

*Full Length Research Paper*

## Novel nano photocatalyst for the degradation of sky blue 5b textile dye

Zulfiqar Ali<sup>1,2</sup>, Syed Tajammul Hussain<sup>2</sup>, Muhammad Nawaz Chaudhry<sup>1</sup>, Syeda Adila Batool<sup>3</sup>, and Tariq Mahmood<sup>2\*</sup>

<sup>1</sup>College of Earth and Environmental Sciences, University of the Punjab, Lahore, Pakistan.

<sup>2</sup>Nano Science and Catalysis Division, National Centre for Physics, Islamabad, Pakistan.

<sup>3</sup>Department of Space Science Punjab University Lahore, Pakistan.

Accepted 10 June, 2013

**A new Nano photocatalyst, CuO-Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>-TiO<sub>2</sub> was synthesized by co-precipitation for the removal of textile dye under ultra violet and direct sunlight. The synthesized catalyst was characterized by using X-rays diffraction, X-rays fluorescent, thermo gravimetric analysis, DRS, scanning electron microscopy and EDX. The dopants reduced the recombination of  $e_{cb}^-$  and  $h_{vb}^+$  and decreased the band gap of TiO<sub>2</sub> from 3.25eV to 1.38eV. Due to this change, light absorption increased under sun light. The photocatalytic activity of the degraded samples of direct sky blue5B was analyzed by UV/Visible spectrophotometer. The results showed an enhanced photocatalytic activity under sun light about 96.8% in time duration of 100 min. It was also found that the degraded samples followed the pseudo first order kinetic model. This technique is cheap, easy and novel for the treatment of textile industrial waste water. In present energy crises of the world it can replace old expensive technologies.**

**Key words:** Nano photocatalysis, direct sky blue5B, photocatalytic degradation, textile dyes, nano catalytic characterization.

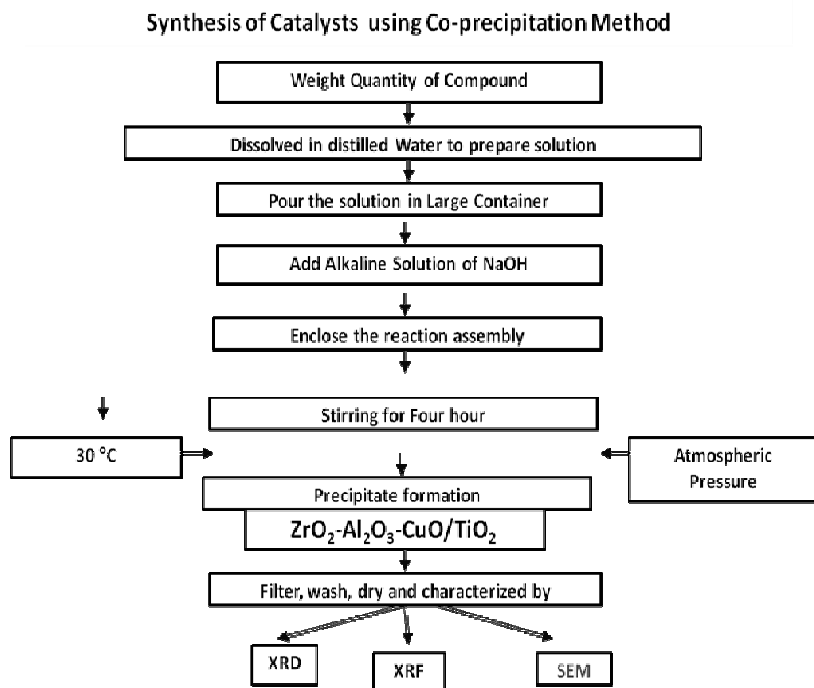
### INTRODUCTION

The extensive disposal of textile and other industrial waste water that contains organic dyes creates a severe contamination throughout the world. About 1 to 20% of the total dyes produced globally are lost during dyeing and other processes. These dyes are released into water as textile effluent (Weber and Stickney, 1993; Rafols and Barcelo, 1997; Houas et al., 2001; Kansal et al., 2009). These organic dyes weathered through oxidation; hydrolysis and other chemical reactions taking place in the wastewater phase can produce toxic metabolites (Bianco-Prevot et al., 2001; Neppolian et al., 2002; Pagga and Brown, 1986; Saquib and Muneer, 2003). These products produce unfavorable effects on human and animal health (Davydov et al., 2001) which requires a suitable treatment of wastewater for environmental

contamination prevention. After the development of novel heterogeneous photocatalytic, oxidation process in the 1970s is of special interest particularly under solar irradiation (Malato et al., 2002). In these processes hydroxyl radicals (OH<sup>•</sup>) and superoxide anion (O<sub>2</sub><sup>•-</sup>), are produced due to absorption of radiation by semiconductor catalyst in contact with water and oxygen (Herrmann, 1999). Amongst a variety of catalysts, semiconductor photocatalyst containing titanium dioxide (TiO<sub>2</sub>) is widely used due to its strong oxidizing power, non-toxicity and long-term photo stability (Pirkanniemi and Sillanpaa, 2002).

On the other hand, the photocatalytic efficiency of TiO<sub>2</sub> regarding the degradation of dyes reduces significantly due to the high recombination ratio of photo-induced

\*Corresponding author. E-mail: [tariqm20002000@yahoo.com](mailto:tariqm20002000@yahoo.com). Tel: +92-333-5178543, Fax: +92-512077395.



**Figure 1.** Summary of synthesis of photocatalyst  $\text{CuO-ZrO}_2\text{-Al}_2\text{O}_3\text{-TiO}_2$ .

electrons ( $e^-$ ) and holes ( $h^+$ ), which are produced due to irradiation under ultraviolet (UV) light (Bao et al., 2004; Malato et al., 2003). For  $\text{TiO}_2$  the ideal wavelength regarding the band-gap energy is of 3.2 eV, which is at near-ultraviolet radiation (300nm) (Adewuyi, 2005; Meena and Pachwarya, 2009; Poullos and Aetopoulou, 2013). Thus the industrial efficacy of this process is bound to limited applications due to the need of ultra violet excitation energy source. As the solar light contains only 5% UV spectrum, hence further research in future is needed for the development of  $\text{TiO}_2$  materials which is able to capture more amount of solar energy spectrum (Sonawane et al., 2004). Therefore the development of solar light active modified  $\text{TiO}_2$  photo-catalyst with high catalytic efficiency in the visible region for the treatment of waste water is always of great interest and demand in both academic and commercial sectors. This paper aims at organic dyes degradation in wastewater treatment by modified  $\text{TiO}_2$  photocatalytic systems. In particular, it focuses on enhancing the degradation efficiency of textile dyes by the use of visible light region, and improving the retrieval and reuse of  $\text{TiO}_2$  photo-catalysts.

## MATERIALS AND METHODS

$\text{TiO}_2$  (Degussa 25) was purchased from Sigma-Aldrich. Copper Nitrate, Zirconium Nitrate and Aluminum Nitrate (99.9% pure) were purchased from Merck Germany. The dye direct sky blue5B was purchased from Sigma-Aldrich. These chemicals were AR grade and there was no need of further purification before use.

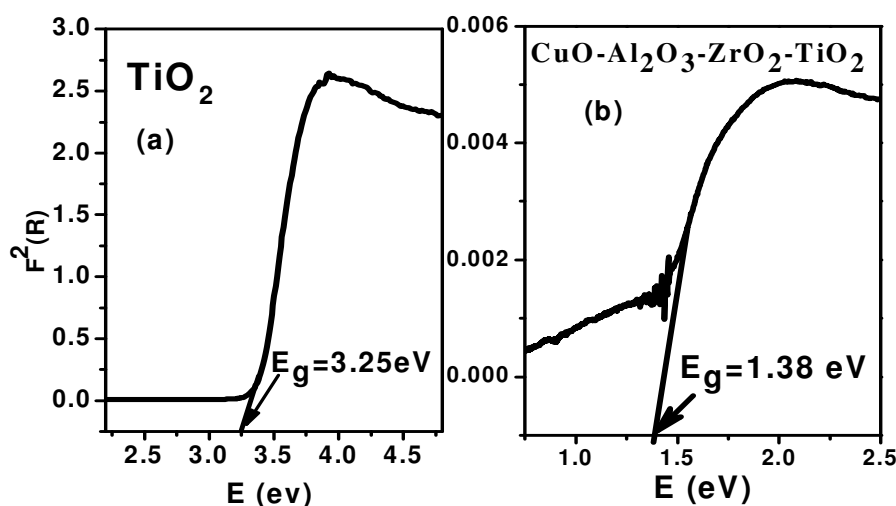
The catalyst was prepared by a facile co-precipitation method as shown in Figure 1.  $\text{CuO-ZrO}_2\text{-Al}_2\text{O}_3\text{-TiO}_2$  composite was synthesized by co-precipitation sedimentation method using ammonium carbonate as precipitating agent (Adewuyi, 2005). In this synthesis, the appropriate amount of  $\text{TiO}_2$  (70 g) was suspended in  $500 \text{ cm}^3$  of deionized water and homogenized for 30 min by stirring. Then equimolar copper nitrate, zirconium nitrate and aluminum nitrate each 10 g were mixed and dissolved in  $100 \text{ cm}^3$  deionized water. The solution was homogenized by standard method. The mixture of these nitrates was then slowly mixed with  $\text{TiO}_2$  solution and homogenized. The suspension, was precipitated against drop wise addition of  $(\text{NH}_4)_2\text{CO}_3$ . The precipitate was then dried overnight with continuous stirring at room temperature. The resultant precipitate was then washed and filtered until the pH of the solution reached near 7 and then dried at  $100^\circ\text{C}$  overnight. It was then calcinated at  $400^\circ\text{C}$  for 4 h in Muffle furnace. The resultant material was grinded and sieved. The prepared sample was characterized by XRD, SEM (Mahmood, 2011), XRF, EDX, TGA and RBS.

The band gap of synthesized catalyst was found by UV/Vis/NIR Spectrometer Lambda 950 diffused reflectance spectroscopy. The Powder XRD of the catalyst was investigated by using Scintag XDS 2000 diffractometer with Cu K $\alpha$  radiation source. The XRD analysis was performed from  $0^\circ$  to  $90^\circ$  ( $2\theta$ ) for the confirmation of structure and crystalline phases. By applying Scherer's equation, the crystallite size was evaluated. For the investigation of morphology of synthesized catalyst, Scanning Electron Microscope (JEOL, JSM 6490-A) was used. The X-Ray fluorescence (JEOL, Model JSX 3202M)) was used for the elemental analysis. The TGA was performed by Perkin Elmer Diamond Series, USA. The photo-degradation of the solution of dye direct sky blue5B was investigated by UV/Vis Spectrometer (Perkin Elmer Lambda 25).

The solution containing different concentration of dye and dosage of catalyst was exposed to UV and solar irradiation. The experimental setup under solar light is shown in Figure 2. The dye



**Figure 2.** Photocatalytic degradation of direct sky blue5B dye experimental set up.



**Figure 3.** Band gap of  $\text{TiO}_2$  and  $\text{CuO-ZrO}_2\text{-Al}_2\text{O}_3\text{-TiO}_2$  nano composite.

solution was taken in a beaker with a magnetic stirrer for stirring and was exposed to the solar irradiation. 4 mirrors were used for focusing the sunlight to enhance the intensity of light. The degraded sample solution of 5 ml was taken after each 10 min interval up to 100 min. After filtering the sample solution, analyzed by UV/V is spectrometer. The removal percent of the dye direct sky blue5B samples were calculated by applying the formula:

$$\text{Degradation/Decolonization (\%)} = (C_i - C_o) / C_o \times 100 = (A_i - A_o) / A_o \times 100$$

Where  $C_o$  and  $C_i$  are the concentrations while  $A_o$  and  $A_i$  are the absorbance values of the dye solution before and after the exposure to sunlight respectively.

## RESULTS AND DISCUSSION

The band gap of the synthesized powder was evaluated by UV-Visible Diffuse Reflectance Spectroscopy (DRS) in

the solid phase. The band gap analysis plots of Kubelka-Munk function versus energy for  $\text{TiO}_2$  and the synthesized sample is shown in Figure 3. The band gap of  $\text{TiO}_2$  is 3.25 eV which shows its anatase character. When  $\text{TiO}_2$  is modified by  $\text{CuO-Al}_2\text{O}_3\text{-ZrO}_2$  its band gap is decreased from 3.25 eV to 1.38 eV which is clear in Figure 3.

The shifting of the band gap from higher to lower wavelength is probably due to enhanced d-d and charge transfer transitions in the solid phase.

A comparison of XRD pattern of the synthesized composite photocatalyst is presented in Figure 4, where it can be observed that the reflections arising from  $\text{TiO}_2$  are dominant in the XRD pattern composite. The XRD patterns were matched with the standard pattern for the  $\text{TiO}_2$  (JCPDS - 71-1168). The reflections at  $25.195^\circ$ ,  $47.772^\circ$ ,  $53.704^\circ$ ,  $54.851^\circ$  and  $62.521^\circ$  represent  $\text{TiO}_2$

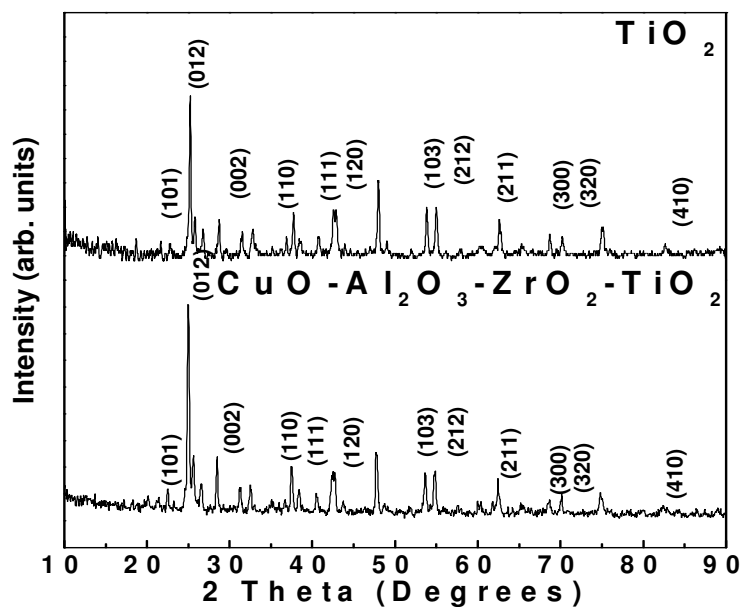


Figure 4. XRD Spectrum of  $\text{TiO}_2$  and  $\text{CuO-ZrO}_2\text{-Al}_2\text{O}_3\text{-TiO}_2$  nano composite.

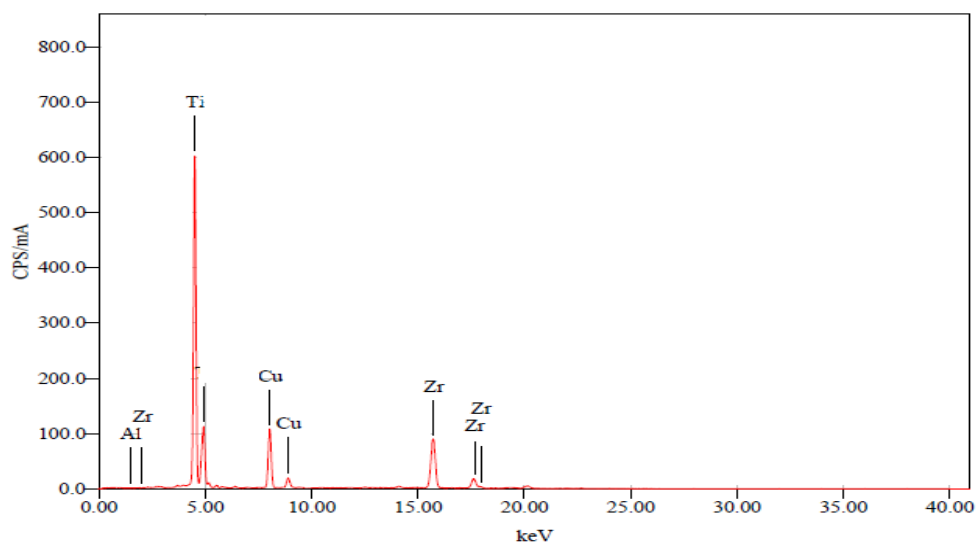


Figure 5. XRF peaks of photocatalyst  $\text{CuO-Al}_2\text{O}_3\text{-ZrO}_2\text{-TiO}_2$ .

(JCPDS -71 - 1168) whereas the reflections at  $26.634^\circ$ ,  $32.281^\circ$  and  $74.398^\circ$  confirmed the presence of  $\text{CuO}$  phase (JCPDS - 34 - 1354). Similarly, the reflections at  $2\theta$  positions of  $35.190^\circ$  and  $67.883^\circ$  were matched with the  $\text{Al}_2\text{O}_3$  (JCPDS - 34 - 0493). Low intensity peaks at the  $2\theta$  positions of  $38.362^\circ$ ,  $60.05^\circ$  and  $70.369^\circ$  were identical with the standard pattern of  $\text{ZrO}_2$  (JCPDS - 17 - 0385). The average crystallite sizes as calculated by Scherrer's equation using FWHM values of most intense peaks, was 29 nm.

The elemental composition of the synthesized sample  $\text{CuO-Al}_2\text{O}_3\text{-ZrO}_2/\text{TiO}_2$  was confirmed by the X-ray Fluorescence analysis shown in Figure 5. It is found that all elements of the prepared catalyst were present and the major peak of  $\text{TiO}_2$  shows that it is present as a base element in the catalyst. It is also confirmed from the analysis that no other peak rather than these elements is present in the catalyst, which shows its purity.

The thermo gravimetric analysis curve shows the weight loss against temperature rise as shown in Figure 6.

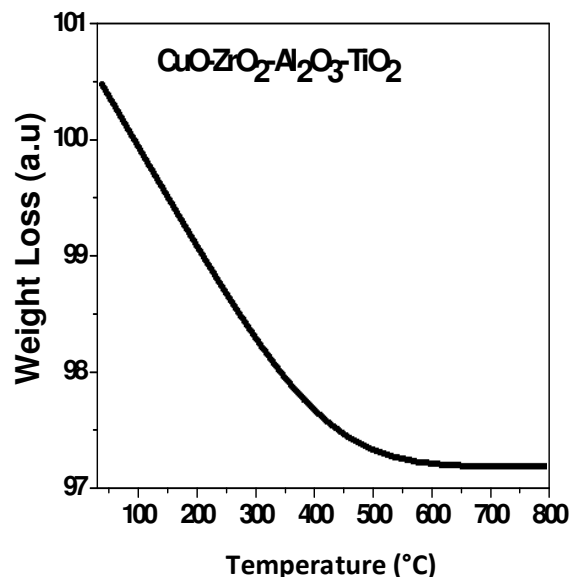


Figure 6. TGA of Photocatalyst (CuO-Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>-TiO<sub>2</sub>).

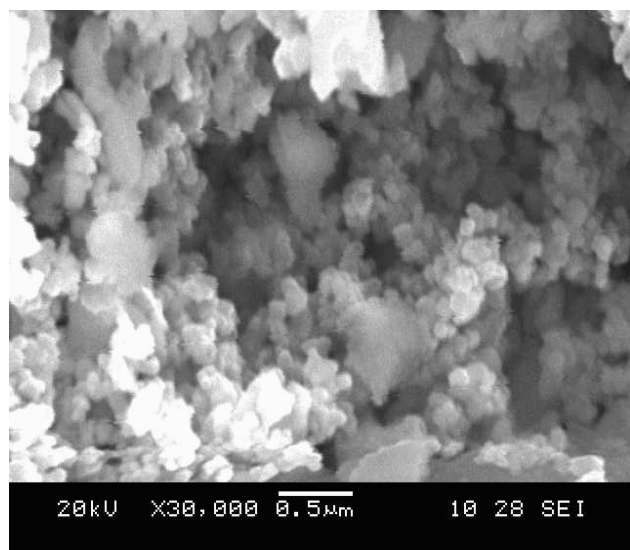


Figure 7. SEM of Photocatalyst (CuO-Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>-TiO<sub>2</sub>).

It was observed in the TGA curve of synthesized catalyst CuO-Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>-TiO<sub>2</sub>, there was a slight weight loss of about 2.49% in the temperature range of 100 °C to 600 °C, which corresponds to the removal of adsorbed water from the catalyst. The weight loss from 600 to 800 °C is about 0.134% which shows that the catalyst is thermally stable and suitable for photo degradation investigation.

The morphology of synthesized catalyst CuO-Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>-TiO<sub>2</sub> was evaluated by SEM as presented in Figure 7. The porous nano-aggregates can be clearly seen in micrograph. It was observed that the metal loading, in the form of oxides, have no significant effect on the

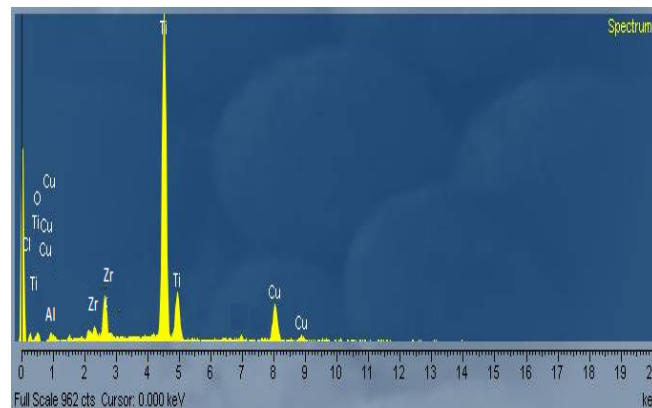


Figure 8. EDX peaks of Photocatalyst (CuO-Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>-TiO<sub>2</sub>).

morphology of TiO<sub>2</sub>, however a meek increase in the particle size is observed due to doping which is in accordance with XRD graph. Metal oxides can amend the surface of the catalyst by increasing the dispersion of active site. The sample composition is determined by the energy dispersive X-ray utility of SEM. The compositions obtained by EDX (Figure 8) and XRF (Figure 5) were in accordance with the theoretical values and within the limits of experimental errors.

The proficient degradation by a photocatalyst in aqueous medium depends upon its ability of absorbing light and its less rate of recombination of electron-hole pair. This ability promotes the generation of oxidizing hydroxyl (OH<sup>•</sup>) radicals that requires suitable band gap energy compared to that of incident photons. To enhance the generation of hydroxyl radicals is dependent on charge carrier recombination rate. The drawback of TiO<sub>2</sub> is that it has high recombination rate suffers, as the life time of excited states is of the order of 10<sup>-9</sup> to 10<sup>-12</sup> s, which in turns suppresses the formation of oxidizing species (Hoffmann et al., 1995). The other drawback is that, it has a wide band gap of 3.2eV, which lies in near-UV radiation (300 nm) (Adewuyi, 2005). This reduces its ability to absorb the photons in the visible spectrum that is, E<sub>photon</sub> ≤ 380 nm limits its use in the sunlight having major portion above 380 nm. The matter of recombination inhibition and light harvesting in the visible region can be made effective through the modification of the surface of TiO<sub>2</sub> by composite formation. This will induce the charge separation through the interfacial charge transfer between the allowed energy states. The possible mechanisms of recombination inhibition through mutual charge transfer between the interfacial energy states of the base material, TiO<sub>2</sub> and the components of the synthesized composites that is, CuO, Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub>.

It is clear in Figure 9a that, when 100ppm solution of the dye was irradiated by a UV source (8 W lamp) by using TiO<sub>2</sub> (5 mg/L) as a catalyst, the degradation rate was about 65%, but under the same concentration of dye and catalyst under solar irradiation, the degradation rate

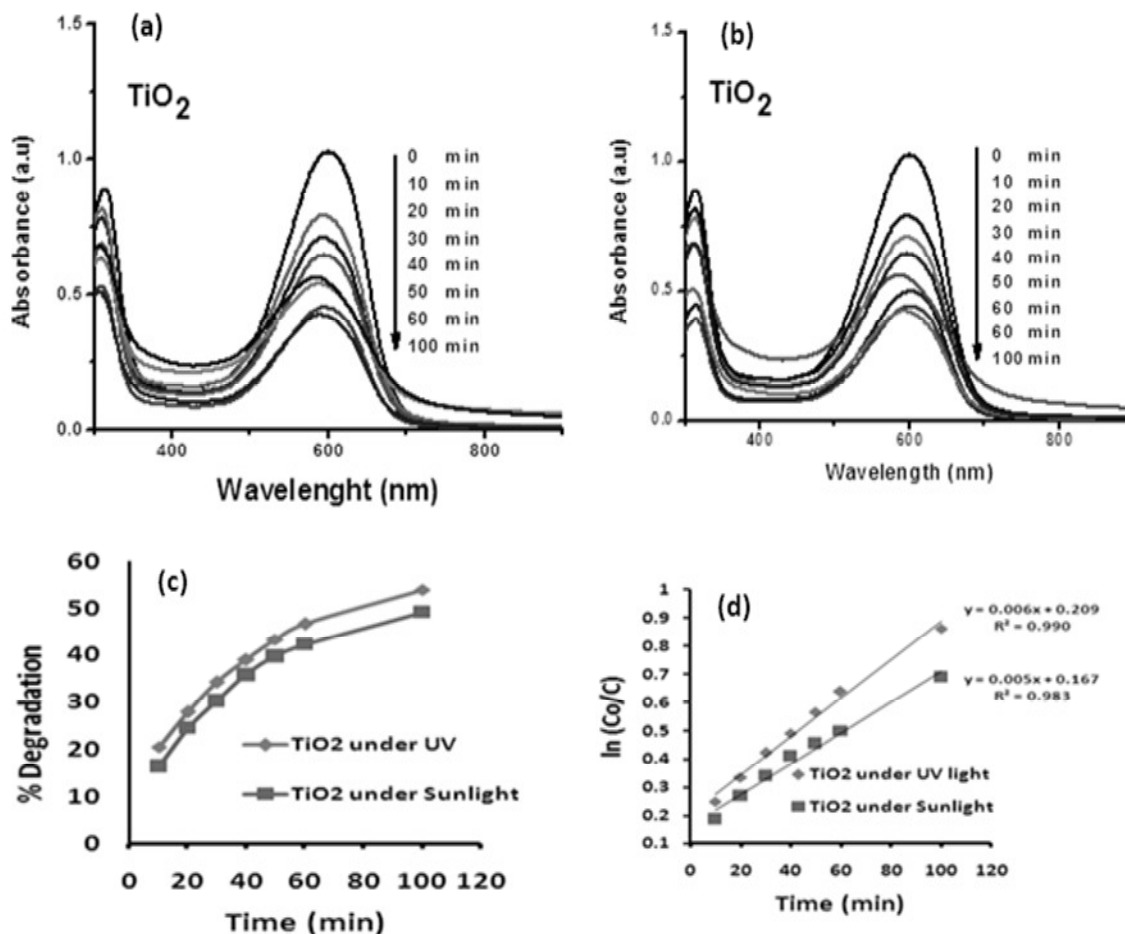


Figure 9. Graphical presentation of TiO<sub>2</sub> based degradation of Textile dye (Direct sky blue5B Dye).

**Table 1.** Comparisons between degradation rates of Direct sky blue5B Dye by TiO<sub>2</sub> and synthesized novel nano catalyst (CuO-Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>-TiO<sub>2</sub>) under UV & Sunlight.

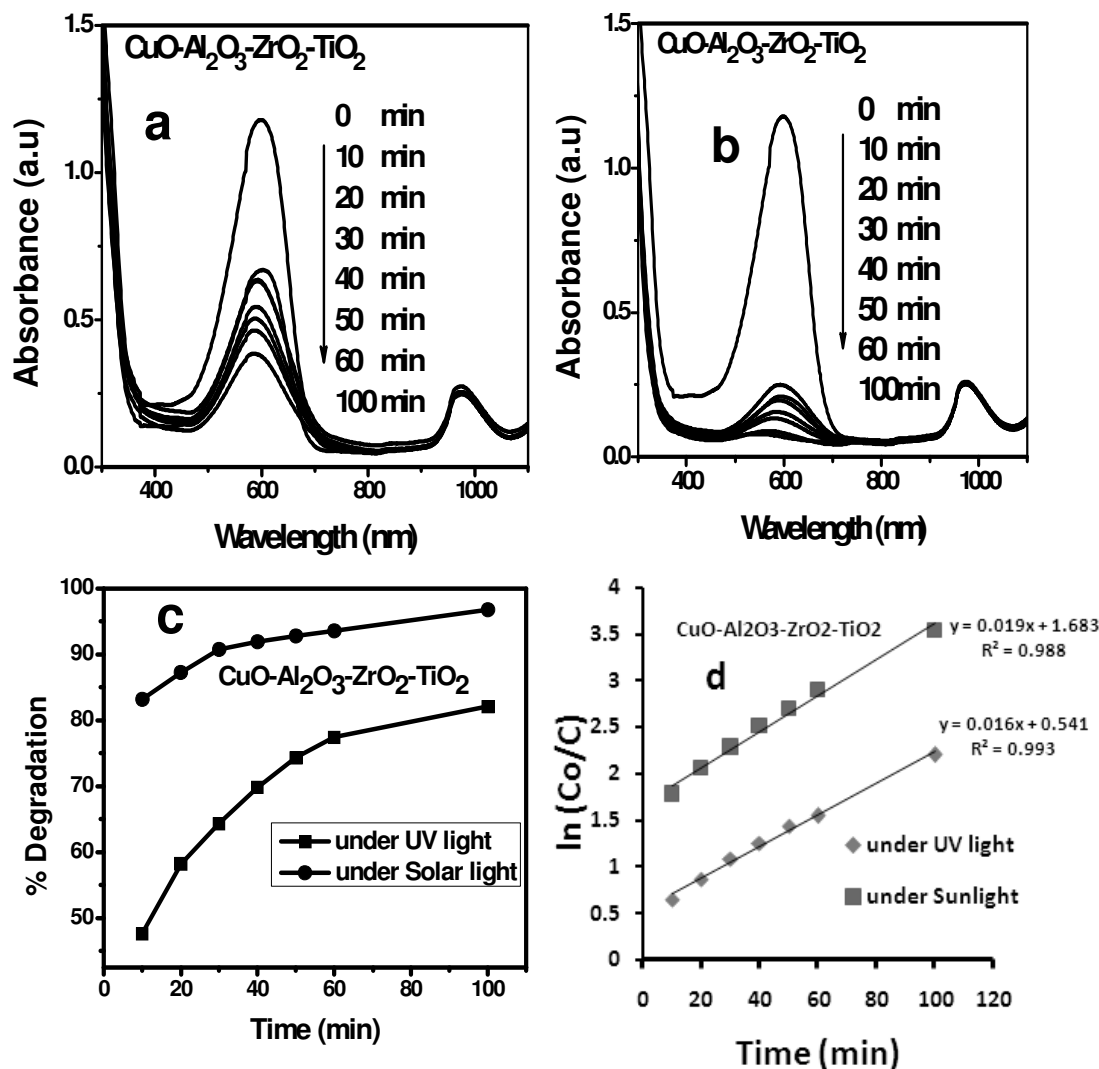
Catalyst	Degradation rate (%) under UV light (100 min)	Degradation rate (%) under solar light (100 min)
TiO <sub>2</sub>	65	58
CuO-Al <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub> -TiO <sub>2</sub>	82.1	96.8

decreases by 58% (Figure 9b). This is due to the fact that the band gap of TiO<sub>2</sub> (3.2 eV) lies in the UV region (Table. 1).

It is clear from Table 1, the degradation rate of TiO<sub>2</sub> is 65% under UV light for 100 min duration, but the degradation rate of TiO<sub>2</sub> is 58% for the same duration of time. The less degradation rate under sunlight is due to band gap of TiO<sub>2</sub> (3.25 eV) which lies in the UV region. But when the TiO<sub>2</sub> is modified by CuO-Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> the band gap was reduced from 3.25 eV to 1.38 eV, which lies in the visible spectrum. From the result in Table 1, it is clear that the catalytic degradation efficiency enhanced up to 96.8% under solar irradiation, rather than 82.1%

under UV light (8W lamp) (Figure. 10).

The comparison of degradation profiles of direct sky blue5B in the presence of TiO<sub>2</sub> and the synthesized catalyst CuO-Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>-TiO<sub>2</sub> shows that as the dye direct sky blue5B is an azo dye with two absorption bands at  $\lambda = 598$  nm and  $\lambda = 313$  nm. The high intensity band with  $\lambda_{\text{max}} = 598$  nm wraps a region of 700 - 500 nm while the low intensity band at  $\lambda_{\text{max}} = 313$  nm covers a region of 370 - 260 nm. The slow response of TiO<sub>2</sub> under solar irradiation is mainly due to its ability to utilize only 5% of solar spectrum ability with additional hindrance due to the low intensity band of dye in 370 - 260 nm, which absorbs a significant number of photons making these



**Figure 10.** Graphical presentation of nano photocatalyst (CuO-Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>-TiO<sub>2</sub>) based degradation of textile dye (direct sky blue 5B dye).

inaccessible to TiO<sub>2</sub> thus causing a significant decrease in the degrading ability. As presented in Figure 9d, the kinetics of dye removal both in UV and under sunlight irradiation was evaluated by plotting ln (Co/C) against time. It is clear from the plots, the degradation of direct sky blue5B follows the pseudo-first order kinetics and the degradation rate depends on the concentration of dye with time.

## Conclusion

From this study it is concluded that photocatalytic activity of TiO<sub>2</sub> can be enhanced by its suitable modification of the absorbing surface. However the best possible efficiency of the multiple photocatalyst can be obtained by selecting a suitable modifier with well-matched

structure, morphological phase and chemical characteristics. It is also possible the photon initiated interfacial electron transfer between the allowed states of the semiconductors involved in the modified catalyst. Analysis of the synthesized catalyst pointed out that the dopants are very well dispersed in the anatase TiO<sub>2</sub>. Optical properties enhancement, greater surface area and high quantum efficiency resulted due to adopted methodology TiO<sub>2</sub> modification. The highly efficient CuO-Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>-TiO<sub>2</sub> nanoparticles of photocatalyst have extraordinary high activity in the degradation of direct sky blue5B under visible light irradiation. The use of visible light receptive nano photocatalysts are appropriate novel technique for the degradation of toxic organic pollutants and a cost effective way by using sunlight which is free of cost. Among other appropriate visible light active photocatalysts, CuO based systems are found to be a



better choice for the modification of  $\text{TiO}_2$  along with  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$ . Nano photocatalysts, due to their low-price, simple synthesis process, high stability, high activity towards photo-induced redox reactions and reducing power are the best choice for degradation of environmental pollutants.

## ACKNOWLEDGEMENTS

Author would like to acknowledge and extend his heartfelt gratitude to the persons who helped me for this research work. I also acknowledge Nanoscience and Catalysis Division, National Centre for Physics, Quaid-i-Azam University Islamabad, for providing me technical and analytical facilities.

## ABBREVIATIONS

**XRD**, X-Rays Diffraction; **XRF**, X-Rays Fluorescent; **TGA**, Thermo Gravimetric Analysis; **DRS**, Diffuse Reflectance Spectroscopy; **SEM**, Scanning Electron Microscope; **EDX**, Energy-Dispersive X-Ray Spectroscopy; **RBS**, Rutherford Back Scattering Ultra-Violet/Visible/Near-Infra Red Spectrophotometer) UV/Vis/NIR.

## REFERENCES

- Adewuyi YG (2005). Sonochemistry in environmental remediation 2. Heterogeneous sonophotocatalytic oxidation process for the treatment of pollutants in water. *Environ. Sci. Technol.* 39(22):8557–8570.
- Bao N, Feng X, Yang Z, Shen L, Lu X (2004). Highly efficient liquid-phase photooxidation of an azo dye methyl orange over novel nanostructured porous titanate-based fiber of self-supported radially aligned  $\text{H}_2\text{Ti}_6\text{O}_{17} \times 1.5\text{H}_2\text{O}$  nanorods. *Environ. Sci. Technol.* 38(9):2729–36.
- Bianco-Prevot AB, Baiocchi C, Brussino MC, Pramauro E, Savarino P, Augugliaro V, Marci G, Palmisano L (2001). Photocatalytic degradation of acid blue 80 in aqueous solutions containing  $\text{TiO}_2$  suspensions. *Environ. Sci. Technol.* 35(5):971–976.
- Davydov L, Reddy EP, France P, Smirniotis PG (2001). Sonophotocatalytic destruction of organic contaminants in aqueous systems on  $\text{TiO}_2$  powders, *Appl. Catal. B: Environ.* 32(1):95–105(11).
- Herrmann JM (1999). Heterogeneous photocatalysis: fundamentals and applications to the removal of various types of aqueous pollutants, *Catal. Today* 53:115–129.
- Hoffmann MR, Martin ST, Choi W, Bahemannt DW (1995). Environmental Applications of Semiconductor Photocatalysis, *Chem. Rev.* 95(1):69–96.
- Houas A, Lachheb H, Ksibi M, Elaloui E, Guillard C, Herrmann JM (2001). Photocatalytic degradation pathway of methylene blue in water, *Appl. Catal. B: Environ.* 31:145–157.
- Kansal SK, Kaur N, Sing S (2009). Photocatalytic degradation of commercial reactive dyes in aqueous phase using Nanophotocatalysts, *Nanoscale Res. Lett.* 4:709–716.
- Mahmood T (2011). Metallic Phytoremediation and Nanobiotechnology of water hyacinth, PhD Thesis, Department of Biochemistry, Quid-i-Azam University Islamabad Pakistan.
- Malato S, Blanco J, Caceres J, Fernandez AR, Agüera A, Rodríguez A (2002). Photocatalytic treatment of water soluble pesticides by photo-Fenton and  $\text{TiO}_2$  using solar energy. *Catalysis Today* 76(2):209–220. ISSN 0920-5861.
- Malato S, Blanco J, Campos A, Cañeros J, Guillard C, Herrmann JM, Fernández-Alba AR (2003). Effect of operating parameters on the testing of new industrial titania catalysts at solar pilot plant scale, *Appl. Catal. B: Environ.* 42(4):349–357.
- Meena RC, Pachwarya RB (2009). Photo catalytic degradation of model textile azo dyes in textile wastewater using methylene blue immobilized resin dowex-11, *J. Sci. Ind. Res.* 68:730–734.
- Neppolian B, Choi HC, Sakthivel S, Arabindoo B, Murugesan V (2002). Solar light induced and  $\text{TiO}_2$  assisted degradation of textile dye reactive blue 4, *Chemosphere*, 46(8): 1173–1181.
- Pagga U, Brown D (1986). The degradation of dyestuffs: Part II Behaviour of dyestuffs in aerobic biodegradation tests, *Chemosphere* 15(4):479–491.
- Pirkanniemi K, Sillanpää M (2002). Heterogeneous water phase catalysis as an environmental application: a review, *Chemosphere*, 48(10):1047–1060.
- Poulios I, Aetopoulou I (2013). Photocatalytic degradation of the textile dye reactive Orange 16 in the presence of  $\text{TiO}_2$  suspensions, *Environ. Technol.* 20:479–487.
- Rafols C, Barcelo D (1997). Determination of mono- and disulphonated azo dyes by liquid chromatography–atmospheric pressure ionization mass spectrometry, *J. Chromatogr. A.* 777(1): 177–192.
- Saqib M, Muneer M (2003).  $\text{TiO}_2$ -mediated photocatalytic degradation of a triphenylmethane dye (gentian violet), in aqueous suspensions, *Dyes Pigments*, 56(1):37–49.
- Sonawane RS, Kale BB, Dongare MK (2004). Preparation and photocatalytic activity of  $\text{FeTiO}_3$  thin films prepared by sol–gel dip coating, *Mater. Chem. Phys.* 85(1):52–57.
- Weber EJ, Stickney VC (1993). Hydrolysis kinetics of Reactive Blue 19-Vinyl Sulfone, *Water Res.* 27(1):63–67.