Enhancing of Textile Wastewater Treatment Using Different Catalysts for Advanced Oxidation Process

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Abstract: The Textile dyeing industry consumes large quantities of water and produces large values of wastewater from different steps in the dyeing units is often rich in color. Containing residues of dyes and chemicals, and requires proper treatment before being released into the environment. The protection and conservation of natural resources is one of the main priorities of modern society. Water is perhaps our most valuable resource, and thus should be recycled. Many of the current recycling techniques for polluted water only concentrate the pollutant without degrading it or eliminating it. In this sense, advanced oxidation processes are possibly one of the most effective methods for treatment of wastewater containing organic products (effluents from chemical and agrochemical industries, the textile industry, paints, etc.). More conventional techniques cannot be used to treat such compounds because of their high chemical stability and/or low biodegradability. This article describes the ozone treatment and its application to the treatment of polluted wastewater in presence and in absence of different catalysts. Ozone oxidation process holds great promise to provide alternative for better treatment and protection of environment, especially when the process enhances by using different catalysts as presented in this paper. The presence of some inert inorganic salts such as Zink sulphate catalyst decreases both the amount of ozone reacted and time of decolourisation. For highly colored water, color removal will usually be performed by combining several types of treatment. Oxidation with chlorine and other oxidizing agents can be lead to satisfactory color abatement, but ozone remains the most efficient oxidizer. The ozonation process degrades refractory, complex and non biodegradable organic compound into simpler and more easily biodegraded compounds. Most molecules responsible for colored matter contain one to several aromatic rings and begin to absorb light at 250 nm. The dyestuffs existed in these wastewater are highly structured organic molecules which are hardly break down biologically. Decolorisation of two types of azo dyes, Direct Red 4BS and Direct Pink3B by ozone in aqueous medium was studied in presence and in absence of some salts as (Zn SO$_4$.7H$_2$O, AgNO$_3$, CuSO$_4$.5H$_2$O and Cr$_2$O$_3$) to see if there is any catalytic effect of such salts at room temperature. In this study, the effect of ozone on the two groups, the azo and the –NHCON- groups for complete decolorisation. It was found that Zink sulfate catalyses the process of color removal more than other catalysts. Equations to describe the process and to allow prediction were developed. In this study, two textile dyes are destroyed by ozone in water solution. These dyes were selected because of their complex chemical structure and extended application in textile industry. This research proved its success and would have an impact on wastewater techniques using ozone, enhancing by different catalysts, so it overcome the problems of textile and other industries wastewater treatment.

Key words: Textile, wastewater Treatment, Catalytic ozonation, Azo Dyes.

INTRODUCTION

The environmental impact of the textile industry is associated with its high water consumption, as well as by the color. Variety, and amount of pollutants that are discharged into the wastewater. Nowadays physical-chemical and biological treatments are mainly applied to these effluents. (Azbar et al., 2004, Kusvuran et al., 2004, Al-Ghouti et al., 2007, Qin et al., 2007, Yu-Li et al., 2006). However these methods concentrate the dye pollutants and necessitate secondary treatment. On the other hand, degradation involving biological processes is not efficient as the synthetic dyes in the effluent are highly structured polymers with low biodegradability (Lucas et al., 2008).
The amount of discharged effluents into the environment can be reduced reusing the textile wastewater once it has been treated. It can also produce savings in water consumption, chemicals and energy. In the same way, the quantity of treated wastewater can be improved if conventional treatments are combined with more advanced processes as reasonable option for efficient removal of color pollutants from contaminated water. (Bandala et al. 2008, Ibadon et al. 2008, Gemey et al. 2008, Mounir et al. 2007).

Advanced oxidation, activated carbon adsorption, ionic exchange, membrane techniques, etc. (Giardelli et al. 2001). Chemical oxidation degrades organic compounds and it does not produce any additional waste. In this kind of oxidation, the most common oxidants are ozone, H\textsubscript{2}O\textsubscript{2} and their combination with UV radiation. Ozone is a very powerful oxidant for water and wastewater treatment. Once dissolved in the water, ozone reacts with high number of organic compounds in two different ways: by direct oxidation, as molecular ozone, or by indirect reaction, through the formation of secondary oxidants such as free radicals, particularly hydroxyl radical. By means of organic matter ozonation, it is expected to achieve color and COD elimination, and an increase of the biodegradable organic carbon for later biological stages (Bes-Pia et al. 2004, Ciardelli et al. 2001, Bertanza et al. 2001, Sevimli, and Kinaci, 2002, and Kweon et al. 2004). Physical-chemical treatment allows reducing dissolved, suspended colloidal and nonsettable matter as well as color from dyes. Depending on the wastewater characteristics, COD of textile effluent can be reduced between 50-70% (Bes-Pia et al. 2003, Bes-Pia et al. 2002).

Oxidation using ozone, H\textsubscript{2}O\textsubscript{2}, and UV was reported to decolorize the wastewater, reduce its COD, and enhanced the biodegradability of its toxic chemicals (Ledakowicz et al. 2001, Arslan and Balcioglu 2001, Dogruel et al. 2002, Lin and Lai 2000, Ciardelli et al. 2001 and Bertanza et al. 2001). Under acid conditions ozone can mainly react directly with organic compounds, while under alkaline conditions ozone can mainly decompose to OH radical, which reacts with the target compound (Von Gunten, 2003 and Koch, 2002).

Catalytic ozonation is one such example of the AOPs that can fulfill the listed criteria because it is easy to operate and the apparatus needed is simple. The presence of some heterogeneous catalyst, which could improve the ozone capability for the degradation of refractory organic pollutant Literature review, showed that the application of ozone in presence of catalyst in the form of metal oxide such as TiO\textsubscript{2} and MnO\textsubscript{2} can increase the generation of hydroxyl radical. (Beltran et al. 2002), or salt such as Mn\textsuperscript{2+}, Mn\textsuperscript{4+} and Fe\textsuperscript{2+} (Sauleda and Brillas 2001), has increased the ozonation rate of organic compounds as compared to ozonation alone.

**MATERIAL AND METHODS**

The experimental set up is shown in Fig (1). It is consisted of an ozone generator, a reactor and washing bottles. The ozone generator is cooled with water, and is supplied by a constant flow rate of oxygen or dry air, which is led through a flow meter that indicates the rate of gas flow; it can be adjusted with a needle valve. If the rate of gas flow is increased, the amount of ozone liberated is increased, but its concentration is decreased, and vice versa. The azonated oxygen stream passes through Tygon tubing into a reactor stirred with magnetic stirrer. The reactor holds the dye solution under investigation, and ozonated gas stream is dispersed into the solution to very small bubbles by means of a sintered glass dispersion stone. The unreacted ozone passes out of the reaction vessel to very small bubbles by means of a sintered glass dispersion stone. The unreacted ozone passes out of the reactor vessel through Tygon tubing into two washing bottles contained a known volume of an acidified 2% KI solution. Finally the excess gas is vented to a hood (it contains no ozone).

![Fig. 1: Schematic Representation of the Ozonation Set-Up](image-url)
The potassium iodide solution reacts with the excess ozone according to the equation:

\[ O_3 + 2KI + H_2O \rightarrow I_2 + 2KOH + O_2 \]  \hspace{1cm} (1)

The resulted iodine is then titrated using standard sodium thiosulfate with starch as indicator.

\[ I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-} \]  \hspace{1cm} (2)

A standard calibration curve for the ozone generated at different oxygen flow rate and different periods of time, without any solution in the reactor is established. From this calibration curve, the ozone input to the reactor could be determined. The unreacted ozone is calculated from the titration. The reacted ozone at any specified conditions can be easily calculated by material balance. Two direct dyes were used in this investigation. The first was direct fast scarlet 4BS and the second was direct pink 3B. Both of them are water soluble used in dying cotton, viscose, wool and natural silk. The chemical structures of the two dyes are:

For each dye the wave length of the maximum absorbance (\( \lambda_{max} \)) and the calibration curves at \( \lambda_{max} \) of the dye were determined. The absorbance curve was carried out at different concentration (5-40 mg/L). The temperature was kept constant 25°C and the dye solution value was 700 mL.

The ozoniser apparatus is laboratory organizer type: 301.7. A product of Erwin sander is supplied with compressed air from air dryer the dried air is subjected to the effect of high voltage for the ozone generation, water is used as cooling medium in the ozoniser.

Specifications:
- Operation gas: oxygen, or dry air
- Capacity: 5-10 g ozone/h
- Concentration: 20 g ozone /m³
- Maximum concentration: 40-90 g/m³

The quantity of ozone generated is to be determined by calibration of the performance of the apparatus. It depends on: Flow rate, current and time. It is to be noted that potassium iodide solution should be kept neutral (using a buffer mixture), otherwise oxygen, whether unconverted to ozone or resulting from ozone consumption according to equation 1, reacts with HI as follows:

\[ O_3 + 4 HI \rightarrow 2 H_2O + 2 I_2. \]  \hspace{1cm} (3)

And a false indication of the quantity of ozone generated is obtained.

RESULTS AND DISCUSSION

The calibration curve for the total ozone generated in gm from the ozone generator as a function of time of ozonation in minutes is shown in Fig.(2). For this calibration curve, conditions were: Oxygen flow rate = 100 L/h and oxygen pressure = 20p.s.i. The curve is not a straight line for the entire time span; it is rather a straight line for a short period of time up to 20 minutes then production rate increases slowly. This will affect results in some published literature when one considers the amount of ozone produced for example after 60 minutes equals 4 times that after 15 minutes. For a correct material balance and to calculate the exact amount of actual ozone reacted in a given system after a specified period of time, knowledge of the actual amount of ozone generated must be correctly known.
Figure (3) shows the minimum time of decolorization of both dyes using ozone. It is clear that the minimum time of decolorization for such direct dyes with ozone is a linear function in the initial dye concentration. This means that:

\[ t = m \cdot c \]

where:
- \( t \) = minimum decolorization time by ozone
- \( c \) = initial dye concentration
- \( m \) = constant, varies only from dye to another.

Figure (4) shows that the amount of ozone reacted increases with increasing the initial dye concentration. A relationship between those two variables is developed to be as follows:

\[ Z = a \cdot C^b \]

where:
- \( Z \) = amount of ozone reacted to cause decolorization
- \( C \) = initial dye concentration
- \( a, b \) = constants

This means that “Z” is a logarithmic function in “C”. On a log—log paper this relation could be easily verified. Approximately 0.17 gm of ozone is required to decolorize one gm of dye, if the initial dye concentration in solution is 1.0 g/L.
Figure (5) shows the effect of adding different catalysts in different concentration on the amount of ozone reacted for a 100mg/L scarlet dye sample. It is clear that some salts are better than others. In this respect zinc sulphate was found to give the best results.

In Figure (6) the effect of these catalysts is shown. The % reduction in time of decolorization increased as the catalyst concentration increased. Zinc sulfate was chosen as the best catalyst that enhances dye decolorization.

**Fig. 4:** Effect of Initial Dye Concentration on Amount of Ozone Reacted for Decolorization of Direct Red 4BS without Catalyst

![Fig. 4](image1.png)

**Fig. 5:** Effect of Different Catalysts Concentration on Reacted Ozone for Decolorization (Initial Dye Concentration= 100mg/L)

![Fig. 5](image2.png)

**Fig. 6:** Effect of Different Catalysts Concentrations on % Time Reduction for Decolorization of Direct Red 4BS by Ozone

![Fig. 6](image3.png)

**Conclusion:**

Decolorization of direct dyes by ozone can be carried out successfully and could be quantitatively predicted. In the decolorization process, increasing the initial dye concentration results in an increase in both the time needed for decolorization and the absolute amount of ozone reacted. Equation (1) and (2) describe the behavior of the process. Calibration curve for total ozone generated over the full span of ozonation time must be determined to insure correct results. The presence of some inert inorganic salts such as zinc sulfate catalyzes the process of decolorization i.e. decrease both the amount of ozone reacted and the time of decolorization.
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REFERENCES


