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Influence of carbon xerogel textural properties on the dynamic adsorption of methyl iodide

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ABSTRACT

X-ray microtomography coupled to image analysis has been used to study the influence of the adsorbent pore texture and the experimental conditions on the dynamic adsorption of methyl iodide in packed filters. By applying this imaging technique the internal axial adsorption profiles for increasing exposure times to the gas stream are analysed. This experimental technique establishes a new technology to study in situ the dynamic adsorption of volatile compounds. Resorcinol–formaldehyde based carbon xerogels have been used as adsorbents, as their pore texture can be tuned by changing the synthesis conditions. The textural characteristics of the adsorbents (surface areas and pore volumes) have been assessed by using nitrogen and carbon dioxide adsorption as well as mercury porosimetry. The methyl iodide dynamic adsorption results show that, for the same gas flow rate and CH_3I inlet concentration, the adsorbed amount is highly dependent on large pore volumes. Thus, samples with almost the same micropore volumes (adsorption volumes) have different methyl iodide adsorption capacities, which are related to, the above mentioned, large pores. The influence of both the gas carrier flow rate and the methyl iodide inlet concentration on the adsorption can be explained using the so-called linear driving force model. This approach takes into account the fact that internal transport limitations are directly related to the pore texture. Moreover, the simulation of the dynamic adsorption process has allowed relating the simulated axial concentration profiles to the experimental X-ray microtomography data.

1. Introduction

Adsorption processes are largely used to separate chemicals or to remove contaminants from gas streams. Such processes are based on the use of suitable porous solids with high surface area and micropore volume. Adsorbent particles are usually packed in a column through which the stream to be treated is forced. The efficiency of the adsorption process depends on two factors: the texture of the adsorbent at the nanometric scale and the macroscopic transport process in the packed bed. The porous texture of the adsorbent has influence on both the adsorption capacity at equilibrium and the kinetic mechanisms. The first one mainly depends on the surface area or micropore volume, while the kinetic is related to the accessibility to microporosity. A good adsorbent must have a reasonably high micropore volume, combined with a network of meso and macropores, allowing easy transport of the adsorbate to the adsorption sites.

Activated carbons are among the most used adsorbents. They have the advantage of being produced by the pyrolysis of several residues, such as wood, nutshells, or plastics [1–5], and of developing a large microporosity, i.e., a very large specific surface area available for adsorption. Nevertheless, they in general have low mesopore or macropore volumes, which can induce diffusional limitations, slowing down the adsorption process. Carbon xerogels [6], obtained from resorcinol–formaldehyde hydrogels appears as an alternative to activated carbons. These materials have the advantage that their pore texture can be tailored for a desired application through the appropriate choice of the gel synthesis conditions. Indeed, it has been shown [7–11] that an appropriate selection of the synthesis procedure as well as the drying and pyrolysis conditions enables to target the desired characteristic of those porous materials, i.e., large porosity and narrow pore size distribution, which can be scaled from nano to micrometers. Due to the possibilities offered by these materials, they are frequently used in several applications, in particular in catalysis [12,13] and adsorption [14 and references therein]. In those cases the possibility of choosing an appropriate pore range size allows to avoid diffusional limitations problems.

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The behaviour of carbon xerogels on the adsorption of several pollutants has been studied by standard adsorption methods [14,15]. Moreover, the dynamic adsorption on carbon xerogels by using techniques as inverse gas–solid chromatography has been reported [16]. This technique allows to determine the adsorption properties of carbon materials and to obtain the adsorption isotherms depending on the inlet concentration of pollutant. Nevertheless, it is not possible to study the adsorption kinetics nor to visualize the mass transport zone (MTZ) [17].

In this work, in situ X-ray microtomography, a technique traditionally not used in adsorption research, is used to study the dynamic adsorption of methyl iodide on carbon xerogels. In a previous work, some of the authors of this paper have reported the feasibility of this technique to analyse dynamic adsorption on activated carbon packed bed filters [18]. It was shown that this non-destructive imaging technique provides additional information to this obtained by the standard adsorption methods.

It must be noticed that transport properties measured by dynamic adsorption are not only determined by the textural characteristics of the adsorbent particles but critically by the filter support, i.e., the size and geometry of the bed as well as by the adsorbent particle packing [19,20]. In previous works, we have used X-ray microtomography coupled to image analysis to determine the characteristic of the bed used in the present work [21,22].

The goal of this paper is threefold: (i) to test the proposed technique, previously applied to a microporous activated carbon [21], in carbon xerogels having hierarchical pore structure, (ii) to compare the microtomography data to these obtained by modelling the process and (iii) to obtain additional information on the influence of the pore texture of carbon xerogels on their performance on the dynamic adsorption of methyl iodide. Heating of containers is usually produced in accidents of electric nuclear plants, among other factors, by the fusion of the reactor and by hydrogen combustion, as it has recently happened in Fukushima. As a result, some radioactive elements tend to react forming volatile products. Thus ^{135}I is released to the environment as CH_3I. For this reason the choice of methyl iodide relies on its adsorption behaviour, which is the same as its radioactive counterpart that is released during nuclear incidents [23]. In the study, two levels of gas flow rate and of pollutant concentration are considered.

2. Experimental

2.1. Synthesis and characterization of carbon xerogels

The aqueous gels used as precursor of the carbon xerogels were obtained by the polycondensation of resorcinol with formaldehyde in water. During the gelation process [6], the condensed aromatic rings form clusters whose size depends on the initial pH of the solution, fixed by a controlled addition of Na_2CO_3 in this case, usually called as 'catalyst' in the literature. Hence, the factor that determines the density, particle size and properties of the resulting gels will be the resorcinol/sodium carbonate ratio, R/C.

The gels were prepared by mixing 160 g of resorcinol with 218 ml of formaldehyde in 300 ml of water. Different amounts of Na_2CO_3 were added to have an R/C ratio of 300, 500, and 1000. Gelation and ageing were carried out at 70 °C for 72 h. Then, the gels were dried by vacuum evaporation without any pre-treatment, producing three different xerogels. Drying was performed in two steps: the first one at a pressure of 10^3 kPa and 60 °C, and the second one at the same pressure at 150 °C for 72 h.

After drying, the xerogels were pyrolysed following a sequential steps heating programme in nitrogen flow [9]: (a) a first ramp at a heating rate of 1.7 °C min^{-1} up to 150 °C and residence time of 15 min, (b) a ramp at 5 °C min^{-1} up to 400 °C and residence time of 60 min, (c) a ramp at 5 °C min^{-1} up to a final temperature of 800 °C and a soak time of 120 min.

The carbon samples were labelled: X300, X500, and X1000, where X refers to the nature of the precursors (xerogels) and the number to the R/C ratio. The textural characteristics of the samples were determined by N_2 and CO_2 adsorption at 77 and 273 K, respectively. The adsorption isotherms were obtained in a Micromeritcs ASAP 2020 apparatus. The BET and Dubinin–Radushkevich (DR) approaches were applied to the isotherm data. In addition, the experimental N_2 adsorption data were combined with those obtained by the Grand Canonical Monte Carlo (GCMC) simulation method in order to obtain a representative micropore size distribution (PSD) of the samples [24–26]. Moreover, the volumes of meso and macropores as well as the meso and macropore size distributions and the densities of the samples were determined by mercury porosimetry and pycnometry, respectively. Mercury porosimetry tests were performed with a PoreMaster 60 (Quantachrome Instruments), which allows to determine pore sizes larger than 3.7 nm. This technique is based on the Washburn's intrusion theory and allows the analysis of pores providing that no collapse occurs during the test [27,28]. The density measured by mercury pycnometry is that of the porous grain. This value is between the bulk density (the density of the powder comprising the volume between the grains) and the true density (the density of the carbon excluding any pore volume).

2.2. Adsorption of methyl iodide

The dynamic adsorption experiments were carried out in a classical breakthrough measurement system [29]. The diagram of the experimental system is shown in Fig. 1. The beds were prepared by filling a plastic canister (length = 33 mm, diameter = 15 mm) with the same amount (2 g) of each carbon xerogel (1 mm particle size). These beds were exposed into the sample batch to two dry air flow rates, namely 5 and 10 L min^{-1}, containing a small amount of methyl iodide vapour, 5 and 10 g m^{-3}, at room temperature and at a relative humidity of less than 6%.

The experiments were carried out at different periods of time. Fresh carbon batch was used for each test. Blank experiments on the carbon xerogel beds were performed prior to any vapour exposure. The samples were weighed before and after each experiment in order to determine the amount of CH_3I adsorbed. It was assumed that the maximum adsorption corresponds to the time after which the grey-level intensity of the microtomogram (see below) did not change.

The static adsorption of methyl iodide on the carbon xerogels has also been measured. This was carried out at 303 K in a conventional gravimetric system. Previous to the adsorption runs the samples were out-gassed to a residual pressure of 10^{-6} Torr during 12 h at 403 K. Two hours of adsorption equilibrium time were allowed for each isotherm point.

2.3. X-ray microtomography

X-ray microtomography is a non-destructive imaging technique allowing the visualisation of the internal structure of an object. In a tomographic experiment, an X-ray beam sent to the sample is attenuated by the solid and the transmitted beam is recorded on a detector. According to the Beer–Lambert law, the transmitted intensity is related to the X-ray attenuation coefficient μ along the path of the beam, which depends on the density of the material, its atomic number, and the energy of the incident beam [30]. This transmitted intensity is recorded as a radiograph (2D projection) for several angular positions by rotating the sample between 0° and 180°. A backprojection algorithm is then applied to these