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EDITORIAL

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Essential role of isoelectric point of skin/leather in leather processing

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Leather, made from animal hide or skin, is mainly composed of collagen. Collagen is a type of fibrous protein. The basic amino acid residues (lysine, arginine and histidine) and acidic amino acid residues (glutamic acid and aspartic acid) of the protein confer zwitterionic character to collagen, making the protein positively or negatively charged at different pH values. The pH at which the net charge of collagen becomes zero is defined as isoelectric point (IEP, the value is labeled as pI).

The IEP is an essential parameter for skin/leather, since it can represent the charged state of skin/leather at any given pH. A variety of chemicals are used to treat skin/leather in leather making. Electrostatic interaction between the chemicals and skin/leather deeply affects the mass transfer and binding of these chemicals in skin/leather. Therefore, clarifying the pI change of skin/leather during leather processing is crucial for exploring the mechanisms of tanning and regulating the whole process of leather manufacture.

The first barrier is how to determine the pI of leather in the solid state precisely and rapidly. Collagen solution was commonly used as the test object in early studies. The conventional zeta potential analyzer which is suitable for solution and colloid was used as the instrument for pI simulation of leather. However, the pI of skin/leather matrix in various processes is quite different from that of collagen solution. Wang et al. [1] drew on techniques from paper industry and established a method for determining zeta potential of leather fibers. Thus, we can conveniently obtain the real pI values of solid-state skin/leather. This tool enables leather chemists to further investigate the mechanisms of various chemical and biochemical treatments on skin/leather.

Beamhouse aims to remove all the useless substances from raw hide/skin and prepare the pelt for tanning. The pI of raw hide or skin is around 7.7–7.9. Figure 1 shows that soaking, the process of rehydration, hardly changes the pI of hide. Subsequently, the pI of limed pelt declines to 7.6 mainly because of the hydrolysis of glutamine and asparagine under strongly basic condition. Bating with protease and pickling with acid further break peptide bonds and reduce the pI to 6.8 and 5.6, respectively. As a result, the pI of hide/skin decreases step by step as the beamhouse proceeds. The variation of pI during beamhouse did not attract much attention in the previous studies. In fact, the mass transfer and reaction of some leather chemicals, such as deliming agent [2], salt-free pickling auxiliary [3] and enzyme [4], is closely related to the pI and charged state of the hide/skin. In particular, enzyme is also a category of amphoteric biomacromolecule. The uniform penetration and satisfactory catalysis of an enzyme are largely influenced by its electrostatic interaction with skin [4, 5]. Skin/leather is known as a 3D hierarchical fiber network with a thickness of 1–8 mm. The mass transfer of enzyme in skin/leather is complicated. Uneven distribution and reaction of enzyme in the network will inevitably damage the grain surface and lead to leather defects. Therefore, much attention should be paid to the surface charge regulation of both enzyme and skin/leather in unhairing, bating and acid bating processes to promote the penetration and performance of the enzyme.

As for tanning, which is the core of leather processing, the pI of leather is highly variable for two reasons. The first one is the introduction of tanning agents with

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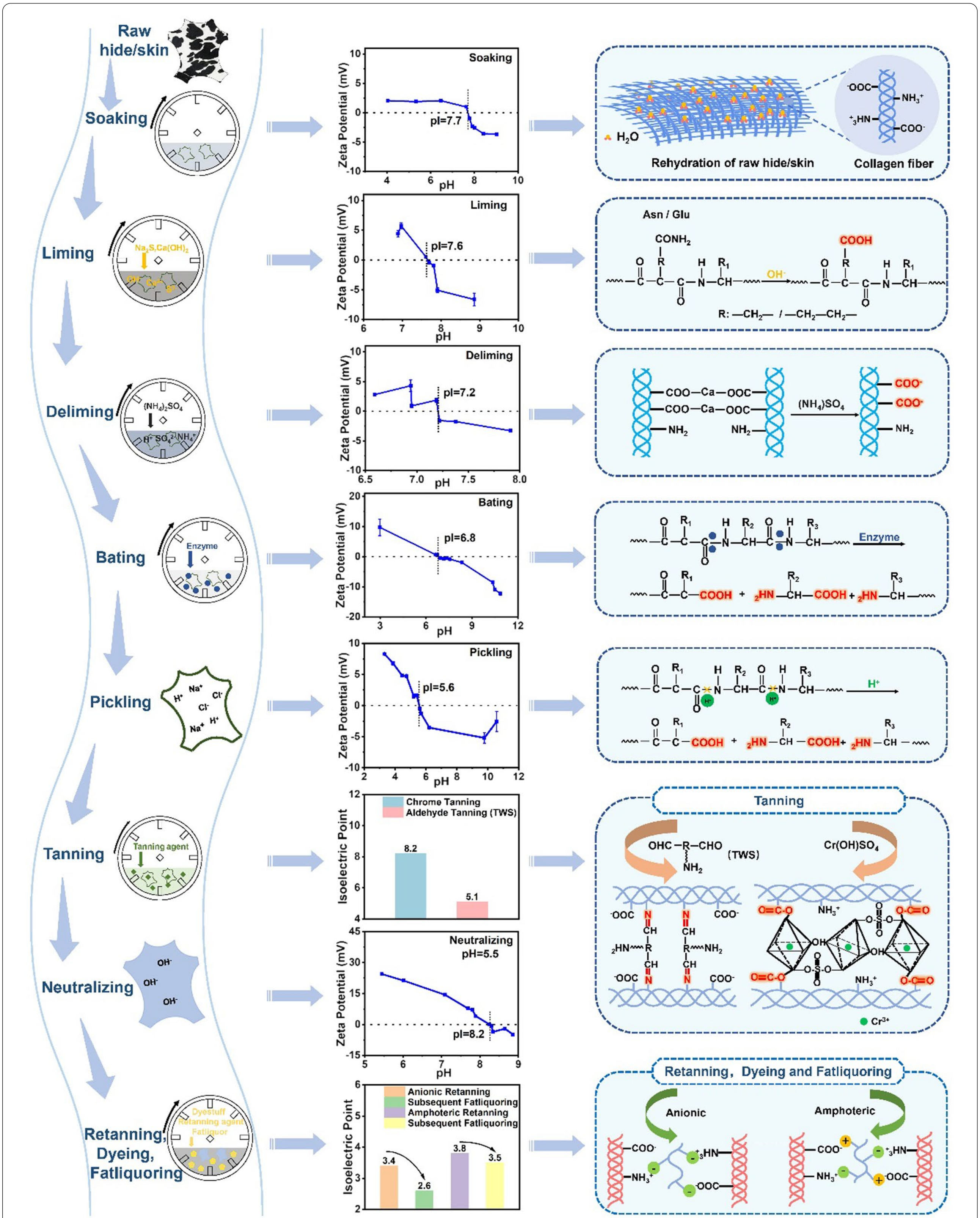

Fig. 1 Flow chart of leather processing and corresponding isoelectric points of skin/leather

charged groups. The second one is the consumption of carboxyl or amino groups on the side chains of collagen via tanning reactions. Conventional chrome tanning raises the pI of pickled pelt from 5.6 to 7–8 (Fig. 1) because of the use of positive charged Cr(III) salts and the consumption of collagen carboxyl through coordination with Cr complexes. Other mineral tannages involving Al, Zr, and Ti salts show similar results [1]. Organic tannages by using aldehyde, cyanuric chloride derivatives, vegetable tannin or other synthetic tanning agents generally form covalent crosslinking between amino groups of collagen, or form salt links between sulfonic groups of tanning agents and amino groups of collagen. Thus, the pI of organic tanned leather often decreases below 5.0 [1]. Notably, the relatively low pI of tanned leather will have a detrimental effect on the fixation of post-tanning chemicals that are mostly negatively charged. Zwitterionic aldehyde tanning agent (TWS) introduces extra amino groups into leather and results in higher pI (5.1) than the other organic tanned leathers (Fig. 1), which benefits the following post-tanning performance. Along with the emergence of chrome-free tanning [6, 7], we should focus on the pI control of chrome-free leather when developing novel tanning technologies.

Post-tanning processes that follow the tanning stage show the diversity and artistry of leather processing. Electrostatic reactions dominate the binding reactions between post-tanning chemicals (retanning agents, dyes and fatliquors) and tanned leather. Conventional wet blue (Cr tanned) leather with high pI of 7–8 exhibits strongly positive charged surface in the late stage of post-tanning ($pH < 4$), thereby achieving firm fixation of the anionic chemicals and excellent properties of crust leather. Thus, the pI of leather shows gradual decline through the post-tanning. This system is also suitable for non-chrome mineral tanned leathers [8]. However, the post-tanning system for organic tanned leathers should be redesigned since the pIs of organic tanned leathers are much lower than that of chrome tanned leather. The use of amphoteric chemicals can enhance the pI of leather during post-tanning (Fig. 1) and sheds new light on the construction of the post-tanning system of organic chrome-free tanned leather. Future work should focus on the adjustment and balance of the pI of both chemicals and leather [9].

In summary, the pI of skin/leather plays an important role in leather manufacture. Accurate determination and ingenious regulation of the pI provide a scientific guide for the design and implementation of leather processes, especially for the challenging enzymatic treatments and chrome-free tanning process.

Author contributions
YW and LH conceived the idea. YW drafted the manuscript. LH performed the experiments and drew the figure. All authors read and approved the final manuscript.

Declarations

Competing interests
The authors declare that they have no competing interests.

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