Research Article

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Removal of methylene blue in water by electrospun PAN/ β -CD nanofibre membrane

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Abstract: The polyacrylonitrile (PAN) nanofiber membrane prepared by the electrospinning technology was used as the matrix, and β -cyclodextrin (β -CD) was introduced into it to synthesize the composite nanofiber membrane. Taking methylene blue as the object, the adsorption performance of nanofiber membranes for dyes in the aqueous solution was studied. The structure, morphology, and specific surface area of the nanofiber membrane were characterized using FTIR, SEM, BET, XRD, and EDS. Meantime, the adsorption equilibrium was also explored. After being modified by cyclodextrin, a large number of cavity structures and hydrophobic binding sites were provided for the nanofiber membrane, and the adsorption performance was significantly improved. The results showed that the maximum adsorption capacity of the PAN/ β -CD blend nanofiber membrane (at 25°C) for methylene blue was 108.66 mg g⁻¹. The effects of pH, adsorption time, ion concentration, and adsorbent dosage on the adsorption capacity were also investigated. In addition, by fitting with the adsorption model, the adsorption process was more complex with the quasi-secondary adsorption kinetics and Langmuir isotherm adsorption model.

Keywords: electrospinning, polyacrylonitrile, cyclodextrin, adsorption, methylene blue

1 Introduction

Methylene blue is a phenothiazine salt that is relatively stable in air and alkaline in aqueous solution. Generally, it is widely used in the manufacture of ink and dyeing of biological and bacterial tissues, and it is also used in the medical field due to its reducing and sterilizing functions. Its chroma is very high, and it will seriously affect the transparency of water. A high concentration of methylene blue is toxic and carcinogenic, which causes great damage to the human body and the environment. Since methylene blue dye is biologically toxic and carcinogenic, it is difficult to carry out biodegradation, photolysis, and oxidative decomposition by conventional methods. In contrast, the adsorption method has the characteristics of lower cost, simple operation, significant effect, and less pollution. In addition, most adsorbents can be reused (1). Materials with higher porosity are often used as adsorbents. Currently, the most widely used adsorbents are zeolite, activated carbon, fiber membranes, and carbon-based materials (2,3).

Among most adsorbents, the nanofiber membrane has a diameter of between 1 and 100 nm and has the advantages of large specific surface area, good adsorption performance, and high porosity. Electrostatic spinning technology is the only technology used to prepare continuous nanofibers in China because it is suitable for all soluble high polymers (4–6). Under the action of the high-voltage electric field, the charged polymer overcomes its surface tension to form a charged jet and finally gets collected on the receiving plate to form ultra-fine fibers (7,8). As an innovative adsorption filter medium, electrospun nanofiber membrane has more pore structure, is low cost, and is an environmentally friendly material. Therefore, nanofiber membranes have a good research prospect in adsorption.

Currently, many researchers have used polyacrylonitrile (PAN) as the matrix to successfully prepare nanofiber membrane materials with the adsorption effect

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using the electrospinning technology. Polyacrylonitrile itself has good spinnability, nontoxicity, good chemical stability, light resistance, and weather resistance. However, the adsorption effect of the nanofiber membrane prepared by pure PAN is not very significant, and it can be modified by chemical modification. The structure of PAN contains $-\text{CN}$, which is easy to be modified, and some groups with adsorption properties such as $-\text{OH}$, $-\text{COOH}$, and $-\text{NH}_2$ can be introduced to improve its adsorption performance. Patel and Hota prepared the PAN nanofiber matrix based on the electrospinning technology and then chemically modified the surface of the obtained PAN nanofiber matrix into different amino (NH_2) functional groups toward the removal of neutral red dye (9). Saeed et al. prepared PAN-oxime nanofibers by the combination of the electrospinning technique and chemical modification of the nitrile group in the PAN. PAN nanofibers were chemically modified with amidoxime groups that are suitable for metal adsorption due to their high adsorption affinity for metal ions (10). Sahoo et al. synthesized the PAN-GO- Fe_3O_4 composite membrane, which improved the adsorption efficiency of $\text{Cr}(\text{VI})$ (11).

As an inexpensive sustainably produced cyclic oligosaccharide, β -cyclodextrin (β -CD) is one of the most promising environment-friendly materials for removing dyes or other pollutants from water by adsorption (12). β -CD is extracted from starch and is a ring composed of seven glucose residues and glycosidic bonds. It has a cavity structure, which can form inclusion compounds with organic dyes, inorganic ions, and so on, and when used as the host, its outer edge is hydrophilic and the inner cavity is hydrophobic, which can provide hydrophobic binding sites for the guest (13–16).

The purpose of this study is to prepare and characterize electrospun PAN/ β -CD-blended nanofiber membranes to effectively treat methylene blue dye in water. The PAN/ β -CD-blended nanofiber membranes have a good adsorption capacity due to hydroxyl groups that enable chelation with dyes. In addition, the morphology of the fibers is not destroyed during the blending of PAN and β -CD.

2 Materials and methods

2.1 Materials

PAN ($M_w \sim 150,000$) was provided by Shanghai Maclean Biochemical Co. β -Cyclodextrin (β -CD; $M_w \sim 113,498$) and N,N -dimethylformamide (DMF) were purchased from Sinopharm Group Chemical Reagent Co.

2.2 Preparation of electrospinning PAN/ β -CD blend nanofiber membrane

Before electrospinning, PAN and β -CD powder were dissolved in the DMF solution at room temperature and magnetically stirred for 36 h. Subsequently, the spinning solution was poured into a 10 mL syringe, and the syringe needle was made of stainless steel. The electrospinning device included a DW-N303-1ACDF0 laboratory high-voltage DC power supply (purchased from Dongwen High Voltage Power Supply (Tianjin) Co.), a TYD01 injection pump, and an aluminum foil receiving plate. During the preparation process, the voltage was 12 kV, the solution feed rate was $15 \mu\text{L min}^{-1}$, and the distance between the syringe needle and the receiving plate was 15 cm. The prepared PAN/ β -CD-blended nanofiber membrane could be easily peeled off from the aluminum foil, and the obtained membrane was stored in a vacuum oven at 80°C for 36 h. At the same time, pure PAN nanofiber membranes were also prepared for comparison.

2.3 Adsorption of electrospinning PAN/ β -CD blend nanofiber membrane

2.3.1 Adsorption experiment

The experiment used ultraviolet spectrophotometry for static adsorption. At the same time, the effects of addition of varying amounts of β -CD, initial concentration, contact time, pH value, and dosage of adsorbent on the adsorption experiment were investigated. Thereafter, the concentration of the solution after adsorption and the corresponding adsorption amount is calculated, and the adsorption amount is obtained by Eq. 1:

$$Q = \frac{(c_0 - c_1) \times V}{1,000 \times m}, \quad (1)$$

where Q is the adsorption capacity (mg g^{-1}), c_0 and c_1 are the initial and final concentrations, respectively, of adsorbate in a solution, V is the volume of the solution (mL), and m is the mass of the adsorbent (g).

2.3.2 Experiment of regeneration and reuse

In the experiment of regeneration and reuse, the reagent regeneration method was adopted. Since methylene blue is soluble in ethanol, ethanol was selected as the

regeneration reagent. After the adsorption experiment, the saturated adsorbent was taken out and placed in a conical flask, and a certain concentration of ethanol solution was added to desorption for 24 h under same conditions as the adsorption experiment. The desorption agent was washed with deionized water, and the desorption experiment was repeated five times after drying.

2.3.3 Adsorption kinetic model

In this article, the adsorption data are analyzed by quasi-first-order and quasi-second-order kinetic models, and the quasi-first-order kinetic model is expressed by Eq. 2:

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t, \quad (2)$$

where t is the adsorption time (min), Q_e is the equilibrium adsorption capacity (mg g^{-1}), Q_t is the adsorption capacity (mg g^{-1}) at time t , and k_1 is the quasi-first adsorption rate constant (min^{-1}).

The quasi-secondary kinetic model is represented by Eq. 3, and the initial adsorption rate h can be calculated by Eq. 4:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e}, \quad (3)$$

$$h = k_2 Q_e^2, \quad (4)$$

where k_2 is the quasi-secondary adsorption rate constant ($\text{g mg}^{-1} \text{min}^{-1}$) and h is the initial adsorption rate ($\text{mg g}^{-1} \text{min}^{-1}$).

The Weber–Morris intraparticle diffusion model (W–M model) is often used to analyze the control steps in the reaction, and the model is usually calculated by Eq. 5. In general, the adsorption process on porous materials can be divided into four stages, of which a certain step or a few steps will become the control stage of the adsorption process, which determines the overall adsorption rate and adsorption capacity:

$$Q_t = k_p t^{0.5} + C, \quad (5)$$

where k_p is the internal diffusion rate constant ($\text{mg g}^{-1} \text{min}^{0.5}$), which is proportional to the internal diffusion rate of the particles, and C is a constant, and its value is related to the thickness of the liquid film. In the fitting results, if $C = 0$, it means that there is only one controllable step in the adsorption process, which is the intraparticle diffusion stage; if $C \neq 0$, it means that the adsorption is a complicated process, and the control step is not only the intraparticle diffusion.

2.3.4 Adsorption isotherm

Adsorption isotherms are often used to judge the nature of the adsorption phenomenon, which can reflect the surface properties of the adsorbent, pore distribution, and the interaction between the adsorbent and the adsorbate (17). In this experiment, the Langmuir and Freundlich isotherm adsorption models were analyzed for the adsorption of methylene blue on PAN/ β -CD composite nanofiber membranes.

The Langmuir adsorption isotherm can be expressed as Eq. 6:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_{\max}} + \frac{1}{Q_{\max} b}, \quad (6)$$

where $Q_{\max}$ is the theoretical maximum adsorption capacity (mg g^{-1}) of the adsorbent and b is the Langmuir equilibrium constant.

Freundlich isotherms assume that adsorption occurs on nonuniform surfaces (18). This model can be represented by Eq. 7:

$$\log Q_e = \log k + \frac{1}{n} \log C_e, \quad (7)$$

where k and n are Freundlich isotherm adsorption constants. It is generally believed that the value of $1/n$ is inversely proportional to the adsorption performance: if $1/n$ is between 0 and 1, it is easy to adsorb; if $1/n > 2$, it is difficult to adsorb.

2.4 Characterization

The surface morphology of blended fiber membranes with different β -CD contents was investigated by Nava 400 Nano SEM. The morphology of the fibers was observed whether there were beads or not. A VERTEX70 FT-IR spectrometer was used to study the specific functional groups of the substance, thereby inferring the structure of the compound. The crystallization properties of the samples were characterized by XRD with a scan range of $0 < 2\theta < 75^\circ$, a scan voltage of 40 kV, and a current of 40 mA. The pore size distribution and the specific surface area of the composite nanofiber membrane were determined by the BET specific surface area test method to determine the pore type of the material. According to the method of the morphology analysis, the adsorbed material can be subjected to EDS detection while performing SEM, and the adsorption effect is analyzed according to the results.

3 Results and discussion

3.1 Surface morphology

The concentration of the spinning solution has a great influence on the fiber morphology and diameter distribution. Because as the concentration of the polymerization solution increases, the viscosity of the solution changes significantly. Studies have shown that the concentration and the viscosity of the polymerization solution have a greater impact on the electrospinning process (19). Figure 1 shows the morphology and the diameter distribution frequency of nanofiber membranes with different mass ratios of PAN and β -CD. It can be seen from the figure that the structure of the pure PAN fiber membrane is relatively loose, with many large pores, fine fibers, and uneven diameter distribution. With the addition of β -CD, a PAN/ β -CD fiber membrane with a smooth surface, a larger fiber diameter, a dense fiber pore structure, and a uniform arrangement can be obtained. This is because when the cyclodextrin is not added or the amount of cyclodextrin is too small, the low-viscosity spinning

solution causes insufficient entanglement of the molecular chains, which cannot effectively resist the electric field force and breaks, and it is easy to form beads. In addition, the jet velocity is relatively fast, resulting in a large electrostatic stretching force and a smaller diameter of the fiber membrane obtained. With the addition of β -CD, the degree of the molecular chain entanglement increases, and a greater electric field force is required to achieve the molecular chain orientation during electrospinning, so the fiber diameter obtained is larger. However, when the β -CD is excessive, the coarser fibers result in the reduction of pores on the surface and inside of the membrane. In addition, due to the high viscosity of the spinning solution, the thickness of the synthesized fiber is uneven, which has a great influence on the adsorption experiment.

3.2 FT-IR analysis

As shown in the curve in Figure 2d, three characteristic peaks appeared in the FT-IR spectrum of β -CD powder,

Figure 1: Fiber diameter distribution frequency diagram and SEM image of different mass ratios of PAN to β -CD: (a) 10:0, (b) 9:1, (c) 8:2, (d) 7:3, (e) 6:4, and (f) 5:5.

Figure 2: FT-IR spectra acquired from (a) PAN/β-CD nanofiber membrane, (b) PAN fiber membrane, (c) PAN powder, and (d) β-CD powder.

and the corresponding wavenumbers were 3,368, 2,930, and 1,026 cm⁻¹, which could be attributed to the groups of -OH, -CH, and C=O, respectively (20). The spectrum obtained by electrospinning pure PAN nanofiber membrane (Figure 2b) had the characteristic band of the center at 2,927 cm⁻¹ (C-H stretching), 3,433 cm⁻¹ (-NH- stretching), and 1,736 cm⁻¹ (C=O stretching). The absorption spectrum of the PAN fiber film obtained by the infrared spectrum was weaker than that of the PAN powder, which might be due to the destruction of the structure of the PAN molecule to some extent during the electrospinning

process. The PAN/β-CD nanofiber membrane (Figure 2a) could identify all characteristic bands of PAN and β-CD, which fully validated the coexistence of PAN and β-CD. At the same time, the absorption peak of the PAN/β-CD nanofiber membrane at 3,421 cm⁻¹ was significantly enhanced compared with the PAN powder, which proved that the hydroxyl group in β-CD was well introduced into the blended nanofiber. Other absorption bands were retained, indicating that the structure of the original molecule was not destroyed after blending.

3.3 Specific surface area and average pore size

The specific surface area and the average pore size are crucial to the adsorption medium and have a great influence on the adsorption effect (21). As shown in Figure 3, the N₂ adsorption-desorption isotherm of the PAN/β-CD nanofiber membrane belongs to the type II isotherm of IUPAC. Such isotherms indicate that the pores of the material are macropores and mesopores. Its linear shape reflected the unrestricted single-layer adsorption, and the inflection point of the curve was not obvious, indicating that the coverage of the monolayer was superimposed with the initial amount of multilayer adsorption. Finally, the calculated specific surface area of the PAN/β-CD nanofiber membrane was 28.1120 m² g⁻¹. Furthermore, the measured pore diameter of the nanofiber membrane was mainly distributed at 5–20 nm.

Figure 3: N₂ adsorption-desorption isotherm and pore size distribution chart of PAN/β-CD nanofiber membrane.

Figure 4: XRD patterns of (a) β -CD powder, (b) PAN powder, (c) PAN nanofiber membrane, and (d) PAN/ β -CD nanofiber membrane before adsorption.

3.4 XRD analysis

In the diffraction pattern of the β -CD powder (Figure 4a), there were obvious diffraction peaks at $2\theta = 10.67^\circ$, 12.52° , 15.45° , 17.73° , 22.80° , and 27.16° , indicating that β -CD had a three-dimensional inclusion structure. In the diffraction pattern of the PAN powder and the PAN nanofiber membrane, there was a sharp peak at $2\theta = 16.82^\circ$. The diffraction peaks of PAN and β -CD powder were relatively sharp, indicating that the crystallinity of the two materials was better. In addition, the narrow diffraction peak of the β -CD powder meant that its particle size was small. The diffraction pattern of the PAN nanofiber membrane and its composite nanofiber membrane with β -CD had a weakened peak at $2\theta = 16.82^\circ$, and there was almost no β -CD diffraction peak in the two patterns. This might be because the crystallinity of the PAN powder was reduced in the process of preparing the membrane by electrospinning, which made the structure lose. The crystallinity of β -CD was also affected when it was introduced, and it also hindered the crystallization of PAN to a certain extent.

As shown in Figure 5, the changes of surface-active groups before and after the PAN/ β -CD nanofiber membrane adsorbed methylene blue were visually compared. It can be seen that the characteristic peaks of the PAN/ β -CD membrane have hardly changed after the adsorption of methylene blue, only the characteristic peaks belonging to PAN at $2\theta = 16.97^\circ$ are slightly weakened, indicating that the adsorption process of the PAN/ β -CD membrane was mainly physical, and the adsorption of methylene blue affected the crystallization of PAN to a certain extent.

Figure 5: XRD patterns of (a) PAN/ β -CD nanofiber membrane before adsorption and (b) PAN/ β -CD nanofiber membrane after adsorption.

3.5 EDS analysis

The EDS mapping images of the PAN/ β -CD nanofiber membrane after adsorption showed that Cl was uniformly distributed on the surface of the adsorbent, and the atomic percentage of S and Cl in the nanofiber membrane after adsorption were 0.21% and 0.44%, respectively. These two elements are the elements contained in methylene blue, which again indicates that the PAN/ β -CD nanofiber membrane has a certain adsorption effect on methylene blue. In the SEM image after methylene blue was adsorbed by the fiber membrane, the fibers were entangled and contracted, showing an irregular distribution, indicating that the obvious adsorption effect occurred on the surface of the material (Figure 6).

3.6 Adsorption studies

3.6.1 Effect of different mass ratios of PAN and β -CD

In the experiments, adsorption studies were performed on nanofiber membranes with PAN: β -CD ratios of 10:0, 9:1, 8:2, 7:3, 6:4, and 5:5. It can be seen from Figure 7 that the adsorption amount of the fiber membrane to methylene blue was the largest (i.e., 66.9 mg g^{-1}) when the mass ratio of PAN to β -CD was 8:2. When the amount of β -CD added was less than the optimal amount, the adsorption performance of the fiber membrane had been significantly improved with the addition of β -CD. This is because the β -CD had a cavity structure that could coat the dye, and

Figure 6: EDS mapping (a, b, and d) and SEM (c) images of PAN/ β -CD nanofiber membrane adsorbed methylene blue.

Figure 7: Effect of different PAN and β -CD mass ratios on adsorption capacity.

the hydroxyl group provided by the β -CD could also adsorb the dye. However, when the amount was too much, the spinning liquid concentration would be too high, which would make the spinnability poor and the adsorption performance decrease. Therefore, the subsequent

adsorption experiments all used composite nanofiber membranes with a mass ratio of PAN and β -CD of 8:2.

3.6.2 Effect of initial concentration and contact time

In the experiment, under the case that other conditions remain unchanged, the trend of the concentration of methylene blue in different solutions (20, 40, 60, 80, 100, and 200 mg L^{-1}) and the same initial concentration over time was explored. It is shown in Figure 8 that the initial concentration was positively correlated with the change of methylene blue adsorption capacity; moreover, at the same initial concentration, the adsorption amount increased rapidly with time, and the adsorption reached equilibrium at 200 min. The adsorption capacity of the PAN/ β -CD nanofiber membrane was higher than that of the PAN membrane, indicating that the adsorption performance of PAN fiber was greatly improved after β -CD was doped into PAN fiber.

This is because the hydroxyl group on the surface of PAN/ β -CD blend nanofibers provided a large number of ion coordination sites. With the increase of the initial concentration of methylene blue, the probability of

Figure 8: Effect of contact time and initial concentration on adsorption capacity.

collision and chelation between the hydroxyl group and methylene blue on the surface of the fiber membrane increased, resulting in an increase in the adsorption capacity. At the same time, under the same initial concentration conditions, the adsorption amount increased rapidly from zero and tended to equilibrium at 200 min. However, in the process of rising, the growth rate of adsorption capacity was also slowly decreasing, and it was the slowest when it is close to equilibrium. The reason is that at first the methylene blue in the solution did not bind to the adsorbent, so there were many binding sites for the adsorbent. At this time, the ionic coordination sites on the surface of the nanofiber membrane were quickly occupied, so the adsorption capacity grew rapidly. However, as the adsorption continued, the binding sites on the adsorbent became less and less, and the free active groups also rapidly decreased. As more and more binding points were occupied, the mass transfer resistance of methylene blue molecules increased, coupled with the decrease of methylene blue concentration, causing the adsorption rate to slow down, and finally gradually equilibrium.

3.6.3 Effect of pH

The pH of the solution is an important influencing factor in the adsorption process, and it affects the surface structure of the adsorbent, the adsorption site, and the morphology of ions and their interactions. At the same time, the concentration of hydrogen ions in the solution will affect the charge distribution on the surface of the adsorbent and the structure of the dye molecule (22). The

effects of different pH values (pH = 3, 4, 5, 6, 7, 8, and 9) on the adsorption performance of the adsorbent were studied in the experiment. As shown in Figure 9, the adsorption performance of the material was poor in an acidic environment, and the adsorption effect was best when the pH was 9. The methylene blue molecule itself has a dimethylamine group, which will be highly protonated under low pH conditions; the hydroxyl groups on the β -CD structure in the composite nanofibers have a positive charge, so the protonated methylene blue molecules are not conducive to the formation of host-guest inclusions with β -CD due to repulsive interaction, so the composite fiber membrane has a small adsorption capacity. When the pH increases, the dimethylamine group gradually becomes neutral, and the methylene blue

Figure 9: Effect of pH value on adsorption capacity.

molecule is deprotonated, thereby enhancing the interaction with the inner cavity of β -CD. At the same time, the surface of β -CD may produce more activated deprotonated carboxyl groups, thereby forming electrostatic interactions with methylene blue molecules, so the adsorption performance is better in an alkaline environment.

3.6.4 Effect of dosage

For the dosage, if the amount of the adsorbent is too small, the ideal adsorption effect cannot be achieved; if the amount of the adsorbent is too much, the adsorption capacity will be reduced based on the same adsorption performance. Therefore, choosing the right amount of adsorbent is very important for adsorption experiments. The experiment explored the effects of different dosages (0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, and 0.08 g) on the adsorption performance and adsorption efficiency. The results are shown in Figure 10. The results show that the adsorption capacity decreased with the increase of the dosage, the adsorption efficiency was the opposite, and the adsorption efficiency tended to be balanced after the dosage reached 0.05 g. The reason is speculated as follows: when the dosage was less than 0.05 g, the adsorbed substance was too small, resulting in too low adsorption efficiency. When the dosage was greater than 0.05 g, the increase of the adsorbent provided more adsorption sites for methylene blue, so that the methylene blue in the solution could have more binding sites with the adsorbent. However, since the concentration of methylene blue was fixed, the removal rate increased slowly. In addition, the amount of material added was still increasing,

so the adsorption capacity had decreased. Therefore, due to this phenomenon, the optimal dosage is 0.05 g.

3.6.5 Adsorption kinetics model

Quasi-first-order and quasi-second-order kinetic models were used to linearly fit the adsorption data. The fitting results and calculated data are presented in Figure 11 and Table 1. From the analysis of the results, it can be concluded that the correlation coefficient of quasi-secondary adsorption kinetics fitting was 0.9991, which was larger than the relevant parameters of quasi-first-order kinetics fitting, and the theoretical equilibrium adsorption capacity was 113.38 mg g^{-1} , not far different from the experimental data of 108.66 mg g^{-1} . Therefore, the adsorption process of the PAN/ β -CD nanofiber membrane to methylene blue was consistent with the former.

The data of the W-M diffusion model are presented in Table 2, and the corresponding model is shown in Figure 12. It can be seen from Figure 12 and Table 2 that according to the W-M diffusion model, the adsorption process of methylene blue by the composite nanofiber membrane was a two-stage model, which was consistent with $k_{p1} > k_{p2}$. That was, the adsorption process was composed of a fast membrane diffusion process and a slow internal diffusion process. This was because when the target ion diffused into the adsorbent, the mass transfer resistance gradually increased, so the diffusion rate decreased, and finally, the diffusion was in a relatively balanced state. The C of the fitted curve was not equal to 0, indicating that intraparticle diffusion was not the only control step in the adsorption process.

Figure 10: Effect of adsorbent dosage on adsorption capacity.

Figure 11: (a) Quasi-first-order adsorption kinetic model and (b) quasi-second-order adsorption kinetic model.

Table 1: Adsorption kinetic fitting parameters

Parameter	Quasi-first order			Quasi-second order			
	$k_1 \text{ (min}^{-1}\text{)}$	$Q_e \text{ (mg g}^{-1}\text{)}$	R^2	$k_2 \text{ (g mg}^{-1} \text{min}^{-1}\text{)}$	$h \text{ (mg g}^{-1} \text{min}^{-1}\text{)}$	Q_e	R^2
	1.622×10^{-2}	58.088	0.9039	4.3×10^{-4}	5.53	113.38	0.9991

Table 2: W–M diffusion model fitting parameter

Parameter	W–M diffusion model					
	$k_{p1} \text{ (mg g}^{-1} \text{min}^{-1/2}\text{)}$	C_1	R^2	$k_{p2} \text{ (mg g}^{-1} \text{min}^{-1/2}\text{)}$	C_2	R^2
	5.9429	32.3757	0.9502	0.1209	105.92	0.7027

Figure 12: W–M diffusion model.

3.6.6 Adsorption isotherm

Adsorption isotherms provide important insights into the interaction between methylene blue and PAN/ β -CD nanofiber membranes, as well as the adsorption changes of methylene blue solution concentration, solution pH, contact time, and temperature under different membrane mass (23,24). In this study, Langmuir and Freundlich isotherm adsorption models were used to analyze the results. The analysis results were presented in Figure 13 and Table 3. The results showed that for the adsorption of methylene blue on the PAN/ β -CD-blended nanofiber membrane, the correlation coefficient (R^2) obtained from the Langmuir equation was higher. Therefore, compared with Freundlich isotherms, the Langmuir model can better describe the isothermal adsorption effect of PAN/ β -CD nanofiber membranes on methylene blue. Moreover, $0 < 1/n < 1$ was calculated based on the Freundlich isothermal

Figure 13: Fitting results of isothermal adsorption model.

adsorption model, indicating that methylene blue was easy to be adsorbed on the PAN/ β -CD fiber membrane.

3.7 Desorption regeneration performance

Figure 14 shows the desorption and regeneration performance of the nanofiber membrane. It can be seen that the adsorption performance of the fiber membrane decreased after five cycles of regeneration. This was because the texture of the fiber membrane itself was relatively soft, and repeated adsorption cycles would cause the blockage of the pores of the fiber membrane and damage of the fiber structure to a certain extent. However, after five adsorption cycles, the adsorption capacity of the fiber membrane could still reach more than 65 mg g^{-1} , indicating that the composite nanofiber membrane had regeneration performance in the adsorption of methylene blue.

3.8 Mechanism analysis

Integrating the FTIR spectra and adsorption experiment results of PAN/ β -CD nanofiber membranes prepared by

Figure 14: Effect of repetition number on adsorption capacity of nanofiber membrane.

doping β -CD, it is confirmed that β -CD is stably present in PAN/ β -CD nanofiber membranes. From the analysis of the XRD diffraction pattern results, the β -CD in the PAN/ β -CD nanofiber membrane is uniformly distributed in the PAN nanofiber membrane in an amorphous form. By comparing the XRD patterns of β -CD powder and PAN/ β -CD nanofiber membranes, it can be obtained that no crystalline substance is formed after PAN and β -CD were mixed, indicating that β -CD is fully dissolved.

Based on the analysis of the characterization results before and after adsorption and the results of adsorption experiments, the adsorption mechanism of PAN/ β -CD film on methylene blue molecules is shown in Figure 15. Combining the FTIR and XRD analysis after adsorption, it can be seen that the physical effect is the dominant process in the adsorption process of methylene blue molecules, mainly the inclusion of methylene blue molecules by the cavity structure of β -CD and electrostatic attraction. It is a carbohydrate molecule with hydrophobic inside and hydrophilic outside. It is nonreductive and easily reacted with various chemical monomers to form stable hydrates. Based on these special structures and physical and chemical properties, β -CD has the characteristics of combining with many inorganic and organic molecules to form host-guest inclusion compounds.

Table 3: Isothermal adsorption model fitting data

Parameter	Langmuir			Freundlich		
	$Q_{\max} (\text{mg g}^{-1})$	b	R^2	$1/n$	b	R^2
	109.9021	0.0087	0.9898	0.4773	5.1631	0.9370

β -cyclodextrin cavity structure

Figure 15: The mechanism diagram of the adsorption of methylene blue by the nanofiber membrane.

4 Conclusion

In this study, PAN/ β -CD-blended nanofiber membranes were prepared using the electrostatic spinning technology. Subsequently, the adsorption properties of the blended nanofiber membranes were studied using methylene blue as the adsorption target. The PAN/ β -CD membranes were characterized by SEM, FT-IR, BET, and XRD, and the results indicated that the fiber diameter increased significantly after blending, the fiber surface was smoother, and the morphology of the nanofibers did not change significantly. The adsorption results show that the PAN/ β -CD-blended nanofiber membrane can effectively adsorb methylene blue from water, presumably due to the cavity structure of cyclodextrin and the chelation of hydroxyl to methylene blue. The effects of pH and contact time on the adsorption capacity were investigated, and the results showed that the optimal pH for methylene blue adsorption by the PAN/ β -CD-blended nanofiber membrane was 9, and the adsorption amount increased with the increase of contact time. For methylene blue, the equilibrium time of adsorption is 200 min, and the results of adsorption studies can fit the quasi-second-order kinetic equation and Langmuir isothermal adsorption equation well. In addition, the research on the absorption and regeneration performance of the nanofiber membrane was also carried out. The final results showed that the prepared membrane had good regeneration performance. What is more, the electrospun nanofiber membrane not only has good performance in dye removal but also has a very broad prospect in the adsorption of heavy metal ions and the competitive adsorption of multiple ions.

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Reference

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