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Preparation of Molecularly Imprinted Sericin/ Poly(vinyl alcohol) Electrospun Fibers for Selective Removal of Methylene Blue

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Abstract Sericin(SS), as an abundant and renewable resource in nature, has been proven to be a good adsorbent for metal ions or organic dyes removal. In this study, glutaraldehyde vapor cross-linked sericin-based electrospun fiber adsorbent was developed for the removal of methylene blue(MB) from wastewater. To overcome the problem of decreasing adsorption capacity by excessive functional group cross-linking, MB-imprinted sericin/poly(vinyl alcohol) (PVA) electrospun fiber adsorbent was prepared. Biocompatible PVA was added to the electrospinning solution to improve the spinnability and mechanical property. Scanning electron microscopy(SEM), Fourier transforms infrared spectroscopy(FTIR), and so forth were used to confirm their structures and composition. The adsorption performance toward the template molecule MB, including pH effect, adsorption isotherm, adsorption kinetics, adsorption selectivity, and reusability, was investigated. By comparison with non-imprinted sericin/PVA electrospun fibers, MB-imprinted sericin/PVA electrospun fiber adsorbent showed an enhanced and selective adsorption capacity toward MB with a good regeneration and recycling ability. The adsorption test suggests that the resulting MB-imprinted sericin/PVA electrospun fibers are promising adsorbents for MB removal from aqueous system.

Keywords Sericin; Molecular imprinting; Electrospun fiber; Adsorbent; Methylene blue

1 Introduction

Water pollution is a quite serious global environment issue and causes severe health and ecological problems to human beings. Dyes discharge, which generated from cosmetics, leather, paper, food, printing, textiles and plastic has become a major water environmental concern[1—3]. Most of the dyes are complex molecules, resistant to aerobic digestion, and stable toward heat, light, and oxidizing agents, which are toxic and carcinogenic to human beings and organisms[4,5]. For this reason, constant efforts have focused on the removal of the dye contaminants before their discharge. To solve this environmental pollution, various methods have been developed for eliminating colored dyes from wastewater[6—8]. As a most common method, adsorption is regarded as a low-cost and highly efficient treating process. The adsorption efficiency mainly depends on the properties of the adsorbents[9,10]. By comparison with bulk materials, nanomaterials have attracted much attention for the removal of organic pollutants[11]. However, in consideration of the cost, efficiency, and secondary pollution, it is significant to develop innovative adsorbents.

In recent years, electrospinning has become a simple, low-cost, and effective technology to fabricate one-dimensional continuous nano- and micro-scale fibers[12]. The obtained fibers possess many remarkable characteristics, such as high porosity, large surface-to-volume ratio, easy preparation, and flexibility, making them good adsorbents for pollutants *via* physical or chemical interactions[13,14]. Much effort has been devoted so far to obtain efficient electrospun fiber adsorbents by choosing suitable polymers, introducing functional groups, or forming special surface structures[13,15,16]. Different types of electrospun fibers, including inorganic nanofibers[17], organic nanofibers[18], and organic/inorganic composite nanofibers[19], have been prepared as pollutant adsorbents. Natural polymers are attractive adsorbent materials due to their low cost and abundant source. Sericin is a water-soluble natural macromolecular protein, which covers the silk fiber. Sericin is usually discarded as a waste product of the silk textile industry with a global yearly production of about 50000 metric tons. Moreover, sericin contains 18 kinds of amino acids, most of which have strongly polar functional groups, such as hydroxyl, carboxyl and amino groups, rendering it a suitable adsorbent candidate[20—22]. Thus, sericin is a low-cost and abundantly available adsorbent material. Although we have verified the good adsorption capacity of sericin-based electrospun fibers toward MB[4], further improvement in enhanced adsorption and selectivity is still required for practical applications.

Recently, molecular imprinting technique is receiving considerable attention as a powerful method to create specific molecular recognition materials[23,24]. The preparation of molecular imprinting polymers(MIPs) involves co-polymerization of

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functional monomers and cross-linkers around template molecules. After removing the template molecules, the imprinting polymers have specific recognition sites for template molecules. Due to their advantages, such as easy preparation, stability, and desired recognition ability, molecular imprinting polymers have been applied in various fields aiming at a wide range of target molecules[25—27]. For adsorption applications, the adsorption capacity and selectivity would be enhanced after removing template pollutant molecules[28,29]. In recent years, ion or molecule imprinted electrospun polymer nanofibers have attracted attention as adsorbents. The template pollutants are usually heavy metal ions or pesticide molecules. Unlike molecular imprinting polymers, the ion or molecule imprinted electrospun polymer nanofibers do not contain the polymerization processes. The as-obtained polymers and template are blending electrospun and followed by a cross-linking process. The templates in the composite could prevent the excessive cross-linking of the functional groups and also create recognition sites for the templates after their elution[30—32]. Recently, Li *et al.*[30] reported a Pb(II) ion-imprinting electrospun cross-linked chitosan nanofiber mat, which showed excellent selectivity for the target ion Pb(II). Chen *et al.*[31] prepared Cu(II)-imprinted PVA/*L*-histidine electrospun nanofibers and the novel material was a promising adsorbent for copper ions removal. In the study of Ruggieri's group[32], pesticide atrazine imprinted polystyrene nanofibers by electrospinning showed an enhanced adsorption capability toward atrazine. However, there are few reports about the preparation of the dye molecule imprinted electrospun nanofiber adsorbents.

Herein, it is interesting to combine the electrospinning technology with molecular imprinting technique to prepare efficient and selective dye-imprinted adsorbents. Sericin, as the abundant and renewable resource in nature, is an ideal material to prepare green and low-cost adsorbent. In this study, we demonstrated the fabrication of the dye-imprinted sericin-based electrospun fibers using cationic dye MB as the templates. To improve the spinnability and mechanical property, synthetic polymer poly(vinyl alcohol)(PVA) with good biocompatibility and mechanical properties was also added to the electrospinning solution. Although some researchers prepared molecular or ion imprinted adsorbents, the preparation of dye imprinted electrospun fiber adsorbents has not been reported. The resulting MB-imprinted sericin/PVA electrospun fiber adsorbent was characterized by various techniques. The adsorption performance, including pH effect, adsorption isotherm, adsorption kinetics, adsorption selectivity, and reusability, has also been investigated in details to verify their enhanced and selective adsorption capacity toward the template MB, which suggests the obtained MB-imprinted sericin/PVA electrospun fibers as good potential adsorbents.

2 Experimental

2.1 Materials

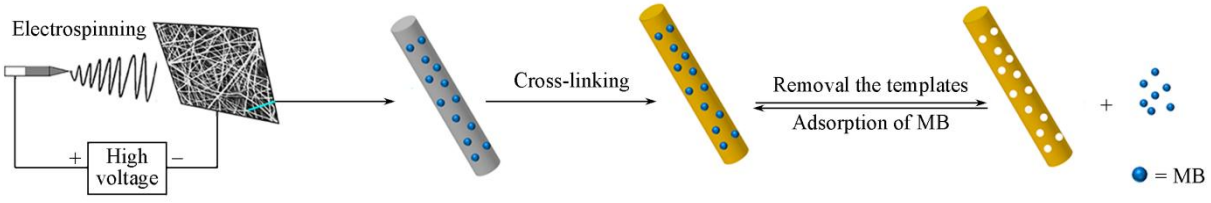
Poly(vinyl alcohol)(PVA, M_w=75000—80000) was purchased from Beijing Chemical Factory(Beijing, China). Sericin (SS, M_w=76000) was purchased from Huzhou Aotesi Biotechnology Co., Ltd.(Huzhou, China). Glutalraldehyde(GA, 50%) was purchased from Tianjin Huadong Product(Tianjin, China). Trifluoroacetic acid was purchased from Aladdin Industrial Corporation. Methylene blue(MB, $C_{16}H_{18}ClN_3S\cdot 3H_2O$), methyl orange(MO, $C_{14}H_{14}N_3SO_3Na$), rhodamine B(RhB, $C_{28}H_{31}ClN_2O_3$) and Congo red(CR, $C_{32}H_{22}N_6Na_2O_6S_2$) were purchased from Sinogharm Chemical Reagent Co., Ltd. All the reagents were used without further purification.

2.2 Preparation of MB Imprinted Cross-linked Electrospun Sericin/PVA Nanofiber Mats

The electrospinning solution containing MB molecules was prepared as follows: the PVA(7%, mass fraction) solution was prepared by dissolving 0.70 g of PVA powder in 9.30 g of distilled water at about 85 °C with constant stirring for 3 h. After the solution was cooled to room temperature, 0.35 g of sericin powder[*m*(sericin):*m*(PVA)=1:2] and 100 mg of MB were added to the PVA solutions and stirred over night to acquire a homogeneous solution.

For the electrospinning process, the solution was loaded into a glass syringe and connected to a high-voltage power supply. The electrospun fibers could be obtained under 15 kV voltage and 18 cm collecting distance between the cathode and anode.

The cross-linking of the obtained electrospun fibers was conducted according to previous report[33]. The obtained electrospun fibers were placed inside a desiccator, containing chemical cross-linking agent glutalraldehyde(GA, 50%), and trifluoroacetic acid as a catalyst at 20 °C for 24 h. The cross-linked fibers containing MB molecules were washed by 0.1 mol/L HCl solutions repeatedly until there was no MB in the solution tested by Shimadzu UV-2501 UV-Vis spectrophotometer at 664 nm. After washing with distilled water and ethanol, the MB imprinted crosslinked electrospun sericin/PVA nanofibers were dried in a vacuum oven at 50 °C overnight for further use. The synthetic route of MB imprinted electrospun sericin/PVA nanofibers is illustrated in Scheme 1. For comparison, cross-linked sericin/PVA composite electrospun fibers without adding the template molecule were prepared and processed under the same conditions.



Scheme 1 Schematic illustration of synthetic procedure for MB imprinted sericin/PVA electrospun fiber

2.3 Characterization

The morphology of the fibers was characterized on a field-emission scanning electron microscopy(SEM, Shimadzu SSX-550) and the mean diameter of the fibers was calculated from measuring the different parts of the fibers at 100 different fibers using commercial software package, Image-Pro Plus. FTIR spectra were recorded on a Bruker Vector-22 spectrometer from 4000 cm^{-1} to 400 cm^{-1} using powder-pressed KBr pellets at room temperature. The mechanical properties of the fiber membranes were performed by assembling the membranes(dimensions: length=30 mm, width=10 mm) between two stainless steel clamps with a tensile speed of 20 mm/min on a mechanical strength microtest device(410R250, Test Resources, Shakopee, MN, USA). For mechanical tests, the results were the average values, which were derived from at least 6 tested specimens. For the stability in water experiments, the fiber mats with squares of 1 cm^2 were immersed in deionized water with different pH values ranging from 3 to 11. After 48 h, the fiber mats were removed from the deionized water and placed in a vacuum oven to dry until a constant mass. The insoluble fraction(%) is determined by Eq.(1):

$$\text{Insoluble fraction}(\%)=(m_i/m_0)\times 100\% \quad (1)$$

where m_0 and m_i are the mass of the fiber mats before and after stability tests, respectively.

2.4 Adsorption Experiments

To evaluate the adsorption capacity, batch adsorption experiments were performed on a model BETS-M1 shaker (Kylin-Bell Lab Instruments Co., Ltd., China) with a shaking speed of 120 r/min. The pH values were adjusted with 0.1 mol/L HCl or 0.1 mol/L NaOH solution, and the pH values of the adsorption solutions were measured using a pH meter (Starter 2100, Ohaus Instruments Co., Ltd.). The concentration of MB in the solution was determined on a Shimadzu UV-2501 UV-Vis spectrophotometer at 664 nm. The adsorption capacity(q, mg/g) of MB adsorbed onto the adsorbents was calculated on the basis of the Eq.(2):

$$q=[(c_0-c_e)V]/m \quad (2)$$

where c_0 and c_e are the initial and the equilibrium concentrations of adsorbate in the test solution(mg/L), respectively, V is the volume of the testing solution(L), and m is the mass of the adsorbent(g).

The initial pH of the MB solution was adjusted to values in the range of 3—10 to investigate the influence of pH. For the isothermal adsorption experiments, imprinted SS/PVA fibers or non-imprinted fibers were added to 20 mL of MB solutions with different concentrations from 40 mg/L to 450 mg/L. For the kinetics adsorption experiments, imprinted SS/PVA fibers or non-imprinted fibers were mixed with 80 mL of MB solution(50 mg/L) and incubated for a certain amount of time from 0 h to 8 h.

The selectivity of MB-imprinted SS/PVA electropsun fibers for MB compared with other dye molecules was evaluated from the selectivity coefficient($\beta_{MB/X}$)[29,34]. The selectivity coefficient is defined as follows:

$$\beta_{MB/X}= D_{MB}/D_X \quad (3)$$

where D_{MB} and D_X are the distribution ratios of MB and other competing molecule(CR, MO, and RhB), respectively. Distribution ratio(D) was calculated by Eq.(4):

$$D = q_e/c_e \quad (4)$$

where q_e is the equilibrium adsorption capacity(mg/g) and c_e is the equilibrium concentration(mg/L).

The relative selectivity coefficient(α), which is used to estimate the effect of imprinting selectivity, can be defined from the following Eq.(5):

$$\alpha=\beta_{MI}/\beta_{NM} \quad (5)$$

where β_{MI} and β_{NM} are the selectivity coefficients of the imprinted and non-imprinted samples, respectively.

For the desorption-readsorption experiment, the saturated MB-adsorbed fibers were regenerated by 0.1 mol/L HCl. After washing thoroughly with deionized water to neutral pH, the adsorbent was reused in adsorption experiments and the process was repeated five times. All experiments were performed at (20±2) °C.

Each adsorption experiment above was conducted twice to obtain reproductive results with error<5%. All the data of adsorption experiments listed in adsorption sections are the average values of two tests.

3 Results and Discussion

3.1 Morphology

Sericin is a water-soluble natural macromolecular protein but it is difficult to prepare electrospun sericin nanofibers from single sericin aqueous solution. Pure electrospun sericin nanofibers have been reported using trifluoroacetic acid as the solvent[35]. To avoid the use of toxic solvent and improve the spinnability, PVA was added to the sericin aqueous solution. In consideration of the sericin content and mechanical strength, we made the mass ratio of sericin to PVA being 1:2. The morphologies of the obtained fibers are shown in Fig.1. Sericin/PVA electrospun fibers are prepared successfully and the fibers are smooth and uniform with few beads[Fig.1(A)]. Cross-linked sericin/PVA fibers still maintain the fibrous morphology[Fig.1(B)]; and the larger average fiber diameter (387 nm) compared with that before cross-linking(334 nm) is likely due to the swelling during the cross-linking process. This phenomenon similarly happens in the cases for dye-loaded sericin/PVA electrospun fibers and cross-linked dye-loaded sericin/PVA fibers. Both the fibers[Fig.1(C) and (D)] show smooth morphology and the average diameter increases from 345 nm to 390 nm after the cross-linking. Also, the elution process doesn't change the morphology or diameter of the fibers[Fig.1(E)], showing high stability. The results reveal that sericin/PVA based electrospun fibers with good fibrous morphology have been fabricated successfully and the cross-linking or elution does not destroy the fibrous morphology. Moreover, the magnified images of Fig.1(B) and (E) are shown in Fig.S1 (see the Electronic Supplementary Material of this paper). Comparing with cross-linked sericin/PVA electrospun fibers, MB-imprinted sericin/PVA electrospun fibers after removing

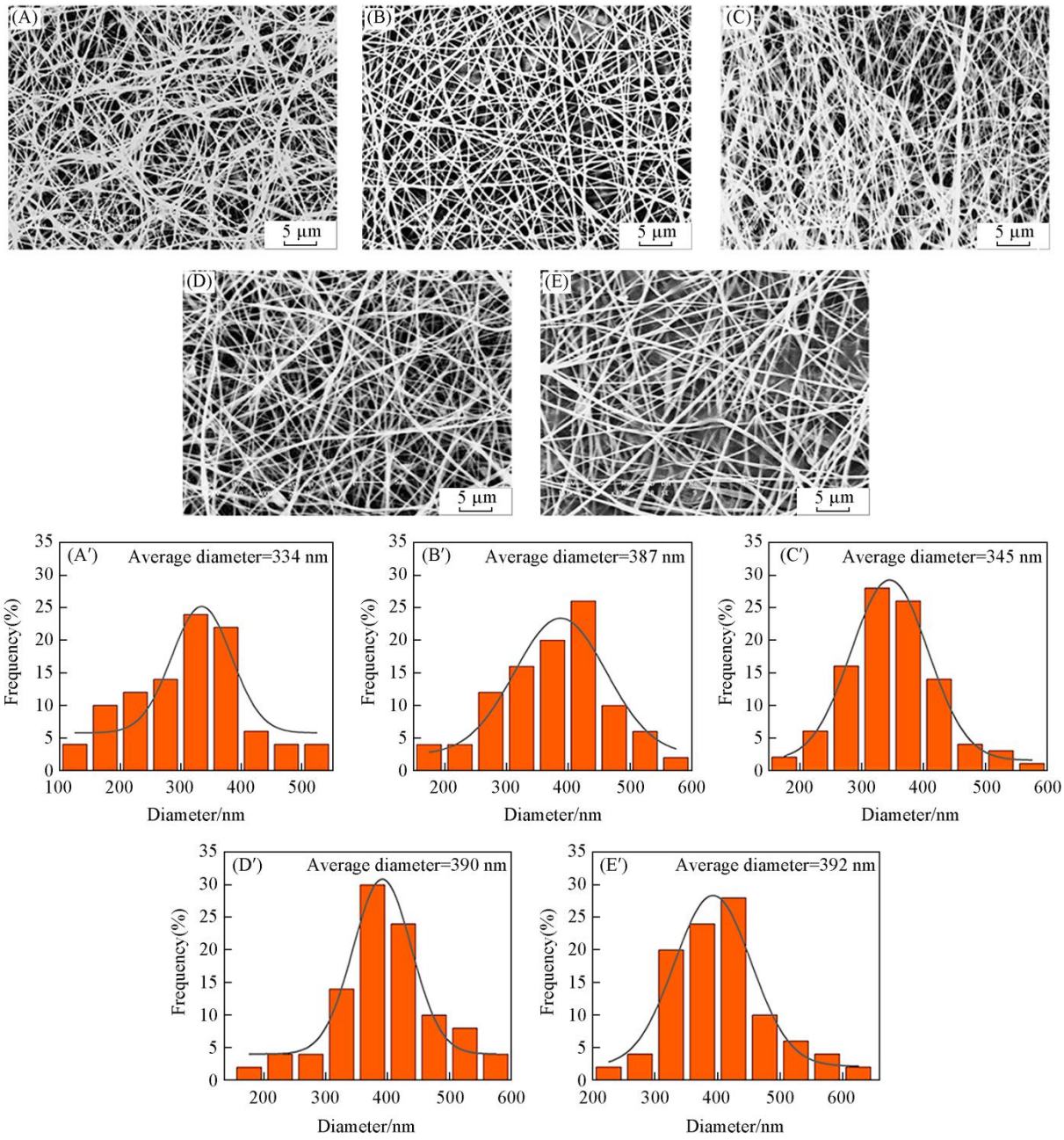


Fig.1 SEM images(A—E) and diameters distributions(A′—E′) of sericin/PVA electrospun fibers(A, A′), cross-linked sericin/PVA electrospun fibers(B, B′), dye-loaded sericin/PVA electrospun fibers(C, C′), cross-linked dye-loaded sericin/PVA electrospun fibers(D, D′) and MB-imprinted sericin/PVA electrospun fibers after removing the templates(E, E′)

the templates show more rough surfaces and collapse due to the elution of MB molecules.

3.2 FTIR Spectra and Water Stability

FTIR spectra are used to verify the structural composition and the cross-linking reaction. The cross-linking is necessary to obtain water-insoluble fibers for adsorption applications; moreover it is the requested step to prepare molecular imprinting polymers. The FTIR spectra of sericin/PVA electrospun fibers and cross-linked sericin/PVA fibers are shown in Fig.2. Both of curves *a* and *b* of Fig.2 show three peaks at 1663, 1541 and 1242 cm^{-1}(regions 2 and 3), belonging to amide I, amide II, and amide III[20,22], respectively, suggesting the existence of sericin component. The broad peak at around 3440 cm^{-1}(region 1) is assigned to —OH groups from PVA or sericin.

After the cross-linking reaction, the peak intensity of —OH groups(at around 3440 cm^{-1}) relatively decreases, indicating that more of the —OH groups are utilized for cross-linking by glutaraldehyde to form the acetal bridge[36]. The band observed at 1000—1140 cm^{-1}(region 4) becomes more broad owing to the formation of —C—O—C— vibration of the acetal group as the result of the reaction between —C═O of glutaraldehyde and —OH groups[37]. Moreover, the intensity of amide I increases due to the formation of —C═N— bonds, indicating the reaction between glutaraldehyde and the free —NH_2 groups from the sericin protein. All the results confirm

the happening of the cross-linked reaction[36]. The FTIR spectra of dye-loaded sericin/PVA electrospun fibers, cross-linked dye-loaded sericin/PVA fibers, and cross-linked imprinted sericin/PVA fibers after the template molecules removal are shown in Fig.3. The spectra of dye-loaded sericin/PVA electrospun fibers and cross-linked dye-loaded sericin/PVA fibers have the similar peaks with curves *a* and *b* of Fig.2, which confirms the functional component sericin and the cross-linked reaction. However, we cannot observe the characteristic peaks for MB[2], such as aromatic ring, C═S or C—N; because these peaks have been overlapped with the peaks of sericin or PVA. After removing the templates in 0.1 mol/L HCl solutions, the peaks have almost no change, suggesting that the elution process does not destroy the cross-linking structure and composition.

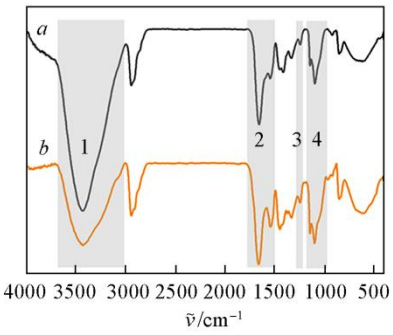


Fig.2 FTIR spectra of sericin/PVA electrospun fibers(*a*) and cross-linked sericin/PVA electrospun fibers(*b*)

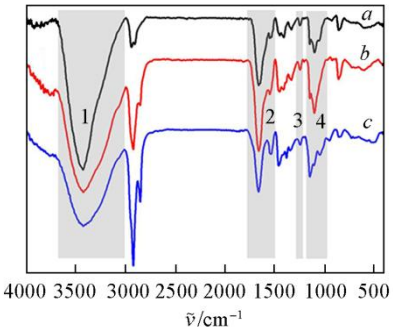


Fig.3 FTIR spectra of dye-loaded sericin/PVA electrospun fibers(*a*), cross-linked dye-loaded sericin/PVA electrospun fibers(*b*) and MB-imprinted sericin/PVA electrospun fibers after removing the templates(*c*)

To observe the cross-linking and imprinting visually, the digital photos for different fiber films after immersing in water are shown in Fig.S1(see the Electronic Supplementary Material of this paper). Before the cross-linking, sericin/PVA electrospun fibers and dye-loaded sericin/PVA fibers lose their fibrous membrane structures and are water-soluble. After the necessary cross-linking step, cross-linked sericin/PVA electrospun fibers and cross-linked dye-loaded sericin/PVA fibers are stable in water. Moreover, the cross-linked dye-imprinted sericin/PVA fibers are blue due to the color of MB. After the removal of the template MB, the MB-imprinted sericin/PVA fibers are still stable in water and the color becomes white, indicating that most of the MB molecules have been washed away. Through measuring the concentration of MB in the eluent, 97.8% of MB in the cross-linked dye-loaded sericin/PVA fibers has been washed out. To further verify the stability in water, the insoluble fractions(Fig.4) for cross-linked sericin/PVA fibers and MB-imprinted sericin/PVA fibers after soaking in water for 48 h are all >95% at the pH values ranging from 3 to 11, showing a good resistance to water. In addition, the morphology of the cross-linked sericin/PVA fibers and MB-imprinted sericin/PVA fibers after soaking in water at pH of 7 for 48 h was observed by SEM(Fig.S2, see the Electronic Supplementary Material of this paper). It can be seen that the fibrous structure of the fibers is well maintained, confirming the excellent water stability and their feasible applications in aqueous medium.

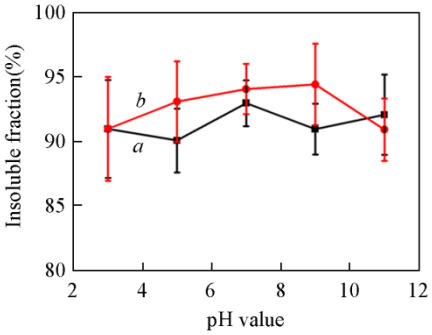


Fig.4 Insoluble fraction of cross-linked sericin/PVA electrospun fibers(*a*) and MB-imprinted sericin/PVA electrospun fibers(*b*) after removing the templates after soaking in water for 48 h

3.3 Mechanical Test Results

As an important characterization paramter, the mechanical properties of the adsorbent films are significant. The stress-strain curves are shown in Fig.5. The tensile strengths of sericin/PVA electrospun fibers and dye-loaded sericin/PVA fibers are 5.53 and 5.22 MPa, respectively; and the elongation at break are 40.24% and 45.71%, respectively. The loading of MB has little impact on the mechanical property. It is reported that the cross-linking of polymers could improve the mechanical property[37,38]. The tensile strength of cross-linked sericin/PVA electrospun fibers increases to 8.21 MPa and the value for

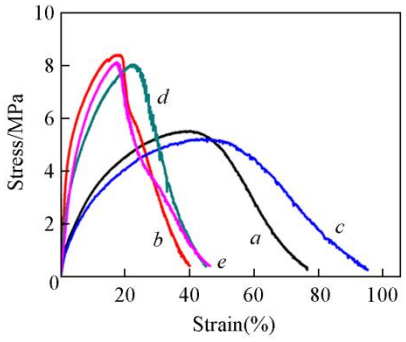


Fig.5 Stress-strain curves of sericin/PVA electrospun fibers(*a*), cross-linked sericin/PVA electrospun fibers(*b*), dye-loaded sericin/PVA electrospun fibers(*c*), cross-linked dye-loaded sericin/PVA electrospun fibers(*d*) and MB-imprinted sericin/PVA electrospun fibers after removing the templates(*e*)

cross-linked dye-loaded sericin/PVA fibers increases to 8.03 MPa. The elongations at break both have relevant decreases to 19.14% and 22.85%, respectively. The improved mechanical property indicates that GA cross-linking makes the fiber films become mechanically more strong and stable. In addition, the mechanical property of dye-imprinted sericin/PVA fibers after the elution changes little, which is compared with cross-linked dye-imprinted sericin/PVA fibers, suggesting that the removal of the templates in 0.1 mol/L HCl solutions has little impact on the mechanical property. In the following discussion, non-MB imprinted cross-linked sericin/PVA fibers are named as NM-SS/PVA and MB-imprinted sericin/PVA fibers after the elution are named as MI-SS/PVA.

3.4 Adsorption Behavior of the NM-SS/PVA and MI-SS/PVA Fibers

Sericin-based electrospun fibers have shown good adsorption capacity toward cationic dye methylene blue(MB) in our previous work[4]. In this work, we further studied the MB imprinted electrospun secirin/PVA composite fibers and evaluated the adsorption behavior of NM-SS/PVA and MI-SS/PVA fibers toward MB. The adsorption performance, including pH effect, adsorption isotherm, adsorption kinetics, adsorption selectivity, and reusability, has been investigated in details.

3.4.1 Effect of pH on MB Adsorption

As an important influence factor for adsorption process, pH values could change both the ionization degree of dye molecules and the surface charge of the adsorbents to affect the adsorption performance. The adsorption capacities of MB onto NM-SS/PVA and MI-SS/PVA fibers were measured over the pH values ranging from 3 to 10, and the results are shown in Fig.6(A). The adsorption capacities for the both adsorbents have the same variation tendency. Both the adsorbents could adsorb less MB molecules at low pH values(between 3 and 5). At low pH values, high concentration of H^+ has a negative influence by the competitive adsorption between the available H^+ and MB molecule with the functional groups(carboxyl groups, amino groups, etc.) from sericin. As the pH values increase, more functional groups become deprotonation, which is beneficial to adsorb more cationic MB by electrostatic adsorption. In our previous study, we have demonstrated that the adsorption process between MB and sericin was electrostatic interaction[4]. The adsorption capacities increase gradually with increasing the pH and keep stable adsorption at pH>7. Therefore, the following studies were conducted at the initial pH value of 7. Through the pH effect results, it is observed that the adsorption capacity of MI-SS/PVA fibers is higher than that of NM-SS/PVA fibers in the selected pH range.

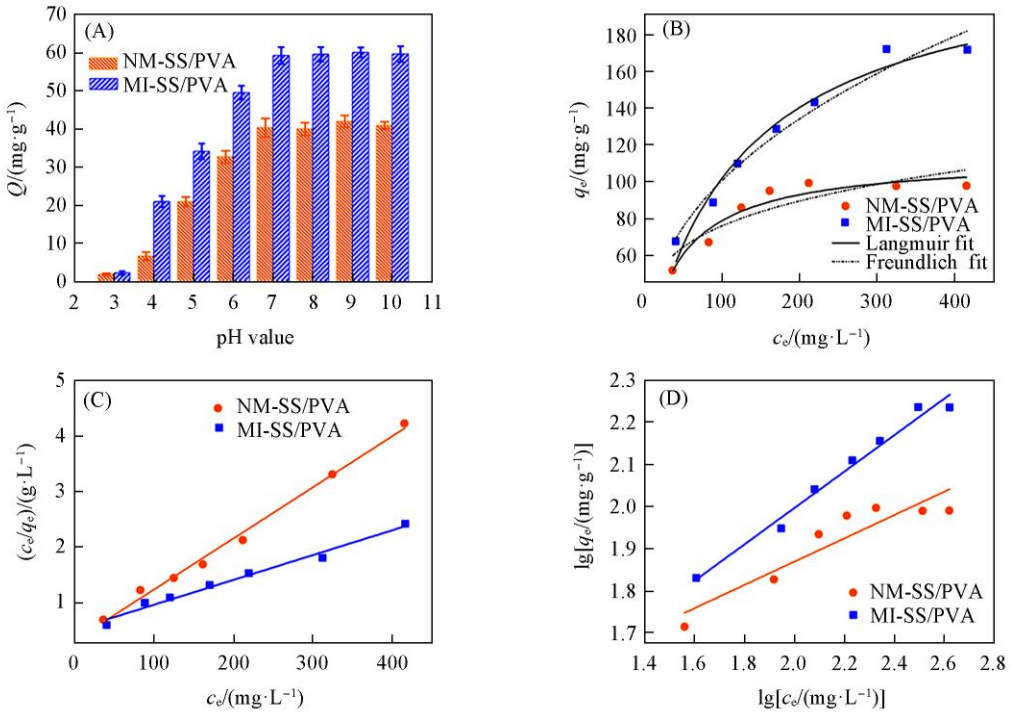


Fig.6 Initial pH value effect on the adsorption(A) and equilibrium adsorption isotherm(B) of MB onto NM-SS/PVA and MI-SS/PVA fibers and the corresponding Langmuir linear fitting plot(C) and Freundlich linear fitting plot(D) of NM-SS/PVA and MI-SS/PVA fibers

Table 1 Langmuir and Freundlich constants for the adsorption of MB

Absorbent	Langmuir isotherm			Freundlich isotherm		
	q_{max}/(mg·g^{-1})	b/(L·mg^{-1})	R^2	K_F	n	R^2
NM-SS/PVA	108.58	2.85×10^{-2}	0.9916	20.66	3.60	0.8307
MI-SS/PVA	223.21	8.57×10^{-3}	0.9812	13.49	2.31	0.9173

3.4.2 Adsorption Isotherm Model

To compare the adsorption capacities directly and better know the interaction between the dye molecules and adsorbents, the adsorption isotherms were conducted with initial dye

concentrations ranging from 40 mg/L to 450 mg/L.

Two classical isotherm models[34], namely Langmuir and Freundlich equations, have been widely used to describe the equilibrium characteristic of the adsorption. Their linear equations are as follows:

Langmuir isotherm(homogeneous and monolayer adsorption):

$$\frac{1}{q_e}=\frac{1}{q_m}+\frac{1}{bq_mc_e} \tag{6}$$

Freundlich isotherm(heterogeneous and multilayer adsorption):

$$\lg q_e=\lg K_F+(1/n)\lg c_e \tag{7}$$

where q_e is the equilibrium adsorption capacity(mg/g), c_e is the equilibrium concentration(mg/L), and q_m and b are the Langmuir constants related to maximum adsorption capacity and binding energy, respectively; K_F and n are empirical constants indica- ting the Freundlich constant(L/mg) and heterogeneity factor, respectively.

The relevant results are shown in Fig.6(B) and Table 1. Through the comparison of correlation coefficient R^2 and linearity data, we observe that the Langmuir equation[Fig.6(C)] represents a better fit to the experimental data than the Freundlich equation[Fig.6(D)] in both the adsorbents for the adsorption of MB, which reflects that both the adsorption processes could be considered as monolayer adsorption and the distribution of the adsorption sites is homogeneous. Through the Langmuir fitting results, the maximum adsorption capacities (q_m) are 108.58 mg/g for NM-SS/PVA fibers and 223.21 mg/g for MI-SS/PVA fibers, suggesting that the adsorption capacity toward template molecules could be greatly enhanced through imprinting method.

3.4.3 *Adsorption Kinetics*

To further investigate the adsorption properties, adsorption kinetics were conducted, which is important for the validation of the efficiency of the process. The kinetic curves for both the adsorbents are displayed in Fig.7(A). As the results shown, both the adsorption processes include two stages: an initial rapid adsorption and a following slower stage. At the initial 2 h, both the adsorption processes show a sharp increase in adsorption capacities, due to the availability of abundant adsorption sites on the surface of the adsorbents. After this stage, MB molecules have to traverse the surface and get deeper into the fibers, resulting in a slow adsorption rate until equilibrium was reached(8 h).

Moreover, the adsorption kinetics was modeled by the pseudo-first-order and the pseudo-second-order rate equations, expressed as follows[21]:

$$\lg(q_e-q_t)=\lg q_e-\frac{k_1t}{2.303} \tag{8}$$

$$\frac{t}{q_t}=\frac{1}{k_2q_e^2}+\frac{t}{q_e} \tag{9}$$

where q_t and q_e(mg/g) are the adsorption capacity at time t and equilibrium time, respectively. k_1(h^{-1}) and k_2[g/(h·mg)] are the pseudo-first order model rate constant and the pseudo-second order model rate constant, respectively. The curves and relevant parameters are shown in Fig.7(B), (C), and Table 2, respectively. According to the R^2, both the adsorption processes for NM-SS/PVA and MI-SS/PVA fibers follow the pseudo-second order model which is based on the assumption that a rate-determining step chemiadsorption process is involved[39].

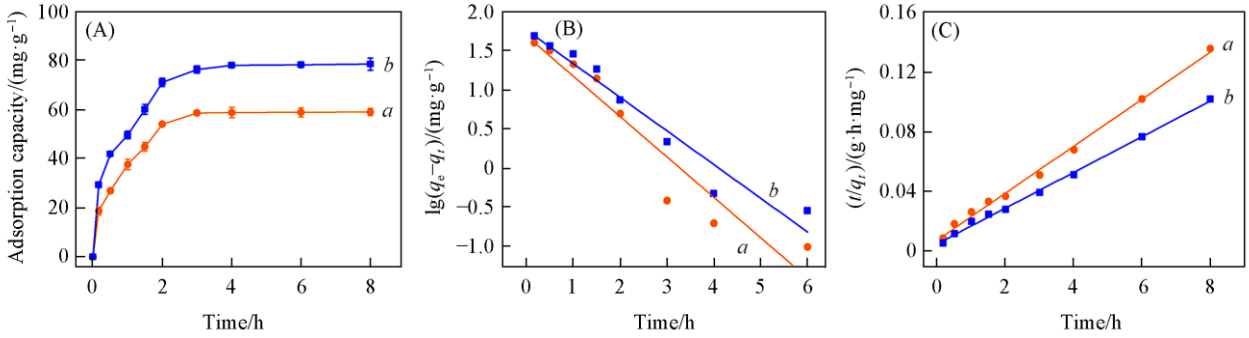


Fig.7 Adsorption kinetic(A), pseudo-first-order kinetic plots(B) and pseudo-second-order kinetic plots(C) of MB onto NM-SS/PVA(*a*) and MI-SS/PVA fibers(*b*)

Table 2 Kinetic parameters for MB absorption by NM-SS/PVA and MI-SS/PVA fibers

Absorbent	Experimental	Pseudo-first-order model			Pseudo-second-order model		
	q_{exp}	q_e/(mg·g^{-1})	k_1/h^{-1}	R^2	q_e/(mg·g^{-1})	k_2/(g·mg^{-1}·h^{-1})	R^2
NM-SS/PVA	59.02	49.22	1.1860	0.9024	63.86	0.0309	0.9955
MI-SS/PVA	78.50	58.42	0.9882	0.9414	83.96	0.0269	0.9967

3.4.4 *Adsorption Selectivity*

Apart from the enhanced adsorption capacity, the adsorption selectivity toward template molecules is another character imprinting polymer. The template molecules firstly interact with the functional monomers; after the cross-linking and elution the special recognition sites toward template molecules are obtained, leading to the selective adsorption ability. To investigate the special recognition ability of MI-SS/PVA fibers, the selective adsorption studies toward MB were carried out under optimal conditions at the solution with pH of 7 in single and binary dye systems. We choose other three dye molecules(CR, MO, and RhB) as the comparative models. As is shown in Fig.8, the NM-SS/PVA fibers have a higher adsorption capacity toward MB than other three dyes in the single dye system; and this is the reason that we choose MB as the template molecules. After the imprinting process, the adsorption capacity toward

MB on MI-SS/PVA fibers is enhanced. As can be seen from Table 3, all the distribution ratios of the MI-SS/PVA fibers are larger than the NM-SS/PVA fibers for the four molecules. It can be seen that the distribution ratio of MB in MI-SS/PVA is 1.42 times as that of NM-SS/PVA. The selectivity coefficients ($\beta_{MB/X}$) of MI-SS/PVA for MB/CR, MB/MO and MB/RhB are 6.271, 8.229, and 54.416, respectively, which are greater than NM-SS/PVA. In addition, the relative selectivity coefficient of MI-SS/PVA for each molecule is considerably larger than 1. The adsorption selectivity toward MB by MI-SS/PVA fibers is also evaluated in the binary mixed dye systems[Fig.9(A) and (B)]. As the results listed in Fig.9 and Table 3, the adsorption capacities of MI-SS/PVA toward MB are also improved in all binary dye systems. The selectivity coefficients($\beta_{MB/X}$) of MI-SS/PVA for MB/CR, MB/MO, and MB/RhB are all greater than NM-SS/PVA; and the relative selectivity coefficients are all larger than 1. The variation tendency is same with the single dye system. These observations prove that the MI-SS/PVA fibers have an excellent selectivity for MB adsorption. The adsorption of MB attributes to the electrostatic interaction between the functional groups from sericin and the MB molecules.

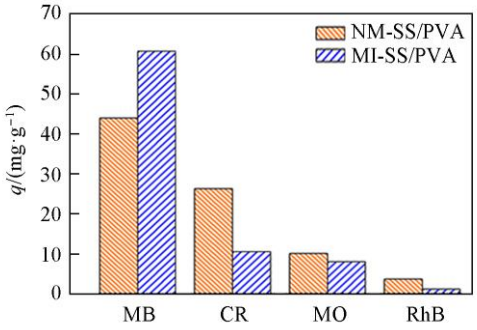


Fig.8 Adsorption capacities of MB, CR, MO and RhB onto NM-SS/PVA and MI-SS/PVA fibers in single system

Table 3 Selective adsorption properties of NM-SS/PVA and MI-SS/PVA fibers

System	Molecule	Distribution ratio/(L·g^{-1})		Selectivity coefficient, $\beta_{MB/X}$		Relative selectivity coefficient, α
		MI-SS/PVA	NM-SS/PVA	MI-SS/PVA	NM-SS/PVA	
Single dye system	MB	1.687	1.187	6.271	1.723	3.640
	CR	0.269	0.689	8.229	4.601	1.789
	MO	0.205	0.258	54.419	12.763	4.264
	RhB	0.031	0.093			
Binary dye system	MB/CR	0.269	0.689	9.171	2.613	3.510
	MB/MO	0.205	0.258	7.381	3.908	1.889
	MB/RhB	0.031	0.093	96.598	21.744	4.442

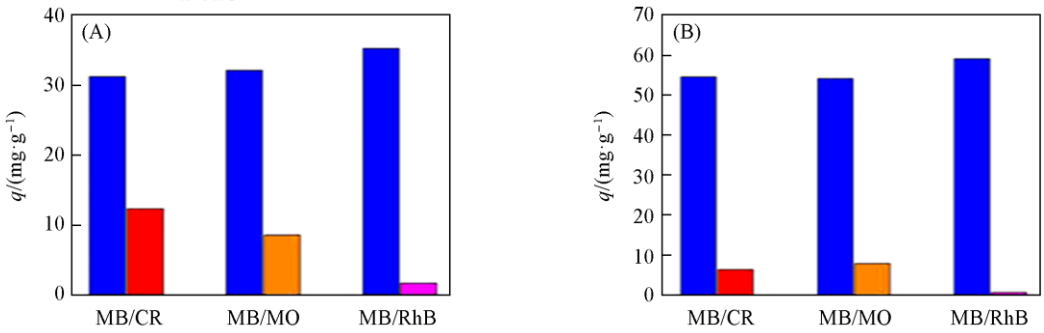


Fig.9 Adsorption capacities of NM-SS/PVA fibers(A) and MI-SS/PVA fibers(B) in binary dye systems

The imprinting process could decrease the excessive functional group(such as amino and carboxyl groups) cross-linking, which have been occupied by the template molecules; thus the adsorption capacity toward MB enhanced after the MB imprinting. Moreover, as shown in Fig.S3(see the Electronic Supplementary Material of this paper), the more rough surfaces and collapse structures of MI-SS/PVA could increase the effective adsorption area, leading to an improved adsorption capacity. MB imprinted sericin/PVA fibers have formed the special recognition sites for MB have formed after the elution process; thus MB imprinted sericin/PVA fibers showed better selective adsorption toward MB.

3.4.5 Cycle Adsorption

Regeneration and reuse are crucial factors for the practical application to reduce the consumption. According to the elution process and pH effect, 0.1 mol/L HCL solutions were used to regenerate the adsorbents. The adsorption-desorption cycle was repeated five times for NM-SS/PVA and MI-SS/PVA fibers. The adsorption capacities for both adsorbents still keep above 94% of the initial capacity after five adsorption-regeneration cycles(Fig.10), which demonstrate the good stability and reusability of the adsorbents. On the basis of the above adsorption

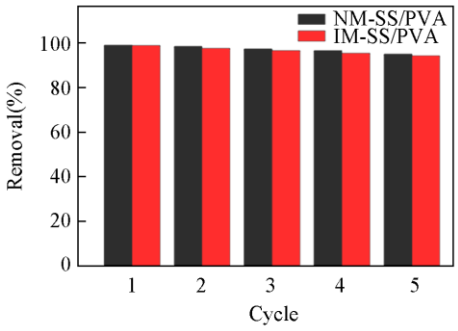


Fig.10 Adsorption-desorption cycles for MB onto NM-SS/PVA and MI-SS/PVA fibers

data, MI-SS/PVA fibers have special recognition selectivity and excellent adsorption capacity for template molecule “MB”.

4 Conclusions

In summary, MB-imprinted sericin/PVA electrospun fiber adsorbent has been synthesized through the combination of electrospinning technology with molecular imprinting technique. The morphology and composition were characterized by SEM and FTIR, respectively. The cross-linked fibers showed good mechanical property and water stability. The adsorption performance toward the template MB, including pH effect, adsorption isotherm, adsorption kinetics, adsorption selectivity, and reusability, has been investigated. It can also be seen that MI-SS/PVA fibers showed enhanced and selective adsorption capacity toward MB comparing with NM-SS/PVA fibers. In addition, the MI-SS/PVA fiber adsorbent could be easily collected due to its membrane structure and mechanical strength and the adsorbent showed a good reusability. With these features, MB-imprinted sericin/PVA electrospun fibers could have the potential application as adsorbents for low-cost and efficient MB removal.

Electronic Supplementary Material

Supplementary material is available in the online version of this article at http://dx.doi.org/10.1007/s40242-017-7115-9.

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