Adsorption of organic molecules from aqueous solutions on carbon materials

Carlos Moreno-Castilla *

Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Granada, Campus Fuentenueva, 18071 Granada, Spain

Received 22 July 2003; accepted 30 September 2003

Abstract

Adsorption of organic molecules from dilute aqueous solutions on carbon materials is a complex interplay between non-electrostatic and electrostatic interactions. Non-electrostatic interactions are essentially due to dispersion and hydrophobic interactions, whereas the electrostatic or coulombic interactions appear with electrolytes when they are ionized at the experimental conditions used. Both interactions depend on the characteristics of the adsorbent and the adsorptive and the solution chemistry. Among them the carbon surface chemistry has a great influence on both electrostatic and non-electrostatic interactions, and can be considered one of the main factors in the adsorption mechanism from dilute aqueous solutions. In this paper the current knowledge about the fundamental factors that control the adsorption process from aqueous phase will be presented.

Keywords: C. Adsorption; D. Adsorption properties; Surface oxygen complexes

1. Introduction

Adsorption of organic solutes from the aqueous phase is a very important application of powdered and granular activated carbons. This covers a wide spectrum of systems such as drinking water and waste water treatments, and applications in the food, beverage, pharmaceutical and chemical industries. Activated carbon adsorption has been cited by the US Environmental Protection Agency as one of the best available environmental control technologies [1].

In spite of the large market for activated carbon, the specific mechanisms by which the adsorption of many compounds, especially organic compounds, takes place on this adsorbent are still ambiguous. This is because liquid-phase adsorption is a more complicated process than gas or vapour-phase adsorption [2].

Thus, current knowledge about the fundamental factors that control the adsorption process from the aqueous phase will be presented, giving examples of the different situations.

2. Adsorption from dilute solutions: generalities

When studying adsorption from solutions on solids it is convenient to differentiate between “adsorption from dilute solution” and “adsorption from binary and multicomponent mixtures covering the entire mole fraction scale”. To judge by the number of papers published annually on adsorption from dilute solution, this subject is more important than the adsorption from binary mixtures. Therefore, reference will be made hereafter to the adsorption from dilute aqueous solutions.

The main differences between adsorption from the gas phase and liquid phase are as follows [3]:

(i) A solution is typically a system of more than one component. In real cases, there are at least two substances that can adsorb. For a dilute solution, adsorption of one type of molecule (say A) involves replacement of the other (B). Thus, adsorption from solution is essentially an exchange process, and hence molecules adsorb not only because they are attracted by solids but also because the solution may reject them. A typical illustration is that the attachment of hydrophobic molecules on hydrophobic adsorbents from aqueous solutions is mainly
driven by their dislike of water and not by their attraction to the surface.

(ii) Isotherms from solution may exhibit non-ideality, not only because of lateral interactions between adsorbed molecules but also because of non-ideality in the solution.

(iii) Multilayer adsorption from solution is less common than from the gas phase, because of the stronger screening interaction forces in condensed fluids.

Adsorption isotherms are normally developed to evaluate the capacity of activated carbons for the adsorption of a particular molecule. They constitute the first experimental information, which is generally used as a tool to discriminate among different activated carbons and thereby choose the most appropriate one for a particular application. The shape of the isotherms is the first experimental tool to diagnose the nature of a specific adsorption phenomenon, and it is expedient to classify the most common types phenomenologically [3]. There are several types of isotherms but those mainly found in carbon materials are the five depicted in Fig. 1.

Long-linear isotherms are not common in adsorption on carbons but are found in the initial part of all isotherms on homogeneous surfaces. The Langmuir type (L) frequently occurs, even when the premises of the Langmuir theory are not satisfied. Type F, typical for heterogeneous surfaces, is perhaps the most common. High-affinity isotherms are characterised by a very steep initial rise, followed by a pseudo-plateau. Sigmoidal isotherms have been obtained with homogeneous surfaces such as the graphitised carbon blacks Graphon and V3G.

Statistically, adsorption from dilute solutions is simple because the solvent can be interpreted as primitive, that is to say as a structureless continuum [3]. Therefore, all the equations derived from monolayer gas adsorption remain valid after replacing pressure by concentration and modifying the dimensions of some parameters.

Some of these equations, such as the Langmuir and Dubinin–Astakhov, are widely used to determine the adsorption capacity of activated carbons.

Batch equilibrium tests are often complemented by dynamic column studies to determine system size requirements, contact time and carbon usage rates. These parameters can be obtained from the breakthrough curves. To study these curves it is usual to apply a macro-approach method based on the mass transfer zone concept (MTZ). The basic principles of this concept are depicted in Fig. 2. The MTZ is the region of the bed between the already-saturated activated carbon and the point where the concentration of the adsorbative in the aqueous phase is at the maximum acceptable limit in the effluent stream. Breakthrough is reached when the leading edge of the zone advances to the end of the bed (point 2 in Fig. 2). The height of this zone is a measure of the adsorption efficiency of the bed. The lower the height, the more efficient is the carbon bed. Under the appropriate experimental conditions, this parameter is independent of the bed depth and generally shows little variation with in the initial concentration.

Adsorption measurements should preferably be amplified by microcalorimetry, such as immersion and flow microcalorimetry. These techniques can give additional information about the surface nature of the adsorbent and the mode or mechanism of adsorption.

3. Factors that control the adsorption process

Adsorption is a spontaneous process that takes place if the free energy of adsorption, $\Delta G_{ads}$, is negative. There is a wide range of energies contributing to the free energy of adsorption, which can be grouped into non-electrostatic and electrostatic.

$$\Delta G_{ads} = \Delta G_{non-elect.} + \Delta G_{elect.}$$
Although at atomic level all ionic and molecular interactions can be interpreted as “electric”, this term is restricted to coulombic interactions and all other interactions are termed non-electrostatic, whatever their origin.

Electrostatic interactions appear when the adsorptive is an electrolyte that is dissociated or protonated in aqueous solution under the experimental conditions used. These interactions, that can be either attractive or repulsive, strongly depend on the charge densities for both the carbon surface and the adsorptive molecule and on the ionic strength of the solution, as we shall see later. The non-electrostatic interactions are always attractive, and can include van der Waals forces, hydrophobic interactions and hydrogen bonding. Factors that influence the adsorption process are the characteristics of the adsorbent and adsorptive, the solution chemistry and the adsorption temperature. These factors will now be discussed.

3.1. Characteristics of the adsorbent

The characteristics of carbon that affect the adsorption process are the pore texture, surface chemistry and mineral matter content. The adsorption capacity of carbon materials is not related in a simple form with their surface area and porosity. The adsorption capacity will depend on the accessibility of the organic molecules to the inner surface of the adsorbent, which depends on their size. Thus, under appropriate experimental conditions, small molecules such as phenol can access micropores, natural organic matter (NOM) can access mesopores, and bacteria can have access to macropores.

Activated carbon fibres have received increasing attention in recent years as a better adsorbent than granular activated carbons, because they normally present much higher adsorption kinetics and adsorption capacity (Fig. 3). Activated carbon fibres only have micropores, which are directly accessible from the external surface of the fibre. Thus, adsorptive molecules reach adsorption sites through micropores without the additional diffusion resistance of macropores, which is usually the rate-controlling step in the case of granular adsorbents.

The surface chemistry of activated carbons essentially depends on their heteroatom content, mainly on their surface oxygen complex content. They determine the charge of the surface, its hydrophobicity, and the electronic density of the graphene layers. Thus, when a solid such as a carbon material is immersed in an aqueous solution, it develops a surface charge that comes from the dissociation of surface groups or the adsorption of ions from solution [2]. This surface charge (Fig. 4) will depend on the solution pH and the surface characteristics of the carbon. A negative charge results from the dissociation of surface oxygen complexes of acid character such as carboxyl and phenolic groups. Therefore, these surface acid sites are of Brønsted type. The origin of the positive surface charge is more uncertain because, in carbons without nitrogen functionalities, it can be due to surface oxygen complexes of basic character like pyrones or chromenes, or to the existence of electron-rich regions within the graphene layers acting as Lewis basic centres, which accept protons from the aqueous solution.

An indication that surface basicity can be mainly due to these electron-rich regions is that, the net enthalpy of neutralization of the total basic sites decreases with the oxygen content of the surface (Fig. 5), whereas the net enthalpy of neutralization of total acid sites increases [4]. Results obtained with activated carbons of different origins can be explained by the fact that oxygen complexes reduce the electronic density of the graphene layers and consequently reduce the basicity of the carbon surface.

The surface charge can be determined by electrokinetics or titration methods. These are complementary methods, especially in the case of granular porous
carbons [2]. The first method primarily measures the surface charge at the more external surface of the particles whereas the second one provides a measure of the total surface charge. The pH at which the external surface charge is zero is referred to as the isoelectric point, pH_{IEP}, while the total surface charge is zero at the point of zero charge, pH_{PZC}.

In addition, surface oxygen complexes also affect the surface hydrophobicity, which determines the hydrophobic interaction. Hydrophobic interaction or, more specifically, hydrophobic bonding describes the unusually strong attraction between hydrophobic molecules and hydrophobic carbon surfaces. The surface hydrophobicity of carbon materials can be determined, for instance, by measuring their contact angle with test liquids of known surface tension, by inverse gas chromatography or by water adsorption.

Hydrophobic bonding occurs exclusively in aqueous solution: in fact it mainly comes from the strong tendency of water molecules to associate with each other by hydrogen bonding and from the characteristic structure of water molecules. Hydrophobic bonding plays an important role in interface and colloid science [5]. For instance, the increasing adsorbability of aliphatic acid molecules with increasing hydrocarbon length, also known as Traube’s rule, is essentially due to the increasing hydrophobic effect [6].

From this it is derived that it is important to plot the adsorption isotherms obtained for adsorptives with different solubilities against the concentration relative to that in saturated solution. This normalisation eliminates the differences in hydrophobicity between the adsorptive molecules, so that the normalised isotherms more truly reflect the affinity for the surface [5,6].

In general, an increase in the oxygen content of carbon brings about a decrease in its hydrophobicity. Thus, Pendleton et al. [7] showed (Fig. 6) that the adsorption of dodecanoic acid on different activated carbons linearly decreased when the oxygen content of the carbonaceous adsorbent increased and that there was no relation with the micropore volume of the adsorbent. Water molecules are bound to the surface oxygen complexes by H-bonds, reducing the accessibility of the hydrophobic aliphatic chain of dodecanoic acid to the hydrophobic parts of the carbon surface.

This model is consistent with that found for the decrease in methyl isoborneol (MIB) adsorption when the oxygen content of carbons increased [8]. In this case, the average enthalpy of displacement of water by MIB (Fig. 7) decreased when the concentration of hydrophilic sites on the surface increased. This finding suggests that it is more difficult for MIB molecules to displace water molecules from carbon surfaces when their oxygen content increases. Results obtained show that the enthalpy of displacement reaches a limiting value when the number of hydrophilic sites is higher than about 0.7 mmol/g.

Finally, surface oxygen complexes also affect the electronic density of the graphene layers [9]. This in turn would affect the dispersion interactions between the carbon surface and the adsorptive molecules. For instance, carboxyl groups fixed at the edges of the graphene layers have the ability to withdraw electrons, whereas phenolic groups release electrons.

Fig. 5. Variation of the net enthalpy of neutralization \( \Delta H \) (NaOH)_{net}, \( \Delta H \) (HCl)_{net}, with the total amount of oxygen on the surface. From [4].

Fig. 6. Relationship between the maximum amount of dodecanoic acid adsorbed on different carbons with their oxygen content and micropore volume. Adapted from [7].

Fig. 7. Enthalpy of displacement of water by 2-methylisoborneol (MIB) versus hydrophilic sites on activated carbons. Adapted from [8].
Thus, Tamon and Okazaki [10] determined by a semi-empirical quantum chemical method the HOMO and LUMO levels of a model aromatic molecule such as a non-substituted phenanthroperylene cluster (AC), and the same cluster substituted with two phenolic groups (AC–OH) and with two carboxyl groups (AC–COOH). Results are shown in Table 1 and indicate that the withdrawing groups, such as carboxyl groups, decrease HOMO and LUMO levels with respect to the original carbon cluster, whereas the donating groups increase these levels.

Finally, the other characteristics of the adsorbent that control the adsorption process is its mineral matter content. This has in general a deleterious effect on the adsorption because it can block the porosity of the carbon matrix and can preferentially adsorb water due to its hydrophilic character, in this case reducing the adsorption of the adsorptive.

### 3.2. Characteristics of the adsorptive

Among the characteristics of the adsorptive that mainly influence the adsorption process are its molecular size, solubility, $pK_a$ and the nature of the substituent if they are aromatic. The molecular size controls the accessibility to the pores of the carbon and the solubility determines the hydrophobic interactions. The $pK_a$ controls the dissociation of the adsorptive if it is an electrolyte. This parameter is closely related to the solution pH and its importance will be discussed later on.

The substituent of the aromatic ring of the adsorptive molecules, as in the case of the substituent of the graphene layers, can withdraw or release electrons from it, which would affect the dispersion interactions between the aromatic ring of the adsorbate and the graphene layers of the adsorbent.

To date, the adsorption of phenolic compounds on carbon materials and the effect of surface oxygen complexes on phenol uptake have been the most studied adsorption processes [2]. Thus, it has long been known that the increase in surface acidity of activated carbons, produced after their oxidation, brings about a decrease in the amount of phenol adsorbed from dilute aqueous solutions. To show this phenomenon (Table 2) sample A was oxidized to increase its surface acidity. Heat treatment of the oxidized sample progressively decreased the surface acidity due to the removal of mainly carboxyl and phenolic groups [11]. A sample heat treated at 950 °C had no acidity and its surface area was lower than that of as-received sample. Fig. 8 shows the adsorption isotherms of phenol on the above carbons. There was a large decrease in phenol uptake after oxidation. This phenol uptake progressively increased as the surface acidity decreased, and the oxidised sample heat treated at 950 °C had the same adsorption capacity as the as-received one, despite the lower surface area of the former sample compared with the latter.

Three mechanisms have been mainly proposed to explain this behaviour, namely: the $\pi-\pi$ dispersion interaction mechanism, the hydrogen bonding formation mechanism and the electron donor–acceptor complex mechanism.

The first two mechanisms were proposed by Coughlin and Ezra [9] in 1968, and the third mechanism was proposed by Mattson et al. [12] in 1969. At that moment it was known that phenol was adsorbed in flat position on the graphene layers, and in this situation the adsorption driving forces would be due to $\pi-\pi$ dispersion interactions between the aromatic ring of phenol and the aromatic structure of the graphene layers.

Thus, Coughlin and Ezra proposed that acidic surface oxygen groups, which are located at the edges of the

![Fig. 8. Adsorption isotherms of phenol on activated carbons with different degrees of oxidation. From [11].](image-url)
basal planes, remove electrons from the \( \pi \)-electron system, creating positive holes in the conducting \( \pi \)-band of the graphitic planes. This would lead to weaker interactions between the \( \pi \)-electrons of the phenol aromatic ring and the \( \pi \)-electrons of the basal planes, therefore reducing the phenol uptake.

Coughlin also proposed that the bonding of water molecules to the oxide functional groups by H-bonding can play an important role in the uptake of phenolic compounds. In this case, Coughlin adopted Dubinin’s proposal that water molecules adsorbed to oxygen groups become secondary adsorption centres, which retain other water molecules by means of H-bonds. As a result, complexes of associated water form within the pores of a carbon adsorbent. These complexes could prevent the migration of organic molecules to a large portion of the active surface area. This mechanism was ruled out by Coughlin, whose results indicated that surface oxygen complexes had no influence on phenol uptake from concentrated solutions (in the second plateau of the isotherms).

Mattson and coworkers suggested that aromatic compounds adsorb on carbons by a donor–acceptor complex mechanism, with the carbonyl oxygen of the carbon surface acting as the electron donor and the aromatic ring of the adsorbate acting as the acceptor. Once the carbonyl groups are exhausted, the aromatic compounds form donor–acceptor complexes with the rings of the basal plane. Thus, Mattson and co-workers explained the decrease in phenol uptake after carbon oxidation as due to the oxidation of carbonyl groups to carboxyl groups. As a result, the electron donor–acceptor complexes cannot be formed.

At this point it is interesting to indicate that Coughlin and Ezra pointed out in their key paper [9] that “evidence for any single explanation (of the decrease of phenol uptake with increase in surface acidity) is not overwhelming” and added that “it is hoped that continuing research will shed more light on this question”. However, this was not, unfortunately, the case in many instances, as can be seen in the recent review published by Radovic et al. [2].

Since the initial proposals by Coughlin and Mattson, many published papers have attempted to elucidate the most appropriate mechanism to explain the adsorption of phenolic compounds, and in general aromatic compounds on carbon materials. Thus, perhaps one of the latest papers published on this topic to date was the one published by Haydar et al. that appeared in 2003 entitled “Adsorption of \( p \)-nitrophenol on an activated carbon with different oxidations” [13]. This paper gives some experimental evidence for the \( \pi–\pi \) dispersion interaction mechanism.

Perhaps the first experimental evidence of this mechanism was given by Mahajan et al. [11] in their study of phenol adsorption on graphite and boron-doped graphite samples (Fig. 9). Results show that the presence of substitutional boron in the lattice of poly-crystalline graphite, which removes \( \pi \)-electrons from the solid, results in a lowering of the phenol uptake from water.

These authors also indicated that both phenol and water can compete to form H-bonds with surface oxygen groups, such as carboxyl groups. In this competition water molecules are preferentially bound by H-bonds [11].

This idea of competition between phenol and water molecules for H-bonding to surface oxygen groups suggested that phenol uptake from its cyclohexane solution would be favoured by the surface oxygen complexes. This is shown in Fig. 10. When adsorption of phenol per unit cyclohexane area is plotted for two heat-treated carbons, the carbon with higher surface acidity exhibited a higher phenol uptake.

More recently, Pinto and co-workers [14] revisited this issue by studying the adsorption of phenol aniline, nitrobenzene and benzoic acid from both aqueous and cyclohexanolic solutions. Although the interpretation of
the authors of the π–π dispersion interactions is confused, their experimental results seem to indicate that the adsorption mechanism is both by water H-bonding with carboxyl groups and π–π dispersion interactions between the aromatic ring of the adsorptive and the graphene layers. These authors also concluded that Mattson’s mechanism is not the driving force for the adsorption of aromatics on activated carbons.

One of the weak points of the Mattson mechanism is that there is much experimental evidence that although oxidation of carbons increases their concentration of CO₂-evolving groups, the CO-evolving groups also increase or remain essentially unchanged.

Additional experimental evidence of the influence of water adsorption comes from the enthalpy of immersion into water of activated carbons, which reflects the specific and non-specific interactions between the liquid and the solid [15] as shown in Fig. 11. The study of a large number of carbons oxidised to different degrees reveals a simple correlation between the enthalpy of immersion, the oxygen content of the surface, the basic groups titrated by HCl, the micropore filling and the wetting of the external surface. Thus, the specific interaction between the surface oxygen and water is 12.1 kJ/mol oxygen, involving an average of two water molecules per oxygen.

More recently, MacDonald and Evans [16] measured the enthalpy of exchange of phenol–water from diluted aqueous solutions on BPL carbons with different oxygen contents. They found (Fig. 12) that phenol exchange enthalpy is inversely proportional to the net molar enthalpy of immersion into water. This indicates that the strong preference of water to H-bond to surface oxygen complexes lowers the phenol exchange enthalpy from aqueous solution.

The two mechanisms proposed by Coughlin can better explain many of the experimental results obtained to date. However, an electron donor–acceptor mechanism cannot be ruled out. Thus, it is well known that adsorption of phenolic compounds is partly physical and partly chemical. The physisorbed part can be desorbed by treating with different solvents or by heat treatments in inert atmosphere. However, the chemisorbed part cannot be desorbed, even at high temperatures, and it is converted to light gases and heavy products that evolve from the surface of the carbon, and also to a polymeric carbon residue that remains on the surface. This residue reduces the adsorption capacity of thermally regenerated activated carbons, as depicted in Fig. 13, which shows that the adsorption capacity for different phenolic compounds decreased when the regeneration cycle increased [17].

Better regeneration results could be achieved by treating the exhausted carbons with liquid water at 150 atm and 350 °C in the absence of oxygen. Some of the results obtained in a recent study [18] of the regeneration of exhausted carbons with ortho-chlorophenol (OCP) are shown in Table 3. In no case was there any loss of carbon due to the treatment. The efficacy of the treatment was slightly above 100% for the first regeneration cycles. However, for successive regeneration cycles there

Fig. 11. Correlation between the enthalpy of immersion into water, the total surface oxygen, the basic groups titrated with HCl, the micropore filling and the wetting of the non-porous surface area. From [15].

Fig. 12. The enthalpy of exchange for phenol–water versus the molar enthalpy of immersion in water for a series of BPL carbons. Adapted from [16].

Fig. 13. Variation of the adsorption capacity of the activated carbon AP-10 as a function of the adsorption–regeneration cycle. Phenol, Δ; m-aminophenol, ◇; p-cresol, ◆; p-nitrophenol, ◊. From [19].
was a slight decrease in the OCP adsorbed, because, according to the authors, part of it was strongly adsorbed and was not completely removed from the carbon surface.

All these data indicate that chemisorbed phenolic compounds are strongly bound by other forces than those of dispersion. These would likely involve charge-transfer complexes in which the direction of the electron transfer could be either similar to that proposed by Mattson or in a reverse direction.

3.3. Solution chemistry and adsorption temperature

Factors from solution chemistry that influence the adsorption process are the solution pH and ionic strength. Solution pH is one of the key factors that control the adsorption process of organic weak electrolytes and polyelectrolytes on carbon materials because it controls the electrostatic interactions between the adsorbent and the adsorbate. Thus, solution pH determines the carbon surface charge and the dissociation or protonation of the electrolyte. At a solution pH lower than the pH_{ZC} or the pH_{IEP}, the total or external surface charge, respectively, will be on average positive, whereas at a higher solution pH they will be negative.

In addition, the solution pH also controls the dissociation or ionization of the electrolyte through its pK_a. Thus, for instance, acidic electrolytes will be dissociated at pH > pK_a. Therefore, the solution pH controls the adsorptive-adsorbent and adsorptive-adsorptive electrostatic interactions, which can have a profound effect on the adsorption process.

Thus, the adsorption of substituted phenols on activated carbon depends on the solution pH (Fig. 14). At acidic pH, the uptake was maximal because phenols were undissociated and the dispersion interactions predominated. At basic pH, however, the uptake was lower because of electrostatic repulsions between the negative surface charge and the phenolate anions and between phenolate-phenolate anions in solution. The pH at which the uptake decreased was found to be dependent on the adsorptive pK_a and the difference between the pH_{ZC} and the pH_{IEP} [19].

Solution pH also affects the characteristics of carbon beds, as shown in Table 4. Thus, adsorption of OCP is favoured at acidic pH, as illustrated by the higher values of the breakthrough volumes and the lower values of the height of the mass transfer zone found at this pH. The lower adsorption at basic pH is due, as explained before, to the repulsion between the net negatively charged carbon surface and the ortho-chlorophenolate anions [20].

The effect of pH and the nature of functional groups of both the aromatic adsorptive and the adsorbent on the adsorption process have recently been investigated by Radovic et al. [21]. For this purpose, they used an as-received activated carbon oxidized with nitric acid and nitrided with ammonia to study the adsorption of aniline and nitrobenzene, which are, respectively, electron-donating and -withdrawing groups. Some of the results obtained from the adsorption of aniline at different pHs are shown in Table 5. At pH 2, anilinium cations were predominant in solution and the surface charge was positive. Carbon oxidation enhanced adsorption with respect to the as-received carbon, whereas nitriding de-

### Table 3

<table>
<thead>
<tr>
<th>Activated carbon</th>
<th>Run number</th>
<th>Amount adsorbed (mmol/g)</th>
<th>Regeneration yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-30</td>
<td>0</td>
<td>1.63</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1.69</td>
<td>104</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.61</td>
<td>99</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1.58</td>
<td>97</td>
</tr>
<tr>
<td>H-13</td>
<td>0</td>
<td>0.92</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.95</td>
<td>104</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.96</td>
<td>105</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.87</td>
<td>95</td>
</tr>
<tr>
<td>RO-0.8</td>
<td>0</td>
<td>1.05</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1.07</td>
<td>103</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.09</td>
<td>104</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1.04</td>
<td>99</td>
</tr>
</tbody>
</table>

### Table 4

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH = 2</th>
<th>pH = 10</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>V_b (cm^3)</td>
<td>H_{MTZ} (cm)</td>
</tr>
<tr>
<td>C-2</td>
<td>4450</td>
<td>1.02</td>
</tr>
<tr>
<td>C-13</td>
<td>6500</td>
<td>0.95</td>
</tr>
<tr>
<td>C-24</td>
<td>10,650</td>
<td>0.48</td>
</tr>
</tbody>
</table>

Fig. 14. Adsorption capacity of activated carbon CP-10 as a function of solution pH. ◯, Phenol (pK_a = 9.96); □, m-chlorophenol (pK_a = 8.80); Δ, p-nitrophenol (pK_a = 7.13). From [19].
Nitrobenzene uptake (mmol/g) at a relative concentration of $10^{-3}$ on Norit GCW carbon at different solution pHs

<table>
<thead>
<tr>
<th>Carbon</th>
<th>pH = 2</th>
<th>pH = 11</th>
<th>pH = $p_{\text{PZC}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>As received</td>
<td>8.0</td>
<td>2.43</td>
<td>2.61</td>
</tr>
<tr>
<td>Oxidized</td>
<td>2.6</td>
<td>0.78</td>
<td>0.70</td>
</tr>
<tr>
<td>Nitrided</td>
<td>8.9</td>
<td>1.30</td>
<td>1.65</td>
</tr>
</tbody>
</table>

Aniline uptake (mmol/g) at a relative concentration of $10^{-1}$ on Norit GCW carbon at different solution pHs

<table>
<thead>
<tr>
<th>Carbon</th>
<th>pH = 2</th>
<th>pH = 11</th>
<th>pH = $p_{\text{PZC}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>As received</td>
<td>8.0</td>
<td>0.48</td>
<td>1.10</td>
</tr>
<tr>
<td>Oxidized</td>
<td>2.6</td>
<td>1.14</td>
<td>0.86</td>
</tr>
<tr>
<td>Nitrided</td>
<td>8.9</td>
<td>0.33</td>
<td>0.86</td>
</tr>
</tbody>
</table>

Aniline $p_K_a = 4.6$. Adapted from [21].

$p_{\text{PZC}}$ values.

Increased it. The authors indicated that in this case the electrostatic adsorbent/adsorbate interactions were more important than the dispersion interactions. Thus, oxidation shifted the $p_{\text{PZC}}$ to a value close to the solution pH, whereas nitriding increased the $p_{\text{PZC}}$, enhancing the adsorbate–adsorbent interactions.

At pH 11, the surface charge was predominantly negative and aniline was not protonated in solution. In this case, oxidation and nitriding were detrimental. These results can be explained because dispersion interactions predominate and are not favoured, because the presence of some oxygen and nitrogen-containing functional groups withdraws electrons from the graphene layers. However, in this case the preferential H-bonding of water to some oxygen and nitrogen surface functional groups can also explain these results.

At a solution pH equal to the $p_{\text{PZC}}$, aniline uptake was relatively high on all adsorbents. According to the authors this is consistent with the minimized electrostatic repulsions.

Some of the results obtained with nitrobenzene are shown in Table 6. In this case solution pH has little effect on equilibrium uptakes because nitrobenzene molecules are the dominant species across the entire range of solution pH. Therefore the effect of surface chemistry is much more important. Across the pH range the as-received carbon exhibits the highest uptake. The authors explained these results as due to the dispersion interactions, which are dominant in this case. Thus, surface oxygen and nitrogen complexes withdraw electrons from the graphene layers decreasing the $\pi-\pi$ interactions. However, as commented above, the H-bonding of water to some surface functionalities can also play an important role in this case. Maximal uptake is obtained at $pH = p_{\text{PZC}}$ because dispersion interactions are maximized.

These results, together with others found in the literature, indicate that functionalization of either the adsorptive or the adsorbent, which increases the $\pi$-electron density, leads to enhanced or stronger adsorption when the adsorption process is governed by dispersion forces. The converse is also true.

Ionic strength is the other key factor that controls the electrostatic interactions. Thus, these interactions, either attractive or repulsive, can be reduced by increasing the ionic strength of the solution. This is due to a screening effect of the surface charge produced by the added salt. Therefore, when the electrostatic interaction between the surface and the adsorptive is repulsive, or the surface concentration is sufficiently high, an increase in ionic strength will increase the adsorption. Conversely, when the electrostatic interactions are attractive, or the surface concentration is sufficiently low, an increase of the ionic strength will diminish the adsorption. These effects have been shown to take place with many weak organic electrolytes and polyelectrolytes, for instance in the case of bisphenol A and NOM [22,23].

In the case of bisphenol A, Fig. 15 shows that its uptake increased with the ionic strength [22]. At solution pH 7, the surface charge would be on average positively charged and screened by the increase in the electrolyte concentration, resulting in an enhancement of the bisphenol uptake.

NOM is found in varying concentrations in all natural water sources. It is a complex mixture of compounds varying from small hydrophilic acids, proteins and amino acids to larger humic and fulvic acids. Newcombe and Drikas [23] have studied the adsorption of NOM (with nominal molecular weight between 500 and 3000 Da) on different activated carbons. Fig. 16 shows the adsorption of NOM at pH 7 on carbon W. At this pH, both the carbon surface and NOM are negatively charged. At very low surface coverage direct surface–adsorbate interactions should predominate. An increase in salt concentration effectively screens repulsive interactions, resulting in increased adsorption.

In the case of carbon C, Fig. 17, the adsorption of NOM was carried out at pH 4. In these conditions the carbon surface will be positively charged whereas NOM will be negatively charged. The adsorption isotherms show an intersection point indicating a transition from a screening-reduced to a screening-enhanced regime. At low surface concentrations below the intersection point of the isotherms, attractive interactions between the adsorbent and the adsorbate are screened by an increase in salt concentration, decreasing the adsorption. Above the intersection point, where the surface concentration is higher, salt screens the repulsion between charged segments of the polyelectrolyte and between adsorbed NOM and NOM in solution, increasing the adsorption.

Table 6

<table>
<thead>
<tr>
<th>Carbon</th>
<th>pH = 2</th>
<th>pH = 11</th>
<th>pH = $p_{\text{PZC}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>As received</td>
<td>8.0</td>
<td>2.43</td>
<td>2.61</td>
</tr>
<tr>
<td>Oxidized</td>
<td>2.6</td>
<td>0.78</td>
<td>0.70</td>
</tr>
<tr>
<td>Nitrided</td>
<td>8.9</td>
<td>1.30</td>
<td>1.65</td>
</tr>
</tbody>
</table>

Adapted from [21].

$p_{\text{PZC}}$ values.
Therefore, both solution pH and ionic strength control the electrostatic interactions between the adsorbent and the adsorptive.

When the adsorption of organic molecules is governed by non-electrostatic interactions, such as \( \pi-\pi \) dispersion or hydrophobic interactions, the area of the adsorbent occupied by the adsorbate depends on the porosity of the former and the molecular size of the latter. Thus, it has been shown [24] in adsorption from diluted aqueous solution and immersion calorimetry measurements (Table 7) that phenol and metachlorophenol are adsorbed as monolayers by both porous and non-porous carbons with basic surface properties, provided that the adsorptive is undissociated at the solution pH. This did not apply where molecular sieve effects reduced the accessibility of the micropore system.

In the case of the adsorption of NOM (Fig. 18) in the molecular weight range between 500 and 3000 on different activated carbons at solution pH 3, where electrostatic interactions are minimal and non-electrostatic interactions predominate, the amount adsorbed depends on the volume of pores between 0.8 and 50 nm [23].

Another example is the adsorption of trichloroethene (Fig. 19) from highly diluted aqueous solutions on activated carbon fibres and granular activated carbons with similar surface chemistry [25]. In this case, the trichloroethene adsorption on the more hydrophobic carbons was primarily controlled by pore volume in the 0.7–1 nm width range. According to the authors, this micropore range is between 1.3 to 1.8 times the trichloroethene kinetic diameter (0.56 nm).

With regard to the effect of temperature on the adsorption, an increasing uptake of organic molecules is expected when the adsorption temperature decreases because adsorption is a spontaneous process. However,

<table>
<thead>
<tr>
<th>Carbon</th>
<th>( S_{\text{Total}} )</th>
<th>( S_{\text{phenol}} )</th>
<th>( S_{m\text{-chlorophenol}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLW</td>
<td>1097</td>
<td>1016 (1037)</td>
<td>1050 (1047)</td>
</tr>
<tr>
<td>AP-5</td>
<td>404</td>
<td>453</td>
<td>453</td>
</tr>
<tr>
<td>CP-5</td>
<td>477</td>
<td>596</td>
<td>522</td>
</tr>
</tbody>
</table>

From [24].

* From CO\(_2\) at 273 K.

* From immersion calorimetry.
some examples have been reported where the amount adsorbed increased with temperature. Thus, for instance, it has recently been reported [26] that the adsorption of paracetamol from diluted aqueous solution increased with adsorption temperature. This effect was independent of the type of carbon, its surface chemistry or solution pH. The authors explained this behaviour as due to phase changes in the crystal form of the adsorptive.

4. Conclusions

Adsorption of organic molecules from dilute aqueous solutions on carbon materials is a complex interplay between electrostatic and non-electrostatic interactions. Electrostatic interactions appear with electrolytes, essentially when they are ionized at the experimental conditions used. Both interactions depend on the characteristics of the adsorbent and the adsorptive, and the solution chemistry. Non-electrostatic interactions are essentially due to dispersion and hydrophobic interactions. The surface chemistry of the carbon has a great influence on both electrostatic and non-electrostatic interactions, and can be considered the main factor in the adsorption mechanism from dilute aqueous solutions.

Aromatic compounds are physisorbed on carbon materials essentially by dispersion interactions between the $\pi$-electrons of the aromatic ring and those of the graphene layers. Functionalization of either the adsorbent or the adsorptive profoundly affects these dispersion interactions. In addition, the presence on carbon surfaces of chemical functionalities that can give rise to H-bonds with water can effectively reduce the adsorption of the adsorptive molecules.

Strongly adsorbed aromatic compounds on the carbon surface, which cannot be desorbed even at high temperatures, would probably be adsorbed on the surface by stronger interactions than the dispersion ones. This likely involves an electron donor–acceptor or charge-transfer mechanism. Thus, further research would be needed in this area.

On the other hand, it has been shown that the surface of the carbon material is more effectively used if non-electrostatic interactions are the driving force for the adsorption. This condition can be reached by controlling the surface chemistry of carbon, and the pH and ionic strength of the solution.

Finally, some research trends on this topic are the study of competitive adsorption, for instance between NOM and micropollutants such as pesticides; adsorption of bacteria which in turn can catalyse the decomposition of the adsorptive; adsorption–desorption of drugs for medical applications and modifications of the adsorptive depending on the solution and carbon surface chemistry.

Acknowledgements

The author wants to acknowledge to Drs. José Rivera-Utrilla and Victoria López-Ramón for fruitful discussions about the manuscript. Financial support from the Ministerio de Ciencia y Tecnología is also acknowledged.

References


