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THE REDUCTION OF BOD, COD AND CHROME IN THE TANNING WASTEWATER

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Abstract

The tannery industry generally uses chrome raw materials in its tanning process. This use results in liquid waste containing chromium. This study aims to determine and analyze the characteristics of the waste from the exhausted chromed tanning process. The material used are sheep skins, which is tanned using conventional methods and the exhausted chrome tanning process. The collected liquid waste is then tested on the parameters of BOD (Biochemical Oxygen Demand), COD (Chemical Oxygen Demand), and total chrome. The results of this test are then analyzed using Independent Sample T-Test, which revealed that the use of the exhausted chromed tanning process is capable of producing waste with lower total value of chromium, BOD, and COD, than that of with conventional method. However, those results are still above the applicable wastewater quality standards, so it still requires further processing in order to meet the requirements in Indonesia.

Keywords

Tanning Wastewater, Chrome, BOD (Biochemical Oxygen Demand), COD (Chemical Oxygen Demand)

1. Introduction

Human activities such as; industries, agriculture, mining, transportations, constructions, all produce waste which contain various substances that can cause environmental pollution. Pollution could be caused by these pollutants when released beyond the assimilation capacity of the environment. Industrial wastes are generated from different processes, and the amount and toxicity of waste released varies with its own specific industrial processes (Shen, 2015).

The tannery industry generally uses chrome as raw materials in its tanning process. This use results in chromium-containing liquid waste. The chromium in the tannery wastewater can cause pollution to the environment and interfere with human health (Ulfin, Harmami, & Rahmawati, 2014). The use of chrome in the tanning industry has always been a major issue and needs to get serious attention. Tannery wastewater is difficult to treat because of complex characteristics like high BOD, COD, suspended solids, sulphide and chromium (Dargo & Ayalew, 2014).

To reduce chromium-containing waste in the leather tanning industry, several methodologies have been developed, including chromed recovery (Pathe, Nandy, Kaul, & Szpyrokwicz, 1996), exhausted chrome tanning (Kanagaraj, Babu, & Mandal, 2008), and chrome adsorption (Mayasari & Sholeh, 2016). Exhausted chrome tanning process as one of the methods that have been developed, is an effort to reduce chrome waste through the use of chrome as efficiently as possible.

The chrome waste produced by the chrome tanning process exhaust method needs to be studied and analyzed further to determine the level of process effectiveness. For this reason, it is necessary to study the waste of exhausted chrome tanning process.

1.1 Aims of the Research

This study aims to determine and analyze the character of waste from exhausted chromed tanning process.

1.2 Benefits of the Research

This research is expected to add information material in the development of education in the field of tannery and leather.

2. Literature Review

Tannery effluents are of large scale environmental concern because the color and it diminish the quality of water bodies into which the wastes are released. Among heavy metals presents in sludge, chromium is one of the most common (Sarker, Basak, & Islam, 2013).

After tanning of the hide (skin after removal of the hair side), 22-35% of the chrome tanning agent remains in the exhausted tanning solutions, which corresponds to a residual chromium concentration of 3-8g/l (recalculated to Cr_2O_3) (Panov, Gyul'khandan'yan, & Pakshver, 2003). For instance, in India alone about 2000–3000tons of chromium escapes into the environment annually from tannery industries, with chromium concentrations ranging 2000-5000 mg/l in the aqueous effluent, compared to the recommended permissible discharge limits of 2mg/l (Altaf, Masood, & Malik, 2008). Chromium waste is formed because not all the chrome used is absorbed into the leather during the tanning process.Varied nature of chromium salts and application methods employed, result in an absorption average level of 40-70% of Cr_2O_3 used in tanning. In the absence of adoption of suitable technological methods, typical concentrations of chromium in sectional waste streams of chromium tanning yard are in the range of 1700-2500ppm (Sreeram & Ramasami, 2003). Conventional chromium tanning spent liquors containing significant amounts of chromium along with different polluting (both organic and inorganic) substances. Only 60-70% of the chromium is utilized from the total used for tanning, while the rest 30-40% remains in the spent (already used) tanning liquor, which is normally sent to a waste water treatment plant (Sarker, Basak, & Islam, 2013). Uncontrolled chromium content in waste which is discharged into the environment, will lead to environmental problems and health risks (Kimbrough, Cohen , Winer , Creelman , & Mabuni, 1999)

Chromium itself is a metal in the VI-B group of the periodic table. Although it is able to exist in several oxidation states, the most stable and common forms are the trivalent Cr (III) and the hexavalent Cr (VI) species having different chemical properties (Carmona, Silva, Leite, & Echeverri, 2007). Trivalent chromium compounds are sparingly soluble in water, while hexavalent chromium compounds are quite soluble. The resulting hexavalent chromium solutions are powerful oxidizing agents under acidic conditions, but less so under basic conditions. (Saha, Nandi, & Saha, 2011). Hexavalent form is five hundred times more toxic than the trivalent (Kumar, Ray, & Chakraborty, 2007) (Kim, Park, & Gu, 2002).

Various efforts need to be done in reducing the release of chrome to the environment which one of them is through exhausted chrome tanning process. The present day high-exhaust chrome tanning methods lead to a wastewater containing 500−1000ppm of chromium. But the discharge limits for trivalent chromium vary broadly ranging from 1-5mg/l in the case of direct discharge into water bodies, and 1-20mg/l in the case of discharge into the public sewer system (Aravindhan, Madhan, Rao, Nair, & Ramasami, 2004).

3. Tools, Materials, and Methods

3.1 Tools

Tools used in this research are drum, knife, and scale.

3.2 Materials

Material used in this research are; 6 sheep skins, Chromosal B, Na-asetat, Novaltan MAP (polycarboxylate), Formic acid, NaCl, Sulfited Fish Oil, MgO, and NaHCO3.

3.3 Methods

6 sheep skin divided in to 2 conditions; conventional tanning process and exhausted-chrome tanning process

Tanning process with conventional system was done by the general process which are 1) repickle by 75% water, 7.5% NaCl, 0,2% FA; 2) tanning sheep skin by 100% water, 8% Chromosal B, 2% Na Acetate, 2% Sulfited fish oil, 0.6% MgO, and 0.65% $NaHCO_3$. The tanning process with exhausted system was done by adding polycarboxylate material during repickle and then proceeds to the tanning process. Repickle 75% water, 7.5% NaCl, 0.1% FA, 2% Novaltan MAP, then tanning sheepskin by 100% water, 0.3% FA, 8% Chromosal B, 2% Na Acetate, 2% Sulfited fish oil, 0.6% MgO, 0.2% $NaHCO_3$. The waste liquid is then collected and tested for the following parameters; Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), and Total Chromium.

3.4 Analysis

The data obtained are then analyzed by Independent Sample T-Test using IBM SPSS 22.

4. Results and Discussions

The results of total chromium, BOD, and COD in wastewater were analyzed with the Independent Sample T-Test method using the SPSS software. The results showed that the average total chromium content in waste water at conventional treatment was 2490mg/L. However after an exhausted chrome process, an average yield of 1102.8 mg/L was obtained. These results indicate that there is a decrease in the total chromium in waste water due to the exhausted chromed tanning process.

Based on the result of the Independent Sample T-Test (Table 2), it is known that the $P<0.05$, so it can be concluded that the exhausted chromed tanning process, with the addition of polycarboxylate, will reduce the total chromium formed in the tanning waste water. This is because the chromium tanning reaction is the creation of covalent complexes between the collagen carboxyl groups and the chromium (III) molecular ions (Covington, 2009).

Thus it can be said that the addition of polycarboxylate in the tanning process by the exhausted chrome process method, will add a carboxylic group that will bind chromium. This will lead to more chrome bound in the leather. This chromium-polycarboxylate bonding is shown in Figure 1. Excessive chromium usage also causes an increase in chromium waste, especially as chromium absorption in leather is limited.

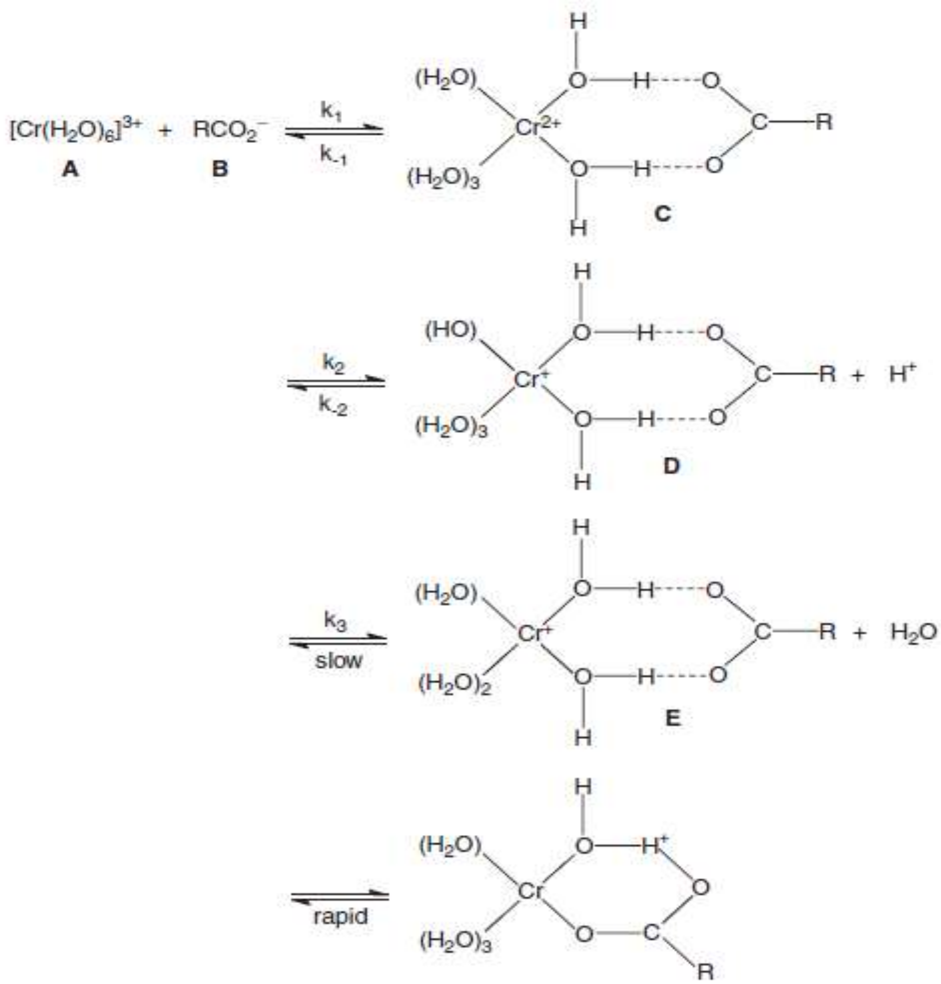

Figure 1: *Chromium Bonding with Polycarboxylate*

Source: (Covington, 2009, p. 217)

Table 1: *Comparison of Exhausted Chrome Tanning Process Wastes with Conventional Processes*

Parameter	Process	N	Mean (mg/ L)
Total Chromium	Conventional	9	2490.00
	Exhausted	9	1102.80
BOD	Conventional	9	2277.00
	Exhausted	9	2187.20
COD	Conventional	9	6606.20
	Exhausted	9	5981.20

Table 2: *Independent Sample T-Test for Exhausted Chrome Tanning Process Wastes with Conventional Processes*

Parameter	Tanning Process	t	df	Sig. (2-tailed)
Total Chromium	Conventional - Exhausted	5945.143	16	0.000^{a}
BOD	Conventional - Exhausted	355.274	16	0.000^{b}
COD	Conventional - Exhausted	3067.494	16	0.000^{c}

a,b,c : different of superscript in the same line showed the highly significant difference ($P \leq 0.05$)

The results also showed that in the conventional tanning process, the average BOD content in waste water was 2277.0 mg/L. Whereas after addition of polycarboxylate, the average value of BOD was 2187.2 mg / L. Hence it can be said that there is a decrease in value for BOD. This is confirmed by the Independent Sample T-Test in Table 2, where the value of $P < 0.05$, thus it can be concluded that the treatment using the exhausted chrome process, with the addition of polycarboxylate, will be able to reduce the BOD value in the tanning waste water process.

The other parameter tested was the COD. The results showed that the average COD content in the waste water from the conventional tanning process was 6606.2mg/L. While in the exhausted chrome process, the value of COD was 5981.2 mg/L. Which means that the value of the COD decreased by 9.46%. The performed Independent Sample t-Test has proven that the exhausted chrome process treatment, with the addition of polycarboxylate, will be able to reduce the value of COD in the tanning waste water process.

However, the addition of polycarboxylate has not been able to produce tanning wastes which have BOD, COD and total chromium content that are in accordance with the regulations enacted in the regulation from the Republic of Indonesia Minister of Environment Number 5 of 2014. Comparison of this can be seen in Table 3.

Table 3: *Comparison of Content in Wastewater with Applicable Regulations*

Parameter	Treatment		Wastewater Quality Standard - Regulation from the Minister of the Environment - Republic of Indonesia No. 5 of 2014 (mg/L)
	Conventional (mg/L)	Exhausted chrome tanning process (mg/L)	
BOD	2277.0	2187.2	50
COD	6606.2	5981.2	110
Chrome total (Cr)	2490.0	1102.8	0,6

Based on the comparison with the Regulation from the Minister of the Environment - Republic of Indonesia No. 5 of 2014, it can be said that the waste water produced in the tanning process still requires further processing of waste in order to meet the standard quality of leather tanning waste.

5. Conclusions

This research was conducted to determine and analyze the characteristics of the waste from the exhausted chrome tanning process. Analysis of BOD, COD and chroumium needs to be done to develop an environmentally friendly tanning method.

Leather tannery using exhausted chromed tanning process method can produce waste with total chromium, BOD, and COD value which are lower than those of conventional method.

Exhausted chrome tanning process is still not able to reduce the value of BOD, COD, and total chromium under the applicable quality standards. Therefore, the waste generated still requires further processing. Proper processing methods for reducing BOD, COD and chromium in tanning wastewater can be further investigated.

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