Water Reuse Strategy in Leather Tannery Process

Aditya Wahyu Nugraha, Ono Suparno, Nastiti S Indrasti

***Abstract:** In leather tannery process, there are some steps which aqueous medium to produce leather. It affects to environment like much amount of wastewater which discharges in the environment. All of the process to produce leather, water is used as reaction medium of chemical material and skins to remove some component of skins are not used to produce leather in the leather tanning process. The aim of the research is to reduce water usage and wastewater with water reuse method in some steps of the leather tanning process. Water reuse application is evaluated such as pollutants in wastewater, water input and water output, and leather (wet blue) characterization. The results showed that water reuse application increased pollutants in wastewater, but it could reduce amount water usage as much as* **35.29%** *and wastewater was* **36.11%**. *The payback period of water reuse was* **5.56** *month. In addition, leather (wet blue) which was produced meet with Indonesian standard quality of jackets.*

***Index Terms*:** *Tannery Process; Water Reuse; Leather (Wet Blue).*

I. INTRODUCTION

Problems and environment handling was described in Al-Qur'an. Some surah in Al-Qur'an told about "And don't you make corruption upon the earth after Allah fix it" (Al-A'raaf: 56) and "Corruption has appeared in land and sea that was caused by people, Allah wants they to feel the consequences of their do, to get them back on the right path (Ar-Rum: 41). Thus, improvements to preserve the environment, it must be solved by their self[7].

The development of leather industries in Indonesia was passably. That industries converted raw hides or skins to leather. After the tanning process, leather will resist from chemical material, biology, physic and mechanic. The process of converting hides to leather give benefit to the stakeholder was joined in this industries. In addition, the tanning process produced a lot of waste. It was solids waste, wastewater, and emission[1].

One of problems in leather processing was produced wastewater. It was caused by quantity of wastewater and high content of pollutant in wastewater[2]. The amount of water usage correlated with amount of wastewater in leather process (1). According (2), total amount of wastewater was 45 – 50 m3 per tons raw hide. Moreover, it will be negative impact for environment. There were toxic and carcinogenic chemical was used in leather process too.

Environment issues that occur in leather industries was caused by poor handling along process production. So, it was need proper handling to increase environmental performance in leather industries. There was method to reduce pollution like reuse wastewater which was produced along leather process. Al-Qur'an said in surah Al An'am: 141, "And be not excessive[3]. Indeed, Allah does not like those who commit excess". That was warning to leather industries to efficiency in all of resource usage. Some research did about reuse wastewater in leather industries such as Na[5], and Gutterres et al (2010). (3) did reuse wastewater in unhairing/liming steps. It affected to decline of chemical material and water usage. And then, wastewater formed could use as long as four times and producing leather was not significant with fresh water. Based on (4), that reuse wastewater in predeliming and deliming/bating steps could reduce water usage and produced leather which similar with fresh water. Wastewater from presoaking/soaking steps could use to others presoaking/soaking [6].In this research will use wastewater washing that formed in presoaking/soaking, liming, and deliming and bating.

II. LITERATURE REVIEW

A. Leather process

Leather industry is an industry which convert raw hides / skins to leather. It resist with chemical material, biology, physic and mechanic. The common product is leather, but there are some by product. There are four process to get leather. It are pretanning (beamhouse), tanning, posttanning and finishing (5).

Pretanning or beamhouse is the process which produced a lot of wastewater along processing. The objective of this process was preparation raw hides or skins to pickle pelt which ready to tanning process. In pretanning or beamhouse process are some steps to get pickle pelt, such as soaking, liming, deliming, bating and pickling (Covington 2009). In addition, there were mechanic steps to support it like fleshing, and or splitting.

1) Soaking.

The materials are used in this steps such as water, salted hides / skins, sodium hydroxide (NaOH), sodium bicarbonate, degreasing agent, and antibacterial. The salted content in raw material varying between 25 – 35% based on weight of raw material. The first step on this process is to remove salt in hides or skins[8]. In addition, this step also remove others material like blood, dirt, dung, and some proteins (6). The others aim of soaking is water rehydration in

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pelt (5). Water usage in soaking is 6,000 – 9,000 L per tons salted hides / skins. The characterization of wastewater in soaking is slightly alkaline.

2) Liming / unhairing

Liming do after soaking. The objectives of liming are to remove hair on the pelt, to remove proteins non collagen to open up fiber structure in the pelt (7). Lime, degreasing agent, antibacterial and sodium sulfide are materials which used in process. In the process, most of protein non collagens will remove (5). Water usage in the process is 4,000 – 6,000 L per ton hides (6). In wastewater there are sludge content and toxic chemical such as sodium sulfide. Lime was caused wastewater characterization is alkaline.

3) Fleshing and splitting

The objective of fleshing and splitting are to remove flesh layer which remain in pelt and subcutis layer. According (7), fleshing do in machine to remove fatty tissue. Input in this step is pelt from liming process. This step is one of steps that produce solid waste.

4) Deliming and bating

Deliming targets to eliminate lime content in the pelt and to neutralize pelt from alkaline condition along liming process (5). The pH value of aqueous approximately is 8.5 (7). The lime can inhibit tanning process. Commonly, Ammonium sulfate is chemical material which used to do it. This step integrate with bating process, so there isn't wastewater. Wastewater will discharge after Bating steps. Bating step is enzymatic reaction. The aims of bating are to remove scud, short hair on the pelt and to upgrade pelt characterization[15]. Bating is also to remove protein no collagen which remain in pelt, so fiber tissue of collagen will more open up. In the deliming and bating process are formed wastewater. In that steps used water as much as 4,500 to 5,000 L per tons hides / skins. The characterization of wastewater is slightly alkaline[16][17][18].

5) Pickling

According (6), pickling is conditioning process after deliming and bating to tanning process. Pelt in pickling step are treated by brine solution to prevent acid swelling. Sulphuric and formic acids is caused acid solution in pickling step (7). In this step pH of pickled pelt is 2.5 – 3 (5). It are caused tanning process is did in low pH and can extend the shelf life of pickle pelt. Chrome will easy to penetration in Collagen tissue at the pH. Water usage in the pickling step is 800 – 1,000 L per tons hides / skins (6).

Tanning is core process that impacted pelt to be resistant by chemical, physics, mechanic and biology. Commonly, chromium salt was used as tanning chemical material. Perhaps 90% of leather industries do it (5). There are others method for tanning process like vegetable tanning, mineral tanning, aldehyde tanning and oil tanning (6). In this way, some industries used pickling solution directly and then add some material like chromium sulfate, sodium format, and sodium bicarbonate. After ascertaining sufficient chrome penetrate to collagen tissue, the pH of solution is raised to 3.8 – 4 (6). Water usage in this process is 1,500 – 2,000 L per ton hides / skins. In addition, the process produce wastewater that toxic content such as chrome.

Retanning, dyeing, and fatliquoring are part process in posttaning. Before it, there are some steps such as wetting back and neutralization. The objectives of retanning is to accomplish a lack in the tanning process like fullness of leather, to modify the properties and performance of the leather [9][10][11]. The material which used in retanning is depending upon the characteristic desired of final leather. Various of retanning materials are used such vegetable tannin (mimosa, quebracho, gambir and others), chrome syntans (to complete tanning process), acrylic and others [12][13]. Dyeing is did after re-tanning. Before Dyeing, some industries discharge water in the drum of re-tanning (7), but others industries used it into dyeing step. According (6), dyestuff materials consider relation of re-tanning and fat liquoring step. Commonly dyestuff is anionic, but there is cationic too. Fat liquoring is to soften the leather, but the main function fat liquoring is to prevent the fiber of leather resticking along drying process[14]. Commonly, retanning, dyeing, and fat liquoring are did together. In this steps was need water as much as 2,500 – 3,000 L per tons of tanned leather (6).

Finishing is last in the leather process. It process isn't much using water. There are some steps in finishing, its are stacking, toggling, embossing, buffing, and spraying or coating. Embossing and buffing is option steps in industries. It was depended finish product of leather.

B. Water Reuse

Some definition is used to explain water reuse such as water reclamation and water recycling (8). Water reuse was defined as the effort to reuse the water because it will give many benefits directly (9). Based on (10), water reuse have a general definition. Water reuse was the using water which has been used at the process to give the effects directly such as irrigation and cooling [19]. Water reuse is rarely to applied in leather industry. Generally, industry discharge the water as the result of treatment of wastewater. Small scale industry did not have wastewater treatment installation, so they discharge the wastewater directly to environment. Water reuse can be used to reduce the waste water from industry[20].

Based on (11), there are two kind of reuse have been developed and applied in the world:

1) Potable Uses

- Direct, use of reclaimed water to increase drinking water supply following high levels of treatment.
- Indirect after coming through the natural environment.

2) Non – potable Uses

- Agriculture irrigation
- Take for irrigating parks, public places of forestry
- Take for aquaculture
- Aquifer refillable
- Take in industry and urban habitation

III. METHODOLOGY

The chemical material that was used in this research were conventional chemical which common in leather industries (Table I). Goat skins was used as raw material to convert leather. Research did in laboratory scale and used multifunction drum. This research only was did till tanning steps (Table I). Weight of skins that used was 1 kg. The research repeated three times.

Table I: Procedure of leather process

Process	%	Remark
Presoaking	Water (200%)	Basis of all material that used was weight of skins. Drum was run along 1 h and stoped along 1 h. Drained.
Washing	Water (100%) x 2	Washing did in two times. Drum run 10 – 15' and drained after washing time.
Soaking	Water (200%) Degresing agent (0.1%) Antibacterial (0.1%) NaOH (0.3%)	Drum run along 2 h. And then drum stopped 50'and run 10'. This procedure was continued for 6 h and overnight. Drained.
Washing	Water (100%) x 2	Washing did in two times. Drum run 10 – 15' and drained after washing time.
Liming	Na_2S (2.5%) Lime (8%) Air (300%) DA (0.1%)	Drum run along 2 h. And then drum stopped 50'and run 10'. This procedure was continued for 10 h and overnight. Drained.
Washing	Air (100%) x 2	Washing did in two times. Drum run 10 – 15' and drained after washing time. **Fleshing**
Deliming and Bating	Ammonium sulfate (2%) Water (100%) Bating agent (0.2%)	Deliming was did for 1 h after addition ammonium sulfate. Then, added bating agent and drum run 1 h. Drained.
Washing	Water (100%) x 2	Washing did in two times. Drum run 10 – 15' and drained after washing time.
Pickling	Water (100%) Salt (10%) Formic acid (0.5%) H_2SO_4 (0.2%)	After Salt was added, drum was run 30'. Then, formic acid and sulfate acid were added. Drum was run 2 h and overnight.
Tanning	Chromium sulfate (8%) Sodium bicarbonate (1.2%) Sodium format (2%)	Drum was run along 30'. Chromium sulfate was added and drum was run 1 h. Added sodium bicarbonate and run along 7 h. Added sodium formate and run 30'. Drained.

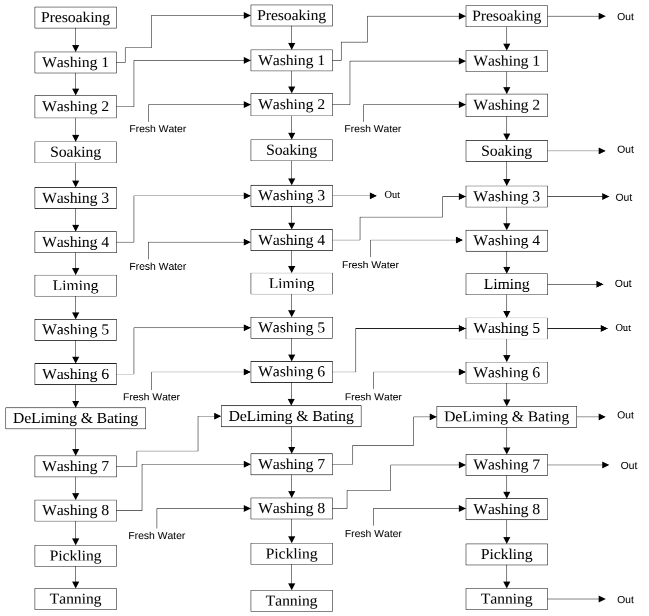

Fig. 1. Design of water reuse

Wastewater formed in water control and water reuse analyzed to know characterization of wastewater was formed. Wastewater analysis refer to APHA (2012) i.eg. pH, conductivity, turbidity, TDS (Total Dissolve Solids) and TS (Total Solids) (12). Leather was analyzed i.eg. tear strength, shrinkage temperature, tensile strength, elongation, chrome oxide content, and organoleptic. Shrinkage temperature was analyzed by SLP 18, tensile strength and elongation used SLP 6, tear strength use SLP 7, chrome oxide content used SLC 8 and organoleptic properties was analyzed with panel[21][22].

IV. RESULT AND DISCUSSION

A. Tensile strength

The result showed tear strength of leather (wet blue) in water reuse was 167.51 N/mm2 and deviation was 18.93 N/mm2. It was smaller than the average value of water control, i.eg. 176.09 N/mm2 with deviation was 16.1 N/mm2 (Fig. 2). The deviation value in water control and water reuse described that data of tensile strength was diverse. Although value of deviation in water reuse is high, but it met with SNI (Indonesian standard) to jacket material. Minimum standard of leather (goat skins) for jacket material is 14 N/mm2 (14).

According (15), the differentiation of leather tensile strength was caused by amount of protein non collagen. They said, if there were many protein non collagen was degraded, it perhaps collagen bonded with tanning material. Meanwhile, leather was formed will has high tensile strength. (16) said, tensile strength were affected by fiber direction, thick skins and location of leather sampling. In addition, (17) in (18), tensile strength was affected by content of fiber protein in skins[23][24][25].

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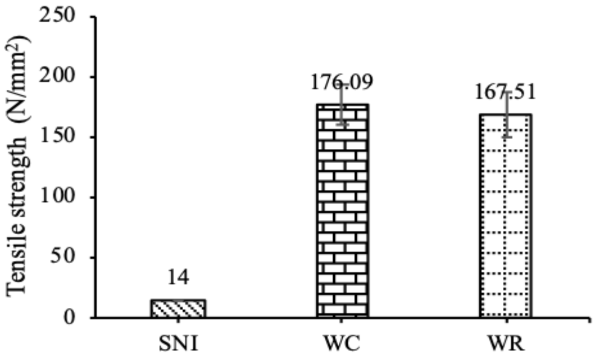

Fig. 2. Tensile strength of leather (Wet Blue)

B. Elongation

The result of leather (wet blue) showed the average value of elongation in water reuse was smaller than water control. Elongation in water reuse was 34.88% with deviation was 1.35%. Meanwhile, elongation of water control was 48.43% with 4.58%. Elongation value of water reuse met with SNI (Fig. 3). Maximum standard of elongation in leather (goat skins) for jacket material was 60% (14).

The differentiation of elongation value in water reuse and water control was caused by thick skins. According Judoamidjojo (1974) in (19), elongation was affected by elastin content in leather. If the leather has many elastin, it caused high elongation value of leather. But, also fatliquoring was gave influence to leather elongation[26].

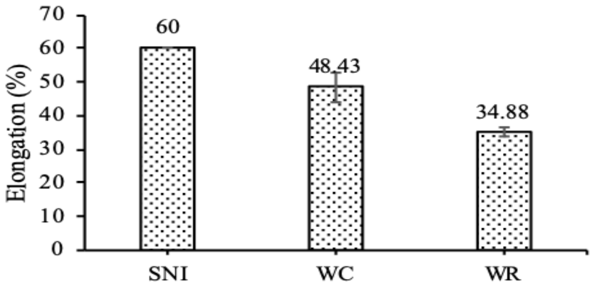

Fig. 3. Elongation of leather (wet blue)

C. Tear strength

Tear strength of water reuse showed that was smaller than water control. The average value of water reuse was 25.19 N/mm with deviation was 2.71 N/mm. Meanwhile, the average value of water control was 27.57 N/mm with deviation 1.56 N/mm (Fig. 4). According SNI, leather (wet blue) was produced with reuse water had met with standard. In tear strength, minimum standard of material jacket from goat skins was 12.5 N/mm (14). According (20), hides or skins which was tanned using high grade tanner will has a high tear resistance[28].

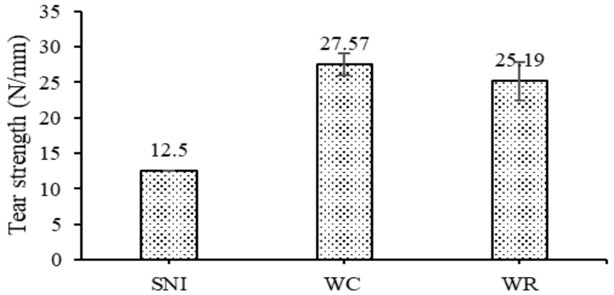

Fig. 4. Tear strength of leather (Wet Blue)

The difference of tear strength in water reuse and water control were caused some factors. According (21), tear strength was affected by thick of skins, direction of collagen fiber, and angle of collagen fibers againt grain layer. Others factor which affected was in beamhouse (pretanning) process, i.eg. liming, deliming and bating. It process determined for fiber opening in skins. Judiamidjojo (1982) said that collagen fibers was not opened will affect penetration of tanner material as skins was not tanned perfectly[27]. According (22) the presence of residual protein non collagen which was caused by not completed process in pelt. It affected tanner chemical penetration in pelt. It effected leather (wet blue) properties like hard, rigid, and fragile.

D. Shrinkage temperature and chrome oxide content

Shrinkage temperature was one of parameters to analyze tanning process. Commonly, shrinkage temperature with conventional tanning was 100 0C. Then, chromium oxide content was parameter to know chrome content bonded in collagen.

Shrinkage temperature test showed that leather was produced in water reuse above 100 0C (Fig. 5). The result also showed water reuse shrinkage temperature below water control. The average of shrinkage temperature of water reuse was 108.32 0C with deviation 0.26 0C, but in water control was 109.85 0C with deviation 1.09 0C. According (5), the high shrinkage temperature in leather was caused Cr^{3+} that formed crosslink with carboxyl group (COO^-) in collagen (Fig. 6). Crosslink which occurs was covalent bond. It caused the bonds that occur between Cr^{3+} and COO^- was strong. Leather could resist with temperature until above 100 0C (23).

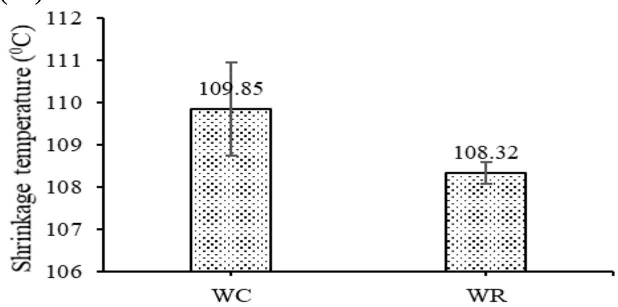

Fig. 5. Shrinkage temperature of leather (Wet Blue)

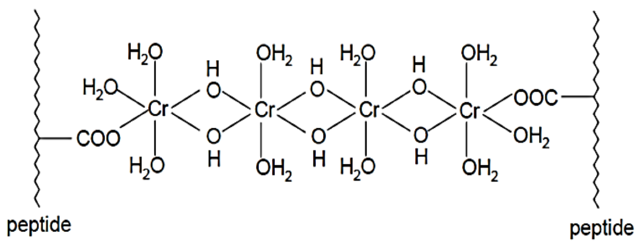

Fig. 6. Reaction of Chrome and Carboxyl group (5)

The result of chrome oxide content in leather (wet blue) has different between water reuse and water control. The average value of water reuse was 2.90% with deviation 0.37%, it was under water control (Fig. 7). Although, there was a decrease in

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chrome oxide content in water reuse, but it met with SNI. Standard of chrome oxide content for jacket material in leather (goat skins) was 2.5%(14). According (24), chrome oxide content in leather (wet blue) affected shrinkage temperature of it. They said there was correlation between chrome oxide and shrinkage temperature. That could see in fig. 5 and fig. 7, where there was a decrease shrinkage temperature in leather (wet blue) with water reuse.

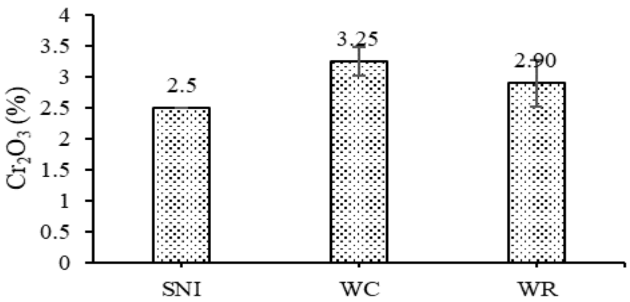

Fig. 7. Chromium oxide content in leather (wet blue)

E. Organoleptic properties of leather

The result showed the average value of organoleptic properties in water reuse nearby water control, it was 7.9. In addition, organoleptic of water control was 7.96 (good). It showed that water reuse did not affect organoleptic of leather (wet blue) was formed (Table II). (4) said, leather was produced without and used water reuse didn't give difference to leather (wet blue). Therefore, design of water reuse in this research could use in leather industries, but will be need scale up before it.

Table II. Organoleptic properties of leather (wet blue)

Treatment	Average value			Organoleptic average
	Feel handle	Colour	Flavor	
WC	7.89	8	8	7.96
WR	7.93	7.8	7.9	7.9

1 – 2 = worse.; 2 – 4 = bad.; 5 – 6 = middle ; 7 – 8 = good.; 9 – 10 = best.

F. Water Analysis of Water Reuse

(25) said that water usage for leather processing among 3,500% from raw hides/skins. According (26), there are variation of water usage for leather process. He said water usage for leather process among 21.1 – 31.45 m3 per ton hides/skins. The variation were caused by some factors, i.e.g. type of products, material quality, good practice, type of machines, water resources, pollution control, and location of industries[29].

Water reuse application in this research was path to reduce wastewater formed in process. (2), wastewater was formed during process production as much as 45 – 50 m3 per ton hides/skins. In addition (27), 1 kg hides/skins would produce wastewater as much as 30 – 35 L to get leather. (28) said, to process 1 tons raw hides need water 21 – 63 m3 and formed 20 – 56 m3 wastewater. More than 80% water used in conversion raw hide to wet blue (28).

The result showed that water reuse reduced water usage and wastewater as much as 35.29% and 36.11% (Table III). (6), cleaner production strategy like water reuse in leather process could decrease water usage as much 25 – 50%. Then, (4) showed there was decline in water usage until 27% from total amount water consumption in beamhouse process.

Table III. Analysis input and output of water usage

Process	% water	Water control		Water reuse		
		Input (ml)	Output (ml)	Input (ml) Fresh water	Output water control	Output (ml)
Presoaking	200	2,000	1,940	1,000	1,000	1,888
Washing 1 [a]	100	1,000	1,000	-	1,000	988
Washing 2 [b]	100	1,000	1,022	1,000	-	1,016
Soaking	200	2,000	1,896	2,000	-	1,910
Washing 3	100	1,000	1,002	-	1,000	994
Washing 4 [c]	100	1,000	1,028	1,000	-	1,036
Liming	300	3,000	2,568	3,000	-	2,556
Washing 5	100	1,000	1,054	-	1,000	1,022
Washing 6 [d]	100	1,000	1,024	1,000	-	1,038
Deliming and bating	100	1,000	1,026	-	1,000	1,016
Washing 7 [e]	100	1,000	1,018	-	1,000	1,000
Washing 8 [f]	100	1,000	1,034	1,000	-	1,024
Pickling	100	1,000	-	1,000	-	-
Tanning	-	-	1,000	-	-	1,000
Total	1,700	17,000	16,612	11,000	6,000	16,488

Note: a, b, c, d, e, and f were processes that it wastewater reuse for input in next batch

Economically, water reuse for wastewater could minimize operational cost for industries. The assumtion is all of process in laboratory scale similar with industrial scale. Production capacity of industrial scale was 1.5 tons hides/skins, so total amount of water usage was 25.5 m^3. It was also assumed that production did 12 times a month. To calculate payback period used formulation 1.

$$Payback\ period = \frac{Investation}{Benefit} \quad (1)$$

The result showed that payback period of water reuse in industries was 5.56 month and after that, industries could save with their operational cost as much as Rp 1,295,848.8,- a month. When compared with other literature like Gutterres et al (2010) with same assumption, so design of water reuse in this research was more profitable. Gutterres et al (2010) only saved as much Rp 991,440,- a month.

G. Wastewater Characterization

Table IV was result of wastewater analysis which formed in some steps of leather process. The result showed that containing wastewater in water control was high pollutant, it also in water reuse (Table IV).

Table IV1. Wastewater analysis before and after water reuse

Process	Parameter									
	pH		TDS (mg/L)		TS (mg/L)		Conductivity (S/cm)		Turbidity (NTU)	
	A	B	A	B	A	B	A	B	A	B
PS	7.4	7.8	47.135	115,120	89,575	120,343	104.2	124.4	1,068	2,234
W1	7.7	8.1	10.556	28,883	38,454	38,960	51.6	60.4	1,014	2,170
W2	7.6	8.0	17.135	9,300	18,782	16,518	28.2	19.8	747	519
W3	8.8	9.0	2.580	3,170	4,249	7,953	6.4	11.1	294	599

W4	8.6	8.9	1.895	1,668	2,220	3,727	3.0	5.5	95	670
W5	12.0	12.2	632	3,720	3,690	8,362	3.5	19.1	536	588
W6	11.8	12.1	218	2,030	2,160	2,988	1.0	5.9	293	550
D	8.6	8.7	3.825	4,125	8,875	9,220	11.5	11.7	87	98
W7	8.5	8.6	3.410	3,454	3,958	4,128	5.4	5.5	45	52
W8	8.3	8.3	1.236	1,365	1,617	1,872	2.4	2.5	7	15

Note: ^{A} water control; ^{B} water reuse;

pH was one of wastewater parameters which must be controlled, so it was not polluted environment when it was discharged. Table IV showed that pH value in effluent in water control was smaller than water reuse. The analysis showed that pH in water control varied 7.4 – 12, then pH in water reuse varied among 7.8 – 12.2. From this analysis, water reuse increased pH in effluent. It was caused by chemical material accumulation in wastewater. Water reuse not only affected to pH, but also influenced to some parameters, such as total dissolve solids (TDS), total solids (TS), conductivity, and turbidity.

TDS and TSS content in water reuse wastewater was higher than water control. It was caused pollutant accumulation from effluent in water control. The result showed TDS and TS in water reuse were 1,125 – 115,120 mg/L and 1,872 – 120.343 mg/L (Table IV). In addition, TDS and TS in water control were 218 – 47,135 mg/L and 1,617 – 89,575 mg/L (Table IV). If it was compared with standard quality from (29), it was not met with the standard.

Conductivity was the ability of solution to conduct electricity. The result showed that conductivity in water reuse were 2.5 – 124.4 S/cm. It was higher than water control. Water control conductivity were 1 – 104.2 S/cm (Table IV). (29)did not has standard of conductivity in wastewater. But, according (30), conductivity could follow Scofield standard, water in medium category has value among 750 – 2,000 µmhos/cm or 0.75 – 2 S/cm, water in high category has value less than 0.75 S/cm. Overall of the process was analyzed, it was not meet with Scofield standard[30].

Turbidity was determination of water saturation optic. Sometimes, turbidity determination was used to analyze water quality based on suspended solids.[31][32], compounds which in suspension was categorized in suspended particles and suspended colloidal. The result showed that turbidity in water reuse was higher than water control, it was 15 – 2,234 NTU. Then, turbidity in water control was 7 – 1,068 NTU. But in W2, there was decline of turbidity (Table IV). (32), turbidity has correlation with total suspended solids (TSS) in effluent. It was showed with value of R^2, it was 0.8. In other side, (33), R^2 value between turbidity and TSS was 0.96. When turbidity was high, so TSS content was high too in wastewater.

V. CONCLUSION

The conclusion of this research is water reuse can uses in leather tannery process. The result showed that leather (wet blue) met with SNI as material of jacket product from goat skins, although there was decline of characteristic if it was compared with water control. Water reuse application reduced water usage 35.29% and wastewater as much as 36.11%. Water reuse application increased pollutant in wastewater which formed during production. Payback period of water reuse was 5.56 month and will save production cost as much Rp 1,295,848.8,- per month.

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