

INVESTIGATION ON ENHANCED PHOTOCATALYTIC ACTIVITY OF NANOPARTICLE FOR THE DEGRADATION OF AZO DYE IN TEXTILE EFFLUENT

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Abstract

Hazardous pollutants, especially dyes and aromatic hydrocarbons constitute the effluents generated from textile Industries. Among the various technologies developed for the treatment of dyes, the heterogeneous photocatalysis is regarded as a promising technology to decompose the recalcitrant dyes into final non-toxic products. Nano TiO₂ has been proved to be a very effective photocatalyst for the degradation of dyes in textile effluent because of its high stability, non-toxicity and low cost. Nano structured titanium dioxide (TiO₂) has been synthesized by modified sol-gel method. The material was characterized by X-ray diffraction (XRD) and SEM micrograph. The results showed that pure nano TiO₂ was composed of uniform distribution nanoparticles of ~ 15 nm and with spherical morphology. The present study aims in the photocatalytic degradation of dye reactive red 198 on the surface of nanoTiO₂ in a batch reactor. Optimisation of parameters such as catalyst weight, concentration of the dye has been studied. All the experiments were performed in a photochemical batch reactor equipped with 8-W UV lamp emitting a peak wavelength around 254 nm. Under optimum conditions complete degradation of the organic dye was achieved and the photodegradation follows pseudo first order kinetics.

Keywords: Textile Wastewater; Degradation; Organic contaminants; Nano TiO₂; Photo catalyst

I. INTRODUCTION

Textile industries produce large volume of colored dye effluents. Among the different types of dyes used in textile industries, 60-70% is azo compounds. These dyes create severe environmental pollution problems by releasing toxic and potential carcinogenic substances into the aqueous phase [1]. Various chemical and physical processes such as precipitation, adsorption, air stripping, flocculation, reverse osmosis and ultra filtration can be used for color removal from textile effluents [2]. However these techniques are non-destructive, since they only transfer the nonbiodegradable matter into sludge, giving rise to new type of pollution, which needs further treatment of solid-wastes and regeneration of the adsorbent which will add more cost to the process [3]. Hence there is a need to develop treatments methods that are more effective in eliminating dyes from the wastewater by conventional chemical treatment systems [4].

The superiority of photocatalytic degradation by semiconductors in wastewater treatment is due to its advantages over the traditional techniques, such as quick oxidation of pollutants. It is an effective and rapid technique for the removal of pollutants from wastewater.

Recently there has been considerable interest in the utilization of advanced oxidation processes (AOPs) for the complete destruction of dyes. AOPs are based on generation of reactive species such as hydroxyl radicals that oxidizes a broad range of organic pollutants quickly and nonselectively [5]. AOPs include photocatalysis systems such as combination of semiconductors and light, and semiconductor and oxidants. Heterogeneous photocatalysis has emerged as an important destructive technology leading to the total mineralization of most of the organic pollutants including organic reactive dyes.

Till now many kinds of semiconductors have been studied as photocatalysts including titanium dioxide (TiO₂), zinc oxide (ZnO), cadmium sulphide (CdS), zinc sulphide (ZnS), stannic oxide (SnO₂) and so on [6]. Titanium dioxide photocatalyst is chemically and biologically inert, photocatalytically stable, relatively easy to produce and to use, able to efficiently catalyze reactions and without risk to the environment or humans. It has become the most promising photo-catalysts due to its chemical-physical stability, thermal and electrical properties, low cost and excellent degradation of organic pollutants [7]. It has much interest in recent years for its highly active photocatalytic

functions, such as the ability to decompose chemical compounds, as well as super hydrophilic and antimicrobial properties. The UV photon is able to activate the photocatalyst, which results in the excitation of an electron from the valence bond (VB) to the conductance band (CB). When titania is irradiated by ultraviolet light, electron hole pairs are generated and then produce a powerful reactive oxygen species (ROS), which can decompose most organic compounds.

The aim of the current work is to prepare the TiO₂ nanoparticle photocatalyst by modified sol-gel method and to characterize the material by XRD, SEM studies. The photocatalytic activity of the nanoparticle is investigated by taking Reactive Red 198(RR198) an azo dye as model compound. Optimisation of parameters such as catalyst weight and concentration of the dye solution in the photocatalytic degradation studies has been studied.

II. MATERIALS AND METHODS

Titanium (IV) isopropoxide, glacial acetic acid and all the organic reagents were analytical grade procured from Merck, India. Dye sample for experimental studies have been obtained from dyestuff suppliers and used without further purification. Solutions have been prepared using double distilled water.

A. Synthesis of TiO₂ nanoparticles

Synthesis of TiO₂ nanoparticle using modified sol-gel method is summarized below. Titanium (IV) isopropoxide, glacial acetic acid and double distilled water were used in a molar ratio of 1:10:350. First titanium (IV) isopropoxide was hydrolyzed by glacial acetic acid at 0°C and double distilled water was added drop wise under vigorous stirring for 4h followed by ultra sonication for 30 minutes to get a clear solution. The solution was kept under dark for 12 h for nucleation and dried at 70°C for 12h. The dried sample was crushed into fine powder and calcined at 500°C for 5h.

B. Catalyst characterization

The XRD analysis was done to analyze the crystallite size of nano TiO₂. Sample for powder X-ray Diffraction (XRD) were prepared by making a thin film of the powder with ethanol on a glass plate and the measurement was performed with a Rigaku Geigerflex X-ray diffractometer with Ni-filtered CuK α radiation

($\lambda = 1.5406 \text{ \AA}$, 30 kV, 15 mA). The XRD patterns were recorded in the range of 20–70°, with a scan speed of 2°/min. The Cary-50 ultraviolet spectrophotometer (Varian), and Scanning Electron microscopy analysis using FESEM- SUPRA55, CARL ZEISS, Germany coupled with dispersive spectroscopy were used in the experiments.

C. Experimental set up

The photodegradation studies have been carried out in a batch reactor system. The slurry is stirred magnetically and low-pressure mercury vapour lamp has been used as an irradiation source. The lamp emits 8W of UV radiation with a peak wavelength of 254 nm. The reactor configuration and operating conditions for the photocatalytic degradation have been optimised by preliminary trial experiments with respect to (i) the total batch volume of reactant solution, (ii) the stirring speed and (iii) the time for adsorption equilibrium prior to exposure to UV light. The optimum conditions consists of a batch volume of 250 ml, stirring speed of 70 rpm and 30 minutes for adsorption equilibrium

The experimental procedure consists of irradiation of the organic dye solution of known concentration mixed with a known weight of catalyst powder at a constant volume of 250 ml. The slurry has been stirred well using a magnetic stirrer throughout the period of experiment. In all the studies the suspensions have been stirred well for about 30 minutes to allow equilibration of adsorption process before exposure to UV light. Samples of 3 ml have been withdrawn at regular intervals of time, centrifuged, absorbance measured at 532 nm, respectively and returned to the reactor. All studies have been carried out at 30°C. The pH of the solution has been adjusted to the desired values between 4.0 and 10.0 by using dilute solutions of HCl or NaOH.

III. RESULTS AND DISCUSSION

A Particle size and structural properties TiO₂ nanoparticle

The patterns of calcined (500°C) nano TiO₂ correspond to anatase phase as shown in Figure.1. The XRD patterns of anatase phase have a main peak at $2\theta = 25.2^\circ$ corresponding to the 101 plane (JCPDS 21-1272). The average particle size was estimated from the scherrer equation on the anatase using the angle

($2\theta = 25.3, 48.1$ and 37.8), width (0.5767, 0.6217 and 0.7810) and the corresponding crystal sizes are 14.4nm, 14.3nm and 10.9 nm from the 3 different diffraction peaks.

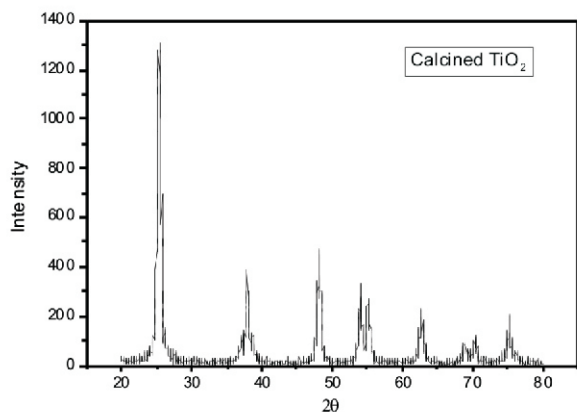


Fig. 1. XRD pattern of TiO₂ nanoparticle

Average crystal sizes of nano TiO₂ was calculated to be around 13-14 nm, respectively. During the synthetic process, a relatively large amount of water was used to enhance the nucleophilic attack of water on titanium (IV) isopropoxide and to suppress fast condensation of titanium (IV) isopropoxide species yielding TiO₂ nanoparticles. Shape and morphology is clearly observed in the SEM micrograph of the sample calcined at that temperature. Figure.2 shows the SEM micrographs of TiO₂ nanoparticles prepared by modified

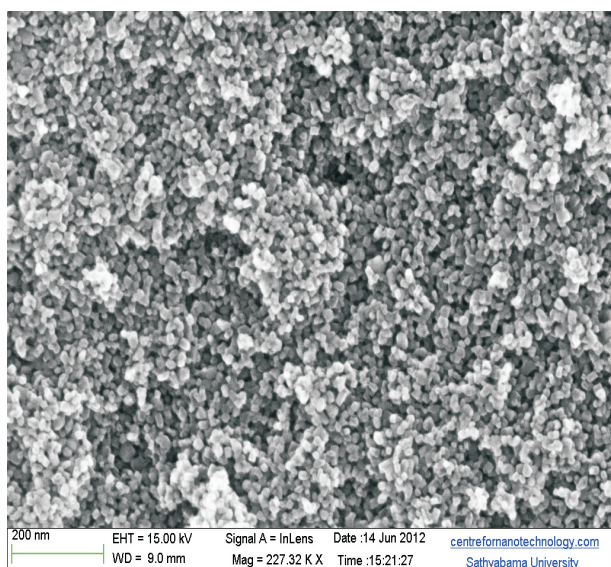


Fig. 2. SEM image of TiO₂ nanoparticle

sol-gel method at the calcination temperature of 500°C consists of spherical in shape and uniform in nature.

B. Photodegradability of reactive red 198

The photodegradability of the dye has been investigated by exposing the dye solution to UV light in the absence and in the presence of nano TiO₂ photocatalyst in a batch reactor. It is seen from the Figure.3 that in the presence of both UV light and TiO₂ about 90% of the dye was degraded at an irradiation time of 1 h. But in the absence of UV light and in the presence nano TiO₂ the dye solution is stable though adsorption has been found to be responsible for the decrease in dye concentration.

For the same experiment performed in the absence of nano TiO₂, only 0.5% of dye undergoes degradation when the UV lamp had been switched off and the reaction was allowed to occur in the darkness. These experiments demonstrated that both UV light and a photocatalyst were needed for the effective destruction of reactive red 198. Because it has been established that the photocatalysed degradation of organic matter in solution is initiated by photo excitation of the semiconductor, followed by the formation of an electron-hole pair on the surface of catalyst. The high oxidative potential of the hole (h^+VB) in the catalyst permits the direct oxidation of organic matter (dye) to reactive intermediates. Very reactive hydroxyl radicals

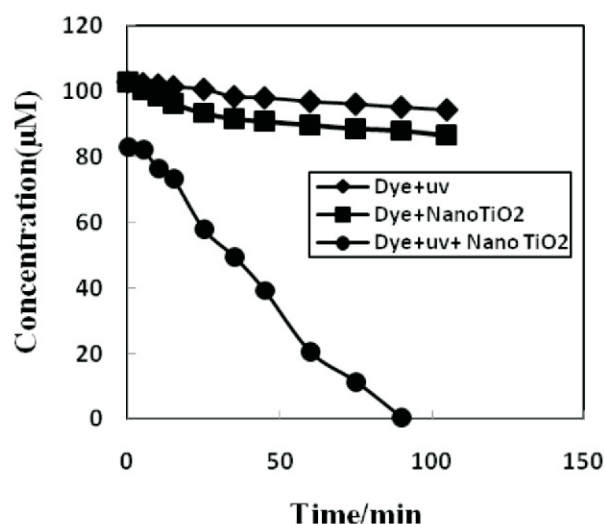


Fig. 3 Photodegradability of RR198. pH = 7.0; Concentration= 100µM; Weight of nano TiO₂ catalyst = 1 g/L Temperature = $30 \pm 0.1^\circ\text{C}$

can also be formed either by the decomposition of water or by the reaction of the hole with OH^- . The hydroxyl radical is an extremely strong, non-selective oxidant ($E^0 = +3.06 \text{ V}$) which leads to the partial or complete mineralization of several organic chemicals.

C. Effect of catalyst weight

Experiments performed with effect of three different catalyst weights showed that the photo degradation efficiency increased with an increase in weight of nano photo catalyst. The total active surface area increases with increasing catalyst dosage. The catalyst concentration above which conversion levels off depends on several factors (e.g. reactor geometry, operating conditions, wavelength and intensity of light source) and corresponds to the point where all catalyst particles are fully illuminated [8].

The effect of catalyst loading on the degradation of RR198 at $\text{pH} = 7$ was studied in the range of 0.5-1g/L of dye solution. It can be seen that the rate of decolorization increases slowly with increase in catalyst loading from 0.5-1g/L is shown in the Figure.4. The observation can be explained in terms of availability of active sites on the catalyst surface and the penetration of visible light in to the suspension. The total active surface area increases with increasing catalyst dosage. And it is important to keep the treatment expenses low for industrial use. So an optimum loading of 1g/L was used for further investigation.

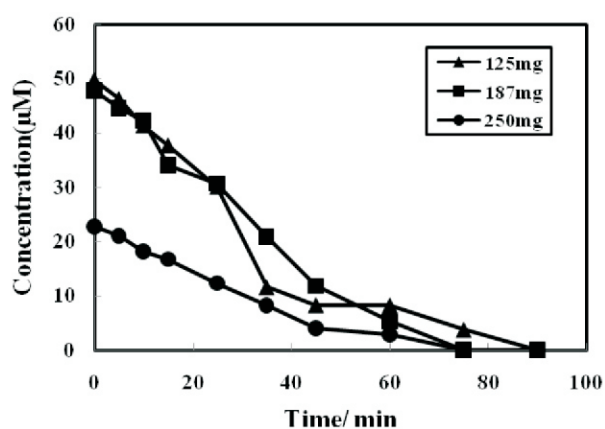


Fig.4. Effect of catalyst weight on the photo catalytic degradation of the dye; $\text{pH} = 7.0$; Concentration = 100(%M); Temperature = $30 \pm 0.1^\circ\text{C}$

D. Effect of dye concentration

The effect of initial concentration of RR198 on photocatalytic decolorization was carried out at fixed amount of the catalyst (1g/L) and varying concentration of the dye from 50%M-120% M.

Fig. 5 shows that the photodegradation efficiency of RR198 decreases with an increase on the concentration of dye. The degradation rate is directly proportional to the probability of formation of hydroxyl radicals (OH°) on the catalyst surface and the probability of hydroxyl radicals reacting with the dye molecules [9]. As the concentration of the dye increase, there should be more interaction with OH° radicals. At high dye concentration the generation of OH° radicals on the surface of catalyst is reduced since the active sites are covered with the dye ions. Also, with increase in dye concentration, less photons reach the photocatalyst surface (UV screening effect), resulting in slower production of hydroxyl radicals.

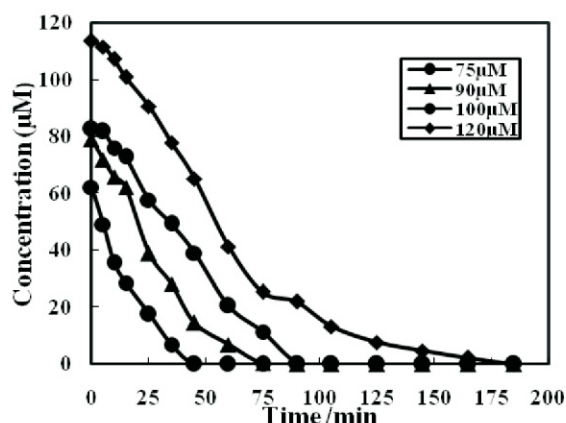


Fig. 5. Effect of concentration on the photo catalytic degradation of the dye; $\text{pH} = 7.0$; Weight of nano TiO_2 catalyst = 1 g/L; Temperature = $30 \pm 0.1^\circ\text{C}$.

E. Kinetics studies on photocatalytic degradation of RR198

Under constant conditions of pH , catalyst weight and photon flux the effect of concentration of the dye on its photodegradability has been studied. The results show that the photocatalytic decolorization of RR198 dye in aqueous TiO_2 follows first order kinetics.

$\ln(C_0/C) = kt$, where C_0 is the initial concentration and C is the concentration at any time, t . Table.1 shows the $\ln C_0/C$ value for the concentration of dye varying from $75 \mu\text{M} - 120 \mu\text{M}$. The plot of $\ln(C_0/C)$ vs. t gave a straight line as shown in the

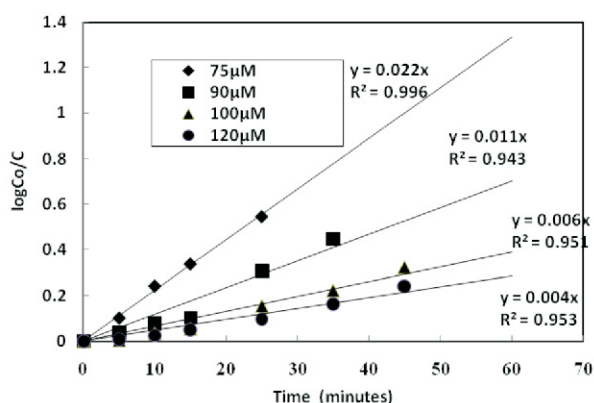


Fig. 6. Linear transform of the disappearance of reactive red 198.

Figure.6. The correlation constant R^2 for the best fit line was calculated to be 0.996, 0.953, 0.951, 0.943 respectively. The rate constants were calculated to be 0.022 min^{-1} , 0.004 min^{-1} , 0.006 min^{-1} , 0.011 min^{-1} respectively. The rate constant values were found to decrease with increase in concentration.

Table.1. $\text{Ln}C_0/C$ value for the concentration of dye varying from $75 \mu\text{M}$ – $120 \mu\text{M}$

S. No	Time in mts	$\text{Ln}C_0/C$			
		$75 \mu\text{M}$	$90 \mu\text{M}$	$100 \mu\text{M}$	$120 \mu\text{M}$
1	0	–	–	–	–
2	5	0.1021	0.0399	0.0047	0.0082
3	10	0.2423	0.0787	0.0366	0.0256
4	15	0.3383	0.1028	0.0545	0.0518
5	25	0.5456	0.3066	0.1562	0.0980
6	35	0.9702	0.4471	0.2236	0.1175
7	45	1.0293	0.7333	0.3245	0.2410

F. Reuse of catalyst:

The catalyst lifetime is an important parameter of the photocatalytic process because its use for longer period of time leads to a significant cost reduction of the treatment. For this reason, the catalyst was recycled which showed a drop in efficiency from 100% in 5h to 90%.

IV. CONCLUSIONS

Nano TiO_2 had been prepared successfully by the sol-gel method and studied by XRD and SEM

micrograph. In conclusion, one of the industrial textile dyes, namely reactive red 198 was studied effectively for its photo catalytic decolorization in UV light using titanium dioxide nanoparticle as photo catalyst. The XRD data showed nano TiO_2 had anatase phase and SEM micrograph showed the uniform and spherical shape of the particle. Introduced at comparatively lower dose, nano TiO_2 was found to be highly efficient in decolorizing and degrading the water pollutant. The photocatalytic degradation rate was improved with increasing amount of nano TiO_2 . All these results indicate that TiO_2 nanoparticle can be a better candidate to handle the waste textile water issue gently, to harmonize water system to its natural state. The photocatalytic degradation of RR198 can be described with pseudo-first order reaction kinetics.

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