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## Copper doped Titania: Characterization and Photocatalytic performance on Rosebengal dye

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### Abstract

In the present study we investigated the activity of the photocatalyst - Copper doped titania for the degradation of the dye-Rosebengal. The characterization of the prepared photocatalyst was done by powder XRD, SEM equipped with EDX and UV-Vis spectrophotometer. The effects of various parameters influencing the dye degradation were studied. The reusability of the catalyst was tested and the performance efficiency was analysed.

**Keywords:** Copper-doped Titania, Photocatalysis, Titanium dioxide (TiO<sub>2</sub>), Rosebengal dye degradation

### Introduction

Nanosized TiO<sub>2</sub> has been widely used because of its stability in aqueous environments and low production cost. However, its light absorption range is limited to the ultraviolet (UV) spectrum of light due to its wide band gap (Approximately 3.2 eV)<sup>[1]</sup>. To shift the absorption range to the visible spectrum, various approaches have been pursued in the past involving size optimization, compositional variation to make sub-oxides, surface modification, and doping to modify the TiO<sub>2</sub> structure. Among these methods, tailoring the band structures by incorporating a dopant into the host nanomaterial is a promising approach<sup>[2]</sup>. Several studies have reported enhancement of absorption in the visible range and photocatalytic activity on doping TiO<sub>2</sub> by transition metal ions like Cu, Co, V, Fe, Nb, and non-metal like N, S, F<sup>[3]</sup>. However, a major challenge is to process low-cost, and stable doped nanomaterials with well-controlled properties that can effectively absorb visible light. Recently, copper has been increasingly investigated as a dopant for titania. Copper oxide is a narrow band gap (cupric oxide, 1.4 eV; cuprous oxide, 2.2 eV) material which has a high-absorption coefficient, but suffers from UV-induced photocorrosion<sup>[4]</sup>. However, copper oxide coupled with TiO<sub>2</sub> has been demonstrated to be stable with improved photocatalytic degradation properties, effective CO<sub>2</sub> photoreduction, improved gas sensing, and enhanced H<sub>2</sub> production<sup>[5]</sup>. Dopants can replace Ti in the substitutional sites or be incorporated in the interstitial sites. In some cases, they may segregate on the surface<sup>[6]</sup>. The creation of new energy states due to the incorporation of the dopant in the host TiO<sub>2</sub> alters the particle properties, electronic structure, and light absorption properties. These affect their functionality, and hence can be used in different applications<sup>[7]</sup>.

Titanium dioxide (TiO<sub>2</sub>) is considered to be one of the most remarkable photocatalysts due to its broad spectrum of applications, and its substantial stability and non-toxicity. TiO<sub>2</sub> has been employed in various applications as a photocatalyst, antimicrobial agent, and a solution to environmental problems, owing to its environment-friendly nature and cost-effectiveness<sup>[8]</sup>. TiO<sub>2</sub> naturally exists in three crystallographic forms namely anatase, rutile, and brookite. In addition to the favorable characteristics mentioned above, it has been possible to improve upon the properties of TiO<sub>2</sub> through various modifications. As a consequence of these alterations, TiO<sub>2</sub> displays absorption in the visible region and in many cases photocatalytic activity under visible irradiation for various reactions<sup>[9]</sup>. The photocatalytic mechanism of titania is constrained by the tendency for electron-hole pairs to recombine, as is the case for

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all semiconductor photocatalysts. As a result of recombination of electron–holes, titania exhibits poor band gap emission, which optically allows for the irradiative recombination of trap states <sup>[10]</sup>. Additionally, decrease in particle size usually leads to an increase in surface recombination. Addition of any species that expedite charge separation serves to reduce recombination phenomenon in the material and enhances overall quantum efficiency of the photocatalytic system. Charge separation in titania supported through various modifiers such as noble metals, heterojunction coupling, and doping with transition metal ions has been reported. Copper incorporated in various concentrations in pure TiO<sub>2</sub> stands out as one of the most favorable dopant materials that compensates for such drawbacks <sup>[11]</sup>. The Cu-based nanocatalysts have significant applications in nanotechnology including photocatalysis, electrolysis, hydrogen production, and anti-bacterial products. In comparison with noble metals (i.e., Au, Pd, and Ag), Cu has been considered as a highly competent co-catalyst of titania due to its ease of availability, and cost-effectiveness in that it is 100 and 6000 times cheaper than Ag and gold, respectively. For photo applications the catalyst should absorb and not block or scatter the incident radiation and should be able to generate charge carriers by band gap excitation. This is possible only with nano sized semiconductor materials with suitable band gap energy.

The high natural abundance of copper and its cost effectiveness when compared to Ag and Au has made the nanoparticles of inexpensive metals, a suitable alternative to the sparse and expensive noble-metal catalysts. It has gained considerable attention in recent years and is used in many conventional commercial processes in different fields such as electrical, catalysis, field emission emitters, inkjets and sensors <sup>[12]</sup>. Moreover, when its location in the periodic table is considered, it is placed in the same group of the periodic table as gold and silver. So, copper has similar properties as that of silver and gold due to its electronic configuration and the face centered cubic (FCC) structure of the atom's location. Therefore, one can expect the comparable potential of improving the photocatalytic activity of TiO<sub>2</sub> on doping Cu along with a higher possibility of successful application it is found that a dopant with an oxidation state of 3<sup>+</sup> or lower produced the oxygen vacancies in the lattice of TiO<sub>2</sub> to maintain the charge neutrality. Therefore, the substitution of Cu<sup>2+</sup> to Ti<sup>4+</sup> increases the oxygen vacancies. A huge difference in valence state suggests that Cu<sup>2+</sup> should not replace Ti<sup>4+</sup> to enable displacement doping at the crystal lattice site. There is only the possibility of incorporating Cu<sup>2+</sup> ions into interstitial positions in the lattice <sup>[13]</sup>. This work deals with the preparation, characterization and analysis of the photocatalytic activity of Cu-TiO<sub>2</sub> on Rosebengal dye.

### Preparation of Copper doped TiO<sub>2</sub> (Cu-TiO<sub>2</sub>) photocatalyst

Copper doped TiO<sub>2</sub> was prepared as follows <sup>[14]</sup>. 0.0018 mol of Cu(NO<sub>3</sub>)<sub>2</sub> was dissolved in 30 mL of distilled water in a porcelain bowl. 0.99 mol of TiO<sub>2</sub> was then added to the solution. The solution was stirred well and allowed to stand for 24 h. The contents were heated at 100 °C to evaporate all the water. The dried solids were first ground and then calcined at 400 °C for 6 h in a muffle furnace.

The photocatalytic activity of the prepared photocatalyst (Fig.1) was evaluated by assessing the degradation rate of

synthetic and toxic dye pollutant Rosebengal dye in aqueous solution. The solution of Rosebengal dye of desired concentration was prepared and mixed with preweighed quantity of catalyst then placed in dark under continuous stirring for 30 minutes to achieve equilibrium between Rosebengal and photocatalyst prior to illumination. After vigorous stirring for 30 minutes, the solution was directly placed under bright sunlight. After complete exposure of light a few ml of solution was extracted to measure dye concentration using UV-vis spectrograph at 545 nm of Rosebengal absorbance. Dye absorbance decreased gradually at ordered time intervals that demonstrated decolorization rate and efficiency of photocatalyst.

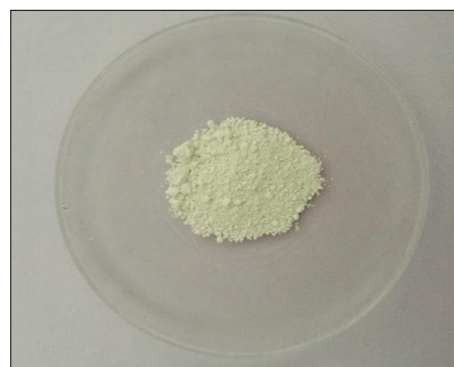


Fig 1: Copper doped TiO<sub>2</sub> (Cu-TiO<sub>2</sub>) photocatalyst

### Characterization of photocatalyst

#### PXRD analysis

The PXRD technique was used to analyze the crystal structure of the synthesized Cu-TiO<sub>2</sub>. The XRD pattern of Cu-doped TiO<sub>2</sub> photocatalyst samples shown in Fig.2 showed no characteristic peaks corresponding to copper oxide crystalline phase. The reason for this might be that the copper doped in titania would be in the amorphous form or the amount of copper would be below the detectable limit by the XRD measurement. Yet another reason might be that the copper ions might have been inserted into the crystalline structure of TiO<sub>2</sub> and located at interstices or occupied some of the Ti lattice sites forming a solid solution of copper-titanium oxides. Applying Debye Scherrer equation, on the diffraction peaks, the calculated average crystallite size for the sample 32 nm.

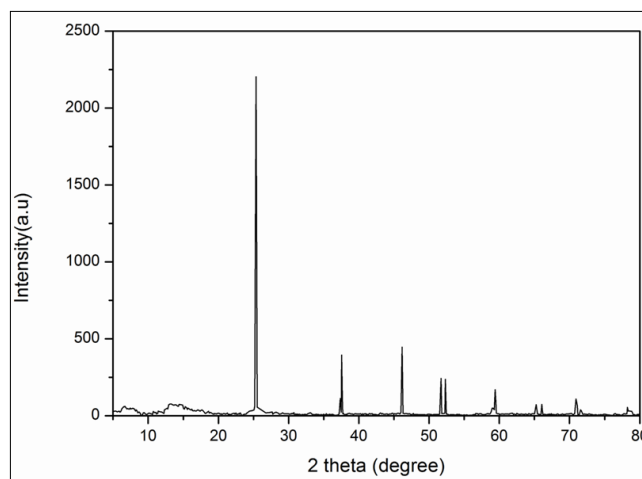


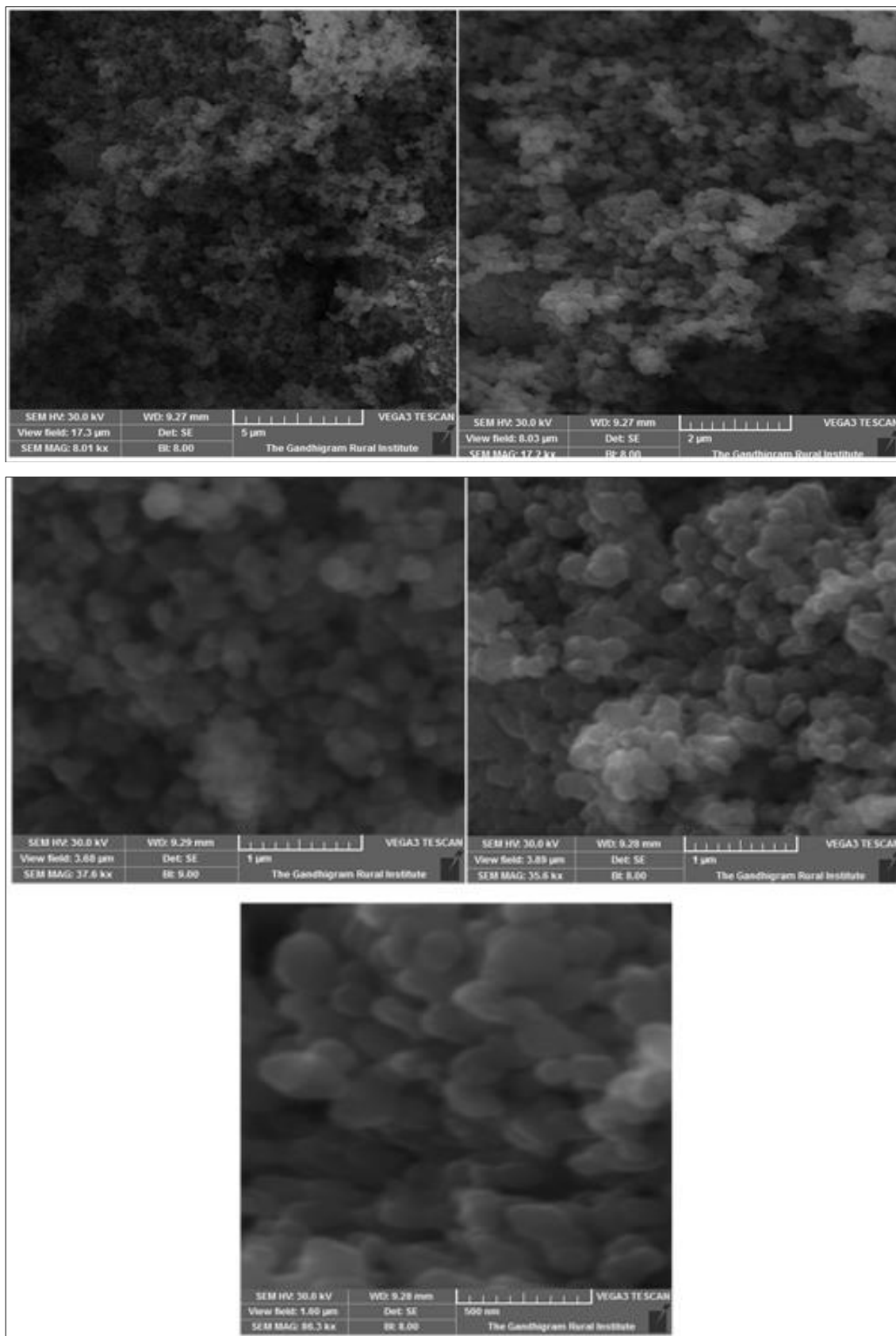
Fig 2: PXRD of Cu-TiO<sub>2</sub>

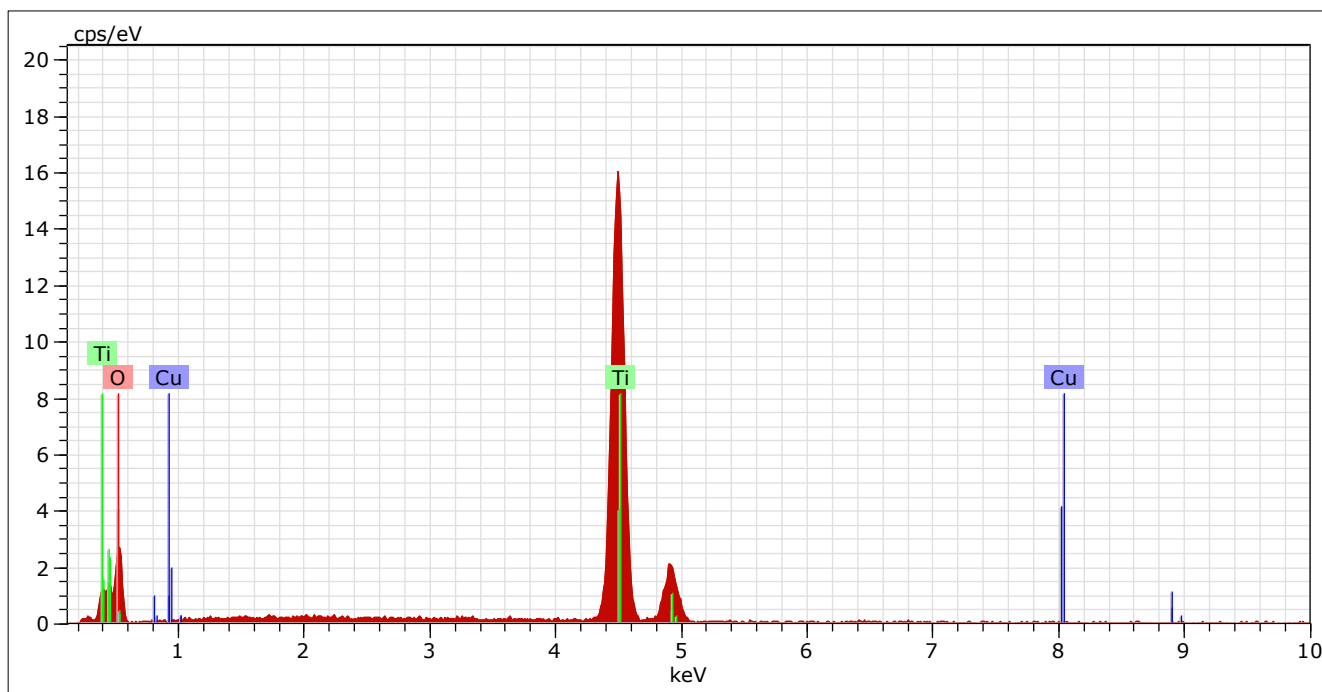
### SEM with EDX analysis

SEM results of the prepared Cu-TiO<sub>2</sub> are shown in Fig.3. It is obvious from the figure that the structures were spherical, and quite identical to each other. The spherical shape in particular is of great significance as it is helpful in the design of surface properties and for tuning the electronic structure. This makes the visible light spectrum more active and provides a better photocatalytic activity [15]. It was

perceived that the doped metal ions were evenly dispersed or incorporated into the crystal structure of TiO<sub>2</sub>.

The elements present in the synthesized Cu-TiO<sub>2</sub> photocatalyst was identified by EDX, a semi-quantitative technique. The EDX spectrum of Cu-TiO<sub>2</sub> is presented in Fig.4 and the elemental composition is shown in Table.1. The EDX spectrum reveals the presence of Cu, Ti and O in the synthesized photocatalyst.



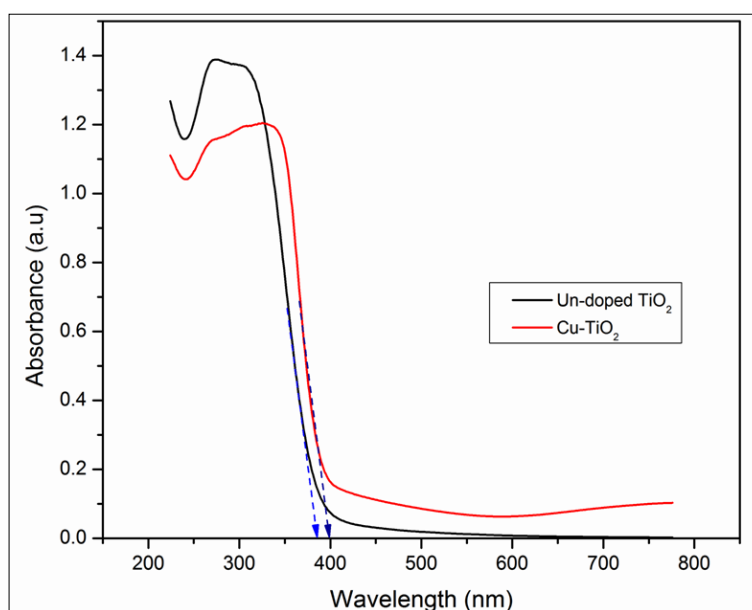
**Fig 3:** SEM images of Cu-TiO<sub>2</sub>**Fig 4:** EDX spectrum of Cu-TiO<sub>2</sub>**Table 1:** Elemental composition of Cu-TiO<sub>2</sub>

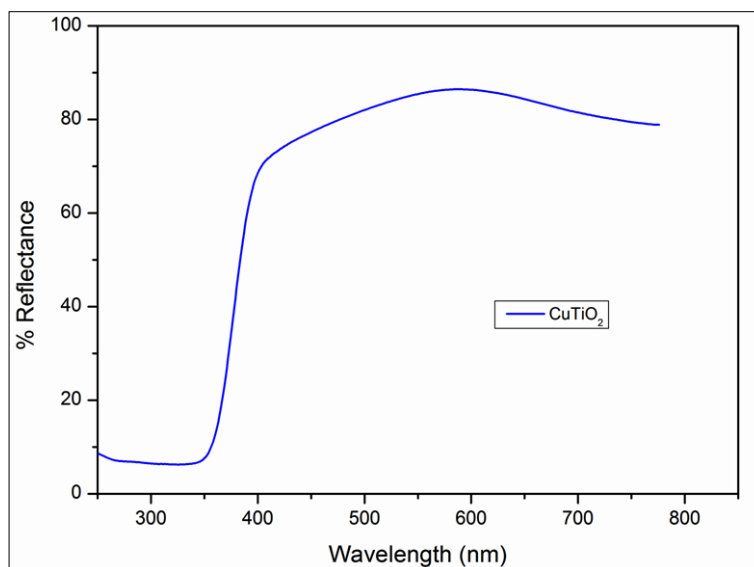
El	AN	Series	Unn. C [wt.%]	Norm. C [wt.%]	Atom. C [at. %]	Error (1 Sigma) [wt.%]
O	8	K-series	40.21	36.72	63.49	9.91
Ti	22	K-series	68.95	62.97	36.38	1.96
Cu	29	K-series	0.34	0.31	0.14	0.07
Total			109.51	100	100	

### UV-vis DRS measurements

The minimum wavelength required to promote an electron depends upon the band-gap energy,  $E_g$  of the photocatalyst [16]. In order to record the absorbance capacity of the photocatalyst and to determine the band-gap energies of the

prepared Cu-TiO<sub>2</sub> samples, the UV-vis diffuse reflectance spectroscopy method was used. The UV-visible absorbance spectra of Cu-TiO<sub>2</sub> and un-doped TiO<sub>2</sub> are shown in Fig.5 and the reflectance spectrum of Cu-TiO<sub>2</sub> is shown in Fig.6. The band gap energy ( $E_g$ ) of the doped samples were determined to be 3.12 eV. Insertion of copper ion into the bulk TiO<sub>2</sub> or on the surface sites resulted in lattice deformation due to the rearrangement of the neighbouring atoms ensuring charge balance. The substitution of Ti<sup>4+</sup> by Cu<sup>2+</sup> inducing this lattice deformation affects the electronic structure of TiO<sub>2</sub> crystalline lattice and this might have led to the change in the optical absorption of Cu doped TiO<sub>2</sub>.

**Fig 5:** UV-vis absorption spectra of Cu-TiO<sub>2</sub>



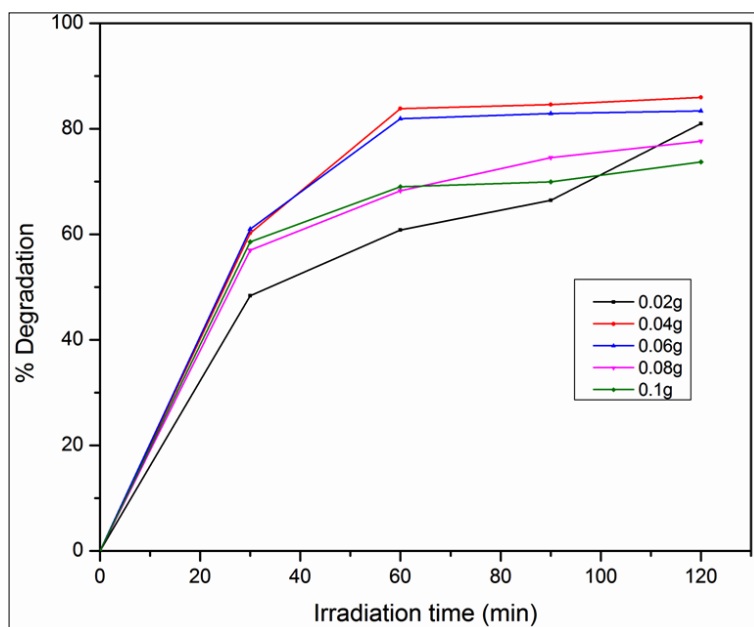
**Fig 6:** Reflectance UV-vis spectra of Cu-TiO<sub>2</sub>

### Factors influencing the photocatalytic degradation

#### Effect of catalyst amount

The reduction in the degradation rate when the catalyst amount increases above the optimum value is attributed to the light scattering effect and the reduction in the penetration of light through the solution. With a higher amount of catalyst, the deactivation of activated molecules by collision with ground state molecules dominates the reaction reducing the rate of degradation<sup>[17]</sup>. Excess amount of adsorbent addition to solution may cause shielding, condensation and settlement leading to the slightly decrease in the adsorption activity. So, it is necessary to determine

the optimal catalyst loading to degrade the dye effectively<sup>[18]</sup>. The optimal amount of Cu-TiO<sub>2</sub> catalyst for the degradation of rosebengal was determined by varying the amount of catalyst from 0.02-0.1g/100mL at a constant dye concentration of 10ppm. The percentage of dye degraded at different time intervals at various catalyst loadings is calculated and depicted in Fig.7. It is evident from figure that with the increase in the amount of catalyst from 0.02-0.1g/100 mL there is an increase in the degradation percentage upto 0.04 g followed by a decrease and hence the optimal amount of catalyst for the present study was taken as 0.04 g/100 mL.



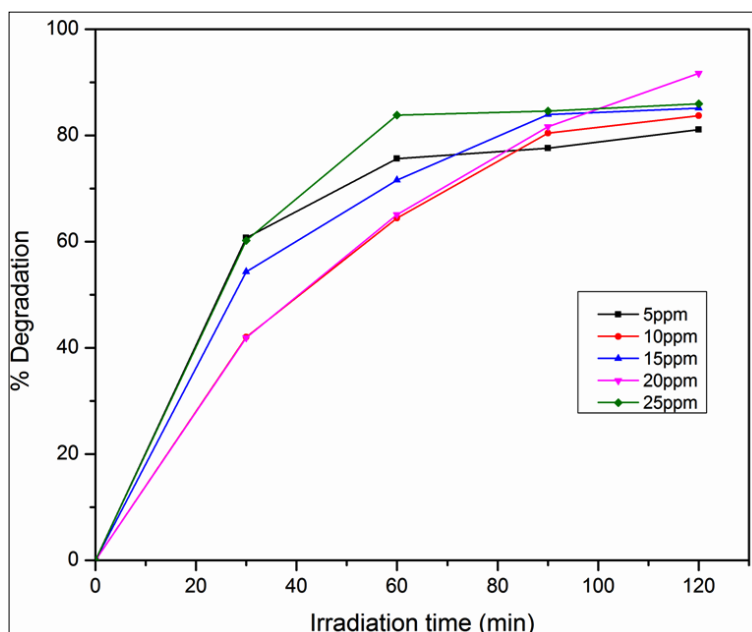
**Fig 7:** Variation of percentage degradation after 120min irradiation as a function of catalyst loading

#### Effect of dye concentration

The probability of formation of hydroxyl radicals (OH<sup>•</sup>) on the catalyst surface and those radicals reacting with the dye molecules directly influence the degradation rate. As the initial concentration of the dye increases, the interaction of OH radical with dye decreases and the light photons are largely absorbed by the dye molecules and prevented from reaching the catalyst surface. So, the degradation efficiency

of the dye decreases<sup>[19]</sup>. Hence, increased dye concentration reduces the light penetration and decreases the relative formation of hydroxyl radicals and superoxide radical anions leading to the decreased photodegradation efficiency. It is evident from the Fig.8 that as the initial concentration of the dye was varied from 5 ppm to 25 ppm in increments of 5 ppm at a constant catalyst loading of 0.04 g/100 mL it is seen that at 20 ppm there is maximum dye degradation. In

this way, the optimum dye concentration was fixed as 20 ppm.



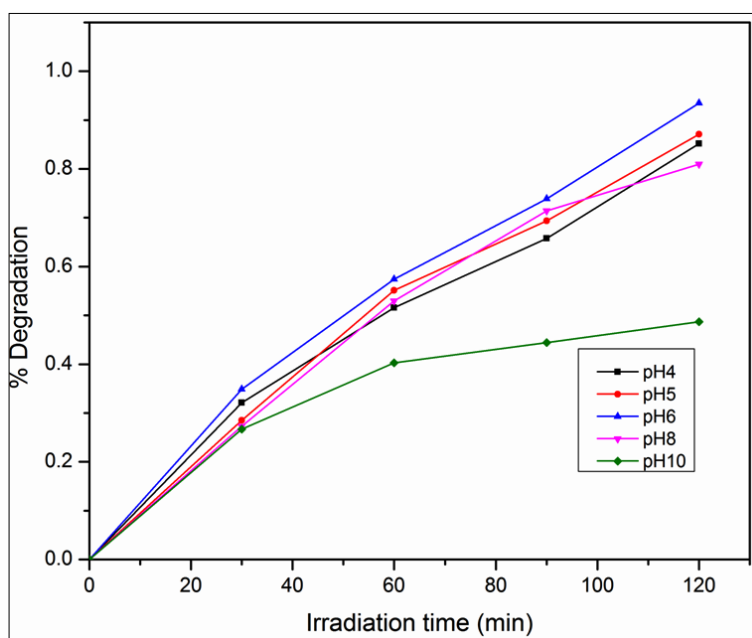
**Fig 8:** Variation of percentage degradation after 120 min irradiation as a function of dye concentration

### Effect of pH

pH changes influence the adsorption of dye molecules onto the  $\text{TiO}_2$  surfaces. So, the effect of solution pH on dye degradation has been investigated in the range 5-9. It is evident from Fig.9 that as pH is increased from 5-9, there is an initial increase in the degradation values upto pH 6 followed by a decrease in rate of degradation.

$\text{TiO}_2$  is reported to have higher oxidizing activity at lower pH, but excess  $\text{H}^+$  can decrease the reaction rate.  $\text{TiO}_2$  behaves as a strong Lewis acid due to the surface positive

charge. The anionic dye acts as a strong Lewis base and can easily adsorb on the positively charged catalyst surface. This favours the adsorption of the dye under acidic conditions while in alkaline conditions this complexation process is not favoured, presumably because of competitive adsorption by hydroxyl groups and the dye molecule in addition to the coulombic repulsion due to the negatively charged catalyst with the dye molecule. This reason can be attributed to the decreased degradation rate at alkaline conditions [20].



**Fig 9:** Variation of percentage degradation after 120 min irradiation as a function of solution pH

### Effect of dissolved oxygen

Another route to an enhanced photocatalytic activity is through external electron acceptors. The species that has a tendency to adsorb on the photocatalyst surface and become reduced by conduction band electrons are referred as

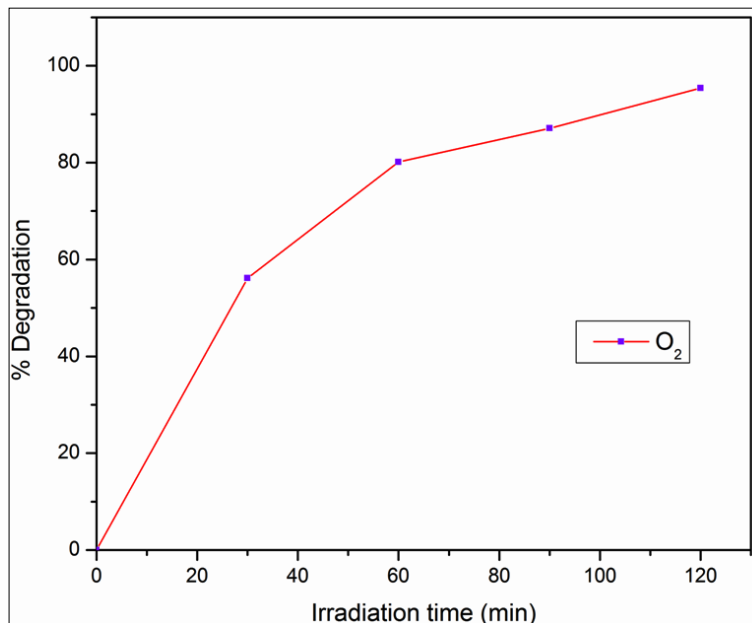
external electron acceptors. One of the simplest molecules that can act as electron acceptor in solution is molecular oxygen. The two main functions of molecular  $\text{O}_2$  in photocatalysis are i. its role as primary electron acceptor which is reduced to  $\text{O}_2^{\cdot-}$ , according to reaction.



and ii. Its ability to combine with organic radicals (That are formed upon oxidation of, or hydrogen abstraction from, organic solutes) forming peroxy radicals.

Depending on the structure of the organic substance, the formed organic peroxy radical may induce further oxidation.

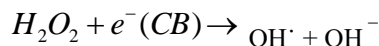
The degradation experiments were carried out in the presence of atmospheric  $\text{O}_2$  by taking rose bengal (20 ppm)  $\text{Cu-TiO}_2$  (0.04 g) at  $\text{pH}$  (6) under sunlight illumination. Fig.10 shows that 100% percent dye degradation was achieved in 120 minutes.



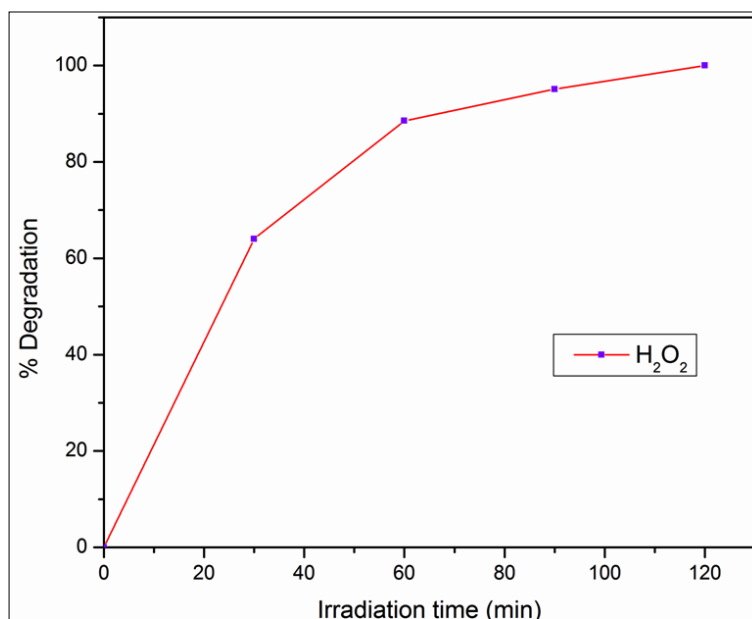
**Fig.10. Effect of dissolved oxygen on dye degradation at optimum conditions**

#### Effect of hydrogen peroxide

Researches show that peroxides significantly improve the rates and efficiencies of photoassisted degradation of organic substrates. One-electron reduction of  $\text{H}_2\text{O}_2$  produces a hydroxide ion and an additional hydroxyl radical as per the reaction given below. Hence,  $\text{H}_2\text{O}_2$  is also a direct source of hydroxyl radicals which boosts the photocatalytic activity more efficiently than  $\text{O}_2$ .



Thus, slightly enhanced degradation with  $\text{H}_2\text{O}_2$  when compared to that in the presence of oxygen was observed as shown in Fig.11 and 100% degradation was achieved in 120 minutes.



**Fig 11: Effect of hydrogen peroxide on dye degradation at optimum conditions**

### Sono-photocatalytic degradation

Ultrasound in a liquid induces cavitation which includes nucleation, growth and collapse of bubbles that generates extremely localised high temperature. The consequence of this is the cleavage of dissolved oxygen molecules and water molecules. The  $H^{\bullet}$ ,  $OH^{\bullet}$  and  $O^{\bullet}$  radicals formed during this process will react with each other as well as with  $H_2O$  and  $O_2$  forming  $HO_2$  and  $H_2O_2$  that is capable of degrading the pollutant.

The deagglomeration of the aggregate catalyst particles brought out by ultrasound can also be considered as a reason for the enhanced degradation rate [21]. The synergy effect of ultrasonic irradiation and light was analysed by carrying out the sono-photocatalytic degradation of rose Bengal dye at optimum conditions and the results are presented in Fig.12 it is observed that 93.95% degradation was observed in 120 minutes in this case as against 93.65% degradation in 120 minutes in the absence of ultrasound.

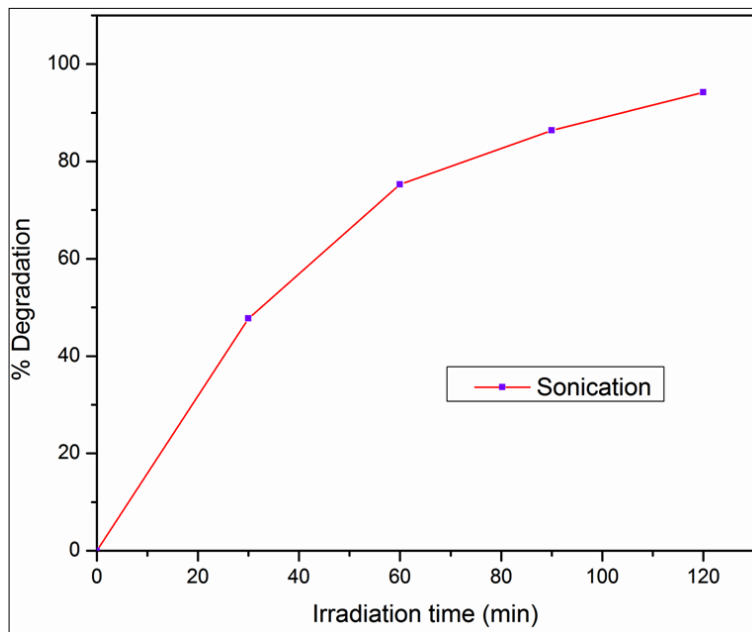


Fig 12: Sono-photocatalytic degradation of dye at optimum conditions

### Degradation of dye during the course of the reaction

The percentage degradation of rose bengal dye achieved at (20 ppm) under sunlight in the presence of Cu-TiO<sub>2</sub> photocatalyst (0.04 g/100 mL) at pH 6 is shown in Fig.14

and the degradation spectra of the dye in the presence of Cu-TiO<sub>2</sub> is shown in Fig. 13. It was observed that as the exposure time increased, the absorbance of the spectra rapidly decreased and reached its minimum at 120 min.

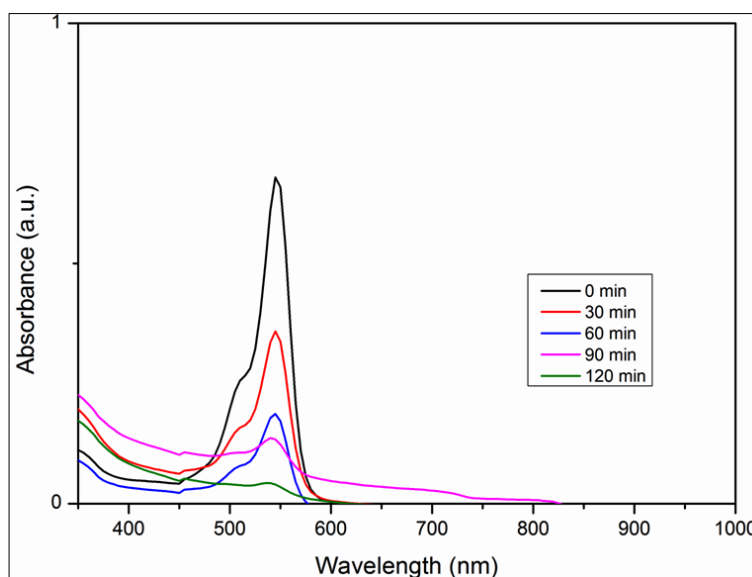


Fig 13: Time dependent photocatalytic degradation of rose bengal dye under sunlight irradiation using Cu-TiO<sub>2</sub>



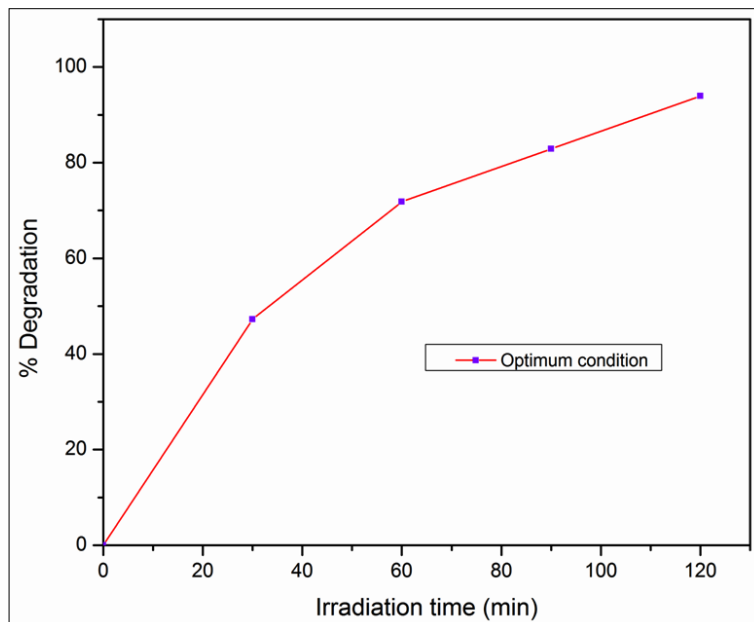


Fig 14: Dye degradation at optimum conditions

### Comparison of degradation rates of rose bengal

Fig.15 shows a comparative study of the degradation of rose Bengal carried out with Cu-TiO<sub>2</sub> at optimum conditions under sunlight, in the presence of oxygen, in the presence of

H<sub>2</sub>O<sub>2</sub> and on sonication. It is observed from the experimental results that maximum degradation is observed in the presence of H<sub>2</sub>O<sub>2</sub> followed by oxygen, sonication and under optimum conditions.

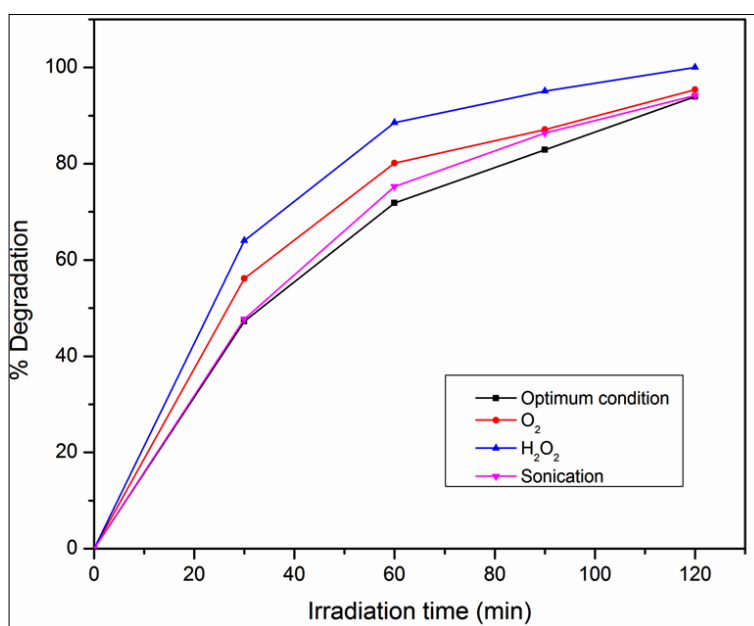


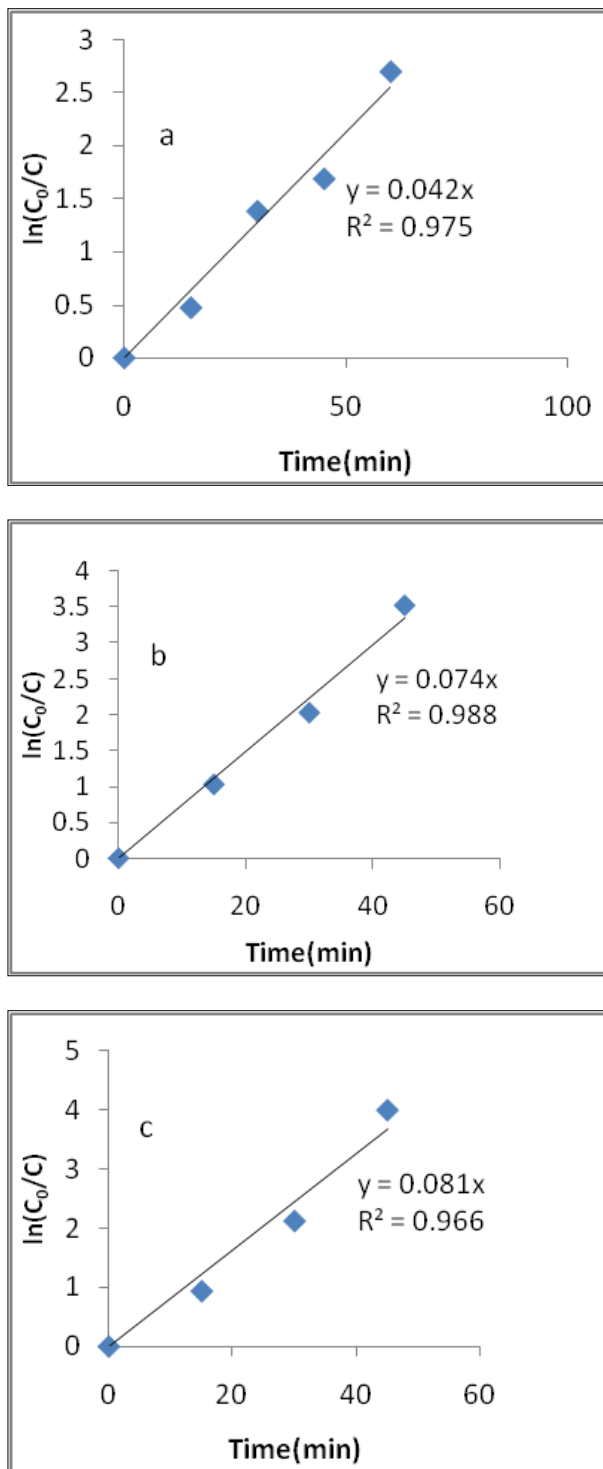
Fig 15: Comparative study of degradation of rose bengal under different operational parameters

### Kinetics of the photocatalytic degradation of rose bengal

In order to determine the order of the reaction, the photo degradation reaction of rose bengal (15 ppm) with photo catalyst (0.06 g) was carried out at pH (6) in sunlight illumination under different conditions and the kinetics plot is shown in Fig.16.

When a graph is plotted between  $\ln C_0/C$  and irradiation time a straight line is obtained in all case.

The regression coefficient  $R^2$  of the experimental values were found to be 0.975, 0.988, and 0.966 when dye degradation was carried out a. at optimum conditions with Cu-TiO<sub>2</sub> alone, b. along with dissolved oxygen and c. along with H<sub>2</sub>O<sub>2</sub> respectively. This confirms that the degradation of the dye molecule obeys pseudo first order linear kinetics.



**Fig 16:** Kinetics plots for the photodegradation of rose bengal dye at a. optimum conditions b. optimum conditions and  $O_2$  c. optimum conditions and  $H_2O_2$

#### Measurement of COD

The Chemical Oxygen Demand (COD) was determined by using the standard dichromate method. The COD varies during the photo catalytic degradation of rose bengal (15 ppm, 100 mL).

The suspension at optimum conditions was irradiated for 2 hours. The proficiency of dye mineralization was estimated. The percentage mineralization was found to be 94.59% after 2 h.

#### Recycling of photocatalyst

To apply photo catalysis on a large scale, the operating cost is a key factor and in this scenario the recycling of photocatalysts becomes important as it cuts down the operating costs to an affordable level. The reusability of the photocatalyst was checked by carrying out the degradation of the rose bengal dye using the recycled catalyst for three more cycles. It was found that the catalyst could be used for one more cycle without much loss in efficiency and after that there was a decrease in efficiency of degradation as obvious from Fig 17.

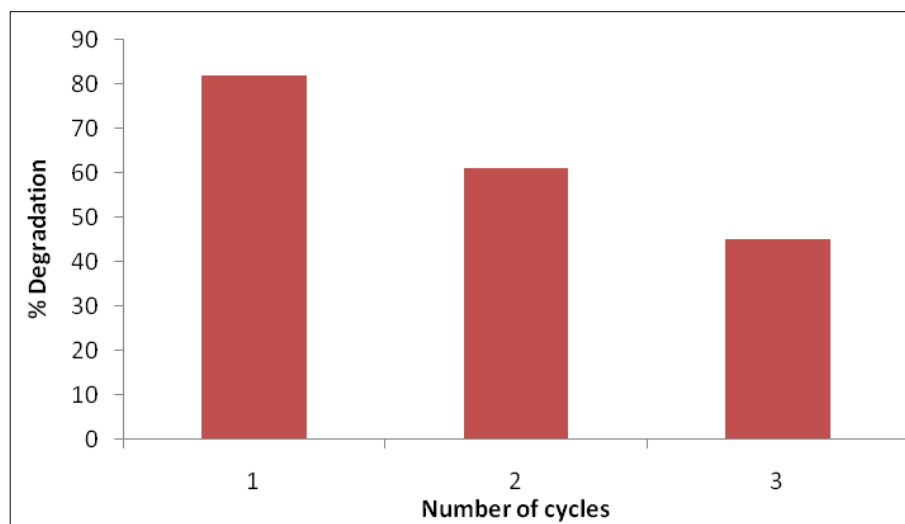


Fig 17: Degradation efficiency of recycled Cu-TiO<sub>2</sub> photocatalyst

### Conclusion

The transition metal ion Copper doped Titania nanoparticles were used to photodegrade the hazardous Rosebengal dye. It has been found that the optimum conditions for the dye degradation were 20ppm dye concentration, 0.04g catalyst loading and pH 6. The maximum dye degradation was observed on addition of Hydrogen peroxide. The catalyst was efficient only for two cycles. The research work opens up the possibility of using Cu-TiO<sub>2</sub> as a photocatalyst for photodegradation of other hazardous dyes that are toxic to the environment.

### Reference

- Ola O, Maroto-Valer MM. Review of material design and reactor engineering on TiO<sub>2</sub> photocatalysis for CO<sub>2</sub> reduction. *J Photochem Photobiol C Photochem Rev.* 2015;24:16-42. <https://doi.org/10.1016/j.jphotochemrev.2015.06.001>.
- Sahu M, Biswas P. Single-step processing of copper-doped titania nanomaterials in a flame aerosol reactor. *Nanoscale Res Lett.* 2011;6:441. <https://doi.org/10.1186/1556-276X-6-441>.
- Thambiliyagodage C, Usgodaarachchi L. Photocatalytic activity of N, Fe, and Cu co-doped TiO<sub>2</sub> nanoparticles under sunlight. *Curr Res Green Sustain Chem.* 2021;4:100186. <https://doi.org/10.1016/j.crgsc.2021.100186>.
- Arulkumar E, Thanikaikarasan S, Rajkumar S, Wondimu W. Influence of solution pH dependency on structure, optical, and photoelectrochemical characteristics of SILAR deposited copper oxide thin films. *Heliyon.* 2024;10(13):e33579. <https://doi.org/10.1016/j.heliyon.2024.e33579>.
- Adamu A, Isaacs M, Boodhoo K, Abegao FR. Investigation of Cu/TiO<sub>2</sub> synthesis methods and conditions for CO<sub>2</sub> photocatalytic reduction via conversion of bicarbonate/carbonate to formate. *J CO<sub>2</sub> Util.* 2023;70:102428. <https://doi.org/10.1016/j.jcou.2023.102428>.
- Dozzi MV, Selli E. Doping TiO<sub>2</sub> with p-block elements: Effects on photocatalytic activity. *J Photochem Photobiol C Photochem Rev.* 2013;14:13-28. <https://doi.org/10.1016/j.jphotochemrev.2012.09.002>.
- Abraham C, Devi LG. Incorporation of Fe<sup>3+</sup> ions into the W<sup>6+</sup> and N<sup>3-</sup> doped TiO<sub>2</sub>: Exploration of the crucial role of Fe<sup>3+</sup> dopant ion and correlation of adsorption characteristics with reaction dynamics. *Surf Sci.* 2022;717:121986. <https://doi.org/10.1016/j.susc.2021.121986>.
- Thakur N, Thakur N, Kumar A, *et al.* A critical review on the recent trends of photocatalytic, antibacterial, antioxidant, and nanohybrid applications of anatase and rutile TiO<sub>2</sub> nanoparticles. *Sci Total Environ.* 2024;914:169815. <https://doi.org/10.1016/j.scitotenv.2023.169815>.
- Mikrut P, Kobielski M, Indyka P, Macyk W. Photocatalytic activity of TiO<sub>2</sub> polymorph B revisited: physical, redox, spectroscopic, and photochemical properties of TiO<sub>2</sub>(B)/anatase series of titanium dioxide materials. *Mater Today Sustain.* 2020;10:100052. <https://doi.org/10.1016/j.mtsust.2020.100052>.
- Etacheri V, Di Valentin C, Schneider J, Bahnemann D, Pillai SC. Visible-light activation of TiO<sub>2</sub> photocatalysts: Advances in theory and experiments. *J Photochem Photobiol C Photochem Rev.* 2015;25:1-29. <https://doi.org/10.1016/j.jphotochemrev.2015.08.003>.
- Ikram M, Umar E, Raza A, *et al.* Dye degradation performance, bactericidal behavior, and molecular docking analysis of Cu-doped TiO<sub>2</sub> nanoparticles. *RSC Adv.* 2020;10(41):24215-24233. <https://doi.org/10.1039/d0ra04851h>.
- Gawande MB, Goswami A, Felpin FX, *et al.* Cu and Cu-based nanoparticles: Synthesis and applications in catalysis. *Chem Rev.* 2016;116(6):3722-3811. <https://doi.org/10.1021/acs.chemrev.5b00482>.
- Janczarek M, Kowalska E. On the origin of enhanced photocatalytic activity of copper-modified titania in the oxidative reaction systems. *Catalysts.* 2017;7(11):317. <https://doi.org/10.3390/catal7110317>.
- Divya N, Bansal A, Jana AK. Photocatalytic degradation of azo dye Orange II in aqueous solutions using copper-impregnated titania. *Int J Environ Sci Technol.* 2013;10:1265-1274. <https://doi.org/10.1007/s13762-013-0238-8>.
- Mugundan S, Rajamannan B, Viruthagiri G, *et al.* Synthesis and characterization of undoped and cobalt-doped TiO<sub>2</sub> nanoparticles via sol-gel technique. *Appl Nanosci.* 2015;5:449-456.

- <https://doi.org/10.1007/s13204-014-0337-y>.
16. Ferrari-Lima AM, De Souza RP, Mendes SS, *et al.* Photodegradation of benzene, toluene, and xylenes under visible light applying N-doped mixed TiO<sub>2</sub> and ZnO catalysts. *Catal Today*. 2015;241:40-46.
  17. Nagaraja R, Kottam N, Girija CR, Nagabhushana BM. Photocatalytic degradation of Rhodamine B dye under UV/solar light using ZnO nanopowder synthesized by solution combustion route. *Powder Technol*. 2012;215-216:91-97.  
<https://doi.org/10.1016/j.powtec.2011.09.014>.
  18. Sahoo C, Gupta AK, Pal A. Photocatalytic degradation of Methyl Red dye in aqueous solutions under UV irradiation using Ag<sup>+</sup> doped TiO<sub>2</sub>. *Desalination*. 2005;181(1-3):91-100.  
<https://doi.org/10.1016/j.desal.2005.02.014>.
  19. Rupa AV, Manikandan D, Divakar D, Sivakumar T. Effect of deposition of Ag on TiO<sub>2</sub> nanoparticles on the photodegradation of Reactive Yellow-17. *J Hazard Mater*. 2007;147(3):906-913.
  20. Rauf MA, Meetani MA, Hisaindee S. An overview on the photocatalytic degradation of azo dyes in the presence of TiO<sub>2</sub> doped with selective transition metals. *Desalination*. 2011;276(1-3):13-27.  
<https://doi.org/10.1016/j.desal.2011.03.071>.
  21. Anju SG, Yesodharan S, Yesodharan EP. Zinc oxide mediated sonophotocatalytic degradation of phenol in water. *Chem Eng J*. 2012;189-190:84-93.  
<https://doi.org/10.1016/j.cej.2012.02.032>.