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EVALUATION OF LEATHER QUALITY AND ECOTOXICITY IN SIMULATED TANNERY WASTEWATERS USING MIMOSA TANNIN

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Abstract: *The leather tanning industry is characterized by the production of different kinds of effluents, generated in each step of leather processing. These effluents have various chemical compounds which may cause toxicity and endocrine disruption and are thus known as endocrine disrupting chemicals (EDC). Tanning stabilizes the protein structure of the hide and imparts heat stability, enhanced tensile properties, and resistance to microbial degradation. Currently most high quality leather is "chrome-tanned," produced by treatment of the hide with salts of the mineral chromium. In this study, the wastewater characteristics and ecotoxicity before and after tanning and retanning processes using mimosa tannin are assessed. Vegetable leather production procedure was followed using one dose mimosa tannin. Leather quality was evaluated according to standard methods. Wastewater characteristics showed that mimosa contributed high organic content to the wastewater. Although vegetable tannin was used the effluent toxicity was observed in tanning and retanning effluents. The preliminary results also showed that leather quality tests failed or at minimum level to comply with the standard values indicating that there is still a need to optimize the procedure including mimosa dose. This study was designed to produce eco-friendly leather using mimosa in tanning and retanning processes. Leather quality and the ecotoxicity of each process during leather production was assessed according to standard methods.*

Key words: *Vegetable tannin, mimosa, wastewater, ecotoxicity, polyphenols*

1. INTRODUCTION

The leather tanning industry is characterized by the production of different kinds of effluents, generated in each step of leather processing. These effluents have various chemical compounds which may cause toxicity and endocrine disruption and are thus known as endocrine disrupting chemicals (EDC) [1]. Tanning stabilizes the protein structure of the hide and imparts heat stability, enhanced tensile properties, and resistance to microbial degradation. Currently most high quality leather is "chrome-tanned," produced by treatment of the hide with salts of the mineral chromium [2]. Because of environmental considerations, and customer preference, there is interest in developing new chrome-free tannages [3, 4]. Thus, alternative tanning chemicals to the chromium tanning process have been evaluated during recent years to produce eco-leather [5]. The most important one among these methods is the vegetable tanning which is performed with vegetable tannins [6]. However, environmental effects of tannins should be addressed well [7, 8, 9] since

During processing, only 40–50% of the applied tannins have been taken up, and the remaining 50–60% has been released as unspent along with the wastewater. The presence of unspent tannins poses challenge to the wastewater treatment processes, due to their recalcitrant nature. In addition, the biological treatments are less effective in degrading the tannins, due to reduced organic content and xenobiotic nature [10]. This study was designed to produce eco-friendly leather using mimosa in tanning and retanning processes. Leather quality and the ecotoxicity of each process during leather production was assessed according to standard methods.

2. MATERIAL AND METHODS

2.1. Leather processing

Raw leather was provided from a leather provider factory to process it with the required chemicals according to standardized procedures [11]. The processes applied on pelts are given in Table 1.

Table 1: *Water and chemicals use during leather processing in this study (leather sample weight: 6.202 gr).*

Processes/Time	Water consumption (v/w leather)	Chemicals used	Consumption (w/w leather)	pH
Deliming (60 min)	100%	Deliming chemicals	3,30%	8,2
Bating (40 min)	100%	Enzyme	0,50%	8,2
Washing+Pickling (180 min)	80%	Formic acid Sulphuric acid	1,60% 0,20%	3,4
Vegetable tanning (120 min)	**80%**	**Mimosa tannin**	**15%**	**3,8**
Retanning step				
Bleaching (80 min)	200%	EDTA	0,50%	
Washing+Neutralization (70 min)	150%	Sodium formate	2%	5,5
Washing+Vegetable retanning (150 min)	**250%**	**Mimosa tannin**	**8%**	
Softening and degreasing (170 min)	100%	Natural and synthetic oils	14%	

Leather samples were taken according to TS EN ISO 2418 (2006) method as detailed in **Fig.1.** Accordingly, the finished leather was submitted to leather quality evaluation tests following standard methods as explained elsewhere [11]. The details of preparation of leather for leather quality testing and samples taken from vertical and parallel to the back bone.

2.2. Wastewater analyses

The wastewater samples originated from pickling, tanning and retanning procedures were analysed for their COD, TOC (Schimadzu, TOC-LCPH/CPN),TSS, nitrogen (TKN and ammonia, Gerhardt, Vapodes VAP 20s) parameters according to Standard Methods (1998) as well as for absorbance (Schimadzu Lambda 1800), electroconductivity, pH, settling properties which are typical parameters and indicators for leather tannery wastewater. Furthermore, polyphenol contents (arbutrine and gallic acids) of the samples were scanned by HPLC (Prominence Modular LC20A) following the method given by Lopez-Velez et al. [12].

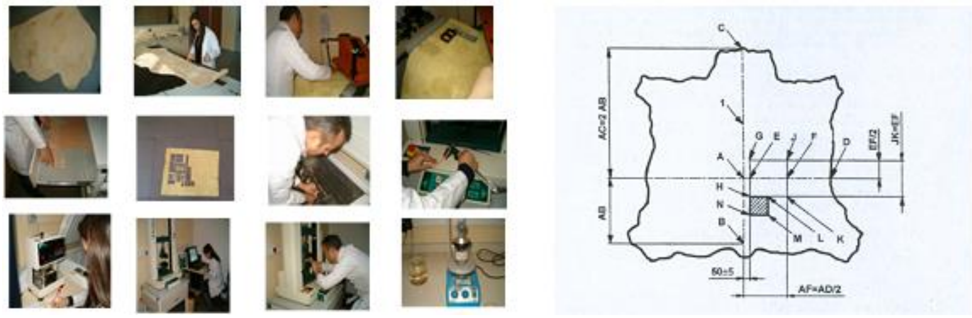


Fig. 1: *Vegetable tanning and retanning steps*

2.3. Toxicity

New born (<24 h) daphnids were exposed to the samples (after 30 min of sedimentation) for 24 and 48 h at different dilution rates to evaluate their toxicity [3, 13].

3. RESULTS AND DISCUSSION

3.1. Water consumption

As seen in Table 1, the ratio between tanning used in tannin and retanning processes is 15/8=1,87 while the ratio of water consumption between two process is 80/250=0.32. This result indicates that tanning process effluents should be more concentrated than retanning process.

3.2. Wastewater characteristics

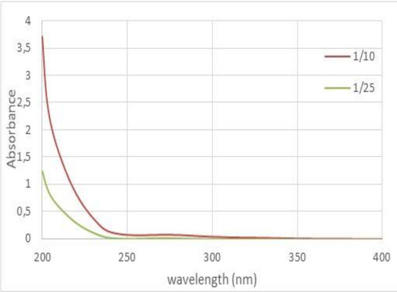
Table 2 shows the characteristics of samples tested in this work. COD and TOC values increased in tanning and retanning effluent samples conforming the contribution of unspent organic chemicals [14]. As seen in Table 1, the water consumption was higher while the amount of chemicals used in retanning process were higher than tanning process. Accordinggly, the ratio between amount of chemicals used and water consumption in tanning and retanning processes is assess to be more than 2. Drastic decrease in TOC in the retanning effluent indicates the organic content contribution of higher mimosa tannin use in the tanning process as 1 gram of mimosa tannin yields 1,153 g COD; 0,47g TOC (98% of TC); 0,576 g TKN and 0,0017 g NH_3 (unpublished data). This drastic decrease in TKN concentration was also observed in retanning effluent. The presence of organics was followed by UV profiles as shown in **Fig.2.** No absorbance peaks were observed (200-300 nm) in pickling wastewater (PW) indicating that no organics were present in the effluent. As explained above, the organics were lesser in retanning process effluent than tanning process since lesser amount of water and chemicals were used in retanning process.

Table 2: *Characteristics of vegetable tanning process wastewaters*

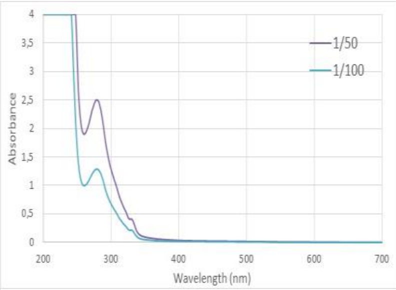
Sample names and codes	COD (mg/L)	TSS (mg/L)	TOC (mg/L)	TKN (mg/L)	Ammonia (mg/L)	UV_{254} (nm)[1]	UV_{280} (nm)[1]
Pickling effluent	3180	405	3030	25,8	25,6	0,001	0,008
Mimosa tanning effluent	19145	330	18030	193	109	>4	>4
Mimosa retanning effluent	8360	280	4325	21,1	6,2	1,68	1,895

3.3. Polyphenols

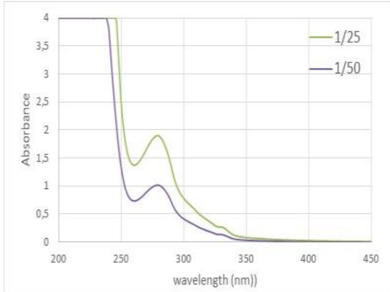
No arbutin was detected in both pickling and tanning processes effluents while Gallic acid (GA) was detected significantly higher in both wastewaters samples than pickling effleunts as seen in **Fig. 3.** High GA concentration (**Fig.3**) was found to be paralel to higher COD and TOC results (Table 2) and UV absorbances (Table 2, **Fig.3**) in tanning and retanning effluent samples**.** As seen in Table 2, UV_{254} and UV_{280} values that indicate aromatic structure and double bound in the organic content, decreased in parallel to COD and TOC parameters.



Pickling effluent

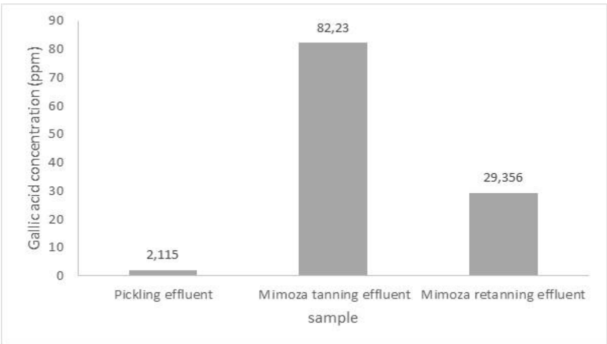


Mimosa tanning effluent

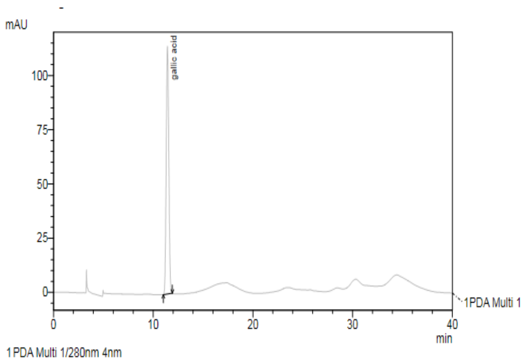


Mimosa retanning effluent

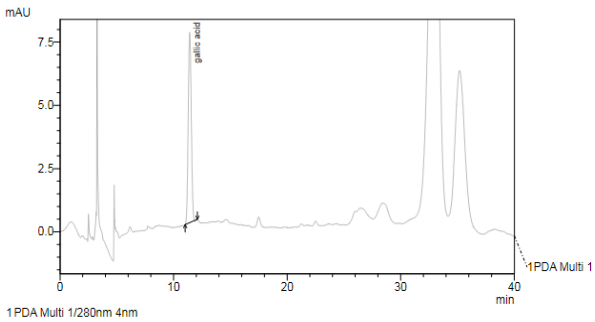
Fig.2: *UV profiles of the samples*



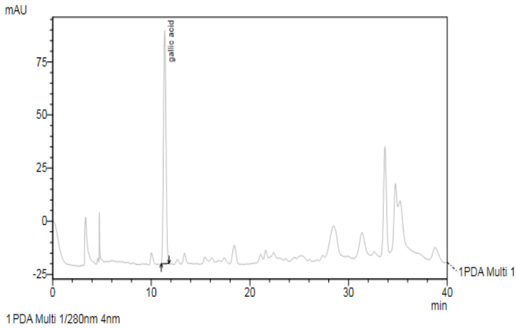
Gallic acid content of the samples



pickling effluent



Mimosa tanning effleunt



Mimosa retanning effluent

Fig. 3*: Gallic acid evolution and HPLC profiles in the samples*

3.4.Toxicity

As seen in **Fig.4**, all samples (pickling, mimosa tanning and mimosa retanning effluents) resulted in 100% toxic to *Daphnia magna* when exposed to non diluted samples. When samples were tested at 50% diluted both mimosa tanning and retanning effluents exhibited higher toxicity than pickling effluent due to higher vegetable tannen content which was explained to be toxic to different species at hihher doses [7,8]. Toxicity of wastewater can be also confirmed with higher gallic acids content as seen in **Fig.3.**

3.5.Leather quality

Table 3 shows the leather quality tests results. Leather quality by means of the resistance coefficient for pulling was obtained significantly higher than standard values. Whereas strengthness and streching resistance were below the stnadrad values indicating that there is still need to imporve the tanning and retanning procedures including the amount of mimosa to be used. Other tests regarding curving resistance measured by Pheleksometer metod, or streching temperature definition tests were in accordance with the standard requirements.

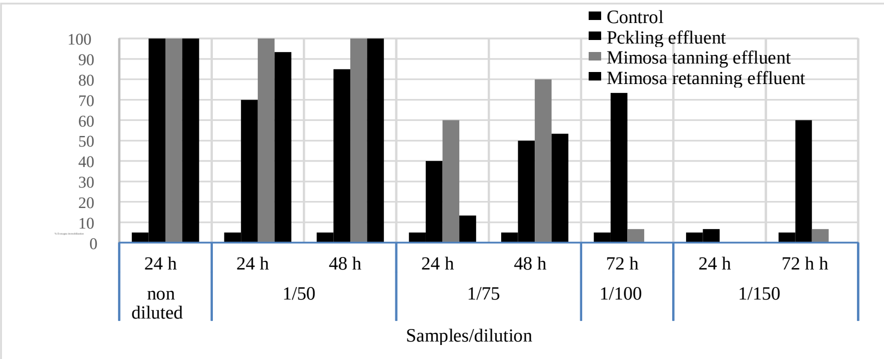


Fig.4: *Toxicity evolution in the effluents of pickling, mimosa tanning and retanning processes.*

Table 3*: Leather quality results obtained according to standart methods*

Tensile strength (N/mm2)		Elongation at break (%)		Tearing Load (N/mm)		Flexing resistance (80000 Flexing)		Shrinkage Temperature (^{o} C)	
Vertical	Parallel	Vertical	Parallel	Vertical	Parallel	Vertical	Parallel	Vertical	Parallel
16,18	21,09	63,3	65,7	72,1	64,6	no effect oberved.	no effect observed.	82	82
EN ISO 3376: 2011 (EN): Nisan 2012				TS 4118–2 EN ISO 3377–2: 2005		TS 4132 EN ISO 5402: 2005		TS 4120 EN ISO 3380: 2005	
> 25 N/mm2		>40 %		>100 N/mm					

4. CONCLUSIONS

All over the abovementioned results vegetable tanning agents can be used for producing ecological high qualiity leather by means of leather quality tests and chromium free wastewater. On the other hand the adverse effect of mimosa tannin of which the amount is still to be optimized for strengther leather product and higher biodegradable wastewater content, is to be better evaluated for safer effluents to protect environment.

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