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X-RAY MICROTOMOGRAPHY: A USEFUL METHOD TO STUDY THE DYNAMICS OF ORGANIC AND WATER VAPOURS ADSORPTION ON CARBON

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Abstract

The suitability of the X-ray microtomographic technique to study the dynamics of vapor adsorption on carbon beds was assessed in this work. This technique was tested using three different systems: CH_3I, water vapor and a mixture of water- and organic vapors. Image analysis of the carbon bed cross-sections obtained by X-ray microtomography allows determining the adsorption front progress in the case of organic vapor and mixture of water and organic vapor whereas the existence of this front was not so obvious in the case of water vapor. The tomographic data show flat profile, *i.e.* a continuous water uptake with time. Experimental results obtained for organic vapors were interpreted on the basis of the Wheeler-Jonas equation: a good agreement was found between experimental and theoretical breakthrough times.

Introduction

Activated carbons are largely used to adsorb organic compounds in industrial processes as well as for civil and military protection. Water vapor is usually present in gas streams, ranging from low concentrations to the saturated state. So, when modeling organic vapor adsorption on activated carbon filters, the effects of water-vapor coadsorption has to be taken into account [1-3]. Both the pre-adsorbed water and the water present in the contaminated air stream can have a deleterious effect on the adsorption capacity of the activated carbon. As organic vapors can go from badly smelling, over noxious and ecotoxic to highly toxic, a correct estimation of filter breakthrough times is essential. This explains the interest in the coadsorption behavior of water and organic vapors on activated carbon. However, this attention has been, almost exclusively, focused on the static adsorption capacity, *i.e.* the usual adsorption isotherm [4]. Even though this static capacity is very important, adsorption and coadsorption are essentially dynamic phenomena.

The first purpose of this work was to assess the suitability of x-ray microtomography to follow an adsorption process taking place in an activated carbon filter. The very first use of X-ray imaging, in radiography mode, to study adsorption in porous materials was performed by Dubinin et al. [5]. In this work, X-ray contrast substances were used to analyze the nature of the mass transfer limiting step, *i.e.* adsorption in micropores or transport in meso and macropores, in activated carbons. X-ray radiographies served as visual supports to explain adsorption kinetics data but no quantification was performed. Fifteen years later Wittwer and Lavanchy [6] used a medical tomograph to visualize the adsorption of organic vapors in activated carbon. To our knowledge, this non-destructive 3D-technique has not been exploited much since the early 90's. During the last decade, microtomographs with improved resolution were developed and commercialized. The objective of the present study was to

contribute to a better understanding of the dynamics of vapor adsorption by leaning on the local information obtained by x-ray microtomography coupled with image analysis.

Materials & Methods

Activated carbon filters

A plastic, cylindrical canister (diameter = 26 mm and height = 23 mm) filled with approximately 5 g of BPL activated carbon was used to perform the adsorption tests in a classical breakthrough measurement system. The corresponding apparent density is approximately 0.45 g/cm³. In- and outlet of the cylinder consist of a metallic grid allowing vapor circulation Experiments were conducted successively for CH_3I in dry air (5 g/m³), CH_3I (5 g/m³) in air at 80% RH (= water-organic coadsorption), and humid air (80% RH) at a temperature of 293 K. For each test, one out of the three gases was forced through the bed with renewed carbon during increasing times. The superficial velocity was close to 34 cm/s.

X-ray microtomography

The X-ray microtomograph used in this study was the "Skyscan-1074 X-ray scanner" (Skyscan, Belgium). Advanced technical details about its conception and operation are described by Sasov and Van Dyck [7]. The cone beam source operated at 40 kV and 1 mA. The detector was a 2D, 768 pixels × 576 pixels, 8-bit X-ray camera giving images with a pixel size of 41 µm. The rotation step was fixed at the minimum, 0.9°, in order to improve image quality, giving total acquisition times close to 10 minutes.

In order to study vapor adsorption on activated carbon, a first tomographic investigation is performed on the bed, in its initial condition. Then, one out of the three gases was forced through the bed with renewed carbon during a determined time. After exposure to the vapor, the sample was removed and placed again in the microtomograph for analysis. Cross section images separated by 205 µm were reconstructed along the plastic canister using a cone-beam reconstruction software.

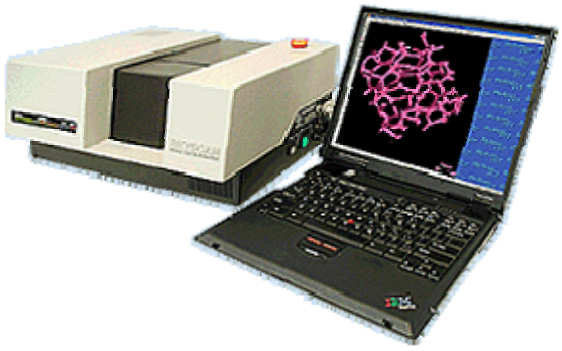

Fig. 1. Skyscan-1074 X-ray scanner (http://www.skyscan.be)

Image analysis

The determination by image analysis of the vapor adsorption in function of the depth of the activated carbon filter was based on the observation that the gray level intensity of carbon grains darkened when vapor was adsorbed (Fig. 2.). According to this behavior, image analysis was performed on each cross section according to methodology recently published [8]. From the original cross section image, a binary mask was automatically constructed in order to isolate the bed from the

background. Finally the image was eroded to eliminate possible borders effects. On this last image, the intensity, *i.e.* the addition of all the pixel values of the gray level image, was calculated. Programs were implemented using Aphelion 3.2 (Adcis SA) software.

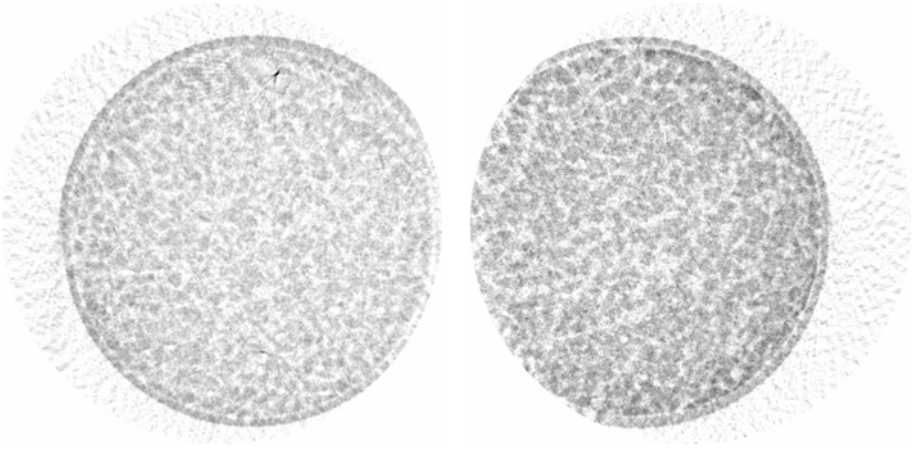

Fig. 2. Cross section image of the carbon filter for (a) virgin and (b) saturated carbon.

Results & Discussion

CH_3I adsorption

The intensity of approximately 100 cross section images per sample was determined and the result drawn in function of the depth of the sample, *i.e.* the distance from the inlet of the carbon bed. As the bottom part of the filter is composed of a screw cap including a metallic grid, it was only possible to reconstruct images along the first 13 mm of the filter. Fig. 3 shows the results obtained with CH_3I in dry air. One can directly observe that microtomography allows to follow-up the adsorption process: after 2 minutes of gas flow through the bed, the change in intensity of the image suggests the development of a well marked adsorption front. Data obtained for longer times clearly show that the adsorption proceeds according to the theoretical model of a plug flow, *i.e.* one can see an adsorption front that moves through the carbon bed. Upstream of this front there is saturation of the carbon (clearly visible after 12 minutes), downstream the carbon is still in its initial state. The existence of a single, constant, front is further proven by the fact that the concentration profiles after 2, 4 and 6 minutes are clearly parallel. These results confirm a recent study performed on the adsorption of CCl_4 [8].

Considering that the breakthrough criterion is fixed at 10% of the inlet concentration, one can say that filter breakthrough was reached after around 12 minutes. This was further verified by modeling the adsorption with the Wheeler-Jonas equation [9] and the annex equations proposed by Wood [10] and Lodewyckx-Wood [11]. A simulated breakthrough time close to 14 minutes was obtained with the model, so that there is quite a good agreement between the theoretical and experimental breakthrough times.

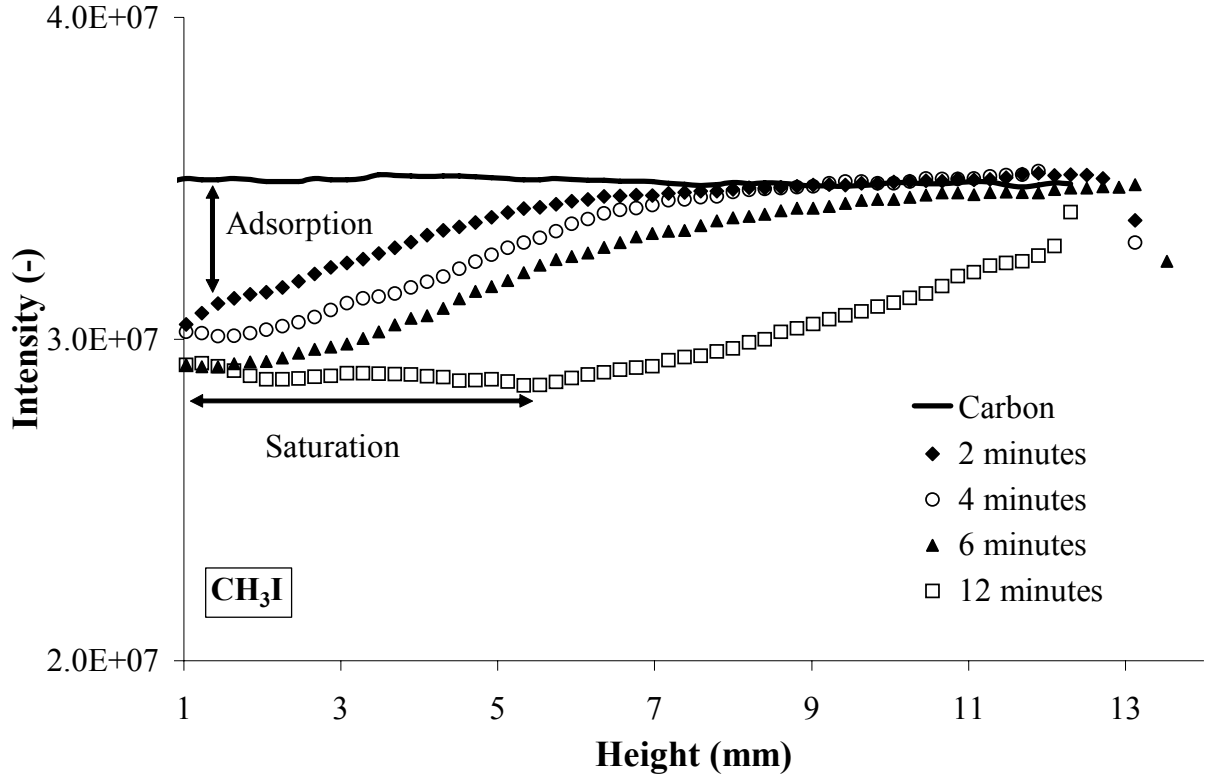

Fig. 3: Intensity *vs.* bed depth for different exposure times to CH_3I in dry air

In order to verify that the results obtained by tomography can be considered as quantitative, the relative mass uptake, *i.e.* the mass of adsorbed CH_3I divided by the mass of activated carbon, was measured after each experiment. These values should be related to the total variation of intensity through the bed, *i.e.* the surface between each intensity curve and the baseline corresponding to the virgin carbon. The surface taken into account is illustrated in Fig. 4 for a gas exposure time of 2 minutes. Fig 5. shows the results obtained after the integration of the curves. As expected, there is a linear relationship between the total intensity change and the mass uptake. This assesses that x-ray microtomography is a technique allowing a quantitative follow-up of a dynamic adsorption phenomenon.

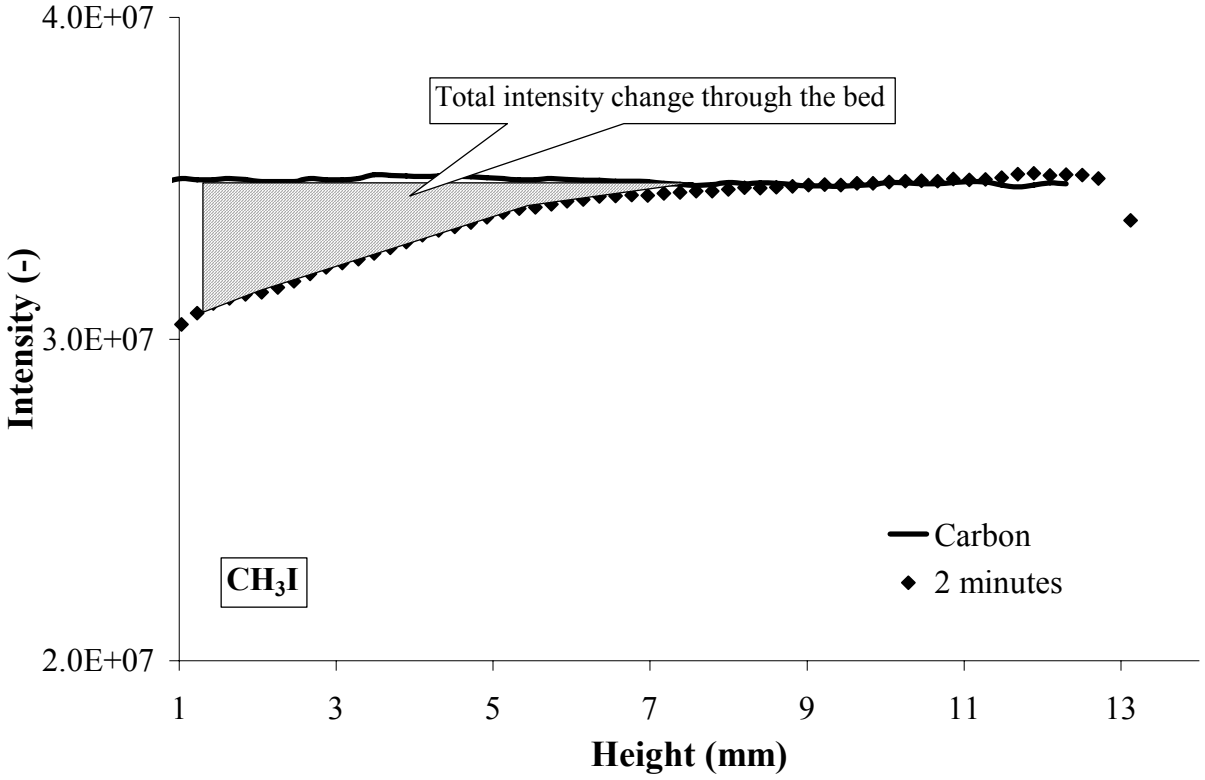

Fig. 4. Surface corresponding to the total intensity change through the bed

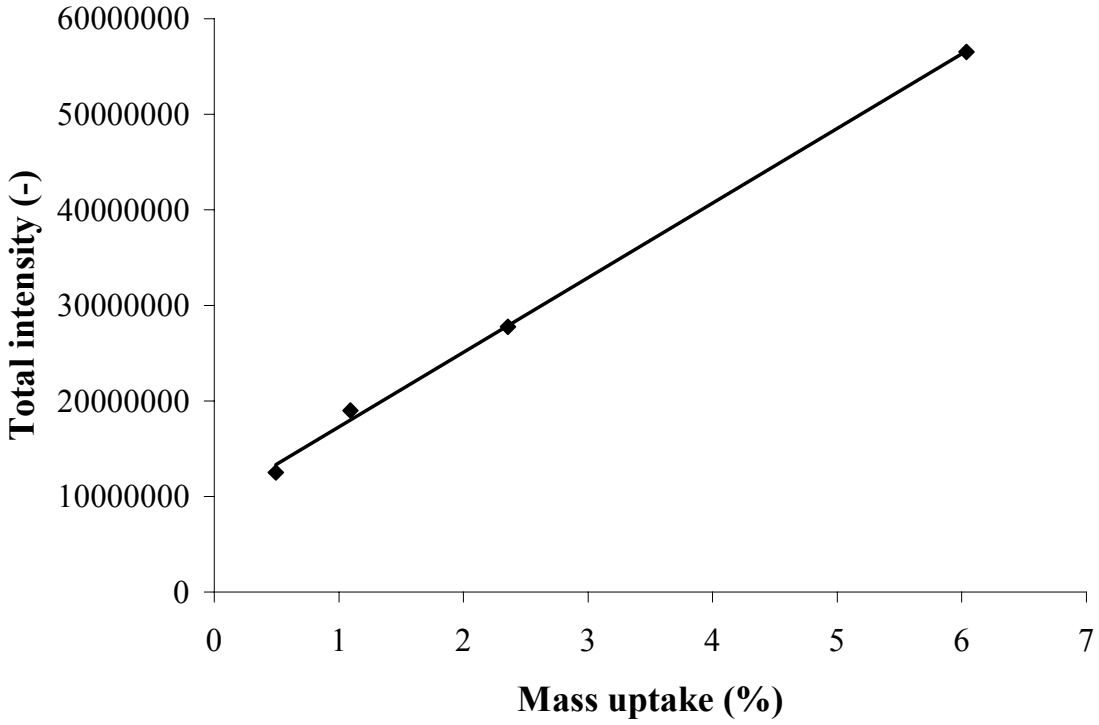

Fig. 5. Total intensity change *vs.* the mass uptake

H_2O adsorption

The results obtained in the case of water vapor adsorption (not shown) were quite different as those obtained for organic vapor. Indeed, no adsorption front was detected but the tomographic data showed flat profiles, with a continuous water uptake throughout the filter with time. These results are in agreement with recent experiments [12-13] and breakthrough data [3].

CH_3I-H_2O coadsorption

The results obtained for coadsorption of CH_3I and H_2O are depicted in Fig. 6. An adsorption front is visible but it is clearly broader than in the case of pure CH_3I. The comparison with the results plotted in Fig. 3. indicates that, for a same exposure time, adsorption reaches a deeper level in the filter. This confirms that the presence of water leads to a drastic decrease of the breakthrough time of the filter. After 6 minutes, one third of the bed is almost saturated, while 12 minutes were required in the case of pure CH_3I. . However, the interpretation of the governing physical mechanisms is not straightforward because the change in intensity is due to both adsorbed organic vapor and water, and it is quite impossible to make a distinction between both phases.

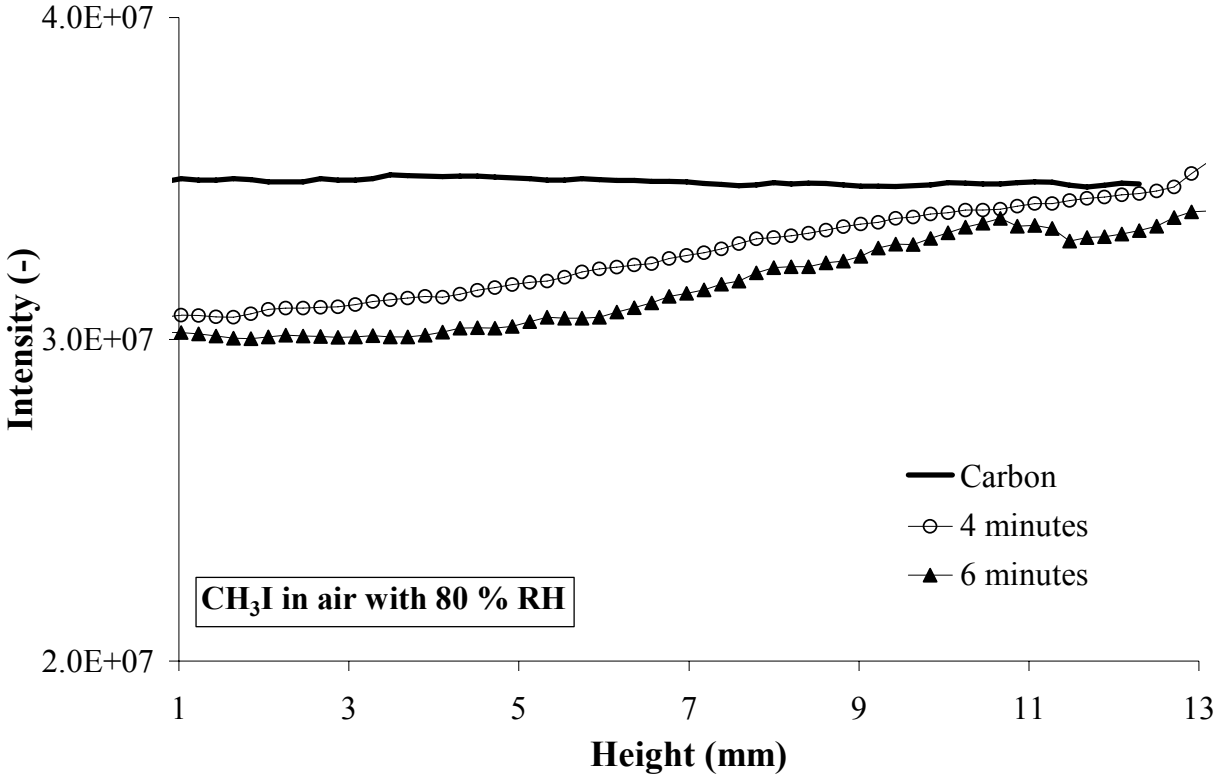

Fig. 6. Intensity *vs.* bed depth for different exposure times to CH_3I in humid air

Conclusions

X-ray microtomography coupled with image analysis is a suitable method to visualize and quantify the dynamic adsorption of organic and water vapors in activated carbon filters. This technique clearly shows the development of an adsorption front that moves through the carbon bed when CH_3I is used. This observation corresponds to the theoretical plug flow model. For water, the image intensity evolution suggests that no front really develops but that there is a continuous water uptake through the whole bed. In the case of coadsorption, the front is clearly detected again, but it is broader than for pure CH_3I. The interpretation is not straightforward, but is seems reasonable to conclude that a mixed front is observed, *i.e.* the combination of water vapor and CH_3I behaviors. For CH_3I in dry air, the breakthrough times determined from microtomography are in agreement with those obtained by simulation.

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