ROLE OF SURFACE CHEMISTRY IN ADSORPTION OF ETHYLMETHYLAMINE ON ACTIVATED CARBONS

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Introduction

Removal of pollutants and contaminants on activated carbons is a well-known method used to clean the environment and prevent its pollution [1-3]. Besides causing unpleasant sensation, some of those substances are hazardous to human health. One of the sources of odor is human sweat. Its odor has the origin in such substances as, for instance, acetaldehyde, valeric acid, and ethylmethylamine (EMA). At present, activated carbon is one of the most promising solid adsorbent for removal of such compounds in the presence of water. This is owing to its commercial availability, high adsorptive capacity, high surface area and the presence of small pores, similar in sizes to adsorbate molecules [1,3,4]. The presence of heteroatoms, such as oxygen, nitrogen, and hydrogen, bonded to the peripheral carbon atoms governs the surface chemistry of activated carbon [2]. These surface features can be altered by oxidation and urea modification of the virgin samples .

The objective of this paper is to study the effects of surface chemistry on adsorption of odoriferous organic molecules being able to interact with the surface via both specific (hydrogen bonding) and dispersive forces. As an adsorbate molecule ethylmethylamine (EMA) was chosen. Its basicity and the presence of nitrogen functionality should be important for removal of trace amounts of this compound from aqueous solution. To identify the role of surface features, carbons of various origins were chosen whose porosities significantly differ. The carbon surface was modified either by introduction of oxygen or nitrogen containing groups. Their presence is expected to help to understand the mechanism of EMA adsorption from aqueous solution on activated carbons.

Experimental

Two activated carbons were chosen for this study. They are as follows: BAX (Westvaco-wood origin, chemical activation with phosphoric acid), and BPL (Calgon Carbon, bituminous coal origin). One sample of each carbon was oxidized with 15 N HNO_3 for 24 h. Two other samples of each carbon were impregnated with urea (saturated solution) for 24 hours and then heated in nitrogen at 723K and 1223K at the rate of 10 K/min for 1 hour, in order to introduce nitrogen groups. Before further experiments, the initial and the modified carbons were washed in a Soxhlet apparatus to remove water-soluble species. The oxidized samples are referred to as BAXO and BPLO whereas the

urea modified ones as BAXN1, BPLN1, BAXN2, BPLN2. N1 and N2 stand for heating temperature of 723 K and 1223 K, respectively.

The surface of the carbon samples was characterized using sorption of nitrogen, Boehm and potentiometric titrations, and thermal analysis.

EMA adsorption isotherms from aqueous solution were measured at 299K. The amount adsorbed was evaluated using GC-MS, and is calculated from the following formula:

$$q_e = \frac{V.\Delta C}{m}$$
(1)

where q_e is the amount adsorbed, V is the volume of the liquid phase, ΔC is the difference in concentration of the solute in the bulk phase before it comes in contact with the adsorbent and at equilibrium, and m is the amount of the adsorbent.

The obtained isotherms were fitted into the modified Freundlich single solute isotherm, which has the following formula:

$$q_e = K_F (A_e)^n$$
(2)

where, A_e is the amount of the EMA at equilibrium (calculated from the concentration and volume) per unit weight of the adsorbent, K_F is Freundlich parameter for heterodisperse system (it is also considered as a unit capacity factor) while exponential term n represents the heterogeneity of the site energies and can be related to the intensity of adsorption (adsorption driving force).

Results and Discussion

As described elsewhere [5,6], oxidation caused the surface of both carbons to become more acidic with an increase in the number of groups in all categories (carboxylic, lactonic and phenolic). As expected for wood based carbon, oxidation effects are more pronounced for BAX than for the BPL samples [7]. Oxidation also caused a decrease in the number of basic groups in the case of BAX carbon. Since after modifications with urea we cannot use the Boehm classification of surface groups due to the similarity in pH values between oxygen and nitrogen functionalities [8,9], the groups on those carbons are considered only as acidic or basic. Heat treatment, regardless of the temperature of heating, resulted in a decrease in the number of acidic groups for both carbons but the effect is the most pronounced for BAXN2. We have to mention here that a significant decrease in the acidity is also observed for this carbon after heat treatment at 1223K, without urea modification [10]. This is the result of an increase in the degree of carbonization since the original BAX carbon is a low temperature chemically activated material [6]. Treatment of urea-modified carbons at 723K resulted in an increase in the number of basic groups, likely due to an introduction of amine-like functionalities to the carbon matrix [6].

The structural parameters are important for the interpretation of our results on adsorption of EMA. It is found that modification has increased $V_{<10A}$ for both samples

whereas volume of micropores was affected mainly for the BAX samples. This is the result of either an introduction of a significant number of oxygen groups blocking pore entrances, or a destruction of pore walls as a result of carbon consumption or shrinkage during heat treatment [12].

Table 1.
Results of Boehm Titration (mmol/g)

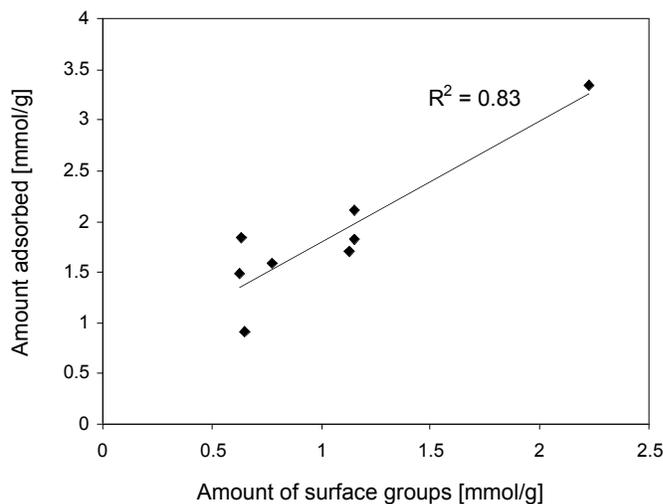| Sample	pH	Carboxylic	Lactonic	Phenolic	Acidic	Basic	Total
BAX	6.55	0.255	0.140	0.367	0.763	0.363	1.126
BAXO	3.68	1.475	0.075	0.600	2.15	0.075	2.225
BAXN1	6.68	---	---	---	0.625	0.525	1.150
BAXN2	6.27	---	---	---	0.325	0.325	0.650
BPL	7.54	0.000	0.025	0.163	0.188	0.450	0.638
BPLO	5.97	0.250	0.25	0.350	0.850	0.300	1.150
BPLN1	7.10	---	---	---	0.150	0.625	0.775
BPLN2	6.53	---	---	---	0.175	0.450	0.625

Figure 1. Dependence of the amount adsorbed at high equilibrium amount of EMA (200 mg of EMA/g of carbon) on the total amount of surface groups.

The adsorption isotherms of EMA from aqueous solutions were measured at 299 K. The isotherms are fitted to the modified Freundlich equation [13,14]. The isotherms showed good fitting with correlation coefficients greater than 0.98 for all samples. In order to better understand the adsorption process, the amounts adsorbed at two equilibrium amounts, 5 mg and 200 mg of ethylmethylamine per gram of carbon, were correlated with the surface features, which we expect to have an influence on the adsorption

process. For 200 mg of ethylmethylamine per gram of carbon the amount adsorbed (Figure 1) shows an increasing trend with an increase in the amount of surface groups suggesting an importance of surface chemistry in the adsorption process. At that concentration, the volume of pores smaller than 10 Å is not expected to be important.
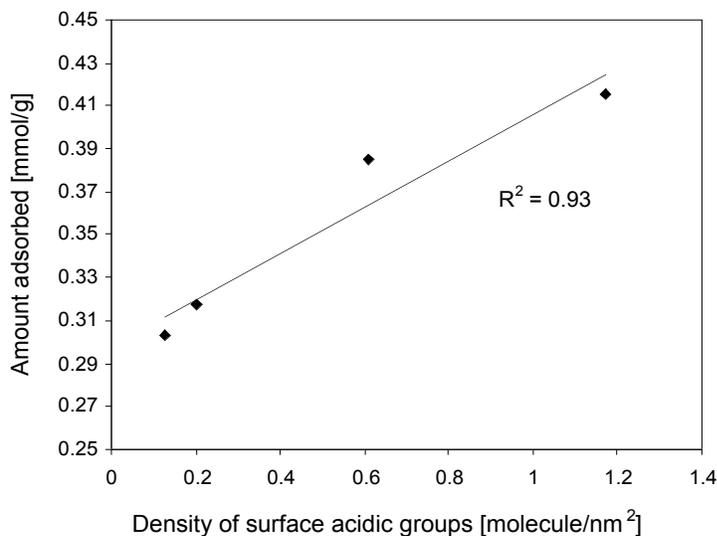

Figure 2. Dependence of the amount of EMA adsorbed on the initial and oxidized carbons at low equilibrium amount (5 mg EMA/g of carbon) on the density of surface acidic groups.
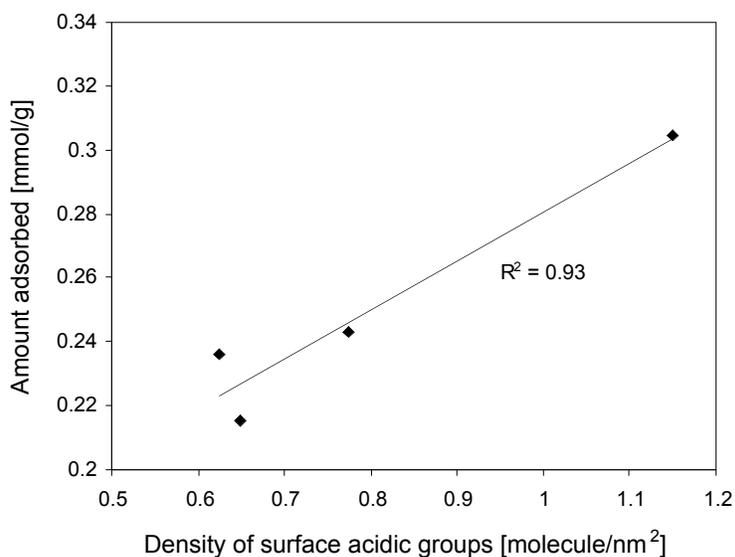

Figure 3. Dependence of the amount of EMA adsorbed on urea modified carbons at low equilibrium concentration (5 mg/g) on the density of surface acidic groups.

The situation should differ at low surface coverage, where more specific sites should play a role. The $V_{<10Å}$ and the number of acidic groups are expected to influence the

amount adsorbed at those conditions. Moreover, oxygen functional groups should affect adsorption differently than those containing nitrogen. Thus the amount adsorbed at low equilibrium amounts of EMA (5 mg/g of carbon) was analyzed separately for carbons containing oxygen groups (initial and oxidized) (Figure 2) and nitrogen functionalities (Figure 3).

In both cases a relatively good linear correlation was found indicating the importance of acid-base interactions at low surface coverage.

Conclusions

The results obtained in this study show that the adsorption of EMA from aqueous solution depends mainly on surface chemistry of activated carbons. It appears that porosity plays an important but not the predominant role in the strength and the extent of the adsorption process.

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