Decolourization of Orange- G Dye using TiO_2 Catalyst

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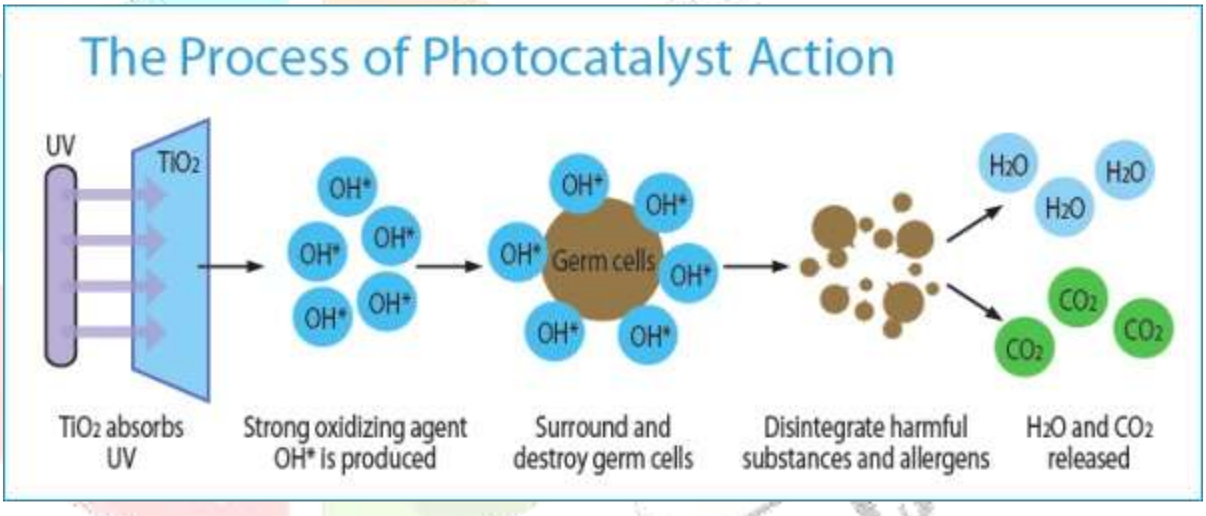
Abstract: **Textile dyes are not efficiently removed from the textile waste water in treatment plants and are released in surface water streams, thus toxicating the pure water streams. The study was carried out through the Photocatalysis technique using TiO_2photo-catalyst. Thus, the Photocatalysis of Orange-G dye (azo dye) was studied under various parameters like the initial dye concentration, catalyst loading and effect of pH. To study the decolourization effect due to Photocatalysis simulated waste water using various concentrations of dye in water were prepared. The process was followed by the studying the decolourization rate of the simulated waste water. Kinetics of the process was also studied by optimizing the various parameters studied earlier. The rate constant was calculated to be 0.0312 min^{-1}. The reduction in chemical oxygen demand of the sample was about 35% after 120 minutes of treatment.**



IndexTerms **- Photocatalysis, TiO_2 catalyst, Ultra- Violet region, Orange-G dye, Decolourization, Chemical Oxygen demand (COD).**

I. INTRODUCTION

Photocatalysis is also referred to as a photo-induced reaction which can be carried out at ambient conditions accelerated by presence of catalyst [Akpan *et al.*, 2009]. Photocatalysis is one of the Advanced Oxidation Processes (AOPs) used for degradation of various unethical elements from water before it can be mixed with fresh water bodies. These days the effluents from printing and textile industries are being addressed as a potential threat [Reisch, 1996]. The textile industry is one of the major generator of waste water due to water used in dying process [Saratale *et al.*, 2011]. Most of the dyes used are N- substituted or their N-substituted transformation product have health hazards [Miao *et al.*, 2015, Shah, 2014]. Azo groups are the compounds containing (-N=N-) N double bond N linkage in their structure.

Removal of such toxic components from water has gained utmost importance and various techniques like homogenous and heterogeneous catalysis, adsorption using activated carbon, fly ash, peat, etc. [Ramakrishna *et al.*, 1997], reverse osmosis and many other methods have come into play.

Here in this article we have used Photocatalysis using TiO_2 and Orange-G dye simulated waste water has been treated. An excellent photocatalyst like TiO_2, has been used in various studies because of its chemical stability, photo-stability under UV as well as visible light, wide band gap semiconductor (3.2 eV) and is relatively inexpensive [Andreozzi *et al.*, 1999, Ibhadon *et al.*, 2013, Munter, 2001, Karla *et al.*, 2011, Yonar, 2011]. Due to near UV- light or UV light illumination the surface of the catalyst material becomes sufficiently oxidizing that it can oxidize the hydroxyl ions on its surface to hydroxyl radicals [Ollis *et al.*, 1990].

II. 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. When exposed to ultraviolet it shows a light blue fluorescence. Having two ionisable groups, it is capable of imparting two colors. It is orange colored under neutral and acidic pH and red coloured at pH greater than 9. The main uses of Orange G are in the OG 6 Papanicolaou stain, to stain keratin, and as a major component of the Alexander test for pollen staining. It is often combined with other yellow dyes and used to stain erythrocytes in the trichrome methods.

Figure 1: Structure of Orange- G dye

The catalyst used is Aeroxide P-25 TiO_2. Aeroxide TiO_2 P-25 is a fine-particulate, pure titanium dioxide (TiO_2) with high specific surface area and marked aggregate and agglomerate structure. Because of its high purity, high specific surface area, and unique combination of anatase and rutile crystal structure, the product is suitable for many catalytic and photocatalytic applications. Its structure also makes it suitable for use as an effective UV filter.

III. METHODOLOGY

The experiment is carried out in a quartz photo-reactor which has a magnetic stirrer and an ozonator. An UV Mercury vapor lamp of Phillips, 250 W was used as source for photons. This lamp was placed in the inner glass holder of the reactor. The solution of 500 ml was prepared with varied concentrations of the Orange- G dye (10 ppm, 50ppm, 100ppm). The reactor was kept in the dark wooden box. The reaction time was 120 minutes for the attainment of equilibrium.

Figure 2: Experimental setup

Experiments were carried in the above arrangement of reactor. A 500 ml volume of dye solution was introduced in the reactor. Predetermined quantity of catalyst was introduced in the reactor after 10 minutes. To study the effect of amount of catalyst various quantities were prepared namely – 0.1 gm, 0.25 gm and 0.5 gm. After the introduction of catalyst, reactor was illuminated with 250 W UV lamps for absorption of 730nm emission. After 15 minutes, samples were withdrawn from the reactor and stored in dark for further analysis. The absorbance spectrum is determined with UV spectrophotometer using cuvettes and the degradation of dye was monitored by recording the absorbance at λ max as a function of illumination time.

IV. DETERMINATION 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 color change will be sharp, changing from a blue green to a reddish hue. The COD of the sample was measured at optimum condition by collecting sample at regular interval of 15 minutes.

V. RESULTS AND DISCUSSION

5.1 EFFECT OF INITIAL DYE CONCENTRATION

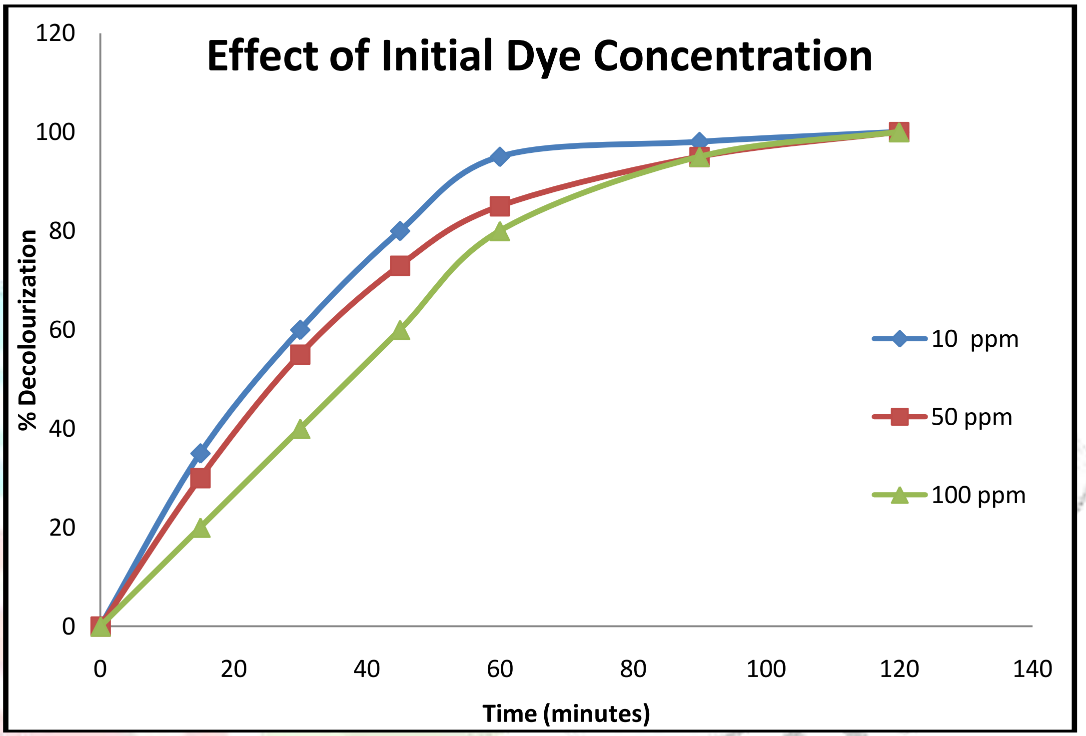


Figure 3: Effect of initial dye concentration.

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, 50 ppm and 100 ppm were introduced in the reactor, keeping the other variables constant for decolourization purpose. For complete decolourization of 10 ppm solution, the time required was 60 minutes. Similarly, time required for 100% decolourization of 50 ppm dye solution was 90 minutes. For 100 ppm dye concentration the time required for 100 % decolourization to take place was approximately 120 minutes.

When the dye concentration increases the amount of dye adsorbed on the active sites per molecule of dye also increases. This affects the active sites of the catalysts hence decreases the efficiency of the TiO_2. An increase in dye concentration also decreases the path length of photon entering into the dye solution. At high dye concentration the dye molecules may absorb a significant amount of UV radiation rather than the catalyst and this may also reduce the catalytic efficiency

5.2 EFFECT OF CATALYST LOADING

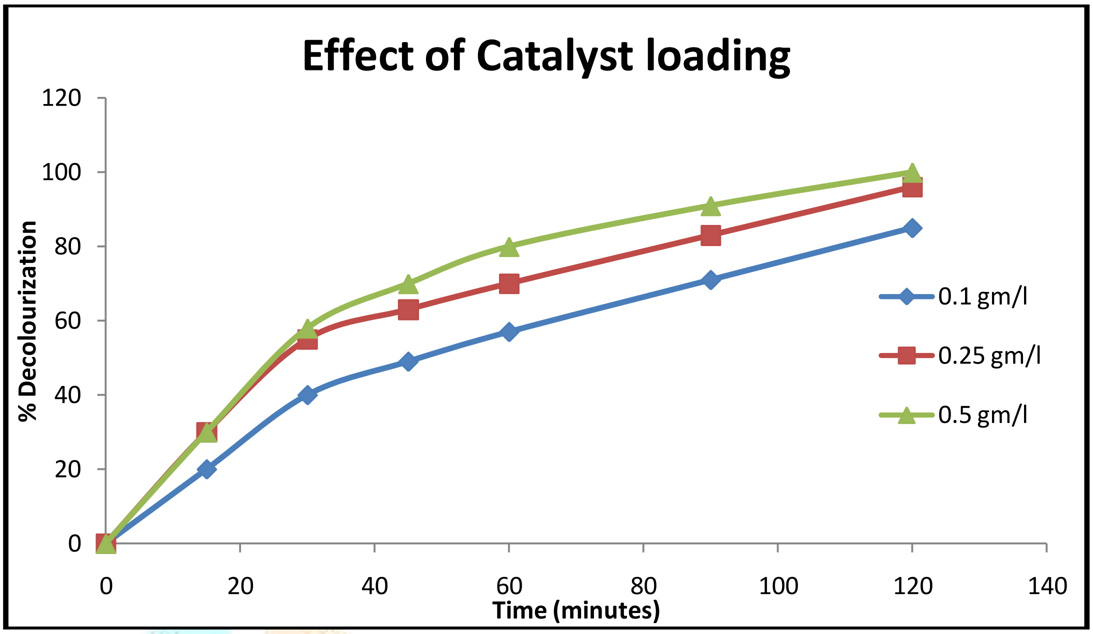


Figure 4: Effect of Catalyst loading

A series of experiments were carried out to assess the optimum amount of catalyst by varying the amount of catalyst. Catalyst loading of 0.1 g/l, 0.25 g/l and 0.5g/l were used for the Orange-G dye solution. The experiments were carried out for 120 min and the percentage change in decolourization was noted. The effect of the amount of TiO_2 catalyst on the decolourization efficiency was pictured in Figure 6.2. Experiments performed with different concentrations of catalyst showed that the decolourization efficiency was around 100% for 0.5 g/l concentration of catalyst. The percentage decolourization showed a proportional relation to 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, also increases the active sites on the catalyst surface area.

But at lower catalyst concentration of 0.1 gm/l, the decolourization efficiency decreased to around 80%. This may be due to decrease in the availability of active sites on the catalyst surface. At lower loading levels, such as 0.1 gm/L, the catalyst surface and absorption of light by the catalyst surface are the limiting factors, and an increase in catalyst loading greatly enhances the process efficiency.

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.

5.3 EFFECT OF pH

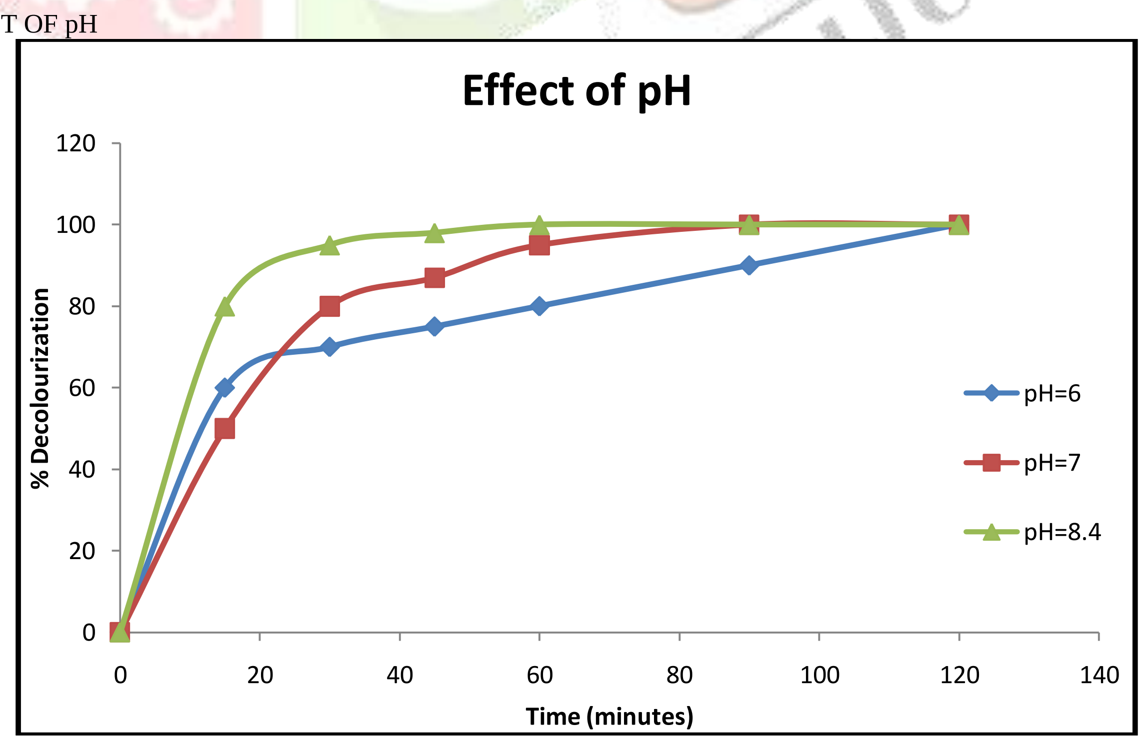


Figure 5: Effect of pH

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 and catalyst loading, 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 100% decolourization takes place at pH 8.4.

In acidic pH range, the decolourization efficiency was around 100% for Orange-G dye. But this was achieved at 120 min, later as compared to pH= 7 and 8.4. 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+ is in excess which reacts with azo linkage decreasing the electron densities of azo group. At 7 pH, percentage color removal of the dye increases due to dye adsorption on the photocatalytic surface decreases. This indicates that the effect of dye adsorption on photocatalytic activity is limited.

This system was optimized on the basis of the three experiments. The optimized conditions are dye concentration= 100 ppm, catalyst loading = 0.5 gm/l and pH= 6.

VI. REACTION KINETICS

The kinetics of decolourization of Orange G dye for a concentration of 100 ppm under optimized conditions of 0.5 gm/l TiO_2 catalyst loading and acidic pH = 6 was studied. The results show that the Photocatalysis of dye can be described by the first order kinetic model,

$$\ln (C_0/C) = k * t$$

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 0.0312 min^{-1}. The k value obtained for Orange G dye under the process of Photocatalysis is consistent with first-order kinetics.

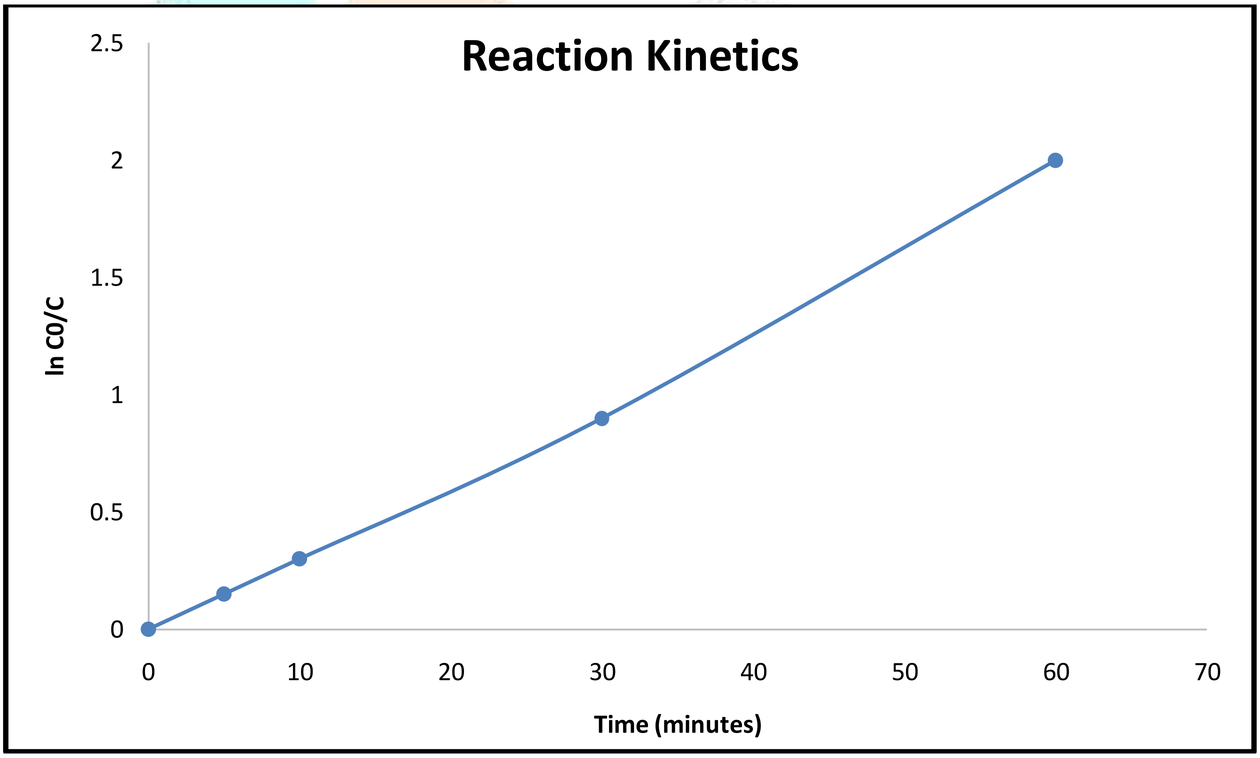


Figure 6: Reaction Kinetics

VII. CHEMICAL OXYGEN DEMAND (COD)

The % COD reduction by Photocatalysis of Orange-G dye solution of 100 ppm under optimized conditions of 0.5 gm/l of TiO_2 catalyst loading and acidic pH = 6 is shown in figure 7. At the end of 120 min; a reduction of 35% COD value was obtained. The reduction of COD reflects the extent of decolourization of an organic species.

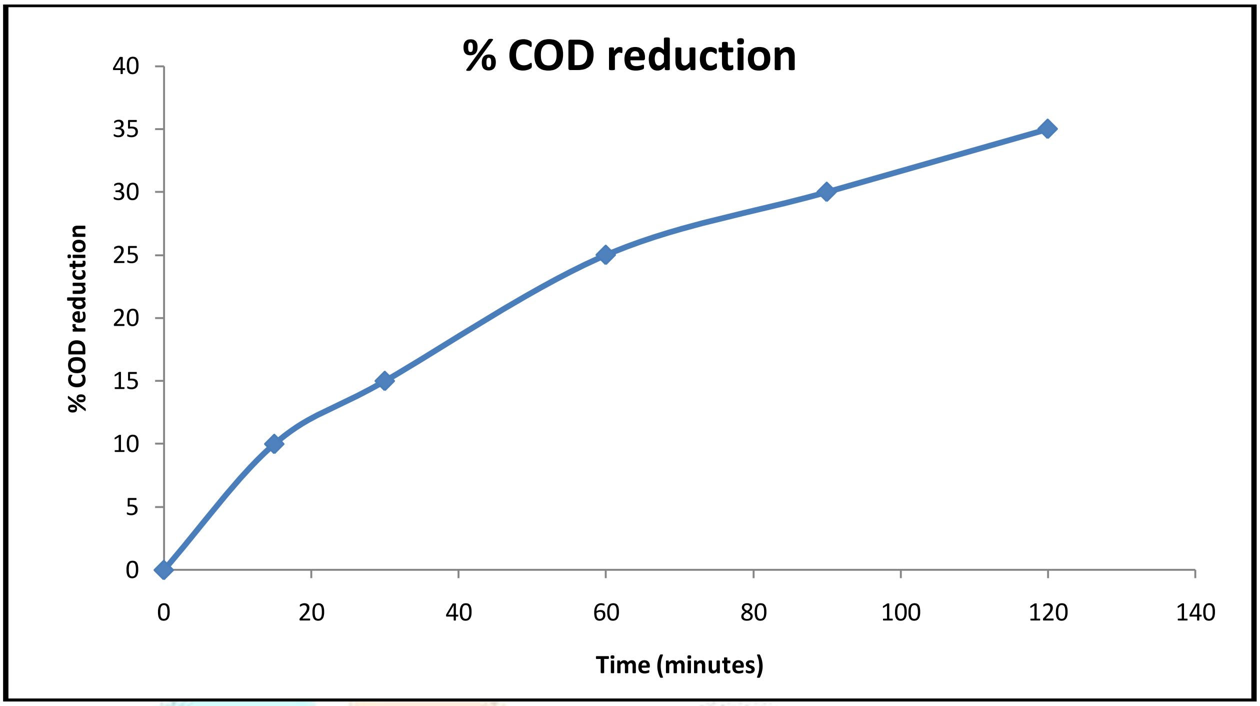


Figure 7: % COD Reduction vs Time

VIII. CONCLUSION

Orange G dye is effectively degraded by TiO_2 assisted Photocatalysis in aqueous dispersion under UV irradiation. The dye is resistant to direct photolysis. Presence of TiO_2 as photocatalyst adsorbs the dye on to its surface making it favorable for processing by photolysis. It was studied that lower concentration simulated waste water were treated quickly, while as the simulated waste increased in took longer time for its complete degradation. Absorption of photons increased with concentration of catalyst, but optimizing the value of catalyst is important to avoid excess cost estimation.

The optimized parameter was found to be 100 ppm dye concentration for 0.5 gm TiO_2 catalyst and acidic pH = 6. The reaction constant was found to be k=0.0312 min^{-1}. The COD reduction being the direct measurement of impurity removed was around 35%. This could have been increased with an increase in reaction time.

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