Preparation of Nanocarbon-Supported Nanofiber Fabric for Purification of Contaminated Water

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Received 13 August 2019; accepted for publication 13 December 2019

Abstract

In this study, a composite fabric was prepared by combining nanofiber having an extremely high specific surface area with nanosized carbon black (CB) having a solute adsorption capacity to purify contaminated water. The nanofiber fabric made of polyacrylonitrile (PAN) with a mean fiber diameter of 400 nm was used as a base material. The CB particles with an original size of 20 nm were used as adsorbent and dispersed in pure water at the concentration of 10 g/L. Before preparation, the CB particles were oxidized by mixing CB with 70% nitric acid at a ratio of 1 g to 1 mL and heating for 2 hours with agitation. The surface of CB particles became hydrophilic by oxidation, and the size of CB particles became the original one in the dispersion. The nanofiber fabric was immersed in the CB dispersion and shaken for 2 hours. After taking out and rinsing it lightly, CB was immobilized on the surface of nanofibers by heating for 1 hour at 150 °C. The adsorption performances of the different CB particles and the prepared CB-supported PAN nanofiber fabrics were evaluated by the static adsorption test using methylene blue (MB) as an adsorbate. The saturated adsorption amount of the oxidized CB-supported PAN nanofiber fabric was as high as 96.2 mg/g. The dynamic adsorption test of MB was also carried out on the untreated CB-supported PAN nanofiber fabric and the oxidized CB-supported PAN nanofiber fabric. Model equations based on the pseudo-first-kinetic model were derived to analyze the various parameters of the dynamic adsorption. The obtained results suggested a potential application of the oxidized CB-supported PAN nanofiber fabric in the contaminated water treatment field.

Key Words : Nanofiber fabric, Carbon black, Composite, Adsorption, Water purification

1. Introduction

Organic dyes are widely used in many industries, such as textile finishing, cosmetics, printing, and plastic [1]. Environmental pollution caused by organic dyes in contaminated water has received increased concern in recent years because of the rapid development of urbanization and industrialization [2, 3]. Almost all of these dyes are synthetic and composed of complex aromatic structures [4]. Water contaminated by these dyes poses a tremendous threat to ecological and human health [5]. A variety of physical and chemical strategies have been developed for the removal of the dyes in water, such as chlorination, ozonation, photocatalytic degradation, adsorption, and electrochemical methods [6-9]. Nevertheless, the use of these techniques is limited by high operation cost and ineffectiveness in treating effluent with low dye concentrations. Among these methods, adsorption has been widely used due to its relatively low-cost, efficiency, and ease of operation.

The adsorption process uses an adsorbent, a material that is able to bind the toxic substance or molecule to its surface. Numerous materials have been prepared for use as adsorbents. Recently, electrospun nanofibers are considered to be promising as an alternative to traditional adsorbents due to high porosity and large specific surface area [10, 11]. Another advantage of electrospun nanofibers over conventional adsorbents is the modifiable nature, as they can be easily designed to obtain the required functional surface adsorption site or specific structure for providing better adsorptive capacity. A lot of researchers have been devoted to developing functional nanofiber fabrics for the removal of dyes from aqueous solutions [12-14]. Shen et al. have prepared a mesoporous alumina nanofiber for the removal of methyl orange dye [15]. The mesoporous alumina nanofiber was obtained after calcining the as-prepared polyvinylpyrrolidone/alumina nanofiber in air above 450 °C for 6 hours. Zarrini et al. have fabricated a type of nylon-6-polyaniline nanocomposite web through coating the surface of nylon-6 nanofibers with polyaniline via in-situ polymerization [16].

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The produced nylon-6-polyaniline nanocomposite web adsorbed up to 370 mg/g methyl orange. Gopakumar et al. used Meldrum's acid as an esterification agent to modify cellulose nanofiber (CNF) based polyvinylidene fluoride (PVDF) membrane via a nonsolvent-assisted methodology [2]. Crystal violet dye's adsorption by the PVDF electrospun fiber was 1.368 mg/g, and that of the unmodified CNF-based PVDF fiber was 2.948 mg/g. In contrast, the crystal violet dye's adsorption by the modified CNF-based PVDF fiber was 3.984 mg/g, which showed 2 to 3 times higher adsorption than the PVDF electrospun fiber. Gao et al. calcined the electrospun polyvinyl alcohol (PVA)- Fe_3O_4 composite fiber at 600°C for 4 hours, and obtained a hollow $\alpha\text{-Fe}_2\text{O}_3$ nanofiber made of rice-like nanorods, which exhibited a methyl orange adsorption capacity of 80.6 mg/g [17]. Methylene blue (MB) is commonly used in the wood, cotton and silk industries, whose chief risk regarding its presence in wastewater arises from its harmful effect upon exposure to eyes, as well as possibility of nausea, vomiting and diarrhea. Aluigi et al. have extracted keratin protein from wool by sulphitolysis and transformed keratin powder into nanofiber fabric through the electrospinning process [18]. The MB adsorption capacity of the obtained keratin nanofiber fabric is 170 mg/g. The main concerns of these reported studies are either a long adsorption equilibrium time or complex preparation processes along with costly adsorbent materials. Therefore, high efficiency and low-cost adsorbent material is the foremost need of adsorption technique. Polyacrylonitrile (PAN) has been used to produce nanofibers due to its excellent characteristics and commercial availability, as well as its non-toxic nature [19]. Carbon black (CB) has been demonstrated to be an excellent adsorbent for diverse organic compounds, including dyes [20, 21]. PAN nanofiber fabrics are able to provide a platform for dye adsorption with CB nanoparticles attributing to their nano-size effect and high specific surface area. Furthermore, the adsorption or filtration process of CB-supported nanofiber fabric can avoid the secondary pollution caused by the generation of a large amount of sludge by using a carbon adsorbent.

The objective of this study was to prepare a composite fabric with an excellent adsorption capacity by combining PAN nanofiber fabric with functionalized CB particles for the purification of contaminated water. Pretreatment of CB particles and its influence on particle size were investigated. Surfaces of the CB-supported nanofiber fabrics were characterized by scanning electron microscope. Methylene blue was selected as a model dye pollutant to investigate the adsorption property of the prepared composite nanofiber fabrics. The adsorption capacity was evaluated through the static adsorption test, and the dynamic adsorption behavior was also studied through the dynamic adsorption test and the analysis by the derived model equations.

2. Preparation of CB-supported nanofiber fabric

2.1 Pretreatment of CB particles

Carbon black (CB) (Nominal diameter 20 nm), purchased from Asahi Carbon Co., Ltd. (Japan), was used as an adsorbent. With the aim of improving the adsorption capacity, the CB particles were subjected to the three following pretreatments: pH control of CB dispersion, activation of CB particles by KOH, and oxidation of CB particles. (1) pH control of CB dispersion: CB particles were added into pure water at a concentration of 1.0 wt% and dispersed under ultrasonic irradiation for 20 minutes. Since the initial pH value of the CB dispersion was 7.3, HCl was added to adjust the pH value to 3.2. (2) Activation of CB particles by KOH: The CB particles were activated by mixing with KOH and heating for 1 hour at 800 °C under an atmosphere of N_2 gas flow of 0.5 L/min. Finally, activated CB particles were rinsed well in water after neutralization with HCl for the removal of residual KOH. (3) Oxidization of CB particles: The CB particles were oxidized by mixing with 70% nitric acid at a ratio of 1 g to 1 mL and heating for 2 hours with agitation. Finally, oxidized CB particles were rinsed well in water for the removal of residual nitric acid.

The particle size distribution of the CB dispersion was measured by a dynamic light scattering device (DLS-7000) manufactured by Otsuka Electronics Co., Ltd. (Japan). Figure 1 shows the size distribution of CB particles by disparate pretreatments. Comparing with the size distribution of the CB particles in the dispersions of pH 7.3 and 3.2, the size of the activated CB particles increased, while the size of the oxidized CB particles reduced as revealed by the distribution data. The calculated average particle size results are displayed in Table 1. The average diameters of CB particles in the dispersions of pH 7.3 and 3.2 are 60.4 nm and 50.7 nm, with a slight change. The activation of CB led to an increase in specific surface area of CB and simultaneously caused the flocculation of CB particles, resulting in the average diameter to enlarge to 72.4 nm. The CB particles had the smallest average diameter of 23.5 nm.

Fig. 1 Size distribution of CB particles.

Table 1 Average particle size of CB.

Pretreatment	$D_{p,av}$ [nm]
CB (pH 7.3)	60.4
CB (pH 3.2)	50.7
Activated CB	72.4
Oxidized CB	23.5

after oxidization, which was close to their original size. Because of the hydrophilic functional groups formed on the CB surface by the oxidation treatment, the oxidized CB particles were hardly aggregated in water and kept in a well dispersed state.

2.2 Immobilization of CB onto nanofibers

The polyacrylonitrile (PAN) nanofiber fabric supplied by Japan Vilene Co. was used as a base material. The mean fiber diameter of the fabric was 400 nm, and the areal weight was 17.2 g/m². Four dispersions were prepared by dispersing raw CB particles at two different pH environments, activated CB particles, and oxidized CB particles separately in pure water. The pH value of one of the raw CB dispersions was 7.3 without adjustment and another one was adjusted to pH 3.2. Round mats of nanofiber fabric with a diameter of 2.5 cm were immersed in 20 mL CB dispersions and shaken for 2 hours. After taking them out from the CB dispersions and rinsing lightly with pure water, the nanofiber fabrics were dried at 50 °C for 2 hours. Subsequently, CB particles were immobilized on the surface of nanofibers by heating for 1 hour at 150°C. In order to remove the unfixed CB particles, the prepared fibers were immersed into 20 mL water and shaken for 30 minutes, then washed by an ultrasonic cleaner for 10 minutes. The samples were washed several times until no CB particles were detected, then again dried at 50 °C for 2 hours.

Photographs of the original PAN nanofiber fabric mat and the CB-supported nanofiber fabric mats fabricated under various conditions are shown in Fig. 2. The fabric mat mass of original fabric, composite with untreated CB at pH 7.3, composite with

Fig. 2 Appearance of PAN nanofiber fabric mats: (a) original fabric, (b) composite with untreated CB at pH 7.3, (c) composite with untreated CB at pH 3.2, (d) composite with activated CB, (e) composite with oxidized CB.

untreated CB at pH 3.2, composite with activated CB, and composite with oxidized CB were 8.5, 10.4, 12.1, 9.4, and 10.1 mg, respectively. As seen in Fig. 2b and Fig. 2c, both of the untreated CB-supported PAN nanofiber fabric mats exhibited pure black, but the carbon amount immobilized on the fabric under acid condition (pH 3.2) is greater. The activated CB-supported PAN nanofiber fabric mat displayed black-gray from the appearance, as presented in Fig. 2d. Activated CB particles were difficult to fix on the surface of the fabric because of a broad particle size distribution caused by flocculation. The CB particles with small size were fixed, while the larger diameter particles were prone to fall off during the rinsing process. In consequence, the amount of CB particles loading on the fabric reduced and CB distribution on the fabric surface became uneven, which resulted in the black-gray color of the fabric mat. The oxidized CB-supported PAN nanofiber fabric mat displayed gray, as shown in Fig. 2e. The diameter of CB particles reduced remarkably due to the oxidation treatment, which led to light wavelength reflection inconsistent to that of usual CB particles. The typical SEM images of original PAN nanofiber fabric mat, composite with untreated CB at pH 7.3, and composite with oxidized CB are shown in Fig. 3. The accumulation of CB particles

Fig. 3 SEM images of PAN nanofiber fabric mats.

can be observed on the fiber surface of the untreated CB-supported PAN nanofiber fabric, which is corresponded to the pure black color on the photograph of Fig. 2b. Interestingly, the CB particles on the fiber surface of the oxidized CB-supported PAN nanofiber fabric were too small to be observed by SEM. The ultrafine and mono-dispersed CB particles distributed evenly on the surface of the fiber, showing the gray color in Fig. 2e. In addition, both untreated CB-supported PAN nanofiber fabric, and oxidized CB-supported PAN nanofiber fabric showed a conventional structure without distinct change in morphological structure compared with the original PAN nanofiber fabric.

3. Adsorption results and discussion

3.1 Static adsorption on CB particles

Methylene blue (MB) ($C_{16}H_{18}N_3SCl \cdot 3(H_2O)$, $M_w = 373.90$) was supplied by Wako Pure Chemical Industries, Ltd. (Japan). A standard stock solution of MB dye was prepared by dissolving a certain amount of dye into pure water to get 200 mg/L of MB solution. Afterwards, different concentrations were obtained from a series of dilution. To investigate the static adsorption properties, 25 mL of CB dispersion was mixed with 25 mL of MB aqueous solution at different concentrations, and the mixed solution was stirred at 300 rpm for 1.5 hours. The CB particles were separated from the solution by a centrifugal filter with a pore diameter of 0.1 μm at 3000 rpm for 5 minutes. The centrifugal filter was washed three times by MB filtrate in advance to reduce the error caused by the adsorption of MB on the centrifuge components. The MB concentration was measured by UV-vis spectroscopy (UV-1800, Shimadzu Corp. (Japan)) at a wavelength of 665 nm. The amount of adsorbed MB was calculated based on the following formula:

$$\Gamma = \frac{(C_0 - C)V}{W} \quad (1)$$

where Γ is the adsorption amount (mg/g), C_0 is the initial concentration of MB (mg/L), C is the final concentration of MB (mg/L), V is the volume of MB solution (L), and W is the weight of the adsorbent (g).

The effect of initial MB concentration on the adsorption capacity was studied in order to determine the maximum loading capacity of various CB particles. The isothermal adsorption process of the CB particles fits the Langmuir isothermal adsorption models well. The Langmuir model is based on the assumption of adsorption homogeneity, such as equally available adsorption sites, monolayer surface coverage, and no interaction between adsorbed species. The adsorption process can be expressed by the following equation:

$$\Gamma = \frac{\Gamma_s K C^*}{1 + K C^*} \quad (2)$$

where Γ_s is the saturated adsorption capacity (mg/g), C^* is the

equilibrium concentration of MB in solution (mg/L), and K is the dissociation constant of the system (L/mg). The linear form of Langmuir equation (2) is depicted as:

$$\frac{C^*}{\Gamma} = \frac{C^*}{\Gamma_s} + \frac{1}{K\Gamma_s} \quad (3)$$

This equation means that the values of Γ_s and K are determined from the slope and the intercept of the linear line by plotting (C^*/Γ) versus C^* .

The adsorption isotherm Γ versus C^* in the static adsorption of MB onto CB particles is shown in Fig. 4, comparing the experimental data with the calculations according to Eq. (2). The amount of MB adsorbed on the CB particles increased with the rise in the equilibrium concentration of MB. Significantly, the adsorption capacity of the activated CB particles and the oxidized CB particles was higher than that of untreated CB particles. The saturated adsorption capacity obtained from Eq. (3) is listed in Table 2. The saturated adsorption capacity of the activated CB particles was 359.5 mg/g, which is 7.6 times greater than that of the untreated CB particles, 47.0 mg/g. The BET specific surface area of the activated CB particles was 773.9 m^2/g , which is 7.4 times larger than that of the untreated CB particles, 105.2 m^2/g . This indicates that the increase of specific surface area contributed to the rise of the adsorption quantity. Otowa et al. argued that the metallic potassium was mobile at the activation temperature, and was intercalated to the carbon matrix [22]. As a result, several atomic layers of carbon widened and formed pores. They found that the petroleum coke placed next to the activation zone of 800 $^{\circ}C$

Fig. 4 Adsorption isotherms of MB onto different CB particles.

Table 2 Saturated adsorption capacity of different CB particles.

Pretreatment	Γ_s [mg/g]
CB	47.0
Activated CB	359.5
Oxidized CB	855.4

was activated, and the BET specific surface area was about $800 \text{ m}^2/\text{g}$ which was very close to $773.9 \text{ m}^2/\text{g}$ obtained in our study. After all, the oxidized CB particles had the largest adsorption capacity of 855.4 mg/g . As seen in Table 1, the average diameter of the CB particles dropped from 60.4 nm to 23.5 nm by the hydrophilic functional groups formed during the oxidation process, which was $1/2.6$ of the untreated CB particles. This indicates that the specific surface area of the oxidized CB particles increased 2.6 times to that of the untreated CB particles. In contrast, the adsorption capacity of the oxidized CB particles presented 18.2 times larger than that of the untreated CB particles as seen in Table 2. The decrease of particle diameter was one of influential factors on the adsorption capacity, but affinity created by the functional groups was the main reason for the increase of the adsorption amount. Asai et al. discussed the functional groups such as carboxyl, carbonyl, and phenolic groups formed on the CB surface by nitric acid oxidation [23]. Due to the affinity of these functional groups, the oxidized CB particles exhibited significantly high adsorption performance in our experiments. EI-Hendawy detected the surface-chemical changes of activated carbon by FTIR to invest the impact of oxidation with nitric acid [24]. They observed the absorption bands assigned to carboxyl, carbonyl, and phenolic groups. Also, they emphasized that the surface oxygen groups enhance the hydrophilic character of the carbon surface.

3.2 Static adsorption on CB-supported nanofiber fabric

The static adsorption test of the prepared CB-supported nanofiber fabrics was conducted by soaking them into the MB aqueous solutions at varied concentrations with shaking until a state of adsorption equilibrium was reached. Then the equilibrium concentration C^* and the equilibrium adsorption amount Γ of MB were measured. The experimental data and the calculations according to Eq. (2) of the adsorption isotherms of MB onto the different fabrics are shown in Fig. 5a. In the static adsorption test of five fabrics, except for the oxidized CB-supported nanofiber fabric,

Table 3 Saturated adsorption capacity of different PAN nanofiber fabrics.

PAN Fabrics	Γ_s [mg/g]
Without CB	1.9
With CB (pH 7.3)	5.0
With CB (pH 3.2)	6.1
With Activated CB	18.3
With Oxidized CB	96.2

the equilibrium adsorption amount of the other fabrics was less than 20 mg/g . An enlargement of Fig. 5a, where the equilibrium adsorption amount was less than 20 mg/g , is displayed in Fig. 5b, excluding the data of the oxidized CB-supported nanofiber fabric. Furthermore, the saturated adsorption capacity obtained from Eq. (3) is listed in Table 3.

As a result, the value of Γ_s was 1.9 mg/g for the original nanofiber fabric, 5.0 mg/g for the untreated CB-supported nanofiber fabric, and 6.1 mg/g for the untreated CB-supported nanofiber fabric prepared under the acid environment. When CB-supported nanofiber fabric was prepared under the acid environment, the amount of supported CB was slightly increased due to the reduction of electrostatic repulsion between CB particles and PAN fiber. The value of Γ_s was 18.3 mg/g for activated CB-supported nanofiber fabric. The adsorption amount was increased by the activation of CB, whose specific surface area increased from $105.2 \text{ m}^2/\text{g}$ to $773.9 \text{ m}^2/\text{g}$, as mentioned before. However, the activation induced the flocculation of CB particles and consequently reduced the rate of increase in the amount of the supported CB, resulting in a smaller adsorption amount than expected. The saturated adsorption capacity of the oxidized CB-supported nanofiber fabric reached 96.2 mg/g . The distinct increase in the amount of adsorption was attributed to the rise in hydrophilic groups and surface area by the process of CB oxidation. Thus, the oxidation of CB is an essential pretreatment to attain high solute adsorption performance.

Fig. 5 Adsorption isotherms of MB onto different PAN nanofiber fabrics.

Fig. 6 Experimental set-up of dynamic adsorption.

3.3 Dynamic adsorption

3.3.1 Process of MB dynamic adsorption

The MB dynamic adsorption test was carried out by permeating the MB solution through the untreated CB or the oxidized CB-supported PAN nanofiber fabric, as schematically shown in Fig. 6. The fabric mats packed into the filter holder had an effective diameter of 2.2 cm and a permeation area of 3.8 cm², and then the filter holder was mounted onto the dynamic adsorption system shown in Fig. 6. Afterwards, MB solution was injected into the filter holder by the syringe pump (SRS-2, AS ONE Co. (Japan)), in the meanwhile, the MB concentration of solution permeating through the fabric was continuously monitored via the UV detector. Dynamic adsorption performance was evaluated under various conditions involving different fabric mat mass W_f (0.01, 0.03, 0.05 g), initial MB concentration C_0 (from 0.08 to 30 mg/L), and permeation rate q_v (from 10 to 50 mL/h).

3.3.2 Mathematical model for MB dynamic adsorption

A mathematical model was derived to analyze the results of the dynamic adsorption test. Assuming that adsorption rate, in accordance with the pseudo-first-kinetic model [25, 26], is proportional to the adsorption sites number of adsorbent, the following formula can be expressed:

$$\frac{d\Gamma_t}{dt} = k(\Gamma_\infty - \Gamma_t) \quad (4)$$

where Γ_t is the adsorption amount (kg/kg) at arbitrary time t (s), Γ_∞ is the adsorption amount (kg/kg) at $t = \infty$, k is the rate constant (s⁻¹). Integrating Eq. (4), Γ_t can be expressed as:

$$\Gamma_t = \Gamma_\infty \{1 - \exp(-kt)\} \quad (5)$$

Rejection R is defined in terms of the fraction of the species in the feed that is retained by the filter medium:

$$R = 1 - C_p / C_0 \quad (6)$$

where C_0 is the MB concentration of feed solution (kg/m³), and C_p is the MB concentration of permeate solution (kg/m³). Rejection can also be defined as the ratio of MB adsorption rate $W_f(d\Gamma_t/dt)$ to MB inflow rate $C_0 q_v$, given by:

$$R = \frac{W_f}{C_0 q_v} \frac{d\Gamma_t}{dt} \quad (7)$$

where W_f is the weight of the fabric mat (kg), q_v is the permeating rate (m³/s). Substituting Eqs. (4) and (5) into Eq. (7), where $t = v/q_v$, v is the permeate volume (m³), results in the following equation:

$$R = \frac{W_f k \Gamma_\infty}{C_0 q_v} \exp\left(-\frac{k}{q_v} v\right) \quad (8)$$

Because the value of rejection cannot be greater than 1,

$$R = 1 \quad \text{at} \quad 0 \leq v \leq \frac{q_v}{k} \ln \frac{W_f k \Gamma_\infty}{C_0 q_v} \quad (9)$$

$$R = \frac{W_f k \Gamma_\infty}{C_0 q_v} \exp\left(-\frac{k}{q_v} v\right) \quad \text{at} \quad v > \frac{q_v}{k} \ln \frac{W_f k \Gamma_\infty}{C_0 q_v} \quad (10)$$

Equations (9) and (10) are obtained for the dynamic adsorption model. According to the two equations, the establishment condition of the dynamic adsorption period of $R = 1$ is as follows:

$$\frac{W_f k \Gamma_\infty}{C_0 q_v} > 1 \quad (11)$$

where the left side of Eq. (11) is R at $v = 0$ in Eq. (8). Taking the logarithm on both sides of Eq. (8),

$$-\ln R = \frac{k}{q_v} v - \ln \frac{W_f k \Gamma_\infty}{C_0 q_v} \quad (12)$$

Therefore, after plotting a linear line with $\ln R$ and v , the values of k and Γ_∞ can be calculated from the slope and the intercept. The fitting curves of the rejection can be obtained by substituting k and Γ_∞ into Eq. (9) or (10).

3.3.3 Discussion of dynamic adsorption

The effects of permeation rate on the dynamic adsorption behavior were studied by varying permeation rate q_v of MB solution through the untreated CB-supported PAN nanofiber fabric. The experimental data and the calculated rejection based on the dynamic adsorption model equations (9) and (10) are plotted in Fig. 7, where the fitting curves of the rejection are indicated by solid lines. The graph shows that the experimental data followed well with the calculated values. With the increase of permeate volume, the rejection revealed a general trend of decrease though the margins of the decline varied. A noticeable reduction in the rejection occurred

Fig. 7 Dynamic adsorption test results and calculated rejection curves at different permeation rates.

during a permeation rate of 50 mL/h. For the fabrics of the same mass, there was the same number of adsorption sites for MB capture, while a jump of MB amount caused by a larger permeation rate resulted in the rapid occupation of MB to the fabric surface. In light of the derived Eq. (8), $k\Gamma_{\infty}$ is considered as a critical parameter for evaluating dynamic adsorption performance. Thus, to clarify the correlation between $k\Gamma_{\infty}$ and other parameters in the dynamic adsorption model, the values of $k\Gamma_{\infty}$ calculated from the untreated CB-supported PAN nanofiber fabric are plotted against the permeation rate q_v in Fig. 8. The graph clearly demonstrates that there was a good linear relation between $k\Gamma_{\infty}$ and the permeation rate. It should be pointed out that $k\Gamma_{\infty}$ had similar values at the fabric mass of 0.03 g and 0.05 g, when the permeation rate was 12 mL/h. The results conclusively demonstrated that $k\Gamma_{\infty}$ is related to the permeation rate and is almost unaffected by the mass of the adsorbent.

The influence of the initial solution concentration on the dynamic

Fig. 8 Correlation between $k\Gamma_{\infty}$ and permeation rate.

Fig. 9 Dynamic adsorption test results and calculated rejection curves at different initial MB concentrations.

adsorption behavior is an important parameter to investigate since it is altering with the source of effluent and affects the service period of the fabric. Figure 9 shows the dynamic adsorption data at different initial MB concentrations C_0 for the oxidized CB-supported PAN nanofiber fabric. The rejections calculated according to the dynamic adsorption model equations are plotted by solid lines in Fig. 9 as well. As can be seen, the experimental values fit the calculated values well. The rejection exhibited a sharp descend at an initial MB concentration of 30 mg/L. This is in agreement with the impact of the permeation rate, since a rise of MB amount attributed to the high concentration led to the speedy migration of MB to the fabric surface. In contrast to the rejection values of the adsorption by 0.01 g fabric, there were dead volume areas in the adsorption by 0.03 g fabric owing to the abundance of MB adsorption sites. To explore how the $k\Gamma_{\infty}$ values respond to the initial concentration C_0 , the values of $k\Gamma_{\infty}$ calculated from the oxidized CB-supported PAN nanofiber fabric are plotted against the initial concentration of MB in Fig. 10. In the experimental range, $k\Gamma_{\infty}$ increased roughly

Fig. 10 Correlation between $k\Gamma_{\infty}$ and initial MB concentration.

Fig. 11 Comparison between static and dynamic adsorption.

in proportional to C_0 . Notably, $k\Gamma_\infty$ had near values at the fabric mass of 0.01 g and 0.03 g, when the initial concentration was 10 mg/L. It is safe to say that $k\Gamma_\infty$ is an MB amount-related value, independent of the mass of the adsorbent. Accordingly, the dynamic adsorption process in various conditions can be estimated by the model equation after clarifying the permeation rate and the initial concentration.

Additionally, the difference in adsorption capacity between static adsorption and dynamic adsorption was examined in the form of Fig. 11. This figure depicts the adsorption isotherm in static adsorption of the oxidized CB-supported nanofiber fabric, along with the corresponding results of dynamic adsorption. The values of Γ_∞ obtained after a sufficient adsorption time in dynamic adsorption at varied initial concentrations C_0 of MB are assumed to correspond to the values of equilibrium adsorption amount Γ at varied equilibrium concentrations C^* of MB in static adsorption. At the corresponding MB concentration, the values of Γ_∞ were slightly smaller than the equilibrium adsorption amount of MB in the static adsorption, nevertheless, extremely close to each other. Therefore, by regarding the values of the equilibrium adsorption amount from the static adsorption test as the values of Γ_∞ and substituting them into the derived dynamic adsorption model equations, the dynamic adsorption process can be estimated approximatively.

4. Conclusions

In this research, the composite fabrics were fabricated by immobilizing various CB particles on the scaffold of PAN nanofiber fabric. The effects of pretreatment on the CB particle size and adsorption properties were investigated. The oxidation process, which increased the CB particles' specific surface area and enhanced the hydrophilicity of the surface, is necessary for CB before loading on the fabric-based material. The prepared CB-supported PAN nanofiber fabrics were examined for the static and dynamic adsorption behavior of MB. The static adsorption performance of the CB particles and the CB-supported PAN

nanofiber fabrics followed the Langmuir isotherm model. The dynamic adsorption process of the CB-supported nanofiber fabric and the oxidized CB-supported nanofiber fabric was in accordance with the pseudo-first-kinetic model. The adsorption amount Γ_∞ in the dynamic adsorption calculated by the derived model equations almost coincided with the static adsorption result. Using the oxidized CB-supported nanofiber fabric as an adsorbent material or filtration medium can avoid the secondary pollution caused by traditional materials in contaminated water treatment process. With its high MB adsorption capacity as well as low-cost preparation process, the oxidized CB-supported nanofiber fabric developed in this work might provide a new option for the removal of dyes in contaminated water.

Acknowledgements

This work was supported in part by JSPS KAKENHI Grant No. 25420801 and No. 16K06824, the Tatematsu Foundation, and Mukai Science and Technology Foundation. The authors would like to express the sincere gratitude for the financial support.

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