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Effect of the Detoxification on the Shrinkage Temperature and pH of Chromium Leather Waste, Another Promising Way for the Tannery Pollution

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Abstract: The leather tannery industry produces a significant amount of solid chromium waste. Environmental concerns and escalating landfill costs are becoming increasingly serious problems to the leather industry and alternative disposal methods are needed. This research describes the possibility of decrease of the shrinkage temperature and to increase the pH value of leather waste by detoxification treatment with use of tartrate potassium. Through this investigation, we have established that is more possible to reduce the shrinkage temperature and neutralizing the acidity of this waste without his degradation or digestion and with decreasing of his chromium content about 95%. The use of reaction time of 72 h generates the optimal decreasing of the shrinkage temperature of waste leather about 42°C close to the one of hide at native state (before tanning process) which reveal another ecological and simple way for the treatment of the chromium containing leather waste.

Key words: Chromium, waste leather, pollution, decontamination, shrinkage temperature

INTRODUCTION

The production of chromium containing solid wastes in leather industry has been recognized as a real problem for many years[1,2]. Using chromium as basic chemical substance in the transformation of the hides and skins into leathers, the tanning process is one of the largest pollutants all over the world[3-5]. Leather industry creates a significant pollution problem due to the large amounts of toxic and inorganic pollutants as Cr(III). The chromium containing leather wastes largely consists of collagen cross linked with chromium[6]. Before tanning process the initial shrinkage temperature and the potential hydrogen value of hides is about respectively 40-45°C and pH ≈7-8[7,8], after tanning the shrinkage temperature increased until 100°C[8] and the pH value decrease of about 3,5-4[7,9-11]. The collagen-Cr (III) complexes produced is chemically stable[10,12] which offers to the waste a no biodegradable and toxic character[13] due to his chromium oxide Cr_2O_3 content about 4,4%[9,14] A large amount of this waste still goes into land disposal[15]. Their incineration generates other forms of pollution more noxious[16-19]. A recent pressure from environmental authorities has given the problem increasing urgency. Since three last decades, leather researchers have made a lot of effort to study the reuse of leather waste.

Several investigations developed some methods of treatment generally based on the previous alkaline hydrolysis of waste[9,20-25], acidic hydrolysis[26] or previous enzymatic hydrolysis[27-30], treatment with one and two-step using alkali and alkaline protease[10,14, 31-35] or with using two consecutive enzymes[36-38]. Unfortunately, most of these processes reported, bring about new residues during treatment such as the chrome cake (mixture of protein and chromium)[35]. Therefore, complicated multi-step chemical operations were used to purify the chrome cake for the chrome recovery[39,40]. These processes produce wastewater with salts and protein residues requiring further treatment which is very expensive. According to the criteria of clean technology processes, this present research consists on the research of an innovative method able to treat such solid tanned waste product as shavings, trimmings and splits. It based on the research of the reversibility of the tanning phenomenon which can decrease the shrinkage temperature and increase the pH value of waste towards their initial value before tanning process by removing of the chromium from the waste, without degradation or digestion of this latter. The influence of the use of potassium tartrate in alkaline medium on the shrinkage temperature and pH of waste leather was studied. Also the relationship between both factors shrinkage temperature and residual chromium content of waste was evaluated.

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MATERIALS AND METHODS

The solid chrome waste (chrome shavings and tanned splits) were collected from a commercial tannery located in great industrial of Algiers (TAMEG - Rouiba). In our experimental research we have used the chrome shavings for determination of the initial values of chromium oxide content (Cr_2O_3), shrinkage temperature and pH. These parameters were analysed using standard methods. For the chromium content the method as reported by O'Flaherty[41] was used. The shrinkage temperature and pH determination is obtained accordingly to the standard method [42].

Determination of the shrinkage temperature: Initial shrinkage temperature of chrome shavings specimens was determined as the following procedure: A series of 10 samples of waste (Initial size of 5 cm^2 each one) were inserted separately in water and gradually heated until bowling. The surface of pieces (size) was continuously measured at different temperature. Once the shrinkage beginning of the sample is observed we fixed the temperature using thermometer. This procedure is also used for determination of the final shrinkage temperature value of specimens after treatment.

Determination of the pH: The tests for the determination of the initial pH value were accomplished as the following way: 5 g of powder of chrome shavings sample was placed in 100 mL of distilled water at room temperature during two hours with agitation. After decantation without filtration of soluble matter (aqueous fraction) we proceed to the determination of the pH of the prepared liquor using the pH-meter. This procedure is also used for determination of the final pH value of specimens after treatment.

Analysis of chromium content: The initial chromium content of chrome shavings is determined. A series of 10 samples of dried shavings (5 g each one) is incinerated in a furnace at 775±25°C. Chromium determination from obtained ashes is performed chemically according to the official standard ALCA D10 method[41]. A mixture of $HClO_4$ (10 mL)/H_2SO_4 (15 mL) is used for oxidizing Cr (III) to Cr (VI) under boiling. This conversion was observed by colour change from green to orange. The chlorine is totally eliminated by boiling. The obtained solution treated with potassium iodide (KI, 50 g L^{-1}) causes the reduction of the hexavalent chromium. The iodine formed being titrated by the thiosulphate $Na_2S_2O_3$ 0.1 N according to the following reactions (Scheme 1), in presence of an indicator of starch powder. This procedure is also used for determination of the final residual chromium content of specimens after treatment.

$$Cr^{3+} + 2\,HClO_4 \longrightarrow Cr_2O_7^{2-} + Cl_2 + H_2O$$

$$Cr_2O_7^{2-} + 14\,H^+ + 6\,I^- \longrightarrow 2\,Cr^{3+} + 3\,I_2 + 7\,H_2O$$

$$I_2 + 2\,Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2\,NaI$$

Scheme 1: Mechanism of oxidizing and chromium III determination

Detoxification procedure with potassium tartrate: A series of 09 baths of detoxification of chrome shavings containing each one 100 mL water and tartrate potassium of 1N, sodium hydroxide (NaOH of 0,25N) and 5 g of chrome shaving sample were prepared. The treatment was carried out at room temperature with different reaction time. For each case of reaction time two samples were treated. At the end the samples were rinsed and dried. The first sample is employed for the final value of shrinkage temperature and pH determination. The second for the final residual chromium content determination.

RESULTS AND DISCUSSION

Shrinkage temperature before treatment: According to the results showed in Table 1 the majority of value obtained can range between 95 and 101°C. The medium value is about 98°C close to this given by the literature (100°C).

This shrinkage temperature value is due the chromium fixed between the collagen fibbers of skin.

Shrinkage temperature after treatment: The treatment of chrome shaving samples was carried out at room temperature with potassium tartrate of 1N in alkaline medium NaOH of 0,25 N. According to the results showed in Fig. 1 more the reaction time increase

Table 1: Initial shrinkage temperature of chrome shavings waste

Waste simples	Shrinkage Temperature(°C)	Medium value (°C)	Literature value (°C)
01	101		
02	98		
03	95		
04	100		
05	96	98	100
06	98		
07	98		
08	100		
09	97		
10	98		

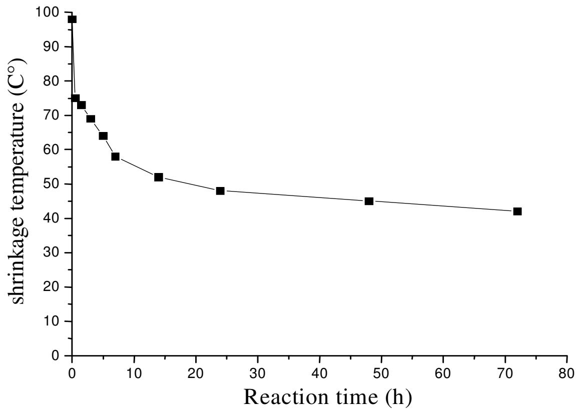


Fig.1: Shrinkage temperature variation according to the reaction time

Table 2: Initial pH value of leather waste samples.

Waste samples	pH value	Average pH value	Literature pH value
01	3.4		
02	3.8		
03	3.6		
04	3.5		
05	3.6	3.051	3.5 - 4
06	3.4		
07	3.7		
08	3.5		
09	3.3		
10	3.3		

and more the reduction of shrinkage temperature of waste samples is significant. Three steps were registered for the shrinkage temperature decreasing: At the end of the first reaction time he is noticeably decreased of about 75°C. Then, from the second to the fourth reaction time he decreased gradually until 58°C. Finally during the lasts reaction time (72 h) the shrinkage temperature is stabilised about 42°C. The finally value of shrinkage temperature obtained is more close to this given by the literature for skin before tanning process. We have unregistered that at the beginning of the treatment with different reaction time the baths are generally colourless but more the reaction time increase the colour of bath change to green more and more concentrated.

pH value of waste samples before treatment: A series of samples of chromium shavings were treated for determination of the initial value of pH accordingly to the procedure above noticed. According to the different result showed in Table 2 the initial pH value is included between 3, 3 and 3, 8. The average value obtained is about pH = 3, 51. This value of initial pH is very similar to those reported in the literature.

Table 3: pH value of waste leather samples after treatment during 72 h

Waste simples	pH value	Average pH value	Literature value of pH of skin before tanning process
01	8.6		
02	8.2		
03	8.4		
04	7.9		
05	7.6	8.1	7 - 8
06	7.4		
07	8.8		
08	8.1		
09	8.9		
10	7.2		

Table 4: Initial chromium content of leather waste samples

Waste samples	Initial Chrome content (%)	Average content (%)	Literature chromiu content (%)
01	3.32		
02	3.66		
03	3.65		
04	4.25		
05	4.10	4	4.30
06	4.33		
07	4.17		
08	4.28		
09	4.28		
10	3.80		

Variation of pH of samples after treatment: For the determination of the final value of pH the chrome shavings sample was treated with a reaction time of 72 h which have allowed us the reduction of the shrinkage temperature of leather waste samples until 42°C. A series of 10 specimens of chrome shavings were treated separately with tartrate potassium of 1N in alkaline medium NaOH of 0.25 N under room temperature and during 72 h. In Table 3 are showed the different final value of pH of chrome shavings after detoxification. Generally the pH values obtained can range between pH = 7.2 and pH = 8.9. The average value is about pH = 8.1. Comparatively to the pH of skin before tanning process (pH = 7-8), the pH obtained after detoxification of waste is weakly superior due to the alkaline medium used. Moreover this alkalinity has not digested or degraded the solid collageneous after decontamination.

Initial chromium contain in leather waste: After the experimental procedure above noticed, the initial chromium content of each samples of chrome shavings is shown in Table 4. The different value obtained can range from 3to 4.25%. The average value about 4% of chromic acid (Cr_2O_3) close to this given by the literature is significant and able to provoke serious environmental problems taking in account the enormous quantities of rejected waste.

Table 5: Chromium residual content according to the reaction time

Potassium tartrat (N)	Alkaline concentration (N)	Reaction time (h)	Residual chromium content (%)
		0	4[a] (100)[b]
		0.5	1.73 (43.25)
		1.5	1.65 (41.25)
		3	1.56 (39)
1	0.25	5	1.44 (36)
		7	1.26 (31.5)
		14	0.8 (20)
		24	0.53 (13.25)
		48	0.27 (6.75)
		72	0.20 (5)

[a]Residual chromium content (%), [b]Percentage of residual chromium content (%).

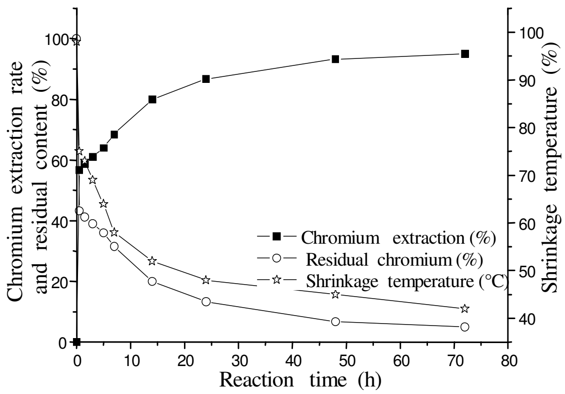
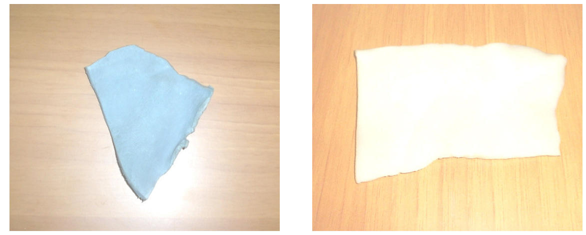


Fig. 2: Residual content and extraction rates of chromium according to the shrinkage temperature variation

Variation of the residual chromium content after treatment with different reaction time: The rates of residual chromium content in waste samples after treatment decrease with increasing of the reaction time (Table 5).

With increasing of reaction time the residual chromium content is reduced according to three principal steps (Fig. 2): The first step is produced during the reaction time of about ½ h where the residual chromium content is considerably reduced until 1.73%. The second step is characterised by a slow decreasing of chromium content from 1.73% to about 1.26%. Finally during the last step the residual chromium content is decreased for about 0.2%. We conclude that the detoxification phenomenon is more and more favoured with the increasing of reaction time. Correlation between shrinkage temperatures decreasing and residual chromium content: According to the results obtained through different experiments it is clear that more the reaction time increased more the shrinkage temperature of waste leather samples



a b

Fig. 3: Sample of leather shavings. (a): Before treatment process. (b): After treatment process

a b

Fig. 4: Sample of leather splits. (a): Before treatment process. (b): After treatment process

decreased (Fig 1). Simultaneously we observed that the decreasing of shrinkage temperature is accompanied with the decreasing of the residual chromium content (Table 5, Fig 2). About 95% of initial chromium content is extracted from the leather waste samples. Consequently the initial blue coloration of the waste samples due to the chromium fixed is increasingly changed towards white coloration due to the phenomenon of detoxification.

In Fig. 3a-b is presented the transformation of the chrome shavings before treatment (Fig. 3a) into white collageneous solid after treatment (Fig. 3b).

After treatment of the chrome shavings accordingly to the following conditions: Potassium tartrate (1N) in alkaline medium NaOH (0,25) under room temperature and during 72 h of reaction time the optimal value of detoxification of the waste obtained is about 95%. This formula of treatment is experimented for the treatment of other case of waste leather. For this the tanned splits waste is treated and the result obtained is very interesting. The rate of the chromium detoxification is in the same importance order (95%). On the Fig. 4a-b is presented the transfo-rmation realized where the initial tanned splits with blue coloration before treatment (Fig. 4a) is changed into white splits after treatment of detoxification (Fig. 4b).

CONCLUSION

The paper reports on the results of an investigation aimed to evaluate the influence of the decontamination by use of tartrate potassium in alkaline medium on the final values of shrinkage temperature, pH and residual chromium content of the waste leather after treatment. For the present study the environmental impact is the principal purpose fixed.

In the first stage, we have determined the initial value of chromium content, pH and shrinkage temperature of waste chrome shavings. Then in the second stage, we have studied the behaviour of the shrinkage temperature of this waste with the increasing of the reaction time of the decontamination process. Simultaneously the pH variation of the chrome shavings after 72 hours of treatment was determined. Also the variation of residual chromium content of chrome shavings with increasing reaction time was evaluated.

According to the experimental results, the waste treatment with the following conditions: Ambient temperature, 72 hours, tartrat (1N), NaOH (0.25N) allowed us the decreasing of the shrinkage temperature of about 42 °C, the increasing of the pH of about 8-9 and the reduction of the residual chromium content from 4% until 0,2%. The colour of decontaminated waste leather is very white (confirmation of removal of chromium). After several tests in similar experimental conditions the repeatability of the results was confirmed. The shrinkage temperature and pH value obtained after treatment during 72 hours were close to the one of skin before tanning process (at native state). These results have significantly revealed the possible reversibility of the mechanism of fixing of chromium to collagen during the tanning process. This hypothesis can be supported by the physics and mechanics properties of waste leather such as his stretching resistance which is unregistered as a preserved character after decontamination. For this we can conclude that the procedure of treatment with tartrate in alkaline medium is very promising and can constitute a novel treatment process for the decontamination of solid tanned leather. Considering the enormous quantities of waste rejected from the tannery industry, the economic and environmental impact of this new way of treatment is considerable. It can allow us firstly to extract chromium about 95% from waste leather and his recycling in tanning process, secondly the totally and easily recovery of the collagen of solid decontaminated and his valorisation in several fields. Comparatively to the others treatments process of this waste reported by numerous authors during the last two decades which are generally complicated, our treatment procedure is simple, non-polluting and likely to ensure a durable environment for this activity. However, our investigation still continues and is oriented towards several objectives such as: The complementary and detailed study on the physics and chemicals properties of the white collagenous solid obtained after decontamination, the study for the understanding and the conception of the possible chemical mechanism of decontamination. Moreover, the development of additional procedures allowing the purification of the decontaminated collagenous solid and its valorization as well as the treatment of the baths of decontamination to recycle chromium in tanning process.

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