Photocatalytic Removal Of Xanthene And Diaryl Methane Dyes By Air Oxidation Using TiO₂ Nanospheres Under Sunlight

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Abstract—Titanium dioxide nanocatalyst was synthesized by simple chemical precipitation method and is characterized by XRD, FE-SEM, EDAX, TEM, BET Surface area analysis, FTIR, UV-DRS and Photoluminescence. The synthesized TiO₂ catalyst is evaluated for its photocatalytic activity towards the degradation of Rose Bengal and basic yellow (Auramine O) dyes under solar irradiation. The parameters such as catalyst dosage, initial dye concentration, pH were optimized for the effective photocatalytic dye degradation. The photodegradation rates of Rose bengal reached 98% within 60 minutes of reaction time and for basic yellow 89% of the dye degradation is achieved within 60 minutes of irradiation and the rate of dye degradation was found to be enhanced by air oxidation using TiO₂ catalyst under sunlight.

Key words: Air oxidation, FE-SEM, Photocatalysis, Solar radiation, TiO₂, TEM, XRD.

1 INTRODUCTION
Among different transition metal oxide nanoparticles, titanium dioxide in its anatase phase have notable applications in waste water management [1], [2]. They are proved to be efficient, less expensive, non-toxic, resistance to corrosion and reusable [3]. These properties of titanium dioxide make it possible to use this metal oxide for a wide variety of applications. Parthasarathi and thilagavathi used titanium dioxide nanoparticles for microbial resistance [4]. Juti Rani Deka and Hong Wen Wang [5] synthesized mesoporous TiO₂ for the photoanodes in dye sensitized solar Cells. Chang Sheng Guo et al., [6] used TiO₂ microspheres catalysts for bisphenol A Degradation. Julie Joseane Murcia et al., [7] utilized fluorinated and platinitized titania for the photocatalytic treatment of dyestuffs and stained wastewater coming from handicrafts factories. Titanium dioxide nanoparticles are prepared by various methods like sol-gel technique, hydrothermal synthesis, chemical vapour deposition, reverse microemulsion method, solid state reaction, solvothermal method, microwave and sonochemical methods [8]. Among all these wide techniques, chemical precipitation method is one of the easiest to yield low temperature, high purity nanoparticles. In the present work, the photocatalytic activity of titanium dioxide nanoparticles is evaluated against two dyes rose Bengal and basic yellow. Rose Bengal (Acid Red 94) falls under the class of xanthene derivatives [9]. It is anionic water soluble and a photosensitive dye widely used in textile, medicinal and photochemical industries [10], [11].

Even though, rose Bengal dye has wide applications, the toxic effects of the dye have also been investigated. Tabery HM studied the Toxic effect of rose bengal dye on the living human corneal epithelium [12]. Lee et al., investigated the In vitro study for staining and toxicity of rose bengal on cultured bovine corneal endothelial cells [13]. Basic yellow Auramine O is a diamethylmethane dye used as a fluorescent stain. Basic yellow 2 dye can be used to stain acid-fast bacteria in a way similar to ziehl-neelsen stain. It can also be used as a fluorescent version of Schiff reagent. It is most commonly used dye in cotton, leather, jute and paper Indus tries [14], [15]. However, the excessive exposure to commercially available auramine dyes induces DNA Damage in Vivo in Liver, Kidney and Bone Marrow Cells [16], [17]. The chemical structures of rose Bengal and basic yellow dyes are shown in the following figure (1a), (1b).

Fig1a. Chemical structure of Basic yellow Auramine O dye.

Fig1b. Chemical structure of Rose Bengal dye.

2 PROCEDURE
The Titanium tetrachloride salt (M.W. 189.679g/ml, purity 99%) was purchased from Sisco Research Laboratories Pvt.Ltd., sodium hydroxide from Merck and ethanol (99.9%) was purchased from Changshu Hongsheng Fine Chemical Co. Ltd. The capacity of the air pump used for the
experiments is 3W and air supplied is 2.5L/min. Basic yellow dye (molecular formula C₁₇H₂₂ClN₃, MW 303.83 and λmax = 432 nm) was obtained from S. D. Fine Chemicals and rose bengal dye (molecular formula C₂₀H₂Cl₄I₄Na₂O₅, MW 1017.628 g/mol and λmax = 559 nm) was obtained from sigma Aldrich chemicals.

2.1. Synthesis of Titanium Dioxide Nanoparticles
Titanium tetrachloride solution (1M) is used as a precursor to prepare the titanium dioxide nanoparticles. Sodium hydroxide is used as a strong base to precipitate the salt solution. The solution is homogenized by continuous stirring at 60°C for two hours. A thick white precipitate is obtained and the stirring is continued for 30 minutes. The obtained precipitate is repeatedly washed with double distilled water and then dried in the hot air oven at 100°C for 6 hours and finally, it is calcined at 400°C for 3 hours.

2.2 Photocatalytic Degradation Experiments
The varying stock solutions of Rose Bengal and basic yellow dyes (10mg to 50mg/L) are prepared, from which 50mL was withdrawn for each experiment. All the photocatalytic experiments were carried out on sunny days between 11 am to 2 pm. Before, exposing the dye solution to sunlight irradiation the initial absorption peak was recorded. Irradiation was carried out in the open air and the solution was continuously mixed by pumping to provide aeration. The experiment was continued for 3 hours, at appropriate intervals 2mL of the dye solution is withdrawn and centrifuged to separate the catalyst. The effect of pH was studied by adjusting the solution using 0.1N NaOH and 0.1N HCl. The blank experiments were performed in the dark at room temperature following the above procedure. The percentage decolourization was calculated using the formula

\[ \frac{C_0 - C}{C_0} \times 100 \]

Where \(C_0\) is the initial concentration of the dye solution and \(C\) is the concentration of the dye solution at time \(t\).

3. RESULTS AND DISCUSSION
3.1 Catalyst Characterization
The morphology of the synthesized Titanium dioxide nanocatalyst is examined by FESEM and TEM analysis.

From figure (2a), (2c), (2d) it is found that the synthesized Titanium dioxide particles posses a moderately spherical shape with the particles size ranging from 12.7nm to 33.6nm which is measured from the FE-SEM images. Additionally the dark spotted circles in the SAED pattern indicates the crystalline nature of the Titanium dioxide nanoparticles. This result is in agreement with that found to Titanium dioxide nanoparticles prepared by similar chemical precipitation techniques [18], [19].
The typical EDAX spectrum of the Titanium dioxide particles in figure (2b) shows the presence of Titanium and oxygen elements in major composition which confirms the successful formation of Titanium dioxide nanoparticles without any impurities. Further, the crystallinity, band gap value, surface area, optical property, and structural disorders and the defects of the as-synthesized TiO₂ nanoparticles were examined by XRD, UV-DRS, nitrogen adsorption-desorption analyzer and room-temperature PL spectrum, respectively.

**Fig3.** XRD pattern of the synthesized TiO₂ nanoparticles.

The crystalline nature of the synthesized titanium dioxide nanoparticles is characterized using X-ray diffraction analysis. The diffraction peaks at 2θ = 25.12°, 37.72°, 47.88°, 67.52° which is in accordance with the anatase phase of titanium dioxide nanoparticles are confirmed from the JCPDS file no. 21-1272 [20] and similarly, the peaks at 2θ = 27.44°, 36.10° 53.82° and 55.04° in accordance with the characteristic peak of rutile titanium dioxide is also observed [18]. However, from the obtained XRD results (shown in fig.3), it is found that peak at 2θ = 25.12° is the most intense one indicating that anatase is the main crystal phase of the sample while there are also some rutile crystals in it. The Band gap energy (Eg) of the Titanium dioxide nanocatalyst is obtained using the following relation

\[
E_g = \frac{1240}{\lambda}
\]

Where Eg is the band gap energy in electron volts (eV) and \(\lambda\) is the wavelength (nm) corresponding to maximum absorption. The Eg of Titanium dioxide nanocatalyst synthesized using chemical precipitation method was found as 3 eV. However, the band gap value of anatase TiO₂ crystals were reported to be 3.2 eV respectively [21], a small decrease in the band gap value of synthesized TiO₂ crystals may be attributed to the presence of some rutile crystals in the synthesized material.

**Fig4a.** shows the UV-DRS plot for the synthesized TiO₂ nanoparticles.

**Fig4b.** shows the Photoluminescence spectrum of the synthesized TiO₂ nanoparticles.

Fluorescence emission (FL) spectrum provides the information about exciton recombination as well as surface defects. PL spectrum of the synthesized titanium dioxide nanoparticles was recorded with 254 nm excitation (Fig 4b). PL emission curve of as formed TiO₂ nanoparticles showed a peak at 355 nm, the observed broad and intense emission peak originates from the recombination of exciton [22], Photon absorption in TiO₂ excites the electron-hole at the valence band. The electron with enough energy which is equal to or greater than the band gap energy will excite from valence band to conduction band. This process also known as radiative transition of bulk anatase TiO₂, contributes to the violet band at wavelength around 400-435nm[23] as shown in fig. and a similar emission band around 468 nm is also found. This strong emission in the region of 400– 550 nm might be assigned to the energy states of surface traps (oxygen vacancies) of the synthesized TiO₂ nanoparticles [24].
Fig 4c. shows the FTIR spectrum of the synthesized TiO$_2$ nanoparticles.

FTIR analysis was used to determine the functional groups of titanium dioxide nanoparticles. As shown in fig 4c, the peaks at 3331 and 1637 cm$^{-1}$ in the spectra are due to stretching and bending vibration of the $–$OH group which may be due to the presence of moisture in the synthesized material. The peaks ranging from 555 cm$^{-1}$ to 657 cm$^{-1}$ shows bending and stretching mode of Ti-O-Ti [25]. The surface area of the catalyst is the most important factor influencing the catalytic activity.

Fig 4d. shows the N$_2$ adsorption-desorption isotherm pattern of TiO$_2$ nanoparticles.

The nitrogen adsorption–desorption isotherms of the as-synthesized zinc oxide nanoparticles are shown in Fig. 4d. From the BET surface area measurements it is found that the specific surface area of the titanium dioxide nanocatalyst is 61.006m$^2$/g and its pore volume is 0.339cc/g.

3.2 Discussion of the Photocatalytic Activity of TiO$_2$ Nanoparticles towards Basic Yellow and Acid Red-94 Dyes

The effects of different experimental factors on the photocatalytic degradation of basic yellow and acid red-94 dyes are studied.

The effect of pH in the range of 3–12 and experimental conditions (15mg of TiO$_2$ catalyst, 10 mg/L dye concentration) on the overall rate of decolorization is studied. The maximum decolorization efficiency was observed at alkaline pH=10 for basic yellow dye and the maximum dye removal was possible at acidic pH 3 for acid red dye as shown in figure 5. From the literature sources, it is found that the point of zero charge (zpc) for TiO$_2$ catalyst is nearly 6.5 and hence, the TiO$_2$ surface was positively charged at pH < 6.5 and negatively charged at pH > 6.5 [26], [27]. Due to the cationic nature of the basic yellow dye it gets attracted to the TiO$_2$ catalyst which carries a negative charge on its surface beyond pH 6.5 hence, at alkaline pH the removal of basic yellow dye takes place more efficiently whereas at acidic pH below 6.5 the TiO$_2$ surface is positively charged and attracts the negatively charged acid red dye towards its surface thus, photocatalytic degradation of acid red dye efficiently takes place at acidic pH in the presence of TiO$_2$ catalyst. Fig. (6a, 6b) shows that increasing TiO$_2$ dose up to 25mg and 15mg increased the removal efficiency for basic yellow and acid red 94 dyes, respectively. Increase in catalyst dosage above these limits showed a decrease in dye removal efficiencies. Even though increase of TiO$_2$ particles in the solution might provide more active sites for the dye molecules to be adsorbed and degraded, excessive amounts of catalyst particles will increase the opacity of solution and consequently reduce the penetration of sunlight and thus decrease the dye removal efficiency. These results agreed with the previous studies [28], [29].
The effect of varying initial dye concentrations were investigated by selecting a concentration range of $3.29 \times 10^{-5}$ mol/L to $1.64 \times 10^{-4}$ mol/L for BY and from $1.96 \times 10^{-5}$ mol/L to $4.91 \times 10^{-5}$ mol/L for AR-94 dye under the experimental conditions of catalyst concentration 25mg and 15mg, pH range 10 for basic yellow dye and acidic pH range 3 for acid red dye and continuous air oxidation which is shown in figure 7a and 7b. The experimental results show that an increase in dye decolourization of 89% up to 98% of $3.9 \times 10^{-4}$ mol/L of acid red dye solution got decolourized within 60 minutes, beyond which there is a decrease in the rate of degradation process. However, under dark condition only 14% of basic yellow and 16% of acid red-94 dyes got decolourized.

The rate of degradation relates to the formation of hydroxyl radicals on catalyst surface and probability of .OH radical reacting with dye molecule. For all initial dye concentrations, the catalyst amount, air oxidation and solar intensity are nearly constant. Since the generation of hydroxyl radical remains constant, the probability of dye molecule to react with hydroxyl radical decreases at higher concentrations and hence there is decrease in the degradation rate.

4 CONCLUSIONS

In summary, we have reported facile and novel synthesis of TiO$_2$ nanoparticles through a simple chemical precipitation technique. Detailed structural and morphological characterizations established the formation of crystalline TiO$_2$ nanoparticles. Considering initial dye concentration, solution pH and catalyst dose as variant factors and the removal percentage as the target response, this study optimized the photodecolorization of AR-94 and Basic yellow dyes by effective air oxidation using TiO$_2$ suspension system under sunlight. Decolourization efficiencies of 98% and 89% were achieved within 60 minutes of reaction time under optimum conditions for AR-94 and Basic yellow dyes, respectively. Results show that a TiO$_2$/Air Oxidation photocatalytic process can be considered as a promising and cost-effective technique for dye removal from textile industry effluents.

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6 REFERENCES


