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# Effect of oxygen surface groups on adsorption of benzene derivatives from aqueous solutions onto active carbon samples

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ABSTRACT

The process of adsorption of selected benzene derivatives from aqueous solution is investigated on two carbonaceous materials of differentiated surface properties – quantity of oxygen functional groups. Carbon samples were prepared by removal of external layers from granules of unmodified and oxidized active carbon. The surface and structure characteristics of carbon samples were estimated by various methods. The experimental isotherms of organics adsorption from liquid phase were measured and interpreted in terms of the theory of adsorption on heterogeneous solid surfaces. The influence of differences in adsorbate and adsorbent properties on adsorption uptake was analyzed. The adsorption effectiveness was regarded as a result of the differences in adsorbate hydrophobicities and the effect of specific interactions of its functional groups with active sites on carbon surface.

## 1. Introduction

The effectiveness of carbon materials in the process of removing organic substances from aqueous solutions depends on adsorbent, adsorbate and solution properties, as well as conditions of establishing adsorption equilibrium [1,2]. Porous structure and surface chemistry of adsorbent affect the adsorption process to a large extent [2,3]. The surface characteristics of active carbons depend on the content of heteroatoms, such as oxygen or nitrogen which determine the charge, hydrophobicity, and electronic density of the graphene layers. Other important factors are the properties of adsorbate molecules: molecular size, solubility, p$K_a$, character of functional group attached to an aromatic ring. The hydrophobicity of adsorbed organic molecules is the main driving force in adsorption from aqueous phase on a hydrophobic surface of active carbon. However, the nature of adsorbate substituent, similarly as in the case of surface groups of adsorbent, affects the interactions in adsorption system resulting in decreasing or increasing adsorption value [4–14].

The aim of the present paper is to estimate dependence between characteristics of surface chemistry of oxidized and unmodified active carbon and adsorption of aromatic substances from dilute aqueous solutions. To investigate the influence of modification of surface properties of active carbons on adsorption from liquid phase the isotherms of adsorption of nitrobenzene (NB), 4-nitrophenol (4-NPh), 4-chlorophenol (4-CPh) and phenol (Ph) from diluted aqueous solutions were measured. The experimental isotherms are discussed in order to find the correlations between the changes in chemical properties of carbon surface and the parameters characterizing adsorption equilibria.

## 2. Experimental

### 2.1. Materials

The studied adsorbent samples were prepared from the commercial granular active carbon Norit R3ex previously demineralized with concentrated HF and HCl acids. Part of this material was then oxidized with concentrated nitric acid (5:1) at 353 K for 3 h and next heated in vacuum at 423 K [15]. From the carbon granules of both unmodified U0 and oxidized O0 samples the external layers were removed by attrition in a spouted bed [15–17] in order to leave granular core samples denoted C2 and OC2, respectively.

The choice of internal cores C2 and OC2 being about 33% of the mass of initial full granules (U0 and O0, respectively) results from their relative homogeneous properties. Changes of oxygen content in function of distance from external surface of granule were

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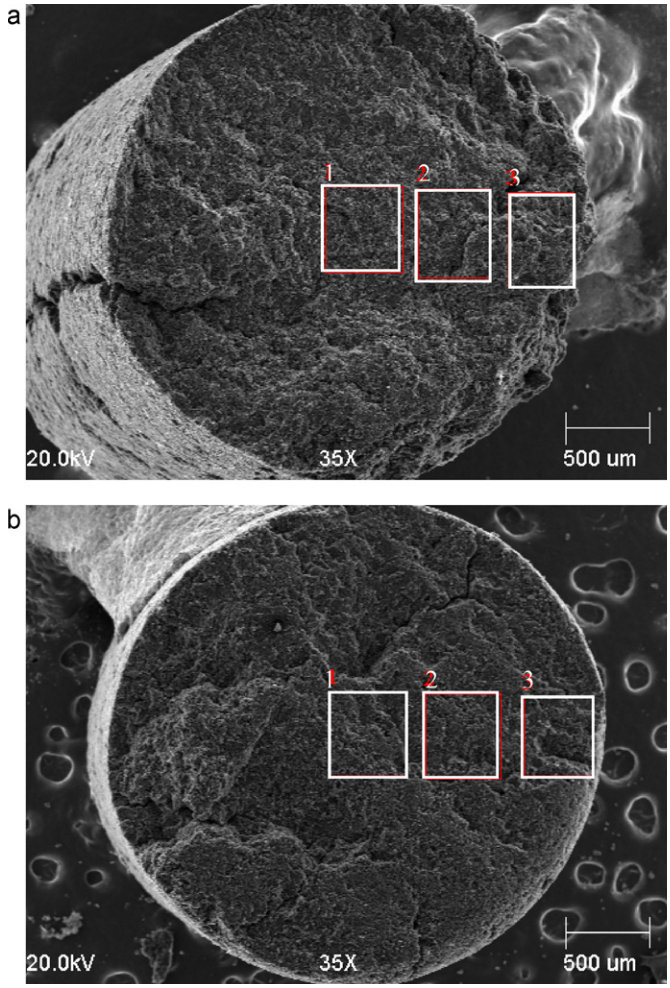

**Fig. 1.** SEM images of cross-sections of active carbon granules (a) U0 and (b) O0 with marked areas of EDS analysis (1 – external layer, 2 – middle layer, 3 – central part of granule).

estimated from EDS measurements of cross-section of granule. SEM pictures of cross-section U0 and O0 carbon granules were obtained on JEOL JMS-5500 LV scanning electron microscope (Japan) with magnification of 35 times. Oxygen determination by SEM-EDS was made by scanning cross-section during 300 s using software IXRF Systems, Inc. The SEM used in this work was provided with EDS detector with a program for ZAF correction.

Analyzed areas are presented in Fig. 1a and b. Contents of oxygen in different parts of carbon granules are presented in Table 1.

**Table 1**
Contents of oxygen in different parts of carbon granules (U0 and O0).

| Part of granule | Oxygen content | |
|---|---|---|
| | at% | wt% |
| External layer of U0 | 4.29 | 5.62 |
| Middle layer of U0 | 3.92 | 5.13 |
| Central part of U0 | 3.46 | 4.54 |
| External layer of O0 | 8.86 | 11.45 |
| Middle layer of O0 | 7.99 | 10.37 |
| Central part of O0 | 7.15 | 9.29 |

### 2.2. Structure characteristics of active carbons

The structural characteristics of active carbons were obtained from the analysis of low-temperature (77.4 K) nitrogen adsorption/desorption isotherms measured by using ASAP 2010 analyzer (Micromeritics, Norcross, USA) (Fig. 2). The values of structure parameters were calculated from Dubinin–Radushkevich equation [18]: micropore volume, $W_0$, adsorption energy in micropores, $E_0$, half width of micropores, $x_o$, surface area, $S_{DR}$. The surface of mesopores, $S_{me}$, was calculated by Dollimore and Heal method [19].

### 2.3. Surface characteristics of active carbons

The Boehm method was used to determine quantitatively the surface functional groups [15,20]. The total oxygen content was determined by using the analyzer CHNS-O model 1108 (Carlo Erba, Milan, Italy) [15]. The hydrophobic/hydrophilic character of adsorbent surface was estimated by water vapor adsorption isotherms (Fig. 3) measured by using the volumetric method of liquid microburetes. The experimental data were analyzed by applying the Dubinin–Serpinsky equation [21]:

$$\frac{a}{h} = b(a_o + a)(1 - ka) \quad (1)$$

where $a$ is the water vapor adsorption, $h = p/p_s$ is the relative pressure of water vapor, $a_o$ is the number of primary adsorption centers, $b$ is the equilibrium constant (relation of rate constants of adsorption and desorption), $k$ is the constant connected with the maximum value of adsorption for $h = 1$.

### 2.4. Adsorption from aqueous solutions

The experimental isotherms for nitrobenzene, phenol, 4-nitrophenol and 4-chlorophenol adsorption from dilute aqueous solutions on the studied carbon samples were measured at 293 K at constant pH (pH = 2.2) and ionic strength ($I$ = 0.1 mol/dm$^3$) by using a static method [22]. The ionic strength and pH were adjusted by adding NaCl and HCl solutions, respectively. The carbon samples of known amounts were brought into contact with 5 cm$^3$ of water and degassed under vacuum. Then, the adsorbate solution of known concentration was added. The initial concentrations of adsorbate solutions were as follows: 0.5–7.5 mmol/l (nitrobenzene), 0.6–11.2 mmol/l (4-nitrophenol), 1.4–15.8 mmol/l (4-chlorophenol), 0.9–24.2 mmol/l (phenol). The adsorption vessels were thermostated at 293 K and agitated until the equilibrium

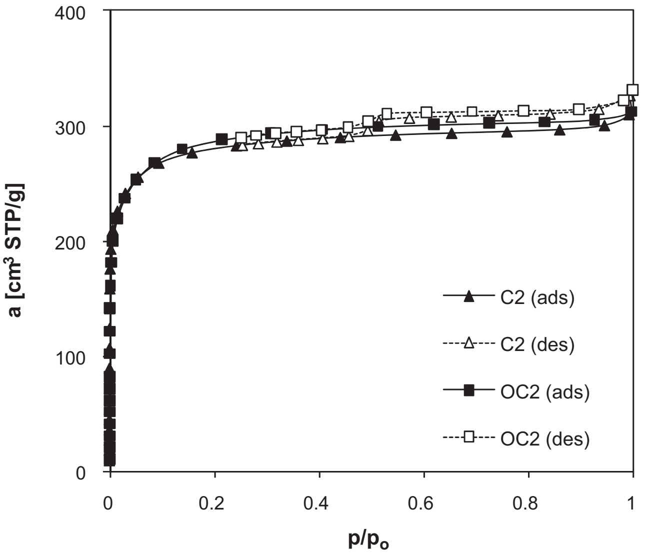

**Fig. 2.** Low temperature nitrogen adsorption/desorption isotherms on the non-modified C2 and oxidized OC2 carbon samples.