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Treatment of textile dye bath wastewater with ozone, persulfate and peroxymonosulphate oxidation

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ABSTRACT

In this study, the treatment of wastewater of two different reactive dye bath wastewater (WW1, WW2) belonging to a yarn dyeing textile industry was evaluated by ozone, heat-activated persulfate (PS) and heat-activated peroxymonosulfate (PMS) oxidation methods. WW1 and WW2 contains azo group dyes and BOD_5 values are 245 and 105 mg/L, Total Organic Carbon (TOC) values are 793 and 3016 mg/L respectively. TOC and color removal and BOD_5/TOC ratio were investigated in samples taken at specific time intervals (15, 30, 45, 60, 90 and 120 min). For WW1, the TOC and color removal rates for heat-activated PS oxidation were 19% and 100%, respectively, and these removal rates were higher than the oxidation results for ozonation (15% and 76%) and heat-activated PMS (16% and 99%). Although the ozone dose applied to WW1 was about 3 times that of the ozone dose applied to WW2, the color removal rate in WW2 (94%) was higher than WW1 (76%) and the TOC removal rates were almost the same. In the result of oxidation studies,no significant increase in BOD value was observed for both wastewater. However, an increase in BOD_5/TOC was achieved by decreasing the TOC value in heat-activated PS oxidation for WW1.

Keywords: Textile wastewater; Ozone; Persulfate; Peroxymonosulfate; TOC

1. **Introduction**

The textile dyeing process consumes huge amount of water and textile waste waters have high pollution potential. The waste water which is released as a result of the dyeing process which takes place in the textile industry, especially during textile finishing, contains a high amount of dyestuff and therefore high color, high organic materials and surface active substances. Treatment of these waste waters by conventional biological treatment methods is difficult due to complex structure and resistance to biological treatment. The purification processes, such as adsorption and flocculation, usually causes a secondary waste stream in the form of a hazardous waste that needs to be disposed of. Alternative methods including electrochemical treatment, membrane processes and different advanced oxidation methods have also been developed for the treatment of wastewater of the textile industry [1,2].

Advanced oxidation processes (AOPs) are treatment technologies based on the production of free radicals such as hydroxyl radicals ($HO^•$) and sulfate radicals ($SO_4^{•}$), which have very high oxidation potential. These radicals usually give rapid and non-selectively reactions with organic pollutants [3,4]. The pollutant is either converted into intermediate and/or end products which are less toxic and biodegradable with partial oxidation, or mineralization is achieved. Therefore, in the elimination and detoxification of toxic and refractory industrial pollutants, it is becoming important to apply AOPs based on the oxidative treatment of organic substances.

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Ozone oxidation has been used in numerous studies on color removal, increasing of biodegradable materials and toxicity removal in textile wastewater [5-7]. Ozonation is used in the oxidation of organic materials and ozone is rapidly decompose to produce hydroxyl radicals and other radical species at basic pH [8].

In recent years, as an alternative to hydroxyl radicals, the number of investigations on AOP based on the reaction of sulfate radicals ($SO_4^{\bullet}$) with a high oxidation potential (2.5–3.1 V) [4] in the removal of contaminants has been rapidly increased [9–23]. Persulfate (PS) and peroxymonosulfate (PMS) oxidants are used for the production of $SO_4^{\bullet}$ and these oxidants are commonly activated by temperature, UV and transition metal ions.

In the case of thermal activation [Eq. (1)], persulfate formation can be slowly initiated even at mild temperatures (30°C). However, at higher temperatures (i.e. 90°C) the activation energy of the "hot persulfate processes" is only 29 kJ/mol in neutral pH solutions. It has already been demonstrated that alkaline conditions can induce the mechanism of $SO_4^{\bullet}$ inter-conversion to $HO^{\cdot}$[Eq. (2)] in the persulfate activation system. In addition, $SO_4^{\bullet}$ may react with water at all pHs to produce $HO^{\bullet}$, in accordance with Eq. (3) [24].

$$S_2O_8^{2-} + \text{heat} \rightarrow SO_4^{\bullet}(30\ ^{\circ}\text{C} < T < 99\ ^{\circ}\text{C}) \qquad (1)$$

$$\text{Alkaline pHs}: SO_4^{\bullet} + OH^{-} \rightarrow SO_4^{2-} + HO^{\cdot} k = 6.5 \pm 1 \times 10^{7}\ M^{-1}\,s^{-1} \qquad (2)$$

$$\text{All pHs}: SO_4^{\bullet} + H_2O \rightarrow SO_4^{2-} + HO^{\bullet} + H^{+} k_{[H2O]} < 2 \times 10^{-3}\ s^{-1} \qquad (3)$$

As a result of the activation of PS and PMS, $SO_4^{\bullet}$ is a powerful oxidant and can oxidize most organic substances in wastewater. Huang et al. [25] studied the decomposition of volatile organic compounds using PS and found that most organic materials were oxidized. Anipsitakis et al. [17] have successfully used PMS oxidant to oxidize chlorophenols, polyaromatic hydrocarbons (PAHs) and pesticides.

The using of $SO_4^{\bullet}$ in oxidation processes has more advantages than $HO^{\bullet}$. $HO^{\bullet}$ is less selective than $SO_4^{\bullet}$ and this leads to a reduction in the removal rate of the target pollutant. $SO_4^{\bullet}$ has a longer half-life than $HO^{\bullet}$. In other words, $SO_4^{\bullet}$ participates only in electron transfer reactions, while $HO^{\bullet}$ is involved in the hydrogen-atom separation reaction and electron transfer reactions at the same time, which causes the $SO_4^{\bullet}$ to have a longer half-life than the $HO^{\bullet}$ [16,17,26]. The rate constants for the reaction of $SO_4^{\bullet}$ and $HO^{\bullet}$ with the organic substances are approximately the same [26]. In addition, $SO_4^{\bullet}$ reacts with lower rate constants with some inorganic materials called radical scavengers which cause radical consumption [27]. $SO_4^{\bullet}$-based AOPs is used for the rapid and efficient treatment of surface water and industrial wastewater in recent years, with less operating problems, smaller reactor volume, shorter contact time, higher organic material removal rate and less sludge than other treatment methods [28]. The most important disadvantage of the $SO_4^{\bullet}$-based AOPs is the additional processes required for the activation of PS and PMS oxidants.

In this study ozone, heat-activated PS and heat-activated PMS processes were applied to treat two different first dye bath wastewater from a textile industry, in terms of TOC and color removal and BOD_5/TOC ratio. The novelty of the study is that the waste waters used in the study were first dye bath waste waters which has average temperature of 80ºC so no additional processing was required for thermal activation.

2. **Materials and methods**

2.1. Wastewater origin and characteristics

In this study, two different kinds of first dye bath waste waters from a textile industry which is dyeing cotton yarn using reactive dye were studied. The wastewater characteristics were determined by analyzing TOC, BOD_5, color, pH, conductivity, alkalinity and chloride parameters. The dyeing process consists of pre-treatment, dyeing, washing and softening phases (Fig. 1). The dyestuffs used are azo group dyes.

Reactive dyeing process to cotton yarn is applied at high pH (10–11) and high temperature, and the temperature of the wastewater is around 80–90°C. The characterization of wastewater samples (WW1 and WW2) is given in Table 1. As can be seen from Table 1, the TOC values for WW2 are higher than WW1 and the BOD_5 values for both waste waters are lower.

The color parameter for WW1 was found to be higher than that of WW2. This is due to the fact that WW1 is originated from black dye bath. The fact that the ratio of BOD_5/TOC obtained for WW2 is rather low suggests that the biological treat ability of the wastewater is weak. The BOD_5 value of raw wastewater for WW2 is low as 105 mg/L, while the TOC is a high value of 3016 mg/L.

2.2. Materials

Potassium persulfate (PS, $K_2S_2O_8$, >99.5%), potassium peroxymonosulfate (PMS, $2KHSO_5 \cdot 3KHSO_4 \cdot 3K_2SO_4$ available as Oxone®, ≥99.5%) and potassium iodide (KI, 99.0%) were purchased from Sigma-Aldrich, (USA). All other reagents were of at least analytical grade and obtained from Merck (Germany) or Sigma-Aldrich (USA).

2.3. Ozone oxidation

An ozone generator manufactured by Degremont with production rate of 2 g O_3 per hour was used to supply ozone. Ozonation system was operated in semi-continuous type, i.e., continuous with respect to the gas flow and batch with respect to solution at room temperature (25°C). 3 liter wastewater was filled into 4 L stainless steel reactor. Samples were taken at 15, 30, 45, 60, 90, 120 min for WW1 and WW2. Excess ozone gas (off gas) passed out through the top of the reactor into a gas-washing bottle containing KI solution. The concentration of ozone in the effluent gas was measured by taking samples from the KI trap during experimental run and titrating the iodine in the samples with $Na_2S_2O_3$ according to Standard Methods [29]. Two gas-washing bottles containing KI solution was connected to the system in parallel with reactor to determine the quantity of ozone applied to the reactor.

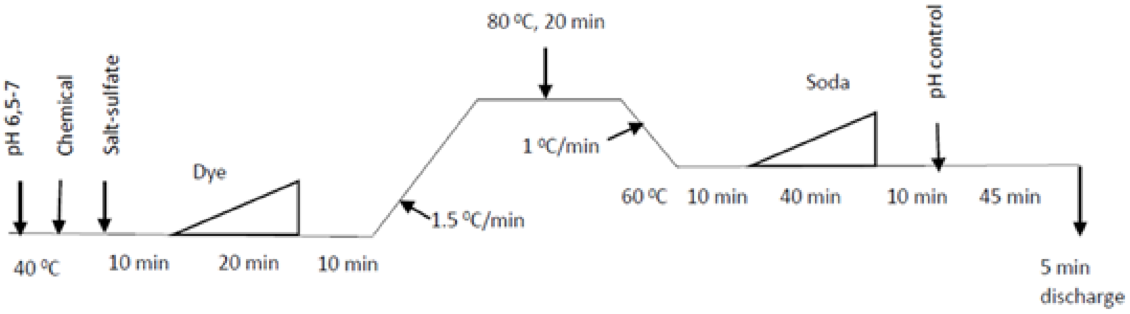

Fig. 1. Dyeing process.

Table 1
Characterization of wastewater

Parameter	TOC, mg/L	BOD_5, mg/L	Color				pH	Conductivity, mS/cm	Alkalinity, mg $CaCO_3$/L	Chloride, mg/L
			RES, m^{-1}	436 nm	525 nm	620 nm				
WW1	793	245	3121.5	8.724	11.314	11.177	9.65	178	12916	91000
WW2	3016	105	220.3	0.399	1.263	0.541	11.00	61.9	40166	2400

2.4. Advanced oxidation with PS and PMS

Heat-activated PS and heat-activated PMS oxidation experiments were performed for 120 min in 1 L-capacity glass beakers. A magnetic stirrer equipped with an electronic contact thermometer (Yellow line MST Basic, IKA-WERKE) was used to ensure constant temperature and perfect mixing at a rate of 300 rpm during all experiments. Oxidation experiments were conducted at a fixed oxidant concentration; 30 mM for PS and 30 mM for PMS. The selection of the studied oxidant concentrations was based on preliminary experiments and former related works that have been reported in the literature [24,28]. In order to determine the treatment performance of heat-activated PS and PMS oxidation, samples were withdrawn at regular time intervals (15, 30, 45 60, 90 and 120 min) and immediately placed in an ice bath (4°C) to quench the reaction. Sample aliquots were analyzed for TOC and color.

Control experiments were also conducted to observe treatment performance of the investigated oxidants at room temperature (25°C) and to understand the individual contribution of oxidants to color and TOC removal.

2.5. Analytical methods

Samples taken during wastewater characterization and oxidation experiments; TOC, BOD_5, pH, conductivity, alkalinity and chloride analyzes were performed according to Standard Methods [29]. TOC analyzes were carried out using a Shimadzu brand V_{PCN} model carbon analyzer. During the experiments, WTW pH 315 i brand pH meter was used for pH measurements. BOD measurements were performed at 20 ± 2°C and as vaccine; activated sludge culture of the plant where the wastewater sample was taken. The evaluation of color removal was made by determining the sample absorbances at the wavelengths of 436, 525 and 620 nm, which were selected in accordance with the European Norm EN ISO 7887:2011 [30] by using a Perkin Elmer brand spectrophotometer.

3. **Results and discussion**

3.1. Ozone oxidation

The experimental results of ozonation process for WW1 and WW2 are given in Table 2 and Fig. 2.

Although ozone doses applied to WW2 were three times less than WW1, TOC removal rates were obtained approximately the same. This can be explained by the fact that the two wastewater have different characteristics. Although the amount of ozone given to wastewater is about as much as oxidizing all organic carbon, the amount of ozone held on the KI traps is big. TOC and color removal rates were determined as 15% and 85% for WW1 and 13% and 94% for WW2, respectively, at 120 min. According to the experimental results, the color removal rate is much higher than TOC removal rate. Similar results were obtained in the literature [31–33]. The amount of ozone applied is enough to disrupt the structure of the chromophore groups of the dyes, but not enough to mineralize organic carbon content. The salts used in dyeing processes affect the ozonation in physically and chemically. Physical changes occur in ozone solubility and ozone mass transfer. However, a more important effect of inorganic salts on the ozone oxidation process is caused by chemical reactions [34]. Halides (ie. Cl^-) and alkalinity may reduce the process efficiency by reacting with ozone or free radicals such as $HO^{\bullet}$ and $SO_4^{\bullet}$ and daughter radicals (eg. CO_3^{-} and $Cl^{\cdot}$) may generated from these reactions. The daughter radicals might act as secondary oxidants, although being more selective than the mother radicals [35]. As can be seen from Table 1, both waste waters have high alkalinity and the type of alkaline used in the dyeing process is important in the ozonation. Sodium carbonate (Na_2CO_3) and caustic (NaOH) are used as alkali source in

Table 2
Experimental results of ozonation

Time (min)	Applied ozone (mg)	Off gas* (mg)	Utilized ozone (mg)	TOC (mg/L)	BOD_5 (mg/L)	BOD/ TOC	436 nm	525 nm	620 nm	RES (m^{-1})
WW1										
0				793	245	0.3	8.724	11.314	11.177	3121.5
15	500	1632	2368	775			8.196	8.890	7.938	2502.4
30	1000			778			7.888	7.547	5.710	2114.5
45	1500			742			6.808	5.39	2.923	1699.3
60	2000			716	257	0.36	5.577	4.019	1.471	1106.7
90	3000			684			4.375	2.661	0.446	748.2
120	4000			676	257	0.38	3.043	1.547	0.001	459.1
WW2										
0				3016	105	0.034	0.399	1.263	0.541	220.3
15	500	1220	2780	2958			0.363	0.741	0.328	143.2
30	1000			2898			0.328	0.272	0.139	73.9
45	1500			2849			0.229	0.114	0.044	38.7
60	2000			2794	115	0.044	0.196	0.081	0.019	29.6
90	3000			2706			0.157	0.046	0.001	20.4
120	4000			2639	115	0.047	0.101	0.027	0.001	12.9

* The amount of ozone in KI traps after 120 min. ozonation

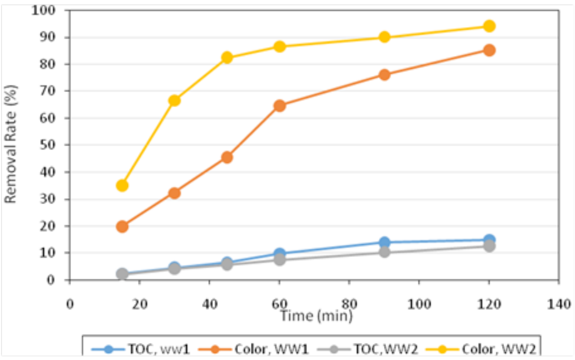

Fig. 2. TOC and color removal rate after ozonation.

textile dyeing. Arslan and Balcıoğlu [36] stated that bicarbonate (HCO_3^-) and carbonate ions (CO_3^{2-}) in the wastewater react with $HO^·$ in case of using Na_2CO_3 in textile industry. The resulting reactions are as follows:

$$HO^· + CO_3^{2-} \rightarrow OH^- + CO_3^{-·} \quad (4)$$

$$HCO_3^- + HO^· \rightarrow HCO_3^- + OH^- \quad (5)$$

Carbonate and bicarbonate ions, known as radical scavengers and they slow down the chain reactions in the ozonation process. This by-products (carbonate and bicarbonate radicals) formed after the reaction of $HO^·$ with these ions do not react with ozone. Chloride ions, which is also a very common salt used in textile dyeing processes, can react with both ozone and $HO^·$[Eqs. (6)–(11)] and due to the direct reaction between ozone and Cl^-, the half-life time of ozone might reduced by a factor of 2 in the presence of 0.1 M NaCl [34,35,37].

$$O_3 + Cl^- \rightarrow O_2 + OCl^- \quad (6)$$

$$O_3 + OCl^- \rightarrow 2O_2 + Cl^- \quad (7)$$

$$HO^• + Cl^- \rightarrow ClOH^{•-} \quad (8)$$

$$ClOH^{•-} + H^+ \rightarrow Cl^• + H_2O \quad (9)$$

$$Cl^• + Cl^- \rightarrow Cl_2^{•-} \quad (10)$$

$$ClOH^{•-} + Cl^- \rightarrow Cl_2^{•-} + OH^- \quad (11)$$

From Table 2 it can be seen that only poor TOC removals were obtained for ozonation for WW1 and WW2 samples. The obtained results might be associated with the scavenging of the radicals with carbonate and bicarbonate ions due to the high alkalinity of both waste waters (12,916 mg $CaCO_3$/L for WW1 and 40,166 mg $CaCO_3$/L for WW2) as well as high chloride content of the samples.

In the study,the BOD_5 value of raw and ozonized wastewater was measured at 60 and 120 min and the effect of ozonation on the BOD_5/TOC ratio was evaluated. The BOD_5 and BOD_5/TOC values obtained by ozonation are given in Table 2. Azo group dyes are resistant to biodegradation due to their nitrogen bonds [38–41]. Ozone cleaves the conjugated bonds of azo dyes and converts high molecular weight compounds of the dye into lower molecules of organic acids leading to color removal and enhancement in

Table 3
PS oxidation results

Time (min)	TOC (mg/L)	BOD_5 (mg/L)	BOD_5/TOC	436 nm	525 nm	620 nm	RES (m^{-1})
WW1							
0	793	245	0.30	8.724	11.314	11.177	3121.5
15	723			0.111	0.022	0.001	13.4
30	690			0.065	0.001	0.001	6.7
45	680			0.050	0.001	0.001	5.7
60	672	306	0.45	0.015	0.001	0.001	1.7
90	659			0.001	0.001	0.001	0.3
120	642	310	0.48	0.001	0.001	0.001	0.3
Control	736	285	0.39	0.711	0.536	0.153	140.0
WW2							
0	3016	105	0.034	0.399	1.263	0.541	220.3
15	2972			0.190	0.043	0.001	23.4
30	2944			0.131	0.015	0.001	14.7
45	2898			0.124	0.014	0.001	13.9
60	2866	112	0.039	0.116	0.013	0.001	13.0
90	2803			0.108	0.012	0.001	12.1
120	2717	112	0.041	0.097	0.009	0.001	10.7
Control	2987	110	0.037	0.362	0.306	0.079	74.7

biodegradability [42]. However, no significant increase in BOD_5 values was achieved for both waste waters by ozonation. As a result of decrease in the TOC parameter, the BOD_5/TOC ratio increased from 0.30 to 0.38 for WW1 and 0.034 to 0.047 for WW2. The fact that the ratio of BOD_5/TOC obtained for WW2 is rather low suggests that the biological treat ability of the wastewater is difficult. The BOD_5 value of raw wastewater for WW2 is low as 105 mg/L, while the TOC is a high value of 3016 mg/L. If the TOC value (3016 g/L) is considered to be originated from residual dyestuff, it can be said that the lower value of BOD_5 is caused by the inhibition effect of this dye.

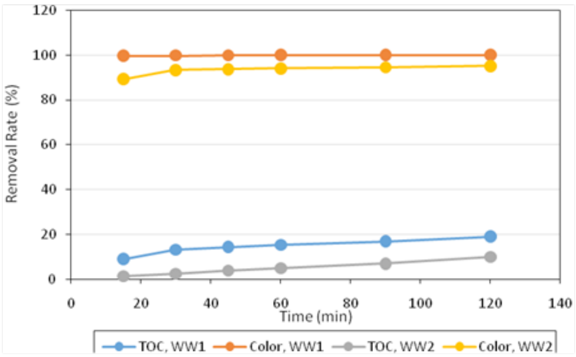

Fig. 3. TOC and color removal rates after PS oxidation.

3.2. Heat-activated PS oxidation

Treat ability results of heat-activated PS process are given in Table 3 and Fig. 3.

TOC and color removal rates were determined as 19% and about 100% for WW1, and 10% and 95% for WW2, respectively, for a 120 min oxidation period. According to the results obtained, the color removal rate is much higher than the TOC removal rate. Since the mineralization is harder than decolorization, longer reaction times are needed for mineralization. Also, the TOC and color removal rates (7% and 96% for WW1, 1% and 66% for WW2, respectively) obtained in control experiments at room temperature (25°C) were lower than 15 min heat activated reaction result. For both waste waters, it could be stated that thermal activation of PS resulted in $SO_4^{\bullet}$ generation and increased TOC and color removal rates.

In the study, the BOD_5 values of raw and heat activated PS treated waste waters were measured at 60 and 120 min and the effect of PS oxidation on the BOD_5/TOC ratio was evaluated. BOD_5 and BOD_5/TOC values obtained as a result of PS oxidation are given in Table 3. Accordingly, no significant increase in BOD_5 values was achieved after PS oxidation for both waste waters. However, as a result of decrease in the TOC parameter, the BOD_5/TOC ratio increased from 0.3 to 0.48 for WW1 and 0.034 to 0.041 for WW2.The BOD_5/TOC ratio for the control sample was 0.39 and 0.037 for WW1 and WW2, respectively. The BOD_5/TOC ratio obtained for the control sample is lower than the values obtained in PS oxidation. According to this result, thermal activation can increase BOD_5/TOC ratio.

3.3. Heat-activated PMS oxidation

The samples (WW1 and WW2) from the dye bath were oxidized by PMS and sampled at time intervals of 15, 30, 45, 60, 90 and 120 min. The results obtained and the removal rates are given in Table 4 and Fig. 4, respectively.

Table 4
PMS oxidation results

Time (min)	TOC (mg/L)	BOD_5 (mg/L)	BOD_5/TOC	436 nm	525 nm	620 nm	RES (m^{-1})
WW1							
0	793	245	0.30	8.724	11.314	11.177	3121.5
15	742			0.658	0.307	0.149	111.5
30	720			0.623	0.301	0.147	107.2
45	692			0.600	0.266	0.104	97.0
60	681	272	0.40	0.588	0.258	0.102	94.8
90	673			0.449	0.164	0.019	63.2
120	664	272	0.41	0.242	0.079	0.045	36.7
Control	729	265	0.36	0.368	0.146	0.085	59.8
WW2							
0	3016	105	0.034	0.399	1.263	0.541	220.3
15	2993			0.326	0.589	0.251	116.6
30	2959			0.296	0.494	0.214	110.4
45	2927			0.286	0.386	0.173	84.5
60	2891	105	0.036	0.282	0.311	0.144	73.7
90	2840			0.232	0.217	0.101	55.0
120	2812	110	0.039	0.153	0.010	0.009	26.0
Control	2978	105	0.035	0.267	0.159	0.065	49.1

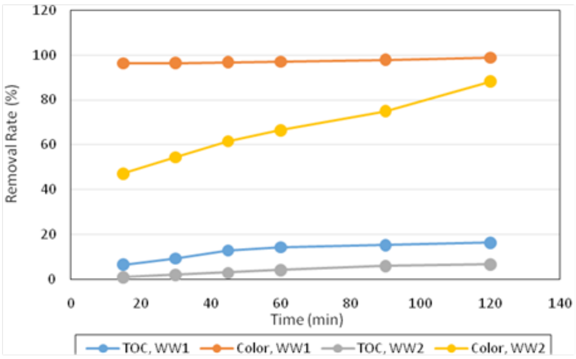

Fig. 4. TOC and color removal rates after PMS oxidation.

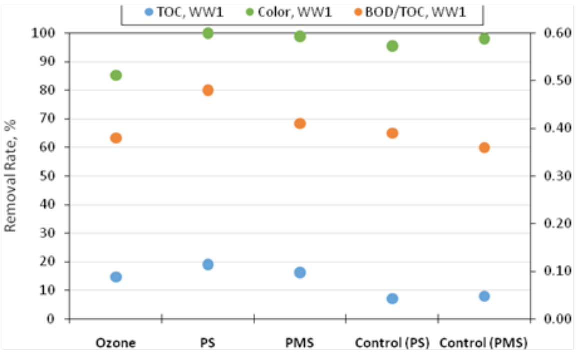

Fig. 5. Comparison of removal rates and BOD_5/TOC ratio for ozone, PS and PMS oxidation for WW1.

TOC and color removal rates were determined as 16%, 99% for WW1 and 7% and 88% for WW2, respectively, for 120 min of oxidation time. According to the results, the color removal rate is much higher than the TOC removal rate. In addition, the TOC removal rate was not higher than 16%. The TOC and color removal rates obtained at room temperature control experiments were 8%, 98% (for WW1) and 1% and 78% (for WW2) respectively.

BOD_5 and BOD_5/TOC values obtained as a result of PMS oxidation are given in Table 4. Accordingly, for both waste waters, no significant increase in BOD values was observed after PMS oxidation. As a results of decrease in the TOC parameter, the BOD_5/TOC ratio slightly increased from 0.3 to 0.41 for WW1 and 0.034 to 0.039 for WW2 as a result of 120 min of PMS oxidation. The BOD_5/TOC ratio for the control sample was 0.36 and 0.035 for WW1 and WW2, respectively. The BOD_5/TOC ratio obtained on the control sample is lower than the values obtained in PMS oxidation.

3.4. Comparison of ozonation, PS and PMS oxidation results

Comparisons of TOC and color removal rate and BOD_5/TOC ratios resulting from ozone, PS and PMS oxidation applied to two different dye bath waste water (WW1 and WW2) of the textile industry are given in Fig. 5 and Fig. 6.

For WW1, the TOC removal rate obtained by PS oxidation did not exceed 19%, although it was better than the obtained removal rate by ozonation. The TOC removal rates obtained for ozonation and PMS oxidation are close to each other (15% and 16% respectively). The highest TOC removal rate for WW2 (13%) was obtained by ozonation. The TOC removal rates for WW2 obtained for PS and PMS oxidation

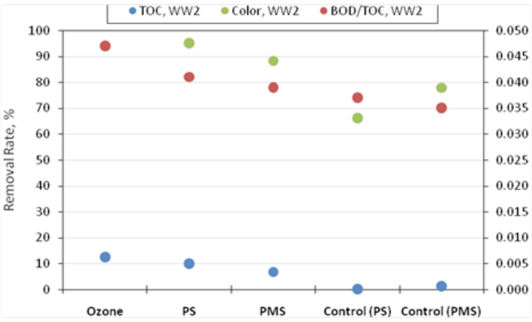

Fig. 6. Comparison of removal rates and BOD_5/TOC ratio for ozone, PS and PMS oxidation for WW2.

were determined as 10% and 7%, respectively. In all oxidation applications it is seen that the highest TOC removal rate for WW1 is achieved in PS oxidation and for WW2 in ozonation application. The TOC removal rates obtained during PMS oxidation are lower than other two applications.

The color removal rates of all oxidation applications were found higher than the TOC removal rates. The highest color removal rate for both waste waters was obtained with PS oxidation of 100% for WW1 and 95% for WW2. Although the removal efficiencies of the ozonation and PS oxidation applications for WW2 are very close to each other, the color removal efficiency of PMS oxidation is lower. Oxidation application with the highest BOD_5/TOC ratio is PS oxidation for WW1 (0.48) and ozone application for WW2 (0.047).

As aforementioned,in order to elucidate the activation of the oxidant (PS and PMS) by heat, resulting in enhancement of color and TOC removals, separate control experiments were carried out on WW1 and WW2 samples at room temperature (25°C) with either 30 mM PS or PMS. It was found that without heat activation, TOC removals employing PS or PMS oxidation resulted in minor TOC removals; 7% and 8% for WW1 and approximately 1% and 1% for WW2, respectively. On the other hand, in case of PS oxidation at room temperature 96% and 66% color removal efficiencies obtained for WW1 and WW2, respectively at the end of 120 min treatment whereas these values were 98% (WW1) and 78% (WW2) for PMS oxidation. PS and PMS are known as the strongest oxidizing agents that are applied in environmental remediation. The standard oxidation–reduction potential (ORP) for the reduction of PS anion equals to 2.01 V, hence it is higher than that of PMS i.e. 1.4 V. The high color removal rates obtained for PS and PMS oxidation at room temperature, while mineralization was limited, implied that the chromophore structures of dye molecules were destructed by PS and PMS themselves. The color removal rate obtained for control samples conducted at room temperature for PMS oxidation was found to be higher than that of PS oxidation and close to the heat activated PMS system (99% for WW1 and 88% for WW2).In the related works it was demonstrated that inorganic ions such as chloride, sulfate, bicarbonate and carbonate could activate PMS. Yang et al. [43] studied the degradation of azo dye Acid Orange7 by three common peroxides (PS, PMS and hydrogen peroxide) under various activation conditions, i.e., heat (25–80°C), UV light (254 nm), or anions (SO_4^{2-}, NO_3^-, CO_3^{2-}, HCO_3^-, HPO_4^{2-}, and Cl^-). They founded that PMS could be activated by CO_3^{2-}, HCO_3^-, HPO_4^{2-}, and Cl^-. The anion decomposition of PMS due to its un symmetric structure, resulted in generation of active species since it would be easily attacked by nucleo phile [43]. The reaction of PMS by halogens (Cl, Br and I) is studied by Lente et al. [44] and they found that combination of PMS with halogen could generate OX^- (X=Cl, Br or I) species. In the case of Cl^-, the generated chlorine/hypochlorite couple might act as oxidants depending on the solution pH (<11) [45]. The chemical reactions involved in (but not limited to) Cl^- ion activated PMS system can be given as follows [44,46,47]:

$$HSO_5^- + Cl^- \rightarrow SO_4^{2-} + HOCl \tag{12}$$

$$HSO_5^- + 2Cl^- + H^+ \rightarrow SO_4^{2-} + Cl_2 + H_2O \tag{13}$$

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- \tag{14}$$

$$HOCl \rightarrow H^+ + OCl^- \tag{15}$$

As can be also seen from Figs. 5 and 6, the anion activation of PMS in WW2 is less than WW1 and as a result lower color removal efficiencies were obtained for WW2 than WW1. This might speculatively be due to the presence of higher chloride concentration in WW1 sample and its lower pH (=9.65).

In the present study the absorbances of the ozone-, PS and PMS-treated WW1 and WW2 samples at wavelength of 280 nm were also measured. By using the absorbances of 120 min treated WW1 and WW2 samples, the aromaticity reduction efficiencies of the investigated treatment systems were established in the following decreasing order; O_3 (25% for WW1 and 8% for WW2) > PS (20% for WW1 and 5% for WW2) > PMS (17% for WW1 and 1% for WW2). Although the removal of aromaticity could be linked to the toxicity removal, it is of major importance to follow the toxicity of oxidation products formed during treatment of textile dye bath waste waters in order to safeguard the investigated technologies especially heat activated PS and PMS systems.

4. Conclusion

In this study, ozone, PS and PMS oxidation were applied to wastewater of two different dye bath belonging to a textile industry which is dyeing yarn. The TOC and color removal rates and BOD_5/TOC ratios were determined for each application and the results were compared. According to this results;

- Although the ozone dose applied for WW1 was approximately three times higher than the ozone dose applied to WW2, the color removal rate obtained in WW2 was found to be higher than that of WW1. On the other hand, the TOC removal rates were limited to 13%–15%. The environmental characteristics of the wastewater samples (especially their chloride and alkalinity levels) affected the ozonation performance considerably.

- PS and PMS oxidation at 25°C were found to be effective in color removal (oxidation of chromophore group) due to the oxidation potential of PS ($S_2O_8^{2-}$) and PMS (HSO_5^-) ions while mineralization (TOC removal) was limited. TOC and color removal rates were higher in PMS oxidation in control experiments conducted at room temperature (25°C) on both wastewater samples speculatively, due the activation of PMS in the presence of anions such as chloride and bicarbonate.
- For WW1, it was determined that heat activated PS treatment gave better results in the terms of TOC and color removal rates. For WW2, while ozone application was better for TOC removal, heat activated PS treatment was better for color removal.
- No significant increase in the BOD_5 value was achieved with oxidation treatments for both wastewater. However, with the application of PS oxidation to WW1, there was a certain increase in the ratio of BOD_5/TOC with the decrease in TOC value.

As a result; it is estimated that high TOC removal rates can be achieved by using PS and PMS oxidation with long retention times in waste waters that has high temperature such as textile industry. It can be predicted that ozone, PS and PMS oxidation can achieve low color values, especially when the color of wastewater will decrease with more colorless waters originating from other processes like rinsing. For this reason, more studies are needed with different wastewater and oxidation applications in different doses and retention times. In addition, further biologic treat ability studies have to be carried out with regard to the waste waters obtained as a result of the oxidation applications carried out.

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