59	(0.44)
	des	9.45	(0.27)	10.40	(0.12)	10.11	(0.41)	9.86	(0.05)

Explanation: see Table 1 and 2; S_{aver} - average surface area ($m^2 g^{-1}$); Q_{aver} - net heat of sorption (kJ mol^{-1}); (...) - standard deviation.

Fig. 3. The BET plot for selected samples of the peat-moorsh soils. Explanation: see Table 1; p/p_0 - relative pressure; a - sorption of water vapour.

namely for the sample No. 12, the surface area obtained from sorption and desorption isotherm was 190 $m^2 g^{-1}$ and 250 $m^2 g^{-1}$, respectively (Table 3). Those values of moorsh surface agree with the results obtained by Sapek *et al.* [20], Sapek and Sapek [21], Chiou *et al.* [4] and Pennell *et al.* [19]. On the other hand, Chiou *et al.* [4] and Peenell *et al.* [19] pointed out that such polar compound as ethylene glycol (EG), can partition into soil organic matter, hampering its use for measuring reliable specific surface area. For the surface area determined by the EG method, Chiou *et al.* [4] proposed term "apparent surface area", which is based on measured by the uptake of an adsorbate that either changes the structure of the solid - dissolves in it, or both.

The average BET specific surface area for the samples of the peaty moorsh (Z_1) and for the proper moorsh (Z_3) were similar. When the sorption curve was the base to obtain the surface area - it was about 292 $m^2 g^{-1}$ (the standard deviation - 42.6) and 301 $m^2 g^{-1}$ (the standard deviation - 46.4) for the samples Z_1 and Z_3 respectively. In the case when the surface was calculated from desorption isotherm, it value was about 380 $m^2 g^{-1}$ (the standard deviation - 52.9) and 399 $m^2 g^{-1}$ (the standard deviation - 62.9) for the samples Z_1 and Z_3, respectively.

There exists a relationship between surface area and water holding capacity index W_1 characterizing the state of secondary transformation of the peat-moorsh

soils, cf. Table 4. The S value increases according to the series: 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), except for completely degraded peat (W_1<0.80).

Nevertheless it can be stated that the moorshing process being involved in phenomena of secondary transformations of peat mass leads to increasing of its total surface area, which is consistent with results of other investigators [20,21].

CONCLUSION

The water vapour sorption on peaty-moorsh soils indicates that the sorption process is not reversible. The sorption-desorption curves do not exhibit hysteresis loop. Generally, the values of the specific surface area obtained from desorption isotherms were higher than those obtained from sorption curves. The shape of all curves was similar, i.e., all the curves belonged to the same class of isotherms according to the BET classification. The values of the correlation coefficients, R, indicated that the BET equation provided a good fit to the experimental data. For all studied samples the BET specific surface area estimated from the sorption isotherm ranged between 250 and 340 $m^2 g^{-1}$ and between 320 and 460 $m^2 g^{-1}$, if the desorption isotherms were used. The average BET specific surface areas for the sample of the peaty muck (Z_1) and the proper muck (Z_3) were similar. The existence of a relationship between surface area and water holding capacity index W_1 characterizing the state of secondary transformation of the peat was proved.

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