Chapter 4

Ultrasound Assisted Synthesis of Pure and Doped TiO$_2$ Nanoparticles
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ULTRASOUND ASSISTED SYNTHESIS OF PURE AND DOPED TiO$_2$ NANO-PARTICLES

The objective of this work was development of simple one step ultrasound mediated synthesis procedure for TiO$_2$ nanoparticles and its comparison with conventional synthesis procedure. The proposed studies included synthesis, characterization and application of TiO$_2$ and doped TiO$_2$ particles for photocatalytic degradation of Crystal Violet dye from waste water.

4.1 Introduction
The most of the advanced industrialized nations are facing environmental problems related to the remediation of hazardous wastes, contaminated groundwaters and the control of toxic air contaminants [1]. Due to the development of industrial sector on a large scale, lot of environmental problems are created with release of toxic chemicals into the receiving streams. For the conventional treatment methods such as incineration, anaerobic digestion, activated sludge digestion the advanced physicochemical processes like semiconductor photocatalysis can be the possible alternative [1]. Recently, attempts are made to study the photochemical processes using semiconductor oxides, such as TiO$_2$, CdS or ZnO in heterogeneous systems [2]. Heterogeneous photocatalysis is a well established technique with a great potential to control aqueous contaminants or air pollutants. Among various oxide semiconductor photocatalysts, titanium dioxide (TiO$_2$) has attracted interest of many researchers because of its applicability for different class of water contaminants such as organic, inorganic and microbiological with a minimum risk of the production of harmful byproducts [3]. Titanium dioxide is most popular due to its peculiarities of chemical inertness, suitable band gap energy, non-photocorrosion and non-toxicity towards microorganisms [4]. Also titanium dioxide is photocatalytically stable, relatively easy to produce and efficiently catalyzes the reactions [5]. It also finds application in cosmetics, paints, electronic paper, filter materials, anti-reflection films, sensors, and dye-sensitive solar cells [6-7]. The titanium dioxide acts photocatalytically by absorbing UV light ($\lambda < 380$ nm) to generate electron-hole pairs. These separated electrons and holes drive reduction and oxidation reactions. But, unwanted recombination of photo generated electrons and holes decrease its catalytic efficiency.
Further its large band-gap energy ($E_g = 3.2$ eV) significantly restricts the exploitation of natural solar light or artificial visible light which is available in plenty and conventional visible light responsive catalysts are unstable under illumination (such as CdS and CdSe) or have lower activity (such as WO$_3$ and Fe$_2$O$_3$) [8]. Efforts have been made to extend the light absorption range of TiO$_2$ from UV to visible light and to improve the photocatalytic activity by slowing down the recombination rate of electron-hole pairs [9]. For preventing the recombination of electron-hole pairs and proper utilization of visible light, TiO$_2$ particles have been modified by selective surface treatments like doping TiO$_2$ with metal ions, dye photosensitization on surface etc. [10].

Dopants, such as transitional metals can be added to TiO$_2$ to improve its catalytic activity and also reduce the recombination of electrons and holes. Noble metals doped or deposited on TiO$_2$ also show effect on the photocatalytic activity by extending excitation wavelength from the UV to the visible light range [7,11-13]. Zeleska [14] has reviewed the preparation methods of doped TiO$_2$ with metallic and nonmetallic species, including various types of dopants and doping methods. Rauf [9] has given an overview on the photocatalytic degradation of azo dyes in the presence of TiO$_2$ doped with selective transition metals.

Among the different types of transitional metals, doping of iron on TiO$_2$ has been reported by many researchers. Owing to the fact that the radius of Fe$^{3+}$ (0.79 Å) is similar to that of Ti$^{4+}$ (0.75 Å), iron has been considered to be an appropriate material for doping on TiO$_2$. Fe$^{3+}$ can be easily included into the crystal lattice of TiO$_2$ and Fe$^{3+}$ has proved to be a successful doping element due to its half-filled electronic configuration [15-18]. As compared to iron there are very few reports of cerium doping on TiO$_2$. Pertaining to the optical and catalytic properties associated to the redox pair Ce$^{3+}$/Ce$^{4+}$, cerium oxides are being studied as doping elements. Ce-doped TiO$_2$ materials are synthesized by the sol–gel and hydrothermal methods and used in the photo-degradation applications [19-22]. The photocatalytic performances of TiO$_2$ catalysts depends strongly on different factors, such as the methods of doping and the amount of doping material, since they have a key influence on the properties of the catalysts. Therefore, it is essential to investigate the effects of doping method and doping material content on the photocatalytic performance of TiO$_2$ catalysts. Conventional physical blending or chemical precipitation processes for the synthesis
of metal-loaded semiconductor oxides have certain disadvantages in terms of limitation in control over size, morphology and dispersion of the metal component. The conventional methods often require longer times and involve multiple step procedures. Ultrasound has been found to be very useful in the synthesis of a wide range of nanostructured materials. The collapse of cavitation bubbles induce localized hot spots with short lived temperature of about 10000 K, pressures in excess of 1000 atm and cooling rates greater than $10^{10}$ K/s. Under such severe conditions, various chemical reactions and physical changes take place and numerous nano-structured materials can be synthesized with required particle size distribution in shorter time [16, 23-25]. The physical and chemical effects of cavitation can be expected to drastically influence the properties of doped materials [16,26]. Many researchers has used ultrasound to prepare TiO$_2$ and doped TiO$_2$ nanomaterials and their photocatalytic activity has been tested for waste water remediation [27-33]. Out of the various water pollutants, synthetic dyes comprise substantial part of industrial water effluents as they are discharged in plenty by many industries. The detrimental effects of those dyes on the environment are a major concern because of the carcinogenic properties of these chemicals [9]. Thus the treatment of these colored effluents before discharging them to various water bodies is of prime importance. Crystal violet a widely used cationic triphenylmethane dye is extensively used in industries such as textile, paper, leather, additives, foodstuffs, cosmetics and analytical chemistry. Crystal violet is a non-biodegradable mutagen and mitotic poison and hence is associated with considerable environmental and health concerns. Considering the widespread use and toxic nature, it is necessary to study its degradation patterns.

In the present work a detailed study on the influence of ultrasound on the phase composition, structure and performance of pure and doped TiO$_2$ nanocatalysts has been done. Cerium and Fe-doped TiO$_2$ nanocatalysts with different doping contents were prepared by a single-step sonochemical method and conventional method at room temperature. The photocatalytic activity of the prepared catalysts has been evaluated for the photodegradation of a model pollutant, Crystal violet dye. The kinetics of the photocatalytic degradation process is also studied.
4.2 Experimental

4.2.1 Reagents
Cerium nitrate, ferric nitrate, propanol and Titanium isopropoxide were supplied by S. D. Fine Chemicals Ltd., Mumbai, India. Crystal violet dye was procured from M/s CDH, India. Sodium hydroxide was obtained from Merck Ltd., Mumbai, India. All the chemicals were of analytical grade and were used as received from the supplier.

4.2.2 Preparation of TiO$_2$ by conventional method (CV)
Titanium (IV) isopropoxide, Ferric nitrate and Cerium (III) nitrate were used as precursors for titanium, iron and cerium respectively. 2-propanol was used as solvent where the main role of the organic solvent is to act as an oxygen source for the metal oxide formation. In conventional synthesis procedure, 5 ml of titanium isopropoxide was added to 50 ml of 2-propanol at room temperature (35 ± 2°C) in a 250 ml beaker and the beaker was placed in a constant temperature bath under continuous stirring. Cerium nitrate solution was prepared in 20 ml distilled water and in another beaker sodium hydroxide was dissolved in 50 ml distilled water. Then 5 ml of sodium hydroxide solution and 2 ml of cerium nitrate solution were added simultaneously to the titanium isopropoxide-propanol mixture after every 30 seconds until a total of 50 ml sodium hydroxide solution and 20 ml of cerium nitrate solution were added into the beaker. Once all the reactants were added the reaction was allowed to proceed for 4 h under stirring at a temperature of 35 ± 2°C. After 4 h of reaction time the resulting precipitate was centrifuged, filtered, dried and calcined at 450°C for 3h. For preparing Fe doped TiO$_2$, ferric nitrate was used as iron precursor and similar procedure was followed. The catalysts prepared by conventional method are hereafter named as TiO$_2$ (CV), Fe-TiO$_2$ (CV) and Ce-TiO$_2$ (CV) where CV stands for conventional method of preparation. Pure TiO$_2$ sample was prepared according to the above procedure without the addition of cerium/iron precursor.

4.2.3 Preparation of TiO$_2$ by sonochemical method (US)
For TiO$_2$ synthesis by sonochemical method 50 ml of 2-propanol was taken in a 250 ml beaker and 5 ml of titanium isopropoxide was added. The beaker was placed in a constant temperature bath and the sonication was carried out using a direct immersion titanium horn. Solutions of five different concentrations of cerium nitrate were prepared to get 0.4, 0.8, 1.2, 1.6 and 2 (mol %) of Ce to TiO$_2$ in 20 ml distilled water. Similar to the procedure followed during conventional synthesis, 5 ml of sodium
hydroxide solution and 2 ml of cerium nitrate solution were added simultaneously after every 30 seconds till a total of 50 ml sodium hydroxide solution and 20 ml of cerium nitrate solution were added into the ultrasound reactor. After the addition of all the reactants, the sonication was continued for further 30 minutes. After 30 minutes of sonication the solution was kept undisturbed for settling of the precipitate. The resulting precipitate was centrifuged, filtered, dried and calcined at 450°C for 3h. Similar procedure was adopted for the synthesis of Fe doped TiO₂ nanocatalyst with molar ratios of 0.4, 0.8, 1.2, 1.6 and 2 (mol %) of Fe to TiO₂. Pure TiO₂ sample was also prepared according to the above procedure except the addition of dopant precursor. Schematic of overall synthesis procedure for cerium doped TiO₂ is shown in figure 4.1. An ultrasonic horn was used as a source of ultrasonic irradiations for the synthesis of TiO₂ doped composite. The specifications of the horn are as follows: Make: Sonics and Materials, USA; Operating frequency: 22 kHz; rated output power: 750 W; diameter of stainless steel tip: 1.3 × 10⁻² m, surface area of ultrasound irradiating face: 1.32 × 10⁻⁴ m², expected ultrasound intensity: 3.4 × 10⁵ W/m² and the horn was operated at 40% amplitude. The catalysts prepared by this method are hereafter described as TiO₂ (US), Fe-TiO₂ (US) and Ce-TiO₂ (US) where US stands for sonochemical method of preparation. The experimental set up for the sonochemical synthesis is schematically shown in figure 4.2. During the conventional synthesis procedure 4 h of reaction time was required while during sonochemical synthesis the precipitate was formed within 30 min of sonic irradiations. The reduction in the reaction time compared to conventional synthesis is attributed to the cavitationsal effects. The rapid micromixing and implosive collapse of bubbles in a liquid solution results in extremely high temperatures during ultrasound induced hydrolysis, which results into accelerated hydrolysis reaction.
Figure 4.1: Synthesis of Ce doped TiO\textsubscript{2} by sonochemical method
4.2.4 Catalyst characterization

The prepared samples have been characterized using X-ray diffraction (XRD), FTIR, transmission electron microscopy (TEM), particle size distribution (PSD) and UV–visible spectra (UV–vis). Phase formation and crystal structure of TiO₂ samples were determined by means of powder X-ray diffractometer (Philips PW 1800). The XRD patterns were recorded at angles between 20° and 70° with a scan rate of 2°/min. Perkin Elmer FTIR spectrometer (Paragon 1000 PC) in the wave number range of 500-4000 cm⁻¹ was used for recording FTIR Spectra of the samples. Transmission electron microscopy (TEM, magnification 7,50,000 X) image was taken on a Philips Tecnai 20 model. The particle size distribution measurements were carried out by Malvern Zetasizer Instrument (Malvern Instruments, Malvern, UK).

4.2.5 Photocatalytic reactivity experiments

Crystal violet dye was selected as model pollutant to test the photocatalytic activity of synthesized catalysts and the experiments were carried out in a laboratory scale reactor. The experimental set up consisted of closed box for UV irradiation with a UV lamp Spectroline XX-15N which emits radiation at 365 nm with intensity of 2000 W/cm². All the photocatalytic degradation experiments were carried out at a temperature of 35°C and pH 6.5 which is the natural pH of the crystal violet solution. In a typical experiment 150 ml of crystal violet dye solution was taken in a beaker and appropriate quantity of catalyst was added. The effect of various operating parameters such as preparation method, doping content, catalyst loading and initial dye concentration was studied for the different photocatalysts.

Prior to the actual photocatalytic degradation experiments (using UV irradiations) the time required for reaching the adsorption equilibrium as well as the maximum amount of dye adsorbed on the TiO₂ surface under dark and stirred conditions was established using preliminary studies. The suspension was stirred in the dark for 120 min to ensure establishment of adsorption–desorption equilibrium of CV dye. The photocatalyst particles were maintained in suspension by continuous stirring. It was observed that maximum of 1.5 % of Crystal Violet dye was adsorbed on the surface of TiO₂ (0.3 g/L loading). Adsorption equilibrium was achieved within first 15 minutes of contact time and the absorbance value did not change with extended time of contact.
beyond 15 min. Hence all the photocatalytic degradation experiments have been carried out with 15 minutes of soaking period under stirring. After that the suspensions were irradiated with UV lamp under stirring. To measure the concentration of Crystal Violet dye, samples were withdrawn from the reactor at regular intervals. The samples were centrifuged prior to analysis, in order to separate any suspended solids. The concentration of CV dye was determined with UV–vis spectrophotometer (SHIMADZU 160A model) and the wavelength of maximum absorbance ($\lambda_{\text{max}}$) of dye was found to be 590 nm. Demineralized water was used as a reference. Conversions were calculated in relation to initial CV dye concentration.

Reproducibility of the obtained experimental data is very important in investigation related to the effects of the operating parameters. In the present work, all the experiments were carried out at least two times to estimate the reproducibility of the obtained data. All the experimental errors were found to be within $\pm 4\%$ of the mean reported value.

4.3 Results and Discussion

4.3.1 XRD analysis

Crystallinity of the produced nanoparticles was confirmed by wide angle X-ray diffraction pattern. The crystallinity and crystal structure of nano-material affects many physical properties. XRD is used for generating the information about the crystal structures and it aids in identifying atomic spacing, unit cell dimensions and phase of the crystalline materials [34]. The XRD patterns of the TiO$_2$ powder samples prepared by ultrasonic method and the conventional method and calcined at 450°C are depicted in figure 4.3. The XRD patterns shows the presence of the main peaks at $2\theta = 25.2^\circ$, $38^\circ$, $47.6^\circ$, $55.1^\circ$ and $61.9^\circ$ for undoped TiO$_2$ prepared by both the methods indicating that the catalysts have been predominantly crystalline in nature with anatase as the major phase.

For both Fe doped and Ce doped catalysts the mole ratio of dopant/Ti was 2 $\%$ for both the synthesis methods. The XRD patterns for Fe doped TiO$_2$ prepared by both the methods shows the peaks at $2\theta = 25.8^\circ$, $36.9^\circ$, $48.1^\circ$, $54.1^\circ$ and $62.4^\circ$ corresponding to the anatase phase and hence it can be concluded that doping with metal ions did not influence the crystal structure of the TiO$_2$ particle. Additionally the peaks at $34.4^\circ$ are observed for Fe doped samples which can be assigned to the presence of Fe in hematite form in TiO$_2$ [6, 35]. Similarly the XRD patterns of Ce
doped TiO\textsubscript{2} samples also showed the presence of main peaks at \(2\theta = 25.4^\circ, 37.4^\circ, 47.8^\circ, 54.5^\circ\) and \(62.7^\circ\). From corresponding characteristic \(2\theta\) values of the diffraction peaks, it can be confirmed that the TiO\textsubscript{2} composites are identified as anatase phase. Other crystalline forms of TiO\textsubscript{2}, namely rutile and brookite, were not detected. Comparing the XRD patterns with JCPDS card No. 21-1272 data files, it was found that all peaks the observed peaks are consistent with anatase (1 0 1), (0 0 4), (2 0 0), (2 1 1) and (2 0 4) spacing, respectively [7, 15, 19, 36] confirming the crystallinity and TiO\textsubscript{2} phase. In addition, a prominent peak was observed at \(2\theta = 29.1^\circ\). As reported in the literature for the Ce-doped TiO\textsubscript{2} materials the presence of prominent peaks at 30° and 30.6° are assigned to cerium titanate -Ce\textsubscript{x}Ti\textsubscript{1-x}O\textsubscript{2}[19, 37]. Thus, in the present case as there was no peak observed at 30°, peak corresponding to 29.1° can be assigned to the presence of cerium as a separate cubic CeO\textsubscript{2}, or as cerium titanate in the TiO\textsubscript{2} phase.

The intensities of peaks prepared by sonochemical method are higher as compared to the conventional method and also the peaks are sharper as well, indicating the increase in the crystallinity of TiO\textsubscript{2}. Fe and Ce doped TiO\textsubscript{2} nanoparticles prepared with sonochemical method leading to the enhanced formation of crystalline particles with anatase phase.

![Figure 4.3: XRD patterns of Ce-doped TiO\textsubscript{2}, Fe-doped TiO\textsubscript{2} and undoped TiO\textsubscript{2} powder prepared by conventional and sonochemical method [A – TiO\textsubscript{2}(CV), B – TiO\textsubscript{2}(US), C – Fe-TiO\textsubscript{2}(CV), D – Fe-TiO\textsubscript{2}(US), E – Ce-TiO\textsubscript{2}(CV), F – Ce-TiO\textsubscript{2}(US)]](image-url)
4.3.2 FTIR analysis

FT-IR spectroscopy is a non-destructive method which provides a fingerprint of a sample with absorption peaks which match the frequencies of vibrations among the bonds of material. Different materials have different combinations of atoms which results in different infrared spectrum [34]. The FTIR spectra of pure TiO$_2$ and doped TiO$_2$ nanoparticles prepared by sonochemical method are shown in figure 4.4. The absorption bands in the region of 3420-3450 cm$^{-1}$ are generally assigned to the stretching vibrations of surface –OH group whereas the bands in the region 1630-1640 cm$^{-1}$ are assigned to the bending vibrations of surface –OH group on the surface of TiO$_2$ catalysts [5,8,13]. The absorption bands in the region of 520-580 cm$^{-1}$ are assigned to the stretching vibration of Ti–O. Results of FTIR analysis of prepared samples shows four main absorption peaks located in the regions 482-507, 1687-1760, 2360-2393, 3568-3651 cm$^{-1}$. The absorption bands in the region of 1687-1760 cm$^{-1}$ are attributed to the bending vibration of the hydroxyl on the surface of TiO$_2$-based catalysts, while the bands in the region of 3568-3651 cm$^{-1}$ may be assigned to the stretching vibration of the hydroxyl on the surface of the catalysts, since there were no absorption peaks in the region of 3420-3450 cm$^{-1}$. The absorption bands in the region of 482-507 cm$^{-1}$ can be assigned to the stretching vibration of Ti–O. In addition, peaks in the range of 883-945 cm$^{-1}$ are observed. These peaks can be assigned to the main band (944 cm$^{-1}$) corresponding to TiO$_2$ [19]. The characteristic peaks of the incorporated Fe and Ce are not detected which indicates the efficient dispersion of the incorporated doping elements. The bulk structure remains virtually unchanged by the incorporation of the metals.
Figure 4.4: FTIR spectra of A) Pure TiO$_2$, B) Fe-TiO$_2$, and C) Ce-TiO$_2$ synthesized by sonochemical method

4.3.3 UV–visible absorbance spectra

The light absorption properties of the catalysts depend on the type of dopant and also on the method of preparation. The method of preparation does have a vital role in controlling the properties of the TiO$_2$ nano-particles which could be identified using UV spectroscopic analysis. Figure 4.5 depicts UV-vis absorption spectra of pure TiO$_2$ and doped TiO$_2$ samples prepared by using conventional and sonochemical methods. Absorption at wavelength of less than 387 nm is caused by the intrinsic band gap absorption of TiO$_2$. Usually, metal ion doping affects the light absorption characteristics of TiO$_2$. The introduction of dopants not only shifts the absorption edge towards the visible region but also increases the absorption of TiO$_2$ in the visible range (higher wavelength 400-600 nm) [3, 15-16, 18].

From the figure 4.5 it can be seen that all the samples has a broad intense absorption below 400 nm which is the characteristic absorption of TiO$_2$ corresponding to the excitation of electrons from the valence band to the conduction band in the anatase TiO$_2$. Significant enhancement of light absorption in the visible region (>400 nm) is seen for doped TiO$_2$ samples compared with the pure samples exhibiting red shifts of absorption edge. The red shift indicates the lowering of band gap energy of TiO$_2$ due
to the adsorption/deposition of doping elements on TiO$_2$ particles causing distortion into its structure. The red shift of the absorption spectra could be attributed to the broad absorption band of transition metals and rare earth elements, and the effect of doping into pure TiO$_2$ is somewhat similar to the influence of adding a photosensitizer to the reaction solution [21]. The extended absorbance of doped TiO$_2$ photocatalyst provides a possibility of enhancement in the photocatalytic performance. Though, it has been presumed that the doping gives the visible light effect, however it is important to note that the UV light effect is more dominant than the visible light as UV light activated photocatalytic reaction is more pronounced [38].

Figure 4.5 also clearly shows the influence of doping and the preparation method on UV/Vis spectral properties of TiO$_2$. Modification of TiO$_2$ with Fe and Ce ions appreciably affected the absorption properties of photocatalysts, whereas for pure TiO$_2$ particles there was no significant increment in the absorption using both the methods (conventional and ultrasound assisted). Amongst all the samples Ce-TiO$_2$ samples exhibited the highest absorbance followed by Fe-TiO$_2$ samples. Further, Ce-TiO$_2$ samples prepared by sonochemical method showed approximately 15% higher absorbance in the visible range as compared to the samples prepared by conventional method indicating that the increase in the visible absorption strongly depended on the method of preparation.

![Figure 4.5: UV-Vis spectra of pure and doped TiO$_2$ nanoparticles prepared by conventional and sonochemical method](image)

A - TiO$_2$ (Conventional)
B - TiO$_2$ (Ultrasound)
C - Fe-TiO$_2$ (Conventional)
D - Fe-TiO$_2$ (Ultrasound)
E - Ce-TiO$_2$ (Conventional)
F - Ce-TiO$_2$ (Ultrasound)
4.3.4 TEM analysis and particle size distribution

The transmission electron microscopy (TEM) images of pure TiO$_2$(A), Fe doped TiO$_2$(B) and Ce doped TiO$_2$(C) nanoparticles prepared by sonochemical method are shown in figure 4.6. It can be seen from the figure that spherical TiO$_2$ particles were formed by the sonochemical method. Formation of microjets due to the cavitational activity during the ultrasonic irradiations helps to form the inorganic oxide particles with smaller and more uniform particle size and uniform shape could also be observed. The primary particle size in all the TEM images seems to be in the range of 10 to 50 nm with aggregation of the individual particles to form secondary particles of larger size. The particle size of the doped TiO$_2$ samples (Figure 4.6 B & C) is smaller than that of pure TiO$_2$(Figure 4.6 A), which signifies that the presence of Fe$^{3+}$ and Ce$^{3+}$ in the reaction media might be used to control the particle and crystallite sizes of the oxides [15]. The crystallite size decreased because Fe, Ce doping restrained the increase in grain size and refined the crystallite size. Moreover the decrease in the particle size is due to an increase in the microstrain effect. The increase in the microstrain may be because of the metal introduction into the anatase lattice and the associated generation of oxygen vacancies [39]. Similar results of decrease in particle size due to doping of Fe$^{3+}$ are reported by Asiltruk et al. [15]. In this work Fe$^{3+}$ ion-doped TiO$_2$ particles were synthesized by the hydrothermal process at 225°C in 1h. The size of prepared particles varied in the range of 1-11 µm. In the present work, the particle size is found to be around 10-50 nm, which is significantly lower than that obtained in the work of Nahar et al. [17]. As well as the reaction is carried out at room temperature and the reaction time is 30 min. The observed trends can be attributed to the fast kinetics of the ultrasound assisted reaction favouring early nucleation and providing insufficient time for particle growth [40].
Figure 4.6: TEM images of (A) pure TiO$_2$, (B) Fe doped TiO$_2$ and (C) Ce doped TiO$_2$ nanoparticles prepared by sonochemical method
The particle size distribution of the samples prepared by sonochemical method and conventional method has been depicted in figure 4.7. All the samples prepared by sonochemical method showed smaller particle size whereas larger particle size is observed for conventional method. The average particle size of undoped TiO₂ prepared by conventional method was found to be 298 nm whereas for undoped TiO₂ prepared by sonochemical method the size is found to be 197 nm. As discussed earlier after doping the reduction in size is observed and the average particle size of Fe and Ce doped TiO₂ for sonochemical method is reduced to 169 and 157 nm respectively.

![Figure 4.7: Particle size distributions of Fe-TiO₂, Ce-TiO₂ and TiO₂ synthesized by sonochemical and conventional method.](image)

### 4.3.5 Photocatalytic degradation of CV dye

The degradation of Crystal Violet dye as a model reaction was studied to investigate the photocatalytic activities of the prepared samples under UV irradiation. The effect of different operating parameters such as preparation method, doping material content, catalyst loading and effect of initial dye concentration on the extent of degradation was investigated and has been discussed in the following sections.

#### 4.3.5.1 Effect of preparation method and irradiation time

Figure 4.8 shows absorbance spectrum of the crystal violet dye with different irradiation times catalyzed by TiO₂. A major absorption band at 590 nm is seen for the
aqueous solution of crystal violet dye of 30 mg/L concentration. With an increasing UV irradiation time the change in the extent of degradation was observed. As the time progressed from 0 to 120 min, the absorption decreased gradually and the peak intensity at 590 nm also decreased. Moreover it was also observed that the extent of decrease in the absorption peak was lower at higher treatment times. This can be attributed to the formation of intermediates and their competitiveness with parent dye molecules in the photocatalytic degradation process. The slow kinetics of dye degradation after certain time limit can also be attributed to the difficulty in converting the N-atoms (N-demethylated products) of dye into oxidized nitrogen compounds [41]. Also, hydroxyl radicals •OH can attack different electron rich sites such as N-C bonds, phenyl rings and the central carbon atom of CV in non-effective way with increased treatment times [42].

In order to measure the maximum possible degradation, initially the experiments were conducted for 180 min but it was noted that there was no appreciable degradation after 120 min irradiation. Hence all the experiments were carried at a constant irradiation time of 120 min.

Figure 4.8: Change in the absorbance spectra of crystal violet with irradiation time in presence of TiO\textsubscript{2} at dye concentration 30 mg/L
The effect of preparation method on the photocatalytic activity of the catalysts prepared by sonochemical and conventional method was studied by doing the experiments for 2% (mol %) of Ce and Fe doped TiO$_2$ and pure TiO$_2$. The degradation curves of CV dye are presented in figure 4.9 as the time-dependent dye concentration, which is the dye concentration remaining at any time divided by the initial dye concentration ($C/C_0$) for the initial dye concentration of 30 mg/L and the catalyst loading of 0.2 g/L. Here it should be noted that $C_0$ is the initial concentration after achieving the adsorption equilibrium. It is observed that the degradation of Crystal Violet increased gradually with UV irradiation time for all the samples. The highest degradation of 84% was achieved with Ce-TiO$_2$ (US) sample followed by Fe- TiO$_2$ (US) (77%) and undoped TiO$_2$ (US) sample gave 71% degradation. The samples prepared by conventional method resulted in 75, 68 and 61% degradation for Ce-TiO$_2$(CV), Fe- TiO$_2$(CV) and TiO$_2$(CV) respectively. The presence of dopant ions improves the absorption in the UV-visible light region and makes a red shift in the band gap transition of the doped TiO$_2$ samples. This results in generation of more electrons and holes to speed up the photocatalytic reactions. Additionally dopant ions help in transfer of interfacial charge [16]. Highest degradation was observed with Cerium doping which can be attributed to the fact that cerium shows the photoresponse in the visible region and the redox pair of cerium (Ce$^{3+}$/Ce$^{4+}$) is also important, since cerium could act as an effective electron scavenger to trap the bulk electrons in TiO$_2$ [19].

The preparation method played a decisive role in deciding the photoactivity of a catalyst. Results indicate that the catalysts prepared by sonochemical method showed higher activity against catalyst prepared by the conventional method. As discussed in particle size analysis, lower particle size of the catalyst was achieved with the sonochemical method which can provide higher surface area for the reaction hence higher degradation. A large surface area may be an important factor in certain photocatalytic degradation reactions, as a large amount of adsorbed organic molecules promotes the reaction rate [43]. Smaller particle size in the case of sonochemical method may be the result of fragmentation of the TiO$_2$ particles because of the increased high-velocity interparticle collisions among the particles during sonication. Further, sonication method can evenly disperse the metal ions into the crystal lattice of TiO$_2$, independent of whether the ions react with Ti-gel or not [27].
This study clearly demonstrated the importance and advantages of sonication in the modification and improvement of the photocatalytic properties of TiO$_2$ and doped TiO$_2$ catalysts. After the first set of experiments, as it was observed that all the samples prepared by sonochemical method gives higher degradation than the samples prepared by conventional method, the studies related to the effect of other operating parameters on the degradation process were performed with the catalyst prepared by sonochemical method.

![Figure 4.9: Degradation vs. time decay curves of crystal violet during the photocatalytic experiments using different catalysts (Dye initial concentration = 30 mg/L, pH 6.5 and catalyst dose = 0.2 g/L)](image)

4.3.5.2 Effect of doping

A prerequisite for an effective dopant involves the possibility of charge detrapping and migration to the surface of catalysts [10]. The concentration ($C/C_0$) vs. time profiles of CV dye conversion under UV irradiation using the cerium doped catalysts are presented in figure 4.10. C is the concentration of CV dye at any time and $C_0$ is the initial concentration after achieving the adsorption equilibrium. The doping
content of cerium was varied from 0.4 - 2 mol %. It can be seen from the figure that the effectiveness of the catalyst strongly depends on the loading of Ce. With increase in the content of cerium doping from 0.4 mol % to 0.8 mol %, the photoactivity of the catalyst increased by 10%, however further increase in doping content resulted in a marginally decreased photoactivity of the catalyst. The results show that the presence of a minute amount of cerium ions can augment the activity, but excessive cerium ions are giving negative effect. The observed results are ascribed to the fact that a small amount of cerium can act as a photo-generated electron trap and inhibit the hole-electron recombination [19-20]. Above that concentration, cerium ions steadily become recombination centers and the activity steadily decreases. Thus, an optimum dopant concentration is needed for the doping of TiO$_2$ to get the best results. Based on the above results, 0.8 mol % cerium doping was considered as the optimum doping concentration.

Similarly figure 4.11 shows the effect of iron doping (0.4 - 2 mol %) on the extent of degradation of crystal violet dye. Similar trend was observed with iron doping also. As doping content of iron increased from 0.4 mol % to 1.2 mol %, the photoactivity of the catalyst increased but beyond 1.2 mol %, the activity decreased with an increase in the iron content. The observed results can be attributed to the fact that the introduction of appropriate quantity of iron in TiO$_2$ is responsible for a reduction in the photo-generated hole-electron recombination rate. But at higher loadings, iron ions can serve as recombination centers and the activity steadily decreases as also demonstrated in some of the earlier investigations [15-17]. Thus, 1.2 mol % iron doping has been considered as the optimal doping concentration.

The high activities of the doped TiO$_2$ powders as compared to pure TiO$_2$ could be ascribed to the results of the synergetic effects of doping elements, small crystallite size and good crystallization during the synthesis. The average particle size for the doped samples was found to be smaller as compared to pure TiO$_2$. An excess amount of dopant at the surface of TiO$_2$ can remarkably screen the TiO$_2$ from the UV light and inhibit the interfacial electron and hole to transfer to the surface resulting in a low photoactivity.

When the results are compared for the doped samples, it can be seen that the photocatalytic activity of Ce doped TiO$_2$ is higher than that of Fe doped TiO$_2$. This may be because when Ce is located in an interstitial site of TiO$_2$, the electron density
of the doped TiO$_2$ may increase, which would increase the photocatalytic activity; while when Fe ions are located in a substitutional site of TiO$_2$, the electron density of the doped TiO$_2$ may have decreased and though TiO$_2$ is an n type semiconductor it may have changed into a p type semiconductor, resulting in decreased photocatalytic activity. Ce 4f level in Ce-TiO$_2$ plays an important role in interfacial charge transfer than Fe 3f level in Fe-TiO$_2$ [20]. Additionally rare earth elements have the capacity to store oxygen. If the concentration of oxygen in the system is low, these elements release oxygen to the reaction system whereas excess oxygen is stored. As reported by Gerischer and Heller [44] oxygen adsorbed on photocatalyst can effectively entrap the photogenerated electrons and it prevents the recombination between electron and hole which results in increases in redox probability and the photocatalytic activity. Moreover, particle size is another important parameter that influences photocatalytic efficiency, since the electron-hole recombination rate may depend on the particle size [16]. As mentioned in Section 3.4 it was observed that Ce doped TiO$_2$ samples had the smallest size of all the samples, hence the advantages associated with the small size can be seen in terms of higher degradation efficiency.

On the whole it can be said that the photocatalytic activity of Fe doped TiO$_2$ is lower than that of the Ce doped TiO$_2$ and the amount of doping of Fe required is also larger. Similar results are reported by Li et al. [10] for Be, Mg and Ca doped TiO$_2$ for photocatalytic production of hydrogen. Another reason for the difference in activities of Ce -TiO$_2$ and Fe-TiO$_2$ is that the cationic dye such as Crystal Violet has different charges in aqueous solution after ionization; so the electrostatic attraction or repulsion occurs between the organic dye ions and the surface of catalysts, may also result in the difference in degradation rates [22].
Figure 4.10: Effect of cerium doping content on degradation of crystal violet dye (Dye initial concentration = 30 mg/L, pH 6.5 and catalyst dose = 0.2 g/L)

Figure 4.11: Effect of iron doping content on degradation of crystal violet dye (Dye initial concentration = 30 mg/L, pH 6.5 and catalyst dose = 0.2 g/L)
4.3.5.3 Effect of catalyst loading

The amount of TiO\textsubscript{2} used in a photocatalytic experiment is directly proportional to the overall photocatalytic reaction rate. However, when the amount of TiO\textsubscript{2} is above certain level, the light photon adsorption co-efficient decreases radially and the excess photocatalyst can create a light screening effect that leads to the reduction in the surface area exposed to irradiation and thus reduces the photocatalytic efficiency of the process [45].

The effect of catalyst loading on the degradation rate of crystal violet was investigated for three different catalyst loadings as 0.1, 0.2 and 0.3 g/L, at dye concentration of 30 mg/L and at pH 6.5 which is a natural pH of Crystal Violet solution. The obtained results are presented in figure 4.12. It is observed that the extent of degradation increased with an increase in the catalyst dosage from 0.1 to 0.3 g/L. If the results are considered for Ce-TiO\textsubscript{2} samples then 74, 89 and 92% degradation was achieved with 0.1, 0.2 and 0.3 g/L catalyst loading respectively. Change in catalyst loading from 0.1 g/L to 0.2 g/L resulted in almost 15% increment in % degradation whereas for change in catalyst loading from 0.2 g/L to 0.3 g/L resulted in mere 3% increment. Similar trend was observed with Fe-TiO\textsubscript{2} and pureTiO\textsubscript{2} samples also. The photodecomposition rates of pollutants are dependent on the number of active sites and the photoabsorption of the catalyst used in the study. Results indicate that an adequate quantity of loading of the catalyst can increase the generation rate of electron/hole pairs for enhancing the degradation of pollutants. And at higher catalyst loadings, the catalysts may block the UV light and restrain the effective usage of light for photo excitation [4, 11, 46]. This behavior is called as ‘shielding effect’ caused by the suspended TiO\textsubscript{2} layers located closer to the radiation source, which reduce the penetration of light. The shielding effect becomes more pronounced as the photocatalyst concentration increases [46]. Thus, the results indicated that an optimal dose of 0.2 g/L of the catalysts was most suitable loading to achieve the best degradation results.
Figure 4.12: Effect of catalyst loading on the crystal violet degradation (Dye initial concentration = 30 mg/L, pH 6.5)

4.3.5.4 Effect of initial dye concentration
Different initial concentrations of CV dye solution, 30 and 60 mg/L were used to assess the effect initial concentrations on degradation. Figure 4.13 illustrates the variation in the relative concentration, \( C/C_0 \) with irradiation time at pH of 6.5 and optimum catalyst loading of 0.2 g/L. From the figure it can be seen that lower the initial concentration of CV dye higher is the observed degradation rate. The possible reasons for these negative results can be as follows: (i) a certain amount of catalyst can only provide a certain amount of light-generated electron-hole pairs during a certain period of time (ii) higher concentrations of CV dye increases the amount of dye adsorbed on the catalyst surface. The increase in dye concentration decreases the path length of photons entering the dye solution. In addition to this, at a higher dye concentration, a considerable amount of UV light may be absorbed by the molecules of the dye instead of the catalyst particles and this results in reduced efficiency of the catalytic reaction (iii) normally the rate of degradation is dependent on the probability of OH\(^\cdot\) radicals formation on the catalyst surface and the probability of OH\(^\cdot\) radicals reacting with dye molecules. But at high dye concentrations active sites on the catalyst surface are covered by dye ions hence the possibility of generation of OH\(^\cdot\)
radicals on the surface of catalyst is likely to be reduced. Thus the limited number of active sites available for the reaction may control the final extent of dye degradation. (iv) the reduction in the degradation of dye can also be ascribed to the filter effect caused by absorption of photon energy by the dye molecules rather than by the photocatalyst (v) the relatively longer chain of crystal violet cannot completely enter the electron- hole and thus reduces the degradation ratio [4, 11,15].

The results clearly confirmed that the photocatalytic oxidation process is promising at low concentrations of the pollutant. This is also true for heterogeneous catalytic systems where the reaction occurs at the interface between two phases [4,11,15].

Figure 4.13: Effect of initial concentration of crystal violet dye (pH 6.5 and catalyst dose = 0.2 g/L)
4.3.5.5 Degradation kinetics

The rate of the heterogeneous photocatalytic degradation of dye has been described by Langmuir–Hinshelwood (L-H) model with the following mathematical formula [4, 47]:

\[-\ln \left( \frac{C}{C_0} \right) = k_{L-H} K_{ad} t = kt\]  

(1)

where \( C \) (mg/L) is the variable concentration of CV dye at any time \( t \), \( C_0 \) is the initial concentration of CV dye prior to irradiation (mg/L), \( k_{L-H} \) is the reaction rate constant, \( K_{ad} \) is the adsorption coefficient of CV dye on photocatalyst, \( k = k_{L-H} K_{ad} \) is the pseudo-first-order reaction rate constant (min\(^{-1}\)) and \( t \) is the irradiation time (min).

The kinetic studies have been performed for the selected three representative samples. Comparison has been done between the sonochemically prepared catalysts with the optimum doping content for cerium and iron as 0.8 and 1.2 mol% and the sonochemically synthesized pure TiO\(_2\). A plot of \(-\ln(C/C_0)\) against time (Figure 4.14) represents the straight lines \((R^2>0.962)\), showing the case of the first-order reaction for photocatalytic degradation of crystal violet dye. The slope of the lines is equal to the apparent first-order rate constant \( k \). From the slopes the first order rate constants were calculated and listed in Table 4.1 for the three samples. It can be seen that the rate constant for 0.8 mol % Ce-TiO\(_2\) sample was twice as compared to that of pure TiO\(_2\) and for 1.2 mol % Fe-TiO\(_2\) it was 0.010 min\(^{-1}\), which is about 45% more as compared to the pure TiO\(_2\). Also for the doped samples the rate constant is higher for Ce doped sample than Fe doped sample. The values of rate constants, \( k \), are consistent with the photodegradation results of individual catalyst samples. Degradation of CV dye was found to be 71%, 82% and 89% with pure TiO\(_2\), 0.8 mol % Fe-TiO\(_2\) and 1.2 mol % Ce-TiO\(_2\) respectively, for 0.2 g/L catalyst loading and 30 mg/L dye concentration and the rate constants are calculated as 0.007, 0.010 and 0.014 min\(^{-1}\) respectively. The results clearly indicated the effect of doping on the degradation efficacy of the doped photocatalyst as compared to the pure form of TiO\(_2\).
Figure 4.14: Reaction kinetics for photocatalytic degradation of crystal violet (Dye initial concentration = 30 mg/L, pH 6.5 and catalyst does = 0.2 g/L)

Table 4.1: Rate constants for first order kinetics

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Rate constant (min⁻¹)</th>
<th>R² Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure TiO₂</td>
<td>0.007</td>
<td>0.962</td>
</tr>
<tr>
<td>1.2 mol% Fe- TiO₂</td>
<td>0.010</td>
<td>0.983</td>
</tr>
<tr>
<td>0.8 mol% Ce- TiO₂</td>
<td>0.014</td>
<td>0.990</td>
</tr>
</tbody>
</table>

4.4 Conclusions
Nanostructured pure and Fe/Ce doped TiO₂ photocatalysts were prepared by hydrolysis reaction of titanium isopropoxide at room temperature by conventional and sonochemical method. The cavitation effect of ultrasound could contribute to grain refinement and uniform dispersion of doping materials. The doped TiO₂ powders showed a strong absorption in the UV-visible light region and a red shift in the band
gap transition. Crystal violet dye was effectively degraded (more than 85% degradation) within 120 min of UV irradiation. An appropriate amount of dopants could obviously enhance the photocatalytic activity of \( \text{TiO}_2 \) powders and the optimum quantities were found to be 0.8 mol % Ce-\( \text{TiO}_2 \) and 1.2 mol % Fe-\( \text{TiO}_2 \). Also, an optimal dosage of 0.2 g/L of the photocatalyst was observed whereas lower initial concentration of the dye was favourable for giving higher extents of degradation. The high activities of the doped \( \text{TiO}_2 \) powders could be attributed to the results of the synergetic effects of doping, small crystallite size and large surface area. The method of preparation played a major role in deciding the photocatalytic activity and catalysts prepared by sonochemical method exhibited higher photocatalytic activity as compared to the catalysts prepared by conventional method. The photocatalytic degradation followed first-order kinetics. Thus, the sonochemical synthesis is fast, simple, convenient, time saving and economical technique for preparing nanostructured materials.

References


