

# VOCs Air Pollutant Cleaning with Polyacrylonitrile/Fly Ash Nanocomposite Electrospun Nanofibrous Membranes

Jun Cong Ge<sup>1</sup>, Zi Jian Wang<sup>2</sup>, Min Soo Kim<sup>3</sup> and Nag Jung Choi<sup>4,\*</sup>

<sup>1</sup>Division of Mechanical Design Engineering, Chonbuk National University, Korea, freedefeng@naver.com

<sup>2</sup>Division of Mechanical Design Engineering, Chonbuk National University, Korea, blove2016@naver.com

<sup>3</sup>Division of Mechanical Design Engineering, Chonbuk National University, Korea, kimms@jbnu.ac.kr

<sup>4</sup>Division of Mechanical Design Engineering, Chonbuk National University, Korea, njchoi@jbnu.ac.kr

\*Corresponding author

**Abstract.** Volatile organic compounds (VOCs) as an environmental pollution, which have many kinds of chemical structures, and many of them are very toxic. Therefore, controlling and reducing the presence of VOCs has become a hot topic among researchers for many years. In this study, the VOCs adsorption capacity of polyacrylonitrile/fly ash (PAN/FA) nanocomposite electrospun nanofibrous membranes were investigated. The results indicated that the PAN with different contents of FA powder (20%, 40%, 60%, 80%, and 100% compared with PAN by weight) could be spun well by electrospinning. The diameter of the fiber was very fine and its arrangement was irregular. The PAN nanofibrous membrane containing 60 wt% FA powder had the highest VOCs absorption capacity compared with other nanofibrous membranes due to its large specific surface area.

**Keywords:** Electrospun; Nanofibrous membranes; Volatile organic compounds; Fly ash.

## 1. Introduction

With the rapid development of modern industry, environmental pollution is increasingly becoming a serious problem. The excessive emissions of carbon dioxide (CO<sub>2</sub>) contribute to the warming of the greenhouse effect and lead to global warming; human excessive use of fossil fuels, which can cause a series of environmental pollution problems, such as: fog and haze, acid rain, particulate matter (PM), volatile organic compounds (VOCs), etc. [1,2]. Among them, VOC is an important pollutant of indoor and outdoor, so it attracts more and more attention from researchers [3,4].

VOCs as an environmental pollution, are volatile organic compounds that volatilize into the air and generate odor and ozone. They are carcinogens that will cause damage to the nervous system through skin contact or inhalation. Which has about 200 different kinds of chemical structures, and many of them are very toxic, they will cause great harm to animals and plants, human, and environment. The most common and most toxic VOCs are Benzene, formaldehyde, toluene, xylene, ethylene, styrene, and acetaldehyde [1,3,5]. Therefore, it is very important to effectively control and reduce the content of VOCs in the air.

In recent years, due to the great progress of nanoscience and technology, especially the further organic combination of nanotechnology, environmental protection and environmental management,



making nanomaterials greatly enhance the ability of human protection of the environment and provide a solution to the environmental problems such as hazardous substances monitoring, water slick treatment, etc. [6,7]. Among them, using nanofibrous membranes to filter the air and absorb VOCs in the air, is a hot topic in the field of nanomaterial technology.

Electrospinning technology is a simple and efficient technology for the fabrication of these nanofibers. The electrospun nanofibrous membranes have high porosity and large specific surface area, Scholten et al. [8], Liu et al. [9], and Ge et al. [3,5] have been successfully spun the nanofiber via electrospinning to filter the air. In addition, the electrospinning have been widely concerned in the field of air filtration, protective clothing, sensors, wound wrap, tissue engineering scaffold, membrane separation materials, and etc. [10-12]. The diameter of the electrospinning fibers is generally distributed in the range of several nanometers to several micrometers. The aggregate material composed of these fibers has a three-dimensional space structure, which not only has the advantages of small nanoparticle size, high specific surface area, but also has good mechanical stability, fiber membrane pore size is small, high porosity, good fiber continuity and other characteristics, has a very wide potential use in the field of environmental.

In this paper, the polyacrylonitrile (PAN) was used as the electrospinning raw material, which has very good spinnability, strong electrical conductivity, low cost, economical and practical. Fly ash (FA), discharged from the power station, was used as the electrospinning functional material. Which has been reported as an adsorbent to filter air, due to its own unique physical characteristics, such as high surface area, porosity, bulk density, particle size, lightweight, nontoxic, and etc. However, there is little research on the use of FA for electrospinning nanofiber membranes. In particular, with the good spinnability PAN material for the fabrication of functional nanofibrous membranes to adsorbed VOCs from air. Therefore, we successfully spun nanofibrous membranes with different FA content via electrospinning, and also optimized the mixing weight ratio of PAN and FA based on the VOCs adsorption capacity.

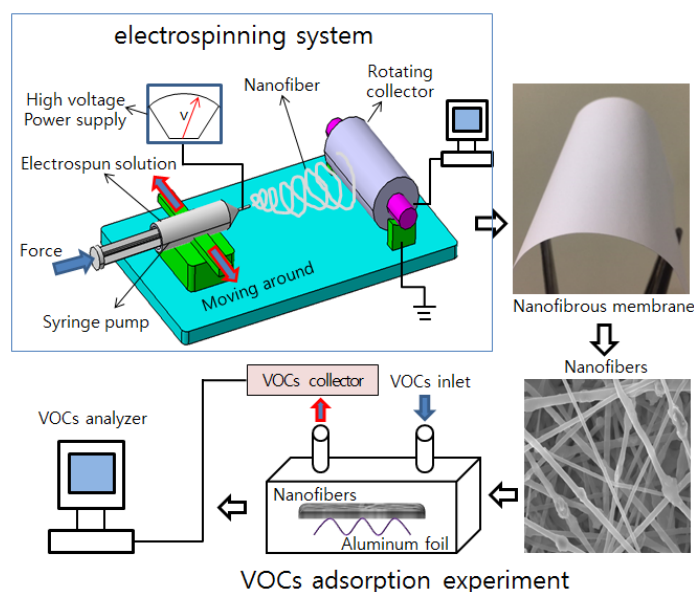
## 2. Experimental Details

### 2.1. Materials

Polyacrylonitrile (PAN,  $M_w=150,000$ ) was purchased from Sigma-Aldrich, Co., USA. N, N-Dimethylformamide (DMF) was purchased from Showa Chemical Co., Ltd., Japan. FA powder obtained from Won Engineering Company Ltd., Korea. Four different kinds of VOCs (chloroform, benzene, xylene, and toluene; purity 99.9%, AR grade) were analyzed.

### 2.2. Fabrication of Nanocomposite Nanofibrous Membranes

10 wt% PAN (in DMF solution by weight) was used as the electrospinning raw material. PAN was completely dissolved in DMF solution using a magnetic stirrer for 12 h at room temperature. Different amounts of ball-milled FA powders (0 wt%, 20 wt%, 40 wt%, 60 wt%, 80 wt%, and 100 wt% with respect to PAN) were respectively dissolved in the prepared DMF solutions using a magnetic stirrer for 12 h. Finally, the prepared mixed solutions were treated by ultrasound for 2 h to obtain a homogeneous electrospinning solution. The electrospinning system and VOCs adsorption experiment are shown in Figure 1. The spinneret voltage used in the experiment was 15 kV, the distance between tip and collector was 18 cm, and the electrospinning solution feed rate was 1 ml/h. The prepared nanofibrous membranes were respectively denoted as FA0 (no FA), FA2 (FA: PAN=0.2), FA4 (FA: PAN=0.4), FA6 (FA: PAN=0.6), FA8 (FA: PAN=0.8), and FA10 (FA: PAN=1) according to different amounts of FA powder.



**Figure 1.** Schematic diagram of the electrospinning system and VOCs absorption experiment

### 2.3. VOCs Absorption Experiment

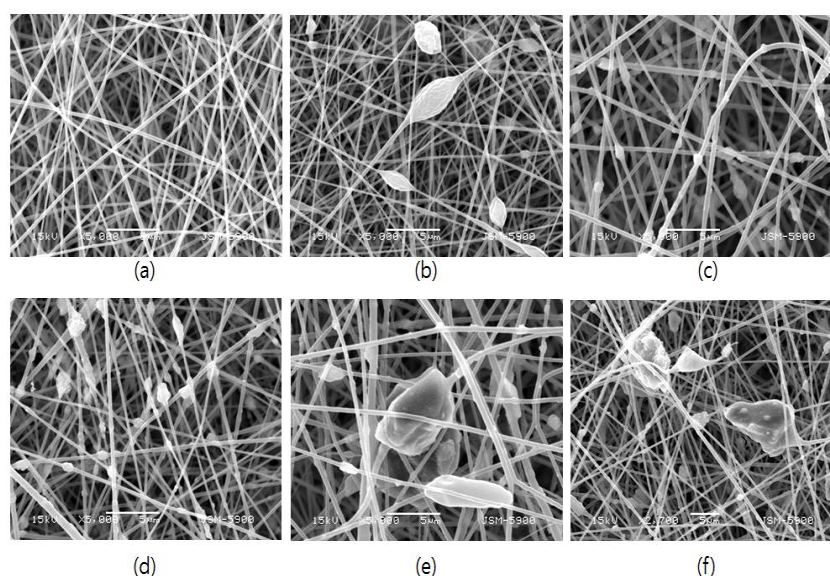
0.1 ml of each of VOCs (chloroform, benzene, xylene, and toluene) were completely mixed into 50ml of MEOH for 2h using a magnetic stirrer. And then 4 $\mu$ l of VOCs was injected into a sealed container with a nanofibrous membrane (11 $\times$ 9 cm). After 2h of VOCs absorption experiment, the non adsorbed VOCs is blown into a gas sampling bag (tedlar bag). Finally, the quantitative and qualitative analysis of VOCs were analyzed by GC/MS analyzer.

### 3. Results and Discussion

Table 1 shows the physical properties of PAN/FA spinning solutions. It can be clearly seen that the viscosity of the mixed spinning solution was decreased with increasing the amount of FA powder to 40 wt%. And the mixed spinning solutions had the higher conductivity compared with previous studies [3, 5], all of them was between 6.6 ~9.9 ms/m. Through these, it can be preliminarily judged that the mixed PAN/FA spinning solutions have a good spinnability.

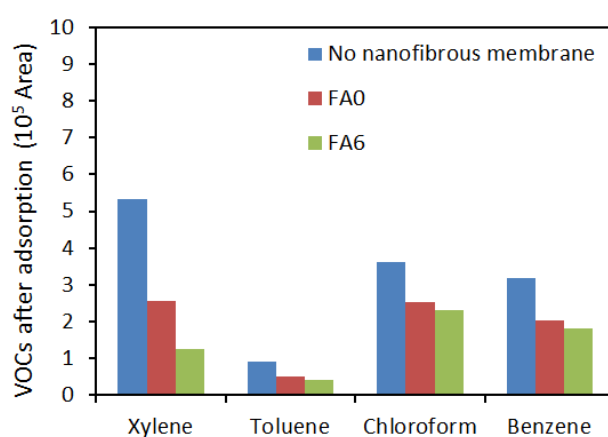
**Table 1.** Physical properties of electrospinning solutions.

Item NO.	Viscosity (cP)	Conductivity (ms/m)
FA0	502.1	9.86
FA2	469.6	7.01
FA4	465.2	6.81
FA6	542.6	6.62
FA8	667.8	6.60
FA10	635.4	6.91



**Figure 2.** SEM images of PAN/FA nanofibrous membrane according to different amounts of FA powder; (a) FA0, (b) FA2, (c) FA4, (d) FA6, (e) FA8, and (f) FA10. The magnification factor of Figure a-e are 5000, and Figure f is 2700.

Figure 2 shows the SEM images of PAN/FA nanofibrous membrane according to different amounts of FA powder. As shown in Figure 2, the morphological changes of PAN/FA nanofibers vary widely. The FA0 (without FA powder) nanofiber surface was smooth and continuous, and the distribution of fibers was random and uniform. With increasing the amount of FA powder, the FA particles began to appear on the PAN fiber, the fiber diameter also began to become smaller. However, a small amount of agglomerate occurred on the PAN fiber when the amount of FA reached 80 wt% (see Figure 2e). In Figure 2f, it can be clearly seen that those agglomerate became much larger and bigger compared with Figure 2e (the magnification factor of two Figures is different). In the electrospinning experiments, the nozzles of the two solutions (FA8 and FA10) were easier to plug compared with other spinning solutions. Therefore, the FA8 and FA10 solutions will be eliminated due to its spinning inconvenience.



**Figure 3.** The amount of VOCs in the tedlar bag after VOCs adsorption experiment.

The VOCs adsorption capacity of the PAN/FA nanofibrous membranes is shown in Figure 3. As shown in Figure 3, the PAN nanofiber containing a certain amount of FA had high VOCs adsorption capacity. The FA6 nanofibrous membrane had the higher VOCs adsorption capacity than FA0, and the total VOCs (TVOCs) of FA6 was reduced by 37.3% compared with no nanofibrous membrane. In addition, FA6 showed a strong adsorption capacity for xylene compared with other VOCs, about 23.8%

of xylene was reduced. This is because there are two adjacent groups of methyl groups in its chemical structure, it led to increased the binding energy [3, 5].

#### 4. Conclusion

In summary, we perfectly combined the PAN and FA by electrospinning, and successfully produced a series of functional membranes that could adsorb VOCs from air. The PAN nanofiber containing a certain amount of FA had high VOCs adsorption capacity. And the PAN/FA nanofibrous membrane showed a strong adsorption capacity for xylene compared with other VOCs.

#### 5. Acknowledgement

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#### 6. References

- [1] X. Zhang, B. Gao, A.E. Creamer, C. Cao, Y. Li, Adsorption of VOCs onto engineered carbon materials: A review, *Journal of Hazardous Materials*, 338 (2017) 102-123.
- [2] J.C. Ge, S.K. Yoon, M.S. Kim, N.J. Choi, Application of Canola Oil Biodiesel/Diesel Blends in a Common Rail Diesel Engine, *Appl. Sci.*, 7 (2017) 1-13.
- [3] J.C. Ge, N.J. Choi, Fabrication of Functional Polyurethane/Rare Earth Nanocomposite Membranes by Electrospinning and Its VOCs Absorption Capacity from Air, *Nanomaterials*, 7 (2017) 1-11.
- [4] N. Hu, J. Tan, X. Wang, X. Zhang, P. Yu, Volatile organic compound emissions from an engine fueled with an ethanol-biodiesel-diesel blend, *Journal of the Energy Institute*, 90 (2017) 101-109.
- [5] J.C. Ge, J.H. Kim, N.J. Choi, Electrospun Polyurethane/Loess Powder Hybrids and Their Absorption of Volatile Organic Compounds, *Advances in Materials Science and Engineering*, 2016 (2016) 1-8.
- [6] N. Bhardwaj, S.C. Kundu, Electrospinning: a fascinating fiber fabrication technique, *Biotechnology Advances*, 28 (2010) 325-347.
- [7] Y. Dzenis, Spinning continuous fibers for nanotechnology, *Science*, 304 (2004) 1917-1919.
- [8] E. Scholten, L. Bromberg, G.C. Rutledge, T. A. Hatton, Electrospun polyurethane fibers for absorption of volatile organic compounds from air, *ACS Appl. Mater. Interfaces*, 3 (2011) 3902-3909.
- [9] Y. Liu, M. Park, B. Ding, J. Kim, M. El-Newehy, S.S. Al-Deyab, H.Y. Kim, Facile electrospun Polyacrylonitrile/poly (acrylic acid) nanofibrous membranes for high efficiency particulate air filtration, *Fibers and Polymers*, 16 (2015) 629-633.
- [10] T. Hyodo, T. Hashimoto, T. Ueda, O. Nakagoe, K. Kamada, T. Sasahara, S. Tanabe, Y. Shimizu, Adsorption/combustion-type VOC sensors employing mesoporous  $\gamma$ -alumina co-loaded with noble-metal and oxide, *Sensors and Actuators B: Chemical*, 220 (2015) 1091-1104.
- [11] X. Fan, B. Du, Selective detection of trace p-xylene by polymer-coated QCM sensors, *Sens. Actuators B: Chem.*, 166 (2012) 753-760.
- [12] H.Y. Yoo, S. Bruckenstein, A novel quartz crystal microbalance gas sensor based on porous film coatings. A high sensitivity porous poly (methylmethacrylate) water vapor sensor, *Anal. Chim. Acta*, 785 (2013) 98-103.