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Reducing chromium discharge in tanning: The salt-free chrome tanning process

Mahdi Haroun * and Manal Mohammed Ahmed

Department of Industries, College of Applied and Industrial Sciences, University of Bahri, P.O. Box13104-Khartoum, Sudan.

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Abstract

Nowadays, there is increasing concern about environmental protection in global industrial activities. The sustainable leather industry is currently focusing on cleaner processing methods to promote a greener environment. However, the discharge of waste streams containing several pollutants poses a significant social threat to the leather sector. The conventional pickling and chrome tanning process is particularly problematic due to the enormous amounts of chlorides and chromium emissions, which have been a longstanding issue that has not been satisfactorily resolved. In order to minimize the emissions of chromium and chloride integrately, a salt-free and high exhaustion chromium tanning method was designed and optimized. The study's results demonstrated that the chrome tanning process could be improved by conducting it in a salt-free environment, resulting in a smooth process and a chromium absorption rate increase to 99% compared to 75% in the conventional process. Moreover, the dosage of Chrome required was minimized from 1.5% to 0.8%, resulting in a significant reduction of residual Chromium concentration in the spent liquor from above 1150 mg/L to 40 mg/L. The novel chrome tanning process significantly decreases the amount of chromium-containing sludge generated and facilitates the disposal of spent liquor with a reduced amount of chrome and chloride. The novel process effectively addresses long-standing problems and meets the requirements of the modern sustainable leather industry.

Keywords: Leather manufacture; Pickling free-salt; Chrome tanning; Aromatic sulphonic acid

1. Introduction

Tanning turns animal skins into leather, making it more durable and resistant to decomposition. Despite the development of other tanning methods, chrome tanning remains the most important and dominant method in the leather industry. This is because chrome-tanned leather offers superior quality, stability, and versatility that cannot be matched by other tanning methods [1]. The standard chrome tanning process has three stages: pickling, tanning, and basification. During pickling, pelts are treated with a salt solution containing sulfuric and formic acid in an amount of 1.0-1.8% on split limed pelt weight. The pickle float should contain at least 6% sodium chloride to protect the collagen from acid swelling, which would negatively affect the leather's properties. The pH of the pickle float is controlled at 2.5-3.0 to modify the reactivity of the carboxyl groups and allow effective penetration of chromium into the pelts' inner layers, while preventing excessive chromium combination on the surface that causes coarse grain. Chrome tanning is initiated during the pickling phase [2]. Typically, 6-8% of basic chromium sulfate (chrome powder) is used in the chrome tanning process, which contains about 25% Cr_2O_3 of 33% basicity. This corresponds to 1.5-2.0% of Cr_2O_3 on the limed pelt weight to ensure minimal chromium levels in the leather and produce high-quality products with excellent properties, including hydrothermal stability, mechanical strength, and organoleptic properties [3]. After the chrome has completely penetrated the pelts, basification occurs to neutralize acids and facilitate the combination of chrome with the collagen. Basification agents such as sodium hydrogen carbonate and magnesia are commonly used to achieve a final pH of 3.8-4.2 in the float, which promotes the combination of chromium to the carboxyl groups and adequate crosslinking of chromium between collagen fibers [4].

* Corresponding author: Mahdi Haroun

In the traditional chrome tanning process, only 60-80% of the offered chrome is utilized, and all sodium chloride remains in the float. As a result, the spent float contains a chrome concentration of 2500-3000 mg Cr/L and a chloride concentration of at least 20,000 mg/L [5]. Disposing of waste chrome and chloride from leather production is a significant challenge, with strict statutory limits in place for their discharge and disposal worldwide. The latest regulations specify a total chrome discharge limit of 1.5 mg/L for discharging into sewage systems and a chloride ion limit of 3000 mg/L for discharging into water bodies [5]. Therefore, developing cleaner chrome tanning processes that maximize chrome uptake while minimizing residual amounts of chrome and chloride in floats is a major concern for all tanners.

An effective way to reduce sodium chloride pollution in chrome tanning process is to use salt-free or low-salt pickling. This method involves the use of non-swelling acids, primarily aromatic sulfonic acids, instead of formic acid and sulfuric acid. By eliminating or reducing the use of sodium chloride, this method can significantly reduce the environmental impact of the tanning process [6-7].

The above pickling methods were found to reduce sodium chloride usage by at least 80% and improve the uptake rate of chrome to some degree. However, in the salt-free or low-salt pickling processes, a greater quantity of aromatic sulfonic acid or syntans were necessary to lower the float pH to approximately 3.0, which is required for conventional chromium tanning at the initial pH level [8-9]. Using a high quantity of aromatic sulfonic acid, particularly syntans, can have a negative impact on leather properties, including color, light fastness, softness, and handling performance. Furthermore, the Chromium concentration in the tanning floats may still be greater than 500 mg/L, making these salt-free or low-salt pickling methods not yet widely accepted commercially.

Increasing the chrome uptake during the tanning process is essential to reduce residual chrome concentration in floats. Two primary methods for achieving this are optimizing process parameters and modifying the tanning process. Modifying the tanning process is often focused on masking the chrome tanning complex and increasing collagen reactivity. Various tanning auxiliaries, including aliphatic dicarboxylates, glyoxylic acid, and low molecular weight polyacrylates, are available to aid in achieving these goals [10], oxazolidines [11] and syntans [12].

To achieve the goals of eliminating sodium chloride usage, minimizing chrome discharge, and ensuring high-quality and desirable properties of chrome tanned leather, a new method has been developed. This salt-free and high exhaustion chromium tanning method combines the benefits of salt-free pickling and chrome tanning at high initial pH.

To implement the salt-free and high exhaustion chromium tanning method, the bated pelts are first preprocessed with appropriate aromatic sulfonic acids to achieve a specific pH value. The pelts are then subjected to chrome tanning using normal chrome powder. Aromatic sulfonic acids can form an electrovalent bond with the amino groups on the collagen side chain under acidic conditions. This process can conceal the positive charges on the side chain of collagen molecules, decreasing their isoelectric point. This prevents possible acidic swelling of pelts in the absence of sodium chloride during the subsequent chrome tanning process. By using a suitable and relatively high initial tanning pH, the chrome uptake and penetration can be improved while minimizing negative impacts on leather quality such as acidic swelling, excessive surface bonding of chrome, and large doses of aromatic sulfonic acid.

2. Material and methods

2.1. Materials

Cattle hides preserved with salts are purchased from Khartoum Tannery. A chromium tanning agent with 33% of basicity and 26% of Cr_2O_3 content and Phenol sulfone sulfonic acid, Naphthol sulfonic acid, and Naphthalene sulfonic acid are of analytic grade.

2.2. Experimental parts

2.2.1. Utilization of Aromatic acids for Pickling and chrome tanning

Cattle hides preserved with salts were soaking, fleshing, liming, splitting, deliming and bating as in conventional method. A whole grain-layer limed cattle hides with thickness of 3-3.2 mm after splitting were divided into pieces adjacently and symmetrically, and they were distributed to different tanning batches for evaluating and comparing tanning effects.

Limed pelts were soaked in drums containing 50% water at 23 ^{o}C. They were pickled using a conventional method with NaCl, formic acid, and sulfuric acid (6%, 0.8%, and 1.0-1.2% respectively). Alternatively, a different aromatic sulfonic acid was used instead of NaCl. The dosage of the acids was determined based on the desired final pickling pH of 2.8 ± 0.1 (Table 1). After pickling overnight, Chromium was added to each drum at a concentration of 6.5%. The drums were run for 180 minutes at 23ºC to allow complete penetration of the chromium into the hide inner-layer. The pH was then carefully increased to around 4.0 using a $NaHCO_3$ solution.

Hot water at 60°C was added to bring the total water amount to 200% of the weight of the limed hides. The drums were run for an additional 120 minutes at 40°C, followed by an overnight stay. The next day, the pH of the tanning liquor was readjusted to 4.0 ± 0.1. The concentration of Chromium in the spent tanning liquor was measured. The distribution of Chromium, shrinkage temperature values (Ts), and grain pattern of the chrome-tanned leather samples from the adjacent and symmetrical parts of the same hide were analyzed and observed.

Table 1 Effect of pickling system with various acid concentrations on chrome tanning

Pickling systems	Doses of Acids, %	Thickness of pelts, %	Chromium In spent liquor (mg/l)	Shrinkage Temperature, T_sºC
Conventional	2.0	-15	1750.9	122
Naphthalene sulfonic acid	5.5	-15	650.5	125
sulfosalicylic acid	4.5	-14	1300.3	120

2.2.2. Utilization of different pickling pH and Naphthalene sulfonic acid on Chrome tanning

Bated cattle hide with thickness of 3.0-3.2 mm after splitting was divided into four pieces were distributed to different tanning groups for evaluating and comparing tanning effects. The bated pelts were pickled with Naphthalene sulfonic acid alone to pH 3.0, 4.0 or 5.0, respectively. As a control, a conventional pickling was also conducted.

2.2.3. Determination of physical and mechanical properties of leather

The leather samples from each tanning group were extracted from adjacent and symmetrical parts of the same hide. To assess their physical and mechanical properties, the samples were dried and conditioned using the IUP method (IUP 2, 2000). Standard procedures (IUP 6, 2000; IUP 8, 2000; IUP 9, 1996) were used to test the samples for physical properties, including tensile strength, elongation at break, tear strength, and bursting strength.

2.2.4. Determination of chromium concentration in spent tanning liquors

The tanning liquid was filtered and treated with a mixture of sulfuric and nitric acid at a high temperature for a specific amount of time. The resulting solution was then diluted and analyzed using AAS to determine its chromium concentration. Finally, the chromium concentration of the original tanning liquid was calculated.

3. Results and discussion

3.1. Effect of pickling free salt with aromatic sulfonic acids on chrome tanning

Extensive research has been conducted to address the issue of high chloride discharge that has troubled tanners for a considerable period. To avoid or eliminate the use of common salt during tanning, various approaches have been explored. Among these methods, the use of aromatic sulfonic acids or their condensates is considered one of the most effective [8-9]. By using these alternatives, the need for common salts in the pickling tanning process can be entirely eliminated.

Two aromatic sulfonic acids were chosen for their superior ability to inhibit acidic swelling. Their effect on the tanning process was then inspected, and the results are displayed in Table 1. Two aromatic sulfonic acids examined were found to be effective in inhibiting acidic swelling of pelts during pickling, as evidenced by the appearance of the pickled pelts and the thickness change rate (Table 1). This success makes it possible to conduct salt-free pickling. Additionally, two non-salt pickling methods were found to enhance chromium exhaustion in comparison to conventional pickling.

When using naphthalene sulfonic acid pickling, the concentration of residual chromium in spent tanning liquor is reduced by at least 65% compared to conventional pickling methods. Additionally, the corresponding chrome-tanned leather exhibits a slight increase in shrinkage temperature (Ts). However, sulfosalicylic acid (SSA) was found to have a detrimental effect on the tanning process. The hydroxyl and carboxyl groups on the benzene ring of the SSA molecule can coordinate with Chromium three ions (Cr^{+3}) and form a hexatomic ring chelate. This leads to a stronger masking effect on Chromium three ions, which inhibits their combination with collagen and hinders the tanning process [13].

Naphthalene sulfonic acid is the best choice for preventing acidic swelling of pelts, improving chromium exhaustion and distribution, and increasing shrinkage temperature, compared to the conventional and sulfosalicylic acid.

3.2. Effect of pickling pH with Naphthalene sulfonic acid on chrome tanning

Using the two selected aromatic sulfonic acids enables salt-free pickling and promotes the uptake of chromium. Our strategy is to eliminate the use of NaCl and reduce the discharge of chromium by using salt-free pickling with aromatic sulfonic acids and chrome tanning at high initial pH levels. To investigate the effect of pickling pH with Naphthalene sulfonic acid on chrome tanning, we conducted an experiment where bated pelts were pickled to different pH levels by adjusting the dosage of Naphthalene sulfonic acid. After pickling, the pelts were tanned with 7.5% chrome powder (equivalent to 1.5% Cr) using conventional dosage. The tanning end pHs were then adjusted to 3.72-3.75. The results of this experiment are presented in Table 2.

Table 2 Effect of the Naphthalene sulfonic acid with initial pH on chrome tanning

Pickling systems	**Pickling, pH**	**Alkalining, pH**	**Chrome in wastewater, mg/l**	**Total organic carbon in spent liquor, mg/l**
Conventional	3.05	3.75	1250.5	1500.4
Naphthalene sulfonic acid, 4%	3.8	3.73	720.4	3000.5
Naphthalene sulfonic acid, 2.5%	4.05	3.72	315.6	2500.4
Naphthalene sulfonic acid, 1%	5.05	3.73	150.5	1800.5

In addition to that Table 2 shows increasing the initial pH results in a decrease in the chromium content in the wastewater. Tanning at a starting pH of approximately 5.0 reduces the residual chromium concentration to only 150.5 mg/L, with a Cr uptake rate of 87%. In contrast, the Chrome uptake rate is only 60% in the conventional pickling process, and the chromium concentration in the effluent is about 1250.5 mg/L, which is 10 times higher than the former. However, the Total Organic Carbon (TOC) in the wastewater is higher in the novel process and increases with the dosage of Naphthalene sulfonic acid. This suggests that excessive use of Naphthalene sulfonic acid is unnecessary and cannot be compensated for by increasing the dosage.

3.3. Efficiency of novel chromium method

One important factor in determining whether a new chrome tanning method will be accepted by tanners is whether it can maintain or improve the original properties of chrome-tanned leather. To assess this, the properties of leather parts of the same hide, tanned with different amounts of Chromium at pH 5.0 and with Naphthalene sulfonic acid pickling, were evaluated. Four different tanning methods were used, and the organoleptic properties of the resulting leathers were examined (Table 3). Results showed no visible differences in terms of color, grain pattern, softness, hand feel, and other properties among the leathers.

Table 3 Effect of Chromium offer on chrome tanning at a high pH

Pickling systems	**Pickling pH**	**Chrome offer, %**	**Alkaline pH**	**Chrome in wastewater, mg/l**	**Chrome uptake, %**	**Shrinkage temperature, oC**
Conventional	2.92	7.5	3.95	1150	75.5	123
Naphthalene sulfonic acid, 2%	5.05	7.5	3.95	130	97.2	124.5
Naphthalene sulfonic acid, 2%	5.12	6.5	4.0	100.5	97.3	124.2
Naphthalene sulfonic acid, 2%	5.0	4.5	3.98	40.5	99.1	109.2

Table 4 shows the physical and mechanical properties of the leathers. Results indicate that tear strength, tensile strength, and elongation at break of all leathers tanned with Naphthalene sulfonic acid at a high initial pH of 5.0 are higher compared to the leather tanned with conventional pickling. These properties were also improved to some degree even with low Chrome dosage. The increase in mechanical properties is believed to be due to more efficient crosslinking between collagen molecules by Chrome at high beginning tanning pH.

Table 4 Physical and Mechanical properties of the leathers tanned with different Chrome offers and Naphthalene sulfonic acid

Pickling systems	**Conventional**	**Naphthalene sulfonic acid,**		
		2%	**2%**	**2%**
Chrome offer, %	1.5	1.5	1.0	0.8
Tensile Strength (N/mm2	15	18	23	22
Tear Strength (N/mm)	75	88	92	90
Elongation at break, %	60	66	64	71

4. Conclusion

Studies have shown that using chrome tanning at a pH of around 5.0 with Naphthalene sulfonic acid pickling under salt-free conditions can offer several advantages. Firstly, it does not cause acidic swelling of the pelts or excessive combination of chromium on the pelt surface. Additionally, this method improves the penetration of chromium and reduces the amount of chromium in wastewater by 87% compared to conventional chrome tanning. The uptake of chromium for this new process is around 99%, which reduces the need for Chrome offering by at least 30% when the Chromium content of the wet blue is equal to that of the conventional process. This method does not compromise the yield, physical mechanics, or esthetic properties of the leather, and the cost of this new process is lower than the conventional processes. This study provides an improved integrated method that is both technically and commercially viable to achieve cleaner pickling-chrome tanning, promoting the sustainable development of the leather industry.

Compliance with ethical standards

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Disclosure of conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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