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A New Isotherm Equation for Single-Solute Adsorption from Dilute Solutions on Energetically Heterogeneous Solids

Short Communication

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A new isotherm equation is proposed for describing single-solute adsorption from dilute solution on energetically heterogeneous solids. This equation comprises all isotherm equations being an extension of simple *Langmuir* isotherm to single-solute adsorption on heterogeneous solids. The phenol adsorption data from dilute aqueous solutions on activated carbon are studied by using this new equation.

(Keywords: Single-solute adsorption; Adsorption from dilute solution; Generalized Langmuir isotherm; Phenol adsorption from dilute aqueous solutions; Adsorption on activated carbon)

Eine neue Isothermengleichung für die Adsorption aus verdünnten Einzelkomponentenlösungen auf energetisch heterogenen Festkörpern (Kurze Mitteilung)

Es wurde eine neue Isothermengleichung für die Adsorption aus verdünnten Einzelkomponentenlösungen auf energetisch heterogenen Festkörpern vorgeschlagen. Diese Gleichung schließt alle bisherigen Isothermengleichungen in sich ein, die Verallgemeinerungen der einfachen *Langmuir*-Isotherme für Adsorption auf heterogenen Festkörpern sind. Es wurden Daten der Adsorption von Phenol aus verdünnten Wasserlösungen auf aktivierte Kohle unter Verwendung der neuen Gleichung untersucht.

The isotherm equations used in single-solute monolayer adsorption from dilute solutions on energetically heterogeneous solids may be divided into two groups[1–3]. The first group contains the isotherm equations reducible to the *Langmuir*-type equation: the generalized

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Freundlich (GF), *Langmuir-Freundlich* (LF) and *Tóth* (T) isotherms. However, the isotherm equations belonging to the second group may be obtained from the exponential absorption isotherm which has been firstly proposed for gas adsorption by *Jaroniec*[4]. The isotherm equations from the second group are very popular in physical adsorption: the *Dubinin-Radushkevich* (DR) and classical *Freundlich* (F) equations. In a recent review[4] *Jaroniec* presented a derivation of equations for single-solute adsorption from the isotherm equations describing adsorption of single gases on energetically heterogeneous solids.

In this communication a new isotherm equation is proposed for single-solute monolayer adsorption. This equation comprises all adsorption isotherms belonging to the first group. It means that these isotherms are special cases of this general equation. Its mathematical form is:

$$\theta = a/a_0 = \left[\frac{(\bar{K}c)^n}{1 + (\bar{K}c)^n}\right]^{\frac{m}{n}} \tag{1}$$

In the above a is the adsorbed amount, a_0 is the monolayer capacity, c is the solute concentration, $\bar{K}$ is the *Langmuir*-type constant, m and n are heterogeneity parameters. The parameters m and n can vary from zero to unity. For $m = n = 1$ Eq. (1) becomes the *Langmuir* adsorption isotherm. The LF equation, discussed in Ref.[2], may be obtained from Eq. (1) by assuming $(m = n) \in (0,1)$. It follows from Ref.[5], that the LF equation corresponds to the symmetrical quasi-*Gauss*ian energy distribution; the parameter n is connected with its width. However, for $m = 1$ and $n \in (0,1)$ Eq. (1) becomes the *Tóth*-type isotherm[6,7] which corresponds to asymmetrical quasi-*Gauss*ian energy distribution with a widened left-hand side[8]. The GF adsorption isotherm may be obtained from Eq. (1) for $n = 1$ and $m \in (0,1)$; it relates to the exponential decreasing energy distribution[9,10]. The parameter m characterizes widening of the distribution in the direction of higher adsorption energies, whereas n characterizes this widening in the direction of lower adsorption energies. The behaviour of isotherm Eq. (1) for $n < m$ is analogous to the *Tóth* isotherm, however, for $n > m$ its properties are similar to a GF isotherm.

For the purpose of illustration the adsorption data of phenol from dilute aqueous solutions on activated carbon at 298 K[11] were represented by Eq. (1). These data were described by *Tóth*[7], classical *Freundlich*[12,13], DR[1] and LF[2,14] isotherm equations. The studies of *Jaroniec* and *Derylo*[1,2,12–14] showed that the classical *Freundlich* and LF equations show small deviations at low and higher solute concentrations. However, the *DR* equation gives the best representation for the above adsorption data. This equation corresponds to an energy distribution with a widened right-hand side[15]. The *Tóth* isotherm gives a worse representation of the phenol adsorption data than a *DR* one because its energy distribution is widened in the direction of lower adsorption energies.

For low solute concentrations Eq. (1) reduces to the classical *Freundlich* isotherm:

$$\ln a = (m \ln \bar{K} - \ln a_0) + m \ln c \tag{2}$$

Plotting the phenol adsorption data for low solute concentrations according to the linear Eq. (2) we calculated the parameter m; it is equal to 0.39. Next, these data were plotted according to the following relationship:

$$\Psi_m = \ln\left[m \cdot \frac{\partial \ln c}{\partial \ln a} - 1\right] = n \ln \bar{K} + n \ln c \tag{3}$$

This relationship is presented in Fig. 1; it gives the parameter $n = 0.44$. Knowing the parameters m and n we can present the adsorption data as follows:

$$a^{\left(\frac{n}{m}\right)} = a_0^{\left(\frac{n}{m}\right)} - (\bar{K})^{-n}\left[\frac{a^{\left(\frac{n}{m}\right)}}{c^n}\right] \tag{4}$$

The dependence $a^{n/m}$ vs. $a^{n/m}/c^n$ is shown in Fig. 1; it gives $a_0 = 5.34\,\mathrm{mmol/g}$ and $\bar{K} = 0.29$. In Fig. 1 the phenol adsorption isotherm is also presented in the logarithmic scale (black circles) with comparison to the theoretical isotherm (the solid line) calculated according to Eq. (1) for parameters presented above. At higher solute concentrations the experimental points deviate from the solid line; it is connected with forming of second and higher adsorption layers. Introduction of the multilayer correction according to the *BET* model gives better agreement with experiment (dashed line). The corrected isotherm was calculated according to the following equation:

$$\theta = \frac{1}{1 - c/c_0} \cdot \left[\frac{(Ac/c_0)^n}{1 + (Ac/c_0)^n}\right]^{\frac{m}{n}} \tag{5}$$

where $A = \bar{K} \cdot c_0$ and c_0 is the saturation concentration of a given solute. Eq. (5) may be obtained by extension of Eq. (1) according to the method used in gas adsorption[6] on energetically heterogeneous solids, when the classical *BET* equation with $A \gg 1$ is applied as the local adsorption isotherm.

It follows from Fig. 1 that new isotherm Eq. (1) gives a good representation for phenol adsorption data from dilute aqueous solutions on activated carbon. As the parameter $n > m$ the energy distribution is an asymmetrical quasi-*Gauss*ian function with a widened right-hand side, which is characteristic for the *DR* isotherm. This result confirms our earlier studies[1] concerning application of the *DR* isotherm for describing single-solute adsorption data.

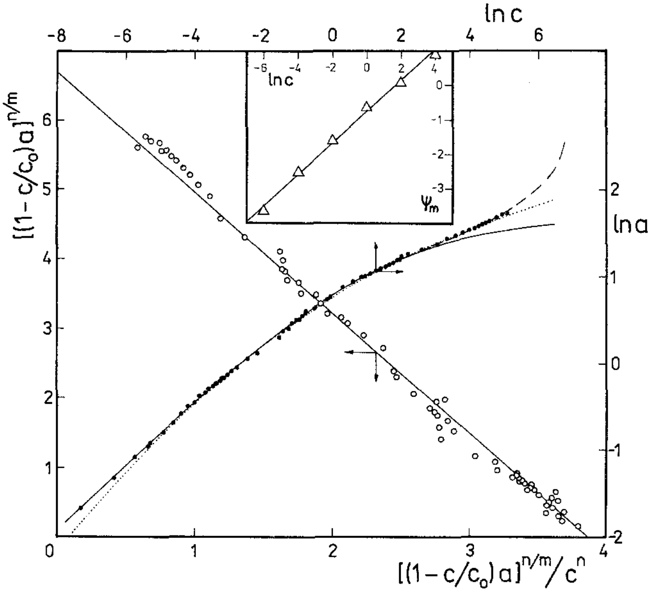

Fig. 1. Experimental points (black circles) and theoretical isotherms calculated according to Eq. (1) (solid line), according to *Tóth* equation [Eq. (1) with $m = 1$] (dotted line) and according to Eq. (5) (dashed line) for adsorption of phenol on activated carbon from dilute aqueous solutions at 298 K. The white circles and straight solid line correspond to linear dependence (4) including the effect of multilayer. The white triangles and straight solid line show the dependence of the function Ψ_m vs. $\ln c$ (Eq. 3) for the experimental and theoretical isotherm

The adsorption isotherm Eq. (1) gives:

$$\varphi = \left(\frac{\partial \ln a}{\partial \ln c}\right)_{(\bar{K}c = 1)} = m/2 \tag{6}$$

This relationship may be used to check the physical reality of the adsorption parameters determined by means of Eqs. (2)-(4). Using $m = 0.39$ we calculated $\varphi = 0.195$, which is very close to the value of φ calculated from the dependence $\ln a$ vs. $\ln c$ at the point $\bar{K}c = 1$ ($\bar{K} = 0.29$). However, for the *Tóth* isotherm [Eq. (1) with $m = 1$] used to describe the above data by *Jossens* et al.[7] Eq. (6) gives $\varphi = 0.5$, whereas the value of φ calculated from the experimental dependence $\ln a$ vs. $\ln c$ at the point $\bar{K}c = 1$ is considerably lower than 0.5. Moreover, the *Tóth* isotherm (dotted line) deviates from experimental data (cf., Fig. 1).

Concluding our analysis of the phenol adsorption data by means of Eq. (1) we can state that this equation gives parameters physically realistic. The energy distribution characteristic for this system is asymmetrical quasi-*Gauss*ian with a widened right-hand side.

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