

## Effect of Ultraviolet and Solar Radiation on Photocatalytic Dye (Black-E and Congo Red) Degradation Using Copper Oxide Nanostructure Particles

Usha Vengatakrishnan<sup>1</sup>, Kalyanaraman Subramanian<sup>1</sup>, Vettumperumal Rajapandi<sup>2</sup>, Dhineshbabu Nattanmai Raman<sup>3</sup>

\* babudhinesh2009@gmail.com

<sup>1</sup> P.G. and Research Department of Physics, Sri Paramakalyani College, Alwarkurichi, India.

<sup>2</sup> Department of Physics, Fodhdhoo School, Noonu Atoll, Republic of Maldives.

<sup>3</sup> Department of Electronics and Communication Engineering, Aditya Engineering College, Surampalem, East Godavari Distt., Andhra Pradesh, India.

Received: February 2021

Revised: May 2021

Accepted: June 2021

DOI: 10.22068/ijmse.2145

**Abstract:** Copper oxide (CuO) nanostructure particles were prepared using KOH/NaOH catalyst by low cost precipitation method and characterized by powder X-ray diffraction (PXRD), scanning electron microscope (SEM) and energy dispersive X-ray spectra (EDX) analysis. The photocatalytic dye degradation study of pure CuO nanostructure particles are analysed against two azo dyes (Direct black 38 (Black-E) and Congo red) under ultraviolet (UV) and solar irradiation. The release of major active species (\*OH) in the photocatalytic degradation by as prepared CuO nanostructure particles were investigated by photoluminescence (PL) spectra with two different excitation wavelength (325 and 355nm). The band gap of CuO nanostructure particles was calculated from diffuse reflectance spectra. The photocatalytic effect of CuO nanostructure particles is confirmed by the UV – Vis and photoluminescence spectra and from the kinetic studies under UV and solar radiations. The photocatalytic degradation results revealed that 16.35 and 7.5% of black E and Congo red dye was degraded under UV, while the degradation was 47.2 and 17.6% under solar light. The influence of pH on the photodegradation and change in the reaction temperature under solar irradiation were also investigated.

**Keywords:** copper oxide, precipitation method, photocatalytic activity, azo dyes, dyedegradation.

### 1. INTRODUCTION

Nanotechnology is based on the smallest units of matter to process new material and devices towards superior scale performance on the basis of atomic scale range. Metal oxide nanoparticles are versatile materials with many scientific and industrial applications. [1] Copper oxide (CuO) is found to be a p-type semiconducting material with indirect bandgap of 1.2-1.51 eV and direct band gap of the order of 3.5 eV. [2, 3] It is also used in wide range of various applications like gas sensors [4], lithium ion batteries [5], solar cells [6], magnetic storage media [7], catalysis [8], field emission devices and semiconductors. CuO nanoparticles have been synthesised by many efficient approaches such as hydrothermal process [9], precipitation [10], microwave irradiation [11], co-precipitation [12], pyrolysis and thermal decomposition method [13], respectively. Among these, sol-gel method is energy efficient and less time-consuming process; however other processes are involved intricate synthesis process and energy intensive.

Nowadays, the water pollution is one of the major

problems in the world. The continuous rise in the population with industrialization causes series number of hazardous organic contaminants disposed into natural water sources which are resistant to conventional chemical and biological treatments [14]. Several types of hazardous pollutants such as dyes, organic compounds, pharmaceuticals, heavy metals, agricultural chemicals and radioactive materials have been detected in the water sources. Among these, dyes are majorly used in different industries where it is estimated that nearly 15% of chemical dyes are directly disposed into the natural environment. Azo dyes are used in a diverse range of industries including paper, textile, food, additives, cosmetics, xerography, laser materials and laser printing industries [15]. Azo dyes are the largest group of synthetic dyes that are characterized by nitrogen to nitrogen double bonds (–N=N–). Therefore, sustainable approach in the waste water management includes novel and improved wastewater treatment technologies that are needed in order to reduce negative impacts on the water bodies. It is used to facilitate recycling and reuse of waste water. Some of the promising

advanced oxidation processes (AOPs) [16] such as photocatalytic degradation, sonochemical degradation, and UV/H<sub>2</sub>O<sub>2</sub> etc., have been developed to eliminate such pollutants [17]. Among these, photocatalytic degradation using semiconductor as a photocatalyst has gained considerable attention in the removal of wide range of harmful water pollutants at ambient pressure and temperature into less harmful substances and the sustainable solar light can also be used for irradiation. It is also the most efficient green technology in decomposition of organic pollutants. Different semiconducting oxides such as TiO<sub>2</sub>, CuO, NiO, MgO, CaO and ZnO etc., are utilized as a photocatalyst for degradation of pollutants have attracted the attention of scientific community all over the world [18]. Among these, p-type semiconducting CuO has obtained considerable attention in photocatalytic degradation studies because of their special properties such as a large surface to volume ratio, increased activity, special electronic properties and unique optical properties as compared to those of the bulk [19].

Since sunlight is abundantly available natural energy source, its energy can be conveniently exploited for the irradiation of semiconducting materials. UV irradiation is yet another high-energy irradiation source for degradation of organic compounds present in the effluents. However, the UV radiation based photocatalytic processes hold serious drawbacks such as low photonic efficiency, requirement of cooling arrangement, less lifetime (1000 h), need of high voltage at initial stage and use of hazardous mercury metal. Therefore, the use of freely available solar light for degradation of pollutants is highly attracted and developed different solar light based processes [20].

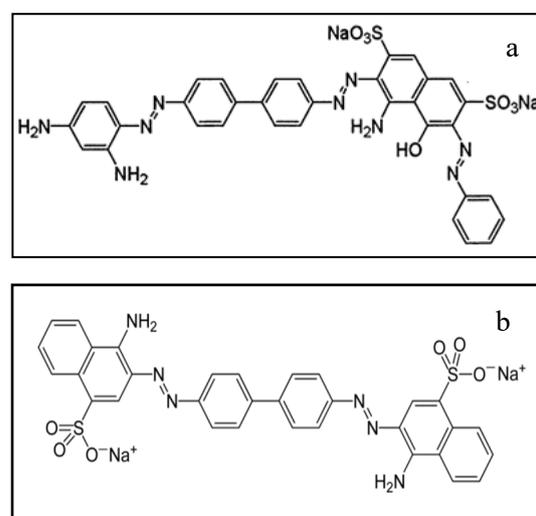
Qamaret.al., [21] investigated the photocatalytic activity of CuO coated ZnO for the degradation of mononitrophenols (2-, 3- and 4-nitrophenol) and dinitrophenols (2,4-, 2,5- and 2,6-dinitrophenol) in the exposure of complete spectrum and in visible region (420-800 nm) of sunlight. Li et.al., [22] demonstrated that the synthesized nano-sized CuO nanoparticles can absorb visible light to produce hydrogen from water. Sundaramoorthy et.al. [23] studied the better photocatalytic degradation of methylene blue dye under solar irradiation in presence of biogenic CuO nanoparticles synthesized using Pyrus

Pyrifolialeaf extract. Umadeviet.al [24] studied the degradation of methyl orange using CuO nanoflower synthesized by combustion method in which glycine was used as a fuel. The reports on degradation of dyes using CuO photocatalyst under solar light irradiation is scarce, so, it was decided to study the influence of solar light and UV light independently on the photocatalytic degradation of dyes.

The present work is to investigate the effect of UV and solar irradiations on the photocatalytic degradation of azo dyes (Direct black-38 (Black E) and Congo red) using pure CuO nanostructure particles prepared by low cost precipitation method. Structural, morphological and optical properties of the CuO nanoparticles are characterized by X-ray diffraction, scanning electron microscope, photoluminescence and UV-Vis spectroscopy analysis.

## 2. MATERIALS AND METHODS

All the chemical reagents used in the preparation were purchased from Sigma Aldrich (99.9% pure) with analytical grade and were used without further purification. The chemical structure of direct black-38 ((Black-E) and Congo red dyes are shown in Figs.1a and 1b.



**Fig. 1.** Molecular structure of (a) Direct Black-38 (Black-E) dye and (b) Congo red dye.

### 2.1. Synthesis of CuO nanoparticle

Copper oxide nanoparticles have been prepared by simple precipitation method. The preparation procedure is reported in our previous work [25]. The mixture of KOH/NaOH solution was

added drop wise into the aqueous solution of copper chloride ( $\text{CuCl}_2$ ) with constant stirring for 2 h. Afterward, the final mixture solution was cooled, the obtained black precipitate was filtered and washed with ethanol and ethyl acetate mixture (3-4 times). Thus, the obtained  $\text{CuO}$  material was dried at  $80^\circ\text{C}$  for 12h under air and then it was further annealed at  $400^\circ\text{C}$  for 1h in air atmosphere.

## 2.2. Characterization

The PXRD spectrum of as prepared  $\text{CuO}$  nanostructure particle was recorded using XPERT\_PRO Diffractometer (Goniometer =PW 3050/60) with  $\text{CuK}\alpha$  radiation ( $\lambda=1.5406 \text{ \AA}$ ) as an X-ray source. PXRD analysis was performed over the  $2\theta$  range of  $10\text{--}80^\circ$ .

SEM images and EDX spectra of the samples were analysed by using JSM 5800 and JSM 6060SEM-EDX microscopes with 20 KV power supply. Photoluminescence spectra were recorded using the F-2500FL photoluminescence spectrometer ROM VERSION (400001) with different excitation wavelengths.

The band gap of synthesized catalysts was determined by UV-Visible diffuse reflectance spectrum recorded at room temperature in the wavelength range of 200-800 nm using Varian Cary 5000 spectrophotometer.

## 2.3. Photocatalytic activity evaluation

The photocatalytic activity of as prepared  $\text{CuO}$  nanostructure particles were evaluated by the photo degradation of Black E and Congo red dyes under UV and solar light irradiation. The required dye solutions were prepared by 50 mg of dye (Black E and Congo red) dissolved in 100 ml of distilled water. After that 500 mg of  $\text{CuO}$  nanostructure particles are added to the solution and it is placed under the irradiation of UV (325 nm and 40 W) and solar light after 30 min stirring in the dark atmosphere.

The change in the absorbance was observed at each 30 min. of time interval by UV-Vis spectroscopy analysis at  $\lambda_{\text{max}}$  of 590 nm (Black E) and 497 nm (Congo red).

The concentration changes ( $C/C_0$ ) during photodegradation was proportional to the maximum absorbance ( $A/A_0$ ) at a given interval of irradiation. The degradation efficiency was calculated from the following relation,

$$\text{Degradation efficiency (D)} = \frac{A_0 - A_t}{A_0} \times 100\%$$

## 3. RESULTS AND DISCUSSION

### 3.1. Structural studies

X-ray diffraction pattern of prepared  $\text{CuO}$  nanostructure particles with  $\text{NaOH/KOH}$  mixture at  $400^\circ\text{C}$  is shown in Fig. 2.

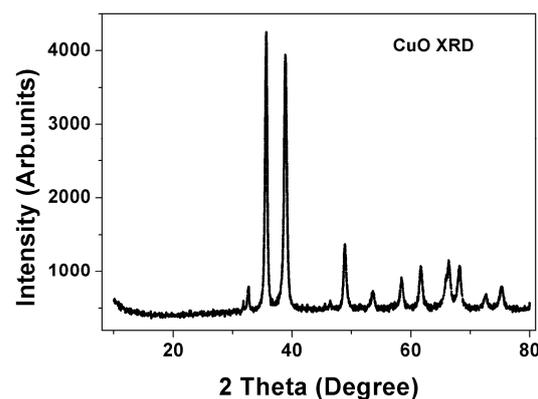


Fig. 2. XRD spectrum of  $\text{CuO}$  nanoparticles.

The diffraction peaks at different  $2\theta$  values of 32.6, 35.6, 38.8, 58.5, 61.7, 66.3, 68.3 and  $75.2^\circ$  were attributed to the monoclinic phase of  $\text{CuO}$  nanoparticles and well consistent with the JCPDS data (card no: 048-1548). The sharp high intense diffraction peaks clearly proved that the synthesized  $\text{CuO}$  nanostructure particles were highly crystalline in nature. Peaks related to  $\text{Cu}(\text{OH})_2$ ,  $\text{Cu}_2\text{O}$  or  $\text{Cu}$  were not observed in the PXRD pattern, indicating the purity of synthesized  $\text{CuO}$  nanostructure particle. The PXRD results are well consistent with the previously reported literature [26]. Lattice constants of  $\text{CuO}$  nanostructure particles were calculated and the values are  $a=4.6876 \text{ \AA}$ ,  $b = 3.4104 \text{ \AA}$ ,  $c = 5.1138 \text{ \AA}$ . Crystallite size of the  $\text{CuO}$  nanostructure particles is calculated by Scherrer formula [27]. The calculated Crystallite size is 42.9 nm.

### 3.2. Morphological studies

Surface morphology of  $\text{CuO}$  nanostructure particles at two magnifications of 2000 and 4000 were analyzed by SEM analysis and it is shown in Fig. 3. The results revealed that surface morphology of the synthesized  $\text{CuO}$  nanostructure particles is constituted by leafy grains, which are tend to agglomerate by getting

the energy from the environment during the annealing process. Moreover, the flower-like

morphology was also observed in some places of

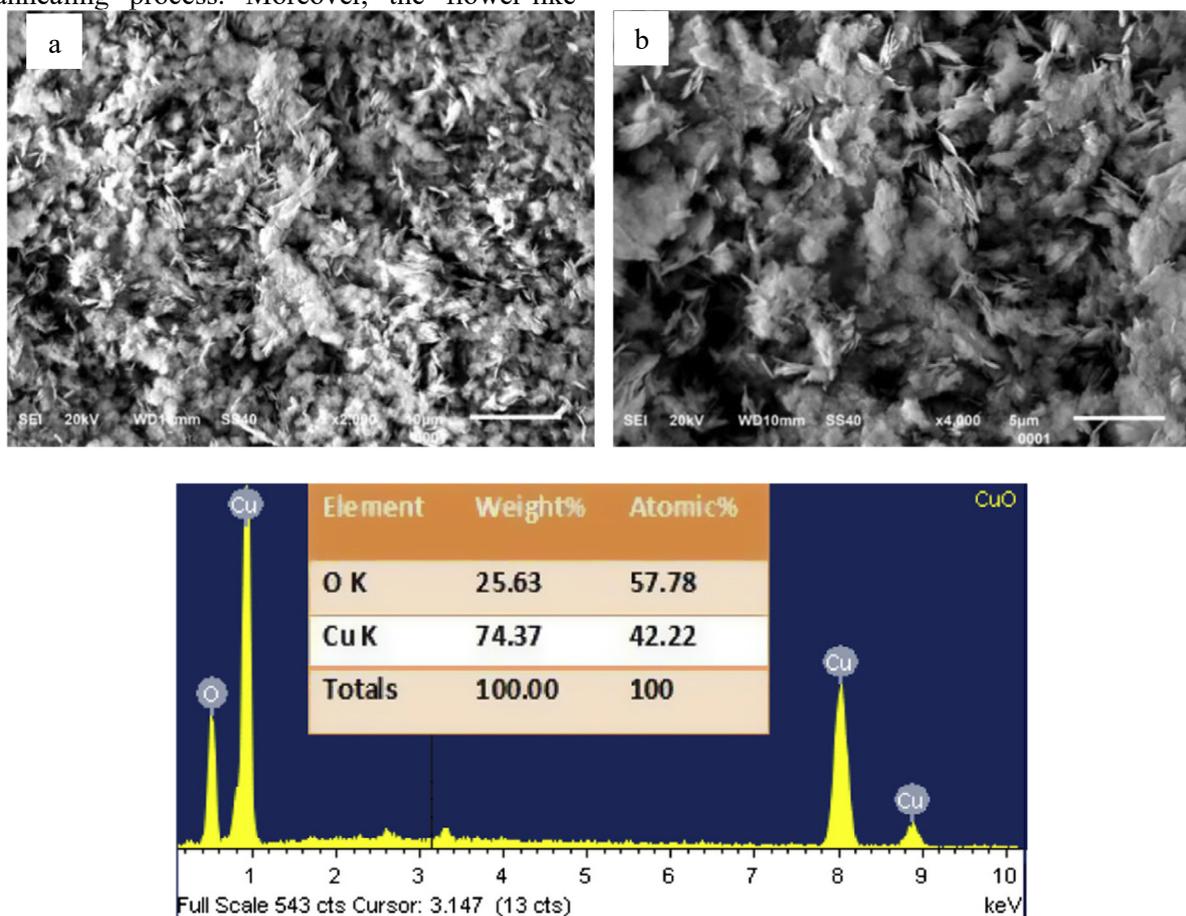


Fig. 3. (a) SEM images of CuO nanoparticles (b) EDAX Spectra of CuO nanoparticles.

the SEM image of CuO, this may be due to the partial conversion of formed leaf like grains to flower-like structure.

The typical CuO grain had sizes in the nano regime and extends up to few micron widths. The close inspection at higher magnifications revealed that morphologies typical of chalcogenides particularly oxides [28, 29]. Elemental composition of CuO nanostructure particles were confirmed by EDX analysis which reveals the presence of CuO nanostructure particles only and no impurities were observed which supports the PXRD results.

### 3.3. Optical studies

Hydroxyl radical is one of the crucial reactive species during photocatalytic reaction which is responsible for oxidative decomposition of pollutants. Photoluminescence technique is one of the methods available to investigate the

production of  $\cdot\text{OH}$  [30].

The photoluminescence spectra of CuO nanostructure particles with two different excitation sources 325 and 355 nm were analysed and the results shown in our previous work mentioned in the experimental section demonstrated that the strong peaks observed at UV region is considered to be near band edge emission and the green emission in the visible region is due to the interaction of oxygen vacancies in the valence band with interfacial Cu vacancies within the band gap [31, 32]. The high relative intensity at UV and visible region inhibits the electron-hole recombination, leading to enhancement in the photocatalytic degradation activity [33].

For any photocatalytic degradation, the band edge position and band gap energy of the material is important for electronic transitions. The reflectance spectrum is shown in Fig. 4.

Using this reflectance the obtained band gap value for CuO catalyst is 3.05 eV and it can be used as a good photocatalyst in the degradation of various dyes.

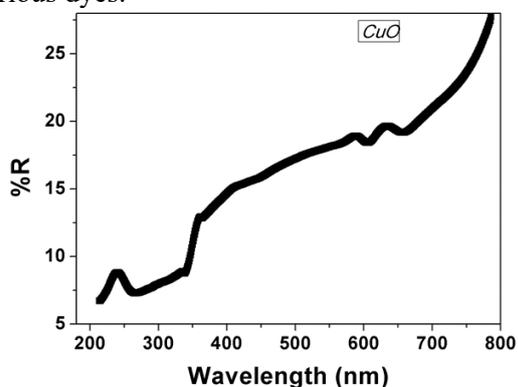


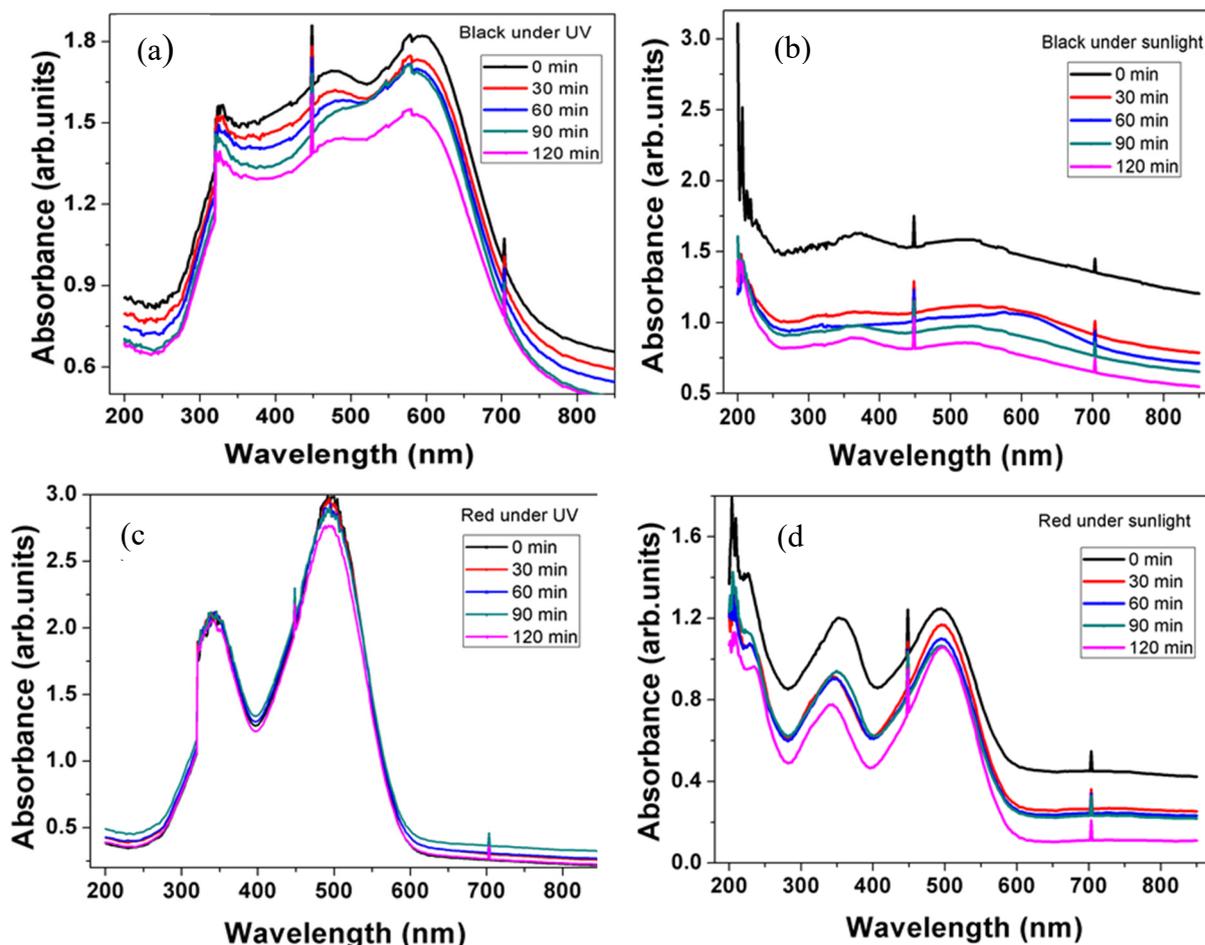
Fig. 4. (a) UV-Vis-DRS spectrum, (b) Tauc plot of CuO nanoparticles.

### 3.4. Photocatalytic degradation of dyes

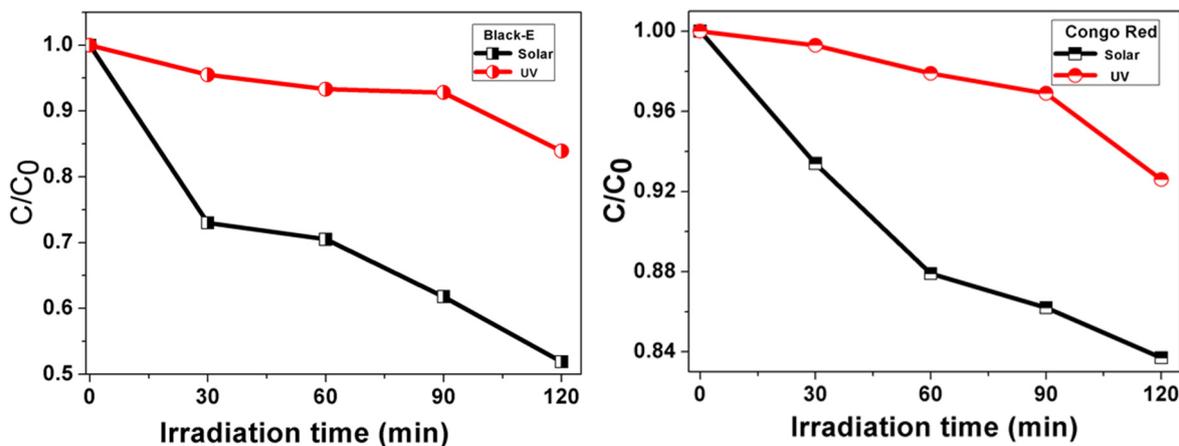
The photocatalytic activity of as synthesized CuO nanostructure particle was investigated by the

degradation of the Black-E and Congo red dyes under the irradiations of UV and solar light. Absorption spectrum of CuO mixed dyes with different irradiation sources and time intervals are presented in Figs. (5a-5d) and photodegradation concentration ( $C/C_0$ ) of dyes changes with respect to the irradiation time is shown in Figs. 6a and 6b. Absorbance of Congo red is observed at 497 and 590 nm for black-E dye. The results revealed that 16.35% and 7.5% of black E and Congo red dyes were degraded after 2 h under UV irradiation, whereas it was 47.2% and 17.6% under solar light irradiation. The PL spectrum reveals that the solar visible) light absorption is efficient and hence a significant enhancement in the degradation efficiency.

The degradation efficiency depends on the availability of active sites on the surface of the catalyst and the penetration of the light intensity into the suspension. The solar light has only 5% of optimum energy for the excitation of electrons in the catalyst.



**Fig. 5.** UV-visible absorption spectrum of Black-E (a, b) and Congo red (c, d) dye solution under irradiation of UV and solar light.



**Fig. 6.** Photocatalytic activity of CuO nanoparticles for degradation of (a) Black-E, (b) Congo red dye in the presence of UV and solar light irradiation.

However, the high photocatalytic activity under solar light irradiation suggested that CuO efficiently utilized the solar light. Therefore, the solar light would be the ultimate sustainable and freely available radiation sources than the UV for degradation these dyes using present reaction conditions. Moreover, under high intense light irradiation, the electron-hole pairs formation is higher, their recombination is largely avoided which produces large number of free radicals causing high percentage degradation of dyes. However, separation and recombination of electron-hole takes place regularly at lower light intensity, which decreases the formation of free radicals following decrease in the photocatalytic degradation of dyes [34]. The input energy of UV is large for the band gap excitation of electrons in the catalysts as compared to solar light. However, UV radiation is hazardous, expensive and need of cooling arrangement, which are undoubtedly impractical in commercialization. Sunlight is a safe and cost-effective source. In case of large surface demanding, photocatalytic dye degradation in Furthermore, the major portion of degradation takes place in the active zone of photocatalyst where the irradiation intensity is higher than the other side [35, 36]. The significant decrease in concentration of the dyes is caused by two main reasons, (i) the adsorption of dye on CuO (ii) the absorption of large amount of light irradiation. The enriched absorption of solar light generates more number of charge carriers which

produces higher concentration reactive hydroxyl radicals for degradation [37, 38]. pH plays an important role in the characteristics of degradation of dyes and in the generation of hydroxyl radicals. The adsorption and dissociation of the dye molecules and the formation of hydroxyl radical depend on the pH of the catalyst [39, 40]. The interpretation of pH effects on the photocatalytic process is a very difficult task because of its multiple roles such as electrostatic interaction between semiconductor surfaces, solvent and charged radicals formed during the progress of reaction [41]. Variations of percentage in the degradation of dyes with change in pH during the photocatalytic process are observed and it is presented in Fig. 7.

pH decreases (changes from acidic to basic nature) during the degradation with the increase in irradiation time. Most of the reactants (e.g. O<sub>2</sub>, OH<sup>-</sup> and organic molecules) should be adsorbed on the surface of photocatalyst resulting in the increase in number of active sites, thus leading to higher degradation efficiency. The percentage degradation of Black-E and Congo red under UV and solar irradiations are 16.35%, 7.5%, 47.2% and 17.6% respectively. The pH study concludes that the rate of degradation was higher in acidic medium than the basic medium. The catalyst shows better degradation within the pH range 6.5 to 8.3[42, 43]. A comparison of the degradation efficiencies of various types of samples with

different dyes are shown in Table. 1. From the table the degradation of dyes using pure CuO nanostructure particles agrees the previous work

[44-48].

Photocatalytic reactions of CuO catalyst follow the pseudo-first order reaction kinetics [49-51]

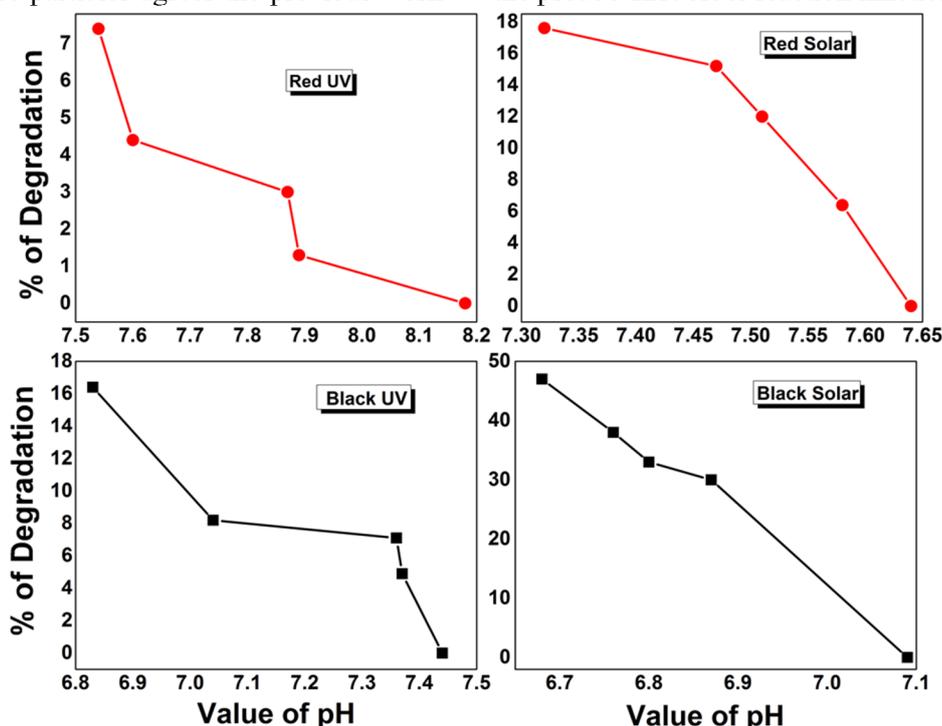


Fig. 7. Effect of pH on the degradation efficiency of Black-E and Congo red dyes under UV and solar light irradiation.

Table 1. comparison of the degradation efficiencies of various types of samples with different dye

Sample	Name of the Dye	Irradiation light source	%of degradation with respect to time	References
CuO annealed 350°C CuO annealed 800°C	Rh-B	Visible	25.58 (2h) 20.64(2h)	45
CuO(without H <sub>2</sub> O <sub>2</sub> ) CuO(with H <sub>2</sub> O <sub>2</sub> )	Rh-B	Mercury	66.24(5h) 100(5h)	46
Fe <sub>3</sub> O <sub>4</sub> /CuO/ZnO Fe <sub>3</sub> O <sub>4</sub> /CuO/ZnO/NGP	Methylene Blue	UV	52 and 87(2h) 57 and 93(2h)	47
Cu <sub>2</sub> O CuO	Malachite Green Methylene Blue Methyl Red Methyl Orange	UV	50 (8h) 90(48h)	48
CuO/ZnO composite	Methylene Blue Methyl Orange	UV	90 (15 min) 85(25 min)	49
Present work (CuO)	Direct Black-38 Congo Red	Solar, UV Solar, UV	47.2, 16.35 (2h) 17.6, 7.5 (2h)	

which is expressed as follows:

$$\ln \frac{C_0}{C} = kt$$

Where k is the first order rate constant, C<sub>0</sub> and C are the initial and final concentrations of dye solution respectively. The linear relationship

between ln (C<sub>0</sub>/C) and irradiation time is shown in Fig. 8.

From the slope of the straight line the rate constant value can be determined and leads to produce kinetic energy, able to move away the

dye molecules from the active zones before achieving the degradation. The calculated rate constants values for degradation of black E and Congo red dyes under UV light irradiation are  $1.26 \times 10^{-3}$  and  $5.92 \times 10^{-4}$ , while it is  $4.92 \times 10^{-3}$  and  $1.43 \times 10^{-3}$  for solar light irradiation.

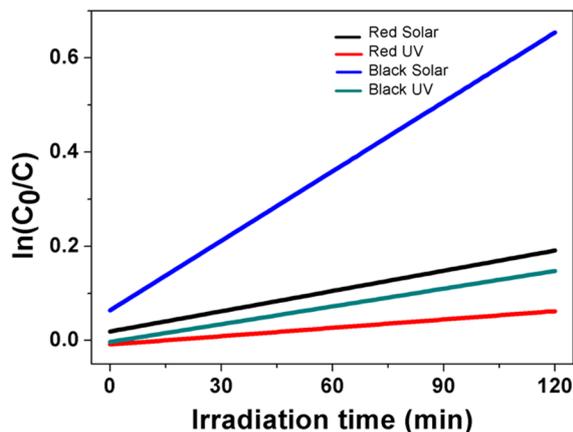


Fig. 8. Kinetics of Black-E and Congo red photocatalytic degradation catalysed by CuO nanoparticles.

From the kinetic studies, we further conclude that CuO is highly beneficial under solar light irradiation. Photocatalytic reactions of CuO catalyst were considered as the pseudo-first order reaction kinetics.

The order of reaction may be affected by the reaction sites. In the first order reaction, curves of  $C/C_0$  versus time are parabolic and the  $\ln(C/C_0)$  curves are straight line. However, in this research  $C/C_0$  – time curves are straight line (specially for red azo). So, reaction is zero-order. It seems that agglomeration of particles led to decrease of reaction sites and consequently, decreased the reaction order from first to zero. Such phenomenon was reported with Khaksar et al. for  $TiO_2$  coated granules [52].

Change of temperature is observed during the photocatalytic degradation performed under the solar irradiation and it is presented in Fig. 9. The photo degradation process is mainly due to the electron transfer through the photocatalyst. In general, in case of semiconductor oxide nanostructure particles the surface to volume ratio is low. If the temperature is increased, more chemical reaction is induced which increases the surface activity resulting in increase in activation energy of the particles. At lower temperature, the

adsorption of dyes with the catalyst becomes high and the activation energy enhances the active zones to increase the oxidation of holes on the surface for better degradation.

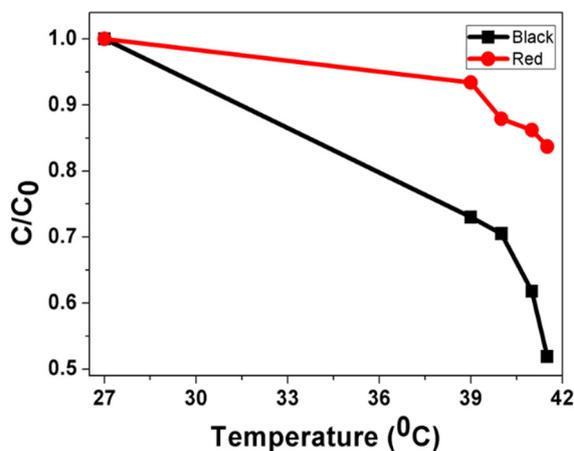


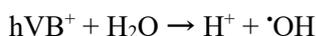
Fig. 9. Temperature dependence of relative concentration under solar irradiation.

However, more increase in the temperature process resulting in decrease in degradation [53].

### 3.5. Photocatalytic degradation mechanism

The photocatalytic mechanism begins when photon energy ( $h\nu$ ) matches or exceeds the band gap energy of the semiconductors. The electrons are promoted from the valance band (VB) to the conduction band (CB), leaving a hole behind. The hole move to catalyst surface where it can either oxidize an adsorbed compound directly or react with electron donors like water to form  $\bullet OH$  radicals, which in turn react with pollutants. Similarly, the electrons reduce the oxygen molecules to superoxide radical anions ( $O_2\bullet^-$ ), which reacts with pollutants [54].

In this the generated  $\bullet OH$  and  $O_2\bullet^-$  react with the black E and Congo red dyes and different range of intermediates products, which are further mineralized into carbon dioxide, water and inorganic anions as shown below and the schematic representation of the degradation mechanism is shown in Fig. 10.



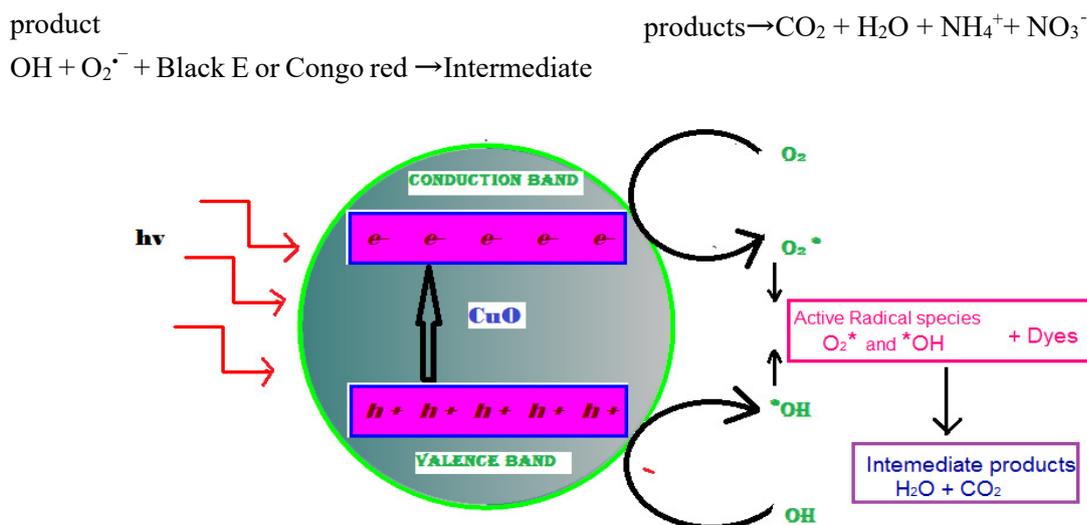


Fig. 10. Schematic representation of photodegradation of Dyes using CuO photocatalyst.

#### 4. CONCLUSIONS

The copper oxide nanostructure particles were prepared by low cost sol-gel method using KOH/NaOH as catalyst. PXRD confirmed the monoclinic crystalline structure of CuO without any secondary phases. The agglomeration of leafy grains in the nanostructure particles was evidenced from SEM analysis. The presence of copper and oxygen was confirmed by EDX spectra. The photosensitive properties were determined using PL spectra and the band gap value was calculated from reflectance which gave an indication that the photocatalytic absorption is high in the UV and solar region. The values obtained showed that the degradation efficiency of pure CuO is in comparable limit with the rest of the samples. Higher rate constant values further confirmed the enhanced photocatalytic activity under solar light. The degradation of dyes was found to be more predominant in the pH range of 6.5-8.3. Better photocatalytic degradation was observed under solar irradiation. CuO nanostructure particle is an efficient and active photocatalytic material for the degradation of black E and Congo red dyes under solar irradiation.

#### REFERENCES

[1] Stark, W. J., Stoessel, P. R. and Wohlleben, W., "Industrial applications of

nanoparticles." *Chem. Soc. Rev.*, 2015, 44, 5793-5805.

[2] Sonia, S., Jayaram, N. D., Suresh Kumar, P., Mangalaraj, D., Ponpandian, N. and Viswanathana, C., "Effect of NaOH concentration on structural, surface and antibacterial activity of CuO nanorods synthesized by direct sonochemical method." *Superlattices Microstruct.*, 2014, 66, 1-9.

[3] Mallick, P. and Sahu, S., "Structure, Microstructure and Optical Absorption Analysis of CuO Nanoparticles Synthesized by Sol-Gel Route." *Nanosci Nanotechnol.* 2012, 2(3), 71-74.

[4] Li, Y., Liang, J., Tao, Z. and Chen, J., "CuO particles and plates: synthesis and gas-sensor application." *Mater. Res. Bull.* 2008, 43, 2380-2385.

[5] Danish, M.S.S., Estrella, L.L., Alemaida, I.M.A., Lisin, A., Moiseev, N., Ahmadi, M., Nazari, M., Wali, M., Zaheb, H. and Senjyu, T., "Photocatalytic Applications of Metal Oxides for Sustainable Environmental Remediation." *Metals*, 2021, 11, 80. <https://doi.org/10.3390/met11010080>.

[6] Kidowaki, H., Oku, T., Akiyama, T., Suzuki, A., Jeyadevan, B. and Cuya J., "Fabrication and Characterization of CuO-based Solar Cells." *J. Mater. Sci. Res.* 2012, 1(1), 138-143.

[7] Vijaya Kumar, R., Diamant, Y. and

- Gedanken, A., "Sonochemical synthesis and characterization of nanometer-size transition metal oxides from metal acetates." *Chem. Mater.* 2000, 12(8), 2301- 2305.
- [8] Ahmady, A. Z., Keshavarz, M. and Kardani, M., "CuO nanoparticles as an efficient catalyst for the synthesis of flavanones." *Orien. J. Chem.*, 2015, 31(3), 1841-1846.
- [9] Kannaki, K., Ramesh, P. S. and Geetha, D., "Hydrothermal synthesis of CuO nanostructure and their characterizations." *Int. J. Sci. Eng. Res.*, 2012, 3(9), 1-4.
- [10] Kshirsagar, J. M., Shrivastava, R. and Adwani, P. S., "Preparation and characterization of copper oxide nanoparticles and determination of enhancement in critical heat flux." *Therm. Sci.*, 2017, 21(1A), 233-242.
- [11] Sutradhar, P., Saha, M. and Maiti, D., "Microwave synthesis of copper oxide nanoparticles using tea leaf and coffee powder extracts and its antibacterial activity." *J. Nanostruct. Chem.*, 2014, 4(86), 1- 6.
- [12] Arora A. K. and Ritu, "Synthesis of nanosized cuo particles: a simple and effective method." *Int. J. Chem. Sci.*, 2013, 11(3), 1270-1276.
- [13] Kanagaraj, M., Sathishkumar, P. and Kalaiselvan, G., "Synthesis of nanosized cuo particles: a simple and effective method." *Ind. J. Pure & App. Chem.* 2014, 52, 124-130.
- [14] Durai, G., Rajasimman, M., "Biological Treatment of Tannery Wastewater - A Review." *J. Environ. Sci. Tech.*, 2011, 4(1), 1-17.
- [15] Maharjan, V. K. and Sonwane, G. H., "Effective degradation and mineralization of real textile effluent by sonolysis, photocatalysis, and sonophotocatalysis using ZnO nano catalyst." *Nano Chem. Res. Summer autumn.*, 2016. 1(2), 258-263.
- [16] Androozzi, R., Caprio, V. and Insola, A., "Advanced oxidation processes (AOP) for water purification and recovery *Catal.*" *Today*, 1999, 53, 51–59.
- [17] Vidhyalakshmi, C., Raji R. J. and Palanivelu K., "Sonochemical degradation of organic dyes using sulphate radicals activated by immobilized iron." *Ind. J. Chem. Tech.*, 2014, 21, 280-284.
- [18] Kum, J. M., Yoo, S. H., Ali, G. and Cho, S. O., "Photocatalytic hydrogen production over CuO and TiO<sub>2</sub> nanoparticles mixture." *Inter. J. Hydro. Ener.*, 2013 3813541-13546.
- [19] Umar, A., Naveed, S. and Ramzan, N., "Selection of a suitable method for the synthesis of copper nanoparticles." *Nano.*, 2012, 7(5), 1230005.
- [20] Khanna, A. and Shetty, V. K., "Solar light induced photocatalytic degradation of Reactive Blue 220 (RB-220) dye with highly efficient Ag@ TiO<sub>2</sub> core-shell nanoparticles: A comparison with UV photocatalysis." *Sol. Energy*, 2014, 99, 67–76.
- [21] Qamar, M. T., Aslam, M., Ismail, I. M. I., Salah, N. and Hameed, A. "Synthesis, Characterization, and Sunlight Mediated Photocatalytic Activity of CuO Coated ZnO for the Removal of Nitrophenols." *ACS App. Mater. Inter.*, 2015, 1, 39.
- [22] Kum J. M., Yoo S. H. , Ali,G. and Cho, S. O., "Photocatalytic hydrogen production over CuO and TiO<sub>2</sub> nanoparticles mixture." *Inter. J. Hydro. Ener.*, 2013, 38, 13541-13546
- [23] Sundaramurthy, N. and Parthiban, C., "Biosynthesis of Copper oxide nanoparticles using *Pyrus pyrifolia* leaf extract and evolve the catalytic activity." *Int. Res. J. Eng. Tech.*, 2015, 2(6), 332-338.
- [24] Umadevi, M. and Christy, A., "Synthesis, characterization and photocatalytic activity of CuO nanoflowers *Spectrochim.*" *Acta Part A.*, 2013, 109, 133–137.
- [25] Usha, V., Kalyanaraman, S., Thangavel, R. and Vettumperumal, R., "Effect of catalysts on the synthesis of CuO nanoparticles: structural and optical properties by sol-gel method." *Superlattices Microstruct.*, 2015, 86, 203-210.
- [26] Kayani, Z. N., Umer, M., Riaz, S. and Naseem, R., "Characterization of copper oxide nanoparticles fabricated by the sol-gel method." *J. Electron. Mater.*, 2015, 44(10), 3704-3709.
- [27] Rejith, S. G. and Krishnan, C., "Synthesis of cadmium-doped copper oxide nanoparticles:Optical and structural characterizations." *Adv. App. Sci. Res.*, 2013, 4(2), 103-109.
- [28] Suleiman M., Mousa M., Hussein A.,

- Hammouti B., Hadda T. B. and Warad I., "Copper(II)-Oxide Nanostructures: Synthesis, Characterizations and their Applications—Review." *J. Mater. Environ. Sci.*, 2013, 4 (5), 792-797.
- [29] Phiw dang K., Suphankij S., Mekprasart W. and Pecharapa W., "Synthesis of CuO Nanoparticles by Precipitation Method Using Different." *Precursors Energy Proc.*, 2013, 34, 740–745.
- [30] Thota S., Rao S. and Tirukkavalluri S., "Visible Light Induced Photocatalytic Degradation of Methyl Red with Codoped Titania." *J. Catal.*, 2014, 7, 962419.
- [31] Lavand A. B. and Malghe Y. S., "Synthesis characterization, and visible light photocatalytic activity of nanosized carbon doped zinc oxide." *J. Saudi. Chem. Soc.*, 2015, 19, 471–478.
- [32] Gopalakrishnan, K., Ramesh, C., Elango, M. and Thamilselvan, M., "Optical and Magnetic Studies on Cu<sub>2</sub>O/PANI Nanocomposite Prepared by Chemical Polymerization Method." *Inter. Scholarly Res. Notices*, 2014, 7, 567927.
- [33] Jinfeng, Z., Yunguang, Y. and Wei, L., "Preparation, Characterization, and Activity Evaluation of CuO/F-TiO<sub>2</sub> Photocatalyst." *Int. J. Photo Energy*, 2012, 12, 139739.
- [34] Neppolian, B., Choi, H. C. and Sakthivel S., "Solar/UV-induced photocatalytic degradation of three commercial textile dyes." *J. Hazard Mater. B*, 2002, 89, 303-317.
- [35] Reutergardh, L. B. and Iangphasuk, M., "Photocatalytic Decolourization of Reactive Azo Dye: A Comparison between TiO<sub>2</sub> and CdS Photocatalysis." *Chemosphere.*, 1997, 35(3), 585-596.
- [36] Zang, L., Liu, C. Y. and Ren, M., "Photochemistry of semiconductor particles 3. Effects of surface charge on reduction rate of methyl orange photosensitized by ZnS sols." *J. Photochem Photobiol. A.*, 1995, 85, 239-245.
- [37] Sima, J. and Hasal, P., "Photocatalytic Degradation of Textile Dyes in aTiO<sub>2</sub>/UV System." *Chem. Eng. Trans.*, 2013, 32, 79-84.
- [38] Tayade, R. J., Natarajan, T. S. and Bajaj, H. C., "Photocatalytic degradation of methylene blue dye using ultraviolet light emitting diodes." *Ind. Eng. Chem. Res.*, 2009, 48(23), 10262–10267.
- [39] Gnanaprakasam, A., Sivakumar, V. M. and Thirumarimurugan, M., "Influencing Parameters in the Photocatalytic Degradation of Organic Effluent via Nanometal Oxide Catalyst: A Review." *Ind. J. Mater. Sci.*, 2015, 15, 601827.
- [40] Kazeminezhad, I. and Sadollahkhani, A., "Influence of pH on the photocatalytic activity of ZnO nanoparticles." *J. Mater. Sci. Mater. Electron.*, 2016, 27(5), 1-10.
- [41] Chen, C., Liu, J., Liu, P. and Yu, B., "Investigation of Photocatalytic Degradation of Methyl Orange by Using Nano-Sized ZnO Catalysts." *Adv. Chem. Eng. Sci.*, 2011, 1, 9-14.
- [42] Giah, M., Badalpoor, N., Habibi, S. and Taghavi, H., "Synthesis of CuO/ZnO nanoparticles and their application for photocatalytic degradation of lidocaine HCl by the trial-and-error and Taguchi methods." *Bull. Korean Chem. Soc.*, 2013, 34(7), 2176-2182.
- [43] Meena, R. C., Himakshi, V. and Disha, "Studies on Photocatalytic Degradation of Azo Dye Acid Red-18 (PONCEAU 4R) using Methylene Blue Immobilized Resin Dowex-11." *Int. Res. J. Environ. Sci.*, 2013, 2(12), 35-41.
- [44] Kumaresan, N., Ramamurthi, K., Mathuri, S., Sinthiya, M. M. A., Manimozhi, T., Mudaliar Margoni M. and Rameshbabu R., "Solid State Synthesis Of CuO Nanoparticles For Photo Catalytic Application." *Int. J. Chem. Tech. Res.*, 2015, 7(3), 1598-1602.
- [45] Tadjarodi, A., Akhavan, O. and Bijanzad, K., "Photocatalytic activity of CuO nanoparticles incorporated in mesoporous structure prepared from bis (2aminonicotinato) copper(II) microflakes." *Trans. Nonferrous Metals Soci. China.*, 2015, 25, 3634–3642.
- [46] Tju, H., Taufik, A. and Saleh, R., "Enhanced UV Photocatalytic Performance of Magnetic Fe<sub>3</sub>O<sub>4</sub>/CuO/ZnO/NGP Nanocomposites." *J. Phys: Conf. Series.*, 2016, 710, 012005.
- [47] Raghav, R., Aggarwal, P. and Srivastava, S., "Tailoring oxides of copper-Cu<sub>2</sub>O and CuO nanoparticles and evaluation of organic dyes degradation." *AIP Conf. Proc.*, 2016, 1724, 020078.

- [48] Chang, T., Li, Z. and Yun, G., "Enhanced Photocatalytic Activity of ZnO/CuO Nanocomposites Synthesized by Hydrothermal Method." *Nano Micro. Lett.*, 2013, 5(3), 163-168.
- [49] Elaziouti, L. N. and Ahmed, B., "ZnO-Assisted Photocatalytic Degradation of Congo Red and Benzopurpurine 4B in Aqueous Solution." *J. Chem. Eng. Process Tech.*, 2011, 2(2), 1-9.
- [50] Collazzo, G. C., Foletto, E. L., Jahn, S. L. and Villetti, M. A., "Degradation of Direct Black 38 dye under visible light and sunlight irradiation by N-doped anatase TiO<sub>2</sub> as photocatalyst." *J. Environ. Manag.*, 2012, 98, 107-111.
- [51] Zaman, S., Zainelabdin, A. and Amin, G., "Efficient catalytic effect of CuO nanostructures on the degradation of organic dyes." *J. Phys. Chem. Sol.*, 2012, 73, 1320–1325.
- [52] Khaksar, E., Shafiee A. M. and Samimi, A., "In situ solvothermal crystallization of TiO<sub>2</sub> nanostructure on alumina granules for photocatalytic wastewater treatment." *J. Mater. Eng. Perform.*, 2013, 23(1), 92–100.
- [53] Barakat, N. A. M., Kanjwal, M. A., Chronakis, I. S. and Kim, H. Y., "Influence of temperature on the photodegradation process using Ag-doped TiO<sub>2</sub> nanostructures: Negative impact with the nanofibers." *J. Mol. Catal. A.*, 2013, 366, 333–340.
- [54] Azam, A., Ahmed, A. S., Oves, M., Khan, M. and Memic, A., "Size-dependent antimicrobial properties of CuO nanoparticles against Gram-positive and -negative bacterial strains." *Int. J. Nanomed.*, 2012, 7, 3527–3535.