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Leather Tannery Wastewater Treatment Using Electro-Fenton Process – Effects on Ammonia, Chromium, Total Suspended Solid, Biological Oxygen Demand and Chemical Oxygen Demand Removal

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ABSTRACT

Electro-Fenton process could remove pollutant in in tannery industry wastewater. The objectives of this is used to know the effect of electro-Fenton on, ammonia (NH_3), chromium (III) (Cr(III), total suspended solid (TSS), biological oxygen demand (BOD), and chemical oxygen demand (COD) removal in tannery wastewater treatment. The voltage variation used to trigger the electro-Fenton reaction was 6 V, 8 V, and 10 V. Observation time at 0, 30, 60, 90, and 120 mins was used to see changes in the sample. The results obtained are electro-Fenton method has an effective time of 30 mins to removal efficiency of 60.7%, 32.9%, 72.8%, 53.4%, and 53.4% for NH_3, Cr(III), TSS, BOD, and COD respectively. Pollution from tannery effluent can be eliminated to a sufficient extent using the electro-Fenton technique.

Keywords: wastewater treatment, leather tannery wastewater, industrial waste, electro-Fenton, removal.

INTRODUCTION

The leather tannery industry is an industry that processes raw animal skin, and semi-finished leather into valuable finished leather [1, 2]. The primary processes in the making of leather are soaking, liming, deliming, bating, pickling, tanning, post-tanning, and finishing [3]. The leather production requires the addition of chemicals and water, the rest of the process becomes liquid waste containing chemical pollutants such as ammonium [2], chromium [4, 5], and organic matter [6]. Improper treatment of leather tannery wastewater is an environmental issue that can pollute soil, surface water, and groundwater.

One of the regions in Indonesia that is the center of the leather tannery industry is the Magetan Regency. The leather tannery industry in Magetan, East Java (Indonesia), is experiencing rapid development [7]. The leather industry environment (LIK) is an area where there is a community to carry out the leather tannery process and a partnership between the tanner community and the Magetan Leather and Leather Products Industry Technical Implementation Unit (UPTI) [8]. There are 35 leather tannery industries in the UPTI-LIK Magetan area that dispose of production waste at the same wastewater treatment plant (IPAL). Based on this, it is necessary to research to determine the suitability of the waste produced with quality standards. Electrochemical process has been widely used in wastewater treatment process [9, 10]. The electro-Fenton (EF) method is one of the most current and sophisticated technologies. It is widely used for treating complicated wastewater and is especially useful for remediating refractory compounds because it can produce in situ reactive species such as hydroxyl radicals (·OH) and sulfate radicals (SO_4^-) [11]. The oxidation process in electro-Fenton depends on the H_2O_2 produced. The mixture of H_2O_2 and $FeSO_4$ produces hydroxyl radicals (-OH) which are more optimal at an acidic pH below 4 [12]. The reduction of Fe_{3+} to Fe_{2+} and these hydroxyl radicals react quickly in an aqueous environment, from which the reaction produces hydroxy (OH) radicals. Previous studies have confirmed the effectiveness of EF-based systems in eliminating a wide range of organic [11], and inorganic matter such as chromium [13].

The chemical organic and inorganic parameters such as NH_3, Cr(III), TSS, BOD, and COD are essential in wastewater characteristics. NH_3 is a chemical compound which has a distinctive odor that can reduce oxygen levels in waters and contains toxins [14]. Chromium (Cr) metal is a heavy metal that is toxic and causes acute poisoning and chronic poisoning [15, 16]. COD describes the total amount of oxygen needed to chemically oxidize organic matter contained in wastewater [17], and BOD is defined as the amount of oxygen required by microorganisms to break down organic materials contained in water [18] TSS is a solid that causes water turbidity, is not dissolved, and cannot settle directly [19].

This study proposes electro-Fenton methods for reducing ammonia, chromium, COD, BOD, and TSS in tannery wastewater treatment. The effect of voltage and time were explored in addition to knowing the optimum condition of the treatment process. The results of this study can be used as an additional treatment for tannery wastewater in the traditional leather tannery industry in Indonesia.

MATERIAL AND METHODS

Samples and chemicals

A leather tannery wastewater sample was taken from the wastewater treatment plant in Magetan City, Indonesia. Sulfuric acid and ferrous sulfate are purchased from Merck (Germany). All analytical reagent was provided at least analytical grade.

Electro-Fenton process

Figure 1 shows a schematic diagram of the electro-Fenton process of leather tannery wastewater. A graphite rod with a 2 mm diameter and 50 mm long was used as a cathode. A carbon rod with an 8 mm diameter and 50 mm long was used as anode. 998 mL of ferrous sulfate (0.18 M) was poured simultaneously with 1000 mL of leather tannery wastewater into each reactor basin. Furthermore, 2 mL sulfuric acid was added to the ferrous sulfate solution to reduce pH < 4. Next, the DC supply was turned on with a distance between electrodes of 6 cm. The magnetic stirrer was set at

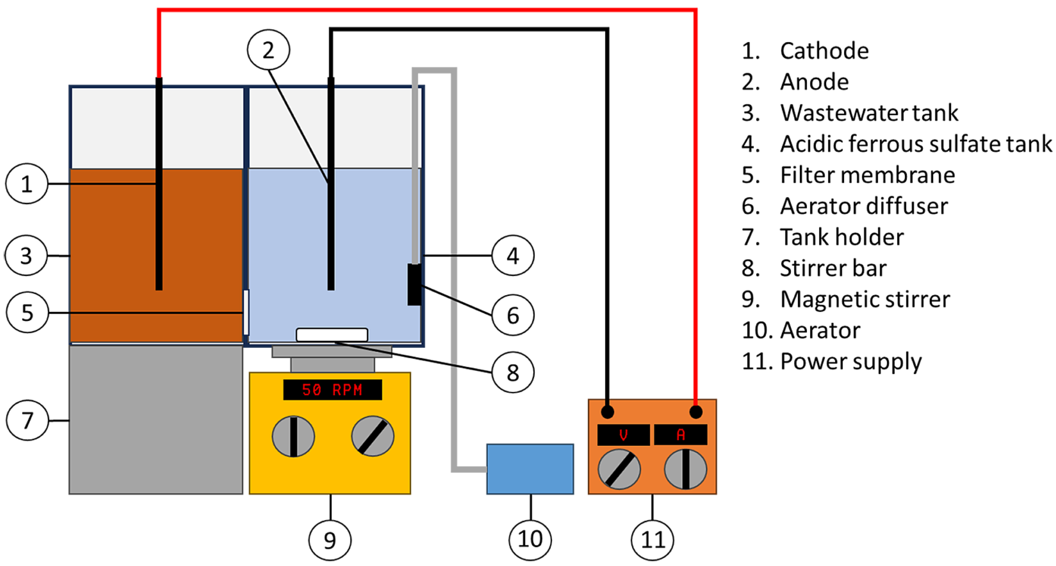

Figure 1. Experimental setup apparatus

50 rpm, while the aerator was set with a flow of 3.5 L/min. The voltage used in this study was 6 V, 8 V, and 10 V with time variations of 30, 60, 90, and 120 min at room temperature. After the electrolysis was completed, the floc formed was allowed to settle completely. The clear part that did not contain floc sediment was removed for analysis.

Analytical methods

All parameter was analyzed using American Public Health Association (APHA) standard methods [20]. Ammonia (NH_3) was analyzed using APHA 4500-NH_3 while Chromium (III) (Cr(III)) was analysed using APHA 3500-Cr. TSS were analyzed using APHA-2540-D. BOD and COD were analysed using APHA-5210B and APHA-5220.

RESULTS AND DISCUSSIONS

Leather tannery wastewater characteristics

Table 1 shows the characteristics of leather tannery effluent collected from tannery wastewater treatment plant in Magetan City, Indonesia. The research data presented in Table 1 highlights concerning deviations from the effluent quality standards for leather tannery wastewater. While the pH level of 7.40 is within the acceptable range of 6.0 to 9.0, several other parameters significantly exceed the maximum allowable concentrations set by Regulation No. 5 of 2014. Specifically, ammonia (NH_3), chromium (Cr(III)), TSS, BOD, and COD levels are substantially higher than permitted limits. Ammonia is measured at 123.10 mg/L, surpassing the 10 mg/L threshold; chromium is at 0.58 mg/L, exceeding the 0.5 mg/L limit; TSS is 373.80 mg/L, well above the 200 mg/L standard; BOD is alarmingly high at 3923 mg/L compared to the 50 mg/L limit; and COD stands at 11413 mg/L, far exceeding the 100 mg/L maximum. These results underscore the urgent need for improved treatment processes and stricter enforcement to mitigate the environmental impact of tannery wastewater [21–23].

Pollutant removal

Ammonia

Figure 2a shows how effectively ammonia (NH_3) is removed during the electro-Fenton process for treating tannery effluent. The results reveal that removal efficiency varies depending on the treatment conditions. The lowest removal efficiency, at just 10.7%, occurred with a voltage of 6 V and a treatment time of 30 minutes. In contrast, the highest removal efficiency of 60.7% was achieved with the same voltage of 6 V but with a longer treatment time of 90 minutes. While the removal efficiency improved up to 60 and 90 minutes, it decreased at 120 minutes. For higher voltages of 8 V and 10 V, the production of hydroxyl radicals was steady, reaching its peak at 60 minutes before tapering off. The drop in efficiency at 120 minutes is due to the saturation of Fe_{2+}, which reacted too much with hydroxyl radicals to form $Fe(OH)_3$, thereby reducing the number of hydroxyl radicals available for ammonia removal [24].

The detention time for the electro-Fenton process shows that 30 minutes is the most effective duration for removing NH_3, although the removal efficiency at 60, 90, and 120 minutes also decreases, the drop is not very significant. NH_3 levels decrease because it reacts with hydroxyl radicals to form NH_2 and hydrogen. However, there were some anomalies in the removal efficiency results, particularly at a voltage of 6V, where parameter levels unexpectedly increased. According to a previous study [25], this increase may be due to the formation of ligands that initially bind

Table 1. Characteristics of leather tannery wastewater

Parameter	Value	*Max. concentration	Result
pH	7.40	6.0–9.0	OK
NH_3 (mg/L)	123.10	10	Exceeds the max. concentration
Cr(III) (mg/L)	0.58	0.5	Exceeds the max. concentration
TSS (mg/L)	373.80	200	Exceeds the max. concentration
BOD (mg/L)	3923	50	Exceeds the max. concentration
COD (mg/L)	11413	100	Exceeds the max. concentration

Note: *regulation of the minister of Environment of the Republic of Indonesia Number 5 of 2014 Concerning Effluent Quality Standards.

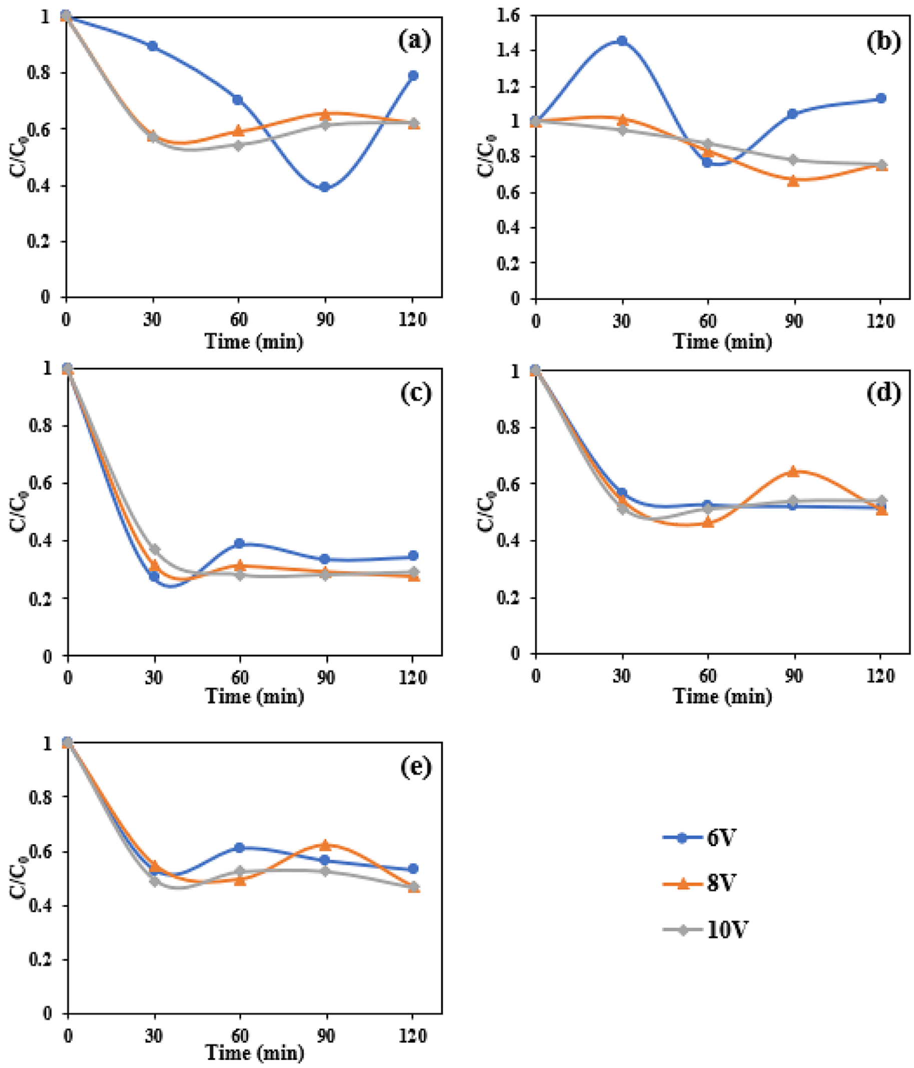

Figure 2. Removal of (a) NH_3, (b) Cr(III), (c) TSS, (d), BOD, and (e) COD during the electro-Fenton process of leather tannery wastewater

with water (H_2O) and then exchange with NH_3. Additionally, since the tannery wastewater contains chromium, this interaction could influence the reaction as follows the Equation 1:

$$(R^-)_2(Cr(H_2O)_4)^{2+} + 4NH_3 \rightleftharpoons \rightleftharpoons (R)_2(Cr(NH_3)_4)^{2+} + 4H_2O \quad (1)$$

The molecular exchange of H2O with NH_3 in the ligand causes the NH_3 content in the tannery industry waste to precipitate which results in the electro-Fenton waste treatment process not occurring perfectly. The NH_3 levels could increase since it can be released by the ligand (Krik, 1981).

Chromium

Figure 2b shows that chromium concentration decreased at voltages of 8 V and 10 V during the electro-Fenton treatment, indicating effective processing at these voltages. However, at 6 V, there were anomalies at 30, 90, and 120 minutes, where chromium levels fluctuated. The most effective detention time was 90 minutes, although efficiency decreased at 120 minutes. This decrease in chromium concentration at higher voltages is attributed to reactions with hydroxyl (OH) radicals. Despite this, an observed increase in chromium (III) concentration after treatment compared to the initial concentration suggests other factors are at play. Specifically, side reactions during the electro-Fenton process may convert chromium from other species to chromium (III), and the formation of complexes that are not fully decomposed could also contribute to higher measured concentrations. Additionally, suboptimal process conditions or parameter settings may exacerbate this issue. As detailed in previous studies [26], chromium (III) can precipitate due to chelate formation with ligands, further influencing chromium concentrations. Therefore, a comprehensive evaluation of reaction mechanisms and process optimization is crucial to address and mitigate the increased chromium (III) concentration.

$$[Cr(H_2O)_5(OH)]^{2+} + H^+ \leftrightarrow [Cr(H_2O)_6]^{3+} \quad (2)$$

The mechanism is interchange associative (IA) the rate at which water molecules are replaced with ligands that act as Lewis bases. In contrast, transition metal atoms (both in the neutral and positively charged state) act as Lewis's acids, i.e. accept (and share) electron pairs from Lewis bases.

TSS

Changes in TSS concentration were up and down in the 6 V and 8 V treatments as shown in Figure 2c. Detention time at 90 mins and 120 mins although decreased but not too significant, this could be due to the Fe^{2+} content of 100 ppm as a catalyst has been used and cannot be reused or due to saturation of the catalyst that reacts with hydroxyl radicals. Based on the hypothesis, the electro-Fenton reaction is effective in the first 30 mins before saturation. The lowest removal efficiency was 61.1% with 6 V treatment and 60 mins of detention time. While the highest removal efficiency was 72.8% with 6 V treatment and 30 mins detention time.

BOD

The lowest removal efficiency was 35.4% with 8 V treatment and 90 mins of detention time. Meanwhile, the highest removal efficiency was 53.4% with 8 V treatment and 60 min detention time as shown in Figure 2d. Based on the observation data, it is hypothesized that the initial 30 mins is the effective time for electro-Fenton to work. With an almost even level of efficiency reduction at different potential differences, the process of decomposing organic matter in waste occurs quickly in the initial 30 mins and slows down afterward. This can happen because the hydroxyl radicals formed saturate the catalyst where $Fe(OH)_3$ begins to form and inhibits the regeneration of Fe^{3+} to Fe^{2+} needed in the Fenton reaction. The chelation of ligands [26] with organics may also affects the BOD degradation process.

COD

Changes in COD concentration decreased most evenly in the initial 30 mins, then experienced ups and downs (Figure 2e). The increase in COD value can be caused by the non-oxidation of Fe^{2+} to Fe^{3+} [13]. This is related to the hypothesis in TSS and BOD where Fe saturation occurs in the form of $Fe(OH)_3$. Based on the same hypothesis in BOD, the formation of Cr ligand chelates is the main factor in the rise and fall of the COD process. The lowest removal efficiency is 37.6% with 8 V treatment and 90 mins of detention time. Meanwhile, the highest removal efficiency was 53.4% with 10V treatment and 120 mins detention time. The effect of electrolysis time is that the longer the electrolysis time causes more Fe^{2+} ions form. The greater the concentration of Fe^{2+} ions, the greater the oxidation of pollutants as indicated by the greater reduction of COD in the waste [27].

Comparison with other oxidation process

Table 2 shows Available studies on tannery wastewater treatment using oxidation methods. Since COD was an important parameter in wastewater, almost all research conducted shows COD removal. The electrochemical oxidation process has been reported could remove the COD containing 32–81.2% [28, 29] with 90% color removal [28]. The electrochemical process has a high efficiency of organic contaminants in wastewater treatment. Electrochemical treatment has specific benefits such as high efficiency, ambient operating conditions, small equipment sizes, little sludge production, and quick start-up [30].

Photochemical process using Fenton [31], ZnO [32], bentonite-Zn [33], and BiVO4–ZnO [23], has variate COD removal of 83%, 97.7%, 64%, 35.3%, 70%, and 95.5% respectively. ZnO photocatalytic process also reported could remove the BOD, total solids (TS), and total organic carbon (TOC) higher than 93% [32]. The use of TiO2 as a photocatalyst also has been reported could remove TOC, Cr(VI), and color nearly 100% [35]. ZnO and TiO2 photocatalysts have the highest COD removal compared to other catalysts. ZnO and TiO2 have been shown in numerous previous studies to be highly promising compounds because they boost the photon's ability to separate electrons from holes as well as the photon's response spectrum [36]. WO3/rGO/

Table 2. Available studies on tannery wastewater treatment using oxidation methods

Method	Initial concentration	Removal efficiency	Reference
Electrochemical oxidation	COD: 3600 mg/L	COD: 32%	[28]
Photo-Fenton	COD: 300 mg/L	COD: 83%	[31]
Ozonation	COD: 5000 mg/L	COD: 70% discoloration: 90%	[21]
Fenton oxidation	COD: 1920 mg/L BOD: 732 mg/L NH_3: 560 mg/L	COD: 78% BOD: 94.8% NH_3: 82.8%	[22]
ZnO photocatalytic process	COD: 15023 mg/L BOD: 4374 mg/L TS: 28500 mg/L TOC: 4683 mg/L	COD: 97.7% BOD: 99.8% TS 93.3% TOC: 99.9%	[32]
BiVO4–ZnO photocatalytic process	COD: 3000 mg/L	COD: 64%	[23]
Bentonite-Zn photocatalytic process	COD: 100 mg/L	COD: 35.3%	[33]
Z-schemed WO3/rGO/SnIn4S8 sandwich nanohybrids photocatalytic process	Cr(VI): 30 mg/L	Cr(VI): 95.4%	[34]
TiO2 Photo electrocatalytic oxidation	Cr(VI): 14.12 mg/L	TOC: 95% Cr(VI): 100% discoloration 100%	[35]
Electrochemical oxidation	COD: 7189 mg/L	COD 81.2%	[29]
Electro-Fenton oxidation	NH_3: 123.10 mg/L Cr(III): 0.58 mg/L TSS: 373.80 mg/L BOD: 3923 mg/L COD: 11413 mg/L	COD: 53.4% NH_3: 60.7% Cr(III): 32.9% TSS: 72.8% BOD: 53.4%	This study

SnIn4S8 sandwich nanohybrids photocatalytic process also reported Cr(VI) and color removal of 95.4% and 88% respectively. In the realm of photocatalysts, titanium dioxide (TiO_2) and zinc oxide (ZnO) are thought to be the most often utilized semiconductors. Because of its broad direct band gap, which is around 3.37 eV, and high ultraviolet (UV) absorption, ZnO has a good photocatalytic power so it was the best choice for organic [37] and inorganic removal [36] in water/wastewater treatment process [37].

Another oxidation process, ozonation, also has significant COD and color removal of 70% and 90% respectively [21]. Fenton oxidation is also reported to have a COD removal efficiency of 77% [22]. In this study, the electro-Fenton process also has sufficient removal of NH_3, chromium, BOD, COD, and TSS removal. However, the removal efficiency was still smaller compared to another oxidation process. Also, compared to other studies, the tannery wastewater from Magetan leather tannery industry has higher BOD and COD concentration. More comprehensive studies should be conducted in the future to explore the ability of the electro-Fenton process in tannery wastewater treatment including the effect of catalyst dose, pH, voltage, and another critical parameter that could improve the pollutant removal efficiency.

CONCLUSION

The electro-Fenton method on the waste of the LIK Magetan leather tanning industry based on observation data has an effective reaction time range of 30 mins. According to the results, the electro-Fenton method can remove 60.7%, 32.9%, 72.8%, 53.4%, and 53.4% of NH3, Cr(III), TSS, BOD, and COD with an effective time of 30 mins. The catalyst plays an important role in the electro-Fenton process, when the catalyst becomes saturated, the electro-Fenton process stops and a stagnation period occurs. The presence of heavy metals encourages the formation of chelate compounds with ligands in the available organic matter. Although has lower removal efficiency compared to other oxidation process, sample used in this study has higher COD concentration. Future research should be more thorough in order to investigate the electro-Fenton process's potential for treating tannery effluent.

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