The influence of activated carbon surface chemical composition on the adsorption of acetaminophen (paracetamol) in vitro

The temperature dependence of adsorption at the neutral pH

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Abstract

The in vitro adsorption and desorption of acetaminophen from water solution on four activated carbons at three temperatures (300, 310 and 320 K) and at the neutral pH (7) were investigated. The carbons were characterized using the low temperature nitrogen adsorption, the mercury porosimetry, Bachmann’s method, Boehm’s method as well as the water immersion calorimetry. As an initial adsorbent, the de-ashed-commercial, ‘non-modified’ carbon D43/1 (Carbo-Tech, Essen, Germany) was applied. To change the chemical composition of its surface, concentrated nitric and sulfuric acids as well as gaseous ammonia were applied as chemical modificators. The acetaminophen adsorption and desorption isotherms on the ‘non-modified’ as well as on the chemically modified carbons were measured, together with the enthalpy of immersion in paracetamol solution. It is shown that, generally, for all the investigated carbons, acetaminophen adsorption increases with temperature. A slightly marked hysteresis on adsorption–desorption isotherms was observed at higher adsorption values. Among the applied procedures of the changing of carbon surface chemical composition, the modification with fuming sulphuric acid leads to the increase in paracetamol adsorption, whilst the opposite effect is observed for the carbon modified with concentrated nitric acid. The modification in the stream of ammonia practically does not change the adsorption properties towards paracetamol. The changes in the adsorption properties of carbons after modification are analysed using isotherms, adsorbability, relative enthalpy of displacement as well as the values of the integral enthalpy of adsorption. To calculate this enthalpy the solubility of acetaminophen in the investigated range of temperatures was determined, and the enthalpy of solution at infinite dilution was calculated using Abraham’s method. © 2000 Elsevier Science B.V. All rights reserved.
1. Introduction

Activated carbons are widely used especially as adsorbents. One of the most spectacular applications is a medical one; it is well known that the oral administration of the activated carbon has been successfully applied in the cases of overdosing different pharmaceuticals [1–3]. Moreover, sometimes the oral administration of carbon, for example, in chloroquine poisoning [4], is the best option. Due to this fact, both in vitro and in vivo investigations on the application of oral charcoal are being still developed.

Among pharmaceuticals, acetaminophen (paracetamol), antipyretic/analgesic drug is widely investigated because of its common use and because of the fact that the overdose results in, for example, acute hepatic failure, liver damage [5–8] and even death [6]. A number of papers have been published on the subject of paracetamol removal using different methods, especially oral carbon administration [2,9–11]. A detailed analysis of the published results, however, leads to the conclusion that only some authors try to associate the adsorption properties of carbon with its porosity [2] and, practically, there are no reports on the influence of carbon surface properties (i.e. a surface chemical composition) as well as the temperature on the ability of drugs adsorption. On the other hand, it is well known that not only carbon porosity but also the chemical composition of carbon surface influence the adsorption properties from the both gaseous [12] and liquid phase [13].

In the presented paper the first attempt is made to determine experimentally the influence of temperature and carbon surface chemical composition on paracetamol adsorption from water solution. To achieve this aim, the commercial activated carbon was de-ashed and modified to increase the surface acidity (surface acidic groups were created using nitric acid and fuming sulfuric acid) and/or basicity (the modification in the stream of gaseous ammonia).

To determine all the factors influencing acetaminophen adsorption, additional data should be collected (i.e. the influence of pH on adsorption should be investigated, as well as kinetic measurements at different initial drug concentrations are necessary to be carried out).

In the first paper of this series, the experimental procedure and the carbon characteristics are reported in detail together with the results of acetaminophen adsorption at pH 7. Simultaneously, the results of the measurements of enthalpy of immersion of carbons in water and in paracetamol solution are presented and the enthalpy of paracetamol adsorption is calculated (to do this, the enthalpy of solution was calculated from the solubility determined at different temperatures).

The results concerning the influence of pH on paracetamol adsorption, as well as the results of kinetic measurements will be published in the future.

2. Experimental

2.1. Materials

Acetaminophen for synthesis (Merck) containing more than 99% of pure compound was used for the preparation of the initial solution. As the adsorbent, the ‘commercial’ activated carbon D43/1 (Carbo-Tech, Essen, Germany) was applied. It was de-ashed using the procedure of Korver (the obtained carbon is called D 43/1–pure). The detailed description of this procedure as well as the analysis of de-ashing on the porosity was discussed previously [14]. This carbon was chemically modified, and as the modifying reagents concentrated (65%) pure HNO₃ (Zaklady Azotowe Tarnow-Moscice, Poland), fuming H₂SO₄ (Polchem, Torun, Poland) and gaseous ammonia (Zaklady Azotowe Pulawy, Poland) were applied.
Table 1
The structural properties of investigated carbons

<table>
<thead>
<tr>
<th>Carbon</th>
<th>( W_0 ) (cm(^3) g(^{-1}))</th>
<th>( V_{\text{water}} ) (cm(^3) g(^{-1}))</th>
<th>( V_{\text{benzene}} ) (cm(^3) g(^{-1}))</th>
<th>( \phi_{\text{av}} ) (nm)</th>
<th>( \phi_{\text{av}} ) (Eq. (3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>D43/1–pure</td>
<td>0.384</td>
<td>0.9702</td>
<td>0.9861</td>
<td>0.543</td>
<td>1113</td>
</tr>
<tr>
<td>D43/1–HNO(_3)</td>
<td>0.492</td>
<td>0.9709</td>
<td>0.9543</td>
<td>0.483</td>
<td>1100</td>
</tr>
<tr>
<td>D43/1–H(_2)SO(_4)</td>
<td>0.450</td>
<td>0.9924</td>
<td>0.9871</td>
<td>0.480</td>
<td>1113</td>
</tr>
<tr>
<td>D43/1–NH(_3)</td>
<td>0.487</td>
<td>0.9832</td>
<td>1.0039</td>
<td>0.523</td>
<td>1200</td>
</tr>
</tbody>
</table>

\( W_0 \) — total micropore volume determined from low-temperature nitrogen adsorption data using Eq. (1), \( V_{\text{water}}, V_{\text{benzene}} \) — total micropore volumes from Bachmann’s method determined using water and/or benzene as an adsorbate, \( \phi_{\text{av}} \) — average micropore diameters determined from Eqs. (2) and (3).

2.2. Carbon surface modification

The modification in the liquid phase (with acids) was performed as follows: 0.5 dm\(^3\) of concentrated acid was added to each 150 g of carbon D43/1–pure, and the solution was heated 3 h at 353 K in an open vessel using water bath. Applying this procedure 2 kg of each carbon sample were obtained. The modified carbons (D43/1 — HNO\(_3\), and D43/1 — H\(_2\)SO\(_4\)) were washed out using warm water to obtain the conductivity of suspension close to that for distilled water. The modification in the gaseous phase was performed in the ammonia stream (the flow 20 dm\(^3\) h\(^{-1}\)) at the temperature of 1023 K (the heating rate was equal to 1023 K h\(^{-1}\)) for 3 h. Then the sample was cooled down to the temperature of 523 K in this stream, and then in the stream of gaseous He (20 dm\(^3\) h\(^{-1}\)) — to the room temperature.

2.3. Carbons porosity determination

For the investigated carbons, the low-temperature (77.5 K) nitrogen adsorption—desorption isotherms were measured, using the ASAP 2010 m (Micromeritics, Atlanta, USA) — an automatic adsorption apparatus. For all the carbons, the measurements using mercury porosimeter (Carlo-Erba, Milano, Italy) were also performed to determine the pore size distribution curve for larger pores. The additional measurements of the total pore volume were performed using the Bachmann’s method [15] which we modified. Three gaskets from stainless steel were closed in some analytical weighing bottles and weighed. Then, they were filled with carbon (\( \approx 3 \) g each) and weighed again. The gaskets filled with carbons were placed in the drier and desorbed in the same way as the samples used for the measurements of adsorption isotherms. After desorption the gaskets were placed in the weighing bottles, closed tightly and weighed after cooling (this was necessary for determining a weight loss). Then the bottles were opened, the samples were placed immediately in a container with the solvent and thermostated for 3 days. After that period the gaskets were dried and weighed again in the weighing bottles. The mass of adsorbed liquid was determined and the pore volume was calculated. It was assumed, that the solvent in pores possesses the same density as in the liquid state. In this case water and benzene were used as adsorbates and the measurements were

Table 2
The comparison of the total carbon pore volumes calculated by typical procedure with determined from Bachmann’s method

<table>
<thead>
<tr>
<th>Carbon</th>
<th>( W_0 + V_{\text{poros}} ) (cm(^3) g(^{-1}))</th>
<th>( \frac{W_0 + V_{\text{poros}}}{V_{\text{water}}} )</th>
<th>( \frac{W_0 + V_{\text{poros}}}{V_{\text{benzene}}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>D43/1–pure</td>
<td>0.927</td>
<td>0.955</td>
<td>0.940</td>
</tr>
<tr>
<td>D43/1–HNO(_3)</td>
<td>0.975</td>
<td>1.004</td>
<td>1.022</td>
</tr>
<tr>
<td>D43/1–H(_2)SO(_4)</td>
<td>0.930</td>
<td>0.937</td>
<td>0.942</td>
</tr>
<tr>
<td>D43/1–NH(_3)</td>
<td>1.010</td>
<td>1.027</td>
<td>1.006</td>
</tr>
<tr>
<td>Average</td>
<td>0.981</td>
<td>0.978</td>
<td>0.978</td>
</tr>
</tbody>
</table>
Table 3
The surface properties of investigated carbons

<table>
<thead>
<tr>
<th>Carbon</th>
<th>$\Delta h_{H_2O}$ (J g$^{-1}$)</th>
<th>$\Delta h_{H_2O}/V_{water}$ (J g$^{-1}$)</th>
<th>$\Delta h_{H_2O}/V_{benzene}$ (J cm$^{-3}$)</th>
<th>$c_a$ (mmol g$^{-1}$)</th>
<th>$c_b$ (mmol g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D43/1–pure</td>
<td>−66.3</td>
<td>−68.3</td>
<td>−67.2</td>
<td>0.446</td>
<td>0.175</td>
</tr>
<tr>
<td>D43/1–HNO$_3$</td>
<td>−92.8</td>
<td>−95.6</td>
<td>−97.2</td>
<td>1.332</td>
<td>0.088</td>
</tr>
<tr>
<td>D43/1–H$_2$SO$_4$</td>
<td>−79.6</td>
<td>−80.2</td>
<td>−80.6</td>
<td>0.999</td>
<td>0.071</td>
</tr>
<tr>
<td>D43/1–NH$_3$</td>
<td>−52.6</td>
<td>−53.5</td>
<td>−53.3</td>
<td>0.100</td>
<td>0.564</td>
</tr>
</tbody>
</table>

$^a$ $\Delta h_n$, the enthalpy of immersion in water; $\Delta h_i/V_i$, the ‘specific’ enthalpy, $c_a$ and $c_b$, total concentration of acidic and basic surface groups, respectively.

Fig. 1. The influence of chemical modification of D43/1 carbon on the enthalpy of immersion in water.

2.4. The analysis of carbon surface chemical acidity and basicity

The surface acidity and basicity of carbons were determined using the well-known procedure proposed by Boehm [16].

2.5. The measurements of the enthalpy of immersion

For each sample the enthalpy of immersion in water, and in paracetamol solution as well at 310 K was measured using the Tian–Calvet isothermal calorimeter constructed in our laboratory. The initial concentration of acetaminophen solution was equal to the $0.07$ mol dm$^{-3}$ i.e. the enthalpy of immersion in solution...
was measured for the maximum concentration applied in the measurement of the adsorption isotherms. Carbon samples were desorbed in the same way as for adsorption measurements (see below). Each measurement was repeated at least three times. The error is equal to \( \pm 1.5 \text{ J g}^{-1} \).

2.6. Analytical method

A widely applied procedure of determining acetaminophen concentration based on Beer’s law calibration plots was applied, using the Specord M 40 (Carl Zeiss Jena, Germany), a UV–VIS spectrophotometer. The maximum absorption wavelength was determined as equal to 244.62 nm. Then the calibration plot was constructed from, on the average, 30 absorption versus concentration points. The calibration was repeated five times during the period of measurements. The linearization of this plot provided usually the determination coefficient close to 99.97%.

2.7. The determination of the solubility of acetaminophen

To determine the solubility of acetaminophen, the excess amount of the compound was added to 0.025 dm\(^3\) of water, closed and thermostated for 72 h (mechanically stirred). The solubility was determined using UV–VIS measurements.

2.8. Adsorption–desorption isotherms

To determine one adsorption–desorption isotherm 20 bottles containing 0.125 dm\(^3\) of acetaminophen solution with different concentra-

![Fig. 2. Adsorption isotherms of acetaminophen on D43/1–pure carbon. Open symbols, adsorption; closed symbols, desorption (\(x_1\) is the mol fraction of acetaminophen in solution).]
tions (from 0.002 to 0.07 mol dm$^{-3}$) were prepared using the initial solution of the reagent described above and the distilled water. The bottles were placed in a thermostat. The temperature was controlled with the accuracy of ±0.2 K. Twenty carbon samples were prepared using analytical balance and desorbed 20 h at 383 K in the drier. For each carbon type the weight loss was determined independently and applied for the calculation of the real mass of carbon sample. The bottles with acetaminophen solutions, after adding carbons, were closed tightly and stirred mechanically for three days. Then from each bottle 0.001 dm$^3$ of equilibrated solution was drawn using automatic variable volume pipette (V3-series, HT Lab) and diluted to 0.2 dm$^3$. The concentrations of the obtained solutions were determined using the UV–VIS method described above. For each solution the absorbance was measured at least three times. To determine the desorption isotherm the additional 0.004 dm$^3$ of equilibrated solution was drawn from each bottle and 0.005 dm$^3$ of water was added to preserve the constant volume of solution. The further procedure was analogous as for adsorption. The adsorption was detected with standard deviations smaller than $2 \times 10^{-5}$ mol g$^{-1}$.

3. Results and discussion

3.1. The influence of carbon modification on porosity

Using the results of low temperature nitrogen adsorption isotherms, as well as porosimetry
data the parameters of porous structure given in the Table 1 were calculated. To evaluate the micropore structure parameters of carbons, the Dubinin–Astakhov [17] adsorption isotherm equation, in the low relative pressure range, (in this paper the relative pressure range applied in calculations was equal $5 \times 10^{-6}$–0.01), is usually used in the form:

$$W = W_0 \exp[-(A/(\beta E_0))^n]$$

(1)

where: $W$ and $W_0$ are the volume of liquid-like adsorbate present in micropores and total micropore volume, respectively, $A$ is the differential molar maximum work of adsorption, $\beta$ is the similarity coefficient (taken as equal to 0.32 for nitrogen), $E_0$ is the characteristic energy of adsorption and $n$ is the equation best-fit parameter (if $n=2$ so called Dubinin–Radushkevich isotherm is obtained).

Moreover, the average widths of carbon micropores ($\varphi_{av}$) were calculated from the relations developed by us recently [18]. Basing on the theory of adsorption in slit-like pores two equations were derived:

$$\varphi_{av} = \frac{0.23028059}{1 - 6.2030475 \exp[-1.8312506n]}
+ \frac{16.051350 - 4.1316959n + 0.53336219n^2}{E_0}$$

(2)

$$\varphi_{av} = 6.5118396(0.25182696)^{1/n}
E_0^{(0.47563536 - 0.056454635n + 0.35312455n^2)}$$

(3)

Eq. (2) was derived assuming that the potential energy formula proposed by Everett and Powl describes the adsorption in the both: micropores

![Fig. 4. Adsorption isotherms of acetaminophen on D43/1–H$_2$SO$_4$ carbon. Open symbols, adsorption; closed symbols, desorption.](image)
and larger pores as well. Deriving Eq. (3) we assumed the cut-off limit equal to 2 nm (the maximal micropore diameter following IUPAC classification).

The results from Table 1 show that for the investigated carbons the volume of micropores is close to the volume of other pores. The detailed analysis of the results from this table confirms the analysis of the results from this table confirms the suggestions that applied conditions of carbon surface chemical modification slightly change the pore diameters of the investigated carbons. A slight increase in pore diameter, in comparison with the initial carbon, is observed for the carbon modified with sulfuric acid. For the carbons modified with nitric acid and ammonia this increase is larger, however not exceeding more than 15%. The application of Bachmann’s method for water (polar adsorbate) as well as for benzene (non-polar one) shows that the changes in total pore volume do not exceed 12%. Taking this fact into account, we postulate that the total pore volume as well as pore diameters after carbon modification remain practically unchanged.

From the Table 2 it can also be concluded that \( W_0 + V_{\text{poros}} \) is practically equal to \( V_{\text{benzene}} \) and/or \( V_{\text{water}} \) determined using the modified Bachmann’s method (and the application of water as an adsorbate leads to slightly better correlation). It is very important for the practical application that this simple method leads to the total pore volumes close or the same as those determined using other methods, moreover, this simple method can be successfully applied for the calculation of the total micropore volume.
3.2. The influence of carbon surface modification on chemical properties of its surface

It is well known that the applied conditions of carbon surface modification lead to the creation of active surface groups. It is widely accepted that the oxidation with concentrated nitric acid leads mainly to the creation of phenolic, carboxyl and lactonic structures [19]. The application of sulfuric acid leads to the creation of acidic sulfone groups [20], sulfates and acid sulfates [21] however, the detailed structure of surface groups created by fuming sulfuric acid modification has not been described yet. The recent XPS investigations on carbon–sulphur surface compounds prepared by heating different carbon materials with compounds containing sulphur suggested that created surface compounds are thiocarbonyls and thiolactons [22].

The annealing of carbon in the stream of ammonia creates mainly amides imides and pyridyne structures that possess basic character [23].

One of the most powerful methods (and not so time-consuming as the measurement of the differential enthalpy of adsorption) of investigation of the changes in surface polarity, caused by chemical modifications, is the measurement of the enthalpy of carbon immersion in water. Though the accuracy of the immersion enthalpy measurement is much lower than that of the displacement one, the simplicity of such a measurement leads to the still increasing number of papers concerning the results of the enthalpy of immersion of carbons in water. Different correlations between the value of this enthalpy and the carbon characteristics have been proposed [24–26], however, it seems that the results concerning the influence of carbon modification with ammonia on enthalpy of immersion in

![Fig. 6. The comparative plot of adsorption isotherms at 300 K.](image-url)
water have not been published yet.

The results of enthalpy of immersion in water are shown in Table 3. In this table the results of the Boehm’s method are also included. It is seen that the modification with acids greatly influences the quality of a surface site. In the case of the modification with concentrated nitric acid greater amount of surface acidic groups is created in comparison with the modification using fuming sulfuric acid. On the other hand, the treatment in the stream of ammonia increases the amount of surface basic groups, and the increase in carbon surface hydrophobicity is observed simultaneously.

Interesting conclusions can be made from the more detailed comparative analysis of the results presented in Table 3. As it was mentioned above, and as it is widely accepted, the changes in carbon surface chemical composition, resulted from carbon modification, play a more important role than the small changes in porosity during adsorption from solution. That is why, the plot of the enthalpy of immersion in water is the linear function of the concentration of acidic groups (determination coefficient is equal to 0.9894); and if this concentration is equal to zero, the enthalpy is equal to $-50.4 \text{ J g}^{-1}$ is obtained (Fig. 1). It is interesting that the linear correlation is obtained only if the concentration of acidic carbon surface groups is taken into account. Those groups interact with higher (oxidised carbons) or lower (carbon modified with ammonia) energy with water than surface groups of non-modified carbon. Moreover, from Fig. 1 it arises that the increase of the concentration of basic surface groups (occurring with acidic ones) leads to the decrease in the enthalpy of immersion.
3.3. Adsorption of acetaminophen

The analysis of the porosity of carbons, described above, leads to the important statement that the changes in the adsorption properties towards paracetamol are mainly caused by the change in the chemical nature of the investigated carbons by modifications.

The obtained adsorption isotherms (Figs. 2–8, $x_1$ is the mole fraction of acetaminophen in solution) possess the shapes leading, following Giles et al. [27], to the conclusion that there exists the high affinity between the adsorbate and adsorbent and it increases with the temperature. Observed at 300 and 310 K decrease in adsorption at low coverages is the result of the increasing adsorption of the solvent. The obtained isotherms can be divided into two regions: in the first of them (up to the equilibrium mole fraction close to $6 \times 10^{-3}$) with plateau, the adsorption takes place in micropores, contrary to the second region (at higher

<table>
<thead>
<tr>
<th>Carbon</th>
<th>$\Delta h_{in}$ (J g$^{-1}$)</th>
<th>$\Delta h_{sw}$ (J g$^{-1}$)</th>
<th>$\Delta h_{ads}$ (J g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D43/1-pure</td>
<td>−109.1</td>
<td>−42.9</td>
<td>−28.1</td>
</tr>
<tr>
<td>D43/1</td>
<td>−120.5</td>
<td>−27.7</td>
<td>−33.5</td>
</tr>
<tr>
<td>−HNO$_3$</td>
<td>−85.8</td>
<td>−6.2</td>
<td>+54.9</td>
</tr>
<tr>
<td>D43/1</td>
<td>−103.2</td>
<td>−50.6</td>
<td>+22.8</td>
</tr>
<tr>
<td>−H$_2$SO$_4$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D43/1−NH$_3$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
mole fractions) where adsorption takes place in larger pores and/or on the external carbon surface.

To determine the influence of carbon surface modification on adsorption at infinite adsorbate dilution, the average adsorbability ($\alpha$, dm$^3$ g$^{-1}$) for investigated temperature range was calculated following Abe et al. [28]:

$$\alpha = \lim_{c \to 0} \frac{a}{c}$$

where $c$ is the equilibrium concentration of paracetamol (mol dm$^{-3}$).

To do that, all adsorption isotherms were re-plotted in the co-ordinates $a/c = f(c)$ and then approximated using the third order polynomial. The fit of experimental data to the third order degree polynomial can be estimated by the determination coefficients equal to 99.8% for isotherms measured at 300 and 310 K and equal to 99.9% for isotherms measured at the highest temperature. The largest adsorbability was obtained for D43/1–NH$_3$ carbon (6.71 dm$^3$ g$^{-1}$). For the pure and modified with fuming sulfuric acid one similar values (3.99 and 4.33 dm$^3$ g$^{-1}$, respectively) were obtained, whilst the smaller value, equal to 1.76 dm$^3$ g$^{-1}$, was obtained for the carbon modified with nitric acid.

From the temperature dependence of the aceticaminophen adsorption–desorption isotherms (Figs. 2–5) it can be noticed that, generally, in the first region of adsorption isotherms i.e. for the region of adsorption in micropores, the influence of temperature on adsorption is smaller than for adsorption in larger pores. For all the systems a slightly marked hysteresis at higher adsorption is
observed as well as the decrease in adsorption at 310 K in this region. For all the studied carbons the increase in adsorption in micropores with temperature is observed. For the adsorption on D43/1–H\textsubscript{2}SO\textsubscript{4} (Fig. 4) this increase is nearly the same for each temperature. For the D43/1–HNO\textsubscript{3} (Fig. 3) it is observed up to 310 K, leading to small differences in adsorption in micropores at the two highest temperatures. On the other hand, for the last two carbons (Figs. 2 and 5) this effect predominates at the highest temperature. This observation, together with the analysis of the values of the enthalpy of immersion in water (Table 3) suggests that the different changes in adsorption with temperature observed for the carbon samples modified with acids are mainly resulted by the differences in energy of interaction between the molecules of solution and surface polar groups.

The influence of carbon surface modification on paracetamol adsorption is shown in Figs. 6–8, where the comparison of the adsorption isotherms for all the investigated carbons is presented, and for all three temperatures. These comparative plots show generally that the differences in adsorption between the applied carbons decrease with the increase in temperature. Moreover, at all the investigated temperatures adsorption properties of the initial and modified with ammonia carbons are nearly the same.

At 300 K adsorption increases in the sentence: D43/1–HNO\textsubscript{3} < D43/1–pure = D43/1–NH\textsubscript{3} < D43/1–H\textsubscript{2}SO\textsubscript{4}. The increase in the temperature to 310 K leads to the same adsorption for the modified with ammonia and nitric acid carbon, and slightly higher adsorption for pure carbon. For the carbon modified with fuming sulfuric acid, adsorption is still the highest at this temperature. The observed adsorption values for the plateau on the isotherms occur for the initial drug concentrations 0.02–0.05 mol dm\textsuperscript{-3}. Although the differences between adsorption values on the pure and modified with sulfuric acid car

![Fig. 10. The relative enthalpy of immersion as function of the concentration of carbon basic surface groups.](image-url)
bons seem to be small, taking into account the fact that the initial dose of charcoal used in intoxinations is 50–100 g in adults [8], leads to the value of the increase in adsorption after modification equal to 1–2 g.

At 320 K both carbons containing acidic surface groups are worse adsorbents than pure and modified with ammonia carbons, however, the modification of carbon with nitric acid leads to more outlined decrease in adsorption.

To determine the enthalpy of acetaminophen adsorption from enthalpy of immersion (Table 4) the procedure described by Kiraly et al. [29] was applied. It is well known that the relative enthalpy of immersion (Table 4) modification of carbon with nitric acid leads to adsorption from enthalpy of immersion (Table 4) is equal to 1–2 g.

The values of enthalpy of adsorption (Table 4) are positive and increase in the following way: D43/1–NH3; D43/1–pure; D43/1–HNO3; D43/1–H2SO4 and it is seen that for the modified with sulphuric acid carbon it is nearly twice as large as for the initial carbon and the modified one with ammonia. It can be noticed that smaller enthalpy of adsorption is observed for more hydrophobic carbons. On the other hand, the non-linear increase in the relative enthalpy of immersion with the increase in basic surface groups concentration is observed (Fig. 10).

The analysis of the adsorbsibility, describing the affinity of the carbon to paracetamol at infinitive dilution, leads to the conclusion that generally the adsorbsibility increases with carbon hydrophobicity. At such dilution, there is plenty of water molecules in comparison with the molecules of solute in solution, and it is possible that these molecules block the entrances to carbon micropores creating water clusters by association with polar surface groups. In such conditions, the increase in carbon hydrophobicity, by incorporation of hydrophobic nitrogen functionalities, leads to the increase in adsorbsibility, by opening the entrances to the smallest micropores with the highest adsorption energy.

At larger mole fractions the interaction of adsorbed acetaminophen molecules with surface groups plays an important role. Adsorption depends on the temperature, and the observed increase in adsorption with the temperature is probably caused by two factors. It is known that the sign and the magnitude of adsorption heat (see Eq. (6)) depends on the value and the sign of the enthalpy of solution [29]. It was established that for the cases of the positive temperature coefficient of solubility, the rise in temperature increases the adsorption especially in polymolecular region. As the adsorption of paracetamol, which was reached in the immunersial experiment, was the same as the maximum adsorption determined from isotherms; the integral enthalpy (calculated from Eq. (6)) is the heat effect belonging.
to the adsorption not only in micropores but in polymolecular region (where the adsorbate–adsorbate interactions predominate) as well. This makes it difficult to speculate about the sign of the adsorption enthalpy in micropores; however, the increase of adsorption in micropores with temperature suggests the positive sign of this enthalpy also. On the other hand, the increase of adsorption with temperature is connected with the less and less distinctive differences in adsorption on carbons with different surface groups. This has led to the conclusion that the second factor increasing the adsorption with temperature (and causing the adsorption on the investigated carbons more and more similar) is the decrease of interactions of water molecules with oxygen surface functionalities of modified adsorbents with temperature.

Paracetamol molecule interacts with active carbon via hydrogen bonding with surface groups and/or by aromatic ring with basal planes of microcrystallites (via dispersive interactions [33]). Moreover, it is well known that the both groups of paracetamol molecule are good electron-donor groups [32]. On the other hand, to discuss the mechanism of adsorption one should remember that the parallel orientation of the solute molecules in micropores should lead to more exothermic enthalpy of adsorption and to lower entropy of adsorbed molecules. The relative enthalpy of immersion with paracetamol solution increases with the number of basic surface groups. On the other hand, the enthalpy of adsorption is the lowest on non-modified carbons, which suggests the lower, than on the modified ones, mobility of adsorbed molecules. The highest polarity of surface oxides created by nitric acid oxidation leads to the highest energy of interaction of water with these groups and the lowest adsorption on this carbon at all temperatures.

4. Conclusions

1. The applied procedures of carbon surface modifications lead to relatively small changes in carbon porosity. This leads to the important statement that the changes in the adsorption properties of investigated carbons towards paracetamol are mainly caused by the change in the nature of the surfaces of investigated carbons by chemical modifications. The applied procedure of carbon surface modification, on the other hand, brings about some remarkable changes in the polarity and acid–base properties of carbon surface layer.

2. The modification of initial carbon with ammonia, leading to the creation of basic surface groups does not cause any remarkable changes in adsorption properties of D43/1 carbon, and the adsorption–desorption isotherms for D43/1–pure and D43/1–NH3 carbons are nearly the same at all investigated temperatures.

3. For acidic carbons the change in the carbon surface chemical composition leads to remarkable changes in adsorption properties. Moreover, these properties change with temperature. It is clearly demonstrated that the presence of surface groups both: acidic and basic influences, in the case of acetaminophen, not only the adsorption but the energetics of this process as well.

4. The modification of activated carbon surface with fuming sulfuric acid is the most effective method improving the in vitro adsorption (at 300 and 310 K) of acetaminophen at intestinal conditions.

5. To determine the detailed mechanism of acetaminophen adsorption the results of the additional measurements are necessary. This problem will be discussed in future.

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