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Degradation of Dyes Using High Temperature Stable Anatase Nanosphere TiO_2 Photocatalyst

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Abstract:

High temperature stable anatase phase TiO_2 was prepared by using titanium(III) chloride precursor. The prepared TiO_2 powder was characterized using XRD, UV, SEM and TEM for their structural, optical and morphological studies. As prepared amorphous nanospheres become crystalline and shows increase in crystallite size with increase in annealing temperature. The lattice (a/b/c) parameters are calculated from XRD diffraction patterns at different annealing temperatures and reported. Obtained anatase nanospheres was used for the photocatalytic degradation of Crystal violet, Methyl red, Thymol blue and Congo red dyes using UV irradiation. The prepared TiO_2 photocatalyst shows good catalytic activity in the order of Methyl red>Thymol blue>Crystal violet>Congo red.

Keywords: TiO_2, Anatase, Nanospheres, Photocatalyst, Dyes

1.0 Introduction:

Due to extensive usage of dyes in many industries particularly textile, ceramic, paper, printing and plastic industries, dyes have now become an integral part of industrial wastewater. Dyes are difficult to degrade because of their stability to light and oxidizing agents and also they are resistant to aerobic digestion. Conventional treatment technologies for dye removal from industrial effluents include biological treatment, coagulation, ozonation, electrochemical process, nanofiltration and activated carbon adsorption (Baran et al. 2008; Adamek et al. 2008; Pouretedal et al. 2008).

The photocatalytic mineralization of organic pollutants using semiconductor oxide particles as photocatalyst is well established and has shown great utility in the complete mineralization of organic pollutants. Among these semiconductors, nanosized TiO_2 has been proved to be an excellent catalyst in the photocatalytic degradation of organic pollutants because it is an effective, photostable, reusable, inexpensive, non toxic and easily available catalyst (Znaidi et al. 2001; Wang et al. 2011; Ananpattarachai et al. 2009; Wang et al. 2002). In brief, photocatalytic reactions of aqueous TiO_2 suspension system can be desired as follows (Tang et al. 1995 and Zou et al. 2007), where, photogenerated holes are highly oxidizing and the photogenerated electrons are reducing to produce superoxide radical which is powerful agents for the degradation of organic pollutants and does not need any chemical additives.

$$TiO_2 + h\upsilon \rightarrow TiO_2 + e^-_{CB} + h^+_{VB}$$
$$h^+_{VB} + OH^-_{surface} \rightarrow \dot{O}H$$
$$h^+_{VB} + H_2O \rightarrow \dot{O}H + H^+$$
$$e^-_{CB} + O_2 \rightarrow O_2^-$$
$$e^-_{CB} + h^+_{VB} \rightarrow Heat$$

The main characteristics of TiO_2 powder which have been reported to influence their photocatalytic activity are the crystalline structure, preparation method, surface area, surface OH groups and morphology (Lee et al. 1999). Particularly, anatase TiO_2 is expected as the most promising photocatalyst than rutile structure. Hence these anatase TiO_2 nanoparticles have the interest of many chemists, who, in the vigorous attempt to characterize, tune and exploit their excellent photochemical activity, have employed the wide range of synthetic approaches as well as structural methods (Yang et al. 2006).

Different methods have been developed to synthesize nanocrystalline anatase TiO_2 viz. Solvent extraction, Solvent evaporation, Crystallization, Layer by layer deposition, Microbial synthesis,, Sol-gel method, Micelle and Inverse micelle methods, Chemical and Physical vapor deposition, Solvothermal, Hydrothermal, Precipitation and Electrodeposition etc (Chen et al. 2007). The chemical synthesis methods are rare but are simple to synthesize anatase TiO_2 for photocatalytic applications. In this present study, we report, the chemical synthesis of nanosized TiO_2 and the study on degradation of different dyes like Crystal violet (CV), Methyl red (MR), Thymol blue (TB) and Congo red (CR) dyes at neutral pH and without the addition of any oxidative reagent under UV light irradiation. This proposed synthetic procedure is simple, fast, and efficient and room temperature based method which produces nanospherical, phase pure, anatase, chemically homogeneous TiO_2 with uniform distribution of particle size. For the authors best knowledge based on the available literature (Table 1), first time we are reporting this synthesis method, characterization of TiO_2 obtained from Titanium(III) chloride with varying annealing temperatures and its effectiveness as a photocatalyst for the degradation of four dyes.

2.0 Materials and Methods:

All the chemicals used were of Analytical grade and were used without further purification. Distilled deionized water was used throughout the experiment.. Titanium hydroxide precipitate was obtained from $TiCl_3$, 15% in HCl (Sigma-Aldrich) by adding aqueous ammonia (Thomas Baker). In the dispersed precipitate, hydrogen peroxide (Loba Chemie) was added to obtain transparent yellow peroxy titanium complex which on constant stirring gives TiO_2 powder (Bandgar et al. 2011, 2012; Sabale et al. 2013). The powder was extracted, dried at room temperature and annealed at various temperatures from 200, 400, 600, 800 and 1000 ^{0}C for 2 hours.

Using BRUKER AXS X-ray deffractometer with monochromatic copper radiation (CuKα) at 40 kV, 25 mA over the 2θ range 10-100^0 the structural properties were studied. The XRD patterns were obtained for as synthesized and annealed samples and particle sizes were estimated by Scherer's formula (Cullity 1978),

$$D = \frac{K\lambda}{\beta \cos\theta}\left(\frac{360}{\pi}\right)$$

The lattice constants *a/b* and *c* for obtained anatase [101 and 200 peaks] and rutile [101 and 002 peaks] phase were calculated from XRD data. The surface morphology of nano TiO_2 was observed by Scanning Electron Microscopy of JEOL JSM 6360 and Transmission Electron Microscopy of Hitachi H-7000 operating at 100 kV with a resolution not less than 3 nm. The optical properties (absorbance study) and photocatalytic properties of nano TiO_2 for dye degradation were carried out using JASCO V-670 DR/UV-VIS-NIR Spectrophotometer with wavelength range from 200-800 nm at room temperature.

The photocatalytic degradation of Crystal violet (CV), Methyl red (MR), Thymol blue (TB) and Congo red (CR) dyes (Fig. 1) (Loba Chem, India) in the TiO_2 suspension under UV illumination was investigated in order to evaluate its photocatalytic activity. A reaction system was set up by adding 50 mg of TiO_2 sample (annealed at 800 ^{0}C-model) in to 50 ppm, 500 mL of dye solution in a photocatalytic multilamp reactor with UV light (125 W, Hg vapor lamp with maximum emission at about 254 nm) at room temperature for constant stirring speed continuously to form a homogeneous suspension. The suspension was irradiated for 1 hr to 6 hr time period. The suspension was withdrawn and centrifuged at each time interval to remove the TiO_2 particles. The absorption of each dye solution was measured using UV-Visible spectrophotometer at its characteristic wavelength. The percentage degradation of each dye at irradiated time intervals was calculated according to the equation

$$\text{Degradation Percentage} = \left[1 - \frac{A_t}{A_o}\right] \times 100$$

where, A_t is absorbance after time 't' and A_o is absorbance of dye solution before degradation.

3.0 Results and Discussion:

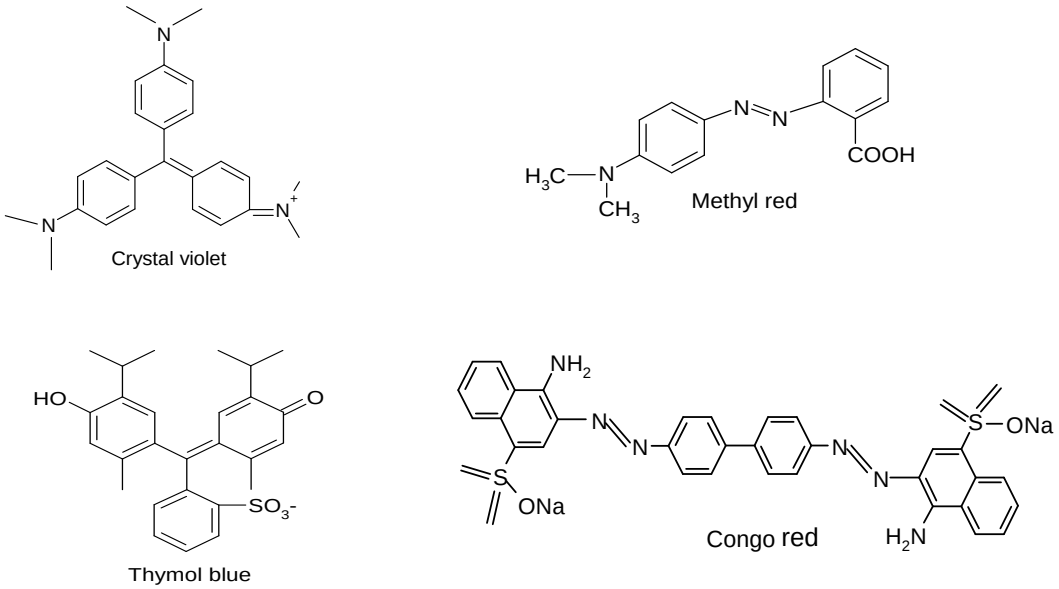

Fig. 1 Chemical structures of the studied dyes

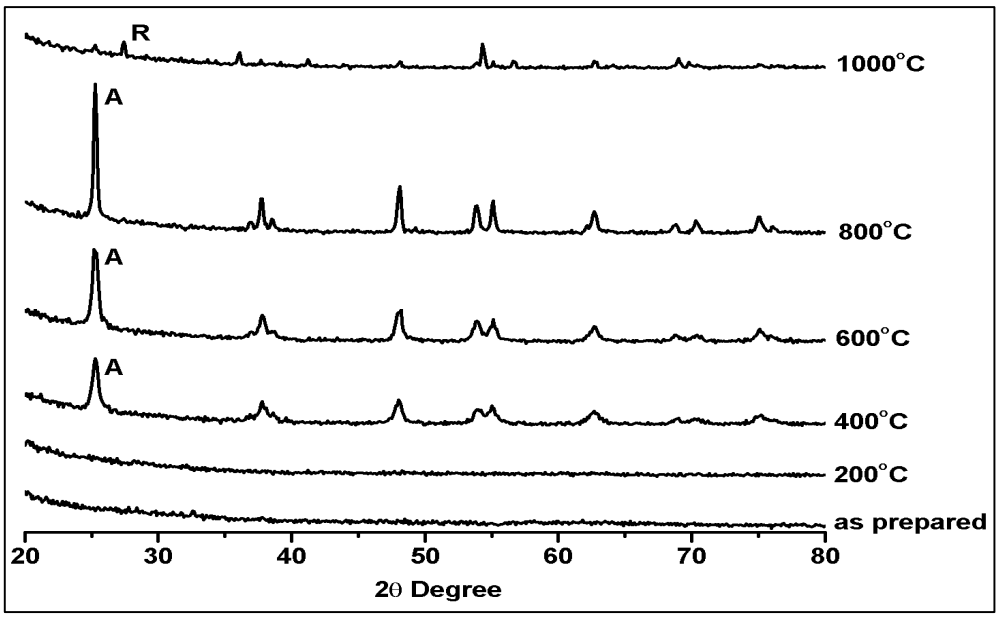

Fig. 2 XRD patterns of nano TiO_2 annealed at different temperatures

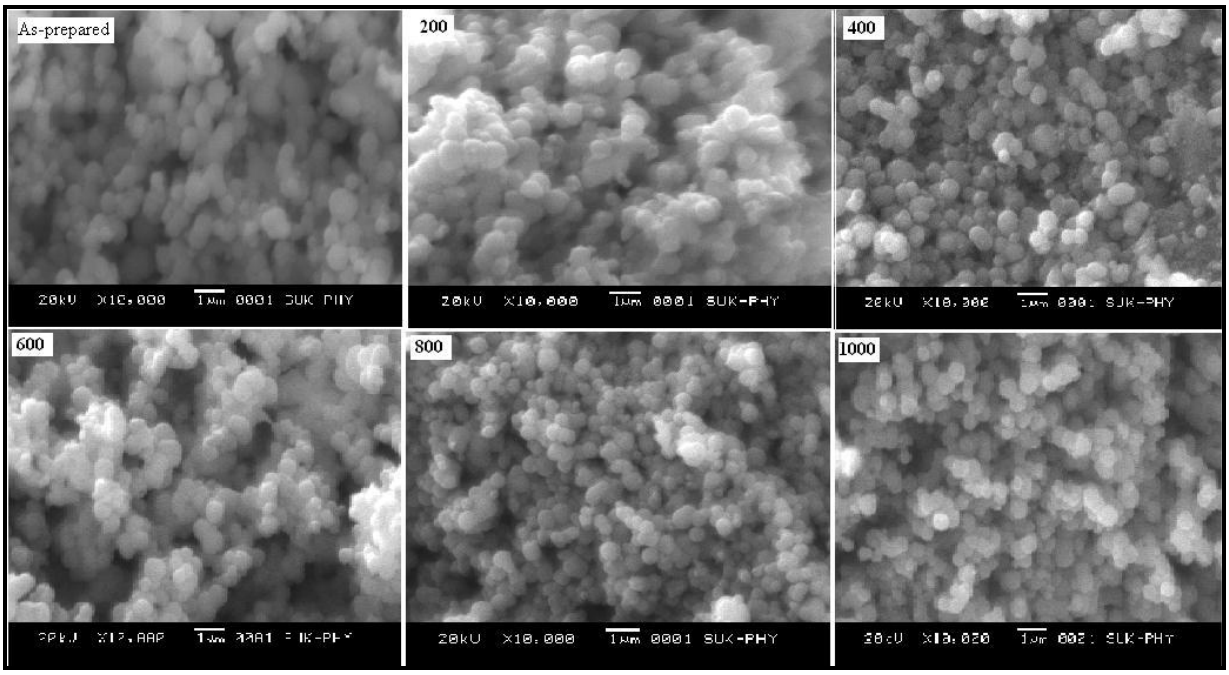

Fig. 3 SEM micrographs of nanosphere TiO_2 annealed at different temperatures

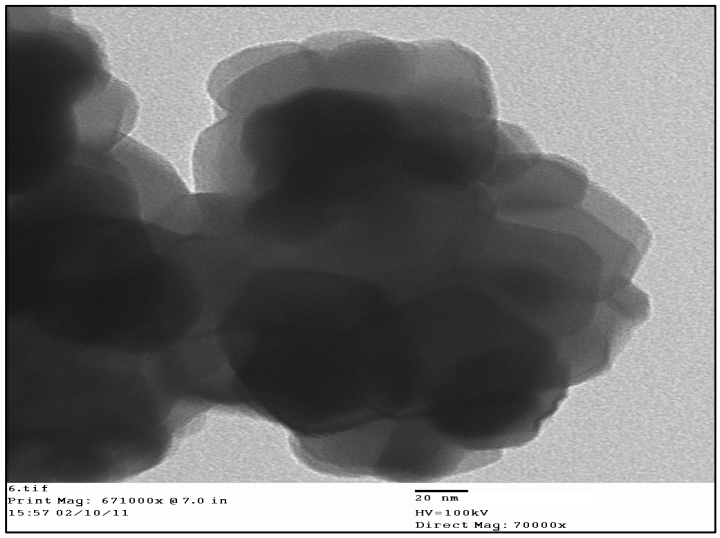

Fig. 4 TEM micrograph for nanosphere TiO_2 annealed at 800 ^{o}C

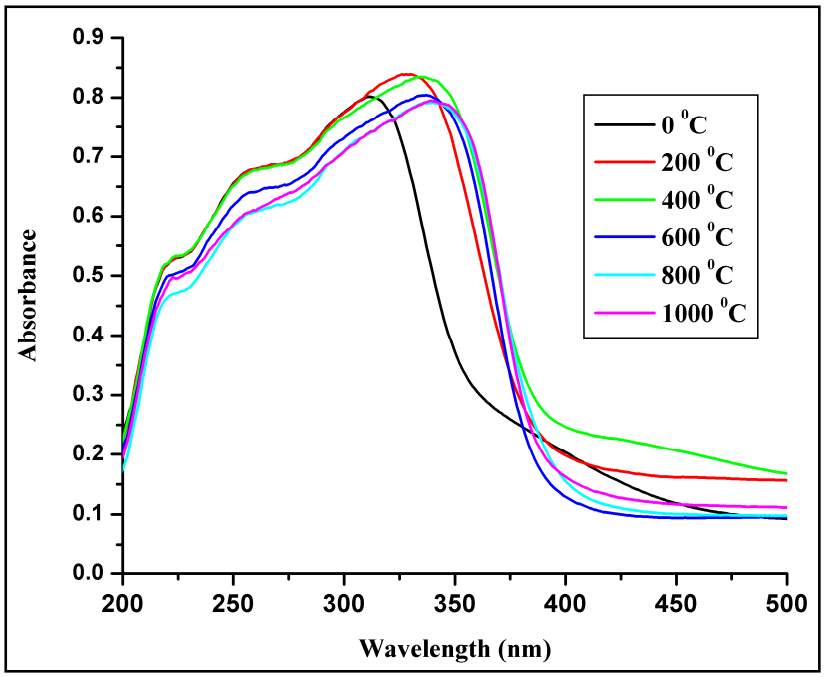

Fig. 5 UV-Vis absorbance spectra for nanosphere TiO_2 annealed at different temperatures

3.1 Structural properties

The X-ray diffraction pattern of the as-prepared sample and samples annealed at 200, 400, 600, 800 and 1000 ^{0}C for 2 hours is as shown in Fig. 1. From XRD pattern it is observed that, the as-prepared and TiO_2 annealed at 200 ^{0}C are amorphous in nature while rest of all diffraction peaks for the samples annealed at 400, 600 and 800 ^{0}C corresponds to phase pure anatase (JCPDS Card File No. 21-1272). Further increase in annealing temperature up to 1000 ^{0}C there is presence of highest intensity peak of rutile phase with a very low intensity of anatase phase (JCPDS Card File No. 21-1276). This study depicts that anatase phase have high thermal stability; even at 800 ^{0}C for 2 hours after which it starts to convert in to rutile phase. The all lattice parameters were calculated from XRD data. The calculated values of lattice parameters are given in Table 2, which shows good agreement with the reported values. Average crystallite size is determined from the highest intensity peak of anatase for the samples annealed at 400, 600 and 800 ^{0}C as well as from highest intensity peak of rutile sample annealed at 1000 ^{0}C using Scherrer's equation. The crystallite size of samples of TiO_2 annealed at 400, 600, 800 and 1000 ^{0}C powder is as shown in Table 3 which indicates the increase in crystallite size with increase in annealing temperature.

3.2Morphological Properties

Fig. 3 shows the SEM micrographs of all the six, as prepared and annealed TiO_2 samples. This surface morphological studies show that, all the obtained TiO_2 samples are with spherical morphology. The annealing temperature does not affect on the morphology of the TiO_2 powder and it retains its spherical morphology. Fig. 4 shows the TEM micrograph of representative sample (Annealed at 800 ^{0}C). From the TEM micrograph it is observed that the TiO_2 nanospheres were formed by the agglomeration of hexagonal titania crystals of average size of 30 nm, which is in good agreement with the XRD evaluation data.

Table 1: Photodegradation study of dyes using TiO_2 nanoparticles

Reference	Method, precursor and property of TiO_2	Dye	Dye /Catalyst concentration	Light source	Observation/Conclusion
Gao et al. (2000)	TiO_2 nanopartiles immobilized on polyethylene foam sheet; Loading density ca. 6.2×10^{-4} g/cm^2	Naphthol blue black	500 mL; 7×10^{-5} M dye solution	Hg lamp; 200W	In 150 min complete disappearance of aromatic absorption; cost effective catalyst system for the degradation of dyes
Rashed et al. (2007)	TiO_2 (Degussa P25); 80% anatase; 20% rutile; 30 nm diameter	Methyl orange	50 mL, 10^{-5} M dye solution; 55 mg TiO_2	Fluorescent light source	34.36 % degradation in 180 min will takes place which is lower than in sunlight
Subramani et al. (2007)	Hydrothermally prepared TiO_2 impregnated activated carbon	Indiago caramine dye	50 mL, 5×10^{-5} M dye solution; 50 mg, TiO_2:AC	UV source; 8 W	Complete demineralization along with decolorisation; TiO_2:AC shows 90% degradation while pure TiO_2 60% in 240 min
Yang et al. (2006)	Sol gel synthesized TiO_2 nanoparticles using $Ti(OBu_4)$ precursor; 16 nm anatase	Methyl orange	150 mL, 3×10^{-3} M dye solution; 100 mg anatase and biphase TiO_2	High press Hg lamp, 125 W, UV light	50 degradation in 120 min was observed; Pure anatase is superior over the biphase TiO_2 containing 65 % rutile
Zou et al. (2009)	H_2O_2 sensitised sulfated titania nanoparticles from $TiCl_4$ precursor; anatase form with size 8-13 nm, 400 ^oC annealed	Methyl orange	200 mL, 20 mgL^{-1}, 0.2 g sulfated TiO_2; 2 mL, 30% H_2O_2	High press Hg lamp, 450 W, visible light	80% degradation in 300 min; the synthesized catalyst show good catalytic activity than Degussa P25 anatase which shows only 20 % degradation at same condition
Wahi et al. (2005)	Anatase TiO_2 by hydrothermal method using Ti(IV) ethoxide precursor; Different morphologies like rod, spherical, flower like, 10 nm size	Congo red	10 mL, 10 mgL^{-1} dye solution; 1.0 gL^{-1} TiO_2 sample	14 UVA lamp (350 nm)	Anatse was superior over rutile TiO_2; catalytic activity depends on the morphology; spherical anatase TiO_2 showed high activity than other
Ling et al. (2004)	Anatase TiO_2 by sol-gel method using titanium isopropoxide precursor; thin film immobilize on glass reactor	Methylene blue	40 $\mu molL^{-1}$; 0.1 gm catalyst	UVL-28 lamp	50 % degradation of dye takes place in 5 circulation with 1.4 min residency time
Hussein et al. (2008)	TiO_2 from BDH Ltd; Phtolysis/ photocatlytic study	Thymol blue	100 mL, 4.3×10^{-3} M; 400 mg catalyst	Solar light	86 % decolorisation in 120 min; catalyst show better activity than ZnO; Photocat. TiO_2 > Photocat. ZnO > Phtolysis

Hosseinnia et al. (2010)	Anatse TiO_2 prepared by precipitation method using $TiCl_4$ precursor; Annealed at 550 ^0C; 20 nm size	Methyl violet; Methylene blue; Methyl red; Rhodamine B; Sudan Blue; Methyl orange	5 mL, 0.2 $mmolL^{-1}$ each dye solution; 2mg TiO_2	500 W white halogen lamp	100 % degradation of methyl violet in 120 min; Methyl violet shows high rate of degradation followed by Methylene blue and rhodamine B
Tayade et al. (2007)	Nanocrystalline TiO_2 synthesised by hydrothermal treatment using titanium isopropoxide	Methylene blue; malachite green	250 mL, 50 ppm dye; 50 mg TiO_2	125 W Hg vapor lamp (200-500 nm)	100 % degradation of both the dyes takes place in 240 min; along with complete removal COD
Rosu et al. (2009)	TiO_2 films prepared by wet chemical method and deposited on ITO glass; Titania P25 degussa AG; 80% anatase and 20% rutile	Violet Gentian; Methylene blue; Methyl green	100 mL, 3×10^{-5} M dye solution	UV-Hg lamp, 100 mW/cm^2	2.5%, 10% and 30% degradation will takes place in 180 min with respective dye; the degradation of all the dyes increases with increase in irradiation time
Yao et al. (2010)	TiO_2 sol using tetrabutyl titanate precursor; Particle size 22.5 nm anatase phase	Methylene blue	0.2 gL^{-1} dye solution; 1.5 gL^{-1} catalyst	UV light, Hg-lamp 40 W, 253.7 nm	92% degradation of methylene blue in 160 min; 71.4 % removal of COD
Ong et al. (2010)	TiO_2 from Degussa, immobilized on glass plate; 30 nm size pure anatase	Congo red	500 mL, 10 mgL^{-1} dye solution	UV light 18 W	60 % degradation in 240 min; rate of degradation increases with time of irradiation
Puzenat et al. (2003)	Degussa P25 TiO_2; 30 nm anatase	Congo red	2.5 gL^{-1} catalyst 50 mL, 10 ppm dye solution	UV-Philips HPK-125 W, 340 nm	100 % decolorisation in 240 min takes place along with complete removal of COD and TOC
Gupta et al. (2006)	TiO_2 Merck; Ag-TiO_2 particle size 1µm	Mixture of Crystal violet + methyl red	5×10^{-5} M; 7.5×10^{-5} M respectively	UV fluorescent lamp 16 W	70% and 99 % degradation in 90 min with respective catalyst; 86% demineralization and 100 % COD removal takes place

Table 2: XRD data for the determination of lattice parameters of as prepared and annealed samples of obtained TiO_2 powder

Amorphous TiO_2						
Temperature	**Peak Position (2θ) (deg)**		**d-spacing (Å)**		**Lattice parameters (Å)**	
As prepared	-	-	-	-	-	-
200 ^{0}C	-	-	-	-	-	-
Anatase TiO_2						
	(101)	(200)	(101)	(200)	a/b	c
400 ^{o}C	25.3137	48.0016	3.5156	1.8938	3.7826	9.4468
600 ^{o}C	25.2905	48.0774	3.5187	1.8910	3.7883	9.5993
800 ^{o}C	25.2900	48.0746	3.5188	1.8911	3.7863	9.5976
Rutile TiO_2						
	(101)	(002)	(101)	(002)	a/b	c
1000 ^{o}C	36.0605	62.7574	2.4887	1.4794	4.6016	2.9588

Table 3: Effect of annealing temperature on crystallite size and band gap

Temperature (^{o}C)	**Crystallite Size (nm)**	**Absorption edge Wavelength, λ (nm)**	**Band gap energy, E (eV)**
As prepared	-	312	3.25
200	-	326	3.14
400	16.2	334	3.14
600	17.4	337	3.14
800	30.0	340	3.11
1000	40.8	339	3.11

Table 4: Photocatalytic activity of prepared TiO_2 nanosphere (800 ^{o}C annealed)

Dye	λ_{max} (nm)	Percentage degradation at time interval (%)					
		60 min	120 min	180 min	240 min	300 min	360 min
Congo red	500	58.49	70.38	83.42	89.18	92.21	95.27
Crystal violet	578	79.12	89.59	92.02	93.25	98.23	99.38
Methyl red	498	100	-	-	-	-	-
Thymol blue	630	78.37	94.50	97.96	-	-	-

3.3 Optical Properties

DR/UV-Visible spectrophotometer was used to study the interactions of the prepared TiO_2 samples with photon energies. Fig. 5 shows the UV-Visible absorption profiles of as prepared and TiO_2 samples annealed at 200, 400, 600, 800 and 1000 ^{0}C. From Fig. 4 it is observed that, as-prepared amorphous titania powder exhibits the absorption at λ=312 nm. The remained annealed anatase as well as rutile titania samples show increase in the absorption wavelength due to the crystallinity and slight increase in the crystallite size. The band gap energy of the titania samples was calculated by using the this UV-Vis spectra using the equation (Tyagi et al. 2007),

$$E(eV) = \frac{hc}{\lambda} = \frac{1239.95}{\lambda}$$

where, E is the band gap energy (eV), h is Planks constant, c is velocity of light (m/s) and λ is the wavelength in nm. The calculated band gap energies and the maximum absorption wavelength of all the titania samples are given in Table 3. The prepared amorphous TiO_2 shows the band gap energy of 3.25 eV which corresponds to the bulk anatase TiO_2; but rest of the samples show decrease in band gap

energy by 0.1 eV due to its regular arrangement to gain crystallinity.

3.4 Photocatalytic Degradation of Dyes

TiO_2 is proved to be an ideal photocatalyst. The photogenerated holes are highly oxidizing than the conventional oxidizing agents as the redox potential for the photogenerated holes is + 2.53 V against the standard hydrogen electrode (SHE) in neutral (pH=7) solution. These holes react with water to produce hydroxyl radicals (·OH), whose redox potential is only slightly decreased. The reduction potential of conduction band electrons is -0.52 V, which is negative enough to produce dioxygen to super oxide. Depending upon the exact experimental conditions the holes, electrons, hydroxyl radicals, super oxide radicals and oxygen itself can play important role in the photocatalytic reaction mechanism (Fujishima et al. 2006).

Table 4 shows the percentage degradation of all the four dyes at different irradiation time intervals using synthesized nanosphere TiO_2 photocatalyst. For this study the anatase TiO_2 sample obtained by annealing at 800 ^{0}C was used as a model photocatalyst. It was observed that among the four dyes under study, Methyl red degrades with faster rate than remained three dyes. Almost 100% degradation of Methyl red takes place within 1 hour which seems that, the as said simple azoic structure is more susceptible to photocatalytic degradation reaction. Both Thymol blue and Crystal violet show the quite similar degradation trend due to the triphenyl methane structure. It was noticed that Congo red dye is resistant for photocatalytic degradation in first hour, which may be due to the more complex structure including biphenyl, sulphoxide naphthol and azoic groups. The dyes under study show Methyl red>Thymol blue>Crystal violet>Congo red degradation pattern. Hence the synthesized TiO_2 photocatalyst is efficient for the degradation of Methyl red.

4.0 Conclusion:

From the study carried out by the researchers, it is concluded that, the high temperature stable phase pure anatase nanosphere TiO_2 particles were synthesized from the peroxo titanium complex using titanium(III) chloride precursor. The obtained TiO_2 powder coverts into crystalline anatase form at annealing temperature 400 ^{0}C which shows high thermal stability to retain the nanatase form. The increase in annealing temperature increases the crystallite size while there is slight decrease in the band gap energy (0.1 eV) due to shift in absorption edge was observed. The synthesized TiO_2 photocatalyst showed good photodegradation of dyes. The catalyst shows strong catalytic degradation for the Methyl red dye followed by Thymol blue and Crystal violet while it is quite inefficient for the degradation of Congo red.

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