

Chemical and hydrophobic modification of activated WD-extra carbon

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Abstract. In this paper commercially available activated WD-extra carbon (Gryfskand) which is applied for water treatment was used. Activated carbon was modified by the following chemical agents: H₂O₂, HNO₃ and HCl. The textural characteristics of the samples were determined by the analysis of physical adsorption isotherms of nitrogen vapor at 77 K. The Boehm titration general procedure was used to determine the distribution of the surface functional groups. Chemical modifications significantly affect the chemical, structural and surface properties of activated carbons. Hydrophobization with ethereal stearic acid was performed on the raw material and samples after chemical modification. Hydrophobic properties of the samples were specified. The relationship of the chemical modification agents with hydrophobization degree was indicated.

1 Introduction

With the increase of population and the development of the industry and energy sector the amount of pollution increases as well. The energy sector is one of the main sources of emissions of coal combustion by-products. Furnace wastes are hazardous to the environment. During storage large amounts of saline waters of sedimentary and leachates contaminated with arsenic and other harmful elements that can contaminate groundwater may be produced [1]. Technological processes in power plants involve the formation of cooling water that goes into surface waters, causing changes in physical, chemical and biological properties, increasing pollution and reducing the amount of oxygen [2]. Oil and organic solvent pollutants are also very harmful.

The variety of types of pollution generated in the energy sector results in the ongoing research in new ways to reduce their emissions or eliminate the effects of their pollution. For many years activated carbons have been used in water treatment processes.

Activated carbons are known to be excellent adsorbents and are therefore used to remove a broad spectrum of dissolved organic and inorganic species from both the gas phase and liquid phase. Their effectiveness in the purification processes primarily depends on structural properties and chemical properties of the surface. Techniques to modify and characterize the surface chemical properties of activated carbons constituted the subject of interest for many scientists [3].

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The chemical modifications may be carried out by various agents, the most common of which include the following: a strong oxidizing nitric acid [4], inorganic acids: hydrochloric acid (HCl) and hydrofluoric acid (HF) [5]. Operation of the carbon-oxidizing agents causes the introduction of the activated carbon surfaces into a variety of oxygen-containing surface groups (carboxyl, lactone, phenol, ketone, quinone and ethereal groups). Many properties of carbon adsorbents are definitely influenced by chemisorbed oxygen, which can be bound in the form of various functional groups [6]. The modifying surface carbon may change the nature of hydrophobic to hydrophilic.

The most widely used treatment-enhancing properties of carbon sorbents are appropriate modifications, which result in the changing of their structural and surface parameters [7, 8]. The change of the hydrophobic properties of the carbon materials, which is applied during production filters for removing oil and organic pollutants [9] or in the purification processes used frying oils, is also possible [10].

The kind of material which is useful for the specific application results directly from its properties. The activated carbons used for the removal of pollution from solutions are characterized by high water absorption. It may be unfavorable during the regeneration process. Due to the heat regeneration of activated carbon, regardless of the type, reactors require drying the wet or moist activated carbon and an increase of the temperature to around 1000 K. Absorbed water-related negatively affects the process of regeneration of waste sorbents. Therefore in this application an important feature of carbons may be there resistance to the water. Water resistance of carbons can be changed by means of the hydrophobization process [11-14].

2 Experimental part

2.1 Sample preparation

During researches a commercially available WD-extra activated carbon (Gryfskand) which is applied for water treatment was used. It was obtained from coal dust and binder and it was used as a raw material (WD). Activted carbon (WD) was modified by the following chemical agents: HCl (1M), HNO₃ (1:1) and H₂O₂ (30%). The 10g sample of adsorbent was poured with 300cm³ of the oxidizing agent and this led to boiling. Modification was carried out at the boiling point during 3 hours. Subsequently the samples were filtered, washed with distilled water to a constant pH and dried. The modified active carbon was obtained which is denoted by WD(HCl), WD(HNO₃) and WD(H₂O₂), respectively. Determination of pH of water extract of activated carbons were done based on PN-85 / C-97555/10 standard. The values of pH of water extract of carbons were the following: WD – 9.6, WD(HCl) – 5.2, WD(HNO₃) – 4.7, WD(H₂O₂) – 7.8. The modification of active carbon with chemical agents exerted a strong influence on the chemical character of its surface. The alkaline raw material after modification with strong HCl and HNO₃ becomes an acidic adsorbent. The modification of the alkaline adsorbent by H₂O₂ was obtained but the values of pH from 9.6 to 7.8 was decreased.

2.2 Structural properties

The standard parameters of the porous structure were calculated by means of low-temperature (77 K) nitrogen adsorption isotherms. Porous texture parameters were determined by means of an apparatus for precise measurement of physical adsorption and chemisorption – AUTOSORB-1-C (Quantachrome Instruments, USA). Before

measurement, the samples were degassed at 200°C for 12 hours using a vacuum degasser system equipped with a turbomolecular pump.

The surface areas (S_{BET}) were obtained from physical adsorption isotherms data using the BET equation. The total volume pores (V_t) were read from the isotherms for the relative pressure equal to 0.995. The micropore volume (W_o), adsorption energy (E_o) and micropore surface area (S_{mic}) were calculated using the Dubinin-Radushkevich (DR) equation. The mesopore volumes (V_{BJH}), surface area of mesopore (S_{BJH}) were determined using the standard Barreta, Joyner, Halendy method (BJH). All structural parameters were summarized in Table 1.

Table 1. Structural parameters for active carbon samples.

Adsorbent	S_{BET} m^2g^{-1}	V_t cm^3g^{-1}	W_o cm^3g^{-1}	E_o $\text{kJ}\cdot\text{mol}^{-1}$	S_{mic} m^2g^{-1}	V_{BJH} cm^3g^{-1}	S_{BJH} m^2g^{-1}
WD	1583	0.845	0.591	18.37	1662	0.302	289
WD(HCl)	1235	0.627	0.448	20.96	1259	0.162	126
WD(HNO ₃)	652	0.299	0.204	21.87	575	0.098	91
WD(H ₂ O ₂)	1129	0.574	0.406	21.50	1142	0.159	138

2.3 Chemical surface characterization

The chemical properties of the surface were estimated by Boehm's method which is a general procedure used to determine the distribution of the surface functional groups [15]. The obtained results are given in Table 2.

Table 2. Concentration of oxygen functional groups determined by Boehm's method.

Adsorbent	Basic groups $\text{mmol}\cdot\text{g}^{-1}$	Acidic groups, $\text{mmol}\cdot\text{g}^{-1}$			
		Carboxyl	Lactone	Phenol	Total
WD	2.210	0.125	0.124	0.359	0.608
WD(HCl)	0.246	0.373	0.371	1.594	2.338
WD(HNO ₃)	0.123	2.455	2.984	4.745	10.184
WD(H ₂ O ₂)	2.094	0.123	0.125	0.374	0.622

The Boehm titration method gives both qualitative and quantitative information only about basic and acidic groups (in the form of carboxyl, lactone and phenol). These groups differ in their acidities and can be distinguished by neutralization with different solutions: HCl (for basic groups) and NaHCO_3 , Na_2CO_3 and NaOH (for acidic groups). The total numbers of the groups of basic character were determined by titration of the NaOH solution, the excess of unreacted HCl. The amount and the type of surface oxygen groups by Boehm titration was examined. Figure 1 contains summarized total basic and acidic groups for all study samples.

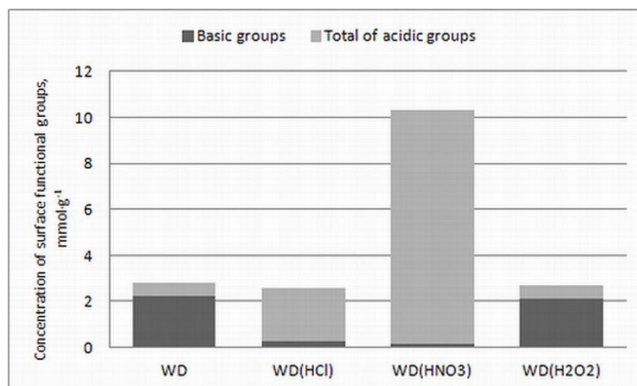


Fig. 1. Concentration of surface functional groups.

2.4 Hydrophobization process

During the hydrophobization process a commercial modifier – stearic acid – was used. The method of carbon hydrophobization with the use of stearic acid was carried out with the use of ether stearic acid solution. The concentration of the ether solution was chosen in such a way that after evaporation of the solvent, the content of stearic acid in a solid material was equal to 1%. Hydrophobization was carried out by mixing stearic acid solution with the carbon in a laboratory evaporator, at an increased temperature. The detailed descriptions of the conducted hydrophobization processes can be found in the author's earlier works [16].

2.4.1 Evaluation of the hydrophobization degree by “floating on water” test

In this work a relative evaluation of the hydrophobization degree of the analysed materials was based on a simple experiment – the so-called “floating on water” test [17]. The experiment consisted in placing a small amount of material on the surface of water in a beaker. The hydrophobization degree of materials modified in the work was evaluated on the basis of the material amount floating on the water surface for a specified period of time. Fig. 2 presents the photographs of the “floating on water” test for the materials, obtained immediately after placing the samples on the water surface.

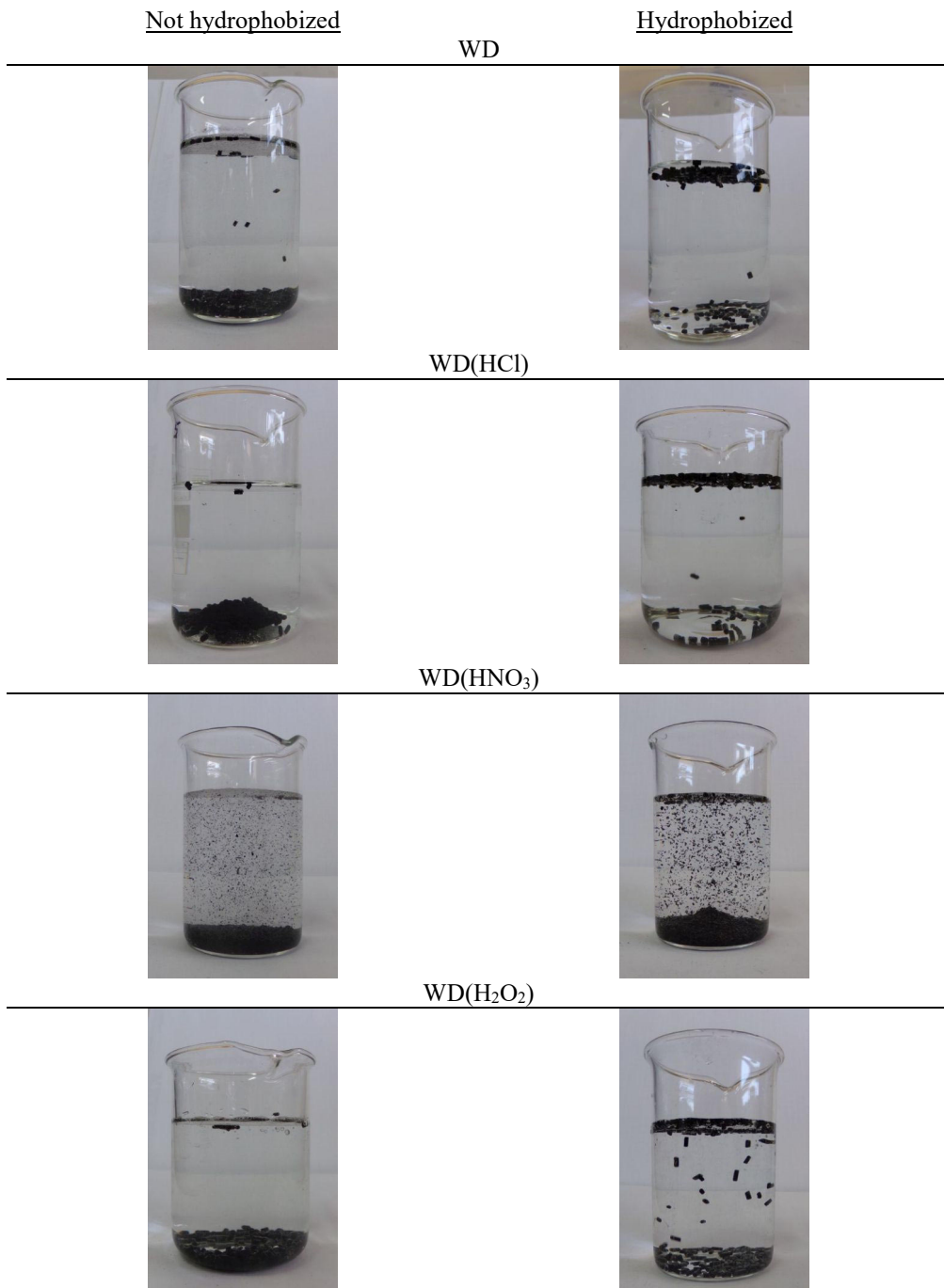


Fig. 2. The photographs of the “floating on water” test for: WD, WD(HCl), WD(HNO₃), WD(H₂O₂).

2.4.2 Evaluation of the water absorption

Water absorption was determined by means of a modified method based on the EN 1097-6:2013 standard [18]. The test portion of material was placed in a beaker and completely immersed in the water. After that the test portion was placed in the wire basket. The sample remained in the basket for a certain time until the water has stopped dripping. In our test absorbent clothes have not been used for draining excess water.

The amount of water determined during a test carried out in this manner is adequate to the amount of water retained in the bed of activated carbon which will be generated in industrial conditions. That is the amount of water, that related negatively affects the process of regeneration of waste sorbents.

The mass m_1 of the saturated test portion of material was obtained. The water absorption (WA) was calculated from the formula:

$$WA = \frac{m_1 - m_2}{m_2} \cdot 100\% \quad (1)$$

Where:

m_1 – mass of the saturated test portion [g]

m_2 – mass of the oven-dried at 105°C, test portion [g].

The obtained results are presented in Table 3.

Table 3. Water absorption.

WA	Type of materials modification				
		WD	WD(HCl)	WD(HNO ₃)	WD(H ₂ O ₂)
	not hydrophobized	164	211	292	167
	hydrophobized	142	124	206	164

3 Results and discussion

The proposed method of the modification of WD-extra active carbon influenced its surface and structural properties. The greatest impact on the structure of the porous active carbon was particularly distinct when use was made of nitric acid at the boiling point. As a result of its modification, it was observed that the resulting material was fragmented. It was demonstrated that the modifying substance (WD(HNO₃)) reduced surface area by almost 60% compared to the raw material, resulting from the partial oxidation of the carbon by a strong oxidizing agent, which is HNO₃. Both the micropore volume (0.204 cm³/g) and particularly the mesopore volume (0.098 cm³/g) is reduced. Nitric acid causes destruction of pore structure due to oxidation. Modification with non-oxidant hydrochloric acid and hydrogen peroxide also influenced the pore structure of the carbon, but they were not quite as big.

The modifying substances applied accounted for an increase in the concentration of the acid functional groups (Table 2 and Fig. 1). The raw carbon contained predominantly the groups of basic character and a negligible amount of acidic groups. The greatest increase of

the acidic groups was observed in the case of nitric acid, which is consistent with the literature [19, 20]. The total concentration of oxygen surface functional groups goes up from 0.608 mmol/g for raw active carbon (WD) to 10.184 mmol/g for WD(HNO₃). The total concentration of basic groups goes down from 2.210 to 0.123 mmol/g for appropriate carbons. Also the increase of concentration of acidic groups was particularly distinct when HCl was used. The total amount of acidic groups was 2.338 mmol/g where 68% is phenol groups and the rest carboxyl and lactone. The use of H₂O₂ had the poorest effect on the nature of the surface. The WD(H₂O₂) modifying material remained as the only alkaline carbon.

On the basis of the results obtained from the “floating on water” test (immediately after placing the samples on the water surface) it was stated (Fig. 2) that the hydrophobization process changed the water resistance of carbons. Non-hydrophobized materials became immediately moist and fell onto the beaker bottom. In the case of hydrophobized materials raw (WD) or HCl modified coals WD(HCl) almost the complete portion of the materials remained on the water surface. In the case of hydrophobized and H₂O₂ modified materials WD(H₂O₂) more than half of the sample fell to the bottom of the beaker. The worst hydrophobic properties were obtained by carbon modified with nitric acid WD(HNO₃) – almost the whole quantity of the material fell to the bottom of the beaker. The material on the water surface was observed for another 2 hours. After that only hydrophobized and HCl-modified WD(HCl)carbon remained on the water surface. This material has the best hydrophobized properties. It floated on the water also on the next day as the only one of all the modified materials.

The water absorption measurements (Table 3) confirm the above-mentioned conclusions. In the case of hydrophobized and HCl modified carbon WD(HCl) the water absorption was the smallest from the values obtained for all samples. The obtained values of water absorption (Table 3) enable us not only to compare the hydrophobic properties of hydrophobized carbons but also tell us how much of water is absorbed. In the case of hydrophobized and HCl-modified WD(HCl) coal this value is almost less than half the value for non-hydrophobized material. This information may be important during the designing of the adsorbent regeneration process. We can state that the types of chemical modification of carbons that are used affect the hydrophobization ability of the material.

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