



Decolorization of a Reactive Dye by UV-Enhanced Ozonation

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ABSTRACT

In the present study the treatment efficiency of O_3 and $UV+O_3$ processes were compared for the oxidation of simulated dyebath effluent containing a mixture of a reactive dye (C.I. Reactive Blue 19) and various dye auxiliary chemicals. The color, COD and TOC removal rates were assessed for different processes. The effect of initial dye concentration and presence of sodium hydroxide and sodium carbonate on decolorization kinetics were studied. The decolorization kinetics decreased by increase of initial dye concentration and addition of sodium hydroxide. The addition of sodium carbonate resulted in a lower COD removal. The experimental results showed that ozonation combined with UV irradiation (9-watt low-pressure mercury lamp) was slightly more efficient than ozonation alone in COD removal with no change in color removal efficiencies. At an initial pH of 6.2, bulk temperature of 25 °C, ozone dosage of 55 g/m³ and initial dye concentration of 800 mg/L, the TOC removal efficiency of RB19 reached 19% and 27% after 90 min for O_3 and $UV+O_3$ processes, respectively. Prog. Color Colorants Coat. 3(2010), 1-8. © Institute for Color Science and Technology.

1. Introduction

Textile effluents have high concentrations of organic and inorganic compounds. Wastewater from spent dye baths and dye rinsing operations in the textile industry contain unfixed dyes that may be highly colored and have serious detrimental effects on aquatic habitats. Through new environmental concerns and regulations, pressure is being placed on textile companies to reduce pollutants and reuse process water and chemicals. Chemical coagulation, activated carbon adsorption, photocatalysis, chlorination and ozonation have been studied to

determine their effectiveness at removing dyes from textile wastewater [1-3].

Recent developments in the chemical treatment of dyes in effluents led to improvement of the oxidative degradation of organic compound in aqueous solution, called advanced oxidation processes (AOPs). AOP methods (UV/H_2O_2 , UV/O_3 , UV photocatalyst and Fenton procedures) have been suggested in the recent literatures as potential alternatives for decolorization of textile effluents by generating hydroxyl with high oxidation potential [4-8]. The following mechanisms

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have been proposed for UV enhanced ozonation process [9-12]. The presence of different oxidants in the solution initiates a synergistic effect which can improve dye degradation in the wastewater.



Reactive dyes, which link to fibers through chemical combining, now are widely used in the textile industry. Some contain typical azo-based chromophores combined with types of reactive groups, such as vinyl sulfone, chlorotriazine, trichloropyrimidine, and difluorochloropyrimidine. This property makes these dyes suitable dyestuffs, but it also makes them hard to degrade in wastewater. Reactive azo dyes are of special environmental concern because they are resistant to aerobic degradation and their degradation products under anaerobic conditions, such as aromatic amines, are considered highly carcinogenic [12, 13].

The literature survey indicated that most of the relevant studies of O_3 and UV+ O_3 processes have been focused on azo dyes [14, 15], and little information is available on anthraquinon reactive dyes such as C.I. Reactive Blue 19 [16-19]. In the present work, the

ozonation and UV enhanced ozonation of C.I. Reactive Blue 19 was carried out extensively. The dye was selected due to its high oxidation resistance, high solubility in water, and its non-biodegradability [20]. The aim of this study was to investigate the application of O_3 and UV/ O_3 processes for degradation of the reactive anthraquinon dye (C.I. Reactive Blue 19). The effect of dye concentration and addition of NaOH and Na_2CO_3 on the decolorization and mineralization were studied.

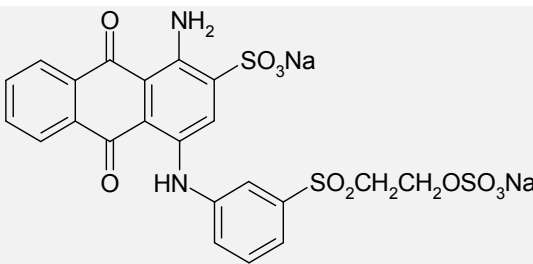
2. Experimental

Commercial C.I. Reactive Blue 19 (RB19) was obtained from Sandal group Ltd. (Pakistan) and used without further purification. The most important physical and chemical properties of this reactive dye are presented in Table 1. Other chemicals, purchased from Merck, were of analytical grade.

The reactor was made from Pyrex glass with a volume of 2000 mL (inside diameter 12 cm, height 15 cm). A UVC lamp (TUV PL-S 9W, Philips) equipped with a quartz tube was located at the center of the reactor vertically and immersed in the dye solution. A schematic diagram of experimental setup can be found elsewhere [15]. The incident UV-light flux inside the reactor was measured by hydrogen peroxide actinometry and it was $2.4 \times 10^{-4} \text{ Einstein.s}^{-1}$ [21].

A peristaltic pump was utilized for mixing the solution and extracting samples. The pH of the solutions was checked using a pH meter (Metrohm 713) and adjusted by adding concentrated H_2SO_4 or NaOH.

Table 1: The most important physical and chemical properties of RB 19.

Chemical structure	
Molecular mass (g/mol)	626.55
C.I. Number	61200
Purity	~60%
Water Solubility	10 g/l
λ_{max} (nm)	595

Decolorization and mineralization of RB 19 by O_3 and UV+ O_3 processes were performed using a 1 L solution containing specified concentration of dye. Solutions were prepared using distilled water to minimize interferences. The initial concentration of RB 19 was generally 200 mg/L. A magnetic stirrer was used for mixing the solution at maximum apparent speed (1100 rpm). Samples were withdrawn from the sample port at certain time intervals and analyzed immediately for decolorization and mineralization. Decolorization of dye solution was measured with the aid of a UV-Vis Lambda 25 Perkin-Elmer spectrophotometer via the decrease in absorbance at 595 nm.

Ozone was produced from dry and pure oxygen (99.99 %) in a commercial ozone generator (Green Technology Co., Iran). The oxygen flow rate was controlled at 0.08 L/min for all experiments using a flow controller (Besta model LZB-3WB, Taiwan). The ozone-oxygen mixture was introduced from the reactor bottom via a diffuser with a cylindrical shaped unit with coarse porosity. Surplus ozone was trapped by gas absorption bottles containing 4-5 % KI solution. The ozone gas concentration was measured in the reactor inlet and outlet with an ozone analyzer (Orbisphere model 3600,

Switzerland).

The COD (chemical oxygen demand) determination was carried out using oxidation with potassium dichromate in sulfuric acid and heating for 2 h at 150 °C according to Hach method no. 8000. The TOC (total organic carbon) tests were carried out according to a close reflux, colorimetric method using a DR/2500 spectrophotometer according to Hach method no. 10128.

3. Results and discussion

3.1. Effect of initial dye concentration on ozonation

In order to study the feasibility of the ozonation process for different concentrations of dye, experiments were carried out at neutral pH, room temperature, and ozone dose of 55 g/m³ by varying the initial dye concentration (200 and 800 mg/L). The effect of RB19 initial concentration on decolorization efficiency is shown in Figure 1. The decolorization of RB19 by ozonation and UV enhanced ozonation are more effective than UV/H₂O₂ process [15]. The decolorization curves of O_3 and UV+ O_3 in different initial dye concentrations almost overlapped implying that the presence or absence of UV radiation hardly affects the decolorization rate [22].

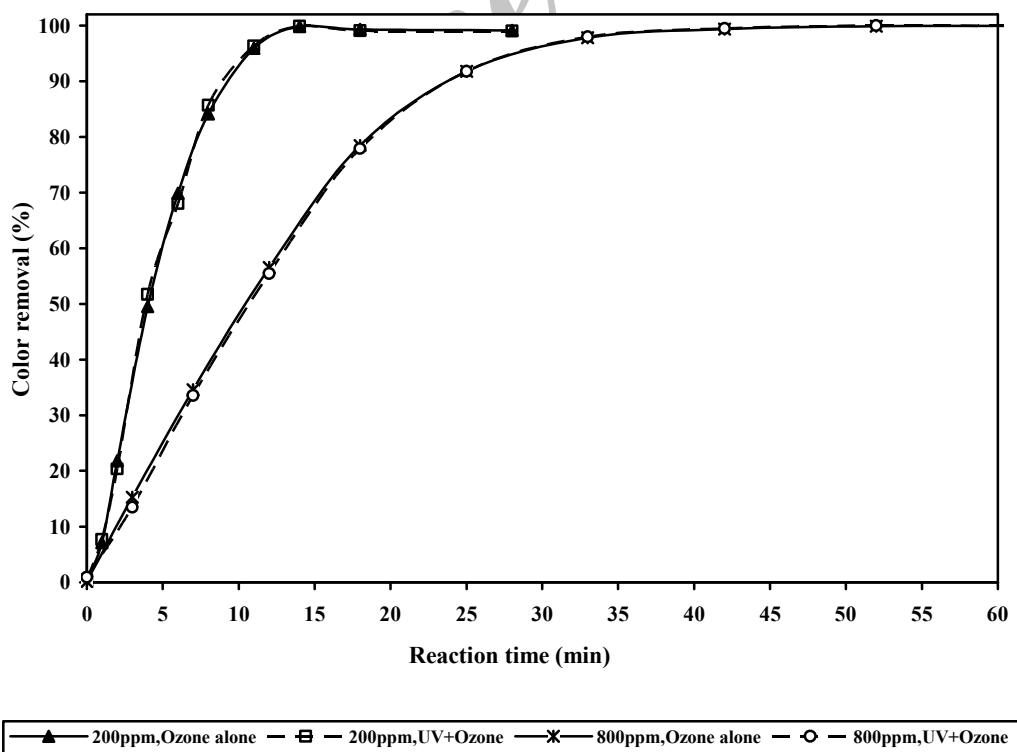


Figure 1: Comparison of O_3 , UV+ O_3 for Color removal at different RB19 initial concentrations (Ozone dose = 55 g/ m³, T = 25 °C, pH=6.5).

It is seen from Figure 1 that by increasing the dye concentration, the decolorization rate is decreased and the complete decolorization is attained more slowly. The reason could be that under the applied conditions the ratio of ozone molecules to dye molecules in the solution decreases with increase of the dye concentration [23]. Increasing the initial dye concentration would cause more ozone to be consumed [24].

In advanced oxidation processes, with an increase in the dye concentration, various intermediates formed upon degradation of the parent dye may interfere with the oxidation. Such suppression would be more pronounced in the presence of an elevated level of degradation intermediates formed upon an increased dye concentration [12]. Thus, the time for complete decolorization would be longer for higher initial dye concentrations.

3.2. Effect of sodium hydroxide addition

In general, ozone oxidation pathways include direct oxidation by ozone or radical oxidation by hydroxyl radical. Hydroxyl radicals are produced from ozone decomposition at high pH values, while the molecular ozone remains as the chief oxidant at low pH values [25]. This indicates that ozone stability decreases with increasing the pH, resulting in generation of secondary oxidants. In acidic pH, the ozone is available as

molecular O_3 and in alkaline pH it decomposes into secondary oxidants which among them hydroxyl radical is most important one. The oxidation potential of ozone decreases in alkaline solutions which indicates the lower solubility and higher decomposition of ozone [26].

The decolorization decreases in the presence of sodium hydroxide in both O_3 and $UV+O_3$ processes as a result of ozone decomposition into hydroxyl radicals (Figure 2), which are less selective but have a higher oxidation potential than ozone [27]. Hydroxyl radicals have a higher oxidizing potential and are less selective than molecular ozone for attacking the dye chromophore, leading to a decolorization decrease and a mineralization increase at high pH values. Thus, pH of the solution plays an important role in ozonation [23, 25, 28]. It should be noted that the dye structure also plays important role here and can affect the decolorization rates by ozone or hydroxyl radical oxidation.

In some research papers [24, 29, 30], it has been observed that decolorization is dependent on the solutions pH; however, others have shown that the decolorization of dye solutions was independent of pH in the range 4-9. The reason for these contradictory results may be explained by the fact that some researchers used buffer solutions to control the pH and others only adjusted the initial pH with a solution of acid or alkali [27].

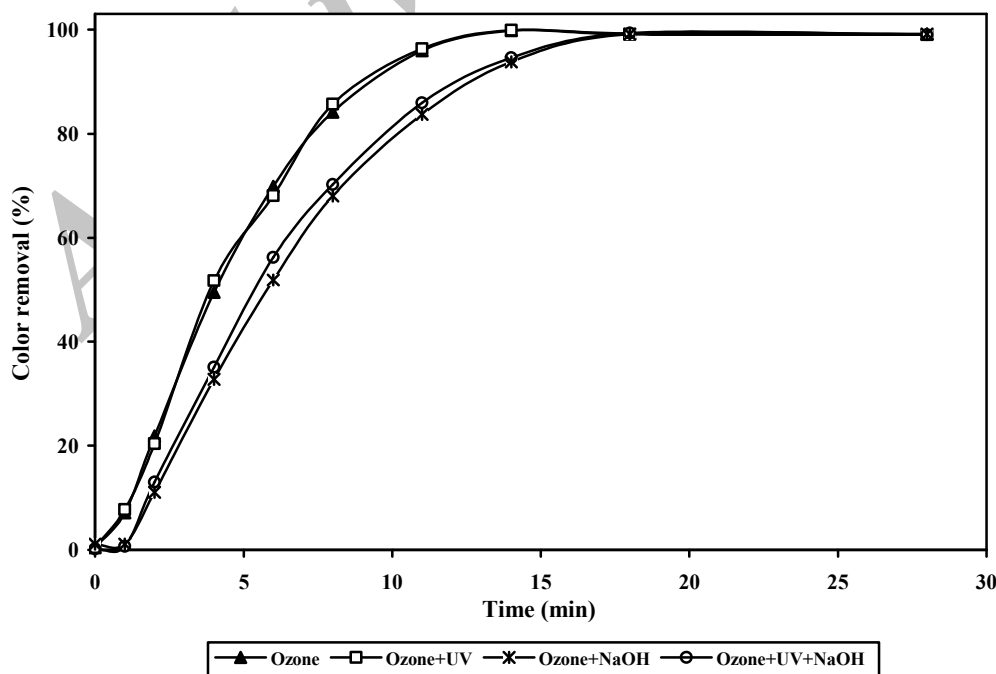


Figure 2: The color removal by O_3 , $UV+O_3$ processes in the presence and absence of sodium hydroxide ($C_{RB19}=200$ mg/L, $C_{NaOH}=1$ g/L, Ozone dose = 55 g/ m^3 , $T=25$ °C).

3.3. Effect of sodium carbonate addition

The decolorization of RB19 (1 L, 200 mg/L) at room temperature and ozone inlet gas concentration of 55 g/m³ has been studied in the presence of sodium carbonate (1 g/L). As can be seen from Figure 3, the addition of Na₂CO₃ does not show any positive or negative effect upon decolorization kinetics. The carbonate species inhibit the decomposition of ozone in both O₃ and UV+O₃ processes. It is significant to note that the decomposition of ozone in wastewater decreases in the presence of materials such as carbonate [25]. It is likely that carbonate is the principal consumer of the hydroxyl radicals. The scavenging effect of bicarbonate also lies in the fact that it reacts with hydroxyl radicals to generate carbonate radicals. These act as a very selective additional oxidation species and which have a much lower reaction rate constant than hydroxyl radicals for oxidation of organic dye [23].

3.4. Dye degradation and mineralization

The results of conventional parameters of O₃ and O₃+UV processes for removal of RB19 in different conditions are shown in Table 2. The pH decrease during ozonation from 6.12 to 3.17 and the conductivity increase from 132 to 466 µS/cm is possibly due to the formation of organic acid anions [6].

By measuring the characteristic wave length at 595 nm, color was removed entirely within 16 min for initial dye concentration of 200 mg/L. The results of absorbance of the ozonated RB19 solution at the

$\lambda=254\text{nm}$ were also recorded and appeared to decrease as ozonation time increased. This suggests that the aromatic structure and/or double bonds were diminished.

Measuring the reduction ratios of COD under different oxidation conditions (about 60% removals) indicated that the oxidation ability of ozone and UV enhanced ozonation processes were not adequate to oxidize all organic carbons into carbon dioxide. Therefore, the smaller organic compounds might be produced along with the oxidation of the target compound in the solution which is more resistant to O₃ and O₃+UV processes. The COD removal yields showed slightly improvement in the presence of UV enhanced ozonation in comparison to ozonation alone. The presence of NaOH decreased the color removal and increased the COD removal possibly because of the formation of hydroxyl radicals which have a higher oxidation potential and are less selective than molecular ozone [31]. The COD, which is a measure of the concentration of all compounds that can be oxidized by the Cr₂O₇²⁻ anion in acidic media, gives a measure of degradation of pollutants and produced intermediates during the dye degradation. Complete removal of the dye is expected to represent the most effective reduction in COD. The fact that the COD reduction in our experiments is low may reflect the decomposition of dye molecules to small organic substances via ozonation process [27]. The lower COD removal (about 60 %) compared with the color removal can be explained by incomplete oxidation of organic materials [24].

Table 2: Conventional parameters during the O₃ and O₃+UV processes
(C_{RB19}=200 mg/L, Ozone dose = 55 g/ m³, T = 25 °C).

Processes	pH _{initial} → pH _{final}	Dye removal (%) (after 10 min)	COD removal (%) (after 30 min)
O ₃	6.12 → 3.17	84.1	57.8
O ₃ + NaOH (1g/L)	12.44 → 12.32	68.9	58.4
O ₃ + Na ₂ CO ₃ (1g/L)	10.89 → 10.05	83.5	55.9
UV+O ₃	6.12 → 3.26	85.7	60.4
UV+O ₃ + NaOH (1g/L)	12.43 → 12.26	70.2	61.4
UV+O ₃ + Na ₂ CO ₃ (1g/L)	10.87 → 10.03	83.1	56.2

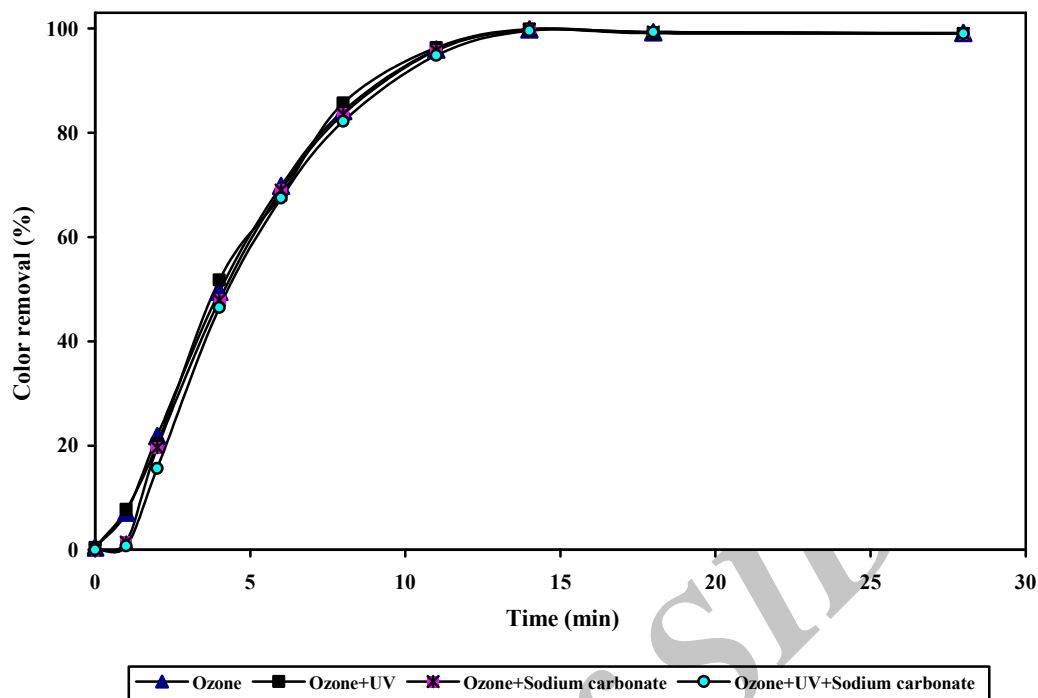


Figure 3: The color removal by O_3 , UV/ O_3 processes in the presence and absence of sodium carbonate ($C_{RB19}=200$ mg/L, $C_{Na_2CO_3}=1$ g/L, Ozone dose = 55 g/ m^3 , $T = 25$ °C).

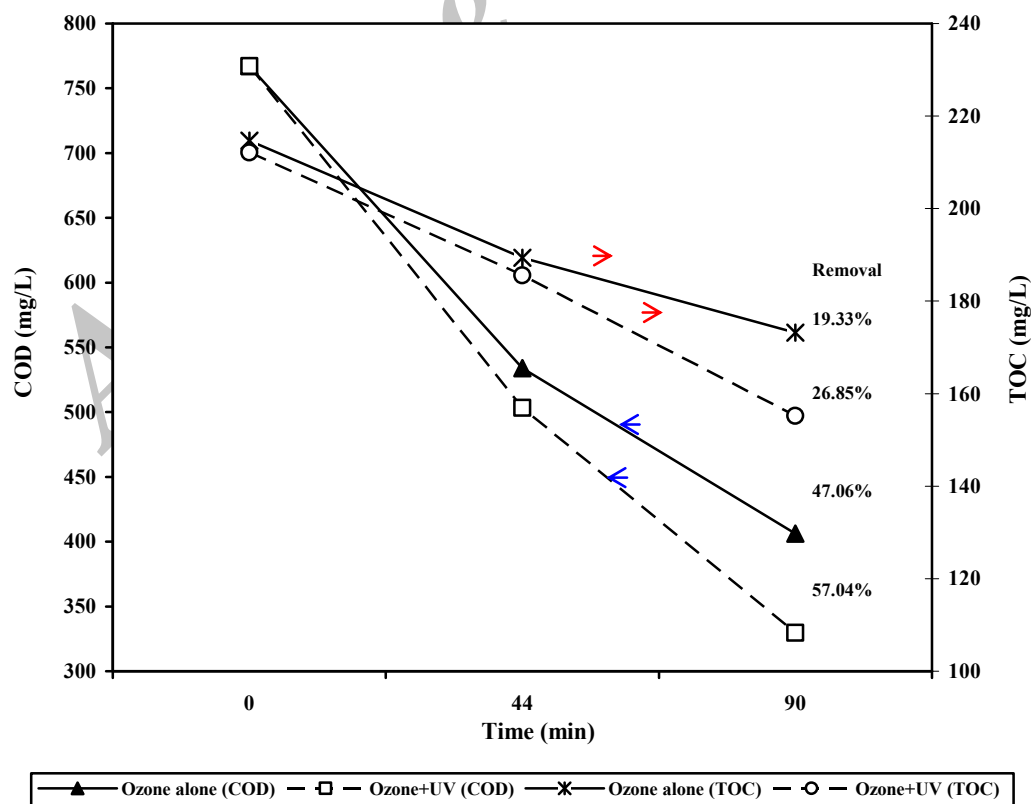


Figure 4: The COD and TOC removal by O_3 , UV/ O_3 processes ($C_{RB19}=800$ mg/L, Ozone dose = 55 g/ m^3 , $T = 25$ °C).

The addition of Na_2CO_3 has no negative effect upon decolorization as can be seen in Figure 3 and Table 2 since color removal can be achieved via both reaction direct and indirect oxidation pathways of ozone. Although ozone molecules decompose readily to hydroxyl radicals at high pH, in the presence of Na_2CO_3 a considerable amount of hydroxyl radicals will be scavenged and wasted by CO_3^{2-} . This will increase ozone life time and there would be no difference in terms of decolorization. However, this will slightly reduce the COD removal as can be seen from Table 2. The same results have been reported in other research papers [32].

The rate of COD and TOC removal of RB19 by O_3 , UV/ O_3 processes is shown in Figure 4. The complete decolorization of RB19 was achieved after 45 min for both O_3 and UV+ O_3 processes. At this stage, the degree of COD and TOC removals were 30 % and 11 % for ozonation and 34% and 13% for UV enhanced ozonation. After 90 min of ozonation, the COD and TOC removals were 47 % and 19 % for ozonation and 57% and 27% for UV enhanced ozonation. This shows the better performance for dye degradation by UV+ O_3 process in comparison to ozonation alone. The UV+ O_3 in comparison to ozonation alone can produce more hydroxyl radicals and is more efficient for mineralization.

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4. Conclusions

Ozonation and UV enhanced ozonation are highly efficient in the decolorization of RB19 solutions. The increase of initial dye concentration increases the time for complete color removal. The ozonation in combination with UV irradiation (9-watt low-pressure mercury lamp) does not show notable differences in decolorization rate and efficiency; but, it has an enhanced effect on the COD and TOC removals. The partial reduction of COD and TOC represents the production of small organic molecular fragments and incomplete mineralization for O_3 and UV+ O_3 processes. In the presence of sodium hydroxide color removal rate slightly decreases and the COD and TOC removals show slightly improvement which can be explained by ozone decomposition into secondary oxidants such as hydroxyl radicals which is stronger oxidant and less selective. In contrast, sodium carbonate acts as a hydroxyl radical scavenger and increase ozone life time and there would be slightly decrease in COD removal with no difference in terms of decolorization rates.

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