



Research article

Chloride or sulfate? Consequences for ozonation of textile wastewater

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ABSTRACT

Ozonation of chloride-rich textile wastewater is a common pretreatment practice in order to increase biodegradability and therefore meet the discharge limits. This study is the first to investigate ozone-chloride/bromide interactions and formation of hazardous adsorbable organic halogens (AOX) in real textile wastewater. Initially effect of ozonation on chloride-rich real textile wastewater samples were investigated for adsorbable organic halogens (AOX) formation, biodegradability and toxicity. After 15 min of ozonation, maximum levels of chlorine/bromine generation (0.3 mg/l) and AOX formation (399 mg/l) were reached. OUR and SOUR levels both increased by approximately 58%. *Daphnia magna* toxicity peaked at 100% for 10 min ozonated sample. Considering adverse effects of ozonation on chloride-rich textile industry effluents, we proposed replacement of NaCl with Na₂SO₄. Comparative ozonation experiments were carried out for both chloride and sulfate containing synthetic dyeing wastewater samples. Results showed that use of sulfate in reactive dyeing increased biodegradability and decreased acute toxicity. Although sulfate is preferred over chloride for more effective dyeing performance, the switch has been hampered due to sodium sulfate's higher unit cost. However, consideration of indirect costs such as contributions to biodegradability, toxicity, water and salt recovery shall facilitate textile industry's switch from chloride to sulfate.

1. Introduction

Textile is one of the most water intensive industries that also uses large quantities of dyes, salts, surfactants, chemicals, and additives of hazardous nature in the process (Arslan-Alaton et al., 2005; Bisschops and Spanjers, 2003; Meric et al., 2005a; Selcuk et al., 2006). Effluents from textile industry are highly colored due to frequently used alkaline dyes and are characterized by high salinity and ecotoxicity. Aside from dyes, effluents may contain biocides, chlorophenols, carcinogenic amines, free formaldehyde, surfactants, disinfectants, solvents, softeners, heavy metals, and salts (Jadhav et al., 2015). Therefore, textile industry wastewater streams may be resistant to biodegradation and photodegradation (Arslan-Alaton et al., 2004; Asghar et al., 2015), passing through conventional treatment plants almost unaltered in form. Nevertheless, some dyes (disperse, vat, direct and basic) are adsorbed onto activated sludge (Frijters et al., 2006) and therefore can be removed successfully. However, due to high solubility and non-biodegradability, reactive dyes are very difficult to remove using biodegradation as the sole treatment method (Khatri et al., 2015). Advanced oxidation processes (AOPs) are emerging technologies for treatment

and detoxification of hazardous chemical compounds. Ozonation is a commercially available AOP which destructs toxic and/or non-biodegradable compounds, provides oxygenation in wastewater and does not generate sludge (Asghar et al., 2015). Therefore, ozonation not only facilitates decolorization, but also enhances biodegradability (Sarayu et al., 2007; Somensi et al., 2010) and detoxification (Asghar et al., 2015; Selcuk, 2005; Somensi et al., 2010) depending on pH. On the other hand, ozonation and electrochemical advanced oxidation systems are known to oxidize chloride to chlorine/bromine and to form chlorinated by-products (Garcia Segura et al., 2018; Ramjaun et al., 2011; Santhanam et al., 2017; Lan et al., 2017; Jalife-Jacobo et al., 2016). Yuan et al. (2012) investigated dye degradation efficiency in UV/TiO₂ process for a wide range of salinity and pH values. Higher Cl⁻ concentration not only inhibited dye degradation, but also increased concentration of halogenated compounds. Moreover, several toxic chlorinated by-products were identified during dye degradation. It is evident that integration of different treatment processes is necessary if we wish to reuse the textile wastewater (Tong and Elimelech, 2016). Recently, a hybrid approach of advanced oxidation prior to biodegradation is found to be the most environmentally friendly and

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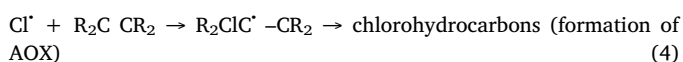
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economically feasible one, among available treatment techniques (Asghar et al., 2015; Imran et al., 2015). Although a multitude of studies on O₃-integrated biological treatment of dyes was reported (Bonakdarpour et al., 2011; Chougule et al., 2014; Eremektar et al., 2007; Liang et al., 2018; S. Meriç et al., 2005b; Popli and Patel, 2015), most of them did not investigate the chloride factor. Chloride cannot be overlooked while studying OH radical-based AOPs, since it is a major ion in textile wastewaters. Especially ozonation and electrochemical oxidation processes are affected due to oxidation of chloride to chlorine/bromine and subsequent formation of halogenated organic/inorganic by-products (Selcuk et al., 2004; Zanoni et al., 2004). Halogenated organic compounds that are adsorbable on activated carbon Adsorbable Organic Halides (AOX) may form by chlorine reacting with many compounds that are present in real textile wastewater (Baycan et al., 2007). Discharge of AOX compounds into environment is a concern due to their carcinogenic, mutagenic, acute, chronic and cytotoxic effects (Turcanu and Bechtold, 2017; Xie et al., 2017, 2018). During ozonation, one of many AOX generation routes is via hydroxyl and chloride radical reactions. Chloride ions may act as OH radical traps (Reactions 1 and 2), forming chloride radicals, which can act upon double bonds of organic compounds (Reactions 3 and 4). Thus chlorinated hydrocarbons are formed and an increase in AOX concentration is observed (Wang et al., 2017).



Thus, chloride ion interferes with decomposition of organic pollutants in oxidation processes. Also, since chlorinated aromatic compounds may be more ecotoxic than the parent dye (Vacchi et al., 2013; Pinheiro et al., 2004), chloride ion may hamper degradation efficiency at the following biological treatment stage (Farooqi and Basheer, 2017; Tomei et al., 2016). In contrast to chloride ions, use of sulfate in dyeing process is expected to produce less AOX due to absence of reactivity with ozone. Also use of sulfate as electrolyte may produce wastewaters that have a potential to increase the overall treatment capacity of anaerobic biological treatment and bioenergy production in microbial fuel cells via sulfur reducing bacteria (Lee et al., 2012; Miran et al., 2018; Zeng et al., 2017).

In this study, our principal aim was to investigate ozone-halogen interaction and to elucidate the formation of AOX in real and synthetic textile wastewater. Since chloride was directly related with a number of issues regarding ozonation of textile wastewater, its replacement with sulfate was proposed. To the best of our knowledge, this is the first study on formation of AOX during ozonation of a real textile wastewater and its effect on biodegradability of real synthetic-cotton textile wastewater. As the pioneering part of this study, use of sulfate instead of chloride was investigated in terms of oxygen uptake rate (OUR) and ecotoxicity to *Vibrio fischeri* and *Daphnia magna*.

2. Material and methods

2.1. Sampling and preparation of synthetic textile sample

Textile wastewater samples were taken from three cotton-synthetic textile factories located in Torbali (Izmir), Gumusler (Denizli) and Esenyurt (Istanbul) industrial zones in Turkey. In those factories, production line included baths of reactive dyeing, rinsing, washing, scoring, and peroxide bleaching. Composite samples (24 h) were collected in spring and winter of 2016 from equalization tanks, which were located at the end of the production line, prior to wastewater treatment plant. Samples were stored at 4 °C to keep chemical composition intact.

Two different synthetic dyeing solutions were prepared using Reactive Black 5 by simulating dyeing procedure of the factories. Also, while one of the solutions contained chloride as the salt ion, the other one had sulfate.

2.2. Ozonation

Ozone (O₃) was generated with a Sander Model 300.5 generator. Pure oxygen with a flow rate of 500 NL/h was fed to the generator which operated at 250 mA current. Generated ozone had a flow rate and concentration of 4.5 g O₃/h and 14 g O₃/m³, respectively. Generated O₃ was fed to a cylindrical glass contact reactor (100 cm length, 10 cm diameter). Ozonation performance was monitored for operation times up to 20 min. Ozone trap with 20 g/l KI was setup at the end of the contact reactor in order to analyze production rate and reacted concentration. At first O₃ gas was directly supplied to O₃ trap filled with KI solution for different time periods and then O₃ analyses were performed according to procedure in method 2350 D (APHA, AWWA, 2012).

2.3. Biodegradability

Oxygen uptake rate analysis is a common technique used in measuring metabolic activities of organisms in aerobic biological wastewater treatment systems. Microorganisms use oxygen as the electron acceptor to oxidize organic matter. High OUR indicates high biological activity. We determined OUR rate through a series of dissolved oxygen (DO) measurements over time. Expression of OUR on the basis of volatile suspended solids data yielded specific oxygen uptake rate (SOUR) as given in Equations (1) and (2). VSS concentrations were obtained from routine daily solids analysis (mg/l).

$$\text{OUR} = \text{mgO}_2/\text{L}/\text{h} \quad (5)$$

$$\text{SOUR} = \frac{\text{Uptake rate} * 1000}{\text{VSS}} \quad (6)$$

2.4. Acute toxicity

In order to estimate the potential toxicity that might arise from ozonation of real textile wastewater, ecotoxicity of effluents prior to and following ozone treatment was assessed by *Daphnia magna* standard acute test (ISO 6341:2012, 2012). Effluents from biological treatment were also tested. Daphnids were grown at 16 h day light - 8 h dark cycles supplying 3000 lux illumination at 20 °C room temperature and were fed *Selenastrum capricornutum* (300,000 cell/ml) and baker's yeast (*Schizosaccharomyces cerevisiae*, 200,000 cell/ml). A minimum 6 mg/l of dissolved oxygen was supplied in vivarium reactors by air pumps and pH of the medium was adjusted to 8.0. Newborn daphnids (> 24 h) were exposed to 50% diluted samples for 24 h. Four replicates were tested in dark at 20 °C, using five daphnids in each vessel with 50 mL sample volume. Toxicity of each sample was assessed by means of immobilization percentage that was determined by dividing total number of immobilized organisms to total number of tested organisms. Bacterial (*Vibrio fischeri*) luminescence inhibition test (Lumistox, Dr. Bruno Lange, Düsseldorf, Germany) was conducted according to ISO guidelines (ISO 6341:2012, 2012) at 15 ± 1 °C and pH 7, with salinity adjustment to 35‰. Exposure time was 30 min. Lyophilized bacterial reagent was obtained from Deutsche Sammlung von Mikroorganismen und Zellkulturen (DSM-7151, Braunschweig, Germany). Each sample dilution (or control) was performed in triplicate. EC₅₀ values for the Lumistox test were calculated by graphical interpolation, in accordance with ISO guidelines (ISO 6341:2012, 2012).

2.5. Analytical methods

Chemical Oxygen Demand (COD), Total Organic Carbon (TOC), 5-day Biological Oxygen Demand (BOD₅), alkalinity, Total Suspended Solids (TSS) and Volatile Suspended Solids (VSS) were analyzed according to Standard Methods (APHA, AWWA, 2012). Hach DR5000 UV-Vis spectrophotometer was used for color and absorbance measurements. Conductivity and pH measurements were done using a HACH HQ40D portable multimeter. TOC measurements were carried out with Shimadzu TOC-CPN TOC analyzer. Chloride and bromide concentrations were measured using ion chromatography. Chlorine generation during ozonation was monitored by standard DPD method. Due to possible bromine interference with chlorine measurement method, from now on we will refer to chlorine measurements as chlorine/bromine measurements. Activated carbon adsorption was used to determine AOX concentration (International code: TS EN ISO 9562:2004).

3. Results and discussion

3.1. Generation of chlorine/bromine during ozone treatment in real wastewater (RW)

Chemical and physical characterization of real and synthetic wastewater samples were given in Table 1. In cotton textile industry salt is used as electrolyte in dyeing process, yielding to chloride concentrations up to 70 g/l. Due to mixing of dyeing effluents with effluents from domestic sources and other processes, average chloride concentration was measured approximately as 1860 mg/l. Chloride concentrations from three factories were observed to be in a wide range (Table 1).

Although there was no direct bromide use in textile processes, it was detected and measured in effluents (Table 1). We believe that domestic wastewater and impurities in bulk NaCl solution that was used in dyeing baths were the major bromide sources in effluents. Furthermore, bulk Cl/Br mass ratios in the range of 1900–8700 have been reported previously (Alcalá and Custodio, 2008; Davis et al., 1998). Although chloride mechanism has been studied extensively, bromide in textile wastewater has not been investigated before. During ozonation, chloride and bromide may react with ozone to produce chlorine and bromine with reaction rate constants of $0.003 \text{ M}^{-1} \text{ s}^{-1}$ and $160 \text{ M}^{-1} \text{ s}^{-1}$, respectively (Table 2). Although concentration of chloride in effluent was significantly higher than bromide concentration (Table 1), O₃-Br reaction rate was 50,000 times faster than that of O₃-Cl (Table 2). Thus bromide level was one of the important factors to control in production of hazardous halogenated by-products in salt rich industrial wastewaters. In textile wastewater, even if chlorine was produced due to high chloride concentration, it rapidly converted to bromine (Table 2).

Hypochlorous/hypobromous acids are dominant reactive species with which majority of organic compounds yield to halogenated products. Real textile wastewater contains many different organic groups

Table 1
Characterization of real (RW) and synthetic textile wastewaters (SW).

Parameter	RW ^a		SW	
			Chloride	Sulfate
BOD ₅	mg/l	128 ± 12	102	95
COD	mg/l	505 ± 67	185	180
TOC	mg/l	527 ± 112	39	41
pH	–	8.1 ± 1	8.0	8.0
Bromide	mg/l	0.68–1.20	–	–
Chloride	mg/l	800–5500	5800	–
Sulfate	mg/l	–	–	6435
Color	Pt-Co	387 ± 204	1352	1413

^a Average values for composite samples taken from three factories except for chlorine and bromide concentration values. Those were reported as range of values.

Table 2
Ozone-chloride, ozone-bromide and chlorine-bromide reactions with corresponding rate constants (Yang and Pignatello, 2017).

Ozone-chloride reactions	Rate constants ($\text{M}^{-1} \text{ s}^{-1}$)
$\text{O}_3 + \text{Cl}^- \rightarrow \text{OCl}_2 + \text{O}_2$	0.003
$\text{O}_3 + \text{OCl}^- \rightarrow 2\text{O}_2 + \text{Cl}^-$	110
$\text{O}_3 + \text{OCl}^- \rightarrow \text{O}_2 + \text{ClO}_2^-$	30
$\text{O}_3 + \text{ClO}_2^- \rightarrow \text{ClO}_3^- + \text{O}_2$	4.10^6
$\text{HOCl} \rightarrow \text{OCl}^- + \text{H}^+$	7.54
Ozone-bromide reactions	Rate constants ($\text{M}^{-1} \text{ s}^{-1}$)
$\text{O}_3 + \text{Br}^- \rightarrow \text{OBr}_2 + \text{O}_2$	160
$\text{O}_3 + \text{OBr}^- \rightarrow 2\text{O}_2 + \text{Br}^-$	330
$\text{O}_3 + \text{OBr}^- \rightarrow \text{O}_2 + \text{BrO}_2^-$	100
$\text{O}_3 + \text{HOBr} \rightarrow \text{O}_2 + \text{BrO}_2^- + \text{H}^+$	< 0.013
$\text{HOBr} \rightarrow \text{OBr}^- + \text{H}^+$	8.8
Chlorine-bromide reaction	Rate constant ($\text{M}^{-1} \text{ s}^{-1}$)
$\text{HOCl} + \text{Br}^- \rightarrow \text{HOBr} + \text{Cl}^-$	2.95×10^3

such as saturated and unsaturated chromophores (Morali et al., 2016; Waring et al., 1990). Azo and anthraquinone are the most important chromophore groups since they are widely used (Farooqi and Basheer, 2017). Although hypochlorous acid reactions with unsaturated bonds are generally slow or negligible, in some cases, chromophore groups in dye molecules may have high chlorine reactivity (Zhang et al., 2009). Real textile wastewater ozonation experiments revealed that with a linear ozone consumption, approximately 1180 mg/l O₃ reacted for the duration of experiment. Chlorine/bromine generation of 0.1 mg/l was observed in 10 min, increasing up to 0.3 mg/l (15 min) and then it started to decrease, reaching a plateau at 30 min (Fig. 1). Results showed that formation and quenching/destruction of chlorine/bromine species occurred simultaneously.

3.2. Formation of AOX during ozonation of real textile wastewater (RW)

In textile industry, although chlorine was replaced by hydrogen peroxide for bleaching, it was still used in scouring solution for dyeing machines. Thus AOX concentration in effluent was mostly attributed to the final cleaning step of dyeing process. AOX concentration was found to be 3.4 mg/l in raw textile wastewater (Fig. 1). During ozonation, AOX concentration reached a maximum of 399 mg/l in 15 min. Following a similar trend as free chlorine/bromine concentration did, AOX concentration decreased sharply after 15 min, becoming almost non-detectable at 45 min. UV-Vis spectra of raw textile wastewater and its ozonated samples were given in Fig. 2. Results for 15 min, 20 min and 25 min ozonated samples converged throughout the spectrum. Thus we concluded that maximum AOX formation and efficient color

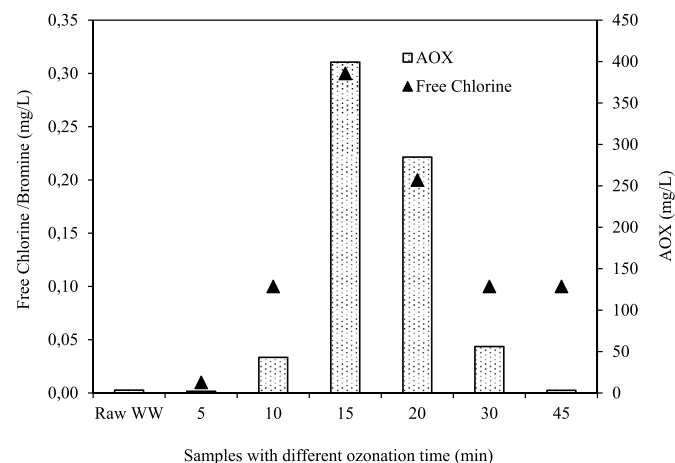


Fig. 1. Formation of AOX and free chlorine/bromine during ozonation of real wastewater.

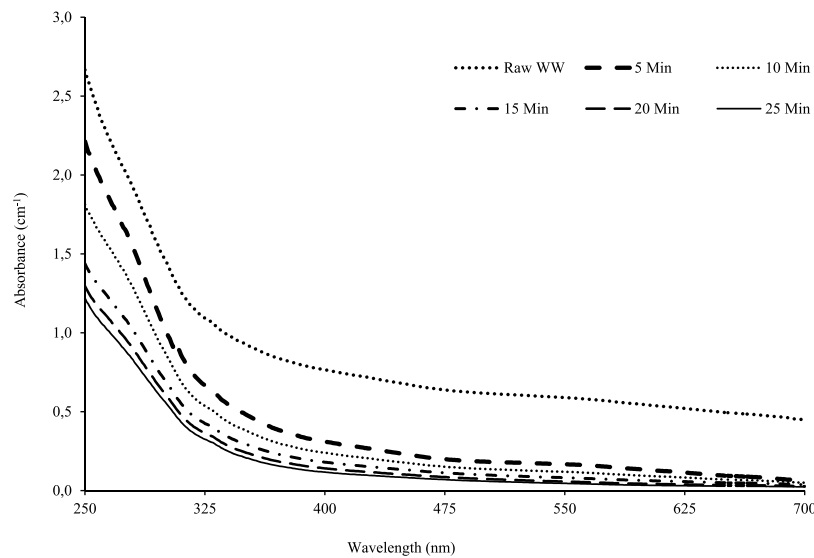


Fig. 2. Color degradation in real textile wastewater due to varying ozonation periods.

degradation occurred in the same ozonation time period. Results also reflected the fact that ozonation of Cl⁻-rich wastewater matrices might not be preferable due to formation of toxic by-products. Furthermore, Grguric et al. (1994) investigated the effect of bromide impurity on formation of brominated by-products in ozonation process. They found that even in an artificial seawater system, where bromide ion was not present, trace bromide impurity was the dominant oxidized species during ozonation. Furthermore, Deudomwongsa et al. (2017) investigated the effect of chloride ions on halogenated by-products and concluded that chloride addition not only induced changes in speciation of halogenated by-products, but also increased halogenated by-product formation potentials by 2-fold. Thus, formation of high concentrations of AOX in ozonated textile wastewater may be also attributable to bromide impurity in used salt.

3.3. Effect of ozonation on the biodegradability and toxicity of real textile wastewater (RW)

As measures of biodegradability we used OUR, SOUR and BOD₅/COD ratio parameters. In microbial processes, stoichiometry and environmental conditions lead the consumption of electron donor and electron acceptor molecules. OUR is the amount of oxygen required to decompose a given electron donor, namely organic matter, at steady state in a given period of time. The change of TOC which required for biological systems, according to pH and temperature during ozonation can be seen Fig. 3.

Specific oxygen uptake rate is obtained by dividing OUR by sludge concentration, establishing the microbial activity connection (Yoon, 2015). If there were any toxic compounds present to deteriorate microbial activity, OUR and SOUR results would decrease. OUR was calculated from dissolved oxygen mass balance in the reactor.

$$OUR = K_L a (C_s - C_{end}) - \frac{dC}{dt} \tag{7}$$

where C, C_s, and C_{end} are dissolved oxygen concentrations (mg/l) of the sample at saturation and during endogenous respiration respectively (Contreras et al., 2008). K_La is Oxygen transfer coefficient. Oxygen used by suspended microorganisms in wastewater depends on gas/bulk liquid/cell membrane transfer rates and microbial growth rates (Garcia-Ochoa and Gomez, 2009). In this study, we investigated substrate utilization rate of aerobic microbial community that was exposed to ozonated real wastewater samples by measuring oxygen uptake. OUR and SOUR results were in agreement to point out that the maximum

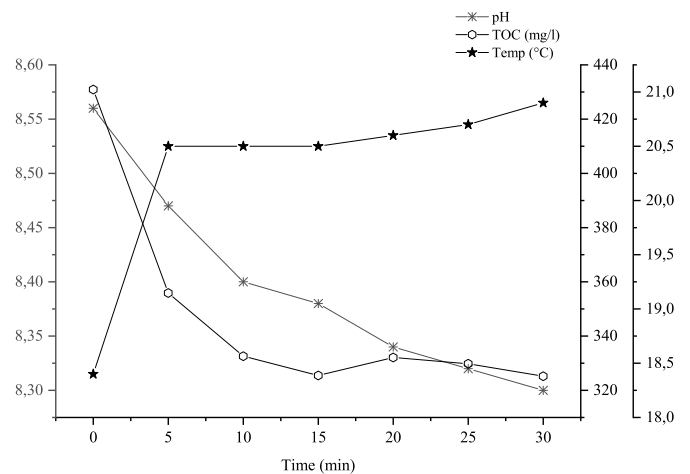


Fig. 3. Change of TOC during ozonation according to pH and temperature.

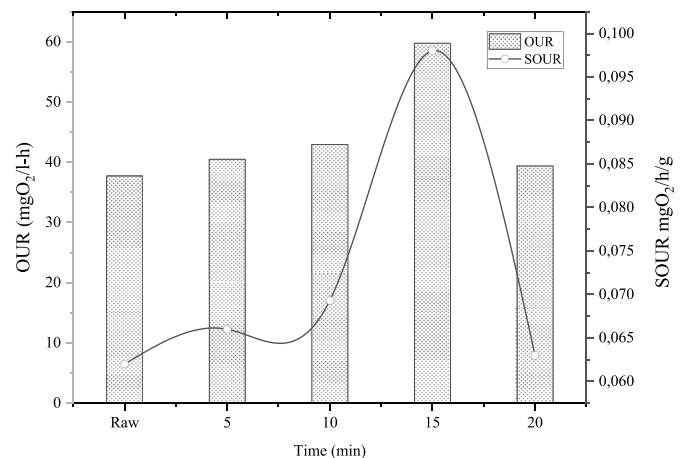


Fig. 4. OUR and SOUR levels at textile wastewater depending on time.

biodegradability was achieved at 15 min ozonation (Fig. 4). While OUR and SOUR results for 5 min and 10 min ozonated samples were following an increasing trend when compared to raw wastewater, 20 min measurement gave a similar result. When maximum AOX formation

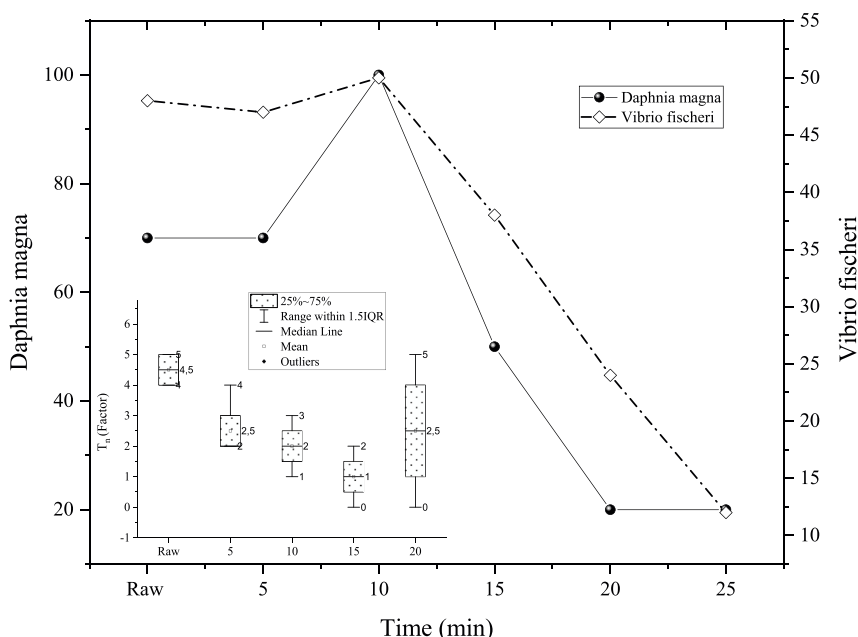


Fig. 5. Acute toxicity levels measured using *Daphnia magna* and *Vibrio fischeri* (Microtox) in real wastewater samples with different ozonation time. Initial chloride concentration was 5500 mg/l for *Daphnia magna* experiments.

was observed (Fig. 1), biodegradability of ozonated wastewater was also at its highest (at 15th min) (Fig. 4).

Ozonation creates a very dynamic environment, where radicals and AOX species were formed and consumed simultaneously. In a mixed microbial consortium, like the one that was used for OUR and SOUR experiments, microorganisms were able to harvest the maximum energy from 15 min ozonated wastewater sample. The decrease in biodegradability for 20 min ozonated sample might be due to formation of less biodegradable by-products. Acute toxicity of raw wastewater to *Daphnia magna* was observed as 70% immobilization (Fig. 5). Five minutes of ozonation did not make a difference in the toxicity level of real textile effluent. However, prolonging ozonation time to 10 min resulted in 100% immobilization. This could be explained by increasing concentration of by-products with ozonation time (Imran et al., 2015; Meriç et al., 2005a). Our findings were in accordance with the study by Fang et al. (2016), where researchers reported a relation between AOX formation and aquatic toxicity during 2,4,6-trichlorophenol degradation in a Co(II)/peroxymonosulfate/Cl⁻ system. Xie et al. (2017) also reported a relation between AOX levels and genotoxicity of AOX-containing pharmaceutical wastewater. By increasing ozonation time to 15 min, toxicity to *D. magna* decreased to 50%, and continued to decrease till 20% by 20 min of ozonation. These results were consistent with AOX profile shown in Fig. 1. Toxicity increased in parallel to chlorine/bromine measurements, however maximum toxicity was observed for 10 min ozonation sample which was caused by dual effect of chloride and AOX on microorganisms. In Microtox experiments (Fig. 5, *Vibrio fischeri*), toxicity results for raw effluent, 5 min ozonated sample and 10 min ozonated sample were similar. Toxicity level increased for prolonged ozonation times in real textile wastewater samples, indicating a similarity with *Daphnia magna* results and with the formation of AOX (Fig. 1).

The difference in toxicity response of two organisms could be explained by their natural habitat. *Daphnia magna* is known to live in freshwater ecosystems, whereas *Vibrio fischeri* is used to salty media as it is a natural inhabitant of seawater. Dual effect of AOX concentration generated in 10 min of ozonation and remaining salt concentration was enough to immobilize whole *Daphnia magna* community, but it affected only half of *Vibrio fischeri* community. Once salt concentration in effluent was spent in formation of AOX, we observed a decrease in

toxicity response of *D. magna*. Our results supported previous findings reported by Somensi et al. (2010), who observed formation of various organic by-products during ozonation of real textile wastewater. Ozonation was reported to be a very efficient oxidation method in improving the biodegradability of textile wastewater, which can thereafter be treated by biological processes (Chougule et al., 2014; Ulucan-Altuntas and Ilhan, 2018). However, in agreement with previous works (Magdeburg et al., 2014; Sarayu et al., 2007; Somensi et al., 2010), our results indicated that there was a risk of toxicity increase depending on ozonation period.

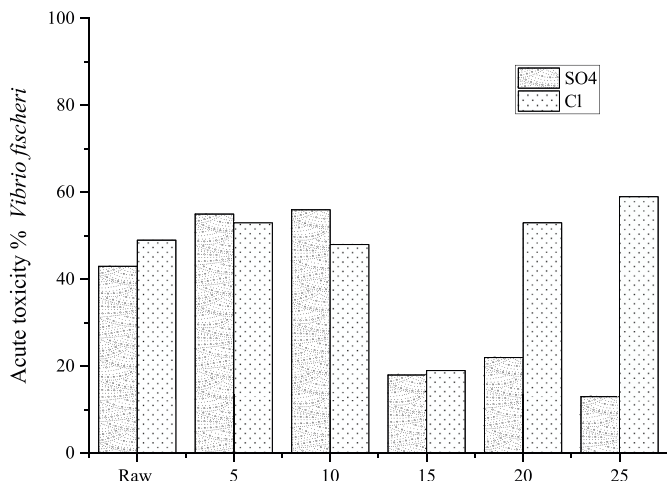
3.4. Comparison studies with synthetic wastewater (SW) containing sulfate salt

During dyeing process, negatively charged ions of dye and cellulose repel each other in the absence of salt, yielding to poor exhaustion. Salt neutralizes the negative charge of cellulose, increases affinity of dye towards cellulosic substrate, and thus facilitates exhaustion. Since reactive dyestuffs have lower affinity, more inorganic salt is required in order to accelerate absorption. Considering effectiveness and cost, both Glauber's salt (Na₂SO₄) and common salt (NaCl) are used in dyeing. While they are basically the same -sodium is the active cation in both-type of anion is important in terms of subsequent reuse of wastewater. Use of sulfate instead of chloride may decrease formation of halogenated by-products and thus decrease toxicity levels in textile effluents. Chloride and its bromide impurity may affect formation and nature of ozonated organic by-products and thus decrease the detoxification efficiency of ozonation process (Yuan et al., 2012). Additionally, presence of sulfate in textile wastewater may form peroxodisulfate (S₂O₈²⁻) ion in (photo)electrochemical advanced oxidation processes. Peroxodisulfate may further oxidize hazardous dyes to either complete mineralization (CO₂) or nonhazardous inorganic ions (Espinoza et al., 2016). Furthermore, communication with textile industry representatives revealed that use of Na₂SO₄ enables a much more efficient dyeing process. However, its use is hampered by its cost, which is higher than cost of NaCl. In order to investigate the effect of salt type on by-product formation and toxicity, two reactive dye solutions were prepared with NaCl and Na₂SO₄, separately. Concentrations of chloride (5800 mg/l) and sulfate (6435 mg/l) were adjusted to simulate

Table 3

Effect of ozonation on biodegradability, oxygen consumption rate and toxicity of chloride and sulfate containing synthetic wastewater.

Sample	Cl ⁻ containing				SO ₄ ²⁻ containing			
	OUR (mg/l)	SOUR (mg/g)	BOD ₅ /COD	Toxicity (%)	OUR (mg/l)	SOUR (mg/g)	BOD ₅ /COD	Toxicity (%)
SW	2,79	0,0035	0,15	56	4,4	0,0053	0,25	43
O ₃ 15 (min)	2,74	0,0033	0,12	36	6,78	0,0086	0,44	18

**Fig. 6.** Acute toxicity on *Vibrio fischeri* in synthetic samples on the presence of chloride and sulfate salts.

electrical conductivity levels required for efficient dyeing. Chloride and sulfate containing solutions were ozonated until color degradation reached a steady state level. Chlorinated compounds might absorb light at UV range of 250–350 nm (Kovács et al., 2016), thus color degradation was followed in both experiments. While biodegradability of SO₄²⁻-SW was higher than that of Cl⁻-SW, 15 min ozonation has increased the difference in favor of SO₄²⁻-SW (Table 3). In Cl⁻-SW, changes in OUR and SOUR levels of pre- and post-ozonation samples were found to be insignificant (< 5%) while BOD₅/COD ratio decreased around 20%. In contrast, after ozonation, BOD₅/COD ratio, OUR and SOUR levels in SO₄²⁻-SW increased from 0.25 mg/mg, 0.44 mg/l and 0.053 mg/l to 0.44 mg/mg, 6.78 mg/l and 0.086 mg/l, respectively (Table 3). Toxicity levels decreased with ozonation for both samples, 25% for SO₄²⁻-SW and 20% for Cl⁻-SW.

Acute toxicity results for sulfate and chloride containing synthetic samples were given in Fig. 6. Comparison of samples revealed that 5 min and 10 min ozonated SO₄²⁻-SW samples were more toxic than their chloride containing counterparts. After 10 min the trend was reversed and sulfate containing samples became less toxic. Especially at 15 min ozonation, which improved biodegradation significantly, toxicity of SO₄²⁻-SW was only 18%. In order to compare ozonation and chlorination, another synthetic dye solution was prepared without adding any salt and it was chlorinated until chlorine residual in solution was 0.3 mg/l. Chlorination of dye solution inhibited biodegradability. Initial 0.25 BOD₅/COD ratio, 4.4 mg/l OUR and 0.053 mg/l SOUR decreased to 0.055 BOD₅/COD ratio, 0.97 mg/l OUR and 0.013 mg/l SOUR, respectively.

4. Conclusions

Textile industry generally uses an advanced oxidation process to pretreat its effluents prior to biological treatment in order to increase biodegradability and subsequently meet the discharge limits. Therefore, ozonation of chloride-rich textile wastewater is a common practice. In this study, we showed that ozonation increased toxicity due to AOX formation and chlorine/bromine generation. Consequently, the biological treatment process that followed ozonation would be expected to

perform poorly and there would be refractory organic compounds remaining in the treated effluent. Since recovery and recycling of water was a requirement for textile industry, we proposed replacing chloride with sulfate. In this study, we showed that switching from chloride to sulfate decreased acute toxicity and improved biodegradability. Although sodium sulfate has a higher unit cost than sodium chloride, indirect contributions such as increased biodegradability, decreased toxicity, facilitation of water and salt recovery shall be considered. In conclusion, we demonstrated the potential benefits that textile industry may gain from switching to sulfate. Our next step will be to investigate treatment of sulfate-rich textile wastewater and its effects on closing the water cycle.

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