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Adsorption of phenols from aqueous solutions: Equilibria, calorimetry and kinetics of adsorption

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ABSTRACT

The brief theoretical description of the phenols adsorption from aqueous solutions on carbonaceous adsorbents, i.e. activated carbons (ACs) and activated carbon fibers (ACFs) has been presented. The description includes adsorption equilibria, calorimetry as well as kinetics of adsorption. The generalized Langmuir–Freundlich (GLF) isotherm equation has been used to study of the cooperative effect of the surface heterogeneity and the lateral interactions between the admolecules. Theoretical isosteric heats of adsorption connected with the GLF model have been estimated too. Knowledge of both adsorption equilibria and heats of adsorption is fundamental for adequate description of any adsorption process. To correlate the kinetic data of the studied systems, the theoretical equations developed from Statistical Rate Theory (SRT) of Interfacial Transport were applied. The most advantageous of the proposed model of calculations is the set of common parameters appearing in each type of expressions, which significantly extends the possibility of their interpretation. Theoretical studies were fully reviewed using the literature experimental adsorption data. They included the data of phenols adsorption both on ACs and ACFs surfaces.

1. Introduction

Phenolic compounds are probably the most widely studied compounds in the field of wastewater treatment, as they are permanent pollutants released into the water by a large number of industries. Considering that adsorption of phenols on activated carbons (ACs) is one of the most important applications of ACs, a large number of studies have been carried out to examine this issue [1–20]. There are two most common physical forms, in which AC is used, i.e. powder-like AC and granular one. The activated carbon fiber (ACF) is a new form of activated carbon which has been extensively developed during the last 20 years. It is known that both ACs and ACFs have strongly heterogeneous surfaces [2,5–8,21–23]. The heterogeneity of surface stems from two sources known as geometrical and chemical. Geometrical heterogeneity is the result of differences in shapes and sizes of pores, but chemical heterogeneity is associated with different surface functional groups. Both chemical and geometrical heterogeneities contribute to the unique sorption properties of ACs and ACFs.

ACFs have drawn increasing attention in recent years as novel adsorbents for purifying wastewaters from phenols [24–30]. The raw materials of ACFs are polyacrylonitrile fibers, cellulose fibers, phenol–formaldehyde resin fibers, pitch fibers, etc. They are first pyrolysed and subsequently activated with the aid of carbon dioxide or steam (temp. 700–1000 °C) [25]. Consequently, there are as many different types of ACFs as there are kinds of precursors. ACFs are extremely microporous materials with high surface areas from 1000 m^2/g to over 2000 m^2/g [31,32]. Adsorption rates of ACFs are several dozen times higher than those obtained on the granulated AC due to the large external surface area of the fibers and to the direct connection of micropores to this area, which involves a decrease in mass-transfer resistance [27,31]. The small and uniform fiber diameter compared with that of granules of ACs allows for faster adsorption (and desorption) for the same AC weight [31,32]. Additionally, ACFs are characterized by narrow and uniform pore size distribution, so stronger interactions of ACF/adsorbate are possible. It is known that some ACFs perform normal adsorption even when the concentration of phenol in wastewater is in the few ppm range, which is not achievable by other adsorbents.

The main objective of the present paper is proposal of the comprehensive theoretical description of the phenols adsorption from aqueous solutions on carbonaceous adsorbents, i.e. ACs and ACFs. Such comprehensive description includes both adsorption equilibria and calorimetry as well as kinetics of adsorption. The generalized Langmuir–Freundlich (GLF) isotherm equation has been applied to study of the cooperative effect of the surface heterogeneity and the lateral interactions between the adjacent molecules. Additionally, theoretical isosteric heats of adsorption connected with the GLF model have been estimated too. It is assumed that the heat of adsorption profile exhibits both the degree of energetic heterogeneity

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of liquid–solid system and the strength of the interactions between the neighbouring admolecules [33,34]. So, the knowledge of both adsorption equilibria and heats of adsorption is fundamental for adequate description of any adsorption process. On the other hand, the adsorbent and the solution are brought into contact for a limited period of time in the industrial process of wastewaters purification [35,36]. Thus, knowledge of kinetic features is indispensible to provide the principal information required for the design and operation of adsorption equipment used for wastewater treatment. To correlate the kinetic data of the studied systems, the theoretical expressions developed from Statistical Rate Theory (SRT) of Interfacial Transport [37–45] have been applied.

Our theoretical studies were fully examined based on the literature experimental adsorption data [46–49]. They included the data of phenols adsorption both on ACs and ACFs surfaces. We used the data of p-nitrophenol adsorption from aqueous solution on viscose-based ACF [46], the data of phenol adsorption from aqueous solution on oil-palm-shell AC [47], 2,4-dichlorophenol adsorption from aqueous solution on polyvinyl alcohol-based ACF [48] and lastly, the data of 2-bromophenol adsorption from aqueous solution on low cost slurry waste-based AC [49].

2. Theory

2.1. Equilibrium adsorption

In the scientific literature on the equilibrium adsorption phenomena, many isotherm equations can be found. Some of them are strictly empirical and others are obtained by using some theoretical assumptions. One of the most important theories describing adsorption equilibrium is the Integral Equation (IE) approach. IE can be used not only to obtain the new isotherm equations but also to make theoretical backgrounds for empirical isotherms. The fundamental expression of IE approach describing single-solute adsorption from dilute solutions on the energetically heterogeneous surface has the form [50–52]:

$$\theta_t(c,T) = \frac{N_t}{M} = \int_\Omega \theta(\varepsilon, c, T)\chi(\varepsilon)d\varepsilon \tag{1}$$

where $\theta_t(c, T)$ is the average fraction of surface coverage by the molecules at an adsorbate concentration c, $\theta(\varepsilon, c, T)$ is the fractional coverage of a certain class of adsorption sites, characterized by the adsorption energy ε (local isotherm), N_t is the adsorbed amount, M is the adsorption maximum capacity, $\chi(\varepsilon)$ is a differential distribution of the number of adsorption sites among various adsorption energies and Ω is a range of possible energy values. For the mathematical convenience Ω is often assumed to be the interval $(-\infty, +\infty)$.

Most of the applications of IE approach relates to the Langmuir model of localized adsorption (as a local isotherm) and its extensions taking into account the interactions between adsorbed molecules.

The really existing adsorption energy distribution functions are expected to have a complicated form. However, they can be approximated by some "smoothed" functions, the shape of which is described by a relatively small number of parameters. To calculate integral (1) many types of adsorption energy distribution functions $\chi(\varepsilon)$ can be used. The Gaussian-like function, the so-called non-symmetrical function and the rectangular function have often been used to represent the real adsorption energy distributions. Use of Gaussian-like function in the Condensation Approximation (CA) and suitable local isotherm results in an isotherm equations which very well describe phenols adsorption. Such isotherm is Langmuir–Freundlich (Sips) [5,6,8,16,22,23,51] assuming lack of lateral interactions between molecules. The isotherm which takes into account lateral interactions is e.g. generalized Langmuir–Freundlich (GLF) isotherm [23,42] as well as isotherms derived in terms of Flory–Huggins and Wilson vacancy solution models [23].

On the other hand, reliability of quasi-Gaussian distribution functions obtained by regularization method was independently confirmed by GCMC simulation method [22].

The Gaussian-like function has the following form [22,23]:

$$\chi(\varepsilon) = \frac{\frac{1}{\eta}\exp\left\{\frac{\varepsilon-\varepsilon_0}{\eta}\right\}}{\left[1+\exp\left\{\frac{\varepsilon-\varepsilon_0}{\eta}\right\}\right]^2} \tag{2}$$

where ε_0 is the most probable value of the adsorption energy and $\eta \in (0, 1)$ is the heterogeneity parameter which is proportional to the distribution width. Eq. (2) is a normalized symmetrical distribution which is defined for $\varepsilon \in (-\infty, +\infty)$.

The simple way to take into account the interaction effects between the adsorbed molecules is to use the Mean Filed Approximation (MFA). When the surface is energetically homogeneous the MFA leads to the relation:

$$\mu_s = \mu_{s,0} + \omega\theta \tag{3}$$

where $\mu_{s,0}$ is the chemical potential of the reference system of non-interacting molecules and ω is the parameter characterizing the interaction energy of a given molecule with those adsorbed on the nearest-neighbour occupied adsorption sites.

The isotherm which takes into account interactions between molecules is e.g. the Fowler–Guggenheim (FG) isotherm [53–55]. It has the following form:

$$\theta(\varepsilon, c, T) = \frac{Kc\exp\left\{\frac{\varepsilon+\omega\theta}{kT}\right\}}{1+Kc\exp\left\{\frac{\varepsilon+\omega\theta}{kT}\right\}} \tag{4}$$

where K is the equilibrium constant, k the Boltzmann constant and T is the temperature.

When the surface is energetically heterogeneous Eq. (4) describes the fractional coverage of the homogeneous patch characterized by the adsorption energy ε.

In the case of the energetically heterogeneous surface and when the adsorption energies are distributed between adsorption sites in the random order the FG equation takes the form:

$$\theta(\varepsilon, c, T) = \frac{Kc\exp\left\{\frac{\varepsilon+\omega\theta_t}{kT}\right\}}{1+Kc\exp\left\{\frac{\varepsilon+\omega\theta_t}{kT}\right\}} \tag{5}$$

In this case, the potential of the average force field acting on adsorbed molecules (created by the presence of other molecules) is the function of the average surface coverage θ_t.

Unfortunately Integral (1) cannot be strictly solved with the energy distribution function (2) and with one of the local isotherms (4) or (5). The Condensation Approximation (CA) in such a common case is the most frequently used method to calculate this integral [50,55–59]. CA is based on the assumption that adsorption proceeds in an ideally "stepwise" fashion in the sequence toward increasing adsorption energies. It means that the local isotherm θ in Eq. (1) is replaced by the following step function:

$$\theta(\varepsilon, c, T) \to \theta_c(\varepsilon, c, T) = \begin{cases} 0 & \text{for } \varepsilon < \varepsilon_c \\ 1 & \text{for } \varepsilon \geqslant \varepsilon_c \end{cases} \tag{6}$$

Then,

$$\theta_t(c,T) = \int_{\varepsilon_c}^{\infty} \chi(\varepsilon)d\varepsilon = -\aleph(\varepsilon_c) \tag{7}$$

where ε_c can be found from the relation:

$$\left(\frac{\partial^2\theta}{\partial\varepsilon^2}\right)_{\varepsilon=\varepsilon_c} = 0 \tag{8}$$