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Original Research Article

Removal of Acute Toxicity with Ozonation in Textile Plant Waste Water

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ABSTRACT

Textile industry is one of the most common and essential sector in the world. The textile industry consumes large quantities of water at its different steps of dyeing and finishing, among other processes. The non-biodegradable nature of dyes and their stability toward light and oxidizing agents complicate the selection of a suitable method for their removal. Moreover, toxicity bioassays have demonstrated that most of them are toxic. The acute toxicity of waste water of textile plant was investigated using *Daphnia magna* (water fleas) and ozonation. In this study, samples were taken from a cotton textile plant in Bursa at the first stage, the treatment was made by ozonation and then the toxicity tests were performed. In ozonation, the appropriate pH, dosage of ozone (O_3) and ozonation time were determined. In toxicity tests, monitoring of toxicity were made at different dilution rates using *Daphnia magna* both in treated water with ozonation and in wastewater. The acute toxicity scale LD_{50} (Lethal Dose) values were determined as 50 % in waste water and 90 % in water treated with ozonation. As a result, it can be concluded that ozonation demonstrated a positive contribution to the removal of acute toxicity in textile wastewaters.

Key Words: Textile Plant, Ozonation, Acute Toxicity, *Daphnia magna*

Tekstil İşletmesi Atık Suyunda Ozonlama Yöntemi ile Akut Toksisite Giderimi

ÖZET

Tekstil endüstrisi dünyada en yaygın ve gerekli temel sektörlerden biridir. Tekstil endüstrisi, boyama ve terbiye işlemlerinin farklı aşamalarında, diğer çeşitli proseslerde bol miktarda su tüketir. Bu sektörde kullanılan boyaların, biyolojik olarak parçalanmayan yapıları ve ışık ile oksitleyici maddelere karşı olan stabiliteleri bu maddelerin uzaklaştırılması için uygun metodun seçimini zorlaştırmaktadır. Ayrıca yapılan toksisite biodeneyleri bu maddelerin büyük bir kısmının toksik olduğunu göstermiştir. Tekstil işletmesi atık suyunun akut toksisitesi *Daphnia magna* (su pire) ve ozonlama yöntemi kullanılarak araştırılmıştır. Çalışmada, atık su numuneleri Bursa'da bulunan bir pamuklu tekstil işletmesinden alınmıştır. İlk aşamada bu numuneler ozonlama yöntemi ile arıtıma tabi tutulmuş, sonra toksisite testleri uygulanmıştır. Ozonlama yönteminde uygun pH değeri, uygun ozon dozu ve ozonlama süresi belirlenmiştir. Toksisite testlerinde, *Daphnia magna* canlıları kullanılarak hem ozonlama ile arıtılmış suda hem de atık suda farklı seyreltme oranlarında toksisite izlemesi yapılmıştır. Akut toksisite ölçeği olan LD_{50} (ölüm dozu) değeri atık su için 50 %, ozonlama yöntemi ile arıtılmış su için ise 90 % olarak belirlenmiştir. Sonuç olarak bu çalışmada ozonlama yönteminin akut toksisite giderimine olumlu katkıda bulunduğu söylenebilir.

Anahtar Kelimeler: Tekstil İşletmesi, Ozonlama, Akut Toksisite, *Daphnia magna*

INTRODUCTION

The textile industry is one of the largest consumers of water in the world, and consequently, one of the largest producers of wastewaters (Mahmoodi and Arami 2009). The wastewater in textile industry is generated in several stages of textile manufacturing and processing, such as sizing of fibres, scouring, desizing, bleaching, washing, mercerization, dyeing and finishing (Rodriguez et al. 2002, Arami et al. 2006, Vilar et al. 2011). Various toxic chemicals such as complexing, wetting, softening, anti-felting and finishing agents, biocides, carriers, halogenated benzenes, surfactants, phenols, pesticides, dyes and many other additives are used in wet processes. As a result, textile plants produce highly toxic wastewater (Navarro et al. 2001, Selçuk 2005, Arslan-Alaton 2007).

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Ozone, due to its high oxidation and disinfection potential, has recently received much attention in water treatment technology (Kasprzyk-Hordern et al. 2003). Ozone oxidation being the most used process, successfully enhanced the biodegradability of different toxic pollutants (Goi et al. 2004). Ozone has high efficiency at high pH levels. At these high pH values (>11.0), ozone reacts almost indiscriminately with all organic and inorganic compounds present in the reacting medium (Steahelin and Hoigne 1982). Ozone reacts with wastewater compounds in two different ways namely direct molecular and indirect radical type chain reactions (mainly, OH radical) (Selçuk et al. 2006). Both reactions occur simultaneously and hence reaction kinetics strongly depend on the characteristics of the treated wastewater (e.g. pH, concentrations of initiators, promoters and scavengers) (Arslan and Balcıoglu 2000). Simplified reaction mechanisms of ozone at high pH is given in below;

$$3O_3 + H_2O \xrightarrow{OH^-} 2OH\bullet + 4\ O_2 \qquad (1)$$

Indirectly, O_3 can generate free hydroxyl radical (OH•). The hydroxyl radical is a powerful and non-selective oxidant that can react through three possible mechanisms: hydrogen abstraction, electron transfer or radical addition after being generated. The waste water characteristics play important role on the process efficiency, hence on the reaction kinetics (Selçuk et al. 2006).

Acute toxicity is defined the adverse effects of a substance that result either from a single exposure or from multiple exposures in a short space of time. Measure of acute toxicity is expressed by LD_{50}. The LD_{50} is defined as the lethal concentration causing 50% death or immobilization in *Daphnia magna*. *Daphnia magna* is often being used as a tool for the evaluation of acute as well as chronic toxicity in industrial wastewater. Many European countries conduct their routine, acute as well long-term toxicity tests with *Daphnia magna*, because of its easy growth, maintenance, relatively simple test procedure and reproducibility, as well as high sensitivity towards industrial pollutants (including heavy metals) and industrial wastewater (Arslan-Alaton 2007, Mahmoodi and Arami 2009).

The complex character of textile industry wastewater composed of dyestuff, surface-active materials and textile additives used in the processes needs to be handling carefully for both effluent toxicity and aesthetic problems. Textile wastewater treatment plant effluent and many azo dyes which cause the effluent color, have been found mutagenic/carcinogenic and toxic to aquatic life (Villegas-Navarro et al. 2001). Because the recalcitrants resist in biological treatment, many advanced oxidation processes such as photocatalytic oxidation, ultrasound, Fenton's oxidation, photo-Fenton oxidation and ozone oxidation have been attempted individually or combined with UV/H_2O_2 oxidants to decolorise, detoxicify and enhance the biodegradability of textile wastewater and dyes (Baban et al. 2003, Lim et al. 2004, Selçuk et al. 2006). Ozone oxidation being the most used process, successfully enhanced the biodegradability of different toxic pollutants (Andreozzi et al. 2003, Goi et al. 2004, Selçuk 2005).

The aim of this study was to apply ozonation methods for detoxification of wastewaters and removal of COD and color originated from cotton textile plant. In the first stage the treatment process was made of ozonation, in the second stage toxicity test was performed. The evaluation of treatment efficiency was made using the parameters of COD, toxicity and color.

MATERIALS AND METHODS

Characterization of the industry

Waste water sample performed in this study was supplied from a cotton textile plant located in Bursa, Turkey. According to the operation manager, various harmful chemicals are used in the processes. Samples are taken from the entrance of wastewater treatment plant and various parameters were examined to determine of water character. For the analysis of these parameters, Standart Methods (APHA 1998) were used. Temperature, pH, conductivity parameters of water were measured using a HACH brand Sension 156 device. Total suspended solids (TSS) was measured by drying the sample under 103-105 ^{0}C (gravimetric method), hardness and alkalinity were measured by the titration method, total phosphorus (Total-P) was measured by the ascorbic acid method. Total Nitrogen (Total-N) were measured by water vapors distillation (Bremner and Mulvaney 1982). Chemical oxygen demand (COD) and color parameters were measured according to the standard methods (APHA 1998).

The results of the wastewater character is given in Table 1. After these studies, wastewater purified by ozone and toxicity tests were performed, at different dilution rates using *Daphnia magna* both in treated water with ozonation and in waste water.

Table 1. Waste water characterization of cotton textile plant.

Parameters	Unit	Waste Water
pH		8,68
Temperature	(^oC)	28,3
Conductivity	(µs/cm)	3720
TSS	(mg/l)	106
COD	(mg O_2/l)	820
Alkalinity	(mg/l $CaCO_3$)	750
Hardness	(mg/l $CaCO_3$)	500
Total-N	(mg /l)	12,6
Total-P	(mg /l)	3,93
$Color_{600}$	nm	0,156

Ozonation

Ozone was generated from air by ozone generator (OG3 OPAL model). A closed cylindrical Pyrex glass reactor with a diameter of 80 mm and height of 400 mm was used in the ozonation experiments. A tubular cylindrical porous diffuser was placed at the bottom of the reactor to transfer input ozone gas into aqueous solution at the regular intervals. Teflon tubing line was used for the connection between ozone generator and reactor. During the experimental studies pressure of pure oxygen was kept at 1 bar constant pressure inlet of generator. All experiments were performed at room temperature. Ozonic color and COD removal experiments were carried out 1 L sample volume. So the amount of ozone that are expressed in a volume of 1 L. Excess gaseous ozone leaving the column was collected in two gas washing bottles connected in series and filled with 2 % KI solution, whereas two other gas washing bottles with 2 % KI solution were directly placed after the gas introduction line in front of the process set-up. The amount of feed and off gas ozone collected in the gas washing bottles was determined via iodometric titration (sodium thyosulfite) and the difference was calculated as the amount of ozone being absorbed (consumed) in the reaction solution throughout the selected ozonation periods.

Removal of acute toxicity and Daphnia magna

The toxicity of waste water and ozone-treated samples was measured using 24 h newborn *D. magna* at different dilution rates (ISO 6341, 1999) for 24 h exposure time. Daphnids were grown in the laboratory at 16 h daylight and 8 h dark periods supplying a 3000 lux illumination. During the experimental method, they were not fed. Room temperature was kept at 20±2°C and minimum 6 mg/l of dissolved oxygen was supplied by air filtered through activated carbon. Experiments were carried out two replicates and 20 daphnids were used in each test beaker with 250 ml of effective volume. Results were evaluated on the basis of immobilization percentage obtained by dividing the number of immobilized animals by total animals.

RESULTS AND DISCUSSION

Ozone treatment

Results of the textile waste water treatment with ozonation are shown in below. Figure 1, shows the percentages of COD and color removal at different pH values of water. Taking into consideration of the literature ozone application dose 23 mg O_3/minute, time 10 minute, total O_3 230 mg/L were chosen (Selçuk et al. 2006, Birgül and Solmaz 2007, Eremektar et al. 2007, Somensi et al. 2010). As shown in Figure 1 the highest removal efficiencies of COD and color values were obtained at pH 12. The efficiency of ozonation in the removal of color and COD from textile waste water is important to achieve to discharge limits (Birgül and Solmaz 2007, Eremektar et al. 2007). Despite achieving high efficiency at pH 11, when results compared with discharge limits, it was determined that this pH value not suitable (Anonymous 2004). Therefore optimum pH value is selected to be 12.

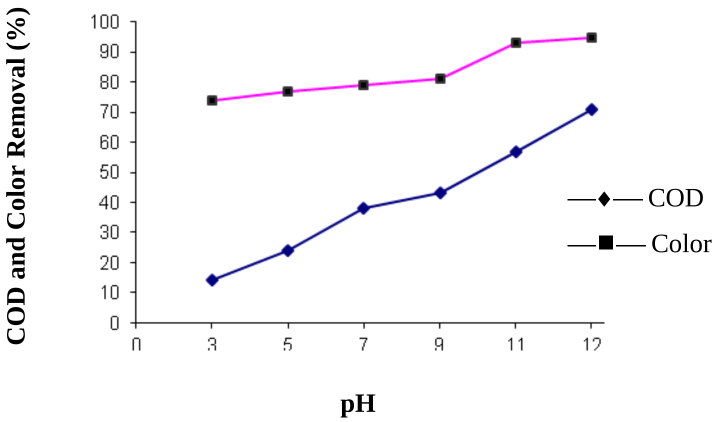

Figure 1. COD and color removal from different pH values

After these studies, the appropriate ozone dose and ozonation time were determined taking into consideration the literature data (Selçuk et al. 2006, Birgül and Solmaz 2007, Eremektar et al. 2007). Eremektar et al. (2007) have achieved 57 % COD, 96 % color and 80 % toxicity removal efficiency during a 20 minute ozonation time. In this study the pH of waste water adjusted 12 and 1000 ml sample taken from the glass reactor. Continuously ozone feding were applied to the samples. Samples taken at different times without opening the cover of the reactor, COD and color analyzes were conducted. The results obtained are given in Table 2.

Table 2. COD and color removal data after ozonation.

Time (min)	O_3 Dose (mg/L)	COD (mg/L)	Removal of COD (%)	Absorbance	Removal of Color (%)
1	23	476	42	0,03	81
2	46	467	43	0,028	82
3	69	467	43	0,023	85
4	92	459	44	0,140	91
5	115	443	46	0,010	93
6	138	443	46	0,010	93
7	161	435	47	0,006	96
8	184	410	50	0,004	97
9	207	369	55	0,004	97
10	230	310	62	0,003	98
15	345	246	70	0,003	98

As shown in the Table 2, after the 15 minute ozonation the rates of removal were determined 98 % for color and 70 % for COD. The results that obtained are consistent with literature studies. As a result of this process the waste water characterization after ozonation (pH 12, 345 mg O_3 / 15 dk) is given in Table 3.

Table 3. Characterization of the waste water is treated with ozone.

Process	COD (mg/L)	$Color_{600}$	pH
Raw Wastewater	820	0,156	8,68
After Ozonation	246	0,003	12

Acute Toxicity

The high conductivity of the waste water (3720 µs/cm) was toxic to *D. Magna* without dilution (Villegas-Navarro et al. 1999, Eremektar et al. 2007). Therefore monitoring of acute toxicity were made at different dilution rates using *Daphnia magna* both in treated water with ozonation and in wastewater (Ileri 2011). Using pure water, different concentrations of waste water and treated water solutions were prepared (e. g. 100 % (250 ml waste water), 80 % (200 ml waste water/50 ml pure water), 50 % (125 ml waste water/125 ml pure water), 20 % (50 ml waste water/200 ml pure water), 5 % (12,5 ml waste water/237,5 ml pure water) and 1 % (2,5 ml waste water/247,5 ml pure water). Treated water with ozone was prepared in the same way (e.g. 100 % (250 ml treated water with ozone), 90 % (225 ml treated water with ozone/25 ml pure water). The percentages of concentrations and the findings of the implementation of toxicity tests are given in Table 4 for waste water and in Table 5 for treated water with ozone. T value refers to the number of active *Daphnia magna* in each concentrations. The value P indicates the percentage of immobility *Daphnia magna* in each concentrations. As shown in Table 4, when the percentage of waste water decreases P values are also decreasing. Because solution rate of 90 % includes 225 ml waste water, also solution rate of 10 % includes 25 ml waste water. Therefore, P values of 90 % which contains more extensive pollution are higher than 10 %.

Table 4. Results of acute toxicity for waste water.

The concentrations of waste water (%)	T (The number of active *Daphnia magna*)	P (The percentage of immobility *Daphnia magna)*
100	2	90
90	3	85
80	4	80
50	10	50
20	15	25
10	16	20
5	17	15
1	19	5

The relationship between the percentage of immobility and the concentration shown in Figure 2. As shown in Figure 2 LD_{50} value was determined as 50 % for waste water.

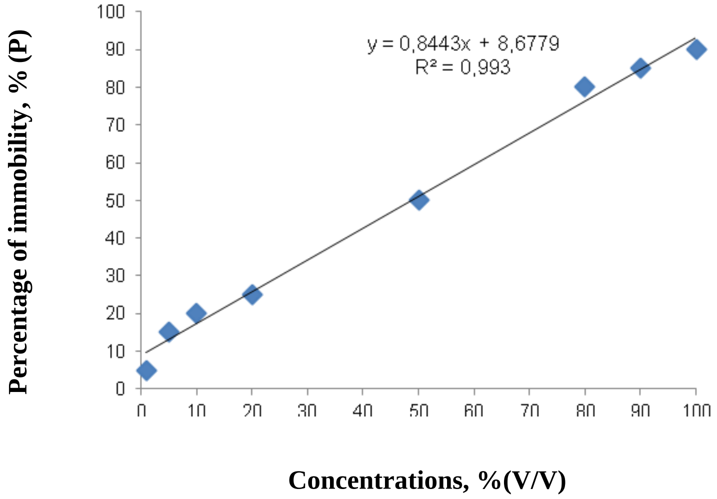

Figure 2. Waste water regression line

In Table 5, T (The number of active *Daphnia manga)* and P (The percentage of immobility *Daphnia magna*) values were obtained for water treated with ozone. The results obtained with the toxicity test showed that the raw textile wastewater was more toxic than the ozonated wastewater.

Table 5. Results of acute toxicity for treated water with ozone.

The concentrations of treated water (%)	**T (The number of active *Daphnia magna*)**	**P (The percentage of immobility *Daphnia magna)***
100	9	55
90	10	50
80	13	35
50	16	20
10	19	5
1	20	0

The relationship between the percentage of immobility and the concentration shown in Figure 3 and LD_{50} value was determined.

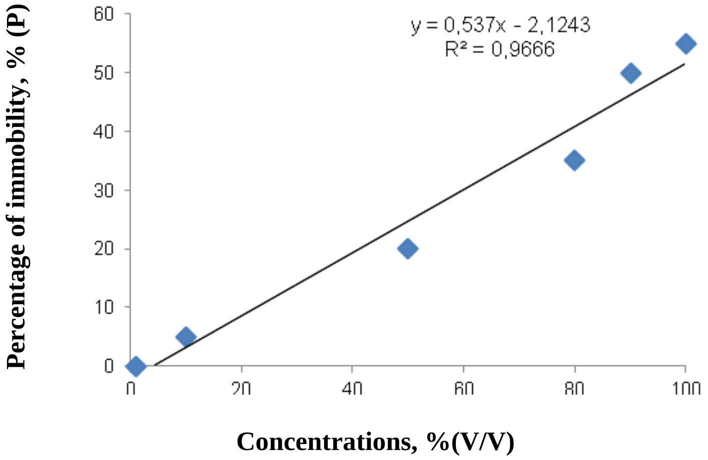

Figure 3. Regression line of treatment water with ozonation

As shown in the Figure 3 LD_{50} value was determined as 90 % for treated water with ozonation.

CONCLUSIONS

This study aimed to evaluate the effects of ozonation on textile plant waste water. Therefore using ozonation that provides a high color and COD removal, also successful results were obtained for the removal of toxicity. Acute toxicity of raw waste water and ozonated samples monitored using *Daphnia magna* were related to the COD and color. High COD and color parameters were determined as a source of toxicity according to the result of the investigations. The optimum pH, ozonation time and dose were found for color absorbances, COD and toxicity removals (pH: 12, 345 mg O_3/15 minute) and in that dose 72 % COD, 98 % color were removed from raw waste water. In toxicity tests, monitoring of toxicity were made at different dilution rates using *Daphnia magna* both in treated water with ozonation and in wastewater. The percentage of immobility (P) for *Daphnia magna* was calculated in each test beaker. Regression lines were created using these values and concentrations (%) for waste water and treated water. The acute toxicity scale LD_{50} (lethal dose) values were determined as 50 % in waste water and 90 % in water treated with ozonation according to the regression lines. It is seen that waste water does not have any toxic effect when diluted by 50 % (or percentage of concentration 50 %), whereas treated water does not have any toxic effect when diluted by 10 % (or percentage of concentrations 90 %). As a result, it can be concluded that ozonation demonstrated a positive contribution to the removal of acute toxicity, color and COD in textile wastewaters.

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