REVIEW

of the official reviewer of the dissertation "Adsorption characterization of composite activated carbon for application in adsorption cooling systems" by Berdenova Bakytnur Amanbayevna, submitted for the degree of Doctor of Philosophy (PhD) in the specialty 6D060300 – Mechanics

Evaluation of the relevance of the topic of the dissertation (compliance with the development of science and technology, the inquiries of public practice).

The relevance of the dissertation is determined by the fact that according to the International Institute of Refrigeration (IIR), about 15% of all electricity produced in the world is used for cooling and air conditioning. Global warming is further aggravated by the need to develop effective devices for such purposes. There are two types of cooling systems: adsorption and compression systems, their operation principle is to use refrigerant with a very low boiling point. Refrigerants after taking the excessive heat of the cooled space begin to boil and evaporate. Thereby evaporated refrigerant particles remove the heat, providing a cooling effect. The main difference between these two systems is how the refrigerant passes from the gas state back to liquid so that the cycle could repeat. In adsorption cooling systems, gaseous refrigerant is absorbed by another material, and the temperature of the material saturated with the refrigerant increases, which leads to the evaporation of the refrigerants. Hot refrigerants pass through a heat exchanger, where they give away their thermal energy outside the system and condense. After all, the condensed refrigerant is sent to the initial compartment, where its next cycle begins.

The dissertation is devoted to the study of the adsorption characteristics of composite activated carbon for use in cooling systems.

This scientific direction of research is practically new in Kazakhstan for the development of new types of adsorbents for refrigeration systems and the analysis of their physical properties. While all over the world this area of adsorption is actively developing and finding more and more new applications.

The dissertation presents experimental and computational-theoretical studies of adsorption and outlines the following results.

1. Experimental studies were carried out on a magnetic suspension balance unit (MSB-GS-100-10 M) to measure CO₂ adsorption onto composite activated carbon and the adsorption capacities of the new material were determined. Experimental data measured gravimetrically gives excessive adsorption value is subject to an additional buoyancy correction procedure to obtain absolute adsorption. The absolute adsorption here is the number of moles of gas contained

in all the accessible pore volume of the porous material in the adsorbed state according to the Gibbs definition.

2. In the dissertation, two methods for assessing absolute absorption are considered: 1) the specific volume of gas in the adsorbed state is equal to the specific volume of pores; 2) assuming that absolute absorption is equal to excess absorption under conditions of low pressure and / or high temperature. The first method determines the upper limit of absolute absorption, and the second - the lower limit.

In the dissertation, the absolute absorption was evaluated by two methods, which allowed more accurately evaluating and building a model of the adsorption isotherm. It is shown that the true absolute value of adsorption is somewhere in between the data obtained using both methods and the average value should give the closest match.

3. To generalize the experimental data, various known adsorption isotherm models have been studied. The absolute adsorption data obtained using two main methods and their average were fitted to the modified Dubinin-Astakhov (D-A) and Tóth models. It is noted that both isotherm models describe well the absolute absorption calculated using two methods. The Tóth model is better for the 1st method, and the D-A model is better for the 2nd method of interpretation of the experimental data.

Also found isosteric heat of adsorption based on the D-A and Tóth models. The average *Q* value estimated using the modified D-A model is 19.742 kJ/mol, and using the Tóth model it is 19.023 kJ/mol.

4. The adsorption kinetics was studied. Experimentally the change in adsorption uptake with time is measured at temperature 20°C for pressures up to 5 MPa in the chamber. Various kinetic models in the literature were discussed: 1) a model with one effective mass transfer coefficient; 2) Maxwell-Stefan model for taking into account the mechanisms of mass transfer, such as surface diffusion, viscous flow and Knudsen diffusion; 3) model of mass transfer in macropores, that correspond to the different system configurations and activated carbon sorts (granular).

Based on the analysis of these works, a mathematical model was constructed for the case of gas adsorption onto consolidated activated carbon. The model implemented using one-dimensional axial dispersed plug flow geometry that excludes the gas penetration through the sides of the tablet. The obtained calculation results correspond to the concentration distribution during diffusion transport with the onset of equilibrium in the system when the adsorption reaches the saturation uptake.

- 5. The effective Knudsen diffusion in nanoporous material was studied. Knudsen diffusion depends on the pore size distribution of the adsorbent and molecular weight and temperature of the adsorbate. The Knudsen coefficient decreases with absorption, and the penetration of gas molecules into the sample becomes more complex. The Knudsen coefficient was calculated for the system under consideration.
- 6. Two different mathematical models with different assumptions listed in Chapter 7 used for experiment simulation. Where in the first model the porosity and Knudsen diffusivity are constants; in the second method to describe the mobile gas mass balance, the well-known model (Chadam et. Al., 1991) of the reaction flow in a porous medium was modified and adjusted to the case of adsorption process. The modified model takes into account the change in adsorption rate due to heat generation, the change in adsorbent porosity and Knudsen diffusion coefficient with uptake. In this case, a more acceptable agreement between the calculation and experiment is possible.

Scientific results within the requirements for the dissertations (paragraphs 2, 5, 6 of the "Rules for awarding academic degrees") and the degree of their validity

In the dissertation, when solving the tasks to achieve the purpose of the study, the following new results were obtained:

- 1. A new composite adsorbent with increased thermal conductivity and volumetric adsorption capacity was synthesized and comprehensively analyzed: the composite adsorbent shows 233% higher thermal conductivity than the parent adsorbent;
- 2. Absolute absorption was estimated by excess adsorption in two stages, which allowed more accurately evaluate and build a model of the adsorption isotherm. The results showed a good approximation between experiment and calculation.
- 3. A non-isothermal reactive mathematical model was constructed taking into account changes in the adsorption rate due to energy release, changes in porosity and Knudsen diffusion coefficient due to gas absorption in the capillaries of the adsorbent. The calculation results are in agreement with the experiment.

Assessment of the internal unity of the obtained results and their focus on solving relevant scientific and practical problems.

The results obtained in the dissertation by Berdenova B.A. represent finished work with inner unity. All the results and the conclusion are internally interconnected; each subsequent statement follows from the previous one. The scientific significance is that the developed mathematical model predicts the dynamics of adsorption with better accuracy, as it takes into account factors such

as changes in porosity and permeability with absorption, as well as the rate of adsorption due to the exothermicity of the adsorption process. Practical value is determined by improving the adsorption characteristics of the working pair (refrigerant / adsorbent) to increase the performance of the ACS. The results can be used in the development of a fully thermally or solar driven ACS prototype.

There are the following remarks for the thesis of Berdenova B.A.

- 1. One of the new results is that the developed consolidated adsorbent shows 233% higher thermal conductivity than that of the parent adsorbent. The dissertation does not explain this phenomenon.
- 2. It is shown that the true absolute adsorption uptake is somewhere in between the data obtained using two methods. Therefore, the average value of the two methods is considered the most suitable for describing the experiments. However, there is no clear explanation for this statement.
- 3. The method of averaging over the local volume of the porous medium, which is used in the dissertation, was first presented in the works of Soviet scientists Nigmatullin R.I., Nikolaevsky V.N. and others. Unfortunately, in the dissertation there is no reference to these works of Nigmatullin R.I., Nikolaevsky V.N. etc.

In conclusion, I believe that comprehensive work was carried out by Berdenova B.A. in combination with experiment conduction, processing the experimental data and the construction of a mathematical model to describe non-isothermal adsorption with heat generation and taking into account the changes in porosity and Knudsen diffusion coefficient in the capillaries of a new composite consolidated adsorbent.

The work of Berdenova B.A. meets all the requirements for the Ph.D. dissertation in the specialty "6D060300 – Mechanics ", and its author deserves the appropriate degree.

Official reviewer

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