

INFLUENCE OF WATER ON THE ADSORPTION OF VOCs ON ACTIVATED CARBON

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Introduction

Activated carbon adsorption is a technique that can be used for removal of volatile organic compounds (VOCs) from the effluent gas pumped from the vacuum wells of a soil vapor extraction (SVE) operation [1,2]. However, the fact that the effluent gas streams are virtually always saturated with water vapor may result in very inefficient performance of the activated carbon for removing VOCs from these gas streams, due to that capillary condensation of liquid water in the pores of the carbon may reduce the rate of diffusional mass transport sufficiently to account for the poor performance of carbon in SVE off-gas treatment [3]. Competition between water molecules and VOC molecules for the adsorption site on the activated carbon may be expected as other possible source of difficulty for VOCs removal by activated carbon. A better knowledge of the effect of water vapor on the adsorption of VOCs on activated carbon is needed to be able to predict activated carbon performance.

In the present work, the influences of water vapor, VOC polarity and activated carbon porosity on the kinetic of adsorption of VOCs on activated carbon have been studied.

Experimental

Different activated carbons have been prepared from acid-precipitated kraft lignin through carbonization at 623 K followed by CO₂-partial gasification at 1123 K, using different reaction times to cover a wide burn-off range, from 21 to about 80%. N₂ (77 K) and CO₂ (273 K) adsorption and mercury porosimetry were used for the porous structure characterization of the activated carbons. Adsorption of three VOC with different polarity, benzene, methyl ethyl ketone and methanol, at different partial pressures, from 0.6 to 12 kPa, in dried and wet air streams were carried out gravimetrically (TGA system) at 293 K and atmospheric pressure, using ~10 mg of carbon. For a total flow rate of 100 cm³/min, the partial water vapor pressures ranged from 0.2 to 2.3 kPa. Desorption experiments were also performed in the microbalance system at 293 K under a dry air stream (100 cm³/g) and

the VOCs in the outlet stream were analyzed by mass spectrometry.

Results and Discussion

Table 1 summarizes the porous structure of the activated carbons prepared for this study. The activated carbons have been designated by the letter H followed by a number indicating the sample burn-off. Increase of micropore volume and widening of micropore size distribution, as indicated by the higher differences between $V_{mic}^{N_2}$ and $V_{mic}^{CO_2}$, take place as activation proceeds. The contribution of mesoporosity become relevant at intermediate burn-off levels and development of macroporosity is achieved at higher activation degrees [4].

Table 1. Micropore, mesopore and macropore volumes (cm³/g), BET and external apparent surface area (m²/g) for the activated carbons

Sample	$V_{mic}^{N_2}$	$V_{mic}^{CO_2}$	V_{mes}	V_{mac}	A_{BET}	A_{ext}
H-21	0.31	0.32	0.06	0.02	822	62
H-54	0.39	0.34	0.48	0.11	1273	333
H-63	0.42	0.38	0.78	0.15	1348	409
H-77	0.57	0.38	0.86	0.53	1853	480

The amount adsorbed and the adsorption rate for benzene and water vapor increased with carbon burn-off as a consequence of an increase of micropore volume, broadening of micropore size distribution and increasing development of meso- and macroporosity [5]. Similar results were found for methyl ethyl ketone and methanol. Adsorption of benzene on the activated carbons studied takes place at a significant higher rate than adsorption of water vapor (an example is shown in Fig. 1 for H-63 carbon). Benzene is only partially desorbed at the adsorption temperature and an appreciable amount of it remains adsorbed on the carbon, most likely, in the narrow micropores. On the contrary, water vapor is desorbed completely at the adsorption temperature and its desorption profile exhibits, clearly, two steps with different desorption rates due to desorption of water vapor from two different adsorption centers, as suggested by Dubinin [6], or to desorption of water vapor from pores of different size. Adsorption of a stream containing a mixture of benzene and water vapor on H-63 carbon takes

place at a similar rate as that of the stream containing only benzene. However, the total amount adsorbed by the carbon, approaching the equilibrium point, is higher than in the case of the stream containing only benzene. The desorption profile, for the case of the inlet stream containing a benzene/water vapor mixture, exhibits, at least, three step clearly differentiated and shows that a significant amount of adsorbate (similar to the amount of benzene retained by the carbon in the case of the stream containing only benzene) remains on the carbon at the desorption temperature. An analysis of the adsorption and desorption profiles of Fig. 1 suggests that the presence of water vapor in the inlet stream does not affect, appreciably, the rate of adsorption of benzene and the total amount of benzene adsorbed in the narrow micropores of H-63 carbon. Similar results were found for the other carbons used in this study. It was observed, however, that the presence of water vapor increased the rate of adsorption of benzene on activated carbon with narrower microporosity, as it was the case for H-21 carbon.

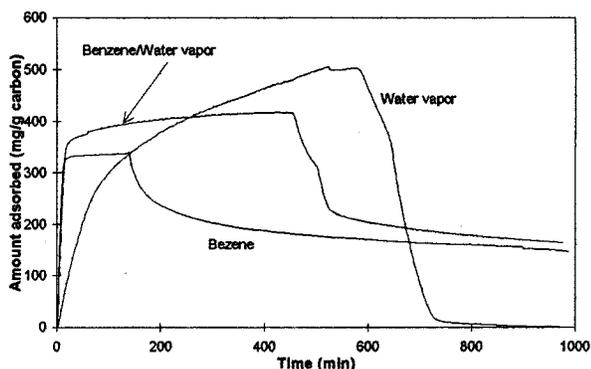


Figure 1. Amount adsorbed as a function of time for the adsorption of benzene (2.06 kPa), water vapor (1.85 kPa) and a mixture of benzene/water vapor (2.06 kPa/1.85 kPa) on H-63 carbon at 293 K.

The rate of adsorption for the VOC studied decreases with VOC polarity. Adsorption of benzene, a non polar organic vapor, is physical and involves dispersion attractive forces and short-range repulsive interactions. The presence of the ketone group confers some polarity to the molecule of methyl ethyl ketone. Methanol molecule exhibits a higher polarity due to the presence of OH group. The adsorption of polar molecules on microporous carbons involves chemisorption or strong specific interaction between the adsorbate and the carbon surface at low relative pressures[7]. The change in the adsorption mechanism may be the cause of the lower adsorption rates exhibited by the polar organic vapors.

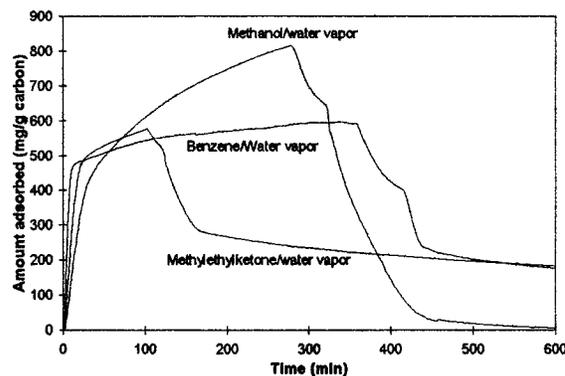


Figure 2. Amount adsorbed as a function of time for the adsorption of benzene/water vapor (2.06 kPa/1.85 kPa), methyl ethyl ketone/water vapor (2.18kPa/1.85 kPa) and methanol/water vapor (2.53 kPa/1.85 kPa) mixtures on H-77 carbon at 293 K.

The effect of VOC polarity and of the presence of water vapor on the benzene, methyl ethyl ketone and methanol adsorption on H-77 carbon are illustrated in Fig.2. The desorption profile for the methyl ethyl ketone/water vapor mixture is quite similar to that for the benzene/water vapor mixture, indicating that the adsorbate is only partially desorbed at the adsorption temperature, with a significant amount of it remaining adsorbed on the carbon. This result suggests that, as in the case of benzene, methyl ethyl ketone remains strongly adsorbed on the narrow micropores of the carbon. Water vapor and methanol are, on the contrary, totally desorbed at the adsorption temperature.

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