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ABSTRACT

Decomposition of Basic Blue 9 (BB-9) in aqueous solution using ozonation and catalytic ozonation system (O_3/granular activated carbon [GAC]) in the bench-scale experiment was investigated. The effect of ozone dose, pH, and GAC contents in removal of BB-9 and biodegradability of effluent such as Biochemical Oxygen Demand (BOD_5); Chemical Oxygen Demand (COD), and BOD_5/COD were studied. Results show that pH of solution and ozone concentration are significant factors on removal of BB-9; COD and BOD_5. Kinetic studies of reactions indicated that reactions followed the first-order kinetics model. The application of GAC as catalyst, in mass concentration of 2 g/l, caused 48% increase in the degradation rate of BB-9. Ozonation process caused an increase in biodegradability of BB-9. However, catalytic ozonation did not have an effect on the biodegradability of the effluent. Acute toxicity tests with *Daphnia magna* show that this applied treatment method can significantly decrease toxicity of dye in aquatic solutions.

Keywords: Decomposition; Decolorization; Basic Blue 9; Catalytic ozonation; GAC; Aquatic solution

1. Introduction

Dyes are organic materials with complex structures, toxic, carcinogenic, teratogenic and non-biodegradable properties. They are the most important pollutants of textile industrial wastewater [1–3].

The removal of organic dyes from wastewater represents an important issue in environmental research. Because of the large number of aromatic rings present in dye molecules and the high stability of the dyes, conventional biological treatment is ineffective for dye degradation [4–6]. Physical adsorption techniques are generally efficient; however, they only transfer the pollutants from the liquid phase to the solid phase, therefore requiring post-treatment of the solid wastes and regeneration of the adsorbent materials. Advanced oxidation techniques (AOTs), based on the generation of strong oxidizers (mainly hydroxyl radicals-OH, ozone-O_3, atomic oxygen-O, hydrogen peroxide-H_2O_2) have been investigated for the degradation of organic dyes in water [7].

The formation of OH radicals is especially desired, because they are among the strongest oxidizers, with a standard reduction potential of 2.56 V [4,5,8]. The objec-

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tive is either complete mineralization (that is, conversion of the target compound to carbon dioxide; water and, eventually, inorganic ions) or only partial degradation of the organic compounds, in order to make the effluent more amenable to conventional treatment (e.g., bio-treatment). Therefore, oxidation is especially needed to remove persistent molecular structures and reduce toxicity.

The chemistry of ozone in pure water is rather complex, and various aqueous reactions have been proposed, as represented by Eqs. (1–7) [9–11]. The following describes various reactions that occur when ozone is dissolved in water:

$$O_3 + OH^- \rightarrow O_2^- + HO_2 \quad (1)$$

$$HO_2 \rightarrow O_2^- + H^+ (\text{pKa} = 4.8) \quad (2)$$

$$O_2^- + O_3 \rightarrow O_2 + O_3^- \quad (3)$$

$$HO_3 \rightarrow O_2 + OH \quad (4)$$

$$HO_2 \leftrightarrow H^+ + O_2^- \quad (5)$$

$$O_3^- + H^+ \rightarrow HO_3 (pH \approx 8) \quad (6)$$

$$O_3 + OH \rightarrow HO_2 + O_2 \quad (7)$$

Eq. (1) describes a reaction of the hydroxide ion with ozone, which initiates a series of chain reactions. The formation of hydroxyl radicals in Eq. (4) via secondary decomposition of ozone is thought to be a rapid process. The hydroxyl radical is an important oxidant because of its high oxidation power. Its formation is also favored at relatively high pH levels [12,13,10].

Unlike ozone, the hydroxyl radical is indiscriminative in its attack and oxidizes organic matter eventually to CO_2 and H_2O. This is the main reason ozonation is mostly conducted under alkaline conditions. An appropriate pathway must exist before ozone can react with pollutants or substrates. Some researchers believe that kinetic factors most often dictate ozone induced oxidation processes even though the thermodynamics may be favorable [14,9,15,13]. This is an important factor because it has direct implications on the engineering and design aspect of a particular treatment system.

Ozone is mainly used for decolorization, degradation of organics, disinfection, oxidation, and elimination of taste and odors. Ozonation of organics in water is a fast process (e.g., color removal), but complete mineralization to CO_2 and H_2O is a very slow process [4,5,1]. The combined use of ozone and activated carbon has recently started to be developed for the treatment of toxic effluents. The combined use of ozone and activated carbon has recently been put forward [16]. It was recently observed that the combination of the high oxidizing capacity of ozone and the high adsorbing capacity of activated carbon in a single process is a highly attractive alternative to advanced oxidation systems. It has also been demonstrated that activated carbon acts as initiator/promoter of the transformation of ozone into $HO^\bullet$ radicals, thereby increasing the treatment efficacy of this system. Studies have demonstrated that basal plane electron s, basic functional groups on the activated carbon surface (chromene, pyrone, and pyrrole) and metallic centers in its mineral matter act as active centers in the transformation of ozone into $HO^\bullet$ radicals. Ever since the discovery of the catalytic activity of activated carbon in the transformation of ozone into $HO^\bullet$ radicals, numerous studies have been designed to improve the treatment efficacy of this system (O_3/activated carbon) and accelerate its full-scale implementation [17]. As we know, there are no studies about the effect of combination of ozone and granular activated carbon (GAC) on biodegradability of by-products and toxicity of treated effluents.

In this work, the decomposition of BB-9 in aqueous solution was investigated using the catalytic ozonation system. The main objectives of this study were the following:

- Quantify the amount of BB-9 removed during the ozonation process.
- Determine the Chemical Oxygen Demand (COD) removal efficiency of the ozonation process.
- Determine the efficiency of the low pH and high pH ozonation treatment processes.
- Survey the effect of GAC as a catalyst in this treatment process.
- Survey the acute toxicity tests of solutions with *Daphnia magna*.

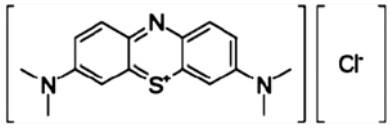
The important parameters studied were Biochemical Oxygen Demand (BOD_5); COD; BOD_5/COD, and color reduction.

2. Materials and methods

2.1. Dye solution preparation

The dye used in this study is BB-9 whose chemical structure is shown in Table 1. Purity of BB-9 is more

Table 1
Physical and chemical characteristics of Basic Blue 9 [1,2]

Characteristics	Value
Dye name	Methylene blue
C.I name	BB-9
C.I number	52,015
Class	Thiazin
λ_{max}	668 nm
Empirical formula	$C_{16}H_{18}N_3SCl$
Molar mass	319.9 g /mol
Molar volume	241.9(Cm^3/mol)
Molecular diameter	0.80 nm
Molecular structure	

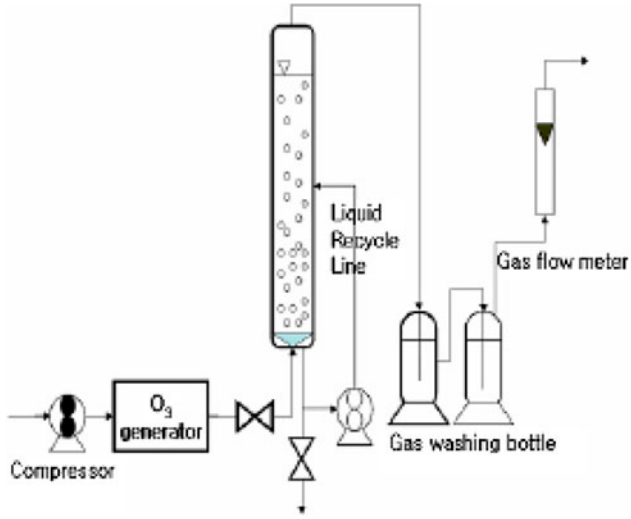


Fig. 1. Schematic diagram of ozonation reactor.

than 98% and was procured from Sigma Aldrich. Stock solutions of BB-9, without further purification, were prepared by dissolving of accurately weighed dye in deionized water at a concentration of 1,000 mg/l. The experimental solutions were obtained by diluting the dye stock in accurate proportions to different initial concentrations. BOD_5 and COD of solution were determined according to the Standard Methods for the Examination of Water and Wastewater, 21st Edition [18,19]. The final concentration of dye in the solution was determined by the three wavelength methods using a spectrophotometer (Model DR-5000, HACH Co., Japan), as American Dye Manufacture Institute (ADMI) method. This method measures the sample's true color, independent of hue. Based on the Adams–Nickerson chromatic value formula for calculating single number color difference values, that is, uniform color differences, this method is applicable to colored waters and wastewaters similar in hue to the standards and with color characteristics significantly different from platinum–cobalt standards [18]. Each color concentration, before and after treatment, was measured by this method immediately after filtration procedure. The gaseous ozone dosage was determined with KI solution per spectrophotometric method [12,10,11]. The efficiency of the dye decomposition is better determined by the yield, defined as the amount of dye decomposed per mg of O_3 spent in the process. The initial pH values of the solutions were adjusted with 0.1 M HNO_3 or NaOH [4].

3. Experimental procedure

The ozonation experiments were carried out with the column reactor being filled with 1liter water containing appropriate concentrations of BB-9 solution for only conducting the O_3 and O_3/catalyst experiment, Column was packed with catalyst (GAC surface area = 880 m^2/g, mesh size = 50-mesh sieve (0.297 mm), iodine number = 750 mg/g) for study of O_3/catalyst experiment. Ozone at a rate of Ozone doses of 0.66–2.66 g/h that were supplied by generation with 1, 2–3 electrodes was diffused continuously into the column through a glass diffuser. Ozone was produced from air using ozone generator (Model HE04-45, Hwangjun Korea), [5,13,20]. Water samples were taken at various intervals corresponding to known applied ozone dosage. The samples were analyzed for concentrations of BB-9, COD, and BOD_5. Dissolved ozone in the water samples collected from the column was removed by pure nitrogen diffused through the sample. The experimental setup included a column reactor made of Plexiglas (20.5 cm high × 2.5 cm diameter) and ozone generator (Fig. 1). To quality assurance and quality control data, all of the experiments were done triplicate and according to the standard methods.

3.1. Acute toxicity test with Daphnia magna

The acute toxicity tests with *Daphnia magna* were carried out according to the ABNT norms. The sensitivity tests were carried out with young organisms (6–24 h of life), which were not fed during the test period. For each concentration, 10 organisms were used, in a 25 ml beaker, in duplicate for each concentration, along with the controls with the dilution water (basic medium). The acute toxicity tests with the effluent samples had duration of 24–96 h, and after this time of exposure, the number of immobile organisms

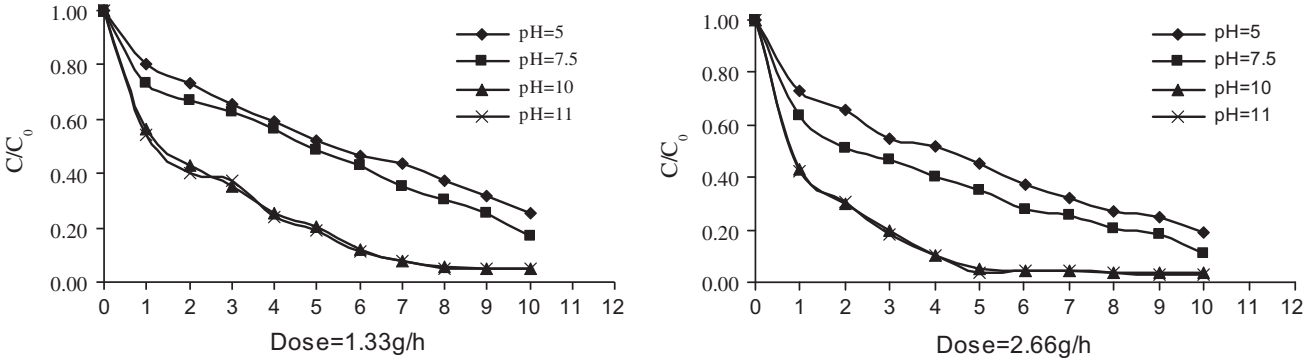


Fig. 2. Effect of pH on decolorization of BB-9 at 1.33 and 2.66 g/h of O_3 ($t = 5$ min).

was observed and noted. The organisms were considered immobile, if they did not show any mobility during 20 s of observation [3]. In order to calculation of LC_{50}, probit analysis, SPSS (ver 11.5) was applied.

4. Results and discussion

4.1. Effect of pH on decomposition of BB-9

In a heterogeneous catalytic ozonation system, pH has two main direct influences on the oxidation, that is, ozone decomposition and the surface property of solid catalyst. Results of the effect of pH on ozonation in bench-scale reactor by different ozone dosages are shown in Fig. 2 Ozone doses of 0.66–2.66 g/h were supplied by generation with 1 and 2 electrodes. Results show that concentration of BB-9 decreased from the initial concentration of 1,500 ADMI to below 75 ADMI, with in 10 min contact time when ozone dosage was 1.33 g/h. Furthermore, the color content dropped to below 75 ADMI with in 5 min when ozone dosage was applied at 2.66 g/h. The highest decolorization rate for BB-9 occurred under basic conditions (pH=10) after 5 min at 2.66 g/h of ozone dosage. Ma et al. (2004a) reported that ozone predominated oxidation process at low pH, while the hydroxyl radical showed more significant effect at high pH [1]. The results of this study show that the highest decolorization rate occurs at pH 10.

4.2. Kinetics of reaction

Color removal rates could be expressed using the first-order kinetics, as illustrated in the following equation:

$$-dC/dt = kC \quad (8)$$

where k = apparent first-order rate constant, C = color value (ADMI value) and t = time of reaction [21,12,22]. Results show that the k values for the decolorization of BB-9 was determined from kinetic profiles, as presented in Table 2. The kinetic analyses show that the decolorization reactions of BB-9 followed the first-order kinetics very well. Results also show that higher k values (apparent first-order rate constants) were observed under higher pH conditions.

Table 2
First-order decay rate constant of BB-9 decomposition with ozone

O_3 dose (g/h)	k (min^{-1}) of BB-9, $r^2 \geq 0.90$		
	pH=5	pH=7.5	pH=10
1.33	0.11	0.25	0.72
2.66	0.42	0.51	0.84

4.3. Effect of ozone dosage

Results of decolorization of BB-9 in different ozone dosages, are shown in Fig. 3. Results show clearly the effect of decolorization of BB-9 was more pro-nounced with higher ozone doses that the efficiency of decolorization in dose of 2.66 g/h was about 95% at pH 10 at

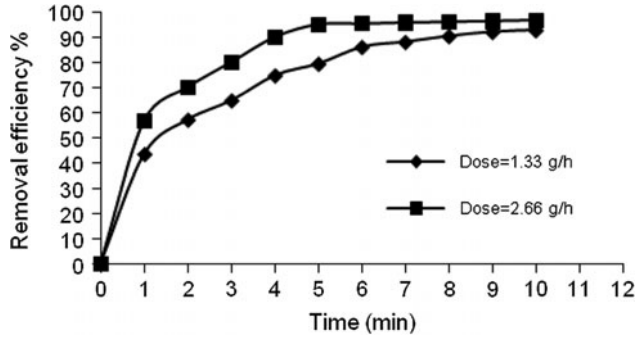


Fig. 3. Effect of ozone dosages and time of ozonation on decolorization of BB-9 at pH=10.

Table 3
BOD_5 and COD of synthetic dyeing wastewater after ozonation (pH=10; $t = 5$ min; characteristics of solution before ozonation, dye concentration = 1,500 ADMI; COD (mg/l)=1,100; BOD_5 (mg/l) = 12.8; $BOD_5/COD = 0.0116$)

O_3 dose (g/h)	After ozonation		
	COD (mg/l)	BOD_5 (mg/l)	BOD_5/COD
0.66	820	220	0.268
1.33	750	320	0.427
1.99	680	412	0.606
2.66	520	460	0.885

6 min of contact time, but in dose of 1.33 g/h was about 80% at pH 10 at 5 min. Results indicated that ozone dosages and time of ozonation have significantly effect on decolorization of BB-9 at pH=10. These results indicated that decomposition of BB-9 was occurred at the first 6 min.

4.4. Effect of ozonation on biodegradability of BB-9

In general, the BOD_5/COD ratio of a textile effluent ranges from 0.011 to 0.015, meaning that the effluent is bio-refractory. Ozonation could increase the biodegradability of some recalcitrant compounds. The ratio of BOD_5/COD is often used as a measurement of biodegradability of solution. The results of this study show that ozonation process cause increased in biodegradability of BB-9, significantly increased of BOD_5/COD, it indicated that refractory materials by ozonation process were decomposed to biodegradable component. These results are presented in Table 3.

4.5. Effect of GAC as catalyst

Tables 4 and 5 present ozonation in presence of catalyst on BB-9 degradation, which generally shows the value of BB-9 degradation was increased with increase ozonation dose and mass of catalyst. The degradation of BB-9 with 0.5–2 g of catalyst was studied. BB-9 absorbed on GAC was calculated as the control experiments that were presented in Table 4. Effect of O_3/GAC on BB-9 decomposition was calculated and presented in Table 5. Results show that ozonation in the presence of catalyst have more significant effect on degradation of BB-9. These results indicated that we can use GAC as a low cost catalyst to degradation of BB-9. These may be because of ozone that caused the oxidation of the carbon and leads to creation of the number of acid groups present on the carbon surface, especially carboxylic groups, whereas the pH of the point of zero charge were decreased. These results are explained by the ozone attack on the carbon and the fixation of oxygen groups on its surface. The integration of ozone with GAC resulted in the regeneration of GAC. The results of biodegradability of effluent of BB-9 after catalytic ozonation is presented in Table 6 indicated that catalytic ozonation process cause increased in biodegradability but according to the BOD_5/COD in Table 3 this is not affected by catalyst activity.

Table 4
The effect of GAC as adsorbent on removal of BB-9 (C_0 (ADMI) = 1,500; volume = 0.3 l; without ozone)

C_e (ADMI)	Mass of GAC (g)	q_e (ADMI/g)
1,420	0.5	48.0
1,324	1	52.8
1,280	1.5	44.0
1,120	2	57.0

Table 5
The effect of GAC as catalyst on degradation of BB-9 at varies dose of ozone (pH=10; $t = 5$ min)

O_3 dose (g/h)	Mass of GAC			
	0.5 g	1 g	1.5 g	2 g
	BB-9 (ADMI) ± SD = $BB\text{-}9_{in}$–$BB\text{-}9_{absorbed\ on\ GAC}$			
0.66	478 ± 8.2	425 ± 5.4	352 ± 6.3	280 ± 4.8
1.33	376 ± 0.4	321 ± 4.6	280 ± 5.4	185 ± 3.2
1.99	257 ± 5.6	208 ± 4.1	187 ± 5.2	135 ± 5.1
2.66	189 ± 7.5	124 ± 8.2	90 ± 2.1	70 ± 2.9

4.6. Toxicity assay

In the present study, toxicity was evaluated at concentrations of 5–100 mg/l for BB-9 to determine LC_{50} ranges. In addition, control solutions (concentration of 0.0 mg/l) were conducted to confirm the accuracy of

Table 6
BOD_5 and COD of synthetic dyeing wastewater before and after catalytic ozonation (GAC = 2 g/l; pH=10; $t = 5$ min; dye concentration = 2,000 ADMI; characteristics of solution before ozonation, dye concentration = 1,500 ADMI; COD (mg/l) = 1,300; BOD_5 (mg/l) = 17.2; $BOD_5/COD = 0.0132$)

O_3 dose (g/h)	After ozonation		
	COD (mg/l)	BOD_5 (mg/l)	BOD_5/COD
0.66	1,100	220	0.200
1.33	950	384	0.404
1.99	870	512	0.589
2.66	705	564	0.800

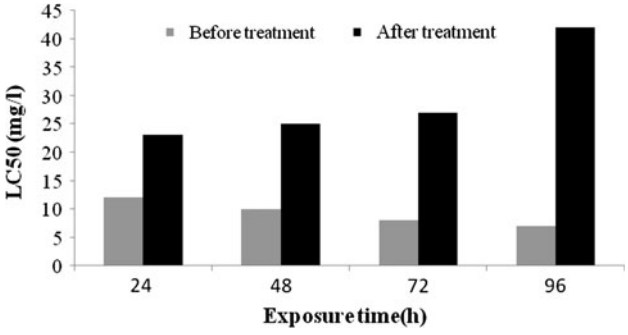


Fig. 4. Acute toxicity of BB-9 to *Daphnia magna* before and after treatment by catalytic ozonation (ozone/GAC) at optimum condition (pH=10, $t = 5$ min).

the test. The results indicate that the LC_{50} of BB-9 for *Daphnia magna* is about 7–12 mg/l. But after treatment of dye by O_3 + GAC toxicity of effluent are decreased. This means that this process can significantly decrease toxicity of dye LC_{50} for *Daphnia magna*. These results are shown in Fig. 4.

5. Conclusions

Chemical oxidation with ozone is one of the techniques that used in wastewater treatment for the removal of organic pollutants. In some cases, ozone was used in combination with other agents to improve the degradation rate of organic pollutants. The degradation of BB-9 using GAC as catalyst has been examined in this study. Ozonation flow rates and pH play a major role in the degradation process. The degradation of BB-9 was higher at a higher ozone flow rate. Similarly, increase in pH and mass of catalyst increasing the rate of degradation. The rate of decomposition of ozone is increased at a higher pH containing a higher concentration of hydroxyl radical that leads to a higher degradation of BB-9. Ozone in combination with GAC as catalyst is an efficient method in eliminating BB-9 from contaminated water. Some researches show that the use of the O_3/GAC system can be considered as a potential advanced oxidation process. During oxidation of the activated carbon by action of the ozone, the catalytic activity of the carbon declines, because of an increase in the number of surface oxygenated groups of acidic character. These functional groups reduce the reductive properties of the activated carbon and, therefore, its reactivity to ozone, preventing its decomposition in aqueous phase [16]. Results of this study (Table 5) can be due to (i) ozone consumption by dye decomposition by product dissolved decreasing the ozone concentration available for $HO^{\bullet}$ generation in O_3/GAC interaction and (ii) adsorption of this by products on GAC surface. These results are the same of research of Rivera-Utrilla et al. [23]. The results of this study show that activated carbon has adsorption and catalytic effect on this oxidation process (see Tables 4 and 5). Also results obtained show that the presence of activated carbon during dye ozonation: (i) increase the removal rate, (ii) reduces oxidation by-product toxicity, and (iii) increase the biodegradability of effluent. The conversion of BB-9 into more biodegradable intermediates provides is an opportunity for integrating advanced oxidation with more conventional biological treatment. GAC because of catalyst and adsorption activity has a good catalyst to enhanced degradation of BB-9. The acute toxicity tests with *Daphnia magna* show that this treatment method can decrease significantly toxicity of solution.

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