Interactions of xanthines with activated carbon
II. The adsorption equilibrium

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Abstract

In the present work, we have studied the adsorption of xanthine derivatives by activated carbon sorbents in aqueous solutions. The study comprised both kinetic, equilibrium and thermodynamic aspects. The kinetic results were reported in a previous paper; the equilibrium-related results are discussed here. The two types of carbon used exhibit some differences but the equilibrium isotherms obtained are all of the H-3 type in the classification of Giles. This suggests a high affinity of the sorbents for the sorbates. We also found that the overall adsorption process comprises more than one individual adsorption–desorption process of which one leads to the formation of a “monolayer” and the other to the “precipitation” of the sorbate on the sorbent surface (multilayer adsorption); the amount of sorbate adsorbed in monolayer form was seemingly greater in C-A14.

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1. Introduction

As stated in a previous paper [1], some xanthine derivatives exhibit pharmacological action and are used as coagents for β-adrenergics and corticoids in the treatment of asthma, bronchitis and emphysema. Such derivatives are usually purified by adsorption of their water-soluble impurities in activated carbon, a process that is also highly useful for treating potential poisoning by these substances [2].

The foregoing, and the fact that a xanthine derivative has been used as a selective sorbate for determining the total surface area of activated carbon [3], led us to study the adsorption of xanthine derivatives by activated carbon sorbents in aqueous solutions. The study comprised both kinetic, equilibrium and thermodynamic aspects. The kinetic results were reported in a previous paper [1]; the equilibrium-related results are discussed here.

The adsorption isotherms of sorbates by solids in dissolution may present different shapes, as can be appreciated in the classification proposed by Giles et al. [4,5]. The individual adsorption isotherm is source of information about both, the solid surface and the interaction process (active sites) with the sorbate. To obtain it, we have to fit the experimental results to the mathematical equation corresponding to a before postulated model. These equations are (oftenly) gases adsorption isotherms, suitably transformed, as them proposed by Henry [6], Freundlich [7], Langmuir [8], Zhukovitsky or that of Dahms and Green [9,10], Frumkin [11,12], Bockris [13], Brunauer [14,15], Tiren [16], Jowet [17], Temkin [18,19] and Derylo-Jaroniec [20].

The Derylo-Jaroniec integrated equation was proposed to describe the overall gas adsorption process by an energetically homogeneous solid, using as point of item different local adsorption isotherms that lead to integral equations, which should describe the global adsorption isotherm.

One of these equations, frequently used in the last years, is that of Töth. The equation called of Töth (or more exactly of Marczewski and Jaroniec), has reached a considerable acceptance. Later, Dabrowski, Jaroniec and Töth [21]
modified it with the goal of adapting it to the needs that appear on studying the adsorption isotherms by solids in dissolution, and proposed a semiempirical one known like “Tóth-modified Equation” [21].

In the present work, we postulate that the experimental isotherms are the result of the sum of the individual ones corresponding to two or more simple reversible adsorption–desorption processes and, in its case, to one sorbate condensation or precipitation process. All the isotherms of the already cited Giles’s classification are satisfactory fitted to the following equation [22]:

\[
\theta = \frac{n^s}{n_{m}^s} = \frac{\sum_{i=1}^{n} K_i C_i^n}{1 + K_i C_i^n} + K_f C_f^m
\]  

(1)

2. Experimental

The sorbents used were a commercially available product (Merck ref. 2514), henceforth, referred to as C-M and one prepared in our laboratory that was designated C-A14 [1]. Both were used in particle sizes over the range 0.50–0.59 mm and characterized by using appropriate methods described elsewhere [1].

The aqueous sorbates used included caffeine (CF), theophylline (TP), theobromine (TB), 1,3,8-trimethyl-xanthine (TM) and 1,3-dimethyl-8-ethylxanthine (ET). Their concentrations in solution were determined by UV spectrophotometry [23,24].

Adsorption isotherms were obtained as described in a previous paper [1], using 100 ml of a 10^{-3} M solution of each sorbate and known amounts of sorbent from 0.030 to 0.900 g. The solid phase and the solution were kept in contact at a constant temperature of 10, 20, 30, 40 or 50 °C for much longer than needed to reach equilibrium. Equilibration times ranged from 150 to 2300 h, depending on the particular sorbent—they were invariably shorter for C-M—and temperature—they decreased with increasing T.

In order to obtain accurate equilibrium isotherms, we initially used near-saturated solutions; this allowed equilibrium concentrations between the lowest analytically detectable level and a value close to the initial one to be obtained. Because the solubility values for some sorbates at specific temperatures were unavailable, we determined their water solubility at each studied temperature.

3. Results and discussion

Table 1 shows the solubility data (C_s) obtained alongside the \( \Delta H_s \) and \( \Delta S_s \) values for the dissolution process, which were determined from ln C_s versus 1/T plots. We checked our values against their reported counterparts where available (e.g. for caffeine [25,26]). Also, we found the ln C_s versus 1/T plot for TM to consist of two straight segments with an apparent inflection at ca. 30 °C; this suggests that, depending on the particular concentration and temperature, the initial solute (the monomer) underwent substantial changes (dimerization or oligomerization) as previously found in caffeine by Lilley [25]. According to this author, the overall process by which caffeine is dissolved in water comprises two individual processes, namely: dissolution proper, with \( \Delta H_1 = 20.9 \) kJ/mol, and dimerization of the solute, with \( \Delta H_2 = 14.2 \) kJ/mol. Based on our solubility data, the enthalpy changes for these steps in TM dissolution would be \( \Delta H_1 = 23.7 \) kJ/mol and \( \Delta H_2 = 12.8 \) kJ/mol, and their combined value 36.5 kJ/mol—the datum listed in Table 1. The fact that ln C_s versus 1/T plots (for the other xanthine derivatives) exhibited no inflection points, probably indicate that both individual processes cannot be separated depending on temperature, inside the studied interval.

The equilibrium results for the studied processes were expressed as moles (n^s) of sorbate adsorbed per gram of sorbent at an absolute (C) or relative (C/C_0) equilibrium concentration and were plotted as a function of C/C_0. Fig. 1 shows a selected plot. While the two types of carbon exhibited some differences, the equilibrium isotherms were all of the H-3 type in the classification of Giles [4]. This suggests a high affinity of the sorbents for the sorbates.

The presence of a more or less well-defined rising portion at the highest equilibrium concentrations is suggestive of multilayer adsorption. This, in turn, suggests that the overall adsorption process comprises one or more individual adsorption–desorption steps of which one leads to the formation of a “monolayer” and the other to the “precipitation” of the sorbate on the sorbent surface (multilayer adsorption). The amount of sorbate adsorbed in monolayer form was seemingly greater in
C-A14; on the other hand, multilayer adsorption was apparently more marked in C-M.

Based on the foregoing, the experimental isotherms may fit the following equation:

$$u = \frac{n_s}{n_{s_m}} = \sum_{i=1}^{j} \frac{K_i C_i^n}{1 + K_i C_i^n} + K_f C^{m}$$  

(1)

where, $\theta$ = fraction of surface active sites in the sorbent occupied by the sorbate, $n_s$ = moles of sorbate adsorbed per gram of sorbent, $n_{s_m}$ = monolayer retention capacity, $C_i$ = equilibrium concentration, $K_i$ = kinetic equilibrium constant, $K_f$ = kinetic precipitation constant, $n$ = partial order of the process respect to the concentration ($C$) and $m$ = constant.

In this case, and based on the results of the kinetic study [1], $j = 2$ and the partial order of the process in $C$ is the unity ($n = 1$).

The experimental data were fitted to Eq. (1). The results for the two reversible adsorption–desorption processes are summarized in Tables 2 and 3. The first individual process may involve the adsorption of the monomer and the second that of the resulting oligomer. As can be seen in Table 2, the xanthine retention capacity of the two sorbents was in the region of $10^{-3}$ mol/g in the first individual adsorption–desorption step and ranged from $5 \times 10^{-4}$ to $10^{-3}$ mol/g in the second. Therefore, the overall amounts adsorbed ranged from $1.5 \times 10^{-3}$ to $2 \times 10^{-3}$ mol/g. The retention capacity of the sorbents remained virtually constant throughout the temperature range studied. However, $n_{s} (1)$ values were greater for C-A14 than for C-M as the likely result of the former being more microporous. On the other hand, $n_{s} (2)$ values were greater for C-M, which was the more mesoporous sorbent.

Fig. 2 shows the isotherms for the adsorption of caffeine (CF) by C-A14 and C-M in water at 20 °C. The combination of the isotherms for the individual processes is quite consistent with the overall process. As can be observed, the experimental data correspond to the sum of the three individual processes. Two first, $n_{s} (1)$ and $n_{s} (2)$, report to a Langmuir process type with $i$ values equals to 1 and 2, respectively. The third-one $n_{s} (3)$ is equivalent to the sorbate crystallization or multilayer retention and follows a Freundlich process type, which is the second part of Eq. (1). As can be deduced from Fig. 2, the contribution of this third process is more important for the C-M due to its larger mesoporosity.

The calculated kinetic equilibrium constants for the two reversible adsorption–desorption steps were in the region of $10^5$.

Table 2

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>$T$ (°C)</th>
<th>First individual process $n_{s_m}10^3$ (mol/g)</th>
<th>Second individual process $n_{s}10^3$ (mol/g)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>CF</td>
<td>TF</td>
<td>TB</td>
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<tr>
<td>C-A14</td>
<td>10</td>
<td>1.08</td>
<td>1.15</td>
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<tr>
<td></td>
<td>20</td>
<td>1.08</td>
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<td>C-M</td>
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<td>20</td>
<td>0.85</td>
<td>1.05</td>
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<td></td>
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<td>40</td>
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<td></td>
<td>50</td>
<td>0.89</td>
<td>1.03</td>
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Table 3

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<thead>
<tr>
<th>Sorbent</th>
<th>$T$ (°C)</th>
<th>$K_1 \times 10^{-3}$</th>
<th>$K_2 \times 10^{-3}$</th>
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<tbody>
<tr>
<td></td>
<td>CF</td>
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<td>C-A14</td>
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for the first and $10^3$ for the second (Table 3), and, as expected from two exothermic processes, decreased with increasing temperature.

The $K_i$ values were used to calculate the “apparent” estimates of the enthalpy of adsorption listed in Table 4. Obviously, the heats of adsorption of the first step were more exothermic than those of the second one; except for CF, the latter were similar to those for the dimerization or crystallization of the solute onto the first retained layer. In those cases, where the enthalpies of adsorption were similar to those of dissolution, the $n$ versus $C/C_s$ isotherms overlapped, as can be observed in Fig. 3, where the adsorption of TB by C-M has been plotted.

### Table 4

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Sorbates</th>
<th>$\Delta H_{(1)}$ (kJ/mol)</th>
<th>$\Delta H_{(2)}$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF</td>
<td>TF</td>
<td>TB</td>
<td>TM</td>
</tr>
<tr>
<td>C-A14</td>
<td>$-48.2$</td>
<td>$-21.3$</td>
<td>$-35.4$</td>
</tr>
<tr>
<td>C-M</td>
<td>$-53.5$</td>
<td>$-29.4$</td>
<td>$-31.9$</td>
</tr>
<tr>
<td>C-A14</td>
<td>$-30.7$</td>
<td>$-16.2$</td>
<td>$-14.9$</td>
</tr>
<tr>
<td>C-M</td>
<td>$-33.6$</td>
<td>$-13.6$</td>
<td>$-17.1$</td>
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</table>

Fig. 2. Isotherms for the retention of CF by C-A14 and C-M at 20 °C.

4. Conclusions

From the results obtained in the present study, the following conclusions may be deduced:

1. The isotherms for the retention of xanthines by active carbons in an aqueous solution correspond to a one adsorption–desorption reversible process that take place in several stages.
2. For the first individual process, and based on the results of the kinetic study, the partial order of the process in $C$ is the unity ($n = 1$), fitting to Langmuir’s equation. The second one involves a multilayer adsorption or crystallization process with an oligomer formation on the sorbent surface.
3. The retention of xanthines answer to an exothermic process.
4. When the heat of adsorption is similar to that of the sorbate dissolution, the $n$ versus $C/C_s$ isotherms overlap to any temperatures.

References