

# Photocatalytic Degradation of Orange-G dye using Cu/Al<sub>2</sub>O<sub>3</sub> photocatalyst

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**ABSTRACT:** Photocatalytic ozonation of Orange-G azo dye is carried out in the presence of Cu/Al<sub>2</sub>O<sub>3</sub> as photocatalyst has been studied. This study comprised of various factors like the effect of initial dye concentration (10, 20, 50, 100 ppm), effect of catalyst loading (0.25, 0.5, 0.75 gm/l), effect of pH (6, 7, 8.4) and effect of ozone flow rate (30, 40, 60 LPH) that were altered to investigate their effect. The amount of Total Organic Carbon (TOC) reduced was plotted against time, with the TOC/TOC<sub>0</sub> ratio being negligible for initial dye concentration of 10 ppm and catalyst loading of 0.75 gm/l. Photocatalytic ozonation process was thus used to produce quality water which could be reused for efficient water management.

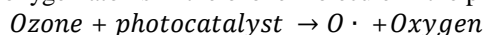
**KEYWORDS:** Advanced Oxidation Process, Photocatalytic Ozonation, Orange- G dye, Cu/Al<sub>2</sub>O<sub>3</sub> catalyst, Total Organic Carbon (TOC).

## I. INTRODUCTION

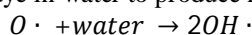
Water soluble dyes are used in many diverse industries like the textile, cosmetic, paper, leather, pharmaceutical and also food industries. Major chunk of these dyes is used in the textile industries for the process of dyeing [1]. Moreover, the release of the coloured effluent water in the fresh-water sources leads to water-pollution. Such release intends to cause eutrophication and perturbation in the aquatic ecosystems [2]. The established processes for industrial waste water treatment like activated sludge process are ineffective. Adsorption with activated carbon is also an option, but the solid adsorb these dyes which need further regeneration.

The research in the Advanced Oxidation Process (AOP) leads to effective eradication of the textile industry effluents including organic and inorganic contaminants which are characterized by elevated chemical oxygen demand (COD), total organic carbon (TOC), pH, salinity etc. These AOPs can be combined with the earlier established waste water treatment techniques or can also be used in isolation [3]. The AOPs are broadly of two types- i) Wet Air Oxidation processes with O<sub>2</sub> under the conditions of 1-20 MPa and 200-300°C and ii) Oxidation with ozone (O<sub>3</sub>) and H<sub>2</sub>O<sub>2</sub> or photons which mainly proceeds with the formation of highly reactive intermediates. The various types of AOPs include: Ozonation at elevated pH (>8.5), Ozone + Hydrogen peroxide, Ozone + Catalyst, Fenton system, O<sub>3</sub>/UV, H<sub>2</sub>O<sub>2</sub>/UV, O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/UV, Photocatalytic oxidation (UV/TiO<sub>2</sub>) [4].

Photocatalytic ozonation is used for the treatment of waste textile water by the formation of highly reactive intermediate of hydroxyl radical. Photocatalytic ozonation can be used for almost all types of organic compounds found in the wastewater contributing to the BOD of wastewater [5]. The mechanism for photocatalytic ozonation initiates by the cleavage of the bonding between oxygen atoms in the ozone molecule in the presence of photocatalyst.



The oxygen radical (O•) generated reacts with dye in water to produce hydroxyl radical.



Further the reactions take place accordingly in multiple steps, as shown in the figure 1

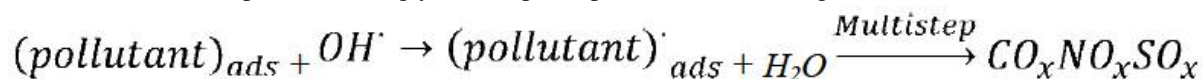


Figure 1: Reaction of conversion of pollutants in simple compounds [6]

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The side reactions taking place are:

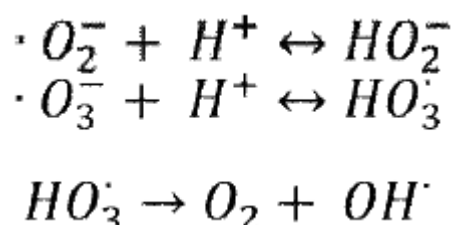


Figure 2: Side reactions taking place in the system [6]

## II. EXPERIMENTAL

### Materials

Orange- G is an azo (-N=N-) dye with a molar mass of 452.38 g/mol with a molecular formula of  $C_{16}H_{10}N_2Na_2O_7S_2$ . It is mainly used in staining purposes. It is an orange powder or crystal. Having two ionisable groups, it is capable of imparting two colours. It is orange coloured under neutral and acidic pH and red coloured at pH greater than 9. Catalyst used was  $Cu/Al_2O_3$ . All the chemicals were obtained from S. D. Fine Chemicals of analytical grade (99% purity).

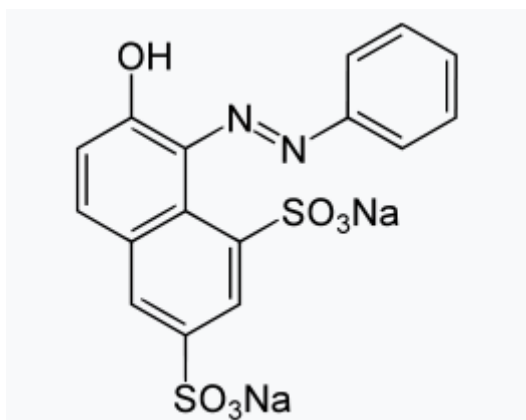


Figure 3: Structure of Orange- G dye

### Method

The experiment is carried out in a quartz photo-reactor which has a magnetic stirrer and an ozonator. An UV Mercury Vapour Lamp of Phillips, 250 W was used as source for photons. This lamp was placed in the inner glass holder of the reactor. Ozone was supplied to the reactor at a flow rate of 30, 40 and 60 LPH respectively while noting the effect of ozone, otherwise it is maintained at 60 LPH. Ozone flow-rate is controlled by a rotameter. The solution of 500 ml was prepared with varied concentrations of the Orange- G dye (10 ppm, 25 ppm, 50ppm, 100ppm). The reactor was kept in the dark wooden box. The reaction time was 120 minutes for the attainment of equilibrium.

Samples were withdrawn at regular time intervals and were checked for absorbance at maximum wavelength of the dye sample. The wavelength was measured by an UV-Vis spectrophotometer. % decolourization is measured by the decrease in the light absorbed by the samples extracted from the reactor at regular intervals. Experiments were carried by altering various parameters namely- Initial dye concentration (10 ppm, 25ppm, 50ppm, 100ppm), catalyst loading (0.25gm/l, 0.5 gm/l, 0.75 gm/l), pH (acidic- 6, neutral- 7, basic- 8.4) and ozone flow-rate (30 LPH, 40 LPH, 60 LPH). pH is controlled by adding 1M of HCl or 1M NaOH according to the pH requirements. pH meter is used to measure the pH of the solution in the reactor.

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## TOC reduction

Total organic carbon (TOC) is the amount of carbon found in an organic compound and is often used as a non-specific indicator of water quality. To determine the level of TOC, the organic carbons must be oxidized. Oxidization helps to convert total carbon into CO<sub>2</sub>. TOC is analysed by TOC analysers which are of two types based, based on their detection systems- non dispersive infrared and conductivity detector. For these experiments a non dispersive infrared type of TOC analyser is used.

### III. RESULTS AND DISCUSSIONS

#### Effect of initial dye concentration:

To study the effect of initial dye concentration on the rate of decolourization, various concentrations of dye were prepared in a 500 ml solution. The dye concentrations of prepared 10 ppm, 25 ppm, 50 ppm and 100 ppm were taken, keeping the other variables were kept constant for decolourization purpose. For complete decolourization of 10 ppm solution, the time required was 60 min. Similarly time required for 100% decolourization of 50 ppm dye solution was 90 min. For 100 ppm and 200 ppm dye concentration the time required for 100 % decolourisation to take place was approximately 120 mins.

The dye concentration, time required for complete decolourization and the amount of ozone required show a proportional variation. With the increase in dye concentration, the time required for complete decolourization and the amount of ozone consumption increases. As the dye concentration increases, the generation of •OH radicals on the surface of catalyst is reduced since active sites are covered by the dyes and at high dye concentration, significant amount of UV is absorbed by the dye molecules. Additionally at higher dye concentrations, the decolourization takes place at a slower rate because the ratio of ozone molecule to the dye molecules in the solution decreases. The possible cause may be due to the increase in dye oxidation by-product which increases the requirement of ozone.

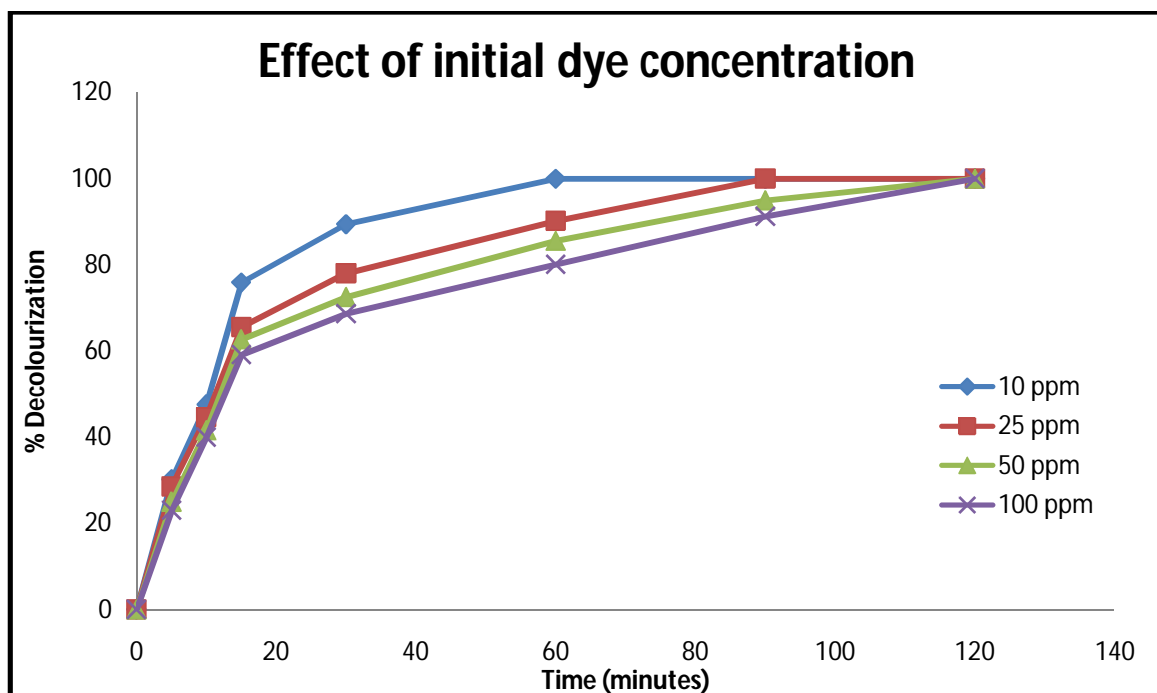


Figure 4: Effect of initial dye concentration (pH = 7; Ozone flow rate = 60 LPH; catalyst loading= 0.25 gm/l)

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### Effect of catalyst loading:

A series of experiments were carried out to assess the optimum amount of catalyst by varying the amount of catalyst. Catalyst loading of 0.25 g/l, 0.5 g/l and 0.75g/l were used for the Orange-G dye solution of 50 mg/l. The experiments were carried out for 120 mins at a pH of 7 and the percentage change in decolourization was noted. The effect of the amount of Cu/Al<sub>2</sub>O<sub>3</sub> catalyst on the decolourization efficiency was pictured in Fig 3. Experiments performed with different concentrations of catalyst showed that the decolourization efficiency was around 95% for 0.25 g/l concentration of catalyst. The % decolourization showed inverse proportion as the catalyst loading increased. The enhancement of removal rate can be explained in terms of availability of active sites on the catalyst surface and the penetration of UV light into the suspension. Increase in the concentration of catalyst which increases the active surface area.

But as increasing the catalyst concentration up to 0.75gm/l, the decolourization efficiency decreased to around 80%. This may be due to an increase in the turbidity of the suspension which causes enhancement of light reflectance by the catalyst and decrease in light penetration. The increased loading of the catalyst, increases the quantity of photons adsorbed and consequently the degradation rates. Hence it is essential to determine the optimum amount of catalyst required in order to avoid unnecessary excesses and also to ensure total absorption of photons for efficient mineralization.

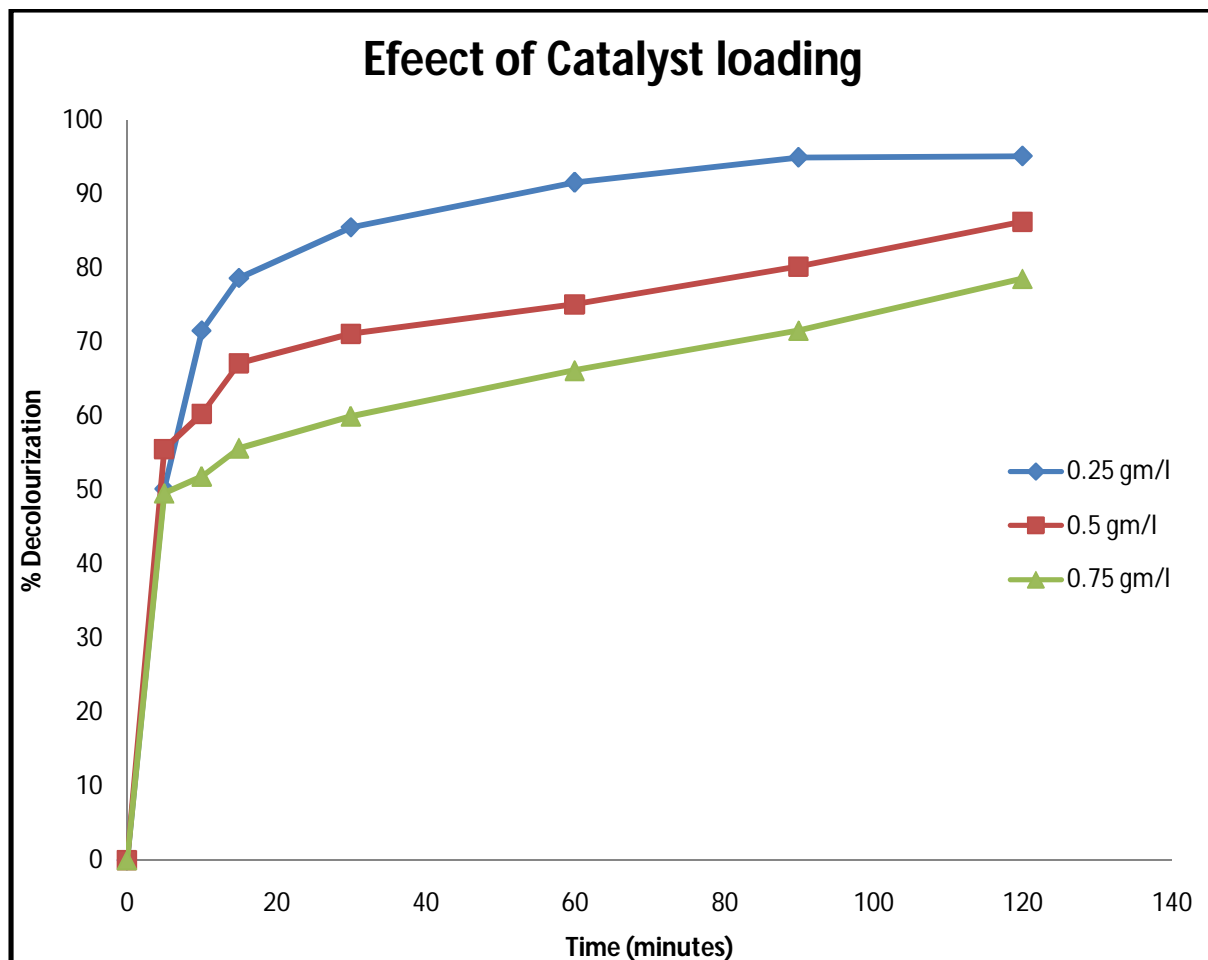


Figure 5: Effect of catalyst loading (Dye concentration = 50 ppm; pH = 7; Ozone Flow rate = 60 LPH)

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### Effect of pH:

The study of the effect of pH on the system variations in pH were made with pH varying in all the three types. Keeping the other parameters constant like dye concentration at 50 ppm, catalyst loading at 0.25 gm/l and ozone flow rate at 60 LPH, the effect was studied with pH at 6, 7 and 8.4 respectively. The desired pH level was achieved by the addition of 2M HCl / 2M NaOH to the dye solution. Maximum of 95% decolourization takes place at pH 7 (neutral).

In acidic pH range, the decolourization efficiency was least around 85% for Orange-G dye. This is because of two reasons: firstly at low pH, catalyst particle agglomeration reduces the dye adsorption as well as photon absorption, secondly the azo linkage (-N=N-) is particularly susceptible to electrophilic attack by hydroxyl radicals. At low pH (pH= 6), concentration of H<sup>+</sup> is in excess which reacts with azo linkage decreasing the electron densities of azo group. At 7 pH, percentage removal of the dye increases though dye adsorption on the photocatalytic surface decreases from pH 6 to 7. This indicates that the effect of dye adsorption on photocatalytic activity is limited. At high pH (pH= 8.4), the hydroxyl radicals are so quickly discarded that they do not have proper time to react with dyes. Hence at basic pH (8.4), % decolourization is low.

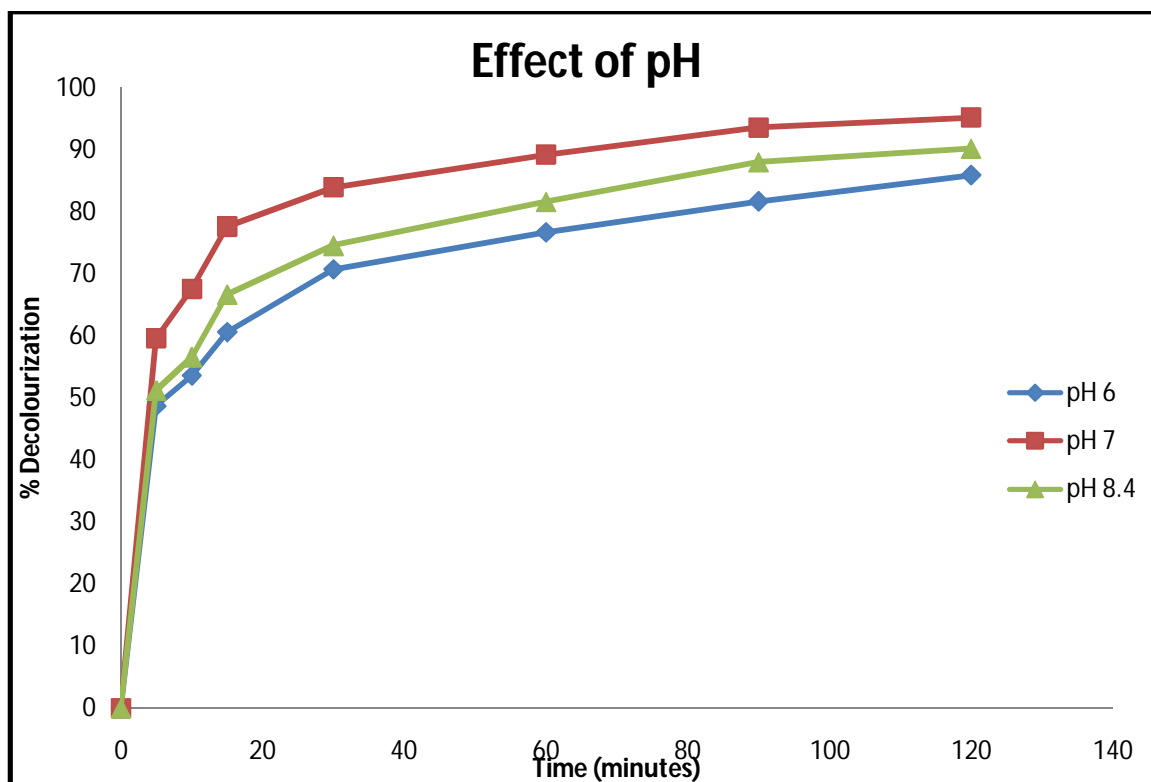


Figure 6: Effect of pH (Dye concentration = 50 ppm; Catalyst loading = 0.25 gm; Ozone flow rate = 60 lph)

### Effect of ozone flow-rate:

The effect of ozone flow rate on the system was studied by varying the ozone flow rate to the system as 30 LPH, 40 LPH and 60 LPH respectively. The rate of decolourization was plotted for the same. The experiments showed that, as the ozone flow rate to the system increased so did the decolourization rate. At 60 LPH ozone inlet, a maximum decolourization of around 98% was observed. For 30 LPH and 40 LPH the % decolourization was found to be 80% and 90% respectively. Breaking of dye molecules occurs by ozonation and hydroxyl radical formation which are activated by UV light. An increment of ozone concentration led to higher oxidation rates and mineralization efficiency.

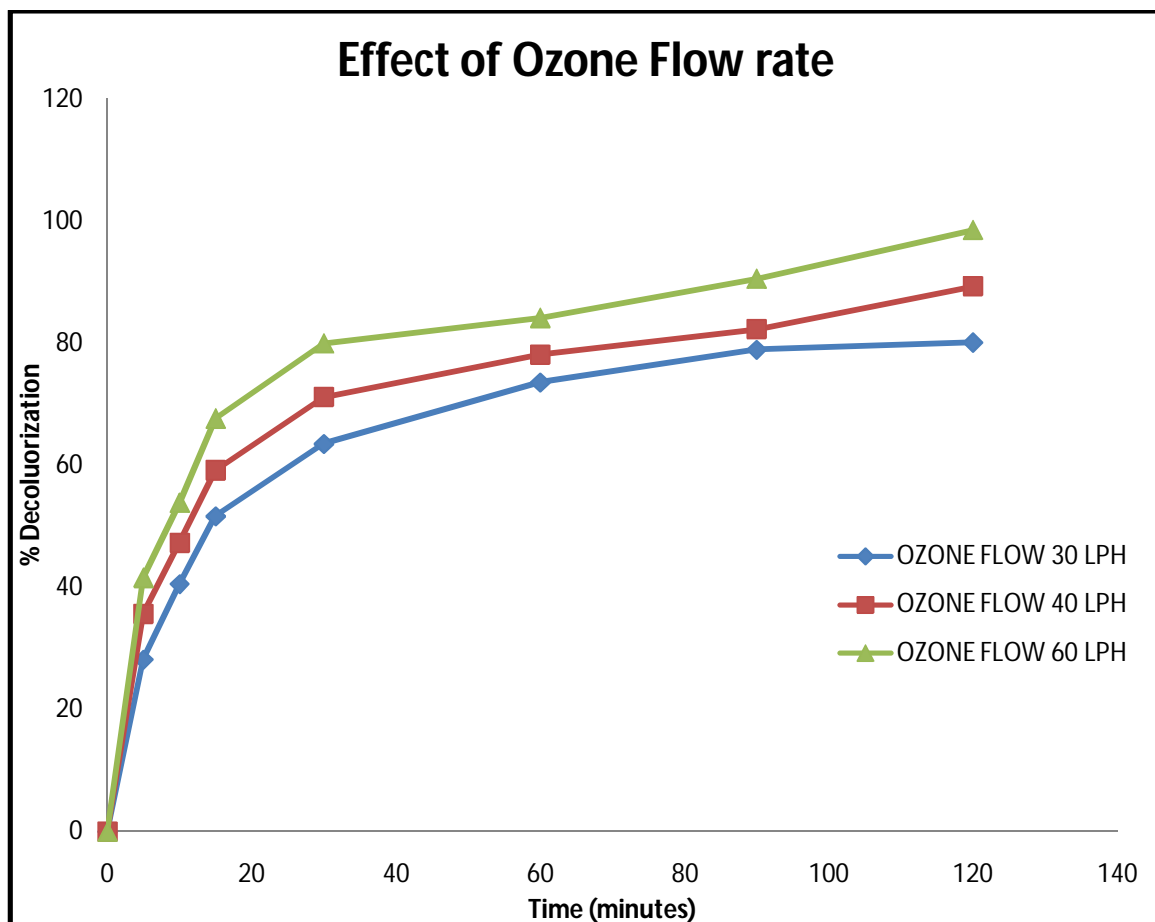


Figure 7: Effect of ozone flow rate (Dye concentration = 50 ppm; Catalyst loading = 0.25 gm; pH = 6.9)

#### IV. TOC REDUCTION:

##### Effect of initial dye concentration:

The amount of Total Organic Carbon (TOC) reduced was investigated by varying the initial dye concentration. The dye solutions of 10 ppm, 25 ppm, 50 ppm and 100 ppm were used for the investigation. It was seen that as the dye concentration was increased, the TOC reduced decreased. The TOC reduction was highest for 10 ppm solution. TOC reductions read as 54% for 10 ppm while it was 46% for 100 ppm solutions. This negative effect can be explained as the dye concentration increases, the equilibrium adsorption of the dye onto the catalyst surface active sites increases, hence competitive adsorption of OH on the same sites decreases, resulting in the lower formation rate of OH radical. Furthermore, as the initial dye concentration increases, the path length of photons entering the solution decreases this means lower photonic absorption on catalyst particles and slower photocatalytic reaction rates.

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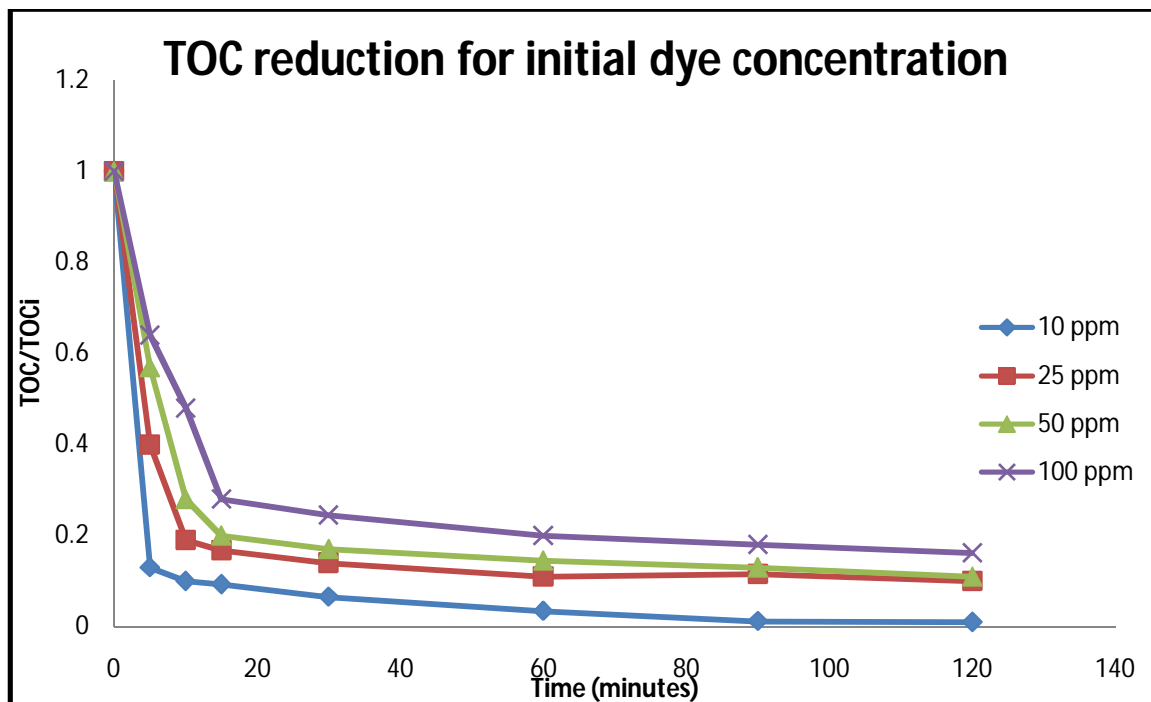


Figure 8: Effect of initial dye concentration (ozone flow rate= 60 LPH; catalyst loading= 0.25gm; pH=7)

### Effect of catalyst loading:

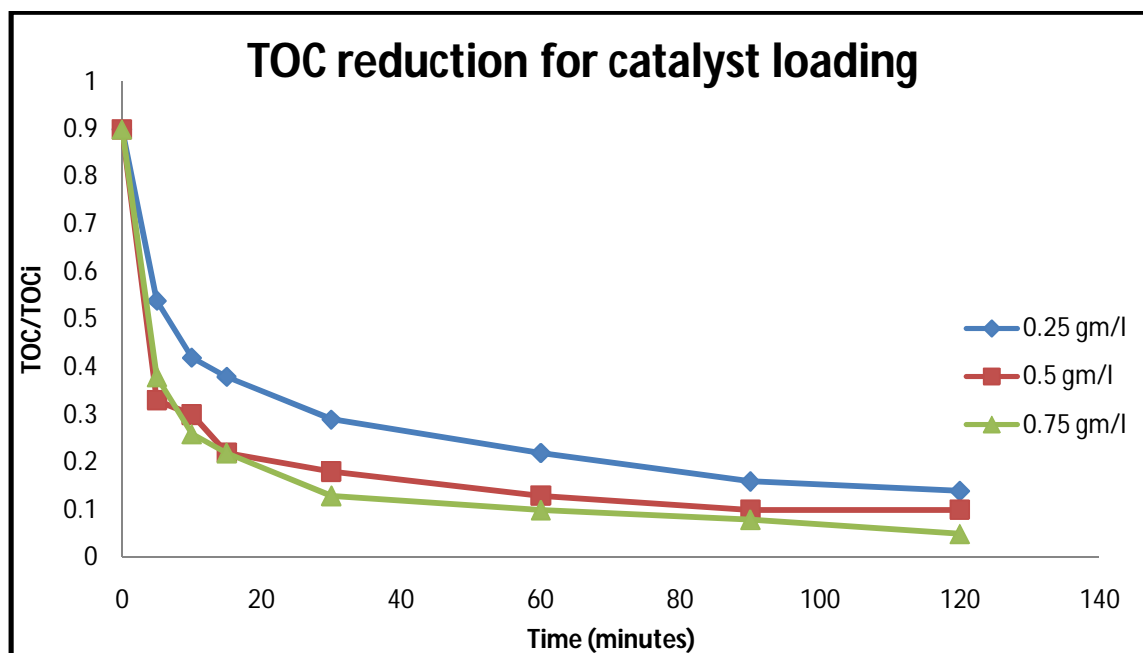


Figure 9: Effect of catalyst loading (pH=7; initial dye concentration=50ppm; ozone flow rate=60 LPH)

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To determine the effect of the catalyst loading, a series of experiments were carried out by varying the amount of catalyst from 0.25 to 0.75g/l. TOC removal are depicted in Fig. Maximal dye degradation, 56.3% TOC removal, was obtained when 0.25g/L of Cu/Al<sub>2</sub>O<sub>3</sub> was added. But further increasing the catalyst loading the rate of dye degradation reduced, i.e., 42%. The increase in catalyst loading decreased the TOC removal of the solution. This is because of formation of complex ion and some unwanted reactions takes place between iron and other types of formed radicals. Catalyst brought resistance to the removal of total organic carbon in the solution.

## V. CONCLUSION

Photocatalytic Ozonation, an AOP is a promising technology and an alternative technique for the treatment of water with textile effluents due to its effective use in dye decolourization. Orange- G dye was readily degraded using this technique. The effects like- initial dye concentration, effect of catalyst (Cu/Al<sub>2</sub>O<sub>3</sub>) loading, effect of pH and effect on ozone flow rate were successfully investigated. TOC reduced was plotted against time for the system for various catalyst loadings and initial dye concentration.

The main problem with the use of AOPs lies in the high cost of reagents such as ozone, hydrogen peroxide and UV light source. On contrary, these problems can be overtaken by the use of solar radiations or electrochemical storage of energy and ozone generation. Photocatalytic ozonation has shown advantageous applications for many organic wastes in water and can be used to eliminate industrial recalcitrant.

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