

H₂ PRODUCTION FROM SULFIDE WASTEWATER USING ZnO DOPED TiO₂ PHOTOCATALYSIS

N.Thangam¹, E.Ezhilarasi², Syed Abuthahir³

^{1,2,3}Assistant professor, Department of Civil Engineering, PERI Institute of Technology, Tamil Nadu, India

Abstract - ZnO-TiO₂ powder synthesized by sol-gel method was used for production of hydrogen from sulfide wastewater. SEM, XRD, UV-DRS, FT-IR were used for characterization of the product. SEM shows that agglomeration of particles was due to cerium. XRD pattern indicates that crystal is tetragonal, body centred cubic lattice in anatase phase with particle size of 34.06 nm. The band gap energy of 1.7 eV and threshold wavelength of 700 nm were found using UV-DRS. Also, the surface adsorption was determined using FTIR. The photocatalytic properties for the production of H₂ from simulated sulfide water were studied using ZnO -TiO₂ a tubular photocatalytic reactor. The results show that 0.1 g suspended in 500 ml of simulated wastewater (10000 mg/L) irradiated at 150W visible lamp produced maximum H₂ of 5189 μmol h⁻¹ by converting sulfide (200 mg/L). The comparison of performance also reveals that ZnO-TiO₂ was better than Nano TiO₂ and TiO₂.

Key Words: ZnO-TiO₂, Band gap, Sulfide, Hydrogen, Photocatalysis, Sol-gel method.

1.INTRODUCTION (Size 11 , cambria font)

During the past few decades, refining crude oil by refiners have significantly reduced sulfur dioxide emissions in the transportation sector. The sulfur present in the crude oil is removed and it generates sulfide rich wastewater which is the biting issue in the industrial sectors. The presence of sulfide in the wastewater exerts a high biological oxygen demand of 2mol O₂/L mol S²⁻ which remains a threat to living organisms in water (Poulton *et al.*, 2002). Hence, if released to the water bodies without treatment can cause serious environmental effects causing adverse threat to the aquatic life and mass fish mortality (Altas and Buyukgungor, 2008). Considering the impacts, the treatment of sulfide from wastewater is often attempted through various treatment processes like

adsorption, coagulation, chemical oxidation, wet air oxidation, membrane technologies, and biological processes to avoid the related environmental concerns but all of them are either expensive or not friendly to environment (El Naas *et al.*, 2009, Demirci *et al.*, 1997, Abdelwahab *et al.*, 2009, Sun *et al.*, 2008, Rahman and Al Malack, 2006). Furthermore, refineries are also in need of large quantities of hydrogen to purify sulfur rich crude oils (World diesel, 2003). To resolve both the problems by framing a suitable strategy, solar photocatalysis is the best and beneficial treatment process which has a high oxidation potential (estimated to be +2.8V) to mineralize all the organic pollutants and the catalyst itself is non-toxic, cost effective and readily available (Al-Rasheed., 2005, Laoufi *et al.*, 2008,

Gaya and Abdullah, 2008). Among the semiconducting materials, more attention is given to TiO₂ because of its high photocatalytic activity, resistance to photocorrosion, photostability, low cost and non toxicity. Nevertheless, Titania has a large band gap (3.2 eV for anatase TiO₂) and therefore small fraction of solar light, about 2-3 % in the UV region can be utilized so that they cannot be installed in refineries to solve the problem. Hence, continuous improvement of photoreaction rate and the solar efficiency via adjusting the band structure of TiO₂ is a promising phenomenon at this stage.

To achieve this goal, metal doped titania is given more focus, testing their efficiency by comparison with pristine TiO₂ (Sampath *et al.*, 1994 and Ranjit *et al.*, 1997). So far, this technology is yet to be commercialized because of the low photocatalytic rate degradation efficiency on the surface of TiO₂ particles, which is due to the fast recombination rate of photogenerated electron-hole pairs. In order to slow

down this process and enhance the interfacial charge efficiency, the properties of TiO_2 particles have been modified by selective surface treatments, such as surface chelation, surface derivatization, platinization and doping of TiO_2 by certain metal ions. (Moser *et al.*, 1991, Hong *et al.*, 1987, Serpone and Lawless, 1994, Lin *et al.*, 1998). In this perspective, many reports using transition metal ion or noble metal as dopants in TiO_2 system have come to the fore. Until last decade, transitional metals are used only in displays and lightings (Zhang *et al.*, 2010 and Eliseeva *et al.*, 2010) but it attained a new rise in the 21st century because of its afterglow property (Huiming *et al.*, 2007, Yan *et al.*, 2010, Mitsuo *et al.*, 2009).

To impart the efficiency in catalytic activity, doping of foreign transition elements into the existing photocatalysts (cationic doping) is one approach and has been studied extensively (Mills *et al.*, 1997, Kato *et al.*, 2002, Ishii *et al.*, 2004). Another approach to synthesize active visible light catalyst is to dope oxygen by N, C or S into a large band gap metal oxide catalyst anionic network (anionic doping). Hara *et al.*, 2004 showed that Ti-O-N system band gap energy could be tuned by adjusting the amount of doped nitrogen and thereby, the electrical properties of the material can be modified. Recently in a brief report (Priya and Kanmani, 2009 and 2011) we have demonstrated the synthesis of CdS-ZnS where the co-precipitation method was used to produce the complex catalyst.

This paper presents the work on the elaborate synthesis of nanosize ZnO- TiO_2 photocatalyst with the extensive characterization by Scanning Electron Microscope (SEM), X-Ray Diffractometer (XRD), Ultraviolet Visible Diffuse Reflectance Spectroscopy (UV-DRS), Fourier transform Infrared Spectroscopy (FTIR). The interesting outcome of this study is that the synthesized ZnO- TiO_2 is found to be an excellent photocatalyst and it is more active than other catalysts under visible light irradiation for the production of hydrogen from sulfide wastewater.

2. MATERIALS AND METHODS

Method of preparing the ZnO- TiO_2 powders was similar to that mentioned in the literature (Liu *et al.*, 2004, Fan *et al.*, 2006) using sol-gel method.

Appropriate cerium nitrate ($\text{Zn}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, HIMEDIA, U.S.A) was dissolved in distilled water in the ratio of 1:8 and the pH of the mixture solution was adjusted to 1.5 using Nitric acid (HNO_3 , MERCK, U.S.A), then titanium Isopropoxide solution ($\text{C}_{12}\text{H}_{28}\text{Ti}$, SPECTROCHEM, India) was added drop by drop to the mixed solution with constant stirring for 10-12 hours,. The white precipitate was formed instantaneously. The resulting colloid solution was concentrated at 35-40°C in a rotary evaporator. The final solution with the precipitate was filtered and dried and given heat treatment at 400°C for 2 hours using muffle furnace.

The phase identification of the powder was conducted at room temperature using X-Ray Diffractometer (XRD, $\text{CuK}\alpha 1$, $\lambda = 1.54$ nm, PANalytical, Netherlands). The phase and particle size were determined using Scherrer equation. Scanning Electron Microscopy (SEM, S3400N, HITACHI, Japan) was used to analyze the particles morphology and the agglomeration.

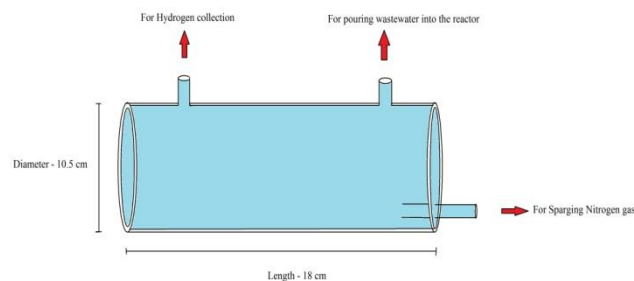


Fig 1. Reactor layout

UltraViolet – Visible Spectroscopy (UV-DRS,) was used to find out the threshold wavelength and bandgap was determined by Getoff and Linselbieger equation and Fourier Transform Infrared Spectroscopy (FT-IR, PERKIN ELMER, U.S.A) which was used to confirm the doping and the surface adsorption of the prepared photocatalyst.

The PCD experiments were conducted using a batch type (Acrylic) reactor holding 500 mL of the respective synthetic wastewater sample batch with ZnO - TiO_2 . Fig 1 provides the reactor details. Batches of synthetic wastewater samples were prepared using distilled water and stock solution was prepared from

using Sodium sulfide (MERCK, U.S.A) and Sodium sulfite (MERCK, U.S.A). For the PCD experiments, effects of various parameters like sulfite concentration, pH of the wastewater, dosage of the catalyst, Volume of the wastewater and finally its performance were compared using various catalysts. The synthetic wastewater batch with ZnO-TiO₂ was transferred to PCD reactor. A 150 W near visible lamp (PHILIPS) that emits rays at a wavelength 615-700 nm with the peak maximum at ~ 682 nm was then positioned at the centre of the reactor. The light source and reactor are separated atleast with a distance of 15 cm. The visible lamp was turned on during the course of the study. The reaction was carried out from 0 to 30 minutes, after which the samples were collected. The hydrogen produced is collected through downward displacement of water. The hydrogen production from sulfide conversion was calculated using the below mentioned formula.

$$\text{Sulfide conversion (Y) in \%} = \frac{\text{Moles of H}_2 \text{ produced}}{\text{Moles of Na}_2\text{S fed}} \times 100$$

The moles of H₂ produced in the reaction have been calculated using Ideal gas equation. The alkaline solution (NaOH, MERCK) was used in order to fix the gas errors. The hydrogen collected in the downward displacement was tested using Gas chromatograph (GC 2014, SHIMADZU, Japan) which was equipped along with the conductivity detector for hydrogen. The Gas chromatograph was calibrated regularly using known concentration of hydrogen. The sulfide conversion in percentage was calculated using the concentration of the simulated sulfide wastewater and from the volume of hydrogen obtained from the reaction. The pH analyses were completed using a pH meter setup (ELICO, India)

3. CHARACTERIZATION OF PHOTOCATALYST

3.1 SEM

The ZnO-TiO₂ powder prepared by sol-gel process method was crystalline with a slight yellow colour. The SEM micrograph of ZnO-TiO₂ is shown in Fig.2 which indicates that the agglomeration of

particles was observed which was due to the result of doping (Liu *et al.*, 2005).

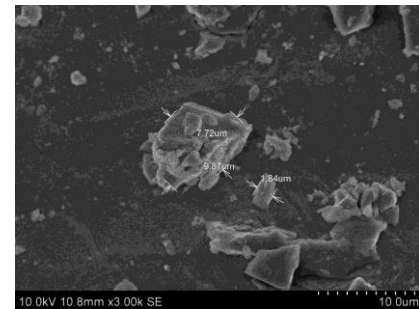


Fig 2. SEM micrograph of ZnO-TiO₂

3.2 XRD

The XRD pattern of ZnO-TiO₂ is shown in Figure. 3. indexed using ISCD no. 86-1157. The indexing study indicates that the powder consists of tetragonal ZnO -TiO₂ in a body centered cubic lattice configuration with a particle size of 32.4 nm which was determined with the strong peak (101) at 2θH'' 25.5° of the ZnO-TiO₂ phase. The particle size is smaller than pure TiO₂ which was due to doping of cerium which can cause the change in quantum size effect (Hoffmann *et al.*, 1995). The pattern also reveals that anatase peaks are more dominant than rutile. The inhibition of phase transition was ascribed to the stabilization of anatase phase by the Ce through the formation of Ti- O- Zn bonds (Zhang *et al.*, 1998). The stability of the anatase peak was due to the electron density imparted by the cerium to TiO₂ (Ranjit *et al.*, 1997).

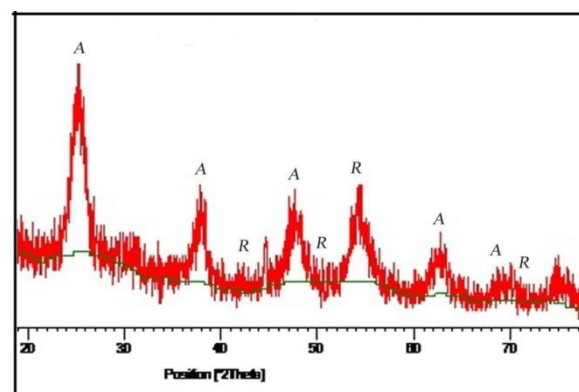


Fig 3. XRD of ZnO-TiO₂

3.3 UV-DRS

The UV-DRS pattern of Figure. 4. was indexed with the UV-DRS spectrum of Gao et al., 2000. The pattern discloses the fact that, after doping, there was a change in band gap and in threshold wavelength. The band gap energy changed from 3.2 eV to 1.7 eV. This modification was due to the dispersion of ceria component in the TiO₂ (Coronado et al.,2002).

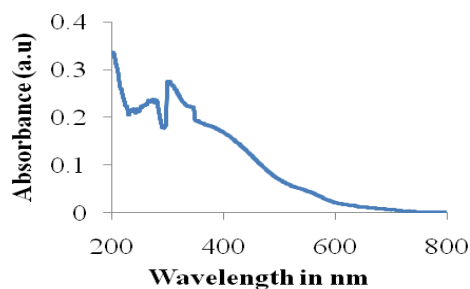


Fig 4 UV_DRS of ZnO-TiO₂

4. RESULTS AND DISCUSSION

Photocatalytic studies for the production of simulated sulfide wastewater were conducted in earlier experiments. First the experiments were conducted at optimizing the sulfite concentration because the sulfite concentration plays a significant role in erratic behaviour of sulfide nature. Three concentrations which were taken for the study are 0.15, 0.25 and 0.35 M. among that; the greater production of hydrogen production and sulfide conversion of maximum was attained at the concentration of 0.25 M. Table. 1 shows the hydrogen production and sulfide conversion with respect to change in sulfite concentration.

Sulfite Concentration in Moles	H ₂ Production in μmol h ⁻¹	Sulfide conversion in mg/L
0.15	3068	204
0.25	5189	207
0.35	2231	63

Table. 1. Effect of Sulfite Concentration

All of these experiments are carried out for 30 minutes of irradiation. The adsorption was maximum at 0.25 M so it attained the higher photocatalytic activity. Also, at some concentrations the wastewater occupies more active sites than the OH⁻ radicals which causes the low photocatalytic activity (Kashif and Ouyang, 2009).

Following the sulfite optimization, pH optimization should be performed because of its prominent role in existing nature of the sulfur compounds. The three basic pH 11, 12 and 13 were tried to find the favourable pH for the maximum hydrogen production and sulfide conversion. Table 2 shows the hydrogen production and sulfide conversion with respect to change in pH.

pH	H ₂ Production in μmol h ⁻¹	Sulfide conversion in mg/L
11	1394	57
12	5245	209
13	2510	100

Table. 2. Effect of pH

pH 12 which is a natural pH of the simulated wastewater was found to have the maximum hydrogen production and sulfide conversion at 30 minutes of irradiation. In photocatalytic treatment of sulfide or thiosulfate wastewater, the natural pH was found to be in favour of the photocatalytic activity (Vohra et al., 2011). The basic pH imparts the hydroxyl group to the surface which causes the increase in adsorption of pollutant to TiO₂ surfaces. The hydroxyl groups when it integrates to the active sites provides a higher photocatalytic activity (Jiangrong et al, 2006). At a low pH, the surface charges of ZnO and TiO₂ would be positive, and at high pH, both particles won't have much effective contact and charge transfer from Zn and TiO₂ (Hoffmann et al, 1995). In order to use the catalyst in efficient manner, effect of dosage was done to know the amount of catalyst needed for efficient

treatment. 0.05, 0.1 and 0.2 g were used for the dosage study.

Catalyst dosage in g	H ₂ Production in $\mu\text{mol h}^{-1}$	Sulfide conversion in mg/L
0.05	1339	53
0.1	5300	212
0.2	2789	111

Table. 3. Effect of Catalyst dosage

Table 3 provides data regarding the hydrogen production and sulfide conversion in table with respect to change in dosage of the catalyst. The greater photocatalytic activity was achieved at 0.1 g proving it as the optimum catalyst dosage, as a large surface area is available for adsorption of dye followed by its degradation. Above the optimum value, the solution opacity increases which affects the light penetration through the solution leading to a decrease in rate of degradation. After optimizing dosage, the volume of the wastewater was taken for the study. Varying amounts of wastewater 100, 300, 500 mL were taken for the study. The hydrogen production and sulfide conversion are presented in table 4.

Volume in mL	H ₂ Production in $\mu\text{mol h}^{-1}$	Sulfide conversion in mg/L
100	1785	0.71
200	2901	1.16
500	5133	2.05

Table. 4. Effect of Volume

The photocatalytic activity increases with the increase in volume of wastewater. Hydrogen production will always depend upon the amount of reactants. Higher the volume of the reactant supplied higher the amount of hydrogen generation (Lin et al., 2011).

After optimizing all the parameters in the treatability studies, the performance of the ZnO -TiO₂ was compared with the existing catalysts, Nano TiO₂ and Degussa TiO₂. The hydrogen production and sulfide conversion in the study were given in the table. 5.

Catalyst	H ₂ Production in $\mu\text{mol h}^{-1}$	Sulfide conversion in mg/L
ZnO-TiO ₂	1339	53
Nano-TiO ₂	5300	212
Degussa TiO ₂	2789	111

Table.5. Comparison of ZnO -TiO₂ with various catalysts

The high activity of the ZnO -TiO₂ is due to the electron density imparted to the TiO₂ surface by the cerium. Li et al (2006a) works also gives the required evidence that using of Cerium with TiO increases the hydrogen production. The photocatalytic activity is Zn -TiO₂ is also stable because of the stabilization of anatase phase by the surrounding earth oxides throughout the formation of Ti-O-Zn element bonds (Zhang et al, 2008) which causes the change in amount of hydroxyl groups resulting from the interaction between the Cerium and TiO₂ (Lin et al, 1999).

5. CONCLUSION

The Tetragonal, body centered cubic crystal structure like ZnO-TiO₂ in the anatase phase was efficiently synthesized with sol-gel method. The powders possess small band gap energy with threshold wavelength in the visible region. The photocatalyst was optimized through treatability studies. 0.1 g of catalyst dispersed in 500 mL of simulated sulfide wastewater (10000 mg/L) irradiated under the visible lamp of 150 W produced the hydrogen of 5189 $\mu\text{mol h}^{-1}$ with the sulfide conversion of 2.07 % (207.5 mg/L). The

performance of ZnO-TiO₂ was found to be best than Nano TiO₂ and Degussa TiO₂.

REFERENCES

- Abdelwahab O., Amin N.K., El Ashtoukhy E, (2009), 'Electrochemical removal of phenol from oil refinery wastewater', *J. Hazard. Mater*, Vol. 163, pp. 711-716.
- Altas L., Buyukgungor H, (2008), 'Sulfide removal in petroleum wastewater by chemical precipitation', *J. Hazard. Mater*, Vol. 153, pp. 462-469.
- Coronado J.M., Maira A.J., Martinez-Arias A., Conesa J.C., Soria J, (2002), 'EPR study of the radicals formed upon UV irradiation of ceria-based photocatalysts', *J. Photochem. Photobiol*, Vol. 150, pp. 213-221.
- Demirci S., Erdogan B., Ozcimder R, (1997), 'Wastewater treatment at the petroleum refinery Kirikkale Turkey using some coagulant and Turkish clays as coagulant aids', *Water Res*, Vol. 32, pp. 3495-2499.
- El-Naas M.H., Al-Zuhair S., Al Lobaney A., Mahloun S, (2009), 'Assessment of electrocoagulation for the treatment of petroleum refinery wastewater', *J. Environ. Manage*, Vol. 91, pp. 180-185.
- Jacack B.V and Belikov S, (2010), Enhanced production of Direct Photons in Au+ Au Collisions at $s_{NN} = \text{GeV}$ and implications for the Implication Temperature, *Phy. Rev. Lett*, Vol. 104, pp. 132301-132307.
- Fan Camei., Xu Peng and Sun Yanping, (2005), 'Preparation of Nano TiO₂ doped with Cerium and its photocatalytic activity', *J. Rare Earths*, Vol. 24, pp 309 -313.
- Gao X., Wachs I.E, (1999), 'Photoreduction of Ag ion on ZnO single crystal', *Catal. Today*, Vol. 51, pp. 233-254.
- Growth in Industrial Gas Supplied Hydrogen to US and European Refiners, (2003), *World Diesel*, pp. 15 and 16.
- Hara M., Takata T., Kondo J.N., Domen K, (2004), 'Photocatalytic reduction of water by TaON under visible light irradiation', *Catal Today*, Vol. 90, pp. 313.
- Hong A.P., Bahnemann D.W., Hoffmann M.R, (1987), " , *J. Phys. Chem*, Vol. 91, pp. 2109.
- Huiming J., Gijiu X., Ying L., Huixiang, (2007), 'A new phosphor with flower-like structure and luminescent properties of Sr₂MgSi₂O₇: Eu²⁺, Dy³⁺ long afterglow materials by sol-gel method', *J. Sol-Gel Sci Technol*, Vol. 44, pp. 133-137.
- Ishii T., Kudo H., Kudo A, (2004), 'H₂ evolution from aqueous methanol solution on Sr₂TiO₃ photocatalyst doped with tantalum and chromium ions under visible light irradiation', *J. Photochem. Photobiol. A*, Vol. 103, pp. 181.
- Jiangrong Xiao., Tianyou Peng., Rang Li and Zhenghe Peng Chunhua Yan, (2006), 'Preparation, phase transformation and photocatalytic activities of cerium-doped mesoporous titania nanoparticles', *J. Solid State Chemistry*, Vol. 179, pp. 1161- 1170.
- Kale BB., Baeg JO., Lee S.M., Chang H., Moon S., Lee C.W, (2006), 'CdIn₂S₄ nanotubes and Marigold nanostructures', *Adv. Func. Mater*, Vol. 16, pp. 1349.
- Kamat P.V, (2002), 'Photophysical, Photochemical and Photocatalytic Aspects of Metal Nanoparticles', *J. Phys. Chem*, Vol. B 106, 7729.
- Kashif Naeem., Ouyang Feng, (2009), 'Parameter effect on heterogeneous photocatalyzed degradation of phenol in aqueous dispersion of TiO₂', *J. Envi. Sci*, Vol. 21, pp. 527-533.
- Kato H., Kudo A, (2002), 'Visible-light response and photocatalytic activity of TiO₂ and SrTiO₃ photocatalyst codoped with antimony and chromium', *J. Phys. Chem. B*, Vol. 106, pp. 5029.
- Laoufi N.A., Tassalit D., Bentahar F, (2008), The degradation of phenol in waste solution by TiO₂ photocatalyst in a chemical reactor, *Global Nest J*, Vol. 10, pp. 404-418.
- Li Y., Xiang C., Hong L.J, (2006a), 'Treatment of oily wastewater by organic-inorganic

- composite tubular ultrafiltration (UF) membranes', *Desalination*, Vol.196, pp. 76-83.
21. Lin J., Yu J.C, (1998), 'An investigation on photocatalytic activities of mixed TiO₂-rare earth oxides for the oxidation of acetone in air', *J. Photochem. Photobiol.* Vol. A 116, pp. 63.
22. Liu Z., Guo B., Hong L., Jiang H, (2005), 'Preparation and characterization of cerium oxide doped TiO₂ nanoparticles', *J. Phys. Chem. Solids*, Vol. 66, pp. 161.
23. Mills A., Le Hunte S, (1997), 'Overview of semiconductor particles', *J. Photochem. Photobiol. A Chem*, Vol. 108, pp. 1.
24. Mitsuo Y., Yusuke O., Tomomi N., Nobou K., Nobuhiro K., Thomas P.J. Han, (2009), 'Long lasting phosphorescence in Ce-doped oxides', *J. Mater. Sci*, Vol. 20, S471-S475.
25. Moser J., Puchihewa S., Infelta P.P., Gratzel, (1991), 'Surface complexation of colloidal semiconductors strongly enhances interfacial electron-transfer rates', *Langmuir*, Vol. 7, pp. 3012.
26. Poulton S.W., Krom M.D., Rijn J.V., Raiswell R, (2002), 'The use of hydrous ion (III) oxides for the removal of hydrogen sulphide in aqueous systems', *Water Res*, Vol. 36, pp. 825-834.
27. Priya R and Kanmani S, (2009), 'Batch slurry photocatalytic reactors for the generation of hydrogen from sulfide and sulfite waste streams under solar irradiation, *Solar Energy*, Vol. 83, pp. 1802-1805.
28. Priya R and Kanmani S, (2011), Optimization of photocatalytic production of hydrogen from hydrogen sulfide in alkaline solution using surface response methodology, *Desalination*, Vol. 276, pp. 222-227.
29. Qifeng Chen., Dong Jiang., Weimei Shi., Dong Wu and Yao Xu, (2009) 'Visible-light-activated Ce-Si co-doped TiO₂ photocatalyst', *J. Appl. Surf. Sci*, Vol. 255, pp. 7918-7924.
30. Ranjit K.T., Viswanathan B, (1997), 'Photocatalytic reduction of nitrite and nitrate ions over doped TiO₂ catalysts', *Photochem. Photobiol. A. Chem*, Vol. 107, pp. 215.
31. Sampath S., Uchida H., Yoneyama H, (1994), 'Photocatalytic degradation of gaseous pyridine over zeolite supported Titanium di-oxide', *J. Catal*, Vol. 149, pp. 189.
32. Serpone N., Lawless D, (1994), 'Spectroscopic photoconductivity and photocatalytic studies of TiO₂ colloids: Naked and with the lattice doped with Cr³⁺, Fe³⁺ and V⁵⁺', *Langmuir*, Vol. 10, pp. 643.
33. Su-Hsia Lin., Chwei-Huann Chiou., Chih-Kai Chang and Ruey-Shin Juang, (2011), 'Photocatalytic degradation of phenol on different phases of TiO₂ particles in aqueous suspensions under UV irradiation', *J. Environ. Mgmt*, Vol. 92, 3098- 3104.
34. Sun Y., Zhang Y., Quan X, (2008), 'Treatment of petroleum refinery wastewater by microwave assisted catalytic wet air oxidation under low temperature and low pressure', *Sep. Purif. Technol*, Vol. 62, pp. 565-570.
35. Sun Y., Zhang Y., Quan X, (2008), 'Treatment of petroleum refinery wastewater by microwave assisted catalytic wet air oxidation under low temperature and low pressure', *Sep. Purif. Technol*, Vol. 62, pp. 565-570.
36. Svetlana V. Eliseeva and Jean-Claude G. Bünzli, (2010), Lanthanide luminescence for functional materials and biosciences, *Chem. Soc. Rev*, Vol. 39, pp. 189-227.
37. Vohra M.S., Selimuzzaman S.M and Al-Suwaiyan M.S, (2011), 'Aqueous Phase Thiosulfate Removal Using Photo catalysis', *Int. J. Environ. Res*, Vol. 5, pp 247 - 254.
38. Yu J.C., Zhang L.Z., Yu J.G, (2002), 'Direct Sonochemical Preparation and Characterization of Highly Active Mesoporous TiO₂ with a Bicrystalline Framework', *Chem. Mater*, Vol. 14, pp. 4647-4653.
39. Zhang H., Banfield J.F, (1998), 'Thermodynamic analysis of phase stability of nanocrystalline titania', *J. Mater. Chem*, Vol. 8, 2073-2076.
40. Zhaolin Liu., Bing Guo., Liang Hong and Huixian Jiang, (2004), 'Preparation and characterization cerium oxide doped TiO₂

nanoparticles', *J. Phys & Chem of Solids*, Vol. 66,
pp.161- 167.