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Ozonation pre and post-treatment of denim textile mill effluents: Effect of cleaner production measures

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ABSTRACT

Denim production, which is one of the leading sub-sectors of textile industry that generates considerable amount of wastewater with high pollution load both from dyeing and finishing processes. This sub-sector is therefore to consider cleaner production opportunities for these processes to reduce its wastewater generation and pollution load. In a denim-producing plant, the wastewater treatability studies have revealed that the most technically applicable cleaner production alternatives are caustic recovery from alkaline finishing wastewaters, and reuse of indigo dyeing wastewaters via the application of membrane filtration. In the present study, impact of the changes in the final effluent quality due to the foreseen cleaner production measures were considered in reference to the evaluation of impact on ozonation treatment of the effluent from a denim-producing plant. Ozonation was applied as pretreatment to the effluent from the plant before the foreseen measures (chemical oxygen demand, COD = 2750 mg/L; color = 3950 Pt–Co), and to the simulated effluent after the foreseen measures (COD = 3100 mg/L; color = 4500 Pt–Co); and also as post-treatment to the biologically treated effluent (COD = 800 mg/L; color = 3700 Pt–Co) before the foreseen measures. When applied to the effluent before the foreseen measures as pretreatment, ozonation provided 86% color and 46% COD removal with 3240 mg/h ozone dose in 70 min. However, less satisfactory results were obtained with the wastewater after the measures; with 86% color and 31% COD removals at 3960 mg/h ozone dose in 80 min. In parallel to the decrease observed in COD removal, ozone consumption was also much higher than that for the wastewater before the cleaner production measures. The findings have indicated that the environmental benefits to be brought by cleaner production measures have to be balanced against the risks to be encountered in the treatment of the final effluent.

1. Introduction

The textile industry is a water intensive sector and production of textiles affords a great variety of processing steps requiring use of large amounts of water and chemicals. This fact has put efforts on the minimization of use of, and where applicable reuse of, raw materials and water within the production steps. Being a water intensive sector (typically 200–400 L per kg of fabric); in textile industry, liquid discharges are of primary concern rather than gaseous emissions and solid wastes. Given the great variety of fibers, chemicals and other auxiliaries in use, textile manufacturing processes generate wastewaters containing metals, phenols, toxic compounds and/or phosphates. These constituents which are mostly resistant to conventional biological treatment, can pass untreated through the conventional wastewater treatment systems (Hu et al., 2016).

For the removal of the recalcitrant organics, conventional treatment methods are inappropriate and chemical oxidation methods are known to be much more effective (Ciardelli et al., 2001). Chemical oxidation with ozone is one of the most suitable chemical oxidation processes for effective color removal from textile effluents, with simultaneous interaction and breakdown of refractory organic matter resistant to biodegradation (Dogruel et al., 2002). Chromophore groups, generally organic compounds with conjugated double bonds can be broken by ozone (directly or indirectly) into smaller forms, decreasing the color of the effluent (Oguz and Keskinler, 2008). However, a complete mineralization by

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ozonation is usually not efficient and economically feasible, whereas, its application in one step for color removal and partial oxidation to improve biodegradability seems to be more promising (Gupta et al., 2015). The conversion of refractory organic matter into more biodegradable intermediates by ozonation, allowing for efficient COD removal by succeeding biological degradation is generally reported to reduce the operational costs (Van Aken et al., 2011). Post-ozonation, on the other hand, may provide better COD removal and have a polishing effect on the effluent quality (Dogruel et al., 2002).

The capability of ozone in oxidizing various pollutants in the water by direct attack on the different bonds; is further enhanced in the presence of H_2O_2 due to the generation of highly reactive OH• radicals. The dissociation of H_2O_2 results in the formation of hydroperoxide ion, which attacks the ozone molecule resulting in the formation of hydroxyl radicals (Gogate and Pandit, 2004). When hydroxyl radical concentration is elevated, the oxidation rate is further increased.

Ozone can be applied either before or after the biological treatment process. Best results concerning color removal are achieved if the wastewater has been previously pretreated in order to remove other constituents so that the ozone oxidizing power is "consumed" only or at least at a maximum proportion in color removal. But still, in some cases, pre-ozonation may be expected to ease biological treatment by converting the more slowly biodegradable COD into simpler compounds or by reducing the amount of inert organic matter.

A study was undertaken as the first application and evaluation of Best Available Techniques (BAT) within the context of the EU's Industrial Emission Directive to a textile mill in Turkey. The objective of the project was to develop a "best practice example" for the textile sector. In the project (CAYDAG-105Y088); for a denim manufacturing textile mill in Kayseri, Turkey, BAT requirements were determined, several better-water management or cleaner production measures were identified targeting at the minimization, and where applicable, reuse of both water and raw materials. In this context; a series of alternative cleaner production opportunities were foreseen for the management of different wastewater streams from the mill. The opportunities considered in the present study are caustic recovery from alkaline finishing wastewaters and water reclamation from indigo dyeing wastewaters by membrane filtration. After these cleaner production measures are taken in the mill, it is expected that there will be reduction in the volume of wastewater from dyeing and finishing operations. Moreover, there will be an increase in the strength of the wastewater from indigo dyeing, as the reject stream from membrane filtration will be going to the already existing wastewater treatment plant applying activated sludge process. On the other side, caustic recovery from finishing wastewaters will yield a finishing wastewater with a lower caustic content which is again the reject stream from the membrane filtration of caustic finishing wastewater. It is expected that these reject streams and the wastewaters from other units will come together to form the overall wastewater flowing into the activated sludge plant. As the reject streams are high in strength, it is expected that the overall wastewater after the foreseen cleaner production measures will be higher in strength and lower in biodegradability.

In the present study which is a part of the above mentioned investigation; ozonation was considered as an option for improving biodegradability of textile wastewater constituents (Asghar et al., 2015) which are mostly resistant to conventional biological treatment due to the chromophore groups of the textile dyes (Vishnu et al., 2008; Souza et al., 2010). As Asghar et al. (2015) indicated, ozone reacts selectively and slowly with organics, it is sometimes combined with catalysts that can convert it to hydroxyl radicals known to be the most important and most reactive oxidants which are capable of reacting with all types of solutes that can be subjected to oxidization. De Moraes et al. (2000) studied the degradation and toxicity reduction of textile effluent combining the photocatalytic process with ozonation and indicated reductions of 95% for color, 60% for total organic carbon and 50% for toxicity of the effluent. Nonetheless, Gianluca and Nicola (2001) reported that color removal from textile wastewater treated biologically was dependent on the initial COD value of the textile wastewater. According to Jianging and Tingwei (2001), ozonation at a dose of 30 mg/cm^3 increased the rate of biodegradability of textile wastewater by a factor of 1.6 and the increase in the degradation rate was influenced by the type of dye and its concentration.

As indicated above, all the studies about the ozonation of textile wastewaters, dealt with various types of textile wastewaters (synthetic or real) without considering possible effects of cleaner production measures such as water reuse or chemical recovery practices on the end-of-pipe treatment process. The studies dealing with the effects of cleaner production measures are all limited to the assessment of decrease in point source pollution (Bezama et al., 2012), environmental impacts (Yilmaz et al., 2015), or econometric influences (Castillo-Vergara et al., 2015). The goal of this study was to explore the possible effects of applying certain cleaner production measures (water reclamation for indigo dyeing wastewater and caustic recovery for mercerizing wastewater) on the end-of-pipe treatment of the resulting effluent and to see the effects on the performance of ozonation when applied as pretreatment.

The research for pretreatment of the overall plant effluents was carried out in two parts; of which the first is with the already existing overall plant wastewater and the second is with the wastewater expected (simulated wastewater) after the application of cleaner production measures which are the reuse of caustic in the alkaline finishing process wastewater and the reuse of indigo dyeing wastewater following membrane filtration. For the post treatment, ozonation experiments were conducted with the wastewater from the effluent of the biological wastewater treatment plant existing in the textile mill. In all the ozonation and ozonation + H_2O_2 application tests; color, COD, 5-day biochemical oxygen demand (BOD_5), ozone utilization ratio and BOD_5/COD parameters were measured to determine the treatment efficiency. As the first stage in experimental studies, pH effect was investigated to determine the optimum pH to be maintained in further ozonation tests.

2. Experimental

2.1. Wastewaters

Ozonation experiments were conducted on three different wastewater samples obtained from denim manufacturing textile mill in Kayseri, Turkey. The first is the so called "before the cleaner production measures" wastewater, which was taken from the influent of the wastewater treatment plant of the mill. This wastewater is mainly from dyeing and finishing processes (Table 1). The second is the wastewater so called "after cleaner production measures" that was prepared using the wastewater samples

Table 1
Wastewater streams forming the overall plant wastewater before and after the foreseen cleaner production measures.

Process	Before measures (% by volume)	After measures (% by volume)
Dyeing	35	24
Finishing	45	31
Other	20	45

coming from dyeing, finishing and other lines of the mill and applying the mixing ratios indicated in Table 1 considering the expected recovery ratios for the foreseen membrane filtration applications. The third is the overall plant wastewater after biological treatment, taken from the effluent of the wastewater treatment plant of the mill.

The wastewater samples were taken as grab samples and transferred to the laboratory in ice-boxes. Then, the samples were passed through a metal filter with 0.8 mm pore size in order to remove coarse fiber and similar large particles. Samples were kept at 4 °C in 25 L plastic containers.

The characteristics of the wastewaters used in the experiments are given in Table 2. As presented, wastewaters were highly variable in composition mainly due to different recipes applied during dyeing or finishing processes.

2.2. Experimental set-up

A glass reactor which is 6 cm in diameter and 78 cm in height was utilized for all the ozonation experiments and operated in the batch mode with regard to wastewater samples. Ozone was generated from air using a bench-scale ITT WEDECO brand Modular 4 H C ozone generator (Germany) with a capacity of 4 g/h ozone at the operating pressure was 0.5 bar. All the ozonation tests were conducted at a constant ozone gas flow rate of 60 L/h, for the elimination of the effect of gas flow rate on experiments.

The ozonation reactor was with three ports; one for the ozone gas coming from the ozone generator, one for the outlet gas, and one for sampling. Ozone gas was given from the bottom port through a sintered glass plate diffuser. Unused ozone in the off-gas from the top port was captured in a 400 mL gas washing bottle containing 2% potassium iodine (KI) solution. The port located at the mid-depth of the reactor was used for taking samples during ozonation tests.

2.3. Ozonation experiments

At the start of each ozonation test, 1.5 L of wastewater sample was placed in the glass reactor. The desired ozone gas flow rate was adjusted, ozonation was applied and the collection of the samples of the reacting solution took place at regular time intervals for a duration of about 60–80 min. All experiments were performed at room temperature (23 ± 2 °C). The pH of the wastewater samples were not adjusted except the experiment performed for the evaluation of pH effect. During the ozonation tests, 25 mL samples were withdrawn at 10 min interval to monitor the change in COD and color removal performance. For ozone + H_2O_2 experiments, H_2O_2 stock was added to the wastewater sample prior to ozone addition to achieve the desired concentration. In the tests with the overall plant wastewater before the foreseen cleaner production measures, ozone application rates of 2340 mg/h, 3240 mg/h and 3960 mg/h were applied. With this wastewater, effect of H_2O_2 was also studied, and H_2O_2 concentrations of 180 mg/L, 600 mg/L and 1800 mg/L were tested. Considering the higher strength of the wastewater after the foreseen cleaner production measures; higher ozone doses, which are 2760 mg/h, 3240 mg/h and 3960 mg/h were applied to the wastewater after the cleaner production measures. The effect of H_2O_2 addition was also tested with this wastewater, applying a H_2O_2 concentration of 1500 mg/L. For the biologically treated wastewater; lower ozone doses of 216 mg/h, 420 mg/h, 960 mg/h and 1320 mg/h were applied.

In all the ozonation and ozonation + H_2O_2 tests; color and COD parameters were monitored to assess the ozonation kinetics. To evaluate the improvement achieved in biodegradability with ozonation, BOD_5 of the ozonated samples were also measured. All experiments were repeated two times and the average values were reported.

2.4. Chemicals

In investigating the effect of pH on ozonation, initial pH of wastewater samples was adjusted using 1 N H_2SO_4 and 1 N NaOH solutions. Hydrogen peroxide with 35% (w/w) concentration was purchased from Merck. Sodium thiosulfate ($Na_2S_2O_3$) and potassium iodine (KI) used in the determination of ozone concentration in off-gas from the reactor were also from Merck.

2.5. Analytical methods

COD measurements were carried out according to USEPA-approved HACH's Method No. 8000. A sample of 2 mL was added into a COD digestion vial and digested at 150 °C for 2 h. After cooling down to room temperature, the vial was transferred into the COD colorimeter for COD determination. BOD_5 analyses were carried out by titrimetric method as per the standard methods (APHA, AWWA, WPCF, 1998).

Color measurements were done by measuring the absorption of the samples at 456 nm using a HACH DR-2000 Model Spectrophotometer (Model No 45600-02, Cole Parmer Instrument Co., USA) according to USEPA approved HACH Method No.8025 (Pt–Co method). Samples were diluted for color measurements darker than 500 Pt Co units using deionized water.

The pH and the conductivity were measured using a HACH Sension 378 pH meter. The ozone concentration was measured according to the Standard Method 8021 (DPD chlorine reagent) (APHA, AWWA, WPCF, 1998).

Mass flow of unused ozone at the outlet gas stream from the reactor was determined by titrating the 2% KI solution from the gas washing bottle with 0.1 N $Na_2S_2O_3$ according to Standard Methods (APHA, AWWA, WPCF, 1998), and using Eq. (1):

$$m_{O3-unused} = \frac{V_{Na_2S_2O_3} \times N_{Na_2S_2O_3} \times 24}{t} \quad (1)$$

Where; $m_{O3\text{-unused}}$ = mass flow of unused ozone (mg/h), $V_{Na2S2O3}$ = volume of $Na_2S_2O_3$ titrate solution used (mL), $N_{Na2S2O3}$ = normality of $Na_2S_2O_3$ solution (meq/mL), t = ozonation period (h), and 24 = conversion factor (24,000 meq/L per 1000 mL/L).

Ozone dose given to the system was calculated from the characteristic curves, according to Eq. (2):

Table 2
Characteristics of wastewaters used in ozonation experiments.

Parameter	Overall plant wastewater (before measures)	Wastewater (after measures)	Effluent of biological treatment plant
Color, Pt–Co	3920–4200	4230–4820	3300–4100
COD, mg O_2/L	2680–2840	3057–3162	743–865
Conductivity, mS/cm	19.75–19.85	13.54–14.01	14.26–14.6
pH	9.3–12.6	12.1–12.2	7.1–7.2

$$m_{O3} = C_{O3} \times V_{gas} \quad (2)$$

where; m_{O3} = ozone dose (mg/h), C_{O3} = ozone concentration in the gas flow (mg/L) from the ozone generator, V_{gas} = gas volume flow (L/h).

The consumed part of the ozone was then calculated as the difference between the ozone dose given to the system (Eq. (2)) and the mass flow of unused ozone (Eq. (1)).

3. Results and discussions

3.1. Effect of pH on ozonation kinetics

Ozone oxidation is either directly by ozone itself or through the formation of highly reactive hydroxyl radicals that to a large extent depends on the solution pH and type of the target molecule. At elevated solution pH values, the production of hydroxyl radicals is favored and therefore the system becomes more effective in oxidizing refractory substances (Van Aken et al., 2011). At low solution pH values, oxidation is more likely to attack electron-rich structures by direct electrophilic reactions.

In this study, in order to evaluate the optimum pH that should be maintained during further experiments, the ozonation tests were conducted at three different pH values: 5.3, 9.3 and 11.0, and the change in color was followed. These experiments were conducted at 1320 mg/h ozone application rate using the wastewater before the cleaner production measures. The pH of 9.3 was the unconditioned pH of the wastewater sample used. The results obtained in these tests are presented in Fig. 1. As seen, wastewater pH did not affect color removal rate seriously. The highest initial decolorization rate was at pH of 11.0 and the lowest was at pH of 9.4. On the other side, at the pH of 9.3, the highest color removal rate of 94.7% from the initial color level of 7145 Pt–Co unit. These findings were in agreement with what has been reported in literature. Even at elevated pH values, direct attack by molecular ozone is reported as the prevailing mechanism when the concentration of fast reacting species with molecular ozone is sufficiently high (Van Aken et al., 2011). Several authors reported high organic matter removal at pH values of around 9 (Tizaoui et al., 2007; Nakamura et al., 2004; Soares et al., 2006). When these truths are considered with the fact that the natural pH of the wastewater is in this range, it was decided that further ozonation tests should be conducted without any pH adjustment. In taking this decision, the fact that ozonation at the natural wastewater pH will reduce the chemical costs, was also a concern.

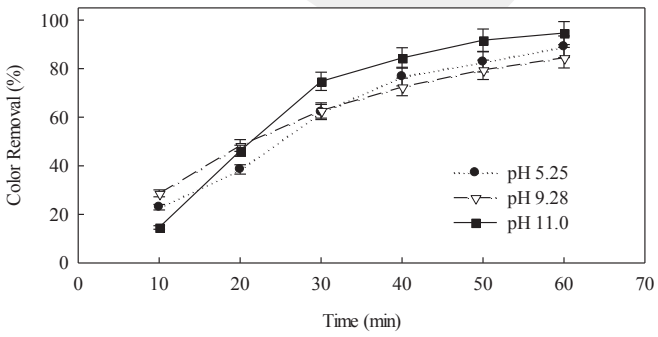

Fig. 1. Color removal at different pH values (Initial wastewater color: 7145 Pt–Co, Ozone dose: 1320 mg/h).

3.2. Ozonation of the wastewater before the cleaner production measures

In this part of the present study, in order to assess the effectiveness of ozonation in the removal of color and COD from indigo dyeing wastewater before the foreseen cleaner production measures, different ozone doses were applied and time-dependent variation in the removal of color and COD were followed. The ozone application rates tested in these experiments were 2340 mg/h, 3240 mg/h and 3960 mg/h without any pH adjustment. The wastewater used was with a COD of 2840 mg/L and color of 3920 Pt–Co. At all these ozone doses; the reaction was followed for a period of 70 min and samples were taken from the reactor at 10 min time intervals. The decrease observed in color and COD of the reactor content with time is presented in Figs. 1 and 2, respectively. As ozonation was considered as a pretreatment technique for the treatment of the wastewater before cleaner production measures, in addition to COD and color removals, the change in BOD_5/COD ratio was also taken into consideration as an indicator of biodegradability (Padoley et al., 2012).

As can be seen from Fig. 1, at all ozone doses tested, color removal was quite rapid during the first 30 min and the initial discolorization rate was higher for higher ozone doses. At the time of 20 min; color removal was about 10% for the ozone application rates of 2340 mg/h, and over 30% for the ozone application rates of 3240 and 3960 mg/h. At the lowest ozone dose tested, i.e. 2340 mg/h, color removal achieved (75%) after 70 min ozonation was not sufficient and the ozonized effluent contained approximately 1000 Pt–Co color which may not be treated biologically. Wu and Wang (2001) reported that subsequent biological treatment has almost no effect on the color of textile effluents. At the dose of 3240 mg/h, the effluent was much better in quality with 85% color removal. However, with an increase in ozone application rate from 3240 to 3960 mg/h, there occurred no considerable improvement in color removal and similar effluent color level was reached. The same color removal observed with 3240 mg/h and 3960 mg/h ozone rates was attributed to the limited degradation of color causing substances with ozone.

When the quantity of ozone consumed in these tests was calculated, the results presented in Fig. 3 were obtained indicating that there was a continuous increase in ozone utilization rate with an increase in ozone application rate. However, this increase was not directly proportional to ozone application rate. While there was almost two folds increase in ozone application rate from 2340 to 3960 mg/h, the increase in cumulative ozone consumption was only from 2850 to 3500 mg by the end of ozonation reaction (Fig. 2).

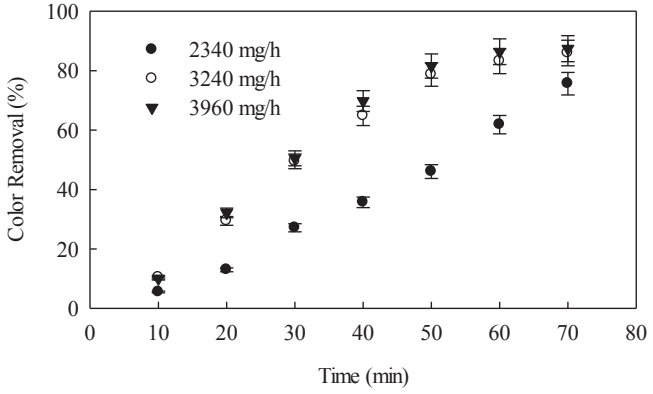

Fig. 2. Color removal at different ozone flow rates from the wastewater before the cleaner production measures.

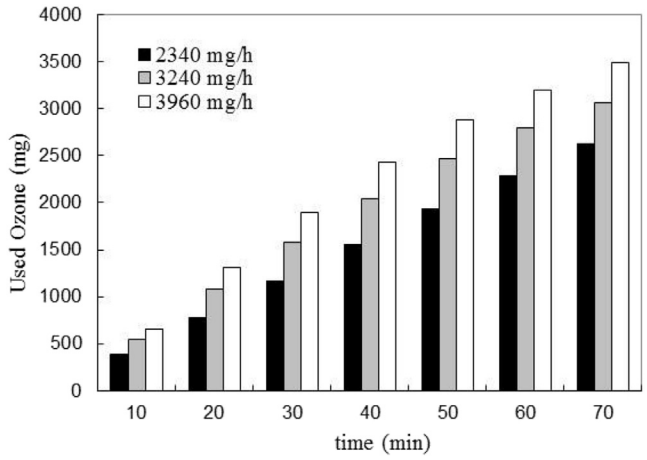

Fig. 3. Consumed ozone amounts in the wastewater before the cleaner production measures.

Fig. 4 shows COD removals achieved when the wastewater before the cleaner production measures was ozonated at three different ozone application rates. Like the case in color removal, the COD removal was the lowest at the lowest ozone dose tested (2340 mg/h); but unlike the case in color removal, COD removal was the highest for the highest ozone application rate. This observation was in agreement with the increase observed in ozone consumption with an increase in ozone application rate (Fig. 2). Consumed ozone to removed COD ratios for the doses studied in the wastewater before measures were 2.75 mg ozone/mg COD for 2340 mg/h ozone dose; 2.31 mg ozone/mg COD for 3240 mg/h ozone dose and 2.26 mg ozone/mg COD for 3960 mg/h ozone dose, respectively (Table 3).

The BOD_5/COD ratio is usually considered as a well-adopted surrogate parameter for biodegradability and used in evaluating the amenability of a waste towards biological treatment (Padoley et al., 2012). The improvement achieved in biodegradability with respect to different ozone doses are given in Table 3. As it is seen, the ozone dose of 2340 mg/h provided no improvement while the ozone dose of 3960 mg/h provided almost 70% increase in biodegradability. At this ozone dose, the BOD_5/COD ratio was almost equal to the limit of 0.40 recommended for a successful biological degradation (Metcalf and Eddy, 2003).

When both color and COD removals achieved and also the improvement observed in biodegradability considered, it can be concluded that the ozone application rate of 3960 mg/h is the best among the three ozone doses tested for the wastewater before the cleaner production measures, and ozonation was able to improve the biodegradability of biorecalcitrant organic constituents of the wastewater up to a level that will allow a subsequent biological treatment.

Table 3
Ozone to COD removed and BOD_5/COD ratio of the wastewater before the cleaner production measures at different ozone doses.

Ozone dose (mg/h)	mg ozone/mg COD ratio	BOD_5/COD ratio
0	–	0.23
2340	2.75	0.21
3240	2.31	0.30
3960	2.26	0.39

3.3. Ozonation of the wastewater before cleaner production measures - addition of hydrogen peroxide

As indicated previously, hydroxyl radicals are produced during the spontaneous decomposition of ozone and this production is accelerated when H_2O_2 is added into ozonated water. Thus, in the presence of H_2O_2, the ozone residual is short, the net result is that the ozone + H_2O_2 is more reactive and much faster compared to the ozone molecular process. In this part of the study, a more efficient oxidation was aimed and three different H_2O_2 doses, 180 mg/L, 600 mg/L and 1800 mg/L, at 2340 mg/h ozone application rate were tested. The observed color and COD removals during a 70 min ozonation period are given in Figs. 5 and 6, respectively.

As can be depicted from Figs. 5 and 6, the color and COD removals achieved when H_2O_2 was added were not better that those obtained with ozone alone. On the contrary, the addition of H_2O_2 affected degradation of organic matter adversely. This result is consistent with the studies of Khadhraoui et al. (2009), Oğuz and Keskinler (2008) and Riaño et al. (2014). Riaño et al. (2014) stated that the combined treatment with ozone + H_2O_2 at pH = 8.1 did not produce any significant COD or color reduction improvement from biologically pre-treated swine manure. Khadhraoui et al. (2009) also reported lower color removal efficiency by ozone + H_2O_2 process as compared to ozone alone, and attributed this outcome to the scavenging effect of high H_2O_2 dose applied. Lopez et al. (2004) observed that the decolorization is inhibited by high H_2O_2 concentrations in their studies with in which Orange Red and Acid Red 27 azo dyes are chosen as a representative model. As indicated in Table 4, the H_2O_2 to ozone dose ratio applied in the present study was in the range 0–0.99 by weight as suggested (Glaze and Kang, 1988).

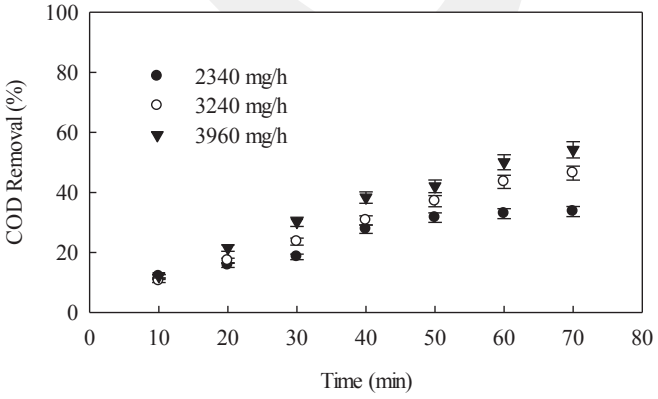

Fig. 4. COD removal at different ozone flow rates from the wastewater before the foreseen cleaner production measures.

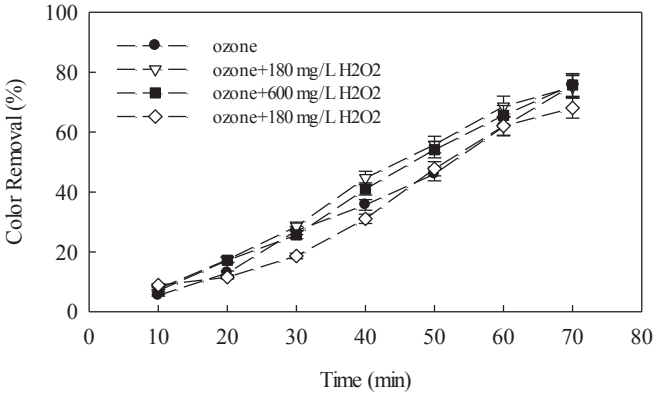

Fig. 5. Color removal when H_2O_2 added at different doses at 2340 mg/h O_3 dose before the cleaner production measures.

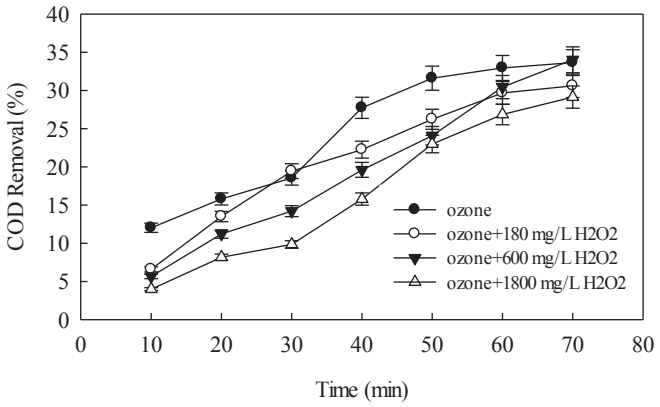

Fig. 6. COD removal (%) when H_2O_2 added at different doses at 2340 mg/h O_3 dose before the cleaner production measures.

Table 4
Effect of H_2O_2/Ozone Dose Ratio on BOD_5/COD ratio of the wastewater before the cleaner production measures.

H_2O_2 concentration, mg/L	H_2O_2/Ozone dose ratio	BOD_5/COD ratio
0	0	0.23
180	0.10	0.25
600	0.33	0.27
1800	0.99	0.27

As the main objective in this part of the research was to use ozonation as a pretreatment to activated sludge process, the improvement in BOD_5/COD ratios was also evaluated for the experiments with the addition of H_2O_2. The calculated BOD_5/COD ratios for the H_2O_2 concentrations tested are given in Table 4. As it can be seen from Table 3, the addition of H_2O_2 did not also provide a considerable improvement of biodegradability. The BOD_5/COD ratio has increased only from its earlier value of 0.23 to 0.25–0.27 when ozone + H_2O_2 process was used.

3.4. Ozonation of the wastewater after the foreseen cleaner production measures

In the textile mill, as stated before, the cleaner production measures are planned to be taken regarding water reuse from indigo dyeing wastewater and caustic recovery from finishing effluent. After these measures are taken, the effluents from these process steps will change both in composition and flow rate, and therefore the influent to the proceeding wastewater treatment plant will differ. Within the scope of this study, the question of "how ozonation treatment would be affected by the cleaner production measures taken in the plant?" was also tried to be answered. For this answer, ozonation tests were run with the simulated, so called "wastewater after the cleaner production measures" and the performance observed was compared to that observed with the wastewater before the cleaner production measures. The characteristics of the simulated "the wastewater the cleaner production measures" prepared using real wastewater samples from indigo dyeing and finishing processes of the mill is given in Table 2. As can be seen, in comparison to "the wastewater before the cleaner production measures", the wastewater so called "after the cleaner production measures", is stronger with respect to color and COD parameters. This situation arises firstly from the foreseen return of concentrate or reject stream from membrane filtration of indigo dyeing wastewater to the overall wastewater stream discharged into the wastewater treatment plant.

Three different ozone doses (2760 mg/h, 3240 mg/h and 3960 mg/h) were applied to the wastewater after the cleaner production measures, and color and COD removals presented in Figs. 7 and 8 were observed. As can be seen, color removal rate was rapid during the first 30 min and then after there was a gradual reduction in the color removal rate. The trend observed in time dependent increase in color removal rate was almost the same for all the ozone doses tested and the final color removal achieved was about 75–85%. With an increase in ozone application rate from 2760 mg/h to 3960 mg/h, there was only about a 5% improvement is color removal. In general, percentage color removals achieved were very similar to those with the wastewater before the cleaner production measures.

However, as presented in Fig. 8, the corresponding COD removals were low; the highest being only 31% at the ozone application rate of 3960 mg/h. COD removals achieved were also low in comparison to removals achieved with the wastewater before the cleaner production measures. For these tests; ozone consumed per COD removed ratios were calculated as 4.46, 4.75 and 4.00 mg ozone/mg COD for 2760, 3240, and 3960 mg/h ozone dose, respectively (Table 5). Thus, in parallel to the decrease observed in COD removal, ozone consumption was also much higher than that for the wastewater before the cleaner production measures. This observation was attributed to the increase in the concentration of aromatic structures in the wastewater as compared to the reference wastewater of before the cleaner production measures. Very recently, Hu et al. (2016) indicated that chromophoric groups in textile wastewaters are easier to be destructed in ozonation comparing with aromatic structures. Thus, color that is predominantly contributed by the dyes possessing complete chromophore, can be removed effectively by ozonation while other substances which contain aromatic rings are not mineralized into inorganics. These findings are a clear indication that the cost of pre-ozonation will increase with the anticipated cleaner measures and possibly influence the proceeding biological treatment adversely as the influent will be with a higher COD.

As regards biodegradability, ozonation of the wastewater after the cleaner production measures did not provide improvement (Table 5). In the wastewater after the cleaner production measures, biodegradability was 0.4 which is not as low as that in the wastewater before the cleaner production measures. This was an interesting finding indicating an increase in biodegradability after the cleaner production measures. Recovery of caustic from finishing process effluent rather than reusing of indigo dyeing wastewater were considered as the possible reason for this increase in BOD_5/COD ratio. The BOD_5/COD ratio of 0.4 is taken as a threshold value for biodegradability. In some studies, BOD_5/COD values less than

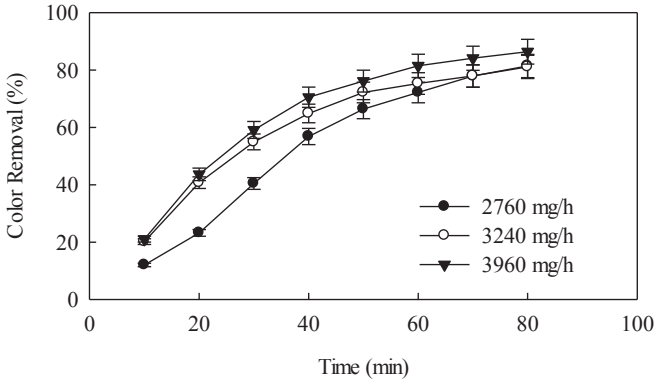

Fig. 7. Color removal at different ozone flow rates from the wastewater after the cleaner production measures.

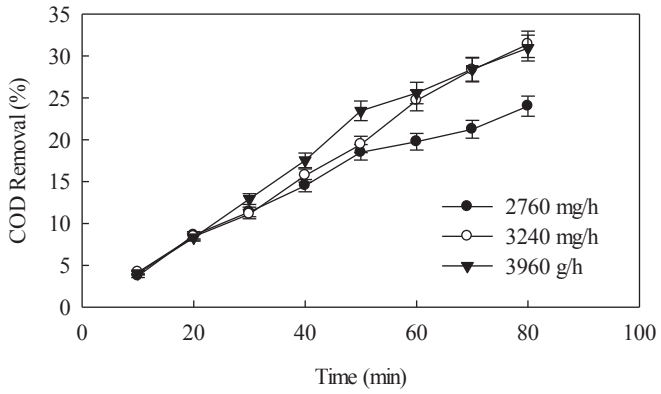

Fig. 8. COD removal at different ozone flow rates from the wastewater after the cleaner production measures.

Table 5
Ozone to COD removed and BOD_5/COD ratio of the wastewater after the cleaner production measures at different ozone doses.

Ozone dose (mg/h)	mg ozone/mg COD ratio	BOD_5/COD ratio
0	0	0.40
2760	4.46	0.43
3240	4.75	0.42
3960	4.00	0.47

0.4 were taken as an indication of difficult biodegradation (Kuo, 1999; Mehrvar et al., 2005; De Morais and Zamora, 2005). The calculated BOD_5/COD ratios for the three applied ozone doses to the wastewater after measures are given in Table 5. As seen, at all the ozone application rates, there was a slight improvement in BOD_5/COD ratio.

All the results achieved with the pre-ozonation of the wastewater after the cleaner production measures indicated that ozonation is less effective as pretreatment for the anticipated wastewater and can only be used for improving color removal performance.

3.5. Ozonation of the wastewater after the foreseen cleaner production measures - addition of hydrogen peroxide

Considering low COD removal achieved from the wastewater after the foreseen cleaner production measures and also the fact that the addition of H_2O_2 did not give satisfactory results in the wastewater before the cleaner production measures, it was decided that the addition of H_2O_2 will be tested but at a higher ozone concentration for the wastewater after the foreseen cleaner production measures. The tests were run at the ozone application rate of 2760 mg/h after the addition of 1500 mg/L H_2O_2 into the reactor. Fig. 9a and b demonstrate the time dependent decrease in color and COD content of the wastewater.

As can be seen, the addition of H_2O_2 provided no significant improvement in COD removal, moreover no effect or slight adverse effect on color removal and almost no effect on BOD_5/COD ratio (Table 6).

3.6. Ozonation experiments on biologically treated wastewater

In this part of the study, ozonation was considered as a post-treatment technique for the biologically treated wastewater and its performance was compared to that obtained for the wastewater before the cleaner production measures. Post-treatment with ozonation is applied to have a polishing effect on effluent quality

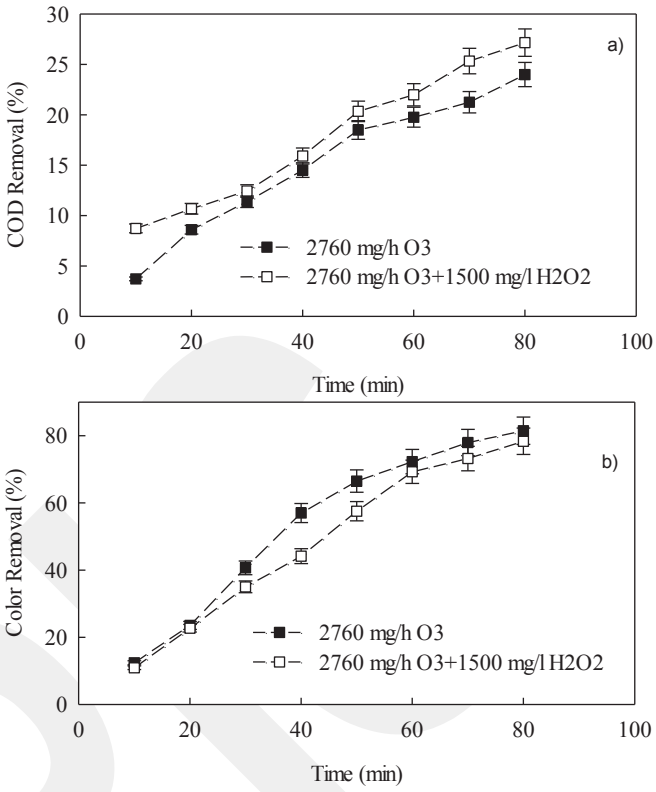

Fig. 9. a) COD removal and b) Color removal dose from the wastewater after the cleaner production measures when 1500 mg/L H_2O_2 added at 2760 mg/h O_3 ozone application rate.

Table 6
Effect of ozone + hydrogen peroxide application on BOD_5/COD ratio in the wastewater after the cleaner production measures.

Oxidizing agent used	BOD_5/COD ratio
0	0.40
2760 mg/h O_3	0.43
2760 mg/h O_3 + 1500 mg/L H_2O_2	0.42

and provide further removal of recalcitrant substances or color causing dye molecules (Yasar et al., 2007). Four different ozone application rates which are lower than those applied during pre-ozonation tests were used for the biologically treated wastewater and the results presented in Figs. 10 and 11 were obtained. As can be depicted, ozonation provided satisfactory color and COD removals from the biologically treated wastewater. Percentage COD removals in the range of 44–56%; and color removals in the range of 93–98% were obtained. These findings have indicated that ozonation provides much better color removal from the biologically treated wastewater as compared to that from the wastewater before cleaner production measures. As can be seen from Fig. 10, color removal was nearly 90% at the ozone application rates of 420, 960 and 1320 mg/h after 20 min ozonation while that from the before the cleaner production measures wastewater was only 10% at a much higher ozone application rate of 2340 mg/h (Fig. 2).

COD removals from biologically treated wastewater were also better; with lower ozone consumption values (Figs. 4 and 11). Ozone consumed to COD removed ratios were in the range of 0.36–1.46 mg ozone/mg COD for the biologically treated wastewater while those for the wastewater before the cleaner production measures were in the range of 2.26–2.75 mg ozone/mg COD

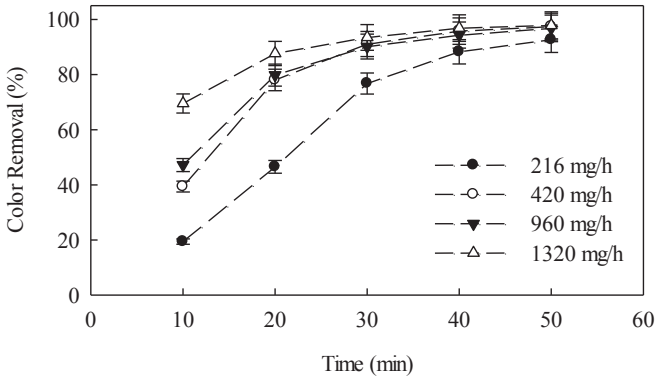

Fig. 10. Color removal at different ozone flow rates from the effluent of biological treatment.

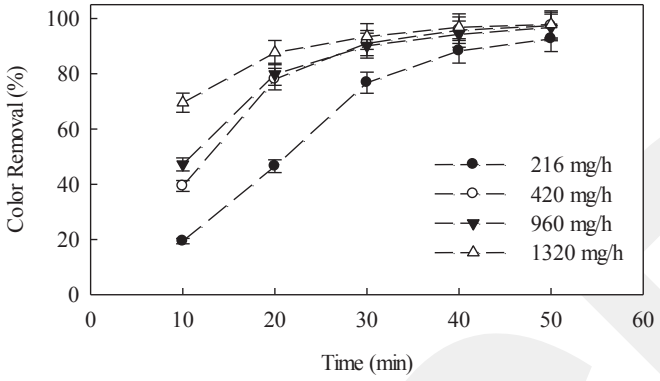

Fig. 11. COD removal at different ozone flow rates from the effluent after biological treatment.

removed. The overall results demonstrate that the usage of ozonation as a post-treatment procedure provides better results in a shorter treatment time and at lower ozone doses when compared to the ozonation as pretreatment conducted on the wastewater before and after measures. In the literature, post-treatment with ozonation has also been reported to result in better treatment performance (Assalin et al., 2009; Blonskaja and Zub, 2009; Aben and Kurnitski, 2006).

A summary of the results for biologically treated effluent is given in Fig. 12. As seen, the cleaner production measures to be implemented in the textile mill resulted in a wastewater which can be treated more difficultly. The COD of the ozonated before cleaner production effluent at all the ozone doses tested was considerably higher than that of after cleaner production measures. This was clearly due to the increase in the concentration of aromatic structures in the wastewater after the application of membrane filtration.

The improvement achieved in the BOD_5/COD ratio of the wastewater before the foreseen measures by ozonation, was also much higher that of the wastewater after the foreseen cleaner production measures. At the highest ozone application rate of 3960 mg/h, there was more than 70% increase in biodegradability of the wastewater before cleaner production measures. However, the improvement observed in the biodegradability of the wastewater after cleaner production measures was only about 10%.

4. Conclusions

In the present study; ozonation and ozonation + H_2O_2 application alternatives were considered as pre- and post-treatment of a denim producing textile mill wastewater, and the effect of the foreseen cleaner production measures (reuse of caustic in the alkaline finishing process wastewater and the reuse of indigo dyeing wastewater following membrane filtration) on ozone treatment was investigated and the removal efficiencies with respect to color and COD were investigated.

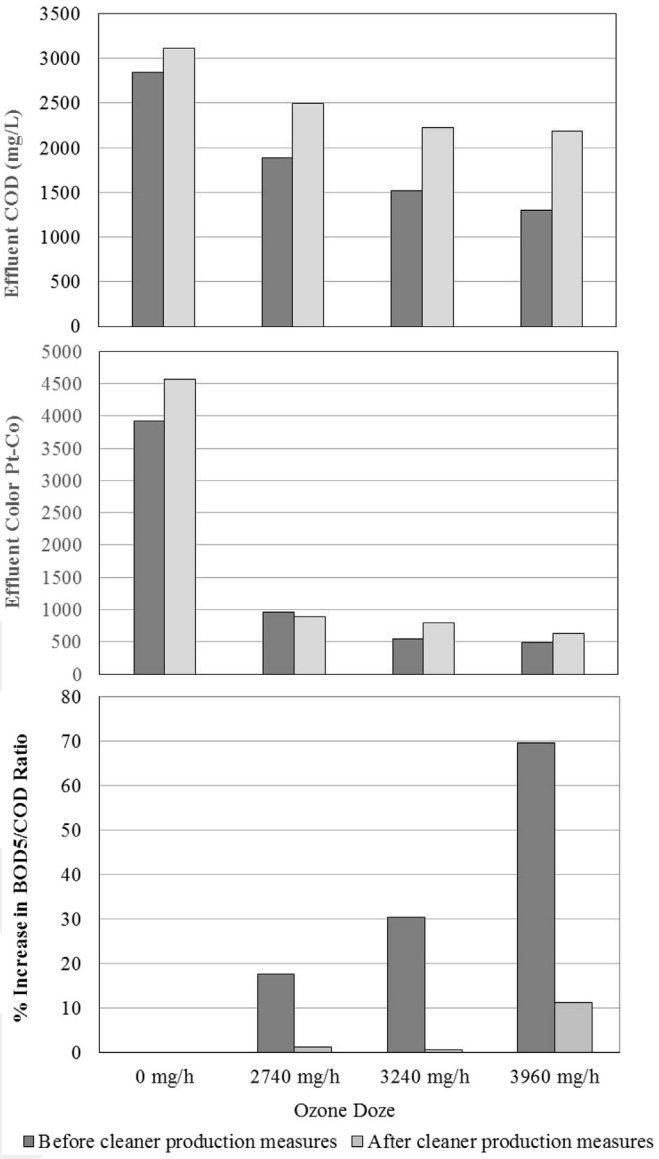

Fig. 12. Effluent color, effluent COD and BOD_5/COD ratio of ozonation effluents.

Both of the cleaner production measures considered were wastewater reclamation practices, therefore foreseen to cause an increase in wastewater strength. It was evaluated that the COD and color of the wastewater will increase from 2750 to 3100 mg/L and 3950 Pt–Co to 4500 Pt–Co, respectively. When the use of ozonation as pretreatment was considered, it was seen that the foreseen water reclamation practices cause an increase in ozone demand and moreover worsen COD removal efficiency. The ozone pretreatment; when applied to the denim textile effluent before foreseen cleaner production measures resulted in 86% color and 46% COD removals with 3240 mg/h ozone dose after 70 min ozonation; whereas when applied to the denim textile effluent after foreseen cleaner production measures, resulted in 86% color and 31% COD removals with 3240 mg/h ozone dose after 80 min of

ozonation. Thus, ozone pretreatment was found to be adversely affected by the water reclamation measures, implying that the concentrate streams from membrane filtration of the mercerizing and dyeing wastewaters influence the ozonation pretreatment process adversely. Furthermore, the improvement achieved in biodegradability by ozonation pretreatment in the wastewater after the foreseen cleaner production was considerably lower than that in the wastewater after cleaner production measures. Therefore, it is concluded that the adaptation of water reclamation practices represent an important concern in the treatment of textile wastewaters, and the environmental benefits to be brought by water reclamation practices have to be balanced against the risks to be encountered in the treatment of the final effluent.

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