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Enhanced Photocatalytic Degradation of Direct Blue-1 Dye by ZnO Nanoparticles Using Visible Light

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ABSTRACT

Photocatalytic degradation of Direct Blue-1 has been studied in ZnO nanoparticles dispersion medium under visible light. The absorbance of Direct Blue-1 dye under investigation has been found to be decreased in the presence of visible light and ZnO nanoparticles. The degradation studies have been carried out under various parameters such as catalyst loading, initial dye concentration, pH, effect of oxidant and effect of light intensity etc. The photocatalyst ZnO nanoparticles have been found to be more efficient for the degradation of Direct Blue-1 dye than other reported catalysts.

Keywords: ZnO NPs, Direct Blue-1 Dye, Photo-Catalytic Degradation, Visible Light

I. INTRODUCTION

The degradation of dyes and other organic contaminants of wastewater effluents has now become the matter of environmental concern. Dyes are carcinogenic and potential pollutants. Hence attention has been paid toward the removal of harmful and these wastewater contaminants [1, 2]. These pollutants are generated from paper; textile and leather industries etc. and when discharged to environment have crucial impact on the aquatic life and human health as well. Thus it resulted into serious consequences to the ecosystem. The main objective of this work is to study the degradation of Direct Blue-1 dye by using ZnO nanoparticles in the presence of visible light [3, 4].

Recently, the heterogeneous photocatalysis is emerging as an effective AOP. Particularly ZnO nanoparticles have been applied as effective, inexpensive and nontoxic photocatalyst for the degradation of a wide range of organic chemicals [5, 6]. In present work, visible light irradiate photo-catalytic degradation of dye wastewater has been investigated using ZnO nanoparticles as photocatalyst. We have investigated this degradation process under different reaction condition to assess the feasibility and optimization of process for industrial dyes effluents [7-10].

II. EXPERIMETAL PROCEDURE

Materials

The dye used Direct Blue-1, was analytic grade reagent. $Zn(NO_3)_2$ and NaOH were obtained from Merck Co. (Germany). Ethanol (99%) was purchased from Aldrich Co. (England). The other chemicals used in present study like H_2O_2, $K_2S_2O_8$, Na_2CO_3, NaCl and $FeCl_3$ were of analytical grade and used as received. The double distilled water was used throughout to carry out experimental work.

Apparatus and experimental conditions

In a specially designed double-walled slurry type batch reactor vessel made up of Pyrex glass (7.5 cm height, 6 cm diameter) and water circulation arrangement was made to keep the temperature in the range of 30 ± 0.5°C. Photocatalytic experiments were carried out with 100ml of dye solution using ZnO NPs as photocatalyst under exposure to visible irradiation. Light irradiation was carried out using 500 W halogen lamp surrounded by aluminum reflector to avoid irradiation loss.

During photocatalytic experiment, after stirring for 10 min. slurry composed of dye solution and catalyst was placed in dark for 30 min in order to establish equilibrium between adsorption and desorption phenomenon of dye molecule on photocatalyst surface. Then slurry containing aqueous dye solution and ZnO NPs were stirred magnetically to ensure complete

suspension of catalyst particle in visible light. At specific time intervals, aliquot (3 ml) was withdrawn and centrifuged for 2 min at 3500 rpm to remove ZnO nanoparticles to assess extent of decolorization spectrophotometrically. Absorption spectra were recorded with UV-Vis. Spectrophotometer (Systronic Model No.166). Intensity of visible radiation was measured by a digital Lux-meter (Lutron LX - 101). The desired pH of the solution was adjusted by the addition of previously standardized 0.050M H_2SO_4 and 1.0M NaOH solutions and measurement was done using digital pH meter. COD & CO_2 estimation were performed and studied by using standard procedure [11-13].

III. RESULTS AND DESCUSSION

a. Effect of ZnO nanophotocatalyst

The amount of catalyst is basic parameter to assess the degradation of Direct Blue-1 dye. It has been studied using 80mg/100 mL to 220mg/100 mL concentration keeping all other parameters constant. (Figure 1) Results showed that the rate increased with an increase in the amount of catalyst till 160mg/100mL and remained almost constant above this concentration. Optimum rate was found at 160mg/100mL and further increase in ZnO nanoparticles concentration increase the number of photons absorbed and consequently absorption of light of dye molecule increases. As the concentration of catalyst was further increased ZnO nanoparticles inhibited the direct contact of light with dye molecule and rate became almost constant [14, 15].

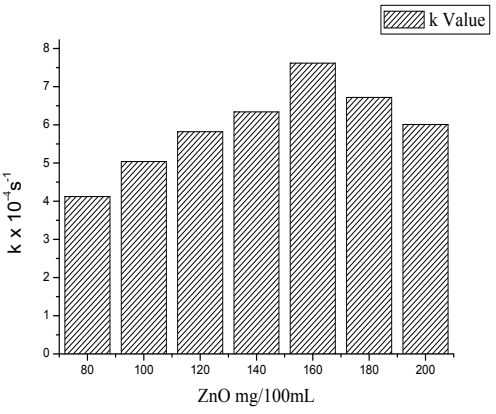

Figure 1. Effect of catalyst loading on photocatalytic degradation of DB-1
[DB-1 = 2.0 x 10^{-5} mole dm^{-3}, pH =6.5, light Intensity = 30 x 10^3 Lux]

b. Effect of pH variation

The effect of pH on the rate of degradation needs to be studied since industrial effluents might not be at neutral pH. Experiments were carried out at pH values, ranging from 3.5 to 9.5 for constant dye concentration (2.0 x 10^{-5} mol dm^{-3}) and catalyst loading (160mg/100ml). The reaction rate increased with increase in pH exhibiting optimum rate of degradation was found at pH 6.5 (figure 2) [16, 17].

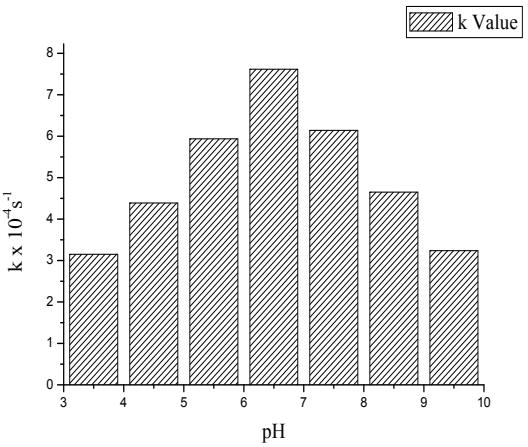

Figure 2. Effect of pH on photocatalytic degradation of DB-1
[DB-1 = 2.0 x 10^{-5} mole dm^{-3}, ZnO NPs = 160mg/100ml, light Intensity = 30 x 10^3 Lux]

c. Effect of initial dye concentration

It is also important to study the dependence of initial dye concentration for the degradation kinetics. The influence of initial dye concentration was studied in the range of 1.0 x 10^{-5} mol dm^{-3} to 3.5 x 10^{-5} mol dm^{-3}. The photocatalytic degradation rate was found to increase from 3.08 x 10^{-4} s^{-1} to 7.62 x 10^{-4} s^{-1} with increase in concentration of dye up to 2.0 x 10^{-5} mol dm^{-3} and increase in dye concentration degradation rate again decreased as found in figure 3. It may be due to that initially as the concentration of dye was increased, more dye molecules were available for excitation and consecutive energy transfer. Since the illumination time and amount of catalyst were constant, therefore, further increase in dye concentration causes virtual masking of greater number of adsorbed dye molecules on the surface of catalyst particles. [18-20]

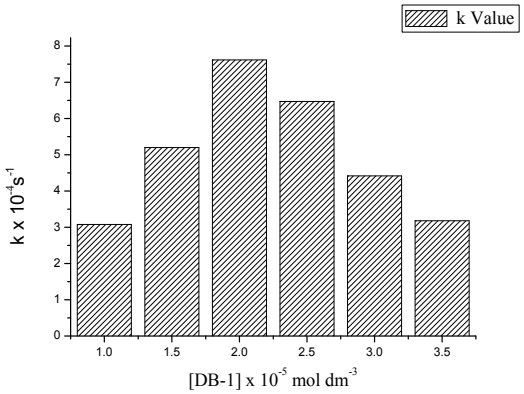

Figure 3. Effect of initial dye concentration on photocatalytic degradation of DB-1
[ZnO NPs = 160mg/100ml, pH =6.5, light Intensity = 30 x 10^3 Lux]

d. Effect of H_2O_2 and $K_2S_2O_8$

The degradation rate has been studied at different H_2O_2 and $K_2S_2O_8$ concentrations. The degradation rate increased with increasing H_2O_2 concentrations from 2.0 x 10^{-6} mol dm^{-3} to 8.0 x 10^{-6} mol dm^{-3}. The reaction rate increased for H_2O_2 from 8.03 x 10^{-4} s^{-1} to 11.23 x $10^{-4}s^{-1}$ (Figure 4). This was because H_2O_2 inhabited the electron-hole recombination and hence, accelerated the reaction by producing an extremely strong and non-selective oxidant hydroxyl radical from scavenging the electrons and absorption of visible light by the following reactions: [21, 22]

$$H_2O_2 + ZnO\,(e^-_{CB}) \longrightarrow {}^{\bullet}OH + OH^- \quad (1)$$
$$H_2O_2 + h\nu \longrightarrow 2{}^{\bullet}OH \quad (2)$$

Further increase in concentration of H_2O_2 beyond optimal concentration, resulted into the decrease in rate constant because at an excess H_2O_2 concentration, it might start acting as hydroxyl radical and hole scavenger [23, 24].

$$H_2O_2 + 2h^+_{VB} \longrightarrow O_2 + 2H^+ \quad (3)$$
$$H_2O_2 + {}^{\bullet}OH \longrightarrow HO_2{}^{\bullet} + H_2O \quad (4)$$
$$HO_2{}^{\bullet} + {}^{\bullet}OH \longrightarrow H_2O + O_2 \quad (5)$$

With increase in $K_2S_2O_8$ concentration from 2.0 x 10^{-6} mol dm^{-3} to 8.0 x 10^{-6}mol dm^{-3}, rate constant increased from 8.12 x 10^{-4} s^{-1} to 10.93 x 10^{-4} s^{-1}. At optimal amount of $K_2S_2O_8$, the rate of degradation has been found to be 10.93 x 10^{-4} s^{-1}. $K_2S_2O_8$ has always been found to be a beneficial oxidizing agent in photocatalytic detoxification due to generation of $SO_4^{-\bullet}$ radicals [25, 26]

$$S_2O_8^{2-} + e^-_{aq} \longrightarrow SO_4^{\bullet-} + SO_4^{2-} \quad (6)$$
$$S_2O_8^{2-} + e^-_{cb} \longrightarrow SO_4^{\bullet-} + SO_4^{2-} \quad (7)$$

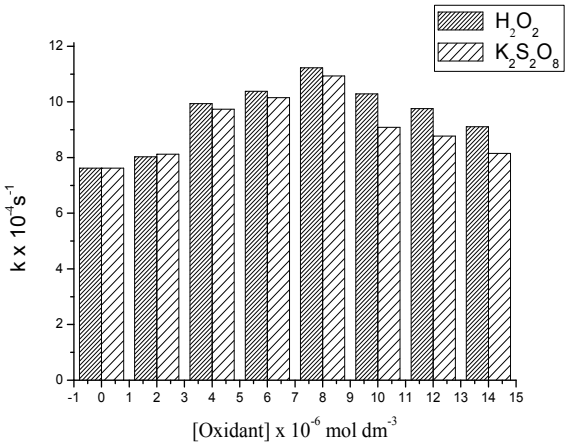

Figure 4. Effect of oxidants on photocatalytic degradation of DB-1
[DB-1 = 2.0 x 10^{-5} mole dm^{-3}, ZnO NPs = 160 mg/100ml, light Intensity = 30 x 10^3 Lux, pH = 6.5]

e. Effect of light intensity

The effect of the variation of the light intensity on the rate of reaction has also been investigated. The data indicated that the degradation rate was accelerated as the intensity of light was increased because any increase in the light intensity increased the number of photons striking per unit time per unit area of the semiconductor powder resulted in more hydroxyl radicals (figure 5) [27].

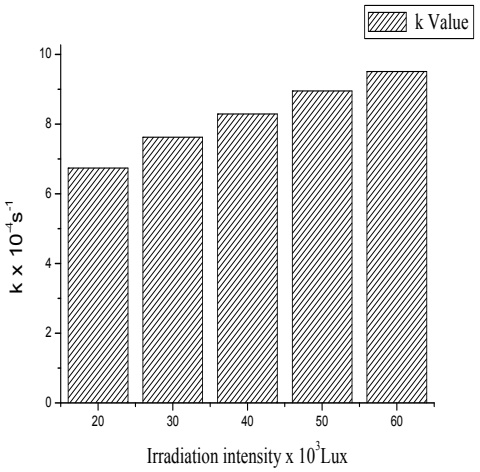

Figure 5. Effect of Light intensity on photocatalytic degradation of DB-1
[DB-1 = 2.0 x 10^{-5} mole dm^{-3}, ZnO NPs = 160 mg/100ml, pH = 6.5]

IV. CONCLUSION

The detailed experimental findings suggest that the use of nano ZnO particles under visible light makes an efficient green degradation technique for complete mineralization of Direct Blue-1 dye.

V. ACKNOWLEDGEMENT

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