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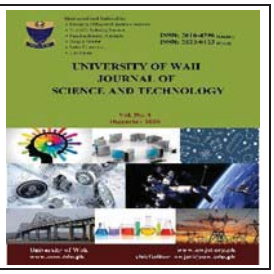

De-Colorization of Azo Dyes C.B-10X Blue and C.B.M-10X Blue by Ozonation for Wastewater Treatment

Muhammad Sajid, Muhammad Irfan Ahamad, Syed Salman Shafqat, Mustafa Kamal Pasha and Muhammad Asim

***Abstract*—Ozonation has strong oxidation potential and is mostly preferred for oxidation processes. Due to its oxidation potential, environment-friendly nature, and process flexibility, ozonation was used for the removal of azo dyes. Different process parameters including the rate of ozone generation, pH, the flow rate of ozone, and initial dye concentrations were optimized for efficient removal of coloring potential of C.B-10X Blue and C.B.M-10X Blue dyes which are mostly used in the textile industry. Under optimized process parameters, the high removal efficiency of 75% for C.B-10X Blue and 72% for C.B.M-10X Blue was achieved at 100 mg concentration. However, removal efficiency strongly decreased with an increase in dye concentrations. Therefore, ozonation can only be used for the treatment of effluents having up to 100 mg/L concentrations of azo dyes.**

***Index Terms*— Ozonation, Azo dyes, De-colorization, wastewater.**

I. Introduction

TEXTTILE industry, the wet process industry uses tones of water and more than 3600 dyes and about 8000 chemicals, which is a major source of wastewater ejection having contamination of organic, inorganic, and strong colored substances[1–4]. Rapid industrialization is continuously increasing the scale of water pollution qualitatively and quantitatively.

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Contaminated water causes harmful effect on biotic life as well as strongly affect human life [5]. The treatment of wastewater is vital considering water security and human life along with aquatic life preservation [6–8]. Azo dyes are the most extensively used textile colored pigments dyes and have nitrogen double bonds (─N=N─). These dyes mostly have 1-4 azo-groups attached to aromatic rings and are used in the range of 10-70 g/L of which ≤90% are mostly consumed in the process [9]. Azo dyes are dangerous for life and can produce carcinogenic compounds by skin microbiota [10].

Different treatment methodologies have been applied considering the types of pollutants, the volume of liquid effluents and the potential of reusability [2]. Principally treatment processes can be categorized into (i) physical, (ii) biological and (iii) oxidation methods. Physical methods mostly applied are; adsorption [7], coagulation [11] and filtration [2], [12]. From these, membrane filtration has been used extensively for the treatment of wastewater [13]. Organic, inorganic, and composite membranes were prepared and used for nanofiltration, ultrafiltration, reverse, and forward osmosis processes depending upon the pore size of the developed membrane [13]. Different biological methods employing enzymes and microorganisms were also used for the treatment of textile wastewater [14]. These methods are divided into aerobic and anaerobic processes based on high and low chemical oxygen demand (COD), respectively. Microorganism secretions contain compounds and enzymes which can degrade the dyes into simpler products [15-16]. For this purpose, Rot White Fungus is used which produces laccase enzyme which has an excellent ability to degrade a wide range of textile dyes [17]. Oxidation methods are mostly categorized as chemical oxidation process (COP) and advanced oxidation processes (AOP) [16]. Oxidation processes are superior to biological processes as wastewater with high

toxicity can be handled. These physical methods have process flexibility without the risk of fouling and sludge generation [2].

Textile effluents are mostly colored due to the presence of different dyes, therefore the color intensity is an indication intensity of dye-pollution. Therefore, de-colorization has been considered a key indicator of the textile wastewater treatment processes. Chemical oxidation is an easy, flexible, and environmentally benign way for the treatment of dyes-polluted industrial wastewater. Multiple oxidants such as chlorides, ozone, and hydrogen peroxide can be used for discoloration of textile wastewater. Among these, Ozonation is most significant and effective for the removal of color pigments present in textile wastewater. Ozone is a powerful oxidizing agent with an oxidation potential of 2.07 volts; however, the exact mechanism of ozonation is still a matter of debate. It is believed that during the ozonation, ozone mostly attacks the double bonds present in the dye structure (carbon-carbon and other functional groups) with high electron densities. This chemical attack results in structure modifications instigating crumbling of color developing groups. Resultantly, the larger macromolecules degraded into small moieties which are easy to decompose by microorganisms present in waste streams [18].

The principal objective of this study is to optimize the ozonation process for Azo Dyes (C.B-10X Blue and C.B.M-10X Blue). The experimental conditions such as pH, dye concentration, and rate of ozone were optimized to achieve the maximum process efficiency. Purposes of ozonation include; disinfection from microorganisms and algal control, oxidation of organic micro-pollutants by altering their structures (increasing the biodegradability of organics) and oxidation of organic micro-pollutants by simple degradation process (Taste, odor compounds, phenolic pollutants, and pesticides). Result elucidated the high decoloration efficiency of the ozonation process under optimized conditions. Ozonation offers an environmentally friendly process for the treatment of textile wastewater, which can play a significant role in the industrial water recycling concept especially in the current water security-sensitive scenario.

II. Materials And Method

A. Materials

Two azo dyes, C.B-10X Blue and C.B.M-10X Blue are purchased from a local supplier and marked as dye 1 and dye 2, respectively for the reader's convenience and better understanding. Ozone generator (Acrona discharge, Model OZX-B300T), with a constant production capacity of 200 mg/h and flow rate of 2 L/h and different set points of 6 min, 12 min, and 18 min is used. A glass cylinder (WERTLAB GERMANY) having length of 45 cm (1000 ml capacity) and diameter of 6.5 cm is used as a reactor. pH meter form JENWAY Model-3510 an Humas Korean spectrophotometer (190 nm to1100 nm, Model-Think Hs 3300) is used to study the absorbance of the dye solution after ozonation. A quartz cuvette is used to load the sample into the spectrophotometer.

B. Solution Preparation

The solution of different dye concentrations (100 mg/L, 300 mg/L, and 500 mg/L) is prepared in the lab. For 100 mg/L solution, 100 mg of dye dissolved in 1000 ml of distilled water and placed in shaking water bath for 15 min at 40 °C to homogenize the solution. The same procedure is repeated for the preparation of dye solutions of 300 and 500 mg. Ozone from ozone generator passed through a small pipe dipped in a glass cylinder. At the end of the pipe, a porous tip is placed for the better mixing of gas in solution. After the ozone generation, bubbling started from the bottom to upward in the cylinder. Pre-calibrations is performed for all pieces of equipment with lab standard procedures of American Public Health Association 1998 [19].

C. λ_{max} Determination

For each dye, the wavelength of the maximum absorbance (λ_{max}) is determined by screening between 380-1100 nm. The maximum wavelength (λ_{max}) of dyes was observed at the concentration of 100 mg. The maximum wavelength of the dyes was; 605 nm and 591 nm for dye 1 and dye 2 repectively as shown in *Fig. 1*. The ozone generator is set at 6 min interval to produce ozone gas. Absorbance and pH of each sample (dye solution) are measured before the ozonation process. Post ozonation pH was measured immediately after the ozonation to minimize the delay time effect. The effect of all the process parameters such as; pH, initial dye concentration, the concentration of ozone used, and time of ozone passed are investigated for the maximum color decrease. The temperature was kept constant at 25°C throughout the experiment [20].

D. Determination of Color Decrease

The percentage color decrease is measured and observed with respect to the λ_{max} of each dye. The formula used for this purpose is;

$$\text{Color decrease (\%)} = \left[\frac{C_0 - C}{C_0}\right] \times 100$$

Here C_0 is the intensity at time "0" and C at the time "t".

III. Results and Discussion

A. Effect of Ozone Dozes

The relation between absorbance and concentration is shown in *Fig. 2*. A linear relationship between concentration and absorbance can be observed according to the Beer-Lambert law in *Fig. 2*. Initial dye concentration, ozone reacted, time of ozonation, and percentage of color decrease as shown in *Fig. 3-5* of dye 1 and dye 2 are checked at different concentration levels [21]. Results elucidated that increase in dye

concentrations decreased the color removal efficiency, similar to reported results [22]. At 100 mg concentration, the maximum efficiency is observed with both dyes as shown in *Fig. 3*. The decoloration efficiency continuously increased with ozonation time directly at low concentration, i.e. 100 mg and 75% removal efficiency is recorded with dye 1 and 72% with dye 2 after 60 min of ozonation as shown in *Fig. 3*. An increase in dye concentration behaved differently, at a relatively high concentration of 300 mg, the color removal efficiency is first increased with time up to 54 minutes and then decreased after 54 minutes as shown in *Fig. 4*. However, the maximum recorded efficiency was only 8% with dye 1 and only 17% with dye 2 as shown in *Fig. 4*. The decrease in color removal efficiency is most probably due to the formation of color pigments with prolonged ozonation.

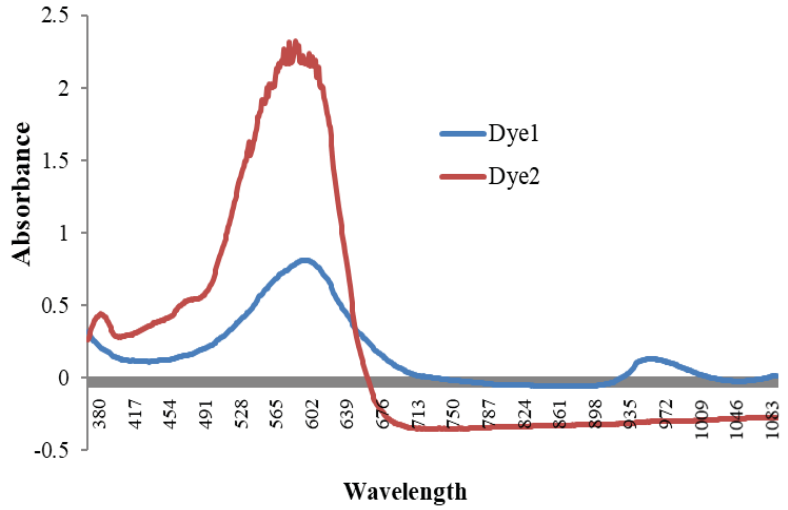

Fig. 1. Determination of λ_{max}

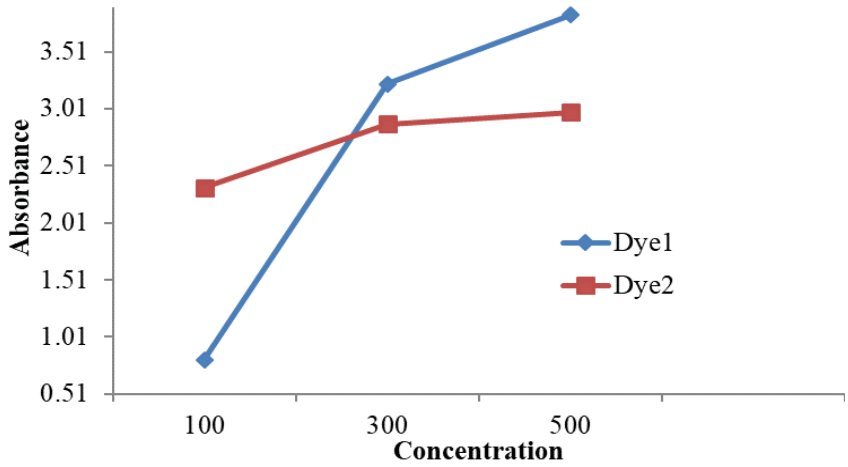

Fig. 2. Effect of initial dye concentration on absorbance for both dyes at their λ_{max}

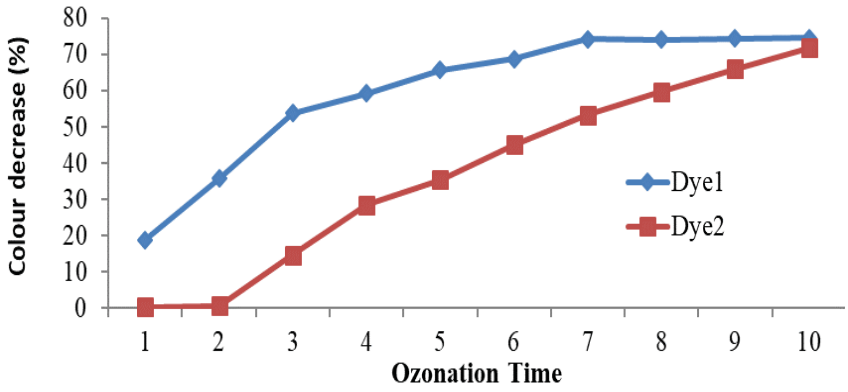

Fig. 3. Effect of ozonation time on concentration decrease at 100 mg concentration

Ozonation for a long time converted the azo structure to a new form of coloring moieties, which is also observed with the change in solution color [23]. Further increase in dye concentration to 500 mg abruptly changed the removal efficiency pattern and a zigzag graph can be observed in *Fig. 5*. At this high concentration (500mg), ozonation is not a good technique for the removal of dye color. Most of the time, absorbance increased instead of decreasing that indicate an increase in color intensity, therefore negative efficiency is noted as shown in *Fig. 5*. This increase in color intensity is possibly due to the (i) formation of new coloring pigments at high dye concentration, and/or (ii) dyes recovered their structure after some time interval with ozonation. However, as the negative values can be observed in absorbance efficiency, which means high color intensity or structure with high absorbance. Therefore, it can be validated that an extended structure is developed with improved absorbance. Therefore, this process of technology cannot be applied for the treatment of wastewater with high dyes concentrations. A similar phenomenon has also been reported in the literature. So, it can be confirmed that an increase in time of ozonation had a direct relation with %age color decrease up to 100 mg dye concentration. For high concentrations, experimental setup with a high dosage of ozone for a longer time of ozonation can be used [24].

B. Effect Of pH

The effect of ozonation on solution pH has been displayed in *Fig. 6-8* for all dye solutions. A decrease in solution pH with an increase in time of ozonation is observed. The decreasing trend is linear with both dyes in all concentrations except dye 2 at 300 mg concentration as shown in *Fig. 7*. However, the peak values and the decreasing rate is different. At lower dye concentrations, decreasing trend and the decreasing rate are quite similar for both dyes and pH is decreased from 5.43 to 4.33 and 5.4 to 4.30 for dye 1 and dye 2, respectively as shown in *Fig. 6*. A similar trend is also observed at lower concentrations with other azo dyes [25]. Therefore, results confirmed the generalized principle of linear decrease in pH with a time of ozonation at lower concentrations of azo dyes. Quite a similar pattern is noted with dye 1 at 300 mg dye concentrations however, abnormal pH swings are observed in dye 2 as shown in *Fig. 7*.

Most probably, the structural changes are the cause of this abnormal increase in pH, which is also validated by an abrupt change in color decrease as shown in *Fig. 4*. At the highest concentration of 500 mg, a rapid decrease in solution's pH is noted as shown in *Fig. 8* as compared to 100 & 300 mg concentrations, similar to reported results in [26]. However, at 500 mg concentration level, repeated swings are observed in color decreasing trend of dye 2 and no decreasing trend is observed in dye 1 as shown in *Fig. 5*. The rapid decrease in solution's pH further confirmed the formation of a new structure as discussed in the previous section. A similar trend of pH change with variable dye concentrations revealed a close relationship and dependency of pH on the time of ozonation.

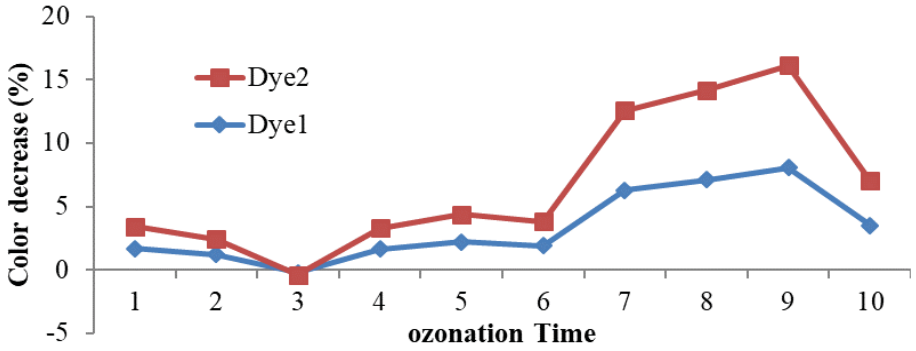

Fig. 4. Effect of ozonation time on concentration decrease at 300 mg concentration.

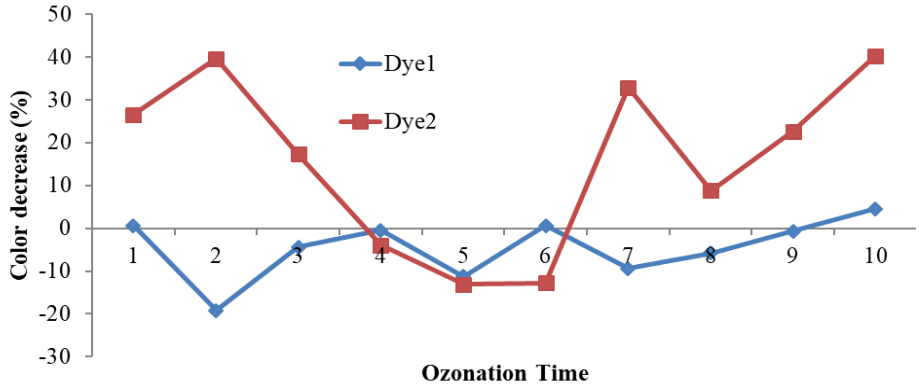

Fig. 5. Effect of ozonation time on concentration decrease at 500 mg concentration

The linear dependency on the time of ozonation elucidated that the reaction of ozone shifted from OH^- to molecular ozone type of oxidation [27]. At higher pH, the OH^- oxidation of ozone is superior and it is stronger than molecular ozone oxidation. At a lower pH level, the molecular ozone oxidation is mostly observed [28]. In this research work, the pH is changed (decrease) and reaction type shifts towards molecular Ozone type oxidation that have the low potential of oxidation as compared to OH^- oxidation. Therefore, the low decrease in color after every time interval of ozonation was observed. However, the decrease in pH at all concentrations with both dyes proved that ozonation can be an effective treatment methodology for the decoloration of textile wastewater.

The study conducted focuses on the effective removal of surface deposited unsettled coloring substances from industrial wastewater. The progress of the technique, though, underwent throughout a variety of stages which integrated a laboratory level learning of ozone de-coloration with the simplest process design having the potential of upscaling for efficient removal of azo dyes. The findings of this process employing two commercial azo dyes indicated that the ozone dosage, time of ozonation and pH have a high impact on de-colorization of all these dyes [29].

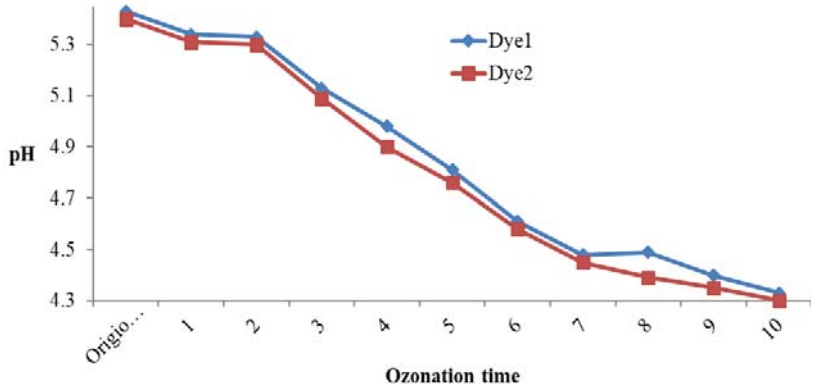

Fig. 6. Effect of ozonation time on pH at 100 mg concentration.

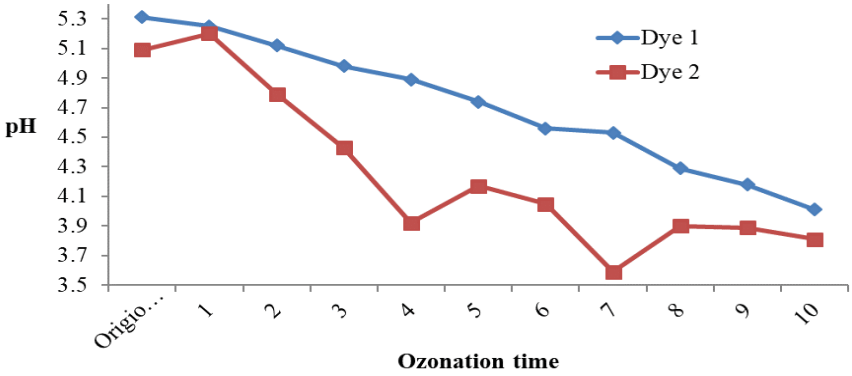

Fig. 7. Effect of ozonation time on pH at 300 mg concentration.

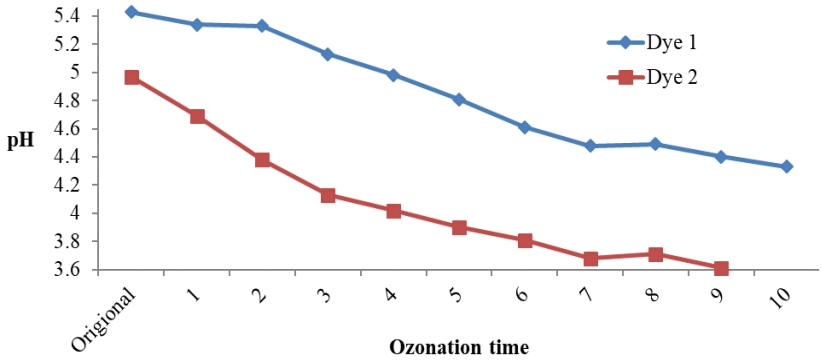

Fig. 8. Effect of ozonation time on pH at 500 mg concentration.

However, the pH change has the most significant effect [30]. Collectively, it can be observed that a pH value of 4 to 4.3 is the optimum pH for the de-colorization of C.B-10X Blue and a pH value of 3.7-4.3 is the optimized value for C.B.M-10X Blue. However, concentration is inversely proportional to a decrease in color intensity and ozonation is highly successful technique for textile effluents having low dye contaminations, which is mostly the case of industrial wastewater. Furthermore, process time is directly proportional to the decrease in color intensity.

IV. Conclusion

In the conducted research work, ozone is used to remove the coloring pigments employing two commercial textile dyes. Results indicate that ozone dosage, time of ozonation, and pH have a high impact on de-coloration. pH is more sensitive toward ozonation as compared to other parameters. Results elucidated that a pH value of 4 to 4.3 and 3.7 to 4.3 is the most effective pH range for C.B-10X Blue and C.B.M-10X Blue decoloration, respectively. The decrease in pH suggests that oxidation type shifts from OH ion to molecular ozone type. Time of ozonation and dye concentration affects the removal efficiency differently. An increase in dye concentration affects the removal efficiency negatively whereas ozonation time affects positively. As the textile effluents mostly have lower coloring pigments, therefore, ozonation can be an alternative technique to be used for the treatment of these effluents. This process is flexible, environmentally benign and without waste sludge generations.

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