Reduction of vegetable tannin amount released in post tanning processes by synergistic effect

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Abstract

An amount of tanning materials remain in the float due to the reason that excessive amount of tanning materials used during the tanning process, or the process is not carried out properly. It is also known that some unbound or weakly bound tanning material remain within leather fibers, and these pass into the float during washing and other processes following tannage and are discharged to the environment through waste waters. These waste waters threaten both environmental and human health when discharged. For this reason, this research was carried out to detect the amount of vegetable tanning materials passing from leather into the float during post tanning processes and to investigate reduction possibility of their amount by forming a complex with another tanning material used in a new float. From the results it is observed that some vegetable tanning material, whose amount was close to the value remaining in the main tanning float, passed into the waste water and this amount of vegetable tanning material passing into waste water could be reduced in significant amounts of approximately 85% with mineral tanning material application after vegetable tannage.

INTRODUCTION

The term "tannin" basically can be defined as the substance which has ability to convert hide and skins that are putrescible without any treatment, to leather that is resistant to microbial attacks and has increased resistance to wet and dry heat.[1] This process is called as "tanning" in leather industry. Vegetable, mineral and synthetic originated tanning materials are used for this purpose.

Vegetable tannins are one of the oldest and most known tanning agents. These materials are any of various soluble astringent complex phenolic substances of plant origin. Despite of decrease in their usage by the introduction of chrome tanning, still vegetable tannins keep their importance in main tannage of sole leathers, retannage of chrome tanned leathers, e.g. upper, upholstery, etc.

In tanning process generally an excess amount of tanning material is used in order to guarantee the tanning process. For this reason some of tanning material remains in residual float. Additionally, an amount of unbound or weakly bound tanning materials within leather fibres pass into the float during washing and other processes following tannage and are discharged to the environment through wastewaters. Discharge of such wastes threatens both environmental and human health.

Today it is generally agreed that vegetable tannins bind with the skin proteins in at least the following two ways:

1) Co-ordination – based on the hydrogen bonding of the phenolic structures of the vegetable tannin on the peptide groups of the skin proteins and

2) Saline bonding – between the vegetable tannins and the amino groups of skin proteins.

Unbound or weakly bound vegetable tannins (polyphenolic compounds), which pass into wastewater during the processes, do not decompose easily, and they are powerful toxic and dangerous organic pollutants.[2,3,4] By discharging the waters containing high concentrations of phenolic material to receiver environment, undesirable changes occur in biologic life. For example, it has been detected that physical circulation of N and P is prevented and mineralization of the organic materials in soil is reduced when polyphenol amounts that pass into soil exceed 3%.[5] At the same time, it is known that 6-7 mg/l of phenol concentration in waters has lethal effects on fish.[6] Legal limitations for tanning and finishing processes concerning the discharging of wastewaters that contain phenolic compounds were restricted to 4.5-5.5 mg/l.[7]

Several methods aiming at purifying tannery wastewaters have been developed and applied; however, it is more important to prevent the formation of wastes in tanneries[8,9]. In the research we carried out, which depends on today's clean technology standards and relies on the idea that preventing is better than reusing, reusing is better than recycling and recycling is better than discharging[10], we aimed to reveal the pollution resulting caused by tanning materials that appear in post-tanning processes and reducing the source of the pollution by making use of the synergistic effect created by the main tanning material (vegetable tannins) and a second tanning material (chrome and aluminum) that will be used in a new float.

MATERIALS AND METHODS

Material

Sheep skin was chosen as research material and 10 pickle sheep skins of Persian origin were used.

Method

Sheep skins were divided parallel at the back bone into two equal pieces, and depickle, acidic bate, fat removal processes were done according to the recipe given in **(Table I)**.

Table I

General formulation for depickling, bating and degreasing processes of the samples

Process	%	Product	Temperature (^{0}C)	Time (min)	pH
Depickle	200	Water	25		
	10	Salt		10	
Pelts added	2	Sodium formate		30	
	1	Sodium bicarbonate		60	5.5-6.0
Drain					
Bate	200	Water	35		
	1	Acidic bate product		60	
Wash	200	Water		2x10	
Drain					
Degrease	5	Degreasing product		60	
Wash	200	Water		3x20	

The skins were randomly selected in 2 groups of 10 samples to be tanned mimosa (Mi) from the condensed vegetable tanning materials, and valonea (Val) from the hydrolysables. The samples to be tanned with mimosa or valonea were adjusted to pH 5 and 4.2 with formic acid in 100% water. Then the skins were tanned with the tanning materials (**Table II**). Samples were taken from the float at the end of the process, and tanning material concentrations and COD (chemical oxygen demand) values were detected in the residual float.

After the tanning process, samples were piled for 2 days, some of them were treated with water without using a second tanning material in order to be kept as blank (B) samples, and the amount of tanning material passing through the water was detected by taking samples from the float at the end of periods of 30, 60, 120 and 180 minutes. Other samples were treated with a second tanning material (chrome or aluminum) in a new float after the main tanning process (**Table II**).

TableII

Treatment with mineral tanning materials after main tannage with vegetable tanning materials

Main Tannage		Main Tannage	
18% Val	-	18% Mi	-
18% Val	+0.25% Cr_2O_3	18% Mi	+0.25% Cr_2O_3
18% Val	+0.25% Al_2O_3	18% Mi	+0.25% Al_2O_3

The purpose of this application was to reduce the pollution load that passed into wastewater by forming a complex between tanning materials. Cr and Al amounts in wastewaters were detected with Perkin-Elmer 2380 Atomic Absorption Spectrophotometer. Cr was measured at 357.9 nm by using air+C_2H_2 mixture; and Al was measured at 309.3 nm by using C_2H_2+air+N_2O gases and at 0.7 slit intervals. The amounts of phenolic materials resulting from the vegetable tannins, and COD values were detected with Merck SQ 300 Water and Wastewater Spectrophotometer by using standard kits (Merck). Cr-phenolic material and Al-phenolic material complexes in wastewater samples, which appeared as the result of using the second tanning material for obtaining synergistic effect after the main tanning process, were precipitated by using NaOH solution (Cr at pH 7.5, Al at pH 6.5) in order to separate Cr and Al from phenolic complexes and to make a precise measurement ($Cr(OH)_3$ $K_{sp}=10^{-30.2}$, $Al(OH)_3$ $K_{sp}=10^{-31.7}$)[11,12]. Finally, their measurements were made after the centrifuge. Additionally, shrinkage temperatures of the leather samples were determined according to SLC 406[13].

RESULTS AND DISCUSSION

When the data obtained from the research was examined, it was found that 2.21 mg/l of phenolic material remained in the float at the end of main tannage with mimosa. It has been detected that there was 1.95-2.23 mg/l of phenol passing into float from leathers treated with only water as blank samples within a period between 30 to 180 minutes at the end of main tannage with mimosa (**Table III**). It can be seen that the amount of tanning material that passed into wastewater from the leather during post-

Table III

Average values of wastewater analysis of Cr and Al usage after main tanning with mimosa

	Phenol (mg/l)	Cr (mg/l)	Al (mg/l)	COD (mg/l)
Mimosa Tannage	**2.21**	**-**	**-**	**12970**
Mi-B. 30´	2.23	-	-	7790
Mi-B. 60´	2.16	-	-	6920
Mi-B. 120´	2.05	-	-	6945
Mi-B. 180´	1.95	-	-	6590
Mi-Al 30´	**0.68**	**-**	**18.7**	**6760**
Mi-Al 60´	**0.43**	**-**	**19.06**	**7180**
Mi-Al 120´	**0.42**	**-**	**12.71**	**7400**
Mi-Al 180´	**0.31**	**-**	**20**	**7360**
Mi-Cr 30´	1.93	276	-	6345
Mi-Cr 60´	2.13	232	-	6705
Mi-Cr 120´	2.30	124	-	6525
Mi-Cr 180´	1.97	84	-	6760

tanning processes is very close to the amount of waste tanning material which remains in the float at the end of tannage. This reveals the fact that a significant amount of polyphenolic material passes into wastewater during the processes applied after vegetable tannage.

It has been detected in the research that chrome, which was used for reducing the amount of phenolic material passing into the float in the following processes after main tanning with mimosa, does not have a significant effect on the rate of phenolic material passing into waste float. Additionally, it has been observed that, after main tanning with mimosa, the amount of phenolic material in waste float decreases depending on the period when Al is used instead of Cr and this amount decreases to 0.31 mg/l in the float at the end of 180 minutes. In this way, a decrease of 85% according to the amount of the tanning material (1.95 mg/l) that passed from unprocessed sample was achieved (**Figure 1**).

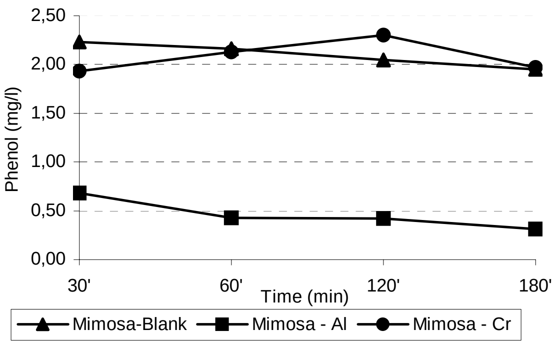

Figure 1: Wastewater Phenolic Material Values of Mimosa Main Tanned Samples

Wastewater samples were taken from the float within the same periods, and the chemical oxygen demand and the amounts of additional tanning material remained in the float after the process were detected (**Figure 2, 3**).

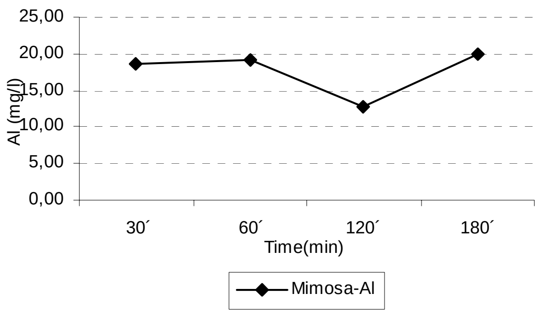

Figure 2: Wastewater Al Values of Mimosa-Al Application

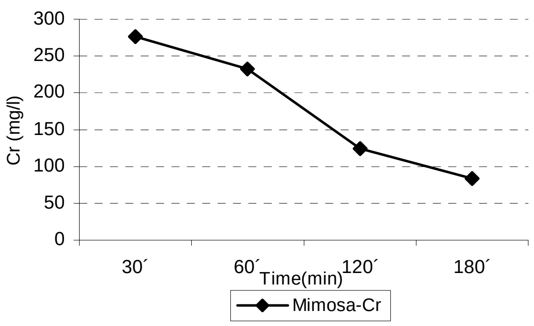

Figure 3: Wastewater Cr Values of Mi-Cr Application

The findings indicated a decrease in the amount of phenolic material in the float, and it was determined that the pollution load (COD) of wastewater increased approximately 2.5-10% after main tanning with mimosa compared to the wastewaters of blank samples.

In the research, it was found that wastewater containing 4.98 mg/l phenolic material arose at the end of main tanning with valonea, and an amount of 4.06 mg/l of additional phenolic material passed into the wastewater during the processes if no precautions were taken (**Table IV**). However a decrease of 65% in the amount of phenolic material that passed into the float was observed by using 0.25% Cr_2O_3 in a new float after main tanning with valonea.

Table IV

Average values of wastewater analysis of Cr and Al usage after main tanning with valonea

	Phenol (mg/l)	Cr (mg/l)	Al (mg/l)	COD (mg/l)
Val. Tanage	**4.98**	**-**	**-**	**30040**
Val-B. 30	2.33	-	-	4860
Val-B. 60	2.92	-	-	5000
Val-B. 120	3.89	-	-	8680
Val-B. 180	4.06	-	-	7220
Val-Al 30	**0.74**	**-**	**13.27**	**4790**
Val-Al 60	**0.58**	**-**	**7.1**	**5160**
Val-Al 120	**0.79**	**-**	**5.05**	**6650**
Val-Al 180	**0.72**	**-**	**4.48**	**6550**
Val-Cr 30	1.90	304	-	5150
Val-Cr 60	1.77	160	-	5250
Val-Cr 120	1.93	92	-	5830
Val-Cr 180	1.45	52	-	5830

The most striking point in this observation is that the amount of phenolic material passed into the float was reduced to 0.72 mg/l with 0.25% Al_2O_3 usage after main tanning with valonea and this meant a significant rate of approximately 82% decrease as in mimosa application (**Figure 4**). Besides, it was discovered that COD values of wastewater decreased at a rate of 10-20% compared to the wastewater COD values of blank samples. **Figures 5 and 6** show the amounts of Cr and Al that remain in wastewater.

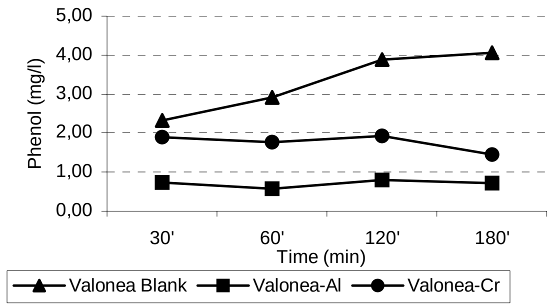

Figure 4: Wastewater Phenolic Material Values of Valonea Main Tanned Samples

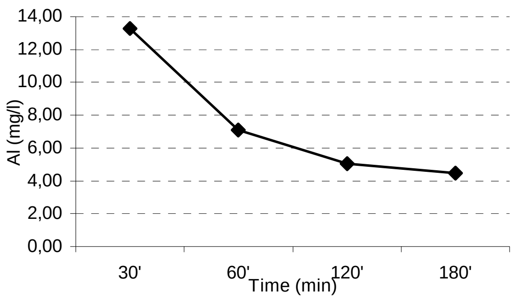

Figure 5: Wastewater Al Values of Valonea -Al Application

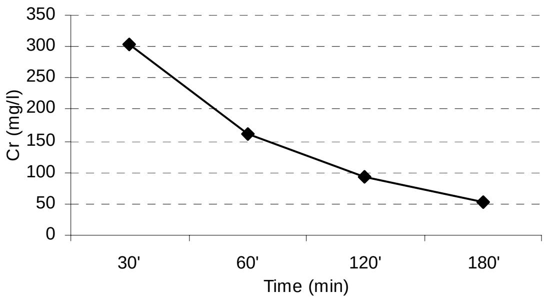

Figure 6: Wastewater Cr Values of Valonea –Cr Application

We discovered also in our research that there was an effective increase in shrinkage temperature as a result of the treatment with aluminium in leather samples which were tanned especially with vegetable tanning materials (**Table V**). As it is known, this increase in the shrinkage temperature depends on the complex-forming features of vegetable tanning materials and aluminium salts considered as synergistic effect (**Figure 7**).

Table V

Average shrinkage temperatures of leather samples

Main Tannage		**Ts (^{0}C)**
18%Valonea	-	73
18%Valonea	+0.25% Cr_2O_3	90
18%Valonea	+0.25% Al_2O_3	94
18% Mimosa	-	82
18% Mimosa	+0.25% Cr_2O_3	91
18% Mimosa	+0.25% Al_2O_3	93

Synergic effect promoted especially with vegetable tanning materials and aluminium, and the studies carried out on Mi-Al and Val-Al combinations have showed that the shrinkage temperature, which is one of the tanning effect criterion, approached to 100 ^{0}C and even exceeded this temperature values[14, 15].

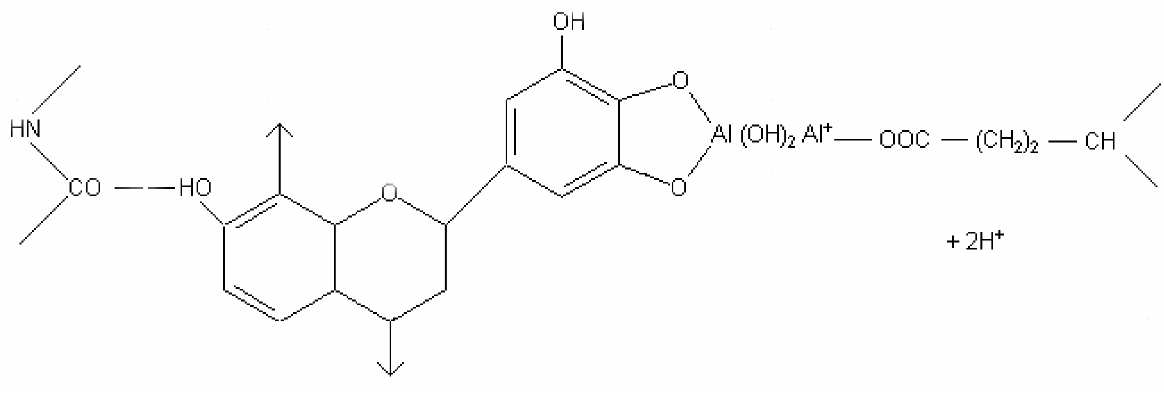

Figure 7: Structure formula of mimosa-aluminium complex[16]

CONCLUSION

From the tanning residual float values, it is clearly seen that some amount of tanning material remained in floats at the end vegetable tanning processes. Considering the research data related to following processes it’s observed that tanning material, whose amount was close to the value remainining in the main tanning float, passed into wastewater. Therefore, the precautions concerning the reduction of the amount of tanning material, which will pass into wastewater during wet processes after tannage, are as important as the precautions to be taken during tannage.

As a result of the research we carried out in order to reveal and reduce this amount, it was concluded that depending on the complex formation shown in **Figure 7**, it is possible to effectively reduce the amount of phenolic material passing into wastewater by using a little amount of aluminium or chrome tanning material after main tanning with mimosa or valonea. Yet, although phenolic material amount was reduced as a result of chrome application after vegetable tanning, the amount of waste caused by chrome was found to be high (52 and 84 mg/l) and the amounts passing into wasterwater was detected to be rather low when aluminium was used (4.48 and 20 mg/l). In addition, the applied method partly reduced the COD values and increased the values of shrinkage temperature.

Notwithstanding the fact that the polluting effects of phenols are not dwelt upon in leather industry as much as the effects of chrome, it is known that phenol and its derivatives are among toxic and dangerous organic pollutants and have negative effects for receiver environments. For example, phenolic compounds constitute a serious threat for the nature of high-quality waters due to their low organic decomposition rates[17,18]. If wastewaters mix with ground waters, even small amounts including phenolic compounds may cause serious pollution in fresh water sources, and more serious problems may arise when chlorine is used for the disinfection of fresh waters. When chlorine reacts with phenols, it forms chlorophenols which gives more harm to human health than phenol alone[18,19]. Considering the fact that such compounds prevent the physical circulation of N and P, and the mineralization of organic materials in soil and pose serious threat for the environment and living beings due to their toxic effects besides many other harmful reactions; the findings obtained in this research constitute significant outcomes, since it concludes that the amount of phenolic material passing into wastewater by aluminium application after valonea or mimosa tannage was reduced approximately 85%, while this amount was reduced 65% with chrome application after valonea tannage.

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