

POSTER

EFFECTS OF ACTIVATED CARBON SURFACE GROUPS ON THE ADSORPTION OF NITROBENZENE AND ANILINE

I. F. Silva¹ and L. R. Radovic²

¹Univ. Nova de Lisboa, FCT, Depto. de Química, Quinta da Torre, 2825 Monte de Caparica, Portugal

²Dept. of Materials Science & Engineering, Penn State University, University Park, PA 16802

INTRODUCTION

A voluminous literature exists on the effects of chemical surface treatment of activated carbons on their capacity to adsorb different organic pollutants in water [1]. The role of oxygen surface groups has received the most attention. There appear to exist considerable inconsistencies among the explanations offered. In particular, the role of electrostatic adsorbate/adsorbent interactions and the consequences of the amphoteric nature of carbon surfaces do not seem to have been clarified. The present communication is part of an ongoing study designed to address these issues. In particular, we contrast the behavior of three chemically different carbons in adsorbing two vastly different aromatic solutes. Nitrobenzene is a very weak Lewis acid that possesses the electron-withdrawing NO₂ group, while aniline is a predominantly cationic species at pH<4.6 that also possesses the electron-donating NH₂ group.

EXPERIMENTAL

A commercial granular carbon (HydroDarco GCW, Norit, sample AR-N) was used as the adsorbent. Oxidation with HNO₃ was performed by contacting the carbon sample with concentrated HNO₃ (65% w/w) at 380 K for 6 h. The sample (O-N) was washed until neutral pH was achieved, and dried at 353 K before use. The reaction with NH₃ (nitriding) was carried out in a tubular furnace flushed at a flow rate of 30 cc/min. The temperature was kept constant for 3 h. Prior to use, the sample (N-N) was washed and dried.

Elemental analysis was performed using LECO CHN-600. Maximum nitrogen incorporation was observed at 673 K. A previously oxidized sample was also subjected to NH₃ treatment. The maximum N uptake (ca. 7%) was achieved at 658 K for 3 h. As the residence time increased, the yield of N decreased.

The oxidized samples were neutralized by reacting 1 g of carbon with 20 mL 0.1 N NaHCO₃, or Na₂CO₃ or NaOH, in mechanically shaken vials for 24 h. The samples were washed and dried prior to the adsorption tests.

The isoelectric point (IEP) and the point of zero charge (PZC) were measured by electrophoresis and mass titration. Physical surface properties of the carbons were determined using an Autosorb adsorption apparatus (Quantachrome). The surface of the as-received and modified carbons was analyzed using XPS (ESCALAB 200A-VG).

Adsorption isotherms were obtained by adding different amounts of carbon to Nalgene flasks containing 0.1 g/L of aniline or nitrobenzene. The pH was adjusted with NaOH or HCl. The suspensions were shaken until equilibrium was reached (ca. 24 h), and the residual adsorbate concentrations were measured by uv spectroscopy.

Table 1. Characteristics of activated carbons.

| Sample | %C | %H | %N | %O | S _{N2} | IEP | PZC |
|--------|------|------|------|------|-----------------|-----|-----|
| AR-N | 96.5 | 0.57 | 1.29 | 1.68 | 859 | 4.0 | 8.0 |
| O-N | 82.9 | 1.30 | 1.60 | 14.2 | 807 | 1.5 | 2.6 |
| N-N | 90.5 | 0.47 | 5.81 | 3.13 | 869 | 5.2 | 8.9 |
| NO-N | 86.7 | 1.48 | 6.72 | 5.10 | 306 | - | 7.1 |

*S_{N2} given in m²/g (BET).

RESULTS

Table 1 shows the physical characteristics of the samples used. For both nitrided and oxidized samples no significant surface area changes were observed, in agreement with our previous studies [2,3]. In contrast, the surface area of the oxidized sample that was subsequently nitrided decreased sharply and its uptake of both adsorbates was quite small. The values of PZC were consistently higher than those of IEP, in agreement with previous studies [2,3] and suggesting surface charge inhomogeneities within the carbon particles [2,3].

Deconvolution of the broad N1s peaks in Figure 1 suggests the presence of amide and amine groups (399.5-399.8 eV), pyridine or nitrile groups (398 eV) and pyrrole groups (401 eV) on the surface of nitrided carbon. No nitrogen oxides were detected. The well known increase in the concentration of

carboxyl groups is illustrated in Figure 2 for the oxidized carbon. The decrease in PZC and IEP also reflects the presence of acidic groups. In addition to carboxyl groups (288.7 eV), carbonyls (287.0 eV) and hydroxyls (286.0 eV) may also be present.

Table 2. Langmuir monolayer capacities (mmol/g).

| Sample | pH=2 | pH=pK _a | pH=PZC | pH=11 |
|--------------|------|--------------------|--------|-------|
| Nitrobenzene | | | | |
| AR-N | 3.28 | - | 4.76 | 1.51 |
| O-N | 0.92 | - | 1.79 | 0.93 |
| N-N | 1.41 | - | 1.92 | 1.23 |
| Aniline | | | | |
| AR-N | 0.68 | 1.27 | 1.01 | 1.45 |
| O-N | 1.13 | 1.96 | 1.75 | 0.79 |
| N-N | 0.28 | 0.63 | 0.97 | 0.98 |

DISCUSSION

In earlier work [3], we concluded that, in contrast to the adsorption of aliphatic carboxylic acids, where electrostatic interactions are dominant, the adsorption of aromatic carboxylic acids is dominated by dispersion interactions between the benzene rings and the graphene layers in carbon. Table 2 and Figure 3 illustrate a complex interplay of electrostatic and dispersive interactions.

For example, aniline is much more soluble in water than nitrobenzene (35 vs. 2 g/L at 25 °C); yet its uptake does not reflect this. This is attributed to the beneficial effect of the electron-donating NH₂ group. Similarly, both oxidation and nitriding of the carbon (which have opposite electrostatic effects) reduce the π electron density on the graphene layers and have a negative effect on the uptake of nitrobenzene, in agreement with our results with benzoic acid [3]. Furthermore, neutralization of oxygen functional groups produced no significant effect on the uptake of nitrobenzene.

The importance of electrostatic interactions is also evident [3], particularly for aniline [3-6], and will be discussed in detail [7].

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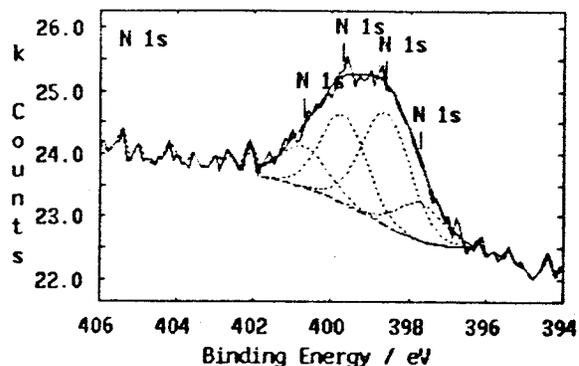


Figure 1. N1s XPS spectrum of nitrated carbon.

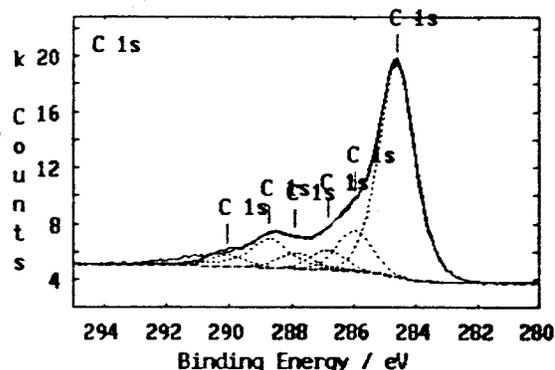


Figure 2. C1s XPS spectrum of oxidized carbon.

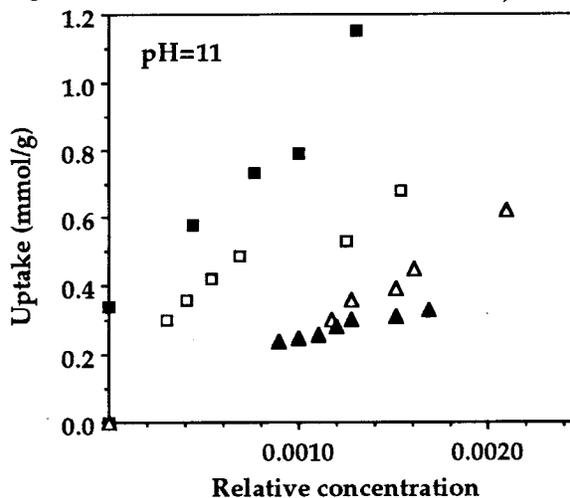


Figure 3. Aniline adsorption isotherms: ■, oxidized; □, NaHCO₃; △, Na₂CO₃; ▲, NaOH.