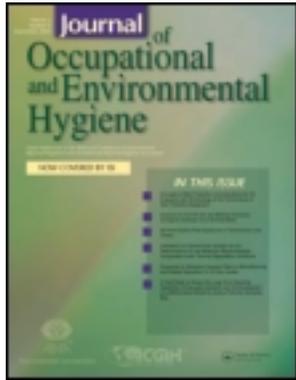


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### Case Study

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## Case Study

# Emission of Carbon Nanofiber (CNF) from CNF-Containing Composite Adsorbents

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### INTRODUCTION

Carbon nanofibers (CNFs) are a new class of synthesized carbonaceous materials receiving increased attention. They have been extensively studied due to their interesting properties (i.e., purity, mechanical strength, high geometric surface area) and potential for use as adsorbents and catalyst supports.<sup>(1–4)</sup> Production costs are significantly lower than those of carbon nanotubes (CNT), and CNFs provide high performance for certain applications.<sup>(5,6)</sup>

CNFs are produced from chemical vapor deposition (CVD), the catalytic decomposition of hydrocarbon gases or carbon monoxide over selected metal particles, including iron, cobalt, nickel, and some of their alloys at temperatures in the range of 400–1000°C.<sup>(5)</sup>

CNFs are characterized by the graphite-like structure at the nanoscale. Variable alignments of laminated hexagonal layers along the fiber axis typically provide three types of CNFs: (1) platelet (aligned perpendicular to the fiber axis), (2) tubular (aligned parallel to the fiber axis), and (3) herringbone (aligned at an angle to the fiber axis).<sup>(2)</sup> These structures differ according to the growing conditions and the metal used as a catalyst.<sup>(7)</sup>

Several studies have shown that CNFs improved adsorbent properties. For example, Lim et al.<sup>(3)</sup> gave activated carbon fiber (ACF) multiple additional properties by growing CNFs on its catalytic surface. This improved the performance of ACFs for such applications as SO<sub>x</sub> and NO<sub>x</sub> removal. Schlogl et al.<sup>(8)</sup> grew carbon nanostructures (CNFs and CNTs) on a carbonaceous carrier (activated carbon-AC) for the removal of metal species in water purification. In a recent study by some of the present study's authors,<sup>(9)</sup> a composite of AC and CNFs (AC/CNF) was prepared. AC was impregnated with a nickel nitrate catalyst, and CNFs with a diameter between 10 to 20 nm were deposited on the catalyst particles in AC micropores using CVD. Prepared samples were then activated by CO<sub>2</sub> to recover the surface area and micropores. The prepared composite adsorbent was tested for VOC adsorption and then employed in an organic vapor respirator cartridge in granular form. The breakthrough time of cyclohexane vapor for a cartridge prepared with CO<sub>2</sub>-activated AC/CNF was significantly longer than for those cartridges prepared with the original AC with the same weight of adsorbents. This study<sup>(9)</sup> suggested that the granular form of AC/CNF composite could be an efficient alternative adsorbent for respirator cartridges due to its larger adsorption capacities and lower weight.

The broad utility of manufactured nanomaterials resulted in increased levels of production, greater risk of human exposure, and the potential for release of these novel materials into the environment. Therefore, close attention to potential health risks, i.e., the potential for exposure and toxic responses to manufactured nanoparticles, including various fibrous nanomaterials, is important.<sup>(10)</sup> A growing body of literature indicates a potential hazard from exposure to CNFs.<sup>(5,11–13)</sup> One study showed that CNFs can penetrate human cells in target organs and cause cellular damage.<sup>(12)</sup> Kisin

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et al.<sup>(6)</sup> showed that CNFs may have a genotoxic effect comparable to asbestos and stronger than single-walled carbon nanotubes (SWCNT).<sup>(6)</sup> Due to the huge number of potential applications for CNFs,<sup>(14)</sup> their possible release during fabrication or usage warrants further investigation. In the present study, the potential release of CNF from a respirator cartridge prepared from AC/CNF composite adsorbent and different particulate filters was evaluated by carbon analysis and electron microscopy analysis.

## MATERIAL AND METHODS

### Cartridge Preparation

The experimental cartridge was designed to correspond to an AC/CNF composite adsorbent prepared for the purpose of respiratory protection against organic vapors. For this purpose, 12 g of granular CNF/AC adsorbent (40% CNF) was placed in a cartridge holder (a plastic case) and retained with particulate filters. Four common types of respirator particulate filters were used in these studies: (1) coarse, (2) pre-filter (3M 6075), (3) FFP2 (3M 9322), (4) and FFP3 (3M 9332). The amounts of adsorbent in the cartridge holder and the airflow rate that passed through were similar to that of a typical respirator cartridge (25–40 g and 30 L/min).<sup>(15,16)</sup> The cartridge was connected to a sampler equipped with a quartz particle filter used to capture the EC and OC present in the potentially released particles (Figure 1). The system was connected to a high-volume flow pump, running continuously at 12 L/min for 12 hr.

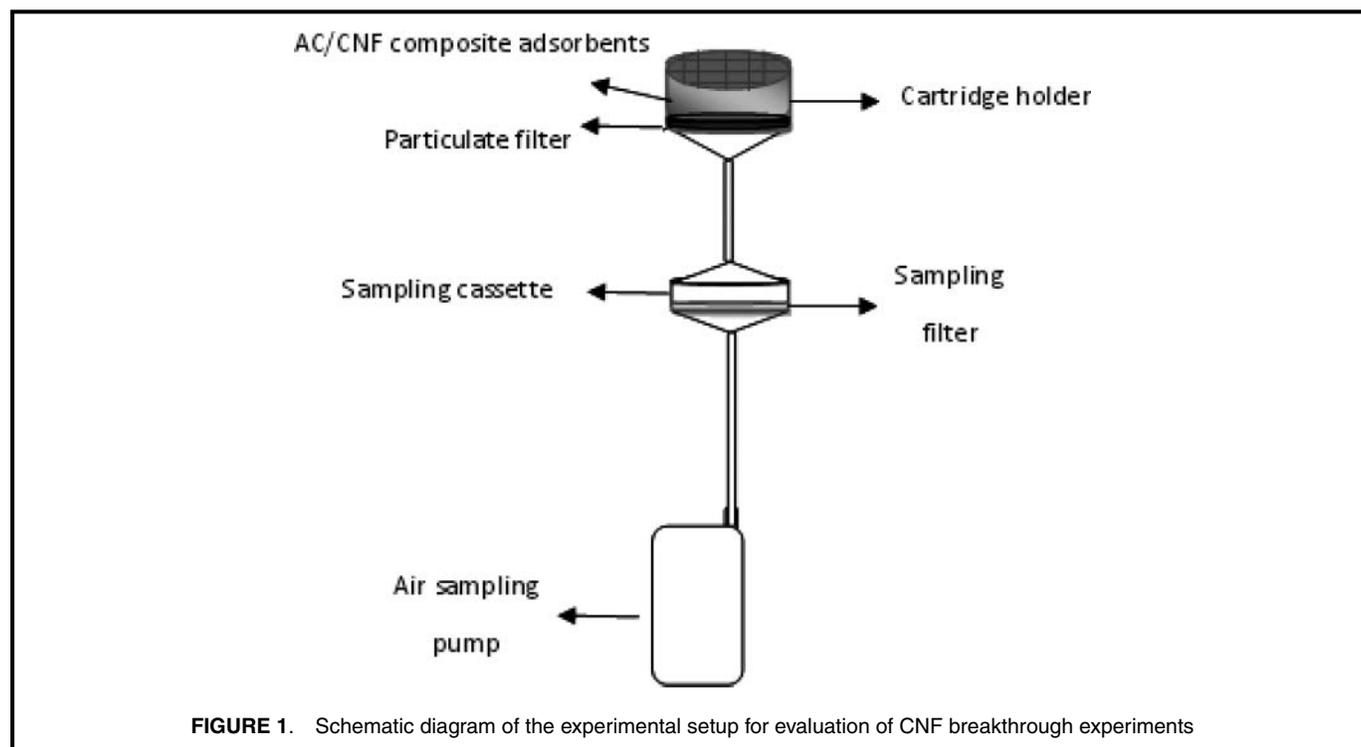
### Carbon Analysis

EC has been proposed as an indicator for exposure assessment with CNFs.<sup>(17–19)</sup> In the present study, the release of carbonaceous particles (CNFs and/or AC) from the composite adsorbent was measured as EC by carbon analysis. Air passed through the cartridge holder (including adsorbents and different particulate filters) and through 37-mm quartz filters (in a 3-piece, 37-mm sampler cassette) using the above experimental setup. For each type of particulate filter, three trials were conducted.

To assess the potential contribution of EC present in the laboratory's ambient air, air was also passed through the particulate filters (pre- and FFP2 filters) without adsorbents in the cartridge. These experiments were done in parallel with the samples collected after passing through the cartridge.

Collected particles on quartz filters were analyzed by a thermal-optical aerosol carbon monitor (Lab OC-EC Aerosol Analyzer; Sunset Laboratory, Tigard, Ore.) according to NIOSH analytical method 5040 for airborne EC.<sup>(19,20)</sup>

In this carbon analysis, a standard-sized punch (1.5 cm<sup>2</sup>) was made from a previously collected quartz filter sample that was placed in a quartz oven and heated under an oxygen-free atmosphere (He 99.999%) to remove OC, then heated again to oxidize the EC. In the NIOSH method, the CO<sub>2</sub> resulting from OC or EC decomposition is catalytically converted to CH<sub>4</sub>. The methane is subsequently measured using a flame ionization detector (FID). In addition, the transmittance of a laser beam through the filter sample is recorded to consider possible pyrolysis of the organic material. The point at which



the value of transmittance becomes the same as the initial value is defined as “the split” between OC and EC. The CO<sub>2</sub> produced before the split is defined as OC and, after the split, is defined as EC.<sup>(21,22)</sup>

The minimum detection limit of this analyzer was 0.15 μg/cm<sup>2</sup>, corresponding to 0.15 μg/m<sup>3</sup> in our experimental conditions. The results obtained from the instrument were corrected for potential OC and EC contamination on the filters by subtraction of results from an unused filter. Then, the mean concentration of OC and EC was calculated by dividing the mass of carbon (OC or EC) by the total volume of air passed through the filter during the sampling period.

### Microscopy Analysis

Qualitative assessment for determining CNF breakthrough was conducted by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Using the above experimental setup in different trials, filter-based air samples were collected on 25-mm MF-Millipore membrane (Merck Millipore, Billerica, Mass.), mixed cellulose esters (MCE), and 25-mm gold-coated polycarbonate membrane filter (in carbon-filled conductive polypropylene sampler cassettes) for TEM (CM 100 operated at 100 kV; Philips, Eindhoven, Netherlands) and SEM (JSM-6300F operated at 10 kV; JEOL Ltd., North Billerica, Mass.) analyses, respectively.

The MCE filters were transferred onto the TEM grids, dissolved by dimethylformamide and acetic acid, and treated in the plasma furnace according to ISO standard 10312<sup>(23)</sup> for filter-based asbestos exposure assessment. Observations were done with a 20,000:1 magnification. Two samples per filter (one on a copper grid and one on a gold grid) were observed, and 100 randomly selected grid fields in each sample were evaluated for CNFs. All experiments for assessing

breakthrough of CNFs were conducted in triplicate for each type of particulate filter evaluated by TEM/SEM.

The calculation of average CNF fiber/agglomerate concentration in TEM grids was done by fiber counting according to the following formula:<sup>(23)</sup>

$$C = Af \times E / (Ag \times k \times V \times 1000)$$

C = concentration of fibers per cm<sup>3</sup>

Af = active surface of the filter [mm<sup>2</sup>] (420 mm<sup>2</sup>)

Ag = surface of one TEM squares [mm<sup>2</sup>] (0.011 mm<sup>2</sup>)

E = number of fibers counted

k = number of TEM squares counted

V = volume of the sampled air

The extrapolated number of fibers was based on the size of one grid: 0.011 mm<sup>2</sup> and total filter surface of 420 mm<sup>2</sup> for 14 hr sampling with a flow rate of 12 L/min.

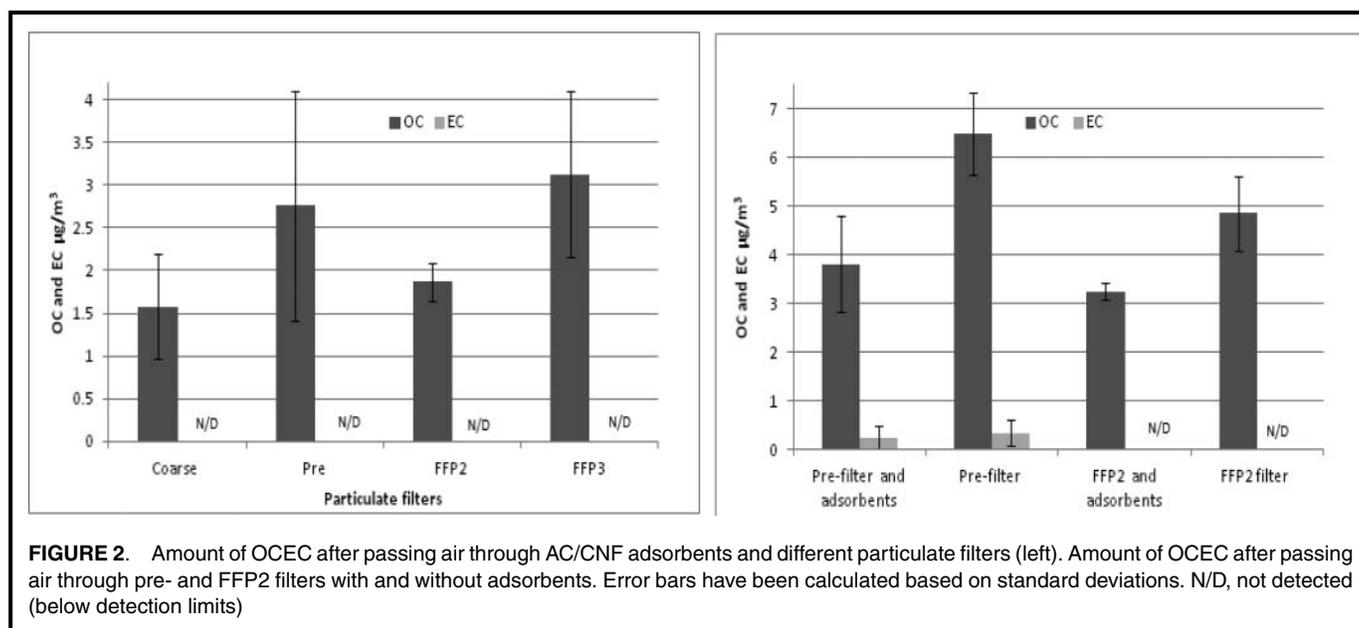
The gold filters were transferred to the grid directly and observed by SEM.

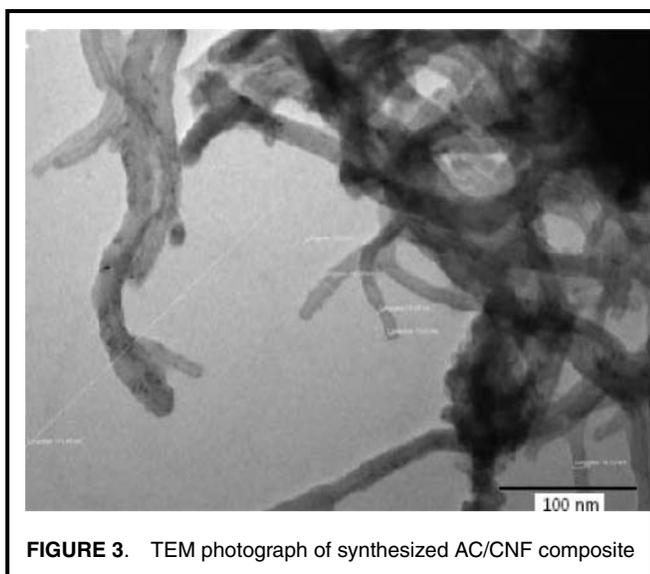
## RESULT AND DISCUSSION

### Carbon Analysis

Figure 2 (left) shows the amount of OC and EC measured after passing air through the AC/CNF adsorbents and different particulate filters. All of the particulate filters (coarse, pre-filter, FFP2, and FFP3) did not show any detectable amounts of released EC (below the detection limit of 0.15 μg/m<sup>3</sup>).

Figure 2 (right) shows the amount of measured OC and EC after passing air through pre- and FFP2 particulate filters with and without CNF-containing adsorbents. Interestingly, the amounts of OC and EC for the samples after passing air through pre- and FFP2 filters (without adsorbents) are higher than the samples collected after passing air through





**FIGURE 3.** TEM photograph of synthesized AC/CNF composite

the adsorbents. This is probably because some of the OC and EC in the ambient air has been removed while passing through the adsorbents.

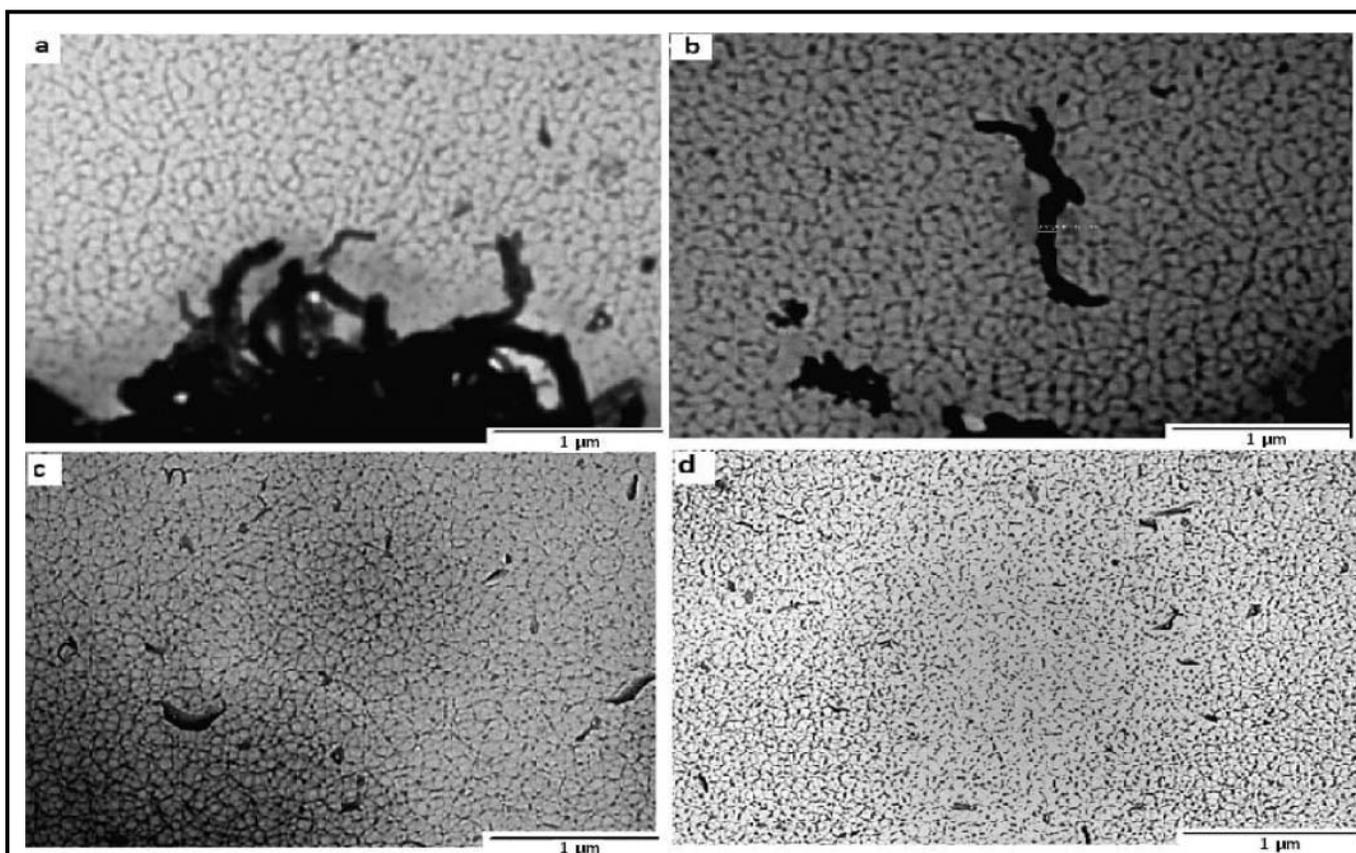
Figure 2 also shows that there is some OC in the filters analyzed. This may suggest that some volatile organic material

became absorbed on the surfaces of adsorbents and filter fibers either during production or storage of these materials, which then led to these small amounts of OC on the filters. However, when considering the values measured from collected samples after passing air through the particulate filters (without adsorbents, Figure 2), a large part of the measured OC values could be attributed to the laboratory's ambient air.

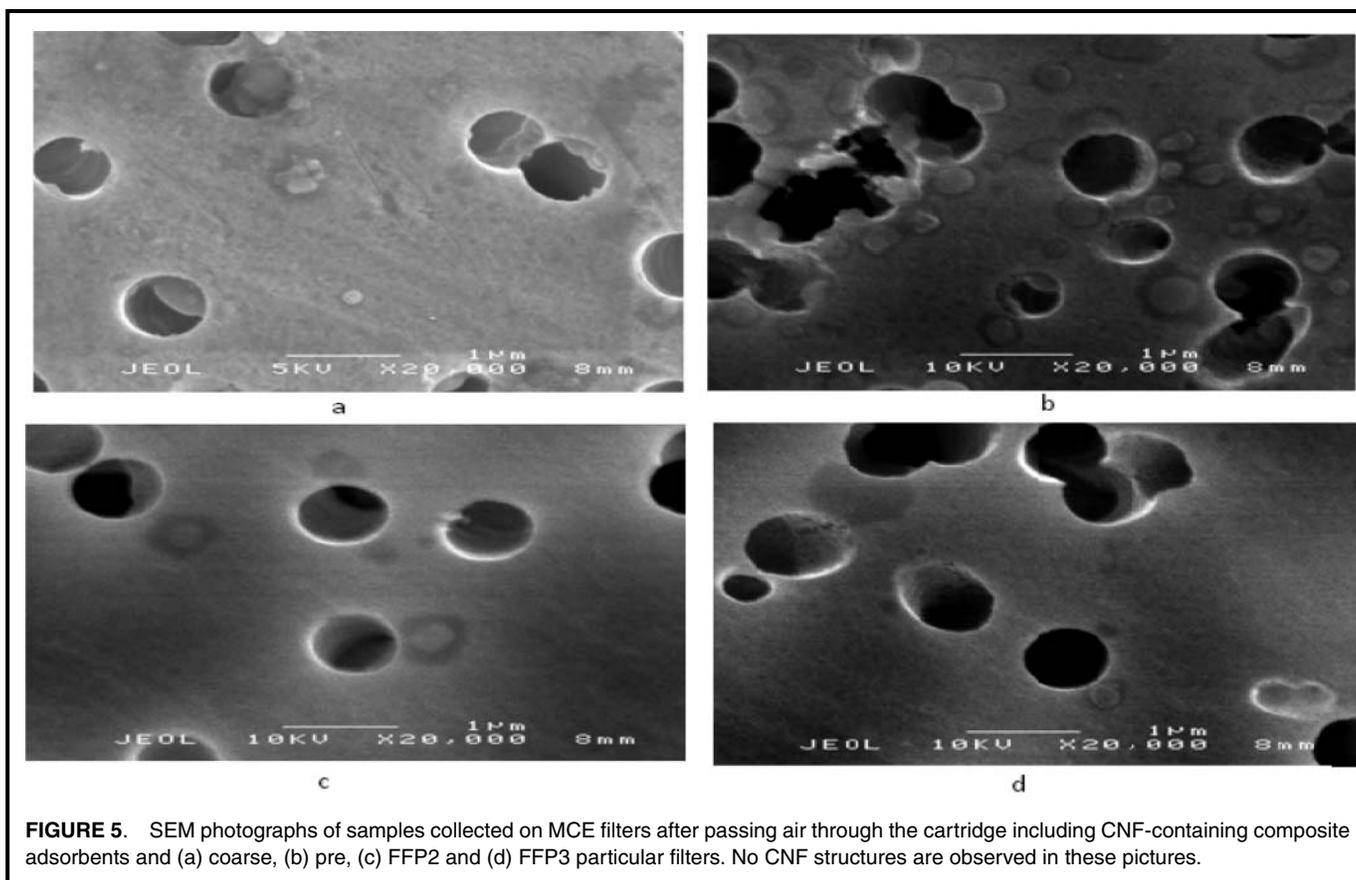
### TEM and SEM Observations

Figure 3 shows the TEM photographs of the original synthesized AC/CNF composite adsorbents used in this study. CNFs with a very thin diameter of about 10–20 nm were formed uniformly on the AC. Many CNFs are intertwined. Such thin CNFs are not of a tubular type but are more similar to a herringbone type.

Figure 4 shows the TEM photographs of samples collected on MCE filters after passing air through the cartridge, including CNF-containing composite adsorbents and (a) coarse, (b) pre, (c) FFP2, and (d) FFP3 particulate filters. We can observe some fibrous agglomerated structures in the photographs for the coarse and pre-particulate filters. It appears that the prepared composite adsorbents released small amounts of CNF that were not retained completely by these two types of particulate filters.



**FIGURE 4.** TEM photographs of collected samples on MCE filters after passing air through cartridges, including CNF-containing composite adsorbents and (a) coarse, (b) pre, (c) FFP2, and (d) FFP3 particulate filters. CNF structures are observed in photos (a) and (b).



**FIGURE 5.** SEM photographs of samples collected on MCE filters after passing air through the cartridge including CNF-containing composite adsorbents and (a) coarse, (b) pre-, (c) FFP2 and (d) FFP3 particulate filters. No CNF structures are observed in these pictures.

Figure 4 shows that the size of these fibers is considerably lower than that used to define asbestos fibers (length  $\geq 5 \mu\text{m}$  and aspect ratio  $\geq 3:1$ ),<sup>(23)</sup> so CNF cannot be considered an analogous hazard to asbestos fibers in terms of penetration into the lung wall.<sup>(24)</sup> Furthermore, the average concentration of CNF fiber/agglomerate in TEM grids after passing air through CNF-containing adsorbents was  $1.32\text{E}^{-4}$  and  $4.41\text{E}^{-5}$  fibers/mL for coarse and pre-particulate filters, respectively. This is significantly lower than the recommended occupational exposure limits in Switzerland for carbon nanotubes and carbon nanofibers (0.01 fibers/mL; this limit is the same as for asbestos fibers).<sup>(24)</sup>

Figure 5 shows scanning electron micrographs of collected samples on the gold-coated filters after passing air through the cartridge including CNF-containing composite adsorbents and (a) coarse, (b) pre-, (c) FFP2, and (d) FFP3 particulate filters. No fiber structures were observed on these SEM monograms.

The number of agglomerated fibers counted on TEM samples collected after the coarse particulate filter was higher than after the pre-filter. Despite this (low) number of CNF structures detected on the TEM grid, SEM analysis did not identify any CNF structures, including the analysis for the coarse particulate filter (Figure 5). For the FFP2 and FFP3 filters, we did not detect any fiber structured object on TEM grids. These results were in agreement with EC measurements.

## CONCLUSION

This study found no detectable release of CNF from fully intact filter cartridges containing AC/CNF composite adsorbent and only minimal amounts if the cartridges were missing the high-efficiency particulate filters they usually contain. The carbon analysis experiments in this study identified only minimal amounts of released elemental carbon while passing air through the cartridge, which was significantly lower than NIOSH's recommended occupational exposure limits for carbon nanotubes and nanofibers.<sup>(19)</sup> Meanwhile TEM photographs showed a few CNF structures for AC/CNF composite adsorbents with coarse and pre-particulate filters that were not in the range defined for asbestos fibers in terms of length and aspect ratio. Therefore, it is concluded that the amount of CNF released from CNF-containing composite adsorbents—prepared by a CVD process followed by a heating process (as a fixation step)—is negligible. This is probably because CNFs are solidly bound to the AC by the process they undergo during synthesis, in which contaminating catalytic metals are frequently removed either by high-temperature vaporization or acid treatment.<sup>(19)</sup> It appears that the synthesis process of heating the composite adsorbents at  $550^\circ\text{C}$  under flowing nitrogen gas has acted as a fixation step, stabilizing the catalyst precursor particles. Consequently, this has controlled and stabilized nanofiber growth on the AC.<sup>(8)</sup>

In this study, the release of CNFs from AC/CNF composite adsorbents was evaluated under conditions equivalent to the normal use of a respirator cartridge in the workplace. Further studies are needed to evaluate the potential release of CNFs in different degradation situations, e.g., chemical exposure, climatic conditions, and shipping conditions. These efforts should be made to ensure that the cartridges are safe by design before the production stage and also to prevent the emission of CNFs during respirator use.

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## REFERENCES

- Iijima, S.: Helical microtubules of graphitic carbon. *Nature* 354:56–58 (1991).
- Rodriguez, N.M., A. Chambers, and R.T.K. Baker: Catalytic engineering of carbon nanostructures. *Langmuir* 11(10):3862–3866 (1995).
- Lim, S., S.H. Yoon, Y. Shimizu, H. Jung, and I. Mochida: Surface control of activated carbon fiber by growth of carbon nanofiber. *Langmuir* 20:5559–5563 (2004).
- Jahangiri, M., S.J. Shahtaheri, J. Adl, A. Rashidi, H. Kakooei, and A.R. Forushani: The adsorption of benzene, toluene and xylenes (BTX) on the carbon nanostructures: The study of different parameters. *Fresenius Environ. Bull.* 20(4a):1036–1045 (2011).
- Genaidya, A., T. Tolaymath, R. Sequeira, M. Rinder, and D. Dionysioua: Health effects of exposure to carbon nanofibers: Systematic review, critical appraisal, meta-analysis and research to practice perspectives. *Sci. Total Environ.* 407:3686–3701 (2009).
- Kisin, E.R., A.R. Murray, L. Sargent, D. Lowry, M. Chirila, K.J. Siegrist et al. : Genotoxicity of carbon nanofibers: Are they potentially more or less dangerous than carbon nanotubes or asbestos? *Toxicol. Appl. Pharmacol.* 252(1):1–10 (2011).
- Serp, P., M. Corrias, and P. Kalck: Carbon nanotubes and nanofibers in catalysis. *Appl. Catal. A General* 253:337 (2003).
- Schlogl, R.: 2006. Nanocarbon-activated carbon composite. U.S. Patent 2009/0220767 A1, filed April 13, 2006, and issued Sept. 9, 2009.
- Jahan-Giri, M., S.J. Shahtaheri, J. Adl, et al.: Preparation of new adsorbents from activated Carbon and Carbon Nanofiber (AC/CNF) for manufacturing organic-vapour respirator cartridge. *Iranian Journal of Environmental Health Science & Engineering*. [In press]
- Shvedova, A.A., V.E. Kagan, and B. Fadeel: Close encounters of the small kind: Adverse effects of man-made materials interfacing with the nano-cosmos of biological systems. *Ann. Rev. Pharmacol. Toxicol.* 50:63–88 (2010).
- Magrez, A., S. Kasas, V. Salicio, et al.: Cellular toxicity of carbon-based nanomaterials. *Nano Lett.* 6(6):1121–1125 (2006).
- Genaidya, A., R. Sequeira, M. Rinder, and A. A-Rehim: Risk analysis and protection measures in a carbon nanofiber manufacturing enterprise: An exploratory investigation. *Sci. Total Environ.* 407:5825–5838 (2009).
- Yokoyama, A., Y. Sato, Y. Nodasaka, et al.: Biological behavior of hat-stacked carbon nanofibers in the subcutaneous tissue in rats. *Nano Lett.* 5(1):157–161 (2004).
- Milne, W.I.: Carbon nanotubes. *enanonewsletter* (Special Issue No. 20/21), 2008.
- Nelson, G.O., and A.N. Correia: Respirator cartridge efficiency studies: VIII. Summary and conclusions. *Am. Ind. Hyg. Assoc. J.* 37:514–525 (1976).
- European Parliament and the Council of the European Union: *Respiratory Protective Device—Gas Filters and Combined Filters—Requirements, Testing, Marking (EN 141:2000)*. [Standard] Brussels: CEN, June 2000.
- Kuhlbusch, T.A.J., and H. Fissan: Particle characteristics in the reactor and palletizing areas of carbon black production. *J. Occup. Environ. Hyg.* 3:558–567 (2006).
- Kuhlbusch, T.A.J., S. Neumann, and H. Fissan: Number size distribution, mass concentration, and particle composition of PM1, PM2.5, and PM10 in bag filling areas of carbon black production. *J. Occup. Environ. Hyg.* 1:660–671 (2004).
- National Institute for Occupational Safety and Health (NIOSH): *Occupational Exposure to Carbon Nanotubes and Nanofibers* (Docket Number: NIOSH 161-A). Current Intelligence Bulletin, 2010.
- National Institute for Occupational Safety and Health (NIOSH): Elemental carbon (diesel exhaust) Method 5040. In *NIOSH Manual of Analytical Methods (NMAM)*. Cincinnati, Ohio: U.S. Department of Health and Human Services, Centers for Disease Control and Prevention, NIOSH, 1999.
- Birch, M.E., and R.A. Cary: Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust. *Aerosol Sci. Technol.* 25:221–224 (1996).
- Mariko, O.-O., and J.S. Thomas: Diesel exhaust particles in the work environment and their analysis. *Ind. Health* 42:389–399 (2004).
- International Organization for Standardization (ISO): *Ambient Air. Determination of Asbestos Fibres. Direct-Transfer Transmission Electron Microscopy Method* (BS ISO 10312:1995). [Standard] Geneva: ISO, 1995.
- Swiss Accident Insurance Institute (SUVA): *Valeurs limites d'exposition aux postes de travail 2011 [Exposure limit values for workstations 2011]*. Lucerne: SUVA, Occupational Medicine Division, 2011.