Usage of Fenton Reagent in Local Tannery Wastewater Bioremediation

N A Fitriyanto1*, A K Sari 1, R A Prasetyo1, N Kurniawati 1

1 Faculty of Animal Science, Universitas Gadjah Mada, Jl. Fauna No.3 Bulaksumur, Yogyakarta, 55281, Indonesia.

Corresponding author’s email address: nanungagusfitriyanto@ugm.ac.id

Abstract. The tannery industry produces liquid wastewater containing high organic and inorganic pollutants. This study aims to determine the effect of Fenton reagent as a bioremediation agent in tannery wastewater treatment. The material used in this study was tannery wastewater from the local leather industry in Bantul, Yogyakarta. This study was arranged in a Completely Randomized Design with triplicates for each treatment, and the result was analyzed using ANOVA and Duncan Multiple range test for the significant difference. The treatment consisted of 4 different concentrations of the Fenton reagent addition P0 (0%), P1 (0.2%), P2 (0.4%), and P3 (0.6%). The BOD, COD, TS, total chrome (Cr), and chrome hexavalent (Cr (VI)) content were observed in this research. This study showed that Fenton reagent's addition at different concentrations had no significant effect (P>0.05) on the BOD content. However, it has a significant effect (P<0.05) on increasing the value of TS, TSS. However, it decreased the value of COD, Total Cr, and Cr (VI). The addition of 0.6% in P3 had the highest effect by reducing 66.7% COD, 11.8% of total chrome (Cr), and 11.5% of Cr (VI). It could be concluded that the addition of the Fenton reagent until 0.6% of this study has not been able to meet the standard quality standard for tannery wastewater. However, it was able to reduce inorganic pollutants, especially in Cr (VI). Combining several methods in bioremediation with the Fenton reagent may important for further study on tannery wastewater treatment.

Keywords: Tannery Industry; Liquid Wastewater; Organic and Inorganic Compounds

1. Introduction
The tannery industry is one of the oldest industries which still exists in recent time. Leather products from various types of animal skins and hides can be produced and processed into materials to make various clothing, accessories, and musical instruments. Human lifestyles also play a role in the development and demand for these leather tanning industry products. The development of the leather in the tannery industry at one of the regional areas affected and increased local economic value and harmed the wastewater's environmental pollution as a by-product. Tannery wastewater contains a high concentration of organic and inorganic compounds, also chemicals hazardous substances. Therefore, it is needed for long periods and must be through various treatment steps of the bioremediation in wastewater before disposal to the environment. One of the dangerous and toxic chemical compounds found in the tannery industrial wastewater is Cr. The hazardous material from Cr compounds in the tannery wastewater originated from the tanning process [1]. The chrome (Cr) from the tannery wastewater is usually in the form of Cr (VI), namely chromate (CrO$_4^{2-}$), which is very toxic. Based on the stability and toxicity of chrome from the lowest form, it can be divided into Cr (0), trivalent Cr
(III), and Cr hexavalent (VI) species [2]. In the previous study, using some strains of bacteria such as *Alcaligenes* sp. LS2T [3][4], *Pseudomonas* sp. LS3K [5][6][7], *Arthrobacter* sp. LM1KK [8] has been attempting in organic compounds bioremediation processing in wastewater treatment.

In this study, we use the Fenton reagent as an additional alternative treatment that can be applied. Fenton reagent is hydrogen peroxide (H$_2$O$_2$) and an iron catalyst (Fe$^{2+}$), which has a high oxidation ability in oxidizing contaminants in wastewater. Fenton reagent's advantage is non-toxic, does not leave harmful residues, simple, and environmentally friendly compounds [9]. The Fenton reagent produces a hydroxyl radical (HO), which effectively destroys organic chemistry because it reacts quickly and none selectively with almost all organic compounds. Fenton reagent also does not cause a new danger to the environment because the Fenton reaction process's final result is CO$_2$ and H$_2$O. Besides that, the Fe ion content in the Fenton reagent also has the potential to reduce Cr (VI) pollutants to Cr (III), which is less toxic and environmentally friendly [10]. This research was conducted to determine the effect of adding the Fenton reagent to the pollutant content in the tannery industrial wastewater at the laboratory scale.

2. Materials and Methods

2.1. Design of Experiment

The untreated tannery wastewater sample in this study was obtained from one of the local tannery industries located in Bantul District, Special Region of Yogyakarta, Indonesia (DMS 7°50'04.0"S 110°23'49.1"E) in August 2019. The application of Fenton reagent to the samples was the following [11]. As much as 500 mL sample of tannery wastewater was filled into Erlenmeyer (1000 mL), continued by stirring with a magnetic stirrer at 25 rpm for 1 hour. pH was adjusted to 3.5 using NaOH and HCl 0.1 M solutions. Several Fenton reagent treatments made by Fe$_2$SO$_4$.7H$_2$O and H$_2$O$_2$ 30% with a proportion of 1:1 (w/v) were added in 3 replications. Concentrations were varied, namely P0 as the control treatment; P1 used 0.2% (0.5 mg Fe$_2$SO$_4$.7H$_2$O + 0.5 mL H$_2$O$_2$); P2 used 0.4% (1 mg Fe$_2$SO$_4$.7H$_2$O +1 mL H$_2$O$_2$) and P3 used 0.6% (1.5 mg Fe$_2$SO$_4$.7H$_2$O + 1.5 mL H$_2$O$_2$). Stirring was carried out in 24 hours using a magnetic stirrer at a speed of 120 rpm. Subsequently, the effluent was taken to be tested in Biochemical Oxygen Demand (BOD) by measuring the Dissolved Oxygen (DO) used the Winkler Titration method [12], Chemical Oxygen Demand (COD) carried out using the open reflux by the Titrimetric method [13]. Total Solids (TS) was measured by the Gravimetric method [14], Total Suspended Solid (TSS) was measured by the Gravimetric method [15], Total (Cr) [16], and Cr (VI) [17] were measured by Atomic Absorption Spectrophotometry (SSA) method

2.2. Data Analysis

The obtained data were statistical analysis with a Completely Randomized Design using One-Way ANOVA and continued with the Duncan Multiple Range Test [18].

3. Results and Discussions

The Characteristics of tannery wastewater treated with the Fenton reagent at different levels are presented in Table 1.

| Parameters | Fenton’s Treatment | Maximum Standards limits* |
|------------|--------------------|---------------------------|
| P0         | P1                 | P2                        | P3                        |
| BOD (mg/L) | 2394.67±237.87     | 2624.67±444.37 690.67±331.93 | 2572±381.90 150          |
| COD (mg/L) | 9156.5±0.7a        | 6363.2±2194b 5587.2±0.00c | 3027.8±1117d 300         |
| TS (mg/L)  | 0.237±0.0001a      | 0.239±0.0004a 0.247±0.0004b | 0.252±0.0006b           |
| TSS (mg/L) | 98±2.83a           | 228±5.66d      144±5.66c  | 118±2.83b 150            |
Based on the results in Table 1, the Fenton reagent addition has no significant effect (P>0.05) on the BOD level of the tannery wastewater. However, it has a significant effect (P<0.05) on increasing the value of TS, TSS and decreasing the value of COD, Total Cr, and Cr (VI). The highest increase in TS value occurred in the addition of 0.4% Fenton reagent (P2), which was observed 6.3% from the TS value in control. The highest increase in TSS values occurred in the addition of 0.2% Fenton reagent (P1), which was observed 132.6% from the control. The highest decrease in COD occurred in the addition of 0.6% Fenton reagent (P3), which was 66.7% from the control. The highest decrease in total Cr value occurred at the addition of 0.6% Fenton reagent (P2), which was determined 11.8% from the control. The highest decrease in Cr (VI) occurs at the addition of 0.6% Fenton reagent (P3), 11.5% from the control. The addition of the 0.6% Fenton reagent to fresh liquid wastewater from the tannery industry with 24 hours of incubation time has not been able to produce waste which under the quality standards of liquid waste for the leather tanning industry in Indonesia (Kep. Men. LH No. 51 Th. 1995). It could be assumed that the doses used in this research were minimum. Fenton reagent’s optimum concentration in the oxidation of pollutant compounds in tannery wastewater depends on the doses, initial pH, and incubation time. In Fenton treatment, maximum waste removal has been observed in the pH range of 3–4. Fenton’s reagents, which made by 6 g/L FeSO4 and 111 g/L H2O2 with 30 minutes of incubation time has removed BOD up to 46% from initial concentration at 977 mg/L, removed COD up to 40.44% from initial concentration at 2533 mg/L, and removed Total Cr up to 5% initial concentration at 258 mg/L. [19].

The high content of pollutants in the tannery wastewater in this study was due to the liquid samples used originating from the equalization bath or shared shelter from various stages of the tanning process from preparation to finishing stages. During the preparation process in raw skin until the finishing tanning will be produced by-products in the form of liquid waste that is high in organic matter and chemical compounds that cause a high concentration of Suspended Solids, BOD, COD, and Total Cr [1]. The advanced oxidation method using the Fenton reagent is one of the additional treatment can be used to destroy the toxic pollutant in tannery wastewater. Fenton reagent is hydrogen peroxide (H2O2) and an iron catalyst (Fe2+), which has a high oxidation ability to oxidize the contaminants in wastewater. Fenton reagent is capable of destroying toxic compounds, whether organic or chemical compounds contained in industrial wastewater. The Fenton reagent is OH radical production occurs with the reaction between H2O2 to Fe2+ (salts). H2O2 + Fe2+ → OH • + OH− + Fe3+. Thus, this is a straightforward way to produce OH radicals without the need for special reactants or special equipment. This reactant is an attractive oxidative system for wastewater treatment because iron is a very abundant and non-toxic element, and hydrogen peroxide is easy to handle and safe for the environment [9]. The Fenton reagent mechanism uses the Fe ions to react with hydrogen peroxide, producing hydroxyl radicals with strong oxidizing abilities to degrade organic and chemical contaminants such as Cr. The presence of Fe2+ ions can reduce and adsorb Cr. The process of degradation of Cr pollutants by Fe ions through the mechanism of adsorption and reduction of hazardous Cr (VI) to Cr (III), which is safer in the form of Cr2O3 and Cr(OH)3 [20].

In this study, the addition of up to 0.6% Fenton reagent was able to reduce the COD value to 66.7%, Total Cr by 11.8%, and Cr (VI) by 11.5%. Thus, it can be an alternative treatment for fresh tannery wastewater. To increase the effectiveness of subsequent processing stages through coagulation, flocculation, sedimentation, and bioremediation. This condition is in line with [6]; the combined treatment on Fenton oxidation with biological treatment can be considered better results in tannery wastewater treatment. The combination treatment has shown a synergistic effect on stimulating the biodegradability of an organic compound in wastewater and reducing the bioremediation treatment time.

| Total Cr (mg/L) | 201.1±2.19a | 193.3±1.00b | 177.6±3.47c | 177.4±1.58c | 2.0 |
| Cr (VI) (mg/L) | 0.382±0.007a | 0.375±0.007a | 0.373±0.009a | 0.338±0.002b |

Notes: *Kep. Men. LH No. 51 th. 1995 is the basis of Indonesian quality standards on liquid wastewater for the tannery industry; a,b,c,d The different superscripts on the different row has a significant effect (P<0.05).
4. Conclusion
Fenton reagent addition up to 0.6% can reduce COD's value by 66.7%, Total Cr by 11.8%, and Cr (VI) by 11.5%. Fenton reagent can be an alternative pretreatment for fresh liquid of tannery wastewater to improve bioremediation effectiveness at the next processing stage and requires further study.

Acknowledgments
This research was supported by the Ministry of Education and Culture of the Republic of Indonesia for funding this research through the Beasiswa Pendidikan Pascasarjana Dalam Negeri/BPPDN program.

References
[1] Durai G and Rajasimman M 2011 Biological treatment of tannery wastewater - A review J. Environ. Sci. Technol. 4 1–17
[2] Oliveira H 2012 Chromium as an Environmental Pollutant: Insights on Induced Plant Toxicity J. Bot. 2012 1–8
[3] Azkarahman A R, Erwanto Y, Hadisaputro W, Yusiati L M and Fitriyanto N A 2017 Characteristics of Alcaligenes sp. LS2T Heterotrophic and Aerobic Ammonium Removal for Potential Livestock’s Wastewater Treatment Proceeding of the 1st International Conference on Tropical Agriculture (Springer International Publishing) pp 337–44
[4] Fitriyanto N A, Gutama R, Wandita T G, Erwanto Y, Hayakawa T and Nakagawa T 2019 Isolation and characterization of Alcaligenes sp. LS2T from poultry farm at Yogyakarta city and the growth ability in animal’s urine medium AIP Conf. Proc. 2099 1–6
[5] Fitriyanto N A, Winarti A, Imara F A, Erwanto Y, Hayakawa T and Nakagawa T 2017 Identification and growth characters of nitrifying pseudomonas sp., LS3K isolated from odorous region of poultry farm J. Biol. Sci. 17 1–10
[6] Prasetyo R A, Pertiwiningrum A, Erwanto Y, Yusiati L M and Fitriyanto N A 2018 Characterization of Pseudomonas sp. LS3K as Nitrate Removal Agent at Different C/N Ratios Under Aerobic Condition Proceeding of the 2nd International Conference on Tropical Agriculture (Springer International Publishing) pp 185–94
[7] Prasetyo R A, Pertiwiningrum A, Erwanto Y, Yusiati L M and Fitriyanto N A 2019 The potency of Pseudomonas sp. LS3K as nitrifying bacteria on inorganic medium at various c/n ratios Asian J. Microbiol. Biotechnol. Environ. Sci. 21 257–63
[8] Fitriyanto N A, Permadi A, Erwanto Y, Hayakawa T and Nakagawa T 2017 Characteristics of High Ammonium-tolerant Arthrobacter sp. LM1KK Isolated from High Ammonia Odorous Region of Laying Hens Farm in the Tropical Area Res. J. Microbiol. 12 118–27
[9] Sharma S, Ruparelia J and Patel M 2011 A general review on advanced oxidation processes for waste water treatment Inst. Technol. Nirma Univ. Ahmedabad-382, 1–7
[10] Vilardi G, Ochando-Pulido J M, Stoller M, Verdone N and Di Palma L 2018 Fenton oxidation and chromium recovery from tannery wastewater by means of iron-based coated biomass as heterogeneous catalyst in fixed-bed columns Chem. Eng. J. 351 1–11
[11] Cristiany A, Rezagama A and Nur M 2017 Perbandingan efisiensi pengolahan air zat warna sintetis indigosol yellow sebagai hasil produksi batik dengan metode fenton dan ozonisasi katalitik terhadap parameter warna J. Tek. Lingkung. 6 1–9
[12] Badan Standardisasi Nasional 2009 SNI 6989.2:2009 Air dan Air Limbah - Bagian 2 : Cara uji Kebutuhan Oksigen Kimiawi (Chemical Oxygen Demand/COD) dengan Refluks Tertutup secara Spektrofotometer pp 1–16
[13] Badan Standardisasi Nasional 2004 SNI 06-6989.15-2004 Air dan air limbah - Bagian 15: Cara uji kebutuhan oksigen kimiawi (KOK) refluks terbuka dengan refluks terbuka secara titrimetri p 9
[14] Badan Standardisasi Nasional 2004 SNI 06-6989.26-2005 Air dan air limbah – Bagian 26: Cara uji kadar padatan total secara gravimetri p 9
[15] Badan Standardisasi Nasional 2004 SNI 06-6989.3-2004 Air dan air limbah – Bagian 3: Cara
uji padatan tersuspensi total (Total Suspended Solid, TSS) secara gravimetri p 10

[16] Badan Standar Nasional 2004 SNI 06-6989.17-2004 tentang Air dan air limbah – Bagian 17: Cara uji krom total (Cr-T) dengan metode Spektrofotometri Serapan Atom (SSA) – nyala

[17] Badan Standarisasi Nasional 2009 SNI 6989.71:2009. Cara uji krom heksavalen (Cr-VI) dalam contoh uji secara spektrofotometri.

[18] Steel R G D and Torrie J H 1995 Prinsip dan prosedur statistika (Terjemahan) (Jakarta: PT. Gramedia Pustaka Utama)

[19] Mandal T, Dasgupta D, Mandal S and Datta S 2010 Treatment of leather industry wastewater by aerobic biological and Fenton oxidation process J. Hazard. Mater. 180 204–11

[20] Diao Z H, Qian W, Zhang Z W, Jin J C, Chen Z L, Guo P R, Dong F X, Yan L, Kong L J and Chu W 2020 Removals of Cr(VI) and Cd(II) by a novel nanoscale zero valent iron/peroxydisulfate process and its Fenton-like oxidation of pesticide atrazine: Coexisting effect, products and mechanism Chem. Eng. J. 397 1–9