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INVESTIGATING PROCESS WATER PROPERTIES FROM DIFFERENT LEATHER INDUSTRY ZONES OF TURKEY

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Abstract: *All the physical and chemical processes in leather production from soaking till dyeing-fatliquoring stages take place in water as medium. Water is also used as carrier for the chemicals in subsequent finishing processes. In leather production many kinds of chemicals are being used in processes. These chemicals are penetrated and chemically bounded to leather collagen in water medium. Therefore, the nature and quality of the process water used in leather industry is crucial. The pH, calcium and magnesium salts, other inorganic salts and organic matters usually affects the chemical reactions, especially in bating, pickling, tanning, dyeing and fatliquoring stages. Thus, determination of the properties of process water used in industry and reveal their affect in leather production is very important. In the present study process water samples were taken from leather industrial zones located in Izmir, Istanbul, Usak, Gerede, Corlu and Bursa regions in Turkiye. Subsequently, the water parameters such as; pH, conductivity, total hardness, permanent hardness, temporary hardness, chloride, nitrate levels as well as the inorganic constituents i.e. natrium, potassium, magnesium, lead, manganese, iron, aluminum, chromium, zinc, copper and nickel were determinated. In this way the properties of the process water used in different leather industrial zones were documented and their possible effects on the regional leather production processes and leather quality have been discussed.*

Key words: *Leather industry, leather production, process water, water quality, water hardness, ICP-OES.*

1. INTRODUCTION

Water is one of the major inputs of leather industry [1]. Almost all chemical reactions in leather production take place in water as medium. All the chemicals used in processes have to penetrate into the three-dimensional skin/hide matrix. Therefore, a transporting medium is required to carry the chemicals into the skin/hide matrix [2-5]. In conventional leather manufacturing, water is used as the transporting medium to carry the chemicals into the matrix and also as a medium for the reaction between the chemicals and the functional groups present in skin matrix [6]. Therefore, water plays an important role in leather manufacturing.

The quality and properties of water have effect on the final leather products. Therefore, the process water is expected to fulfill some requirements. The water used in the production has to be periodically controlled in terms of qualitative, organoleptic and quantitative methods. In this manner, the color, pH, hardness, turbidity, organic and inorganic constituents of the water have to be determined [7]. The general requirements for process water to be used in leather production are summarized in Table 1 [8].

Table 1. *General requirements for water used in leather manufacturing [8]*

Parameter	Required level	Parameter	Required level
Appearance	Clear, no suspended solids	Nitrate	30 mg/L
Temperature	≤ 20°C	Nitrite	n.d
pH	7.0 ± 0.5	Ammonia	n.d
Bacteria	< 200 count in 1m^3	Fe	< 0.1 mg/L
Total hardness	Max 15 °A	Mn	< 0.05 mg/L
Temporary hardness	Max 12 °A	Pb	< 0 mg/L
Salts (Chloride and sulfate)	Max. 100 mg/L	Phosphate	n.d
Sulfate ion	20 mg/L	Free carbon acid	n.d
Chloride ion	30 mg/L	$KMnO_4$ consumption	2-5 mg/L

Whilst the role of water in leather production is so crucial, the quality parameters of process water are usually not investigated. Hence, the penetration efficiency and the reaction ability of the chemicals through the skin/hides are highly affected by the quality and constituents of process water. The number of studies investigated the properties of process water and their effect on leather quality is very limited. Among them the most comprehensive one was reported by Devikavathi and Muralidharan [9]. They showed the effect of different hardness and chloride content of water on some leather quality parameters. In their results they revealed that chloride content up to 20.000 ppm and high hardness values could be tolerated in soaking stage while the chromium uptake was significantly affected in tanning stage. They also observed increased chromium content in wastewater effluents. In another study Devikavathi et al. [10] examined the effect of water with different hardness level on the dyeing properties of leathers. In their study they showed that the hardness level of water affected the shades of leather color. In a similar study Hauber ve Germann [11] the effect of water hardness level on dyeing properties of leathers was also shown. They studied different types of dyestuff and compared the color properties of leathers. In their results they also pointed out the significant influence of water hardness on color shades of leathers. Some other researchers also mentioned about the importance of water properties in leather production and their possible effects on leather quality [12,13,14].

The characteristics of the water differ due to the region where industry is located. Thus, there might be quite differences of water quality between different regions. Although there is a few individual companies, most of the leather companies are located in certain organized industrial zones in Turkey such as Istanbul-Tuzla, Izmir-Menemen, Usak, Manisa, Bolu-Gerede, Tekirdag-Corlu, Bursa. In the present study process water samples were taken from these industrial zones and their parameters such as pH, hardness, conductivity, chloride, nitrate content were investigated. Many inorganic constituents including trace elements like Na, K, Ca, Mg, Pb, Mn, Fe, Al, Cr, Zn, Cu, and Ni were also determined by using ICP-OES. Therefore, many important quality parameters of the process waters from different leather industrial zones were shown comparatively and their possible effects on leather quality were discussed.

2. MATERIAL AND METHODS

2.1 Material

In this study, ten water samples obtained from six different leather industrial zones in Turkey were used as material of the study. The sources of water samples are given in Table 2. The samples were coded as Wx for water sample number(x), following two letters for first two letters of city, S for source water, G for ground water and C for city water.

Table 2. *The codes and sources of the water samples*

Code	Water Source
W1GES	Spring Water - Gerede Leather Specialized Organized Industrial Zone, Bolu
W2GEG	Ground Water - Gerede Leather Specialized Organized Industrial Zone, Bolu
W3BOG	Ground Water - Bursa Specialized Leather Industrial Zone, Bursa
W4BOC	City Water - Bursa Specialized Leather Industrial Zone, Bursa
W5ISC	City Water - Istanbul Leather Organized Industrial Zone, Istanbul
W6USC	City Water - Usak Leather (Mixed) Organized Industrial Zone, Usak
W7COG	Ground Water - Corlu Leather Specialized and Mixed Organized Industrial Zone, Tekirdag
W8COG	Ground Water - Corlu Leather Specialized and Mixed Organized Industrial Zone, Tekirdag
W9COG	Ground Water - Corlu Leather Specialized and Mixed Organized Industrial Zone, Tekirdag
W10IZC	City Water - Izmir Free Zone, Izmir

2.2 METHOD

Conductivity and salinity of water used in the leather production process were determined by using YSI brand 30 model Conductivity meter (USA). The pH values were measured with Metrohm brand 827 model pH Meter (Switzerland). Determination of chloride (Cl^-) content of the water was done according to potentiometric titration method by Metrohm brand 848 titrino plus model Potantiometer (Switzerland). Determination of hardness in water by titration was made according to ASTM D1126-17 test method [15]. The nitrate (NO_3^-) content in process water was examined according to spectrophotometric method in 220 nm by Shimadzu brand 1601 model UV Spectrophotometer (Japan). Trace and basic elements in were detected by using PerkinElmer brand Optima 2100 DV model ICP-OES instrument (USA) equipped with WinLab32 software for ICP according to EPA method 6010D [16].

3. RESULTS AND DISCUSSIONS

When conductivity and salinity values of process waters taken from different regions were investigated, it was seen that especially W2GEG and W10IZC samples had fairly high salinity and thus conductivity values. A high content of electrolytes in the float can affect the solubility of most dyes, with direct consequences on levelness, penetration and fastness and use of unstable fatliquors can lead to precipitation of fat emulsion [17]. All process water samples' pH values fit well to recommended 7.0±0.5 pH for leather production (Table 3).

Table 3. Conductivity, pH, chloride, nitrate, nitrate nitrogen contents data of process waters

Water Sample	Conductivity (μS) (25ºC)	Salinity (gL^{-1})	pH	Chloride (Cl^-)	Nitrate Nitrogen (NO_3^-N)	Nitrate (NO_3^-)
W1GES	372	0,2	7,3±0,1	10±1	2,7±0,3	11,7±1,2
W2GEG	3572	2	6,7±0,1	910±39	5,1±0,4	22,7±1,6
W3BOG	813	0,4	7,4±0,1	117,6±2,1	2,0±0,4	8,8±1,8
W4BOC	849	0,8	7,4±0,1	50,9±0,7	17,4±0,9	76,9±4,2
W5ISC	1295	0,6	6,8±0,1	191,8±3	18,1±1,1	80,2±4,9
W6USC	732	0,4	7,0±0,1	28,7±0,3	16,9±1,0	74,6±4,9
W7COG	559	0,5	6,9±0,1	138,5±2,3	9,7±0,9	42,7±4,3
W8COG	1551	0,7	6,5±0,1	208,8±3	15,0±1,2	67,3±5,2
W9COG	683	0,3	6,8±0,1	109,8±3	1,5±0,3	6,8±1,4
W10IZC	2378	1,2	6,8±0,1	498±19	16,1±1,2	71,0±4,9

Evaluating chloride (Cl^-) content results of the process waters (Table 3); it was detected that except W1GES and W6USC samples, rest of the water samples had chloride contents higher than recommended value (30 mg L^{-1}) for leather process water cloride content. Within them particularly W2GEG and W10IZC water samples had fairly high chloride contents. Chlorides, sulphates from permanent hardness constituents can cause a retardation of reaction or precipitations only in higher concentrations. They may also lead to the destruction of cement pipes or cement vessels by corrosion[17].

Examining the Table 4 in which hardness values of process waters are given, it is seen that W10IZC, W2GEG and W8COG samples were in very hard waters group, W1GES was in medium hard waters and rest of the samples were in hard waters group. When conductivity and salinity values were recalled, as expected they were in accordance with the hardness values. Use of waters with high carbonate hardness, the poorly soluble calsium carbonate; can lead to precipitations, color changes, retarded reactions and staining in many processes of leather production such as soaking, liming, rinsing and washing floats, bating, manufacture of vegetable tanning agents, during vegetable tanning, dyeing and fatliquoring. It also causes dangerous scale formation in steam boilers [17, 18].

Process water used in tanneries has direct and indirect effect on dyeing and fatliquoring processes. For example use of very soft waters result with flat leathers. High temporary hardness has negative effect on fatliquoring and dyeing processes, and causes cloudy lime stains. Dyestuffs are also very sensitive to calcium in water; it may lead to precipitations of dyes [13]. In fatliquoring process especially fatliquors with low stability, hard water prevents and breaks emulsions. This also can lead to precipitation of fat emulison. Especially when natural fats which were stored for long time are used, hard water causes calcium soaps [7].

Considering water hardness recomended for leather processing (slightly hard 14,5-21,5 FS°) [8]; except W1GES water sample, all other water samples are not suitable for directly use and a necessity for softening or purifying before using in processes is appeared.

Table 4. *Hardness data of process waters*

Water Sample	Total Hardness (°fH)	Permanent Hardness (°fH)	Temporary Hardness (°fH)
W1GES	18,8±0,2	6,0±0,2	12,8
W2GEG	49,6±0,3	10,9±0,2	38,7
W3BOG	24,2±0,3	10,6±0,2	13,6
W4BOC	31,4±0,3	6,6±0,2	24,8
W5ISC	23,0±0,3	12,3±0,2	10,7
W6USC	23,2±0,2	20,0±0,2	13,2
W7COG	30,4±0,3	23,4±0,3	7,0
W8COG	44,4±0,4	23,8±0,3	20,6
W9COG	22,6±0,3	7,8±0,1	14,8
W10IZC	53,7±0,5	23,0±0,3	30,7

From the investigation of heavy metal contents of the water samples (Table 5); in none of them noticable amounts of lead (Pb), aluminium (Al), copper (Cu) and nickel (Ni) ions could be detected. Only in W8COG sample approximately 7 ppm zinc (Zn) was found. Iron (Fe) content for leather process water is recommended to be <0.1mgL^{-1}. From the investigation of the iron (Fe) content results of the samples; it was seen that in the mean time W1GES and W2GEG samples were having fairly high iron content, W8COG and W7COG samples' iron contents were over the recomended value. Recommended value for manganese (Mn) content for leather processing water is<0.05 mgL^{-1}. Considering the manganese content results of water samples it was seen that W5ISC, W1GES and W2GEG samples were containing respectively 10 and 2 times of recomended value. Free metal salts such as chromium, aluminum, zirconium or lime components may react with unstable fats, natural oils or content of natural fats; and can cause soap formation in fatliquoring process. Iron content in the case of vegetable or some synthetic tanning or retanning processes result in grey or blue staining over the entire surface of the leather or in patches. This also results bluish-grey blunt dyeing [17]. Furthermore metal contents in water can lead to unsolubility problems in leather dyeing and colour shifts in metal complex dyes.

From the evaluation of alkali and alkaline earth metal contents of water samples such as natrium (Na), potassium (K) and magnesium (Mg); it was found out that W1GES, W1GEG and W10IZC samples were very rich from these ions. W5ISC and W10IZC water samples followed them with high natrium (Na) and potassium (K) contents. Also, W8COG sample was containing remarkably high amount of calcium. Calcium and magnesium salts react with vegetable tanning agents or also synthetic phenolic tanning agents to produce insoluble precipitation compounds. Lead to stains in leather which cannot be dyed, and also to crackiness of the grain in these parts [17].

Table 5. *Inorganic constituents of water samples*

Water Sample	Na	K	Ca	Mg	Pb	Mn	Fe	Al	Cr	Zn	Cu	Ni
W1GES	279.4	18.04	278.4	75.45	n.d.	0.101	2.774	n.d.	0.077	n.d.	0.013	n.d.
W2GEG	273.4	15.36	248.7	68.84	n.d.	0.151	2.312	n.d.	0.025	n.d.	0.011	n.d.
W3BOG	58.46	5.181	34.20	26.57	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.015	n.d.
W4BOC	45.66	5.290	48.66	38.25	n.d.	n.d.	n.d.	n.d.	n.d.	0.52	0.017	n.d.
W5ISC	141.5	15.05	59.98	10.37	n.d.	0.471	0.09	n.d.	0.002	0.04	0.015	0.037
W6USC	12.55	4.518	49.39	33.88	n.d.	n.d.	n.d.	n.d.	0.003	n.d.	0.018	n.d.
W7COG	54.74	3.864	74.98	17.09	n.d.	n.d.	0.1	n.d.	n.d.	0.298	0.019	n.d.
W8COG	68.4	4.991	118.7	25.85	n.d.	0.05	0.242	n.d.	n.d.	6.993	0.014	n.d.
W9COG	27.58	3.694	55.49	13.82	n.d.	0.033	0.492	n.d.	n.d.	0.162	0.016	n.d.
W10IZC	215.9	19.71	164.8	31.97	n.d.	n.d.	0.006	n.d.	0.083	n.d.	0.013	n.d.

4. CONCLUSIONS

Water, one of the main inputs of leather processing, may have more or less impact on chemicals and processes used. Therefore, process waters should have certain criteria not to cause any problems in processes and to assure quality of final products. In this study properties of water samples from different industrial zones were examined and findings were discussed with possible problems based on literature. It was concluded that none of the water samples was appropriate for direct use in leather processes. Use of these process waters can lead to precipitations, color changes, retarded reactions and staining in many processes of leather production such as soaking, liming, rinsing and washing floats, bating, tanning, dyeing and fatliquoring. Therefore, waters available in Gerede, Bursa, Istanbul, Corlu, Usak and Izmir leather industrial zones should be softened and purified before using in leather processing to avoid problems and obtain quality.

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