

Removal of COD and color of Carmine Dye by Photocatalytic Ozonation with effect of Zinc Oxide catalyst

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Abstract- Photocatalytic ozonation is found to be one of the most effective ways to degrade dye waste water. Photocatalytic ozonation facilitates ozone decomposition and hydroxyl radical formation. For this study Carmine dye (non azo) was used as dye model. Carmine dye has UV max absorption (water) of 500 nm. The carcinogenic effects of dye include asthma, rhinoconjunctivitis, anaphylaxis, allergic contact, dermatitis, hypersensitivity and skin damage caused from prolonged exposure and consumption. The effect of various dye concentrations (50 ppm, 100 ppm and 200 ppm), catalyst ZnO loading (0.125 g/l, 0.25 g/l, 0.5g/L), pH (5.5, 7, 8.5) and ozone flow rate (30, 45, 65 lph) have been studied. The optimum parameters were found to be 200 ppm dye concentration, 0.25 g/l ZnO catalyst loading, acidic pH of 5.5 and maximum ozone flow rate of 65 lph. The reaction kinetics and % COD reduction have also been investigated. The reaction was found to follow first order kinetics with rate constant k equal to 0.0255 min^{-1} . Photocatalytic ozonation process was found to reduce COD % of dye effluent by 60%. Samples of dye were analyzed by UV-Vis spectroscopy. Photocatalytic Ozonation method can be used to produce high quality water which can be reused and gives better management of waste water.

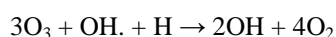
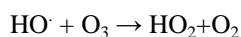
Index Terms- Advanced Oxidation Process; Photocatalytic ozonation; Carmine dye; Zinc Oxide catalyst; UV-Vis Spectrophotometer

1. INTRODUCTION

Water pollution has been a main reason of concern since years for the mankind. Water pollution has taken a toll mainly because of reasons such as industrial effluents having contaminants such as toxic chemicals, nutrients, pathogens. Change in the chemical, physical, biological quality of water is injurious for consumption of human beings and aquatic life. Contaminants have a significant impact on ecosystems. More than 60% of the world dyes production is consumed by textiles industries [3]. The presence of dye in water may have other environmental negative effects such as reflection of sunlight, low quality of the treated water since the presence of residuals affect water properties such as pH, hardness, etc., non-soluble salts that cause partial or complete blocking of process tube lines [5]. Textile industry effluents can be classified by extreme fluctuations in many parameters such as high concentrations of recalcitrant organic and inorganic chemicals and are characterized by high chemical oxygen demand (COD) and total organic carbon (TOC), pH, salinity. Traditional physical and chemical methods such as coagulation, adsorption, ion exchange or ultra-filtration, though, can generally be used efficiently, result in the generation of solid waste which needs further disposal [5]. Such methods have been helpful in

removing colour but are costly and do not at times meet the discharge criteria. Therefore some studies suggest employing advanced oxidative processes (AOPs) in isolation, combined or for preliminary assessment. Several methods are available for generating OH radicals. These include both non-photochemical and photochemical methods such as Ozonation at elevated pH (>8.5), Ozone + hydrogen peroxide ($\text{O}_3/\text{H}_2\text{O}_2$), Ozone + catalyst (O_3/CAT), Fenton system ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$), O_3/UV , $\text{H}_2\text{O}_2/\text{UV}$, $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$, Photo-Fenton/Fenton-like systems, Photocatalytic oxidation (UV/TiO₂) [16]. The toxicity reduction and decolourisation of textile effluent combining the photocatalytic process with ozonation found to be very efficient.

Photocatalytic ozonation controls the decomposition of ozone and hydroxyl radical formation using catalyst. Cleavage of dye takes place both by direct ozonation and radical pathways, involving the generation of hydroxyl radicals which can be activated by UV light. The reaction between hydroxide ions and ozone leads to the formation of super-oxide anion radical O_2^- and hydroperoxyl radical HO_2 . By the reaction between ozone and the super-oxide anion radical the ozonide anion radical O_3^- is formed, which decomposes immediately giving OH radical [15].



In this work we have carried out photocatalytic ozonation of carmine dye (non azo dye). Experiments were carried out in a batch quartz photo-reactor equipped with magnetic stirrer and Ozonator. The irradiation source was a UV Mercury Vapor Lamp (250W, Philips), which was placed in the inner glass holder of the reactor. At the same time ozone is supplied through ozonator at a flow rate of 65 lph in reactor. Reaction is carried out with the help of UV light and ozone gas for time limit of 2 hrs. Samples were withdrawn at regular time intervals and analyzed for dye degradation. Percent decolorization of Carmine dye was measured at different time intervals by UV-Vis spectrophotometer using absorbance at maximum wavelength (λ max) of the dye. Parameters such as Effect of initial dye concentration (with and without catalyst loading), effect of pH, effect of catalyst loading, effect of ozone concentration, reaction kinetics and cod reduction were studied.

1.1 Carmine dye properties:

Carmine is a non azo dye. Cochineal (the primary extract) is purplish-red liquid. Carmine is made by precipitating carminic acid from the primary extract onto an alumina hydrate substrate, using aluminum or calcium cations. Carmine is insoluble in water and oil. It is stable if pH is held above 6. It is soluble in alkaline solution, where it is a bright burgundy/violet color. Its molecular weight is 492.3864 g/mol. Its molecular formula is $\text{C}_{22}\text{H}_{20}\text{O}_{13}$. Carmine is Soluble in alcohol, concentrated sulfuric acid; slightly soluble in ether; practically insoluble in petroleum ether, benzene, chloroform. Its solubility in water is 1.30 g/L (1.30X10+3 mg/L) at 25°C and less than 1 mg/mL at 70 ° F. Carmine has pH of 4.8 (yellow) and 6.2 (violet). Carmine's spectral properties show maximum UV absorption (water) at 500 nm.

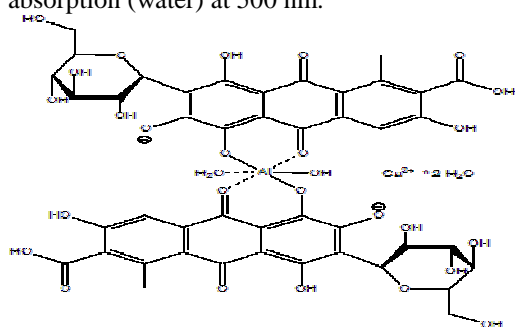


Fig1. Structure of carmine dye

2. MATERIALS AND METHODS:

Carmine dye, a typical non- azo dye, was selected for the study of effect of photocatalytic ozonation on dye effluent. Carmine dye ($\text{C}_{22}\text{H}_{20}\text{O}_{13}$, molecular weight 492.3864g/mol) of analytical

grade was purchased from S.D. Fine Chemicals (Mumbai). KI solution was prepared from KI powder which was purchased from S.D. Fine Chemicals (Mumbai) for excess ozone trapping. Catalyst Zinc Oxide of analytical grade (99% purity) was purchased from NIMCO Chemicals (Mumbai). The irradiation source was a UV Mercury Vapor Lamp (250W, Philips). Ozone is supplied through ozonator (Le' Pure, 400 mg/l maximum ozone flow). UV-Vis spectrophotometer was used for analysis. The pH of solution was measured using pH meter. Experiments were carried out in a batch quartz photo-reactor equipped with magnetic stirrer and Ozonator. UV Mercury Vapor Lamp was placed in the inner glass holder of the reactor. Decolorization by Photocatalytic ozonation processes was performed using a 500 ml solution containing specified concentration of dye. Ozone was supplied at a flow rate of 65 lph. Reaction was carried out for time limit of 2 hrs. The suspension was stirred for 20 min in dark for the attainment of equilibrium.

Samples were withdrawn at regular time intervals and absorbance at maximum wavelength (λ max) of the dye was measured by UV-Vis spectrophotometer. The absorbance is used to measure the % decolorization of dye. Effect of various parameters such as dye concentration, catalyst loading, and pH and ozone flow rate was studied. The pH was varied using 1M NaOH solution. Ozone flow rate was varied using rotameter. COD analysis of the optimum sample was performed using standard laboratory procedure.

2.1 Determiation of chemical oxygen demand (COD)

COD is a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant. This was analyzed by laboratory method. Organic and inorganic substances in the sample are oxidized by potassium dichromate in 50% sulfuric acid solution in reflux temperature. Silver sulfate is used as a catalyst and mercuric sulfate is used to remove chloride inference. The excess dichromate is titrated with standard ferrous ammonium sulfate by adding ferroin indicator. The colour change will be sharp, changing from a blue green to a reddish hue.

3. RESULTS AND DISCUSSIONS:

3.1 Effect of initial dye concentration:

To study the effect of dye concentration on the rate of decolorization, various dye concentrations are taken. The dye concentrations of 50 ppm, 100 ppm and 200 ppm were studied for decolorization purpose. For 50 ppm dye concentration, the % decolourisation at 60 min was found to be 100%. For 100 ppm dye concentration, the % decolourisation at 90 min was found to be 100%. For 200 ppm dye concentration the maximum 100 % decolourisation takes place at 120 mins. As the concentration of dye increases the time required for max %

decolourisation increases. 50 ppm dye concentration shows max % decolourisation in less time (fig .2).

With the increase in dye concentration, the time required for complete decolorization and the amount of ozone consumption increases. When the dye concentration increases, the amount of dye adsorbed on the active sites per molecule of dye also increases. At high dye concentration the dye molecules may absorb a significant amount of UV radiation.

Also at increased dye concentration, the decolorization takes place slowly as the ratio of ozone molecules to dye molecules in the solution decreases. This happens because when there is increase in dye concentration, the dye oxidation by-products increases due to which ozone consumption increases. These may be the possible causes of decrease in the rate of dye decolorization with increase in dye concentration.

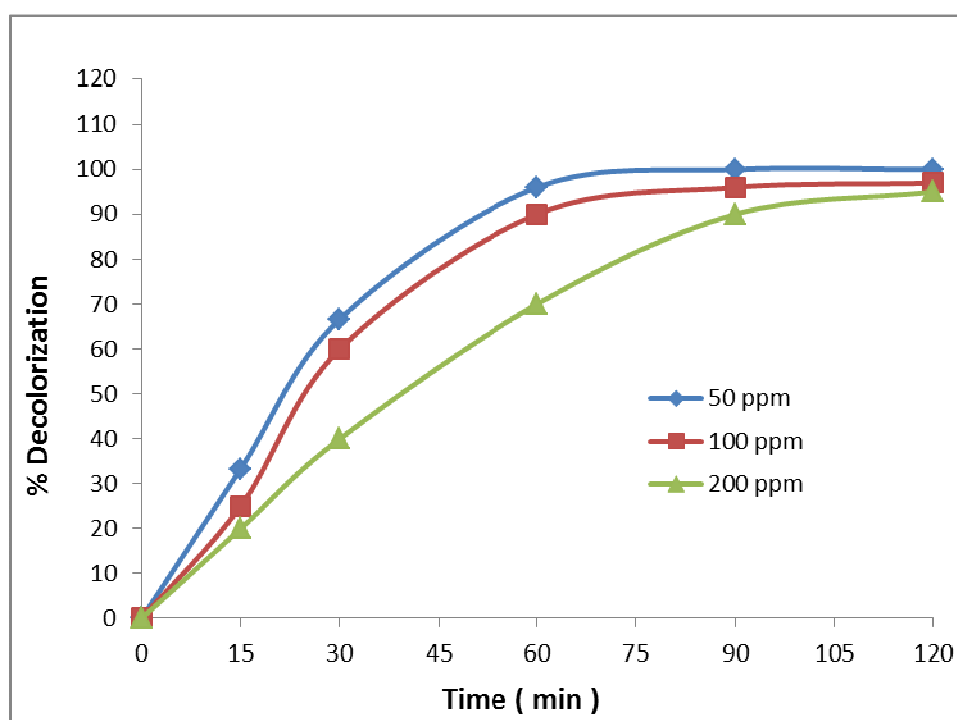


Fig2. Effect of initial dye concentration (Dye concentration = 50 ppm, 100 ppm, 200 ppm; pH = 5.5; Ozone flow rate = 65 lph)

3.2 Effect of catalyst loading:

To study the effect of catalyst loading on the rate of decolorization, the dye concentrations of 50 ppm, 100 ppm and 200 ppm were studied at the catalyst loading of 0.5g/L. Catalyst Zinc Oxide (ZnO) was used for this system. The rate of percentage decolonization increased with ZnO dosage in the range 0.5–1.5g/L. The 50 ppm solution that initially decolorized completely in 30 mins was now found to completely decolorize in 15 mins. Similarly, the 100 ppm and 200 pm solution were now found to decolorize completely in half the time taken without ZnO catalyst loading, i.e., within 30 mins and 90 mins respectively (fig 3).The removal percentage of carmine increased with ZnO dosage. The decolorization rate

of Carmine increased with ZnO dosage in the range 0.5–1.5g/L. Photo generated holes and hydroxyl radicals are produced and the yield of holes and radicals increases with ZnO dosage. Hence, the proportion of hydroxyl radicals that attack Carmine and the reaction intermediates increases with ZnO dosage. However, adding a large amount of ZnO may reduce UV penetration and have a UV screening effect, inhibiting decolorization [18, 19]. This study also found that the UV screening effect of 0.5g/L ZnO was associated with the highest decolorization rate. The decay of the absorbance at the UV band is considered to indicate aromatic fragment decolorization in the dye molecule and its intermediates[17].

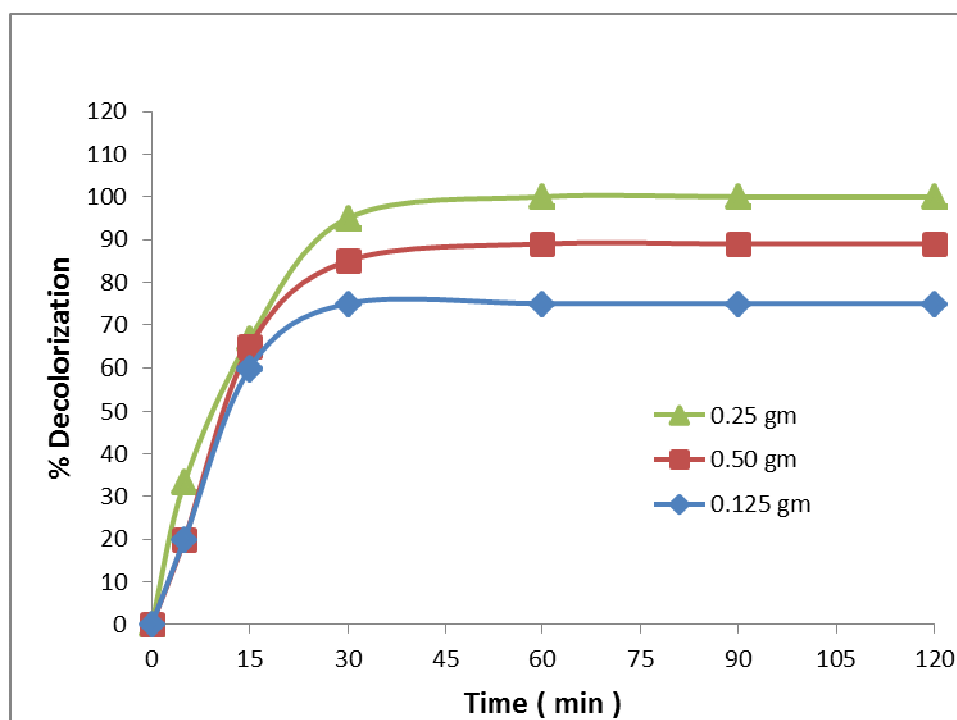


Fig3. Effect of catalyst loading (Dye concentration = 200 ppm; catalyst loading = 0.125 gm, 0.25 gm, 0.5 gm; pH = 5.5; Ozone flow rate = 65 lph)

3.3 Effect of pH:

Experiments were carried out at pH values of (5.5–8.5) using 200 ppm Carmine dye concentration and 0.5g/L ZnO. The rate of % decolorization increased with increasing pH. The stock solution with pH = 5.5 (acidic) was found to achieve 100% decolorization in 120 mins. Whereas, the solutions with pH = 7 (neutral) and pH = 8.5 (basic) were found to decolorize completely within 90 mins and 60 mins respectively (fig 4).

The interpretation of pH effects on the efficiency of dye decolorization process is a very difficult task since it has multiple roles. Because of the amphoteric behavior of most semiconductor oxides, an important parameter governing the rate of reaction taking place on semiconductor particle surface is the pH of the dispersions, since; it influences the surface-charge properties of the catalysts. The extent of photocatalysis increased with increasing pH. The formation of hydroxyl

radical from OH⁻ is favoured at high pH. The decrease in the decolorization at acidic pH may be due to dissolution of ZnO at low pH. the decolorization at acidic pH may be due to dissolution of ZnO at low pH.

Ozone decomposition is directly affected by the solution pH. Hydroxyl radicals have a greater oxidative power and are less selective than molecular ozone, leading to a decrease in decolorization and an increase in mineralization at higher pH. Ozone decomposes quickly at high pH and forms hydroxyl radicals, and this shift is fast at alkaline pH values. Since oxidation potential of OH radicals is higher than that of the ozone molecule, the decomposition reaction is faster in basic condition. At high pH value, ozone decomposes to non-selective hydroxyl radicals. Photocatalytic ozonation allows for the effective formation of hydroxyl radicals also at a low pH [7, 8]. The highest % COD reduction is obtained at low pH and hence acidic pH (5.5) is selected as optimum parameter

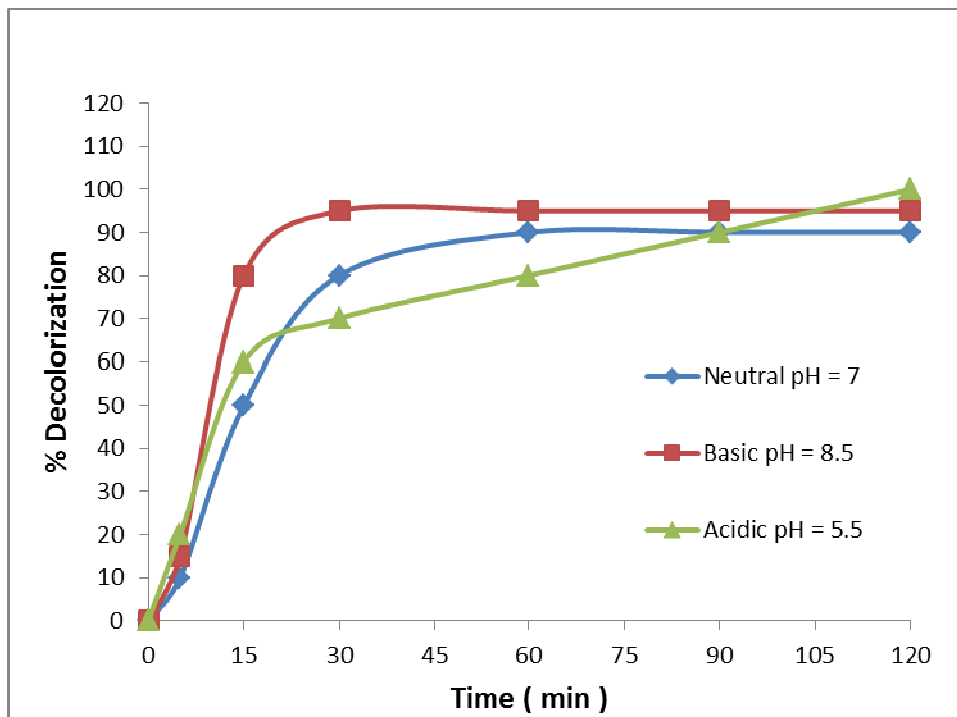


Fig4. Effect of pH (Dye concentration = 200 ppm; Catalyst loading = 0.25 gm; pH = 5.5, 7, 8.5; Ozone flow rate = 65 lph)

3.4 Effect of Ozone Flow rate:

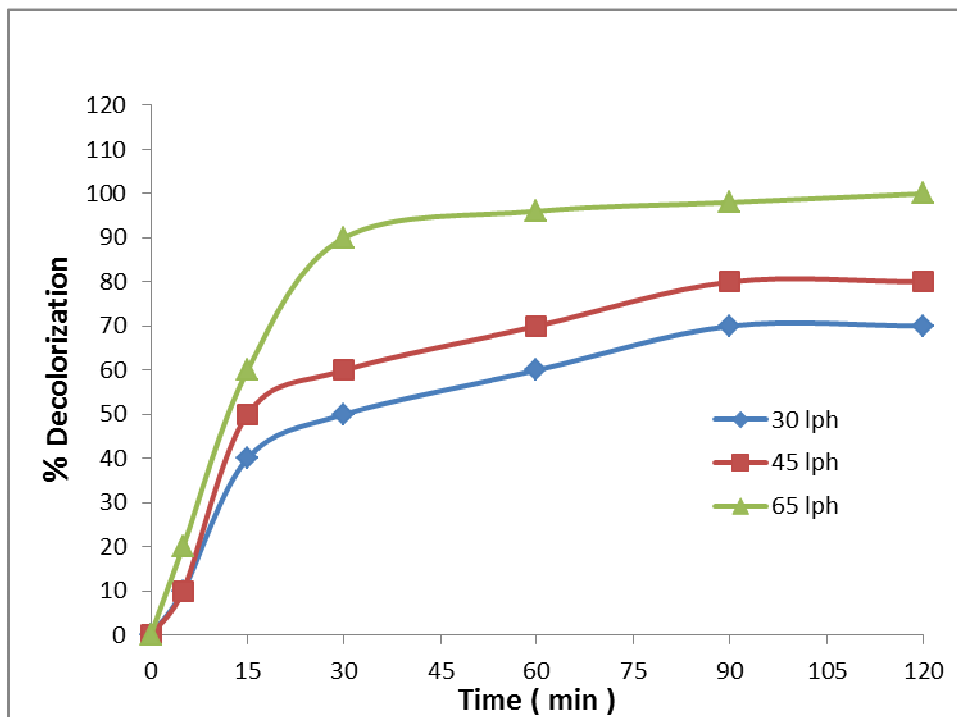


Fig5. Effect of ozone flow rate (Dye concentration = 200 ppm; Catalyst loading = 0.25 gm; pH = 5.5; Ozone flow rate = 30, 45, 65 lph)

The effect of ozone flow rate was studied in the range of 30–65 lph. The ozone flow to the system was varied using a rotameter. It was observed that highest % decolorization takes place at the maximum ozone flow, i.e., 65 lph. Ozone flow rates of 30 lph and 45 lph do not result in 100% decolorization. The % decolorization achieved using 30 lph and 45 lph is only 70% and 80% respectively (fig 5). It can be observed that depletion of carmine concentration along time increases when increasing of flow rate. Breaking of dye molecules occurs by ozonation and hydroxyl radical formation which are activated by UV light.

4. REACTION KINETICS:

The kinetics of decolorization of Carmine dye for a concentration of 200 ppm under optimized conditions (0.5 g/L ZnO catalyst loading, acidic pH = 5.5 and max ozone flow rate of 65 lph) was studied. The results (fig 6) show that the photocatalytic ozonation of dye can be described by the first order kinetic model, $\ln(C_0/C) = kt$, where C_0 is the initial concentration and C is the concentration at any time, t . The logarithmic plots of the concentration data gave a straight line. The rate constant k was found to be 0.0255 min^{-1} . The k value obtained for Carmine dye under the process of photocatalytic ozonation is consistent with first-order kinetics.

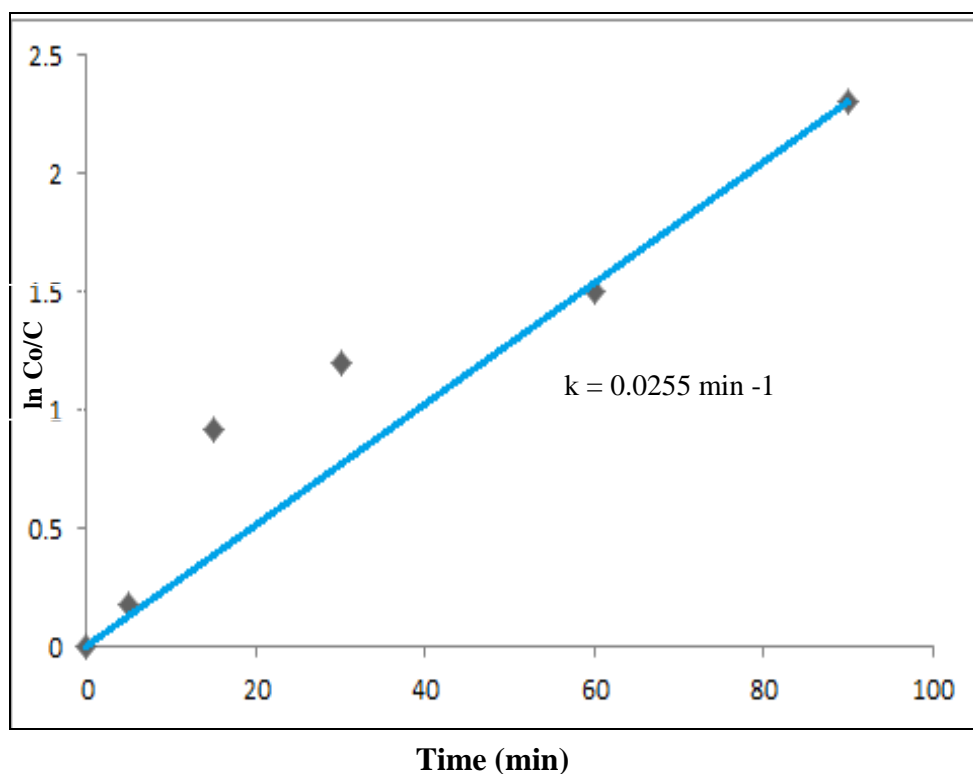


Fig6. Plot of $\ln C_0/C$ vs time (min)

5. COD REDUCTION :

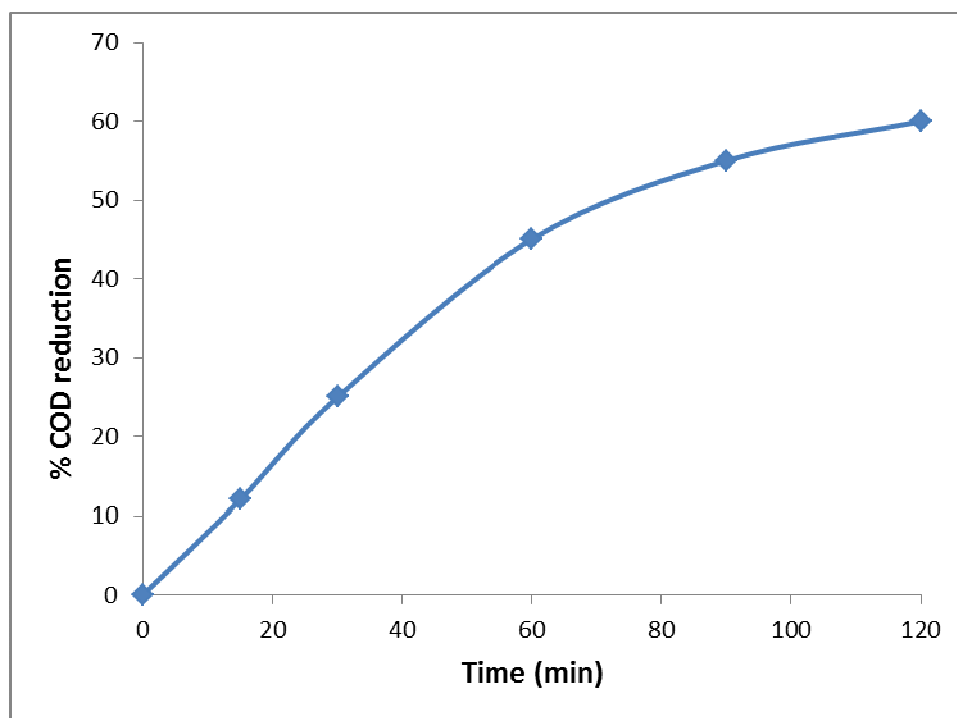


Fig7. % COD reduction vs time (min)

The % COD reduction by photocatalytic ozonation of Carmine dye solution of 200 ppm under optimized conditions (0.5 g/L) ZnO catalyst loading, acidic pH = 5.5 and maximum ozone flow rate 65 lph is shown in figure 7.

Ozone flow rate of Percent cod reduction was found to increase with time. At the end of 120 mins; a reduction of 60% COD value was obtained. The reduction of COD reflects the extent of decolorization of an organic species.

6. CONCLUSION

Advanced Oxidation Processes are promising alternative of traditional treatment processes for the treatment of textile effluent. Photocatalytic ozonation has proved to be very efficient in dye decolorization. In the present study, the efficiency of photocatalytic ozonation process on carmine dye solution using ozone and by suspending it in aqueous media in

presence of UV light has been studied. The effect of initial concentration of the dye effluent, effect of zinc oxide catalyst loading, effect of pH and effect of ozone flow rate have been investigated. Also, the reaction kinetics and the % COD reduction for photocatalytic ozonation of Carmine dye have been studied. The dye decolorization rate decreased with increase in dye concentration and increased with increase in ZnO catalyst loading. Photocatalytic ozonation along with ZnO catalyst helped to achieve controlled decomposition of ozone and hydroxyl radical formation. Therefore decolorization occurred using both direct and indirect attack at low pH. The highest % decolorization took place at the maximum ozone flow rate, i.e., 65 lph.

The kinetics of decolorization for the photocatalytic ozonation process was found to be of first order kinetic model. The rate constant k was found to be 0.0255 min^{-1} . The process of photocatalytic ozonation of Carmine dye solution resulted in 60% COD reduction.

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