

Preparation and Characterization of *Carex meyeriana* Kunth Cellulose Nanofibers by Electrospinning

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Abstract

Carex meyeriana Kunth is a renewable cellulose resource with abundant reserves in nature and has a large research space, but its application is limited and still under development. Hence, *Carex meyeriana* Kunth is worth developing. *Carex meyeriana* Kunth's cellulose is abbreviated as CMKC. This study aims to produce cellulose nanofibers (CMKN) from CMKC by electrostatic spinning. The electrostatic spinning solution was prepared by mixing the self-made cellulose solution with 15% polyacrylonitrile, and a CMKN was obtained by electrostatic spinning. The influence of adding cellulose concentration, voltage, the receiving distance, and the pushing speed on the fiber surface morphology was considered. In the tests, the feed rate of the spinning parameters varied in the range of 0.2–1.0 mL/h, the distance from the tip to the acquisition board varied in the range of 10–25 cm, the voltage was 15–25 kV, and the relative humidity was 65%. The fibers were characterized by scanning electron microscopy, X-ray diffraction (XRD), and Fourier transform infrared spectroscopy. The optimal process route was explored. At 21 kV, 20-cm receiving distance, and 0.5 mL/h pushing speed, the spun nanofibers have a smooth surface, a high overall orientation, strong uniformity, and fiber diameter. According to XRD, infrared spectroscopy, and the single-fiber tensile strength test, the crystallinity of cellulose decreases and the tensile strength increases after the transformation from cellulose to nanofiber. Through chemical and mechanical means, we effectively removed the non-cellulose components and increased the cellulose content. The cellulose in the nanofiber is type I. Response surface diagrams help to understand the interaction of these parameters. Langmuir adsorption isotherm is the best fitting model for MB removal by CMKN. The kinetic model is better explained using a pseudo-second-order model. It can be seen from the experiment that the best dye removal conditions are 30°C, MB solution concentration 40mg/L, shock time 90min, 15% cellulose nanofilm removal rate is 63.24%.

1. Introduction

Carex meyeriana Kunth, from the monocotyledon class sedge family *Carex* genus, is a perennial herbaceous plant that grows in swamps and wetlands[1]. Given its parallel hollow vein structure, *Carex meyeriana* Kunth will form a circulation channel that can lock water and air, resulting in good moisture absorption[2]. This herbaceous plant is one of the few plants in nature that can resist the invasion of foreign parasitic fungi[3]. The chemical composition of *Carex meyeriana* Kunth is usually determined by the GB5889-86 Quantitative Analysis of Ramie Chemical Composition. The plant's chemical composition is very similar to that of hemp fiber, mainly containing cellulose, hemicellulose, pectin, lignin, wax lipids, and water-soluble substances[4]. *Carex meyeriana* Kunth has good oxidation resistance[5], good adsorption[6], and other remarkable characteristics. The focus of the research on *Carex meyeriana* Kunth is on the extraction of natural fiber and the application of the plant's components. Hong Wang et al. determined the Cr, Zn, Cu, Cd, Pb, and Ni contents in the aboveground soil and plants along the highway and studied the absorption behavior of *Carex meyeriana* Kunth in mud. The results show that *Carex Meyeriana* Kunth mainly absorbs lead from atmospheric sediments through its stomata. *Carex* plants can be candidates for Cd uptake in soil[7]. B H C A et al. studied *Carex meyeriana* Kunth and used

response surface methodology to optimize the extraction process. They also studied the chemical composition and antioxidant and antibacterial activities of essential oil. They found that *Carex* essential oil has strong antioxidant and antibacterial activities and great application potential in food, medicine, chemical, and other fields[8]. Zhengyu et al. adopted the analytical hierarchy process and the response surface method to optimize the macroporous purification of *Carex* polysaccharide resin. The optimal purification conditions are as follows: elution volume of 2.74 BV, flow rate of 1.88 BV/h, and injection concentration of 2.10 mg/mL. Two fractions of polysaccharides (CMKP – 1 and CMKP-2) were obtained by the DEAE-52 column. CMKP-1 and CMKP-2 could stimulate RAW264.7 cells in a certain concentration range. It is a potential immunomodulator and can be used in medicine and functional food fields[9].

Carex Meyeriana Kunth has a huge amount of cellulose. Cellulose is an important renewable resource in nature due to its high degree of polymerization, good molecular orientation, and strong chemical stability[10]. When cellulose is combined with nanomaterials to form nanocellulose, their advantages are exploited. Nanocellulose has high mechanical properties, dimensional stability, and good absorbability[11]. In recent years, many studies have been conducted on the preparation of nanocellulose. Electrostatic spinning is one of the main methods of preparing nanocellulose. Many examples of cellulose electrospinning currently exist. For example, cellulose nanofiber nonwovens were prepared by electrospinning cotton cellulose in a LiCl/DMAc solution[12]. Cellulose was removed from wheat straw, pretreated by tempo-mediated oxidation, and then dissolved into trifluoroacetic acid by electrostatic spinning to prepare highly absorbent and environment-friendly nanocellulose fibers[13]. The dissolution of toilet paper in 0.5–8.5wt % lithium dimethyl acetamide (LiCl/DMAc) or trifluoroacetic acid solution was attempted to produce cellulose nanofibers by the electrostatic spinning method[14].

Figure 1 presents the principle of cellulose electrostatic spinning. The configured cellulose solution is placed in a syringe of a certain specification, which is fixed on the clamping port of the machine; then, the needle is connected to the required high voltage static electricity, and the parameters on the control panel are adjusted[15–16]. The solution in the syringe is pushed out at constant speed. The needle solution is sprayed over the receiver in a Taylor cone shaped jet under the action of voltage. After the jets gradually volatilize, cool, and solidify, they eventually accumulate on the receiver to form a fibroid[17]. In this process, environmental temperature and humidity, surface tension, air resistance, voltage, solution ratio, and other factors affect the results of finished products, requiring further exploration and adjustment[18].

2. Experimental

2.1 Materials

Carex Meyeriana Kunth herb (purchased from Jiamusi City, Heilongjiang Province, China). The *Carex meyeriana* Kunth's cellulose (CMKC) used in this study was self-made in the laboratory. The other reagents used in this experiment are as follows: N, N-dimethyl acetamide (DMAc, ≥99.0%, SCR) and polyacrylonitrile (PAN, with an average molecular weight of 150,000 g/mol); methylene blue(MB, ≥98.5%, Tianjin Zhiyuan Chemical Reagent Co., LTD). All chemicals used in this study were

analytical grade reagents without any further treatment, and all solutions were prepared with distilled water.

2.2 Preparation of Cellulose Nanofiber

2.2.1 Preparation of Eletrospinning Solutions

PAN powder was dissolved in DMAc to prepare a 15% PAN solution. The resulting solution was magnetically stirred until evenly mixed. Then, the self-made CMKC solution was mixed with 15% PAN solution in different proportions to prepare 5%, 10%, 15%, and 25% CMKC-PAN electrospinning solutions. The mixed solution was cleaned by an ultrasonic cleaning machine for a certain time to produce an evenly mixed solution.

2.2.2 Electrostatic spinning process

The evenly mixed solution was electrospun into ultrafine fibers by an electrostatic spinning equipment (YFSP-T, YunFan antijet nano electrostatic spinning machine). The parameters, such as the applied voltage, the pushing speed, and the accepting distance, can be manually adjusted via the control panel on the equipment. The applied voltage was within 15–25 kV, and the feed rate of the solution was controlled at 0.2–1 mL/h. The collector wrapped in aluminum foil was placed 10–25 cm away from the tip of the nozzle to collect the fibers. Electrospinning was performed at room temperature and 60% relative humidity. The fibers were removed from the aluminum foil and completely dried in vacuum at 65°C.

2.3 Response surface optimization of dye adsorption process

After *Carex Meyeriana* Kunth cellulose nanofilm and methylene blue dye are dried in the drying oven, methylene blue solution of a certain concentration is configured, and then *Carex Meyeriana* Kunth cellulose nanofilm is cut into small pieces of different quality and added to methylene blue solution. Use a constant temperature oscillator for a period of time to promote dye adsorption. After the adsorption is completed, the dye solution after adsorption is taken and tested in the UV-visible near-infrared spectrophotometer. The dye removal rate is calculated according to the absorbance of the residual solution.

2.3.1 Single factor experiment

The effects of CMKC dosage, MB initial concentration, temperature and shock time on dye removal by CMKN were investigated in simulated wastewater containing methylene blue.

2.3.2 Response surface method was used to optimize the experimental design

According to the analysis of single factor experimental results, according to the design principle of Box-Behnken central combination experiment, with temperature (A), shock time (B) and MB concentration (C) as independent variables and total dye removal rate as response value, response surface analysis method with three factors and three levels was used to obtain the optimized process parameters. The design of experimental factor level is shown in Table 1.

Table 1
Three Factors Levels and Codes of Box-Behnken Design

The coding level	A Temperature (°C)	B shock time (min)	C MB concentration (mg/L)
-1	25	80	30
0	30	90	40
1	35	100	50

3. Characterizations And Measurements

3.1 SEM analysis

Scanning electron microscopy (SEM) images of the fiber surface were taken with an S-3400 (Hitachi) scanning electron microscope. The microscope was operated at 10 kV, 20 °C, and RH of 65%. Prior to SEM evaluation, the samples were coated with a thin layer of gold using a plasma sputtering apparatus.

3.2 XRD analysis

X-ray diffraction (XRD) patterns were recorded from 2θ = 10°–90° with a D/max-RB diffractometer equipped with a graphite monochromator and Cu Kα radiation at λ = 0.154 nm (45 kV, 200 mA).

3.3 FT-IR analysis

The chemical functional groups in CMKC and CMKN were determined by infrared spectroscopy. The changes between the two were analyzed. The optical fibers were analyzed using a Spectrum One Infrared spectroscopy analyzer (PE, USA). The spectrum obtained is the result of 30 scans at 4 cm⁻¹ resolution in the range of 400–4000 cm⁻¹.

3.4 Mechanical and Physical Test

The CMKN samples were treated in a vacuum oven (65 ± 2 °C) for 24 h and then cut into 5 mm × 3 cm strips for testing. The fiber strength and elongation at break were measured by an LY – 06E fiber strength tester at 20 °C and RH of 65%. The pre-tension was 0.6 CN/dtex, and the tensile length and speed were maintained at 10 mm and 30 mm/min, respectively. The results from the five specimens were averaged[19].

3.5 Adsorption rate test

Using CMKN as adsorbent for static experiment, the specific operation process is: A certain mass of CMKN was added to the methylene blue solution with a certain concentration, and the methylene blue wave length was known to be about 650nm after shaking on the digital display constant temperature oscillator for a certain time. The absorbance and concentration of the remaining dye were measured by UV spectrophotometer, and the removal rate was calculated. As shown in the following formula, C_0 : Initial dye concentration (mg/L); C_t : Is the dye concentration in solution at time t (mg/L)[20].

$$\text{Dye removal rate} = \frac{C_0 - C_t}{C_0} \times 100\%$$

4 Results And Discussion

4.1 SEM analysis

4.1.1 Effect of different proportions of cellulose and PAN on electrospinning

In electrospinning, the spinning fluid has a very important effect on fiber formation[21]. The cellulose solution of pure *Carex meyeriana* Kunth has poor stability and low viscosity and is difficult to spin by electrostatic spinning. Therefore, a certain proportion of PAN should be used to improve the spinnability[22–23]. Figure 2 shows the SEM images of different proportions of cellulose and PAN electrospinning fibers. In this experiment, the effects of 5%, 10%, 15%, and 25% cellulose in the cellulose and PAN mixture on the electrospinning effect were investigated. Electrospinning was performed at 18 kV, the receiving distance of 15 cm, and the propulsion speed 0.5 mL/h.

Figure 2a clearly shows that when the cellulose/PAN ratio is 5%, the diameter of the polymer fiber formed is irregular, and a large gap exists between the fiber diameters. The fiber diameter is mostly distributed between 400 and 500 nm, and the surface is rough and greatly curved. Figure 2b indicates that when the cellulose/PAN ratio is 10%, the fiber diameter distribution is mostly between 250 and 300 nm. Thus, the fiber surface is obviously smooth, but some bending remains. Some improvement can be observed compared with adding 5% cellulose. Figure 2c shows that when the cellulose/PAN ratio is 15%, the overall fiber distribution is relatively uniform under electron microscopy, and the fiber diameter is mainly concentrated in the range of 300-350nm. The overall uniformity of fiber is high, the fiber surface is smooth and smooth, relatively continuous, without too much bending, and the spinning effect is good. Figure 2d shows that when the cellulose/PAN ratio is 25%, the fiber diameter is mainly distributed between 160–230 nm. Although the fiber generally becomes fine, certain beads remain, and the bending degree of the fiber increases. Thus, the spinning condition is poor.

When the cellulose/PAN ratio is 15%, the fiber diameter distribution is uniform, the fiber morphology difference is small, the fiber surface is flat, and the fiber fineness is good. If the concentration is extremely low, then the fiber diameter will be thick and the uniformity will be worse. Increasing the concentration to

more than 25% will result in liquid beads, poor stability, and reduced spinnability. Therefore, the optimal blending ratio of 15% can be adopted for the subsequent experimental research.

4.1.2 Effect of voltage on electrospinning

Spinning voltage also has a great influence on fiber formation in electrostatic spinning[24]. If the electrostatic spinning voltage is extremely low, the effect of the electric field force in the electric field will be weakened, and the solution pushed out by the syringe will be affected by its own viscosity and surface tension resistance, so it cannot spin smoothly[25]. If the voltage of electrostatic spinning is too high and the charge load is too large, the discharge phenomenon will cause damage to the nozzle and receiver[26]. In this experiment, 15% cellulose ratio, liquid pushing speed of 0.2 mL/h and receiving distance of 20cm were selected to study the influence of different voltages on CMKC electrostatic spinning.

Figure 3 shows the SEM and fiber diameter distribution histogram of the nanofibers prepared by the spinning solution at 15, 18, kV and 25kV. As shown in the figure, regular nanofibers can be spun within the voltage range of 15–25 kV. However, the fibers spun at 15 kV (Fig. 3a) and 18 kV (Fig. 3b) still had certain beads, and the spinning effect was unstable. In contrast, nanofibers spun at 21 Kv (Fig. 3c) exhibited high uniformity and few disorderly fibers, and the diameter of the fibers was generally distributed between 200 and 250 nm. Meanwhile, the observation of the fibers spun at 25 kV (Fig. 3d) revealed that the fiber diameter distribution widened; although the fiber became fine for a short time, the uniformity decreased. The electric field force increased with the voltage, causing the solution ejection speed to increase sharply. The spinning solution was sprayed on the receiver without good stretching in the electric field within a short time, making the overall effect of the fiber gap large, indicating that it is unsuitable for high voltage. Thus, 21 kV is suitable for the electrostatic spinning of CNKC. According to the above analysis, 21 kV voltage was selected for the follow-up study.

4.1.3 Effect of liquid pushing speed on electrospinning

Meanwhile, selecting a reasonable pushing speed is also the key factor affecting the morphology of the electrostatic spinning fiber. In electrostatic spinning, the fiber with a low flow rate is fully polarized, and the morphology of the fiber is good[27]. According to the above analysis, we selected 15% cellulose spinning solution, 21 kV spinning voltage, and 20 cm receiving distance as the fixed parameters for exploring the influence of different pushing speeds on the electrostatic spinning fiber morphology. As shown in FIG. 4, the pushing velocity is 0.2, 0.5, 0.8, and 1 ml/h, respectively. The overall morphology and diameter distribution of the fiber are the same, and the main diameter of the fiber is basically distributed between 250 and 300 nm. From 0.2 mL/h to 1 mL/h, the fiber output increased gradually with the increase of the liquid pushing speed. The fiber diameter distribution diagram indicates that when the fiber pushing speed increased, part of the fiber diameter gradually increased, and the overall fiber uniformity decreased. Moreover, increasing the fiber pushing speed will have a great influence on the fiber morphology, forming filaments in the jet and even beads on the fiber of the receiver and decreasing the stability of electrostatic spinning [27]. Through experimental research and analysis, we selected the liquid

pushing speed of 0.5 ml/h as the best parameter. At this speed, the fiber fineness is relatively neat, that is, mainly between 250 and 300 nm, and the surface is smooth.

4.1.4 Effect of receiving distance on electrospinning

Figure 5 shows the SEM images and fiber distribution histograms of the spinning solution with 15% cellulose ratio at 21 kV, 0.5 mL/h pushing speed, and different receiving distances. In this experiment, 10 cm (FIG.5a), 15 cm (FIG. b), 20 cm (FIG. c), and 25 cm (FIG. d) were selected for reference.

The figure shows that when the receiving distance of the fiber was 10 and 15 cm, the fiber morphology showed no obvious problems, but the fiber diameter distribution was wide, the thickness gap was obvious, and the fiber was not neat. At the receiving distance of 20 cm, the overall uniformity of the fiber improved significantly, and the fiber diameter was mainly concentrated between 60 and 100 nm. When the fiber was lit 25 cm, the fiber began to become coarser and the overall uniformity decreased. As the receiving distance increased, the voltage remained constant and the electric field intensity decreased[28]. The jet velocity decreased, and the fiber was not fully stretched and did not thicken. The range is extremely small and will cause inadequate fiber stretching and incomplete solvent volatilization, resulting in fiber adhesion and pile knot. The fiber surface morphology at the 20 cm receiving distance (Fig. 5c) is better than that at other distances. Furthermore the spinning effect is better with higher uniformity and good fiber orientation at the 20 cm receiving distance than in the other distances. Therefore, 20 cm is the best receiving distance.

4.2 XRD analysis

The crystallinity of fiber can be determined by XRD analysis[29]. Fiber crystallinity is commonly used to measure the mechanical properties of fiber, that is, the higher the crystallinity of the fiber is, the better the relative mechanical properties are; but an extremely high crystallinity will lead to fiber rigidity, that is, elasticity reduction[30]. In the diffraction pattern, the crystalline and amorphous regions of the fiber can be inferred from the XRD structure[31]. Figure 6 shows the XRD patterns of CMKC and CMKN and the diffraction patterns of fiber changes under XRD. The initial CMKC was transformed into CMKN, and the crystal ratio changed. Figure 6 shows that the main crystal peak occurred when CMKC $2\theta = 22^\circ - 23^\circ$, which corresponds to cellulose crystal type I[32]. In addition, the spectra of CMKN and CMKC have similar variation trends and diffraction peak intensities. However, the crystallization index of CMKN, which becomes cellulose nanofibers after treatment, is much lower than that of CMKC before treatment. During electrospinning, the crystal structure of natural cellulose was obviously disturbed, decreasing the crystallinity after the deposition of nanofibers[33]. When the crystallinity of fiber is affected by mechanical or chemical factors, the hydrogen bonds between cellulose segments will be destroyed, and the crystallinity of CMKN will be much lower than that of CMKC[34].

4.3 FT-RT analysis

Infrared spectrometer is used for analyzing the molecular structure and the chemical composition on the basis of the absorption characteristics of different wavelengths of infrared radiation[35]. In Fig. 7, we mainly compare and analyze the changes of the infrared spectrum of CMKN after PAN and electrostatic spinning. The figure shows that certain changes occurred in the structure of cellulose to nano fiber. In the CMKN spectrum, a strength band formed by O-H bond stretching was observed at 3400 cm^{-1} , and a medium strength band formed by C-H bond stretching was observed at 2862 cm^{-1} [36]. The changes at 1733 and 1558 cm^{-1} were due to the disappearance of the glycofurfural ester and acetyl hemicellulose or carboxyl ester bond lignin in the fiber[37]. This result indicates that our nanofibers effectively removed some non-cellulose components and increased the cellulose components compared with the original product. The absorbance of 1330 – 970 in the CMKN region is due to the stretching of the C-O bond[38], and the 900 cm^{-1} band is characteristic of the β -glycoside bond between sugar units[39]. The peaks of 1421, 1364, 1323, 1142, 1050, 1029, and 900 cm^{-1} are significantly correlated with the cellulose peaks[40]. A small band was found at 712 cm^{-1} , which is the type I form of cellulose[41], which is currently the dominant cellulose form of PAN. The changing structure of the infrared spectrum shows that after chemical or physical treatment, some non-cellulose structures were effectively removed, making the composition of cellulose prominent, and the form of cellulose is cellulose I.

4.4 Mechanical and Physical Test

Given the small size of electrospun nanofibers, no specific method is suitable for measuring them. Therefore, a single-fiber strength tensimeter is widely used to measure the mechanical properties of nanofiber membranes[42]. The tensile strength of materials can be measured by their physical quantities, such as the maximum tensile strength, the breaking force, the elongation at break, and the elastic modulus [43]. FIG. 8 shows that this experiment compares the effects of different proportions of the cellulose/PAN spinning solution on the mechanical properties of CMKN under 21 kV, the pushing speed of 0.5 mL/h, and the receiving distance of 20 cm.

The figure shows that the strength of the spinning solutions with different cellulose ratios also varies. The mechanical properties are greatly improved with the increase of the cellulose ratio in the spinning solution. The strength of the CMKN spun from 5% and 10% spinning solutions did not improve significantly, but the mechanical properties began to improve greatly when it was added to 15%. This phenomenon may be attributed to the generally small effect of the very small cellulose content on the spinning solution or insufficient solution uniformity of the ultrasonic spinning solution. Although the addition of cellulose can improve the mechanical properties, excessive addition will lead to a poor spinning effect and many defects in fiber appearance, leading to the failure of normal spinning.

4.5 Dye removal rate analysis

4.5.1 Single factor experimental analysis of dye removal rate

As shown in FIG. 9a, Under the conditions of 30°C, methylene blue (MB) concentration of 40mg/L, adding 2.5mol/L H₂O₂, shaking for 90min, 0.5mg carex meyeriana kunth cellulose nanomembrane was selected, and the cellulose content in the membrane was divided into 5%, 10%, 15%, and 25% for the experiment. As can be seen from Table 1, the dye removal rate will increase with the increase of cellulose ratio, but the performance of 25% nanofilm is not good enough. Therefore, the nanomembranes with a cellulose ratio of 15% were selected for discussion.

As shown in Fig. 9b, Cut 0.5mg nanomembrane with 15% cellulose content, add 2.5mol/L H₂O₂ in methylene blue (MB) concentration of 40mg/L dye solution, shake for 90min, the above conditions are fixed. The temperature is set to 20°C, 30°C, 40°C, 50°C, etc. The dye removal rate can be seen from the table. When the temperature is below 30°C, the dye removal rate can only reach about 20%, and when it reaches 30°C, the dye removal rate is significantly increased. The dye removal rate gradually decreased after 30°C. When the temperature is changed, the ions will move faster with the increase of temperature, and the dye will quickly find the attachment point of the film. However, when the attachment point is basically coated by the dye, the removal rate will be stable, and the adsorption effect will not increase significantly. Rising temperature will also decompose H₂O₂, leading to a decrease in removal rate. Therefore, the next 30°C will be selected for the experiment.

As shown in FIG. 9c, At 30°C, 0.5mg nanofilm with 15% cellulose added, 2.5mol/L H₂O₂ added, methylene blue (MB) concentration selected 40mg/L dye solution for the test, the above conditions are fixed. The shock time is set to 30min, 60min, 90min and 120min respectively. As can be seen from the table, the dye removal rate gradually increased with the increase of the oscillation time, but after 90min, the removal rate did not increase, but decreased to a certain extent. In the process of adsorption, the dye fully binds to the binding point on the membrane surface with the increase of time, but when the binding point is completely occupied, the adsorption amount of dye will not rise and a certain degree of dissociation will occur. After that, no matter how the adsorption time increases, the removal rate will not be affected, and the adsorption and dissociation of the dye will reach a dynamic equilibrium.

As shown in Fig. 9d, At 30°C, 0.5mg nanofilm containing 15% cellulose was used, 2.5mol/L H₂O₂ was added, and the shaking time was 90min. The above conditions were fixed. Dye solution methylene blue (MB) concentration of 20mg/L, 30mg/L, 40mg/L and 50mg/L were selected for the test. As can be seen from the table, between the concentration of dye solution and the removal rate, the removal rate will increase with the increase of concentration, but the removal rate will decrease when the concentration exceeds a certain range. Since the dye concentration is low and the attachment points are many, increasing the concentration will increase the dye, so as to effectively adhere to the membrane surface. However, if the concentration is too high, the dye will increase, and the attachment point is limited, and the solution is too concentrated, the dye will not spread well, leading to the poor adsorption effect of the film, and the removal rate will decrease.

4.5.2 Response surface analysis

According to the single factor test, the optimal experimental range of significant factors was selected, and the total dye removal rate was taken as the optimization index CMKN adsorption MB staining solution process conditions for response surface analysis, so as to optimize the process again. The experimental results, regression equation diagram and response surface analysis of variance are shown in Table 2 and Table 3.

Table 2
Box-Behnken Design Test Results

No.	Temperature (°C)	shock time (min)	MB concentration (mg/L)	dye removal rate(%)
1	30	80	50	47.81
2	30	90	40	63.24
3	25	80	40	45.08
4	25	90	30	44.79
5	30	100	30	58.04
6	30	90	40	61.16
7	30	90	40	62.72
8	30	90	40	62.87
9	30	90	40	63.21
10	30	80	30	57.82
11	35	100	40	55.52
12	35	90	50	52.58
13	30	100	50	53.94
14	25	100	40	40.88
15	35	90	30	51.35
16	25	90	50	37.08
17	35	80	40	50.67

Table 3
Analysis-of-variance results.

Source	Sum of squares	Degree of freedom	Mean square	F	P
Model	1069.38	9	118.82	54.65	< 0.00001
Residual	15.22	7	2.17		
Lack of Fit	12.28	3	4.09	5.58	0.0651
Pure Error	2.93	4	0.7337		
Cor Total	1084.60	16			

Figure 10 shows the interaction of three factors: shock time, MB concentration and temperature. The significant level of influencing factors can be seen from the surface conditions and contour plots of each figure. The steep surface indicates that the influencing factors are significant, and the shape of the contour line can reflect the strength of the interaction effect. The oval indicates that the interaction between the two factors is significant, while the circle indicates that the interaction effect is not obvious [44]. The surface in Fig. 10 is steep and the contour lines approach the ellipse, indicating that the interaction effect is significant.

Combined with the above analysis, the software was used for further analysis, and the optimal experimental conditions were as follows: shock time 90min, MB concentration 40mg/L, temperature 30°C, removal rate of 63.24%. In order to validate the result of the prediction, using the optimal conditions for experiments, the removal rate of CMKN, comparing the regression equation of predicted value, its deviation was 0.6%, the fitting of the correlation between experimental value and predicted value is good, prove that the conditions of the model analysis and prediction is more accurate and reliable, has certain practical value.

Multiple regression analysis was conducted on the experimental results of CMKN adsorbing MB dye. According to the variance analysis results of each item in the regression equation (Table 2), F value of Model was 54.65, P value was < 0.0001, indicating that Model was extremely significant. A (temperature), B (shock time) and C (MB concentration) were significant factors, and the order of influence of each factor on MB removal rate was as follows: A > B > C. Among them, the interaction between AB and AC was significant, and the influence of the other terms was not significant enough, indicating that the relationship between each factor and the response value could not be explained by a simple linear relationship, but a nonlinear relationship. The correlation coefficient R^2 of the model is 0.9860, 98.60% of the variation in response value was due to the three selected variables. And F value of the misfitting term is 5.58, P value is 0.0651, indicating that the model has a high degree of fitting to the actual situation, and the regression equation can be used The removal rate of MB solution under different experimental

conditions was predicted and the optimal experimental conditions were obtained. According to the results of regression analysis (Table.2) Make the corresponding surface diagram.

5. Conclusions

The influence factors of the cellulose in nature on the electrostatic spinning process were systematically studied. After discussing the influence factors, namely, electrostatic spinning voltage, liquid pushing speed, receiving distance, and cellulose/PAN ratio, the optimal process route was explored. At 21 kV, 20 cm receiving distance, and 0.5 mL/h pushing speed, the spun nanofibers have a smooth surface, a high overall orientation, strong uniformity, and fiber diameter. According to XRD, infrared spectroscopy, and the single-fiber tensile strength test, the crystallinity of cellulose decreases and the tensile strength increases after the transformation from cellulose to nanofiber. Through chemical and mechanical means, we effectively removed the non-cellulose components and increased the cellulose content. The cellulose in the nanofiber is type I. Response surface diagrams help to understand the interaction of these parameters. Langmuir adsorption isotherm is the best fitting model for MB removal by CMKN. The kinetic model is better explained using a pseudo-second-order model. It can be seen from the experiment that the best dye removal conditions are 30°C, MB solution concentration 40mg/L, shock time 90min, 15% cellulose nanofilm removal rate is 63.24%.

The results show that the nanofibers prepared by combining cellulose with existing electrostatic spinning methods have good properties and a strong application prospect. Nanocellulose composite membrane material has good adsorption, filtration, barrier and mechanical properties. At present, functional membrane is widely used in food industry, water treatment industry, new energy field, battery manufacturing and other industries. This study opened a new development direction for the application of natural resources, improved the commercial potential of *Carex meyeriana*, and made a new exploratory attempt to alleviate the consumption of fossil energy and the environmental pressure on the earth.

Declarations

All the methods were carried out in accordance with local, China and Qiqihar University guidelines and regulations.

Data availability

Data Availability Statement: The figures used and analyzed during the current review are available from the publisher and corresponding author on reasonable request.

Author contributions

Ying SUN wrote the main manuscript text; Yang YU participated in experimental research and wrote part of the manuscript text; Duanxin LI prepared Table. 1, 2, 3; Weishuai KONG and Feng YANG prepared Figs.1-10. All authors reviewed the manuscript.

Competing interests

The authors declare no competing interests.

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Figures

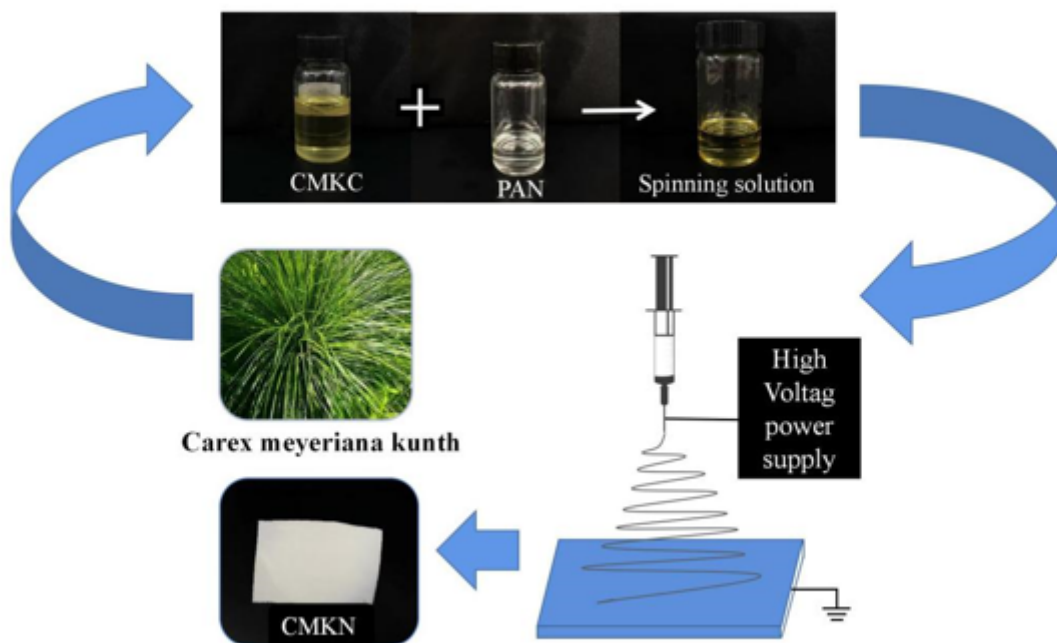


Figure 1

Route of electrospinning experiment

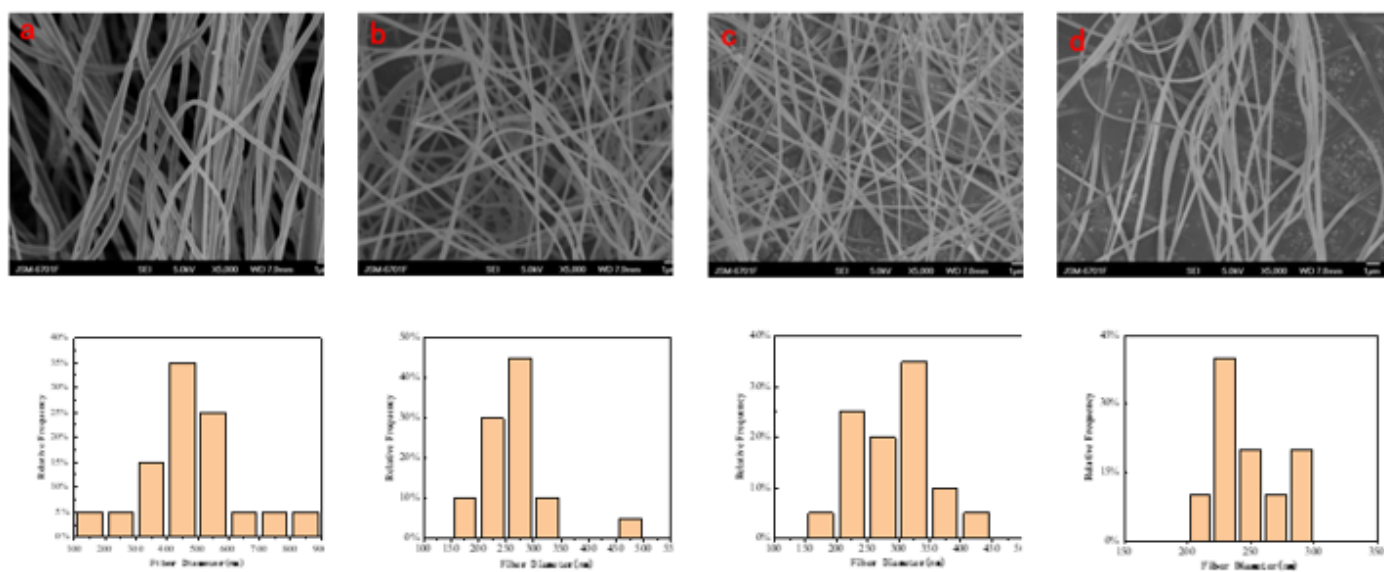


Figure 2

SEM images of electrospinning CMKN fibers with different cellulose ratio and fiber diameter distribution (a: 5%;B:10%; C:15%;d:25%)

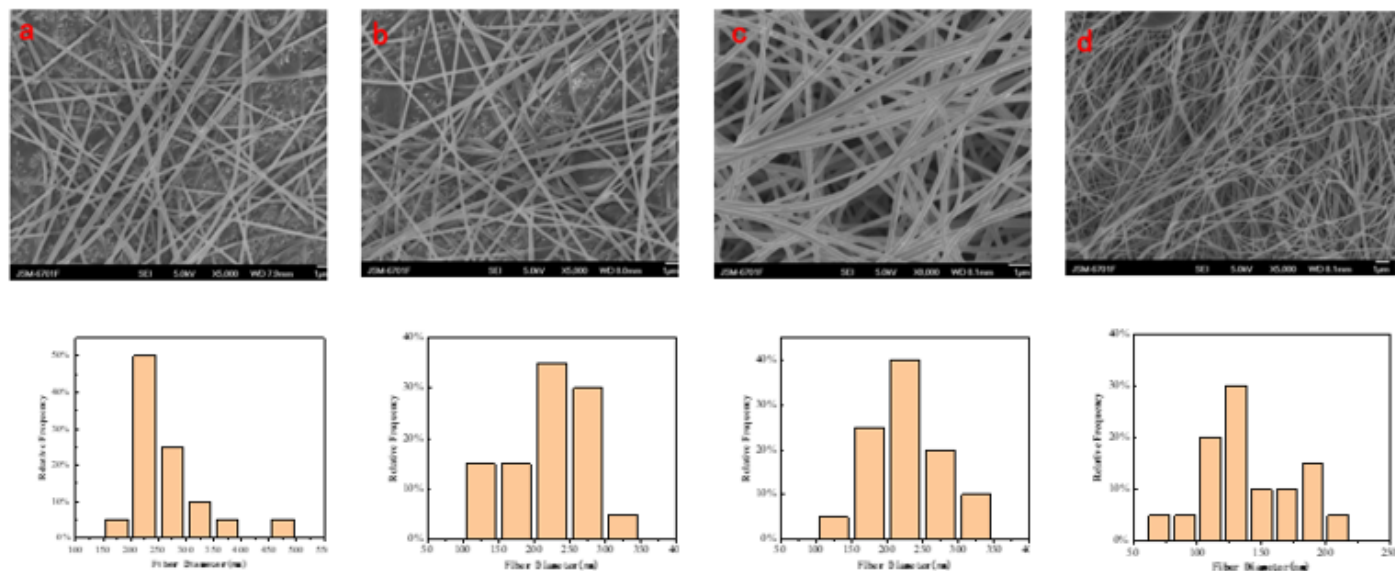


Figure 3

SEM images of electrospun CMKN fibers at different voltages and fiber diameters (A:15kV;B:18 kv;c:21kv;d:25kv)

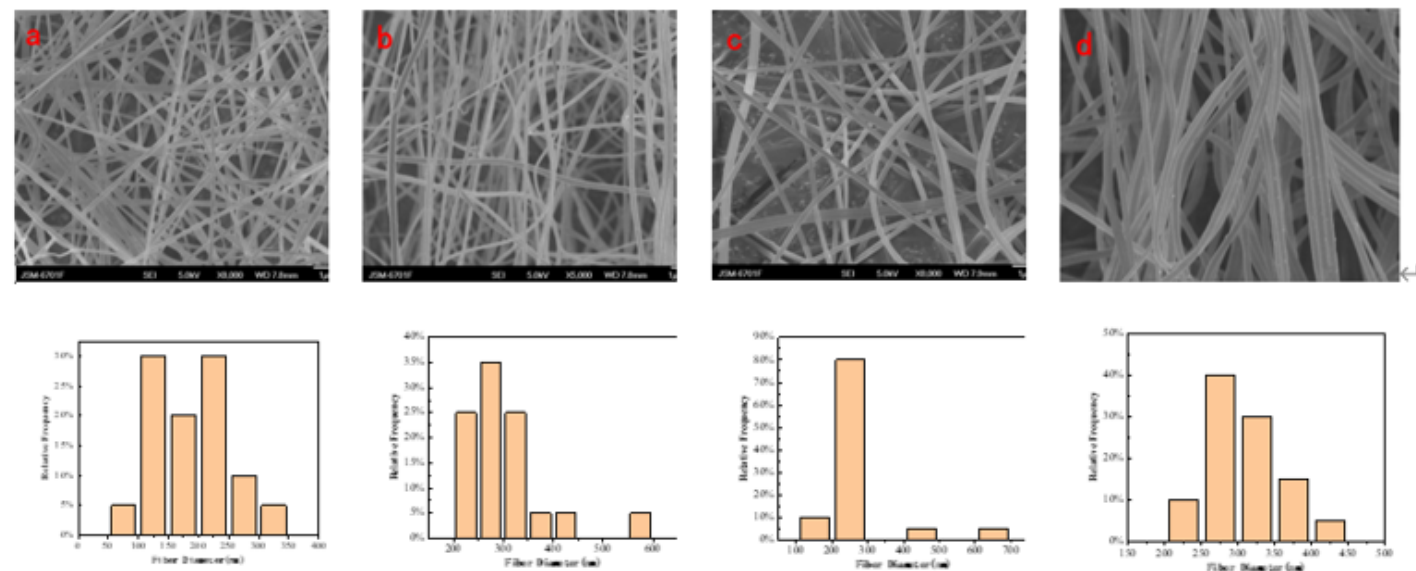


Figure 4

SEM images of electrospinning CMKN fibers at different pushing speed and fiber diameter distribution (a:0.2ml/h;B:0.5 ml/h;C:0.8 ml/h;d:1ml/h)

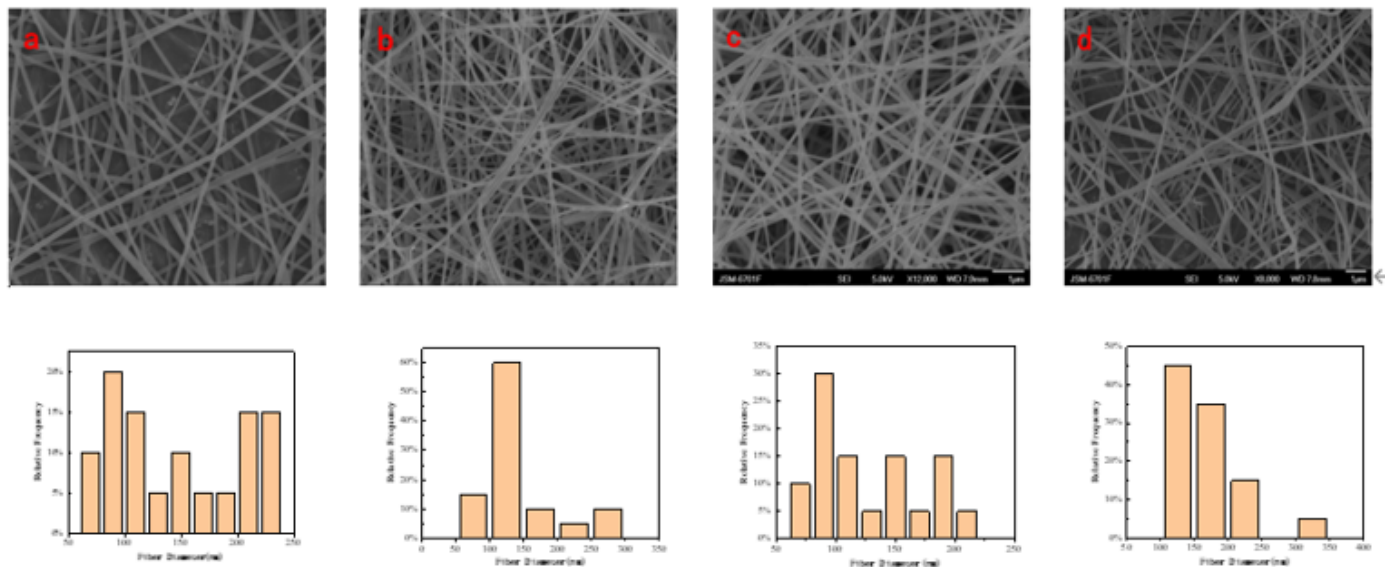


Figure 5

SEM images of electrospun CMKN fibers at different collection distances and fiber diameter distribution (a:10cm;b:15cm;c:20cm;d:25cm)

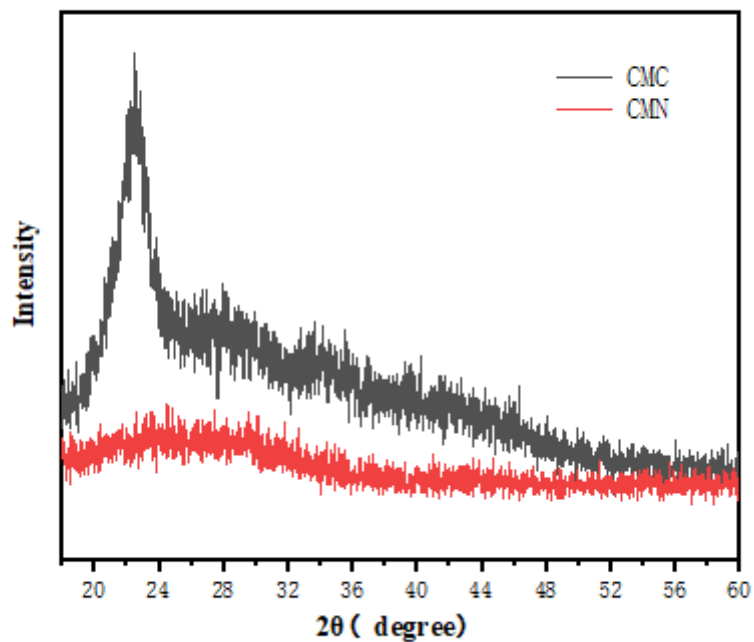


Figure 6

X-ray diffractograms of CMKC and CMKN

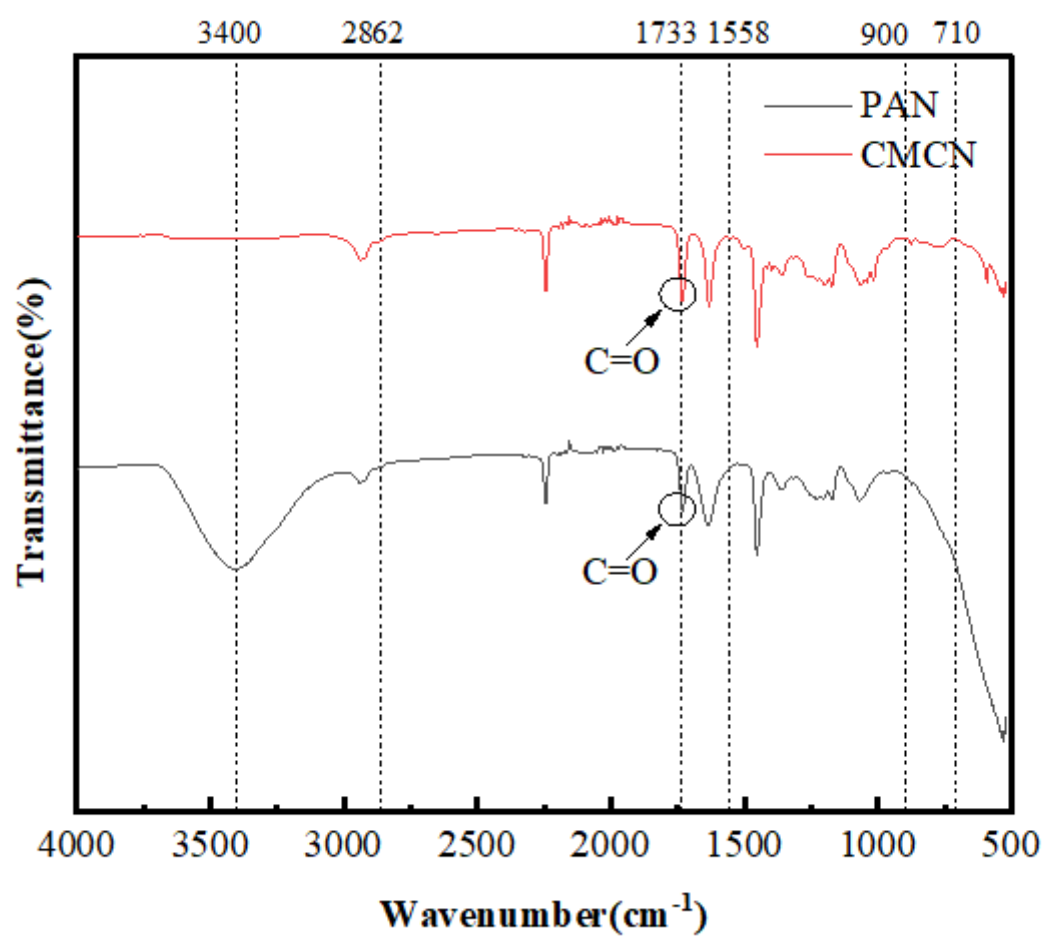


Figure 7

FTIR spectra of PAN and CMKN

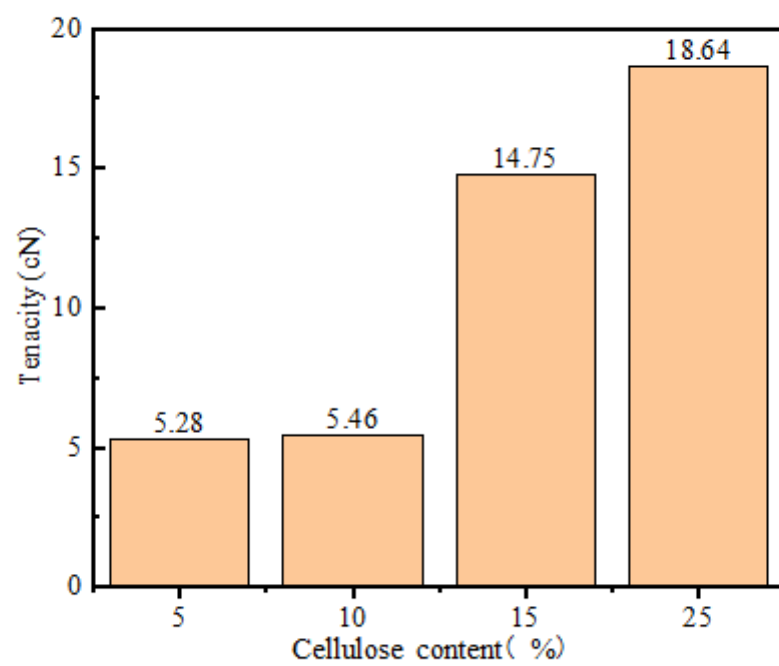


Figure 8

Tensile strength of a spinning fluid with different cellulose content

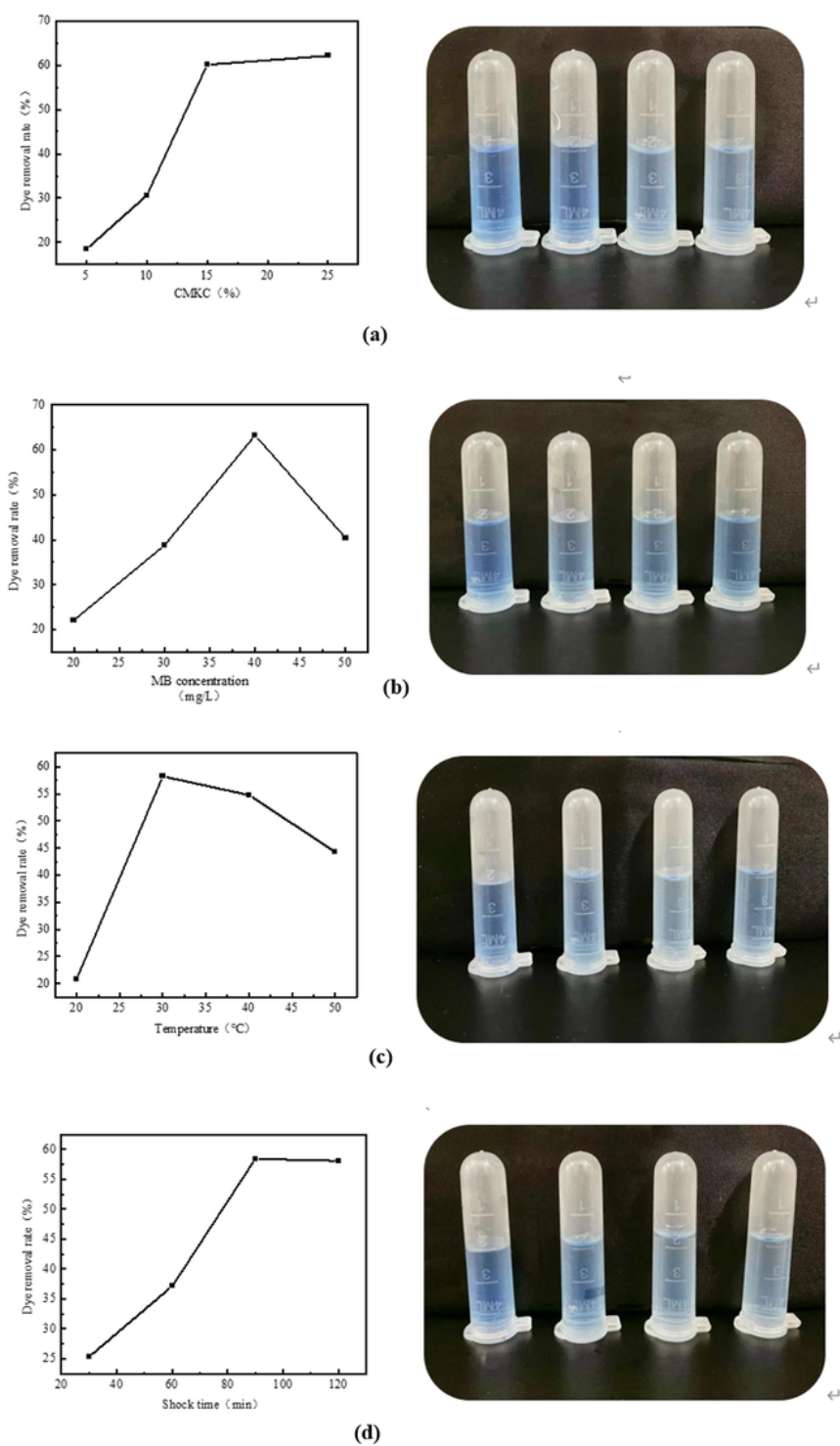


Figure 9

(a) Effect of CMKC ratio on dye removal rate (b) Effect of MB concentration on dye removal rate (c) Effect of Temperature on dye removal rate (d) Effect of different shock time on dye removal rate

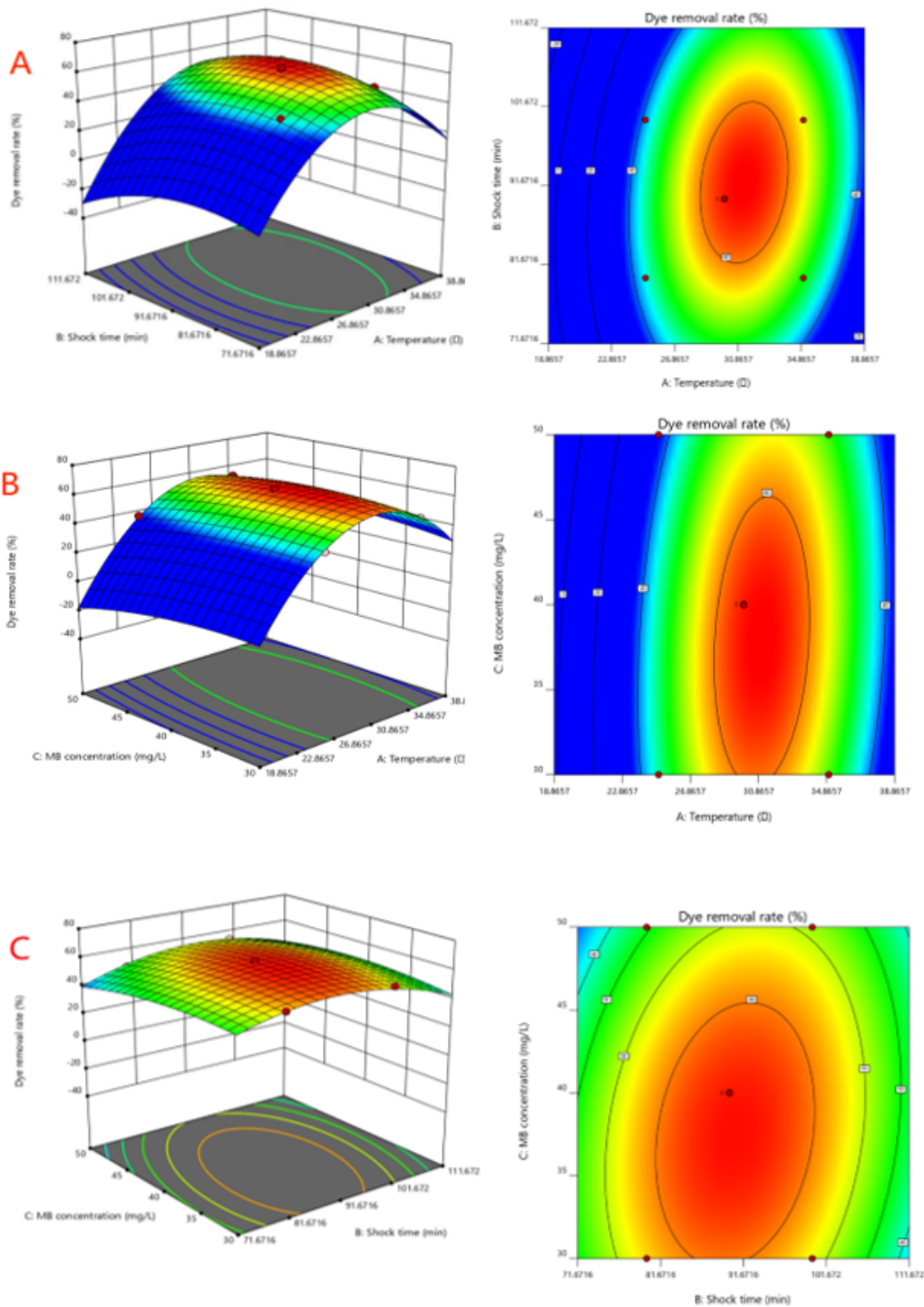


Figure 10

Response surface plot and contour plot of the influence of Various factors on removal rate (A:Temperature and Shock time;B :MB concentration and Temperature; C:MB concentration and Shock time)