REDUCTION OF COD IN WASTEWATER FROM A TEXTILE INDUSTRY BY ELECTRO-FENTON PROCESS

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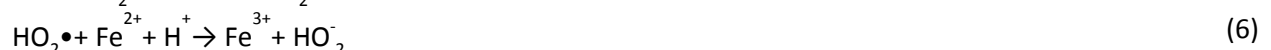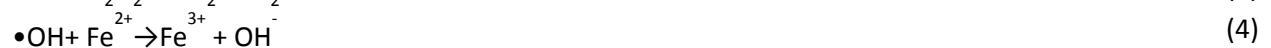*Istanbul, TURKEY*

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 of textile industry wastewater by electro-Fenton (EF) oxidation, was studied at batch experimental conditions. The wastewater samples with a COD of 590 mg l^{-1} in average were taken from the outlet of an equalization tank of a textile industry in the Marmara Region in Turkey. The wastewater samples were treated in a batch reactor equipped with two iron electrodes. The EF tests were conducted at different H_2O_2 doses such as 313, 626, 940, and 1253 mg l^{-1} and constant electrical power of 24 W and pH of 3. For each EF test electricity consumption was determined based on per unit of COD mass removed (kW kg^{-1}). The COD removal increased with decreasing H_2O_2 dose. The highest treatment efficiency was attained at 313 mg l^{-1} of H_2O_2, by which more than 85% of COD was removed within 10 min of reaction time. These results indicate that the EF process can be considered as an alternative method for textile wastewater treatment.

Keywords: Advanced oxidation processes, COD removal; electro-Fenton process, iron electrodes, textile wastewater.

1. Introduction

Mechanism for decomposition of H_2O_2 in acidic solution in dark and in the absence of organic compounds consists of the sequence of reactions [1-8] (Pignatello *et al.*, 2006). Among these reactions, the production of hydroxyl radicals occurs in the cycle of Fe^{3+} to Fe^{2+} and the quenching of •OH by Fe^{2+} and H_2O_2.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + \bullet OH \tag{1}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2\bullet \tag{2}$$

$$\bullet OH + H_2O_2 \rightarrow HO_2\bullet + H_2O \tag{3}$$

$$\bullet OH + Fe^{2+} \rightarrow Fe^{3+} + OH^- \tag{4}$$

$$Fe^{3+} + HO_2\bullet \rightarrow Fe^{2+} + H^+ + O_2 \tag{5}$$

$$HO_2\bullet + Fe^{2+} + H^+ \rightarrow Fe^{3+} + HO_2^- \tag{6}$$

$$2HO_2\bullet \rightarrow H_2O_2 + O_2 \tag{7}$$

$$2H_2O_2 \rightarrow O_2 + 2H_2O \tag{8}$$

An increase in H_2O_2 dose usually results with an increase in the formation of hydroxyl radicals, but at somewhere it reaches to an optimum value, above which the •OH generation does not change significantly. If H_2O_2 is used in excessive amounts, •OH radical generation might be lowered due to the formation of less reactive radicals such as $HO_2^\bullet$, as shown by the reactions 2 and 3, and therefore Fenton oxidation becomes less effective for the treatment organic or inorganic compounds. Oxidation potentials of hydroperoxyl radicals (1.25 volt) are lower than H_2O_2 (1.31 volt) (Parsons, 2004).

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

Wastewater type	Process	Reaction time, hour (min)	UED, kWh kg^{-1} pollutant^{-1} removed^{-1}	Pollutant (removal)	Reference
Textile wastewater	Electro-chemical Anode: Iron Cathode: Iron	0.17 (10)	0.008	COD (86 %)	(Current study)
Textile dyeing	Electro-coagulation Anode: Iron Cathode: Steel	-	4.7	Dye (75 %)	(Daneshvar et al., 2006)
		-	7.57	Dye (98%)	
Dyeing wastewater	Electro-coagulation Anode: Boron-doped diamond (BDD) Cathode: Stainless steel (SS)	-	15.0	COD (90%)	(Chen et al., 2003)
			20.1	COD (89%)	
Dyeing wastewater	Electro-coagulation Anode and Cathode: Mild Steel	-	50	COD (98%)	(Golder et al., 2005)
Tannery wastewater	Electro-chemical Anode: Iron Cathode: Iron	0.17 (10)	3.1	COD (72 %)	(Kurt et al., 2007)
Domestic wastewater	Electro-chemical Anode: Ti/Pt, Cathode: SS 304	1 (60)	12.4	COD (89 %)	(Vlyssides et al., 2002)
Methylene parathion pesticide in aqueous solution	Electro-chemical Anode: Pt/Ti, Cathode: SS 304	2 (120)	8-18	COD (80%)	(Arapoglou et al., 2003)
Synthetic wastewater	Electro-chemical Anode and Cathode: RuO2	--	1880	Phenol (99.7%)	(Yavuz and Koparal, 2006)
			2112	COD(88.9%)	
Petroleum refinery wastewater	Electro-chemical Anode and Cathode: RuO2	-	-	COD (70.1%)	
Olive oil industry	Electro-chemical Anode: Ti/Pt, Cathode: SS 304	1 (60)	1.3	COD (41%)	(Vlyssides et al., 1999)
Olive oil industry	Electro-chemical Anode: Ti/Pt, Cathode: SS 304	10 (600)	12.3	COD (93%)	(Israilides et al., 1997)

In this study, EF trials at different H_2O_2 doses such as 313, 626, 940, and 1253 mg l^{-1} corresponding to 25%, 50%, 75%, 100% of theoretical H_2O_2 dose, respectively were performed using 24.0W, 31.0V, 0.75A of electrical power. As can be seen from Equation-8, required theoretical H_2O_2 dose for removing all COD compounds is equal to 1253 mg l^{-1}. Iron electrode, which was used during the electrolytic processes, increased the concentration of Fe^{2+} ions in electrolyte with increasing reaction time. The Fe^{2+}

ions diffuse from iron anode and catalyze the formation of hydroxyl radicals ($\bullet$OH) in Fenton reaction which can be seen from equation 1. In EF and electro-coagulation (EC) processes, the amount of electrical energy required for the treatment of a wastewater depends on desired treatment efficiency and wastewater characteristics such as organic loading, pH, turbidity etc. Some data from literature on the unit energy demand for pollutant removal in wastewater treatment were given in Table 1. From these studies it appears that prolonged times such as hours are required to attain high treatment efficiencies.

2. Materials and methods

Wastewater samples were taken from a treatment plant of a Textile industry. COD and conductivity of the wastewater were 590 mg l^{-1} and 2.3 mS cm^{-1} (at 20 °C), respectively. According to guidelines for industrial wastewater discharge in study area, effluent pollution of treated wastewater for textile factory has to be 200 mg COD l^{-1}. The treatment plant includes an equalization basin which collects wastewaters from small process units in the textile industry. The sample was put into PE containers and taken to the laboratory and protected at +4 °C prior to performing the experiments. The experimental set-up used in the study is presented in Figure 1.
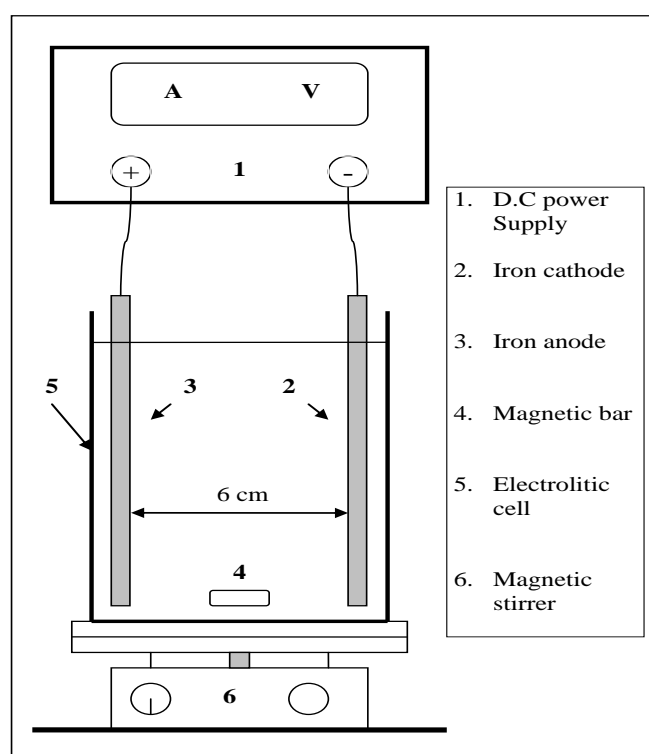

Figure 1. Experimental Set-up

Experimental studies were performed in a 0.5 l glass-made batch reactor, equipped with a cathode and anode, both of which made of iron and installed in parallel. Distance between the electrodes was 6.0 cm (dimensions of electrodes were 2.0mmx6.2cmx7.4cm). Electrodes were plunged into the beaker containing 0.4 l of samples of textile wastewater. The total effective electrode area was 46.0 cm^2.

The electrodes were connected to a Good Will GPC 3030D model digital DC power supply. All the runs were performed at initial temperature of 20 °C. pH, temperature and conductivity measurements were performed by a HACH-Lange HQ40D model pH meter. A sample of 0.4 l of wastewater was first placed into the electrochemical cell, and subsequently pH was adjusted to 3 with 1N H_2SO_4. After that, H_2O_2 was added in appropriate amounts to come up with initial concentrations of 313, 626, 940, or

1253 mg l^{-1}. The current density was adjusted to a desired value, and then electrolysis was started and kept on till all H_2O_2 was consumed up.

The analysis of H_2O_2 was done by the permanganometric method (www.h2o2.com). During each EF trial, samples were taken at appropriate intervals, and then left settling for 30 min. In the study, all analyses were carried out on treated samples taken out the limpid phase of the beaker. All chemicals (Merck) used in this study were in analytical grade. All chemical analyses used in this work were carried out in accordance with the Standard Methods for Examination of Water and Wastewater (APHA, 1998). Closed reflux titrimetric method was used for COD analysis and HACH-Lange DRB 200 model thermoreactor was used as a digester. Furthermore, HACH-Lange DR 5000 model spektrofotometer was used to determine absorbance values of the samples.

It is known that treatment cost is important factor for treatment processes. So, treatment cost per kg COD removal was estimated via oxidant doses and given as unit energy demand (UED). UED of the EF process was calculated from equation 9 (Apaydin et $al.$, 2009).

$$UED_{(t)} = \frac{[A \times V \times t]}{[10 \times C_i \times n(t)]} \tag{9}$$

Where UED for each m^3 wastewater is the unit energy demand (kWh kg^{-1} COD^{-1} removed^{-1}); C_i is beginning COD concentration, kg m^{-3}, n is COD removal efficiency (%), t is reaction time, hour, A is the total current applied, Ampere, and V is the overall cell voltage, Volt.

3. Results and discussion

The EF treatments were performed using different oxidation doses and constant electrical power of 24 W. Results have demonstrated that wastewater began to become clear in the reaction beaker and ultimately appear totally visible after 2 min from the start of the reaction. It was also observed that the volume of the precipitating mud increased with the presence ferrous irons in the solution. Amounts of residual H_2O_2 were presented in Figure 2 via reaction time. COD removals based on H_2O_2 doses were presented at Figure 3 via reaction time.
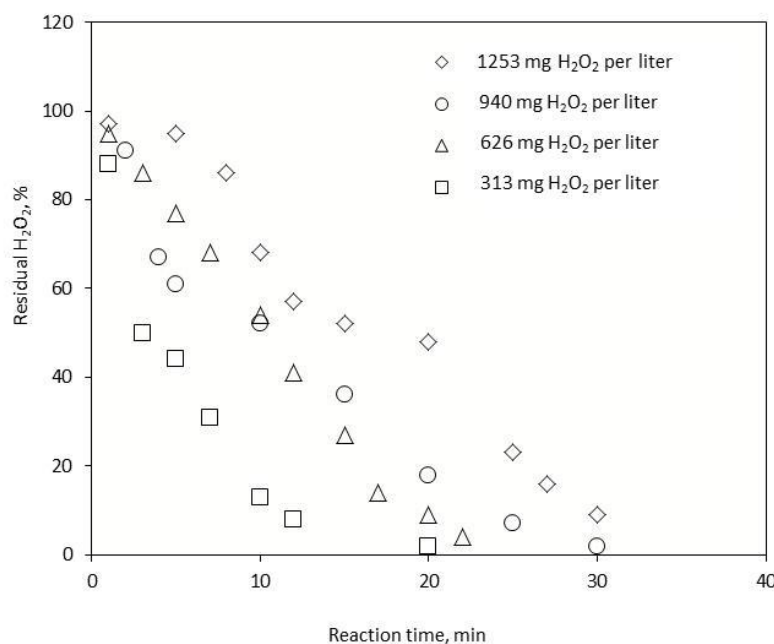

Figure 2. Residual H_2O_2 for different oxidant doses via reaction time.

As can be seen from Figure 2, residual H_2O_2 decreases with reaction time. It might be recalled that, for the EF application to take place, the presence of residual oxidant and adequate catalyst (Ferrous ions) concentration are essential. Otherwise, undesirable reactions through equations [3, 4 and 5] could occur resulting with a decrease in the treatment efficiency.

It is observed from Figure 3 that, in the case of the presence of 1253 mg H_2O_2 l^{-1} (100% theoretical dose) and the application of electrical power of 24.0 W, the removal of COD was around 75%, 67%, and 25% after 30, 20, and 10 min of reaction period, respectively. In the case of the presence of 940 mg H_2O_2 L^{-1} (75% theoretical dose) and the application of electrical power of 24.0 W, about 73%, 55%, and 40% of COD removals were attained within 30, 20, and 10 min of reaction time. Using 626 mg H_2O_2 l^1 (50% theoretical dose) and the electrical power of 24.0 W, the removal of COD was 79% in 30 min, 60% in 20 min and 50% in 10 min. Finally, in the case of the presence of 313 mg H_2O_2 l^{-1} (25% theoretical dose) and the use of similar electrical power, the removal of COD was 99% in 30 min, 99% in 20 min and 86% in 10 min. According to these experimental results, the optimum dose for H_2O_2 seems to be 313 mg l^{-1}, which was, in fact the lowest dose used in the experiments. It appears that H_2O_2 concentrations above 313 mg l^{-1} hamper the formation of hydroxyl free radicals, which in turn lowers the COD removal efficiency by the EF treatment. It is also important to note that the chemical and energy consumption rates can be significantly minimized with reducing the dose and treatment time, which was actually the case at 313 mg l^{-1} of H_2O_2 where more than 85% of COD reduction was achieved within just 10 min of reaction time.
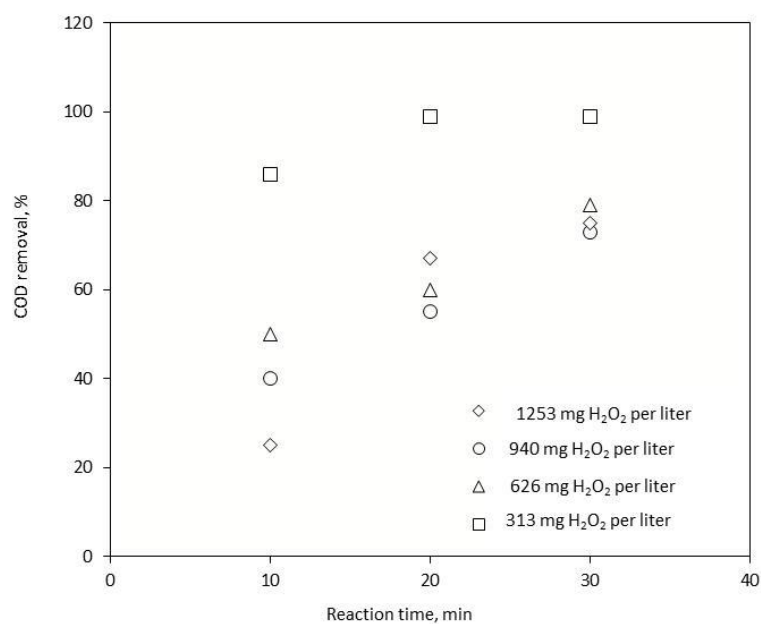

Figure 3. COD removal via reaction time during EF process.

In the presence of H_2O_2; dissolved ferrous ion (Fe^{2+}), which originates from anode, is converted to the ferric ion (Fe^{3+}). Ferric ion is a coagulation material and forms the sludge with $Fe(OH)_3$. In the case of maximum COD removal efficiency of 86% obtained from 313 mg H_2O_2 l^{-1} dose (10 min, 24.0 Watt), the energy consumption was calculated as 0.008 kWh kg^{-1} COD^{-1} removed^{-1} based on Equation 9.

Color and turbidity are two of the physical parameters in wastewater treatment processes. Absorbance values at specific wave length of visible light are important to determine treatment efficiency of wastewater. Absorbance values with different wave lights at EF process were determined using a spectrophotometer, having 10-mm absorption cells and an effective operating range from 400 to 700

nm. Results obtained from the analysis were given at Figure 4 based on reaction time and oxidant doses. According to Figure 4, absorbance values in different wave lengths (436, 525, 620, and 700 nm) obtained from EF processes are lower than absorbance values of original textile samples. The lowest absorbance values were obtained at the highest H_2O_2 doses, used in the experiments.
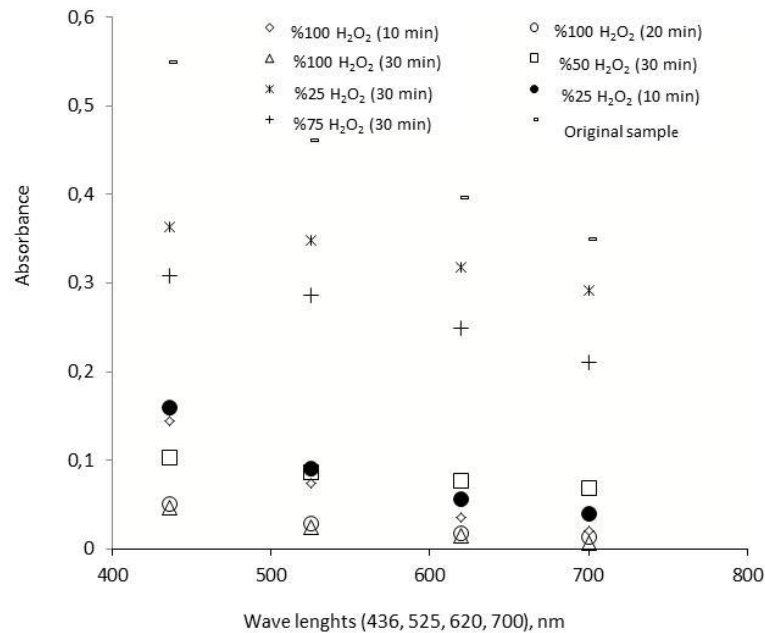

Figure 4. Absorbance values for the samples obtained in the study

Experimental results in Figure 4 show that absorbance value is decreased by 80% using 100% H_2O_2 theoretical dose during 20 min of reaction time. Moreover, both 100% H_2O_2 theoretical dose during 20 min and 50% H_2O_2 theoretical dose during 30 min of reaction time, absorbance values were found to be similar. But, the reaction time of the latter was longer than that of the former. Therefore, the former seems to be more cost effective in terms of energy consumption, while the latter is favorable because of requiring lower chemical doses.

According to results obtained from the studies, optimum requirements to supply to guidelines for industrial wastewater discharge in study area are:

1)1253 mg H_2O_2 l^{-1} dose and 20 min reaction time (effluent COD=195 mg l^{-1}) or 30 min reaction time (effluent COD =147 mg l^{-1}).

2) 940 mg H_2O_2 l^{-1} dose and 30 min reaction time (effluent COD =160 mg l^{-1}).

3) 626 mg H_2O_2 l^{-1} dose and 30 min reaction time (effluent COD=124 mg l^{-1}).

4) 313 mg H_2O_2 l^{-1} dose and 10 min reaction time (effluent COD=83 mg l^{-1}) or 20 min reaction time (effluent COD=6 mg l^{-1}).

EF treatability studies gave the best results for 313 mg H_2O_2 l^{-1} (10 min reaction time). The dose supplies both minimum H_2O_2 dose and requires lowest energy consumption as 0.008 kWh kg^{-1} COD^{-1} $removed^{-1}$ for treating textile wastewater.

4.   Conclusions

The electro-fenton (EF) treatment was found to be effective in removing the COD of textile wastewater. The major reaction mechanisms in the EF process include coagulation and hydroxyl free radical oxidation. While the coagulation occurred directly with ferrous ions, the hydroxyl free radical oxidation

was achieved based on the reaction between hydrogen peroxide and Fe^{2+} ions. According to the previous studies, the efficiency of COD reduction ranges from 41 to 99% depending on several variables such as wastewater type, energy consumption, reaction time, or pH. In our study, the overall COD removal efficiencies were found to be between 65% and 99% with respect to the amount of H_2O_2 used in the experiments. The lower the dose of hydrogen peroxide, the higher the removal efficiency obtained by the EF treatment. About more than 85% COD reduction was attained within 10 min when the oxidant dose was adjusted to 313 mg l^{-1}, recorded as the optimum dose for the electro-fenton treatment of the textile wastewater. Hence, EF process can be used as a suitable alternative treatment for the textile wastewaters.

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