

New numerical method as a tool for analysing the microporous structure of carbon materials on the basis of multiple gaseous adsorption isotherms

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Abstract

The aim of this work was the computer analysis of numerical properties of the original mathematical method of the description of adsorption process and the reliability of the identification of structure parameters. The method is based on the theory of multilayer adsorption, the derivation and further theoretical discussion of which was presented in the author's earlier works. The influence of the assumed structure parameters, the influence of the high-pressure section of adsorption isotherms and the influence of the number of simultaneously fitted adsorption isotherms on the quality of identification and the errors of microporous structure parameters. This research provides a basis for the evaluation of the reliability of the parameters calculated for real adsorption systems. Keywords Computer calculation. Heterogeneous. Isotherms. Microporous. Physical adsorption Introduction and theoretical basis

At the present time, the microporous materials occupy a major position among adsorbents due to their adsorption, chemical and mechanical properties. The characteristic adsorption properties of those materials are connected to the occurrence of micropores, defined as pores with internal width of less than 2 nm. The use of carbonaceous materials requires their characterization, which includes, among others, description of microporosity and heterogeneity in terms of adsorption energy. Different methods for the characterization of micropores are available, including spectroscopy, electron and tunnel microscopy and adsorption methods. However, the results obtained are not always compatible, resulting in problems with the credibility of the obtained structure parameters. Therefore in the majority of cases applying a single technique does not suffice to provide for precise and reliable information regarding the structure of the pores. Consequently, the acquired data should be compared with those obtained otherwise. The most popular method is the physical adsorption measurement, used widely for the analysis of the texture of porous carbons. Gas and vapours adsorption methods are the techniques applied particularly often for the characterization of microporous carbonaceous materials.

Several various equations have been proposed to describe the adsorption equilibrium of small molecules, and many different theories of physical adsorption processes have been developed. They are used for obtaining the characteristics of adsorbents including adsorption energy distribution, pore volume, pore size

distribution and surface area on the basis of the empirical adsorption data obtained at lower pressures. Those theories assume different mechanisms of physical adsorption processes and various simplifications of the real adsorption systems. For microporous materials, the Dubinin-Radushkevich (DR) and Dubinin-Astakhov (DA) equations are usually recommended. The DR equation is empirical, but it is based on the adsorption theory of the volume filling of micropores proposed by Dubinin and Radushkevich which has its origins in the potential theory of physical adsorption.

The DR equation is used widely for the description of vapours adsorption on a variety of microporous carbonaceous adsorbents, including activated carbons. However, it is often emphasized that there are several defects in the Dubinin-Radushkevich equation, which affect the accuracy of the results. In particular, the DR equation does not reduce to the Henry equation as p/p_0 approaches zero. Moreover, adsorption isotherms of many microporous carbonaceous materials usually cannot be fitted to the DR equation and in many cases the fittings are unsatisfactory.

Additionally, one can find objections in the literature that the energy parameter of the DR equation is not defined clearly enough. Another popular equation applied to the description of the physical adsorption process is the BET equation. The adsorption model on which the BET equation is based describes the multilayer physical adsorption on the basis of the kinetic model proposed by Langmuir. According to the Langmuir theory the adsorption process is limited to a monolayer and the dynamic equilibrium is reached between the gas phase and the adsorbed state when the rates of adsorption and desorption are equal. The principal assumption of the BET theory is that the Langmuir equation applies to every adsorption layer. Similar to the Langmuir theory, the first adsorption layer is formed on active centers, which are located on the adsorbent surface. Moreover, it is assumed that the probability of occupying a given site is independent of the neighboring sites and the molecules, which may already be placed at these neighboring sites. It is also assumed that there are no lateral interactions between the adsorbed molecules situated on the neighboring sites.

Applicability of the linearity range for the BET equation is usually restricted to the range of relative pressures between 0.05 and 0.35 p/p_0 and for the number of layers equal to 1 this equation reduces to the Langmuir equation.