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Characterization of materials toward toluene traces detection for air quality monitoring and lung cancer diagnosis

Geoffrey Gregis [a], Sébastien Schaefer [b], Jean-Baptiste Sanchez [a, c, *], Vanessa Fierro [b], Franck Berger [a, c], Igor Bezverkhyy [d], Guy Weber [d], Jean-Pierre Bellat [d], Alain Celzard [b]

[a] Laboratoire Chrono-environnement, UMR CNRS 6249, Université de Bourgogne – Franche Comté, 16 Route de Gray, 25030 Besançon, France
[b] Institut Jean Lamour UMR, Université de Lorraine – CNRS 7198, ENSTIB 27 rue Philippe Séguin, CS 60036, 88026 Épinal Cedex, France
[c] Institut FEMTO-ST, UMR CNRS 6174, Université Bourgogne – Franche-Comté, 15B Avenue des montboucons, 25030 Besançon, France
[d] Laboratoire Interdisciplinaire Carnot de Bourgogne, UMR CNRS 6303, Université de Bourgogne – Franche Comté, 9 Avenue Alain Savary, BP 47870, 21078 Dijon, France

HIGHLIGHTS

- Adsorption capacities of toluene at very low pressure onto activated carbon materials and zeolites were estimated.
- High-resolution adsorption–desorption isotherms of toluene are measured by TGA.
- Zeolite NaY and W5 activated carbon microspheres have the best adsorption affinities and capacities.
- Toluene adsorption capacity onto W5 activated carbon microspheres was the highest.
- Carbonaceous microspheres W5 and the zeolite NaY appear as the best candidates to adsorb toluene traces.

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ABSTRACT

The aim of this work was to identify a nanoporous material able to trap toluene traces in order to develop a gas detection device for indoor air quality monitoring or biomedical diagnosis. A set of various adsorbents such as zeolites and activated carbon microspheres was studied here. First a detailed characterization of their porous properties was performed by nitrogen adsorption. Then adsorption of toluene and other interfering compounds which can selectively adsorbed with it, such as water and carbon dioxide, was studied in order to select the most suitable material. Results revealed that the activated carbon microspheres W5 and the zeolite NaY, which exhibit high specific surface areas and large micropore volumes, are the best adsorbent materials to capture toluene present at very low concentration in the gas phase.

1. Introduction

Toluene is an important organic solvent used for example in the preparation of paints, varnishes and shellacs, thinners, nail polishes, adhesives and glues, metal cleaners, rust preservatives, fuel system antifreezes and flame retardants. It also finds applications in the production of chemicals, dyes and inks, plastics, perfumes and detergents [1]. Although it is widespread, this chemical compound is harmful and mainly affects the central nervous system (the brain), causing headache, nausea, dizziness, clumsiness, drowsiness, and other effects. Toluene is indeed toxic and has serious clinical implications. This compound is then a significant contributor to indoor air pollution [2]. The average concentration reported for indoor air levels measured in several countries is close to 80 μg m^{-3} (21 ppb) [3,4].

On the other hand, with respect to medical applications, toluene can also be considered as a very important cancer biomarker. Indeed, abnormally high concentration of toluene was observed in the breath of patients with lung cancer compared to healthy non-smokers [5–7]. In that case, the concentration of this volatile

* Corresponding author. Institut FEMTO-ST, UMR CNRS 6174, Université Bourgogne – Franche-Comté, 15B Avenue des montboucons, 25030 Besançon, France.
E-mail address: jbsanche@univ-fcomte.fr (J.-B. Sanchez).

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biomarker ranges from 10 to 100 ppb in human breath.

Whether it is for indoor air quality monitoring or for biomedical diagnosis, the detection of very low concentration of toluene (ppb level) cannot be realized without a concentration step prior to detection. The concentration process consists in adsorbing the target compound at room temperature inside the porosity of highly porous materials such as zeolites, polymers or activated carbons. This first step is followed by thermal desorption, allowing to generate a higher concentration of the target molecule in the surrounding atmosphere of the gas detector [8]. An efficient adsorbent should therefore exhibit not only a high adsorption capacity at low concentration and a strong adsorption affinity, but also fast adsorption and desorption rates, as well as a good thermal stability and durability in use [9]. Adsorption selectivity toward interfering compounds in particular water and carbon dioxide is also a determining criterion for the choice of the adsorbent.

Materials such as zeolites and activated carbons have been widely studied due to their high micropore volume and controllable pore size distribution [10,11]. In particular, activated carbon microspheres have received considerable attention during the last decade due, for example, to their good adsorption performances and high purity [12,13].

The main objective of the present paper was to identify and to characterize a suitable adsorbent for concentrating toluene traces in air. Toluene adsorption isotherms onto porous sorbent materials (such as activated carbons (ACs) or zeolites) have been thoroughly studied in the literature [14–18]. However, those studies were mainly conducted at high concentration ranges (>500 ppm), and some of them were even carried out at relative pressures close to saturation. The purpose of this study is to evaluate the adsorption/desorption capacity of toluene onto various high quality nanoporous materials at room temperature and under very low toluene pressures (P < 0.2 hPa, i.e. 200 ppm).

After a presentation of the adsorbents, standard analysis techniques were used to select the best adsorbent able to capture toluene in the gas phase. The adsorption of water vapor (H_2O) and carbon dioxide (CO_2) on the selected adsorbents was also investigated because these adsorbates, which are present at high concentrations in indoor air and in exhaled human breath, may be interfering compounds during the adsorption process of toluene.

2. Experimental

2.1. Materials

2.1.1. Adsorbents

Four adsorbents were investigated for the adsorption of toluene in the gas phase:

- A pure hydrophobic dealuminated faujasite zeolite supplied by Degussa and referenced as DaY. Its chemical formula was $Na_2(Al_2Si_{190}O_{384})$ and the particle size was in the range 1–5 μm.
- A pure hydrophilic cationic faujasite zeolite NaY synthesised by Union Carbide with the chemical formula $Na_{52}(Al_{52}Si_{140}O_{384})$. The particle size was around 1 μm.
- Two activated carbon microspheres prepared by hydrothermal carbonisation of a 0.8 M sucrose solution at 453 K for 24 h in an autoclave. Then, the carbonaceous or hydrochar microspheres obtained were chemically activated with KOH at 1023 K with a weight ratio of KOH to hydrochar equal to 4 or 5, to give activated carbon microspheres labelled W4 and W5, respectively. The particle size of both activated carbon microspheres was lower than 50 μm. More information on KOH activation can be found elsewhere [19].

2.1.2. Adsorbates

High purity nitrogen (*ALPHAGAZ*™ 1 NITROGEN, 99.999%) was used for the characterization of the porosity of the adsorbents without any additional purification. For adsorption measurements, toluene of analytical grade with purity higher than 99.5% was purchased from Aldrich; after outgassing, it was transferred to a flask containing an activated zeolite 3A in order to trap any residual water. Distilled water was employed as adsorbate after degassing. Carbon dioxide gas of 99.999% purity distributed by *ALPHAGAZ*™ 2 was also employed for adsorption measurements.

2.2. Methods

2.2.1. Characterization of the porosity of the adsorbents

The pore structure of the adsorbents was characterized by nitrogen adsorption-desorption at 77 K using an automatic sorptometer (Micromeritics ASAP 2020 instrument). Before each experiment, the adsorbents were first out-gassed under vacuum (10^{-5} hPa) at 673 K for the faujasite zeolites and at 573 K for the activated carbon microspheres, in order to desorb any molecule previously adsorbed at room temperature. Then, adsorption-desorption isotherms were measured for relative pressures P/P_S ranging from 10^{-5} to 0.99.

The specific surface area (S_{BET}) of each material was determined using the Brunauer, Emmet and Teller (BET) equation [20]. The total pore volume (V_T) was determined at $P/P_S = 0.97$.

The micropore volume (V_μ) was determined by the t-plot method and the mesopore volume (V_{meso}) by the difference between the total pore volume (V_T) and the micropore volume (V_μ). The non-local density functional theory (NLDFT) was used to calculate the pore size distribution (PSD) and thereby the average micropore diameter (d_μ) taking into account the pores narrower than 2 nm.

The adsorption data were analyzed with the help of the SAIEUS (Solution of Adsorption Integral Equation Using Splines) routine provided by Micromeritics. The PSDs of the activated carbons were determined by using simultaneously the nitrogen and carbon dioxide isotherms and the 2D-heterogenous surface model [21].

The PSDs of the zeolites were determined considering only nitrogen adsorption data. In this case, carbon dioxide adsorption data was not used for the characterization of the pore structure because the CO_2 molecule has a high quadrupole moment, which strongly interacts with the functional groups of the zeolite. Nitrogen adsorption data on DaY and NaY were analyzed with the H-form and Me-form, respectively, of the NLDFT model for zeolites with cylindrical pores.

2.2.2. Measurements of the adsorption-desorption isotherms for toluene, water and carbon dioxide

Toluene and water adsorption/desorption isotherms were measured by thermogravimetry (McBain thermobalance) under controlled vapor pressure. The experimental set-up is shown in Fig. 1 [22].

The sample (around 15 mg) was first evacuated *in situ* under a dynamic vacuum (10^{-5} hPa) for 5 h at 673 K for the zeolites, and at 573 K for the activated carbon microspheres. Then, the sample was cooled down to room temperature. The adsorption/desorption isotherms were drawn step-by-step using a static method by introducing successively toluene or water vapor doses into the thermobalance. Once a constant mass was reached, the next equilibrium state was performed by increasing or decreasing slightly the vapor pressure. All adsorption/desorption isotherms were measured at 298 K. The vapor pressure ranged from 10^{-4} to about 0.2 and 29 hPa for toluene and water, respectively.

Carbon dioxide adsorption-desorption experiments were