

Minimization of Process and Wastewater Load in a Low-Pressure Environment through Vacuum Application for Fiber-Based Materials: Leather and Cotton Products

Ersin Onem^{1,,}, Ali Yorgancioglu^{1*}, Behzat Oral Bitlisli¹, Onur Yilmaz¹,
Yalcin Yilmaz¹, Saltanat Sabyrkhanova², Alperen Isbecer³

¹ Department of Leather Engineering, Faculty of Engineering, Ege University, 35100 Bornova-Izmir, Turkey

² Department of Technology and Design of Textile Materials, Higher School of Light and Food Engineering, SKU Auezov University, 160012 Tauke Khan Avenue-Shymkent, Kazakhstan

³ Demaksan Tannery Machines Co. Ltd., 35730 Kemalpasa-Izmir, Turkey

* Corresponding author. E-mail: ali.yorgancioglu@ege.edu.tr

Abstract

Our study aimed to eliminate the negative aspects of conventional fiber-type materials. First, leather dyeing was considered by designing a vacuum-operated reaction vessel/drum and a suitable production recipe for sheepskins, based on the analyzes of float uptake and color strength regarding water usage, dyestuff usage, and process time. Acid dyes were used for leather dyeing under a vacuum. The dyeing time decreased from 60 minutes to 30 minutes with the application of low pressure. Float uptake increased from 71.18% to 92.02% by analyzing the residual dye floats with a 30-minute vacuum process. Process water was considerably saved, and float water eliminated. The success of the process was demonstrated by float uptake and color strength (K/S) values after dyeing. Metal complex and cotton dyeing applications were also conducted under a vacuum to demonstrate the system's effectiveness on fiber-type products. The results showed that vacuum-operated dyeing procedures were highly effective and promising for the sustainable production of fiber-type materials.

Keywords

Leather, cotton, dyeing, coloration, vacuum, low pressure, sustainable production.

1. Introduction

Almost all wet processes in leather production are carried out in conventional wooden cabinet/drum systems (production tanks/reaction vessels). The purpose of these drums is to penetrate the chemical materials into the leather with the help of water and the mechanical effect caused by the rotational movement of the cabinet, and to carry out skin-related reactions. In traditional drums, there is no pressure control and no vacuuming of the ambient. Inside the drums, there are some parts placed to increase the mechanical impact. The rotational motion in conventional drum systems agitates the chemicals, helping to keep the chemical concentration in the aqueous solution homogeneous. In addition, with the help of agitating the drum, a pumping effect is created by the continuous movement of the leather fibers, and the diffusion of chemicals is aimed to be realized. However, in traditional drum systems, the desired effect cannot be achieved sufficiently, the processing time is long and the amount of wastewater containing chemicals is high. Because the distance

between the fibers of the skin cannot be opened sufficiently, the penetration process is very slow and can only be achieved with a higher concentration of dyestuff in the dyeing bath [1].

In addition to the production of footwear, clothing and leather goods, natural leather is now in high demand in the aircraft, yacht, automotive and furniture sectors and its market volume has grown steadily. The turnover of leather and their articles reached approximately 600 billion US dollars [2]. On the other hand, the environmental problems of the industry is huge and brings more and more environmental challenges [3-5].

Looking at the recent activities of the Leather Working Group (LWG), which consists of member countries around the world, it is seen that an awareness is being raised for sustainable leather production [6]. Companies engaged in leather production are explicitly required to use less water and chemicals, use less energy, minimize waste volume and pollution load, and reuse the waste generated. Again, there are policies of

various brands to make purchases from companies having eco-labels in the sale of leather products. As can be seen, it will be an inevitable fact that companies that do not act in accordance with sustainable environmental production criteria will have difficulties in exports in the future. It is also foreseen that this situation may become more serious in the coming years with the sanctions imposed.

Dyeing is an economically and ecologically important process step in leather and textile production. The dyeing process, in which the appearance characteristics of leather are improved and the leather is brought to the desired color, constitutes one of the highest budget items in leather production, and anionic acid dyestuffs are used in this process step [1]. One of the difficulties encountered in aqueous dyeing is that the dyestuffs cannot penetrate the leather cross-section and superficial dyeing occurs. This is due to the unique structure of leather and the insufficient mechanical effect of current technologies. The corium layer of the leather prevents the penetration of the dyestuff due to

the tight structure formed by elastin and collagen fibers. The inability of the dyestuff to penetrate under the fibrous structure in the corium layer prevents the homogeneous and balanced distribution of the dyestuff and causes more water, dye and auxiliary chemicals to be used for dyeing. Again, the chemicals used in leather production remain as a layer on the surface, resulting in quality problems such as hardness and low fastness values in the finished leather [7]. There are some studies on increasing dyestuff exhaustion in conventional production systems [8,9].

When we look at the studies on water management in the leather and textile industry, it is seen that there are very few studies on reducing the proportion of water used in the processes [10-12], which generally remains at the point of preventing the hazard of wastewater after it is formed. In recent years, efforts have been made to ensure sustainability in the leather and textile industry [13-16] and waste management plans are enforced [17,18]. The need to develop technologies that reduce the use of water and chemicals and to save energy by enabling reactions to take place in a shorter time is emphasized [19]. Reducing the use of process water is recommended, but hypotheses on how to ensure the penetration of chemicals into the matrix are not developed. Efforts to save water have not been sufficient, and effective results have not been put into practice. In these studies, chemical consumption was low when the carrier medium was kept low, so the final leather quality could not be achieved at the desired levels [20]. However, the main objective should be to improve processes and reduce water use without compromising the performance characteristics of the finished leathers. So far, the most successful results in this direction have been obtained with studies carried out in supercritical fluid ambient. The system is based on the use of a supercritical fluid medium under high pressure as a carrier instead of water [2, 21-25].

In a study on the application of a vacuum in leather production, Gudro et al. (2014) examined the usability and preservation time of the vacuum effect in the conservation of raw hides [26]. In

the study, it was determined that when a vacuum was applied, raw hides could be stored for up to 21 days at +4 °C storage conditions without deterioration and microorganism activity remained very low. It was emphasized that with the method raw hides could be preserved without the use of salt, and the pollution load caused by salt could be eliminated. However, this study, which was carried out for the protection (conservation) of raw hides until they are put into production in factories, could not be used in the leather industry due to the short duration of the protection and the impossibility of putting it into practice in international transportation operations. This study does not address the process steps of leather production in an aqueous environment, i.e. water and chemical savings.

In this study, in order to solve the problems of the traditional dyeing system, it was aimed to design special production recipes to reduce the water and dyestuff ratios used and shorten the process time under low atmospheric pressure by creating a controlled vacuum in the leather production drum, and to determine the properties of the finished leather and wastewater. By placing the system under a controlled vacuum; it is aimed to open collagen fiber bundles faster and more efficiently, thus using low volumes of water and dyestuff as a carrier medium, easier/faster penetration of dyestuff between the opened fiber bundles and significantly reducing the dye load in the waste. Vacuum conditions were also tested for cotton and metal complex dyeing, demonstrating the effectiveness of the system for fibre type products.

2. Experimental Programme

2.1. Materials

Commercial domestic pickled sheepskins with a thickness of 0.6 mm were used as

leather material. After tanning and post-tanning applications, the leathers were ready for dyeing experiments with both the conventional and vacuum methods. A cotton sample woven with yarn number (68/1) was used, made for the experiment at the AZALA textile mill. The composition of the sample is given in Table 1 below.

2.2. Conventional dyeing experiments

After pre-treatments, leathers were dyed conventionally according to Table 2. Variations to be studied for vacuum experiments were marked in bold. These are water, dyestuff usage and time parameters. By reducing these ratios with the advantages offered by the vacuum system, more economical and environmentally friendly recipe designs were attempted to be created.

Black colored acid dyestuff of anionic character was used as dyestuff. "Acid Black 210" dyestuff of Turkuaz Chemical Company (Turkey) (CAS: 99576-15-5), which is widely used in the industry, was preferred because it shows surface and cross-sectional color properties more clearly [27]. A metal complex dyeing agent was also used with the same recipe to make a comparison between dyestuffs.

2.3. Vacuum operated dyeing drum

Technical properties of the vacuum dyeing drum were as follows:

- Stainless steel chrome nickel material for the drum,
- Cr304 chrome body, resistant to acidic chemicals,
- Height: 1631 mm,
- Width: 832 mm (with rotating heads),
- Inner chamber diameter of the vacuum drum: 600 mm,

Yarn number in warp	Yarn number in weft	Fabric composition		Interlacing
68/1	68/1	-	100%c	5/2

Table 1. Composition and identification of cotton sample

Process	%	Substances	Temperature (°C)	Time (min.)	Remarks
Dyeing	100	Water	40		
	2	Dye auxiliary		30	
	5	Dyestuff		60	
	1	Formic acid		40	pH: 4.0
Drain-Washing-Horsing-Mechanical operations					

Table 2. Conventional dyeing recipe

- Inner chamber width of the vacuum drum: 300 mm,
- Vacuum drum rotation drive motor power: 0.37 kW
- Vacuum cabinet rotation drive reducer: NMRV050,
- Vacuuming pressure of the vacuum pump: Up to 600 mm Hg,
- A pump that draws the air inside the leather production cabinet and allows the fibers in the leather to open and/or close the gap between the opened leather fibers by providing air pressure into the cabinet at any time by exhausting the air pressure,
- Vacuum pump motor power: 3 kW
- Viewing window to observe the reactions inside the cabinet,
- Thickness of observation glass panes: 10 mm,
- A pressure sensor to continuously measure the air pressure inside the processing cabinet and monitor it from the outside,
- Protrusions on the inside of the cabinet that allow the leathers to be attached and lifted upwards during the rotation and to increase the mechanical movement that occurs when the lifted leather falls down due to gravity,
- Heating element for heating the fluid in the process ambient,
- A shut-off valve that allows the liquid flow to be interrupted at any time,
- Swivel head connection to shaft hubs: 2 pcs,
- Chemical dosing chamber from rotating head to vacuum cabinet,
- Control panel for monitoring production parameters,
- Chemical discharge drain valve under the cabinet,
- Bidirectional rotation of the cabinet.

2.4. Drum testing steps

A prototype vacuum cabinet was manufactured in line with the specifications

specified without compromising the shape of traditional leather production drums. In order to test the vacuum leather production cabinet manufactured; 5 sheepskins and 100% water by weight were taken into the cabinet and a vacuum environment created inside, where the cabinet was rotated for 1 hour, material was given from the chemical dosing unit from time to time, and it was checked whether there was any vacuum leakage during the cabinet movement. According to the test result, during the opening and closing of the chemical dosing chamber, the vacuum pressure could not be kept constant during the time in the internal environment, and some pressure losses were observed. In order to eliminate this problem, it was aimed to install a separate section between the chemical dosing unit and the cabinet, to transfer the chemicals from the external unit to the intermediate unit first and then to the drum. Thanks to the double-stage transmission system, it is planned to prevent air leaks and pressure changes. The prototype produced is given in Figure 1.

The arrangement between the cabinet and the chemical dosing unit is shown in Figure 2.

According to the tests of the new setup, the vacuum pressure remained constant in the internal environment and no increase or decrease in the internal pressure of the cabinet was observed.

2.5. Dyeing experiments in vacuum operated drum

In the dyeing processes carried out in the traditional system, 100% of the bath and 5% of the dyestuff were used and the process time was 60 minutes. In the production recipe in the vacuum environment, water usage rates were specified as variable A, dyestuff usage

rates as variable B, and dyeing time as variable C. The parameters were as follows;

A1: 80% water usage (on leather weight),

A2: 50% water usage,

A3: 25% water usage,

A4: Free of water use; in water-free productions; no bath was taken into the vacuum cabinet, only the dye was dissolved with the amount of water in which the dyestuff would dissolve and taken into the drum (50 mL).

B1: 4% dyestuff,

B2: 3.5% dyestuff,

B3: 3% dyestuff,

B4: 2.5% dyestuff.

C1: 45 mins,

C2: 30 mins,

C3: 15 mins.

Variables by recipe are shown in Table 3.

After application of the dyeing recipe, post processes such as retanning and fatliquoring of the leathers were completed and the finished products produced. Float uptake was measured immediately after dyeing according to the UV-spectrophotometer method, and color measurements on leathers were made on finished products after all processes as in the conventional system. The float uptake and color measurements on leathers were considered as target parameters for optimization studies for comparison.

2.6. Cotton dyeing procedures

The cotton fibre samples were wiped with a stain remover at 40°C for 30 minutes, and then thoroughly rinsed and dried at 25°C temperature. The cleaned material was soaked in clean water for 30 minutes before dyeing. The dyeing of the samples was carried out with an initial temperature of 50°C, and the temperature was raised

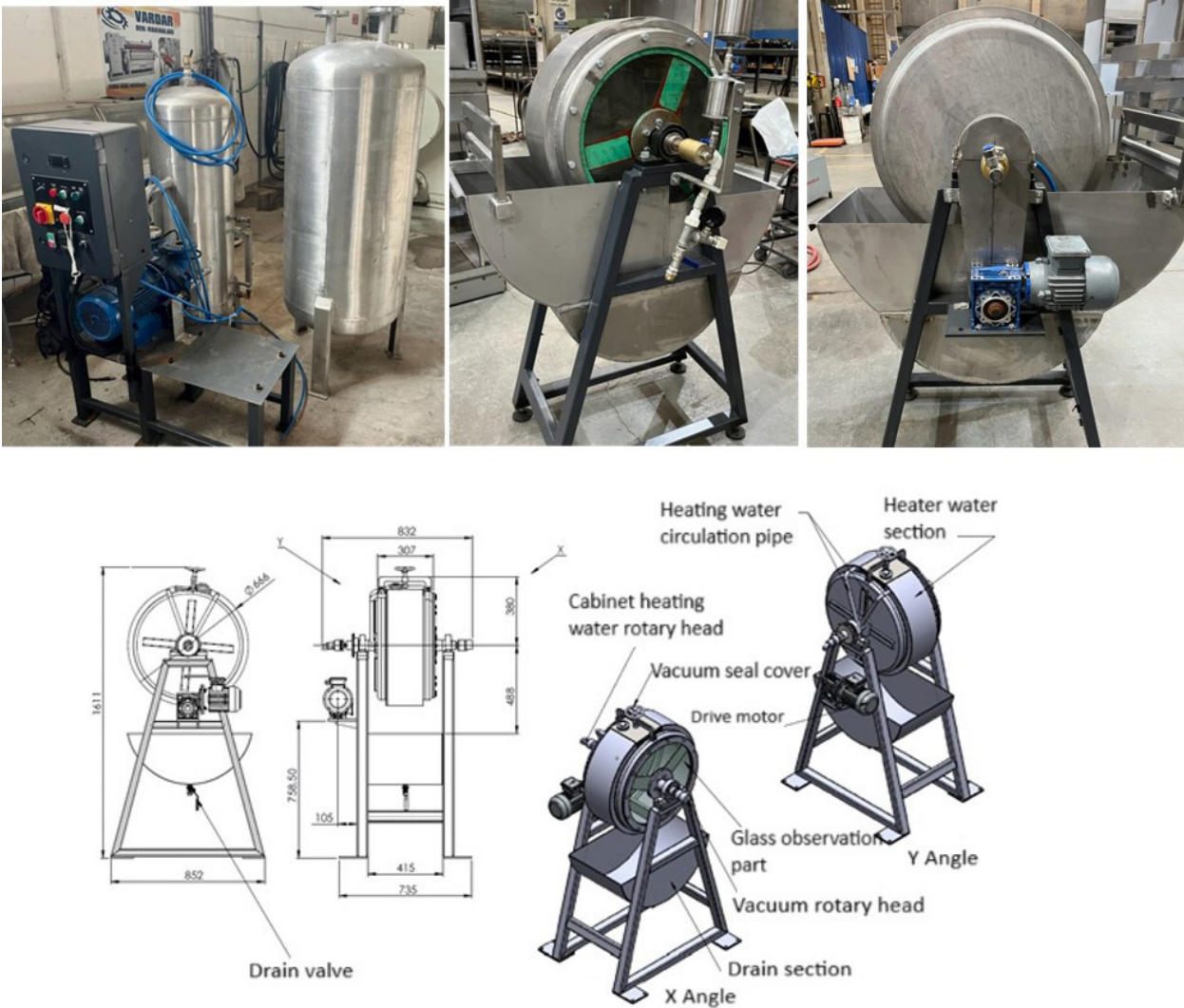


Fig. 1. Visuals of a vacuum leather production drum (pressure/vacuum tanks, vacuum pump, rotary drum/reaction medium, control panel) and schematic diagram of the experimental system



Fig. 2. Chemical dosing unit, and the set-up between the drum and dosing unit

Process	%	Substances	Temp. (°C)	Time (min.)	Remarks
Dyeing	A	Water	40		A1-A4
	2	Dye auxiliary		30	
	B	Dyestuff		C	B1-B4, C1-C3
	1	HCOOH		40	pH: 4.0
Drain-Wash-Horsing-Mechanics					

Table 3. Leather dyeing recipe under vacuum

to 100°C. Then the samples were wrung out to a weight gain of 90%, dried at a temperature of 25°C, followed by washing with hot water at a temperature of 45°C and then with cold water [28]. The conventional method was applied by using 10 g of dye and 1000 mL of process water. The same process was also applied under vacuum conditions, using half the amount of process water and with the hypericum extract dissolved.

2.7. Determination of dyestuff concentration in residual floats by UV-spectrophotometer

Spectrophotometric measurements were performed to determine the amount of dye remaining in the bath and float uptake after the dyeing process. A Shimadzu UV-1800 spectrophotometer was used

for these measurements. Floats were examined before and after dyeing, and exhaustion values (%) were reached. The absorbance differences were compared with the absorbance value of the dyestuff itself before dyeings, and the necessary dilutions were made in order to operate in a healthy reading range in the device. Dyestuff exhaustion (E%) was calculated according to the following formula;

$$E\% = \frac{A_0 - A_d}{A_0} \times 100 \quad (1)$$

Where A_0 is the absorbance values of the dye solution in the liquor before dyeing and A_d the absorbance values of the dye solution in the liquor after dyeing. Measurements were made at the wavelength at which the dye solution showed maximum absorbance ($\lambda_{\max}$: 438 nm).

2.8. Color measurements and Kubelka-Munk theory

A Konica Minolta spectrophotometer CM-3600d device was used for color measurements of dyed leathers. After the dyeing process of the finished leathers, the leathers were kept in a special conditioning room at 50% relative humidity for 48 hours in order to minimize the color difference due to moisture. The prepared samples were read on the device and color intensity values determined.

Kubelka-Munk theory is based on the premise that the absorption and scattering of light by a sample can be described using two parameters, defined as the absorption coefficient (K) and scattering coefficient (S). The absorption coefficient describes the fraction of incident light absorbed by the sample, while the scattering coefficient describes the fraction of incident light scattered by the sample. K/S is expressed as color intensity.

Using the reflectance value at the maximum absorbance ($\lambda_{\max}$) at the visible wavelength (360-700 nm) for each dyeing, the color intensity values of the leather samples were calculated with the Kubelka-Munk equation given below.

$$K/S = (1 - R)^2 / 2R \quad (2)$$

In this equation, K is the absorption coefficient of the sample, S the scattering coefficient of the sample, and R corresponds to the reflectance value of the sample at the maximum absorbance [29].

2.9. Rub fastness on dyed leathers

Determination of color fastness to-and-fro rubbing cycles of leathers dyed in the conventional system and vacuum ambient was carried out according to the TS EN ISO 11640 standard test method [30]. This method is based on the determination of the behavior of the leather surface against rubbing with felt.

2.10. Hypothesis of vacuum dyeing

In dyeing studies in vacuum system production ambient, it was aimed to reduce water usage ratios, dyestuff usage ratios and dyeing time, and as a target it was determined to reach at least the quality values of the leathers produced in the conventional system under the planned conditions. If the limit values in the conventional system were not met using vacuum applications, the process was deemed unsuccessful. However, if dyeing designs using less water, time, and chemicals matched the conventional system's results, the vacuum process was considered successful. For this reason, obtaining better data than the leather properties obtained with the conventional method or reaching at least the values achieved in the conventional system with reduced economic burden recipe designs was accepted as a success criterion. Leather color intensity/strength (K/S) and float uptake were based on optimization indicators for vacuum processes.

2.11. Statistical analysis

For all trials 2 sheepskins were taken into the same drum and 3 replicate

productions carried out. Thus, all analyses were carried out on 6 leathers and residual waters (3 pcs-3 replicates). Means and standard deviations of the results were calculated by using an SPSS 15.0 statistical software package.

3. Results and Discussion

In our study, since it was planned to carry out completely water-free production in a vacuum ambient, the vacuum environment and the leathers inside were subjected to trials in water-free applications, but in the absence of water, breaks in the leather fibers were detected with the rotational movement of the cabinet and the mechanical effect. The determinations made as a result of the preliminary trials were useful in shaping the experimental design, and completely waterless productions were abandoned. However, it was planned to investigate the minimum water usage rates so as not to damage the leather fibers.

The dyestuff float uptakes and color intensity/strength values of the leathers obtained as a result of the dyeing processes carried out in the conventional system are given in Table 4. A complete cross-sectional dyeing of the dyed leathers was obtained.

As a result of repetitive and parallel dyeing processes, full cross-sectional dyeing was obtained in each leather, and the average dyestuff bath exhaustion for the conventional system was determined as 71.18%. Leather color intensity values varied depending on the proportion of dyestuff consumed by the leather from the bath. As a result of 71.18% float exhaustion, the average color intensity value was determined to be 12.36 (K/S). Considering the consumption rates in the conventional system, approximately 30% of the dyestuff is disposed of with the remaining bath after the process. This situation brings both a significant loss in terms of dyestuffs, which are the most serious cost burden in leather production, and disadvantages in terms of environmental pollution caused by dyed wastewater. Eliminating these disadvantages under vacuum production

conditions was the aim of the study. In the vacuum cabinet system; it is aimed to use less dyestuff with the realization of high consumption dyeing processes, a more environmentally friendly application thanks to the decrease in the rate of waste dyestuff remaining in the bath, and, at the same time, it is aimed to obtain stronger color intensities on the leathers with high bath consumption. At the point of realizing the process with less dyestuff, it is aimed to obtain at least the color intensity obtained in the conventional system by using less dyestuff with the vacuum cabinet system. For dyeing applications, the vacuum system was used to consume less water as a carrier medium.

Optimization studies for dyeing studies in the vacuum cabinet were started primarily on water usage rates. The results obtained after the productions and analyses are given in Table 5.

As a result of dyeing studies in a vacuum cabinet; the float exhaustion was 92.15% with 80% water use, 91.45% with 50% water use, 90.32% with 25% water use, and 86.56% in water-free (only dye solution) production. Considering that the bath consumption rate in the traditional system is 71.18%, it is seen that a significant bath consumption is achieved in the vacuum environment. It is observed that the color intensity of the leathers increased with the float uptake. As a result of conventional production, the color intensity (K/S) value was determined as 12.36, while in vacuum production, the color intensity varied depending on the use of water. It was observed that even at the lowest water usage rate, the color intensity reached higher levels in the vacuum environment compared to the conventional system. The K/S value was 20.36 with 80% water use, 19.20 with 50% water use, 18.78 with 25% water use, and 16.45 in waterless production. It was decided that the most suitable condition for dyeing studies in a vacuum environment was the dyeing application carried out in anhydrous ambient compared to the values obtained from the conventional method, and the optimization of dyestuff usage ratios was started for the next stage.

Process	Dyestuff float exhaustion (%)	Color strength on leather after dyeing (K/S)
Conventional dyeing process	71.18 $\pm$ 3.28	12.36 $\pm$ 0.57

Table 4. Leather and float analyses after conventional dyeing process

Process	Float exhaustion (%)	Color strength on leather (K/S)
80% water use	92.15 $\pm$ 1.47	20.36 $\pm$ 1.61
50% water use	91.45 $\pm$ 1.77	19.20 $\pm$ 1.13
25% water use	90.32 $\pm$ 2.63	18.78 $\pm$ 2.05
Free of water use (only dissolving water)	86.56 $\pm$ 2.82	16.45 $\pm$ 1.16

Table 5. Leather and float analyses after dyeing processes carried out in a vacuum cabinet in dependence on water usage ratios

The results obtained after the productions and analyses are given in Table 6.

As shown in Table 6, the float uptake was 94.02% with 4% dyestuff use, 95.25% with 3.5% dyestuff use, 93.35% with 3% dyestuff use, and 92.86% with 2.5% dyestuff use. Considering that the float exhaustion ratio in the conventional system was 71.18%, it was seen that higher bath consumptions were achieved even at decreasing dyestuff ratios in the vacuum environment. However, it was revealed that the color intensities of the leathers decreased with decreasing dyestuff ratios, and only 4% and 3.5% dyestuffs gave higher levels of color intensity compared to the conventional system, while 3% and 2.5% dyestuffs gave leathers with lower color intensity. Accordingly, it was determined that the use of 3.5% dyestuff is the optimum parameter for vacuum productions. Thus, it turns out that the use of dyestuff can be reduced by 30% in vacuum ambient compared to the conventional system. Finally, optimization of the dyeing/ process time was carried out. The results obtained after the productions and analyses are given in Table 7.

As shown in Table 7, the float exhaustion at the end of the 45-minute process was determined as 94.05%, at the end of the 30-minute process as 92.02%, and after the 15-minute process as 80.11%. Considering that the float exhaustion rate in the conventional system was 71.18% and the K/S value 12.36, it was revealed that higher color intensity was

achieved at the end of only 45 and 30 minutes of the processes compared to the conventional method, and the 15-minute dyeing period yielded leather with lower color intensity. Although higher float exhaustion was achieved in a vacuum ambient with a 15-minute dyeing time compared to the conventional system, a lower K/S was obtained because of the lower dyestuff ratio used. Accordingly, it was decided to determine the 30-minute dyeing time as the optimum parameter for vacuum production. Thus, it turns out that the dyeing time could be reduced by 50% compared to the conventional method in a vacuum ambient. It was observed that full cross-section dyeing of the leathers was achieved for each dyeing study. When organoleptic evaluations such as the fullness and handling/touch of the leathers obtained were made, it was determined that they showed very similar properties to the leathers produced with the conventional system. Prokein et al. (2023) indicated that it was possible to produce waterless leather and that an almost 100% float uptake could be achieved with the effect of the pressure ambient in their leather dyeing studies in supercritical pressure conditions. [31]. In our study, promising and successful results were also achieved with vacuum processes for sustainable leather production.

The uptake of the dyestuff by collagen matrix is demonstrated with Figure 3 as computer simulation.

Process	Float exhaustion (%)	Color strength on leather (K/S)
4% dyestuff	94.02 ± 2.42	15.49 ± 1.90
3.5% dyestuff	95.25 ± 2.91	12.41 ± 1.29
3% dyestuff	93.35 ± 4.30	11.32 ± 1.37
2.5% dyestuff	92.86 ± 3.19	9.45 ± 0.76

Table 6. Leather and bath analyses after dyeing processes carried out in a vacuum cabinet in dependence on dyestuff usage ratios

Process	Float exhaustion (%)	Color strength on leather (K/S)
45 mins	94.05 ± 2.87	15.18 ± 1.52
30 mins	92.02 ± 1.96	12.38 ± 2.39
15 mins	80.11 ± 3.69	10.77 ± 1.10

Table 7. Leather and float analyses after dyeing processes carried out in a vacuum drum in dependence on the process time

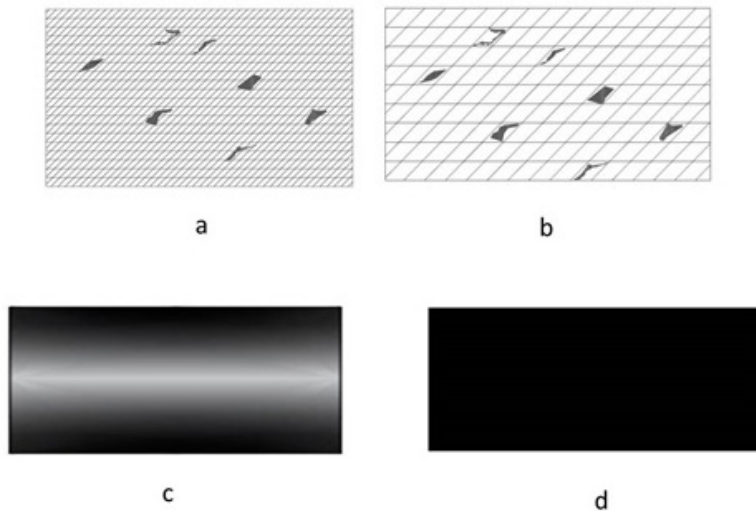


Fig. 3. Opened collagen matrix by vacuum and full dyeing of leather

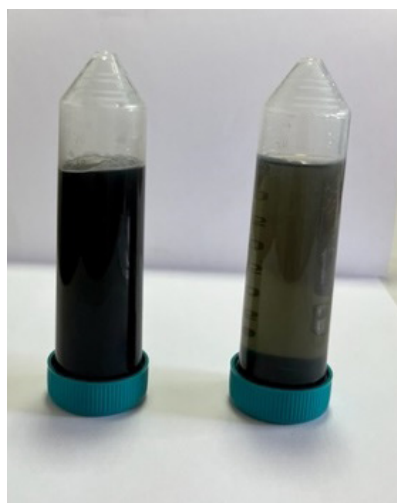


Fig. 4. Residual floats of conventional dyeing (left) and vacuum dyeing (right)

Figure 4 shows the residual floats after conventional dyeing and after production in vacuum ambient with optimized parameters.

The color difference of the floats in Figure 5 shows the differences in exhaustions. After the dyeing studies with acid dyestuff, it was aimed to investigate the behavior of metal complex dyestuff under both conventional and optimized vacuum process conditions, for the purpose of which the same dyeing recipe was tested by changing only the type of dyestuff. Moreover, cotton dyeing was also applied under a vacuum with half water according to the conventional system. Table 8 presents the results of leather analyses with metal complex dyestuff and cotton dyeing results obtained using the conventional process and vacuum ambient.

Conventional dyeing with acid dyestuff has a float exhaustion of 71.18% and a K/S value of 12.36. As a result of the conventional process with metal complex dyestuff, a float exhaustion of 74.05% was achieved and the K/S value was found to be 14.81. These values are higher than for the dyeing processes performed with acid dyestuff. Again, in the vacuum system these values were exceeded; the float uptake was determined as 96.79% and the K/S color intensity as 15.23. It should be noted here that higher color intensity was achieved with lower dyestuff (3.5%), less water use (only dissolving the dyestuff) and a shorter process time (30 minutes) under optimized conditions in a vacuum. Again, for cotton dyeing, while 92.21% float uptake was achieved in the conventional system with hypericum dye, with the exhaustion reaching 98.76% with less water under a vacuum, and the K/S value increasing from 8.91 to 9.06.

In the last stage, the rubbing fastness properties of leather and cotton products dyed with the optimized vacuum cabinet parameters and, leather and cotton products dyed with the conventional system were compared. It was examined whether dyestuff was sufficiently bound to the surface of the material in vacuum ambient. Analyses were performed on acid dyed leather, metal complex dyestuff treated leather and hypericum treated cotton. Table 9 shows the results of rubbing fastness analyses of leathers and cottons dyed in a vacuum and by the conventional method.

When Table 9 is examined, it is seen that the rubbing fastness values of the leathers dyed with both acid dye and metal complex dye in vacuum ambient are equivalent to the values of the leathers produced with the conventional system (4/5). For cotton dyeing, the fastness to rubbing values of the products dyed with the conventional and vacuum systems were also found to be same (4). Therefore, as a result of the dyeing processes carried out in the vacuum system, it was concluded that there was no problem in terms of the binding of dyestuff to fibre type materials in the ambient where less water was used.

Process	Float exhaustion (%)	Color strength (K/S)
Conventional system (metal complex dye, leather)	74.05 ± 4.47	14.81 ± 3.35
Vacuum system (metal complex dye, leather)	96.79 ± 2.24	15.23 ± 0.74
Conventional system (hypericum dye, cotton)	92.21 ± 1.93	6.91 ± 1.23
Vacuum system (hypericum dye, cotton)	98.76 ± 2.01	7.06 ± 1.19

Table 8. Results of leather dyeing with metal complex dyestuff and cotton dyeing carried out in a conventional and vacuum cabinet

Process	Rub fastness
Conventional system (acid dye, leather)	4/5
Conventional system (metal complex dye, leather)	4/5
Conventional system (hypericum dye, cotton)	4
Vacuum system (acid dye)	4/5
Vacuum system (metal complex dye)	4/5
Vacuum system (hypericum dye, cotton)	4

Table 9. Rubbing fastness values of dyed samples

4. Conclusions

The success criteria for vacuum dyeing processes focused on achieving high float exhaustion, reducing dyestuff usage, and shortening dyeing times. These objectives were successfully realized. The primary goal was to enhance color intensity within the matrix by increasing the float uptake as compared to conventional methods. While similar or slightly improved color intensities were achieved, this was accomplished with reduced water consumption, shorter processing times, and lower dye usage. Despite higher float uptake, the reduction in dye concentration resulted in color intensities comparable to those of traditional methods.

Throughout the experiments, maintaining color intensity values equivalent to or better than those obtained with conventional systems remained a key objective, with no compromise on quality. The principle of meeting or exceeding the standards of classical methods was upheld in all vacuum system productions. By comparing vacuum system outcomes with those of conventional methods, the success criteria and optimal vacuum production conditions were effectively identified. Achieving all target values within a vacuum atmosphere marked the study's success.

The findings demonstrate that dyeing processes with higher exhaustion, significant time savings, and reduced water and dyestuff consumption are achievable under vacuum conditions. Vacuum dyeing proved successful and advantageous for both leather and cotton products, with no issues observed in the binding of dyestuffs to fiber materials. As sustainable production systems gain prominence, these promising results suggest substantial potential for industrial adoption. Various initiatives are being planned to capitalize on these findings and advance sustainable dyeing practices.

Acknowledgement

The authors gratefully acknowledge the financial support from “The Scientific and Technological Research Council of Turkey” (TUBITAK – Project number: 122M048).

References

- Covington, A.D. Tanning Chemistry, The Science of Leather, The University of Northampton, Northampton, UK, 2009.
- Deng, W., Chen, D., Huang, M., Hu, J., Chen, L. Carbon dioxide deliming in leather production: A literature review. *Journal of Cleaner Production*, 2015; 87: 26-38.
- Simeonova, L.S., Dalev, P.G. Utilization of a leather industry waste. *Waste Management*, 1996; 16: 765-769.
- Kanagaraj, J., Velappan, K.C., Chandra Babu, N.K., Sadulla, S. Solid wastes generation in the leather industry and its utilization for cleaner environment - a review. *Journal of Scientific & Industrial Research*, 2006; 65: 541-548.
- Hu, J., Xiao, Z., Zhou, R., Deng, W., Wang, M., Ma, S. Ecological utilization of leather tannery waste with circular economy model. *Journal of Cleaner Production*, 2011; 19: 221-228.
- Leather Working Group (LWG), Improving Environmental Stewardship, <https://www.leatherworkinggroup.com/who-we-are/un-sdgs>.
- John, G. Possible Defects in Leather Production: Definitions, Causes, Consequences, Remedies and Types of Leather”, Lampertheim, 379p, ISBN: 3-00-001555-8, 1996.
- Kanagaraj, J., Panda, R.C., Senthilvelan, T., Gupta, S. Cleaner approach in leather

- dyeing using graft copolymer as high performance auxiliary: Related kinetics and mechanism. *Journal of Cleaner Production*, 2016; 112: 4863-4878.
9. Mia, M.A., Refat, E.A., Nurnabi, M., Alam, M.Z. Eco-friendly leather dyeing using ultrasound technique. *Journal of the American Leather Chemists Association*, 2020; 115(6): 199-206.
 10. Halilovic, N., Krdzalic, E., Basic, A., Dacic, M., Avdic, N. Electrochemical treatment of leather industry wastewater. *Glasnik Hemicara I Tehnologa Bosne I Hercegovine*, 2017; 48: 15-20.
 11. Jallouli, S., Wali, A., Buonerba, A., Zarra, T., Belgiorno, V., Naddeo, V., Ksibi, M. Efficient and sustainable treatment of tannery wastewater by a sequential electrocoagulation-UV photolytic process. *Journal of Water Process Engineering*, 2020; 38: 101642.
 12. Azhar, A., Shaikh, I.A., Abbasi, N.A., Firdous, N., Ashraf, M.N. Enhancing water efficiency and wastewater treatment using sustainable technologies: A laboratory and pilot study for adhesive and leather chemicals production. *Journal of Water Process Engineering*, 2020; 36: 101308.
 13. Onem, E., Gulumser, G., Akay, S., Celiktas, O.Y. Optimization of tannin isolation from Acorn and application in leather processing. *Industrial Crops and Products*, 2014; 53: 16-22.
 14. Onem, E., Gulumser, G., Renner, M., Oelbermann, A.L., Celiktas, O.Y. Pressurized fluid extraction (PFE) of valonea tannin with binary H_2O-CO_2 and ternary $H_2O-CH_3OH-CO_2$ systems and phase equilibrium studies. *Separation and Purification Technology*, 2015; 146: 101-107.
 15. Shirmohammadli, Y., Efhamisisi, D., Pizzi, A. Tannins as a sustainable raw material for green chemistry: A review. *Industrial Crops and Products*, 2019; 126: 316-332.
 16. Yorgancioglu, A., Onem, E. New lubricating natural polymer for water-repellent upper leather production. *Annals of the University of Oradea-Fascicle of Textiles, Leatherwork*, 2020; 21(1): 163-168.
 17. Onem, E., Renner, M., Prokein, M. Green separation and characterization of fatty acids from solid wastes of leather industry in supercritical fluid CO_2 . *Environmental Science and Pollution Research*, 2018; 25(22): 22213-22223.
 18. Yorgancioglu, A., Onem, E., Basaran, B. Preparation, characterization and application of lubricating protein filler for sustainable leather production. *Journal of Natural Fibers*, 2020. 18(11): 1946-1956.
 19. Aquim, P.M., Hansen, E., Gutterres, M. Water reuse: An alternative to minimize the environmental impact on the leather industry. *Journal of Environmental Management*, 2019; 230: 456-463.
 20. Basaran, B., Yorgancioglu, A., Onem, E., Bitlisli, B.O. Performance assessment of green practices in liming with reductive potential chemicals for environmental sustainability. *Revista Leather and Footwear Journal*, 2019; 19(3): 177-184.
 21. Marsal, A., Celma, P.J., Cot, J., Cequier, M. Supercritical CO_2 extraction as a clean degreasing process in the leather industry. *Journal of Supercritical Fluids*, 2000; 16: 217-223.
 22. Renner, M., Weidner, E., Björn, J., Helmut, G. Free of water tanning using CO_2 as process additive-An overview on the process development. *The Journal of Supercritical Fluids*, 2012; 66: 291-296.
 23. Sathish, M., Madhan, B., Sreeram, K.J., Rao, J.R., Nair, B.U. Alternative carrier medium for sustainable leather manufacturing: A review and perspective. *Journal of Cleaner Production*, 2016; 112: 49-58.
 24. Prokein, M., Renner, M., Weidner, E., Heinen, T. Low-chromium- and low-sulphate emission leather tanning intensified by compressed carbon dioxide. *Clean Technologies and Environmental Policy*, 2017; 19: 2455-2465.
 25. Prokein, M., Renner, M., Weidner, E. Fast high-pressure tanning of animal skins by accelerated chromium sulphate complexation. *Clean Technologies and Environmental Policy*, 2020; 22(5): 1133-1143.
 26. Gudro, I., Valeika, V., Sirvaityte, J. Short term preservation of hide using vacuum: Influence on properties of hide and of processed leather. *Plos One*, 2014; 9(11): e112783.
 27. Piccin, J.S., Gomes, C.S., Feris, L.A., Gutterres, M.. Kinetics and isotherms of leather dye adsorption by tannery solid waste. *Chemical Engineering Journal*, 2012; 183: 30-38.
 28. Sabyrkhanova, S., Efendioglu, N.O., Yeldiyar, G., Bitlisli, B.O. Investigation of dyeing, antibacterial and antifungal properties of blended fabrics treated with plant-based dyestuffs and mordants as shoe materials. *Coloration Technology*, 2024; 140(4): 598-611.
 29. Needles, H.L. Textile Fibers, Dyes, Finishes and Processes, Noyes Publications, USA, 1986.
 30. TS EN ISO 11640. Leather- Tests for colour fastness- Colour fastness to cycles of to-and-fro rubbing. Turkish Standards Institution, 9p, 2013.
 31. Prokein, M., Hoffmanns, D., Renner, M. Determination of dye uptake in leather coatings for waterless leather dyeing by $ScCO_2$ impregnation. *The Journal of Supercritical Fluids*, 2023; 198: 105933.