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Optimization of ozonation in the removal of Basic Blue 41 in aqueous solution

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This study involved the use of ozonation to decrease the content of a commercial basic dye, Basic Blue 41 (BB41), in synthetically produced wastewater. The optimization of this process was examined by assessing the chemical oxygen demand (COD) outcomes. Experiments were conducted in a 7-L reactor utilizing a batch bubble column of laboratory size. This study focused on investigating the optimal operating conditions by examining experimental factors such as pH, ozone dose, and reaction time. At pH 10, the COD of the basic dye wastewater decreased by 79.82%. Additionally, a significant reduction in color took place within a period of 9 min. The process of ozone depletion in the reaction medium continued for 16 min, and most of the degradation processes (94.56%) were successfully completed during this time. The ozonation kinetics were investigated and found to fit pseudo-first-order. The research showed that the rate constant exhibited a positive correlation with the applied ozone dosage and basic pH conditions and showed a logarithmic decrease with the initial dye concentration. These findings indicate that ozonation is more efficient for basic dyes when conducted under alkaline pH conditions than under acidic or neutral pH conditions.

Keywords: Basic blue 41; Ozonation; Decolorization; Optimization; Wastewater; Basic dyes

INTRODUCTION

The textile sector significantly contributes to global economic growth and provides job opportunities for a large workforce. While the textile sector may meet environmental rules in many nations, it is now facing stricter constitutional pollution laws that demand higher-quality wastewater treatment. Physical, biological, and chemical techniques can partially eliminate wastewater pollutants. However, dyes present a challenge since they cannot be adequately broken down and are not easily eliminated from wastewater using traditional treatment systems.

The advanced oxidation process is a promising alternative for removing color and reducing the high wastewater levels generated by textile dyeing and finishing wastes. The decolorizing impact of ozone on dyes in water is due to its ability to react with unsaturated dyes to form ozonides. These ozonides then undergo rapid hydrolysis, causing the molecules to break down. Decolorization of wastewater using O_3 depends on ozone dosage, solution temperature, reaction time, and solution pH. Ozonation is an ideal method for removing dyes from aqueous solutions because of its quick reaction time, cost-effectiveness (excluding installation expenses), and high efficiency. Nevertheless, it is important to note that ozone typically generates harmless substances that transform into carbon dioxide (CO_2) and water (H_2O), depending on the prevailing circumstances.

Azo dyes are the predominant category of artificial colorants, accounting for approximately 60-70% of all such dyes. The azo group (-N=N-) is a defining characteristic of these dye groups, along with aromatic systems and auxochromes (OH, SO_3, etc.). The combination of these chemical groups in the dye molecules presents a complicated challenge for their removal from wastewater. Several techniques employed to remove color from dyes rely on physical or chemical procedures. These methods [1] encompass membrane filtering [2-4], electrochemical technology [5, 6], and advanced oxidation processes (AOP), such as photochemical oxidation [7], photocatalysis [8, 9], and ultrasonic waves [10].

Dyes with cationic properties of their molecules are referred to as cationic or basic dyes. Basic Blue 41 (BB41) is a cationic azo dye widely used in dyeing nylon, acrylic, and woollen textiles. BB41 is highly resistant to degradation *via* chemical oxidation, photocatalysis, and biodegradation [11]. Compared to anionic dyes, cationic dyes exhibit higher toxicity and can easily penetrate cells by accumulating in the cytoplasm because of interaction with the negatively charged surfaces of cell membranes. Hence, the removal of these dyes before they are emitted into wastewater has emerged as a significant concern.

Several studies have been published on the removal of color from Basic Blue 41 waste. Abbasi and Asl [10] on the sonochemical degradation of

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nano TiO_2 and H_2O_2; Bouhelassa *et al.* [12] on the process of optimizing the photocatalytic decolorization of BB41 in a solar photoreactor prototype; and Humelnicu *et al.* [13] have studied the removal of BB4 from a water-based solution by an adsorption process using natural zeolite tuff in a batch method. Saravanan *et al.* [14] conducted research on the biological decolorization process of BB41 using composts enriched with beneficial microorganisms.

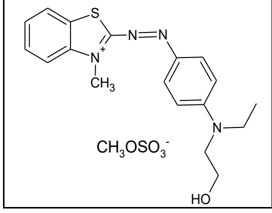
When ozone gas encounters organic substances, it enters into molecular or radical reactions. The degradation rate of ozone depends on pH and initial dye concentration. Under alkaline conditions, ozone rapidly decomposes, producing hydroxyl radicals and some other types of radicals in solution. Under acidic conditions, it can enter direct electrophilic reactions with organic substrates. Ozone is frequently used to decolorize dye wastes due to its capacity to react selectively with conjugated double bonds normally responsible for color. Molecular reactions of ozone can show selectivity and occur mostly through electrophilic attack; however, they can also proceed *via* nucleophilic or oxygen transfer pathways. Electrophilic attacks occur at sites with a significant concentration of negative charges, including atoms such as N, P, O, and S, as well as molecules with many bonds such as -C=C- or -N=N-. It can directly react with molecules containing functional groups such as $–OH$, $–CH_3$, $–OCH_3$ and $–NH_2$ at the ortho- and para- substitution positions. Research has shown that the molecular ozone reaction mechanism is responsible for partial oxidation [15, 16]. The electron-rich chromophoric azo linkage is susceptible to direct attack and degradation by ozone, leading to immediate reduction of color. This process does not require the breakdown of bonds into hydroxyl radicals as a secondary oxidant [17-19]. Various variables, such as pH, contact time, ozone amount, and dye properties, affect the effectiveness of ozone in decolorizing wastewater dyes.

This study includes the relationship between varying ozonation time (ranging from 0 to 120 min), initial dye concentration (ranging from 150 to 600 mg/L), and ozone concentration (ranging from 4.21 to 24.03 g/m^3). The effects of various factors, including initial pH (ranging from 2 to 12) depending on the concentration and removal of the dye, were evaluated. Efficient degradation of BB41 was achieved by maximizing both COD and color removal. The pH of the dye solutions was observed to change over time as the initial dye concentrations changed.

EXPERIMENTAL

The azo dye Basic Blue 41 (Table 1), along with all other chemicals, was acquired from Sigma-Aldrich.

Table 1. Characteristics of the azo dye studied in this work.

Disperse Dye	Formula	CAS No
C.I. Basic Blue 41 	$C_{20}H_{26}N_4O_6S_2$	12270-13-2

The dye solution’s color was quantified using a previously established integration approach [19]. This technique entailed measuring the absorbance of a sample across a range of wavelengths from 200 to 800 nm and calculating the total area under the absorbance curve. The integrated area is measured in integrated absorbance units (IAU), which are directly correlated to the color of the sample. The integration approach is less complex compared to the tristimulus filter method used by the American Dye Manufacturers Institute (ADMI), however, studies have demonstrated that both methods yield comparable outcomes [20, 21]. The indigo technique was used to assess the quantity of dissolved ozone in the research.

Figure 1 depicts the Fischer 502 model ozone generator, which is a laboratory-scale device. It consists of a cylindrical column reactor with a volume of 2 L, measuring 5 cm in diameter and 110 cm in height. Additionally, the setup includes a dye solution reactor with a capacity of 5 L, a dosimeter, washing bottles, oxygen gas, a gas cylinder, peristaltic pumps, and a temperature control unit. The temperature was maintained at a constant level of 20±1°C for all trials. Various pH values were utilized to conduct ozonation reactions to examine their impacts. The pH was regulated by adding 1 M H_2SO_4 and 1 M NaOH. At 15-min intervals, samples were extracted from the reactor and the concentrations of the dyes in the solutions were measured using the Agilent 8453 spectrophotometer.

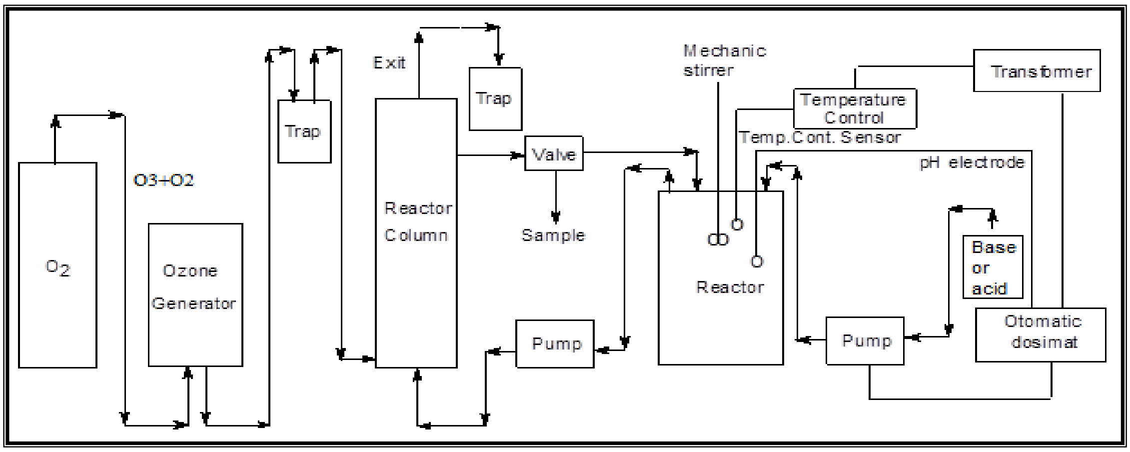


Figure 1. Schematic diagram of the bench-scale reactor system.

Decolorization

The assessment of dye removal was conducted by analysing the reduction in the maximum wavelength using a UV-Vis spectrophotometer. The percent removal values of dyestuffs were computed using Equation 1.

$$Dye\ removal(\%) = \frac{(Abs(i)-Abs(f))}{Abs(i)} = x\ 100 \qquad (1)$$

Abs (i): Absorbance value of the dyestuff at its maximum wavelength.

Abs (f): Absorbance value at the maximum wavelength at the end of the time after the adsorbent is added to the dyestuff.

A rubber tube was used to send ozone that hadn't been broken down from the top of the column reactor to the washing bottles that held 2% KI solution.

$$O_3 + 2KI + H_2O \rightarrow I_2 + 2KOH + O_2 \qquad (2)$$

As we did in earlier studies, we found out how much unused ozone there was by titrating iodide with $Na_2S_2O_3$ while a starch indicator was present. [16, 19, 22-26] The tests were done with an ozone air flow rate of 120 L/s because a high ozone flow rate and concentration are needed to treat wastewater effectively with ozone.

- *Decolorization kinetics of BB41.* Kinetic study is an important part of the ozone method to determine how well contaminated wastewater is treated. When hydroxyl radicals form, they consume the starting molecule and existing intermediates. If the ozone source is strong or the ozone concentration at the contact point remains the same, the oxidation rate follows the first-order dynamics of the decomposed organic matter concentration. This ratio is given in equation [3]:

$$-[C_{dye}] / dt = k[C_{dye}] \qquad (3)$$

To study the ozonation of dye solutions, the dye content (C_{dye}) and the observed rate constant (k) were used [22-26]. Multiplying the intrinsic rate constant by the dissolved ozone concentration (C_{ozone}) gives the apparent rate constant (k):

$$k = -0.2461 \times C_{BB41}^{-0.5459} \qquad (4)$$

Figure 2 shows that as the applied ozone dose (D_{ozone}), temperature, and k increased, the initial dye concentration logarithmically decreased.

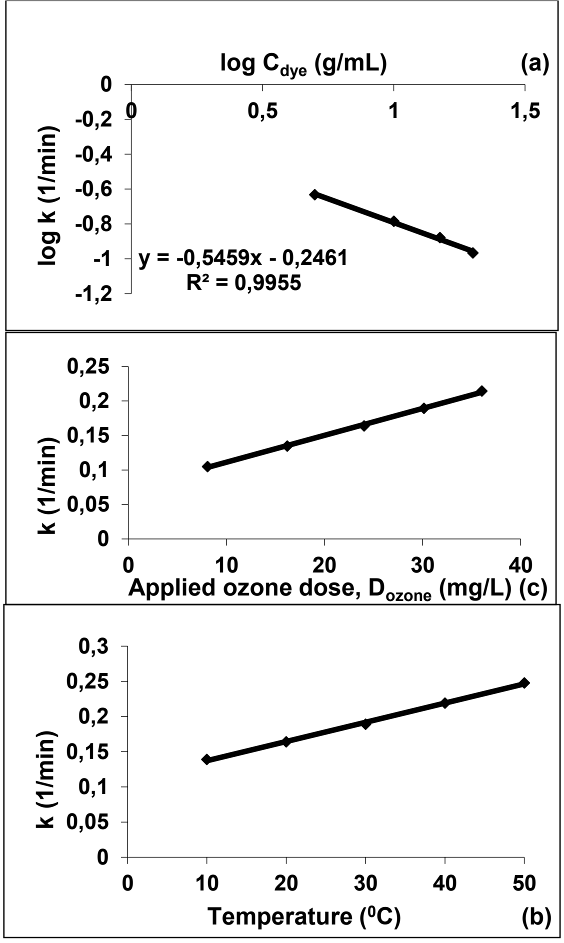


Figure 2. Dependence of the apparent rate constant of decolorization k on initial dye concentration, applied ozone dose and temperature for BB41. **(a)** D_{ozone} = 24,03 mg/L.min, T = 20 ^{0}C **(b)** C_{dye} = 300 mg/L, T = 20 ^{0}C **(c)** C_{dye} = 300 mg/L, D_{ozone} = 24,03 mg/L.min

The units for k and C_{dye} are given as L per min and g per L, respectively. It is important to observe that the rate constant that is observed, rather than the actual rate constant, varies with the initial concentration while keeping the temperature constant. This is because the actual rate is determined solely by the temperature. It is believed that the decrease in k is a result of the increased formation of intermediate compounds caused by the higher C_{dye} concentration. As the initial dye concentration increased, the consumption of ozone by these intermediates resulted in a decrease in C_{ozone}. Due to this, the rate constant appears to decrease as the dye concentration increases. The apparent rate constant and initial dye concentration in this study show a logarithmic relationship, which aligns with the findings of our previous studies [22-26].

Observing Figure 2, one can see that k rises as D_{ozone} and temperature increase. This can be attributed to the higher concentration of dissolved ozone. Decolorization happens more quickly with a higher amount of ozone applied, and the rate constant increases at higher temperatures. Table 2 presents the pH and corresponding k value for the dye under investigation. For further experiments, it was found that a basic pH environment yielded higher rate constant values, as indicated in Table 2.

Impact of initial solution pH on COD

At the start of the ozonation process, a volume of 7000 mL of BB41 solution with a concentration of 300 mg/L was introduced into the column. The experiment began with the introduction of ozone gas into the column. Regular time intervals were used to collect samples and measure the concentration of BB41 and COD at the sample port.

The pH of the raw basic dye wastewater was measured as 7.1. After 90 min of ozone bubbling treatment, the COD of the basic dyestuff wastewater decreased from 1358 mg/L to 546 mg/L. Considering the potential impact of pH on the results, a series of ozone treatment experiments were conducted using samples at different pH levels. The COD measurement after ozone treatment was conducted at different pH values ranging from 2 to 12. The corresponding results can be found in Figure 3. Under a basic condition of pH 10, the COD reduction observed in the direct dye wastewater was quite remarkable. At a pH of 10.0, the wastewater's COD with basic dyestuffs decreased to 274 mg/L, as observed. It has been noted that a significant number of bubbles are produced when the gas flow rate at the inlet is high, and a higher concentration of ozone has proven to be effective in reducing COD. A pH of 10 was chosen for the following experiments.

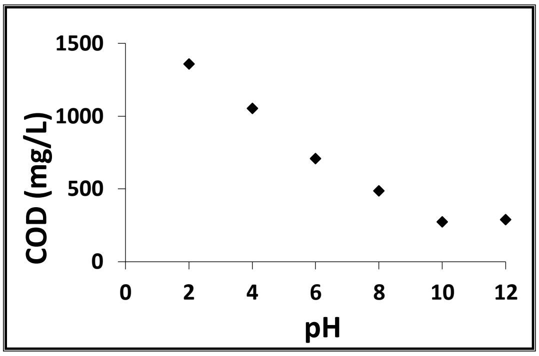


Figure 3. Effect of pH of the initial solution on COD (COD raw disperse dyestuff: 1358 mg/L for BB41); ozone concentration: 24 g/m^3; dye concentration: 300 mg/L; dye solution: 7000 mL; ozone-air flow rate: 120 L/h; ozonation time: 90 min.).

Table 2. Line-fitted values of rate constant k, (L/min).

		k (L/min)			
Disperse dye	pH	C_0 = 5 mg/L	C_0 = 10 mg/L	C_0 = 15 mg/L	C_0 = 20 mg/L
C.I. Basic Blue 41	6.0	0.159	0.140	0.122	0.099
	8.0	0.184	0.156	0.127	0.102
	10.0	0.233	0.174	0.132	0.108
	12.0	0.378	0.205	0.159	0.115

Spectrophotometric analysis of the process

As the reaction time advanced, the absorption intensity of BB41 in solution gradually diminished. It was observed that BB41 molecules underwent degradation in the presence of ozone.

The absorption maximum of the BB41 solution at λ_{max}=609 nm indicated a rapid degradation of the solution.

Impact of reaction time

Measurement of COD was also conducted during the reaction. According to Figure 4, the COD removal efficiencies of dye wastewater reached 79.82% after a 90-min reaction using ozonation at pH 10.0.

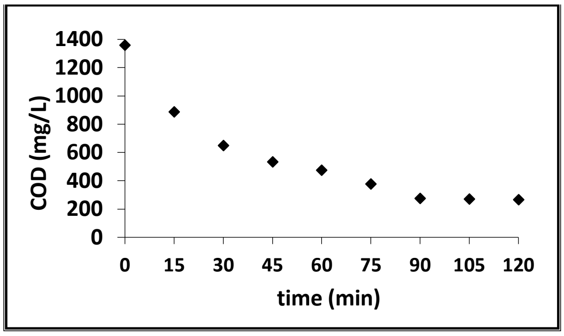


Figure 4. CODs of BB41 with ozone after different reaction time at pH 10 (ozone conc.: 24 g/m^3; dye concentration: 300 mg/L; dye solution: 7000 mL; ozone-air flow rate: 120 L/h).

Impact of initial dye concentration on the rate of dye decolorization

Figure 5 illustrates the variation in dye concentration over time during ozonation at various initial dye concentrations. The rate of dye removal starts off strong and gradually decreases as time goes on.

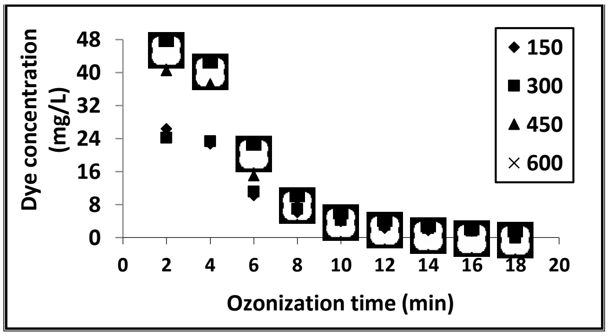


Figure 5. Ozonation time data for different dye concentrations treated with ozone (ozone conc.: 24 g/m^3; dye solution: 7000 mL; ozone-air flow rate: 120 L/h; pH: 10).

Effect of initial dye concentration on decolorization time

Figure 6 shows the effect of initial basic dye concentrations on the time required for the decolorization process. The decolorization time increases with increasing the initial dye concentration in the waste. The data fit equation [5]:

$$t_D = m.c \tag{5}$$

where t_D is the dye decolorization time (min), m - a constant, and c - the initial dye concentration (mg/L).

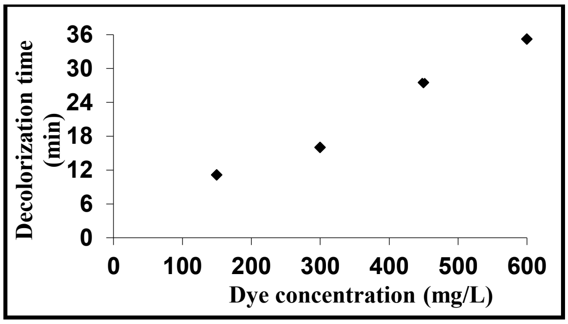


Figure 6. Effect of initial dye concentration on the decolorization time of BB41 (ozone conc.: 24 g/m^3; dye solution: 7000 mL; ozone-air flow rate: 120 L/h; pH: 10).

Impact of ozone concentration on decolorization time

Figure 7 illustrates the relationship between ozone concentration and decolorization time. It is evident that as the ozone concentration increases, the decolorization time linearly decreases. Increasing ozone concentration in the gas phase from 4.21 to 24.03 g/m^3 lowers the time it takes to decolorize a 300 mg/L dye solution by about 91.23%. This outcome aligns with the mass transfer theory, which posits that as the ozone concentration in the air bubbles (which carry ozone) rises, the force that facilitates ozone transfer to the dye solution increases. Hence, both the ozone concentration in the solution and the rate of dye oxidation increase.

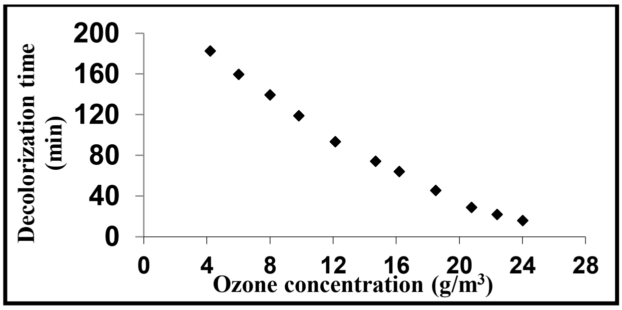


Figure 7. Effect of ozone concentration on dye decolorization time (dye conc.: 300 mg/L; dye solution: 7000 mL; ozone-air flow rate: 120 L/h; pH: 10).

Impact of initial dye solution pH on decolorization time

Figure 8 illustrates the impact of varying starting dye solution pH on the duration required for dye decolorization. Observations indicate that the duration of decolorization diminishes as the starting solution pH increases. The rate of ozone breakdown is enhanced by the generation of hydroxyl radicals at elevated pH levels. The dye decolorization time was reduced by 56.42% when the pH value was increased from 2 to 12.

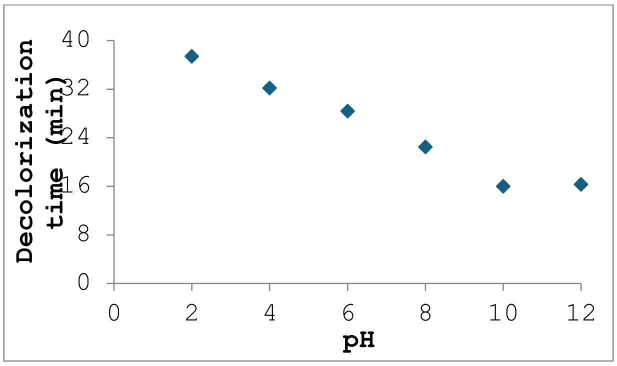


Figure 8. Effect of initial solution pH on decolorization time (dye concentration: 300 mg/L; dye solution: 7000 mL; ozone-air flow rate: 120 L/h; ozone concentration: 24 g/m^3).

The untreated dyestuff wastewater samples exhibited a blue hue. The ozone treatment effectively decolorized the wastewater containing basic dyestuffs. After around 9 min of the reaction, an observable color change occurred, resulting in a translucent yellow hue. The process of decolorization was accomplished within a time frame of around 16 min. After a reaction time of 16 min, the absorbance of the basic dyestuff wastewater decreased by 94.56%.

RESULTS

The textile-finishing business generates wastewater with intense pigmentation, necessitating specialized treatment and assessment of the ecotoxicological impacts resulting from the discharge of process wastes into the surrounding environment. Scientific evidence has demonstrated that ozone treatment is highly successful in eliminating color; however, it only slightly reduces COD. Ozonation is a promising method for removing color and reducing the COD in wastewater that contains basic dyes. When dealing with ozone procedures, it is crucial to consider both the color and toxicity of the treated wastewater products. Hence, it is imperative to attain a suitable duration for ozonation.

For this experiment, we treated water-based solutions of a representative basic dye used in the textile industry with ozone in a reactor that operates in a semi-batch mode. The purpose of our experiment was to see how well indirect ozonation with radical reactions could help the breakdown of model BB41 persistent pollutants in water solutions.

An in-depth analysis of the findings yields the following conclusions: The study found that wastewater containing primary dyestuffs underwent a reduction of 79.82% in COD. Additionally, a substantial decrease in color was detected at a pH level of 10.

The decolorization and degradation of the dye were fully accomplished during a duration of 16 min. A multitude of bubbles were generated when the gas flow rates at the entrance were high. The relationship between high ozone concentration and COD decrease was evident and substantial.

The study investigated the rate of ozonation and determined that it adheres to pseudo-first-order kinetics. The findings of this study suggest that the process of ozonation is more efficient in degrading basic dyes when conducted at alkaline pH, as opposed to acidic or neutral pH. The study found that color and COD were removed to a significant degree when the starting dye concentration was 300 mg/L, the pH was either acidic or neutral, and the ozonation time was short.

The results demonstrate that the ozonation procedure is an effective technique for treating azo dyes present in textile effluents.

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