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WATER TREATMENT INSTALLATION BASED CHROME CONTENT ANALYSIS IN INDONESIAN LEATHER TANNING INDUSTRY

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ABSTRACT

Cleaner production programs have become a requirement for a leather tanning industry, including the wastewater treatment installation (WTI) of leather tanning industry, so that the qualified WTI procurement needs to be developed since liquid waste from the tanning industry process is quite large and harmful to environment. The samples of 330 (three hundred thirty) tanneries from Garut, Indonesia, that need to be considered on the issue of wastewater treatment installation so that the environment is maintained. The availability of chrome waste of 1300 ppm resulted from the leather tanning industry process that has been dumped into the environment caused pollution of the rivers, the agricultural area, the well and the community pool around tannery industry center of. In order not to pollute the environment, the wastewater of tannery industry must first perform coagulation process, and the supernatant of coagulation process results is then filtered and normalized of pH. The chrome content and pH of the liquid waste to be dumped into the environment shall comply with the quality standard in accordance with the decree of the State Minister of Population and Environment of the Republic of Indonesia Number: KEP-03/MENKLH/ II/1991 February 1, 1991 where the chrome content dumped into the environment shall ≤ 2 ppm, with normal pH. This is a result of innovation program for the community as a real step for the implementation of pollution-free area as well as to improve production efficiency program for small and medium industries especially leather tanning industry since the industry was originally able to donate considerable foreign exchange for the country. The dregs of the coagulation process are then recrystallized and filtered until producing 11% of chromium sulfate. Optimally recycled chrome sulfate is used on chrome process with 100% composition using recycled chrome sulfate. As evidenced by the results of leather testing that meets the requirements, 6 sub-variables are in rank 1, and 1 sub variable is in rank 4. The total of 7 variables from 21 variables tested, the results of the test approached the tannery result using chrome sulfate (Chromosal-B).

KEY WORDS : Cr, Waste, Pollutant, Clean production

INTRODUCTION

The tannery industry uses many chromium compounds (chromosaris-B) where chromium compounds are still imported from Germany, so the price is relatively expensive. As a consequence of the use of chrome in the process of tannery, the industrial waste of tannery contains many chromium metal ions as a source of pollution for plants, animals, and humans (Chernicharo and Vliet, 1996). Metal ions dumped into the environment must go through a process that can reduce and even eliminate the presence of chromium metal ions in wastewater (Nazer, *et al.*, 2006).

The tannery industry at Garut, Indonesia shows that the condition has a very potential liquid waste to be processed/chrome metal ions to be recycled. Average total waste during the production process is between 55-60% in which the tannery waste can

reach more than 12,000 m3 (twelve thousand cubic meters) per day. Results of mapping of chromium content in sediment and in river water, well water population, and plants around the watersheds showed significant chromium content (Garut, 2003).

To overcome this problem, on the processing strategy the tannery liquid waste that contains many chromium metal ions will be recycled into chrome sulfate as raw material of hide tanning process.

MATERIALS AND METHODS

In the tannery industry, chrome compounds are widely used tannery materials. If the residual tanning solution is dumped into the water environment, it increases the amount of metal ions in the water environment. The water environment containing excessive metal ions generally cannot be consumed as drinking water. It is mentioned in Government Regulation No. 82/2001 on Water Quality Management and Water Pollution Control that defines water pollution as living organisms, substances, energy, or other components that are entered into water by human activities, so the water quality falls to a certain level that causes water not to function in accordance with its designation (P.P.R.I.N.T. 2001).

To avoid chromium contamination (Cr) in the environment water, a particular enzyme as a substitute for chromium was used as a tannery material. But in this way there is also a disadvantage in which the enzyme carried by the tannery waste material together with fat and residual hides will contribute to increase the population of microorganisms in the water.

Fat, residual skin, and enzymes will be degraded easily by microorganisms to produce volatile compounds, and it generally smells foul (Fidiastuti and Suarsini, 2017). This stench is the result of the decomposition of proteins and amine groups.

The increasing population of microorganisms in the water is worried to also increase the possibility of bacterial/ microbial pathogen breeding that is harmful to humans.

Heavy Metal of Chromium

The tanning process aims to transform the raw skin which is susceptible to damage by the activity of microorganisms, chemicals, or physics into tanned skin that is more resistant to such effects. The method of skin tanning uses vegetable tanners and mineral tanners.

Chrome tanning is a tanning that is started with a low pH or acidic state that is from 2 to 3, so the skin needs acidification in order to get the desired conditions. The length of the chrome tanning process usually takes from 4 to 8 hours. This is not a standard, but it depends on the thickness of the skin. After the tanning process, the skin moistness is tested with boiling water for 2 minutes. If there is no more than 10% shrinkage, it means that the skin condition is ripe. The factors that are important in affecting the physical properties of tanned skin include the raw skin structure. Tensile strength is one of the factors that need to be noticed in the assessment of the finished skin.

Coagulation Process

Coagulation is the process of clumping colloidal particles due to the addition of chemicals so that the particles are neutral and form precipitates due to the force of gravity. Coagulant mechanism can be done in several ways, namely:

Using Electrophoresis Principle

Electrophoresis process is the movement of charged colloid particles to the electrode with opposite charge. When the particle reaches the electrode, the colloidal system will lose its charge and will be neutral;

Colloid addition

The addition of colloids can occur as follows: The negatively charged colloids will attract positive ions (cations) while the positively charged colloids will attract negative ions (anions). The ions will form a second layer sheath. If the second layer cover is too close, it will neutralize the colloid charge, so coagulation occurs. The greater the ionic charge, the stronger the appeal with the colloidal particles, so the faster the coagulation occurs.

Chromium Sulphate

Chromium sulphate is usually an inorganic compound. The heavy metal chromium is widely used in the leather tanning industry where the liquid waste can potentially pollute the environment. Chromium compound is shaped like a green crystal.

The densities are various. Those are for the form; 3.10 g/ cm^3 (anhydrous), 1.86 g/ cm3 (pentadecahydrate), and 1.709 g/ cm3 (octadecahydrate). The melting point is at 90 °C while the boiling point breaks down into chromic acid. For water anhydrous insoluble in water, while

hydrate dissolves in water, dissolves in alcohol, but practically dissolves. The chromium sulfate at high pH undergoes a process called olation which produces active polychromium compounds as tanners, cross linked collagen subunits. After the application of chromium substances, the milk basin is treated with sodium bicarbonate to increase the pH to 4.0-4.3 and to increase cross-induction between chromium and collagen. An increase in pH is usually accompanied by a gradual rise in temperature up to 40 °C.

The ability of chromium to form the stable bond proves that chromium sulfate as one of the most efficient tanning compounds. The efficiency is characterized by the increasing hydrothermal stability in the skin and its resistance to shrinkage in hot water.

d. Production Process Steps of Recycled Chromium Sulfate

The steps of chromium sulphate production process with recycling system of tannery industry wastewater, including identification of factual problem in tannery industry center in Sukaregang of Garut Regency, studying result of field survey, recycling process of wastewater of leather tannery industry in laboratory scale.

RESULTS

Data of Research Results

This process produced a supernatant liquid that was almost chromium-free and could also lower Biological Oxygen Demand (BOD). The equalization stage can be performed, so the nitrogen removal is through nitrification or denitrification process. Physicochemical treatment was performed in the coagulation stage to remove BOD and solids. The relatively easy and simple physicochemical treatment can remove > 95% of suspended solids and BOD by about 70%.

The above liquid waste treatment technique is in accordance with the standard of waste treatment installation, but not all tannery industries can apply it to the industry, especially in small industries. This is due to cost constraints and resources that support. In order that the liquid waste of leather tanning industry is not dangerous, the handling to make wastewater treatment installation with the recycling system can be done, that is to take back the chromium sulfate to be reused during chromming and re-chroming process. The pH research result data and chromium content can be seen in Table 1, pH after filtration in Table 3, and chromium content at 4.

Table 1. The average of Chromium and pH levels of Tanning Industry Liquid Waste

Sample from drum	pH	Chromium levels (ppm)
1	3.5	13.238,8
2	3.5	13.654,6
3	3.5	12.925,5
Average	3.5	13.272,9

Goat leather test data by utilizing the recycled chromium sulfate during the process of chroming and re-chroming is with the following composition:

a. Sample 1 used 100% chromium sulfate;
b. Sample 2 used 75% sodium chloride + 25% water;
c. Sample 3 used 75% chromium sulphate + 25% chromosal B (Import);
d. Sample 4 used 75% chromium sulfate left for 1 hour + 25% chromium B (Import);
e. Sample 5 used 100% chromosal B (Import) commonly used by the company (made as standard).

Goat leather test data which includes organoleptic, physical, and chemical can be seen in Table 4.

DISCUSSION

The analytical method used on the best test results from four groups of samples is the analysis of variance (Analysis of Variance or ANOVA) which will be further tested by (Post Hoc) Tukey if the ANOVA test results are stated significant.

In ANOVA test, the focus of the test is to determine whether in the five sample groups, there is a difference in the average of variable. The first step to do is the distribution test. The test results are normally distributed. The Test Results of Variance Homogeneity state that the data of all variables are declared to be homogeneous.

The average difference in the five groups is significant if p-value produced is less than 0.05, and otherwise if p-value> 0.05, the mean of the variables in the five samples is not significantly different or the same.

The difference of the mean value on the group

Table 2. The pH Average Value of Liquid Waste of Tannery Industry After the Filtration Process

MeasurementSample	1	2	3	4	Total	Average
A-1	6	7	7	7	27	6.8
A-2	7	6	7	7	27	6.8
A-3	6	6	6	7	25	6.3
Total	19	19	20	21	79	19.9
Average	6.3	6.3	6.7	7.0	26.3	6.6
B-1	7	7	6	7	27	6.8
B-2	7	7	7	6	27	6.8
B-3	6	7	6	7	26	6.5
Total	20	21	19	20	80	20.1
Average	6.7	7.0	6.3	6.7	26.7	6.7
C-1	7	7	6	6	26,	6.5
C-2	7	6	6	7	26	6.5
C-3	7	7	7	7	28	7.0
Total	21	20	19	20	80	20.0
Average	7.0	6.7	6.3	6.7	26.7	6.7
Total Average	20.0	20.0	19.3	20.4	79.7	20.0
Average	6.7	6.7	6.4	6.8	26.6	6.7

Table 3. The Average Value of Chromium Liquid Waste Level of Tanning Industry After Filtration Process

Measurement/Sample	1	2	3	4	Total	Average
A-1	1.73	2.05	1.65	1.63	7.06	1.77
A-2	1.83	1.86	1.48	1.66	6.83	1.71
A-3	1.71	1.68	1.54	1.48	6.41	1.60
Total	5.27	5.59	4.67	4.77	20.30	5.08
Average	**1.77**	**1.86**	**1.56**	**1.59**	**6.77**	***1.69***
B-1	2.15	1.93	1.86	1.88	7.82	1.96
B-2	1.97	1.75	1.63	1.82	7.17	1.79
B-3	1.71	1.77	1.79	1.65	6.92	1.73
Total	5.83	5.45	5.28	5.53	21.91	5.48
Average	**1.94**	**1.82**	**1.76**	**1.78**	**7.30**	***1.83***
C-1	2.27	2.18	1.98	2.10	8.53	2.13
C-2	2.18	2.17	2.12	1.98	8.45	2.12
C-3	1.96	1.86	1.93	1.78	7.53	1.88
Total	6.41	6.21	6.03	5.86	24.51	6.13
Average	**2.14**	**2.07**	**2.01**	**1.95**	**8.17**	***2.04***
Total Average	5.85	5.75	5.33	5.32	22.24	5.56
Average	**1.95**	**1.92**	**1.78**	**1.77**	**7.41**	***1.85***

value is significant if the p value is less than 0.05, and otherwise if the p value is 0.05, the mean value is not significant or the same.

ANOVA test results are stated to produce a significant conclusion, meaning that there is a significant difference in mean values on the samples compared, and then the test is continued with Tukey test. In Tukey test we will get a specific comparison among samples and between samples with Company samples. In Tukey test it will be known which samples have similarity levels with the Company, which are indicated by insignificant differences. The mean values placed in the same column showed no significant difference, but if placed in different columns, it showed significant differences ($p < 0.05$).

The results of the ANOVA test for all variables were then recorded for 13 quantitative variables, and it was concluded which group of samples produced the highest similarity with the results given by Company sample. The best sample closest to Company, the recap of the ANOVA test results can be seen in Table 5.

Referring to Table 5, it can be summarized based on the sample ranking recapitulation that equals the Company sample as a standard. See Table 6.

Table 4. The Result Data of Goat Leather Test

No	Test Types	Sample	Test results	Test Method
I.	Organoleptic			
1.1	Color	1	Overally Black	SNI.06-4593-1998
		2	Overally Black	
		3	Overally Black	
		4	Overally Black	
		5	Overally Black	
1.2	Nerf Release	1	Not out of nerf	SNI.06-4593-1998
		2	Not out of nerf	
		3	Not out of nerf	
		4	Not out of nerf	
		5	Not out of nerf	
1.3	Elasticity	1	Springy	SNI.06-0258-1998
		2	Springy	
		3	Springy	
		4	Springy	
		5	Springy	
1.4	Skin Area, Sq ft	1	5,50 5,45 5,50	SNI.06-0257-1998
		2	5,25 5,30 5,35	
		3	4,00 4,10 4,15	
		4	4,50 4,60 4,40	
		5	6,00 6,15 6.10	
II	Physic			
2.1	Thickness, mm	1	0,52 0,54 0,55	SNI.06-7128-2008
		2	0,48 0,48 0,50	
	.	3	0,52 0,53 0,52	
		4	0,60 0,59 0,63	
		5	0,56 0,53 0,55	
2.2	Tear Strength, N/mm	1	28,06 26,31 27,00	SNI.06-1794-1990
		2	9,03 9,33 7,81	
		3	20,54 22,24 19,37	
		4	21,50 21,93 22,25	
		5	21,15 19,76 21,22	
2.3	Tanning/ Depreciation (%)	1	4,90 6,12 4,90	SNI.06-0235-1989
		2	10,72 9,70 9,66	
		3	4,90 4,90 6,86	
		4	5,94 5,00 6,00	
		5	10,73 8,76 10,72	
2.4	Tensile strength, N/mm^2	1	14,90 15,31 14,78	SNI.06-1795-1990
		2	10,55 9,54 11,32	
		3	20,45 17,68 19,12	
		4	17,64 17,50 17,77	
		5	12,36 13,15 14,75	
2,5	Diligence, %	1	55,75 67,10 54,51	SNI.06-1795-1990
		2	54,78 66,43 56,20	
		3	71,75 69,43 62,28	
		4	77,26 78,68 80,70	
		5	89,00 91,61 99,08	
2.6	Cat Brush Resistance			SNI.06-0996-1989
a.	Dry	1	¼ faded (faded slightly)	
		2	¼ faded (faded slightly)	
		3	¼ faded (faded slightly)	
		4	¼ faded (faded slightly)	
		5	¼ faded (faded slightly)	

Table 4. *Continued ...*

No	Test Types	Sample	Test results	Test Method
b.	Wet	1	2/3 faded	SNI.06-1795-1990
		2	2/3 faded	
		3	2/3 faded	
		4	2/3 faded	
		5	2/3 faded	
2.7	Translucent to Water Vapor, mg/cm^2/hour	1	8.62 8,67 8,64	ISO 5403 : 2002
		2	10,26 9,85 10,06	
		3	9,88 9,5510,21	
		4	14,35 16,02 15,29	
		5	9,87 9,32 9,60	
2.8	Enervation	1	8.62 8,67 8,64	ISO 17235 : 2002
		2	10,26 9,85 10,06	
		3	9,88 9,55 10,21	
		4	14,35 16,02 15,29	
		5	9,87 9,32 9,60	
III	Chemistry			
3,1	Water Level, %	1	16,98 17,05 17,08	SNI.06-0644-1989
		2	17,00 17,10 16,95	
		3	17,00 16,97 16,94	
		4	17,00 17,02 17,05	
		5	16,99 16,92 16,89	
3,2	Chromite Oxide Level, %	1	3,44 3,47 3,48	SNI.06-0645-1989
		2	3,46 3,42 3,45	
		3	3,60 3,55 3,63	
		4	3,56 3,50 3,52	
		5	3,49 3,52 3,47	
3,3	Ash Level, %	1	6,33 6,39 6,36	SNI.06-0563-1989
		2	6,30 6,21 6.27	
		3	5,80 5,80 5,93	
		4	5,19 5,20 5,04	
		5	6,48 6,54 6,43	
3,4	Fat/ Oil content, %	1	11,34 11,31 11,36	SNI.06-0564-1989
		2	11,55 11,50 11,52	
		3	9,94 9,92 9,90	
		4	9,60 9,57 9,62	
		5	11,28 11,31 11,27	
3,5	pH	1	4,29 4,33 4,37	ISO 4045 : 2011
		2	4,27 4,27 4,25	
		3	4,23 4,20 4,24	
		4	4,25 4,22 4,24	
		5	4,06 4,10 4,08	

Source: Central for Leather, Rubber, and Plastics-Ministry of Industry of RI

CONCLUSION

Based on the first rank that most closely matches the values in the Company sample, Sample 1 ranks first with a fit in rank 1 of 6 indicators (46%), and Sample 3 ranks second with rank 1 of 4 indicators (31%). Likewise, if we look at the total number of categorized samples, it has similarities with Leather Company samples, from first to fourth rank. Sample 1 ranks first as a sample resulting in similarity with Leather Company samples (7 indicators) followed by Sample 3 (5 indicators).

From the analysis above, it can be concluded that Sample 1, which is a hide tanning process using 100% recycled chromium sulfate, is a sample that produced the highest level of conformity with that Leather Company samples get as standard.

Table 5. The Recapitulation of Sample Ranking that Equals Company Results

Test category	No	Variables	A	B	C	D
I. Organoleptic	1.4	Skin Area (sqft)	1			
II. Physic	2.1	Thickness (mm)	1	3		
	2.2	Tear Strength (N/mm)	3	4		
	2.3	Taning/ Depreciation (%)	2			
	2.4	Tensile Strength (N/mm^2)	1			
	2.5	Glossary (%)	4			
	2.7	Translucent to Water Vapor (mg/cm^2/jam)	3	2		
	2.8	Enervation	2	4		
III. Chemistry	3.1	Water Content (%)	3	2	4	1
	3.2	Chromite Oxide Content (%)	1	4		
	3.3	Ash Content (%)	1			
	3.4	Fat/ Oil content (%)	1			
	3.5	pH	3			

Information:
1. The numbers in the table show Samples from 1 to 4;
2. Letter A is rank 1, B rank 2, C rank 3, and D rank 4.

Table 6. Recapitulation of Sample Ranking that Equals Company as A Standard

Sample	Rank 1	Rank 2	Rank 3	Rank 4	Total
Sample 1	6			1	7
Sample 2	2	2			4
Sample 3	4	1			5
Sample 4	1	3	1		5
Total	13	6	1	1	21

Description: The numbers in the table show the appearance frequency of the sample number according to the Ranking

Suggestion

a. The recycled chromium sulphate in liquid should be formed into crystals such as crommosal B (import) and then implemented in the hide tanning process to find out whether the effect is very significant or not;
b. Review the utilization of recycled chromium sulfate from leather tanning industry wastewater with cowhide as a research object.

REFERENCES

Chernicharo, C. and Vliet, M.V. 1996. Strategies for pollution control in tanneries located in Minas Gerais State, Brazil case study. *Water Science and Technology.* 34 (11) : 201-207.

Garut, B.P.D.P.D.K. 2003. *Laporan Penelitian Pemetaan Aliran Limbah Krom*, Garut, Indonesia.

Fidiastuti, H.R. and Suarsini, E. 2017. Potensi Bakteri Iindigen Dalam Mendegragasi Limbah Cair Pabrik Kulit Secara *In vitro. Bioeksperimen.* 3 (1) : 1-10.

Nazer, D. W., Al-Sa'ed, R.M. and Siebel, M.A. 2006. Reducing the environmental impact of the unhairing - liming process in the leather tanning industry. *Journal of Cleaner Production.* 14 : 65-74.

P. P. R. I. N.T. 2001. *Pengelolaan Kualitas Air and PengendalianPencemaran*, Pemerintah Republik Indonesia, Jakarta, 2001.