



CURRENT TRENDS IN MATERIALS CHEMISTRY

Editors

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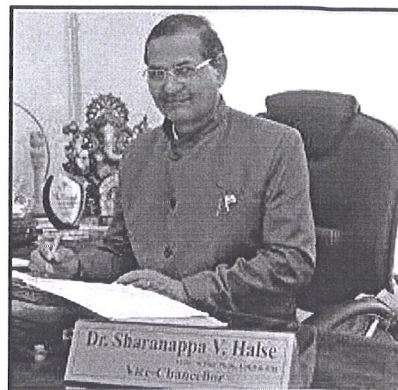
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Message



It is my great pleasure to introduce you the book “**Current Trends in Materials Chemistry**”. This book is being published by Davangere University to highlight the rapid developments that are taking place in the field of Materials Chemistry. Materials Chemistry is rapidly emerging as a key component of contemporary science. The strongly interdisciplinary nature of the field requires input from all branches of science from crystallography, solid state physics and nanotechnology. In this book, a compiled set of chapters from researchers representing some of the highlights of materials chemistry. This book benefits scientists, researchers from academia and industry as well. I hope the book will be well received and motivates students, teachers, scientists and Engineers.

Prof. Sharanappa V Halase
Vice Chancellor, Davangere University,
Shivangothri, Davangere – 577 077.


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Relative Study of TiO₂ and Pd doped TiO₂ Nano Catalysts for Water Purification under Solar and Ultraviolet Irradiation

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Abstract

The photo degradation of Congo Red (CR.) by using TiO₂ and Pd doped TiO₂ nanoparticles was investigated. The TiO₂ and Pd doped TiO₂ nanoparticles were prepared by solution combustion method using Glycine as fuel, and they are characterized by Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), and band gap was determined by using UV-absorption spectroscopy. All experiments were carried out under natural Sunlight and UV light. The rate of degradation was highly efficient in 20 ppm dye concentration, with constant catalyst concentration 0.1g/1000ml for both nanoparticles. It proves that synthesized TiO₂ and Pd doped TiO₂ nanoparticles are useful in removing the Congo red from the aqueous solution through degradation.

Keyword: TiO₂, Pd doped TiO₂ (Ti_{0.97}Pd_{0.03}O_{1.97}), Congo red, Photo-catalysis.


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1. Introduction

Titanium dioxide (TiO₂), as a photocatalysts is promising due to its merits of strong photo-oxidizing power, chemical stability, non-toxicity, and low cost. Unmodified TiO₂ suffers from a narrow light-response range, difficult catalyst recovery with low efficiency, and fast recombination [1]. Titania, a semiconductor, has attracted more research interest due to its large band gap ~3.0–3.2 eV. the decolorization of CR has been carried out by many types of research over different catalysts such as TiO₂ and Pd doped TiO₂, etc., a higher percentage of decolorization with less catalyst loading (Catalyst weight in mg/Dye concentration in ppm=20mg) at a shorter time was obtained over our catalysts [2,3]. However, it exhibits unique structural, thermal, and electronic properties based on the preparation methods where the size, shape, crystal structure, and phases are tuned for specific applications. Improvising the characteristics of TiO₂ by affecting its synthesis route by doping, impregnation, and band gap engineering have evolved Nanostructured TiO₂ for dye degradation, pesticide redemption, micro pollutants mitigation, and for solar cells [4-6]. Congo red (C.R.) dye is one of the most important secondary diazo dyes used for dyeing cotton in textile industries and also in wood pulp and paper industries. It has an intense red color, complex chemical structure, and has a maximum absorbance at the wavelength of 498 nm (λ_{max}), but it is a carcinogenic dye. Hence it is most important to study the degradation profile of CR [7, 8]. The most important research was investigated the degradation of CR in the presence of different catalysts [9-15]. From literature, in 2011, Obuya and coworkers photo-deposited Pd NPs of diameters within 2-5 nm on electro spun TiO₂. In 2014, Nasrollahzadeh and his group dispersed 40 nm Pd NPs on commercial TiO₂ using a simple drop drying process. To improve catalytic ability and widen application fields, modification of TiO₂ with noble metals such as Pt, Pd, and Au is often adopted due to their high effectiveness and good stability [12]. Palladium (Pd) is a known noble metal with new properties; Palladium is one of the most active elements for interacting with the surface of oxides as support. Previous studies have reported that the photocatalytic performance of Pd-doped TiO₂ is affected by crystal size and morphology of Pd. The Pd-doped TiO₂ catalysts with highly dispersed small Pd particles are reported to be more active concerning strong metal-support interactions (Banerjee et al., 2016). To our best knowledge, fewer studies have been reported to evaluate photocatalytic degradation of dye mixtures using Pd-doped TiO₂, including the effect of the chemical structure of dyes. Although some researchers suggested that such

catalysts are promising to treat dye-containing solutions (Abdelaal and Mohamed, 2013; Kuvarega et al., 2011; Leelavathi et al., 2013), it is not enough to convince because the chemical structure of the pollutants is an important factor affecting the directly photocatalytic performance of the catalysts. The possible photocatalytic reaction can be proposed as follows (Abou-Gamra and Ahmed, 2016; Amreetha et al., 2016; Chen et al., 2008; Hu et al., 2015; Kaur and Singhal, 2014; Trandafilović et al., 2017) Palladium doped Titania is most useful for the high oxygen storage capacity. The photocatalytic degradation of various organic dyes such as Methylene blue (MB), Alizarin S (AS), Methyl red (M.R.), Congo red (C.R.), and Orange G (O.G.) was investigated using nanosized anatase Titania TiO_2 and Pd doped titania ($\text{Ti}_{0.97}\text{Pd}_{0.03}\text{O}_{1.97}$) were prepared by solution combustion method, which absorbs the UV and most of the visible light of the solar spectrum. The catalyst has been characterized using the X-ray diffraction (XRD) technique, gravimetric-differential thermal analysis (TG-DTA), FTIR SEM, and UV-Vis spectrophotometer.

In this present study was mainly focused on the investigation of photocatalytic degradation of Congo Red (CR) and examine the effectiveness of synthesized TiO_2 and Pd doped TiO_2 . The identification of degradation product of Congo red using solar and UV light irradiation technique. The effect of parameters, such as pH, initial dye concentration, catalyst loading, transition metal doping on TiO_2 by substitution, and impregnation, was examined, taking Congo red as a specific dye for analysis. The photocatalytic degradation obtained with Sunlight has been compared with that obtained by irradiation with mercury vapor lamp using the same TiO_2 and Pd doped TiO_2 catalyst.

2. Materials and Methods

2.1. Chemicals Required

Chemicals required: $\text{Ti}(\text{OC}_3\text{H}_7)_4$, PdCl_2 , $\text{NH}_2\text{CH}_2\text{COOH}$ and $(\text{C}_{32}\text{H}_{22}\text{N}_6\text{Na}_2\text{O}_6\text{S}_2)$

2.2. Synthesis of TiO_2 and $\text{Ti}_{0.97}\text{Pd}_{0.03}\text{O}_{1.97}$ powdered catalysts

TiO_2 and Pd-doped TiO_2 catalysts were synthesized using solution combustion method. The compound $\text{Ti}_{0.97}\text{Pd}_{0.03}\text{O}_2$ can be prepared by using the starting materials are $\text{Ti}(\text{OC}_3\text{H}_7)_4$, PdCl_2 , and Glycine as fuel. For the synthesis of $\text{Ti}_{0.97}\text{Pd}_{0.03}\text{O}_2$, the stoichiometric ratio of starting materials were to be taken as 9.89 mmol of $\text{TiO}(\text{NO}_3)_2$ which is prepared from $\text{Ti}(\text{OC}_3\text{H}_7)_4$, 0.31 mmol of PdCl_2 and 10.99 mmol of Glycine in a 300 ml capacity crystallizing dish. The compounds were fully dissolved in 15 ml

of H₂O. The solution was kept in preheated furnace at 350° C. The combustion takes place after dehydration and the solid product is left behind.

2.3 Experiment Procedure

Photocatalytic experiments were conducted under direct Sunlight and U.V. light. The C.R. solution was prepared by dissolving 0.06 g of Congored dye with double distilled water using a 1000 ml volumetric flask and degradation in the presence of TiO₂ and Pd doped TiO₂ nanoparticles. Initially, 100ml of 20ppm of dye samples were tested with catalyst dosage (60 mg), under Sunlight and U.V. light. All the experiments were carried out in the presence of direct Sunlight and U.V. light. The whole experimental set-up was placed under Sunlight between 11 a.m. and 2 p.m. and the average intensity of Sunlight during this period is 834×100 lux unit using lux meter and U.V. light were carried out in the dark conditions at room temperature. After the photocatalytic degradation, the extent of degradation was estimated by recording absorbance of the dye solution using spectrophotometer (Elico, SL 177). The percentage degradation was calculated by equation 1,

$$D = (C_0 - C_t / C_0 \times 100) \quad (\text{Eq. 1})$$

Where, C₀ is the initial absorbance of the dye solution C_t is the absorbance at time interval t, i.e., after 120 minutes. The photo degradation of Congo red follows the first-order reaction kinetics that obeys the equation $\ln (C_0/C) = kt$, where k is the rate constant, t is the irradiation time; C₀ and C are the initial and concentration at time t. The first order rate constant value is higher for the both TiO₂ and Pd-doped TiO₂ catalysts

3. Results and discussion

3.1. XRD analysis

The XRD pattern of undoped and palladium doped TiO₂ was obtained using an X-ray Diffractometer Shimadzu model: XRD 6000 with CuK α radiation in the range of 20-70° ($\lambda=0.154\text{nm}$). The XRD patterns of the undoped and palladium doped TiO₂ nanoparticles obtained by the solution combustion method was shown in Fig. 1 a) 1 b) and 1 c) respectively. All the peaks in the XRD patterns can be indexed as anatase phases of TiO₂, and the diffraction data were in good agreement with JCPDS No: 21-1272. Crystallite size was obtained by Debye-Scherrer's formula given by equation 2.

$$D = K \lambda / (\beta \cos \theta) \dots \dots \dots (2)$$

Where D is the crystal size; λ is the wavelength of the X-ray radiation ($\lambda=0.15406 \text{ nm}$) for CuK α ; K is usually taken as 0.89, and β is the line width at half-maximum height.

The crystallite size obtained using this formula is 6.24 nm for undoped and 7.8 nm palladium doped TiO₂. This reveals that Pd ions are uniformly doped in the TiO₂ matrix. In the region of 2θ=10°-85°, the shape of diffraction peaks of the crystal planes of pure TiO₂ is moderately analogous to those of Pd/TiO₂. The average crystal sizes of TiO₂ and Pd doped TiO₂ nanoparticles were calculated, and also the average crystal size was not significantly altered due to the addition of the Pd²⁺. The Rietveld refined XRD profiles of undoped and palladium doped TiO₂ are shown in Figure.2. The pattern is indexed to anatase TiO₂ (tetragonal) one to two atomic percent Pd metal can be detected by slow scan in the XRD. If Pd ion was substituted for Ti⁴⁺ atom in six coordination, there should have been a measurable increase in lattice parameters and, if at all, a slight decrease in cell volume from 135.6 to 135.2 Å as indicated in Table 2. Therefore, Pd ion in these oxides is not in octahedral coordination. The ionic radius of Pd²⁺ atom in square planar coordination is 0.64 Å, which is close to Ti⁴⁺ ion in octahedral coordination. Because for every Pd²⁺ ion substitution, one oxide ion vacancy needs to be created for charge balance, Pd is likely to be in square-planar coordination.

Table.1. Rietveld refined lattice parameters of TiO₂ and Ti_{0.97}Pd_{0.03}O₂ (0.03)

Catalysts	a	c	Cell volume	R _f	R _B
TiO ₂	3.779(1)	9.497(1)	153.62	2.8	2.6
Ti _{0.97} Pd _{0.03} O ₂	3.778(1)	9.473(0)	153.21	2.7	2.5

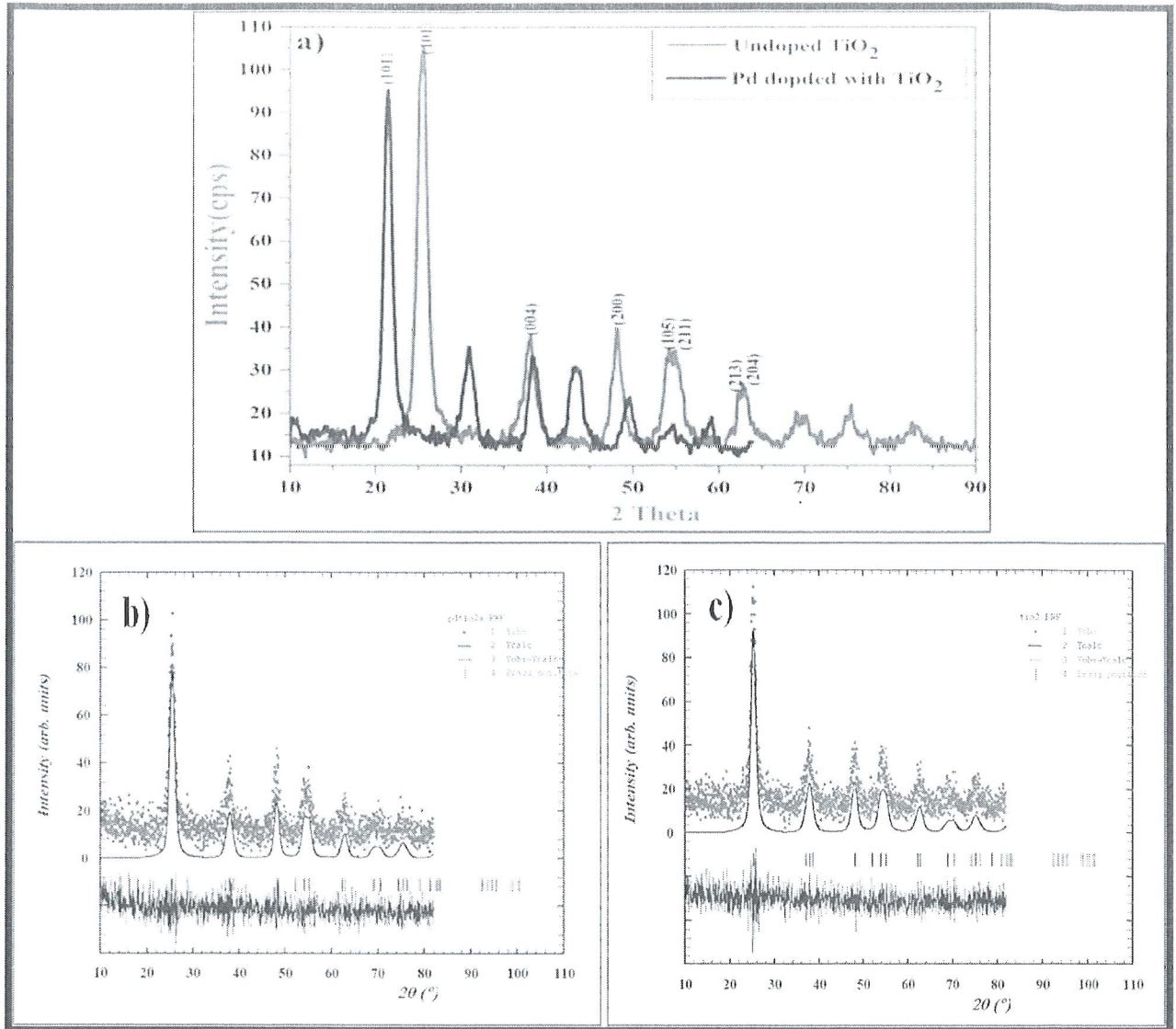


Fig.1. XRD Pattern of a) TiO_2 , Palladium doped TiO_2 and Rietveld refined images of b) Palladium doped TiO_2 and c) TiO_2

3.2 Scanning Electron Microscope Analysis

SEM images of the palladium doped TiO_2 prepared are shown in Fig. 2 a) and Fig 2 b). In Fig.2 a), the bright nanostructures can be seen as having a grain size of $\sim 1\mu\text{m}$ to 200nm and the tetragonal morphology with uniform particle distribution. In Fig 2 b), demonstrating the particles are in little accumulation and tetragonal morphology. The

SEM analysis showed that the doped palladium on TiO₂ does not affect the morphology and structure of the TiO₂ nanoparticle.

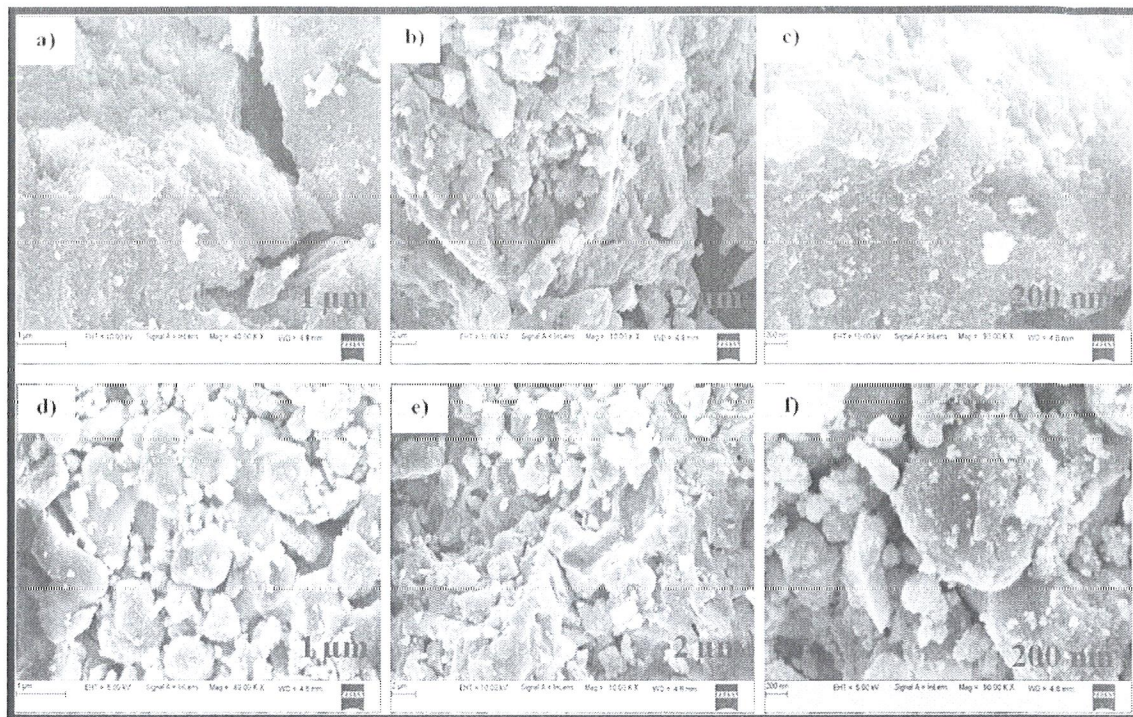


Fig.2. SEM images of a) 1 μm b) 2 μm and c) 200 nm of Undoped TiO₂ and Palladium doped TiO₂

4. Photocatalytic studies

4.1 UV light determined photocatalysis.

The photocatalytic activity of both the TiO₂ and Pd doped TiO₂ Catalyst has been investigated under UV irradiation. Congo red has been selected as a model dye for the evaluation of the photocatalytic activity. Congo red is a structurally stable anionic dye, which is represented in the inset of Fig. 3. The absorption spectrum of an aqueous solution of Congo red is illustrated in Fig. 3. The absorption band at 343 nm is associated with the $\pi-\pi^*$ transition of the aromatic ring and the band at 496 nm can be assigned to the $n-\pi^*$ transition of the lone pair present in the N atom of the chromophoric $-\text{N}=\text{N}-$ azo moiety [16]. The degradation of the dye by photocatalysis can be followed by monitoring the decrease in the intensity of the absorption band at 497 nm, indicating cleavage of the $-\text{N}=\text{N}-$ bond. Initially, a new experiment was conducted where the dye and the catalyst suspension were stirred magnetically in the dark before irradiation. Congo red degradation was negligible in the absence of light. The experiment was also conducted in the presence of light but without the catalyst to ensure that there is no photolysis of the dye in the absence of a catalyst. Fig. 3 displays

the degradation profile of Congo red in the presence of TiO_2 and Pd doped TiO_2 Catalysts under UV irradiation. For comparison, the degradation of Congo red by anatase TiO_2 nanoparticles with Pd doped TiO_2 under UV irradiation in the same experimental conditions is also shown. It is evident from the degradation profile (Fig. 3) that TiO_2 exhibits a slightly higher photocatalytic activity than Pd doped TiO_2 .

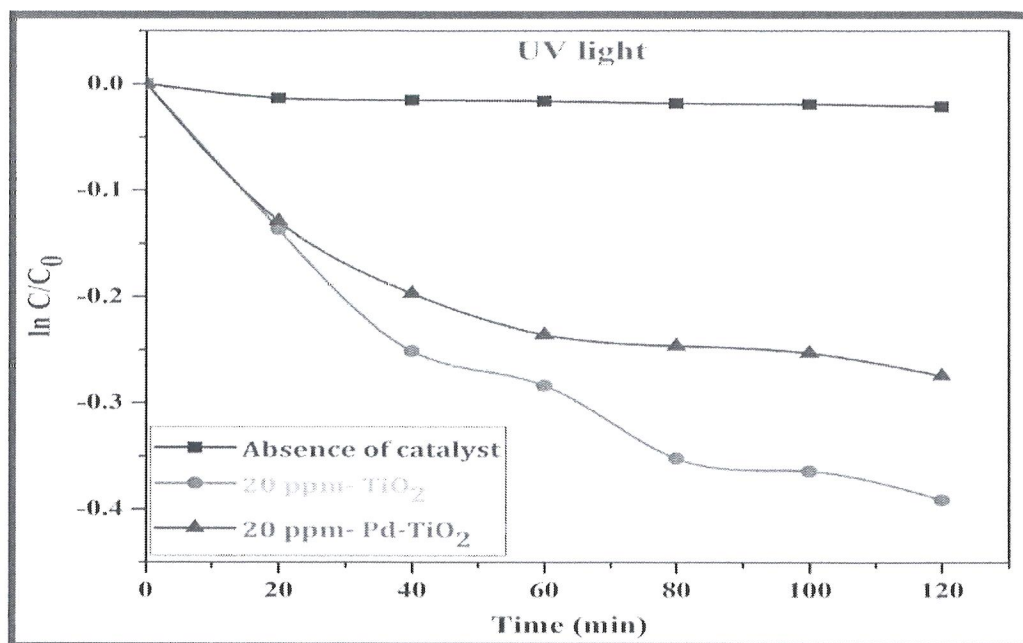


Fig. 3: Degradation profile for the Congo red dye under UV irradiation.

4.2 Visible light determined photocatalysis.

Fig. 4 represents the degradation of the dye under sunlight using nano TiO_2 and Pd doped TiO_2 . It is unsurprising that the photocatalytic activity of anatase is vastly diminished in the presence of the sun. The broad band gap of anatase results in the inability of the catalyst to absorb energy in the visible region. From Fig. 4, it can be discerned that the photocatalytic activity of nano TiO_2 is more than Pd doped TiO_2 . It is well recognized that as the redshift in the absorption edge extends towards the visible region, the utilization of photons in the visible region increases. This indicates that the smaller the band gap, the higher the photocatalytic activity in the visible area. Accordingly, Pd doped TiO_2 , with the lowest band gap as calculated from the DRS data, should have shown higher photocatalytic activity than nano Pd doped TiO_2 under sunlight irradiation. On the contrary, it is observed that although the absorption edge of nano Pd doped TiO_2 being smaller in the visible region, it degrades the dye faster than its bulk counterpart. Therefore, it is likely that the higher activity of nano TiO_2 is due to the particle size effect. It is believed that as the particle size becomes smaller, in

addition to the increase in the surface area, the distance to reach the reaction site will be shortened for the excitons on the surface of the catalyst. [17] Therefore, the electron-hole recombination rate decreases, thereby enhancing the photocatalytic activity. [17] Hence, it can be surmised that not only the band gap but also the particle size plays a crucial role in determining photocatalytic activity. Furthermore, the recyclability of the bulk and nano catalyst after three photoreactions in the presence of solar radiation follows the same trend as the photocatalytic activity already discussed in the previous section. It must be mentioned that, to our knowledge, since this is the first study reporting the synthesis of nanoparticles by combustion synthesis in this class of materials, more research is required to understand the effect of the particle size on the photocatalytic activity. From the above discussion, it can be established that TiO_2 shows slightly high photocatalytic activity in the UV as well as the visible region. Furthermore, in comparison with UV irradiation, the rate of Congo red degradation under solar irradiation is higher. Hence, the degradation and removal rate of Congo red is more feasible under sunlight rather than in UV light for the TiO_2 catalyst.

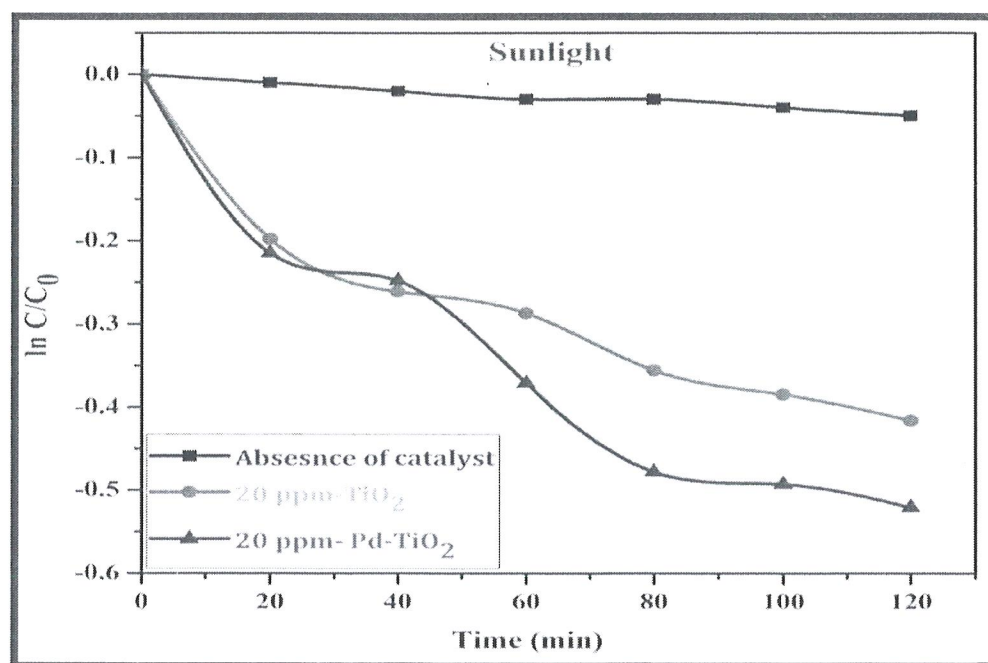


Fig.4. Degradation profile for the Congo red dye under sunlight irradiation.

4.3 Photocatalytic Studies of Sunlight and UV-light

The photocatalytic activity of TiO_2 and Pd doped TiO_2 Catalysts was studied by the degradation of CR under UV light irradiation concerning time. The aqueous solution of CR initially shows an absorption maximum at 498 nm. Fig.5 shows a tremendous decrease in absorption maxima resulting in 90.55 % of degradation in just 120 mines.

For comparison sake, we have also performed a similar experiment using synthesized Pd doped TiO₂, and degradation reached only 90.23 % in 120 min. Further, The orange color of the initial solution changes to almost colorless at 120min in the presence of TiO₂, and Pd doped TiO₂ catalysts under UV light irradiation concerning time indicates destruction of dyes. The degradation of Congo red is further established by UV Vis absorption of the dye recorded at different intervals of degradation, as represented in Fig.5. The results of the absorption spectra are concurrent with the above FTIR analysis. Aqueous solutions of Congo red exhibit well defined maxima at 497 nm, which is associated with the n-p* transitions of the non-bonded electron present in the N atom of the azo group. It is evident from the spectra that there is a gradual reduction of the –N=N– peak with time, which indicates cleavage of the azo group leading to the degradation of the dye. In general, photo degradation of the dye over a semiconductor is driven either by photosensitization of the dye or by photocatalytic oxidation. [18] In the photosensitization process, the dye is stimulated by absorbing visible light photons and the subsequent transfer of electrons to the conduction band of the catalyst, which reacts with the oxygen present in the media to produce a superoxide oxidant. Photo catalytically induced -OH radicals are believed to carry out the oxidation process.5 these highly reactive oxidants primarily attack the –N=N– group, destroying the chromophoric group of the dye. As the band gap widens due to the reduction in the particle size, the charge carrier transport in photocatalysis also differs. The electrons in the conduction minima and the holes present in the valence maxima have relatively higher oxidation and reduction potentials, respectively [18]. As a consequence of the higher redox potential, smaller particles are able to degrade the dye faster than bigger particles in the bulk. The influence of the particle size is also reflected in the higher amount of absorption of photons, thus facilitating the faster removal of the dye over the surface of the catalyst. [19] Since the surface energy is higher in nano TiO₂, photocatalytic oxidation of the organic moiety present on the catalyst is expected to be higher than in the Pd doped TiO₂. The presence of these defects in the semiconductor hinders the migration of electron-hole pairs to the surface and also promotes the recombination rate. Therefore, the probability of the diffusion of photo-generated excitons to reach the reaction site decreases, causing diminished photocatalytic activity.

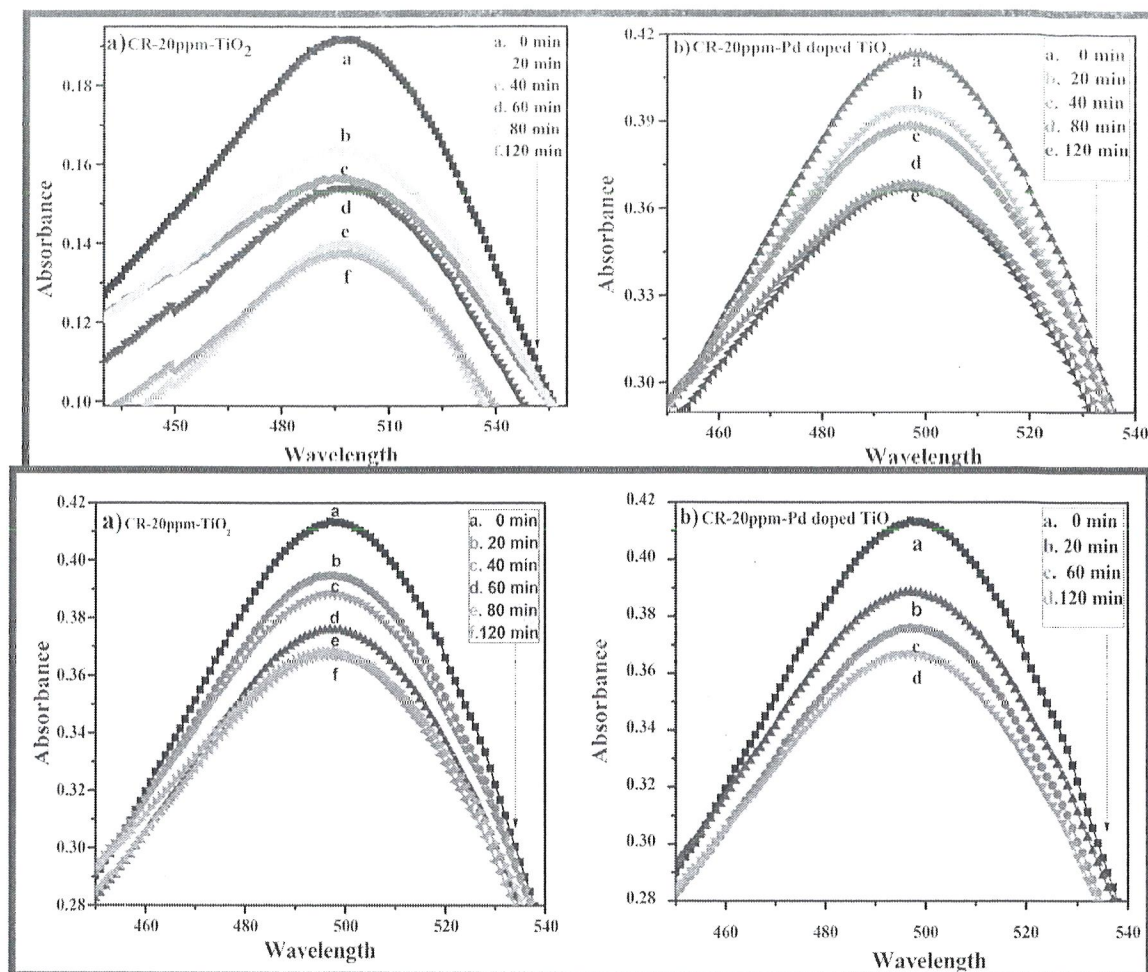


Fig.5. Successive UV-Vis spectra of CR degradation at different time intervals in the presence of nano TiO_2 and Pd doped TiO_2

4.4 Degradation efficiency of Congo red using TiO_2 and Pd doped TiO_2 catalyts.

It is found that nano TiO_2 degrades 99.58% of the CR dye, Pd doped TiO_2 99.26%, whereas anatase TiO_2 removes 99% of the color (Fig.6). Though anatase has a band gap of 3.2 eV and thus is expected to degrade the dye faster, it is remarkable that the rate of degradation is higher with the TiO_2 catalyst. It can be inferred from this experiment that anatase TiO_2 is more efficient than Pd doped TiO_2 for the photocatalytic degradation of Congo red. This could imply that TiO_2 prohibits effective electron-hole pair recombination due to its layered structure, thereby enhancing its photocatalytic activity. The higher activity exhibited by nano TiO_2 under UV irradiation can be attributed to its higher band gap of 3.2 eV compared to Pd doped TiO_2 . Hence, efficient utilization of photons under UV irradiation is more probable for nano TiO_2 than the Pd doped material to facilitate the photo degradation of the dye.

Table.2 .Comparison of photocatalyst performance

Sl No	Light Source	Catalysts	Amount of catalyst dosage	The concentration of dye solution	Degradation time (min)	% of degradation
1	Sunlight	TiO ₂	60 mg	20 ppm	120 min	99.38
2	UV light	Ti _{0.97} Pd _{0.03} O ₂	60 mg	20 ppm	120 min	99.40

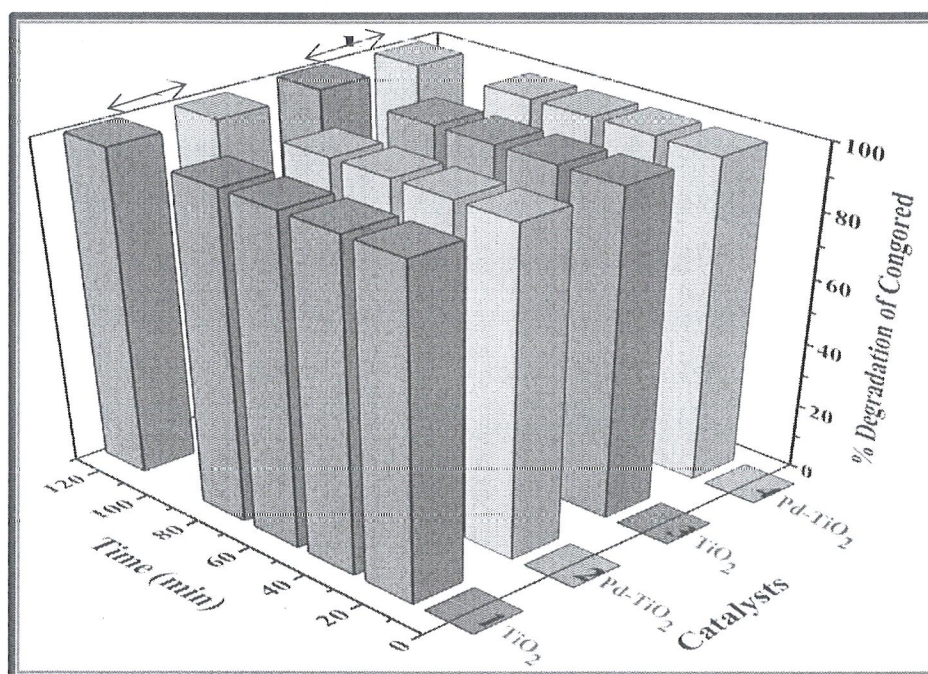


Fig.6: Effect of irradiation time on photo degradation; (a) Degradation percentage under sunlight radiation, (b) Degradation percentage under UV-radiation.

5. Conclusion

The synthesized particles are in the tetragonal structure and showed that doped palladium on TiO₂ doesn't change the morphology of the material. In Fig 3 b), demonstrating the particles are in little accumulation and tetragonal morphology. The SEM analysis showed that the doped palladium on TiO₂ does not affect the morphology and arrangement of the TiO₂ nano particle. The solar photocatalytic degradation of various organic dyes was studied using combustion synthesized nano TiO₂. The higher solar photocatalytic activity of combustion synthesized TiO₂ can be attributed to the nano-size, crystal structure (anatase), crystallinity, large amount surface hydroxyl

groups and decreased band-gap energy of the catalyst which enhances the solar energy absorption. Photocatalysis is a very effective method for the degradation of industrial or textile dyes. In this study, TiO₂ and Pd doped TiO₂ nanoparticles were synthesized and characterized by XRD, SEM, EDX, and UV-Vis reflectance. It was observed that the synthesized, effective in degrading selected azo dye (CR) entirely in a short interval of time (120 minutes). From this experiment, we can conclude that the TiO₂ and Pd doped TiO₂ did degrade the dye over a short interval of time with the help of sunlight. Even though the result was achieved more than 97%, we still believe that if this experiment was done over a more extended period that the concentration of the dyes would have been zero. This protocol developed may be employed effectively in the treatment of textile dye effluents, which are hazardous to the environment.

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