

Reduction of COD in wastewater from an organized tannery industrial region by Electro-Fenton process

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Received 27 April 2006; received in revised form 8 August 2006; accepted 28 August 2006

Available online 1 September 2006

Abstract

Advanced oxidation processes (AOPs) have led the way in the treatment of aqueous waste and are rapidly becoming the chosen technology for many applications. In this paper, COD reduction potential of leather tanning industry wastewaters by Electro-Fenton (EF) oxidation, as one of the AOPs, was experimentally evaluated. The wastewater sample was taken from an outlet of an equalization basin in a common treatment plant of an organized tannery industrial region in Istanbul, Turkey. Treatment of the wastewater was carried out by an electrochemical batch reactor equipped with two iron electrodes, which were connected parallel to each other. The oxidation process was studied for optimization of H₂O₂ and the electricity consumptions were observed at different contact times under different pH conditions (3.0, 5.0 and 7.2). In each case, electricity consumption for decreased COD mass was estimated. In this process, COD was reduced by 60–70% within 10 min. By taking into consideration the local sewerage discharge limit, applicability of EF process for the tannery wastewaters was evaluated.

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Keywords: Advanced oxidation processes; COD; Electro-Fenton; Iron electrodes; Tannery wastewater

1. Introduction

The uncontrolled release of tannery effluents in natural water bodies increases the environmental pollution and the health risks. The characteristics of tannery wastewater vary widely depending on the nature of the tanning process adopted, the amount of water used, the process of hide preservation, the hide processing capacity, the inplant measures followed, and no minimization of water used to reduce pollution [1]. Tannery wastewater treatment represents a serious environmental and technological problem. In fact, after conventional treatment (i.e., chromium precipitation–primary sedimentation–biological oxidation–secondary sedimentation), effluents still do not meet the required limits, at least for some parameters such as COD, salinity, ammonia and surfactants [2]. Conventional biological treatment methods are often inadequate to completely remove pollutants in tannery wastewater [3]. Furthermore, biological

treatment of wastewaters containing resisting and toxic compounds requires a long period of time in order to remove the pollutants. The kinetics of the electrochemical process are about 100-fold faster than biological oxidation process [4]. A lot of pollutants, such as ammonia [5–7], nitrite [8], benzoquinone [9], benzene [10], thiourea dioxide [11], phenols [12], chlorophenols [13,14], dyes [15,16], formaldehyde [17], cyanides [18], toluene [19], and alcohols [20] are effectively removed by electrochemical technics. Electrochemical treatment seems to be a good prospect since the discharge flow from most tannery plants is not large; hence it is worth exploring the application of this method as an alternative to the conventional biological processes [5]. EF treatment evaluated in this paper is one of the electrochemical treatment applications. That includes the combined advantages of electrochemical and Fenton treatment methods, and each of them is a powerful treatment choice.

The mechanism for decomposition of H₂O₂ in acidic solution in the dark and in the absence of organic compounds consists of a sequence of reactions (1)–(8) [21]. An optimum dose can provide expected results better than excess oxidant doses. If H₂O₂ dose is excessively increased, two reactions (2)–(3) could be involved leading to the formation of less reactive radicals from the hydroxyl radical. Fenton reaction becomes ineffective

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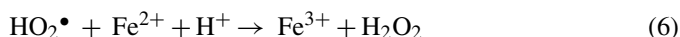
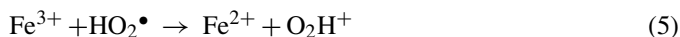
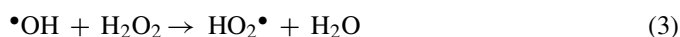
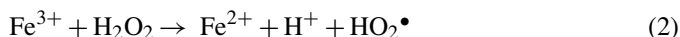
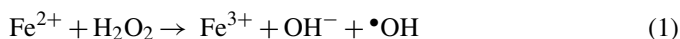
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Table 1
Unit energy demand for pollutant removal in wastewater treatment by electro-chemical process

Wastewater type	Process	Reaction time (h)	UED (kWh/kg) pollutant removed	Pollutant removal (%)	Reference
Synthetic wastewaters	Electro-chemical, anode and cathode: RuO ₂	–	1880	Phenol (99.7%)	[12]
Synthetic wastewaters	Electro-chemical, anode and cathode: RuO ₂	–	2112	COD (88.9%)	[12]
Petroleum refinery wastewater	Electro-chemical, anode and cathode: RuO ₂	–	–	COD (70.1%)	[12]
Textile dyeing	Electro-coagulation, anode: iron; cathode: steel	–	4.7	Dye (75%)	[16]
Textile dyeing	Electro-coagulation, anode: iron; cathode: steel	–	7.57	Dye (98%)	[16]
Methylene–parathion pesticide in aqueous solution	Electro-chemical, anode: Pt/Ti; cathode: SS 304	2	8–18	COD (80 %)	[23]
Dyeing wastewater	Electro-coagulation, anode: boron-doped diamond (BDD); cathode: SS	–	15.0	COD (90%)	[24]
Dyeing wastewater	Electro-coagulation, anode: BDD; cathode: SS	–	20.1	COD (89%)	[24]
Dyeing wastewater	Electro-coagulation, anode and cathode: mild steel	–	50	COD (98%)	[25]
Domestic wastewater	Electro-chemical, anode: Ti/Pt; cathode: SS 304	1	12.4	COD (89 %)	[26]
Olive oil industry	Electro-chemical, anode: Ti/Pt	1	1.3	COD (41%)	[27]
Olive oil industry	Cathode: SS 304	10	12.3	COD (93%)	[28]

because of undesired reactions. Among these reactions, the production of hydroperoxyl radicals occur in the cycle of Fe³⁺ to Fe²⁺ and the quenching of •OH by Fe²⁺ and H₂O₂. Oxidation potentials of hydroperoxyl radicals are lower than H₂O₂. Oxidation potentials of H₂O₂ and hydroperoxyl radicals are 1.31 and 1.25 as compared to chlorine: 1.0 [22]



In this study, EF trials for different pH values (3.0, 5.0, and 7.2), for different H₂O₂ doses (840, 1670, 3340, and 5010 mg/l which are equal to 14%, 28%, 56%, and 84% of the theoretical H₂O₂ dose, respectively), and for different electrical powers (15.0 W as 1.5 A and 10 V, 4.0 W as 0.8 A and 5 V, and 1.2 W as 0.35 A and 3.4 V) were performed. As can be seen from Eq. (8), the required theoretical H₂O₂ dose for removing all COD forming compounds is equal to 5970 mg H₂O₂/l. Iron electrodes, which were used during the electrolytic processes, increased the concentration of Fe²⁺ ions in electrolytic media depending reaction time. The ions diffuse from the iron anode and catalyze the formation of hydroxyl radicals (•OH) in the Fenton reaction as can be seen from Eq. (1).

During the pollutant removal from wastewaters with different organic pollutant loads, the energy consumption changes with both intended efficiency for the purification and the characteristics of the wastewater at the EF and electro-coagulation (EC) processes. Some data from the literature on the unit energy demand for pollutant removal in wastewater treatment were

given in Table 1. These studies, from which the data were obtained, were performed using reactions in order to have a higher efficiency.

2. Materials and methods

Wastewater sample was taken from an outlet of an equalization basin in a common treatment plant of Organized Tannery Industrial Region located in the Tuzla district of Istanbul, Turkey. The equalization basin collects the wastewater of about 100 small tannery plants. Equalized wastewater is mainly based on chrome and vegetable tanning processes in the tannery plants. The common treatment plant has the following sequential steps: equalization, settling, aerobic activated sludge, and physico-chemical treatment by chemical coagulation. The composition of the wastewater sample is given in Table 2.

The sample was put into PE containers and taken to the laboratory in one hour and protected at +4 °C during the experiments. The experimental set-up used in the present study is presented in Fig. 1.

Experimental studies were performed in a batch laboratory reactor consisting of a 0.5 l glass beaker equipped with a cathode and an anode, both made of iron and installed in parallel. The distance between the electrodes was 6.0 cm (dimensions

Table 2
The characteristics of the wastewater sample taken from the equalization tank

Parameters	Unit	Value
pH	–	7.2
Chloride	mg/l	6400
Conductivity	mS	19,950 (at 21 °C)
Sulfide	mg/l	89
COD	mg/l	2810
BOD ₅	mg/l	910
Total chromium	mg/l	62
Ammonia-N	mg/l	130
Suspended solids	mg/l	1520
Volatile suspended solids	mg/l	1060
Total iron	mg/l	0.62

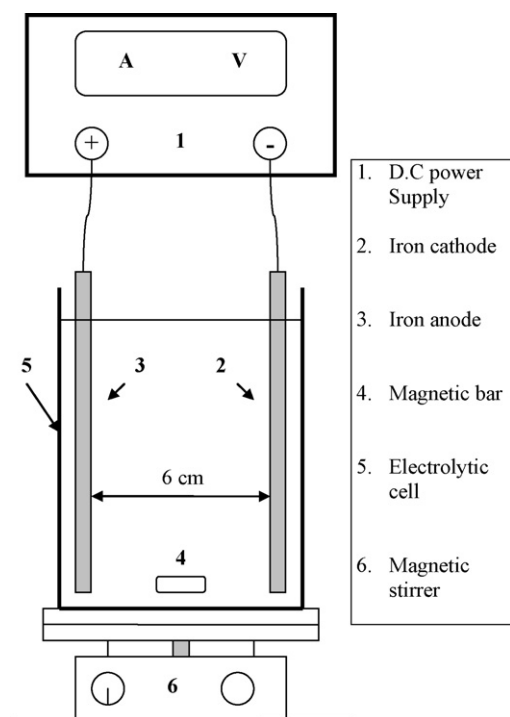


Fig. 1. The experimental set-up.

of electrodes were $2.0 \text{ mm} \times 6.0 \text{ cm} \times 7.5 \text{ cm}$). Electrodes were plunged into the beaker containing tannery wastewater with a 0.41 working volume. The total effective electrode area was 45.0 cm^2 . Ferrous ions acted as coagulation materials in the electro-chemical treatment. On the other hand, ferrous ions create hydroxyl radicals and catalyze the Fenton reaction. The electrodes were connected to a digital DC power supply (GW Instek, GPS 3030 DD, 0–30.0 V, 0.0–3.0 A). All the runs were performed at an initial temperature of 20°C and the temperature was increased up to 29°C in 40 min. In each run, 400 cm^3 of wastewater was placed into the electrochemical cell. The pH was adjusted to 3 and 5 with 1N H_2SO_4 solution. Then H_2O_2 was added as 840, 1670, 3340, and 5010 mg/l for each experimental set-up. The current density was adjusted to the desired value; and electrolysis was started and maintained until all H_2O_2 was consumed. The analysis of H_2O_2 was done by the permanganometric method [29]. The samples treated by the EF process were settled for 30 min after electro-oxidation reactions. In the study, all analyses were carried out on treated samples taken out of the limpid phase in the beaker. Merck analytical quality chemicals were used in the preparation of reagents. All the chemical analyses were carried out in accordance with the Standard Methods for Examination of Water and Wastewater [30]. A Jenway 3040 brand a pH-meter was used for pH measurements.

Unit energy demands (UED) of the EF process were calculated from the following equation:

$$\text{UED}(t) = \frac{A \times V \times t}{10 \times C_i \times \eta(t)} \quad (9)$$

where UED for each m^3 of wastewater is the unit energy demand (kWh/kg COD removed); C_i is beginning COD concentration

(kg/m^3); η is COD removal efficiency (%); t is the reaction time (h); A is the total current applied (A); V is the overall cell voltage (V).

3. Results and discussion

EF processes were performed for three different initial pH levels (3.0, 5.0, and 7.2), different levels of oxidant doses (840, 1670, 3340, and 5010 mg $\text{H}_2\text{O}_2/\text{l}$), and different amounts of electrical power (1.2, 4.0, and 15.0 W). In all applications, it was observed that the efficiency of 99.5% of the sulphide removal was obtained within the first 15 min. The flock constitutions became visible after 2 min. It was also observed that the volume of the precipitating mud increased with the presence ferrous irons in the solution, the duration of the reaction, and the amount of power applied. Below, the results obtained from the EF treatments of the sample with three different pH values are given and evaluated.

3.1. The EF studies at pH 3.0

As can be seen from Fig. 2, the time for the disappearance of residues of H_2O_2 is shorter as the amount of electrical power used increases. However, as the dose of oxidant increases, the time interval required for residual oxidant to disappear increases as well. Therefore, the conditions for fastest removal of H_2O_2 , which was 15 min, were 15.0 W for the greatest electrical power, and 840 mg $\text{H}_2\text{O}_2/\text{l}$ for the smallest dose. The longest interval of time for oxidation to occur was observed for 1.2 W of electrical power. In this situation, even after 90 min, there was 68 mg $\text{H}_2\text{O}_2/\text{l}$ residual concentration present. It might be recalled that, for the EF application to take place, the presence of residual oxidant and adequate catalyst (ferrous ions) concentrations are essential. Otherwise, undesirable reactions occur such as Eqs. (3)–(5), which decrease pollutant removal efficiency.

It is observed from Fig. 3 that, in the case of the presence of 840 mg/l H_2O_2 (14% theoretical dose) and the application of electrical power of 4.0 and 15.0 W, the removal of COD was 70% in 15 and 10 min, respectively. The same ratio of efficiency was obtained in 25 min when 1670 mg $\text{H}_2\text{O}_2/\text{l}$ (28% theoretical

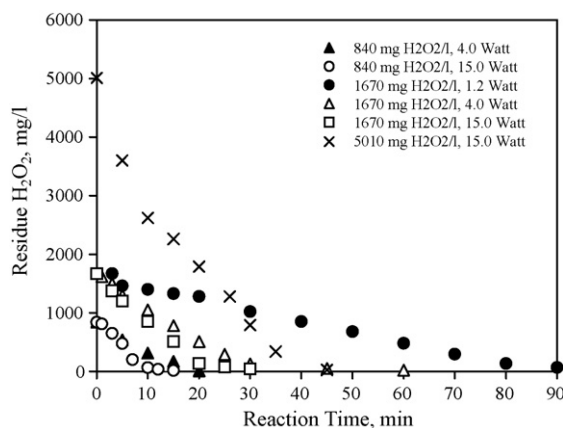


Fig. 2. H_2O_2 residues developing for different applications at pH 3.0.

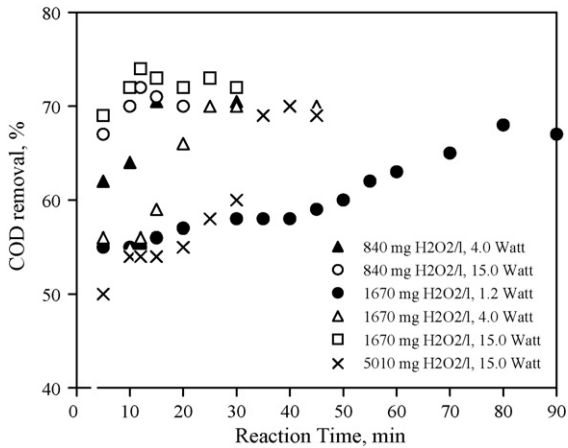


Fig. 3. COD removal at pH 3.0 during EF process.

dose) and the electrical power of 4.0 W were used; in 5 min when 1670 mg $\text{H}_2\text{O}_2/\text{l}$ (28% theoretical dose) and the electrical power of 15.0 W were used; in 40 min when 5010 mg $\text{H}_2\text{O}_2/\text{l}$ (84% theoretical dose) and the electrical power of 15.0 W were used. The highest efficiency (73%) was obtained in 12 min when the electrical power of 15.0 W and the dose of 1670 $\text{H}_2\text{O}_2/\text{l}$ were used. In the case of the highest dose (5010 $\text{H}_2\text{O}_2/\text{l}$), the COD removal efficiency of 70% is obtained after 40 min. According to these experimental results, in a short period of time like 5 min, the optimum result in terms of the energy consumption of 4 W and the chemical consumption of the dose of 840 mg/l H_2O_2 , which was the only 14% of the theoretical dose, the efficiency of COD reduction was 62%. Data given in the figure seems to be in contradiction because a lower H_2O_2 dose supplies higher COD removal rate. As mentioned in literature section, if the H_2O_2 dose is excessively increased, undesired reactions like the formation of less reactive radicals from the hydroxyl radical and the quenching of $\bullet\text{OH}$ may occur. On the other hand, the energy consumption rate had a linear relationship with the COD removal rate. For that reason, the highest removal rate (69%) was obtained for 15 W when applied to 1670 $\text{H}_2\text{O}_2/\text{l}$. Another exciting observation from the figure is jumps in COD removal rates during the oxidation process. These are probably due to cleavage of some groups of resisting organics and after that it is possible that they may be readily oxidized.

Experimental results in Fig. 4 established that, sulfide removal in the process of EF is 93% in 5 min, 98% in 10 min, and 99% in 12 min. Moreover, the amount of biologically degradable organic compounds increased relative to the amount of time that the reaction proceeded. It was observed in this case that some organic compounds can be transformed into biologically degradable forms.

When the energy consumption is considered, the case of 1.2 W was the case with the least consumption of energy. However, in that case, the efficiency of COD removal was between 50% and 60% (See Fig. 3). In the case of the maximum efficiency of 70% (12 min., 1670 mg $\text{H}_2\text{O}_2/\text{l}$, 15.0 W), as can be seen from Fig. 5, the energy consumption was 3.6 kWh/kg COD removed. Indeed, if the energy consumption of 1.2 W with the COD removal efficiency of 55% provided sufficient treatment,

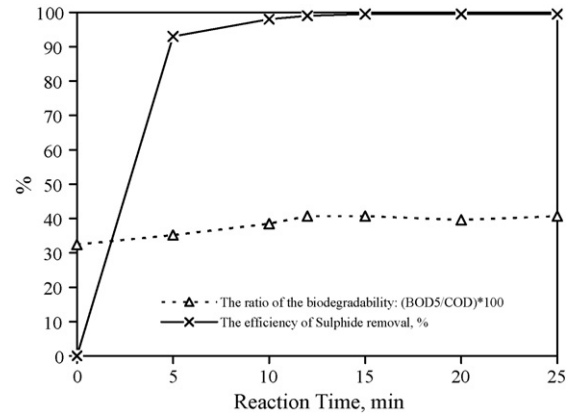


Fig. 4. BOD5/COD variation and sulfide removal at pH 3.0 (1670 mg $\text{H}_2\text{O}_2/\text{l}$, 15.0 W).

then the amount of 0.16 kWh/kg COD removed would be very small. However, it was observed that some extra energy needs to be consumed in order to have a treatment that is dischargeable.

3.2. The EF studies at pH 5.0

Studied at pH 5.0, the results of oxidant concentration versus time were shown in Fig. 6, the efficiency of COD removal was shown in Fig. 7, and the energy consumption per kg per COD removed was shown in Fig. 8.

As can be detected from Fig. 6, similarly to the case of pH 3.0, the reaction time was inversely proportional to the electrical power used. While the applied dose of oxidant increases, the time required to consume residual oxidant increases as well. When the electrical power used kept constant at 15.0 W, the smallest dose (840 mg $\text{H}_2\text{O}_2/\text{l}$) is consumed in shortest time (8 min). When the same dose (1670 mg $\text{H}_2\text{O}_2/\text{l}$), and different electrical power (15.0, 4.0, and 1.2 W) are used, the degradation speed of H_2O_2 decreases as the electrical power used decreases and, therefore, the time required for the oxidation reaction increases. For instance, in the case of the electrical power of 1.2 W, in 60 min there was still H_2O_2 in the wastewater.

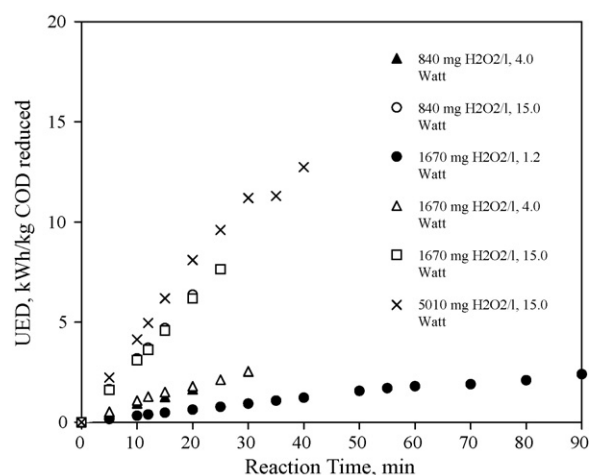


Fig. 5. Energy consumption for COD removal at pH 3.0.

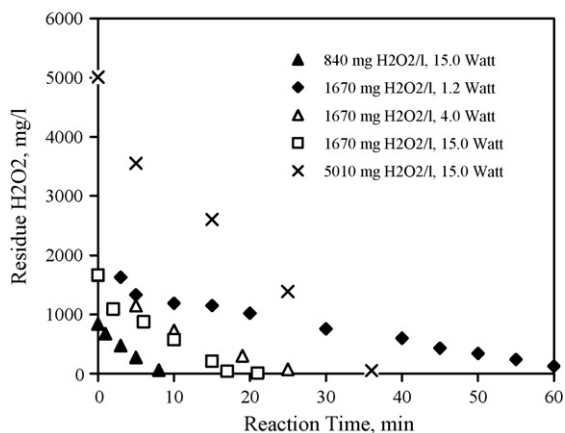


Fig. 6. H₂O₂ residues developing for different applications at pH 5.0.

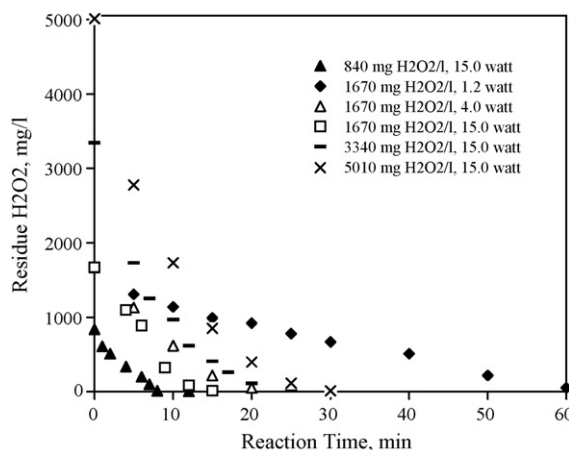


Fig. 9. H₂O₂ residues developed for different applications at pH 7.2.

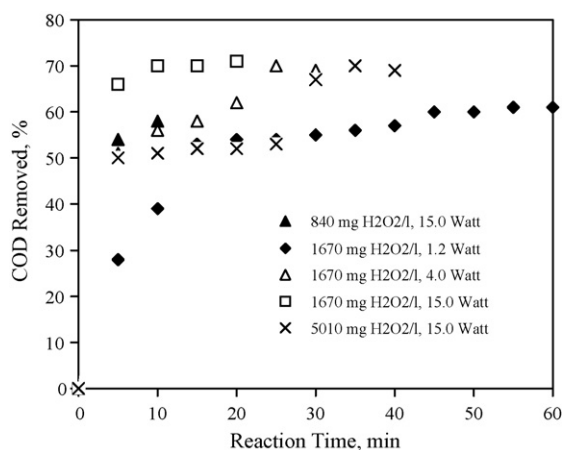


Fig. 7. COD removal at pH 5.0 during EF process.

The experimental results in Fig. 7 shows that 70% COD reduction can be achieved during applications of 840–5010 mg H₂O₂/l and 1.2–15 W at pH 5. The results show similar main trends in pH 3 applications: 1. Oxidant dose increment does not always cause elevation of COD reduction rate always because of excess oxidant that results in slowed oxidation reactions 2. Electrical power application increments supply elevations

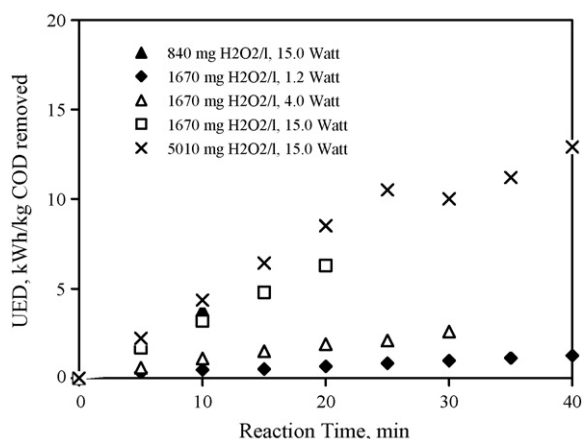


Fig. 8. Energy consumption for COD removal at pH 5.0.

in COD reduction rates. The difference between pH 5 and 3 experiments is some decrement in COD decomposition rate, as expected. In the case of 1670 mg/l H₂O₂ (28% theoretical dose) and the 15.0 W electrical power consumption, the removal of COD was 70% in 10 min. The same ratio of efficiency was obtained in 25 min when 1670 mg H₂O₂/l (28% theoretical dose) and the electrical power of 4.0 W were used; in 35 min when 5010 mg H₂O₂/l (84% theoretical dose) and the electrical power of 15.0 W were used.

Fig. 8 indicated that, when the energy consumption was considered, similar to the case of pH 3.0, 1.2 W energy consumption was the smallest one. However, the COD removal efficiency was observed to be between 50% and 60% (see Fig. 7). When the maximum efficiency of 70% was obtained (10 min, 1670 mg H₂O₂/l and 15.0 W), the electric consumption was 3.2 kWh/kg COD removed.

3.3. The EF studies at pH 7.2 (original wastewater)

The results obtained from the original wastewater of the pH 7.2 of oxidant level versus time were shown in Fig. 9, whereas the efficiency of COD removal was shown in Fig. 10; and the

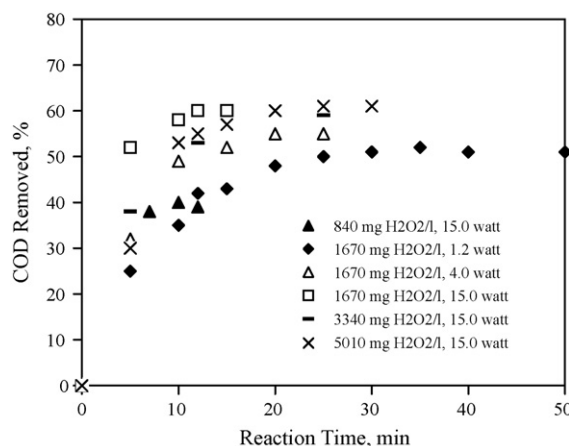


Fig. 10. COD removal at pH 7.2 during EF process.

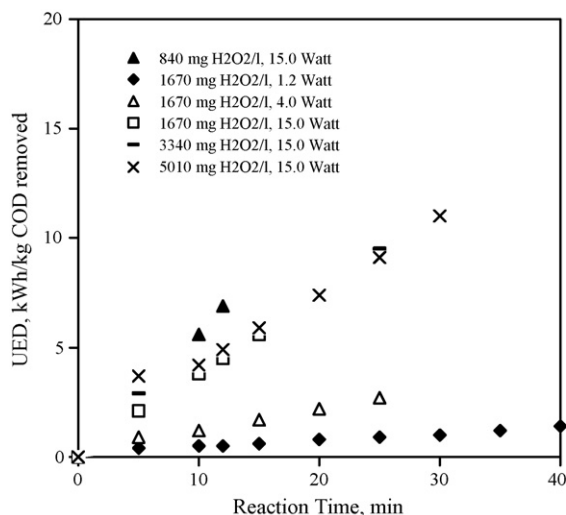


Fig. 11. Energy consumption for COD removal at pH 7.2.

electrical power consumption per kilogram per COD removed was shown in Fig. 11.

The H_2O_2 decomposition experiments at pH 7.2 for different oxidant doses and electricity power values were similar to the two previous cases (Fig. 9). The ending time of decomposition or consumption reactions of the oxidant was inversely proportional to the electrical power used. Accordingly, while the applied dose of oxidant increases, the time required to consume residual oxidant increases as well. When the same amount of electrical power (15.0 W) was applied to four different doses, the smallest dose of 840 mg $\text{H}_2\text{O}_2/\text{l}$ consumed the oxidant in shortest period of time (12 min). When the dose of 1670 mg $\text{H}_2\text{O}_2/\text{l}$ and the power consumption of 15.0, 4.0, and 1.2 W were compared, it was observed, as expected, as the electrical power used decreases, the speed of the reaction decreases as well, so the duration of the reaction increases. (When the electrical power of 1.2 W was applied, the H_2O_2 was not consumed even after 60 min).

When pH 7.2 was considered, as seen from Fig. 10, when 1670 mg/l H_2O_2 (28% theoretical dose) was utilized and the electrical power of 15.0 W was applied, COD removal was 60% in 12 min. The same efficiency levels were obtained in 20 min when 15.0 W of electrical power was used with 3340 mg $\text{H}_2\text{O}_2/\text{l}$ (56% theoretical dose) and 5010 mg $\text{H}_2\text{O}_2/\text{l}$ (84% theoretical dose), while keeping the electrical power at 15.0 W, the highest efficiency (60%) was reached with 1670 $\text{H}_2\text{O}_2/\text{l}$ in 12 min. The application of the highest dose (5010 $\text{H}_2\text{O}_2/\text{l}$) had a 60% efficiency after 20 min.

As can be seen in Fig. 11, when the electrical consumption was considered, similar to the previous cases, 1.2 W consumed

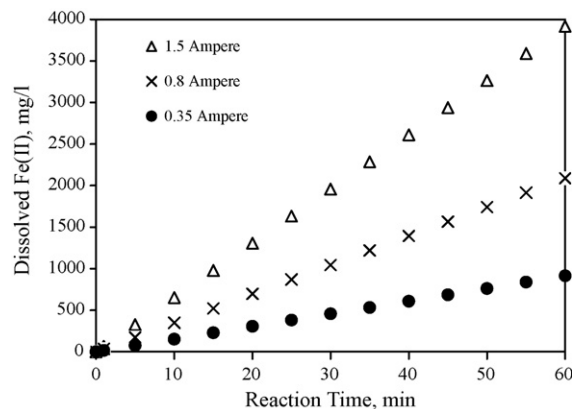


Fig. 12. Fe(II) concentrations in solution for different electrical currents.

the least power. However, again in this case, the efficiency of COD removal was between 40% and 50%, which was relatively low compared to Fig. 10. However, the maximum efficiency of 60% was obtained with a reaction time of 12 min and with 1670 mg $\text{H}_2\text{O}_2/\text{l}$ and with the electrical power of 15.0 W. In this case, the consumption of electricity was 4.5 kWh/kg COD removed.

When all the studies conducted at different pH levels were considered, it was observed that, the oxidant doses, which were applied at various pH levels, altered the COD removal. It was also observed that, the application of a mean oxidant level might provide the maximum removal. This shows that, without conducting research with wastewater at different pH levels, the full scale treatment cannot be initiated.

Another result was the direct proportion of increased power consumption to the removal efficiency. Consequently, when the unit energy applied (kWh/m³) and the amount of removed COD were considered, it was observed that the lowest electrical power applications were more energy effective. Furthermore, in these processes, for the first 5–10 min the removal occurred rapidly and afterwards, the amount of removed COD showed an increasingly decreasing tendency although the energy consumed was held constant. All these results show that the application of EF can be chosen for pre-treatment since it consumes very small amounts of energy when it is performed in the first 5–10 min. The only restricting reason against this idea is that the efficiency of COD removal was about 40%. If we evaluated acidic conditions, the efficiency might exceed 50%.

In the presence of H_2O_2 dissolved ferrous ions originating from the anode change to ferric ions. It is known that ferric ions are a coagulation material and form a sludge with $\text{Fe}(\text{OH})_3$. The concentrations of dissolved Fe(II) ions from anode material during EF process at pH 7.2 were given in Fig. 12. It is determined

Table 3
The characterization of the sludges formed for different operational conditions

Operational conditions			Settleable solids in 1 l treated solution		
A, ampere	W, watt	Reaction time, min	Volumetric rate, ml/100 ml	Gravimetric rate, g/100 ml	Organic fraction in the solids, %
1.5	15	20	13	0.31	33.87
0.35	1.2	30	10	0.22	47.47

from the figure that the concentrations of dissolved Fe(II) ions increase linearly depending on current density (A) and reaction time.

The characterization of sludge formed from 1.2 and 15 W (0.35 and 1.5 A) studies were given in Table 3. The table shows that electrochemical treatment processes increase inorganic content in the sludge as precipitations of Fe(OH)₃. The organic fraction in the sludge originates from suspended solids in the wastewater. Sludge volume and metal content of sludge is proportional to the reaction time and ampere applied.

4. Conclusions

According to the literature data given in Table 1, COD reduction changes from 41% to 99% based on different variables such as wastewater type, energy consumption, reaction time, etc. In this study, the efficiency of pollutant removal is evaluated for different variables such as oxidant doses, energy consumption, reaction time, etc. The significant result was, that although these variables varied uniformly, the COD removal did not show any pattern of direct or inverse proportionality. For this reason, for a specific wastewater, very detailed laboratory work would be required before the EF application.

EF treatability studies gave the best results (over 70% COD removal) for pH 3. At a neutral pH, greater than 60% COD removal was obtained. These results showed that, wastewater samples from organized tannery industrial regions could be treated up to the level of the local sewerage system discharge limit (800 mg COD/l). The process under study provides a solution in 10 minutes instead of long periods of chemical and biological treatments. In neutral pH with 1670 mg/l oxidant dose and 15.0 W, 58% COD removal was obtained in 10 min. During this process, 3.8 kWh/kg COD removed is consumed. In acidic conditions, when readjustments are required, in the same conditions 72% COD removal is obtained with the energy consumption of 3.1 kWh/kg COD removed. However, the process requires acid consumption for a reduced pH and might make the system invulnerable to corrosion. For these reasons, it seems that it would be more convenient perform the process at neutral pH.

If the lower energy consumption (with the energy consumption of 1.2 W) is the goal instead of reaching the sewerage discharge limit, consumption can be reduced until 0.5 kWh per COD is removed per kg. But, due to the energy savings, the efficiency of COD removal turns out to be 35%. An additional treatment would be necessary due to the insufficiency of tannery wastewater treatment.

It is determined that energy consumed is used to decompose organic substances. The BOD tests showed that there still were biological degradable organic molecules in solution.

It was observed that the sulfide concentration in the tannery industry wastewater was almost 100% removed in 10 min.

Consequently, the applicability of this process will increase since there are organic and toxic inorganic substances present in the tannery industry wastewater and these substances have high resistance to biological degradation.

Acknowledgement

We would like to give our special thanks to Yildiz Technical University Scientific Projects Coordination Department for the financial support (Project no. 25/05/02.01).

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