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The inhibition effect of ozonation in textile wastewater

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Abstract

The textile industry effluent includes toxic, mutagenic, carcinogenic compounds. Color containing substances are one of the most important effluents among these compounds. These substances should be treated and for the treatment of these substances, biological wastewater treatment processes are frequently preferred. However, biological wastewater treatment processes might not be adequate, therefore, advanced treatment processes could be applied for textile effluent to meet the discharge limits. One of the often-used advanced treatment processes is ozonation. Ozone is a disinfectant and a powerful oxidant The aim of this study is to show the effects, which include decolorization and inhibition effects, of ozonation on real textile wastewater after anaerobic treatment. For evaluating of ozonation efficiency DOC, alkalinity, pH, ORP and color were measured. The change of color was measured at 436 nm, 525 nm and 620 nm wavelengths. In conclusion, with 10 minutes of ozone contact time, color and DOC are removed by 80% and 65%, respectively. The inhibition tests indicate that the effluents should be considered slightly toxic with 10 min ozonation time.

Keywords: ozonation, textile wastewater, decolorization, inhibition effect.

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1. Introduction

The textile industry is an important industry. Its wastewaters include heavy metals, strong color, high concentrations of organic and inorganic compounds (Soares, Órfão, Portela, Vieira & Pereira, 2006; Wijannaronga, Aroonsrimorakota, Thavipokea, Kumsopaa & Sangjanb, 2013). These compounds generally arise from sizing, wetting, washing, anti-felting and finishing agents, biocides, halogenated benzenes, surfactants, phenols, pesticides, dyes, and others (Rodriguez Sarria, Esplugas &Pulgarin, 2002). Among these, dyes hold an important role in the textile industry and its wastewaters. Based on their chemical structure, dyes are categorized as azo, triphenylmethane, heterocyclic, polymeric dyes. The azo dyes play a big part in textile dyestuffs and consist of 70% of all organic dyes in the world (Carliell, Barclay, Shaw, Wheatley & Buckley, 1998; Yang, Zhao, Liu, Zheng & Qian, 2009; Bafana, Devi & Chakrabarti, 2011). Many synthetic dyes, including azo dyes, do not degrade easily (Lin, Zhang & Lei, 2010). Textile dye effluent has toxic effects on aquatic life, leading to environmental problems (Saratale, Chang & Govindwar, 2009). Most synthetic azo dyes are mutagenic, carcinogenic with toxic effects, which impact the germination rates, ecological function, wildlife, providing of organic substance, soil from erosion, and biomass (Meric, Selcuk & Belgiorn, 2005; Ghodake, Telke, Jadhav & Govindwar, 2009; Khan, Bhawana & Fulekar 2013). As such, textile wastewaters require treatment.

Many different processes could be used to treat textile wastewaters, such as; biological, simple physicochemical and advanced treatment processes (Tehrani-Bagha, Mahmoodi & Menger, 2010). Advanced oxidation processes (AOP) are generally used to treat hazardous organic substances content or degrading dyes. These processes are based on ozonation, UV irradiation, Fenton, catalytic peroxide oxidation, and others. Ozonation is an expensive process; however this is one of the alternatives with the most potential for color removal in textile wastewater (Soares et al., 2006; Tehrani-Bagha et al., 2010; Laconi, 2012). Ozonation is the most commonly used process, because it increases the biodegradability of different toxic pollutants (Selcuk, Eremektar & Meric, 2006). Ozonation generated from ozone (O3) a direct reaction of molecular ozone and indirectly reaction of a hydroxyl radical, is a powerful oxidizing agent and degrades most of organic, inorganic compounds in aqueous solution (Souza, Bonilla & Souza, 2010).

This study focuses on providing the treatment of the hazardous components of textile wastewater. For this, ozonation is operated to effluent after textile wastewater treatment by lab-scale reactor. The effect of ozonation was based on the following parameters; color removal, inhibition test, dissolved oxygen carbon (DOC) and alkalinity.

2. Material and Methods

2.1. Wastewater

The wastewater was taken from a local textile wastewater treatment plant, which has a capacity of 8000-10000 m3/day in Kahramanmaras, Turkey. This wastewater was biologically treated in a bioreactor (New Brunswick BioFlo, CelliGen 115, USA) by anaerobic process. Characterization of real textile wastewater and continuous flow stirred-tank reactor CSTR-treated effluent is shown in Table 1. The hydraulic retention time (HRT) for the reactor was one day. In the effluent of anaerobic wastewater; DOC, pH, and alkalinity were measured.

Table 1. Characterization of real textile wastewater and CSTR-treated effluent used in study

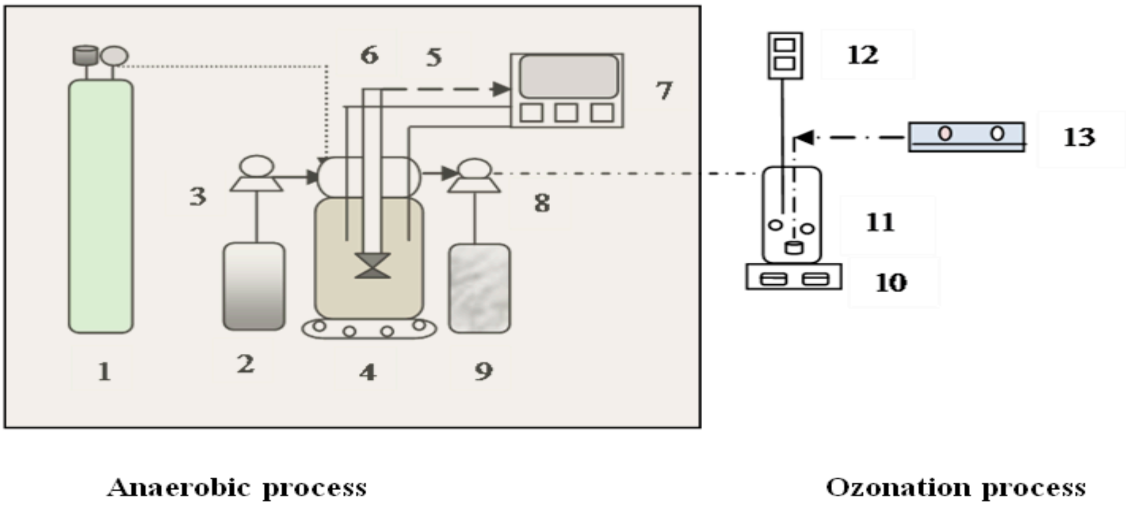
Parameters		Unit	Real textile wastewater	CSTR effluent
pH		-	11±0.5	7±0.5
Temperature		(^{0}C)	25.6±3.5	25.6±3.5
DOC		(mg/L)	680±11	60±10
NH_4-N		(mg/L)	4.83±1	0.05±0.01
Color (RES)	λ_{436} nm	m^{-1}	52.07±0.5	25±0.1
	λ_{525} nm	m^{-1}	55.01±0.2	17,45±0.05
	λ_{620} nm	m^{-1}	68.04±0.5	19,09±0.2
Color		Pt-Co	1600±22	900±09

2.2. Ozonation

An ozone generator (Opal OG-400, Ankara, Turkey) was used to produce ozone from air and was bubbled at the bottom of the reactor by means of a diffuser at the rate of 400 mg/h. Flow rate of ozone generator was 0.042 m3/h. A tubular cylindrical porous diffuser was placed at the bottom of the glass beaker to transfer input ozone gas into effluent. Ozonation experiments were carried out at ozonation dose of 5 and 10 min and samples were taken at regular intervals to measure pH, alkalinity DOC and color.

2.3. Experimental Design

Ozone was provided as a fixed dose in a 250 mL glass beaker filled of textile wastewater effluent and the stirrer (Heidolph MR Hei-Standard, Germany) was operated at 250 rpm for a complete mixing. Oxidation–reduction potential (ORP) in the system was measured continuously using an ORP Meter (M 300, Mettler Toledo, Greifensee, Switzerland) equipped with a redox electrode. The pH was measured using a probe (WTW Multi 340i, Germany). The experimental design is shown Figure 1.



1 Nitrogen gas, **2** Influent wastewater, **3**&**8** Peristaltic pump, **4** Biologic reactor **5**&**12** pH probe, **6**&**13** ORP probe, **7** Monitor, **9** Effluent wastewater, **10** Reactor applied ozone, **11** Magnetic stirrer, **12** Ozone generator

Figure 1. Experimental design of system

2.4. Analytical Methods

Dissolved oxygen carbon (DOC), alkalinity and color were measured at regular time intervals. Alkalinity was measured according to EPA standard methods (EPA, 1999). Samples were centrifuged using Eppendorf Centrifuge 5415R centrifuge 3000 rpm for 5 minutes, before the measurement of color and DOC concentrations from the supernatant.

For color measurements, RES parameter (m-1) was applied according to the standards of European Norm EN ISO 7887. The absorbance measurements at three wavelengths, namely 436 nm, 525 nm and 620 nm, were yellow, red and blue color, respectively. Absorbance measurements were carried out on a HACH DR-5000 model spectrophotometer in 1 cm glass cuvettes. The color was measured (HACH DR 5000) in platinum-cobalt (Pt-Co unit).

DOC analysis was carried out by means of a Shimadzu TOC-VCSH (Japan) total carbon organic analyzer. DOC was measured by direct injection of samples filtered through 0.45 µm syringe-driven filters into a TOC analyzer.

2.5. Inhibition Analysis

ToxTrak TM kit (10017 method HACH, USA) was used in detection percent inhibition. This kit includes resazurin dye, accelerator solution, Lauryl tryptose broth tube and ToxTrak TM reagent powder pillow. Resazurin dye changes from pink to blue when it is reduced. Respiration of the bacteria with the ToxTrak TM kit is based on reduction of resazurin dye. Absorbances of samples were measured in 603 nm wavelength (HACH DR 2500, Hach Lange, USA) and inhibition percentage was determined for textile wastewater. The samples were measured in triplicate.

3. Results

The color is an important parameter in textile wastewater because of dyes and theirs metabolites that can be toxic, mutagenic and carcinogenic. Anaerobic treatment is an efficient and cost-effective process for color removal. However, it is not sufficient to remove all of the color. For better color removal some treatment plants are designing anaerobic and aerobic process together, however using this approach, the color removal efficiency could be low and odor problems could occur. The color measurements of influent samples was 900 Platinum-Cobalt (Pt-Co) colors and absorbance at 436 nm, 525 nm, 620 nm wave lengths were 24.8, 18.11, 18.5 m-1. Because of low color removal values in biological treatment, textile wastewater could require advanced treatment process, such as ozonation. In the present study, ozone was given in 0.042 m3/h flow rate in fixed dose as 0, 5 and 10 min. Figure 2 shows the DOC profile of the textile wastewater effluent over ozone contact time. The DOC value was 60.39 mg/L at 0 min. This value decreased to 21.2 mg/L applying 5 min and 19.06 mg/L at 10 min. The removal efficiency was initially 65% at 5 min and after 69% at 10 min.

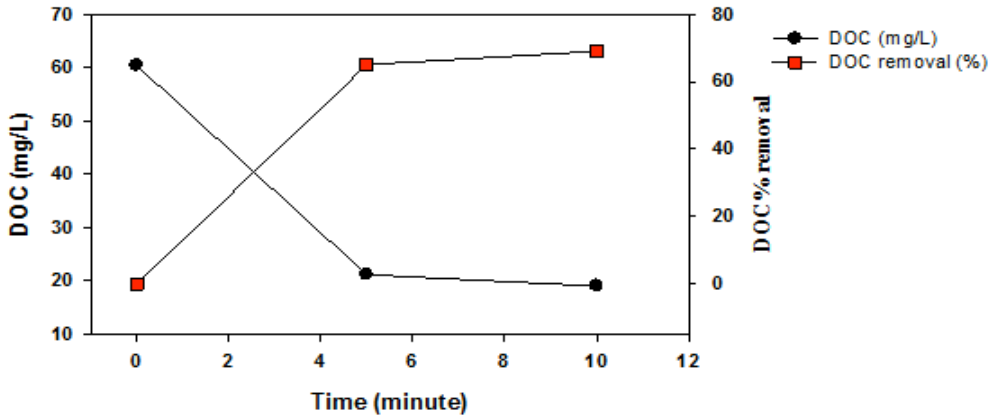


Figure 2. DOC removal

The oxidation-reduction potential (ORP) parameter is more sensitive than DO parameter and in some cases it should be measured to monitor the system performance. In this study, ORP values were 27.4 mV at 0 min, 121.2 mV at 5 min and 182.7 mV at 10 min. The alkalinity and pH values were at 0, 5 and 10 min. According to these results, pH value increased to 8.35, 8.74, and 8.9. The alkalinity value decreased at 0, 5 and 10 min measuring 2950, 1600, and 927.5 mg $CaCO_3$/L, respectively. The removal efficiency was 46% at 5 min and 65% at 10 min. The decrease of alkalinity results showed an increase of organic matter removal as shown in Figure 3.

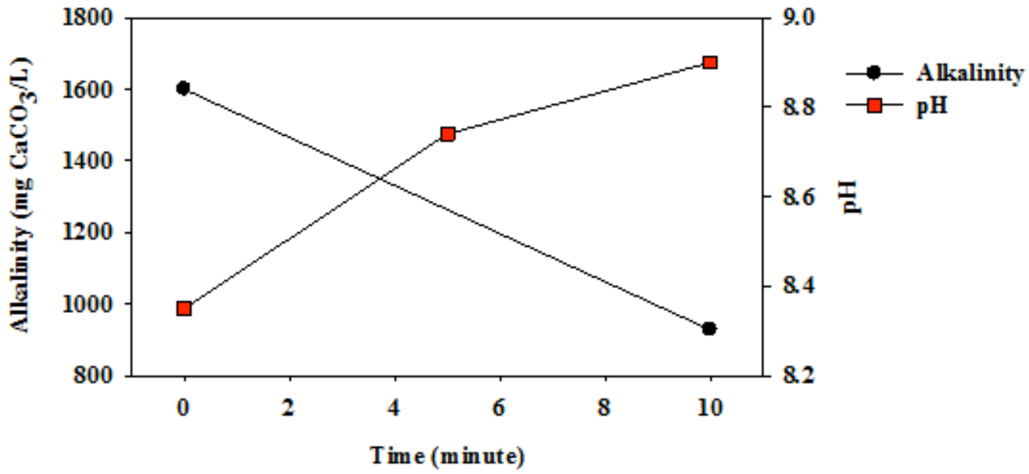


Figure 3. Alkalinity and pH

Figure 4 shows the color removal profile of the textile wastewater effluent. The value of Pt-Co, and colors in 436 nm, 525 nm and 620 nm wave lengths are 190, 7.48, 3.54, 2.36 by 10 minutes ozone contact time and color removal average was 79±7%. İleri and Karaer, (2013) reported that the highest removal efficiencies of COD and color values were obtained at pH 12. However, in this study, color discharge criteria are provided in a lower pH.

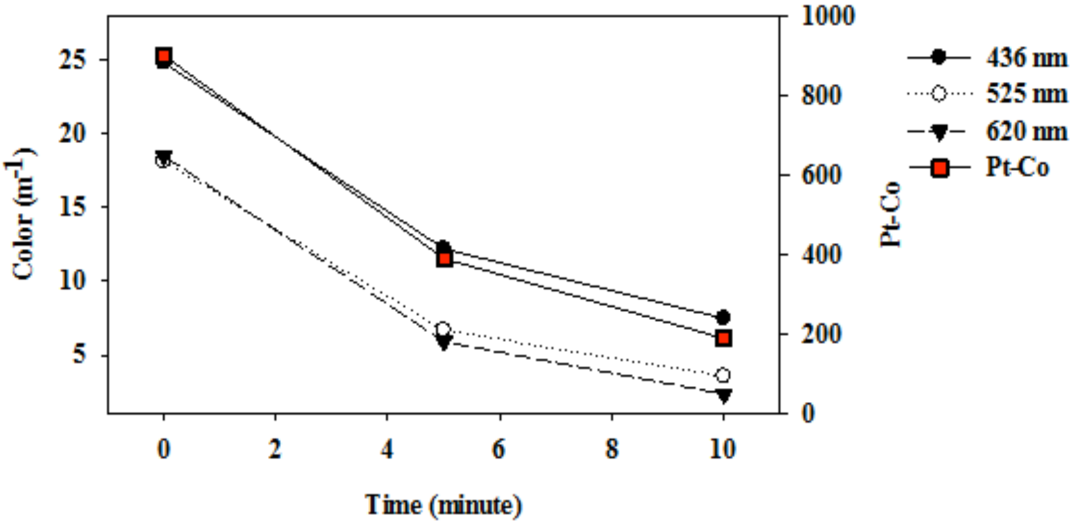


Figure 4. Color removal

Results of the removal efficiency showed that the resazurin dye color changed from blue to pink as a consequence of the reaction. Inhibition percent of raw and ozonated textile wastewater is more than >-10%, this means that the ozonation in this study does not have an inhibition effect. According to ToxTrak TM method a minus value indicates slightly toxic effect, therefore the toxic effect of the samples should be thoroughly investigated.

4. Discussion

The textile industry is an important industry. According to Selcuk (2005), the textile industry can produce high amount of toxic wastewater. However, the textile wastewaters are not completely treated, especially for color, after conventional wastewater treatment. Therefore, advanced treatment processes such as ozonation or fenton could be used. Laconi (2012) has reported that the DOC removal efficiency of textile wastewater at 76% with 180±30 mg/L.h ozonation dozes. In the present study color and DOC removal efficiencies of 79±7% and 69% have been achieved after 10 min ozone. The study of Laconi, (2012) indicated that the process was better at color and DOC removal efficiencies than present study because of high ozone dose used in the study of Laconi.

In another study, the evaluation effectiveness of Fenton's oxidation (FO) and ozonation oxidation processes, the ozone dose used was 1.4 g/L.h at 20 min. The COD removal was determined as 59% in FO and 33% in ozonation oxidation of textile wastewater. Saratale et al. (2009) and et Meric al. (2005) noticed that the color removal efficiency was 89% in FO and 91% in ozonation oxidation. The color range of Pt–Co was 150–250 units for assessment of toxicity. In this study, DOC removal was observed at 69% and the color removal efficiency was approximately 79±7%. Because of the different characteristics of textile wastewaters a comparison with the existing literature cannot be undertaken.

The inhibition effect of textile wastewater on activated sludge was determined by ToxTrak TM kits. The inhibition value was more than > -10% and according to the test method this value means that the samples are slightly toxic. Because of both of wastewater before and after ozonation had same value, for better understanding toxicity tests should be applied.

5. Conclusions

The present study was aimed to research the decolorization of real textile effluent with ozonation and after biological treatment with an anaerobic lab-scale reactor. For evaluating of ozonation efficiency; DOC, alkalinity, pH, ORP and color were measured. The change of colors was measured by absorbance at 436 nm, 525 nm, 620 nm and 465 nm (Pt-Co) wavelengths. The color and DOC were removed approximately by 80% and 69%, respectively; with 0.042 m3/h flow rate at 10 minutes ozone contact time. The inhibition effect of raw textile wastewater and ozonated samples was determined using ToxTrak TM kits. According to the results there was no inhibition effect, even though the samples were slightly toxic. Ozonation process has no inhibition and toxic effect on this wastewater. However, a detailed toxicity test should be undertaken.

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