



ISSN 0975-413X  
CODEN (USA): PCHHAX

Der Pharma Chemica, 2016, 8(1):61-66  
(<http://derpharmachemica.com/archive.html>)

## Effective visible light photocatalytic degradation of Brilliant green using H<sub>2</sub>O<sub>2</sub> sensitized BiVO<sub>4</sub>

A. M. Umabala\*, P. Suresh and A. V. Prasada Rao

*Department of Inorganic and Analytical Chemistry, Andhra University, Visakhapatnam, India*

### ABSTRACT

*Photocatalytic degradation of Brilliant green is studied over monoclinic BiVO<sub>4</sub> in presence of H<sub>2</sub>O<sub>2</sub> under visible light irradiation. Experimental results indicate a synergetic effect between BiVO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub> in generating more ·OH free radicals which are responsible for the degradation of dye molecular structure. Complete degradation was achieved for 90min of irradiation.*

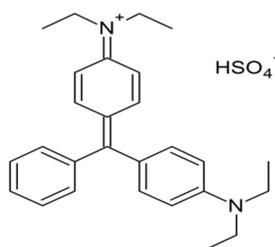
**Key words:** Photocatalytic degradation, Brilliant green, Bismuth vanadate, Solid-State metathesis.

### INTRODUCTION

Semiconductor mediated heterogeneous photocatalysis has become increasingly important for the remediation of several toxic organic pollutants from industrial waste water effluents. It offers several advantages namely (i) the process is cost effective since it involves no coagulation and subsequent filtration (ii) the hazardous pollutants can be completely mineralized leaving no harmful intermediates (iii) utilizes inexhaustible solar radiation and (iv) effectively removes pollutants at ppm level. Several studies projected TiO<sub>2</sub> as a potential photocatalyst because of its chemical inertness, photostability, easy synthesis and high quantum efficiency. But the wide band gap of 3.2 eV restricts the absorption of TiO<sub>2</sub> to U.V region which is less than 5% of available solar radiation. In order to shift the absorption of TiO<sub>2</sub> from U.V to visible region, three different approaches have been reported in literature – (i) doping with transition metal atoms, cations and/or anions (ii) sensitize TiO<sub>2</sub> surface with a more visible light absorbing compound and (iii) form a composite with higher surface in the form of nano/meso phase. Nevertheless, these methods yield only limited success because of some inherent drawbacks which limit their applicability for industrial use. Consequently, the focus is now shifted to explore alternate photocatalysts with good quantum efficiency [1]. Among the many binary and ternary metal oxides that have been explored, BiVO<sub>4</sub> is highly promising because of its visible light absorption efficiency with a band gap of 2.4 eV. BiVO<sub>4</sub> exists in three crystalline modifications - tetragonal zircon, monoclinic scheelite and tetragonal scheelite of which only monoclinic polymorph has been found to be a good visible light responding photocatalyst [2-7]. Different synthetic approaches have been reported to enhance the photocatalytic efficiency of monoclinic BiVO<sub>4</sub> in terms of crystalline structures with high energy facets and special hierarchical nano architectures [8-11]. To our knowledge no studies have been reported on the photodegradation of Brilliant green using BiVO<sub>4</sub>.

Brilliant green (BG) is a member of triphenyl methane dyes which are extensively used in textile industry for dyeing nylon, wool, cotton, silk as well as for coloring of oils, fats, waxes, plastics and varnishes. BG is also used as a biological stain, dermatological agent and in poultry feed to prevent fungus formation. BG is considered as highly toxic to both humans and animals since it causes irritation of respiration and gastrointestinal tracts leading to

vomiting and diarrhea. BG has been banned in many countries due to its carcinogenic nature [12-14]. Though a number of methods have been reported for the degradation of remnant dyes in terms of chemical oxidation and reduction, ion exchange, adsorption, coagulation, electrochemical oxidation etc, none of these methods has been found to be satisfactory as a unique remediation technique. On the other hand, heterogeneous photocatalysis under visible light offers distinct advantages besides being an energy saving green technology. The aim of this study is to investigate the photocatalytic degradation of BG under visible light irradiation using H<sub>2</sub>O<sub>2</sub> sensitized monoclinic BiVO<sub>4</sub>. Molecular formula of BG is C<sub>27</sub>H<sub>34</sub>N<sub>2</sub>O<sub>4</sub>S (Mol. Wt = 482.62g/mole) and its chemical structure is as given below.



Structure of Brilliant green Dye

## METERIALS AND METHODS

### Synthesis of Photocatalyst:

BiVO<sub>4</sub> is prepared by room temperature solid-state metathesis synthesis reported elsewhere [15]. Stoichiometric amounts of BiOCl (Loba Chemie PVT. Ltd.) and NaVO<sub>3</sub> (98% 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:

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<sub>α</sub> radiation (λ= 1.54059 Å), with a scan rate of 2° min<sup>-1</sup>. Microstructural investigation of the sample was performed on the powdered sample using SEM (JEOL-JSM-6610LV, Tokyo, Japan).

### Photocatalytic studies:

Photo catalytic activity of BiVO<sub>4</sub> was evaluated in terms of degradation of BG under visible light. 100 mg of the catalyst was dispersed in 100ml BG aqueous solution (10 mg/L) and the suspension was magnetically stirred for half an hour in dark to ensure adsorption/desorption equilibrium between photo catalyst 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 (Schmadzu corp.). The extent of photodegradation was calculated using the following equation

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

where A<sub>0</sub> and A<sub>t</sub> correspond to the initial absorbance and absorbance at time 't' respectively.

## RESULTS AND DISCUSSION

Photodegradation of BG to an extent of 65% was reported by Ankit Kumar Jain and coworkers over N,S- codoped nano TiO<sub>2</sub> for 90min irradiation of visible light [16]. Khaled Elsony [17] studied kinetics of degradation of BG under vacuum ultraviolet radiation. Shamalah Munuswamy et al [18] reported the effect of Zn and Cu in the photocatalysis of TiO<sub>2</sub> on degradation of BG. Hae Soo Park and Weon Bee Ko [19] reported photodegradation of BG over Nb<sub>2</sub>O<sub>5</sub>-Graphene nanocomposites under U.V irradiation. Sudha and Subrhamaniyan [20] reported 90%

degradation of BG in 180min over CeO<sub>2</sub>-Zeolite (Nax) under visible light. Ching-Chang Chen *et al* [21] identified four intermediates mono, di-, tri-, and tetra-N-deethylated BG species during degradation of BG over TiO<sub>2</sub> under U.V irradiation. Swati Sood *et al* [22] reported 95% degradation of BG over Sr-TiO<sub>2</sub> for 60min of U.V irradiation. Weiyang Dong *et al* [23] studied degradation of BG over TiO<sub>2</sub>-SiO<sub>2</sub> mesoporous nanocomposite under U.V irradiation and concluded that degradation activity was better than that for P-25. Thakare and Jadhav [24] reported degradation of BG using ultrasound (US), US+H<sub>2</sub>O<sub>2</sub>, US+Nb<sub>2</sub>O<sub>5</sub>, US+U.V+Nb<sub>2</sub>O<sub>5</sub> and concluded that the combined technique is more effective comparative to individual techniques. Shanmugam *et al* [25] reported photodegradation of BG to an extent of 90% over doped SnO<sub>2</sub> nanoparticles under solar light for 105min. Ragupathy and coworkers [26] reported photodegradation of BG under solar radiation for 90min over TiO<sub>2</sub> nanoparticles loaded on activated carbon.

X-ray diffraction pattern of BiVO<sub>4</sub> sample synthesized by solid-state metathesis is given in Fig. 1. All peaks in the XRD pattern coincide with the diffraction peaks reported for monoclinic BiVO<sub>4</sub> of JCPDS File No. 75-2480. Absence of peaks that could not be indexed ascertains that BiVO<sub>4</sub> formed is phase pure and monoclinic in crystal structure.

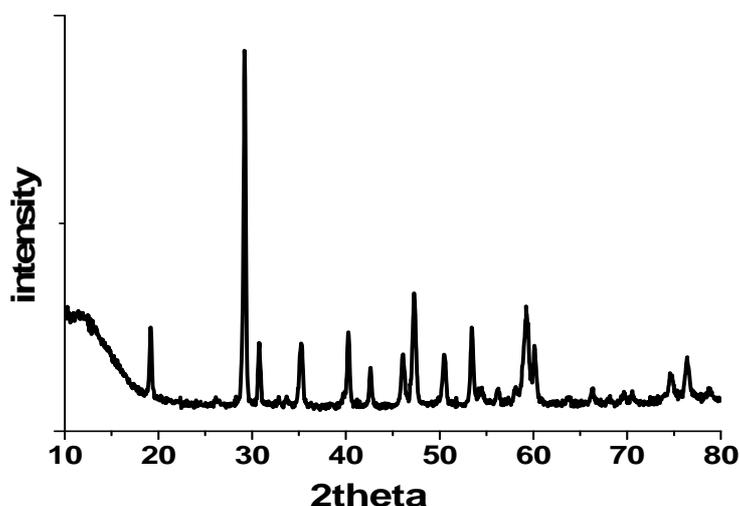


Fig. 1. X-ray diffraction pattern of BiOCl+NaVO<sub>3</sub> mixture in 1:1 mole ratio after grinding and washing

Micro structural investigation of the catalyst powder depicted in Fig. 2 shows particles of < 1μm with lot of agglomeration and no characteristic morphology.

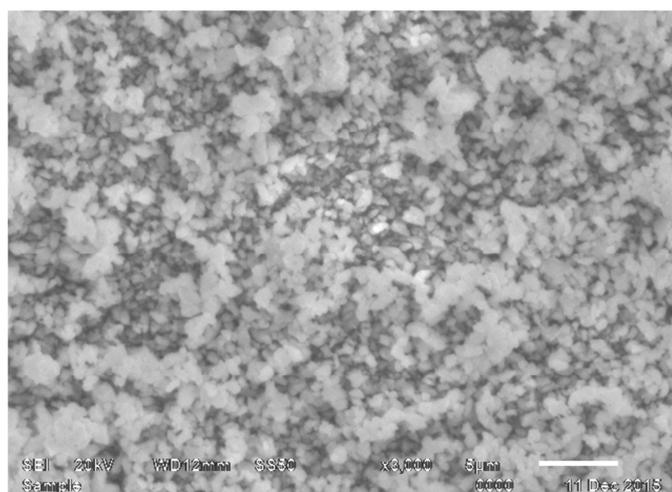
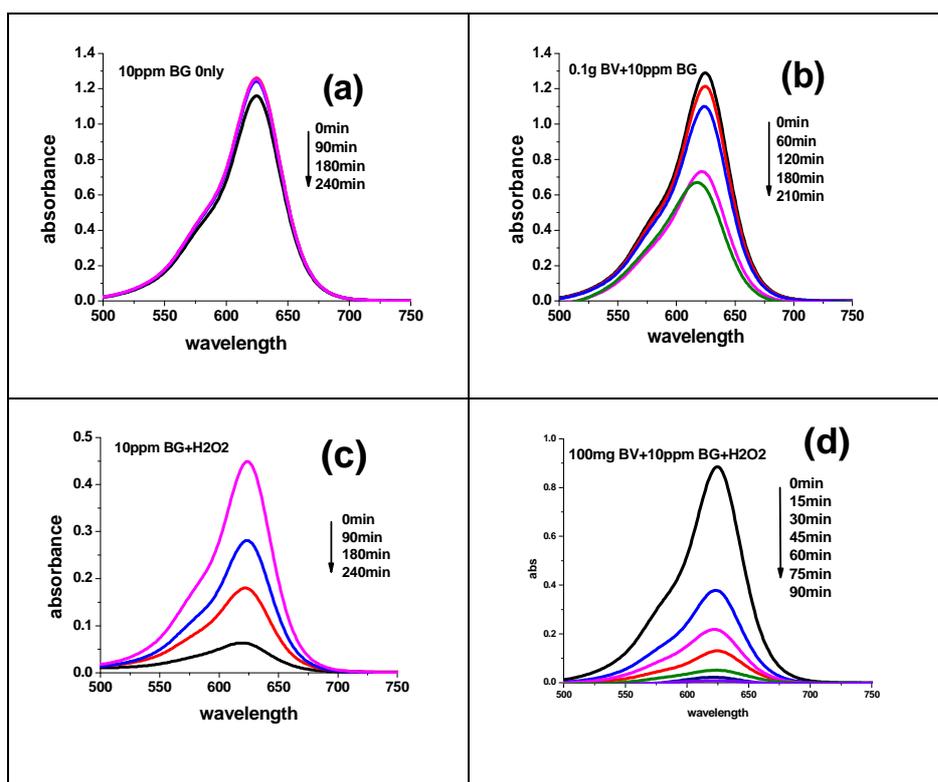


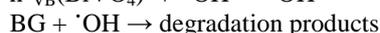
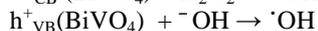
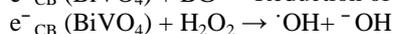
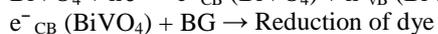
Fig. 2. SEM image of BiVO<sub>4</sub> photocatalyst

Temporal variation of spectral contours as a function of irradiation time for aqueous BG, BG+H<sub>2</sub>O<sub>2</sub>, BG+BiVO<sub>4</sub> and BG+BiVO<sub>4</sub>+H<sub>2</sub>O<sub>2</sub> are shown in Fig. 3. From the figure it can be seen that the characteristic absorption peak for BG is centered at  $\lambda_{\max} = 610\text{nm}$  and aqueous solution of BG does not show any appreciable photolysis even for 240min. of irradiation (Fig. 3(a)). In presence of BiVO<sub>4</sub>, BG shows photodegradation to an extent of 50% for irradiation of 210min (Fig. 3(b)). Presence of H<sub>2</sub>O<sub>2</sub> led to decrease in absorption intensity of BG upto to 85% for irradiation of 240min as seen in Fig. 3(c). However, in presence of both BiVO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub>, absorption intensity decreased rapidly and complete degradation is achieved for 90min of irradiation indicating synergetic effect between BiVO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub>. (Fig.3(d)).



**Fig.3.** variation of spectral intensities as a function of irradiation time for (a) aqueous solution of BG, (b) BG +BiVO<sub>4</sub>, (c) BG +H<sub>2</sub>O<sub>2</sub> and (d) BG +BiVO<sub>4</sub>+H<sub>2</sub>O<sub>2</sub>

There is no observable shift in  $\lambda_{\max}$  with progressive degradation indicating that dethylation process is not the degradation mechanisms as was suggested in Ref. (22) with TiO<sub>2</sub> under UV irradiation. Based on the above results photocatalytic degradation of BG may be explained in terms of the following mechanism.



#### Effect of amount of catalyst:

In order to optimize the amount of catalyst required for complete degradation of 10ppm BG, spectra are recorded as a function of irradiation time with 25, 50, 150 and 200mg photocatalyst. From the time dependent variation of spectral intensities as a function of irradiation time shown in Fig.(4), it can be concluded that 50mg is the optimum amount of photocatalyst.

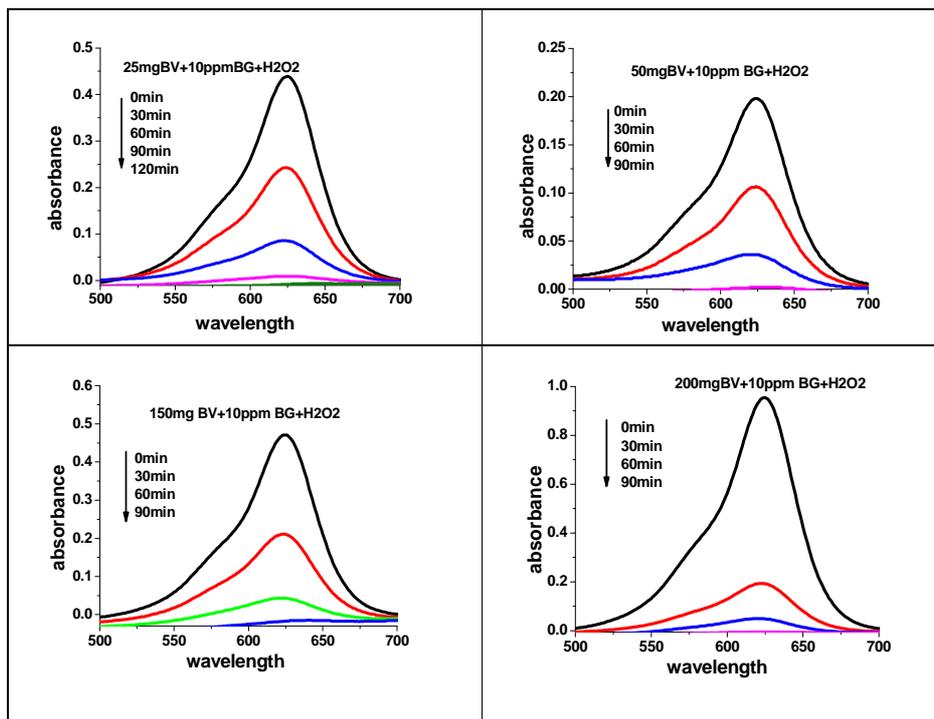


Fig. 4. variation of spectral intensities as a function of irradiation time for aqueous solution of BG with (a) 25mg, (b) 50mg, (c) 150mg and (d) 200mg photocatalyst and H<sub>2</sub>O<sub>2</sub>

Langmuir-Hinshelwood model is generally used to describe the kinetics of photocatalytic degradation reactions in aqueous solution, according to which, degradation is represented by a pseudo first-order equation given by

$$\ln(C_t/C_0) = -kt$$

where C<sub>0</sub> is the initial concentration and C<sub>t</sub> is the concentration at time 't'. The slope k is the apparent rate constant. Fig. 5 depicts a plot of ln(C<sub>t</sub>/C<sub>0</sub>) vs time for photodegradation of BG, BG+BiVO<sub>4</sub>, BG+H<sub>2</sub>O<sub>2</sub> and BG+BiVO<sub>4</sub>+H<sub>2</sub>O<sub>2</sub>. Rates of degradation as calculated are given below.

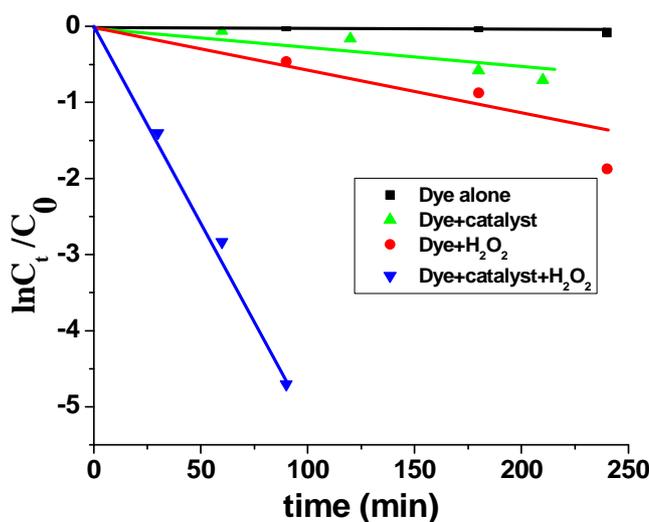


Fig. 5. Plot of ln(C<sub>t</sub>/C<sub>0</sub>) vs irradiation time for BG, BG+BiVO<sub>4</sub>, BG+ H<sub>2</sub>O<sub>2</sub> and BG+BiVO<sub>4</sub>+H<sub>2</sub>O<sub>2</sub>

Table. 1. Calculated rate constants for photodegradation of BG with and without catalyst and H<sub>2</sub>O<sub>2</sub>

photodegradation	Rate constant k <sub>BV</sub> (min <sup>-1</sup> )
BG only	-
BG+BiVO <sub>4</sub>	1.0×10 <sup>-5</sup>
BG+H <sub>2</sub> O <sub>2</sub>	3.0×10 <sup>-5</sup>
BG+BiVO <sub>4</sub> + H <sub>2</sub> O <sub>2</sub>	5.2×10 <sup>-4</sup>

The above results indicate that 10ppm of BG can be successfully photodegraded over BiVO<sub>4</sub> in presence of H<sub>2</sub>O<sub>2</sub> for just 90 min of visible light irradiation. The present method is more economical since the bulk catalyst is synthesized at room temperature and photodegradation performed in visible region which constitutes a large part of solar radiation.

### CONCLUSION

Monoclinic BiVO<sub>4</sub> prepared by solid-state metathesis showed enhanced photocatalytic efficiency in presence of external oxidant H<sub>2</sub>O<sub>2</sub>. Complete degradation of 10ppm Brilliant green was achieved over 100mg of BiVO<sub>4</sub> in presence of 10µm of H<sub>2</sub>O<sub>2</sub> for 90min of irradiation. Significant photolysis of Brilliant green was noticed in presence of H<sub>2</sub>O<sub>2</sub> for 240min of irradiation. But BiVO<sub>4</sub>+H<sub>2</sub>O<sub>2</sub> showed a synergetic effect and caused complete degradation of Brilliant green dye for 90min of visible light irradiation.

### REFERENCES

- [1]A.V. Prasada Rao, A.M. Umabala, P.Suresh, *J. Aplic. Chem.*, **2015**, 4(4), 1145-1172.
- [2]R. Ran, J. G. McEvoy, Z. Zhang, *Inter. J. Photoenergy.*, **2015**, <http://dx.doi.org/10.1155/2015/612857>.
- [3]S. Chala, K. Wetchakun, S. Phanichphant, B. Inceesungvorn, N. Wetchakun, *J. Alloys Compds.*, **2014**, 597 (5), 129–135.
- [4]T. Saison, N. Chemin, C. Chanéac, O. Durupthy, L. Mariey, F. Mauge, V. Brezova, J. P. Jolivet, *J. Phys. Chem. C.*, **2015**, 119 (23), 12967–12977.
- [5]A.M. Umabala, *Int. J. Eng. Appl. Sci.*, **2015**, 2(4), 122-125.
- [6]A.M. Umabala, *Int. J. Sci. Res.*, **2015**, 4(12), 1521-1524.
- [7]S. Wu, H. Zheng, Y. Lian, Y. Wu, *Mater. Res. Bullet.*, **2013**, 48, 2901–2907.
- [8]G. Liu, S. Liu, Q. Lu, H. Sun, F. Xu, G. Zhao, *J. Sol-Gel Sci. Technol.*, **2014**, 70, 24–32.
- [9]H.K. Timmaji, W. Chanmanee, N.R. de Tacconi, K. Rajeshwar, *J. Adv. Oxid. Technol.*, **2011**, 14 (1), 93-105.
- [10]W. Wei, X. Yue, H. Cui, X. Lu, J. Xie, *J. Mater. Res.*, **2013**, 28 (24), 3408-3416.
- [11]U.M. Garcia-Perez1, S. Sepulveda-Guzman, A. Martinez- de la Cruz, J. Peral, *Int. J. Electrochem. Sci.*, **2012**, 7, 9622 – 9632.
- [12]P.R. Gogate, G.S. Bhosale, *Chemical Eng. Processing: Process Intensification*, **2013**, 71, 59–69.
- [13]B.K. Nandi, A. Goswami, M.K. Purkait, *J. Hazard. Mater.*, **2009**, 161 (1), 387-395.
- [14]A. Vachalkova, L. Novotny, M. Blesova, *Neoplasma*, **1996**, 43, 113.
- [15]U. Sujana Kumari, P. Suresh, A.V. Prasada Rao, *J. aplic. Chem.*, **2014**, 3(1), 366-371.
- [16]A.K. Jain, S. Benjamin, R. Ameta, *Oct. Jour Env. Res.*, **2015**, 3(1), 001-006.
- [17]K.M. Elsousy, *Adv. Pure and Applied Chem.*, **2012**, 2(1), 91-97.
- [18]S. Munusamy, R. sai laxmi aparna, R. Gunneswara subramanya vara Prasad, *Sustainable chemical processes*, **2013**, 1:4, 1-8.
- [19]H.S. Park, W.B. Ko, *Elastomers and Composites*, **2014**, 49 (4), 330-335.
- [20]G. Sudha, E. Subramanian, *J. Adv. Chem. Sci.*, **2015**, 1(3), 17-120.
- [21]C.C. Chen, C.S. lu, H.J. Fan, W.H. Chung, J.L. Jan, H.D. Lin, W.Y.Lin, *Desalination*, **2008**, 219, 89-100.
- [22]S. Sood, A. Umar, S.K. Mehta, A.S.K. Sinha, S.K. Kansal, *Ceramics Inter.*, **2015**, 41(3), 3533-3540.
- [23]W. Dong, Y. Sun, Q. Ma, L. Zhu, W. Hua, X. Lu, G. Zhuang, S. Zhang, Z. Guo, D. Zhao, *J. Hazard. Mater.*, **2012**, 229-230, 307-320.
- [24]Y. D. Thakare, S.M. Jadhav, *Int. J. Adv. Engg. Tech.*, **2013**, /IV/IV/, 31-36.
- [25]N Shanmugam, T. Sathya, G. Viruthagiri, C. Kalyanasundhaam, R. Gobi, *J Applied Surface Sci.*, **2016**, 360, 283-290.
- [26]S. Ragupathy, K. Raghu, *Inter. J. Current Res.*, **2014**, 6 (9), 8427-8432.