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Mechanochemical activation of humic acids in the brown coal

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Abstract

The paper reports the impact of the conditions of mechanical activation for the preparation of ultra-fine coal powders with an increased content of humic acids (HA). With an optimum grinding time of 20 min and revolution amplitude of 400, a double increase of HA contents can be achieved. In the process of activated coal grinding insignificant specific surface area (SA) changes occurs due to the increased HA contents. Distribution curves of the active powder culminate at 22 nm and with an agglomerated coal sample at 35 nm. The aggregation of grains influences the surface properties of the coal powders.

Keywords: Mechanical activation; Handlova brown coal; Humic acid; Zeta potential

1. Introduction

The non-traditional use of coal are currently important from the point of view of the development of new carbonaceous technologies, mainly the use of activated carbon in the environmental technologies, constructional materials for chemical industry equipment like the production of electrodes, battery charges, carbon fibres, carbides for cutting and abrasive materials, artificial diamonds, etc. [1]. In terms of coal treatment science, the physical [2,3], chemical [4] and biological procedures with the use of thermodynamic models [5–8] play an important role and are termed “advanced coal treatment technologies” [9,10].

One non-fuel usage of coals is the production of humic preparations to be used in different branches of industry and agriculture. Humic acids (HA) of coal, as a group of natural substances, have much in common with natural humus as far as the character of their structure is concerned. There are no principal differences between the humic acid of soils, though there are differences in the structural details as their formation depends on bioclimatic factors, stage of coalification and degree of weathering [11]. Their colloidal character and high surface functionality make them excellent adsorbent, possessing a superior capacity for the retention of ionic and molecular pollutants, and for facilitating the processes of mobilization/immobilization of these in the environment [12]. Many constituent of HA from different continents and of various origins are of the same or similar structure [13].

HA are the major constituent of organic oxidation products and are formed on coal surface with various molecular weights for different oxidation conditions. They are insoluble in acidic solutions but become soluble in alkaline solutions, their solubility varying with their molecular weight. Usually, the lower molecular weight humic acids dissolve at lower alkaline solution strengths. It was also found that most short chain soluble organic acids from oxidized coal did not show much effect on the zeta potential of unoxidized coal [14]. The zeta potential of HA was reported as being approximately −35 mV over the whole range of pH [15]. For the pH range of 5.4–12.2 with lowering pH, a decrease in the adsorbed amount of HA is observed. This can be explained by the tendency of HA molecules to coil and form aggregates through hydrogen bonds with decreasing pH, which leads to bigger sizes of adsorbate molecules [16]. The variation of the colloid’s zeta potential and size, with pH, reflects the ionisation of the carboxylic and phenolic acidic groups, and a linear dependence of size on zeta potential [17].

2. Materials and methods

The research was carried out with the samples of Slovak brown coal from locality Handlova. Coal samples (the basic sample and the sample of coal after hydrocyclone washing-product) were processed to the size of grain—0.5 mm.

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Table 1
Analysis of the Slovak brown coal from locality Handlová

Sample	A^d (%)	W^a (%)	S_{sulp} (%)	$S_{sulphate}$ (%)	S_{total} (%)	HA (%)
Basic-feed	45.35	8.09	1.87	0.53	2.3	7.09
Product (washed coal)	7.43	12.26	0.96	0.11	1.2	4.10

Hydrocyclone washing was performed in the laboratory equipment UGT SAV. For the washing test, the cyclone made of steel with the 150 mm in diameter was used. The cyclone's cone consisted of three angles 135–75–20°. The ratio of spigot finder to apex diameter was 68:14.5 mm. The products of hydrocyclone treatment were cumulated, and after refining and drying phase a product was obtained whose characteristics are presented in Table 1. The chemical analysis was performed by standard analytical procedures.

Brown coal sample was activated by grinding using planetary Pulverisette 6 mill (Fritsch, Germany) in air and argon atmosphere in the following conditions: granularity of input 0.5 mm, mass of sample 20 g, grinding speed 400 rev/min, time of grinding 10 and 60 min.

The specific surface of samples was measured by Micromeritics Gemini 2360 apparatus using BET method. The granulometric analysis was carried out using Sympatec Helos apparatus, Rodos, Germany, in wet conditions.

The granulometric analysis of sub-microns particles smaller than 1 μm (nano-particles) was carried out with dynamic laser radiation dispersion using ALV detection equipment, Germany, with ALV 5000 correlator. The experimental equipment consisted of an argon laser Spectra Physics Stabilite 2017-0.4 S, USA, working within the wave length of 514.5 nm at the out put of 400 mW. The data were analysed using CCNTIN method and ALV 800 transputer. Scanning electron microscopy (SEM) of sample of Slovak brown coal was performed using microscope type TESLA BS 340.

Electrokinetic potential (ξ potential) was measured using a Zetaplus instrument. Laser Doppler electrophoretic light scattering determinations were performed with the instrument purchased from the Brookhaven Instruments (USA), with the reference beam mode at the wavelength of the laser light source of 670 nm, sampling time 256 μm, modular frequency 250 Hz, and the scattering angle 15°. The standard error of the zeta potentials (ξ), converted from the experimentally determined electrophoretic mobilities according to the Smoluchowski limit of the Henry equation, was typically <1.5% and the percentage error was 5%. The zeta potential distributions were obtained by averaging two or three runs. A desired pH of the individual aqueous dispersions of 20 ml of mechanical activated coal was adjusted with hydrochloric acid. Small accounts (1.5 ml) were transferred into the cell of the instrument where the zeta potential distribution was measured in sequence.

3. Results and discussion

Coal is a very heterogenous material and the mechanism of surface change is very complex. In general, when a freshly fractured coal surface is exposed to the atmosphere, the exposed carbon atoms in the lattice react with atmospheric oxygen (natural weathering). The surface charge of low-ranking lignitic coals is specifically determined by the degree of dissociation of weakly acidic oxygen-containing functional groups, such as phenolic (OH) and carboxylic (COOH). At high pH, the surface carboxylic will tend to dissociate and the surface acquires a strong negative charge. At low pH the groups will be protonated and the surface charge diminishes. At a very low pH, the surface may even become positively charged [18]. In a previous study [19] the specific surface of ground samples and content of HA increased with increasing time of mechanical activation. The agglomeration of grains occurs due to longer grinding periods. This was accompanied by an unwanted secondary process, namely, the degradation of HA, as confirmed by stagnation of values of specific surface and HA^{daf}_{total}.

Activating grinding of brown coal in the equipments of intensive grinding induces significant surface structural changes of ultra-fine active powders [20] depending on the grinding intensity, i.e. grinding time and revolutions of a grinder.

Comparing the curves of dependency of the grain fineness on the grinding time at different grinding speeds, it may be noticed that in all of the three samples (Fig. 1), a significant drop of the size of the grains of active powders occurs. In the case of the lowest level of grinding speed, i.e. curve 1–300 rpm, active grinding is the longest and takes 60 min. With increasing the grinding speed the effective phase of grinding is shortened, i.e. 20 min, which represents an optimum grinding time. After this phase aggregation of the grains occurs which can increase the grain size on curve 3 (550 rpm) or lead to stagnation of the values on curves 1 and 2 (300 and 400 rpm). The process of aggregation of ultra-fine coal powders (grinding at 400 rpm, $t > 20$ min) with a mean grain size of 7.7 μm is accompanied with a 50% increase of the specific surface (SA: 5 min—3.30 $m^2\,g^{-1}$; SA: 20 min—3.80 $m^2\,g^{-1}$; SA: 60 a 120 min—5.5 $m^2\,g^{-1}$) due to an increased content of the total humic acids in the carbon structure of the ground stock.

In the process of active dry grinding, there occurs a double increase of the contents of the total HA: after 5 min + 6.20%, after 20 min + 14.30%, after 60 min + 15.61%. The content of the free HA increased in the process of active grinding 5 min + 1.38%, 20 min + 10.96%, 60 min + 12.65% at 400 rpm. Activated coal grinding in argon atmosphere increases the HA insignificantly, i.e. about 2% (Table 2), the specific surface of aggregated grains increases similarly as in the case of the grinding in air.

Fig. 2a–c shows SEM images of the grains in mechanically active coal powders after active grinding time (20 min) and grain agglomeration (60 min). In Fig. 2b and c, there is an obvious

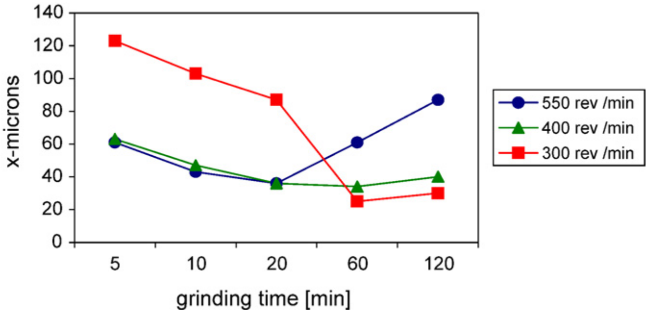

Fig. 1. Grain size × dependence on activation grinding time.

Table 2
The comparison of total HA (%) after activation grinding in air and argon atmosphere

Sample	Air atmosphere		Argon atmosphere	
	10 min/400 rpm	60 min/400 rpm	10 min/400 rpm	60 min/400 rpm
HA in the basic-feed (%)	13.00	12.98	14.98	15.00
HA in the product (washed coal) (%)	19.93	22.98	22.88	26.46

aggregation of the grains in the ground stock. The mechanism of aggregation of ultra-fine grains cannot be definitely specified. There is, however, a significant impact of particles of nano size that participate in this process. Fig. 3a and b shows weighted distribution of the particles with radius *R* in an optimum (20 min) ground sample (Fig. 3b) and agglomerated sample after grinding time of 60 min (Fig. 3a). Comparing the culminations of the weighted distribution curves it is obvious that with the most activated powders, the maximum is at 22 nm and in the case of the agglomerated sample it is at 35 nm. In both weighted distribution curves, the initial section of the curve displays the breaking point at 14 nm. The content of the ultra-fine nano-grains in an optimum ground sample attains 0.15%, which is half the value of the weighted share of the finest grains in an aggregated sample of the ground stock. The literature [17] states that the aggregation significantly influences the surface charge of active powders as consequence of the ionisation of COOH groups in HA.

Fig. 4 shows dependence of the zeta potential on pH in various mechanically activated coal powders. The figure shows that the aggregation moderately decreases the values of the zeta potential in the range of pH 4–7, where the literature indicates ionisation of COOH groups in mechanically activated HA in coal powders.

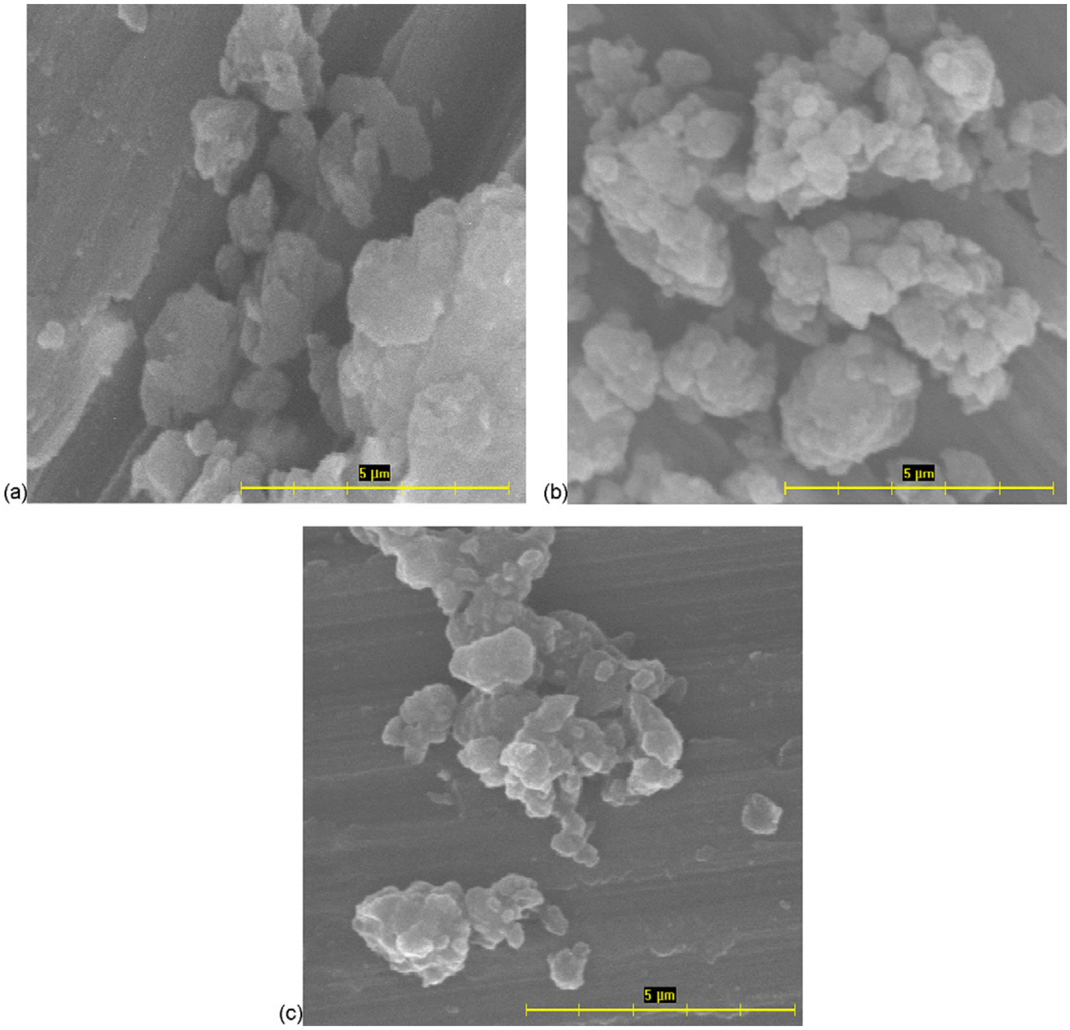

Fig. 2. SEM images of the Slovak brown coal (Handlová locality) at a enlargement of 20,000 times: (a) 400 rpm, 20 min; (b) 550 rpm, 60 min; (c) 550 rpm, 20 min.

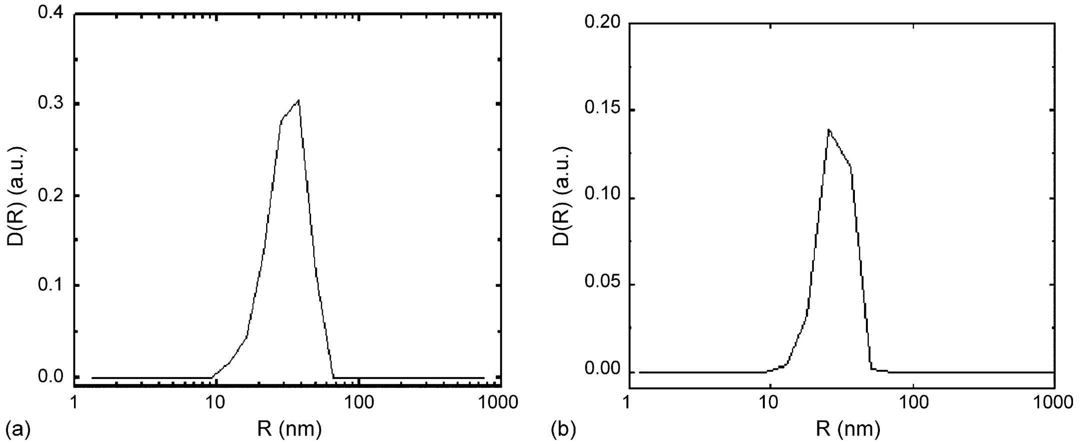

Fig. 3. Weighted distribution of particle radius *R*: (a) product of 60 min/550 rpm (dry grinding) and (b) product of 20 min/550 rpm (dry grinding).

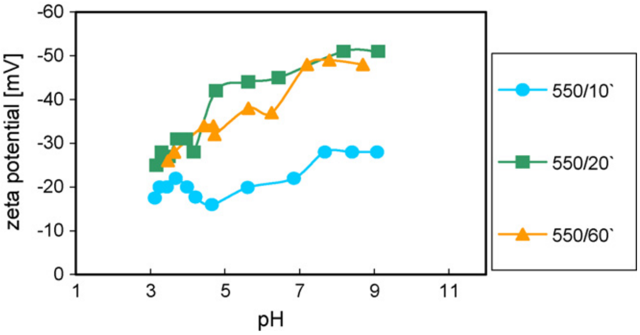

Fig. 4. Dependence of zeta potential on pH.

4. Conclusions

Experimental results presented in this study indicate that:

- The influence of grinding revolutions on the preparation of active coal powders is most significant at the level of 550 rpm.
- At the optimum grinding time (t_G 20 min, 400 rpm) the increase of the contents of humic acids is $HA^{daf}_{t=20\,min} + 14.30\%$ compared to $HA^{daf}_{t=5\,min} + 6.20\%$.
- Impact of the atmosphere of grinding on the process of HA creation is rather insignificant.
- Maximum of particle size distribution curves of an actively ground sample is at 22 nm and for the agglomerated sample at 35 nm.
- Grain aggregation decreases the values of the zeta potential in the range of pH 4–7 where the literature indicates ionisation of COOH groups.

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