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Visible Light Induced Innovative Technique for the Remediation of Wastewater containing Organic Contaminants using ZnO Nano Photocatalyst

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Abstract: Advanced oxidation processes (AOPs) have been found to be highly efficient in wastewater treatment specially containing hazardous organic pollutants such as dyes. In present study, we have carried out photocatalytic degradation of Acridine Orange (AO) dye using ZnO NPs in presence of visible light. An effective and green reaction procedure has been established. ZnO as nanocatalyst has been found to be highly efficient for dye degradation particularly Acridine Orange. Several reaction parameters such as amount of catalyst, reaction pH, addition of H_2O_2 and $K_2S_2O_8$ and addition of Na_2CO_3, and NaCl have been studied.

Keywords: ZnO NPs, Acridine Orangedye, Photo-catalytic degradation, Visible light

I. INTRODUCTION

Hazardous organic waste materials found in the water related by industries and domestics source are an emerging issue of modern industrial time. The colored wastewater related by industries particularly textile industries effluent create a potential environmental problem to ecosystem and its treatment is must before discharging into natural water sources. Still there is no proper method available in reports available which is economical and technically fit for effective degradation, mineralization and decolorization of toxic and hazardous organic compounds present wastewater released by textile industry [1-3].

To overcome these problems cost effective and environmental procedure is the demand of present time for degradation and mineralization of organic waste produced by industries and domestic water as well [4-5]. AOPs are efficient technique to remove organic contamination and fulfill all the above requirements in very easy way [6].

AOPs are a set of processes involving the producing of very reactive oxygen moieties able to destroy a wide range of organic materials. AOP using heterogeneous semiconductor photocatalyst is widely applied alternate method for industrial wastewater treatment. Hydroxyl radicals generated by AOPs can completely degrade pollutant non-selectively into harmless products [7].

ZnO nanostructure have high surface area are excellent material for various catalyst degradation and with this cause in mine we have chosen it for Acridine Orange (AO) dye degradation under visible light. Acridine orange (AO) is water soluble dye and used in colorization of textile, leather, paper and lacquer industries[8-9].

II. EXPERIMENTAL PROCEDURE

A. *Photocatalytic Degradation Study*

All the chemicals used were of AR grade and used as received without further purification. Solutions were prepared by dissolving the desired amount of substance in distilled water. The photocatalytic degradation reaction was carried out in a Pyrex cylindrical photoreactor (as shown in figure 1) was used in the experiment, in which 500 W halogen lamp (Philips, India) was positioned at the center of the cylindrical vessel surrounded by a water circulation to control the temperature at 30+-0.5°C. For photocatalytic experiment, 80 mg of the photocatalyst powder was added to 100 mL of the Acridine Orange (AO) aqueous solution. The suspension was magnetically stirred in dark for 15 min to establish adsorption–desorption equilibrium. The aqueous suspension containing Acridine Orange and the photocatalyst was then irradiated under the visible light. At specific time intervals, an aliquot (3mL) of the mixture was withdrawn and centrifuged for 2 min at the rate of 3500 rpm to remove the catalyst particles in order to assess rate of decolorization and degradation photo-metrically using visible Spectrophotometer (Systronic Model No.166).The intensity of visible radiation was measured by a digital lux-meter (Lutron Lx-101). The pH was constantly monitored using a pH meter. The COD was determined by the potassium dichromate reflux method. The efficiency of photocatalytic process was calculated as:

% efficiency = $C_0 - C / C_0 x 100$. Where, C_0 and Care initial and final values for dye concentration or COD or CO_2 for reaction time t. [10-11].

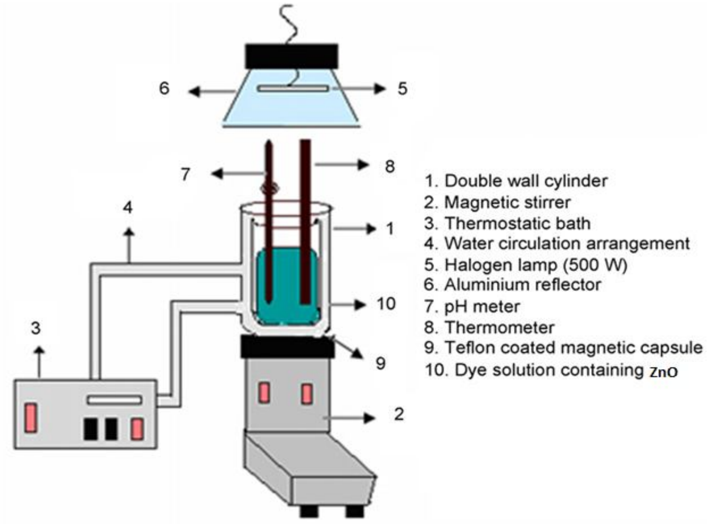

Fig. 1:Schematic view of the reactor set-up used during the photocatalytic experiments.

III. RESULTS AND DISCUSSION

A. *Effect of pH Variation*

An important parameter to be studied in photo-catalytic processes is pH. The effect of pH on the rate of reaction was investigated in the pH range 5.5 to 11.5. The photo-degradation of Acridine Orange (AO) dye was studied form 5.5 to 8.4 and found to increase first and then decreased from pH 8.4 to 11.5 and it has found to be optimum at pH 8.4. The results are reported in graphical form presented in Figure 2 clearly indicate that the value of rate constant increased from 0.97x $10^{-4}s^{-1}$ to 3.86x $10^{-4}s^{-1}$on increasing pH from 5.5 to 8.4. Thereafter, rate constant values decreased to 1.06 x 10^{-4} s^{-1} on further increase in upto pH 11.5[12-13].

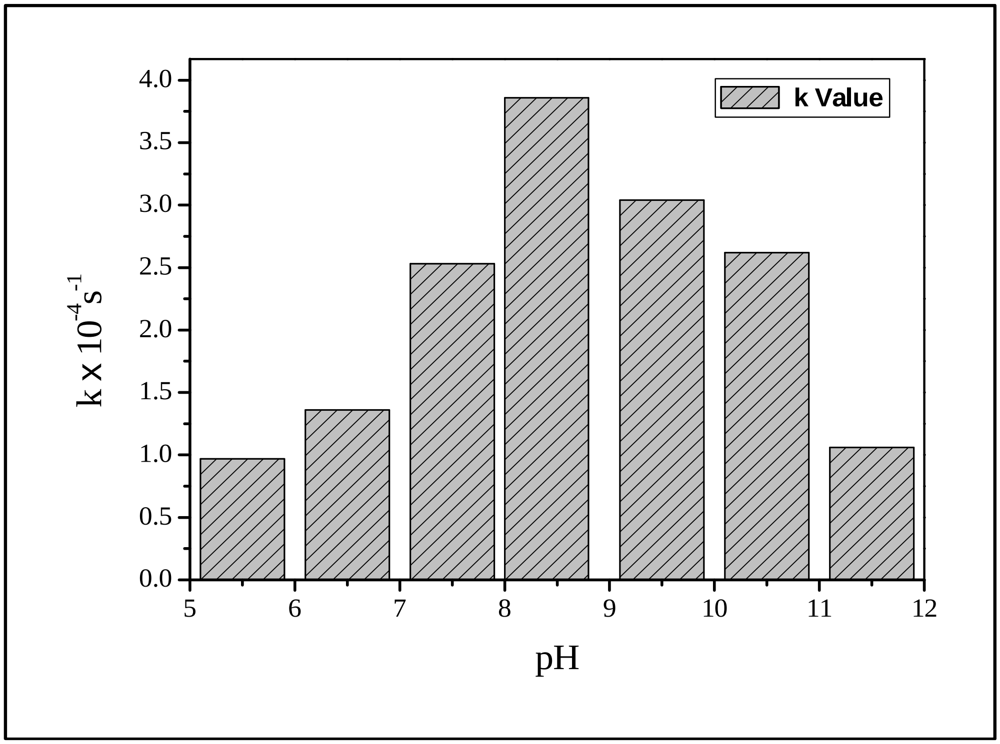

Fig. 2:Effect of pH on photocatalytic degradation of AO

Reaction conditions AO:[AO] = 2.5× 10^{-5}mol dm^{-3}, amount of ZnO NPs = 80 mg/100mL, Light intensity = 30 x 10^{3}Lux.

B. *Effect Of Zno Nanophotocatalyst*

The amount of photo-catalyst is primary parameter for dye degradation studies. It has been observed that less than 50 mg of catalyst was not effective for high degradation yield and higher amount of photo-catalyst also suppressed the dye degradation decreased. It has been also observed that ZnO nanoparticles were more effect than commercial ZnO particles because of high surface area available than commercial and as the surface area increased the photo-catalytic degradation of Acridine Orange (AO) dye increased[14].

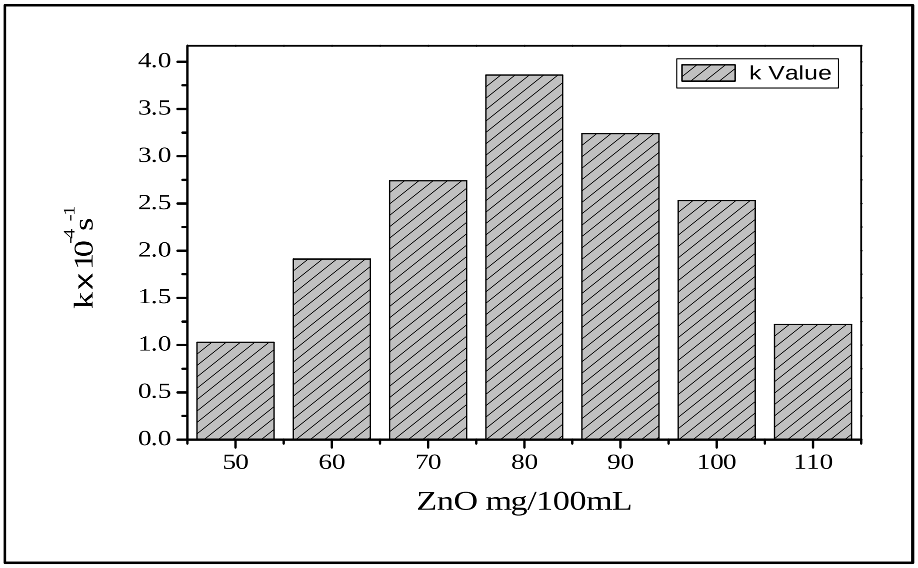

Fig.3**:** Effect of catalyst loading on photocatalytic degradation of AO

Reaction conditions AO: [AO] = 2.5x10^{-5}mol dm^{-3}, pH = 8.4, Lightintensity = 30 x 10^{3} Lux.

C. *Effect Of Initial Dye Concentration*

he initial dye concentration from 1.0 x 10^{-5}mol dm^{-3} to 4.5 x 10^{-5}mol dm^{-3} in order to find out the suitable amount was varied dye concentration. Under optimum degradation conditions as we increased the concentration of Acridine Orange (AO) dye photo-degradation rate decreased and 2.5 x 10^{-5}mol dm^{-3} was found to be the maximal initial dye concentration. It was also reported that when we increased the Acridine Orange dye concentration the rate of photocatalystdecolorization also increased and observed optimum at 2.5 x 10^{-5}mol dm^{-3} higher the initial dye concentration promoted the number of dye molecules by absorbing visible light and thus prevent photons to reach the photocatalyst surface and subsequently the rate of photo-degradation [15-16].

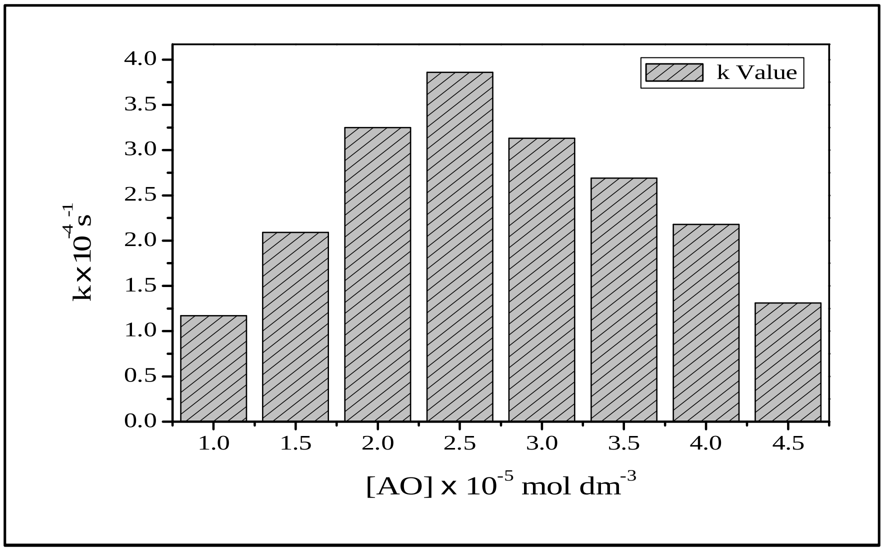

Fig.4: Effect of initial dye concentration on photocatalytic degradation of AO

Reaction condition amount of ZnO Nanoparticles = 80 mg/100mL, pH =8.4, Lightintensity = 30 x 10^3Lux.

D. Effect of H_2O_2 and $K_2S_2O_8$

The addition of oxidizing species such as H_2O_2 and $K_2S_2O_8$ to catalyst suspensions in process led to an increase in the rate of photo-degradation. The effect of concentration of H_2O_2 on the initial reaction rate of Acridine Orange (AO) dye degradation shown in Figure 5. The photo-catalytic efficiency increased as we increase the concentration of $H_2O_2$2.0 x 10^{-6}mol dm^{-3} to 10.0 x 10^{-6}mol dm^{-3} and found optimum at 10.0 x 10^{-6}mol dm^{-3} after this it again decreased. Therefore, the rate constant decreased as the concentration of the H_2O_2 increased beyond the optimum. H_2O_2 is considered to have two functions in the process of photocatalytic degradation, i.e. it accepts a photo-generated electron from the conduction band and thus promotes the charge separation [17-19]. At optimum concentration of $K_2S_2O_8$, rate constant has been found to be 7.87x 10^{-4} s^{-1}. Consequently degradation rate decreased as the concentration of the $K_2S_2O_8$ increased beyond the optimum condition [20-21]

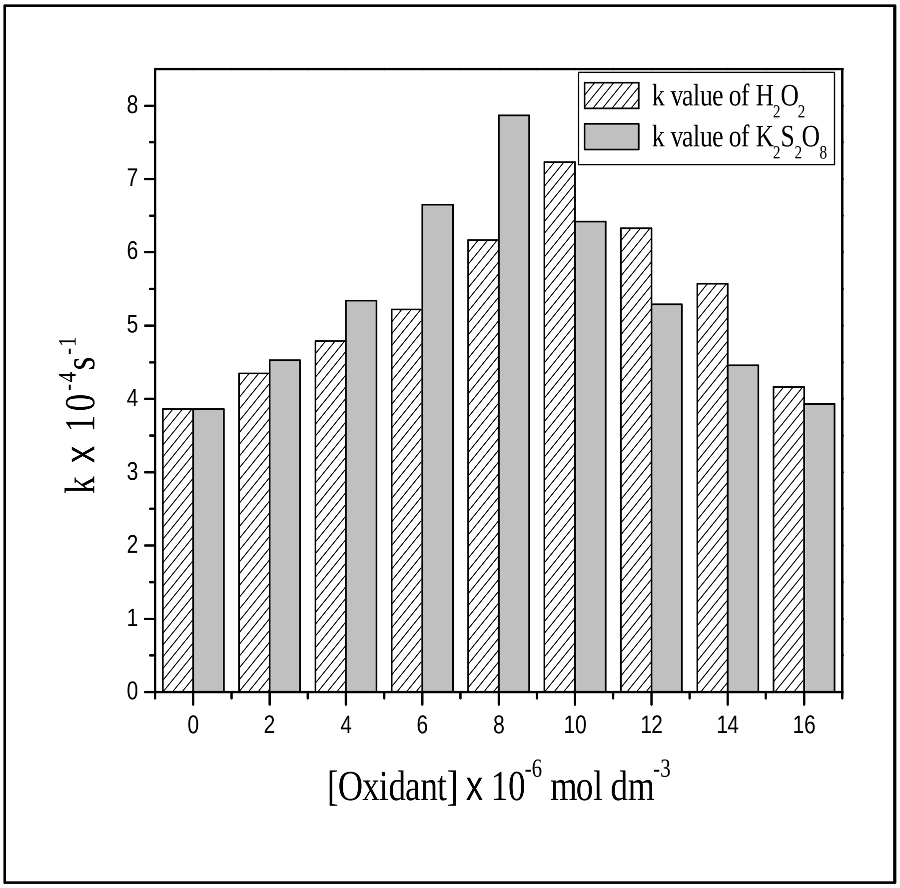

Fig. 5: Effect of oxidantson photocatalytic degradation of AO

Reaction condition AO: [AO] = 2.5 x 10^{-5}mol dm^{-3}, ZnO NPs = 80 mg/100mL, pH =8.4, Light intensity = 30 x 10^3 Lux.

E. Effect Of Sodium Carbonate And Sodium Chloride

Presence of other substances like $Na_2CO_3$and NaCl which is commonly used in dye industry has also showed influence on the photo-catalytic degradation efficiency. Two possible influences of inorganic ions on the photo-catalytic reaction are: (1) change in the ionic strength of reaction medium and (2) inhibition of catalytic of the photo-catalyst. Results showed the dependency of rate constant on the concentration of Na_2CO_3 and NaCl(Fig. 6). Therefore, the effects of added Na_2CO_3 and NaCl on the removal of Acridine Orange (AO) dye have been studied. Degradation rate decreased from 3.59 x 10^{-4} s^{-1} to 1.45 x 10^{-4} s^{-1} and 3.68 x 10^{-4} s^{-1} to 1.54 x 10^{-4} s^{-1} on increase in concentration of Na_2CO_3 and NaCl from 2.0 × 10^{-5} to 12.0 × 10^{-5}mol dm^{-3} respectively. Na_2CO_3 strongly retarded the degradation rate due to the hydroxyl radical scavenging effect of carbonate ions. It has been very well reported that anions like carbonate, bicarbonate, and chloride ions retard the degradation of organic compounds by scavenging the hydroxyl radicals to form the respective anion radical[22-24].

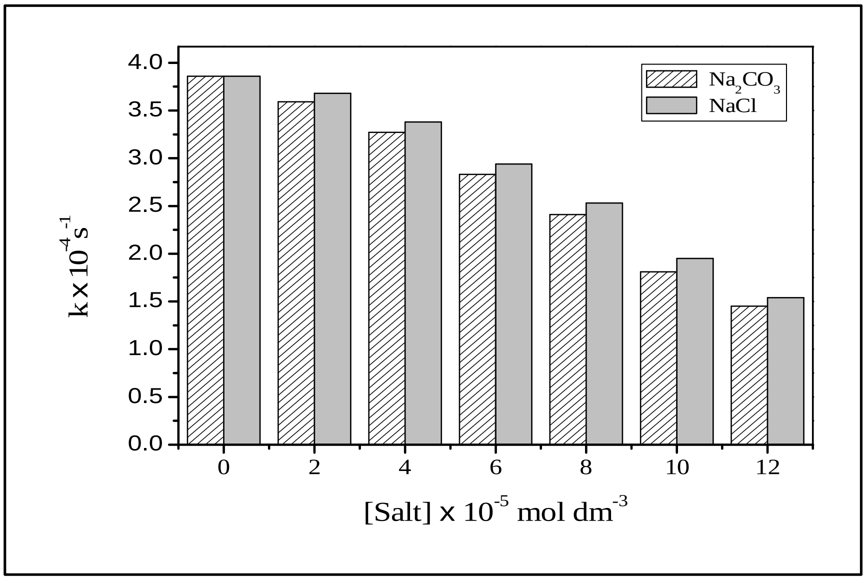

Fig. 6:Effect of oxidants on photocatalytic degradation of AO

Reaction conitionAO: [AO] = 2.5 x 10^{-5}mol dm^{-3}, ZnO NPs = 80 mg/100mL, pH =8.4, Light intensity = 30 x 10^{3} Lux.

F. Cod And Co$_2$ Measurements During Mineralization Of Acridine Orange Dye

COD has been taken as one of the important parameter to study the feasibility of the photochemical processes for the photocatalytic degradation of Acridine Orange (AO) dye. The COD test allowed the measurement of waste in terms of total quantity of oxygen requirement for organic material oxidation to carbon mono oxide and water. Amount of COD before and after degradation was calculated and observed the reduction of COD values of treated dye solution indicated the mineralization of Acridine Orange dye molecule along with decolorization. The reduction in the estimated COD values from 218 mg/L to 0 mg/L and increase in CO_2 values from 21 mg/L to 192 mg/L in 140 min. of illumination indicated the complete mineralization of dye solution under investigation. The results are shown in fig. 7[25-26].

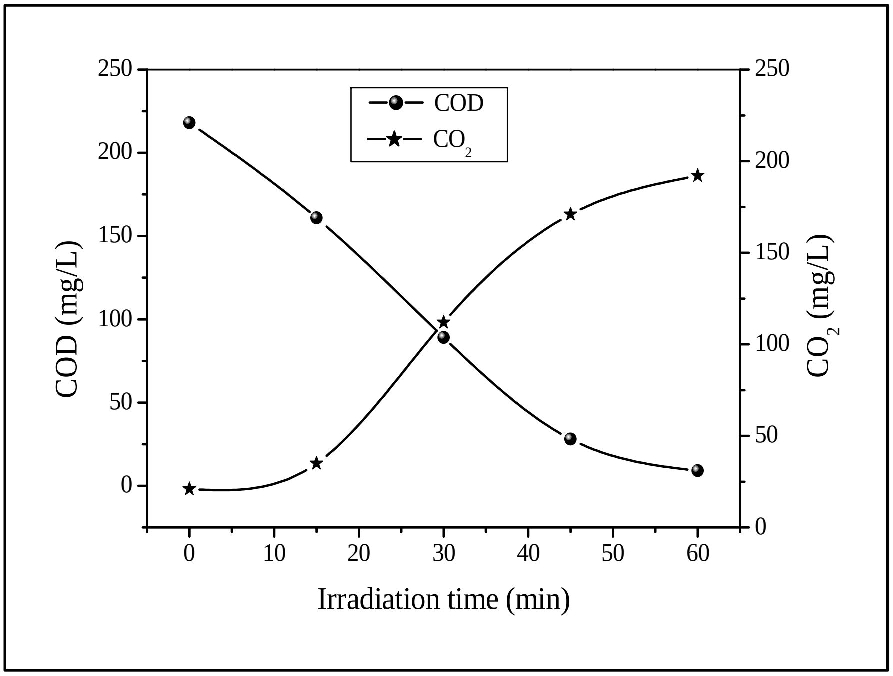

Fig. 7: COD and CO_2 trend during mineralization of AO

Reaction condition AO: [AO] = 2.5 x 10^{-5}mol dm^{-3}, ZnO NPs = 80 mg/100mL, pH =8.4, Light intensity = 30 x 10^{3} Lux.

IV. CONCLUSION

Present study confirmed that ZnO NPs photocatalytic degradation technique is efficient and environment friendly procedure for decolorization and mineralization of Acridine Orange (AO) dye. This process is mainly depend on pH of solution, initial dye concentration and amount of photocatalyst as well as its sizeH_2O_2 and $S_2O_8^{2-}$, NaCl and Na_2CO_3. From the results obtained by UV-visible spectrophotometer, estimation of COD and evolution of CO_2 further confirmed the mineralization of Acridine Orange (AO) dye. Optimum reaction conditions have been established for the degradation of Acridine Orange dye, which are crucial and can be used for another dyes in further which also follows the environmental friendly procedure.

V. ACKNOWLEDGEMENT

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