Adsorption 11: 769–773, 2005

Preparation of Active Carbons for Adsorption Cooling System

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Abstract. Among the gas–solid adsorption processes the active carbon methanol adsorption seems to be interesting for use in thermodynamic systems such as heat pumps and cooling systems. The porous structure of active carbon modified by successive removal of external layers from a particle surface as produced by abrasion in spouted bed, next by demineralization and oxidation was evaluated on the basis of nitrogen adsorption data and those for methanol. The aim of this study was to test the improvement of texture and nature of surface of active carbon for adsorption refrigeration system.

Keywords: adsorption, refrigeration, active carbon-methanol pair

1. Introduction

Adsorption processes have been proposed for heat management as a consistent alternative to vapor compression systems. Gas adsorption phenomenon is strictly correlated to energy transfer and transformation because they are regulated by temperature and pressure. Taking into account these properties and combining endothermic desorption with exothermic adsorption processes in closed cycles, it is possible to realize several attracted features for both heat pump and heat transformers applications (Critoph, 1989).

Adsorption systems show some advantages: the adsorbent is not submitted to any change of volume during the sorption processes, as in solid absorption; it does not need a rectifying column as in liquid absorption. Moreover, adsorption techniques allow large amounts of refrigerant liquid to be cycled.

In the design of adsorption refrigeration/heat pump systems, the characteristics of both adsorbent—adsorbate (refrigerant) pairs and adsorption cycles play an important role in various kinds of applications. A number of suitable adsorbents can be used to sorb refrigerants from the air with the simultaneous release of energy. At present two pairs dominate in refrigeration systems: zeolite–water and active carbon–methanol. Methanol is easily desorbed from active carbon when it is heated and can evaporate at a temperature largely below 273 K.

In adsorption cooling system as important as choice of adsorbate is appropriate choice of adsorbent. Recently we can observe increasing interest porous structure of carbon adsorbent which work effective in cycles adsorption—desorption. The adsorption depends on the surface area and pore size distribution, which in turn arises due to the nature of the raw material and the method of activation used. The adsorbent should not only have a high surface area, but should also be able to provide a high packing density. It seems that the carbon - methanol pairs appears to be a most promising medium for the heat storage systems (Buczek et al., 2003).

The effective work presented systems depends on: adsorption capacity, heat of adsorption, rate of adsorption/desorption and facility regeneration. Optimization heat exchange has become one of the most important conditions of effective work for adsorption cooling systems.

The aim of this study was to test the improvement of texture and nature of surface of active carbon for adsorption refrigeration systems. The methods of successive removal of external layers from a particle surface,

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demineralisation and oxidation of active carbon were used for the preparation of samples. In order to characterize the changes in properties of active carbons physicochemical measurements were made. The samples were characterized by nitrogen adsorption at 77 K. Methanol adsorption isotherms were measured volumetrically using a device for simultaneous determination of isotherms and kinetics of adsorption.

2. Experimental

Granulated active carbon of type N (Poland) obtained by activation of hard coal with steam was selected to study as commercial adsorbent originally used for organic vapors recovery. Carbon was subjected to working in a spouted bed (Buczek et al., 1987; Buczek, 1993). The time of the process was chosen in order that the amount of carbon abraded from the surface of the particles in the form of dust was increased by about 33 wt.% for each successive sample. As a result of this process, particles of active carbon with surface layers removed to different degrees were obtained and designated N33 and N66.

Next, both the initial sample (N0) as well as, abraded samples were treated three times with concentrated HCl and HF acids, then washed several times with distilled water.

In order to enhance the content of oxygen-containing groups on the surface, demineralized samples were oxidised with concentrated HNO_3 (H_2O:HNO_3; 1:5 v/v). After oxidation active carbon was washed with distilled water. Obtained samples were designated as carbons N0U, N33U, N66U. Modification and preparation procedure of active carbon are presented in Fig. 1.

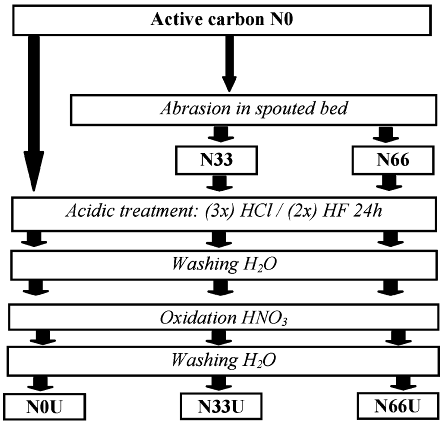

Figure 1. Modification of active carbon.

Methanol adsorption isotherms were measured volumetrically using a liquid microburettes for simultaneous determination of isotherms and kinetics of adsorption (Ciembroniewicz et al., 1985). Maximum experimental error is 2%. A manometric pressure stabiliser of manostate type guaranteed that the measurements were isobaric, and a system of thermostats ensured that the process was isothermal. The measurements were carried out in the temperature range 273–373 K.

3. Results and Discussion

The samples of active carbon were characterized by nitrogen adsorption and desorption at 77 K. The values of volume of micropores (W_o), characteristic energy of adsorption (E_o) and micropores surface area (S_{DR}) have been determined according to the Dubinin - Radushkevich equation (Dubinin, 1987). The value of mesopores surface area (S_{me}) and mean mesopores dimension (d_{me}) have been determined using Dollimore-Heal method (Dollimore et al., 1964), whereas specific surface by Brunauer, Emmett and Teller equation. The results of calculations obtained from isotherms are summarized in Table 1.

The oxidation process causes that the specific surface of activated carbons grow up. The decrease of micropore width and increase of mean mesopores dimension were observed. Value of characteristic energy of adsorption is greater for oxidized active carbon.

The adsorption isotherms of methanol vapours for oxidized active carbon N33U are presented in Fig. 2.

All of the samples readily adsorb methanol giving reversible isotherms of type I. Adsorption capacity decreases simultaneously to the temperature rises. Oxidized active carbon achieves greater adsorption capacity than samples obtained by attrition in spouted bed, as shown in Fig. 3.

The universal adsorption function (also called the “characteristic curve”) was calculated for the system under study. The points of characteristic curve thus calculated for observed temperatures are plotted in Fig. 4.

The procedure proposed gives a good representation of the data. Analysis of the data for a given temperatures results in a temperature—independent characteristic curve. Thereby, if the characteristic curve for an adsorbate is known, than adsorption values of can be predicted at any pressure and temperature. In practice, only one adsorption isotherm is necessary to obtain the characteristic curve and this is sufficient to describe the adsorption at all other temperatures and pressures.

Table 1. Sample textural properties.

Property	N0	N33	N66	N0U	N33U	N66U
Volume of micropores, W_o (cm^3g^{-1})	0.334	0.299	0.252	0.320	0.312	0.273
Characteristic energy of adsorption, E_o (kJ mol^{-1})	17.7	19.3	21.6	20.3	20.1	22.0
Micropore width, x_{mi} (nm)	0.74	0.67	0.56	0.49	0.48	0.48
DR surface area, S_{DR} (m^2 g^{-1})	942	842	710	900	878	769
Mesopores surface area, S_{me} (m^2 g^{-1})	102	76	46	111	88	78
Mean mesopores dimension, d_{me} (nm)	5.1	5.2	4.1	5.8	7.7	7.1
Specific surface, S_{BET} (m^2 g^{-1})	803	724	596	819	778	668

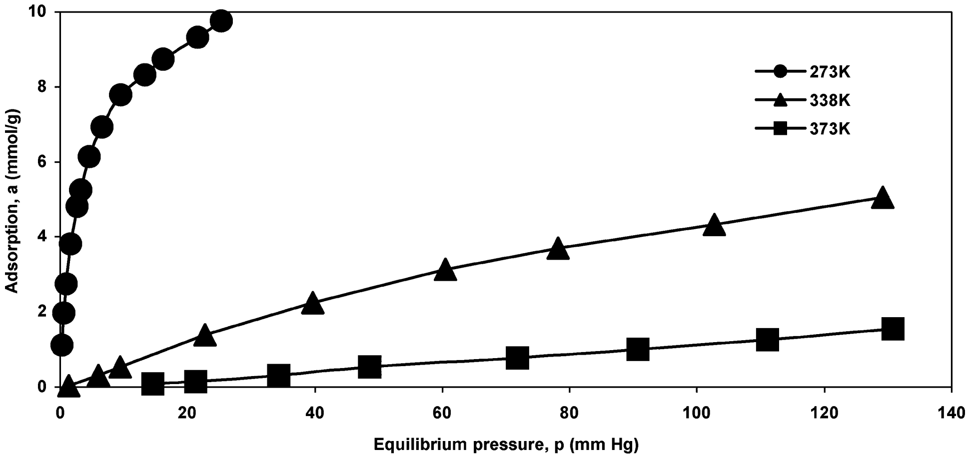

Figure 2. Methanol adsorption isotherms for active carbon sample N33U.

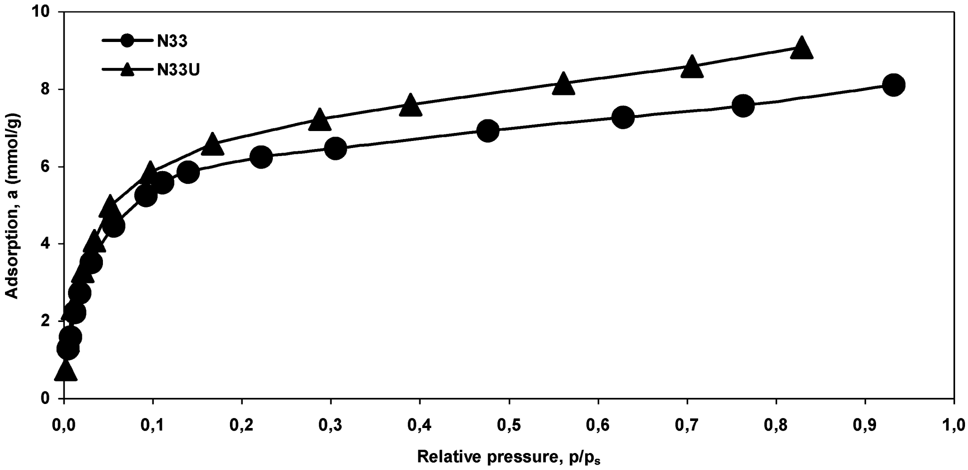

Figure 3. Methanol adsorption isotherms in temperature 273 K.

Adsorption isotherm data were also fitted using the thermal—type virial adsorption equation (Czepirski and Jagiello, 1989) to obtain the temperature and pressure dependence simultaneously. Although the equation used can be considered as an empirical, it allows a description and prediction of the isothermal data over a wide range: of pressures and temperatures.

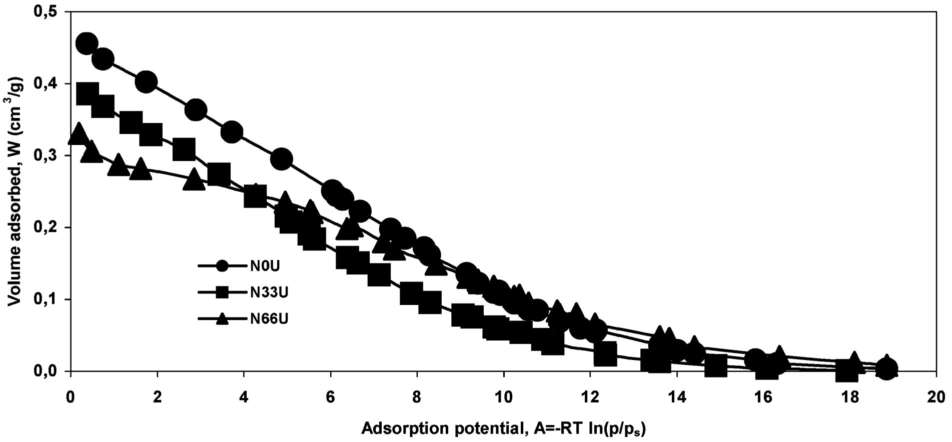

Figure 4. Characteristic curves for methanol adsorption on oxidized active carbons.

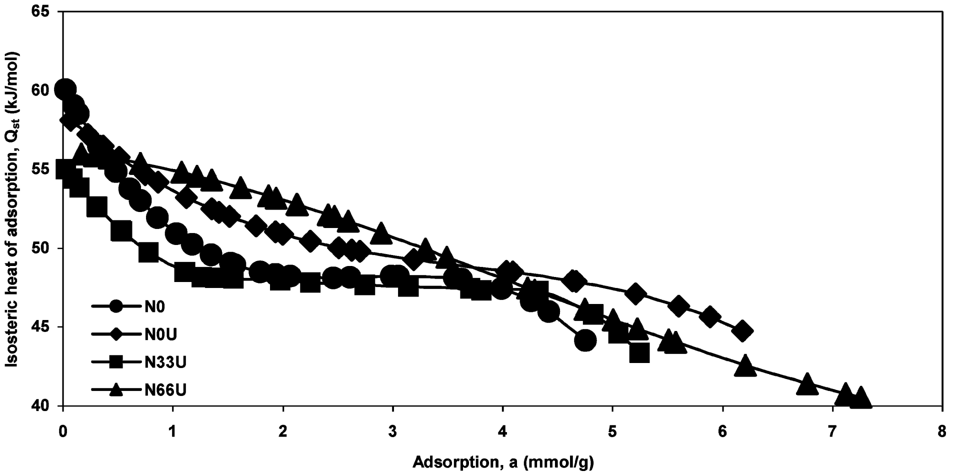

Figure 5. Isosteric heat of adsorption vs. amount adsorbed for oxidized active carbons.

It was considered that equation would be sufficient for numerical calculations of adsorption data for a given sample as a method facilitating and speeding up calculation for various operative conditions.

The virial adsorption equation can be used for estimating an isosteric heat of adsorption as a function of coverage. The run of adsorption heat (Fig. 5) shows adsorption heterogeneity associated with active carbons texture. Particularly interesting is run for carbon N66U, which curves can be possible connected with oxidation the surface of carbon samples with the most faintly developed the micro- and mesopores structure (N66). For all systems under study the isosteric heat of adsorption was higher than the heat of condensation and of the sufficient magnitude to be characterized as physical adsorption.

4. Conclusions

In this study modification and preparation of active carbon was made. The material of increased adsorption capacity was obtained. The change nature of surface of active carbon by oxidized improvement of the properties of carbon for adsorption refrigeration systems. The preparations of active carbon improve its densimetric characteristics and heat effects of methanol adsorption. The reduction of the adsorbent bed volume and simultaneous increase of the adsorption heat leads to the improvement for description adsorption cooling systems.

Porous structure parameters obtained for nitrogen and methanol agreed reasonably well and Dubinin-Radushkevich approach could be useful method for characterization of these systems. The methods for calculation of heat effects of methanol adsorption in wide range of temperature and pressures are discussed.

The approach proposed in description of equilibrium data in wide range of temperatures and pressures is very convenient to use in numerical calculations and the simplicity of the procedures allows rapid screening of many active carbon types in different conditions.

Active carbon adsorption cycles have great promise for small refrigeration systems. The porosity characteristics of available carbons give reasonable performance compared to the maximum that can be achieved with physical adsorption. Also, an improvement in the mechanical strength and conductivity of adsorbent is needed and the actual design of the total system, including heat exchangers, still needs to be considered in order to realise these systems.

Acknowledgments

The authors are grateful to the State Committee of Scientific Research (KBN) for its financial support of this work (Project No. 4 T08D 023 22).

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