Int. Agrophysics, 2006, 20, 121-128

INTERNATIONAL
Agrophysics
www.ipan.lublin.pl/int-agrophysics

Selected physical and chemical properties for evaluating brown coals used for soil reclamation

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Received December 14, 2005; accepted February 2, 2006

A b s t r a c t. In this study some selected physical and chemical measurable parameters were determined and discussed. These parameters can be used for screening brown coals with respect to their suitability for soil reclamation purposes. Structural parameters, such as total cumulative volume, specific surface area, average pore radius, pore size distribution and total porosity were evaluated as a tool for the final selection of the suitable brown coal materials for reclamation purposes. The investigations were carried out using samples of brown coal from the opencast in Livno (Bosnia and Herzegovina) and brown coal material (BC1) from the Konin (Poland) deposit. Samples were taken from different depths to evaluate the effect of depth on the studied properties.

Based on results of S, C, N, ash, humic acids contents, it can be stated that the brown coal from Livno (BC4) was the worst material to be used as a soil conditioner and/or for soil reclamation purposes. Brown coal samples from Livno were characterized by a very high acidity, thus in the case of their application for reclamation of soil contaminated with heavy metals, they have to be mixed with lime. The specific and bulk density of brown coal from Konin were lower than for brown coals from Livno. The structural parameters can be recommended as a tool for final selection of suitable brown coal materials for soil reclamation.

K e y w o r d s: brown coals, physical and chemical properties, surface area, mercury porosimetry, structural parameters

INTRODUCTION

Anthropopression results in severe soil deterioration due to both contamination, mainly with heavy metals, and enhanced erosion processes. Thus, soil reclamation requires not only remediation but improving the structural characteristics, as well. Brown coal is recognized as a suitable material to address both issues mentioned above (Raychev *et al.*, 2001a; Raychev *et al.*, 2001b; Maciejewska, 1995; Maciejewska and Kwiatkowska, 2002).

Useful deposits in Poland are mainly found in lower Jurassic, upper Cretaceous tertiary Miocene formations (Bielikowski, 1995). The most important deposits are located near Turów, Konin, Bełchatów and Sieniawa. There are three types of brown coal: compact shiny (type I), smudge with xylithe (type II) and soft-smudge (type III). Polish brown coals belong mainly to type III (soft smudge), in which the moisture contents range from 20 to 45%. The ash contents are from 20 (type I) to 12% (type III). The smudge brown coal consists of substances with properties that are similar to the humic substances in soils. The most specific property of brown coal is strongly developed porous system, and consequently the ability of sorption and ion exchange between soil solution and solid phase, as well as complexation of ions (Tengler, 1985).

Gas adsorption and intrusion of a non-wetting liquid are the principal methods available to characterize a porous solid. The International Union of Pure and Applied Chemistry (IUPAC) has classified pores according to different adsorption mechanisms (Sing, 1982). The IUPAC classification of pore width is as follows: micropores <2 nm; mesopores 2-50 nm; macropores >50 nm.

Mercury intrusion porosimetry (MIP) is commonly accepted as a standard of total pore volume (TPV) and pore size distribution (PSD) determination in the macro- and mesopore ranges. The PSD and pore volumes, as determined by MIP are in the range from 3.7 to 7500 nm. Low-temperature measurements of nitrogen adsorption are commonly used to determine the surface area and mesopore size distribution (Gregg and Sing, 1978; Rouquerol *et al.*, 1994). When the nitrogen isotherm is used for analysis of porous texture, the PSD curve can be recalculated from 1.7 nm.

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A number of different theories have been proposed for interpretation of adsorption data. The best know and probably the most frequently used theory is the one proposed by Brunauer-Emmett-Teller (BET). It leads to the equation called 'the BET equation', which is widely applied for determination of the specific surface area (SSA) from isotherms of the type II. The another equation that has been often applied to describe adsorption isotherms of water on coals is the equation proposed originally by Dubinin (1975) and modified by several authors (Gauden and Terzyk, 2002). The Dubinin and the modified Dubinin isotherms allow for evaluation of parameters characterizing the porous structure of adsorbents *ie* SSA, pore volume and average pore radius (APR). Furthermore, since the size of water molecule is smaller in comparison with that of nitrogen, water adsorption isotherms can be effectively applied for analysis of porous texture with narrow pores, into which nitrogen molecules cannot penetrate.

The objective of this research is to determine physical-chemical characteristics that may be used for screening brown coals with respect to their suitability for soil reclamation purposes. Structural parameters such as total cumulative volume (TCV), specific surface area of pores (SSAP), APR, PSD, total porosity (TP) and SSA have been evaluated as indicators for final selection of suitable brown coal materials for reclamation purposes. The methods for determination of these parameters are discussed.

MATERIAL AND METHODS

Material

Samples of brown coal (BC2-5) from the opencast in Livno (Bosnia and Herzegovina) are used in this study. Their physical-chemical parameters are compared with those for brown coal material (BC1) from the Konin deposit (Table 1). Samples were taken from different depths to evaluate the effect of depth on the studied properties.

Methods

Basic parameters

The following parameters of brown coals were determined: pH in H_2O and 1M KCl potentiometrically, hydrolytic acidity (Hh) in 1M $(CH_3COO)_2Ca$ solution by the Kappen's method, specific density by a helium pycnometer. Humic acids (HAs) were extracted from the incubated materials according to the IHSS standard method (Dziadowiec *et al*., 1999). Elemental composition were determined based on coal dry mass using CHN 2400 Perkin-Elmer Analyzer.

Structural parameter

Mercury intrusion porosimetry (MIP)

The measurements were carried out using the Carlo Erba 2000 Porosimeter. Detailed description of this method has been given by Hajnos and Świeboda (2004). Total cumulative pore volume (TCV) and pore size distributions (PSD) were analysed. Using computer programme Milestone 100, and assuming the cylindrical pore model, the following parameters were calculated: bulk density, specific surface area of pores (SSAP), average pore radius (APR) and total porosity (TP).

Adsorption isotherms and the SSA

Adsorption isotherms of the nitrogen at liquid nitrogen temperature of 77 K, were obtained using Sorptomatic 1990 (Fisons) apparatus. Before adsorption measurements brown coal samples were dried at 105°C and desiccated (Bowanko, 2004). Adsorption-desorption isotherms of water vapour were determined by a gravimetric method (Sokołowska, 2004). All the measurements were replicated three times at the constant temperature T=20°C (±0.5°C). The standard deviation of replicates did not exceed ±5% at the lowest vapour pressure and ±1% at the highest vapour pressure. The averaged values were used to obtain the SSA.

T a b l e 1. Selected properties of tested brown coals

Place/Sample	Depth of sampling (m)	Type	Texture (grain size; cm)	Actual density ($g\ m^{-3}$)
Konin (BC1)	18.2-20.9	soft-smudge	mine run (up to 2)	$1.2\ 10^6$
Livno (BC2)	4.4-5.6	xylithe	shales	$0.5\ 10^6$
Livno (BC3)	7.8-11.3	smudge-xylithe	lumps	$1.0\ 10^6$
Livno (BC4)	14.7-17.4	smudge	mine run (up to 1)	$1.4\ 10^6$
Livno (BC5)	18.5-20.9	smudge-xylithe	lumps	$1.0\ 10^6$

The TPV (total pore volume) were derived from amount of vapour adsorbed at a relative pressure close to unity, assuming that under such conditions the pores are filled with liquid adsorbate (Sing, 1982; Rouquerol *et al*., 1994). The SSA of brown coal samples was evaluated from adsorption-desorption isotherms in the BET range of relative water vapour pressure $0.015<p\ p_o^{-1}<0.35$, using the BET method (Gregg and Sing, 1978; Ościk, 1982; Sing, 1982). The first step in the BET method is to obtain the monolayer capacity, N_m, from the BET plot. The second step is to calculate the SSA from the formula:

$$SSA=N_m M^{-1} L\ \omega,$$

where: L is the Avogadro number (6.02 10^{23} molecules mole^{-1}), M is the molecular weight of water (gram mole^{-1}) and ω is the molecule cross-sectional area (10.8 10^{-20} m^2 for water and 16.2 10^{-20} m^2 for nitrogen molecule).

This procedure is in agreement with the Polish standard (PN-Z-19010-1, 1997) for measuring the SSA of soil (Sokołowska, 2004).

RESULTS AND DISCUSSION

Basic parameters

The basic characteristics of brown coals from Livno and Konin are presented in Table 2. The S content is the highest in BC4; in other samples it is nearly the same. In the case of C contents the opposite situation is observed. The N content varies from 9.96 to 27.57% in brown coal from Livno, as compared to 18.9% in BC1.

In the case of BC4 the ash content is the highest (27.57%), while the HA content is the lowest (30.6%); for BC1 these values are 11.1 and 51.1%, respectively. Also, particularly high HA contents characterize the brown coals from the deposits near Konin (Maciejewska, 1995). The suitability of brown coal to improve the soil characteristics is due to its petrogaphic structure and chemical composition, as well as due to a series of specific physicochemical properties (Augustyn, 1980). Polish brown coals are generally rich in fatty acids that are main source of organic matter (Fabiańska, 2004).

Based on the characteristics given above it can be stated that the BC4 sample is the least suitable material for soil conditioning and/or for soil reclamation. Brown coal from Livno is characterized with a very high acidity (Table 2), thus it has to be mixed with lime when used for reclamation of soils contamined with heavy metals.

Structural parameters

Mercury porosimetry

The specific (true) density and structural parameters of investigated brown coals are presented in Table 3.

Well-developed pore structure and low density characterize coals with a chaotic arrangement. On the other hand, coals with a well-ordered structure have less developed pore structure and higher density. The specific density of 1.311 g cm^{-3} for BC1 is lower than for brown

Table 2. S, C, N, ash and humic acids (HA) contents (in % ww), hydrolytic acidity (Hh) (in cmol(+) kg^{-1}) and pH of brown coals

Sample	S	C	N	Ash	HA	Hh	pH in H_2O	pH in 1M KCl
BC1	0.44	40.45	18.90	11.10	51.1	1.45	6.87	6.47
BC2	0.47	39.95	11.45	18.90	40.1	16.72	3.74	2.04
BC3	0.49	37.39	27.57	11.45	33.3	11.25	2.85	1.91
BC4	0.70	21.60	9.96	27.57	30.6	10.42	3.29	3.10
BC5	0.50	36.96	20.74	9.96	36.6	9.60	3.80	2.80

Table 3. Specific density and structural parameters of brown coals samples determined using the mercury intrusion porosimetry and assuming the cylindrical pore model

Sample	ρ_s* (g cm^{-3})	TCV (mm^3 g^{-1})	ρ_b (g cm^{-3})	SSAP (m^2 g^{-1})	APR (μm)	TP (%)
BC1	1.311	522.67	0.76	1.30	1.580	39.83
BC2	1.432	33.45	1.41	0.52	4.761	4.71
BC3	1.431	28.70	1.42	1.68	3.824	4.07
BC4	1.460	15.49	1.51	0.07	2.953	2.33
BC5	1.428	31.43	1.44	2.59	0.005	4.52

ρ_s* - specific density (measured by helium pycnometer), TCV – total cumulative volume of pores, ρ_b – bulk density, SSAP – specific surface area of pores, APR – average pore radius, TP – total porosity.

coals from Livno (1.428-1.460 g cm^{-3}). The bulk density of BC1 (0.76 g cm^{-3}) is almost two times lower than for BC2-BC5 (1.41-1.51 g cm^{-3}). For investigated brown coal samples the TCV that was obtained by a direct MIP measurement ranges from 15.5 to 523 mm^3 g^{-1}. The TCV for BC1 was over 10 times higher, as compared to samples BC2-BC5. On the contrary, the SSAP was the highest for BC5. The APR values generally decrease with increasing depths of brown coal deposition. The TP of 39.83% determined for BC1 is *ca*. 10 times higher than that of BC2-BC5. It should be emphasized that all structural parameters were calculated on basis of TCV and assuming particular model of pores. One should remember, however, that MIP measurements yield the pore size ranging from 3.5 to 7500 nm, thus the TCV has been evaluated taking into account only the pores from this interval and, consequently, the TP does not include macropores, as well as closed and bottle-neck pores.

The TCV curves for investigated brown coals are presented in Fig. 1. The curves show the total mercury volume intruded into the pores versus the pore size. It is worth to notice an increasing APR in the case of BC2-BC5. It can be related to its deposition 'age'. A similar behaviour is observed for TP with exception of sample BC5.

The PSD curves for investigated brown coals are shown in Fig. 2. The shape of the curves for BC2-BC5 is similar (with 2 peaks) but it significantly differs from BC1 with only one peak. The peak for BC1 is much higher (approximately 1.5 order of magnitude), as compared to BC2-5. The PDS curves exhibiting single and narrow peaks indicate that from the geometrical viewpoint the BC1 sample is more homogenous.

The knowledge of TCV, PSD and TP parameters is not-sufficient for complete soil characterisation, because they do not contain information about the types and number of pores, which are important for evaluating the air-water relations in soil, and, consequently for availability of pore water to plants. The micro- (V_{micro}) and mesopore (V_{meso}) volume is obtained from mercury porosimetry data. Mesopores appear to be the main type of pores in investigated brown coals,

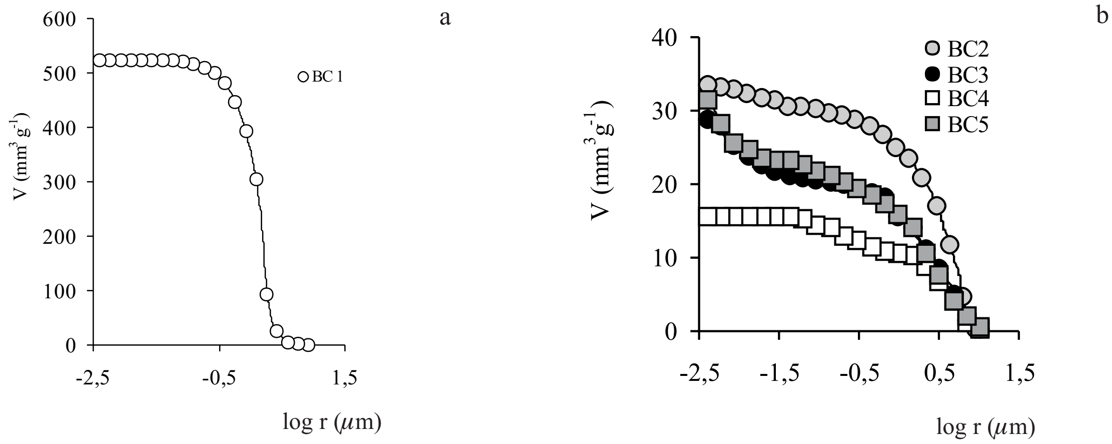

Fig. 1. The cumulative curves for brown coal from: a) Konin and b) Livno.

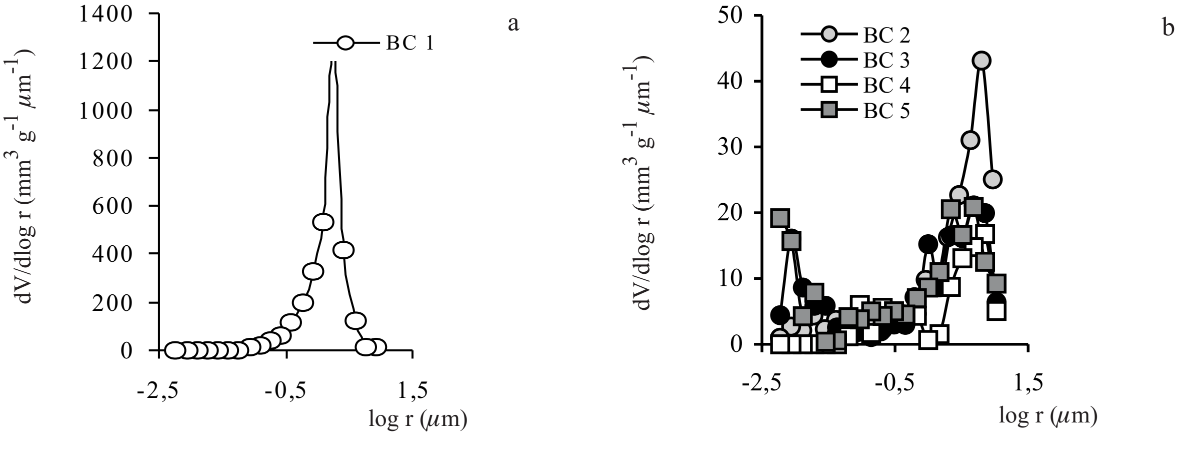

Fig. 2. The pore size distribution (PSD) curves for brown coal from: a) Konin and b) Livno.

their content of the TCV is 97% in BC1, *ca*. 80% in BC2 and BC4, and *ca*. 60% in BC3 and in BC5. The pore radius of 20 μm is the boundary of aeration *ie* the boundary between non-capillary and capillary pores (Konstankiewicz, 1985). It can be assumed that the volume of mesopores corresponds to the volume of capillary pores participating in transport of water in soil. This characteristics of investigated brown coals indicates their applicability as a material for modifying soil structure. It has to be emphasized, however, that only part of capillary pores ranging from 20 to 0.2 μm can be determined by using the MIP method.

Adsorption study and specific surface area (SSA)

Generally, coals are known to be extremely heterogeneous microporous materials with high SSA.The values of S_w determined from adsorption isotherms of water vapours on brown coal are within the range of 160-210 $m^2 g^{-1}$ (Fig. 3a). In the case of evaluation based on nitrogen isotherms (Fig. 3a) the value of S_w for BC1 (*ca*. 250 $m^2 g^{-1}$) is about 5 times higher than for BC2-BC5. Grzybek *et al.* (1997) observed that the SSA of coals from Polish mines Makoszowy and Borynia was of 285 and 74 $m^2 g^{-1}$, respectively. Tarasevich (2001) studied the sorption properties of young hard coal from Donbass. Analysing adsorption of hexane vapours, he calculated volumes of micro- and mesopores, half widths, and SSA of mesopores of coals. The total SSA of coals obtained using the BET equation applied to hexane isotherm was of 151 $m^2 g^{-1}$. The SSA of young long-flame coals determined by low-temperature adsorption of nitrogen ranged from 10 to 100 $m^2 g^{-1}$. For most coals SSA is small, S<1 $m^2 g^{-1}$ (Ettinger and Shulman, 1975; Tarasevich, 2001). Amarasekera *et al.* (1995) calculated the SSA of Australian and US coals from adsorption isotherms of nitrogen at a range of relative pressures between 0.02-0.15 using the BET model. They found the presence of very fine micropores of equivalent sizes from 1.3 to 1.4 nm and volumes of 0.06-0.08 $cm^3 g^{-1}$, for which the SSA was from 160 to 200 $m^2 g^{-1}$.

Figure 3b shows the relationship between the water-surface area and hydrolitic acidity (Hh). The value of S_w increases when Hh increases. The regression coefficient is high (R^2=0.852). Chemical composition of the coal surface and functional groups, as well as microporosity and surface heterogeneity (energetic and structural heterogeneity) play an essential role in adsorption. In the adsorption process of water vapour the surface polar functional groups are the sorption sites for water molecules. These groups bound water molecules via hydrogen bonds or van der Waals forces. Nishino (2001) studied the adsorption of water vapours and carbon dioxide on a surface of coals. The amounts of adsorbed water vapours and carbon dioxide increased when the content of oxygen in coals was of 6%. Similar dependence was observed for carboxylic groups present on coals' surfaces. The SSA of studied coals was in the range from 40 to 780 $m^2 g^{-1}$.

The effect of cation content of brown coals and equilibrium moisture content at 25% relative humidity were studied by Schafer (1972). In all cases the equilibrium moisture content increased with increasing the cation content, and the extent of this increase varied with the type of cation.

No correlations were observed between the S_W and the basic and structural characteristics of brown coal samples. In the process of nitrogen adsorption the type of adsorption

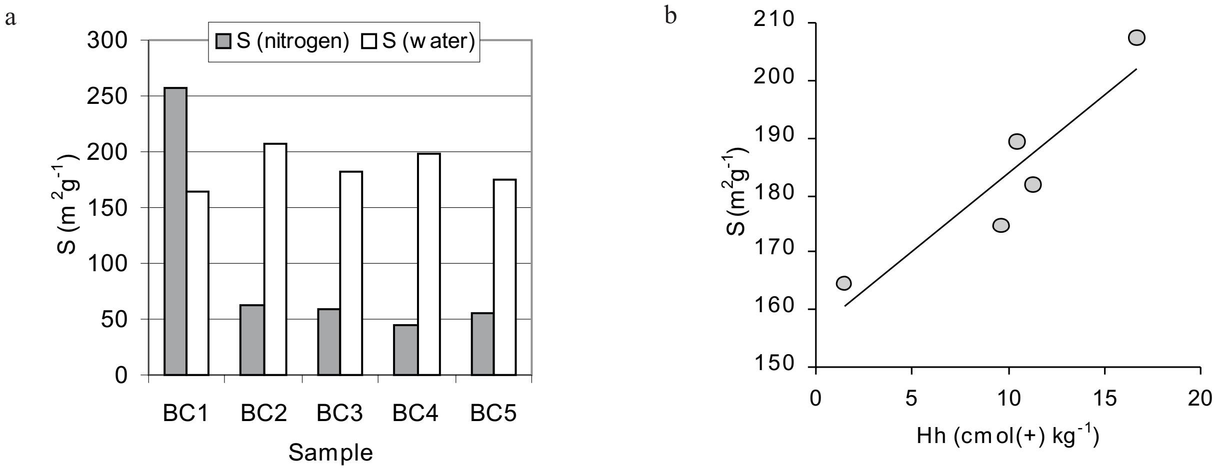

Fig. 3. Specific surface areas (SSA) of brown coals obtained from water vapours (S_w) and nitrogen (S_{N2}) adsorption data using the BET method (a), relations between the specific surface area (S_w) determined using the water vapours adsorption isotherm and the hydrolytic acidity (Hh) (b).

centres plays smaller role than the pore structure because nitrogen is an inert adsorbate.

Figure 4 exhibits a linear regression plot of the nitrogen surface area (S_{N2}) *vs.* the coal density (Fig. 4a), ash content and TCV, evaluated using MIP (Fig. 4b).

In the case of brown coals density the regression R^2 was of 0.976 and 0.998 for the bulk and specific densities, respectively. Unfortunately, in many cases the coefficient R^2 is rather poor statistic for deciding wheather an observed correlation is statistically significant. Therefore, we have also evaluated standard errors in determining the slope and the constant of regression line. For example, for the density obtained from Hg measurements the standard errors for regression line slope and constant are lower than 3% and 1%, respectively. Thus, despite that one data point lies for from four other, the relationship between density ans surface area can be rightly modelled by linear function. No correlation was found for the ash content (R^2=0.434). The nitrogen-surface area increases with an increase of TCV, and an increase of ash contents causes a decrease of S_{N2}.

We also found a high correlation (R^2=0.895) for nitrogen surface area and the TCV (Fig. 4b). The errors in the slope and the constant of the regression line are lower than 3% and 8%, respectively.

Figure 5a shows the correlation between nitrogen SSA of brown coals and the content of mezo and micropore volumes, which are expressed as percentage of the TCV. The regression coefficient is low (R^2 = 0.508) in this case. However, the regression coefficients between SSA evaluated from nitrogen adsorption and TCV from mercury porosimetry (Fig. 4b) are high. We also found that the value of mesopore volume obtained from the MIP and the TPV

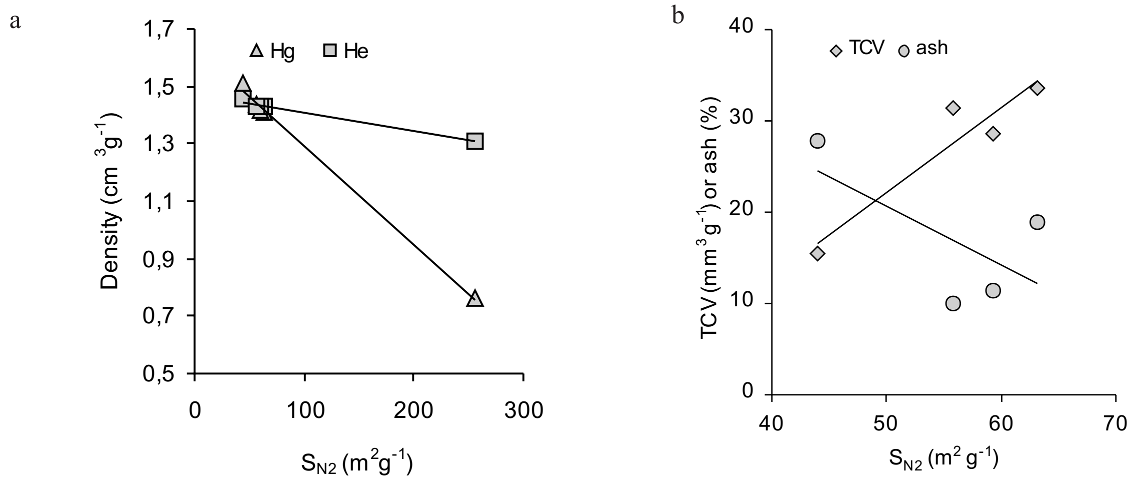

Fig. 4. Relation between the nitrogen specific surface area (S_{N2}) and density (a) (triangle - specific density (ρ_s) measured by helium pycnometer, square - bulk density (ρ_b) measured using MIP), and the total cumulative volume (TCV) (rhombus) and the ash content (circle) of brown coals (b).

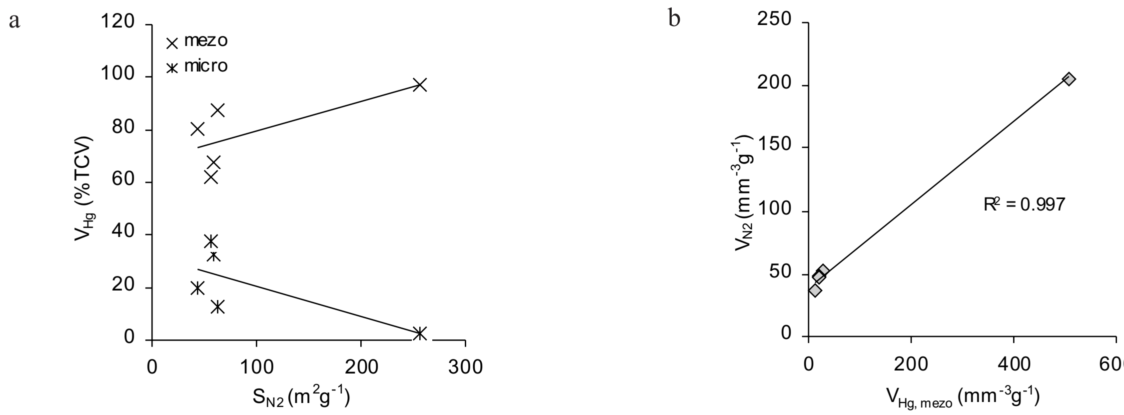

Fig. 5. Nitrogen surface area (S_{N2}) vs. the mezo- (V_{mezo}) and micropore (V_{micro}) volume of investigated coals (a); the regression between nitrogen pore volume (V_{N2}) and mezopore volume (V_{mezo}) obtained from mercury porosimetry data (b).

determined using nitrogen adsorption were similar, and the regression coefficient between these quantities is very high, R^2=0.997 (Fig. 5b). The errors in the slope and the constant of the regression line are again small – lower than 3%.

Generally, the investigated brown coals are characterized by mezoporous structure and SSA determined from water adsorption isotherms of *ca*. 160-210 $m^2 g^{-1}$ and of 40-260 $m^2 g^{-1}$ obtained from nitrogen adsorption. Figure 6 shows TPV evaluated from MIP and nitrogen and water adsorption data. The TPV obtained from nitrogen adsorption and MIP are in a good agreement.

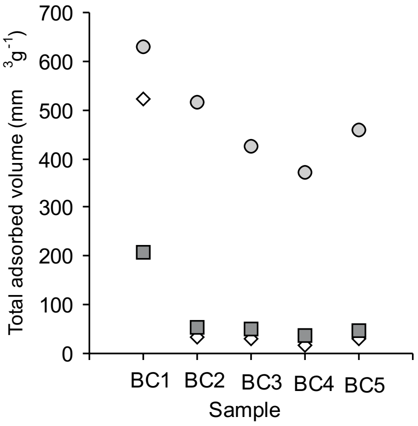

Fig. 6. Comparison of the pore volume (TPV) of coal samples determined from mercury porosimetry (diamonds), nitrogen (grey squares) and water vapour (grey circles) adsorption data.

There are definite needs for investigations of adsorption of water on coal materials because sorption and desorption of gases and water is a basic physicochemical phenomenon taking place in hard coals, and it is the reason of changes of carbon proprieties (Nodzenski, 1998). Water is the most often applied solvent for investigation of adsorption from solutions. The studies on adsorption of water on coals are connected with a practical aspect *ie* the enlarging the hydrophobic properties of surfaces.

CONCLUSIONS

1. The physical-chemical measurable parameters that may be used for screening brown coals with respect to their suitability for soil reclamation purposes were evaluated. Based on the results of elemental composition (S, C, N), ash and humic acids contents it can be stated, that the BC4 (brown coal from Livno) was the worst material to be used as a soil conditioner and/or for soil reclamation purposes.

2. Brown coal from Livno (BC2-BC5) were characterized by a very high acidity, thus in the case of their application for reclamation soil contaminated with heavy metals they have to be mixed with lime.

3. The structural parameters *ie* total pore volume, specific surface area, average pore radius, and total porosity, could be recommended for the final selection of suitable brown coal materials to be applied for soil reclamation.

4. Well-developed porous structure (TP) and low density characterize brown coal from Konin. On the other hand, brown coals from Livno with a well-ordered structure have less developed porous structure and higher density, thus in the case of their application for reclamation soil, brown coal from Livno is worse than from Konin.

5. The average pore radius was generally decreasing with the increasing depths of brown coal deposition.

6. The total cumulative volume, pore size distribution, and total porosity do not contain information about the types and number of pores. Mesopores appear to be the main type of pores in investigated brown coals. It can be assumed that the volume of mesopores corresponds to the volume of capillary pores. This characteristics of investigated brown coals indicates their applicability as a material for modifying the soil structure. It has to be emphasized, however, that by using the MIP method only part of capillary pores ranging from 20 to 0.2 μm can be determined.

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