An antibacterial strategy on chrome-free tanned leather: based on *β*-cyclodextrin aldehyde derivatives and small molecule antimicrobial agent

Wen Huitao[1,2], Yu Guofei[1,3], Ding Zhuang[1,3]

Chen Yining[1,3], Dan Nianhua[1,3], Dan Weihua[1,2]*

[1]National Engineering Research Center of Clean Technology in Leather Industry, Sichuan University, Chengdu 610065, China

[2]Fujian Key Laboratory of Green Design and Manufacture of Leather, Xingye Leather Technology Co., Ltd., Jinjiang 362271, China;

[3]Key Laboratory of Leather Chemistry and Engineering of Ministry of Education, Sichuan University, Chengdu 610065, China

*Corresponding authors.

E-mail: danweihua_scu@126.com

Fax: (+86)-028-85468589; Tell: (+86)-028-85468589

Abstract

Chrome tanning has dominated in leather production up to now, while facing a significant challenge in terms of chromium. Therefore, the chrome-free tanning process becomes an inevitable choice. However, chrome-free tanned leather (CFTL) is poor in antibacterial properties, which limits its practical application in leather production. In this work, a new environment-friendly antibacterial strategy based *β*-cyclodextrin (*β*-CD) aldehyde derivatives and ciprofloxacin hydrochloride (CH) as a small molecule model antibacterial agent was developed to address this issue along with improving the comprehensive performances of leather. The structure and properties of obtained leather were characterized by Fourier transform infrared

spectroscopy, scanning electron microscopy, differential scanning calorimetry, thermogravimetric, and its antibacterial effect against *E. coli* and *S. aureus* was investigated. The results showed that compared with CFTL without *β*-CD modification and CH treatment, the T_s, T_d and T_p of the leather with this method possessed increased 5.7°C, 4.9°C, and 6.9°C, respectively. After being treated by CH with 90 days of storage, the antibacterial rates against *E. coli* and *S. aureus* still reached 99.8% and 97.4%, respectively, which were 29.9% and 34.4% higher than those without *β*-CD treatment. It, that antibacterial agent is included in the cavity of *β*-CD on CFTL, will improve the poor antibacterial durability due to the release of the small molecule antimicrobial agent. These findings, therefore, indicated that a new antibacterial method on CFTL with *β*-cyclodextrin aldehyde derivatives and ciprofloxacin hydrochloride has potential practical application prospects in leather production.

Keywords: chrome-free tanned leather, antibacterial performance, *β*-cyclodextrin, ciprofloxacin hydrochloride

1. Introduction

Leather is a natural material used by mankind for a long time, and it plays an important role in daily life, economy, military, and other aspects (Sathish *et al.*, 2016). Up to now, Chrome tanning has dominated in leather production, while facing a significant challenge in terms of chromium (Kanagaraj *et al.*, 2020). Therefore, the chrome-free tanning process, such as tannin extract, organic tanning agent and metal complex tanning agent, had become an inevitable choice (Krishnamoorthy *et al.*, 2012). However, chrome-free tanned leather (CFTL) is poor in antibacterial properties (Orlita, 2004), which limits its practical application in leather production.

The conventional solution was to add antibacterial agents during the tanning process, and the antibacterial agents were mainly distributed on the surface of the leather and between the collagen fibers. It should be noted that to reduce the adverse impact of antibacterial agents on leather performance and the environment, the addition amount should be little (only 0.1-0.3% of the weight of wet leather), so that the antibacterial performance was poor and difficult to last. Related researches tend to choose more efficient and safe fungicides such as nanosilver (Velmurugan *et al.*, 2014), chitosan (Barros *et al.*, 2011), quaternary ammonium salts (Xiao et al., 2014), compound fungicides (Cuadros *et al.*, 2012), and encapsulated fungicides (Geng *et al.*, 2018), but the effects were not ideal, and the problem has not been completely solved so far.

Herein a strategy is to introduce a complete β-CD cavity on CFTL, and fix the small molecule antibacterial agent in the cavity, and use its slow-release effect to

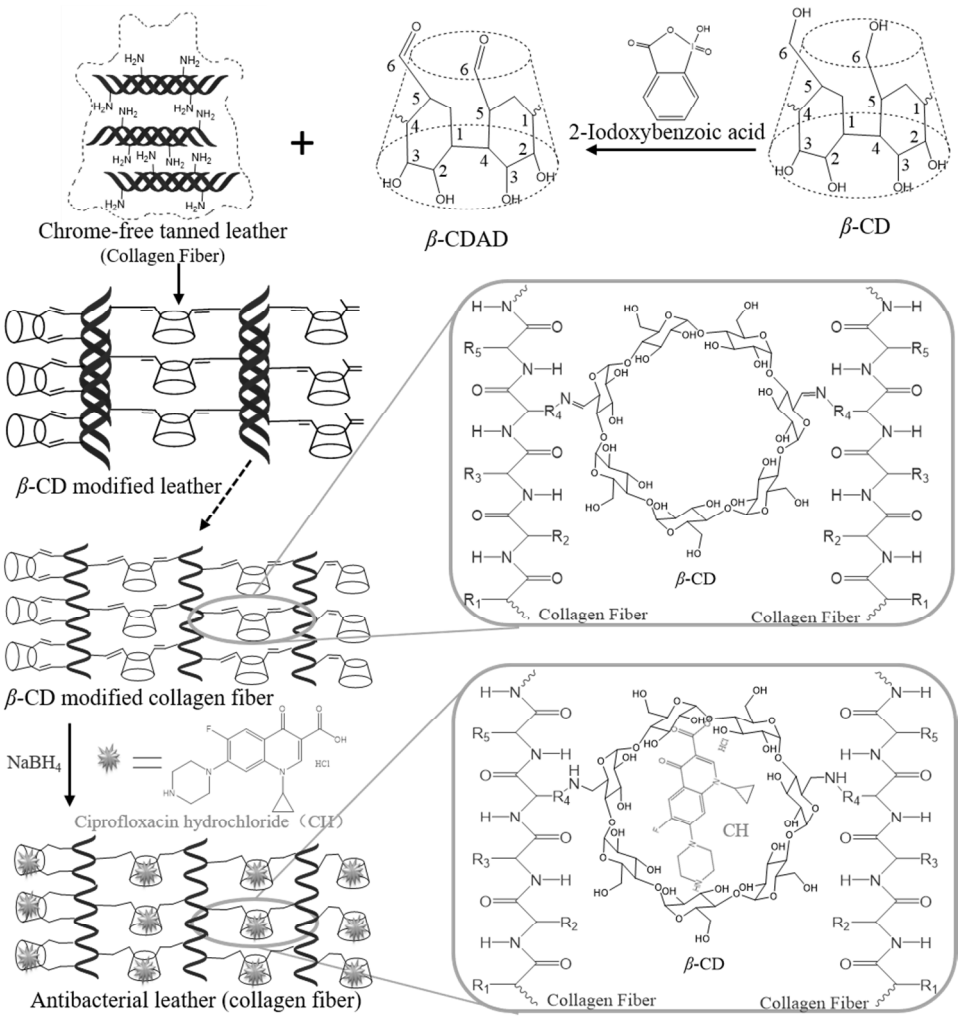
achieve the purpose of long-term antibacterial. *β*-CD, a natural product of CGTase acted on starch (Valle and Martin, 2004), was a cyclic oligosaccharide consisting of seven glucopyranose units linked by α-(1,4) bonds, had a hydrophilic outer surface and a hollow hydrophobic interior cavity. The most notable feature was that it could form stable inclusion complexes (host-guest complexes) with a wide variety of hydrophobic guest molecules in the cavity (Eastburn and Tao, 1994; Radu *et al.*, 2016; Matencio *et al.*, 2020). Inclusion complexes had a significant influence on the physicochemical properties of guest molecules, and the guest molecules were temporarily locked or caged within the host cavity, such as improved stability, reduced volatility, and sublimation, as well as controlled and sustained release.

To enhance the force between *β*-CD and leather, *β*-CD was oxidized into *β*-CD aldehyde derivatives (CDAD). Meanwhile, for achieving the effect of multi-point cross-linking, each molecule of CDAD should have more than two aldehyde groups. Different from the commonly used 2, 3-dialdehyde *β*-CD, CDAD used in this work is multiple-6-deoxy-6-formyl-*β*-CD, prepared by oxidizing the primary hydroxyl group on the C_6 position, without destroying the cavity structure of *β*-CD (Wen *et al.*, 2021).

Ciprofloxacin hydrochloride (CH), a quinolone carboxylic acid derivative, could be used as a model antibacterial agent to apply in textile antibacterial materials (Hou *et al.*, 2021). *β*-CD and CH could form a 1:1 inclusion compound (Chao *et al.*, 2002). After the inclusion, CH could have a slow-release effect, which made the antibacterial performance more stable and lasting (Choi *et al.*, 2017).

In this work, CDAD modified CTFL (CD-CFTL) was prepared by Schiff base

reaction, and CH antibacterial treated CFTL (CH/CD-CFTL) was prepared by inclusion reaction of β-CD on CD-CFTL (Fig. 1). The structure and properties of as-formed leather was characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), differential scanning calorimetry (DSC), thermogravimetric (TGA), and its antibacterial effect against *E. coli* and *S. aureus* was investigated. The results show that modified CFTL had improved thermal properties and excellent antibacterial properties, which not only provides a new way to improve the antibacterial properties, but also provides a new idea to prepare



multifunctional leather products.

Fig.1 Preparation of antibacterial CFTL

2. Experimental

2.1 Materials

CH, for research use only, Beijing Solarbio Science & Technology Co., Ltd. *β*-CD was a biological reagent and purchased from Chengdu Kelong Chemical Co., Ltd (China). *β*-CD aldehyde derivatives (*β*-CDAD) was prepared according to an improved method (Hu *et al.*, 1999), the content of aldehyde groups of the per *β*-CD molecule was 2.2, measured by hydroxylamine hydrochloride-potentiometric titration method (Zhao and Heindel, 1991). All the other reagents used were of analytical grade and purchased from Chengdu Kelong Chemical Co., Ltd (China).

The chrome-free tanned leather (CFTL) was prepared by the combination tannage (Wen et al., 2021) based on an organic tanning agent F-90 (Granofin® Easy F-90), tannin extract and Zr-Al-Ti complex tanning agent (CAT), which has a tanning effect comparable to that of chrome tanning, and the tanning process was shown in Tab. 1.

Tab.1 The tanning process of the chrome-free tanned leather

Process	Chemicals	Dosage /%	Temp. /°C	time / min	pH
Washing	H_2O	250	25	10	7.0
Tanning I	H_2O	30	30		
	F-90	5.0		120-180	
	H_2O	30	38-42	120	5.5
Tanning II	HCOOH(1:10)	0.5	25	30	4.0-4.5
	sulfite fish oil	1		30	
	tannin extract	15		180	drain
Tanning III	H_2O	50	35	120	
	HCOOH(1:10)	0.5	25	30	2.8-3.0
	HCOONa	1.0			
	CAT	6.0		180	
	$NaHCO_3$	2.0			
	H_2O	150	40	180	3.8-4.0
Washing	H_2O	150		10	Drain

2.2 Samples preparation

2.2.1 *β*-CDAD modified CFTL

First, the CFTL was put into a drum with a speed of 6-8 r/min, containing 50-80% of 30-32°C water, and the pH was adjusted to 2.5-4.5, rotated for 30 minutes. Then *β*-CDAD (3-7%, based on the weight of CFTL) was added, reacted for 2-6 hours. And then the pH was adjusted to 4.5-6.5, the temperature was adjusted to 38-42°C, and the reaction time was 2-6 hours. Finally, add a certain amount of sodium borohydride and continue the reaction for 2-6 hours. The *β*-CDAD modified CFTL (CD-CFTL) were made by natural drying after washing.

Theoretically, the weight gain rate of CFTL after *β*-CDAD modification was the *β*-CD graft rate, which was calculated according to formula (1):

$$W\% = \frac{m_1 - m_0}{m_0} \times 100\% \qquad (1)$$

where W represents the weight gain rate of CFTL after CDAD modification, %; m_1 was the weight of CFTL after *β*-CDAD modification, g; m_0 was the weight of CFTL, g.

2.2.2 CH antibacterial treated CD-CFTL

First, the CD-CFTL were put into a drum with a speed of 6-8 r/min, containing 200% of 25-45°C water, and the pH was adjusted to 4.0-6.0, rotated 30 minutes. Then CH (0.01-0.05%, based on the weight of CD-CFTL) was added and reacted for 2-10 h. Finally, the resultant antibacterial leather was washed twice with water, and then piled for further evaluation.

The included rate of CH and the CH loaded degree of CD-CTFL were calculated according to Eq. (2) and Eq. (3), respectively.

$$N = \frac{C_0 - C_1}{C_0} \times 100\% \quad (2)$$

$$L = \frac{N * C_0 * V}{m_{CTFL}} \quad (3)$$

where N represents the included rate of CH, %; L represents the CH load degree of CD-CTFL, mg/g; C_0 and C_1 is the concentration of CH at the start and certain time during the load process, mg/L, V is the volume of CH solution and m_{CTFL} is the weight of CTFL.

2.3 Characterization

2.3.1 FTIR spectra

The FTIR spectra were recorded using an FTIR spectrometer (Nicolet is10, Thermo Scientific, USA). Each about 1 mg sample was pressed into a thin sheet with 200 mg KBr pellet, and measured in the range of 400-4000 cm^{-1} at room temperature, using 32 scans and 4 cm^{-1} resolution under the conditions of a temperature of about 25°C and a humidity of about 65%.

2.3.2 UV-vis Spectra

The UV-vis spectra were recorded using a UV-vis spectrometer (U-3900H, HITACHI, Japan). After UV-vis full-wavelength scanning, in an acetic acid-sodium acetate buffer solution with a pH of about 4.0, CH has an absorption peak at 276 nm. The waste liquid after the CH antibacterial treatment was adjusted to pH 4.0, and the absorbance at 276 nm was measured.

2.3.3 SEM

The morphologies were observed using an SEM (Apreo S, Thermo Scientific, America). Samples were frozen section, removed the surface layer of equal thickness, fixed on the conductive adhesive, sputter and coated with gold, and then observed with an accelerated voltage of 15 kV.

2.3.4 Thermal properties

Shrink temperature (T_s) was tested using a digital leather shrinkage temperature tester (MSW-YD4, Shaanxi University of Science & Technology, China) in light of ISO 3380:2015. Thermal properties were recorded using a DSC analyzer (204 F1, Netzsch, German) and a TGA analyzer (209 F1, Netzsch, German).

2.3.5 Antibacterial performance test

The antibacterial performance test against *E. coli* and *S. aureus* were carried out refers to GB/T 21510-2008 Appendix II: Material antibacterial performance test method: oscillation method (Chao *et al.*, 2014). And the antibacterial rate was calculated according to Eq. (4):

$$A=\frac{N_0-N_1}{N_0}\times 100\% \quad (4)$$

where A represents the antibacterial rate, %; N_0 and N_1 were the number of viable bacteria in the blank group and the test group, respectively.

3. Results and discussion

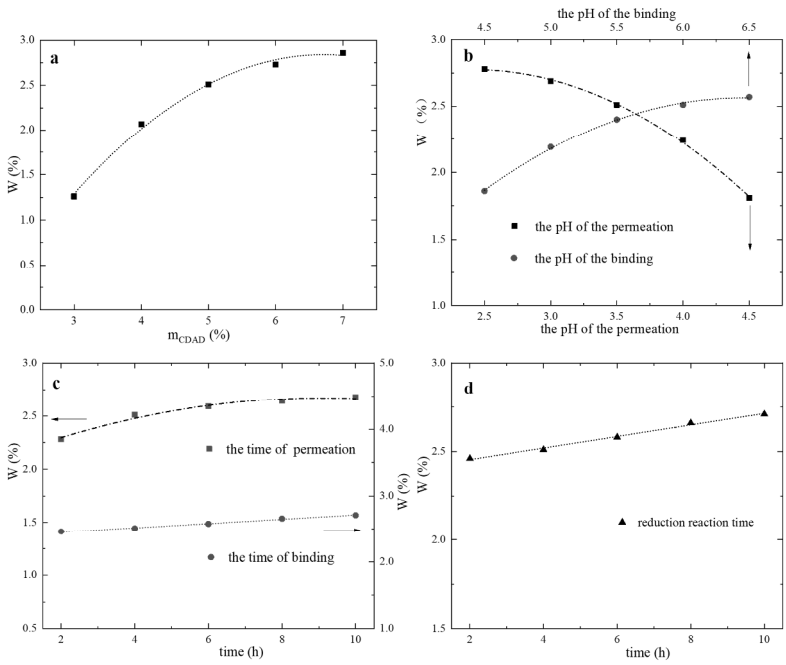
3.1 Preparation and characterization of CD-CFTL

CD-CFTL was prepared by Schiff base reaction between aldehyde groups on β-CDAD and amino groups on CFTL (Bowes and Cater, 1968) . The important

structural feature was the introduction of the β-CD cavity, while the content of amino groups decreased and the content of hydroxyl groups increased.

3.1.1 Experimental optimization

The experimental design was performed to evaluate the influence of the following variables on the modified process, to determine the best process conditions: the amount of β-CDAD, the pH of the permeation and binding, and the time of permeation, binding reaction, and reduction reaction.



(a) the amount of CDAD, (b) the pH of permeation and binding reaction,

(c) the time of permeation, binding, and reduction reaction

Fig.2 Effect of reaction conditions on weight gain rate

Using a single factor experimental method and the weight gain rate as an evaluation index, the dosage of β-CDAD, pH and time of osmotic reaction, pH and time of

binding reaction, and reduction reaction time were optimized one by one. The results (Fig.2) show when the amount of *β*-CDAD is 5%, the pH and time of the osmotic reaction are 3.5 and 4 hours, the pH and time of the binding reaction are 6.0 and 4 hours, and the reduction reaction time is 2 hours, an ideal weight gain effect can be achieved, with a weight gain rate about 2.51%.

3.1.2 FTIR analysis

CDAD is composed of multiple hydroxyl glucose units, the peak at 3402 cm^{-1} is O–H tensile vibration, the peak at 2925 cm^{-1} is C–H tensile vibration, the peak at 1610 cm^{-1}, 1160 cm^{-1}, 1075 cm^{-1}, 1030 cm^{-1}, 850 cm^{-1} are all characteristic peaks of D-glucopyranose. Since the 6-position primary hydroxyl group is partially oxidized to an aldehyde group, a characteristic peak of the aldehyde group appears at 1732 cm^{-1} (Chao *et al.*, 2014).

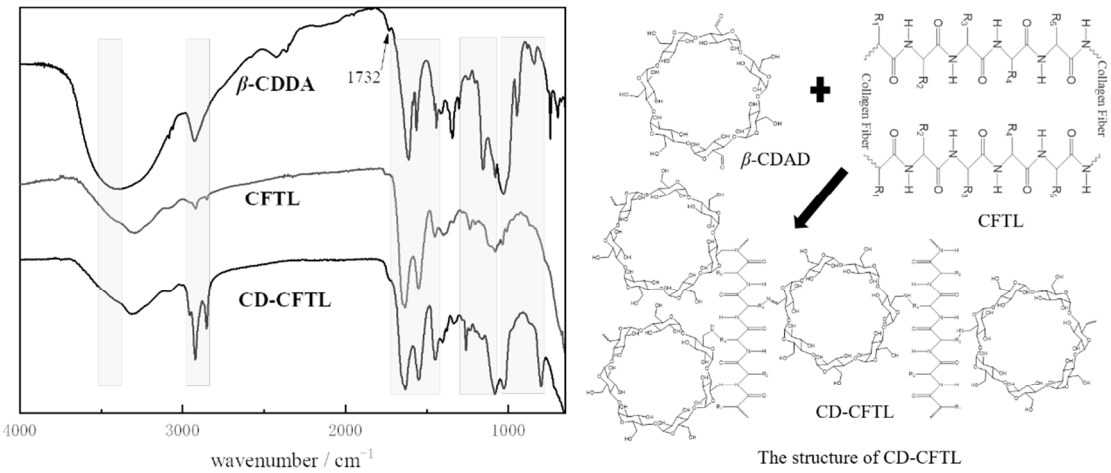


Fig. 3 The FTIR and structure of CD-CFTL

CFTL was tanned by combining F-90, tannin extract and Zr-Al-Ti complex tanning agent. F-90 could react with the carboxyl and the amino groups, the tannin extract

could be combined with the peptide bonds and amino groups, and the Zr-Al-Ti complex tanning agent could react with the carboxyl group of CFTL, and the synergy effect between a variety of chromium-free composite tanning agents, giving the excellent tanning effect. The principle to prepare CD-CFTL was based on the Schiff base reaction between the aldehyde group of *β*-CDAD and the amino group of CFTL, which was similar to the aldehyde tanning of leather. Fig.3 showed the amide A peak was blue-shifted, the peak intensity of amides I, II, and III decreases, and the characteristic peaks of the *β*-CD structure appear. All these changes indicate that *β*-CD has been grafted onto CFTL (Wen *et al.*, 2021).

3.1.3 SEM analysis

The SEM of CFTL and CD-CFTL were showed in Fig. 5, which was removed the surface of equal thickness by a freezing section. The collagen fiber bundles of CFTL were relatively regular and arranged relatively tightly (Fig. 5a). After *β*-CDAD modification, many dots appeared on the SEM of CD-CTFL. These dots were considered to be the grafted *β*-CD, which was closer to the SEM of *β*-CD grafted wool (Yu *et al.*, 2016).

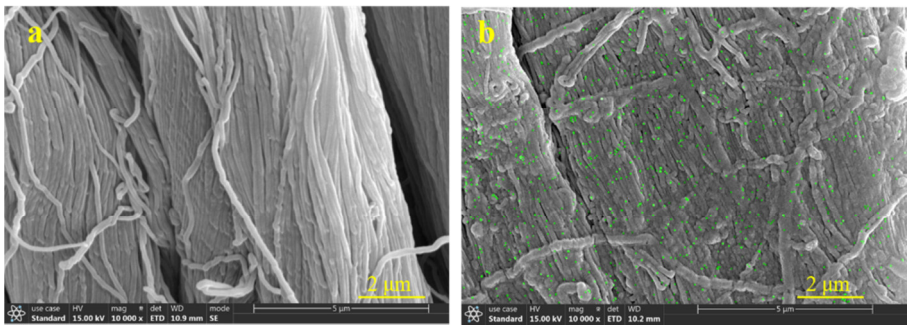


Fig.5 SEM of CFTL and CD-CFTL

3.1.3 Thermal analysis

The thermal shrink temperature (T_s), denaturation temperature (T_d), and decomposition temperature (T_p) of CFTL and CD-CFTL were shown in Fig. 6. After modification by CDAD, the T_s, T_d and T_p of CFTL increased 5.7 °C, 4.9 °C, and 6.9 °C, respectively, which showed CDAD could effectively crosslink the collagen fibers of CFTL and has a better tanning effect.

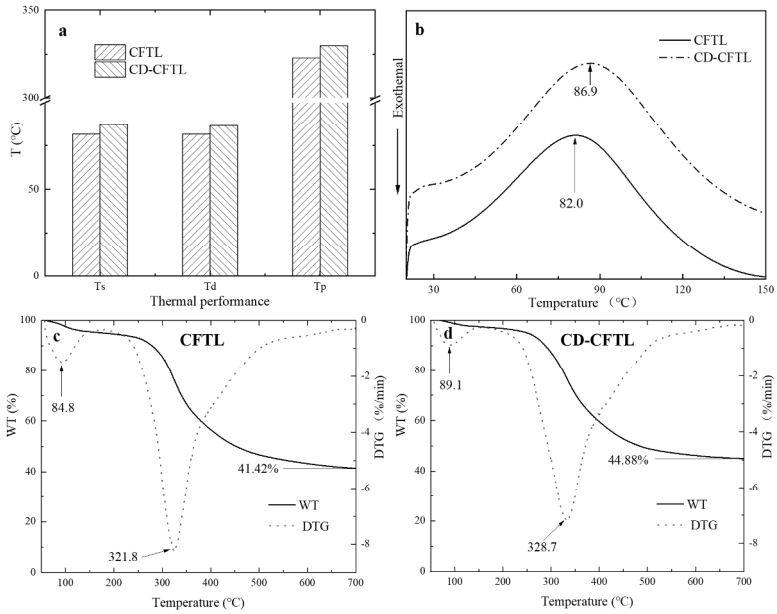


Fig. 6 The T_s, T_d, and T_p of CFTL and CD-CFTL

3.2 Preparation and characterization of CH/CD-CFTL

The characterization of CD-CFTL proved that β-CD has been grafted onto CFTL and maintains its original three-dimensional cavity, so it has a inclusion ability for small molecules. As far as β-CD is concerned, it is very suitable for the inclusion of small molecules with the five-membered ring, benzene, or naphthalene structures, such as imidazole, thiazoles, phenols, fluoroquinolones, vanillin, etc. Among these

organic antibacterial agents, CH has good antibacterial activity against both gram-positive bacteria and gram-negative bacteria. It has the advantages of a wide antibacterial spectrum, strong antibacterial activity, low dosage, and small toxic and side effects, and can form a 1:1 inclusion compound with β-CD (Gauzit *et al.*, 2020), so CH is selected as a model antibacterial agent.

3.2.1 Experimental optimization

The experimental design was performed to evaluate the influence of the following variables on the antibacterial treatment process, to determine the best process conditions: the amount of CH, the pH, temperature (T), and time (t) of the antibacterial treatment process.

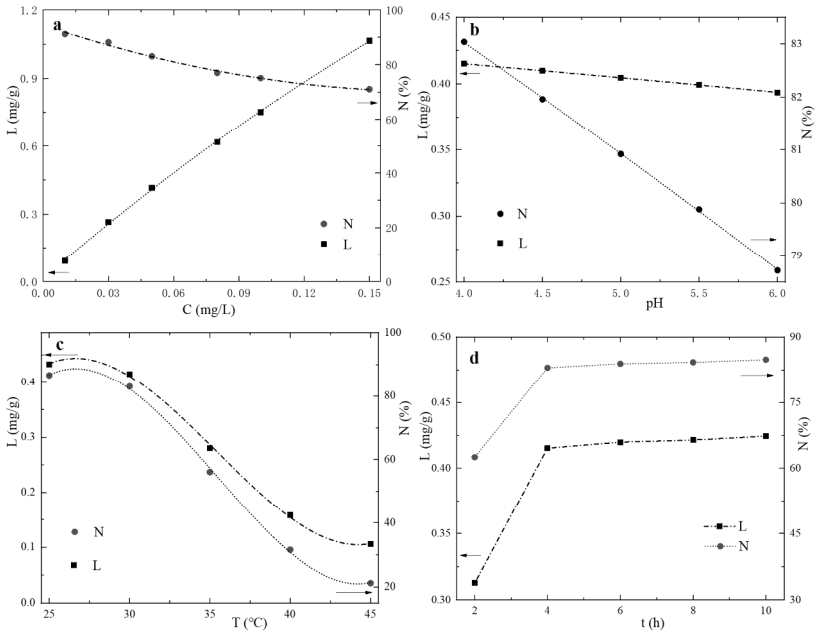


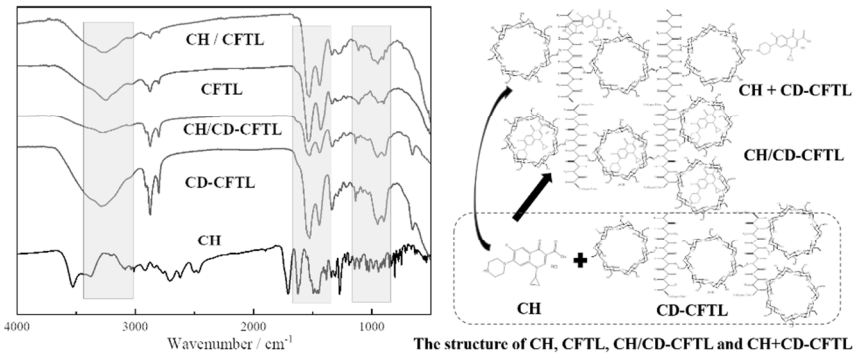
Fig.7 Experimental optimization of the antibacterial treatment process

Using a single factor experimental method, the included rate of CH and the CH loaded degree as evaluation indexes, the dosage of CH, pH, T, and t of antibacterial

treatment process were optimized. The results (Fig.7) show that when the concentration of CH is 0.05 mg/L, the pH is 4.0, the T is 30°C, and time is 4 hours, an ideal included effect can be achieved, with the included rate of CH is 83.04% and the CH loaded degree of CD-CFTL is 0.42 mg/g.

3.2.2 FTIR analysis

Fig. 8 showed the FTIR and structure of CH, CFTL, CD-CFTL, CH/CFTL, and CH/CD-CFTL. The characteristic peaks of CH could be observed in CH/CFTL, but disappear in CH/CD-CFTL. The reason was that CH was included in the cavity of *β*-CD. Compared with the FTIR spectrum of CD-CFTL, the intensity of the amide I and amide II peaks on the CH/CD-CFTL spectrum had decreased and blue-shifted, amide A had a redshift, and the intensity of the CO vibration peak attributable to the D-glucopyranose unit of *β*-CD had decreased (Yap *et al.*, 2005). It could be found that the intensity of all peaks on CH/CD-CFTL has been weakened to varying degrees, which was caused by the obstruction of the molecular vibration after inclusion (Liu, 2008). All phenomena indicated that CH was included in the cavity of *β*-CD on CD-CFTL.



The structure of CH, CFTL, CH/CD-CFTL and CH+CD-CFTL

Fig. 8 The FTIR and structure of CH, CFTL, CD-CFTL, CH/ CFTL and CH/CD-CFTL

3.2.3 Thermal analysis

The T_s, T_d, and T_p of CH/CFTL and CH/CD-CFTL were shown in Fig. 9. Compared with CFTL, CD-CFTL after CH antibacterial treatment had better thermal properties. The reason was that CH and CD could form an inclusion compound, and the thermal stability of the inclusion compound was stronger (Zhang *et al.*, 2012). After CH was loaded, an exothermic peak appears at 157.4°C in CH/CFTL, which was confirmed to be a characteristic peak of CH (Zhu, 2008). And the peak did not exist in CH/CD-CFTL, which also showed that CH was included in the cavity of β-CD.

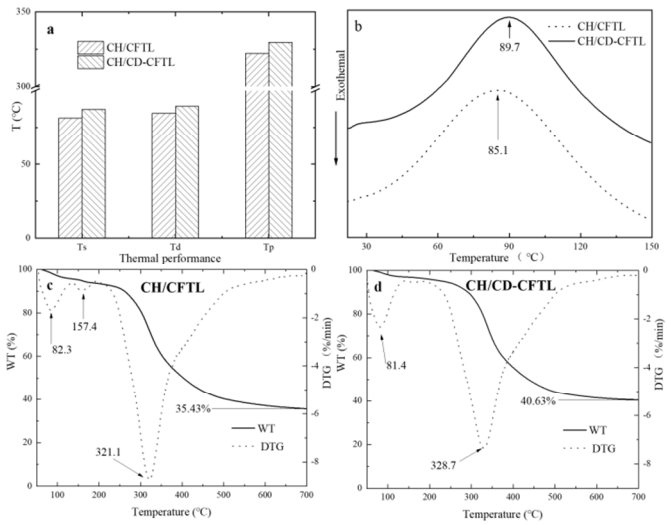


Fig.9 The T_s, T_d, and T_p of CH/CFTL and CH/CD-CFTL

Compared with CFTL and CD-CFTL in Fig. 6, the T_s, T_d, and T_p of CH/CFTL and CH/CD-CFTL has very little change. For CH/CFTL, the reason is that CH adsorbed by CFTL is easily released completely in a humid and hot environment. For CH/CD-CFTL, the reason is that the inclusion-release reaction is an equilibrium reaction.

Although the inclusion compound has higher stability, CH could be completely released under certain conditions. However, the inclusion-release reaction could be used to prepare antibacterial, sweet-scented, and other functional materials.

3.3 Antibacterial properties

The characterization of CH/CD-CFTL proved that the antibacterial agent has been included in the cavities of β-CDs on CD-CFTL, so theoretically it should have better antibacterial properties. The gram-negative bacteria *E. coli* and the gram-positive bacteria *S. aureus* were selected as the test bacteria and the antibacterial properties were investigated by the natural colony counting method using the oscillation method.

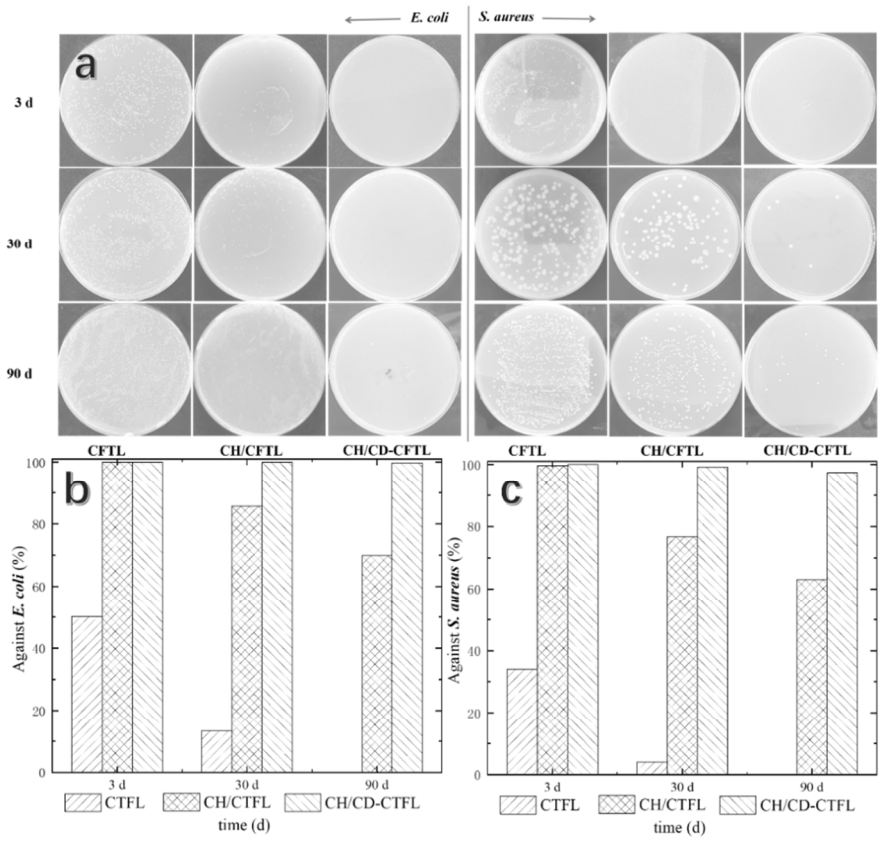


Fig. 10 Against *E. Coli* and *S. aureus* for 3 days, 30 days, and 90 days

The antibacterial results of CFTL, CH/CFTL, and CH/CD-CFTL after being stored in natural conditions for 3 days, 30 days, and 90 days were shown in Fig.10a, and the statistical results were shown in Fig. 10b and Fig. 10c. CFTL had slight antibacterial properties, which might be related to the used tannin extract and organic tanning agent. But after 30 days, CTFL had a poor antibacterial ability, which could not meet the antibacterial requirements. CH/CFTL has a certain antibacterial effect, however, the antibacterial effect decreases with the increase of time. The reason might be the weak force between CH and CFTL, and the low usage of CH (0.05%) which was only half of the conventional minimum dosage.

Different from CH/CFTL, CH/CD-CFTL has excellent long-lasting antibacterial properties, and the antibacterial rates after 90 days of storage against *E. coli* and *S. aureus* still reached 99.8% and 97.4%, respectively, which were 29.9% and 34.4% higher than those without β-CD treatment. It showed that the CH included in the cavity of β-CD had a slow-release effect and could prolong the antibacterial effect. At the same time, the antibacterial effect of *E. Coli* was better than that of *S. aureus*, which might be related to the performance of the antibacterial agent itself.

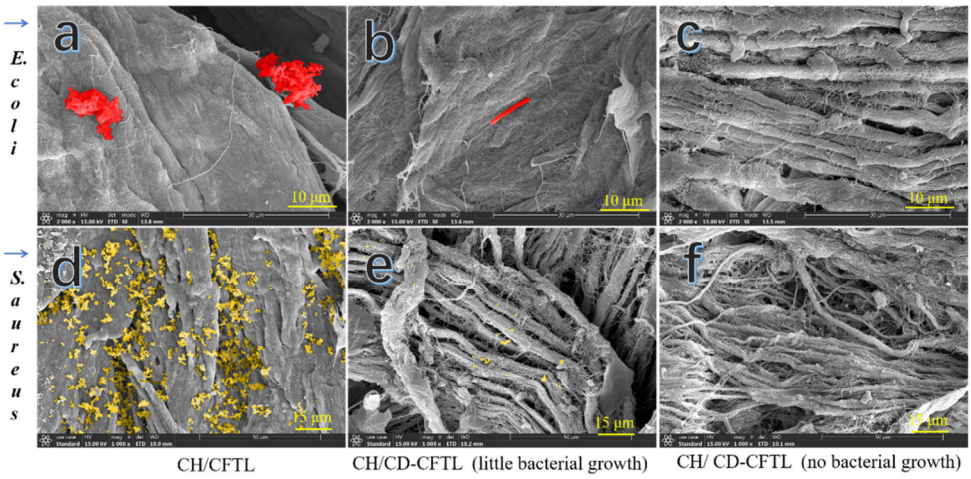


Fig.11 SEM against *E. coli* and *S. aureus* of CH/CFTL and CH/CD-CFTL after 90 days

Fig. 11 showed the SEM of the antibacterial test of CH/CFTL and CH/CD-CFTL after 90 days of storage. The *E. coli* and *S. aureus* grew wildly on samples of CH/CFTL, caused serious damage to the surface. But there were almost no bacteria on the surface of CH/CD-CFTL, and occasionally a few bacteria that have been inhibited and unable to grow were found. In summary, the obtained leather has an excellent long-term antibacterial ability.

4. Conclusion

An antibacterial strategy to improve the long-term antibacterial effect of CFTL had been proven to be successful, that is, to introduce a complete β-CD cavity on the CFTL and to fill the cavity with a small molecule antibacterial agent such as CH. The optimized CD-CFTL preparation process is 5% CDAD, the pH and time of the permeation reaction are 3.5 and 4 hours, the binding reaction is 3.5 and 4 hours, and the reduction reaction time is 2 hours, which can make the CD grafting rate reach

2.51%. The optimized CH/CD-CFTL preparation process is 0.05% CH addition, the pH, temperature, and time of inclusion reaction are 4.0, 30℃ and 4 hours, which can make the inclusion rate of CH and the CH loading degree of CD-CFTL reach 83.04% and 0.42 mg/g, respectively. It should be noted that CFTL is based on the combined tanning of organic tanning agent F-90, tannin extract and Zr-Al-Ti complex tanning agent, and CDAD is obtained by oxidizing the primary hydroxyl group at the C_6 position of *β*-CD, which has the complete *β*-CD cavity structure.

The structure and properties of CD-CFTL and CH/ CD-CFTL were characterized by FTIR, SEM, DSC, TGA, and the antibacterial rate against *E. coli* and *S. aureus* was calculated according to the oscillation method. The results showed that the T_s, T_d, and T_p increased 5.7 °C, 4.9 °C, and 6.9 °C, respectively. After being treated by CH with 90 days of storage, the antibacterial rates against *E. coli* and *S. aureus* still reached 99.8% and 97.4%, respectively, which were 29.9% and 34.4% higher than those without *β*-CD treatment.

Since both antibacterial properties and heat resistance could meet the requirements of production applications, the application prospects were promising. In conclusion, a new antibacterial method could improve the long-term antibacterial performance and heat resistance of the chrome-free tanned leather, and be expected to be applied to the leather industry.

Declarations

Competing interests

The authors declare that they have no competing interests.

Funding

This work was financially supported by the Fujian Provincial Natural Science Foundation Projects [2019J06025], the National Key R&D Program [2017YFB0308500], and the Fundamental Research Funds for the Central Universities [20826041E4156].

Acknowledgements

The authors gratefully acknowledge the Xingye Leather Technology Co., Ltd for their providedthe wet salt hides, and would thanks to Prof. Hui Wang (Analytical＆Testing Center, Sichuan University) for her help in SEM observations.

References

Barros M. C., Fernandes I. P., Pinto V., et al., (2011): Chitosan as an antimicrobial agent for footwear leather components. Biodegradable Polymers and Sustainable Polymers (BIOPOL-2009), 151-166.

Bowes J. H., Cater C. W., (1968): The interaction of aldehydes with collagen., Biochimica et Biophysica Acta (BBA) - Protein Structure., 168(2), 341-352.

Chao D., Qian L., Zhao G., et al., (2014): Preparation of antimicrobial cellulose fibers by grafting β-cyclodextrin and inclusion with antibiotics., Materials Letters., 124, 181-183.

Chao J., Chen L., Hao X., et al., (2002): Preparation and study on the solid inclusion complex of ciprofloxacin with β-cyclodextrin., Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy., 58(13), 2809-2815.

Choi J. M., Park K., Lee B., et al., (2017): Solubility and bioavailability enhancement of ciprofloxacin by induced oval-shaped mono-6-deoxy-6-aminoethylamino-beta-cyclodextrin., Carbohydrate Polymer, 163, 118-128.

Cuadros S., Manresa M. A., Font J., et al., (2012): Alternative Fungicides for the Leather Industry: Application in Various Processes., 96(6), 225-233.

Eastburn S. D., Tao B. Y., (1994): Applications of modified cyclodextrins. Biotechnology Advances, 12(2), 325-339.

Gauzit A. A., Palomino D. C., Maton M., et al., (2020): Designed sponges based on chitosan and cyclodextrin polymer for a local release of ciprofloxacin in diabetic foot infections., International Journal of Pharmaceutics., 587, 119677.

Geng X., Li W., Yin Q., et al. , (2018): Design and fabrication of reversible thermochromic microencapsulated phase change materials for thermal energy storage and its antibacterial activity., Energy, 159, 857-869.

Hou D., Wang R., Wang Z., et al., (2021): A light-activatable antibiotic with high activation efficiency and uncompromised bactericidal potency in the activated state. Journal of Leather Science and Engineering, 3, 8.

Hu J., Ye C., Zhao Y., et al., (1999): A Facile Synthesis of β-Cyclodextrin Monoaldehyde., Chinese Chemical Letters., 10, 273-274.

Kanagaraj J., Panda R. C., Vinodh K. M., (2020): Trends and advancements in sustainable leather processing: Future directions and challenges - A review. Journal of Environmental Chemical Engineering., 104379.

Krishnamoorthy G., Sadulla S., Sehgal P. K., et al., (2012): Green chemistry approaches to leather tanning process for making chrome-free leather by unnatural amino acids. Journal of Hazardous Materials., 215, 173-182.

Liu H., (2008): Study on changes of the IR absorption bands for the Guest Molecule in β-cyclodextrin inclusion complex., Spectroscopy and Spectral AmIySis., 28(10), 91-92.

Matencio A., Navarro-Orcajada S., García-Carmona F., et al., (2020): Applications of

cyclodextrins in food science. A review., Trends in Food Science & Technology, 104, 132-143.

Orlita A., (2004): Microbial biodeterioration of leather and its control: a review. International Biodeterioration & Biodegradation., 53(3), 157-163.

Radu C. D., Parteni O., Ochiuz L., (2016): Applications of cyclodextrins in medical textiles — review. Journal of Controlled Release, 224, 146-157.

Sathish M., Madhan B., Sreeram K J., et al., (2016): Alternative carrier medium for sustainable leather manufacturing – a review and perspective. Journal of Cleaner Production., 112, 49-58.

Valle D, Martin E M., (2004): Cyclodextrins and their uses: a review., Process Biochemistry, 39(9), 1033-1046.

Velmurugan P, Cho M, Lee S M, et al., (2014): Antimicrobial fabrication of cotton fabric and leather using green-synthesized nanosilver. Carbohydr Polymer., 106, 319-325.

Wen H., Chen J., Yang Y., et al., (2021): Redesign and application of chrome-free tanning and its performance endowed process technology., China Leather., 50(11), 1-7.

Wen H., Yu G., Zheng X., et al., (2021): Improving the antibacterial properties of wet leather based on grafting β-cyclodextrin and inclusion with ciprofloxacin hydrochloride., Journal of Society of Leather Technologists and Chemists., 104(5): 1-14.

Wen H., Zheng X., Yu G., et al., (2021): Preparation of fragrant collagen fibers by cross-linking with β-cyclodextrin and inclusion of l-menthol: characterization, release behavior and reusability evaluation. The Journal of The Textile Institute., doi: 10.1080/00405000.2021.1992856: 1-10.

Xiao S., Zhu J., Dan W., et al., (2014). Application of n-(2-hydroxy) propyl-3-trimethyl ammonium chitosan chloride as an antibacterial and antifungal agent in wet-blue cattle hides. Journal of the Society of Leather Technologists and Chemists., 98(6), 264-268.

Yap K. L., Liu X., Thenmozhiyal J. C., et al., (2005): Characterization of the 13-cis-retinoic acid/cyclodextrin inclusion complexes by phase solubility, photostability, physicochemical and computational analysis [J]. Eur J Pharm Sci, 2005, 25(1): 49-56.

Yu Y., Wang Q., Yuan J., et al., (2016): A novel approach for grafting of beta-cyclodextrin onto wool via laccase/TEMPO oxidation., Carbohydrate Polymer., 153, 463-470.

Zhang H., Hou X., Liang L., (2012): Study on the supramolecular systems of ciprofloxacin with cyclodextrins., Journal of Molecular Science., 28(3): 214-220.

Zhao H., Heindel N. D. , (1991): Determination of Degree of Substitution of Formyl Groups in Polyaldehyde Dextran by the Hydroxylamine Hydrochloride Method., Pharmaceutical Research., 8(3), 400-402.

Zhu X., (2008): Thermal Stability and Thermal Decomposition Kinetics of Ofloxacin., Chemical World., 19(6), 333-334.