



Toward an effective adsorbent for polar pollutants: Formaldehyde adsorption by activated carbon



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HIGHLIGHTS

- Activated carbon fiber with mild activation condition is useful as adsorbent for polar pollutants.
- Diverse variations are investigated for developing an effective adsorbent.
- Surface functional group is the most important factor for capacity as a adsorbent.
- Surface functional groups on ACFs are investigated using micro-ATR FTIR.

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ABSTRACT

Due to increasing concerns about environmental pollutants, the development of an effective adsorbent or sensitive sensor has been pursued in recent years. Diverse porous materials have been selected as promising candidates for detecting and removing harmful materials, but the most appropriate pore structure and surface functional groups, both important factors for effective adsorbency, have not yet been fully elucidated. In particular, there is limited information relating to the use of activated carbon materials for effective adsorbent of specific pollutants. Here, the pore structure and surface functionality of polyacrylonitrile-based activated carbon fibers were investigated to develop an efficient adsorbent for polar pollutants. The effect of pore structure and surface functional groups on removal capability was investigated. The activated carbons with higher nitrogen content show a great ability to absorb formaldehyde because of their increased affinity with polar pollutants. In particular, nitrogen functional groups that neighbor oxygen atoms play an important role in maximizing adsorption capability. However, because there is also a similar increase in water affinity in adsorbents with polar functional groups, there is a considerable decrease in adsorption ability under humid conditions because of preferential adsorption of water to adsorbents. Therefore, it can be concluded that pore structures, surface functional groups and the water affinity of any adsorbent should be considered together to develop an effective and practical adsorbent for polar pollutants. These studies can provide vital information for developing porous materials for efficient adsorbents, especially for polar pollutants.

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1. Introduction

Increasing concerns about harmful pollutants in the environment have pushed for a need to develop an efficient adsorbent or a highly sensitive chemical sensor for toxic materials [1,2].

Porous materials, such as activated carbons [3], mesoporous silica or carbons [4,5], zeolite [6,7], and metal organic frameworks (MOF) [8,9] have been utilized as adsorbents or sensing transducers. Activated carbon materials, including activated charcoal and activated carbon fiber (ACF), are considered to be some of the most promising adsorbents due to their abundant micropores, large surface area, fast adsorption/desorption rate, excellent adsorption capacity and, most importantly, cost-effectiveness compared with other materials [10–13]. In certain cases, however, the decisive factor in determining adsorption ability is not just surface area or pore volume, but the nature of surface functional groups and pore size [14–17]. In particular, when adsorbents are required to

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have high selectivity for certain adsorbates, for instance, in energy storage applications, chemical conversion of adsorbates to useful compounds (regeneration technologies), and selective removal of certain compounds from mass pollutants, delicate control of surface functional groups on adsorbents should be achieved.

The surface functional groups on the porous materials prepared by bottom-up approaches, for example Zeolite and MOF, can be readily predicted and adjusted [6–9]. Particularly, in the case of MOF, these are constructed using a combination of metal ions and certain organic linkers. Alternating the functional groups of organic linkers by organic synthesis can make it possible to generate diverse functional groups on the MOF materials, on demand. Therefore, porous materials produced using bottom-up approaches have several advantages; for example, it is possible to generate tailored pore structure and functional groups, corresponding to higher selectivity for certain adsorbates. Conversely, porous materials made using top-down approaches are generally dependent on calcination or carbonization of a certain precursor. These materials are greatly competitive in terms of cost-effectiveness compared with MOF or Zeolite, but it is relatively difficult to anticipate and control their surface functional groups or pore structures. This is potentially a major obstacle to using activated carbon materials in advanced adsorption applications, even though carbon materials provide diverse advantages over other porous materials in terms of their large pore volume and cost-effectiveness.

It is noteworthy that the development of an effective, low-cost adsorbent for polar pollutants is warranted because most airborne pollutant contains carbonyl functional groups. Carbonyl pollutants, including formaldehyde, are some of the most concerning airborne chemicals and are considered as the main cause of the recent increase in childhood asthma and atopic hypersensitivity, as well as the cause of symptoms such as headaches, nausea, coryza, pharyngitis, among other things [14]. However, the development of an effective adsorbent for pollutants with carbonyl functional groups using activated carbon is challenging. Here, we report on the role of surface functional groups and pore structure of the diverse ACFs on the removal efficiency of formaldehyde. Based on sequential characterization, including nitrogen adsorption/desorption isotherm, elemental analysis, formaldehyde breakthrough traces, water adsorption/desorption isotherm and surface characterization by micro-ATR-FTIR methods, the pore structure and surface functional groups of activated carbon fibers (ACFs) were determined. More abundant heteroatoms lead to a greater adsorption ability of polar pollutants, but also an increased affinity of water molecules, resulting in decreased adsorption performance under humid conditions. Basic clues to be used in developing porous materials as effective adsorbents for polar pollutants are provided.

2. Materials and methods

2.1. Materials

Several different pitch-based ACFs (OG series: OG5A, OG7A, and OG15A) and PAN-based ACFs (FE series: FE100, FE200, FE300, and FE400) were obtained from Osaka Gas Co. Ltd. (Japan), and TOHO Tenax Co. Ltd. (Japan), respectively. Standard dry formaldehyde gas with 20 ppm of concentration, balanced with pure nitrogen, was purchased from Asahi Gas Co. in Japan.

2.2. Porosity measurements of ACF by nitrogen and water adsorption/desorption isotherm

Nitrogen adsorption/desorption isotherms of ACF were measured at 77 K using BELSORP-max-S (BEL Japan Inc.). Samples were

out-gassed at 200 °C in vacuum ($p < 10^{-8}$ bar) for 4 h before measurements were taken. Surface area was calculated according to the Brunauer–Emmett–Teller (BET) model [18]. Total pore volume was estimated from the amount of nitrogen adsorbed at a relative pressure of 0.95, with the assumption that all pores are totally filled with liquid nitrogen. The non-localized density function theory (NLDFT) method was used to determine the micropore volume and the pore size distribution. Water adsorption/desorption isotherms of ACF were also obtained at 298 K by HYDROSORB-1000 (Quantachrome).

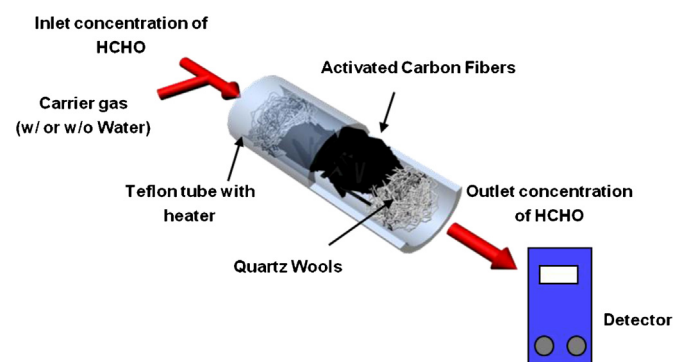
2.3. Characterization of the surface functional groups of ACF

Elemental analysis of carbon, hydrogen, nitrogen and oxygen of the ACF was carried out using a Perkin–Elmer CHN Elemental Analyzer, Model 2400. The samples were desiccated thoroughly before measurements (in a vacuum oven at 60 °C for 4 h). The surface structure was determined by XPS (ASCLab220i-XL electron spectrometer from VG Scientific using 300-W AlK α radiation) and micro-ATR FTIR (Bomem MB-100 series) equipped with a deuterated triglycine sulfate (DTGS) detector. A schematic of the micro-ATR FTIR analysis is represented in Figure S1 (supporting information). The sample chamber was continuously purged with dry nitrogen to prevent interference between carbon dioxide and water vapor. The micro-ATR FTIR technique, which is based on the internal total reflection, is among the most sensitive techniques for surface analysis [19]. A micro-ATR accessory was purchased from the Harrick Co., USA. In this micro-ATR FTIR, a 45° incident angle Ge prism with dimension of 10 mm \times 5 mm \times 1 mm was selected as the micro-ATR cell. The Ge prism (refractive index of 4.0) was used to induce the total reflection, because the refractive index of carbon materials exhibited the high value of ca. 3.5. Each spectrum was obtained with 4-cm $^{-1}$ resolution and 200 coadditions. The absorbance spectra were subtracted from raw spectra collected with ACF-KBr disk referenced to the raw spectra of pure KBr. The detailed procedure of the micro-ATR technique has been described elsewhere [19].

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jhazmat.2013.04.049>.

2.4. Formaldehyde adsorption on ACF

The detailed procedure to obtain the formaldehyde breakthrough curves has been denoted in previous work [20], and is schematically illustrated in Scheme 1. A fixed-bed unit with a column of 40 mm in length and 8 mm in diameter was constructed and 0.05 g of ACF was loaded into the apparatus. The 20 ppm formaldehyde-containing standard gas balanced with pure nitrogen and the additional dry nitrogen were fed into the system at a



Scheme 1. Schematic diagram of the experiment set-up for adsorption of formaldehyde.

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