Applied Surface Science 257 (2011) 8912–8922

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Analysis of relative pressure range influence on the identification quality during computer identification of adsorption system parameters by employing the new multilayer adsorption models

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ARTICLE INFO

Article history:
Received 7 November 2010
Accepted 18 May 2011
Available online 26 May 2011

Keywords:
Adsorption
Heterogeneity
Micropores
Isotherms
Computer modeling

ABSTRACT

The aim of this work has been to analyze the problems related to the identification of microporous structure parameters of carbonaceous materials. The new methods for microporous structure parameters identification have been explored with special focus on the influence of the analyzed relative pressure range on the reliability of parameters identification. For that purpose, the adsorption isotherm of nitrogen on active carbon for different ranges of relative pressures p/p_0 was analyzed. The conducted research was to provide for an answer to the question of whether the range of the analyzed relative pressures has any effect on the quality of adsorption system parameters identification, as well as what range of the relative pressure permits execution of the reliable identification of microporous structure parameters.

1. Introduction

The term ‘microporous carbonaceous adsorbents’ define a large group of materials with highly developed internal surface area and porosity, and consequently high capacity for adsorbing gases and liquids. The microporous carbonaceous adsorbents are extremely versatile adsorbents of industrial and everyday life significance, which are used, in a wide range of applications, concerned principally with the removal of undesired substances by adsorption from water [1–4] or air [5–7]. Additionally, microporous carbonaceous adsorbents have been applied widely in such fields of application as environmental protection [8,9], food [10,11] and petrochemical industry [12–14], air-conditioning [15–19], dehumidifying [20–22], gases storage [23–27] and separating gases mixtures technology [28–31].

The pores in carbonaceous adsorbents are scattered over a wide range of size and shape. The mentioned pores are usually classified by their sizes into three groups: the macropores with the average diameter of more than 50 nm, the mesopores with the diameter within 2–50 nm, and the micropores having the average diameter of less than 2 nm. These are further divided into supermicropores (0.7–2.0 nm) and ultramicropores of the diameter of less than 0.7 nm. The pore structure of the carbonaceous adsorbents is derived from the structure of the raw material, which is particularly evident in the case of wood-based products. It is therefore important to select appropriate original material in order to obtain the expected porous structure [32].

The different techniques have been used to determine pore size distribution in the porous carbonaceous adsorbents. These are mercury porosimetry and gas adsorption isotherms, and the scanning tunneling microscopy, which has been used increasingly often nowadays. However, the most popular and frequent method is that based on the adsorption of gases and vapours by determining adsorption isotherms [33–35].

In the 20th century there were developed numerous theories and methods for describing microporous structure of carbonaceous adsorbents and the adsorption processes, which occur, on their surface. Many equations describing the relation between the amount of adsorbed gas or vapour and the relative pressure of the adsorbed substances in the volatile phase were derived at that time as well [36]. Originally, these formulas had the form of empirical equations, although with the development of science and the growing knowledge of the adsorption process parameters the thermodynamical models with parameters having clearly definite the physical interpretation were developed. Parallel to the development and popularization of the computational methods, more sophisticated methods for microporous structure description based on the advanced numerical algorithms were developed [37–41], based on molecular simulations [42–46], the density functional theory [47,48], fractal approach [49–53] and neural networks [54–57].

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doi:10.1016/j.apsusc.2011.05.064

2. The classical models and equations

One of the most popular equations applied in the description of the adsorption process is the Dubinin–Radushkevich (DR) equation [58–66]. This equation describes well the adsorption on homogeneous materials, characterized by the narrow distribution of micropores, such as microporous active carbons [59], microporous carbon fibres, or microporous soots [60]. However, it should be mentioned that the description of porous structure using the DR equation is too distant from the real structure of carbonaceous adsorbents. Moreover, on the basis of this equation it is hard to qualify the real function of micropore volume distribution depending on their linear dimension [63]. It has been emphasized in many publications that there are doubts regarding the application of the DR equation to the description of the microporus structure of active carbons, connected in particular with the impact of temperature on the obtained values of the structural parameter and the volume of micropores caused by the presence of submicropores.

In their work, Choma and Jaroniec [67] presented very interesting results of the research in which the parameters of the microporous structure were determined using the DR equation on the basis of the isotherms of nitrogen, argon and benzene adsorption for three microporous active carbons. The comparison of the obtained results enabled obtaining information on the varying accessibility of the smallest micropores for the adsorbate molecules with different molecular sizes.

This means that the application of a single adsorbate to examine the microporous structure of carbonaceous adsorbents can be insufficient [67]. Therefore there arises the issue of using several simultaneously analyzed adsorption isotherms in structure analysis. When applying various temperatures or adsorbates with different molecule sizes, more precise information regarding the distribution of micropores can be obtained.

Numerous active carbons have bimodal structure, i.e. they contain in their structure two predominant average sizes of micropores. Therefore an attempt was made to analyze such materials as the superposition of two independent microporous structures. The sum of two DR equations was proposed to describe the bimodal structures [68], taking into account two microporous structures: micropores and supermicropores. This equation was called the Dubinin–Radushkevich bidispersion equation of adsorption isotherm.

Yet, another equation describing the process of adsorption on microporous carbonaceous adsorbents is the Dubinin–Astakhov equation (DA) [69,70]. The Dubinin–Radushkevich equation discussed above is the special case of the general Dubinin–Astakhov equation for which the exponential index is equal to 2 [70–73]. The DA equation characterizes the microporous structure by means of the following three parameters: the volume of micropores, the characteristic energy of adsorption of standard vapours, and the exponent. This equation describes well the process of adsorption on microporous carbonaceous adsorbents [71–74], even better than the DR equation, as evidenced experimentally [75–77].

However, it should be emphasized that both the Dubinin–Radushkevich and the Dubinin–Astakhov equations are only the empirical formulas. Therefore they should not be considered as the theoretical basis for analyzing the nature of the adsorption processes.

The present theory of adsorption was originated only by Langmuir, the author of the first thermodynamically correct theory which has been arising considerable interest until today, and the approach applied in that theory has been the starting point for many new theories and equations of adsorption isotherms derived from [78]. Langmuir assumed that the definite quantity of active places is located on the adsorbent surface, proportional to the surface size, and only one molecule of the adsorbate can place itself in each of such places. The monomolecular localized adsorption layer is developed this way.

According to the Langmuir's theory the energy of states of each adsorbed molecule does not depend on the presence of different atoms or molecules of the adsorbate in the surroundings of the active place under consideration, and therefore the occurrence of side-interactions is ignored. The interactions between the neighbouring molecules of the adsorbate were taken into account only in the Kisarov equation derived from the Langmuir theory [79].

In the case of using the Langmuir equation, it can be observed that considerable volume of the experimental data comply with the theoretical isotherms. However, a range of discrepancies may appear due to the multilayer adsorption parallel to reducing the temperature, as well as due to the inhomogeneity of the adsorbent surface. Having regard to the above, it is recommended to apply this equation mainly to describe the processes of chemical adsorption.

Based on the Langmuir theory, the BET theory of multilayer adsorption was derived by Brunauer, Emmett and Teller [80]. This theory is based on a series of assumptions bearing that: the adsorbent surface is homogeneous; there is a definite number of active places on the surface of the adsorbents; one or more molecules will be adsorbed on each active place; the adsorption is localized; multimolecular layer can develop on the surface of the adsorbent; and each layer can be described using the Langmuir equation. The scope of applicability of the BET equation is contained within the range of relative pressure p/p_0 from 0.05 to 0.35, and this equation can exceptionally be applied to the pressure value of 0.5 [80].

However, it should be pointed out that the physical model on which the BET theory was based contains a number of flaws, related to the fact that the Brunauer–Emmett–Teller theory is founded on a simplified extension of the Langmuir's adsorption mechanism. For instance, the BET theory does not take into account the side interactions between the adsorbed molecules, the significant influence of which on the mechanism of the adsorption process was discussed in the literature [81].

Many attempts have been made to modify the BET equation, and one of the interesting examples is the multilayer adsorption equation by Anderson which correctly describes the process of multilayer adsorption within the range from 0.1 to 0.8 p/p_0 [82]. Another interesting proposal for the modification of the BET equation was presented by Hütting [83], who assumed that during the adsorption process the layers of adsorbate are formed on the adsorbent, and additionally it is possible to desorbed the adsorbed molecules from the deeper, already formed adsorption layers.

Ross [83] derived Hütting equation using the BET theory and compared it to the derivation of the BET theory, showing that these two theories differ only in the assumed desorption mechanism. According to Hütting equation, the process of molecule desorption from the nth layer does not come across any restrictions caused by the molecules adsorbed in the layer $n+1$, while according to the BET theory the molecules adsorbed in the layer $n+1$ totally disable the desorption of the molecules located in the lower layers [83]. In the Hütting equation the number of molecules adsorbed under the pressure $p = p_0$ is not infinite, as in the BET equation, but equal to the number of layers.

Considering the fact that the BET equation determines too high adsorption in the area above $p/p_0 = 0.35$, while the Hütting adsorption isotherm equation determines too low adsorption in the corresponding area, it was proposed to calculate the mean from the above equations, and consequently no additional parameter was introduced [83]. However, this approach has not been accepted widely.

When discussing the classical equations of the adsorption process, one should also mention very popular empirical adsorption equation derived by Freundlich [84], applied widely in technology. However, when using this equation one should remember that sat-