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An integrated technology to minimize the pollution of chromium in wet-end process of leather manufacture☆

Chunxiao Zhang [a, b], Fuming Xia [a], Jiajun Long [a], Biyu Peng [a, b, *]

[a] National Engineering Laboratory for Clean Technology of Leather Manufacture, Sichuan University, Chengdu 610065, PR China
[b] Key Lab. of Leather Chemistry and Engineering of Ministry of Education, Sichuan University, Chengdu, Sichuan 610065, PR China

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ABSTRACT

In order to minimize chromium pollution, based on tracing the life cycle of chromium in whole leather wet-end processing, an integrated technology comprising of a novel salt-free and high-exhaustion chrome tanning process, modified chrome retanning, direct recycling of tanning wastewater and highly efficient removal of Cr from post-tanning floats was developed. The results indicated that, in the novel technology, the total Cr utilization ratio reached to 98.6% (conventional 91.2%), the total chromium discharge was reduced by 84.2% from the source, and the spent tanning liquor could be completely recycled for at least 10 cycles, whilst the leather properties were not impaired. Furthermore, the remained Cr in the wastewater without reused value was removed by means of precipitation with optimized bases, and the residual Cr was at the level of 1.0–1.2 mg/L, the produced chrome-contained sludge was reduced by 28.1%. The novel technology integrating reduction at source and end treatment can reduce the total Cr discharge with effluent to 4.604 g/t salted-wet hide and the chrome concentration in mixed wastewater streams is 0.354 mg/L, and achieve near zero emission of chromium in leather processing.

1. Introduction

Nowadays, environmental protection has become one of the most concerned issues in global industrial activities. Among typical pollutants from leather industry, chrome discharge is especially concerned, because chrome is put in the list of the strict controlled discharging metals in most countries, and chrome tanning is still the most important and widely used tanning method for quite a long time in the future, which is characterized by giving leather top handing quality, high hydrothermal stability, user-specific properties and versatile applicability. (Sundar et al., 2011).

However, in the conventional chrome tanning process, only 60%–80% of the offering chrome is effectively utilized. As a result, the chrome concentration in spent float is in a range of 2500–3,000 mg/L, (Sundar et al., 2002) which poses a significant disposal problem. Hence, minimizing the residual chrome, together with chloride ion, in effluent to near zero emission is a matter of great concern to tanners.

There is a huge volume of research work in reducing chrome discharge, which can be classified into two categories, i.e. reduction from the source and by end treatment. High-exhaustion chrome tanning is the major technology focused on reducing chrome concentration in the residual float, which is the foremost source of chrome discharge (Rivela et al., 2004). There are two main approaches to increasing the chrome uptake, which mainly involve modifying chrome complexes by use of sodium citrate, sodium oxalate and orthophtalate (Gregori et al., 1993), and increasing the collagen reactivity with the participation of auxiliaries including oxazolidine (Sundarapandiyan, et al., 2011), the multi-functional group agent containing carboxyl, hydroxyl and tetra-amino (Shifang et al., 2007), glyoxylic acid (Fuchs et al., 1993). Modifying tanning process through raising the beginning pH can also increase the chromium absorption ratio. (Jiping et al., 2006; Legesse et al., 2002) However, there are some problems limiting their widely commercial acceptability, i.e., it is still necessary to add enough dosage of neutral salts, the operations are more complicated, the residual chrome in the effluent is still at a rather high level, and lastly but most significantly, the leather properties and the following

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* Corresponding author. National Engineering Laboratory for Clean Technology of Leather Manufacture, Sichuan University, Chengdu 610065, PR China.
E-mail address: pengbiyu@scu.edu.cn (B. Peng).

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recycling of the spent tanning float may be negatively affected.

By measured the residual Cr concentrations in the wastewaters of the operations during leather processing, Jian et al. (2011) found that, besides the high-concentration chrome wastewater from chrome tanning and retanning processes, the low-concentration chrome wastewater from post-tanning processes resulting from chrome leaching out from chrome-tanned leather should be paid more attention, because the limit of total chrome discharge in effluent is set on 1.5 mg/L for discharging into sewage systems in most countries. The former can be direct recycled back into tanning, or the residual chrome can be recovered and reused. All chrome-tanned floats should be further treated to separate chrome before bumped to the integrated wastewater treatment plant in order to avoid chrome-containing effluents mixing with other wastewater, thus producing a huge amount of chrome-containing sludge.

Recycling the high-concentration chrome-containing effluent directly back into tanning and recovering chrome from effluent are the practicable methods to prevent Cr from being discharged into sewage systems (Sreeram et al., 2005; Panswad et al., 1995; Panov et al., 2008). However, the chemical constituents of the spent chrome effluent in the conventional tanning process, comprising of neutral salts, chromium complexes, masking agents, etc., are so complex that it's hard to maintain the chemistry equilibrium of recycled floats after several cycles. The chrome tanning effectiveness will be negatively influenced by the accumulation of residual components. In addition, because of high concentration Cr residual in spent float, it is difficult to completely replace fresh water with the wastewater, otherwise, the residual Cr will quickly combine with the surface of pelts to cause coarse grain (Cranston et al., 1997), hence usually more float is available for recycling than can actually be used. The compositions of the spent liquors in the above high-exhaustion chrome tanning processes are more complicated with the introduction of auxiliaries; therefore, the recycling process becomes unmanageable. (Nacheva et al., 2004).

Generally, it is not considered to recycle and reuse the low-concentration chrome wastewater from post-tanning processes, because the chemical constituents are more complicated. Some approaches have been researched to remove Cr from spent liquors, including nanofiltration (Das and De, 2006), constructed wetlands (Dotro et al., 2012), activated carbon (Fahim et al., 2006), brown seaweed (Aravindhan et al., 2004a, b), cation exchange resin (Sahu et al., 2009) and the alkalis of sodium carbonate, magnesium oxide, calcium hydroxide (Guo et al., 2006). Hitherto, alkali precipitation is one of the effective and practical ways. The alkali precipitation effectiveness is adversely affected by residual organic chemicals (Remoudaki et al., 2003). The keys are how to improve the precipitation efficiency and reduce the amount of produced chrome-containing sludge, which mainly depends on the amount of residual chrome.

Aiming at realizing the near zero discharge of chromium in leather processing, an integrated technology composing of a novel salt-free and high-exhaustion chrome tanning conducted at a high initial pH with aromatic sulphonic acid, modified chrome retanning, recycling of chrome tanning wastewater and highly efficient removal of Cr from post-tanning wastewater is designed. Firstly, with the use of the novel high-exhaustion chrome tanning and modified chrome retanning methods, the chrome emission is reduced to a maximum degree at the source in tanning processing, the constituents of the spent tanning liquor are simplified because of high exhaustion of added chemicals and being free of sodium chloride and additional masking agents. Secondly, the high-concentration chrome-containing floats can be completely recycled back into process as many times as possible because of the low chrome concentration and less accumulation effect of other components. Thirdly, the releasing amount of chrome from the leather tanned under the novel process into floats will also go down in the post-tanning processes, thus reducing the amount of produced chrome-containing sludge from alkali precipitating. According to the above design, the key process parameters and effectiveness were optimized and evaluated.

2. Experimental and methods

2.1. Materials and instruments

Salted-wet cattle hides from Sichuan, China, were purchased from a local tannery (Chengdu Xinshi Leather Industry CO., Ltd.). Chromosal B (a chromium tanning agent with 33% of basicity and 26% of Cr_2O_3 (0.177% of Cr) content) was purchased from LANXESS Inc. Naphthalene sulfonic acid (NSA), was synthesized as per the standard synthesizing procedures in our laboratory. The following applied leather chemicals, including syntans, fatliquors, polymers, filling agents, etc. were of industrial grade and from Sichuan Dowell Science & Technology Co., Ltd China. The other chemicals were of analytic grade.

Stainless Experimental Drum (GSD400-4, Wuxi Xinda Light Industry Machinery Co., Ltd.), Inductively Coupled Plasma Emission Spectrometer (AES-ICP, 2100DV, Perkin Elmer Inc. America), Precision Slice Machine (C520L, Camog (a) Inc., Italy), Digital Determinator of Shrinkage Temperature (MSW-YD4, Shanxi University of Science and Technology, China).

2.2. Methods

2.2.1. Novel salt-free and high-exhaustion chromium tanning and retanning processes

Ten pieces of salted-wet cattle hide conducted soaking, fleshing, liming, splitting, deliming and bating procedures as normal, and then were divided into two groups. Among them, a whole grain-layer limed cattle hide with thickness of 2.8–3.0 mm after splitting was cut into two half sides along with the backbone line, symmetrically, and they were distributed to different tanning groups for evaluating and comparing tanning effects. As shown in Fig. 1, the two groups were carried out a conventional chrome tanning (at pH 2.8 around with 6.5% Chromosal B) and a novel high-exhaustion (at pH 5.0 around with 5.0% Chromosal B), respectively. After stacked and aged for 7 days, the tanned leathers were carried out sammying, shaving (thickness 1.1–1.2 mm), wetting as normal operations. Then the shaved tanned leathers were put back to a drum and conducted a normal chrome retanning (at pH 3.5 around with 3.5% Chromosal B) and a modified retanning (at pH 4.5 around with 3.0% Chromosal B) correspondingly. Following on that, the chrome retanned leathers were neutralized, retanned with organic syntans, dyed and fatliquored as the normal shoe upper leather procedures (See Table A, Appendices).

2.2.2. The recycle of spent chrome tanning liquors

As shown in Fig. 1, the spent chrome tanning liquors from the above two tanning processes were completely collected and reused after filtrated through a 20 mesh filter. A whole grain-layer limed cattle hide with thickness of 3.0–3.2 mm after splitting was divided into pieces adjacently and symmetrically, and they were distributed to different tanning groups for evaluating and comparing tanning effects in spent liquors. The spent liquors were reused in two steps, i.e., used as the pickling float and supplement water at the later stage of tanning. The bated pelts were soaked in 50% of the filtered spent tanning liquors at 23 °C with or without adding 6% of sodium chloride, and the float pH was adjusted to about 2.8 or 5.0 with a certain amount of sulfuric acid or NSA, respectively, corresponding to the conventional or novel high exhaustion chrome