



# New approach of depollution of solid chromium leather waste by the use of organic chelates Economical and environmental impacts

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## ABSTRACT

Herein, we describe an original novel method which allows the decontamination of the chromium-containing leather wastes to simplify the recovery of its considerable protein fractions. Organic salts and acids such as potassium oxalate, potassium tartrate, acetic and citric acids were tested for their efficiency to separate the chromium from the leather waste. Our investigation is based on the research of the total reversibility of the tanning process, in order to decontaminate the waste without its previous degradation or digestion. The effect of several influential parameters on the treatment process was also studied. Therefore, the action of chemical agents used in decontamination process seems very interesting. The optimal yield of chromium extraction about 95% is obtained. The aim of the present study is to define a preliminary processing of solid leather waste with two main impacts: Removing with reusing chromium in the tanning process with simple, ecological and economic treatment process and potential valorization of the organic matrix of waste decontaminated.

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## 1. Introduction

Economical and ecological concepts are nowadays part of everyone's preoccupations and will still be in the future. In our country, the production of chromium containing leather wastes (including chrome shavings and tanned splits) in leather industry has been recognized as a real problem for many years [1]. Using chromium basic salts which contain about 25% of  $\text{Cr}_2\text{O}_3$  at 33° S of basicity as basic chemical substance in the transformation of the hides and skins into leathers made the tanning process one of the largest pollutants all over the world [2–5]. The chromium leather wastes are generated principally during mechanical treatments carried out after tanning process. In this latter, chromium is bound with the collagen matrix, by cross linking with collagen carboxylic groups through coordinate covalent linkage [6–10]. The final chemical structure of the waste illustrated in Eq. (1), is obtained through two chemical phenomena “olation and oxolation”. As reported by numerous authors [6–12], the ololation phenomenon is observed gradually with the increase of the alkalinity of the tanning medium. The ololated complex continues its evolution through time and an acid discharge takes place while the oxygen-chrome coordinate links are transformed into covalent links (oxolation bridges) Eq. (2).

The great stability of the collagen–chromium complex produced makes the waste a non-biodegradable and toxic material, due to the chromium and nitrogen content about 4.3% and 14%, respectively [13,14]. A large amount of waste still goes into land disposal [15]. Incineration in air atmosphere generates other forms of residual pollutant (gaseous emission and ashes) more noxious [16–21]. A recent pressure from environmental authorities has increased urgency and obliged the leather industry to develop cleaner technology by minimizing generated wastes and to find a practical solution to the disposal of potentially noxious waste. Since last three decades, several leather researchers have tried to improve the valorization of leather waste. They developed some methods of waste treatment for recovery and isolation of protein fraction, generally based on the previous alkaline hydrolysis of waste using CaO, MgO, NaOH [13,15,22–28], acidic hydrolysis [29] or enzymatic hydrolysis [14,22,30–40]. Unfortunately, most of these processes reported bring about new residues during treatment such as the chrome cake (mixture of chromium and protein). Therefore, complicated multi-step chemical operations were used to purify the chrome cake to the chrome recovery [37,41,42]. Some other studies related to the valorization of chromium waste leather have been made. The chromium recovery conditions in the form of soluble chromate from the chrome shavings by air oxidation, oxygen and  $\text{Na}_2\text{O}_2$  were investigated [43]. The chrome tanned leather shavings were used after multi-step disintegration, to prepare a powder, as filler of butadiene-acrylonitrile rubber [44]. Used at raw state, the

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solid leather wastes were also studied for their ability to remove oils, oily wastes and hydrocarbons from contaminated water [45]. The ash of chromium leather shavings has constituted the subject of several researches. In this field, materials prepared with alumina and ashes of chrome tanned shavings were reported [46]. The effect of the incorporation of the chromium leather shavings ash in the Portland cement clinker process on the properties of clinkers was studied [47]. It is important to indicate that the chromium recovery from solid leather waste based on the incineration method can cause enormous environmental problems because of the gaseous pollutant generated. Moreover, the concept of recycling is above all, a procedure allowing the assurance of the sustained development. Actually, it can be stated that waste management is the most important issue for Algerian leather industry. In this latter, generally, 1 ton of wet salted hide yields 400 kg of solid chromium wastes (40% of the initial hide weight) due to the bad quality of the raw material. In the absence of adequate solution, these enormous quantities of waste represent a real problem able to threaten the continuity of this activity. Applying the criteria of “clean technology processes”, this present work contributes to help the Algerian leather industry in the development of alternatives to land disposal (or storage inside the production unit) for solid tannery waste. In the literature, it has been reported that the adding of masking agents as mono and/or polycarboxylic (organic chelates) in chromium tanning bath provides optimum fixation of chrome to skin and allows the best tanning results. This phenomenon is explained by the strong aptitude of these masking agents to react with chromium by their carboxylic reagent groups. However, the stability of the chrome–chelate complex formed depends of the organic radical used. As reported, the masking activity of these chelates on the chrome during tanning process can prevent in some conditions, the fixation of the chromium to the skin [6–10]. In the present work, we showed the organic chelates efficiency to decontaminate the solid leather waste. In the light of this fact, potassium oxalate, potassium tartrate, acetic and citric acids were tested. The aim of the present study is to define a preliminary processing of leather waste with two main impacts: Removing with reusing chromium in the tanning process with simple, ecological and economic treatment process and potential valorization of the collagen matrix.

## 2. Materials and methods

### 2.1. Chromium leather wastes and chemicals

The solid leather waste (chrome shavings and splits), technically called “wet blue”, was collected from a commercial tannery located in great industrial area of Algiers (TAMEG–Rouiba). The samples were kept at room temperature. All the chemicals agents used in the experimentation were laboratory grade chemicals, and supplied by Merck KGaA Darmstadt Germany (VWR International SAS France).

### 2.2. Determination of the initial chromium content of leather waste

Firstly, the initial chromium content of waste is determined. A series of 10 samples of dried leather waste shavings (5 g each one) is incinerated in a furnace at  $600 \pm 25^\circ\text{C}$ . Chromium determination from obtained ashes is performed chemically according to the official standard ALCA D10 method of the American Leather Chemists Association [48]. A concentrated mixture of  $\text{HClO}_4$  (10 mL)/ $\text{H}_2\text{SO}_4$  (15 mL) is used for oxidizing Cr (III) to Cr (VI) under boiling. This conversion was observed by color change from green to orange. The chlorine is totally eliminated by boiling (a negative test when potassium iodide paper is held in the vapor indicates the absence of chlorine). The obtained solution treated with 10 mL of potassium

iodide (10%) causes the reduction of the hexavalent chromium. The iodine formed being titrated by the sodium thiosulfate solution  $\text{Na}_2\text{S}_2\text{O}_3$  (0.1 N) in presence of starch powder as an indicator Eq. (3).

The chromium content was determined by the following expression:

$$\text{Chromium oxide content (\%)} = \frac{(A \times N \times 0.02533 \times 100)}{W}$$

where  $A$  is the milliliters of titrating reagent used,  $N$ , the normality of the titrating reagent,  $W$  is the weight of the specimen in grams and 0.02533 is the standard quantity in grams of  $\text{Cr}_2\text{O}_3$  titrated by one milliliter of  $\text{Na}_2\text{S}_2\text{O}_3$  (0.1 N).

### 2.3. Treatment procedures of chromium leather waste

Organic salts and acids as potassium oxalate, potassium tartrate, citric and acetic acids have been tested for their capacities to extract the chromium from the organic matrix of leather waste. This ability is determined by the chromium amount extracted with each organic chelate. The present experiment series is carried out with 5 g dried leather waste samples shaken with 100 mL of distilled water. The chemicals were used with a concentration of 2 N. Waste samples have been treated according to two distinct procedures:

#### 2.3.1. Procedure 1

The treatment was done in a one step process under neutral pH and room temperature for 72 h of contact time.

#### 2.3.2. Procedure 2

The second procedure consists of two-step experiments: The first step is similar to the first procedure. During the second step, the waste samples have been treated in three baths containing each one 100 mL of distilled water with different mediums: Acidic ( $\text{H}_2\text{SO}_4$  0.5 M), alkaline (NaOH 0.5 M) and neutral (distilled water), for 30 min of contact time and under room temperature. At the end of each procedure, the samples are rinsed, dried then incinerated for the determination of chromium extraction yield and residual chromium content in ashes produced. Firstly, these procedures allow to define the best organic chelates which present the high chromium removal efficiency and secondly, the favourable treatment medium.

### 2.4. Effect of several influential parameters on chromium removal

After the determination of the efficient organic chelate and the favourable medium, most effective parameters having a significant effect on chromium extraction yield, like concentration of chemicals, bath temperature and the reaction time, were investigated.

## 3. Results and discussion

### 3.1. Initial chromium content in leather waste

A series of 10 samples of dried shavings (5 g each one) is incinerated. Firstly, the initial chromium content of waste is determined. Chromium determination from obtained ashes is performed chemically according to the official standard ALCA D10 mentioned above.

Initial chromium content of experimented waste samples can range from 4.15% to 4.33% (Table 1). The average value about 4.23% of chromic acid ( $\text{Cr}_2\text{O}_3$ ) close to that given in the literature, i.e., 4.30% [13,14] can be considered as the initial chromium content for all the following experimental parts.

**Table 1**  
Initial chromium content of leather waste samples.

Samples	Initial chromium content (%)	Average content (%)	Literature chromium content (%)
01	4.15		
02	4.22		
03	4.19		
04	4.25		
05	4.27	4.23	4.3
06	4.33		
07	4.17		
08	4.28		
09	4.28		
10	4.21		

**Table 2**  
Chromium extraction yields after treatment according to procedure 1.

Chemical agents	Initial chromium content (%)	Residual chromium content (%)	Chromium extraction yields (%)
K <sub>2</sub> C <sub>2</sub> O <sub>4</sub>		1.40 <sup>a</sup>	2.83 <sup>a</sup> 66.9 <sup>b</sup>
CH <sub>3</sub> COOH		1.83	2.40 56.7
K <sub>2</sub> C <sub>4</sub> H <sub>4</sub> O <sub>6</sub>	4.23	1.28	2.95 69.7
H <sub>3</sub> C <sub>6</sub> H <sub>5</sub> O <sub>7</sub>		1.73	2.50 59.1

<sup>a</sup> In relation to the initial chromium content (4.23%).

<sup>b</sup> Percentage of chromium extraction (%).

### 3.2. Chromium removal with procedure 1

The chromium extraction efficiency is dependent on the organic chelate used. Through the obtained results, we noticed that the effect of organic salts on the chromium extraction yield was more important than that of organic acids. The presence of alkaline medium in the first case, can constitute a good explanation (formation of strong interaction between the carboxylic groups of the different chelates and chromium). In the second case, the acidic medium is unfavourable and can inhibit the reaction. Among the different chelates tested, tartrate gives the best results about 69.7% of chromium extraction yield (Table 2). It seems to be the extractant of choice for the chrome–collagen separation. Nevertheless, taking into account the importance of the residual chromium content after treatment, the extraction efficiency remains insufficient for all chemicals tested.

### 3.3. Treatment according to procedure 2

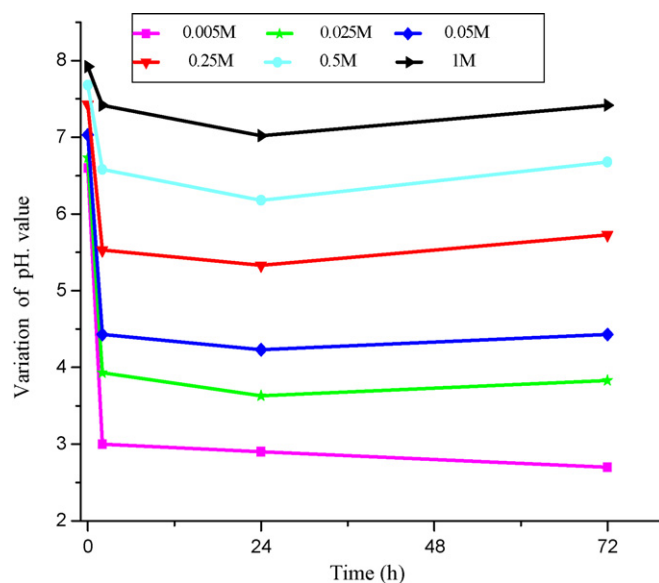
The most interesting results were observed with all chemicals tested in alkaline medium. A chromium extraction yield of almost 94.3% is obtained with potassium tartrate (Table 3). Generally, after treatment in basic medium, the residual chromium content obtained in each case is strongly reduced towards the range 0.24–1.1% (Table 4). On the other hand, neutral and acidic medium significantly affected the extraction efficiency, and a great amount of residual chromium content still remains in waste samples. According to the obtained results from both procedures, we can conclude that alkaline medium is the most favourable way

**Table 3**  
Chromium extraction yields after step 2 of treatment according to procedure 2.

Chemical agents	Chromium extraction yields (%)					
	Neutral medium (H <sub>2</sub> O)		Acidic medium (H <sub>2</sub> SO <sub>4</sub> )		Alkaline medium (NaOH)	
K <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	2.95 <sup>a</sup>	(69.7) <sup>b</sup>	2.87 <sup>a</sup>	(67.8) <sup>b</sup>	3.78 <sup>a</sup>	(89.3) <sup>b</sup>
CH <sub>3</sub> COOH	2.44	(57.6)	2.43	(57.4)	3.13	(73.9)
K <sub>2</sub> C <sub>4</sub> H <sub>4</sub> O <sub>6</sub>	3.04	(71.8)	2.97	(70.2)	3.99	(94.3)
H <sub>3</sub> C <sub>6</sub> H <sub>5</sub> O <sub>7</sub>	2.58	(60.9)	2.53	(59.8)	3.38	(79.9)

<sup>a</sup> Extraction yields in relation to the initial chromium content (4.23%).

<sup>b</sup> Percentage of chromium extraction (%).



**Fig. 1.** pH behaviour during chromium removal in neutral medium with different concentrations of tartrate.

and potassium tartrate is the most efficient medium for chromium extraction.

### 3.4. Study of influential parameters on chromium removal

On the basis of the obtained results, effects of potassium tartrate, alkali concentrations, pH, bath temperature and reaction time were investigated.

#### 3.4.1. Effect of potassium tartrate concentration

The treatment of 5 g dried leather waste samples was carried out at neutral pH, under room temperature for 72 h. Several baths of chromium removal containing each one 100 mL of distilled water and potassium tartrate with various concentrations 0.005 M, 0.025 M, 0.05 M, 0.25 M, 0.5 M and 1 M were prepared. The pH of baths has been recorded at different periods of treatment. At the end, the samples were rinsed, dried and then incinerated. The chromium extraction yields determination from obtained ashes of each sample, was performed chemically according to the official method ALCA D10 mentioned above.

We can notice that final pH of the various baths decreased with the weak concentrations of tartrate. With the increasing tartrate concentration, final pH is stabilized and close to its initial value (Fig. 1). The progressive pH stability exhibits a significant increasing of chromium extraction yields (Table 5). The most important values of 65.4% and 69.7% were recorded respectively for a potassium tartrate concentration of 0.5 M and 1 M. The residual chromium content obtained with tartrate 0.5 M and 1 M was almost in the same order of significance. Consequently, in the following experi-

**Table 4**  
Residual chromium content after step 2 of treatment according to procedure 2.

Chemical agents	Residual chromium content (%) <sup>a</sup>			
	After step 1	After step 2		
		Neutral medium	Acidic medium	Alkaline medium
K <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	1.40	1.28	1.36	0.45
CH <sub>3</sub> COOH	1.82	1.79	1.80	1.1
K <sub>2</sub> C <sub>4</sub> H <sub>4</sub> O <sub>6</sub>	1.28	1.19	1.26	0.24
H <sub>3</sub> C <sub>6</sub> H <sub>5</sub> O <sub>7</sub>	1.73	1.65	1.7	0.85

<sup>a</sup> In relation to the initial chromium content (4.23%).

**Table 5**  
Chromium extraction yields according to the tartrate concentration.

Tartrate concentration (M)	Residual chromium content (%)	Chromium extraction yields (%)
0.005	3.45 <sup>a</sup>	18.4 <sup>b</sup>
0.025	3.22	23.8
0.05	2.71	35.9
0.25	2.17	48.6
0.5	1.46	65.4
1	1.28	69.7

<sup>a</sup> In relation to the initial chromium content (4.23%).

<sup>b</sup> Percentage of chromium removal (%).

mental part, the potassium tartrate concentration of 0.5 M will be adopted.

### 3.4.2. Effect of the alkali concentration

The samples of 5 g dried waste leather were treated in different extraction baths constituted of 100 mL of distilled water, potassium tartrate 0.5 M and various alkali (NaOH) concentrations: 0.01 M, 0.05 M, 0.1 M, 0.25 M, 0.5 M and 1 M. The experimentation was carried out at room temperature during 72 h of reaction time. During the treatment, the initial and final pH values of baths were recorded. In parallel, some pilot tests of treatment with various concentrations of NaOH 0.1 M, 0.25 M, 0.5 M, 1 M and 5 M, in absence of potassium tartrate, in similar conditions as previously were done. At the end of experimentation, the samples were rinsed, dried and then incinerated. The chromium extraction yields determination was carried out according to the official method. During treatment, a significant decrease of initial pH value of baths is observed with weak concentrations of alkali (Table 6). Consequently, weak yields of chromium extraction were observed. On account of the progressive alkali concentration increase, the initial pH of the baths tends to be increasingly stabilized and chromium extraction efficiency follows this tendency.

A maximum of chromium extraction yields about 95.2% was obtained with potassium tartrate 0.5 M in the presence of NaOH 0.25 M. At higher alkali concentrations 0.5 M and more, samples degradation was recorded. In the case of pilot tests, the chromium extraction yields were insignificant for lower concentrations of alkali due to the slight hydrolysis of chromium complexes. Otherwise, with higher concentrations of alkali, a total degradation of

waste was observed, due principally to the strong hydrolysis action of the hydroxyl groups (OH<sup>-</sup>) on chromium complexes and collagen.

It appears clearly that potassium tartrate plays an important role in the chromium extraction. Its reaction with this latter allows the hydrolysis limitation by the groups OH<sup>-</sup> (competitive reactions) and the reduction of the ability of the chromium complexes lately formed to condense inside waste. Moreover, it promotes the formation of new more stable chromium complexes, in the light of this fact, the desorption in the baths is much easier, and the chromium extraction efficiency is more important.

### 3.4.3. Effect of bath temperature and reaction time

Potassium tartrate (0.5 M) in alkaline medium (NaOH 0.25 M) has been investigated. The influence of the temperature and the reaction time on the chromium extraction, were studied simultaneously. The fixing of reaction time and the variation of the baths temperature, have been respected. We have constituted 9 baths of extraction divided into three groups of three samples each one. These latter were treated at various reaction time 30 min, 90 min, and 180 min. For each reaction time, progressive temperatures of bath extraction 25 °C, 30 °C and 40 °C have been experimented. At the end of the treatment, the samples were rinsed, dried and incinerated. The chromium extraction yields determination from obtained ashes, was carried out according to the official method.

The recorded results show that the temperature and reaction time are both parameters having a significant effect on the chromium extraction efficiency. Nevertheless, this latter seems to be more promoted by increasing in temperature (Table 7). The best result of chromium extraction yield of about 95.7% was observed with a temperature of 40 °C and 90 min as reaction time. The fixing temperature value with the variation of the reaction time caused a lower decreasing of residual chromium rate, however this latter is considerably reduced with both fixing reaction time and bath temperature variation. During the decontamination process, the progressive extraction of chromium causes the decreasing of the shrinkage temperature value of waste. At higher bath temperature and reaction time of about respectively 40 °C and 180 min, a waste degradation was observed.

### 3.4.4. Probable mechanism of chromium removal

During the tanning process, chromium fixation into skin is obtained according to several simultaneous chemical reactions,

**Table 6**  
Chromium extraction yields according to the alkali concentration.

Tartrate concentration (M)	Alkali concentration (M)	Initial pH	Final pH	Residual chromium content (%)	Chromium extraction yields (%)
0.5	0.01	11.3	6.1	2.26 <sup>a</sup>	46.5 <sup>b</sup>
	0.05	11.6	7.5	1.92	54.6
	0.1	11.8	8	0.86	79.6
	0.25	12	9.8	0.2	95.2
	0.5	12.3	11.2	Degradation	Degradation
	1	12.5	11.6	–	–

<sup>a</sup> In relation to the initial chromium content (4.23%).

<sup>b</sup> Percentage of chromium removal (%).



**Table 7**  
Influence of the baths temperature and reaction time on the chromium extraction yields.

Concentration of tartrate (M)	Concentration of alkali (M)	Reaction time (min)	Bath temperature (°C)	Residual chromium content (%)	Chromium extraction yields (%)
0.5	0.25	30	25	1.73 <sup>a</sup>	59.1 <sup>b</sup>
		30	30	1.01	76.1
		30	40	0.76	82
		90	25	1.65	60.9
		90	30	0.64	84.8
		90	40	0.18	95.7
		180	25	1.56	63.1
		180	30	0.26	93.8
		180	40	Degradation	Degradation

<sup>a</sup> In relation to the initial chromium content (4.23%).

<sup>b</sup> Percentage of chromium extraction (%).

such as reported by numerous authors Eqs. (1) and (2) [6–12], which cause on the one hand stable chemical bonds between chromium atoms through oxygen bridges, due to the phenomenon of oxolation and oxolation and on the other hand, a stable chemical bond between chromium atom and carboxylic groups of collagen. In the decontamination process, these two kinds of bonds must be destabilized through successive chemical reactions which cause their breaking (rupture of Cr–Cr and Cr–Collagen bonds). These ruptures are better promoted in alkaline medium than in other mediums. The chemical process which can be involved in this treatment may be explained by the following approach with two steps: The first step is based on the rupture of the chrome-collagen bonds of the chemical structure of waste Eq. (1), according to the following pathway: Substitution reaction (exchange) of one water molecule (aqua group) surrounding the first chromium atom by ionised carboxylic group of tartrate, with the breaking of the first chromium–collagen bond for restoring the chromium coordination (see A in Eq. (4)). The second step consists of an attack of ionized carboxylic groups of tartrate on the second chromium atom. The break of the bond between collagen and the second chromium atom is obtained according to the same way (see B in Eq. (5)). The chromium complexes separated from collagen matrix of waste are obtained in the form (C) presented in Eq. (6). The oxygen bridges between chromium atoms are very stable as reported in the literature [6–12]; therefore their rupture may be obtained by the protonation of the oxygen atom of oxo bridges by the aqua ligand (H<sub>2</sub>O).

This phenomenon can cause the weakness and rupture of the two oxo bridges around the chromium atoms and promotes a second attack of ionized carboxylic groups of another tartrate chelate. The likely final form of the chromium complexes separated from the waste is presented in Eq. (7) (form D). Among several chromium complexes formed in the bath during decontamination process, two probable forms (1) and (2) could be admitted (Fig. 2), where the first structure is more stable. Its stability is due to the limitation of the

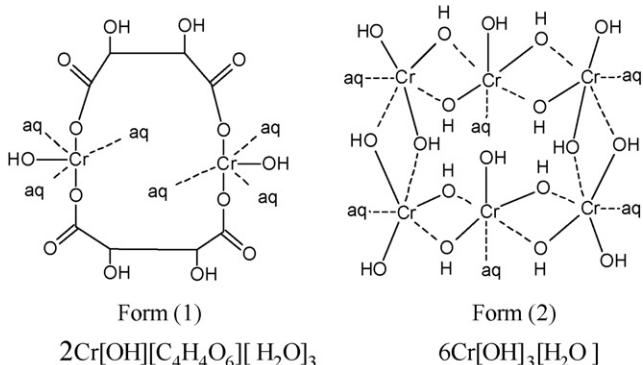
number of the hydroxyl groups (OH<sup>-</sup>) surrounding the chromium atoms, by tartrate chelate which prevent its condensation inside the protein sample and promotes its extraction (NaOH 0.25 M). It is not the case for the structure (2) where the protein samples degradation is observed, due to the flocculation phenomenon, consequently to the fixation of a more significant number of the hydroxyl groups OH<sup>-</sup> to the chromium atoms (NaOH > 0.5 M).

#### 4. Conclusions

Through the present work, we have developed a new approach to help the Algerian leather industry in solving the potentially difficult relative to the solid leather waste problems. This paper reports the results of an investigation aimed to evaluate the performances of an innovative tannery solid leather waste process. It is based on the use of organic chelates as decontamination agents. We could demonstrate the feasibility of using chemical substance as part of a process to isolate chromium from the organic matrix of leather waste. In the first step, it appears clearly that the most efficient chromium extraction occurs in alkaline medium. Various chemical agents were compared in this medium and potassium tartrate was found to be the most important extractant agent. In the second step, we have studied appropriate parameters likely to affect chromium extraction yield. According to the experimental results, the improving of chromium extraction yield of about 95% from the waste treatment is obtained with the following operating conditions: potassium tartrate 0.5 M, alkali (NaOH) 0.25 M, room temperature and 72 h of contact time. The repeatability was confirmed after several tests under similar experimental conditions. The temperature plays an important role in reducing the length of time of the chromium extraction process.

During the treatment process, the initial chromium content of leather waste sample of about 4.3% was reduced towards about 0.2%. The color of decontaminated product obtained is very white and almost devoid of residual chromium. The decontamination procedure with tartrate in alkaline medium is very promising and can constitute an original new treatment process. It is easy in the absence of complicated multi-steps of treatment, non-polluting (absence of incineration), economic by the less use of energy and allow a good recovery of the waste leather parts, likely to ensure a sustainable development for this activity.

Considering the enormous quantities of generated leather waste, the impacts of this way of treatment is considerable. It is clear that it will enable us to put an end to the multiform pollution (incineration process being very noxious), but this study is a possible alternative to the storage inside the production unit or to land disposal. Nevertheless, our investigation still continues and will be oriented towards several objectives, such as the development of additional procedures allowing the optimization of the treatment procedure and then, the purification of decontaminated



**Fig. 2.** Structure of chromium complexes produced during waste leather treatment.



## References

- [1] L.F. Cabeza, A.J. Mcaloon, W.C. Yee, et al., Process simulation and cost estimation of treatment of chromium-containing leather waste, *J. Am. Leath. Chem. Assoc.* 93 (12) (1998) 2990–3135.
- [2] A. Vulliermet, M.C. Carre, *Tannery and Environment*, Technical Center of Leather, CTC, Lyon, France, 1983.
- [3] V. Van der Bossche, G. Gavend, M.J. Brun, *Chromium Tanned Leather and its Environmental Impact*, International Chromium Development Association, CTC, Lyon, France, 1997.
- [4] F.B. Stern, J.J. Beaumont, W.E. Halperin, L.I. Murthy, B.W. Hills, J.M. Fajen, Mortality of chrome leather tannery workers and chemical exposures in tannery, *Scand. J. Work. Environ. Health* 13 (1987) 108–117.
- [5] E. Heidemann, Disposal land recycling of chrome-tanned materials, *J. Am. Leath. Chem. Assoc.* 86 (9) (1991) 331–333.
- [6] I. Jullien, *Chromium Tanning*, Technical Center of leather, Lyon, France, 1981.
- [7] R. Martinetti, *Theory of Chromium Tanning*, *Industry of Leather Review*, 5, IDC, France, 1995.
- [8] E. Robert, *Physical Chemistry of Leather Making*, Chap, Collagen Tanning, Original English ed., Krieger Publishing Company, Malabar, Florida, 1983, pp. 308–354.
- [9] T.C. Thorstensen, *Practical Leather Technology*, Chap: Chrome Tanning, Fourth ed., Krieger Publishing Company, Malabar, Florida, 1993, pp. 118–133.
- [10] S.G. Shuttleworth, *The Chemistry and Technology of Leather*, vol. II, Types of Tannages, the Mechanism of Chrome Tannage, Tanner's Council Laboratory, Krieger Publishing Company, Malabar, Florida, 1978, pp. (554) 281–322.
- [11] J.P. Jolivet, M. Henry, J. Livage, *Aqueous Chemistry of Metal Cation, Hydrolysis, Condensation and Complexation, Structure and Banding*, Springer-Verlag, Berlin, 1992, pp. 153–206.
- [12] J.P. Jolivet, *De la solution à l'oxyde, Condensation des cations en solution aqueuse* Inter ed, CNRS, Paris, 1994.
- [13] S. Tahiri, M. Bouhria, A. Albizane, A. Messaoudi, M. Azzi, S.Y. Alami, J. Mabrou, Extraction of proteins from chrome shavings with sodium hydroxide and reuse of chromium in the tanning process, *J. Am. Leath. Chem. Assoc. (JALCA)* 99 (2004) 16–25.
- [14] M.M. Taylor, E.J. Diefendorf, C.J. Thompson, E.M. Brown, W.N. Marmer, L.F. Cabeza, Extraction of value added byproducts from the treatment of chromium containing collagenous leather industry waste, *J. Soc. Leath. Technol. Chem.* 81 (1) (1997) 5–13.
- [15] M. Brown, M.M. Taylor, W.N. Marmer, Production and potential uses of co-products from solid tannery waste, *J. Am. Leath. Chem. Assoc.* 91 (10) (1996) 270–276.
- [16] Z.R. Zahid, Z.S. Al-Hakkak, A.H.H. Kadhim, E.A. Elias, I.S. Al-Jumaily, Comparative effect of trivalent and hexavalent chromium on spermatogenesis of the mouse, *Toxicol. Env. Chem.* 25 (1989) 131–136.
- [17] E.T. Oppelt, C.R. Dempsey, *Incineration of hazardous waste: a critical review update*, *Air Waste* 43 (1993) 25–73.
- [18] E.T. Oppelt, *Air emission from the incineration of hazardous waste*, *Toxicol. Indust. Health* 6 (5) (1990) 23–31.
- [19] P.I. Williams, *A review of pollution from waste incineration*, *J. Institute Water Environ. Manag.* 4 (1) (1990) 26–34.
- [20] N. Andre, O. Paut, J. Arditti, P. Fabre, V. Bremond, T. Alhmana, J.F. Bellus, J. Jouglard, J. Camboulives, Severe potassium dichromate poisoning after accidental nasal introduction, *Arch. Pediat.* 145 (1998), pp. 8–5.
- [21] P. Gikas, P. Romanos, Effect of trivalent (Cr(III)) and hexa-valent (Cr(VI)) chromium on the growth of activated sludge, *J. Hazard. Mater.* B133 (2006) 212–217.
- [22] C.D. Mu, W. Lin, M.R. Zhang, Q. Zhu, Towards zero discharge of chromium-containing leather waste through improved alkali hydrolysis, *Waste Manag* 23 (2003) 835–843.
- [23] G. Guardini, *Extraction of proteins and chromium sulphate from chromium-tanned skin waste*, US Patent 4,483, 829 (1983).
- [24] D.F. Holloway, *Recovery and separation of nutritious proteins hydrolysates and chromium from chrome leather scrap*, US Patent 4,100,154 (1978).
- [25] A. Galatik, J. Duda, L. Minarik, *Pressure hydrolysis of leather waste with sodium hydroxide*, Czech Patent CS 252, 382 (1988).
- [26] M.S. Maire, V.A. Lipsett, *Offal enhancement*, *J. Am. Leath. Chem. Assoc.* 75 (1) (1980) 16–33.
- [27] S. Tahiri, M. Azzi, A. Albizane, A. Messaoudi, M. Bouhria, Y.S. Alami, A. Mourid, J. Amrhar, Study of quality of a pigment prepared by complexation of chromates recovered from treated chrome shavings and tanned splits, *J. Am. Leath. Chem. Assoc.* 96 (2001) 426–436.
- [28] F.J. Berry, N. Constantini, L.E. Smart, *Synthesis of chromium-containing pigment from chromium recovered from leather waste*, *Waste Manag.* 22 (2002) 761–772.
- [29] L. Wojciech, G. Mieczyslaw, M. Urszula, et al., *Leather treatment to remove chromium*, *PCT Int. Appl.* (1998), WO 9803685.
- [30] M. Sivaparvathi, K. Suseela, S.C. Nandy, *Hydrolytic action of pseudomonas aeruginosa on chrome shavings*, *Leath. Sci.* 33 (1) (1986) 8–11.
- [31] M. Sivaparvathi, K. Suseela, S.C. Nandy, *Purification and properties of pseudomonas aeruginosa protease causing hydrolysis of chrome shavings*, *Leath. Sci.* 33 (11) (1986) 303–307.
- [32] M.M. Taylor, E.J. Diefendorf, G.C. Na, *Enzymatic treatment of chrome shavings*, *J. Am. Leath. Chem. Assoc.* 85 (9) (1990) 281–282.
- [33] M.M. Taylor, E.J. Diefendorf, G.C. Na, W.N. Marmer, *Enzymatic processing of materials containing chromium and protein*, US Patent 5, 094,946 (1992).
- [34] M.M. Taylor, E.J. Diefendorf, W.N. Marmer, *Efficiency of enzymatic solubility of chrome shaving as influenced by choice of alkalinity-inducing agent*, *J. Am. Leath. Chem. Assoc.* 86 (6) (1991) 199–208.
- [35] M.M. Taylor, E.J. Diefendorf, E.M. Brown, W.N. Marmer, *Characterisation of products isolated by enzyme treatment of chromium-containing leather waste*, *J. Am. Leath. Chem. Assoc.* 87 (10) (1992) 380–388.
- [36] M.M. Taylor, E.J. Diefendorf, W.N. Marmer, E.M. Brown, *Effect of various alkalinity-inducing agent on chemical and physical properties of protein isolated from chromium-containing leather waste*, *J. Am. Leath. Chem. Assoc.* 89 (7) (1994) 221–228.
- [37] L.F. Cabeza, M.M. Taylor, G.L. DiMaio, E.M. Brown, W.N. Marmer, R. Carrio, P.J. Celma, J. Cot, *Processing of leather waste pilot scale studies on chrome shavings. Isolation of potentially valuable protein products and chromium*, *Waste Manag* 18 (1998) 211–218.
- [38] L.F. Cabeza, M.M. Taylor, E.M. Brown, W.N. Marmer, *Influence of pepsin and trypsin on chemical and physical properties of isolation gelatine from chrome shavings*, *J. Am. Leath. Chem. Assoc.* 92 (8) (1997) 200–207.
- [39] L.F. Cabeza, M.M. Taylor, E.M. Brown, W.N. Marmer, *Chemical and physical properties of protein products isolated from chromium-containing leather waste using two consecutive enzymes*, *J. Soc. Leath. Technol. Chem.* 82 (5) (1998) 173–179.
- [40] L.F. Cabeza, M.M. Taylor, E.M. Brown, W.N. Marmer, *Use of tryptec enzyme preparations in treatment of chrome shavings*, *J. Am. Leath. Chem. Assoc.* 94 (7) (1999) 268–287.
- [41] L.F. Cabeza, M.M. Taylor, G.L. DiMaio, E.M. Brown, W.N. Marmer, R. Carrio, P.J. Celma, J. Cot, *Processing of leather waste pilot scale studies on chrome shavings. Part II: purification of chrome cake and tanning trials*, *J. Am. Leath. Chem. Assoc.* 93 (3) (1998) 83–98.
- [42] L.F. Cabeza, M.M. Taylor, E.M. Brown, W.N. Marmer, *Isolation of protein products from chrome-containing leather waste using two consecutive enzymes and purification of final chromium product pilot plant studies*, *J. Soc. Leath. Technol. Chem.* 83 (1) (1999) 14–19.
- [43] M. Erdem, *Chromium recovery from chrome shavings generated in tanning process*, *J. Hazard. Mater.* B129 (2006) 143–146.
- [44] A. Przepiorkowska, K. Chronska, M. Zaborski, *Chrome-tanned leather shavings as a filler of butadiene-acrylonitrile rubber*, *J. Hazard. Mater.* 141 (2007) 252–257.
- [45] A. Gammoun, S. Tahiri, A. Albizane, M. Azzi, J. Moros, S. Garrigues, M. de la Guardia, *Separation of motor oils, oily wastes and hydrocarbons from contaminated water by sorption on chrome shavings*, *J. Hazard. Mater.* 145 (2007) 148–153.
- [46] T. Basegio, C. Haas, A. Pokorny, A.M. Bernardes, C.P. Bergmann, *Production of materials with alumina and ashes from incineration of chromium tanned leather shavings: Environmental and technical aspects*, *J. Hazard. Mater.* B137 (2006) 1156–1164.
- [47] M.A. Trezza, A.N. Scian, *Waste with chrome in the Portland cement clinker production*, *J. Hazard. Mater.* B147 (2007) 188–196.
- [48] H.B. Merrill, *Chemistry and Technology of Leather*, vol. IV, Evaluation of Leather, Chap: Determination of Mineral Tanning Agents, Tanner's Council Laboratory, Cincinnati University, Ohio, Florida, 1978, pp. 243–251.