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# Ozonation of high strength segregated effluents from a woollen textile dyeing and finishing plant

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**Abstract**

Effluents from dyeing processes of woollen textile finishing industries are highly polluted with recalcitrant compounds compared to effluents from rinsing and finishing processes. Oxidation of woollen textile dyeing effluent consisting of wastewater generated from spent dye baths and first and second rinses (remaining composite wastewater) were investigated. Ozone oxidation ($C_{O3}$ = 18.5 mg/l; input rate) was applied on remaining composite wastewater, before and after the biological treatment, for various time intervals. Treatment efficiency was monitored by decolorization and by COD removal rates. Additionally, toxicity tests (bioluminescence test) were carried out to determine the effect of oxidation process. The results indicated that 40 min ozonation of biologically treated wastewater yielded almost colorless effluent with a decolorization efficiency of around 98–99% and with a corresponding ozone absorption rate of 58.0 mg/l. Biological treatment followed by 10 min ozone oxidation reduced the overall toxicity significantly (92%). However, ozonation was found to have only slight effect on COD removal.


*Keywords:* Decolorization; Ozonation; Woollen textile; Remaining composite wastewater; Bioluminescence test; Toxicity

## 1. Introduction

Considerable amount of high quality water is needed for textile industry for dyeing and finishing operations. Color and recalcitrant compounds are among the vital environmental concerns in effluent treatment. Wastewater from these industries represents a variety of pollutants, high strength load and high in color depending on the stage of the process and nature of discharge. The high pollution load is generated from spent dyeing baths, first and second rinses carried out after dyeing processes. These effluents consist of unbound colorants or reaction products, which remain in the substrate and are washed out in subsequent rinses, dye impurities, auxiliaries and surfactants. These compounds exhibit slow degradation kinetics for conventional

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biological processes and resulting effluent is still high in color and violates the discharge limits imposed by legislation [1–5]. There is an increasing interest in utilization of advanced oxidation processes (AOPs) for destruction of recalcitrant compounds. AOPs is based on the production of hydroxyl radicals as oxidizing agents to mineralise many synthetic organic chemicals. The physical, chemical and biological methods applied to textile effluents include chemical oxidation by ozone, UV, hydrogen peroxide, hypochloride, fenton reagent and their combinations, advanced oxidation processes with and without heterogeneous catalysis, sorption, photooxidation and activated sludge type biological oxidation processes [6–11]. Ozone oxidation studies have demonstrated relatively low rate of mineralization so far. However, it was shown that ozonation improved biodegradability of textile baths [12–17]. Aerobic and anaerobic biological oxidation processes are also often applied to dye-baths for decolorization and degradation purposes [18–20]. Biological treatment processes applied on strong textile effluents resulted in quite small amount of decrease in color characteristics. Therefore, it is advisable to employ oxidative treatment techniques preferably in combination with other treatment technologies as reported by several researchers [21–23]. Furthermore, use of fungi for degradation and decolorization purposes [24–27], membrane separation techniques, especially for remaining salts, for reuse purposes of textile wastewater showed also a promising future [28].

Along these lines, ozone oxidation process for the treatment of segregated high strength wastewater (remaining composite), generated from a woollen and woollen–PES blends enterprise was explored. Oxidative treatment was applied on the remaining composite wastewater, consisted of dye bath effluents and first and second rinse wastewaters as well as the biologically treated remaining composite effluent as post treatment for decolorization and advanced oxidation purposes. In addition, bioluminescence test was applied as a reproducible and sensitive screening method [29–31] to different types of samples as described above to evaluate their toxic potential.

## 2. Experimental

The enterprise involves, processing of wool, polyester blends of yarn and fabric. Reactive, disperse and metal-complex dyes are used for batch type of dyeing operations. The remaining composite waste stream can be described as the flow proportional composition of the wastewaters generated by the recipes, *Acidol, Lanaset, Forosyn* and *Diamant* dyeing. The effluents of dye baths and first and second rinses were selected as remaining composite wastewater, which had total and soluble COD concentration of 1700 and 1590 mg/l respectively. The remaining composite wastewaters before (raw wastewater) and after biological treatment were subjected to ozonation experiments. The ozone input rate was 20 mg/l. Conventional pollutant parameters for untreated and ozonated samples were determined accordingly to predict the effect of ozonation as an advanced treatment option. Varying ozone contact times (10–60 min) were applied to both samples; color decrease was taken as an indication of efficiency of the treatment at first. Samples (20 ml) were withdrawn and analyzed for UV/Vis-absorbance, total COD, pH and conductivity. In addition to that, bioluminescence test was applied to the samples, before and after the ozone treatment as a pre-toxicity screening test using the luminescence bacterium *Vibrio fischerii* in LUMIStox 300. All tests were conducted by Dr. LANGE LUMIStox 300 photometer. Luminescent bacteria and all other reagents required for the assay were also obtained from the same company. Dilution series were prepared according to German standards DIN 38412 L34 and L341 and the international standard ISO DIS 11348. The effect of the test compounds on the luminescent bacterium was evaluated using the GL-values. The GL-value, as referred in DIN 38412 L34/341, gives the dilution level at which a sample causes less than 20% inhibition.

## 3. Results and discussion

The applied and absorbed rates of ozone for chemical oxidation of raw and biologically treated remaining composite wastewater are given in Table 1. The results stated that although ozone application rates are virtually identical for both experiments, ozone uptake (absorption) rate for raw remaining composite wastewater was about 30% higher as compared to the ozonation of biologically treated effluent. High organic matter content of raw wastewater was considered to exert the excess amount of ozone uptake [15]. The data obtained through the experimental runs can be utilised for designing the system or making feasibility analysis for full-scale implementations. The variation between the amount of ozone induction and uptake indicates the relatively low efficiency of the ozonation reactor due to the large bubble size generated by the porous plate or short contact time because of the configuration of the reactor [13]. The results of the analysis of monitored parameters for the ozonation experiments including the toxicity measurements with respect to ozonation period are listed in Table 2. Remaining absorbance as the percentage of its initial value and COD removal rates as a function of ozone oxidation time are illustrated in Figs. 1 and 2, respectively.

It should be pointed out that only a slight reduction in COD for the ozonated raw and biologically treated wastewater samples were

Table 1
Ozone induction and uptake rates for raw and biologically treated remaining composite textile wastewaters ($C_{O3}$ = 18.5 mg/l)

| Ozonation period (min) | Raw | | Biologically treated | |
|---|---|---|---|---|
| | Applied (mg/l ww) | Absorbed (mg/l ww) | Applied (mg/l ww) | Absorbed (mg/l ww) |
| **10** | 61.1 | 23.8 | 61.9 | 18.8 |
| **20** | 122.1 | 43.1 | 123.8 | 35.2 |
| **30** | 183.2 | 62.5 | 185.7 | 49.1 |
| **40** | 244.2 | 80.2 | 247.5 | 58.0 |
| **60** | 366.3 | 111.4 | 371.3 | 77.4 |

Table 2
Conventional parameters and GL-values for raw and biologically treated remaining composite textile wastewaters during ozonation ($C_{O3}$ = 18.5 mg/l)

| Contact time (min) | Absorbance ($m^{-1}$) | | | Toxicity GL-value | COD ($mg\ l^{-1}$) | Conductivity (mS/cm) | pH[a] |
|---|---|---|---|---|---|---|---|
| | 625 | 525 | 437 (nm) | | | | |
| *Raw ww* | | | | | | | |
| 0 | 40.1 | 49.3 | 56.5 | 24 | 1700 | 41.4 | 8.30 |
| 10 | 28.9 | 36.2 | 32.2 | 16 | 1570 | 4.13 | 7.58 |
| 20 | 29.4 | 38.3 | 32.8 | 12 | 1490 | 4.08 | 7.70 |
| 30 | 17.9 | 20.6 | 23.9 | 16 | 1380 | 4.04 | 7.73 |
| 40 | 17.0 | 19.8 | 24.6 | 8 | 1450 | 4.13 | 7.07 |
| 60 | 10.8 | 12.8 | 17.1 | 8 | 1430 | 4.10 | 7.02 |
| *Biologically treated ww* | | | | | | | |
| 0 | 20.9 | 25.4 | 31.8 | 6 | 450 | 3.85 | 8.30 |
| 10 | 12.0 | 16.0 | 20.5 | 2 | 380 | 3.98 | 8.69 |
| 20 | 7.6 | 10.1 | 14.2 | 2 | 320 | 4.25 | 8.54 |
| 30 | 3.9 | 5.8 | 9.1 | 2 | 385 | 4.40 | 8.64 |
| 40 | 0.7 | 1.1 | 2.8 | 2 | 365 | 4.13 | 8.50 |
| 60 | 0.5 | 1.5 | 0.2 | 2 | 355 | 3.93 | 8.03 |

[a] pH of raw remaining composite was adjusted to 8.3 prior to commencement of ozonation experiments with 1 M NaOH from its original value 4.1.

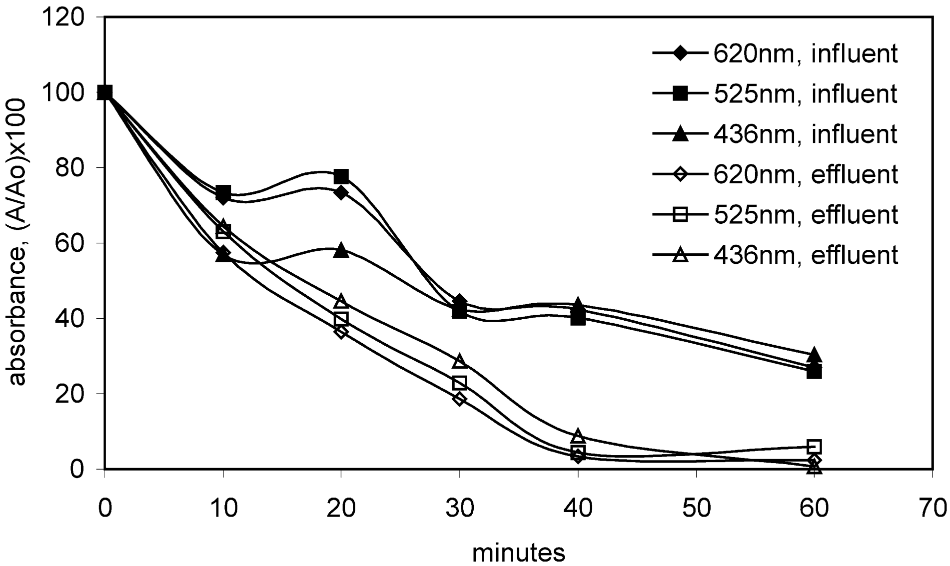


Fig. 1. Remaining absorbance (%) as a function of ozonation time for raw (influent) and biologically treated remaining composite (effluent) wastewater ($C_{O3}$ = 18.5 mg/).

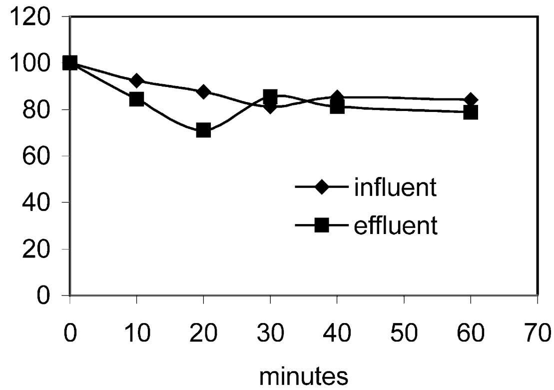


Fig. 2. COD removal as a function of ozonation time ($C_{O3}$ = 18.5 mg/l).

attained. Color reduction was significant for both cases. The achieved COD removal rate was slightly higher for ozonated biologically treated composite wastewater as compared to raw composite wastewater. The differences in removal rates can be attributed to about four times less initial COD concentration of treated remaining composite wastewater resulting in rapid degradation during ozonation period. In addition to that 50% less absorbance values of treated wastewater may result in high COD removal efficiency which might have been caused by previous color and suspended solid removal by biological treatment. Related phenomena is also described in the literature [2,6,8] as the combination of biological (activated sludge) and oxidative treatment of wastewaters from dyeing and finishing processes from several finishing and dyeing plants.

Results shown in Table 2 indicate that the remaining color for the biologically treated sample was virtually 1–2% of its initial value following to the 40 min ozonation. Besides, 70–75% color removal was achieved by means of 60 minutes ozonation of untreated remaining composite wastewater. The decrease in color was much faster during the first 40 minutes of ozonation of remaining composite wastewater. Hence, it can be stated that 30 and 40 minutes of ozonation is sufficient for decolorization of raw and biologically treated wastewater, respectively [32].

The composition of textile wastewater depends on a large extent of the dyed substrates, dyes, textile auxiliaries, and chemicals used, which makes the statement of average values impossible. The quality of segregated effluents varies with the typical processes and chemical used. Routine analysis is necessary in order to monitor the quality of effluents to decide the further reuse or discharge.

As shown in Table 2 the highest GL value of 24 was obtained after 10 min ozonation of remaining composite wastewater. This resulting inhibition can be described as a moderate toxicity referring the categorisation by Wang et al. [29]. With a GL-value of 2, the biologically treated wastewater caused very weak inhibition as it was first treated biologically and then subjected to ozone oxidation for a period of 10 min. This result supports the importance of the combination of biological and oxidative treatment methodology to treat wastewater containing compounds exhibiting slow degradation kinetics for conventional biological processes. Thirty minutes ozone contact time was necessary to obtain 50% reduction in bioluminescence inhibition for raw wastewater whereas, only 10 min ozonation was sufficient to obtain 70% inhibition reduction for biological treated remaining composite wastewater.

Electrical conductivity, which represents the indirect measure of dissolved matter in solution, has not varied notably during both ozone oxidation experiments. A slight decrease was observed in pH with respect to ozonation period. The decrease in pH was comparatively higher for the oxidation study of raw remaining composite wastewater.

## 4. Conclusions

Oxidative treatment was carried out for the remaining composite wastewaters of a woollen textile finishing enterprise before (raw wastewater) and after biological treatment. Although, COD removal rates for both wastewaters were low, high decolorization efficiency was obtained. Forty minutes ozonation of biologically treated wastewater yielded almost colorless effluent. In addition to that significant reduction of the luminescence in the test solutions was attained by ozone oxidation. The results obtained from the study indicated that a combination of biological and oxidative treatment methodology as described above can be proposed for implementation purposes or an industrial scale. In this case, depending on the process requirements the treated wastewater can be used for reuse options in the enterprise.

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