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

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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 Ts, Td and Tp 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 C6 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.

![Image of preparation of antibacterial CFTL](image)

**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.
| Process       | Chemicals                        | Dosage /% | Temp. /°C | time / min | pH    |
|--------------|----------------------------------|-----------|-----------|------------|-------|
| Washing      | H₂O                              | 250       | 25        | 10         | 7.0   |
| Tanning I    | H₂O                              | 30        | 30        |            |       |
|              | F-90                             | 5.0       | 120-180   |            |       |
|              | H₂O                              | 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  | H₂O                              | 50        | 35        | 120        |       |
|              | HCOOH(1:10)                      | 0.5       | 25        | 30         | 2.8-3.0|
|              | HCOONa                           | 1.0       |           | 180        |       |
|              | CAT                              | 6.0       |           |            |       |
|              | NaHCO₃                           | 2.0       |           |            |       |
|              | H₂O                              | 150       | 40        | 180        | 3.8-4.0|
| Washing      | H₂O                              | 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):

\[ W\% = \frac{m_1 - m_0}{m_0} \times 100\% \quad (1) \]

where W represents the weight gain rate of CFTL after CDAD modification, %; m1 is the weight of CFTL after β-CDAD modification, g; m0 is 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.

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

\[ L = \frac{N \times C_0 \times V}{m_{CTFL}} \quad (3) \]

where N represents the included rate of CH, %; L represents the CH load degree of CD-CTFL, mg/g; C0 and C1 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 mCTFL is the weight of CTFL.

2.3 Characterization

2.3.1 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 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):

\[
A = \frac{N_0 - N_1}{N_0} \times 100\% 
\]

where A represents the antibacterial rate, %; N0 and N1 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 reaction, and the time of permeation, binding reaction, and reduction reaction.

![Graphs showing the effect of reaction conditions on weight gain rate.](http://dx.doi.org/10.15677/jallpa.2021.v6i1.22)

(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-CFTL. 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).
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.

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 an 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.

![Experimental optimization of the antibacterial treatment process](image)

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.
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 $\beta$-CD.

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 \( \beta \)-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](image)

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, CFTL 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 \( \beta \)-CD treatment. It showed that the CH included in the cavity of \( \beta \)-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 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°C 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 C6 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 Ts, Td, and Tp 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.

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