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Visible light assisted photocatalytic degradation of 2-aminophenol using H_2O_2 sensitized $BiVO_4$

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ABSTRACT

Visible light photocatalytic degradation of 2-aminophenol is investigated using $BiVO_4$ synthesized by room temperature solid-state metathesis reaction using the precursors $BiOCl$ and $NaVO_3$. Addition of external oxidant H_2O_2 enhanced the rate of degradation of 2-aminophenol. Complete photodegradation of 10ppm 2-aminophenol occurred for 5h of visible light irradiation in presence of 100 mg of $BiVO_4$. Synergetic effect is noticed between $BiVO_4$ and H_2O_2 .

Key words: 2-aminophenol, photocatalytic degradation, $BiVO_4$, Synergetic effect

INTRODUCTION

Heterogeneous photocatalysis based on combined use of UV-visible light and a semiconductor material proved to be a promising technique for remediation of several hazardous organic pollutants like aromatic compounds, pesticides and pharmaceuticals in water [1-3]. Several semiconductor binary metal oxides such as TiO_2 , Fe_2O_3 , ZrO_2 , CuO , MoO_3 , ZnO , Bi_2O_3 , SnO_2 [4-11] and metal sulphides like CdS and ZnS [12-13] have been studied as photocatalysts under U.V. irradiation. These studies revealed that TiO_2 is an extremely useful photocatalyst because it is inexpensive, easy to synthesis, non corrosive and photo stable. Despite these advantages, TiO_2 suffers from two important limitations namely limited absorption in solar radiation because of its wide band gap and, rapid recombination rate of charge carriers generated consequent to photoabsorption. In order to extend photo response of TiO_2 in to visible region and to enhance life times of generated e^- s and holes, different strategies have been pursued in terms of doping, codoping and tridoping with transition metal atoms/anions and/or cations, surface sensitization with dyes/ pthalocyanins/porphyrins, and fabrication of nano/meso form of composites with high surface to volume ratio. These techniques though yielded better results compared to TiO_2 , yet suffer from some serious limitations. For instance, dopants when exceed an optimum concentration level tend to act as traps. Likewise in the dye sensitization process, one has to contend with competing oxidative degradation of dye sensitizer along with pollutant. Similarly, formation of nanoheirarchial structures involves special methods and not cost effective. Alternately, several investigations revealed that ternary metal oxide semiconductors can also function as good photocatalysts in the largely available visible region of solar radiation unlike the majority of binary metal oxides whose absorption is restricted to relatively less available U.V. region of solar radiation [14]. These ternary metal oxides include $ZnWO_4$ [15], $BiVO_4$ [16], $CoFe_2O_4$ [17], $Zn_3(VO_4)_2$ [18], $BaBiO_3$ [19], FeV_3O_8 [20], Bi_2MoO_6 [21], Bi_2WO_6 [22], α - $Bi_2Mo_3O_{12}$ [23], $NaBiO_3$ [24], $Fe_2Mo_3O_{12}$ [25], $BiFeO_3$ [26] etc. of which composite oxides of Bi-V, Bi-Mo and Bi-W forms a major portion of visible light active photocatalysts. Among these three families, $BiVO_4$ in presence of external oxidant H_2O_2 has been shown to photocatalytically degrade several organic pollutants that include Brilliant green [27], Eosin

blue and Eriochrome black-T [28], Fast sulphon black-F [29], Nitrobenzene [30], 2, and 4- nitrophenols [31], acetophenone [32], Rhodamine -B and phenol [33], Methylene blue [34] and Methyl orange [35] under visible light irradiation.

2-aminophenol is an important intermediate in the synthesis of several dyes, Benzoxazoles and agrochemicals [36]. Maurino *et al* [37] reported photocatalytic degradation of 2-, 3-, and 4-amino phenols using TiO₂ under U.V irradiation at pH 5.5. Pulgarin and Kiwi [38] reported that pretreatment step of photocatalysis mediated by α -Fe₂O₃ enhanced the biodegradability of 2-aminophenol. Andreozzi and coworkers [39] investigated Iron (III) hydroxide (FeOH) mediated photooxidation of 2-aminophenol. Lafta and Kadhim [40] studied photocatalytic degradation of 2-aminophenol over ZnO and riboflavin sensitized ZnO and observed that U.V. light illumination was more active than sun light in the reaction. Present paper describes heterogeneous photocatalytic degradation of 2-aminophenol using H₂O₂ sensitized monoclinic BiVO₄ under visible light irradiation.

MATERIAL AND METHODS

Synthesis of Photocatalyst:

BiVO₄ is prepared by room temperature solid-state metathesis synthesis reported elsewhere [30]. Stoichiometric amounts of BiOCl (Loba Chemie PVT. Ltd) and NaVO₃ (HIMEDIA) in the molar ratio of 1:1 are mixed in an agate mortar and ground for 2hrs in ethanol. With progressive grinding, the mixture exhibited a canary yellow colour. After 2hrs of grinding, the mixture is washed several times with distilled water to completely remove the by product NaCl and the residue is dried at 80°C in an air oven. The dried powder is subjected to phase identification, microstructural investigation and photocatalytic studies.

Characterization Techniques:

Phase purity of the resultant powder was investigated with X-ray diffractometer (PANalytical- X' Pert PRO, Japan) at room temperature, using Nickel filtered Cu-K_α radiation ($\lambda = 1.54059 \text{ \AA}$), with a scan rate of 2° min^{-1} . Microstructural investigation of the sample was performed on the powdered sample using SEM (JEOL-JSM-6610LV, Tokyo, Japan).

Photocatalytic studies:

Photocatalytic activity of BiVO₄ was evaluated in terms of degradation of 2-aminophenol under visible light. 100 mg of the catalyst was dispersed in 100ml 2-aminophenol aqueous solution (10 mg/L) and the suspension was magnetically stirred for half an hour in dark to ensure adsorption/desorption equilibrium between photocatalyst powder and dye. The suspension was then exposed to 400 wt metal halide lamp; 5ml aliquots were pipetted at periodic time intervals and filtered through 0.45 micron Millipore filters to remove the suspended powder. The spectra as a function of irradiation time were recorded using UV-Visible spectrophotometer (Schimadzu). The extent of photodegradation was calculated using the following equation

$$\% \text{ Photodegradation} = [(A_0 - A_t) / A_0] \times 100$$

where A₀ and A_t correspond to the initial absorbance and absorbance at time 't' respectively.

Photoluminescence studies:

50 mg BiVO₄ catalyst is added to the beaker containing 100 ml of terphthalic acid (TPA) solution (0.25 mmol L⁻¹ in 1mmol L⁻¹ NaOH solution) and 10 μm H₂O₂. The solution is stirred for 15 min in dark followed by irradiation by 400 w metal halide lamp for 30 min. The reacted solution was centrifuged and the clear solution is used for photoluminescence measurements in a fluorescence spectro fluorometer (Fluoromax 4) with the excitation wavelength of 315 nm.

RESULTS AND DISCUSSION

BiVO₄ has been reported to exist in three different crystalline modifications of tetragonal Zircon, tetragonal Scheelite and monoclinic Scheelite type crystal structures among which only monoclinic form proved to be a visible light active photocatalyst. Also, it is established that high temperature synthesis methods generally yield monoclinic phase while low temperature synthesis leads to tetragonal scheelite form [41]. Room temperature solid state metathetic reactions have been reported to provide a simple route for the synthesis of several mixed metal oxides

[42, 43] in which the high gain in lattice energy for the by product NaCl acts as the driving force for solid-state metathetic exchange. X-ray diffraction pattern of the ground mixture of BiOCl+NaVO₃ after washing is shown in Fig. 1. All the experimentally observed diffraction peaks could be indexed to monoclinic BiVO₄ reported in JCPDS File No. 75-2480. Absence of any extra peaks due to contaminants, ascertains that resultant BiVO₄ is phase pure. Micro structural investigation with SEM shown in Fig. 2 revealed particle size in the range of μm with no characteristic texture or orientation.

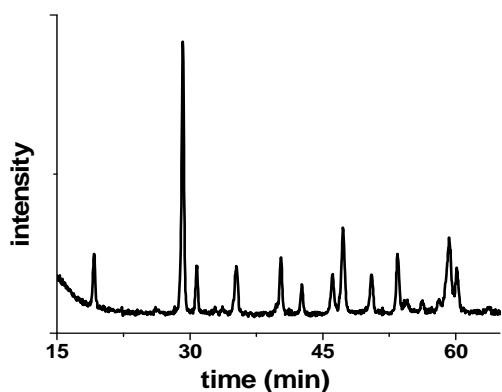


Fig.1. X-ray diffraction pattern of BiOCl+NaVO₃ mixture in 1:1 mole ratio after grinding and washing

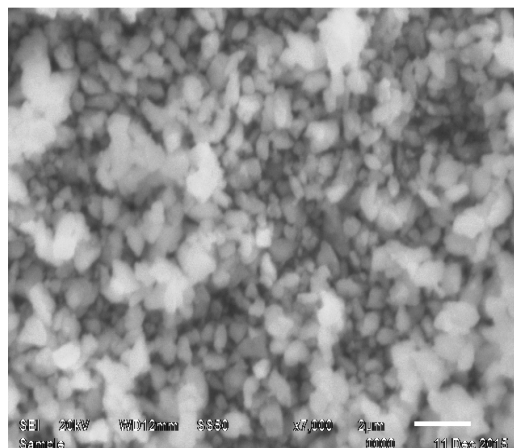
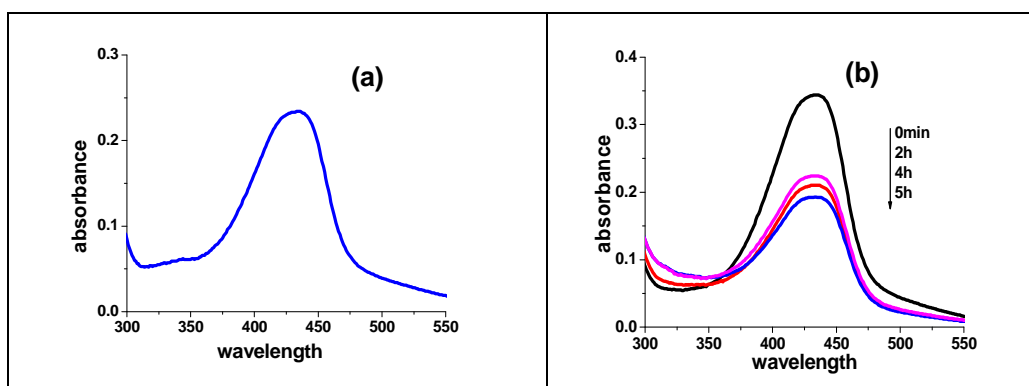


Fig. 2. SEM image of BiVO₄ Photocatalyst

Temporal variation of spectral intensities for 2-aminophenol aqueous solution, 2-aminophenol+H₂O₂, 2-aminophenol+BiVO₄ and 2-aminophenol+BiVO₄+H₂O₂ are shown in Fig. 3. 2-aminophenol shows an absorption peak at $\lambda_{\text{max}} = 425 \text{ nm}$ and no photolysis was observed for exposure up to 5h irradiation (Fig. 3a). In presence of H₂O₂, 2-aminophenol showed photodegradation to an extent of 44 % for 5h of irradiation (Fig. 3b). In presence of BiVO₄, an increase in intensity is observed for the first 3h of irradiation followed by a slight decrease in intensity for irradiation of 4 and 5h (Fig. 3c). The initial increase in intensity may be ascribed to release of adsorbed pollutant on to BiVO₄. In presence of BiVO₄+H₂O₂, initially the intensity increased for first 2h of irradiation followed by a quick decrease in spectral intensity to near zero for 5h of irradiation (Fig. 3d) indicating complete decoloration due to 100% photo degradation.



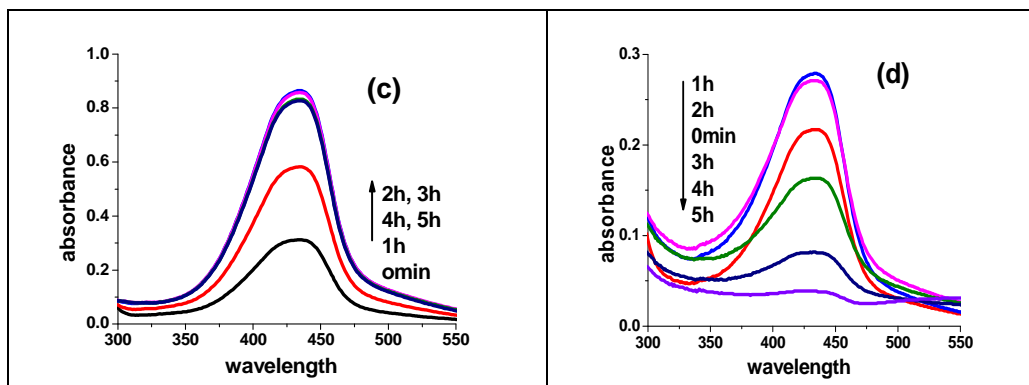


Fig. 3. U.V-visible absorption spectra of (a) 2-aminophenol, (b) 2-aminophenol + H₂O₂, (c) 2-aminophenol + BiVO₄, and (d) 2-aminophenol + BiVO₄ + H₂O₂ as a function of irradiation time (2-aminophenol 10ppm, BiVO₄ 50mg, H₂O₂ 10 μ m)

Fig. 4 depicts time dependent UV-visible spectra for 10ppm 2-aminophenol separately with 20 mg and 100 mg of BiVO₄ to optimize the amount of catalyst. With 20 mg of BiVO₄, it may be noticed that photo degradation was incomplete even for 5h of irradiation (Fig. 4a), whereas with 100 mg BiVO₄ the extent of photo degradation was 100% for 5h of irradiation (Fig. 4b). This is the same as observed for 50 mg of BiVO₄ (Fig. 3d). This data suggests that 50 mg BiVO₄ is the optimal amount of catalyst.

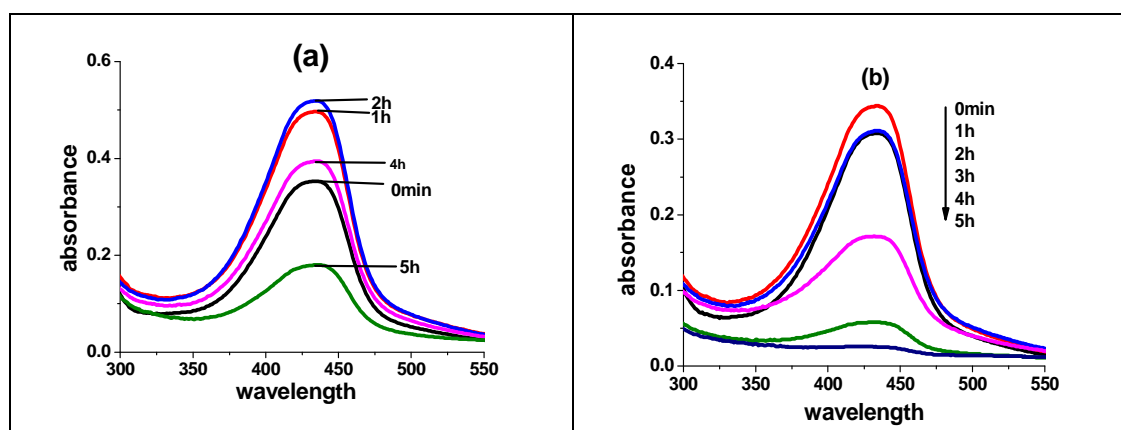


Fig. 4. Variation of spectral intensities for 2-aminophenol as a function of irradiation time with (a) 20mg and (b) 50mg of BiVO₄

In order to differentiate photo degradation from possible desorption, time dependent spectra of 2-aminophenol for 1 to 5h of stirring in dark (without any irradiation) are recorded and shown in Fig. 5, which show only a slight decrease in intensity for first 3h of irradiation followed by a very small increase in intensity for 5h of irradiation. These observations clearly suggest that photo catalytic degradation is the important step and contribution due to adsorption is minimal in lowering the spectral intensity.

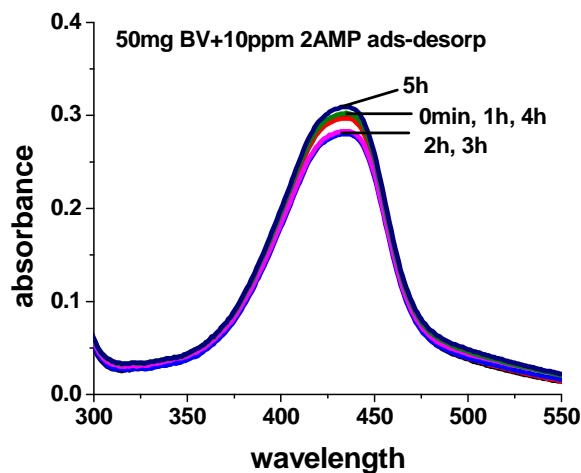


Fig. 5. Adsorption-desorption spectra of 2-aminophenol

Further, since H_2O_2 enhanced the rate of degradation, the role of formation of $\cdot OH$ free radicals is investigated with Terphthalic acid (TPA) as a probe molecule. TPA is known to couple with $\cdot OH$ to form hydroxy terphthalic acid (HTPA) which exhibits a characteristic photoluminescence at 419 nm. Fig. 6 portrays the photoluminescence spectra for TPA+ $BiVO_4$ aqueous solution, TPA+ $BiVO_4 + H_2O_2$ prior to irradiation and TPA+ $BiVO_4 + H_2O_2$ after irradiation. The steep increase in intensity of the peak at 420 nm after irradiation clearly indicate generation of more $\cdot OH$ free radicals in presence of H_2O_2 .

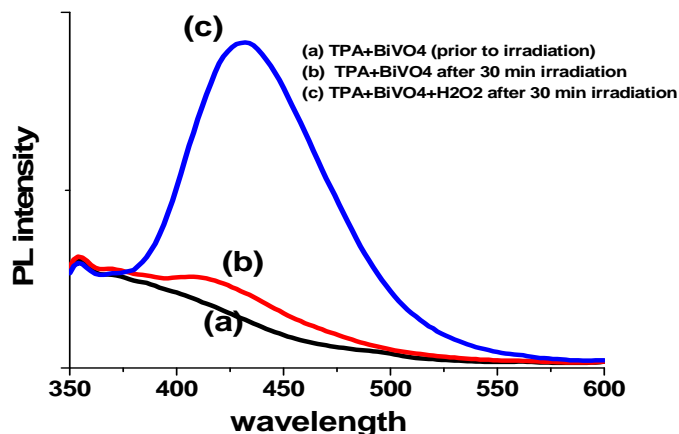
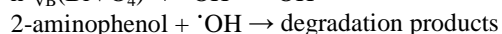
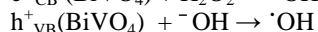
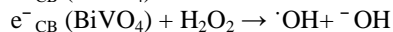
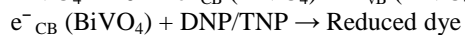
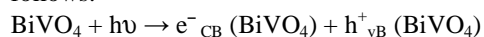


Fig. 6. Photoluminescence spectrum of TPA solution containing $BiVO_4$ photocatalyst in presence and in absence of H_2O_2 before and after irradiation for 30 min

Based on the above observations, the possible photo catalytic degradation mechanism involved is suggested as follows:



The above results clearly indicate that 2-aminophenol can be completely photo degraded over H_2O_2 sensitized $BiVO_4$ under visible light irradiation.

CONCLUSION

Monoclinic BiVO₄ synthesized by solid-state metathetic reaction is found to be effective in the photo catalytic degradation of 2-aminophenol under visible light irradiation. Presence of H₂O₂ enhanced the rate of degradation and resulted in 100% photo degradation of 10ppm 2-aminophenol for 5h of irradiation. More ·OH free radical formation was ascertained due to synergetic effect between BiVO₄ and H₂O₂.

REFERENCES

- [1] D. Chatterjee, S. Dasgupta, *J. Photochem. Photobiol. C: Photochem. Reviews.*, **2005**, 6, 186–205.
- [2] S. Ahmed, M.G. Rasul, R. Brown, M.A. Hashib, *J. Environ. Manag.*, **2011**, 92 (3), 311–330.
- [3] K. Ikehata, N.J. Naghashkar, M.G. El-Din, *Ozone: Sci. Eng.*, **2006**, 28, 353–414.
- [4] C.C. Chen, C.S. Lu, Y.C. Chung, J.L. Jan, *J. Hazard. Mater.* **2007**, 141 (3), 520–528.
- [5] P. Sharma, R. Kumar, S. Chauhan, D. Singh, M.S. Chauhan, *J. Nanosci. Nanotech.*, **2014**, 14: 1.
- [6] H.R. Pouretedal, M. Hosseini. *Acta Chim Slov.*, **2010**, 57, 415.
- [7] M. Umadevi, A. Jegatha Christy, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, **2013**, 109, 133–137.
- [8] A. Chithambararaj, N.S. Sanjini, S. Velmathi, A.C. Bose, *Phys. Chem. Chem. Phys.*, **2013** 15(35), 14761–14769.
- [9] A.R. Daniel Souza, M. Gusatti, C. Sanches, V.M. Moser, N.C. Kuhnen, H.G. Riella. *Chem. Eng. Trans.*, **2013**, 32, 2275.
- [10] H. Oudghiri-Hassani, S. Rakass, F.T. Al Wadaani, K.J. Al-ghamdi, A. Omer, M. Messali, M. Abboudi, *J. Taibah University for Sci.*, **2015**, 9, 508–512.
- [11] H. yuan, J. Xu, *Int. J. Chem. Eng. Appl.*, **2010**, 1, 241.
- [12] V. Rajendran, M. Lehnig, Ch.M. Niemeyer, *J. Mater. Chem.*, **2009**, 19, 6348–6353.
- [13] M. Shamsipur, H. Reza Rajabi, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, **2014**, 122, 260–267.
- [14] A.V. Prasada Rao, A.M. Umabala, P.Suresh, *J. Aplic. Chem.*, **2015**, 4(4), 1145–1172.
- [15] T. Montini, V. Gombac, A. Hameed, L. Felisari, G. Adami, P. Fornasiero, *Chem. Phys. Lett.* **2010**, 498, 113–119.
- [16] A. Martínez-de la Cruz, U.M. Garcia Perez, *Mater. Res. Bulletin.* **2010**, 45, 135–141.
- [17] L. Gan, S. Shang, Ch. Wah Marcus Yuen, S.X. Jiang, E. Hu, *Appl. Surface Sci.*, **2015**, 351, 140–147.
- [18] H. Guo, D. Guo, Z. Zheng, W. Wen, J. Chen, *J. Mater. Res.*, **2014**, 29(24), 2934–2941.
- [19] J. Tang, Z. Zou, J. Ye, *J. Physical Chem. C.* **2007**, 111, 12779–12785.
- [20] L.F. Zhang, J. Zhou, C.Y. Zhang, *J. Mater. Chem. A.*, **2014**, 2, 14903–14907.
- [21] A. Martínez-de la Cruz, S. Obregón Alfaro, *J. Molecular Catal. A: Chem.*, **2010**, 320, 85–91.
- [22] B.L. Yi-Hsien, W. Jian Xun, L. Jia-Shi, Ch. Wen-Hsin, L. Wan-Yu, Ch. Chiing-Chang, *Catal. Today*, **2011**, 174, 148–159.
- [23] P. Suresh, A.M. Umabala, A.V. Prasada Rao, *Inter. J. Eng. Apli. Sci.*, **2015**, 2, 42–46.
- [24] X. Chang, G. Yu, J. Huang, Z. Li, S. Zhu, P. Yu, Ch. Cheng, S. Deng, G. Ji, *Catal. Today*, **2010**, 153, 193–199.
- [25] P. Suresh, U. Sujana Kumari, T. Siva Rao, A.V. Prasada Rao, *J. Aplicble. Chem.*, **2014**, 3, 2047–2054.
- [26] Y. Huo, Y. Jin, Y. Zhang, *J. Molecular Catal. A: Chem.*, **2010**, 331, 15–20.
- [27] A.M. Umabala, P. Suresh, A.V. Prasada Rao, *Der Pharma chem.*, **2016**, 8, 61–66.
- [28] A.M. Umabala, P. Suresh, A.V. Prasada Rao, *Inter. J. Recent Scientific Res.*, **2016**, 7(2), 8893–8998, 2016.
- [29] A.M. Umabala, P. Suresh and A.V. Prasada Rao, *J. Applic. Chem.*, **2016**, 5 (1), 248–254.
- [30] A.M. Umabala, *Inter. J. Sci. Res.*, **2015**, 4, 1521–1524.
- [31] A.M. Umabala, *Inter. J. Eng. Apli. Sci.*, **2015**, 2, 122–125.
- [32] A.M. Umabala, P. Suresh and A.V. Prasada Rao, *Inter. J. Curr. Res. Chem. Pharm. Sci.*, **2016**, 3, 10–15.
- [33] M. Shang, W. Wang, S. Sun, J. Ren, L. Zhou, L. Zhang, *J. Phys. Chem. C*, **2009**, 113, 20228–20233.
- [34] S. Chala, K. Wetchakun, S. Phanichphant, B. Inceesungvorn, N. Wetchakun, *J. Alloys Compds.*, **2014**, 597, 129–135.
- [35] G. Lei, *Mater. Chem. Phys.*, **2008**, 107, 465–470.
- [36] H. Naeimi, S. Rahmatinejad, *Metal-Organic, and Nano-Metal Chem.*, **2016**, 46, 471–476.
- [37] V. Maurino, C. Minero, E. Pelizzetti, P. Piccinini, N. Serpone, H. Hidaka, *J. Photochem. Photobiol. A: Chem.*, **1997**, 109, 171–176.
- [38] C. Pulgarin, J. Kiwi, *Langmuir*, **1995**, 11 (2), 519–526.

- [39] R. Andreozzi, V. Caprio, R. Marotta, *Water Res.*, **2003**, 37, 3682–3688.
- [40] A.J. Lafta, A.A. Adrea, S.H. Kadhim, https://www.researchgate.net/publication/268216430_Photocatalytic_degradation_of_2-amino-phenol_over_naked_and_riboflavin_sensitized_zinc_oxide.
- [41] S. Tokunaga, H. Kato and A. Kudo, *Chem. Mater.*, **2001**, 13, 4624-4628.
- [42] U. Sujana Kumari, P. Suresh and A.V. Prasada Rao, *Inter. J. Appl. Chem.*, **2013**, 9(1), 51-58.
- [43] U. Sujana Kumari, Solid state metathetic synthesis and characterization of some ABO₃ and ABO₄ type mixed metal oxides, **2013**, Dept. of Inorganic and Analytical Chemistry, Andhra University.