



Photocatalytic degradation in silver doped TiO₂

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Abstract. Many intriguing ways have been identified to mitigate the low photocatalytic activity of Titanium dioxide (TiO₂). One of the ways is to adulterate the structure of TiO₂ with foreign substances like metals i.e., Ni²⁺, Zn²⁺, Cr³⁺ and Fe³⁺, which are having similar radii with Ti⁴⁺. In this study, the introduction of silver into the structure of TiO₂ by Liquid Impregnation (LI) method with various mole fractions have been presented. Comparison has been made to degrade one model pollutant: Direct Blue 71 (DB71) by using both doped and undoped TiO₂. Study was further supported by studying the Langmuir and Freundlich isotherms. Enhancement in the photocatalytic degradation of the dye was observed with silver doped TiO₂ at 2.0% mole fraction as compared to undoped TiO₂. While studying the photocatalytic activity, the reaction mixture pH was kept unchanged with doped TiO₂, wherein with undoped TiO₂ demanded acidic pH to have more photocatalytic activity.

Keywords. Isotherm; silver doped TiO₂; adsorption; irradiation; metals; TiO₂.

1. Introduction

To solve the issues related with refractory nature of organic molecules in the wastewater, Advanced Oxidation Processes (AOPs) are merged as next generation environmental engineering techniques [1]. Of all the AOPs, Heterogeneous Photocatalysis proves to be more promising [2, 3], which work on the generation of electrons (e⁻) and holes (h⁺) by using semiconducting transition metal oxides as catalyst in the presence of light [4, 5]. These electrons and holes are called as charge carriers, which lead to the formation of various radicals, potent species for breaking the bonds [6]. Basically it is a redox reaction, where the big organic molecule gets oxidized to various smaller species [7]. The photogenerated electrons and holes and various radical species play vital role in the photocatalytic reactions are shown in figure 1.

Therefore, this whole process can be defined as an organic reaction, using organic substances as a substrate and reaction conditions are the use of catalyst, light, pH, temperature, etc. Among the semiconductors, Titanium dioxide (TiO₂) has been found to be more efficient due to its high efficiency and stability having band gap energy (E_g) of 3.2 eV [8, 9]. Retarding point in this reaction is the recombination of electron and holes. Retardation can be reduced by doping with transition metals (i.e., Ni²⁺, Zn²⁺,

Cr³⁺ and Fe³⁺), which are having similar radii with Ti⁴⁺ [10], thus fitting into the structure of TiO₂. Moreover, doping with metal reduces the recombination [11, 12]. Oxygen species are the electrons acceptor in the processes of photocatalysis. By preparing silver doped TiO₂, Ag⁰ and Ag⁺ act as electron accepting species rather than oxygen. Since the fermi level of titanium dioxide film is high, the electrons gets migrate from the surface of titanium dioxide film to the silver metal, which results in the formation of charge layer at the boundaries of titanium dioxide film and Ag. Hence silver doping has the advantage of increasing the efficiency of charge separation, leading to increase the lifetime of charge carriers. Methyl Orange degradation was studied by using CeO₂ and 0.50-5.00 mol% Fe- doped CeO₂ prepared by homogeneous precipitation method combined with homogeneous/impregnation method. 1.5% mol Fe-doped CeO₂ showed maximum percentage removal under visible light [13]. Photocatalytic degradation of Acid Red 88 (AR88) was enhanced by using silver doped nanoparticles prepared through liquid impregnation (LI) and photodeposition (PD) method as compared to TiO₂ [3]. In another study, decomposition of chloroform and urea was found to be more effective with Ag-loaded TiO₂ as compared to TiO₂ [14]. The Present study deals with the testing the activity of silver doped TiO₂ (Ag⁺-TiO₂) and undoped TiO₂ on the degradation process of Direct Blue 71 (DB 71). Liquid impregnation was the method used for the preparation of Ag⁺-TiO₂ [15]. To further support the study,

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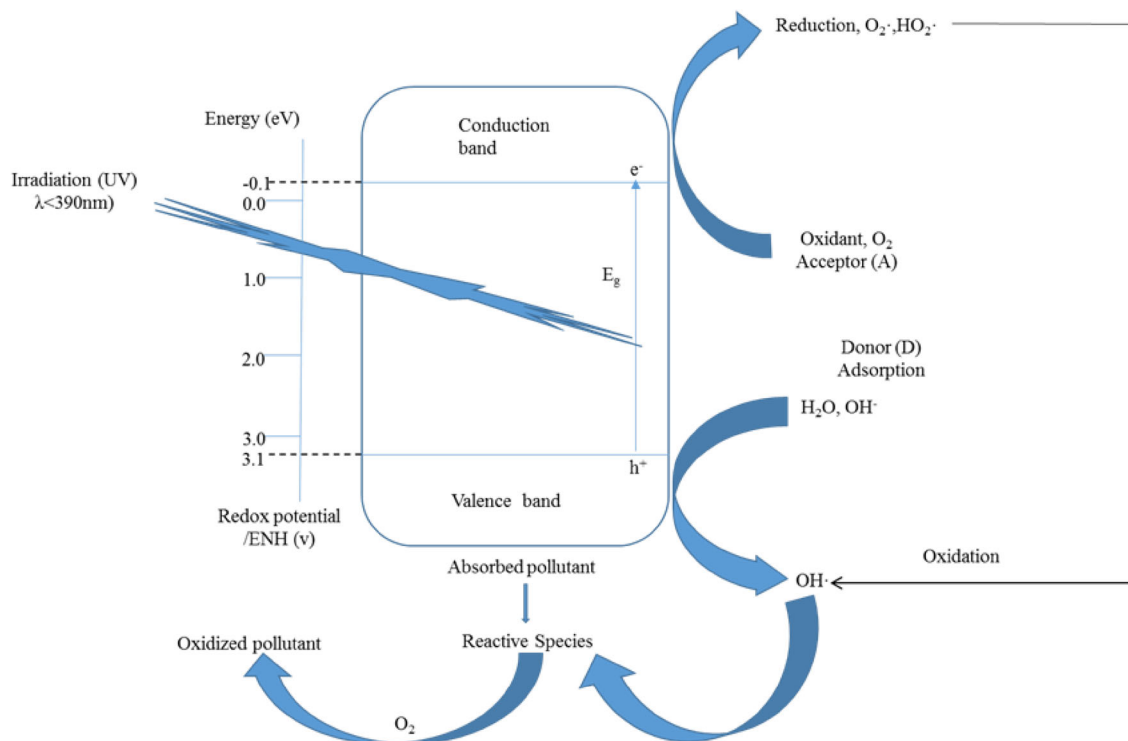


Figure 1. Mechanism of photocatalysis by TiO_2 .

activity was compared by studying the rate kinetics and change in concentration of the dye. Langmuir and Freundlich isotherms have been studied for the adsorption process.

2. Experimental

2.1 Materials

Direct Blue 71 dye (55% dye content) (DB71) was procured from Sigma Aldrich. Direct Blue 71 is triazo dye (figure 2) with λ_{max} 594 nm. The catalyst used was Degussa P25 Aeroxide TiO_2 procured from Degussa Company, Germany. AgNO_3 was purchased from Qualigens Fine Chemicals.

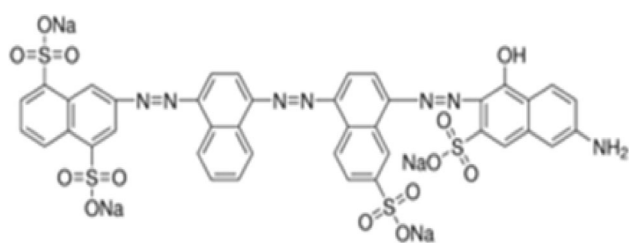


Figure 2. Structure of direct blue 71 dye.

2.2 Photoreactor

Photoreactor used was manufactured from galvanized aluminium sheet to convert it into box having 8 UV tubes of 40 W each mounted on the top of the reactor. The intensity of the UV was kept at 10 W/m^2 (figure 3).

2.3 Method of preparation of doped TiO_2

Ag^+ - TiO_2 was prepared by Liquid Impregnation (LI), in which slurry of different mole fractions (0.5, 1.0, 1.5 and 2.5) were prepared by dissolving TiO_2 and making the solution up to 100 ml with distilled water. Resultant slurry was allowed to stir well and rested for 24 h in hot air oven for 12 h at 100°C for drying. Big mass solid formed was

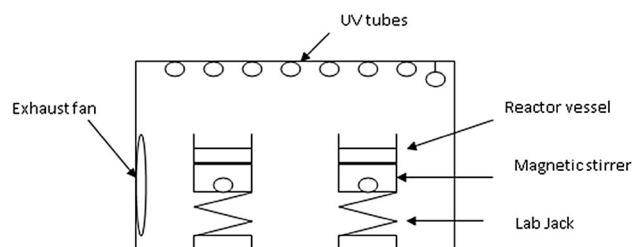


Figure 3. Schematic diagram of photoreactor.

grounded into pieces in agate mortar and calcined at 400°C in muffle furnace for 5 h [15].

2.4 Procedure

Known amount of dye (say 100 mg/l) was first absorbed on both TiO₂ and Ag⁺-TiO₂ in dark. The dye solution with the catalyst was mixed vigorously in a stirrer with catalyst for 30 min in dark. After 15 min centrifugation at 14500 rpm, the supernatant was taken out and the dye concentration was spectrophotometrically determined at 594 nm. Adsorption step was followed by Photocatalytic treatment done by stirring minimum of 60 min in the presence of UV light.

3. Results and discussion

3.1 Kinetics of adsorption of undoped and doped TiO₂

Before getting degraded photo catalytically, the dye should be absorbed on the surface of the catalyst, which was done by stirring magnetically for some time in dark. Adsorption is a surface phenomenon, which depends on the number of active sites available onto the catalyst surface. Therefore, initially when more active sites are available, the rate of adsorption will be more as can be seen in figure 4 with undoped TiO₂, and becomes slower as it reaches the equilibrium. It takes longer contact time to get chemically adsorbed onto the surface of the catalyst. The effect of contact time on adsorption is shown in figure 4 using undoped TiO₂ at pH = 3 and 100 mg/l dye concentration.

Remaining vacant sites are difficult to occupy after certain time because of the steric hindrances between the solute molecules on the solid and bulk phases. Initial concentration of the dye is also a driving force to overcome the mass transfer issues of the dye molecules from solid phase to the liquid phase. The adsorption reached its equilibrium

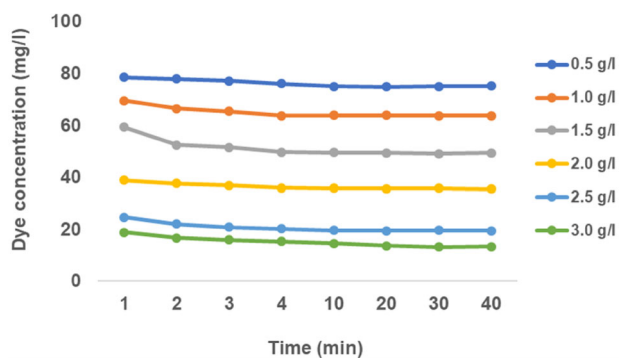


Figure 4. Adsorption studies of DB 71 by undoped TiO₂ (Dye conc. = 100 mg/l, pH = 3).

point after 10 min with undoped TiO₂. However as shown in figure 5 with doped TiO₂, the adsorption was poor at pH=3 and 200 mg/l dye concentration even after stirring for 40 min.

The kinetics of the reaction constants with undoped TiO₂ were studied for the pseudo-first order and pseudo-second order were calculated. Pseudo first order reaction constant is obtained if the concentration of one relative reactant remains stable which is applied in excess. The pseudo-first order can be described as a physisorption process because the rate determining step is the physical exchange between one of the reactant and substrate [16]. The equation representing the pseudo-first order kinetic model is represented as follows.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (1)$$

In the processes following, pseudo second order reaction, the chemical reaction seems significant in the rate-controlling step [16]. The equation corresponding to the pseudo-second order kinetic model is represented as follows

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (2)$$

q_e is the dye absorbed (mg/g) at equilibrium, q_t is the dye absorbed (mg/g) at time t (min), k_1 is equilibrium rate constant of the pseudo-first sorption (1/min), and k_2 is the equilibrium rate constant of the pseudo-second-order adsorption (g/mg/min)

From the values of coefficient of determination (R^2) (table 1), it can be concluded that the adsorption of DB 71 on the undoped TiO₂ follows pseudo-second order reaction. The efficacy of the adsorption process was estimated by studying the isotherm. The Langmuir and Freundlich isotherms were studied. The equilibrium adsorption test provides the physico-chemical data on the applicability of the adsorption for bare TiO₂. The Langmuir isotherm equation (Eq. 3) is as following

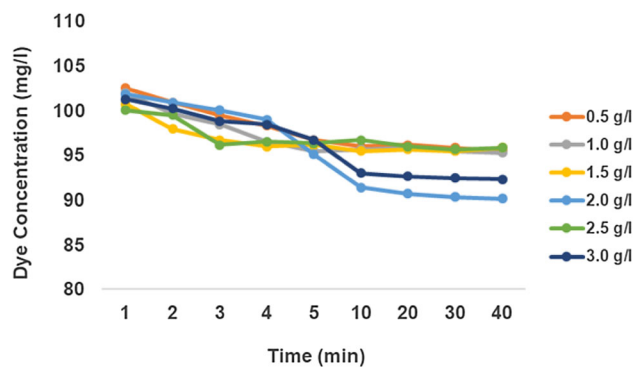
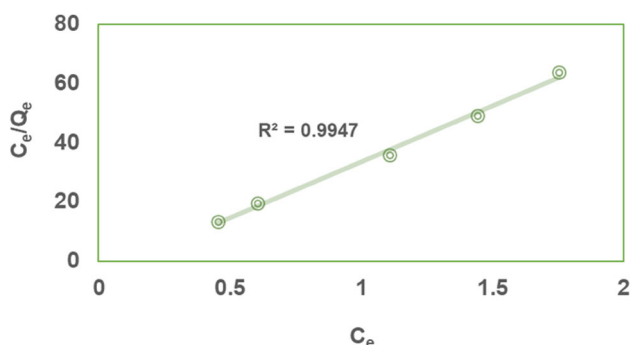
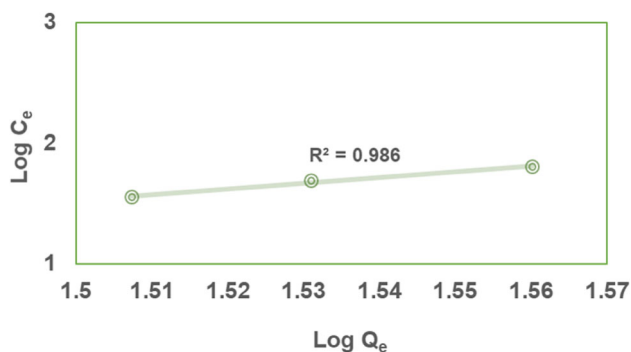


Figure 5. Adsorption studies of DB 71 by doped TiO₂ (Dye conc. = 100 mg/l, pH = 3).

Table 1. Adsorption kinetic parameters for TiO₂ (initial dye concentration = 100 mg/l, pH = 3).

Catalyst load (g/l)	First-order kinetic model				Second-order kinetic model		
	q _e (exp.) (mg/g)	k ₁ (min ⁻¹)	q _e (cal) (mg/g)	R ²	k ₂ (g/mg/min)	q _e (cal) (mg/g)	R ²
02.00	35.55	00.65	10.58	0.97	0.27	34.45	0.99

**Figure 6.** Langmuir adsorption isotherm of DB 71 onto TiO₂ surface (Dye conc. = 100 mg/l, pH = 3).**Figure 7.** Freundlich adsorption isotherm of DB 71 onto TiO₂ surface (Dye conc. = 100 mg/l, pH = 3).

$$q_e = \frac{q_{\text{mon}} K_L C_e}{1 + K_L C_e} \quad (3)$$

K_L represents Langmuir constant related to the energy adsorption (L/mg). q_{mon} is the maximum amount of adsorption corresponding to complete coverage on the surface (mg/g).

The Freundlich isotherm is expressed by the following equation:

$$q_e = K_F C_e^{1/n} \quad (4)$$

Table 2. Adsorption isotherm for parameters on TiO₂ (Dye conc. =200 mg/l, pH=3).

Langmuir Isotherm	Q _{mon} (mg/g)	35.38	Freundlich Isotherms	K _F (L/g)	22.12
	K _L (L/mg)	0.25		N	6.70
	R ²	0.98		R ²	0.98

K_F is a rough indicator of the adsorption capacity $1/n$ is the adsorption intensity

Figures 6 and 7 represent the Langmuir and Freundlich isotherms for undoped TiO₂ from where R² values calculated show that both the isotherms are well suited. Table 2 shows the values of parameters for Langmuir and Freundlich isotherm. In the homogeneous adsorption systems, sorbate molecules showing no interaction between each other, the Langmuir model is applied, while in heterogeneous systems where there is no monolayer formation, Freundlich model is applicable [17].

3.2 Photocatalytic degradation using undoped and doped TiO₂

The photocatalytic degradation rate of the DB 71 in the presence of undoped and doped TiO₂ is shown in figure 8.

The rate approached first order using Langmuir-Hinshelwood kinetic model [17], represented by the equation

$$r = -\frac{dC}{dt} = kK_{\text{ads}}C = k'C \quad (5)$$

k' is apparent rate constant for the pseudo-first order kinetics. For the photocatalytic treatment of binary dye mixture of Acid Blue 13 (AB13) and Acid Red (AR 14), the graph between $-\ln(C_0/C)$ and time showed the first order kinetics [18]. For the current study, K_{ads} is calculated by plotting graph between $1/k_{\text{aapp}}$ and C (figure 9).

The degradation of DB71 dye was better at pH=3 for undoped TiO₂ and in the case of doped TiO₂ demanded no change in the pH of the solution mixture for the same percentage degradation of the dye. With the undoped TiO₂, after the photocatalytic treatment for 6 h, there was 87% degradation of the dye (with initial conc. = 200 mg/l, catalyst load = 2 mg/l and pH = 3). While with doped TiO₂, with same initial dye concentration and catalyst load but at reaction mixture pH, the dye degradation was 99%. Figure 10 shows the DB71 degradation process of Ag⁺-TiO₂ prepared by LI method was much higher than of undoped TiO₂.

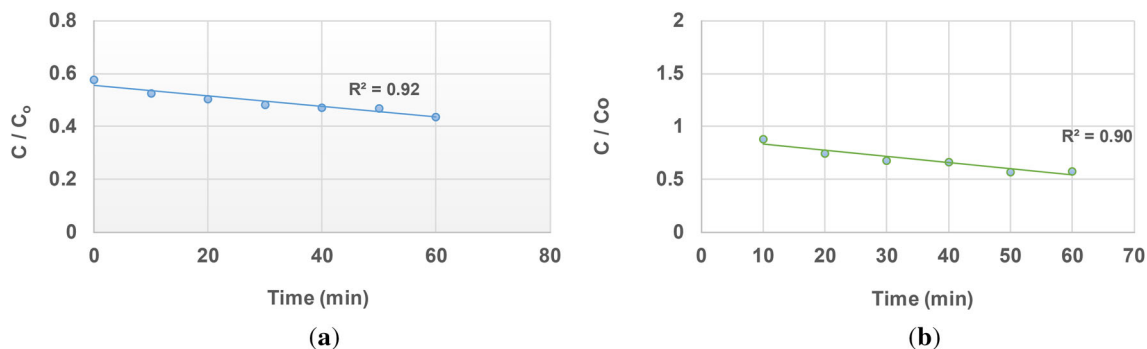


Figure 8. Photodegradation of direct blue 71: (a) TiO_2 surface; (b) doped TiO_2 surface. (Dye conc. = 100 mg/l, catalyst load = 2.5 g/l, pH = 3).

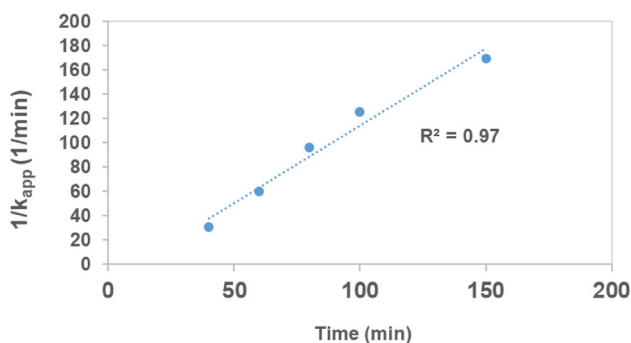


Figure 9. Langmuir – Hinshelwood model graph for doped TiO_2 .

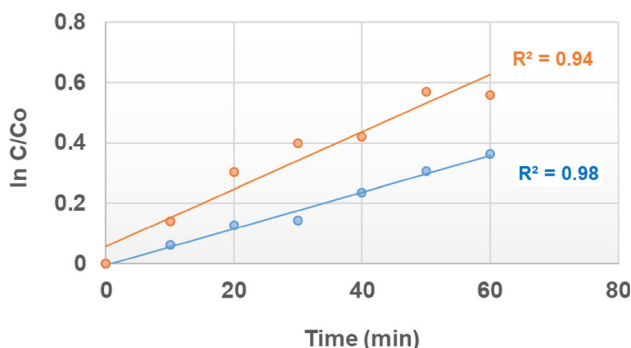


Figure 10. Effect of dye concentration of doped and undoped TiO_2 at the degradation of DB 71 (dye conc. = 100 mg/l, catalyst load = 2.5 g/l and 2.5% doping).

The difference in photoactivity of silver doped and undoped TiO_2 can be because of the oxidation state of silver on TiO_2 . LI preparation method results into the positive charge on silver at TiO_2 . Ag^+ accepts the electrons generated by the absorption of light by TiO_2 , and gets reduced to Ag^0 , leading to the reduction in the e^-h^+ recombinations. This scavenging of e^- by O_2 is slower as compared to Ag^+ [19]. Moreover, present study showed the importance of pH in the process of degradation.

4. Conclusions

- Doping TiO_2 with silver can be an economical way to degrade TiO_2 by not changing the reaction mixture pH, as changing pH demands the use of more chemicals.
- With undoped TiO_2 , the adsorption data were fitted with two order equation but pseudo-second order was best suited ($R^2 = 0.99$). The calculated sorption capacity at equilibrium was 34.45 mg/g such data was not calculated with doped TiO_2 , as it showed poor adsorption properties in dark.
- Percentage degradation of DB71 with doped TiO_2 was found to be more as compared to undoped TiO_2 at the reaction mixture pH. Undoped TiO_2 worked well in acidic pH.

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