Decolorization of industrial wastewater by ozonation followed by adsorption on activated carbon

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ABSTRACT

The decolorization of industrial wastewater containing direct dye (Drimarene Red CL-3B) by advanced oxidation process using ozonation in a semi-batch bubble column reactor followed by granule activated carbon (GAC) adsorption process was studied. The effect of initial dye concentration, ozone concentration, pH and ozone-air flow rate on the rate of dye decolorization were investigated. It was found that the rate of dye decolorization increases with increasing ozone concentration, ozone-air flow rate, and pH but decreases with increasing initial dye concentration.

This study is a hybrid system conducted in combination between ozonation process and GAC adsorption to reveal higher and efficient removal of color and TOC. The process started with ozonation for efficient and rapid decolorization of dyeing wastewater, followed by GAC adsorption process to gain efficient removal of color and TOC. The adsorption process was found to be very efficient in removal of ozonation residual TOC, in view of high TOC removal, up to 37% TOC removal was obtained.

Numerical correlation using regression analysis for decolorization time with the operating conditions of the ozonation process were presented.

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1. Introduction

The public demand for color-free waste discharge to receive water and the tougher color standards have made decolorization of a variety of industrial wastes a top priority. Unfortunately, with the complicated color-causing compounds, the decolorization of these wastes is a difficult and challenging task [1,2]. The major pollutants in textile wastewater are higher suspended solids, TOC, color, and other soluble substances. The release of these colored wastewaters in the environment is a considerable source of non-aesthetic pollution and eutrophication [3,4].

The advanced oxidation processes such as ozonation, UV/H_2O_2, UV/O_3 have proved to be powerful tools that are widely used to treat organic contaminants into carbon dioxide and water [5]. The decolorization ability of ozonation process for dye wastewater is receiving growing attention in view of the fact that ozone and hydroxyl radicals (OH) generated in the aqueous solution are able to open the aromatic ring [6–8]. However the industrial applications of ozonation have been limited by the high production cost of ozone and the low ozone utilization due to poor mass transfer rate of ozone [9]. This calls for more research to improve the process. The combined catalytic and non-catalytic ozonation of dyeing wastewater have been investigated by various researchers and found to be more efficient than only ozonation for the decolorization of dye wastewater [10–13]. Furthermore, it has been documented that color removal using ozonation process from textile wastewater is depended on dye concentration, as higher initial dye concentration of textile wastewater causes more ozone consumption [14–16]. Moreover according to Arslan and Balcioglu [17], 40–60 min ozonation of bio-treated textile wastewater yielded 99% of decolorization efficiency. Previous researchers documented that the rate of dye oxidation increased slightly with increasing solution pH [15,18]. Arslan and Balcioglu [17] documented that high color removal of simulated reactive dye bath effluent was achieved at pH 12 when using ozone concentration of 2340 mg/l. Moreover, According to Koch et al. [19] ozonation of the hydrolyzed dye (Reactive Yellow 84) decreased as solution pH decreased from 6.1 to 3.2 when ozone concentration was 18.5 mg/l. Konsowa [16] who used O_3 to decolorize direct fast red 8B dye from a textile waste solution, documented 32% reduction in the decolorization time when the pH changed from 2 to 12. It is also reported that the TOC destruction by ozonation was not high during the process of decolorization, since only 7–37%, as max of TOC removal from the wastewater was obtained by ozonation [20,21]. In view of this result it is highly

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desirable to use extra measures to reduce TOC of the ozonated dye solution.

The main aim of the present work is to study the factors affecting the rate of decolorization of a synthetic waste solution containing a water-soluble direct dye (Drimarene Red CL-3B) by ozonation. The present study also explores the possibility of using granular activated carbon adsorption after ozonation as a complementary measure to further reduce the TOC of the ozonated dye solution. The study was conducted using Plexi-glass bubble column followed by activated carbon adsorption process in a simple agitated vessel. Numerical correlations using regression analysis for decolorization time with operating conditions of the process were presented.

2. Material and methods

The experimental setup shown in Fig. 1a consists of an air dryer consisting of two columns which are filled with high adsorption molecular sieve and two compressors working alternatively, laboratory ozonizer model 301.7 (Erwin Sander) to generate ozone and Plexi-glass bubble column reactor. The reactor had a glass column of 10-cm diameter and 50-cm height with pyrex sintered glass at the bottom through which O_3 was bubbled through the dyeing wastewater. The ozonated dyeing wastewater was subjected to GAC adsorption in a batch stirred tank reactor of 15 cm diameter. The tank was stirred by 45° pitched 4 blades turbine impeller mounted on a shaft which was driven by a variable speed motor. In order to eliminate swirl motion, the tank was fitted with 4 baffles (Fig. 1b).

Before each run the bubble column was filled with 2000 cm³ of dye wastewater. Compressed air was allowed to pass through the ozonizer where ozone formation takes place. The outlet stream from the ozonizer containing O_3, O_2, and N_2 mixture was allowed to pass through tygon tubing connected to the bottom of the bubble column. The gas flow rate was controlled by a needle valve and was measured by air flow meters, the gaseous ozone concentrations were verified by iodometric method using potassium iodide solution [22]. A sample of the decolorized wastewater was taken and analyzed for TOC and the decolorized wastewater is subjected directly after ozonation to GAC adsorption for 30 min [23,24] in a batch stirred tank reactor. Temperature was ambient temperature (20 ± 1 °C) during all experiments. Finally GAC treated wastewater sample was taken to measure its total organic carbon (TOC). The activated carbon used was Norit Nederland B.V. – NRS CARBON GA (0.5–2.5), iodine number 850, total surface area 975 m²/g, apparent density 500 kg/m³, and particle size 0.5–2.5 mm.

The dye concentration time data during decolorization was followed using spectrophotometer. The dye used in the present work was water soluble (Drimarene Red CL-3B) having the following structure:
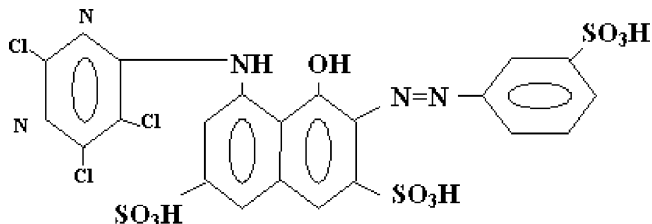
3. Results and discussion

Fig. 2 represents the change of dye concentration with time at different initial dye concentration.

Fig. 3 shows the effect of initial direct dye concentration (150–600 ppm) on the decolorization time. It was found that decolorization time increases with increasing initial dye concentration
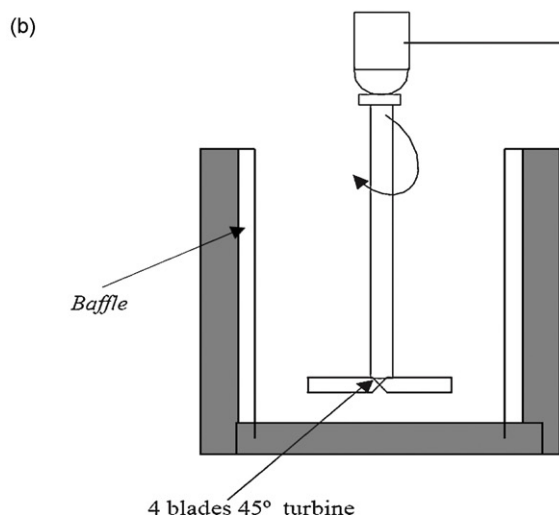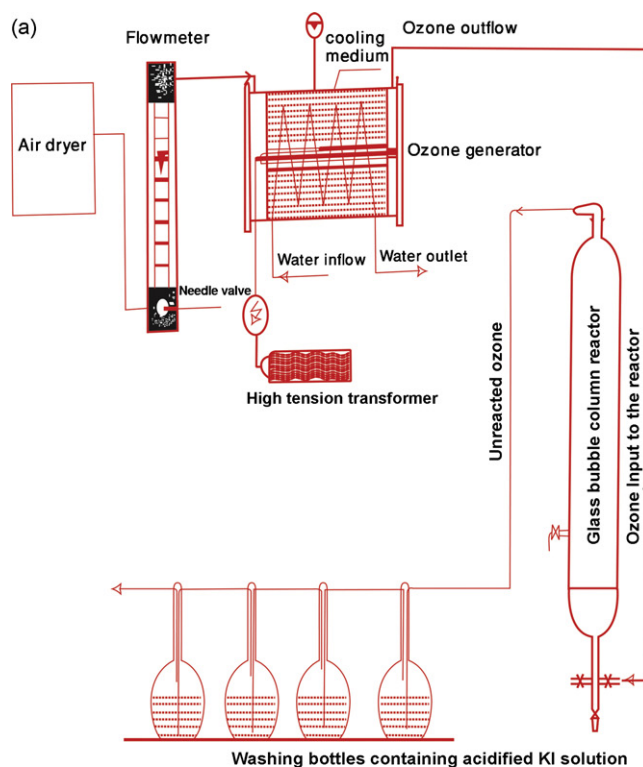

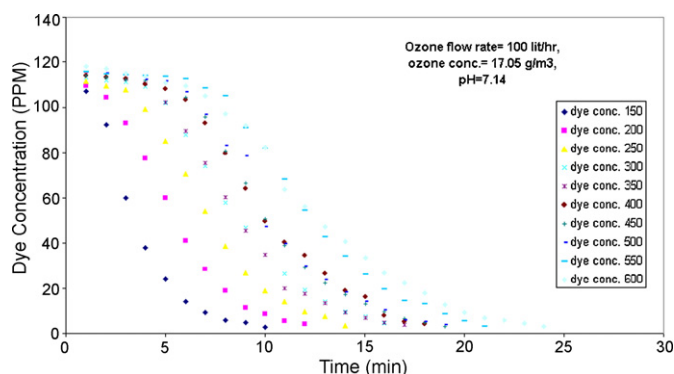**Fig. 1.** Apparatus used in (a) ozonation and (b) adsorption.

Fig. 2. Concentration vs. time for different direct dye concentration.

Fig. 3. Effect of initial dye concentration on decolorization time.

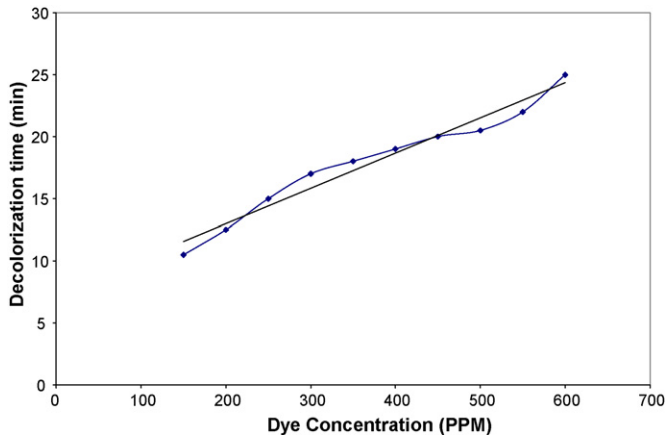**Fig. 5.** Dye concentration vs. time at different ozone concentration.

Fig. 6. Effect of ozone concentration on decolorization time.

and this is due to the decrease in the rate of dye oxidation as the ozone is no longer present in excess. Furthermore the reduction of available ozone at high dye concentrations favors the partial oxidation of the dye and retarding the oxidation of intermediate compounds [25,26]. The time for complete decolorization ranges from 8 to about 20 min depending on dye concentration while 150 ppm dye needs 8 min and 600 ppm dye needs 20 min for complete decolorization, i.e. the rate of dye removal (r) decreases with increasing dye concentration, this in consistent with the law of mass action [27]:

$$r = \frac{dc}{dt} = kC_d^m C_o^n \tag{1}$$

where k is the rate constant (cm/s), C_d the dye concentration, and C_o the ozone concentration; in view of the complexity of the reaction it was difficult to determine m and n.

The data in Fig. 3 was found to fit the following equation:

$$T_d = 0.0284C_d + 7.2909, \quad R^2 = 0.96 \tag{2}$$

where T_d is the decolorization time (min) and C_d is the initial dye concentration (ppm).

Fig. 4 shows the relation between the TOC after ozonation, the TOC remaining after adsorption process and the %TOC removed by GAC adsorption. It is clear from the figure that the adsorption process is efficient in removal of TOC in view of a higher value of TOC removal of 37% at initial dye concentration of 150 mg/l. The percent removed TOC was found to decrease with increasing initial dye concentration and this may be ascribed to the limited adsorption and exchange capacity of the GAC at constant GAC to wastewater ratio.

Fig. 5 shows the decrease of the dye concentration with time at different ozone concentration. The rate of dye removal increases with increasing ozone concentration in the gas bubbles, this is in consistent with the law of mass action [Eq. (1)], the theory of mass transfer and gives us a good indication in view of mass transfer that this reaction is limited by the mass transfer step [28].
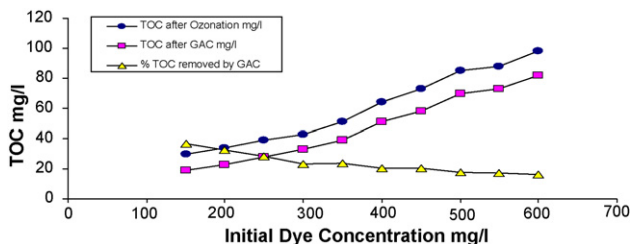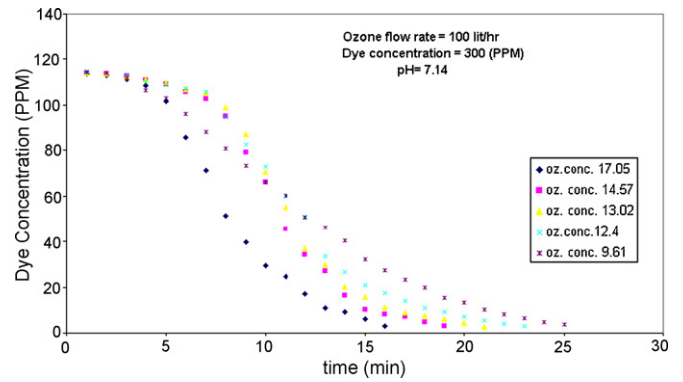
Fig. 6 shows the effect of ozone concentration on the decolorization time. It is clear that the decolorization time decreases linearly with increasing ozone concentration.

As the ozone concentration increased from 9.61 to 17.02 g/m³ (ppm) the decolorization time of 300 ppm (initial dye concentration) reduced by about 41.07%. This result is consistent with the theories of mass transfers [29]. According to these theories, as ozone concentration increases in the air bubbles, the driving force for the transfer of ozone to the dye solution increases with a consequent increase in ozone concentration in the solution and the rate of dye oxidation.

The data fit the following equation:

$$T_d = -1.5564C_o + 42.747, \quad R^2 = 0.98 \tag{3}$$

where T_d is the decolorization time (min) and C_o is the ozone concentration (ppm).

Fig. 7 shows the relation between TOC after ozonation and TOC after GAC adsorption and the percent TOC removed with reference

Fig. 4. Total organic carbon (TOC) of ozonated wastewater for different initial dye concentration.

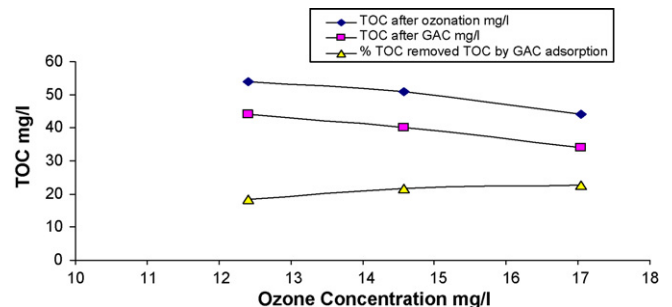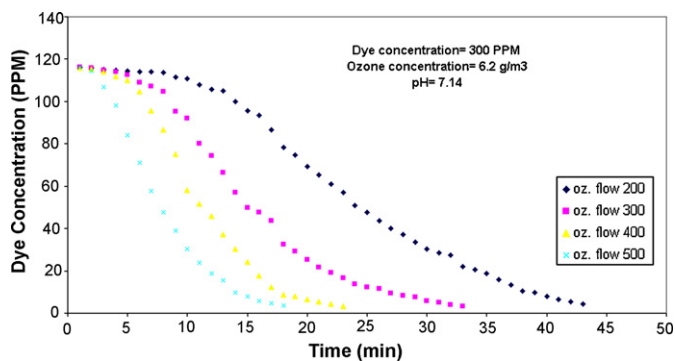**Fig. 7.** Total organic carbon (TOC) vs. ozone concentration.

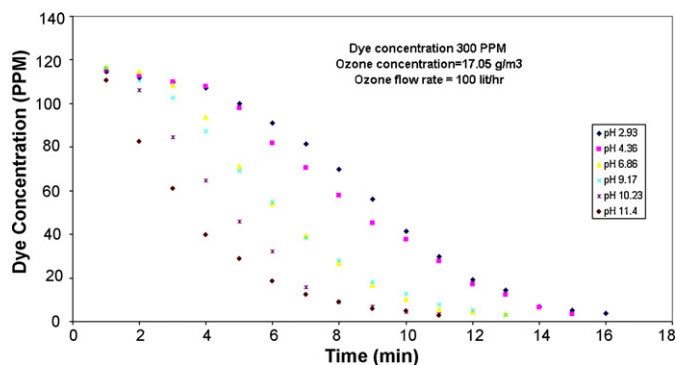**Fig. 8.** Dye concentration vs. time at different ozone flow rate.

Fig. 10. Dye concentration vs. pH at different ozone concentration.

to TOC after ozonation. It is clear from the figure that the adsorption process efficiency in TOC removal ranges from 19% at ozone concentration of 12.4 g/m^3 to 23% at O$_3$ concentration of 17.05 g/m^3. The increase in %TOC removal at different O$_3$ concentrations may be ascribed to the increase in the mineralization rate by ozonation process.

Figs. 8 and 9 show the effect of ozone-air flow rate on the decolorization time. The decolorization time decreases with increasing gas flow rate by a maximum of 58.5%.

The data in Fig. 6 fit the following equation:

$$T_d = -0.0915F_o + 63.9, \quad R^2 = 0.98 \tag{4}$$

where T_d is the decolorization time (min) and F_o is the ozone-air flow rate (l/h).

The decrease in decolorization time with increasing gas flow rate (V_g) is attributed to the enhancement of the rate of mass transfer of ozone from air-ozone bubbles to the liquid phase as a result of: (1) The ability of the rising bubbles to induce radial momentum [30] beside the eddies generated in the wake of the rising bubbles reduce the diffusion layer thickness that surrounds the bubbles [31,22] with a consequent increase in the rate of mass transfer of O$_3$ from the gas bubbles to the solution; (2) increase in the gas hold up (ε), according to the equation [32]:

$$\varepsilon \alpha (V_g)^n \tag{5}$$

where n ranges from 0.7 to 1.2 in the bubbly regime which prevails at a relatively low gas flow rate. The increase in the gas holdup increases the interfacial mass transfer area with a consequent increase in the volumetric mass transfer coefficient KA of O$_3$ dissolution in the solution; (3) As the gas velocity increases, solution entrained in the wake of the gas bubbles is recycled downward at the walls of the column. This improves the mix-
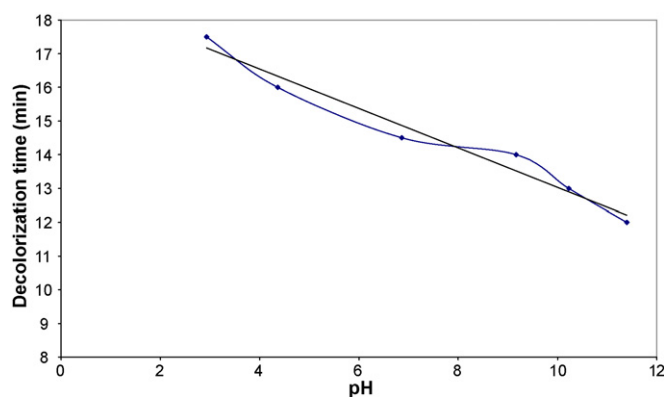

Fig. 11. Effect of solution pH on decolorization time.

ing conditions inside the batch bubble column with a consequent increase in the rate of mass transfer of O$_3$ dissolution in the solution [33].

Figs. 10 and 11 show the effect of different solution pH on the dye concentration and decolorization time. The decolorization time decreases with increasing pH of the solution by a maximum of 31.4%. The data fit the following equation:

$$T_d = -0.5847\,\text{pH} + 18.881, \quad R^2 = 0.97 \tag{6}$$

where T_d is the decolorization time (min).

According to Chu and Ma [34] and Shu [35], the pH affects the decolorization process by affecting the rate of ozone decomposition and ozonation kinetics. The rate of ozone decomposition is favored by formation of hydroxyl radicals at higher pH values. So the increase in pH value enhances the mineralization during the ozonation process as shown from Fig. 12.

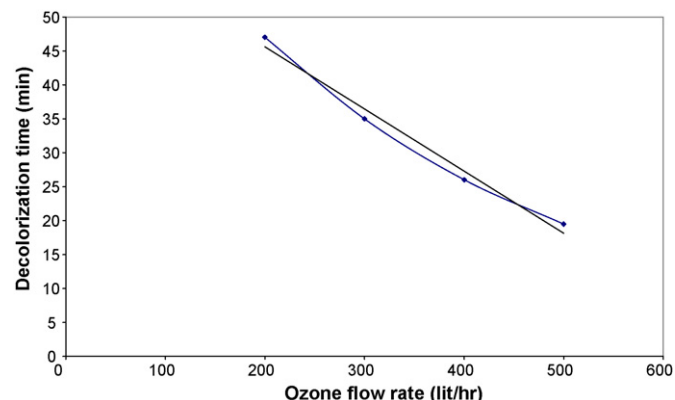Fig. 12 shows that alkaline medium will reduce the TOC.

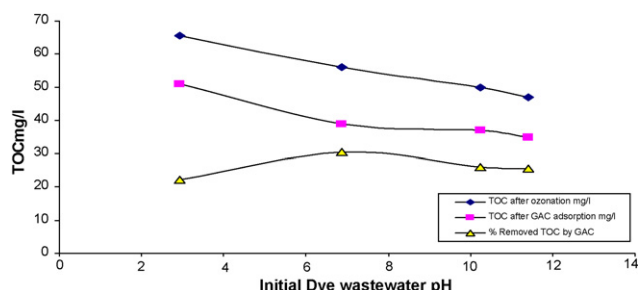**Fig. 9.** Effect of ozone flow rate on decolorization time.

Fig. 12. Total organic carbon (TOC) vs. pH.

Effect of different variables on the decolorization time lead to the following numerical overall correlation using regression analysis:

$$T_d = 60.046 - 0.58728\,\text{pH} - 0.05393 F_o - 2.64558 C_o$$
$$+0.0341 C_d, \quad R^2 = 0.88 \tag{7}$$

This equation can be used to predict the decolorization time in terms of the operating conditions (initial dye concentration, ozone-air flow rate, ozone concentration, and pH of the dye solution).

The aforementioned beneficial effect of post ozonation GAC adsorption in reducing the TOC calls for future detailed study to optimize the GAC adsorption parameters such as particle size, bed height, solution flow rate, using a continuous packed column instead of the simple batch agitated vessel used in the present study. It is expected that the TOC will be reduced by decreasing particle size and solution flow rate, and increasing bed height. As higher bed height and lower particle size will increase the specific surface area of the activated carbon which provide more fixation binding sites for adsorption while at a higher flow rate, the adsorption capacity will be lower due to insufficient residence time of the solute in the column and diffusion of the solute into the pores of the adsorbent [36]. Therefore, the performance of the activated carbon bed could be enhanced by applying a higher bed height or a lower solution flow rate.

4. Conclusion

The study of direct dye (Drimarene Red CL-3B) decolorization by ozonation followed by granular activated carbon adsorption has revealed that:

(1) The integrated treatment of textile waste solution by ozone oxidation followed by carbon adsorption is a promising process which needs further studies on a continuous pilot plant scale to delineate the effect of factors such as relative ozone and wastewater flow rates and the role of packing the bubble column on the process efficiency.

(2) Increasing ozone concentration, gas flow rate and pH was found to reduce the decolorization time and increasing initial dye concentration was found to increase the decolorization time. A methodology was developed to calculate the deodorization time as function of initial dye concentration, ozone dose, pH, and ozone-air flow rate by regression analysis. An overall numerical correlation was developed, which can be used to predict the decolorization time in terms of the operating conditions:

$$T_d = 60.046 - 0.58728\,\text{pH} - 0.05393 F_o - 2.64558 C_o + 0.0341 C_d$$

(3) Adsorption on active carbon after O_3 oxidation reduced the TOC by a maximum of 37%.

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