



# A new model for calculating the adsorption equilibrium constant of water vapor in micropores of activated carbon



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## ABSTRACT

A new model for calculating the adsorption equilibrium constant of water vapor in the micropores of activated carbon was established, the mechanism of which is based on the penetration of water clusters into micropores. Two kinds of carbon materials with significantly different pore and surface structures were prepared for water vapor adsorption, and the adsorption experiments were conducted in different conditions to test the accuracy of the new model. The new model was also applicable to water adsorption on bituminous-based activated carbon. Furthermore, being able to calculate the values for enthalpy of activation and entropy of activation, the new model can provide universal thermodynamic criteria for the water adsorption on activated carbon.

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## 1. Introduction

Activated carbon mainly suffers from water vapor adsorption in gas separation and purification, such as hydrogen gas from steam methane reforming and volatile organic compound (VOC) removal from air [1,2]. Despite the hydrophobicity of activated carbon, water affects the separation of hydrogen and methane as well as the adsorption of VOCs, especially in high relative humidity conditions where water is considerably adsorbed that interferes significantly with organic gas adsorption. Therefore, studying on water vapor adsorption in activated carbon has been paid particular attention from both theoretical and experimental perspectives.

In the beginning, water vapor adsorption was analyzed by theoretical methods. Dubinin and Serpinsky (DS) [3,4] studied the kinetic theory of water sorption onto sorption sites, and obtained an equation applicable to the experimental data. Stoeckli et al. [5] studied water vapor adsorption in activated carbons using the Dubinin–Astakhov (DA) equation. The equation becomes S-shaped at medium relative pressures and provides a good basis for the fitting of the adsorption branch of type V isotherms at near room temperature. Müller et al. [6] proposed a molecular model for water vapor on activated carbon pores based on the grand canonical Monte Carlo

simulation method. The simulation results at low pressures accorded with the experimental data. Finally, Talu and Meunier [7] presented another equation that basically involved the clustering of water molecules around chemisorption sites. The theory is highly effective in correlating temperature variation, and provides physically meaningful parameter values in line with carbon properties.

Do et al. [8] developed a new model (DD model) based on cluster formation and penetration of clusters into micropores. This model accounts for the micropore structure of activated carbon, with functional groups at the basal plane edges of graphitic units. Hysteresis in the adsorption–desorption isotherm relies on the relaxation of water clusters inside micropores. Besides, this model accounts for the different shapes of water adsorption isotherms for carbonaceous materials, and presents a mechanism for water vapor adsorption in activated carbon, i.e. water molecules, which are adsorbed in the clusters surrounding functional groups, enter the micropores once they grow to sufficiently large. The DD model has been modified diversely. For example, Horikawa et al. [9] extended the model by adding an additional term to describe the adsorption in mesopores, and Neitsch et al. [10] assumed cluster size was variable. Furmaniak et al. [11] developed a heterogeneous DD model to elucidate the distribution of adsorption energy of functional groups, and Cossarutto et al. [12] used a Langmuir equation to describe the adsorption on functional groups.

Although the DD model can describe the different shapes of water adsorption isotherm in activated carbon, many physical parameters, such as the equilibrium constant of micropore adsorption and the size of water clusters, cannot be directly measured.

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Thus, it is necessary to develop a new theory or to establish a novel model to calculate these factors with measurable macroscopic parameters.

Thereby motivated, a new model was proposed herein to calculate the equilibrium constant of micropore adsorption in this paper. In addition, water vapor adsorption experiments were carried out and the adsorption data for two different kinds of activated carbon were determined. The applicability of the new model was also tested against those of other scholars' research.

## 2. Material and methods

### 2.1. Material preparation

A commercial granular activated carbon, purchased from Shanxi Xinhua Activated Carbon Co., Ltd. (KZ15-2), was used as the raw activated carbon (RAC). Prior to use, it was washed in deionized water to remove impurities and was kept in a drying vacuum oven at 573 K for over 24 h to remove functional groups. A portion of RAC was further immersed into a 1 M calcium acetate ( $(\text{CH}_3\text{COO})_2\text{Ca}$ ) solution at room temperature for 72 h, put into the drying vacuum oven again, and kept at 398 K for 24 h to produce the modified activated carbon (MAC).

### 2.2. Analysis of materials

Porous texture of RAC and MAC were determined by  $\text{N}_2$  isotherms at 77 K using an SA3100 specific surface area analyzer (Beckman-Coulter Instrument Co., USA). The samples were grinded to a powder and degassed in vacuum at 293 K for 24 h before the test. Their surface area ( $S_{\text{BET}}$ ) and pore volume ( $V_{\text{total}}$ ) were calculated using Brunauer Emmett Teller (BET) equation [13]. The micropore surface area ( $S_{\text{mic}}$ ), as well as its volume ( $V_{\text{mic}}$ ) were calculated using the  $t$ -Plot method [14].

### 2.3. Adsorption experiments

Configuration of the experimental apparatus used in the fixed-bed adsorption experiments is shown in Fig. 1. Dry compressed air was pushed through an electronic mass flow controller (MFC, Qixin Huachuang Instruments, China) to regulate air flow through the system. Then the air was divided into two parts. One part was passed through saturated water to obtain moist air, and the other one was connected with a mixing tank to dilute the moist air. To elevate the relative humidity of moist air, the saturated water was heated with a thermostatic water bath (TWB, Tiandi Instruments, China), and then the super heated vapor was condensed with a graham condenser (GC) before entering the mixing tank. The mixed air was held at 2.0 l/min by a flow meter. Relative humidity ( $RH$ ) in the system was adjusted by a flow meter (FM, Suzhou Beida Instruments, China) installed upstream of the mixing

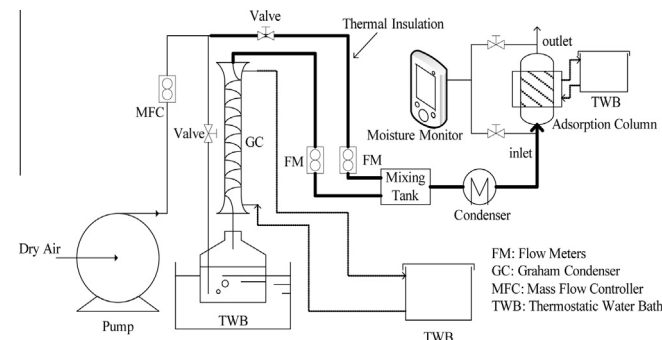


Fig. 1. Configuration of the experimental apparatus.

tank. The adsorption column was constructed out of glass (inner diameter: 0.8 cm) pipe and the temperature kept from 293.15 to 313.15 K during adsorption. For each test, 4–6 g sample was put into the adsorption column. Relative humidity and concentrations of water vapor at the inlet and outlet of the column were measured by a Center 310 moisture monitor (Center Technology Corp., Taiwan). The test results were automatically recorded per 5 s by a computer. The concentration at the column outlet was increased gradually until adsorption equilibrium which was defined as a concentration variation less than 3% with in more than an hour. The adsorption amount of water in activated carbon ( $q_u$ ) is calculated as follow:

$$q_u = \frac{\int (C_{\text{in}} - C_{\text{out}}) V dt}{m} \quad (1)$$

where  $C_{\text{in}}$  and  $C_{\text{out}}$  are the concentration at the inlet and outlet of column, respectively,  $V$  is the flow rate of water vapor and  $t$  is the adsorption equilibrium time.

## 3. Theory

The original model was proposed by Do et al. with assumptions of the DD model [8]. The DD equation describing adsorption is:

$$q_u = q_{u,s} \cdot \frac{k_u \sum_{n=\alpha+1}^{\infty} x^n}{k_u \sum_{n=\alpha+1}^{\infty} x^n + \sum_{n=\alpha+1}^{\infty} x^{n-\alpha}} + q_s \cdot \frac{k_f \sum_{n=1}^{\alpha} x^n}{(1-x)[1+(k_f-1)x]} \quad (2)$$

where  $q_u$  is the adsorption amount of water vapor in activated carbon,  $q_{u,s}$  is the saturated adsorption amount of water vapor in the micropore,  $q_s$  is the amount of functional groups participating in water vapor adsorption,  $\alpha$  is the water cluster size,  $k_u$  is the equilibrium constant of micropore adsorption,  $k_f$  is ratio of (equilibrium constant of adsorption and desorption per unit functional group)/(equilibrium constant of adsorption and desorption on the water vapor adsorbed on functional group), and  $x$  is the relative humidity of water vapor.

During adsorption, a portion of water molecules have sufficient potential energy to enter a micropore and then to be adsorbed inside. On the other hand, some water molecules adsorbed on activated carbon surfaces leave the micropore because of heat activation. Having described a mechanism for water adsorption-desorption in the micropores of activated carbon, a mathematical

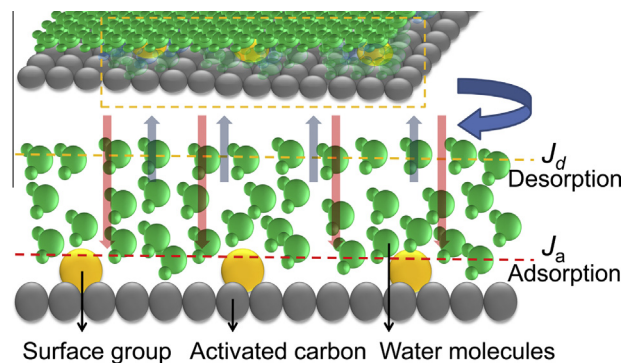


Fig. 2. Schematic of water vaporizing theory in activated carbon.

Table 1  
Specific surface area and pore volume of RAC and MAC.

Sample	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	$S_{\text{mic}}$ ( $\text{m}^2/\text{g}$ )	$V_{\text{total}}$ ( $\text{ml}/\text{g}$ )	$V_{\text{mic}}$ ( $\text{ml}/\text{g}$ )
RAC	947.7	845.6	0.466	0.396
MAC	756.4	621.1	0.348	0.299

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