Textile wastewater treatment with Ozone/Fenton process: Effect of pH

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ABSTRACT: In this study, ozone/Fenton process was applied to biologically treated textile wastewater (Dissolved organic carbon, (DOC): 150 mg/L, color 500 Pt-Co) to investigate residual color and DOC removal. Ozone dose and Fe^{+2}/H_2O_2 molar ratio was kept constant at 1.28mg/min and 1:1, respectively. Initially, ozone and Fenton process (Fe^{+2}/H_2O_2) was optimized separately under varying pH (4-9). Afterwards, effect of the varying pH values (4-6-8) on combined ozone/Fenton process was studied to optimize the color removal performance. System performance was evaluated by color, organic carbon and mixed liquor suspended solids (MLSS) parameters. Increasing pH increased color removal efficiency, which was evaluated based on influent and effluent parameters, for ozone process. However, relatively lower pH values (pH 4) were efficient for Fenton process. When combined ozone/Fenton process was applied, maximum color and DOC removal was obtained at pH 4, corresponding to 73%, 4% removal efficiencies, respectively. In this study, combination of ozone and Fenton processes provided higher color removal efficiency and lower sludge formation compared to separate ozone and Fenton process.

Keywords: *Ozone, Fenton, pH, Color Removal, Textile Wastewater*

Ozon/Fenton Prosesi ile Tekstil Atıksularının Arıtımı: pH'nın Etkisi

ÖZET: Bu çalışmada biyolojik olarak arıtılmış tekstil atıksularındaki (Çözünmüş Organik Karbon, (ÇOK): 150 mg/L, renk:500 Pt-Co) kalıntı renk ve ÇOK giderimi için ozon/Fenton prosesinin uygulanabilirliği araştırılmıştır. Ozon dozu ve Fe^{+2}/H_2O_2 molar oranı sırasıyla 1.28 mg/dk ve 1:1 olarak sabit tutulmuştur. Başlangıçta, birbirinden bağımsız olarak işletilen ozon ve Fenton prosesi (Fe^{+2}/H_2O_2) farklı pH (4-9) değerlerinde optimize edilmiştir. Bu aşamadan sonra renk giderim performansını optimize etmek için farklı pH değerlerinin birleşik ozon fenton prosesi üzerine etkisi incelenmiştir. Sistem performansı renk, organik karbon ve askıda katı madde parametleri ile değerlendirilmiştir. Ozon prosesinde pH değeri arttıkça giriş ve çıkış parametrelerine bağlı olarak değerlendirilen renk giderim verimi artmıştır. Ancak düşük pH (pH 4) değerlerinin fenton prosesi için daha verimli olduğu gözlemlenmiştir. Birleşik ozon/Fenton prosesi ile pH 4'de maksimum renk (%73) ve ÇOK (%4) giderim verimi elde edilmiştir. Sonuç olarak birleşik ozon/Fenton prosesi, birbirinden bağımsız ozon ve Fenton prosesine göre yüksek renk giderim verimi ve düşük çamur üretimi sağlamıştır.

Anahtar Kelimeler: *Ozon, Fenton, pH, Renk Giderimi, Tekstil Atıksuları*

1. INTRODUCTION

The textile industry covers a wide range of activities which are all energy- and water-consuming as well as highly chemically polluting. Large amounts of water are used in wet-processing operations like dyeing and washing process in a textile industry and, consequently, important volumes of wastewater are generated. The most problematical parameters in this wastewater are toxic agents, chemical oxygen demand (COD), and color. Textile wastewater need to be treated beacuse discharge of untreated textile wastewater can cause serious damage to environment. The traditional treatment of textile wastewater is usually based on physicochemical, mechanical and biological treatment methods.

A wide range of chemicals, color and non-biodegradable organic compounds is detected in textile industry wastewater. Therefore, textile industry wastewater is difficult to biologically proceeds and the application of biological treatments of textile industry wastewater is limits. Then an alternative method can be evaluated. As one of alternative method can be used ozonation process which posses high oxidative power with an oxidation potential (E_0) of 2.08 V.

Ozone which is powerful chemical oxidant and high capacity for oxidation has recently accepted much attention on biologically treated textile wastewater [1-3].Although ozone is effective in COD and color removal from biologically pre-treated textile wastewater, its effectiveness can be improved using advance oxidant materials and techniques. For example, combination ozone and hydrogen peroxide accelerates

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the efficiency of color removal [4]. Ozone specifically attacks the conjugated chains that give the color to the dyestuff [5]. Fenton process can have the dual functions of oxidation and coagulation and, therefore, this technology is capable to remove almost all parts of the organics which consists of both soluble and particulate fractions of COD formed during the biological treatment [6].

The aim of this study was to evaluate the effectiveness of combined ozone and Fenton process under varying pH as post-treatments for biologically pre-treated textile wastewater. The performance of combination was evaluated in terms of organic matter removal, colour removal and total suspended solid.

2. MATERIALS AND METHODS

2.1. Wastewater Sampling and Characteristics

Textile wastewater was collected from activated sludge reactor in a textile company (indusrty) in Kahramanmaras, Turkey. Then, textile wastewater was biologically treated as biological using anaerobic biorector under lab. conditions. The wastewater was used in COD and color removal with ozone/fenton process. Characteristics of biologically treated textile wastewater used in the experiments are shown in Table 1.

Table 1. Characteristics of biologically pre-treated raw wastewater

Parameters		Unit	Value
pH		-	7.2±0.2
Temperature		(^{0}C)	25±2
Conductivity		(mS/cm)	9.355±1
Suspended solid		(mg/L)	120±10
COD		(mg/L)	89.65±10
DOC		(mg/L)	159,9±20
Color	λ436 nm	(m^{-1})	18,9±2
	λ525 nm	(m^{-1})	17,9±2
	λ620 nm	(m^{-1})	9,9±2
Color		Pt-Co	500±50

2.2. Experimental Set up

2.2.1. Experimental Procedure of Ozonation Stage and Combined Ozone/Fenton Stage

The ozone and combined ozone/fenton experiments were conducted in a 1000 ml glass reactor which wasn't available for the absorbation of the color, at room temperature and batch mode. An ozone generator (Opal OG-400, Ankara, Turkey) was employed to produce ozone from air and was bubbled at the bottom of the reactor by means of a diffuser at the rate of 1.28mg/min. Ozonation experiments were carried out at ozonation time of 5 to 30 min and samples were taken at regular intervals to measure DOC, color and MLSS. The pH values were operated at around 4, 6 and 8 over the experimental period.

2.2.2. Experimental Procedure of Fenton Stage

The Fenton experiments are conducted on six beakers with jar equipments, at room temperature. Rapid mix the beakers at 150 rpm for 5 minutes. Then slow mix the beakers at 30 rpm for 25 minutes. During experiments, effectiveness of Fenton process under varying pH (4-9) was evaluated.

2.3. Analytical Methods

DOC, color and MLSS were measured at regular time intervals. pH was measured using a pH probe (340i, WTW, Oslo, Norway). Samples were centrifuged using Eppendorf Centrifuge 5415R centrifuge 3000×g for 5 min, before the measurement of color and DOC concentrations from the supernatant. Absorbance measurements were carried out by a Hach DR-5000 model spectrophotometer in 1 cm glass cuvettes according to German environmental legislations at three different wavelengths, namely 436 nm, 525 nm and 620 nm, representing yellow, red and blue color, respectively. Standart test method for color was measured (HACH DR/5000) using platinum-cobalt (Pt-Co unit). DOC anlyses were caried out using a total organic carbon analyzer (Shimadzu TOC-VCPN, Kyoto, Japan). MLSS was analyzed using a Standart Methods.

Ozone consumption was calculated as described by Sevimli et al. [7].

3. RESULTS AND DISCUSSION

3.1. Effect of pH on Ozonation

Fig. 1 illustrates the effectiveness of ozonation process under varying pH by means of color (Figure 1A), DOC (Figure 1B), and ozone consumption (Figure 1C). The influence of pH on ozonation process was evaluated at pH 4, 6, and 8, respectively. Increasing pH increased ozone consumption and color removal efficiency. Color removal of 25% and 45% was observed at pH 4 and 6, respectively which was raised to 54% at pH 8. Similar results were obtained in previous works argueing that high pH values are benefical in ozonation process when treating textile wastewaters [8-10]. Thus, in this study, the maximum removal of DOC, color, ozone comsuption were 11%, 54%, 3.7 mg O_3/L respectively, at pH 8.

Generally, direct ozone oxidation or radical oxidation by OH* radicals played key role on oxidation mechanism. It has known that direct oxidation predominates under acidic contiditions and it is slower than radical oxidation [11]. In our study, alkaline pH values are found favarouble as ozone decomposition by hydroxyl radicals are enhanced at alkaline conditions. Therefore, higher removal rate of color was obtained at high pH values. Arslan et al. [12] reported high color removal at pH 7. However, Lidia et al. [13] found low DOC removal (10%) at pH 8 when textile wastewater contain largly disperse dyes which have high solubility. In a study performed by Cortez et al. [14] COD removal was reported to increase from 18% at pH 5.5 to 49% at pH 11. Similar results were obtained in the ozonation of landfill leachate with COD removal efficiencies of 24%, 29%, and 41% at the initial pH values of 4.5, 8.1, and 11, respectively [15]. As a result, higher pH values are favarouble for color removal of textile wastewater when using ozonation process. However this process is insufficient for DOC removal from this kind of wastewater.

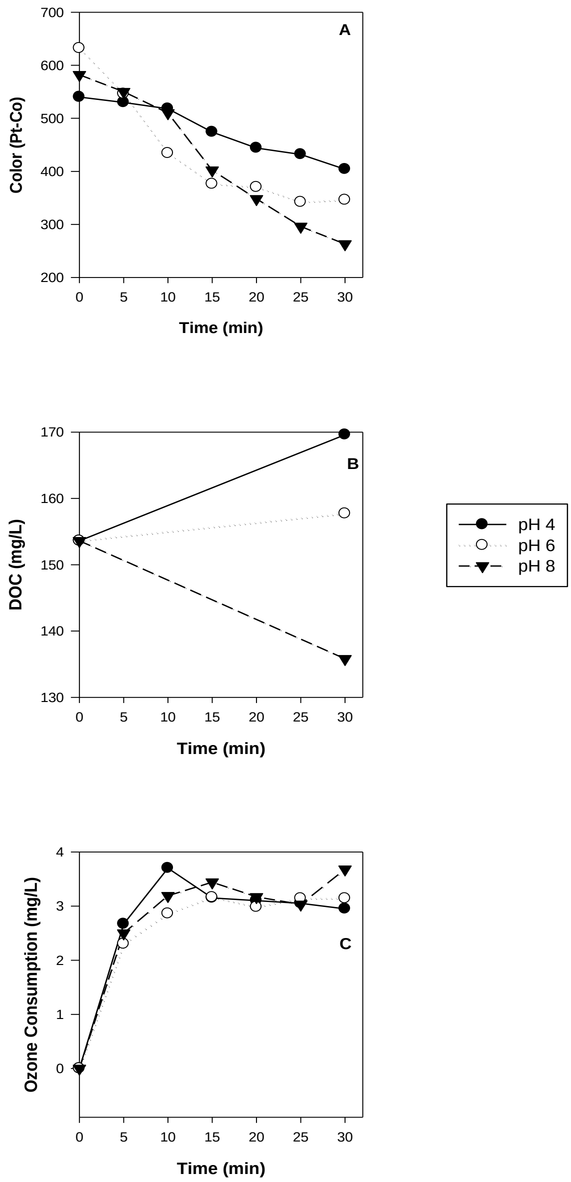

Figure 1. Color (A), COD (B) removal and Ozone consumption (C) during ozonation process

3.2. Effect of pH on Fenton Process

Fenton's reagent is a mixture of H_2O_2 and ferrous iron, which generates hydroxyl radicals according to the following reactions Equation (1-7). Equations (1) and (2) will prefer low pH while Equations (3) and (6) prefer higher pH [16, 17].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\cdot} + OH^{-}$$
$$k_1 \approx 70 M^{-1}s^{-1} \qquad (1)$$

$$OH^{\cdot} + Fe^{2+} \rightarrow OH^{-} + Fe^{3+}$$
$$k_2 = 3.2 \times 10^{8} M^{-1}s^{-1} \qquad (2)$$

$$Fe^{3+} + H_2O_2 \leftrightarrow Fe-OOH^{2+} + H^{+}$$
$$k_3 = 0.001 - 0.01 M^{-1}s^{-1} \qquad (3)$$

$$Fe-OOH^{2+} \rightarrow HO_2^{\cdot} + Fe^{2+} \qquad (4)$$

$$Fe^{2+} + HO_2^{\cdot} \rightarrow Fe^{3+} + HO_2^{-}$$
$$k_5 = 1.3 \times 10^{6} M^{-1}s^{-1} (\text{at pH } 3) \qquad (5)$$

$$Fe^{3+} + HO_2^{\cdot} \rightarrow Fe^{2+} + O_2 + H^{+}$$
$$k_6 = 1.3 \times 10^{6} M^{-1}s^{-1} (\text{at pH } 3) \qquad (6)$$

$$OH^{\cdot} + H_2O_2 \rightarrow H_2O + HO_2$$
$$k_7 = 3.3 \times 10^{7} M^{-1}s^{-1} \qquad (7)$$

As Fenton oxidation occur at acidic pH close pH must be raised again to neutral conditions to help in coagulation and precipitation of ferric ions (Fe^{+++}). Calcium hydroxide can be used fort this aim. Generally fenton reactions are known to be affected by pH parameter as genaration of OH* radicals depend on the pH [18].

Fig. 2 shows the color removal, DOC removal and MLSS profile which is an indicator of sludge production during Fenton studies at varying pH values (4-9). In the Fenton treatment system, the optimal pH values for the degradation of organics are generally reported between 2 and 4.5 [19, 20]. Similarly, in this study, the maximum removal of color, and DOC were observed as 65,6%, 14%, respectively, at pH 4. It can be concluded that fentone alone is more effcicient for coor and DOC removal compared to ozone alone process. Also, in this study, the low removal of DOC, and color was obtained when pH value was higher than 7 (Figure 2). The reason can be probably due to the fact that the ferrous catalyst may be deactivated by the formation of ferric hydroxo complexes at high pH values [21].

Similar to our results, high COD and TOC removals were observed at low pH values in previous studies [17]. In a study performed by Szpyrkowicz et al. [22], lower pH values than 3 decreased the COD removal effciciency pobably due to the lower reaction rate of $[Fe(H_2O)]_2$ and H_2O_2 or the inhibition of the reaction between Fe^{3+} and H_2O_2 due to high concentrations of H^{+}. Generally it is suggested that to ensure that the maximum amount of OH* radicals is available for organic compound oxidation neither H_2O_2 nor Fe^{2+} must be overdosed in Fenton treatment [23]. In the previous part, Fig. 1 shows that the efficiency of ozone alone is insufficient for the removal of DOC. Thus; the Fenton reagent is more efficient for textile wastewater treatment than O_3 alone as post treatment.

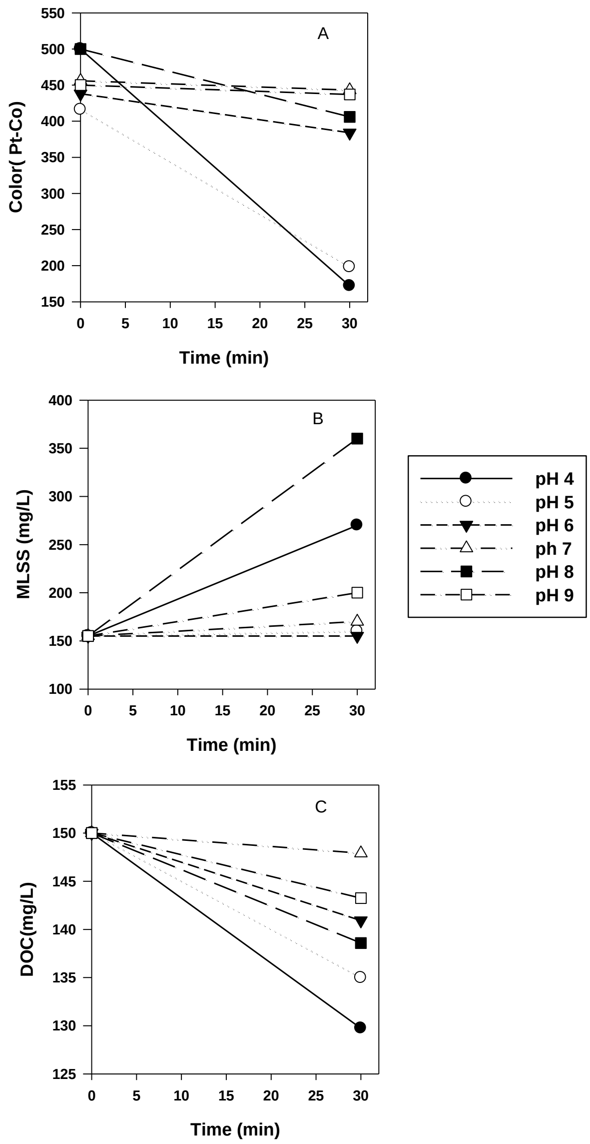

Figure 2. Color (A), DOC (B) removal and MLSS profile (C) during Fenton process

3.3. Effect of pH on Combined Ozone/Fenton Process

The performance of combined ozone/Fenton in terms of color removal, DOC removal, ozone consumption and MLLS generation is presented in Fig. 3A, 3B, 3C and 3D, respectively. Decreasing the pH from 8 to 4, resulted in increase color (Pt-Co unit) and DOC removal efficiency. Effluent color value was lower when compared to seperate ozone and fenton processes, corresponding to 133Pt-Co. The DOC removals were releatively low at all pH values. However the best removal was observed at lowest pH of 4, corresponding to 4% removal efficiency. Since the wastewater is previously treated as biologically, the remaining organic matter is hardly degradable. For this reason low DOC removals were observed. Recently, Abu Amr and Hamidi [24] improved COD removal efficiency from 15% to 65% by using combined Ozone/Fenton process, when raw wastewater was used.

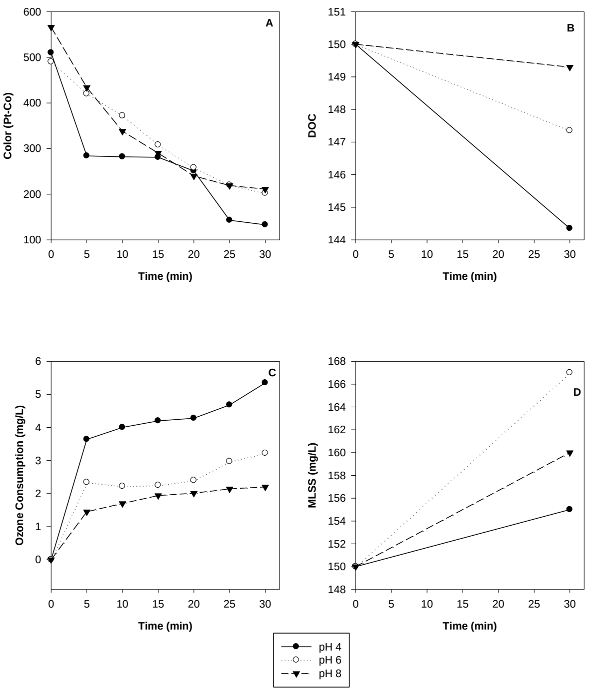

Figure 3. Color (A), DOC (B) removal, Ozone consumption (C) and MLSS concentration (D) during combined ozone/Fenton process

The color removal efficiency had its highest value at pH 4, however it decreased when pH was decreased. Additionally highest ozone comsumption was observed at pH 4 where contaminant removals were higher. The sludge production was relatively low as 3% when compared to fentone alone process (80%). Combination of ozone and fenton improved color removal from 65% in fenton alone to 73% in combined ozone-fentone process.

4. CONCLUSIONS

In the current study, the effect of pH on Fenton, ozonation, and combined fenton-ozonation process for post treatment of biologically pretreated textile wastewater. At pH value of 4, the performance of combined Fenton and ozone is more efficient for post treatment of textile wastewater than the seperate Fenton or ozone process. The initial DOC and color was about 150 mg/L and 500 Pt-Co. Accordingly, the color removal efficiencies were 54% at pH 8, 65% at pH 4, and 73% at pH 4 for ozone alone, Fenton alone and combined ozone-fentone process, respectively. DOC removals were low, however fenton alone process found efficient, corresponding to 14% DOC removal. As a result, the implementation of combined Fenton and ozonation processes resulted in the highest color removal and lowest sludge production among all the treatment methods applied, while the highest DOC removal was observed during the Fenton -treatment only. This study findings shows that combined ozone-Fenton process is an efficient method for post treatment of textile wastewater, especially for the removal of residual color.

5. REFERENCES

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