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Anti-Felting Treatment of Wool Fabric by Fenton-Like Oxidation System

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Abstract: Wool fabric is prone to felting under hot and humid conditions due to the scale layer structure, impairing its appearance and durability. A novel Fenton-like oxidation system for anti-felting treatment of wool fabric was proposed in this study. The composite catalyst, prepared by loading Fe_3O_4 onto chitosan (CS) and hydroxyapatite (HA), denoted as CS/HA/Fe_3O_4, was used to catalyze H_2O_2 to generate free radicals, thereby reducing felting shrinkage by destroying the scale structure of wool fibers. The optimal reaction conditions were determined as CS/HA/Fe_3O_4 4.5% on mass of fabric (omf), H_2O_2 30.0% omf, 1-hydroxyethylidene-1, 1-diphosphonic acid (HEDP) 18.0% omf, and Na_2CO_3 5.0% omf. Fourier transform infrared (FTIR), scanning electron microscopy (SEM), and water contact angle (WCA) characterizations confirmed that the Fenton-like treatment effectively cleaved wool disulfide bonds, stripped surface scales, and reduced hydrophobicity. Preliminary reusability tests of the CS/HA/Fe_3O_4 composite catalyst showed that after three cycles, the felting shrinkage rate of wool fabric slightly increased from 4.0% to 4.7%, which still met the international standard (≤5.0%).

Keywords: wool fabric; surface modification; anti-felting treatment; Fenton-like oxidation
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0 Introduction

Wool fibers, natural fibers derived from the outer coat of sheep, possess numerous outstanding properties and thus have extensive applications[1]. Composed predominantly of proteins, they are characterized by a high degree of elasticity, softness, and comfort, along with excellent thermal insulation properties[2]. The felting shrinkage of wool fabric can be attributed to the unique scale layer structure on the fiber surface. Under hot and humid conditions, interpenetration, entanglement, and felting phenomena occur[3]. The surface scale layer structure of wool fibers, owing to the directional friction effect, leads to the cross-overlapping of the scale layer, which in turn gives rise to the felting shrinkage phenomenon[4]. Specifically, the surface of wool fibers is covered with tightly arranged scales oriented in the direction of the wool tip. Consequently, the frictional resistance from the wool root to the wool tip (anti-scale direction) is higher than that from the wool tip to the wool root (para-scale direction). The difference between the coefficient of friction in the anti-scale direction and that in the para-scale direction is referred to as the directional friction effect. The felting of wool fabric is closely associated with the directional friction effect. Therefore, anti-felting treatment is mainly targeted at treating the scale layers of wool fibers, aiming to reduce the directional friction effect and thus minimize or prevent the occurrence of the felting shrinkage.

At present, the anti-felting treatment methods for wool fabric are mainly classified into three types: addition, reduction, and a combination of addition and reduction. The addition methods involve applying a polymer to the scale layer on the surface of wool fibers to form a coating or polymer film, which can effectively reduce the directional friction effect of wool fibers, thereby achieving the anti-felting effect[5]. The reduction methods aim to damage the scale layer on the surface of wool fibers. When the scale layer becomes flattened, the directional friction effect of wool fibers is also reduced[6]. The combination of the addition and reduction methods first employ the reduction method to remove the scale layer, and then, polymerization treatment is applied, making the scale layer of wool fibers flatter and reducing the directional friction effect.

The common reduction methods include the chlorination method, peroxide method, bio-enzyme method, etc. Among these, the chlorination method is the most effective one. However, during its application, it can cause fabric yellowing and generate organic halides (AOX), which lead to environmental pollution[7]. The peroxide method is a common treatment method that contains a large amount of reactive oxygen species. It mainly decomposes into water and oxygen during the treatment process, posing no pollution to the environment. However, this decomposition process is

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usually slow[8]. Pu et al.[9] found that when the wool fabric was pretreated with H_2O_2 under appropriate conditions and then co-treated with a self-made environmentally friendly protein-based anti-felting agent and sodium sulfite, the felting shrinkage rate of the wool fabric was reduced by 6.7% compared with that of the wool fabric pretreated without H_2O_2. Wang et al.[10] investigated the effect of H_2O_2 pretreatment on the properties of the wool fabric. Owing to the destruction and removal of the scale layer and the bleaching effect of H_2O_2, the anti-felting property and the whiteness of the wool fabric were significantly improved. When the wool fabric is treated with H_2O_2, H_2O_2 acts as a strong oxidizing agent to oxidize the disulfide bonds in the scales of wool fibers, converting them into oxidized sulfonyl alanine. Meanwhile, it decomposes the peptide chains of protein molecules, thereby destroying the scales on wool fibers and reducing the frictional effect. As the frictional effect is weakened, the anti-felting property of wool fabric is enhanced, and the hydrophilicity of the wool fabric is also improved[11]. However, the drawback of H_2O_2 lies in its extreme instability. The entire oxidation process is hard to control, and the utilization rate of H_2O_2 is extremely low. A common approach to enhancing the utilization of H_2O_2 is to add a catalyst.

Fe^{2+} is commonly used as a catalyst to enhance the utilization rate of H_2O_2, and this process is the traditional homogeneous Fenton reaction[12]. However, the homogeneous Fenton reaction has some drawbacks. For example, the reaction occurs at a pH value of about 3 and is sensitive to particulate matter[13]. Scientists have attempted to replace Fe^{2+} in the homogeneous Fenton reaction with iron-containing solid materials as catalysts, thus developing the Fenton-like (heterogeneous Fenton) technology. The Fenton-like technology has broad application prospects due to its advantages, such as high catalytic activity, non-toxicity, a wide application pH range, and easy recyclability[13]. An important heterogeneous catalyst is magnetite (Fe_3O_4), which has an octahedral structure capable of accommodating Fe^{2+} and Fe^{3+}[14]. These ions can be reversibly oxidized and reduced within the crystal lattice. Moreover, it also has excellent magnetic and electrical properties, making it easy to collect after use[15]. Currently, the application of the Fenton-like oxidation system is mainly concentrated in wastewater treatment. The use of this technique in textile finishing is not common, and only a few researchers have made preliminary attempts. Li et al.[16] used $FeSO_4$ as a catalyst to catalyze H_2O_2 and combined it with ultrasound to bleach the wool fibers. The experimental results indicated that Fe^{2+} could enhance the decomposition rate of H_2O_2 by 20.9%, and the rate increased by a further 35.9% after the introduction of ultrasound. This further verifies the feasibility of metal matrix-catalyzed H_2O_2.

Fe_3O_4 is frequently loaded onto other substrates. If this system is applied to the treatment of the wool fabric, the loading substrate is required to have the ability to adsorb both metal ions and the wool fabric. Chitosan (CS), a natural polymeric compound, exhibits good biocompatibility and renewability. Moreover, it possesses a variety of functional groups (amino and hydroxyl groups), endowing it with a strong metal adsorption capacity[17]. It is an ideal material for loading Fe_3O_4. However, CS exhibits poor mechanical strength, which may lead to the instability of the loaded material. Hydroxyapatite (HA), which is abundantly present in animal bones and teeth, has been proven by some studies to be able to improve the stability and mechanical strength of CS[18-20]. These studies demonstrate the feasibility of immobilizing CS on HA for the loading of Fe_3O_4.

The primary objective of this research is to construct a novel Fenton-like oxidation system for wool fabric anti-felting treatment. This novel Fenton-like oxidation system consists of a CS/HA/Fe_3O_4 composite catalyst and H_2O_2. CS/HA/Fe_3O_4 was prepared by loading Fe_3O_4 onto a composite material made of CS and HA. By optimizing the Fenton-like treatment, in which the amounts of CS/HA/Fe_3O_4, H_2O_2, the oxygen bleaching stabilizer 1-hydroxyethylidene-1,1-diphosphonic acid(HEDP), and Na_2CO_3 were determined, and the optimal process parameters for wool fabric anti-felting treatment were derived. In addition, the reusability of CS/HA/Fe_3O_4 was preliminarily investigated. The findings of this research will contribute to an understanding of the potential application of a novel Fenton-like oxidation system in the anti-felting treatment of the wool fabric. In the following schematic diagram, wool fiber is used for illustrative purposes. The flowchart of this study is presented in Fig. 1.

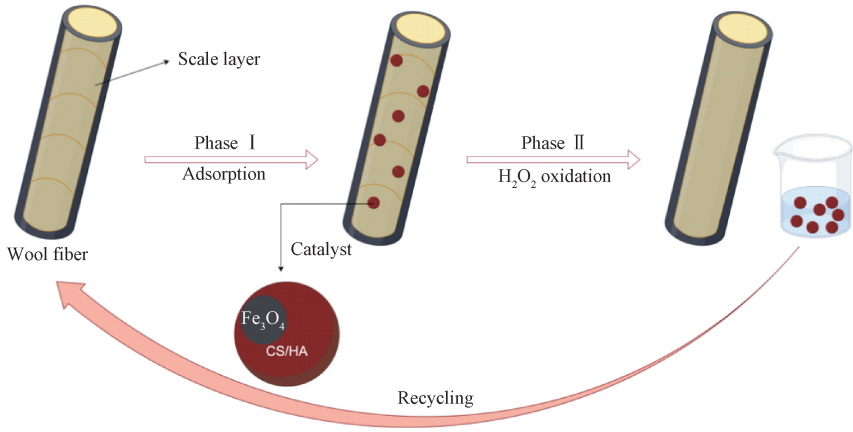

Fig. 1 Fenton-like anti-felting treatment of wool fabric

1 Materials and Methods

1.1 Materials

Wool fibers and the wool knitted fabric were supplied by Hebei Duoweikang Additive Co., Ltd., China; CS, HA, $FeCl_3 \cdot 6H_2O$, $FeCl_2 \cdot 4H_2O$ and HEDP were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd., China; nonionic surfactant CN and penetrating agent JFC were purchased from Chuanhua Chemical Co., Ltd., China; H_2O_2 and other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd., China.

1.2 Preparation of CS/HA/Fe_3O_4

CS/HA/Fe_3O_4 was prepared following the procedure described in Ref. [21]. CS (1 g) was dissolved in a four-necked flask with acetic acid solution (a mass fraction of 2%) under stirring. After 30 min, the $Ca(NO_3)_2 \cdot 4H_2O$ solution was slowly poured into the flask under constant stirring. The pH was adjusted to 1 with HCl solution (0.1 mol/L) to prevent the formation of $Fe(CH_3COO)_3$ and $FePO_4$ precipitates during the reaction. Then, a mixed solution of $FeCl_2$ and $FeCl_3$ at a molar ratio of 1∶2 was added to the flask. At the same time, $(NH_4)_2HPO_4$ and $NH_3 \cdot H_2O$ solutions were added dropwise, and the pH was adjusted to about 10. The mixture was stirred vigorously under nitrogen protection in an oil bath at 80 ℃ for 3 h. It was cooled to room temperature and aged overnight in isolation. The obtained catalyst was washed with deionized water to neutral and then filtered. Finally, the catalyst was freeze-dried for 48 h. The CS/HA/Fe_3O_4 composite catalyst was obtained.

1.3 Treatment of wool fibers and fabric

Wool fibers and fabric were pretreated with a solution of the non-ionic surfactant CN (2 g/L) at 50 ℃ for 20 min at a bath ratio of 1∶50. After gently squeezing out the excess water, they were dried at 40 ℃. The purpose of this treatment was to enhance the adsorption of CS/HA/Fe_3O_4 on wool fibers and fabric in subsequent treatments.

The Fenton-like treatment was divided into two stages: the Fenton-like oxidation pretreatment and the H_2O_2 treatment. In addition, three sets of control experiments were carried out, namely the untreated, H_2O_2 treatment, and NaClO treatment.

1) Fenton-like oxidation pretreatment. Immerse the pretreated wool fibers and fabric in a mixed solution containing CS/HA/Fe_3O_4, $Na_2S_2O_4$ (4.0% on mass of fabric (omf)), and JFC (2.0% omf). After ultrasonic treatment at 50 ℃ for 1 h at a bath ratio of 1∶30, the fibers and fabric were taken out and rinsed with water.

2) H_2O_2 treatment. Put the wool fibers and fabric (treated with CS/HA/Fe_3O_4 or untreated) into an oxidation solution composed of H_2O_2, HEDP, and Na_2CO_3, and treat them at 60 ℃ for 1.5 h at a bath ratio of 1∶30. Rinse the treated wool fibers and fabric three times with water to remove the residual chemical reagents and dry the fibers and fabric at 50 ℃.

3) NaClO treatment. Put the wool fibers and fabric into a solution of NaClO (2% omf), and treat them at 30 ℃ for 60 min at a bath ratio of 1∶50.

1.4 Characterization of CS/HA/Fe_3O_4

The structure of CS/HA/Fe_3O_4 was determined by an X-ray diffractometer (Dynamic 500, Anton Paar, Austria).

1.5 Decomposition rate of H_2O_2

Referring to the standard GB/T1616—2014 Industrial Hydrogen Peroxide, the concentration of H_2O_2 in the treatment solution was determined by using the $KMnO_4$ standard titration procedure, and then the decomposition rate of H_2O_2 was calculated.

1.6 Characterization of wool fibers and fabric

The surface scales of wool fibers were observed by using a field emission scanning electron microscope (S-4800, Hitachi, Japan). Wool fiber samples, both before and after treatment, were placed on a glass slide, covered with a coverslip that had a drop of bromine solution on it, and then photographed under an optical microscope equipped with a digital camera to observe the

formation of fluid vesicles. A Fourier transform infrared (FTIR) spectrometer (Nicolet670, Thermo Fisher, USA) was used to analyze the structural property of wool fibers. The water contact angles (WCAs) of the wool fabric samples before and after treatment were tested by using a contact angle and surface tension meter (DSA30, Kruss, Germany). The tensile property of wool fibers was tested by using an electronic single-fiber tensile strength machine (YG(B)008E, Wenzhou Darong Textile Instrument Co., Ltd., China), according to the standard ASTM D3822/D3822M-14 (2020) Standard Test Method for Tensile Properties of Single Textile Fibers. The tensile property of the wool fabric samples was tested by using a universal material testing machine (H10K-S, Tiniius Olsen, USA), according to the standard ASTM D5035-11(2019) Standard Test Method for Breaking Force and Elongation of Textile Fabrics (Strip Method). The anti-felting property of wool fabric samples was evaluated according to the standard FZ/T 70009—2021 Test Method for Relaxation Dimensional Change and Felting Dimensional Change to Washing of Wool Textiles. Wool fabric samples with dimensions of 15 cm × 15 cm were washed by using an European standard shrinkage tester (Model FOM71CLS, Electrolux, Sweden). All results were reported as the average of three parallel samples.

2 Results and Discussion

2.1 Structure of CS/HA/Fe_3O_4

XRD patterns of HA, Fe_3O_4, CS and CS/HA/Fe_3O_4 are shown in Fig. 2.

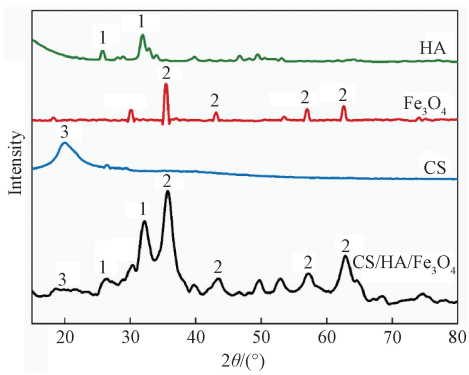

Fig. 2 XRD patterns of HA, Fe_3O_4, CS and CS/HA/Fe_3O_4

The broad peak of CS at around 20.0° (labled as 3) almost disappears on CS/HA/Fe_3O_4, indicating that the hydrogen bond between the amino and hydroxyl groups in the CS molecule is broken by the inorganic phases of HA and Fe_3O_4, as reported in Ref. [22]. The characteristic peaks of Fe_3O_4 at 37.1°, 42.9°, 57.1°, and 62.6°, labeled as 2, and those of HA at 27.9° and 32.3°, labeled as 1, are clearly visible. By comparing the XRD patterns of Fe_3O_4 and CS/HA/Fe_3O_4, it is evident that, in addition to the characteristic peaks of Fe_3O_4, the XRD pattern of CS/HA/Fe_3O_4 also contains the characteristic peaks of HA. This indicates that Fe_3O_4 particles are successfully loaded on the HA/CS composite.

2.2 Optimization of treatment conditions

The optimal amounts of various chemicals in the Fenton-like treatment were explored to optimize the anti-felting effect and tensile property of the wool fabric. This study divides the analysis process into the following two parts for detailed discussion.

Firstly, during the Fenton-like oxidation pretreatment stage, the amount of CS/HA/Fe_3O_4 was optimized by evaluating the decomposition rate of H_2O_2, thereby enhancing the catalytic effect. Secondly, we explored the optimal combination of the amount of H_2O_2, HEDP, and Na_2CO_3 during the Fenton-like treatment process.

2.2.1 Optimization of Fenton-like oxidation pretreatment

When investigating the optimal amount of CS/HA/Fe_3O_4 during the Fenton-like oxidation pretreatment stage of the wool fabric, the catalytic effect was assessed based on the decomposition rate of H_2O_2. To prevent potential interference from HEDP and Na_2CO_3 on the decomposition rate, these two chemicals were excluded from this experiment.

Figure 3 illustrates the decomposition rate of H_2O_2 with different amounts of CS/HA/Fe_3O_4 (1.5%, 3.0%, 4.5% and 6.0% omf, respectively). The results indicate that the decomposition rate of H_2O_2 gradually increases as the amount of CS/HA/Fe_3O_4 increases.

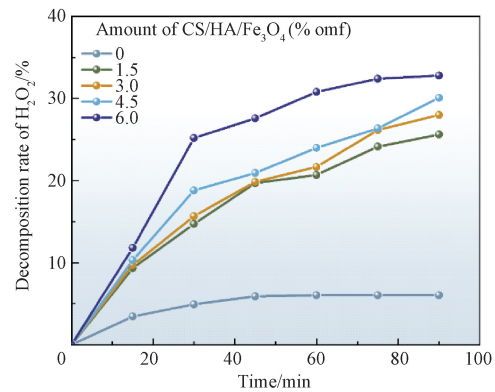

Fig. 3 Decomposition rate of H_2O_2 during pretreatment of wool fabric with different amounts of CS/HA/Fe_3O_4

When no CS/HA/Fe_3O_4 is added, the decomposition rate of H_2O_2 is merely 6.0% after 90 min. When the amount of CS/HA/Fe_3O_4 is 6.0% omf, the decomposition rate increases to 32.8%. However, when the amount of CS/HA/Fe_3O_4 is 6.0% omf, the rapid oxidation rate may result in the transient generation of a large number of superoxide radicals, some of which may become ineffective[14]. When the amount of CS/HA/Fe_3O_4 is 4.5% omf, the decomposition rate of H_2O_2

reaches 30.1%, which can significantly enhance the utilization efficiency of H_2O_2. Based on this finding, the optimal amount of CS/HA/Fe_3O_4 is determined to be 4.5% omf.

2.2.2 Optimization of H_2O_2 treatment

H_2O_2 treatment was carried out following Fenton-like oxidation pretreatment. In this experiment, the amounts of H_2O_2 (A), HEDP (B), and Na_2CO_3 (C) were identified as the key factors. A response surface analysis was conducted by using these three factors, with the tensile strength and elongation at break of the wool fibers, and the felting shrinkage rate of the wool fabric serving as evaluation indices. The Box-Behnken design was employed to optimize the factors. Each factor was set at three levels: low (−1), medium (0), and high (1), and the corresponding responses were measured to construct the regression models. The levels of the factors are presented in Table 1, and the results are shown in Table 2.

Table 1 Levels of factors

Factor	Coded symbol	Level/(% omf)		
		Low (−1)	Medium (0)	High (1)
H_2O_2	A	30.0	60.0	90.0
HEDP	B	6.0	12.0	18.0
Na_2CO_3	C	5.0	10.0	15.0

Table 2 Results of response surface design test

Number	A	B	C	Wool fiber		Wool fabric
				Tensile strength/cN	Elongation at break/%	Felting shrinkage rate/%
1	1	0	−1	8.0	46.8	6.0
2	−1	0	−1	8.7	45.7	5.1
3	−1	−1	0	7.7	49.9	4.7
4	0	0	0	7.8	42.9	5.7
5	0	0	0	7.8	43.6	5.4
6	1	−1	0	7.9	48.5	5.0
7	−1	1	0	8.3	48.7	5.3
8	1	1	0	7.6	49.8	5.7
9	0	0	0	7.8	42.8	5.5
10	0	−1	−1	7.5	50.3	4.0
11	0	0	0	7.8	43.2	5.7
12	0	0	0	7.7	42.9	5.7
13	0	−1	1	7.4	51.7	3.9
14	0	1	−1	7.6	45.6	4.3
15	1	0	1	7.9	48.5	5.0
16	−1	0	1	8.5	47.5	4.9
17	0	1	1	7.3	58.6	3.9

The experimental results were analyzed by using Design-Expert10 software. The analysis of variance (ANOVA) results are shown in Tables 3, 4, and 5. The regression models 1, 2 and 3 are highly significant (p-value less than 0.01); the model determination coefficients R^2 are 0.9568, 0.9402, and 0.9653. The results indicate that the models are well-fitted.

According to the experimental model, the predicted process parameters are H_2O_2 30.0% omf, HEDP 18.0% omf, and Na_2CO_3 5.0% omf. The predicted experimental results are tensile strength of 8.6 cN, elongation at break of 46.3%, and felting shrinkage rate of 4.6%.

Table 3 ANOVA for tensile strength of wool fibers

Source	Sum of squares	Degree of freedom	Mean square	*F*-value	*p*-value
Model 1	2. 210 0	9	0. 245 2	17. 240 0	0. 000 6
A	0. 400 5	1	0. 400 5	28. 160 0	0. 001 1
B	0. 012 8	1	0. 012 8	0. 899 8	0. 374 4
C	0. 090 3	1	0. 090 3	6. 350 0	0. 039 8
AB	0. 164 0	1	0. 164 0	11. 530 0	0. 011 5
AC	0. 003 6	1	0. 003 6	0. 253 1	0. 630 4
BC	0. 009 0	1	0. 009 0	0. 634 4	0. 451 9
A^2	0. 960 0	1	0. 960 0	67. 490 0	<0. 000 1
B^2	0. 640 4	1	0. 640 4	45. 020 0	0. 000 3
C^2	0. 003 2	1	0. 003 2	0. 223 8	0. 650 5
R^2	0. 956 8				
R'^2	0. 901 3				

Notes: in the first column, A, B, and C represent the main effect of factors A, B, and C, respectively; AB, AC, and BC represent the first-order interaction effect between factors A and B, A and C, and B and C, respectively; A^2, B^2, and C^2 represent the quadratic effect of factors A, B, and C, respectively; R'^2 is the adjusted determination coefficient.

Table 4 ANOVA for elongation at break of wool fibers

Source	Sum of squares	Degree of freedom	Mean square	*F*-value	*p*-value
Model 2	254. 18	9	28. 24	12. 230 0	0. 001 6
A	0. 446 5	1	0. 446 5	0. 193 4	0. 673 4
B	0. 690 3	1	0. 690 3	0. 299 0	0. 601 5
C	40. 500	1	40. 50	17. 540 0	0. 004 1
AB	1. 430 0	1	1. 43	0. 618 5	0. 457 4
AC	2.84×10^{-14}	1	2.842×10^{-14}	1.231×10^{-14}	1. 000 0
BC	33. 760	1	33. 76	14. 62	0. 006 5
A^2	2. 970 0	1	2. 97	1. 29	0. 294 1
B^2	119. 16	1	119. 16	51. 61	0. 000 2
C^2	42. 910	1	42. 91	18. 58	0. 003 5
R^2	0. 940 2				
R'^2	0. 863 4				

Table 5 ANOVA for felting shrinkage rate of wool fabric

Source	Sum of squares	Degree of freedom	Mean square	*F*-value	*p*-value
Model 3	6. 980 0	9	0. 775 8	21. 61	0. 000 3
A	0. 340 3	1	0. 340 3	9. 48	0. 017 8
B	0. 328 1	1	0. 328 1	9. 1400	0. 019 3
C	0. 382 8	1	0. 382 8	10. 670	0. 013 8
AB	0. 000 2	1	0. 000 2	0. 006 3	0. 939 1
AC	0. 152 1	1	0. 152 1	4. 240 0	0. 078 5
BC	0. 024 0	1	0. 024 0	0. 669 4	0. 440 2
A^2	0. 683 8	1	0. 683 8	19. 050	0. 003 3
B^2	2. 790 0	1	2. 790 0	77. 830	<0. 000 1
C^2	2. 260 0	1	2. 260 0	62. 860	<0. 000 1
R^2	0. 965 3				
R'^2	0. 920 6				

2.3 Property of wool fibers and fabric

2.3.1 Tensile and felting shrinkage property

Based on the aforementioned analyses, the optimized process parameters were set as follows: H_2O_2 30.0% omf, HEDP 18.0% omf, and Na_2CO_3 5.0% omf. To validate the optimized analytical results, three replicate validation tests were performed under identical conditions. Furthermore, three comparative experimental groups were established: untreated, H_2O_2 treatment, and NaClO treatment. The results are shown in Table 6.

Table 6 Tensile and felting shrinkage property of wool samples treated by different methods

Method	Wool fiber		Wool fabric	
	Tensile strength/cN	Elongation at break/%	Tensile strength/N	Felting shrinkage rate/%
Fenton-like treatment	8.3	46.8	74.7	4.0
H_2O_2 treatment	8.6	44.7	86.3	10.5
NaClO treatment	5.7	51.0	46.5	3.6
Untreated	9.1	43.3	107.7	15.7

As shown in Table 6, the tensile strength and elongation at break of untreated wool fibers are 9.1 cN and 43.3%, respectively. After Fenton-like treatment and H_2O_2 treatment, the tensile strengths of wool fibers decrease to 8.3 cN and 8.6 cN, respectively. This phenomenon can be ascribed to the hydroxyl free radicals generated from the decomposition of H_2O_2 in both treatments, which attack the scale layer of wool fibers, leading to a reduction in the tensile strength of the fibers[23]. Further comparison shows that the tensile strength of the Fenton-like treated wool fibers is lower than that of the H_2O_2 treated fibers. This can be attributed to the addition of CS/HA/Fe_3O_4 in the Fenton-like oxidation system, which accelerates the decomposition of H_2O_2 and leads to the generation of more hydroxyl free radicals. Consequently, the scale layer of wool is damaged more severely. As a result, the felting shrinkage rate of the wool fabric after Fenton-like treatment is lower than that of the H_2O_2 treated wool fabric. The tensile strength and elongation at break of wool fibers treated with NaClO are 5.7 cN and 51.0%, respectively. Compared with untreated wool fibers, the tensile strength decreases by 37.4%. When comparing NaClO treatment with Fenton-like treatment, there is little difference in the felting shrinkage between the two methods. However, the tensile strength of the wool fabric after Fenton-like treatment is higher than that of NaClO treatment.

In summary, the anti-felting property of the Fenton-like treatment is superior to that of H_2O_2 treatment, and comparable to the traditional NaClO treatment. Moreover, the Fenton-like treatment avoids the reduction in fiber breaking strength caused by NaClO treatment, thus exhibiting better tensile properties while maintaining excellent anti-felting effect.

2.3.2 Chemical structure

FTIR tests were conducted on the untreated and Fenton-like treated wool fibers, and the results are presented in Fig. 4. The peak at 3 275 cm^{-1} represents the unique amide A structure of wool fibers, while the peaks at 2 920 cm^{-1} and 2 850 cm^{-1} correspond to the vibrational peaks of —CH_2 and —CH_3 groups in wool fibers[24]. After Fenton-like treatment, the absorption intensities at 2 920 cm^{-1} and 2 850 cm^{-1} decrease, indicating damage to the secondary structure of wool fibers[25]. Moreover, a peak corresponding to the sulfinyl group (S═O) emerges at 1 040 cm^{-1}, suggesting that Fenton-like treatment can effectively break the disulfide bonds in wool fibers.

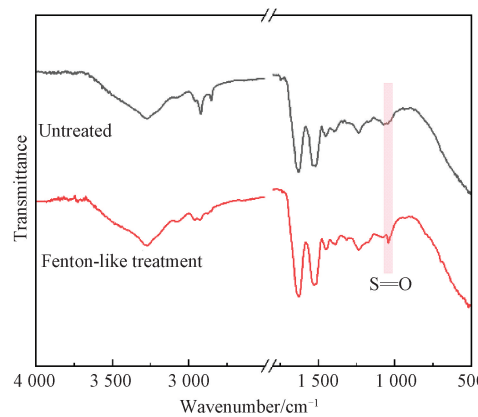

Fig. 4 FTIR spectra of wool fibers before and after Fenton-like treatment

2.3.3 Surface morphology

Scanning electron microscopy (SEM) images of wool fibers treated with different methods are shown in Fig. 5. Sharp and intact scales are visible on untreated wool fibers (Fig. 5(a)). After H_2O_2 treatment (Fig. 5(c)), the scales are removed to a greater extent. In contrast, the scales become relatively flat in the Fenton-like treated (Fig. 5(b)) and NaClO treated (Fig. 5(d)) samples. From a microstructural perspective, this etching and stripping effect renders the wool fiber surface smoother, reduces inter-fiber entanglement and friction, and thus improves the anti-felting property.

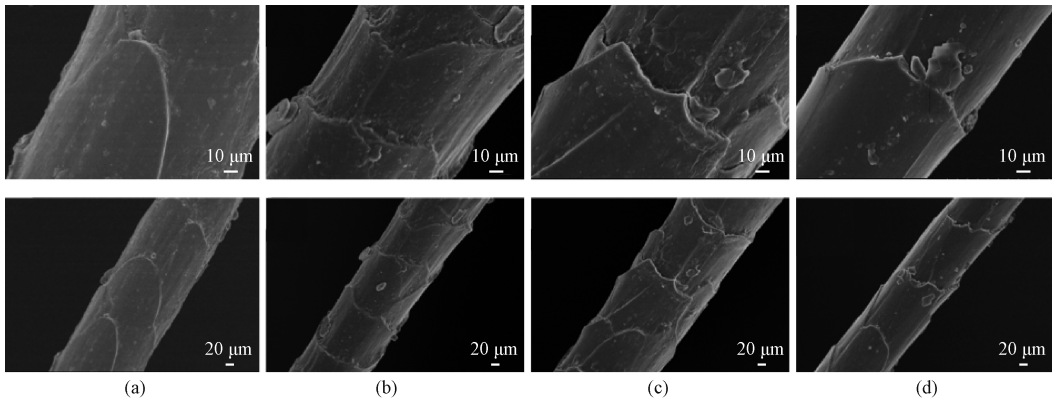

Fig. 5 SEM images of wool fibers after different treatments: (a) untreated; (b) Fenton-like treatment; (c) H_2O_2 treatment; (d) NaClO treatment

The Allworden reaction results of wool fibers before and after Fenton-like treatment are presented in Fig. 6.

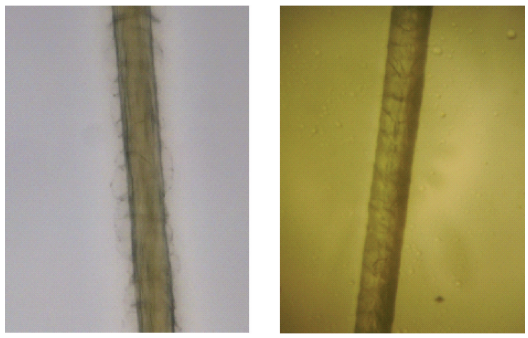

Fig. 6 Images of wool fibers after Allworden reaction: (a) untreated; (b) Fenton-like treatment

Large and dense bubbles form around the untreated wool fibers, which arise from the internal and external pressure difference across the wool fiber scales after applying saturated bromine solution. After Fenton-like treatment, the size and morphology of bubbles generated by the Allworden reaction are significantly changed, with only tiny bubbles observed on the scale surface. This phenomenon indicates that the Fenton-like treatment not only cleaves the disulfide bonds on the wool fiber scale surface but also hydrolyzes partial proteins and breaks peptide bonds. Consequently, the binding force at the scale edge and inside the fiber is weakened, reducing the pressure difference across the fiber during the Allworden reaction and making it more difficult for large bubbles to form.

2.3.4 Surface property

The removal of scales has an impact on the wettability of the wool fabric. The WCAs of wool fabric samples after different treatments are shown in Fig. 7. The untreated wool fabric is hydrophobic, with a WCA of 148.90°. After Fenton-like treatment, the WCA decreases significantly to 103.20°. This can be attributed to the fact that CS/HA/Fe_3O_4 catalyzes H_2O_2 to generate more superoxide radicals, which attack the wool fiber scale layer and introduce more hydrophilic groups (such as —OH and —NH_2) on the wool fiber surface[26]. The WCA of the wool fabric after H_2O_2 treatment is 102.00°, which is very close to that of the Fenton-like treatment. In contrast, NaClO treatment leads to a more obvious reduction in WCA, with a value of 91.23°.

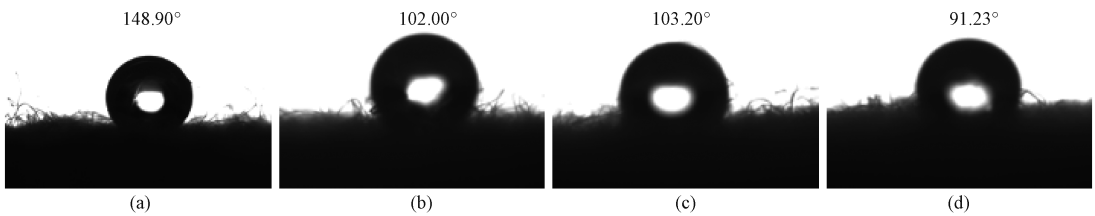

Fig. 7 WCAs of wool fabric after different treatments: (a) untreated; (b) H_2O_2 treatment; (c) Fenton-like treatment; (d) NaClO treatment

2.4 Recycling performance of CS/HA/Fe_3O_4

The above analyses verified the effectiveness of the constructed novel Fenton-like treatment. The composite catalyst CS/HA/Fe_3O_4 employed in this system is a magnetic iron-based catalyst, characterized by recyclability. The recyclability of the catalyst is crucial for cost reduction. For this purpose, following the treatment, CS/HA/Fe_3O_4 was recovered by magnetic adsorption, and the supernatant was decanted. Subsequently, the recovered CS/HA/Fe_3O_4 was washed with deionized water and then recycled.

This study preliminarily investigated the effect of

the recycled CS/HA/Fe_3O_4 on the decomposition rate of H_2O_2 and the anti-felting property of the wool fabric. The results are presented in Fig. 8. It can be observed that the decomposition rate of H_2O_2 decreases from 30.1% to 23.0% after three cycles, and decreases notably after three cycles. This may be attributed to the disruption of the organic phase, the formation of pores, and the saturation of adsorption sites during the Fenton-like treatment[27]. The felting shrinkage rate of the wool fabric remains at a low level for the first three cycles, increasing only slightly from 4.0% to 4.7%, which still meets the international standard of less than 5.0%. This indicates that the catalyst maintains good recoverability and stable catalytic performance within three cycles. However, a significant decline in performance is observed after the third cycle. These results suggest that CS/HA/Fe_3O_4 exhibits good recyclability and stable anti-felting property for up to three cycles, but its effectiveness deteriorates with further reuse.

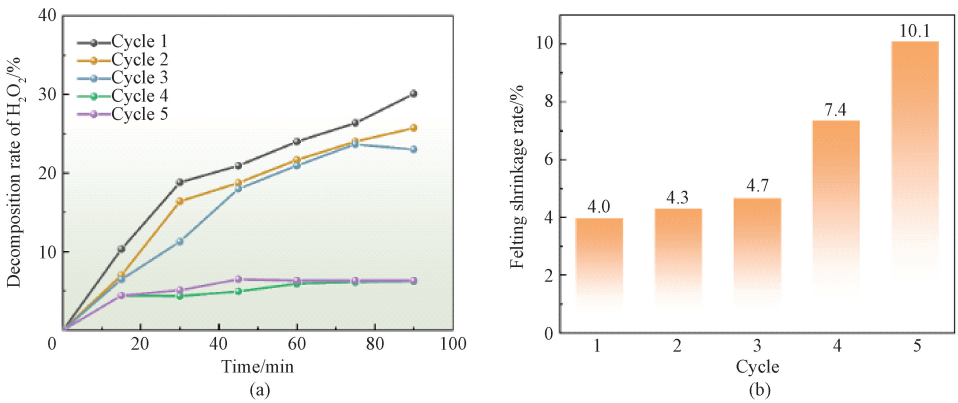

Fig. 8 Performance of CS/HA/Fe_3O_4 after five cycles: (a) decomposition rate of H_2O_2; (b) felting shrinkage rate of wool fabric

3 Conclusions

In this study, a novel Fenton-like oxidation system, denoted as CS/HA/Fe_3O_4, was explored and proposed to enhance the anti-felting property of wool fabric. The optimal treatment conditions were obtained by the response surface analysis. The Fenton-like treatment achieved an anti-felting property superior to H_2O_2 treatment and comparable to traditional NaClO treatment, while avoiding the fiber strength reduction associated with NaClO treatment. CS/HA/Fe_3O_4 exhibited good recyclability and stable anti-felting property for three reuse cycles, after which its effectiveness declined due to structural and adsorption-site changes. Overall, the Fenton-like treatment proposed herein is environmentally friendly, operationally feasible, and effective for enhancing wool fabric anti-felting, thus holding broad application prospects.

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羊毛织物类芬顿氧化防毡缩整理

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摘　要：羊毛织物因具有鳞片层结构，在湿热条件下极易发生毡缩，从而影响其外观与耐用性。本研究提出一种用于羊毛织物防毡缩整理的新型类芬顿氧化体系，采用壳聚糖（chitosan，CS）和羟基磷灰石（hydroxyapatite，HA）负载 Fe_3O_4 制备复合催化剂 CS/HA/Fe_3O_4，用于催化 H_2O_2 产生自由基，通过破坏羊毛纤维鳞片结构来降低毡缩现象。确定的最优工艺条件为：CS/HA/Fe_3O_4 4.5% omf（对织物质量分数）、H_2O_2 30.0% omf、羟基乙叉二膦酸（1-hydroxyethylidene-1,1-diphosphonic acid，HEDP）18.0% omf，Na_2CO_3 5.0% omf。傅里叶变换红外光谱（Fourier transform infrared，FTIR）、扫描电子显微镜（scanning electron microscopy，SEM）及水接触角（water contact angle，WCA）表征结果表明，类芬顿处理可有效断裂羊毛纤维二硫键、剥蚀表面鳞片并降低疏水性。对 CS/HA/Fe_3O_4 复合催化剂的初步循环利用实验显示，经 3 次循环利用后，羊毛织物的毡缩率由 4.0%略升至 4.7%，仍满足国际标准要求（≤5.0%）。

关键词：羊毛织物；表面改性；防毡缩整理；类芬顿氧化