

A Research on treatability of leather industry wastewater by using electro-fenton process

Uğur KURT*, Ömer APAYDIN, M. Talha GÖNÜLLÜ
Yildiz Technical University Environmental Engineering Department
34349 Besiktas/Istanbul/Turkey
ukurt@yildiz.edu.tr
Fax:0212-2597070/2347

Abstract

In this study, treatment performance of Electro-Fenton Process as one of Advanced Treatment Processes (AOPs) on Leather Industry Wastewater was exposed.

Leather Industry Wastewater (LIW) is composed quite resistive organic pollutants and toxic substances such as chromium and sulfide. LIW, to treat as biological is very difficult. Microorganisms are inhibited by toxic substances.

Electro-Fenton Process is removal pollutants and toxicities both fastly and efficiently.

LIW samples were supplied from primary settling tank in Biological Treatment Plant of Istanbul Leather Organize Industry Region. Experimental studies were realized in a glass electrolyses cell with mixing in one liter volume. Iron sheet was used as anode and cathode electrodes. Electron transfer area was 45 cm² and distance between electrodes was 6 cm.

In the experiments, treatment performance was determined measuring COD in different electrical current and oxidant doses.

By the experimental works, in only five minutes, maximum COD and sulfide removals were obtained as % 69 and % 95, respectively. The lowest energy consumption for each kg COD removed in the solution was 1.66 kWh.

Key Words: AOPs, Electro-Fenton and Tannery Wastewater.

INTRODUCTION

Manufacturing of leather and leather goods produces numerous by-products, solid wastes, high amounts of wastewater containing different loads of pollutants and emissions into the air. The uncontrolled release of tannery effluents to natural water bodies increases environmental pollution and health risks.

In the sector, the water used varies extremely depending on the type of applied manufacturing technology. Advanced technologies involve processes usually termed low-waste or cleaner technologies. The minimum volume required is 2-3 m³/t raw hide under very good conditions. Tanning is a process of making leather from skin involves a complex combination of mechanical and chemical processes. The heart of the process is the tanning operation itself in which organic or inorganic materials become chemically bound to the protein structure of the hide and preserve it from deterioration. 80-90% of the world-wide tanneries use Cr (III) salts in their tanning processes. In some parts of the world, the Cr (III) is obtained from Cr (VI) species, which are a hundred times more toxic, but generally tannery effluents are unlikely to contain this form. Effluents from raw hide processing tanneries contain compounds of trivalent chromium (Cr) and sulphides in most cases. Due to these two foremost constituents of the wastewaters, different organic ingredients being responsible for high BOD and COD values expose an immense pollution problem. Treatment of tannery effluents is also known as causing technical problems, sophisticated technologies and high costs in concern with effluent

treatment. In common, a satisfying treatment of organics in this type wastewater is quite difficult.

Treatment of tannery effluents has been searched for physical, chemical and biological methods. Toxic structure of tannery effluents required application of these methods all together. After physical treatment, physico-chemical treatment methods are usually performed, which involves the chrome precipitation and sulphide treatment. Physico-chemical pre-treatment supplies an effluent containing easily biodegradable organics in standard aerobic biological treatment plants. However, each of chemical and biological treatment options has associated problems (Gate Information Service).

Oxidants especially hydrogen peroxide has been used to reduce the COD and BOD of industrial wastewaters for many years. H_2O_2 due to its redox properties find application in bleaching of paper pulp, sugar and textile. In a work three different oxidizing agents i.e. Hydrogen peroxide (H_2O_2), Sodium Hypochlorite ($NaOCl$) and Calcium Hypochlorite $\{Ca(OCl)_2\}$ have been used to reduce COD from tannery wastewater (Awan). The search showed that all the three oxidants i.e. Hydrogen peroxide (H_2O_2), Sodium Hypochlorite ($NaOCl$) and Calcium Hypochlorite ($Ca(OCl)_2$) can be used independently for the treatment of organic matter of tannery wastewater. Treatment by Hydrogen peroxide (H_2O_2) has supplied 44% COD removal in 1440 min. The maximum COD reduction (68% removal in 1440 min) was observed for Calcium Hypochlorite ($Ca(OCl)_2$) as oxidant. Treatment by $Ca(OCl)_2$ is also economically viable as compared to two other oxidants.

The purpose of this research is to perform electro fenton advanced oxidation method, and to put forward the applicability of the method by means of provided relevant data. In the experiments, optimization of doses of ferrous iron and hydrogen peroxide was carried out using a tannery wastewater sample. For that purpose, theoretical H_2O_2 doses required for Fenton oxidation of COD in wastewater theoretical have been calculated according to equation 1.



Theoretical H_2O_2 dose for one mole COD : $34/16 * COD = 2,125 * 2810 = 5970 \text{ mg } H_2O_2/l$. During the electrolytic processes using iron electrode, the concentration of Fe^{+2} ions in electrolytic media increases depending on reaction time. The ions are diffused from iron anode and catalyze forming of hydroxyl radicals ($\bullet OH$) in Fenton reaction can be seen from equation 2:



Hydroxyl radicals ($\bullet OH$) is the second strong oxidant after fluorine which standard oxidation potential (E^0) 2.87 volt. Hydroxyl radical has 2.33 volt standard oxidation potential.

MATERIAL AND METHODS

The tanning wastewater sample was taken from outlet of equalization basin in wastewater treatment plant of an Organized Industrialized (composed of heavily tannery plants) Region located Tuzla District in Istanbul-Turkey (Gonullu, 2004). The sample representing combined sewer system belonging to the region has had a characterization shown in Table 1, determined by using standard methods (APHA, 1998).

Electro-Fenton oxidation of wastewater was conducted in an undivided reactor of 0.5 dm³ volume. The overall experimental setup mainly consists of a cell unit, as shown in the following Fig. 1. Iron plates as cathode and anode (thickness: 2.0 mm, length: 6.0 cm and width: 7.5 cm) were arranged in parallel. Distance between electrodes was 6 cm. The total effective electrode area was 45 cm². The electrodes were connected to a DC power supply (GW Instek, GPS 3030 DD, 0-30 V, 0-3 A). Electrochemical treatment was conducted at 10V DC and 1.5 ampere (15 W). Electric current density was kept at 3.33 A·dm⁻². All the experiments were made at room temperature.

Before the process, the filled wastewater up was adjusted to pH=3. The study was performed for three different H₂O₂ doses (600, 1500 and 4500 mg/l which are equal to 10%, 25% and 75% of theoretical H₂O₂ dose, respectively). Electro-Fenton experiments were naturally realized until H₂O₂ residue in the solution is not exist. The measurement of H₂O₂ was made by permanganometric method (h2o2.com).

After termination of EF reactions due to being exhausted oxidant, solution was left for settling of ferric flocs for 30 min. The COD concentrations examined from limpid phase. The pH was measured by a pH meter (Jenway 3040 Ion Analyzer).

Table 1 Characterization of the sample taken from the organized industrialized region.

Parameter	Unit	Value
pH	-	7.2
Chloride	mg/l	6400
Conductivity	mS	19950 (at 21°C)
Sulfide	mg/l	89.0
COD	mg/l	2810
BOD	mg/l	910
Total Chromium	mg/l	62
Ammonia	mg/l	130

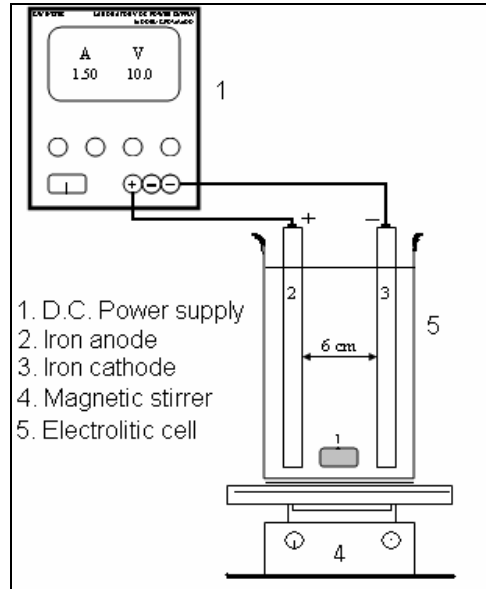


Figure 1 The Experimental Set-up

Unit energy demand of the electrolytic process were calculated from

$$UED_{(t)} = \frac{SEC_{(t)}}{C_i * \eta_{(t)}} * 100 \quad (3)$$

Where UED is the unit energy demand (kWh/kg COD removed); C_i is the initial COD concentration, kg/m^3 , η is COD removal percentage. Where SEC is the specific energy consumption (kWh/m^3) and calculated from

$$SEC_{(t)} = 10^{-3} * J * U * t \quad (4)$$

Where t is the time needed for the removal of a given pollutant, hour; J is the total current applied, Ampere; U is the overall cell voltage, Volt.

EXPERIMENTAL RESULTS AND DISCUSSION

Existence durations of residual oxidant in the solution determined for three different oxidant doses have been illustrated in Figure 2; as rounded, 15, 30 and 45 minutes for increasing dose order. These values give a suggestion for upper limit of electro-fenton application time, for each dose.

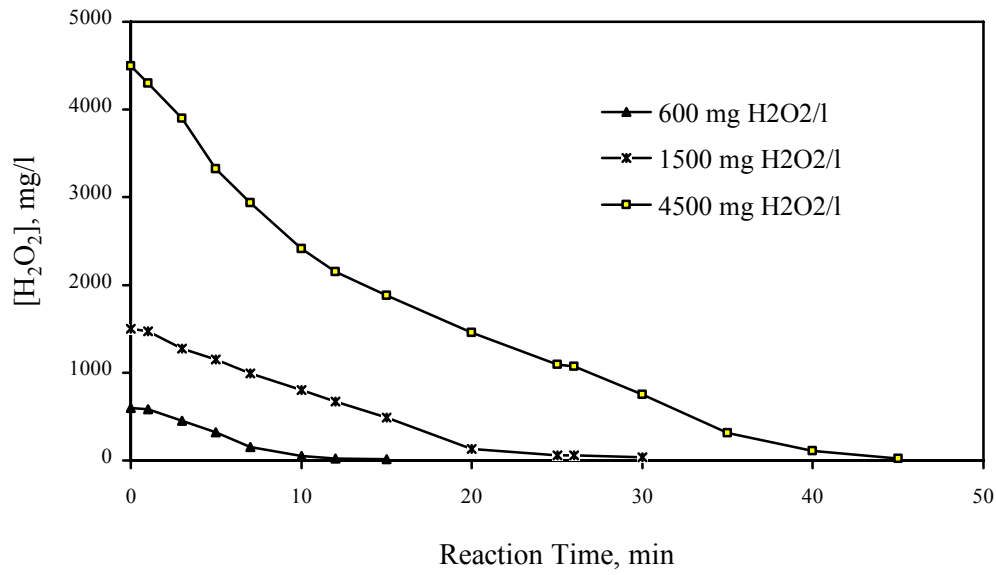
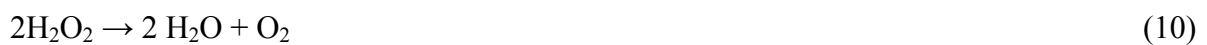


Figure 2 Variation by time of residual H₂O₂ for changing doses

The oxidation capability results of the three oxidant doses for COD destruction in the sample and oxidation durations are given in Figure 3. According to these destruction data, it can be expressed that the maximum COD reduction was obtained for 1500 mg/l oxidant dose. Surprisingly, three times higher dose (4500 mg/l) did not give higher COD destruction. That means that oxidant doses higher than an optimum dose can not provide expected results. If H₂O₂ dose is increased excessively, in this case two reactions (see Eq 5-6) could be involved leading to the formation of less reactive radicals from hydroxyl radical. Fenton reaction is made ineffective by undesired reactions. Among these reactions, the production of hydroperoxyl radicals, the cycling of iron(III) to iron(II) and the quenching of OH• by iron(II) and H₂O₂, occur, as given below (Mohanty and Wei, 1993).



On the other hand, 600 mg/l oxidant dose supplied too close COD reduction result to 1500 mg/l dose. In case each dose application; a drastic COD reduction was achieved in initial five minutes. After this period, no substantial increment in the reduction of COD was observed. If the reaction time is increased to many hours the best results could be achieved. But in this case, more time and more electric energy will be consumed for the overall reaction. In five

minute, for 1500 mg/l oxidant dose, 69% COD was removed. But, 600 mg oxidant per liter being two and half times lower dose was supplied 67% COD. Therefore 600 mg/l dose can be accepted as the most affected dose.

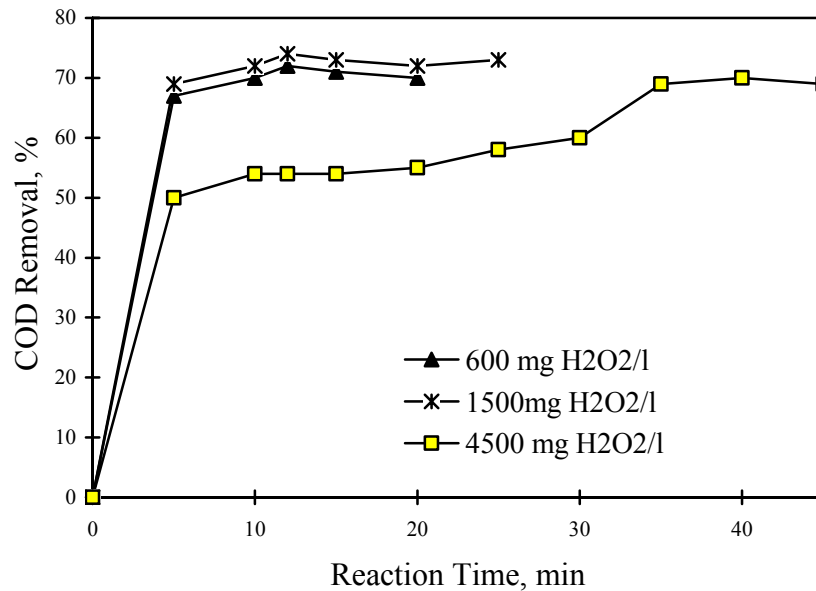


Figure 3 COD removals with altering oxidant doses

Figure 4 demonstrates variations of sulfide removal and BOD₅/COD ratio with time or oxidant addition. Sulfide oxidation after five minutes was higher than 95%. 32% initial BOD₅/COD*100 value in the sample was not change remarkably (could change by 40%).

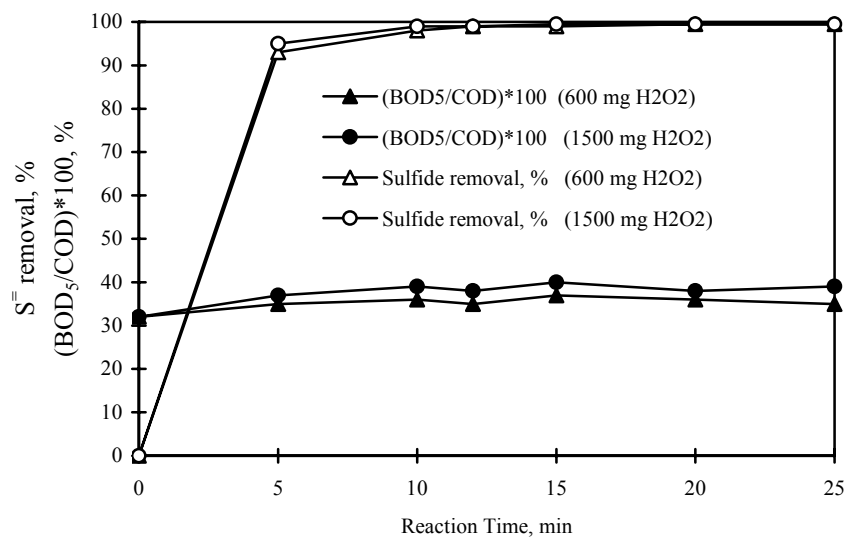


Figure 4 Variation of BOD₅/COD ratio and sulphide removal

In order to make an evaluation of the EF process, energy consumption (SEC) with time for each oxidant dose should be considered meanwhile. As can be observed from Figure 5, consumed energy by increasing time increases. For example, SEC in fifth minute will be realized as 3.1 kWh/m³.

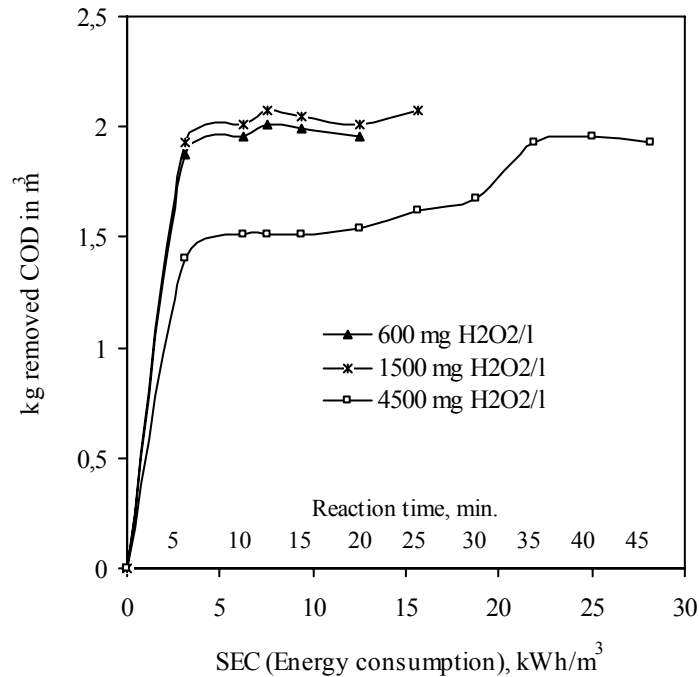


Figure 5. COD mass removed depending on energy consumption

Figure 5 shows also that COD mass removed in 1 m³ effluent is about 1.88 kg COD/ m³ if 600 mg/l H₂O₂ oxidant dose is applied. Incases using 1500 and 4500 mg H₂O₂ doses, COD removals are obtained as 1.93 and 1.40 kg COD/ m³. This comparison of the doses brings a consideration which optimization of energy consumption regarding to removed COD mass to be calculate for each dose is more sensible. For that purpose, Unit Energy Demand (UED) values for each dose in order increasing dose were estimated as 1.66, 1.71 and 2.22 kWh/kg COD removed, respectively. When examined these findings, it is confirmed that 600 mg oxidant/ liter dose would be economically viable.

CONCLUSION

The study showed that EF process can be used for the treatment of organic matter of tannery wastewater. The maximum COD reduction was obtained as about 70% for five minutes contact duration. 1.66 kWh/kg COD removed was provided by 600 mg/l optimum dose application. The study also puts forward that the EF process will be a time saving treatment option.

References

1. APHA Standard Methods for the Examination of Water and Wastewater, 20th Ed., American public Health Association, American Water Works Association, Water Environmental Federation, Washington D.C. 1998.
2. Awan, M.A., Reduction of Chemical Oxygen Demand from Tannery Wastewater by Oxidation, EJEAFChe, Electronical Journal.
3. Gate Information Service (Eschborn, Germany), Treatment of Tannery Wastewater, <http://www.gtz.de/gate/gateid.afp>
4. Gonullu, M.T., 2004. Industrial Pollution Control, V. I Birsen Yayinevi, 418 (in Turkish).
5. Mohanty, N.R., Wei, I.W., 1993. Oxidation of 2,4-dinitrotoluene Using Fenton's Reagent: Reaction Mechanisms and Their Practical Applications., Hazard. Waste & Hazard. Mater. 10, 171-183.
6. www.h2o2.com