



COLOR REDUCTION IN DYES USING PHOTOCATALYST MATERIALS

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Abstract- The ability to degrade organic and inorganic pollutants comes from the redox environment generated from photo-activation of TiO₂, which is a semiconductor material. TiO₂ or titania is a very well-known and well-researched material due to the stability of its chemical structure, biocompatibility, physical, optical and electrical properties. The possible application for this material as a photocatalyst is nowadays widely used in a commercial scale water treatment facility. In the last decade, however, TiO₂ has been developed and used as a photocatalyst for the purification and remediation of contaminated waters loaded with low concentrations of toxic organic pollutants. In the present investigation, we have reported the photocatalytic efficiency of commercial TiO₂ and lab made modified TiO₂ using a batch photocatalytic reactor for the color reduction of dye solutions in textile wastewater.

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Introduction

Textile dyes are an abundant source of colored organic compounds that present an increasing environmental danger. With the increased demand for textile products, the textile industry and its wastewaters have been increasing proportionally making it one of the main sources of severe pollution problems worldwide. Textile wastewater includes a large variety of dyes and chemical additions that make the environmental challenge for textile industry not only as liquid waste but also in its chemical composition [1]. In particular, the colored effluents into the environment are undesirable, not only because of their color, but also because of presence of many dyes in wastewater whose breakdown products are toxic and / or mutagenic to life. During dye production and textile manufacturing processes, a large quantity of wastewater containing dyestuffs with intensive color and toxicity can be introduced in the aquatic systems. Due to the large degree of organics present in these molecules and stability of modern textile dyes, conventional biological treatment methods are ineffective for their decolorisation and degradation. Traditional methods for treating the textile dye wastewaters consist of various chemical, physical and biological processes. The use of conventional textile wastewater treat-

ment processes becomes drastically challenged to environmental engineers with increasing more and more restrictive effluent quality by water authorities. Conventional treatment methods such as biological treatment discharges not acceptable as 47% of 87 colors are identified as non-biodegradable [2]. Advanced oxidation processes hold great promise to provide alternative for better treatment and protection of environment. AOPs have shown great potential in treating pollutants at both low and high concentrations and have found applications as diverse as treatment of ground water and municipal wastewater sludge. Advanced oxidation processes (AOPs) have been developed to generate hydroxyl free radicals by different techniques. Among the many AOPs, the most studied method is probably the photocatalysis by TiO₂ / UV. Due to the advantages of photocatalytic decomposition of organic pollutants using TiO₂ particles or films, advanced oxidation by TiO₂/ UV has been gaining industrial and academic attention. However, most of the studies investigate only some and not all factors that might influence the degradation rate of organic compounds in aquatic systems [3]. Heterogeneous photocatalysis is a process in which the illumination of an oxide semi-conductor, usually anatase or rutile phase titania, produces photo-excited

electrons (e^-) and positive charged holes (h^+). The photo-excitation of the semi-conductor particles by UV light changes the energy state of the electrons from the valence band of the solid to the conduction band. This paper is based on the original efforts that have been made to investigate photocatalytic materials for removal of color from aqueous reactive dye solutions in textile wastewater. The following objectives were delineated and investigated which included the preparation of a photocatalyst, colour removal studies under photocatalytic conditions using reactive dyes employing photocatalysts-kinetic studies and comparison of photocatalytic efficiency of laboratory made as well as commercially available TiO_2 catalysts using an immersion well batch reactor.

Materials and methods

The solutions of variable concentrations of reactive dyes namely Reactive Black 5 (RB5) and Reactive Red 2 (RR2) were prepared in aqueous medium were prepared using analytical grade water from a Millipore, Water Purification Unit. The glassware used was washed thoroughly with chromic acid and rinsed with Millipore water before use. The commercially available titanium dioxide was procured from Degussa AG (Germany). The catalyst is generally referred to by its trade name as P-25 TiO_2 . The modified lab made titania catalysts namely 0.5% Ag/ TiO_2 and 0.5% Cu/ TiO_2 were prepared in the laboratory to test the photoactivity of selected reactive dyes. Surface doped Ag/ TiO_2 and Cu/ TiO_2 were synthesized by the method of photodeposition of metals on irradiated TiO_2 [4]. The commercial samples of the reactive dyes namely Reactive Black 5 (RB5) and Reactive Red 2 (RR2) were procured from M/s Color Chemicals, Ahmedabad.

Photocatalytic Batch Reactor

The cylindrical photocatalytic batch reactor used for the investigations was made up of quartz and provided with a water circulation arrangement in order to maintain the temperature. The top portion of the photochemical quartz immersion well was provided with inlet and outlet ports for aeration and sampling. The irradiation was carried out using a UV Medium Pressure Mercury emitting a UV radiation in the range of 200 nm to 400 nm with a peak emission at 365 nm. The photochemical reaction vessel for holding wastewater samples was fabricated out of borosilicate glass with a capacity of 400 ml. The quartz assembly was inserted into the reaction vessel and irradiation commenced. This complete immersion well photoreactor was jacketed in a cylindrical metal compartment in order to avoid the UV radiation exposure. The samples representing color removal were collected at different intervals during illumination period and filtered through 0.20 micron syringe filters for further analyses.

Batch Photoreactor Experiments

Experiments were performed with aqueous solutions of dyes RB5 and RR2 in batches. Photocatalytic treatment of two variable concentrations namely 25 and 100 $mg\ l^{-1}$ of each dye was performed in the photoreactor. Initially 400 ml of 25 $mg\ l^{-1}$ concentration of RB5 in water was taken into the immersion well photocatalytic batch reactor. To this, 0.08 g of TiO_2 (Degussa P - 25) photocatalyst was added with respect to an optimized dose of 0.2 g/l TiO_2 required for efficient photocatalytic treatment [5,6]. The reaction

mixture was aerated using aquarium pump. The photocatalytic treatment was commenced by irradiation through the UV source (MPML 400W). The progress of photocatalytic degradation of the dye was monitored by withdrawing aliquots of the reaction mixture at regular intervals and measuring the absorbance at wavelengths of maximum absorbance in each case for decolorization. In a similar manner, 100 $mg\ l^{-1}$ concentration of RB5 and RR2 were also subjected to photocatalytic degradation in the immersion well batch reactor. Further, similar procedure was carried out for concentrations of all the reactive dyes for other lab made photocatalysts namely; Ag/ TiO_2 and Cu/ TiO_2 .

Analysis

Color reduction in the test samples collected at various stages in the present study was analyzed by determining the absorption peaks and absorbance values using a double beam UV - VIS spectrophotometer (Shimadzu 1650 PC). The dyes examined have a characteristic color and absorbance in the visible region. The wavelength of maximum absorption (λ_{max}) was determined by recording absorption spectra of each dye for a particular known concentration. A calibration plot of concentration versus absorbance was plotted at λ_{max} for the dyes.

Kinetic Studies

This involved determination of initial rates of photocatalytic degradation of the chosen reactive dyes as a function of initial concentration of each reactive dye and fitting into the existing kinetic models such as Langmuir - Hinshelwood kinetic model popularly adopted for similar studies elsewhere [7]. Alternatively, $\log C_t/C_0$ vs time linear plots were constructed and first order rate constants were deduced and compared. The experimental color concentration data was used to deduce photo degradation kinetic constant from the slope of linear plots between $-\log (C_t/C_0)$ vs. time. The pseudo first order rate constant of photodegradation was deduced by plotting $\log (C_t/C_0)$ vs. time plots and performing the linear regression analysis. Regression coefficient > 0.9 (R^2) was considered best. The slope of the straight line represented rate constant (k) of the photodegradation. The unit of ' k ' is reported in min^{-1} .

Results & Discussion

The degradation of the dyes is evidenced from the decrease in the absorbance values with time and was tested by the absorption curves determined for the collected periodic samples during the experiments. The Fig.1 shows a typical time-dependent colour reduction kinetic linear plot of the individual dye solution during photo irradiation. The absorption peaks corresponding to the dye diminish and finally disappear under reaction, indicating the degradation of the dye in each individual case. The percentage color reduction of reactive dyes using all three catalysts is reported according to the Table1, Table 2 and Table 3.

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Table 1- Percentage color removal of dyes under photocatalysis using TiO_2

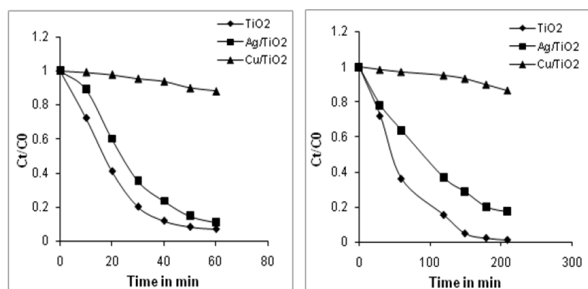
Dyes	25 $mg\ l^{-1}$	100 $mg\ l^{-1}$
RB5	92.82	98.87
RR2	93.04	100

Table 2- Percentage color removal of dyes under photocatalysis using Ag/ TiO₂

Dyes	25 mg ^l -1	100 mg ^l -1
RB5	88.99	82.62
RR2	77.57	70.55

Table 3- Percentage color removal of dyes under photocatalysis using Cu/ TiO₂

Dyes	25 mg ^l -1	100 mg ^l -1
RB5	11.7	13.5
RR2	20	23.9



a) Decolorisation of 25 mg^l-1 RB5 using titanium dioxide and titania modified catalysts

b) Decolorisation of 100 mg^l-1 RB5 using titanium dioxide and titania modified catalysts

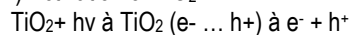
Fig 1: Decolorization of Reactive Black 5 (RB5) using TiO₂ and titania modified catalysts in an immersion well UV batch reactor

Semiconductor photocatalysis takes advantage of the valence/conduction band gap specific to semiconductor molecules. Incoming photons with energies at or above the band gap will cause valence electrons to become excited and move to the conduction shell, leaving holes in the valence band. These excited charge carriers can then react with molecules adsorbed on the semiconductor surface thus acting as catalytically active species. There are several competing effects, which might limit the effectiveness of the catalysts. Most of the charge carriers will undergo recombination before reaching the surface to interact with adsorbed molecules. In fact upto 90% of the generated charge carriers are lost within a nanosecond of their generation, leading to low photoactivity [8]. It is proposed that the addition of certain metal ions offers a way to trap the charge carrier and extend the lifetime of one or both of the charge carriers improving the efficiency of the catalyst thus increasing the surface charge transfer by stabilizing the electron-hole pairs once they reach the catalyst surface. The adopted method used for the synthesis of the doped catalysts in the study allowed the metal ions to be located in the interstitial positions of the TiO₂ lattice.

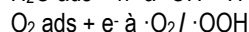
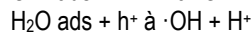
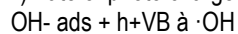
Titanium dioxide is a semiconductor with a band gap of 3.20 eV. It implies that light with energy equal to this or higher will only activate TiO₂. In terms of wavelength this may be equated to 385 nm. This explains the need for UV illumination. When UV light is absorbed by titanium dioxide, two primary charge carriers are generated namely electrons (e⁻) and holes (h⁺). A large part of photo charges undergo recombination in the absence of competitive interfacial reactions viz. oxidation of H₂O, OH⁻, O₂, dye molecules etc. Therefore, the carriers, which succeed in reaching the space charge layer/interface, will react with adsorbed molecules and

generate chemical oxidants such as ·OH, ·O₂⁻, ·O₂H, etc. that in turn react with dyes. In successive steps, the dyes are decolorized and mineralized to final oxidation products. Owing to very high oxidation potential, the hydroxyl and hydro-peroxy radicals oxidize the dyes leading to several degradation intermediates initially and carbon dioxide finally. The following reaction steps illustrate the complexity of photocatalytic degradation reactions.

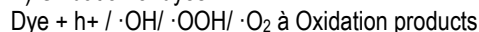
i) Activation of TiO₂



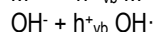
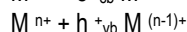
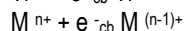
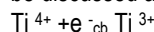
ii) Fate of photo charges at TiO₂ solution interface



iii) Oxidation of dyes



Many reaction conditions viz. light intensity, dose of catalyst, concentration of dyes and their specific absorptivity (extinction coefficients), presence of metal ions and other inorganic ions can be expected to influence the rate of photodegradation of dyes. It is reported [9] that the addition or impregnation of metals on the TiO₂ surface can enhance the photocatalytic degradation activity due to charge trapping. The process involved in the charge trapping may be discussed as follows;



Here the metal ion is the impregnated metal ion. The energy level of Mⁿ⁺ / M⁽ⁿ⁻¹⁾⁺ lies below the conduction band edge. Thus, the energy level of the metal ion affects the trapping efficiency. The trapping electrons makes it easy for holes to transfer onto the surface of TiO₂ and react with OH⁻ in the organic compound solution and form active hydroxyl radicals which participate in the degradation of organic compounds. For effective degradation reaction, the lifetime of electrons and holes is critical. The lifetime of the holes can be enhanced by trapping electrons, thereby reducing the recombination of rate and allowing holes to diffuse to the particle surface and participate in oxidation reaction. If the energy level of the dopant moves towards the conduction band edge, the efficiency of trapping becomes higher. In that case, the traps have a larger tendency to act as shallow traps so that the holes generated by following photons cannot recombine with the already trapped electrons. Consequently, the lifetime of free holes can be extended. Among the four catalysts studied, the photocatalytic activity is different for different catalysts probably due to the different effects on impeding the transportation of electrons and holes from the interface to the surface, thereby having different effects on catalyst efficiency. The higher photoactivity of Ag/ TiO₂ as compared to that of Cu/ TiO₂ may be due to maximum charge trapping of the silver metal ion. The order of initial rate shows that the higher photocatalytic activity obtained for Ag/TiO₂ as particularly compared to Cu/ TiO₂ may be due to the silver metal ion onto TiO₂ which causes better charge separation and hence less recombination (Wang et al, 2009). The behavior of the Cu²⁺ in the Cu²⁺ system is more complicated. Cu²⁺ may scavenge electrons with the formation of Cu⁺ but the latter can be re-oxidised by the positive holes or by the hydroxyl radicals. Thus the first step enhances the oxidation of the substrate and the second step inhibits it. However,

the overall influence of Cu^{2+} on the photocatalytic activity of TiO_2 is very minor [10].

In the present study it has been observed that photocatalytic degradation efficiency of all the four textile dyes with TiO_2 and modified titania catalysts was found to be of the order; $\text{TiO}_2 > \text{Ag/TiO}_2 > \text{Cu/TiO}_2$ respectively. A number of researchers have earlier shown that mixing different semiconductors with appropriate energy levels can produce a more efficient photocatalyst owing to better separation of e^- and h^+ [11]. But this effect was possible to see with nanocrystalline and quantum sized semiconductor materials. In the present study, we have found that crystallites of TiO_2 and dopant ions are quite larger in size (in a range of 3- 20 μm). Therefore, the expected charge separation and accompanying photoactivity could not be found.

Among the catalysts used, TiO_2 (commercial Degussa P25) was found out to be the most effective. This may be due to (80:20) anatase:rutile. Further, Ag/ TiO_2 catalyst was also found relatively more efficient as compared to Cu/ TiO_2 . Hence the photocatalytic degradation of dyes can be effectively carried out using these photocatalysts in slurry and immobilized photoreactors for the reduction of color in textile wastewater and hence has a prominent application in wastewater treatment.

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