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Research Paper

Solar Photocatalytic Degradation of Commercial Azo Dye Acid Orange 7 by Synthesized $CaZnO_2$ Nanoparticle as an Effective Catalyst

Gopalappa H.[1], *Yogendra K.[1], Mahadevan K. M.[2]
[1]Department of P.G studies and Research in Environmental Science,
Kuvempu University, Jnana Sahyadri, Shankaraghatta, Shivamogga, Karnataka,INDIA
[2]Department of Chemistry, Kuvempu University,
Jnana Sahyadri, Shankaraghatta, Shivamogga, Karnataka,INDIA

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Abstract: *The degradation of acid orange 7 (AO7) widely used as a textile dye, can be photocatalysed by $CaZnO_2$ nanoparticle using Advanced oxidation process (AOPs). Calcium zincate nanoparticles were synthesized by solution combustion method and characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). Calcium zincate appears to be a suitable alternative to TiO_2 for water treatment. In this study a detailed investigation of photocatalytic degradation of acid range 7 is presented. Photo degradation efficiency was small when the photolysis was carried out in the absence of sunlight and it was zero in presence of sunlight without catalyst. It was found that 99 % degradation occurs with catalyst in presence of sunlight. The effect of parameters such as pH, amount of photocatalyst, irradiation time and dye concentration were also examined.*

Keywords: photocatalytic degradation, advanced oxidation process, $CaZnO_2$ nanoparticle, Azo dye, Acid orange 7.

Introduction

During the past decade, there has been considerable interest in the preparation of metal oxide nanoparticles with carefully controlled size, morphology and surface nature, because they serve as key materials in the enormous fields of catalysts and catalyst supports, inorganic additives, micro electronics, electro optics, photochromics, photovoltics and photocatalysts [1-3]. The textile industry produces large quantities of highly colored effluents, which are generally toxic and resistant to degradation by biological treatment methods, Acid orange7 (AO7) is widely used in the textile industry [4,5].

Various chemical and physical processes such as chemical precipitation and separation of pollutants, coagulation, electro coagulation [6], elimination by adsorption on activated carbon, etc are applied for color removal from textile effluents. In recent years an alternative to conventional methods is advanced oxidation process (AOPs). It is more effective than other methods in the way that, the conventional methods are not destructive but only transfer the contamination from one phase to another, therefore, a new and different kind of pollution is faced which calls for further treatment [7]. AOPs are based on the generation of very reactive species such as hydroxyl radicals, that oxidizes the organic pollutant quickly and effectively [8,9]. TiO_2 is found to be more efficient for photocatalytic degradation of pollutants due to a faster electron transfer to molecular oxygen [10]. However widespread use of TiO_2 is uneconomic for large scale water treatment operations. $CaZnO_2$ appears to be a suitable effective and alternative to TiO_2. Since its photo degradation mechanism seems to be similar to that of TiO_2. The efficiency of $CaZnO_2$ has been reported in the photocatalytic degradation of Coralene dark red 2B [11].

The aim of the present work is to study the photocatalytic degradation of an acid orange 7 an azo dye extensively used by the textile industry in presence of $CaZnO_2$ as a suitable alternative to TiO_2 irradiated by sunlight (sunlight/$CaZnO_2$ process). The effect of sunlight irradiation, pH and the amount of catalyst and concentration of dye were examined.

Material and Methods

Acid orange 7, Calcium nitrate ($Ca(NO_3)_2.4H_2O$), Zinc nitrate ($Zn(NO_3)_2.6H_2O$) and urea (NH_2CONH_2), A.R grade and used without further purification.

Apparatus and instruments: A 119(UV.VIS) single beam spectrometer from Systronics has been used for recording absorbance at λ_{max}. Later the absorbance was recorded in uv.vis spectrometer 169 (Systronics).

Synthesis of $CaZnO_2$ nanoparticle: The photocatalyst Calcium Zincate was synthesized by solution combustion method. The chemicals like Calcium nitrate ($Ca(NO_3)_2.4H_2O$) (99%, A. R.), Zinc nitrate ($Zn(NO_3)_2.6H_2O$) (99%, A. R.) and Urea (NH_2CONH_2) (99%, A.R.), were obtained from Hi media chemicals Mumbai and were used without further purification. Stoichiometric compositions of Calcium nitrate, Zinc nitrate, and Urea were calculated using the total oxidizing and reducing valencies of the components which serve as numerical coefficients for Stoichiometric balance [12]. In a typical experiment $Ca(NO_3)_2.4H_2O$ and $Zn(NO_3)_2.6H_2O$ were dissolved in minimum quantity of water along with Urea in a silica Crucible (with volume of 100 cm^3). The reaction mixture was introduced into the muffle furnace which was preheated at 500^0C. The reaction mixture was then undergoes dehydration followed by decomposition with the release of CO_2, N_2 and H_2O. The mixture then froths and swells forming foam which ruptures with a flame and glows to incandescence. The product of combustion is a voluminous and foamy $CaZnO_2$. The obtained Calcium Zincate was crushed in a mortar to make it amorphous. According to propellant chemistry the reaction is as shown.

$$3\,Ca(NO_3)_2 + 3\,Zn(NO_3)_2 + 10\,NH_2CONH_2 \rightarrow 3\,CaZnO_2 + 10\,CO_2 + 20\,H_2O + 16\,N_2$$

SEM and XRD of prepared Calcium zincate nanoparticles: XRD was performed by Rigaku diffractometer using Cu-K_α radiation (1.5406 Å) in a θ-2θ configuration. The XRD pattern of the prepared $CaZnO_2$ nanoparticle was as shown in Figure 1. According to the Debye–Scherrer's formula ($D = K\lambda/(\beta\cos\theta)$, where K is the Scherrer's constant, λ the X-ray wavelength, β is the peak width at half-maximum and θ is the Bragg diffraction angle) the average crystallite size D is 39.17 nm.

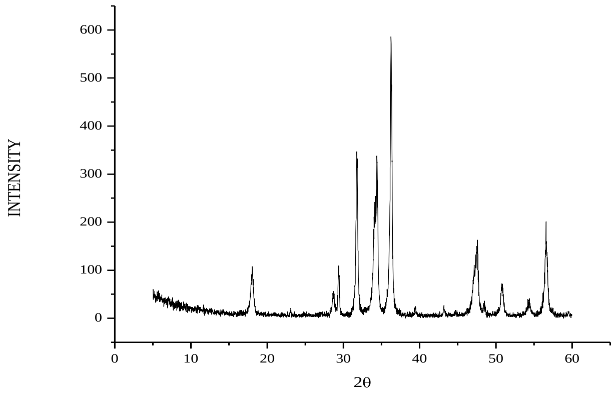

Figure 1: X-ray diffractograms of the nanoparticle $CaZnO_2$

The SEM images of prepared $CaZnO_2$ nanoparticle have shown the typical texture and morphology. SEM images obtained were depicted that the synthesized nanoparticles were both rod and cluster shaped (Figure 2).

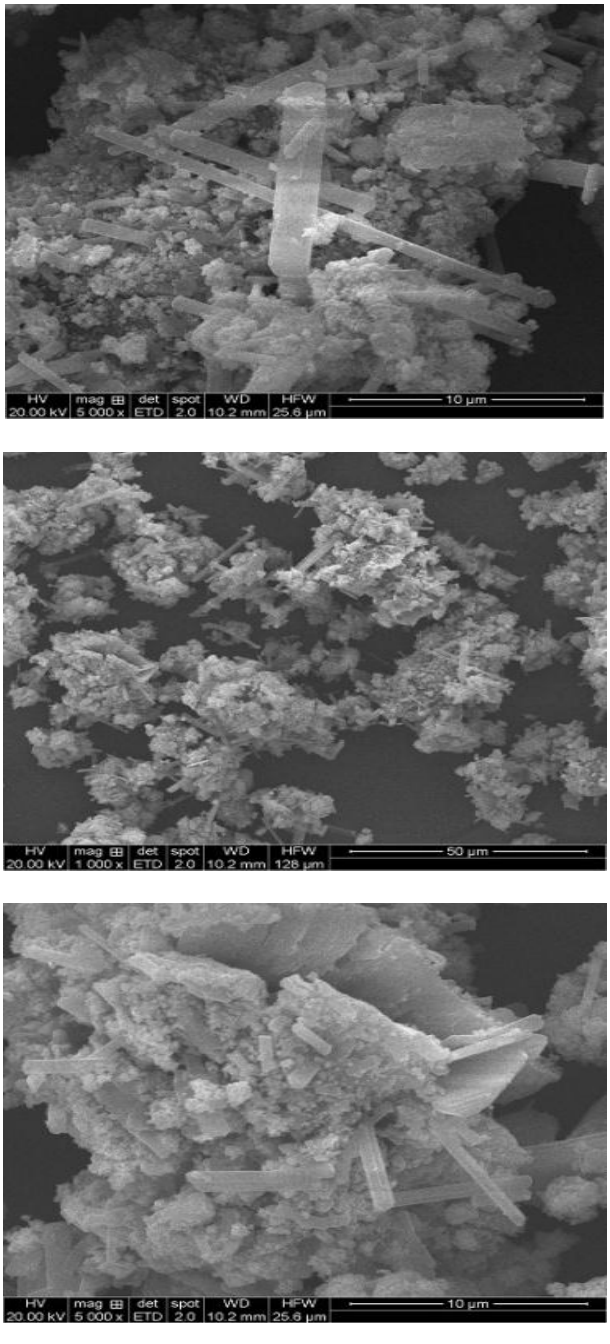

Figure 2: SEM micrographs of the nanoparticle $CaZnO_2$

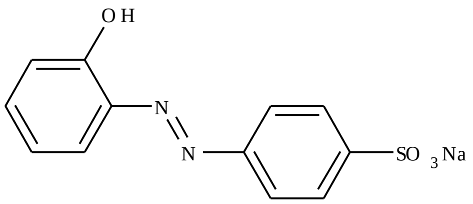

Figure 3: Structure of Acid orange 7

Procedure: For the photo degradation of AO7 a solution containing known concentration of dye (50 mg/L) and $CaZnO_2$ was prepared and it was stirred vigorously and allowed to equilibrated for 20 min in the darkness.. The suspension pH values were adjusted at desired level using dilute NaOH and H_2SO_4 and then the pH values were measured with pH pen. After that the beaker was kept in the sunlight. During irradiation, agitation was maintained to keep the suspension homogenous. The concentration of dye in each degraded sample was determined with UV-VIS spectrophotometer 169 (Systronics) at λ_{max}=507.5nm. The percentage of photo degradation D was determined by using the equation,

$$D= \{(C_0 - C_t) \div C_0\} \times 100,$$

Where C_0 is initial concentration of AO7 and C_t is the concentration of AO7 at time‘t’

Results and Discussion

Effect of sunlight irradiation and catalyst: It can be seen from Figure 4 that in presence of both $CaZnO_2$ and sunlight, 88.6% of dye was degraded at the irradiation time of 2hrs. Only 15% degradation occurs for the same experiment in the darkness and no degradation takes place without $CaZnO_2$ in presence of sunlight. These experiments demonstrated that both sunlight and photocatalyst such as $CaZnO_2$ were needed for the effective destruction of AO7, because it has been established that the photocatalysed degradation of organic matter in solution is initiated by the photo excitation of the semiconductor, followed by the formation of electron-hole pair on the surface of the catalyst. The mechanism of photocatalytic degradation for an azo dye are characterized by nitrogen to nitrogen double bonds (N =N). The color of azo-dyes is determined by the azo bonds and their associated chromophore and auxochromes. Azo bonds are the most active bonds in azo-dye molecules and can be oxidized by positive hole or hydroxyl radical or reduced by electron in the conduction band. The cleavage of N=N leads to the discoloration of dyes [13].

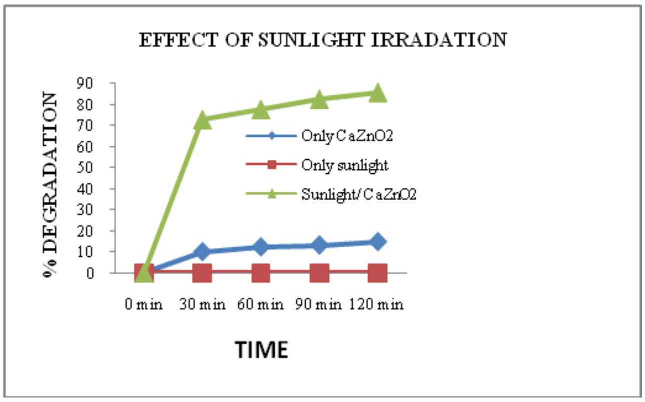

Figure 4: Effect of sunlight irradiation on Photocatalytic degradation of AO7. [$CaZnO_2$=0.4 g/L, AO7=50mg/L, pH=8]

Mechanism of the photocatalytic degradation

$CaZnO_2 + h\nu \rightarrow (e^-_{CB} + h^+_{VB})$ ……………………..(1)

$e^-_{CB} + O_2 \rightarrow O_2^{\bullet -}$ ……………...……………………..(2)

$H_2O + O_2^{\bullet -} \rightarrow OOH^\bullet + OH^-$ ……………………...(3)

$2OOH^\bullet \rightarrow O_2 + H_2O_2$ ………………………….…..(4)

$O_2^{\bullet -} + AO7 \rightarrow AO7\text{-}OO^\bullet$ ……………………….(5)
$OOH^\bullet + H_2O + e^-_{CB} \rightarrow H_2O_2 + OH^-$ ……………(6)
$H_2O_2 + e^-_{CB} \rightarrow OH^\bullet + OH^-$ …………….................(7)

$H_2O_2 + O_2^{\bullet -} \rightarrow OH^\bullet + OH^- + O_2$ ……….............(8)

$OH^\bullet / O_2^{\bullet -} / CaZnO_2^{\bullet +} + AO7$ Dye degradation...(9)

The mechanism of photocatalytic activity of $CaZnO_2$ nanoparticle can be predicted. Under sunlight irradiation $CaZnO_2$ molecules get excited and transfer electron to the conduction band (Eq 1). Electron in the conduction band of $CaZnO_2$ can reduce molecular oxygen and produce the super oxide radical (Eq 2). This radical may form hydrogen peroxide or organic peroxide in the presence of oxygen and organic molecule (Eq 3, 4, 5). Hydrogen peroxide can be generated in another path (Eq 6). Hydrogen peroxide can form hydroxyl radicals which are powerful oxidizing agents (Eq 7, 8). The radicals produced are capable of attacking dye molecules and degrade them (Eq 9).

Effect of catalyst concentration: The effect of concentration of $CaZnO_2$ on the photo degradation efficiency was shown in Figure 5. Experiments performed with different concentration showed that photo degradation efficiency increases with an increase in $CaZnO_2$ concentration up to 0.5g/L and is then decreased.

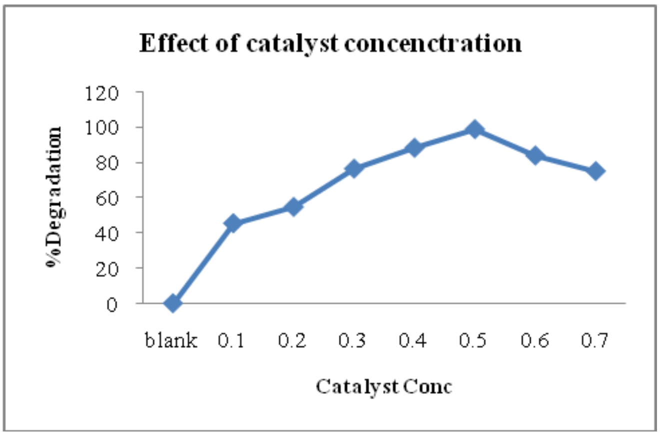

Figure 5: Effect of $CaZnO_2$ concentration on photocatalytic degradation of AO7at irradiation time 2hrs [AO7= 50 mg/L, pH=8, Sunlight]

The increase in degradation rate can be explained in terms of availability of active sites on the catalyst surface and sunlight penetration into the suspension as a result of increased screening effect and scattering of light. Further increase in the catalyst amount beyond 0.5g decreased the photo degradation. This may be due to overlapping of adsorption sites as a result of overcrowding owing to collision with ground state catalyst [14,15]. Since the photo degradation was most effective at 0.5g/L catalyst concentration, other experiments were performed in this concentration of $CaZnO_2$.

Effect of pH: In order to study the effect of pH on the degradation efficiency of $CaZnO_2$ catalyst, the experiments were conducted at various pH ranging from 2 to 11. The results showed that pH significantly affected the degradation efficiency. As shown in Figure 6, the degradation rate of AO7 increased from 77.6% to 99.2%when the pH was increased from 2 to 8 and then decreased to 80.2% at pH 11. The maximum degradation rate of AO7 was achieved at pH 8. AO7 is an anionic dye which contains sulphonated groups. Its photocatalytic activity is maximum at pH 8. More efficient formation of hydroxyl radicals occurs in alkaline medium. Excess of hydroxyl anions increases the formation of $OH^{\cdot}$ radicals. These $OH^{\cdot}$ radicals are the main oxidizing species responsible for photocatalytic degradation.(Eq 7-8) [16,17].

At pH more than 9, the decrease in the degradation efficiency could be explained on the basis of amphoteric nature of $CaZnO_2$ catalyst. $CaZnO_2$ surface becomes negatively charged for higher pH values. This causes the electrostatic repulsion between the catalyst and negatively charged AO7 dye [18].

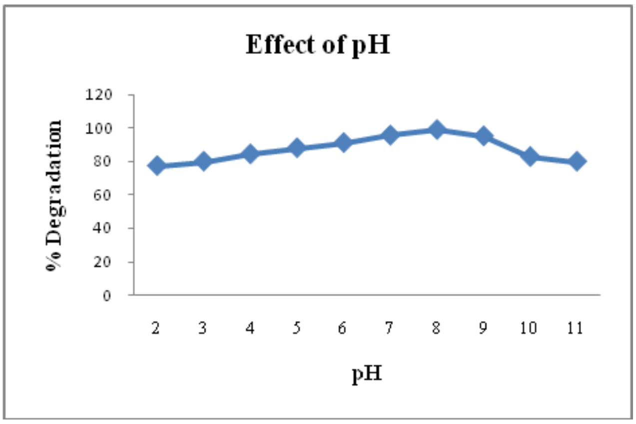

Figure 6: Effect of pH on photocatalytic degradation of AO7 at irradiation time 2hrs [$CaZnO_2$ =0.5g/L, AO7= 50 mg/L, Sunlight]

Effect of initial dye concentration: The effect of initial dye concentration on the decolorization efficiency was investigated by varying the initial concentration from 30 to 120 mg of catalyst loading (0.5g/L at solution pH 8) and results are shown in Figure 7. As seen in the figure, degradation efficiency is inversely affected by the dye concentration. The decrease in the degradation with increase in dye concentration is ascribed to the equilibrium adsorption of dye on the catalyst surface active sites increases, hence competitive adsorption of OH^- ions on the same sites decreases.

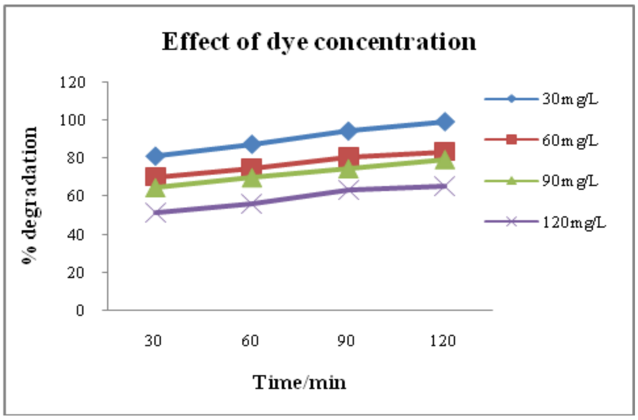

Figure 7: Effect of initial dye concentration on photocatalytic degradation of AO7.[$CaZnO_2$= 0.5 g/L, pH=8, Sunlight]

This phenomenon results in the lower formation of $OH^{\cdot}$ radicals which are considered as primary oxidizing agents of the organic dye [19]. Further, considering Beer Lambert law, as the initial dye concentration increases, the path length of photons entering the solution decreases. This results in lower photon adsorption on the catalyst particles, and consequently decreases photocatalytic reaction rate [20].

Conclusion

In this study solar photocatalytic degradation of textile dye acid orange 7 has been investigated using newly synthesized $CaZnO_2$ nanoparticle catalyst. $CaZnO_2$ has been found to be most active catalyst, exhibiting high photocatalytic activity. From the studies, it has been found that

- $CaZnO_2$ nanoparticle can be synthesized economically conveniently and quickly. Preparation cost of $CaZnO_2$ is many times less than TiO_2.
- At lower catalyst concentration, the catalyst surface and adsorption of light on catalyst surface are the limiting factors. Thus an increase in catalyst concentration greatly enhances the process efficiency. On the other hand, at high concentration, overlapping of adsorption site and deactivation of activated catalyst reduces the process efficiency.
- The degradation efficiency increases with increase in pH, attaining maximum value at pH 8. Above pH 9 the catalyst surface is negatively charged by means of adsorbed OH^- ions, which causes electrostatic repulsion between catalyst and negatively charged AO7, this deceases the degradation efficiency.
- Photodegradation is directly related to irradiation time and inversely related to the dye concentration. By increasing the dye concentration the equilibrium adsorption of dye on the catalyst surface increases and consequently $OH^{\cdot}$ radicals formation rate decreases. Further the path length of photons entering the solution

decreases also according to Beer-Lambert law which results in lower photon adsorption on catalyst particles.

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References

1. Gerko Oskam, Metal oxide nanoparticles: synthesis, characterization and Application, *J. Sol-Gel Sci Techn.,* **37**, 161 **(2006)**

2. Faraji M., Yamini Y. and Rezaee M., Magnetic Nanoparticles: Synthesis, Stabilization, Functionalization, Characterization, and Applications, *J. Iran. Chem. Soc.*, **7(1)**, 1 **(2010)**

3. Mohapatra M. and Anand S., Synthesis and applications of nano-structured iron oxides/hydroxides – a review, *Int. J. Eng. Sci. Tech.,* **2(8)**, 127 **(2010)**

4. Rajalakshmi Gopalakrishnan and Sudha Sellappa, Decolourisation of Methyl Orange and Methyl Red by Live and Dead Biomass of Fungi, *Asian J. Exp. Biol. Sci.,* **2(4)**, 569 **(2011)**

5. Joshni Chacko T. and Kalidass Subramaniam, Enzymatic Degradation of Azo Dyes – A Review, *Int. J. Environ. Sci.,* **1(6)**, 1250 **(2011)**

6. Mehmet Kobya, Orhan Taner Can and Mahmut Bayramoglu, Treatment of textile wastewaters by electrocoagulation using iron and aluminum electrodes, *J.Hazard. Mater. B,* **100,** 163 **(2003)**

7. Harrelkas F., Paulo A., Alves M.M., El Khadir L., Zahraa O., Pons M.N. and van der Zee F. P., Photocatalytic and combined anaerobic–photocatalytic treatment of textile dyes, *Chemosphere,* **72,** 1816 **(2008)**

8. Abdurrahman Akyol, Treatment of paint manufacturing wastewater by electrocoagulation, *Desalination,* **285,** 91 **(2012)**

9. Kuo W.S. and Ho P. H., Solar Photocatalytic decolorization of methylene blue in water, *Chemosphere,* **45**, 77 **(2001)**

10. Daneshvar N., Salari D. and Khataee A. R., Photocatalytic degradation of azo dye acid red 14 in water on ZnO as an alternative catalyst to TiO_2, *J. Photochem. Photobiol. A: Chem.,* **162,** 317 **(2004)**

11. Madhusudhana N., Yogendra K., Mahadevan K.M, and Suneel Naik, Photocatalytic Degradation of Coralene Dark Red 2B Azo Dye Using Calcium Zincate Nanoparticle in Presence of Natural Sunlight: An Aid to Environmental Remediation, *Int. J. Chem. Eng. Appl.*, **2(4),** 301 **(2011)**

12. Gerko Oskam, Metal oxide nanoparticles: synthesis, characterization and application, *J Sol-Gel. Sci. Techn.,* 37, 161 **(2006)**

13. Ya-Li Song, Ji-Tai Li and Bo Bai, TiO_2 Assisted Photodegradation of Direct Blue 78 in Aqueous Solution in Sunlight, *Water Air Soil Pollut.,* **213,** 311 **(2010)**

14. Fernandez Ibanez P., Malato S. and de las Nieves F. J., Relationship between TiO_2 particle size and reactor diameter in solar photoreactors efficiency, *Catalysis Today,* **54(2),** 195 **(1999)**

15. Ismail A.A., Ibrahim I.A., Ahmed M.S., Mohamed R.M. and El-Shall H., Sol–gel synthesis of titania–silica photocatalyst for cyanide photodegradation, *J. Photochem. Photobiol. A: Chem.,* **163(3),** 445 **(2004)**

16. Pinki Punjabi B., Rakshit Ameta, Anil Kumar and Madhu Jain, Visible light induced photocatalytic degradation of some xanthene dyes using immobilized anthracene, *Bull. Chem. Soc. Ethiop.,* **22(3),** 361 **(2008)**

17. Rakshit Ameta, Pinki Bala Punjabi and Suresh Ameta C., Photodegradation of Naphthol green B in the presence of semiconducting antimony trisulphide, *J. Serb. Chem. Soc.,* **76(7),** 1049 **(2011)**

18. Antoine Piscopo, Didier Robert and Jean Victor Weber, Influence of pH and chloride anion on the photocatalytic degradation of organic compounds Part I. Effect on the benzamide and para-hydroxybenzoic acid in TiO_2 aqueous solution, *App. Catal. B: Environ.,* **35,** 117 **(2001)**

19. Akpan U.G. and Hameed B. H., Parameters affecting the photocatalytic degradation of dyes using TiO_2-based photocatalysts: A review, *J. Hazard. Mater.,* **170**, 520 **(2009)**

20. Akyol A., Yatmaz H.C. and Bayramoglu M., Photocatalytic decolorization of Remazol Red RR in aqueous ZnO suspensions, *App. Catal. B: Environ.,* **54,** 19 **(2004)**.