전기방사법을 이용하여 PAN / Pitch Blend로 제작된 나노 섬유의 흡착 특성

황경준, 심왕근[1], 김찬[1], 양갑승[1], 문희[1], 이재욱*
서남대학교 환경화학공학부
[1]전남대학교 응용화학공학과 기능성 나노 신화학소재센타
(jwlee@seonam.ac.kr*)

Preparation and Adsorption Characteristics of PAN / Pitch Blend Nanofibers by Electrospinning Method

Kyung-Jun Hwang, Wang-Geun Shim[1], Chan Kim[1], Kap-Seung Yang[1],
Hee Moon[1], Jae-Wook Lee*
Department of Environmental and Chemical Engineering, Seonam University
[1]Center for Functional Nano Fine Chemicals and Faculty of Applied Chemical Engineering,
Chonnam National University
(jwlee@seonam.ac.kr*)

INTRODUCTION

Compared to granular and powdered activated carbon, activated carbon fibers (ACF) have many advantages such as high adsorption capacities, high mass transfer rates for both adsorption and desorption[1]. Recently, therefore, they have been receiving much attention as adsorbents and catalysts. It has been known that the porous structure and adsorption properties of ACF are highly influenced by the nature of the precursors and the method of activation. In general, many precursors including PAN, cellulose, phenolic resin and coal tar pitch have been widely used for the preparation of ACF by physical activation with CO_2 or steam or chemical activation with KOH and NaOH. Electrospinning provides a simple and highly versatile method of fabricating nanofibers from a polymer solution at high voltage by using an electrostatically repulsive force and an electric field between two electrodes[2,3]. It seems to be very interesting to investigate the preparation and adsorption properties of PAN / pitch blend nanofibers. However, experimental and theoretical adsorption studies of composite PAN / Pitch nanofibers have been very limited to date. In this study, ACF was fabricated by electrospinning the PAN and pitch dissolved in dimethylformamide. The samples were characterized by SEM, BET, and XRD. To understand the adsorption properties of ACF, the adsorption equilibrium and kinetics of two adsorbates (BPA and congo red) were studied. Adsorption kinetics was evaluated by the pseudo-second-order model.

EXPERIMENTAL DETAILS

Polyacrylonitrile (PAN, 10wt%) and pitch were dissolved in dimethylformamide. The solution was spun into the fiber web through the capillary positively charged using an electrospinning apparatus at DC 10-25 kV (HYP-303D Power Supply, Han Young Co., Korea). The negative electrode was connected to the drum winder collecting the webs. The details have been reported elsewhere[1,2]. The adsorption experiments were carried out using

BPA and CR, purchased from Aldrich Co. (USA). The adsorption experiments were conducted by adding different amounts of ACF into a flask containing 100 ml of dye solution. After shaking in a constant temperature incubator at constant temperature (298.15 K) for 3 days to give sufficient contacting time for equilibrium, samples were taken from the flask and filtered through a Whatman glass microfilter. The filtrate was then measured for the dye concentration. In the meantime, the adsorption kinetic experiments were conducted in a Carberry-type batch adsorber (1.0 10^{-3} m^3) at 300 rpm to obtain the concentration decay curves as a function of time. The concentration was evaluated using a UV spectrophotometer (Shimadzu UV-160A, Japan). Solution pH was determined by using the pH meter (Orion, USA).

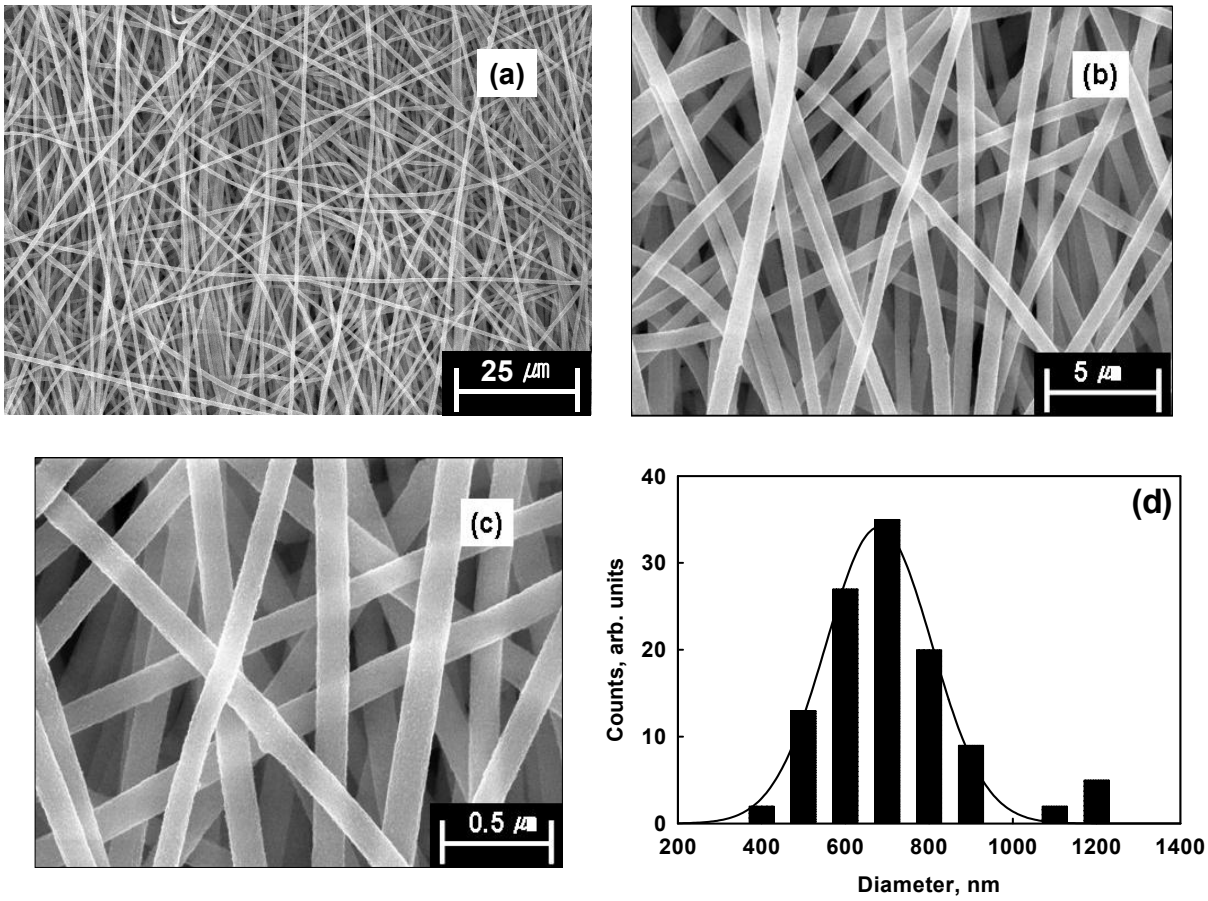

Fig. 1. FE-SEM images at PAN / Pitch : (a) 1k, (b) 5k, (c) 10k, and (d) size distribution.

RESULTS AND DISCUSSION

Nitrogen adsorption-desorption isotherms were measured on an ASAP 2010 volumetric adsorption apparatus (Micrometrics) at 77.4 K. The surface area was calculated by using the BET method. The pore size distribution was obtained by density functional theory. The surface area was found to be 1420 m^2 g^{-1} and the average pore diameter 18 Å. Fig. 1 shows an example of scanning electron micrographs (SEM) (Hitachi, S-4100, Japan) for ACF-800 showing a highly uniform diameter distribution. The specific surface area and pore size

increased with increasing activation temperature. The progressive temperature rise from 700 to 800 ^{o}C resulted in increasing the reaction rate of carbon burn-off. The reaction enhanced the existing pores and created new porosities. However, there is no significant change in average pore diameter although the micropore volume fraction was changed with increasing activation temperature.

Adsorption kinetics is one of the most important properties that determine the potential applications of ACFs[4-6]. The adsorption kinetic experiments were carried out at different types of ACF and PAC, temperatures (298.15, 308.15, 318.15 K), pH (3, 7, 10), and concentrations (10, 30, 50, 70, 100 mg l^{-1}). It was observed that the pseudo-first-order model explains the initial stages where rapid adsorption occurs well but cannot be applied for the entire adsorption process. Thus, the kinetic data were analyzed with the pseudo-second-order model[7,8]

$$\frac{dq}{dt} = k_2(q_e - q)^2 \quad (1)$$

Integrating for the boundary conditions q = 0 to $q = q_t$ at t = 0 to $t = t$, gives,

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e}, \quad (2)$$

$$h = k_2 q_e^2, \quad (3)$$

where k_2 (g mg^{-1} min^{-1}) is the second-order rate constant determined by the plot of t / q_t vs. t. Figs. 2 and 3 show the typical examples of the effect of adsorbates and different adsorbents. Note that the correlation coefficients (R^2) of the pseudo-second-order model are very close to 1. This result implies that adsorption kinetics can be successfully described by the pseudo-second-order model. The rate constant, k_2 determined in this study was in the range of 0.05~1.25 g mg^{-1} min^{-1}. Especially, ACF prepared using PAN / Pitch blend solution by electrospinning technique shows higher adsorption kinetics compared to commercialized PAC.

CONCLUSION

For the application of ACF fabricated by electrospinning of polyacrylonitrile and pitch solutions, adsorption equilibrium and kinetics were investigated. Adsorption equilibrium data of BPA and CR were correlated well with Toth equation. The internal mass transfer coefficients of BPA were much faster than that of CR because of the different molecular dimensions and solubility. The adsorption equilibrium and kinetics studies indicate that ACF can successfully be applied for many adsorption fields.

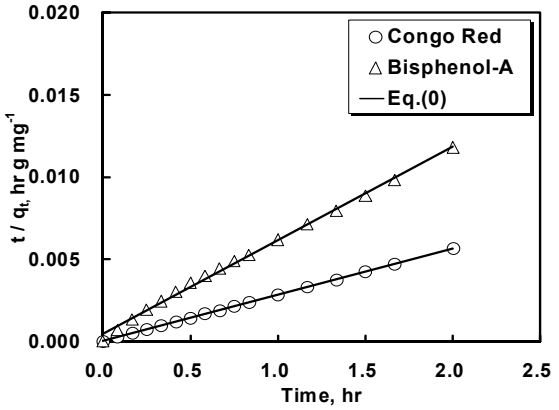

Fig. 2. Adsorption kinetics of CR and BPA.

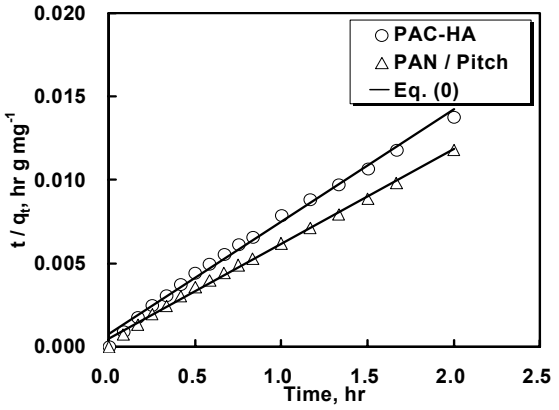

Fig. 3. Adsorption kinetics of PAC and ACF.

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