

Letter to the Editor

Developing the solution analogue of the Toth adsorption isotherm equation

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Abstract

The well-known Toth adsorption isotherm equation developed formerly for adsorption of vapors is converted into its solution analogue. It is shown that this equation can be successfully applied to the description of adsorption data of organics on activated carbons.

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1. Introduction

The empirical adsorption equation proposed by Toth [1,2] describes well many systems with submonolayer coverage. As was pointed out recently by Do [3], the Freundlich equation is not valid at the low and high ends of the pressure range, and the Sips equation is not valid at the low end, as they do not possess the correct Henry-law-type behavior. In contrast, the Toth equation is one of the empirical and popularly used equations since it satisfies the two end limits [3]. It has the form

$$\Theta = \frac{K_T p}{[1 + (K_T p)^t]^{1/t}}, \quad (1)$$

where $\Theta = a/a_{\max}$, a and a_{\max} are the adsorption and the maximum adsorption, respectively, K_T and t are the equation constants, and p is the equilibrium pressure. It is obvious that for $t = 1$ this isotherm reduces to the Langmuir adsorption isotherm equation; therefore the parameter t is said to characterize the system heterogeneity. If it deviates further away from unity, the system is said to be more heterogeneous.

2. The general procedure of derivation of the solution analogue

Garbacz et al. [4,5] proposed a very interesting procedure for derivation of the solution analogue of an adsorption isotherm equation formerly developed for vapors. To illustrate this method one can consider the Langmuir adsorption isotherm equation,

$$\Theta = \frac{K_L p}{1 + K_L p}, \quad (2)$$

where K_L is the Langmuir constant. This equation can be rewritten assuming that $p = p_s$, and the latter is a saturation vapor pressure. Thus,

$$\Theta_s = \frac{K_L p_s}{1 + K_L p_s}. \quad (3)$$

Dividing Eqs. (2) and (3) and denoting $\vartheta = \Theta/\Theta_s$, after simple manipulation one obtains

$$\vartheta = \frac{K^* h / (1 - h)}{1 + K^* h / (1 - h)}, \quad (4)$$

where $h = p/p_s$ and $K^* = K_L p_s + 1$.

It is obvious that Θ is the degree of surface filling and defined in this way ϑ describes the degree of filling of the internal adsorption space of an adsorbent. The solution analogue of Eq. (4) is the isotherm developed by Everett [6]

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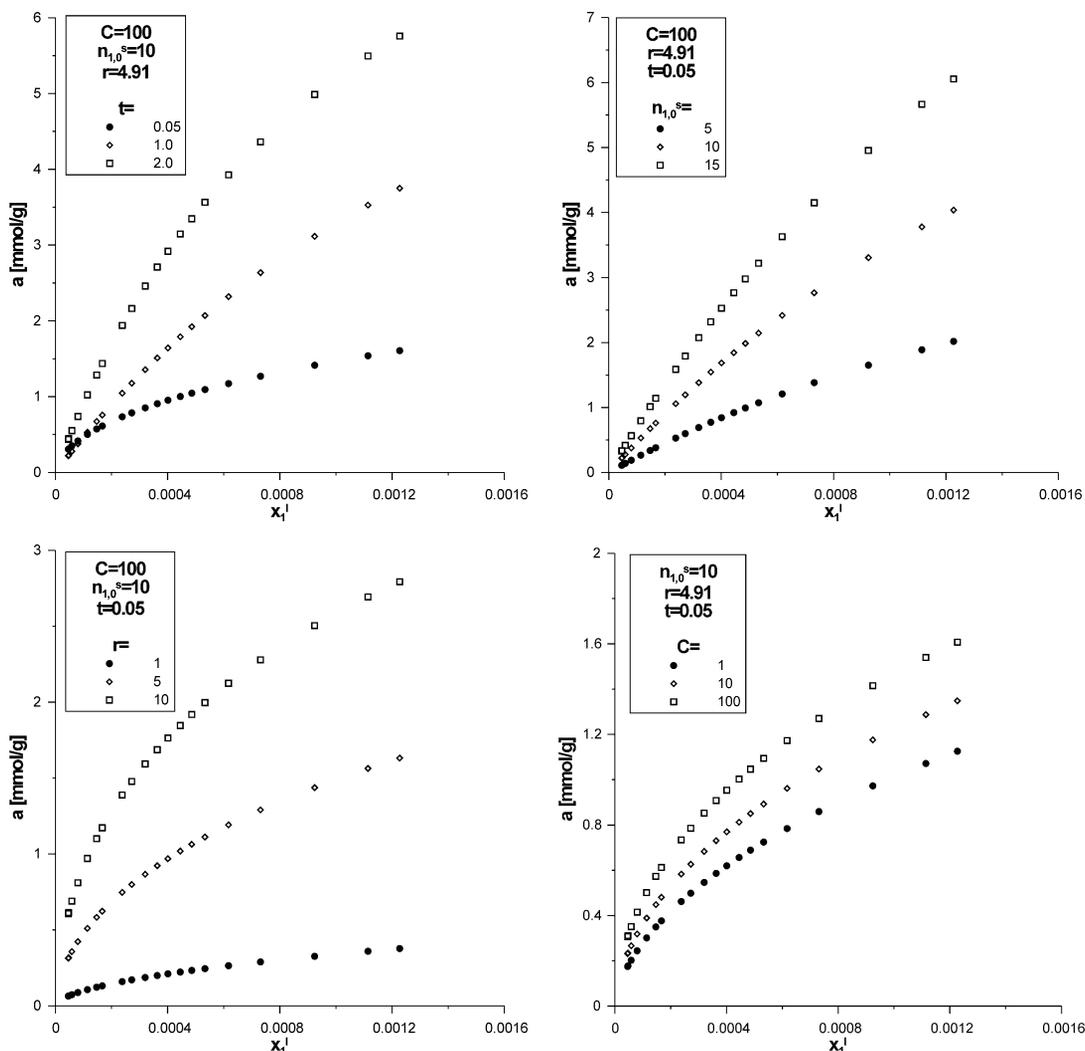


Fig. 1. The features of the solution analogue of the Toth adsorption isotherm equation (13) connected with Eqs. (14) and (15).

based on the thermodynamics of adsorption from solution,

$$x_1^s = \frac{Ca_1/a_2}{Ca_1/a_2 + 1}, \tag{5}$$

where C is the equilibrium constant of the exchange process in the system: bulk phase/adsorption layer, a_1 and a_2 are the activities of components 1 and 2 in the bulk phase, and x_1^s is the equilibrium mole fraction of the component 1 in the adsorbed phase.

It can easily be shown that Eqs. (4) and (5) are equivalent if one assumes that

$$\vartheta \rightarrow x_1^s, \quad h/(1-h) \rightarrow a_{12} = a_1/a_2, \quad K^* \rightarrow C. \tag{6}$$

Garbacz and co-workers [4,5], postulating that Eqs. (6) are general, developed in this way a method of simple derivation of the solution analogs of well-known adsorption isotherm equations. As an example, the solution analogs of the Dubinin–Radushkevich and Freundlich adsorption equations are

$$x_1^s = \exp \left[- \left(B_{DR} \ln \frac{1+a_{12}}{a_{12}} \right)^2 \right] \tag{7}$$

and

$$x_1^s = \left(\frac{a_{12}}{1+a_{12}} \right)^{B_F}, \tag{8}$$

where B_{DR} and B_F are constants.

3. The solution analogue of the Toth equation

Adopting the procedure described above and denoting

$$\alpha = \frac{h}{1-h}, \tag{9}$$

Eq. (1) can be rewritten as follows:

$$\Theta = \left[\frac{(K_T p_s \frac{\alpha}{1-\alpha})^t}{1 + (K_T p_s \frac{\alpha}{1-\alpha})^t} \right]^{1/t}. \tag{10}$$

If $p = p_s$ it becomes

$$\Theta_s = \left[\frac{(K_T p_s)^t}{1 + (K_T p_s)^t} \right]^{1/t} \tag{11}$$

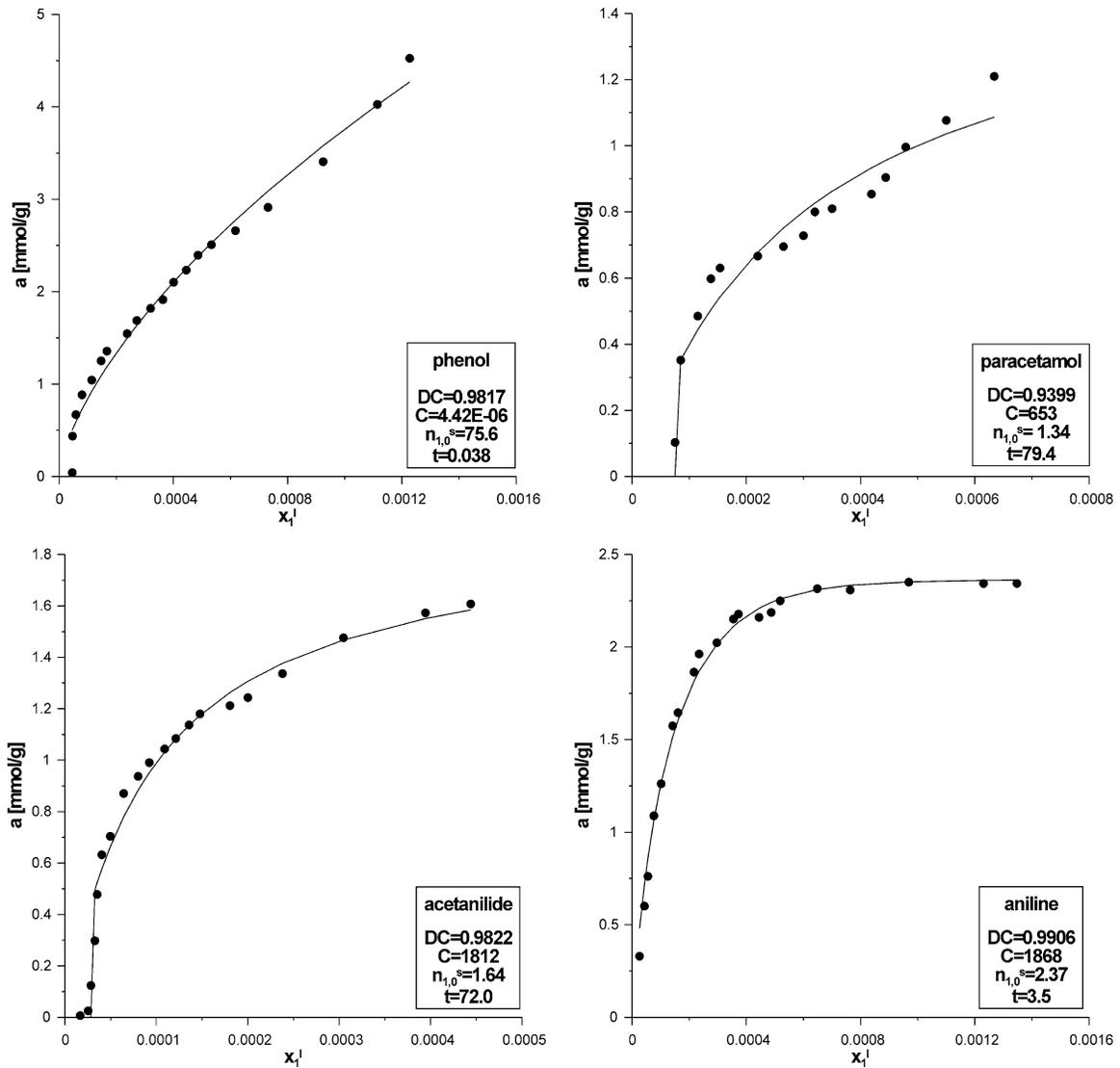


Fig. 2. The results of fitting of the solution analogue of Toth isotherm (solid line) to the experimentally measured adsorption data of phenol [7], paracetamol [9], acetanilide, and aniline on D43/1–HNO₃ carbon at 300 K. DC is the determination coefficient describing the goodness of the fit of the theoretical data to the experimental ones.

and finally

$$\vartheta = \frac{\Theta}{\Theta_s} = \left[\frac{(1 + (K^\#)^t) \left(\frac{\alpha}{1-\alpha}\right)^t}{1 + (K^\#)^t \left(\frac{\alpha}{1-\alpha}\right)^t} \right]^{1/t}, \quad (12)$$

where $K^\# = K_T p_s$. Assuming $t = 1$ and $K^* = K^\# + 1$, Eq. (12) can be easily transformed into Eq. (4).

Taking into account Eqs. (6),

$$x_1^s = \left[\frac{(1 + (C)^t) \left(\frac{a_{12}}{1-a_{12}}\right)^t}{1 + (C)^t \left(\frac{a_{12}}{1-a_{12}}\right)^t} \right]^{1/t}. \quad (13)$$

Summing up, Eq. (13) is the solution analogue of the Toth adsorption isotherm equation (1).

4. The basic features and the experimental verification of Eq. (13)

Equation (13) was verified for four adsorbate–activated carbon systems. Recently reported phenol [7] and paracetamol adsorption data [8,9] measured at 300 K on D43/1 carbon (Carbo-Tech, Essen, Germany) oxidized by conc. nitric acid, labeled as D43/1–HNO₃, were applied. Adsorption data of acetanilide and aniline on the same carbon measured at this temperature are new and have not been published yet. The procedure of measurement, as well as the carbon characteristics, has been published elsewhere [7–12].

It is well known that in describing adsorption from solution, the presence of both components should be considered and [13]

$$n_1^{\sigma(n)} = n^s (x_1^s - x_1^l), \quad (14)$$

where $n_1^{\sigma(n)}$ is the adsorption amount, x_1^s is the molar fraction of a solute in the adsorbed phase, and x_1^l is the mole fraction of a solute in the liquid phase. The differences in the molecular volumes of the two components of the solution must be taken into account by [5]

$$n^s = rn_{1,0}^s / [1 + (r - 1)x_1^s], \quad (15)$$

where $r = (V_s/V_l)$ is the ratio of the molar volumes of solute and solvent (the following values were taken in calculations: phenol–water system, $r = 4.91$ [7], paracetamol–water, $r = 5.81$ [8], acetanilide–water, $r = 6.12$, and aniline–water, $r = 5.25$), and $n_{1,0}^s$ is the number of moles of a solute adsorbed by a mass unit of an adsorbent in the absence of a solvent.

Figure 1 shows the main features of Eq. (13) connected with Eqs. (14) and (15). The influence of the parameter t is exactly the same as for the original Toth equation (1) (see p. 65, Fig. 3.2-10 in [3]). It can be mentioned that the more this parameter is lower than unity, the more heterogeneous is the system. On the other hand, as was mentioned by Toth [2], if the lateral interactions between the adsorbed molecules are greater than the adsorptive potential, $t > 1$. As was expected, Fig. 1 shows that the rise in the $n_{1,0}^s$ leads to the increase in adsorption. Exactly the same effect is observed when the molecules of a solute are larger than those of a solvent (i.e., if r increases) and if the affinity of adsorbed molecules to the surface increases (the rise in C value).

Equations (13)–(15) were fitted to experimental data by applying a minimization procedure using the differential evolution (DE) algorithm constructed by Storn and Price [14]. It is a vectorized variant of DE which, however, has properties differing from the original version of DE. The random selection of vectors is performed by shuffling the population array. Hence a certain vector cannot be chosen twice in the same term of the perturbation expression.

Figure 2 shows the graphical comparison of the theoretical and experimental isotherms (Eqs. (13)–(15)). It can be concluded that the solution analogue of Toth equation describes the analyzed data satisfactorily, and only for paracetamol data is the DC value low, due to a stepwise type of adsorption isotherm. Since it is well known that the modification of D43/1 carbon with conc. nitric acid leads to a

rise in surface acidity [7,9,10], the increase in C value is observed with the rise in basicity of the adsorbate (i.e., from phenol up to aniline). Therefore, strong repulsion between phenol molecules and acidic undissociated surface groups, as well as water adsorption on active sites [7], lead to pronounced heterogeneity of the phenol–carbon system (and the lowest t value). For other systems $t > 1$, suggesting strong adsorbate–adsorbate interactions similar to those for paracetamol and acetanilide molecules.

Finally, it can be concluded that the solution analogue of the Toth equation describes the analyzed data satisfactorily. The applicability of this equation to other experimental systems will be the subject of our forthcoming study.

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