Treatment of Tissue Paper Wastewater: Application of Electro-Fenton Method

Umran Tezcan Un, Seher Topal, Emre Oduncu, and Ulker Bakir Ogutveren

***Abstract*—The Fenton process is one of the most powerful advanced electrochemical processes based on the production of hydroxyl radicals ($OH^{\cdot}$) as a result of the reaction of hydrogen peroxide (H_2O_2) with catalyst ferrous ions (Fe^{2+}) under acidic conditions. In this study, tissue paper wastewater with the initial COD concentration of 1200 mg/L was treated using Electro-Fenton method. The cylindrical iron electrochemical reactor was used as a cathode. The turbine impeller with 8 flat blades were used as an anode. The effects of initial pH, current density and concentration of H_2O_2 on COD removal efficiency were determined. The removal efficiency of 80 % were obtained after 60 minutes of electro-fenton process at the current density of 20 mA/cm^2 with the addition of 0.1M H_2O_2. Additionally, the electrical energy consumptions were also evaluated. It can be concluded from the study that reactor designed dissimilar from those in the literature, can be used successfully for COD removal from the tissue paper industry wastewater.**

***Index Terms*—Tissue paper wastewater, electro-fenton, wastewater treatment, COD.**

I. Introduction

High consumption of freshwater is one of the most important environmental concerns in the paper industries [1]. Effluents of the pulp and paper industry contain a number of toxic compounds and may cause deleterious environmental impacts upon direct discharge to receiving waters [2].

The pulp and paper industry is the sixth largest polluter discharging a variety of gaseous, liquid and solid wastes into the environment [3]. The most significant sources of pollution in paper and paper industry are wood preparation, papering, paper washing, bleaching and coating operations. Papering processes utilize large amounts of water, which reappear in the form of an effluent [4]. This kind of paper mill wastewater, containing many toxic and intensely colored, mainly organic substances, is characterized by a high level of chemical oxygen demand (COD) [5].

Traditional methods for dealing with the wastewater consist of biological, physical, and chemical processes and various combinations of these [6]. The most of the pulp and paper mills treat their effluents by using biological treatment systems. The effluent from the biological treatment still contains significant amount of color compounds, microorganisms, recalcitrant organic compounds and suspended solids. Also, chemical oxygen demand (COD) cannot be removed effectively by biological treatment. Hence, advanced treatment is necessary to improve wastewater discharge quality and to reuse wastewater as process water [1].

The method of electrochemical oxidation for treatment of the organic contaminants contained in wastewater has become a hot focus in recent years because of its convenience and effectiveness than traditional methods [5].

The Fenton process is one of the most powerful advanced electrochemical processes. Its oxidation mechanism is based on the production of hydroxyl radicals ($OH^{\cdot}$) as a result of the reaction of hydrogen peroxide (H_2O_2) with catalyst ferrous ions (Fe^{2+}) under acidic conditions, as shown as equation (1).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{-} + OH \quad (1)$$

Fe^{3+} produced can react with H_2O_2 and hydroperoxyl radical in the so-called Fenton-like reaction, which leads to regenerating Fe^{2+} (reactions (2) and (3)). Fe^{2+} regeneration is also possible by reacting with organic radical intermediates (reaction (4)) [7].

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + + HO_2 + H^{+} \quad (2)$$

$$Fe^{3+} + HO_2 \rightarrow Fe^{2} + + O_2 + H^{+} \quad (3)$$

$$Fe^{3+} + R \rightarrow Fe^{2} + + R^{+} \quad (4)$$

The purpose of the work was to investigate the performance of the reactor designed differently from those in the literature to obtain direct dischargeable effluent from the paper mill wastewater. The effects of operation parameters are initial pH, current density and concentration of H_2O_2 are examine. Energy consumption was also analyzed.

II. Experimental Studies

A. Wastewater

In the experimental studies, tissue paper industry wastewater obtained from Kocaeli/Turkey. The wastewater taken from paper industry not only has specific odor but also has a specific color, between yellow and green. The wastewater has 1200 mg/L COD, and pH of 7. The wastewater was stored at refrigerator.

B. Experimental Setup and EC Apparatus

The electrochemical system consisted of a reactor, a mechanical stirrer, and a direct current (DC) power supply (Statron 2257); its schematic representation and picture were shown in Fig. 1. A cylindrical iron reactor operated as anode has an internal diameter of 8.2 cm and height of 10 cm. Anode has 8 pedal blade with a dimensions of 1.8 cm × 3 cm while acting as mechanical stirrer. It submerged into the reactor

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containing wastewater and maintained uniform composition by stirring the mixture at 100 rpm. The performance of the reactor was evaluated in the batch mode.

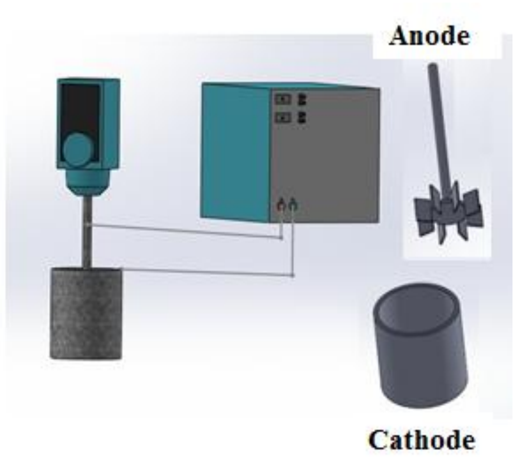

Fig. 1. The experimental set-up and anode and cathode.

C. Experimental Procedure

In each run, 0.5 L of model solution was poured into the electrolytic cell, and the pH, conductivity, and current density were adjusted to the desired value. The mechanical stirrer was submerged into the reactor. Constant agitation speed rate at 100 rpm was selected to enable the agglomeration of flocs in the solution. The reaction was started by switching the DC power supply on. Electrocoagulation experiments were performed for 60 min for each run and samples were taken every 15 min interval, filtered and analyzed to determine COD concentrations using Close-Reflux Methods. All the samples were analyzed in duplicate to ensure data reproducibility, and an additional measurement was carried out, if necessary.

The effects of initial pH, current density and the concentration of H_2O_2 on removal efficiency and energy consumption was investigated. The removal efficiencies (RE%) and energy consumptions (E_c; kWh/m^3) were calculated using following equations;

$$RE\% = \frac{(C_O - C)}{C_O} \times 100 \qquad (5)$$

where C_o and C are the concentrations of COD before and after E_C, respectively, in mg/L.

$$E_C = \frac{V \times I \times t}{v_W} \qquad (6)$$

where V is Voltage (V), I is Current (A), t is operation time (h) and v_w is the volume of the wastewater (m^3).

III. Results and Discussion

A. Effect of Initial pH

pH has a significant impact in Electro-Fenton process because of controlling the variation of iron (Fe^{+2}-Fe^{+3}) and the oxidation ability of hydroxyl radical generated [8]. The initial pH of the wastewater was adjusted using 4N H_2SO_4. As known, Electro- Fenton process may occur more efficiently in lower pH. Therefore, experiments were run in the acidic range. In all experiments, pH was not controlled but monitored during operation. As seen from Fig. 2, for the initial pH of 2, 3 and 4 the removal efficiencies of 76 %, 76 % and 80 % were obtained respectively after 60 minutes at the current density of 20 mA/cm^2 and addition of 0.1M H_2O_2.

At low pH the reaction may slow down due to the complex species of iron $[Fe(H_2O)_6]^{2+}$, which reacts slower with peroxide compared to $[Fe(OH)(H_2O_5)]^{2+}$. Additionally, at the high concentration of H^+ ions, hydrogen peroxide gets solvated and more stable form named oxonium ion $[H_3O_2]^+$ was occurred [9].

As seen from Fig. 3, the energy consumptions were 127, 284, 285 kWh/m^3, at pH 2, 3 and 4, respectively. The decrease in the pH of solution may increase conductivity of the solution. Therefore, when the conductivity increases, ability to carry electricity is also increased and low energy needed [10]. Therefore subsequent experiments were performed at pH 2 because of lower energy consumption.

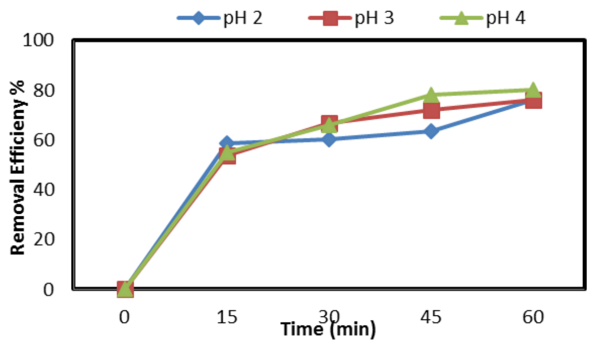

Fig. 2. Effects of initial pH on COD removal efficiency (i = 20 mA/cm^2; $C_{H_2O_2}$= 0.1 M).

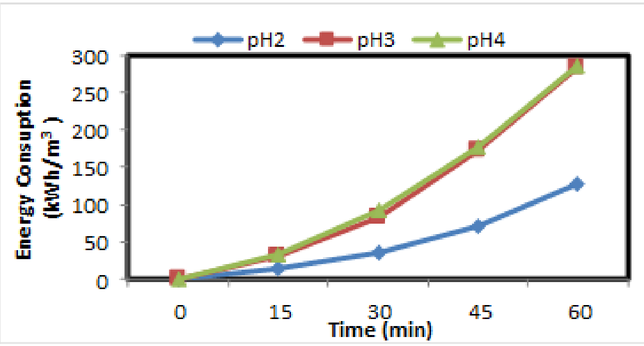

Fig. 3. Effects of initial pH on energy consumption (i = 20 mA/cm^2, $C_{H_2O_2}$ = 0.1 M).

B. Effect of Current Density

Current density has an important role in the electrochemical processes. According to Faraday's law (Eq. 7), the amount of oxidized iron generated from electrode released from anode increases with increasing current (I). Therefore, iron may have more possibility to make complex species to reduce COD.

$$m = \frac{I \times t \times M}{z \times F} \qquad (7)$$

where m is the mass of generated metal ions (gram); I is the current(Ampere), t is the operation time (min, h); M is the atomic weight of metal (g/mol), z is the number of electrons transferred in the anodic dissolution, and F is Faraday's constant (96 486 C/eq).

As seen from the results in the Fig. 4, removal efficiencies were 74%, 75%, 76% and 78%, at the current densities of 10, 15, 20, 25 mA/cm^2, respectively.

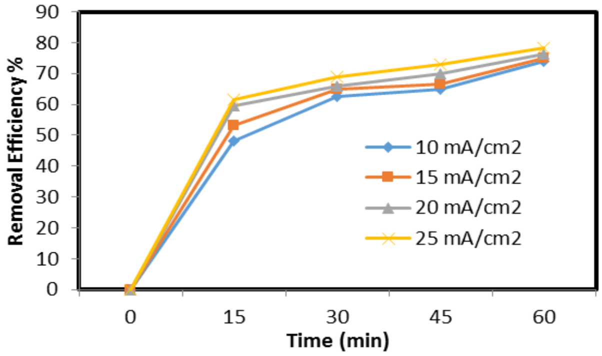

Fig. 4. Effects of current density on COD removal efficiency (pH 2 , $C_{H_2O_2}$ = 0.1 M).

Energy consumption depends on current that applied. Increasing current results with increasing energy consumption. As seen from the Fig. 5, energy consumptions of 5, 28, 48, 58 kWh/m^3 were obtained at current densities of 10, 15, 20, 25 mA/cm^2, respectively.

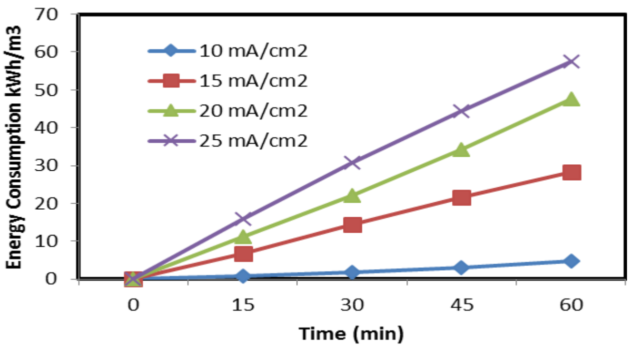

Fig. 5. Variation of energy consumption with time for different current densities (pH 2, $C_{H_2O_2}$= 0.1 M).

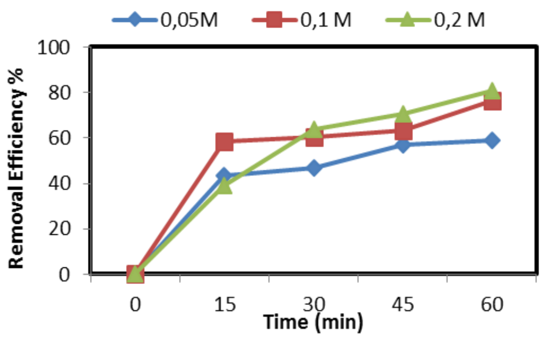

Fig. 6. Effects of H_2O_2 concentration on COD removal efficiency (pH 2 , i= 20mA/cm^2).

C. *Effect of Concentration of H_2O_2*

Dosage of H_2O_2 is also important parameter for COD removal in the Electro-Fenton process. With increasing dosage of H_2O_2 the hydroxyl radicals which is important for complex formations are also increased. The removal efficiencies of 60%, 76% and 81% were obtained at 0.05, 0.1, 0.2 M of H_2O_2 , respectively. As it can be easily seen from the results in the Fig. 6 that, COD removal was increased with increasing dosage of H_2O_2.

It is also observed that, after 60 minutes Electro-Fenton process, energy consumptions of 126, 123, and 96 kWh/m^3 were consumed at the presence of 0.05, 0.1 and 0.2 M of H_2O_2 respectively (Fig. 7).

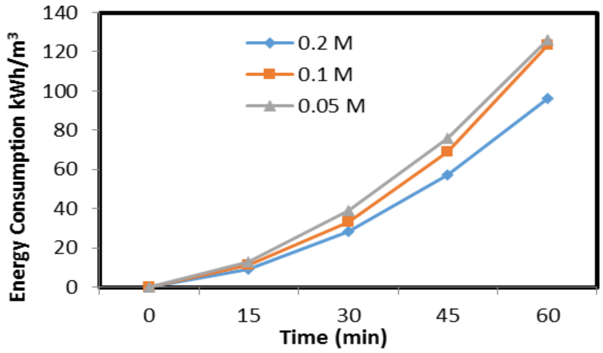

Fig. 7. Variation of energy consumption with time for different H_2O_2 concentration (pH 2, i=20mA/cm^2).

IV. Conclusion

In this study the performances of Electro-Fenton process on COD removal from the paper mill wastewater were investigated. Based on the results achieved from the experiments, the following conclusions may be outlined:

1) Electro-Fenton with iron electrode could be applicable for COD removal from the tissue paper wastewater.
2) The removal efficiencies increased by increasing the current density. However, increasing the current density caused the energy consumption to increase.
3) The initial COD of 1200mg/L was reduced to 228 mg/L with the removal efficiency of 81% at pH 2, 20 mA/cm^2 and addition of 0.2M H_2O_2.

It can be concluded from the study that iron reactor and anode with 8 paddle blade, designed dissimilar from those in the literature, can be used successfully for COD removal from the paper industry.

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