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Investigation of Photocatalytic Degradation of Rhodamine B by Using Nano-Sized TiO_2

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Abstract

In present work investigation of photocatalytic degradation of Rhodamine B dye has been done using nano-sized TiO_2. In photocatalytic degradation the decomposition of rhodamine-B dye has been done using UV illumination using TiO_2 Nanoparticles. In present work the absorbance of the reaction mixture has been measured at various time intervals using Spectrophotometer. Control experiments confirm the necessity of light, semiconductor catalyst and oxygen to follow the photocatalytic path to proceed the photobleaching of dye. Effect of pH, amount of photocatalyst [TiO_2], initial dye concentration has been studied over photocatalytic degradation of Rhodamine B. A tentative mechanism has also been proposed.

Keywords: Rhodamine-B ,Photocatalytic degradation, TiO_2 Nanoparticles

Introduction

Rhodamine B represents one of the most important dyes, extensively used in the textile industry due to its high stability. Its release into the environment is dangerous for aquatic life as in many cases; it is carcinogenic and mutagenic for both humans and animals. Thus, decomposition of such organic dyes is significantly important[1-5]. Semiconductor photocatalysts such as TiO_2 nano-particles have attracted much attention in recent years due to their various applications to the photocatalytic degradation of organic pollutants in water and air and dye sensitized photovoltaic solar cell [6-9]. Advanced oxidation processes are of ample interest currently for the effective oxidation of a wide variety of organics and dyes [10]. Present study deals with the effect of catalyst dosage, concentration of dye, pH of the dye solution, light source on photocatalytic degradation.

Experimental

To study photocatalytic degradation stock solution has been prepared. For the stock solution dye Rhodamine B has been dissolved in of double distilled water so that the concentration of dye solution become 1 X 10^{-3} M . This solution has been further diluted as per requirement. The absorbance of the dye solution has been determined with the help of spectrophotometer. Control experiments confirm that both light and semiconductor photocatalyst are necessary for the photodegradation and oxygen increases the rate of photodegradation. Photocatalytic degradation of Rhodamine B has been carried out by taking 100 ml of 3 X 10^{-5} M dye solution in round bottom flask and 0.15 gm of TiO_2 nanoparticles have been added to it. The pH of the reaction mixture has been made alkaline (9.0) by adding 0.1 N NaOH. The mixture has been then irradiated under visible light source (2 x 200 W, Tungsten lamps). A water filter has been placed between light source and reaction vessel to cut off thermal radiations. Air has been purged continuously through reaction mixture with the help of an aerator for stiring purpose and availability of oxygen.

Results and discussion

About 3 ml of dye solution has been taken after a specific time interval (40 min) and its absorbance has been measured using spectrophotometer at 554 nm after removing TiO_2 . The rate of change in absorbance of the reaction mixture with time has been continuously measured. It has been observed that absorbance of rhodamine B decreases with increase in time of irradiation. It has been observed that the photocatalytic degradation of rhodamine B follows the first order kinetics.

Effect of variation in pH

pH plays an important role in generation of hydroxyl radicals. pH value effects the surface properties of TiO_2 nanoparticles. Attempts have been made to study the influence of pH to the photocatalytic degradation of rhodamine B dye. The pH of the dye solution has been varied using HCl and NaOH solution. Effect of variation in pH to photocatalytic degradation and hence to rate constant has been tabulated in Table 1

Table 1 Effect of variation in pH

[Rhodamine B] = 3 x 10^{-5} M **pH** = 9.0

Irradiation Time = 200 min λ_{max} = 554 nm

pH	Rate constant K x 10^{-5} (sec^{-1})
5	3.4
6	4.1
7	4.9
8	5.8
9	6.4
10	5.2

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Fig. 1 depicts the effect of pH on rate of photocatalytic degradation. It is evident by fig 1 that rate of degradation increases in pH range 5 to 9. Maximum degradation has been occurred at pH = 9 whereas it decrease after pH = 9. As the pH increases the oxidizing ability of holes of semiconductor increases. The hydroxyl radical production made possible the oxidation of hydroxide ions by holes. The more alkaline, the more readily hydroxide ions underwent oxidation to generate hydroxyl radicals on the catalyst surface. Therefore, the photocatalytic degradation of Rhodamine B has become more efficient due to the increase in pH value.

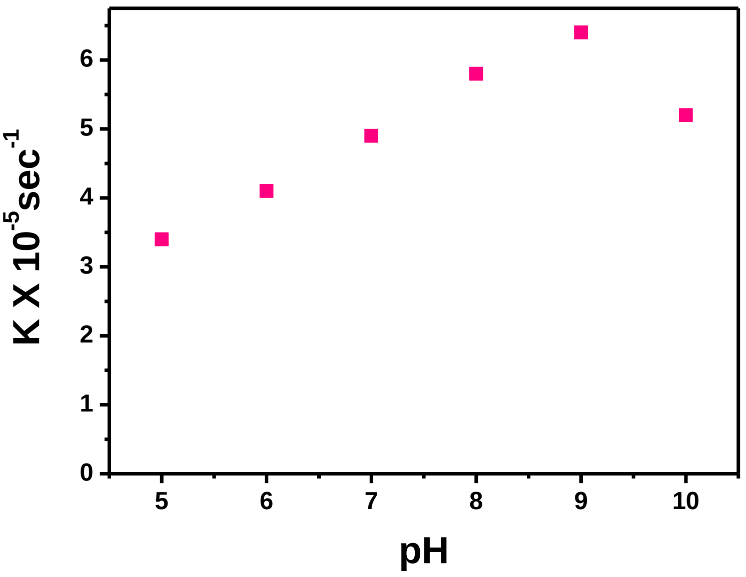

Fig 1: Effect of variation in pH to photocatalytic degradation of Rhodamine B dye

Effect of amount of photocatalyst [TiO_2]

In many studies it has been observed that amount of photocatalyst have a great deal of influence on the photocatalytic degradation of dyes. In present study keeping all the factors identical, amount of TiO_2 has been varied from 0.05 gm to 0.30 gm, and rate constant has been evaluated. Results have been listed in table 3.3 and showed in fig.3.3.

Table 2 Effect of amount of photocatalyst [TiO_2]

[Rhodamine B] = 3 x 10^{-5} M

pH = 9

Irradiation Time = 200 min

λ_{max} = 554 nm

Amount of TiO_2 (gm)	Rate constant K x 10^{-5} (sec^{-1})
0.05	4.4
0.10	5.2
0.15	6.4
0.20	6.9
0.25	7.3
0.30	7.7

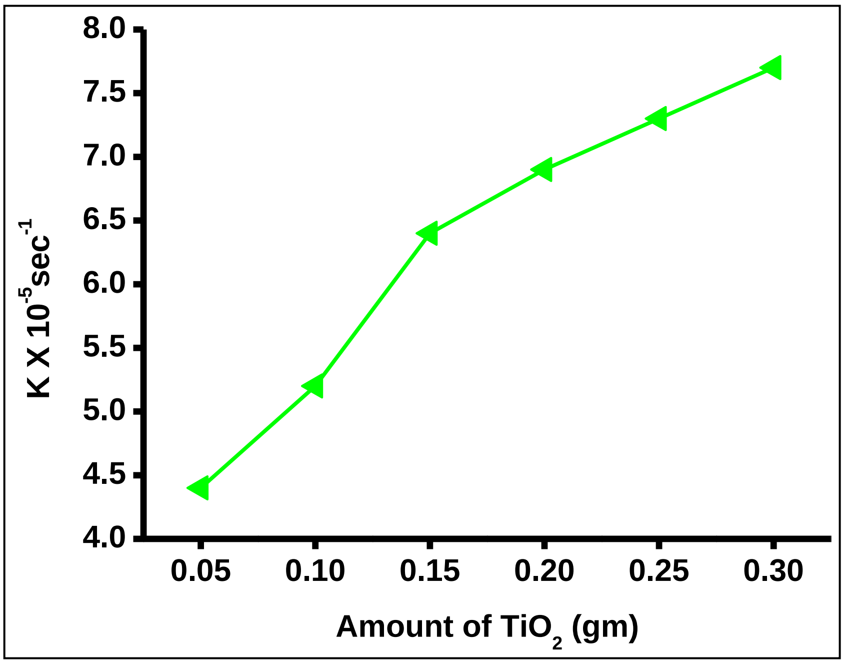

Fig 2: Effect of variation in amount of TiO_2 to photocatalytic degradation of Rhodamine B dye

Results revels that the increase in the TiO_2 catalyst concentration leads to an increase in the rate constant. The observed increase in rate constant as a result of increasing the amount of the catalyst could be attributed to the increase in the number of photons absorbed and the number of dye molecule adsorbed. Increase in the amount of catalyst increases the number of TiO2 active sites on the surface that in turn increases the number of hydroxyl and oxygen radicals. As a result rate of degradation increases. At higher amount of TiO_2 the number of substrate molecules is not enough to fill active sites of TiO_2 which reduces the light transmission through the solution and catalyst does not lead to enhance the degradation rate.

Effect of variation in initial dye concentration

The effect of the initial concentration of the dye on the efficiency of the photocatalytic degradation has been investigated by varying the initial dye concentration in the range of $1X10^{-5}$ to $7X10^{-5}$ M and the results has been shown in table 3 and Figure 3 .

Table 3 Effect of variation in rhodamine B dye concentration

Nano TiO_2 = 0.15 gm **pH** = 9

Irradiation Time = 200 min λ_{max} = 554 nm

[Rhodamine B] X 10^{-5} M	Rate constant K x 10^{-5} (sec^{-1})
1	**8.2**
2	**7.3**
3	**6.4**
4	**5.2**
5	**4.5**
6	**3.1**
7	**2.3**

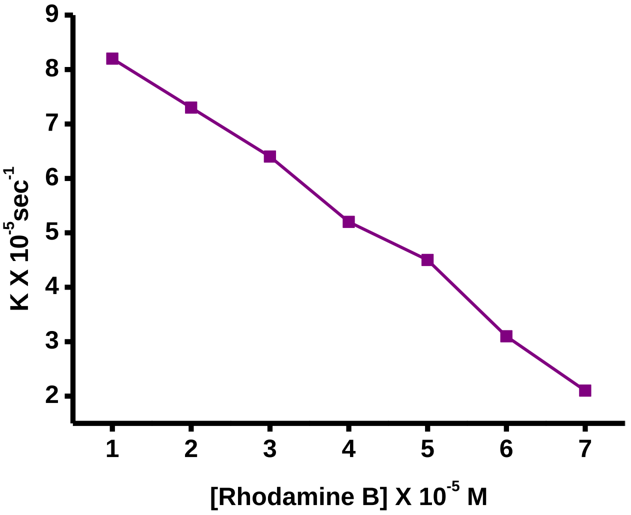

Fig 3: Effect of variation in dye concentration to photocatalytic degradation of Rhodamine B dye

It has been observed that efficiency of photocatalytic degradation of rhodamine B tend to decrease with increasing the concentration of rhodamine B. A possible explanation for this behaviour is that as the initial concentrations of the dye increase the production of $^{\bullet}OH$ radical on the surface of the catalyst has been reduced hence the number of active sites available for the •OH adsorption dramatically decreases, also dye molecules has been adsorbed on the surface of the catalyst and significant amount of light has been absorbed by the dye molecules rather than the TiO_2 particles. Hence, the penetration of light to the surface of the catalyst decreases.

Mechanism and product study

Explanation of Mechanism of semiconductor photocatalytic oxidative degradation of dyes has been specified by a band gap model of semiconductors. The photocatalytic degradation of dyes has been supposed to takes place by the following mechanism. When a catalyst absorbs a photon with energy equal or higher than the band gap energy (Eg), electrons (e^-) are promoted from valence band (VB) to conduction band (CB) and leaving an electron vacancy or hole (h^+) in the valence band as shown in Eq. (1).

$$\mathbf{TiO_2 + h\nu \rightarrow TiO_2\,(e_{cb}^{\;-} + h_{vb}^{\;+})\ (Electron\text{-}hole\ generation)\ldots\ldots\ldots\ldots(1)}$$

These formed e^- and h^+ pairs can move to catalyst surface, where they reacts with the surface hydroxyl group or water and dissolved oxygen to produce hydroxyl, peroxide and superoxide radical anions as shown in Eqs. (2)–(7).

$$\mathbf{TiO_2\,(h_{vb}^{\;+}) + H_2O \rightarrow TiO_2 + H^+ + {}^{\bullet}OH \qquad (2)}$$

$$\mathbf{TiO_2(h_{vb}^{\;+}) + OH^- \rightarrow TiO_2 + {}^{\bullet}OH \qquad (3)}$$

$$\mathbf{TiO_2(e_{cb}^{\;-}) + O_2 \rightarrow TiO_2 + O_2^{\bullet-} \qquad (4)}$$

$$O_2^{\bullet -} + H^+ \rightarrow HO_2^{\bullet} \qquad (5)$$

$$2O_2^{\bullet -} + 2H^+ \rightarrow O_2 + H_2O_2 \qquad (6)$$

$$H_2O_2 + TiO_2\,(e_{cb}^-) \rightarrow {}^{\bullet}OH + OH^- + TiO_2 \qquad (7)$$

The hole generated can react with surface oxygen ions of the TiO_2 lattice to produce $^{\bullet}OH$ radicals as in Eq. (9). These generated radicals, which further react with a dye producing a whole range of intermediates including radical and radical cations to achieve complete mineralization with the formation of carbon dioxide, water, and inorganic nitrogen with nitrate ion.

$$HO_2^{\bullet} + H^+ + TiO_2\,(e_{cb}^-) \rightarrow {}^{\bullet}OH + OH^- + TiO_2 \qquad (8)$$

$$> Os^- + H_{aq} + TiO_2(h_{vb}^+) \rightarrow TiO_2 + {}^{\bullet}OH_s \qquad (9)$$

$$RhB + {}^{\bullet}OH \rightarrow \text{Intermediate products} \rightarrow CO_2 + H_2O + NO_3^- + NH_4^+ \qquad (10)$$

The formed oxidized products have been mineralized into CO_2, H_2O, NO_3^- and NH_4^+. To confirm the mineralization, the photocatalytic degradation reactions have been carried out and then the irradiated samples have been analyzed by COD and TIC.

Identification of possible intermediate products during the photocatalytic reaction is the best way to understand the photocatalytic degradation reaction mechanism. The end product have been dected and their presence in the reaction mixture has been ascertained by chemical test. The formations of N-deethylated intermediate has been observed after the photocatalytic degradation of Rhodamine B dye. In addition to Rhodamine B dye, the N-deethylated intermediates such as N,N-diethyl-N_- ethylrhodamine, N,N-diethylrhodamine, N-ethylrhodamine have been observed at the retention time.

Conclusion

Photocatalytic degradation of Rhodamine B dye in presence of TiO2 nanoparticles has been studied. Absorbance of the reaction mixture has been measured at various time intervals. The control experiments have also been performed in different conditions. It has been observed degradation follows the first order kinetics. Results reveals that the photocatalytic degradation of Rhodamine B has become more efficient due to the increase in pH value. the increase in the TiO_2 catalyst concentration leads to an increase in the rate constant. It has also been observed that efficiency of photocatalytic degradation of rhodamine B tend to decrease with increasing the concentration of rhodamine B. mechanism reveals that In addition to Rhodamine B dye, the N-deethylated intermediates such as N,N-diethyl-N_- ethylrhodamine, N,N-diethylrhodamine, N-ethylrhodamine have been observed at the retention time.

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