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Potassium hydroxide modified active carbon for adsorptive refrigerators

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Abstract Active carbon-methanol pair appears to be suitable for adsorptive cooling systems. The porous structure of commercial active carbon was modified by potassium hydroxide treatment at 750 °C. Such treatment develops the specific surface area of carbon, changes nature of its surface and significantly increases the heat of wetting. The applied way for active carbon modification gives possibility of modeling porous structure, character surface and heat effects of carbonaceous materials for adsorptive refrigerators.

Keywords Refrigeration · Active carbon-methanol pair · Heat effects of adsorption

Abbreviations

C_{wA}	specific heat of methanol, J/g °C
C_{wC}	specific heat of carbon, J/g °C
E_0	characteristic energy of adsorption, kJ/mol
Q	heat of wetting, J
S_{BET}	specific surface, m^2/g
S_{me}	mesopores surface area, m^2/g
W_0	volume of micropores, cm^3/g
V_A	volume of methanol used in the measurement, cm^3
V_p	volume of pores, cm^3/g
d_A	density of methanol, g/cm^3
d_{HK}	slit pore width, nm
m_C	mass of carbon, g
ΔT	increase of temperature, °C

1 Introduction

Extensive theoretical and experimental work has shown that the application of carbon adsorbents for heat storage can be used in adsorptive cooling systems/adsorptive refrigerators utilizing closed thermodynamic cycles (Meunier 2001). The most interesting system is methyl alcohol and microporous carbon material pair (Leite et al. 2005; Wang et al. 2003). Because of its ability to selectively adsorb vapours and gases, extended internal porosity and large specific surface area, active carbon is a good solid adsorbent for storage of mass and energy (Marsh and Rodriguez-Reinoso 2006). It is a significantly cheaper than, for instance, zeolites working in water vapour pairs. In addition, methanol is a very good adsorbate because it can work at temperatures considerably lower than 0 °C (melting point for $CH_3OH = -94\,°C$) and its molecules are sufficiently small and easily adsorbed in microporous carbon systems. Methanol is more easily desorbed and its working pressure is always lower than atmospheric pressure, which allows for a rapid identification of any faults in a cooling system. The temperature of desorption of methanol from an adsorbent is considerably lower than for water vapour systems. For all these reasons the methanol-active carbon pair can be used for storage of food and medicines, ice production, in air conditioning systems and heat pumps (Wolak and Buczek 2005).

Performance of an adsorbent in a thermodynamic system depends upon properties such as specific area, type and number of pores, adsorbent form and adsorption enthalpy of the adsorbate and its thermal conductivity. Therefore, any method of modification of active carbon has to improve carbon structural features and to increase the heat and mass transfer.

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Contemporary methods of chemical activation of carbon materials lead to the production of 'superactive' adsorbents. Activation with alkalis, in particular with potassium hydroxide, is a known method of obtaining microporous adsorbents of high specific surface area and a relatively narrow distribution of pore sizes. This method has been used by AMOCO researchers. The first installation to produce 'superactive' carbons on an industrial scale was designed by the Anderson Development Company. Its products have a specific surface area of 2800–3500 $m^2\,g^{-1}$ and a volume of 1.4–2.0 $cm^3\,g^{-1}$. They are sold as powders and granulates under the brand name of Maxsorb, PX-21 and AX-21 (Rouquerol et al. 1999).

Potassium hydroxide activation process is actively researched and its current understanding indicates that the reactions that proceed on the surface of active carbon (Otowa et al. 1996):

$$2KOH \rightarrow K_2O + H_2O \tag{a}$$

$$C + H_2O \rightarrow H_2 + CO \tag{b}$$

$$CO + H_2O \rightarrow H_2 + CO_2 \tag{c}$$

$$K_2O + CO_2 \rightarrow K_2CO_3 \tag{d}$$

$$K_2O + H_2 \rightarrow 2K + H_2O \tag{e}$$

$$K_2O + C \rightarrow 2K + CO \tag{f}$$

It was found that K_2O, a product of dehydration of KOH, reacts with CO_2 and gives K_2CO_3. At 700 °C the liberation of metallic potassium as a result of K_2O reduction by carbon or hydrogen can be observed. It seems that metallic potassium is responsible for such a high increase of carbon material structure and formation of large surface areas and volume of pores.

Investigations of the KOH activation of various carbon raw materials (Kierzek et al. 2004) are part of the search for porous materials of properties specific to the storage of fuels. Particularly attractive are the processes of adsorptive storage of methane and hydrogen, which are an unconventional energy carriers, used for instance in driving mechanical vehicles or in systems of adsorptive refrigeration (Buczek et al. 2005).

2 Experimental and results

A commercial active carbon CWZ type, produced by Carbon Raciborz Ltd, was used in the investigations. It is a powdery carbon obtained from charcoal in the process of steam activation. In industry CWZ carbon is used for decolorization and purification of liquids. It is also used in the cosmetic and food industry. This carbon is denoted by CWZp in the paper.

2.1 Modification of active carbon

CWZp active carbon was subjected to additional activation with KOH. Dried carbon was mixed with solid KOH, in a mass ratio of 1:3. The process was carried out in a muffle furnace under a nitrogen atmosphere, flowing at the rate of 30 L/h. The mixture was first heated rapidly to 700 °C, and afterwards at the rate of 10 °C/h to 750 °C. After cooling to ambient temperature, the product was neutralized in 5% HCL solution. After activation and washing off the reaction products, the carbon suspension was washed with distilled water until the pH of the solution reached a value close to 5. Afterwards the carbon was separated from the solution by filtration through a Büchner funnel in a vacuum of 10–15 mm Hg. The modified carbon was then dried at 120 °C. It is denoted as CWZpK.

2.2 Porous structure analysis

Both active carbons were characterized by nitrogen adsorption and desorption at 77 K (Fig. 1).

The volume of micropores (W_0), characteristic energy of adsorption (E_0) have been determined according to Dubinin-Radushkevich equation (Dubinin 1987), mesopores surface area (S_{me}) using Dollimore-Heal method (Dollimore and Heal 1964), whereas specific surface was obtained using BET equation.

In order to understand better the changes in microporous structure of active carbons, pore size distribution were calculated by the method of Horvath and Kawazoe (Horvath and Kawazoe 1983). The size distribution of micropores was analyzed in terms of slit width d_{HK} (Fig. 2). The results of calculations obtained from isotherms are summarized in Table 1.

KOH activation leads to a significant increase of the specific surface area and the number of mesopores in the studied materials. An increased volume of micropores is also observed. The structure of micropores and mesopores is considerably enhanced. The maximum of the micropore size distribution appears at 0.57 and 0.55 nm for CWZp and CWZpK respectively. The adsorbent obtained has significantly better structural properties than the initial active carbon.

2.3 Nature of surface

One of the most commonly used methods of the identification and determination of the content of superficial oxygen groups is the method of selective neutralization (acid-base titration). To characterize the acidic functional groups present on the investigated carbons the Boehm method is used (Boehm 2002). The aim of this method is the neutralization of oxygen groups of acidic character with alkalis

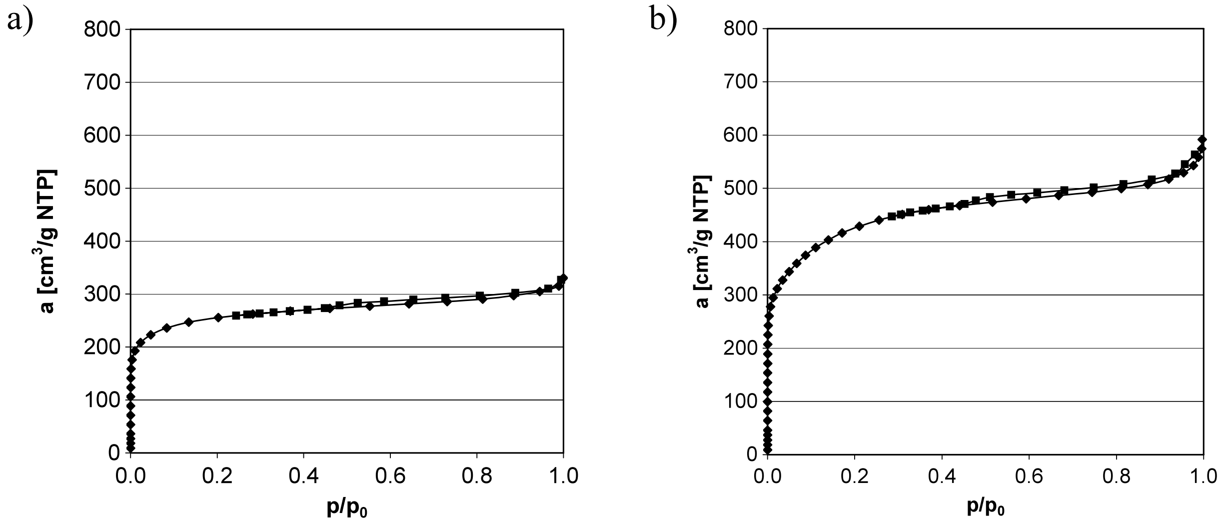

Fig. 1 Adsorption-desorption isotherms (**a**) CWZp and (**b**) CWZpK active carbons

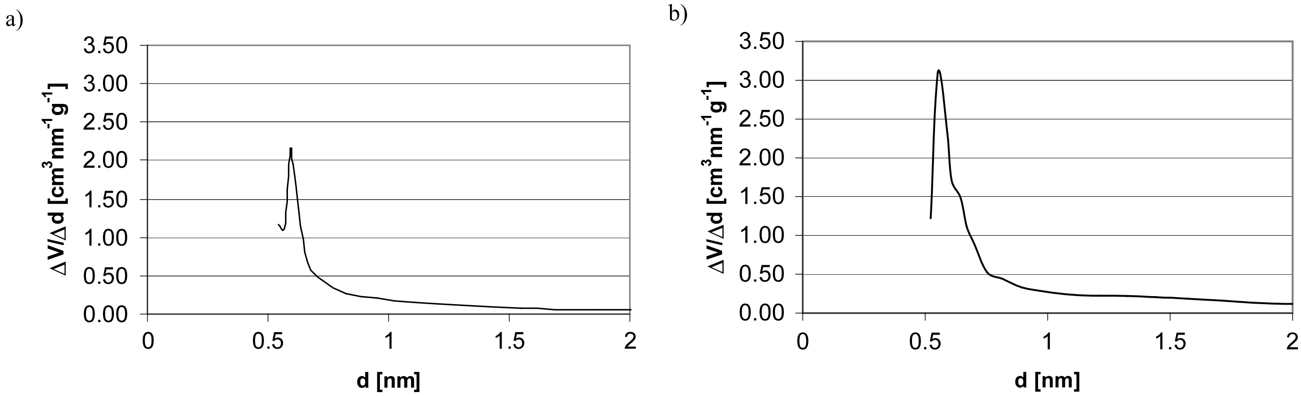

Fig. 2 Micropore size distribution by HK method (**a**) CWZp and (**b**) CWZpK active carbons

Table 1 Structural properties of active carbons

Carbon	W_0 cm^3/g	E_0 kJ/mol	S_{me} m^2/g	S_{BET} m^2/g	V_p cm^3/g	d_{HK} nml
CWZp	0.366	19.7	73	900	0.484	0.57
CWZpK	0.564	18.6	124	1510	0.845	0.55

Table 2 Acidic oxygen groups [μmol/g] determined in activated carbons

Carbon	pK = 6.37	pK = 10.75	pK = 15.74
CWZp	–	–	28.90
CWZpK	50.08	268.89	165.67

of increasingly strong base. $NaHCO_3$ neutralizes the acidic groups of pK = 6.37, Na_2CO_3 neutralizes the carboxylic and lactone groups of pK = 10.75, NaOH neutralizes carboxylic, lactone and phenolic groups of pK = 15.74, while $NaOC_2H_5$ neutralizes all above mentioned groups and additionally carbonyl groups (Jankowska et al. 1985).

This neutralization proceeds by addition of Na^+ ions by the dissociated acidic groups. The excess of OH^- ions is titrated with a standard HCl solution. The results of the determinations are presented in Table 2.

The Boehm method enables the determination of the number of particular types of oxygen groups. The analysis of the results presented in Table 2 shows that, for the initial carbon and the KOH activated carbon, strongly, moderately and weakly acidic oxygen groups have been found. The moderately acidic groups are the most numerous on the surface of CWZpK. The initial CWZp carbon has a considerably lower number of oxygen groups, of weakly acidic character only. Strongly and moderately acidic groups were not detected with this method. Clear differences in the chemical structure of the surface of the both adsorbents are visible.

2.4 Heat of wetting

The important factor of designing systems of adsorptive refrigerating, decisive for their performance, are the thermal effects of the process. Energetic effects of adsorption can be directly determined by calorimetric measurements. They can also be estimated by computing methods from the adsorption isotherms measured at various temperature values (the isosteric heat of adsorption).

For the estimation of the energetic effects characterizing the carbons investigated, 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.

The measurements of the heat of wetting were carried out in the original apparatus, presented in Fig. 3.

Prior to measuring, the active carbons were heated at 120 °C for circa 2 hours. Afterwards a weighed sample of ca. 2 ± 10^{-4} g of the adsorbent was placed in a isolated calorimetric cell (1). The studied carbons are powdery. Therefore a metallic net, protecting against material float, was placed on their surface. The whole calorimetric cell, containing the adsorbent was degassed by opening valve K2. During degassing of the carbon, a vacuum was maintained in the measuring cell (1). After equilibrating the system and closing the valve K2 (vacuum valve), a well defined volume of the wetting liquid (10 cm^3 methanol from the container (2) was introduced. The temperature in the apparatus was measured with an accuracy of 0.1 °C. During the whole measurement procedure the electronic system registered the temperature every 2 seconds. Afterwards readings of the increase of temperature were carried out as a function of time. The measurement was stopped when successive temperature measurements showed a decrease.

The heat of wetting was calculated from the following formula:

$$Q = (C_{wA} V_A d_A + C_{wC} m_C)\Delta T \tag{1}$$

where:

C_{wA}—specific heat of methanol, $C_{wA} = 2.334 \frac{J}{g\,°C}$
V_A—volume of methanol used in the measurement
d_A—density of methanol, $d_A = 0.792 \frac{g}{cm^3}$
C_{wC}—specific heat of carbon (variable value, dependent upon the degree of the expansion of the carbon sample).

In the calculations the following value was assumed: $C_{wC} = 1.257 \frac{J}{g\,°C}$

m_C—mass of carbon used in the experiment

ΔT—increase of temperature measured between the equilibrium state and the maximum value of temperature observed in the system.

Fig. 3 Scheme of the apparatus measuring the heat of wetting

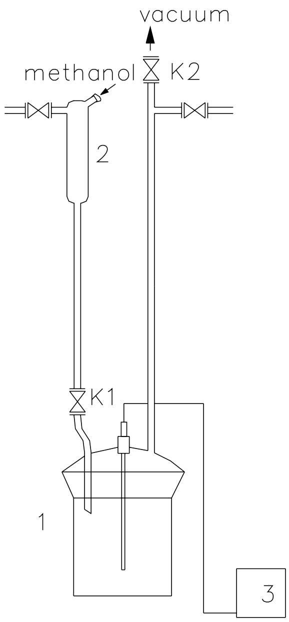

Table 3 Heat of wetting and its indices for the active carbons

Heat of wetting	CWZp	CWZpK
Q [J]	74.5	89.3
ΔT [°C]	4.3	4.8
dT/dt [°C/s]	11.0	15.5
$\frac{dT/dt}{Q}$	0.15	0.17

Changes of temperature in time were graphically analysed. The method of the least trapezoids was used to determine the surface area under the curve by calculating the rate of temperature increase with time, dT/dt. The calculation was carried out from the injection of methanol to the system up to the time when two successive decreases of temperature were noted. The values of the heat of wetting, the values of the temperature increase, dT/dt and the ratio of $\frac{dT/dt}{Q}$ are collected in Table 3.

The proposed method of measuring the heat of wetting makes it possible to compare the thermal effects of the process. The comparison of the values of the heat of wetting, calculated for the investigated adsorbent, shows that the heat evolved by the modified carbon is considerably greater. The large amount of heat evolved during the wetting process is an indication of a more developed adsorbent structure and a hydrophilic surface. In the case of the carbon subjected to modification, the rate of temperature increase is also higher. The ratios of temperature increase to the value of heat of wetting are close for these carbons. This may indicate a linear relationship between the increase of temperature and the heat of wetting. The results correlate well with structural parameters and the nature of the surface of the active carbons.

3 Conclusions

The KOH activation process of commercial active carbon significantly improves the properties important for acting as an adsorbent in systems of adsorptive refrigeration. Such modification expands the specific area of carbon, changes the nature of its surface and increases the heat of wetting. The chemical character of the surface of the active carbon, together with its porous structure, is the most important factor in determining its adsorptive properties. The methanol adsorptive capacity of carbon is also influenced by the presence of superficial oxygen functional groups.

The modified adsorbent is also characterized by larger energetic effects related to the heat of wetting with methanol. The KOH activation makes possible modification of the surface and nature of carbon adsorbents. All these advantages improve the performance and efficiency of the system in adsorptive refrigeration.

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