



MODIFICATION OF ACTIVATED CARBONS FOR APPLICATION IN ADSORPTION COOLING SYSTEMS

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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: H_2O_2 , HNO_3 and HCl. 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. The thermal effects of wetting by methanol was measured. The heat of wetting was calculated. The purpose of the work was to modify the WD carbon properties to obtain an adsorbent for cooling systems characterized by both good thermal capacity and moisture resistance. The modifying chemical substances applied accounted for an increase in the concentration of the acid functional groups. The hydrophobized and HCl-modified WD(HCl) carbon has the best hydrophobized properties. The results of studies describing such modifications allow to conclude that the use of hydrophobic materials may lead to the production of sorbents with new functions facilitating their storage and use.

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Introduction

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 the liquid phase. Coals applications are also known and widely used, but the specific properties of this material may be useful in other areas as well. Theoretical and experimental work has done that the application of carbon adsorbents for heat storage in adsorptive cooling systems/adsorptive refrigerators is useful (MEUNIER 2001). The most interesting system may be methyl alcohol pair and microporous carbon materials (LEITE et al. 2005). Carbon is a good solid adsorbent for storage of mass and energy because of its good internal porosity and large specific surface area. (MARSH, RODRIGUEZ-REINOSO 2006). It is worth to add that are much cheaper than systems with the use of zeolites. Additionally methanol is a very good adsorbate because it can work at temperatures considerably lower than 0°C (WANG et al. 2003). Carbons effectiveness in such applications 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 (MENEDEZ et al. 1996).

The chemical modifications may be carried out by various agents, the most common of which include the following: a strong oxidizing nitric acid (EL-HENDAWY 2003), inorganic acids: hydrochloric acid (HCl) and hydrofluoric acid (HF) (BAGREEV et al. 2001). 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 (KALIJADIS et al. 2011). The modifying surface carbon may change the nature of hydrophobic to hydrophilic what is not always beneficial when they are used. So, it is very important what kind of modification rewords treatment-enhancing properties (structural and surface parameters) of carbon sorbents are used (REPELEWICZ et al. 2009, BUCZEK, WOLAK 2008).

The change of the hydrophobic properties of the carbon materials, which is applied during production filters for removing oil and organic pollutants (LEE et al. 2011) or in the purification processes used frying oils, is possible (BUCZEK, CHWIAŁKOWSKI 2005). Hydrophobization is a beneficial process from the economic point of view since, as it is commonly known, hydrophobic materials are sensitive to the harmful effect of humidity to a much lower degree than solids with similar applications but not possessing this characteristic. The results of studies describing such modifications allow to conclude that the use of the hydrophobized materials can lead to production of less amount of the solid waste during the industrial purification process, moreover new features of the sorbents

make its storage and dosage easier. The topic of the hydrofobization different material is actual and such researches could have a potential to contribute to improvements of waste purification processes.

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. In the case of cooling systems, the damp material will have a lower thermal capacity. Therefore in this application also an important feature of carbons may be resistance to the water. Water resistance of carbons can be changed by means of the hydrophobization process (DUONG DO 1998, THOMAS, CRITTENDEN 1998, YANG 2003, KERRY 2006).

Experimental part

Sample preparation

During the preparation of this paper 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). Activated carbon (WD) was modified by the following chemical agents: HCl (1 M – with a molar concentration 1 mol/dm^3), HNO_3 (1:1 – 65% acid diluted with 1:1 distilled water) and H_2O_2 (30% – with a percentage concentration). The 10 g sample of adsorbent was poured with 300 cm^3 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 carbon was obtained which is denoted by WD(HCl), WD(HNO_3) and WD(H_2O_2), respectively. pH values were measured for all modifying substances. The values of pH for the raw materials were the following: WD – 9.6, WD(HCl) – 5.2, WD(HNO_3) – 4.7, WD(H_2O_2) – 7.8. The modification of activated 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 HNO_3 becomes an acidic adsorbent. The modification of the alkaline adsorbent by H_2O_2 was obtained but the values of pH from 9.6 to 7.8 was decreased.

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 BET equation presents a formula (1).

$$a = \frac{a_m \cdot c \cdot x}{(1 - x) \cdot [1 + (c - 1)] \cdot x} \quad (1)$$

where:

- a – equilibrium adsorption with a relative pressure $x = p/p_0$ [mole],
- a_m – adsorption capacity of the monolayer [mole],
- c – constant dependent on the adsorption heat.

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, Joynera, Halendy method (BJH). All structural parameters are summarized in Table 1.

Table 1

Structural of activated carbon samples

Adsorbent	S_{BET} [m ² g ⁻¹]	V_t [cm ³ g ⁻¹]	W_o [cm ³ g ⁻¹]	E_o [kJ·mol ⁻¹]	S_{mic} [m ² g ⁻¹]	V_{BJH} [cm ³ g ⁻¹]	S_{BJH} [m ² g ⁻¹]
WD	1,583	0.845	0.591	18.37	1,662	0.302	289
WD(HCl)	1,235	0.627	0.448	20.96	1,259	0.162	126
WD(HNO ₃)	652	0.299	0.204	21.87	575	0.098	91
WD(H ₂ O ₂)	1,129	0.574	0.406	21.50	1,142	0.159	138

As a result of the chemical modification, the obtained materials were characterized by a less developed microporous structure. This is evidenced by lower values of the specific surface area and the volume of micropores. The smallest specific surface area of S_{BET} was obtained for activated carbon modified with strong acid HNO₃.

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 (BOEHM 2002). 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. The obtained results are given in Table 2.

Table 2

Adsorbent	Basic groups [mmol·g ⁻¹]	Acidic groups [mmol·g ⁻¹]			Total
		Carboxyl	Lactone	Phenol	
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_2O_2)	2.094	0.123	0.125	0.374	0.622

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 (VOGT 2008).

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 (VOGT 2012). 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. Figure 1 presents the photographs of the “floating on water” test for the materials, obtained immediately after placing the samples on the water surface.

Evaluation of the water absorption. Water absorption was determined by means of a modified method based on the EN 1097-6:2013 standard (EN 1097-6:2013 standard). Water absorption is the amount of water that is retained

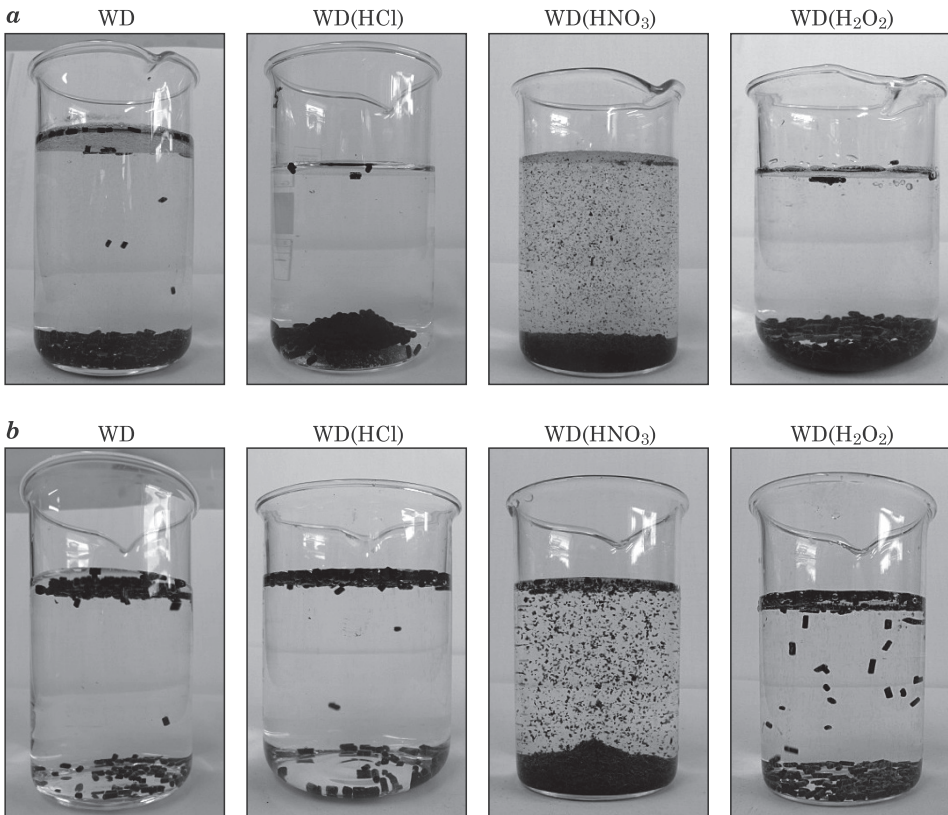


Fig. 1. The photographs of the “floating on water” test: *a* – not hydrophobized, *b* – hydrophobized

in the entire volume of the test sample immersed in the water. 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.

The mass m_1 of the saturated test portion of material was obtained. The water absorption (*WA*) was calculated from the formula (2):

$$WA = \frac{m_1 - m_2}{m_2} \cdot 100\% \quad (2)$$

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.

Carbons lose their natural hydrophobic properties after acid modification. Water adsorption results obtained for acid-modified carbons are higher than for raw material WD (Tab. 3). The hydrophobization process allows both the reproduction of this natural hydrophobicity and, in the case of WD(HCl)–H material even decreases the water adsorption value as compared to the raw material of WD.

Table 3

Water absorption			
Water absorption [%]			
WD	WD(HCl)	WD(HNO ₃)	WD(H ₂ O ₂)
164	211	292	167
WD–H	WD(HCl)–H	WD(HNO ₃)–H	WD(H ₂ O ₂)–H
142	124	206	164

Heat effects

For the estimation of the energetic effects characterizing the investigated carbons, the heat of their wetting by methanol has been determined. The heat of wetting, evolved as a result of the mutual interaction of the molecules of the wetting liquid and the adsorbent surface, is a valuable source of information. The heat of wetting can be used to determine the relative surface area of carbon, heat of adsorption, as well as for the determination of its hydrophilicity and the degree of the oxidation of the adsorbent surface (LÓPEZ-RAMÓN et al. 2000, SZYMAŃSKI et al. 2002).

The measurements of the heat of wetting were carried out in the original apparatus, which was presented in (BUCZEK, WOLAK 2009). At first, the activated carbon samples were heated at 105°C for about 3 hours. The investigated adsorbents were measured in the amount of 2 g samples. As the wetting liquid 10 cm³ of methyl alcohol was used. The temperature in the apparatus was measured with an accuracy of 0.1°C. During the whole measurement procedure the electronic system registered the changes of temperature in time. The measurement was stopped when successive temperature measurements showed a decrease. Temperature changes as a function of time is presented in Figure 2.

Analyzing the course of temperature changes over time, it was noticed that for all hydrophobic coals thermal effects of wetting with methanol are slightly lower than for non-hydrophobic coals. The function is similar for all samples tested. Such values allow to conclude that the hydrophobization process does not significantly reduce the thermal effects during the adsorption of methanol

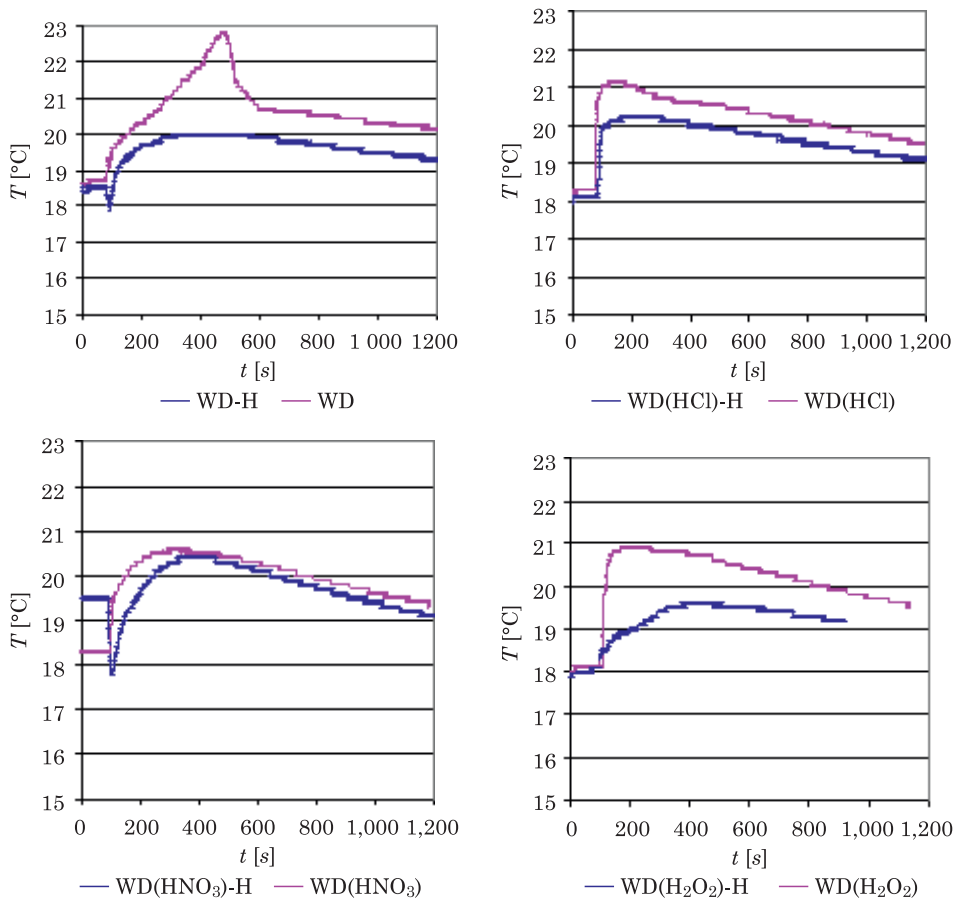


Fig. 2. Temperature variation in time

vapors. This effect is profitable when using hydrophobized carbons in cooling systems. What's more, the hydrophobic carbons will not get wet with ambient water during storage or use. Thus, their efficiency as a sorbent used in cooling systems will be higher.

On the basis of the measurements carried out, the heat of wetting with methanol was calculated with Equation (3).

$$q = (C_{wA}V_A d_A + C_{wC}m_C) \Delta T \quad (3)$$

where:

C_{wA} – specific heat of methanol [$\text{J} \cdot \text{g}^{-1}$],

V_A – volume of methanol [cm^3],

d_A – density of methanol [$\text{g} \cdot \text{cm}^{-3}$],

C_{wC} – specific heat of carbon, constant for all samples [$\text{J} \cdot \text{g}^{-1}$],

m_C – mass of activated carbon [g],
 ΔT – temperature rise from steady state to maximum.

The values of the heat effect (ΔT) and the heat of wetting (q [J] and Q [J/g]), are collected in Table 4.

Table. 4

Heat effect and heat of wetting of activated carbon samples			
Adsorbent	ΔT	q [J]	Q [J·g ⁻¹]
WD	4.2	88.0	44.8
WD-H	1.6	33.5	17.1
WD(HCl)	2.9	61.0	30.1
WD(HCl)-H	2.2	46.1	23.5
WD(HNO ₃)	2.3	48.3	24.2
WD(HNO ₃)-H	0.9	19.0	9.1
WD(H ₂ O ₂)	2.9	61.2	29.3
WD(H ₂ O ₂)-H	1.6	33.4	17.5

For the modified HCl coal WD(HCl) after the hydrophobization process WD(HCl)-H, the smallest reduction in thermal effects was determined. It can be concluded that such a procedure for modifying WD carbon to obtain a hydrophobic material is most advantageous for obtaining a sorbent for a cooling system (WD carbon-methanol). What's more, such hydrophobic coal will not take water from surrounding during storage or use. Thus, its efficiency as a sorbent used in cooling systems may be higher in the case of high humidity.

Results and discussion

The proposed method of the modification of WD-extra activated carbon influenced its surface and structural properties. The greatest impact on the structure of the porous activated carbon was particularly distinct when use was made of nitric acid at the boiling point. It was demonstrated that the modifying substance (WD(HNO₃)) reduced surface area by almost 60% compared to the raw material. Both the micropore volume (0.204 cm³/g) and particularly the mesopore volume (0.098 cm³/g) is reduced. Nitric acid causes too much destruction of pore structure so it isn't good modification for obtaining new sorbent for cooling systems. 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 (Tab. 2). 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 (PRADHAN, SANDLE 1999, REPELEWICZ et al. 2009). Also the increase of concentration of acidic groups was particularly distinct when HCl was used. The WD(H₂O₂) modifying material remained as the only alkaline carbon.

In adsorptive cooling systems, better sorbents are materials with a developed microporous surface, greater adsorptive capacity with respect to methanol and better thermal conductivity. The introduction of acidic/basic groups onto the carbon surface can increase the adsorption efficiency of polar methanol molecules.

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. 1) 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.

Conclusion

The aim of the work was to modify the WD carbon properties to obtain an adsorbent for cooling systems characterized by both good thermal capacity and moisture resistance.

The water absorption measurements confirm the hydrophobization process changed the water resistance of carbons. 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 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)-H carbon this value is almost less than half the value for non-hydrophobized material.

Such hydrophobic carbon WD(HCl)-H will not take water from surrounding during storage or usage. Thus, its efficiency as a sorbent used in cooling systems may be higher in the case of high humidity. The procedure of obtaining a sorbent for a cooling system (WD carbon – methanol) consisting on connecting

activation process by HCl (WD(HCl)) and hydrofobization process (WD(HCl)-H)) it seems to be the best of the used methods.

It was found that the types of chemical modification of carbons that are used affect the hydrophobization ability of the material. The results of studies describing such modifications allow to conclude that the use of hydrophobic materials may lead to the production of sorbents with new functions facilitating their storage and use.

The work was carried out within the research to keep the research potential AGH (11.11.210.374).

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