AMMAR MALEK[1], BENAMAR BENOTMANE[1], CHOUAIB ARIBI[1], MESSAOUD HACHEMI[1]

CHEMICAL TRANSFORMATION OF CHROMED LEATHER WASTES INTO ENVIRONMENTALLY HARMLESS FIBROUS BIOMASS

Chemical transformation of leather waste into chromium free biomass has been investigated. The conversion was performed by extracting the toxic metal. The effects of several influential factors on the process have been studied using design of experiments. Optimal conditions of chromium extraction have been determined. The collagen fiber of the biomass obtained has been analyzed by the Fourier transform infrared spectroscopy (FTIR). The chemical mechanism allowing this transformation has been suggested. The infrared analysis showed that the collagen fiber of the obtained biomass presents chemical composition similar to that of native collagen fiber of non-chromed leather. These results demonstrated the almost complete extraction of chromium from leather waste and the conversion of these latter into an environmentally harmless biomass.

1. INTRODUCTION

During tanning process, skins are converted into leather by tanning agents. The mineral tanning agent most commonly used is the basic chromium sulfate [1, 2]. The tanning process is based on the cross-linkage of chromium with free carboxyl groups of collagen amino-acids of skin [1, 3–6]. Through the tanning process several forms of effluents are generated such as liquid discharges [7, 8] and solid leather wastes [9–14]. Chromium leather wastes like shavings, splits and trimmings are mainly generated at the mechanical treatment of leather. The high stability of the chromium-collagen compound obtained makes the leather waste a non-biodegradable character [9, 10]. The leather wastes are generally deposited in landfills and burned at open-air [2, 11]. Unfortunately, toxic hexavalent chromium residues Cr(VI) are generated [15–20]. Owing to

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[1]Research Unit of Materials – Processes and Environment (UR-MPE), Laboratory of Matter Chemistry and Environment, Faculty of Engineer Sciences, M'hamed Bougara University, Avenue of Independence, 35000 Boumerdes, Algeria), corresponding author A. Malek, e-mail: amirouchmalek@gmail.com

the escalating restrictions from environmental authorities, numerous scientific groups have focused their research to recycle these wastes [9, 12–14].

However, the solutions advocated involve not only multi-step chemical treatments, which are expensive, but additionally the investigations conducted are generally based on empirical methods. To study a chemical process which depends on several factors, the only efficient way is the use of design of experiments [21, 22]. The aim of the present investigation is to study the chemical transformation of leather waste into chromium free biomass, rich in collagen fibers. This conversion has been experimented by using tartrate ligand as an extracting agent of chromium in alkaline medium. The effects of several influential factors on the chromium extraction rate have been studied by the use of design of experiments. Optimal conditions of extraction have been determined after modelization of the extraction process. The dechromed collagen fiber (DCF) of the biomass obtained has been analyzed by the Fourier transform infrared spectroscopy (FTIR) to compare its chemical structure with those of chromed collagen fiber (CCF) of leather wastes and of the native collagen fiber (NCF) of non-chromed skin as reference.

This analysis was conducted to verify the conversion of leather waste into chromium-free biomass. In addition, the chemical mechanism allowing this transformation has been suggested.

2. MATERIALS AND METHODS

Leather wastes and chemicals. The samples of leather waste used in the present study (Fig. 1) originate from the tannery TAMEG of great industrial zone of Algiers similarly as in our previous work [23], All analytical re agents used in the experiments: potassium tartrate, sodium hydroxide, perchloric acid, sulfuric acid, sodium thiosulfate and potassium iodine have been supplied from the Biochem Chemopharma (USA).

Fig. 1. Chromium leather shavings

Experimental procedures. The effects of four factors such as tartrate concentration (C_t), alkaline concentration (C_a), bath temperature (B_t) and contact time (T_c) on the chromium extraction rate have been studied (Fig. 2). The interactions between factors that seem relevant to study are as follows: (C_tC_a), (C_aB_t) and (C_tB_t).
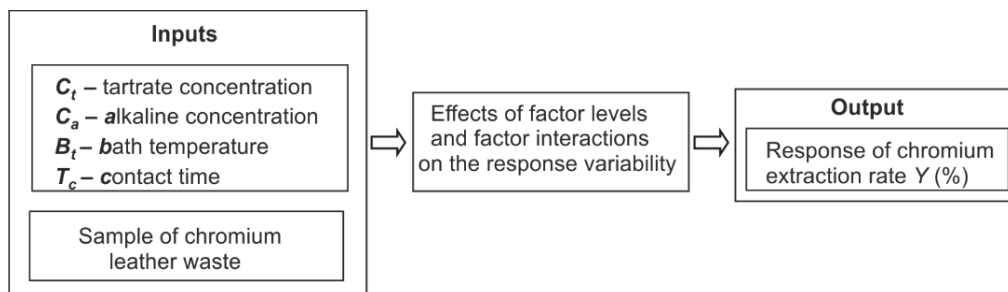

Fig. 2. Diagram of effects in the chromium extraction process

To achieve this objective, a Taguchi orthogonal array L_8 (2^7) obtained from STATISTICA software has been used (Table 1). In order to estimate the responses variability of chromium extraction rates and to perform the ANOVA of the experimental results, the orthogonal array has been repeated five times.

Table 1

Orthogonal array L_8 (2^7) of Taguchi

Combination numbers	Factors and factor interactions						
	C_t	C_a	Interaction [C_tC_a]	B_t	Interaction [C_tB_t]	Interaction [C_aB_t]	T_c
01	−1	−1	1	−1	1	1	−1
02	−1	−1	1	1	−1	−1	1
03	−1	1	−1	−1	1	−1	1
04	−1	1	−1	1	−1	1	−1
05	1	−1	−1	−1	−1	1	1
06	1	−1	−1	1	1	−1	−1
07	1	1	1	−1	−1	−1	−1
08	1	1	1	1	1	1	1

In Table 1, the factors and factor interactions are attributed to corresponding columns of the Taguchi orthogonal array avoiding aliases. The interest domains and levels of individual factors are given in Table 2. The 5g samples of leather waste treated through all the experiments were elaborated from the same lot collected during our previous work [23], the reason why the initial chromium content of this waste of about 4.23%, has been used. A series of forty samples were first dried for 6 h in an oven at

105 °C to eliminate the excess of moisture until constant weight, then distributed into 8 groups of 5 samples each.

Experimental domains and levels of each factor

Factor	Factor level	Interest domains	
		Level 1 (–1)	Level 2 (1)
C_t, tartrate concentration, mol/dm^3	2	0.25	0.5
C_a, alkaline concentration, mol/dm^3	2	0.1	0.25
B_t, bath temperature, °C	2	20	40
T_c, Contact time, h	2	0.5	2.5

Chromium extraction procedure. For each combination, five leather waste samples were treated separately. The bath of treatment of each sample was prepared by dissolving potassium tartrate ($K_2C_4H_4O_6$) and sodium hydroxide (NaOH) in 100 cm^3 of deionised water at concentrations given in Table 2. To regulate the bath temperature at 40 °C a thermostatic heating plate was used. The leather waste samples were treated with strict respect of the experimental conditions for each combination of factor levels. After treatment, the samples were removed from the baths, then rinsed in 100 cm^3 of distilled water during 30 min.

Determination of the chromium extraction rate. The treated waste samples were dried in the open air before being incinerated at 600±25 °C in an incinerator with adjustable temperature. Ashes containing trivalent chromium Cr(III) obtained from each leather waste sample were introduced into an Erlenmeyer flask, then oxidized under heater into hexavalent chromium Cr(VI) by addition 15 cm^3 of concentrated sulfuric acid (98%) and 10 cm^3 of concentrated perchloric acid (70%). The trivalent chromium content of ash samples was determined by titration using sodium thiosulfate $Na_2S_2O_3$ (0.05 M), potassium iodide KI (50 g/dm^3) and starch powder solution as an indicator.

Optimal conditions of chromium extraction. The optimal conditions of chromium extraction were evaluated from a mathematical model describing the extraction process. The general form of the model used in this study is as follows:

$$Y = g(C_t, C_a, B_t, T_c, C_{t*}C_a, C_{t*}B_t, C_{a*}B_t) + h(w) \tag{1}$$

The model is composed of a deterministic part (*g*) and a random part (*h*) such as the two parts are additive, where: *Y* is the predicted response of the chromium extraction rate, *g* represents the factors and factor interactions effects, *h* represents the variability of the response *Y* estimated by the analysis of variance. The optimal value of chromium

extraction rate is obtained applying the optimal levels of each factor in the mathematical model.

Analysis by the Fourier transform infrared spectroscopy (FTIR). The analysis was carried out successively on the DCF of the biomass obtained after chromium extraction, NCF of non-chromed skin as reference as well as on the CCF. Infrared analysis was conducted on pellets containing 4–5 mg of dry collagen powder mixed with 100 mg of KBr. The infrared spectrometer used allowed us to record the transmittances produced by vibrations of different functional groups and chemical bonds contained in the organic molecules of collagen fibers. The range of transmittances recorded is in mid-infrared from 500 to 4000 cm^{-1}. The purpose of this analysis was to compare the chemical structure of the three types of collagen fiber: DCF of obtained biomass, NCF of non-chromed skin and CCFin order to check the conversion of leather waste into chromium free biomass.

3. RESULTS AND DISCUSSION

The results obtained from the design of experiments are presented in Table 3. For each combination of factor levels, we determined five responses about the chromium extraction rates. The average experimental response (y_m) of each combination is indicated. Also, the average response (Y_M) for all the experimental design is also presented. To analyze the results obtained, all the statistical indicators allowing this aim have been determined. The sample variance (S^2) and the coefficient of variation of each experimental combination are successively presented in Table 3.

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Results of the experimental design

Run	C_t	C_a	B_t	T_c	y_m	Y_M (exp.)	Var (S^2)	Coefficient of variation [%]
01	–1	–1	–1	–1	39.20		0.191	1.12
02	–1	–1	1	1	70.79		0.415	0.91
03	–1	1	–1	1	68.71		0.273	0.76
04	–1	1	1	–1	74.58	65.63	1.155	1.44
05	1	–1	–1	1	52.83		0.262	0.97
06	1	–1	1	–1	62.66		0.204	0.72
07	1	1	–1	–1	61.24		0.374	1.00
08	1	1	1	1	95.08		0.483	0.73

The factor effects on the studied response (Y) have been determined and shown in Fig. 3 with a confidence level of 95%. The effects of all the main factors are important.

The average responses Y obtained for each factor, with lower level are: C_t (–1) = 63.32%, C_a (–1) = 56. 37%, B_t (–1) = 55.49% and T_c (–1) = 59.42%. These values are less significant than the total average response (Y_M) of about 65.63% indicated in Table 3. Contrarily, when the higher level is applied, the average responses (Y) obtained for each factor are: C_t (1) = 67.95%, C_a (1) = 74.91%, B_t (1) = 75.77% and T_c (1) = 71.85%. With the higher level (1), all the obtained responses were more significant than the total average response (Y_M) (Table 3). However, in accordance with the correlation equations and correlation coefficients obtained for the response Y (%) of each factor (Fig. 3), a disparity between factor effects is observed.
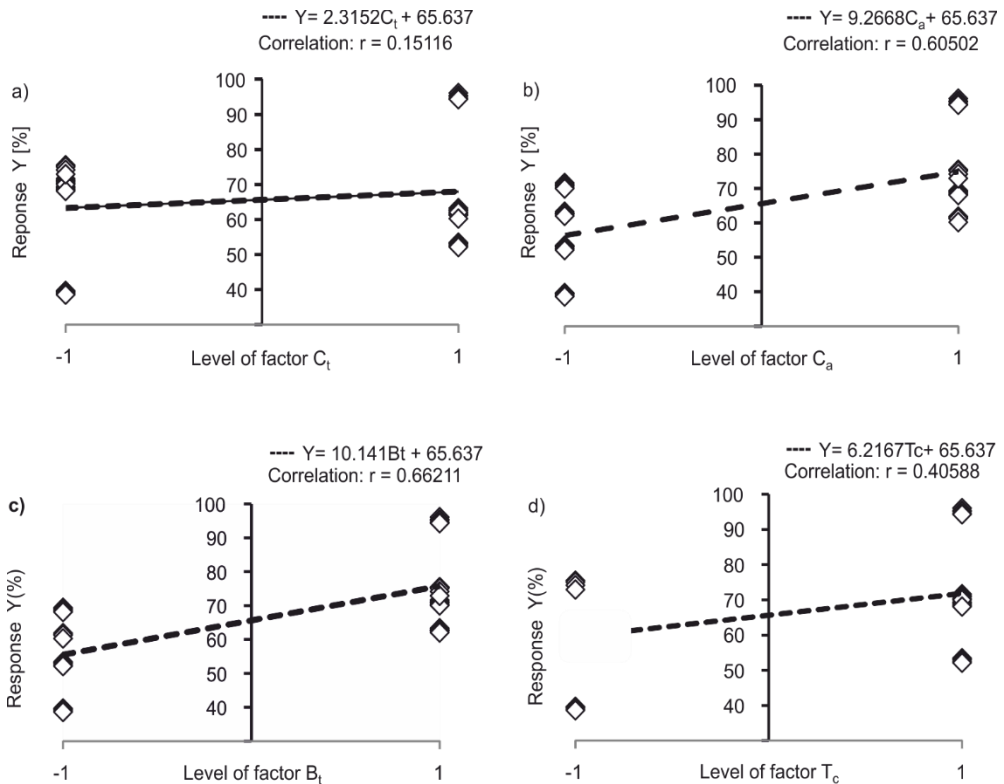
Fig. 3. Factor effects on the chromium extraction response Y (%)
a) factor C_t, b) factor C_a, c) factor B_t, d) factor T_c

It can be deduced that bath temperature (B_t) is the most important factor in the chromium extraction process. The concentration of alkaline (C_a) is the second important factor followed by the contact time (T_c) and lastly the tartrate concentration (C_t). According to the responses variation between level (–1) and level (1) of each factor, the studied factors can be classified according to their increasing effects as follows:

$$C_t < T_c < C_a < B_t$$

We can conclude that the use of higher level (1) for all the studied factors allows one to increase the chromium extraction rate Y. Contrary, with lower level (–1) of factors the extraction rate has tendency to decrease.

The effects of the factor interactions studied have been approved (Fig. 4). However, we observe that the interactions C_tC_a and C_tB_t, are more important than the interaction C_aB_t. For the interactions C_tC_a and C_tB_t we record the presence of two non-parallel lines. The interaction C_aB_t is less important which explains the presence of two parallel lines.

The coefficients estimated are presented in Table 4, where $C_{nf}L_{mt}$ is the confidence limit. The coefficient values obtained are variable and depend on the effect of each factor. The factors C_t, C_a, B_t and T_c have the following coefficients 2.32, 9.27, 10.14 and 6.22, respectively, which are firstly coherent with those previously shown in the correlation equations of each factor (Fig. 3), secondly with the classifying factor effects previously made. According to the coefficients of the factor interactions determined, we can conclude that the two interactions (C_tC_a) and (C_tB_t) are more considerable compared to the interaction (C_aB_t), being much lower and unimportant. The coefficient of the interaction (C_aB_t) is insignificant, this is why it has been eliminated.

Table 4

Estimated coefficients of factors and factor interactions

| Effect	Coefficient	$C_{nf}L_{mt}$	
		–95%	95%
Intercept	65.6372	65.4285	65.8459
C_t	2.3152	2.1065	2.5239
C_a	9.2667	9.0580	9.4754
B_t	10.1412	9.9325	10.3499
T_c	6.2167	6.0080	6.4254
C_tC_a	0.9417	0.7330	1.1504
C_tB_t	0.7762	0.5675	0.9849
C_aB_t	–0.2132	–0.4219	–0.0045

To identify the significance of all the actions studied, the contribution of each factor and factor interaction in the chromium extraction process was determined (Table 5). The contributions are given as the sum of squared deviations (SSD) .

The analysis of variance (ANOVA) of the system was conducted with 33 degrees of freedom in order to eliminate the interaction C_aB_t. With the confidence level α of 5%, a low residual variance of about 0.5 was obtained (Table 5). That is confirmed by the results of the standard deviation analysis (Fig. 5). Almost all the values of the residual variance are homogeneous. Hence, we can conclude that all the contributions of the actions: C_t, C_a, B_t, T_c, C_tC_a and C_tB_t, are significant.

Significances of the factors and factors interactions

Effect	SS contribution	Degree of freedom	MS variance	F ratio
Intercept	172 329.9	1	172329.9	372654.1
C_t	214.4	1	214.4	463.7
C_a	3434.9	1	3434.9	7427.8
B_t	4113.8	1	4113.8	8895.9
T_c	1545.9	1	1545.9	3343.0
C_tC_a	35.5	1	35.5	76.7
C_tB_t	24.1	1	24.1	52.1
Error	15.3	33	0.5	
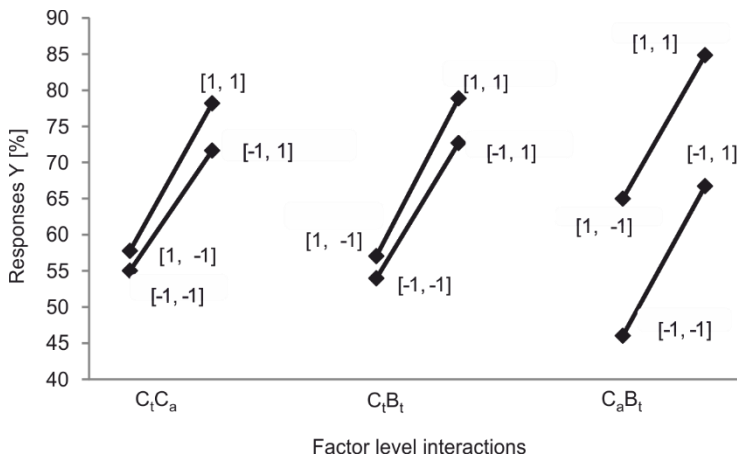
Fig. 4. Effects of the factor interactions on the chromium extraction response Y

In order to determine the optimal response Y of chromium extraction rate from leather waste, we have beforehand determined the mathematical model describing the influence order of factors and factor interactions on the response Y. Only the most influential factors and factor interactions previously defined have been retained in the formulation:

$$Y = 65.637 + 2.315C_t + 9.266C_a + 10.141B_t + 6.216T_c + 0.941C_tC_a + 0.776C_tB_t \qquad (2)$$

The adequacy of the mathematical model obtained was checked by the determination coefficient (R^2). This latter is determined to be 0.9983. This implies that the experimental data obtained were compatible with the data predicted by the model. Moreover, the value of the adjusted R^2 (0.998) is also close to 1.0 which shows a good fit of the model obtained. We can conclude that the resulting model is adequate to

describe the chromium extraction process. The optimal response of chromium extraction rate Y (%) is obtained applying the high level (1) of factors in the model obtained, Eq. (2). This choice was made in accordance with the results obtained (Table 3 and Fig. 5). The response Y of chromium extraction rate of about 95.29% was achieved.
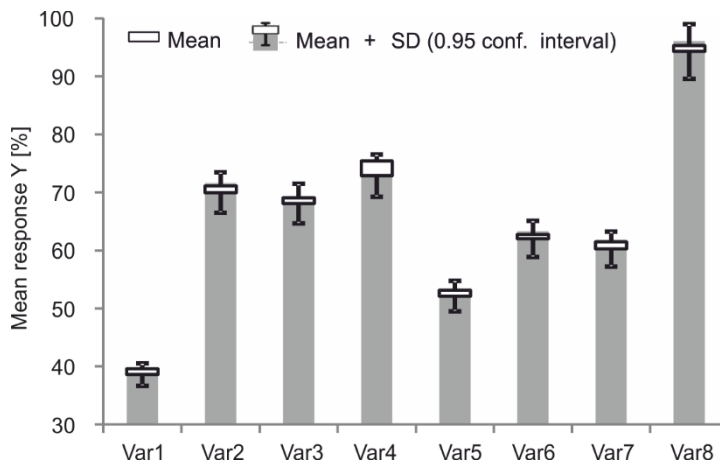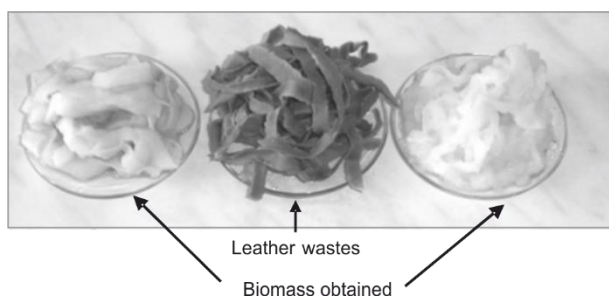

Fig. 5. Mean responses and standard deviation

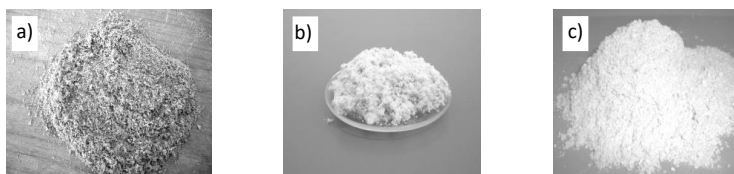Fig. 6. Leather waste and biomass obtained after chromium extraction

Fig. 7. Collagen fibers analyzed: a) CCF, b) DCF, c) NCF

Figure 6 shows two samples of leather waste treated according to the optimal experimental conditions. The leather wastes colored to blue due to the presence of chro-

mium are converted after chromium extraction into white and harmless biomass. Spectral analysis was performed on three types of collagen fibers: chromed collagen fiber (CCF); dechromed collagen fiber (DCF) of the biomass obtained and native collagen fiber (NCF) of non-chromed skin as reference (Fig. 7).

The spectra of the three types of collagen fibers are shown in Fig. 8. The spectra were recorded in the range of 500–4000 cm^{-1}.
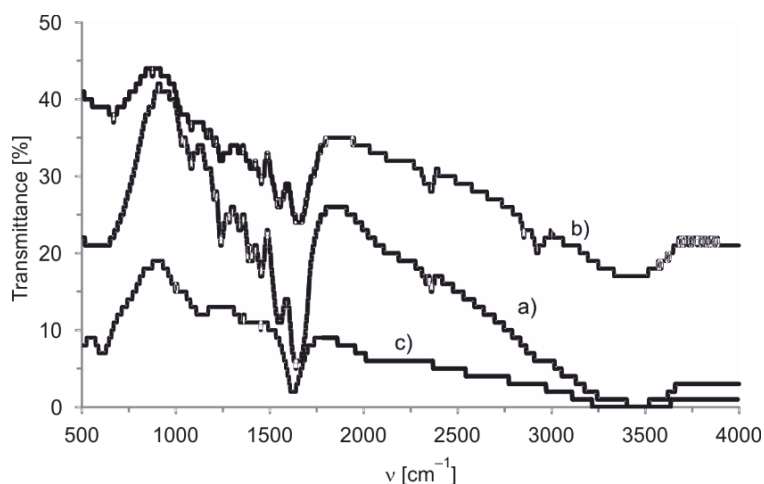

Fig. 8. Infrared spectra of the three types of collagen fibers:
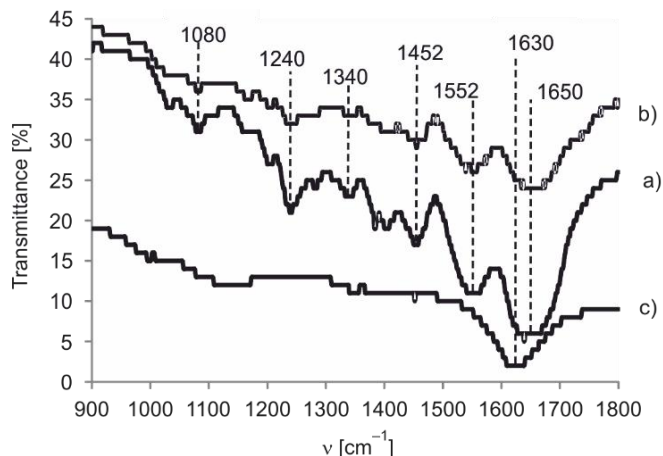a) DCF (obtained biomass), b) NCF of non-chromed skin, c) of leather waste

Fig. 9. Vibration bands in the range of 1000–1800 cm^{-1}
for the three types of collagen fibers

The infrared spectrum of CCF (c) differs from the infrared spectrum of NCF (b, reference spectrum). The peaks in spectrum (b), located between 1000 cm⁻¹ and 1600 cm⁻¹ (Fig. 9), are not visible in spectrum (c). This is due to the presence of chromium, chemically linked to the reactive groups of collagen during the tanning process. On the other hand, the spectrum (a) closely resembles the spectrum (b). This allows us to conclude that the CCF of leather waste, corresponding to the infrared spectrum (c), is transformed after treatment into chromium-free biomass which corresponds to the infrared spectrum (a). However, from Fig. 9 we notice that the peaks recorded in spectrum (a), relating to the DCF of the obtained biomass, are slightly more intense than those in spectrum (b) of the NCF. This is probably due to a slight hydrolysis of the collagen fibers in the alkaline medium during the chromium extraction process.

In Figure 9, we present the frequency range from 1000 cm⁻¹ to 1800 cm⁻¹, which covers the main vibration bands characterizing the chemical bonds and functional groups of the collagen fiber. The transmittance peaks located at 1630 cm⁻¹ and 1650 cm⁻¹, are due to stretching vibrations of the NH bonds of the free primary amine groups. The emergence of the peak at 1630 cm⁻¹ in the case of spectrum (c) can be explained by the fact that the primary amino groups do not react with chromium during the tanning process [4].
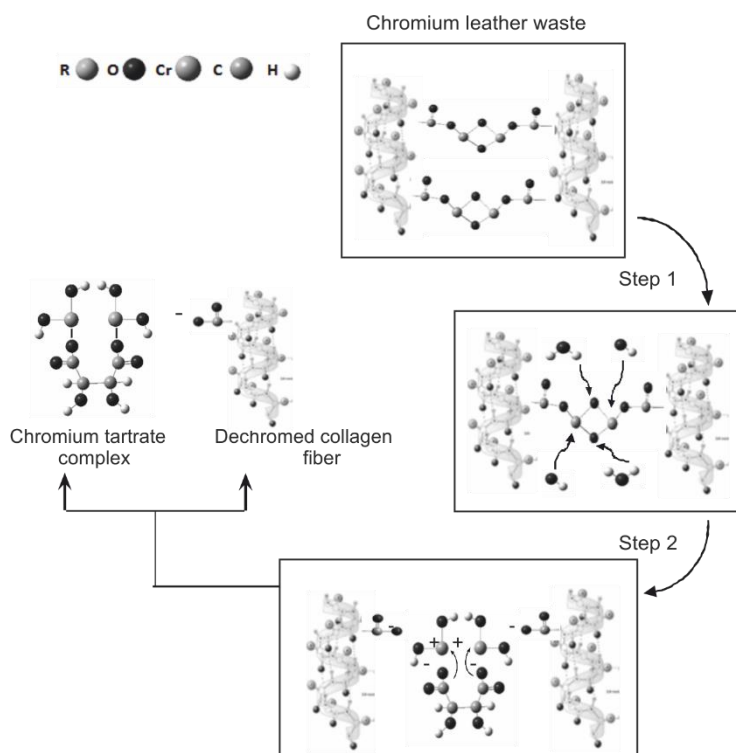

Fig. 10. Scheme of chromium extraction from leather wastes

The bands recorded inn spectra a) and b) at 1552 cm^{-1} and 1452 cm^{-1} correspond to the stretching vibrations of C=O bonds of carboxylic acids. Similarly, the peaks observed at 1340 cm^{-1} and 1240 cm^{-1} correspond to the stretching vibrations of the C–O bonds of carboxylic acids. The amide bonds contained in the collagen fiber have been identified by the presence of a peak at 1080 cm^{-1}, corresponding to the stretching vibration of C–N bonds.

The results of the experimental design allow us to conclude that chromium extraction occurs through two stages (Fig. 10). In the first step, the hydroxyl and aqua groups start the destabilization of the chemical bonds of chromium-collagen compound. Firstly, nucleophilic attacks by the hydroxyl ligands (OH$^-$) on the chromium atoms and secondly electrophilic attacks by the aqua ligands (H$_2$O) on the oxygen bridges. During the second step, the tartrate ligands react with the chromium atoms, which are under a state of unstable cationic transition, what causes the masking of chromium. This chemical interaction prevents the precipitation of chromium inside the organic matrix of leather wastes and promotes its diffusion in the treatment bath in the form of chromium-tartrate compound.

4. CONCLUSIONS

The study on the transformation process of leather waste into chromium free biomass, has been performed. The transformation was performed by chromium extraction in alkaline medium in the presence of tartrate as masking ligand. The effects of several parameters on the extraction process, as the concentrations of tartrate and alkaline concen, bath temperature and the contact time were studied. The temperature plays an important role in the chromium extraction process. This is a factor that greatly enhances the extraction kinetics. Also, the treatment time of leather waste has a significant effect on the result of chromium extraction.

The effect of tartrate concentration is less important compared to that of the alkaline concentration. However, the tartrate ligand plays several roles: first as a stabilizing agent of chromium, secondly as a promoting agent for the increase of the extraction, and lastly as protective agent for the fibrous structure of the organic matrix.

Therefore, we obtained biomass composed of collagen fibers almost completely devoid of chromium. This was verified by the infrared analysis of three types of collagen fibers including: chromed collagen fiber, collagen fiber of the biomass obtained, in addition to the native collagen fiber of non-chromed skin. The chemical composition of the collagen fiber of the biomass obtained is almost similar to the native collagen fiber of non-chromed skin, which explains the transformation of leather waste, after chromium extraction, into environmentally harmless biomass. This conversion has been clarified by a chemical mechanism that we advocated in accordance with experimental results. The results obtained through this work are very interesting. The implementation

of these results to industrial scale can constitute a practical solution expected by the industrials. In view of the enormous quantities of leather waste generated worldwide, this procedure can be an effective way for the treatment of this waste and recovery of invaluable amount of fibrous biomass. This last can be exploited in various fields such as civil engineering, as filler for the reinforcement in polymers and composites. In addition, taking into account its high nitrogen, it can be used as fertilizer in agriculture.

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