IJIRST –International Journal for Innovative Research in Science & Technology| Volume 2 | Issue 10 | March 2016
ISSN (online): 2349-6010

Removal of Reactive Black 5 Dye from Aqueous Solution using Photo Catalysis

Joysmita Panja
UG Student
Department of Chemical Engineering
Heritage Institute of Technology, Kolkata

Shilpi Sarkar
UG Student
Department of Chemical Engineering
Heritage Institute of Technology, Kolkata

Uttiya Raybarman
UG Student
Department of Chemical Engineering
Heritage Institute of Technology, Kolkata

Sangita Bhattacharjee
Assistant Professor
Department of Chemical Engineering
Heritage Institute of Technology, Kolkata

Abstract

Textile industries use different synthetic dye and generate huge volume of textile effluent containing complex mixtures of many polluting substances. The removal of colour from textile wastewater represents a major environmental concern. In this work, the removal of reactive black 5, a textile dye, from aqueous solution has been studied using photocatalysis in a UV annular reactor using TiO2 as catalyst. Photocatalysis is the acceleration of a photoreaction in the presence of a semiconductor catalyst. In this work, effects of reactor operating time, flowrate, solution pH on percent demineralization of dye has been studied. A 94% dye removal was achieved in near neutral solution (pH=6.4) compared to 75% removal in case of alkaline medium (pH=8.4). The kinetic of the photo-reaction has been found to follow Langmuir-Hinshelwood model.

Keywords: Reactive Black 5, Photocatalysis, UV annular reactor, pH, Langmuir-Hinshelwood model

---

I. INTRODUCTION

Industrial effluents are one of the most important sources of pollution in the environment. The dye effluents from textile industries are significant sources of environmental pollution [1]. Synthetic dyes have been used in many industries such as textile, paper printing, food, pharmaceutical, leather and cosmetics [2]. Traditionally, synthetic dyes are classified into acid, reactive, direct, basic, metal complex, and sulphur dyes.

Reactive black 5 (RB-5) like other reactive dye have good fastness properties owing to the bonding that occurs during dyeing. RB-5 is an azo dye. Azo dyes, have one or more azo bonds (-N=N-) and because of their solubility, low expense, stability and color variety, are widely used in many applications [3]. Removal of azo dyes from colored effluents due to their complex composition, toxicity, poor degradability and high solubility, have attracted great interest in the last few years [4]. Conventional methods such as chemical precipitation and biological treatment cannot effectively remove of dyes from effluents, so finding an effective technique is necessary.

The purification of wastewater by heterogeneous photocatalysis is one of the most rapidly growing areas of interest to both research workers and water purification plants. Commercial application of the process is called advanced oxidation process (A.O.P). In recent years, TiO_2 has been chosen as a photocatalyst for the destruction of polluting materials due to its efficiency, non toxicity, high activity, photochemical inertness and low cost [5]. In some recent work, photocatalytic degradation of reactive black-5 dye using TiO_2 impregnated ZSM-5 was investigated in a batch reactor [6]. With some optimum formulation of supported catalyst, 98% degradation of 50mg/L RB-5 solution was obtained in 90 minutes.

Hosseinia *et.al.* [7] has synthesized nanosize TiO_2 particles and investigated photocatalytic degradation of different chromophores under visible light irradiation at different catalyst loading and different dye concentrations. In another work [8] phenol degradation had been examined with combined photocatalysts TiO_2 and ZnO under illumination of a 500W super high pressure mercury lamp mounted axially. The results revealed that, both TiO_2 and ZnO were effective though the latter was much superior in activity. Very recently [9], photocatalytic degradation of formaldehyde in indoor air was studied using nanoparticulate TiO_2 photocatalyst. The degradation rate was found to be affected with initial concentration, light intensiy, stream flow rate and reaction temperature.

In the light of the above discussion, the work in this paper was undertaken to study the photocatalysis of Reactive black-5 dye using TiO_2 as catalyst in a indigenously designed UV irradiated annular reactor. Effects of influencing parameters such as flow rate, reactor operating time, solution pH etc. on degradation of azo dye were investigated in detail. The model proposed by Langmuir-Hinshelwood was employed to describe the kinetics of the photodecomposition reaction and the rate constant was evaluated under specified operating conditions.

II. THEORY

The heterogeneous photocatalysis permits total degradation (mineralization) of the most toxic organic molecules in aqueous solution in the presence of a catalyst. In this process, excitation of TiO_2 by a UV light of wavelength $\lambda \leq 380$ nm generates electron-hole pairs (e^-_{cb}, h_{vb}^+). Dissolved oxygen of the solution scavenges the electron generated, preventing the recombination of electrons and holes. Conduction band electrons and valence band holes generated from UV irradiated TiO_2 interact with TiO_2 surface adsorbed molecular oxygen and water to generate superoxide radical $O_2\bullet$, and the highly reactive $HO\bullet$ respectively. The hydroxyl radicals generated in this process are powerful oxidant due to high reactivity [10]. This species is unstable and is continuously produced due to photochemical reactions. The mechanism [11] of the photocatalysis is shown below stepwise.

$$TiO_2 + h_v \longrightarrow e^-_{cb} + h_{vb}^+ \qquad (1)$$

$$e^-_{cb} + O_2\,(ads) \longrightarrow O_2^{\cdot\,-} \qquad (2)$$

$$h_{vb}^+ + H_2O \longrightarrow HO_{ads}^{\cdot} + H^+ \qquad (3)$$

$$HO_{ads}^{\cdot} + \text{Reactants} \longrightarrow \text{Photo oxidized products} \qquad (4)$$

The photodegradation efficiency or conversion was calculated by the following relation

$$X\,(\%) = 100 \times (C0-C)/C0 \qquad (5)$$

Where X is the photodegradation efficiency or conversion.

III. EXPERIMENTAL PROCEDURE

A. Materials and methods

Reactive black dye ($C_{26}H_{21}N_5Na_4O_{19}S_6$) procured from Sigma Aldrich was chosen as a simple model of reactive dye, largely used in textile industries. It is a heterocyclic aromatic compound whose structure is given in Fig.1. When dissolved in water, the UV-Visible spectrum gives maximum absorbance at 599nm (λ_{max}).The natural pH of aqueous dye solution is 6.4.The pH of the solution was adjusted using NaOH or H_2SO_4. The aqueous solutions were prepared with deionised water.

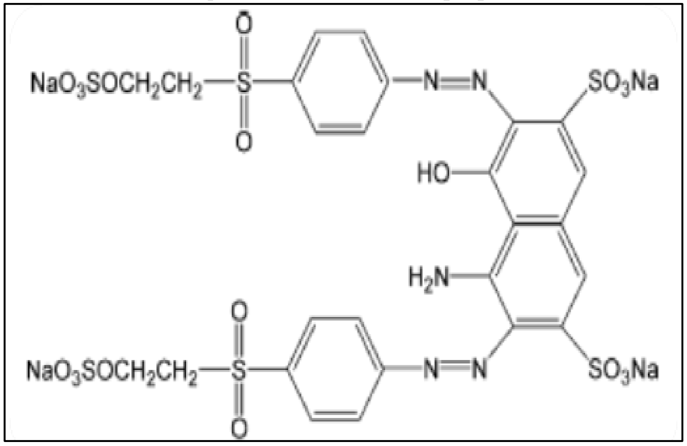

Fig. 1:

The catalyst TiO_2 (more than 99.9% purity) procured from Sigma, Aldrich was used without any pre-treatment. From XRD analysis (Fig.2), it was found that TiO_2 contained only anatase form. The anatase form of TiO_2 has low band-gap energy (approximately 3.2eV), which is almost equivalent to 400nm wavelength of light.

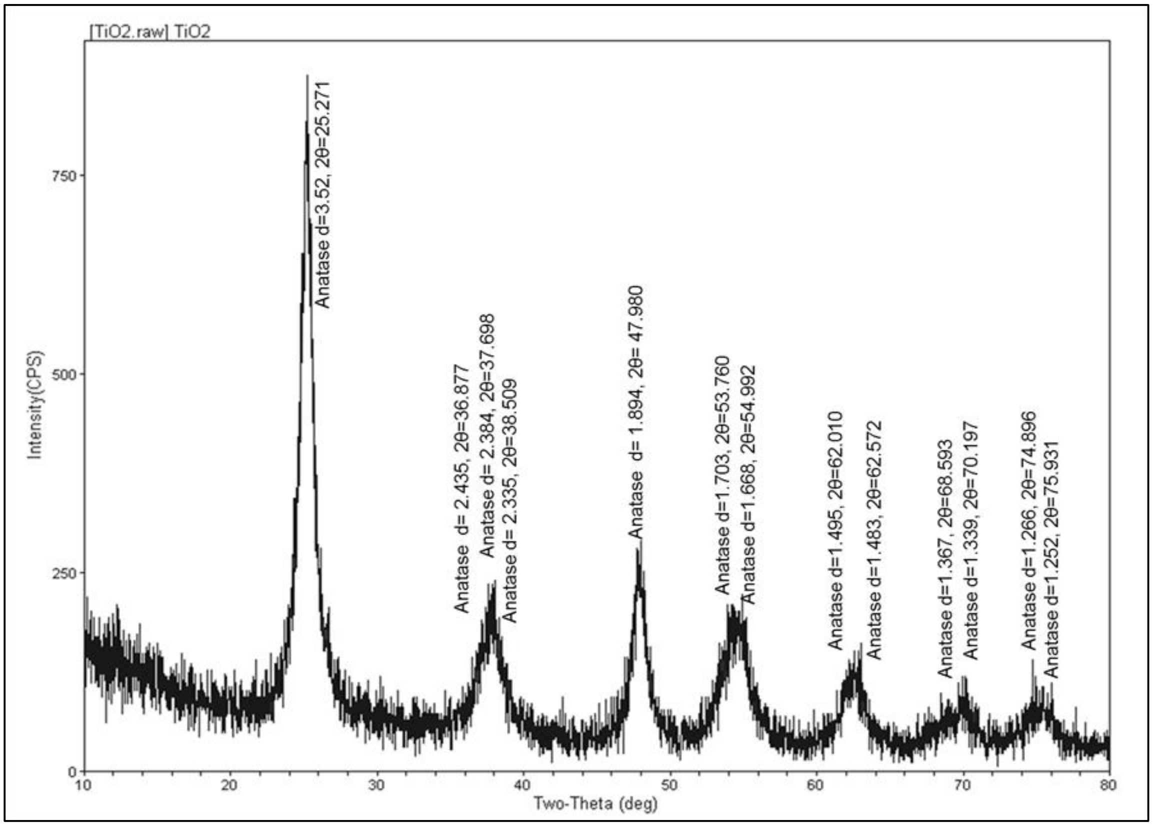

Fig. 2:

IV. CALIBRATION CURVE

Five no. of dilute solutions of Reactive Black-5 were prepared for construction of standard curve. Aqueous Reactive black-5 solution was scanned for maximum absorbance and was found to give peak absorbance (λ_{max}) at 599 nm in a UV-visible spectrophotometer (Thermo: Genesys). The absorbance vs. concentration data was plotted in fig.3. The curve was used extensively to determine Reactive Black-5 concentration during experimental runs.

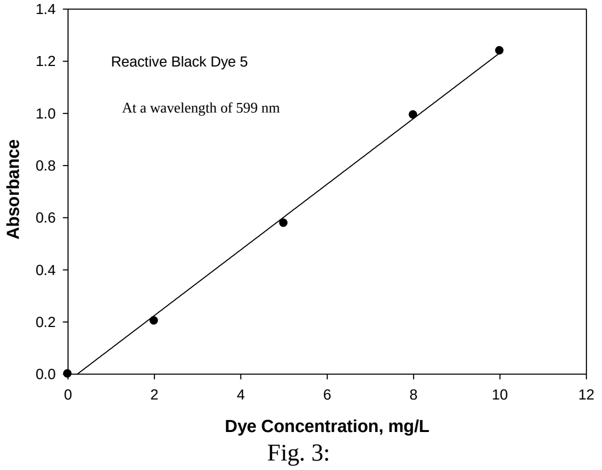

Fig. 3:

V. PHOTO REACTOR

The photoreactor of capacity 1720 ml contained 305 mm long, four no. UV lamps each with flux 13.5 W/m^2. The sources of irradiation were placed uniformly inside the reactor to assure the maximum energy exchange between the source of irradiation and reaction mixture that would flow out continuously. A pump was used to circulate the mixture between the reactor and the reservoir containing the feed solution. The schematic diagram of the experimental setup is furnished in Fig 4.

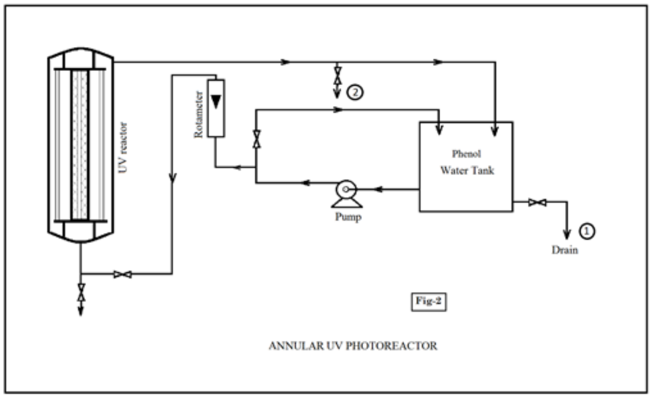

Fig. 4:

VI. METHODS

5 litres of the Reactive Black-5 solution of 50 mg/L was prepared by accurately weighing Reactive Black-5 dye in an electronic weighing balance (supplied by Sartorius, India Ltd.) and dissolving in deionised water. Specified amount of TiO_2 (0.5 g/L) was accurately weighed and was mixed thoroughly with the dye solution . The solution was then placed in the feed reservoir. The suspension was stirred for about half an hour in the absence of UV light in order to reach adsorption equilibrium before irradiation with UV light. Photocatalysis reaction was carried out for a period of 2 hrs. The same procedure was followed in each of two flow rates of 10 and 15 Litre per hour (LPH) respectively and for different solution pH. The solution coming out of the reactor was directed to the reservoir and was allowed to mix thoroughly with the solution. The sample of reaction suspension (5ml) was withdrawn with a syringe from the reservoir at regular interval of 30 minutes. Each sample collected was then filtered and then analyzed in the UV-Visible spectrophotometer by measuring the absorbance at 599 nm. Using the calibration curve, the remaining Reactive Black-5 concentration of the samples was determined. Dye concentration was measured at different time interval (30,60, 90 and 120 mins.) and the kinetics of the photocatalysis reaction was determined.

VII. RESULTS AND DISCUSSION

A. Effect of flowrate

Adsorption and photodegradation of Reactive Black-5(RB-5) was carried out with varying flowrates 10 and 15 LPH. The concentration of RB-5 was plotted against time by measuring the residual RB-5 concentration in solution. The conversion of RB-5 into harmless products was calculated using Equation no. (5). Fig. 5 depicts the change in concentration of RB-5 against time for a reactor operating time up to 120 minutes or 2 hrs at a flowrate of 10 LPH. From the experimental results it was observed that higher conversion (95.4%) had been achieved at a flowrate of 15 LPH compared to that (88.5%) at 10 LPH. The increase in percent degradation of RB-5 at higher flowrate could be due to the formation of turbulence in the solid liquid reaction medium. With the formation of turbulence at higher flowrate, the external mass transfer resistance from the bulk solution to the catalyst surface had been reduced. This might have indirectly increased the global rate of reaction between the catalyst and RB-5 resulting in increase in degradation efficiency.

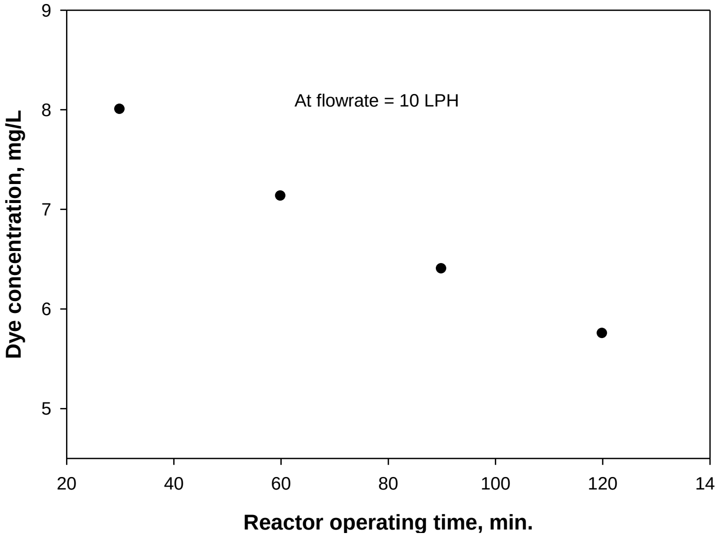

Fig. 5:

B. Effect of pH

The effect of pH on the photo catalytic degradation efficiency of Reactive Black-5 by UV/TiO_2 process is one of the major factors affecting the rate of mineralization of various organic compounds. The degradation of Reactive Black-5 was carried out under UV irradiation at different pH (4.2, 6.4, 8.4). It is evident that there is an optimum pH that would result in maximum Reactive Black-5 conversion which was obtained in mildly acidic to neutral region. The process of the photocatalytic degradation would involve radical oxidation, direct electron transfer and surface sorption reaction. At mildly acidic condition (pH=6.4) the TiO_2 surface carries a net positive charge, while the RB-5 and the intermediates are basically negatively charged. This results in better adsorption and subsequent better degradation of RB-5. However at stronger acidic condition (pH=4.2) RB-5 degradation rate (i.e. conversion) got retarded, probably due to the presence of excess hydrogen ion in the system. At alkaline medium (pH=8.4), formation of OH radical, the main agent causing photocatalytic oxidation got retarded; Moreover in the vicinity of this pH, RB-5 became ionized (negatively charged) and got repelled from the negatively charged surface of the adsorbent, TiO_2. Due to these causes, at higher pH, the
adsorption of RB-5 on TiO_2 active sites decreased and hence the RB-5 degradation rate got lowered.

Table – 1
Removal of RB-5 dye at different solution pH

Time of Contact (in min.)	*Removal at acidic range (pH=4.2)*	*Removal near neutral range (pH=6.4)*	*Removal in alkaline range (pH=8.4)*
30	*88%*	*92.4%*	*66%*
60	*90%*	*94.0%*	*75%*

C. Kinetic studies

The Langmuir-Hinshelwood kinetic model was used to describe the mineralization process kinetics. The Langmuir-Hinshelwood (L-H) model was initially developed to quantitatively describe gaseous–solid reactions. This model was recently employed to describe solid–liquid reactions. In this model, the rate of reaction (r) is proportional to the fraction of surface covered by the substrate (θ), as shown below:

$$r = -dC/dt = k_r\theta \qquad (8)$$

Considering Langmuir's equation

$$\theta = KC/(1+KC) \qquad (9)$$

Combining Eq. (8) and (9),

$$r = k_rKC/(1+KC) \qquad (10)$$

In Eq. (10) k_r is the true rate constant, K is the Langmuir constant and C is the concentration of the organic substrate at any time t. Since in this case, the solution is highly diluted, C (mol/L) $<10^{-3}$ [12] the term KC becomes <<1, and the reaction transforms to an apparent first order reaction, whose kinetic expression may be written as follows :

$$r = -dC/dt = k_rKC = k_{app}C \qquad (11)$$

where k_{app} is the apparent rate constant of a pseudo first order reaction.
Integrating we get

$$\ln\frac{c}{c_o} = -k_{app}t \qquad (12)$$

By plotting $\ln\frac{c}{c_o}$ against t, k_{app} has been computed from the slope of the straight line (Fig.6).

The apparent rate constant thus obtained is found to be 3.83×10^{-3} min^{-1}

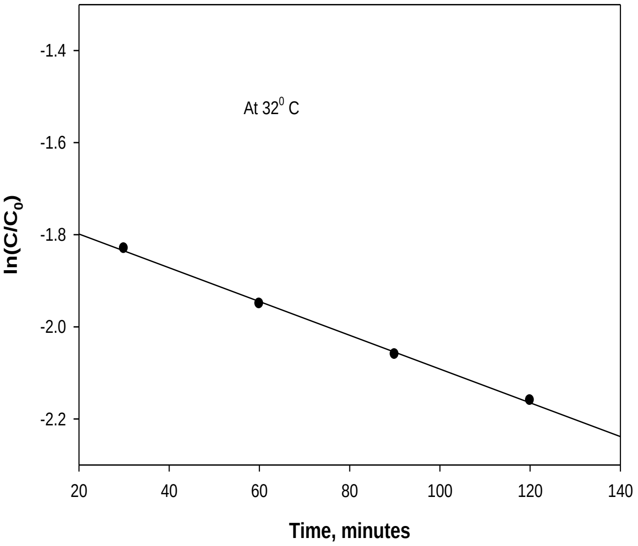

Fig. 6:

VIII. CONCLUSION

From present investigation, it had been found that photocatalysis in UV/TiO2/O2 system was quite effective in degradation of Reactive Black-5. Effect of solution pH and flow rate were found to influence the extent of mineralization substantially. Slightly acid to neutral region solution pH was found to be favourable for the photocatalysis reaction. Due to higher turbulence, the degradation was found to get enhanced considerably. The photodegradation of RB-5 dye using TiO2 as a catalyst has been found to follow Langmuir-Hinshelwood model.

REFERENCE

[1] Wang, K-S, Chen, H-Y, Huang, L-C, Su, YC, Chang, S-H., Degradation of Reactive Black 5 using combined electrochemical degradation-solar-light/immobilized TiO2 film process and toxicity evalution, Chemosphere, 72, 299 (2008).
[2] Choi, H-D, Shin, M-C, Kim, D-H, Jeon, C-S, Beak, K., "Removal characteristics of reactive black 5 using surfactant-modified activated carbon", Desalination, 223, 290 (2008).
[3] Mahmoodi, N.M., Arami, M., "Bulk phase degradation of Acid Red 14 by nanophotocatalysis using immobilized titanium (VI) oxide nanoparticles", J. Photochem. Photobio. A: Chemistry, 182, 60 (2006).
[4] Baocheng, Q., Jiti, Z., Xuemin, X., Chunli, Z., Hongxia, Z., Xiaobai, Z., "Adsorption behavior of Azo Dye C. I. Acid Red 14 in aqueous solution on surface soils", J. Env. Sci, 20, 704 (2008).
[5] R.W. Matthews, Purification of water with near UV illuminated suspensions of titanium dioxide, Water Research, 24 (1990) 653-660.
[6] O.K Mahadwad, P.A.Parikh, R.V. Jasra and C Patil, Photocatalytic degradation of reactive black-5 dye using TiO2 impregnated ZSM-5, Bull. Mater. Sci., 34(3), (2011) 551–556.
[7] Hosseinnia, M. Keyanpour-Rad and M. Pazouki, Photo-catalytic Degradation of Organic Dyes with Different Chromophores by Synthesized Nanosize TiO2 Particles, World Appl. Sci. Journal, 8 (2010) 1327-1332.
[8] S.P. Devipriya and S. Yasadharan, Photocatalytic Degradation of Phenol in Water using TiO2 and ZnO, Journal of Env. Bio., 31 (2010) 247-249.
[9] C.N. Satterfield, Mass Transfer in Heterogeneous Catalysis, MIT Press, Cambridge MA, 1970
[10] J.M. Herrmann. Heterogeneous photocatalysis : fundamentals and applications to the removal of various types of aqueous pollutants. Catalysis Today, 53 (1999) 115-129.
[11] N.A.Laoufi, D. Tassalit and F. Bentahar, The degradation of phenol in water solution by TiO2 photocatalysis in a helical reactor, Global Nest Journal,10 (2008) vol. 10, 404-418.
[12] C.S. Turchi and D.F. Ollis, Photocatalytic degradation of organic water contaminants: mechanisms involving hydroxyl radical attack, J.Catal.122 (1990).