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RESEARCH ARTICLE

VISIBLE LIGHT HETEROGENEOUS PHOTOCATALYTIC DEGRADATION OF EOSIN-B and ERIOCHROME BLACK-T USING H_2O_2 SENSITIZED MONOCLINIC $BiVO_4$

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ABSTRACT

Visible light photo catalytic degradation of Eosine Blue and Eriochrome Black-T dyes is investigated over monoclinic $BiVO_4$ prepared by room temperature solid-state metathesis. XRD pattern showed formation of phase pure monoclinic $BiVO_4$. Complete photo degradation of Eosin Blue and Eriochrome Black-T occurred for respective irradiation times of 120 and 210 min. in presence of H_2O_2. A synergetic effect between $BiVO_4$ and H_2O_2 led to enhanced degradation of both dyes.

INTRODUCTION

Effective remediation of toxic organic pollutants has become a prime concern for a sustainable environment because waste water discharges from industries relating to manufacture of dyes, polymers, pesticides, pharmaceuticals etc., continue to contaminate world's aquatic sources posing a severe threat to human health, animal life and the ecosystem. Several methods were proposed from time to time for elimination of hazardous pollutants in terms of adsorption, bio-sorption, ion exchange, ultra filtration, solvent extraction, reverse osmosis, wet chemical oxidation, electro catalytic, electro chemical and sono degradation. But, none of these methods is adequately satisfactory because these methods suffer from some inherent draw backs of either generating secondary pollutants due to phase transfer, or operate under restricted conditions involving cumbersome technology and hence not cost effective. During the past few decades, semiconductor based heterogeneous photo catalysis is claimed to be a superior technique for the remediation of organic pollutants because of its ability to mineralize them non selectively and possibly completely at ambient temperature avoiding expensive filtration methods. A wide number of investigators projected TiO_2 as most useful photo catalyst because it is inexpensive, easy to synthesize, non-toxic, chemically inert and highly photo stable. Nevertheless, the wide band gap associated with TiO_2 restricts absorption to U.V region of wave length < 380nm which constitutes hardly 5% of solar radiation. Since setting of artificial UV light requires lot of power consumption and is also harmful to humans, different strategies have been advanced to extend photo response of TiO_2 to visible region and reduce the recombination rate of charge carriers in terms of doping, surface sensitization and nano composite formation with large surface to volume ratio (Prasada Rao *et al*., 2015). Though these modifications are moderately successful they are limited in enhancing photo catalytic efficiency upto an optimal range only. Alternately, studies on ternary metal oxides revealed a new bunch of visible light active photo catalysts that include $ZnWO_4$ (Montini *et al*., 2010), $BiVO_4$ (Martínez-de la Cruz. *et al*., 2010), $BaBiO_3$ (Tang. *et al*., 2007), $NaBiO_3$ (Chang *et al*., 2010), Bi_2MoO_6 (Martínez-de la Cruz. and Obregón Alfaro, 2010), Bi_2WO_6 (Yi-Hsien *et al*., 2011), $Bi_2Mo_3O_{12}$ (Suresh *et al*., 2015), $Fe_2Mo_3O_{12}$ (Suresh *et al*., 2014), $Bi_2Mo_2O_9$ (Li *et al*., 2009) etc. In the composite Bi-oxide system with V/Mo/W oxides, monoclinic $BiVO_4$ is reported as the most useful visible light active photo catalyst. Recently photo degradation of nitro benzene Umabala (2015), nitro phenols Umabala (2015), acetophenone (Umabala *et al*.,

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2016) and Brilliant Green (Umabala *et al*., 2016) using $BiVO_4$ has been reported from this laboratory. Present paper describes visible light photo degradation of Eosin Blue and Eriochrome Black-T using H_2O_2 sensitized $BiVO_4$. Molecular formulae and chemical structures of Eosin Blue and Erichrome Black-T are given below.

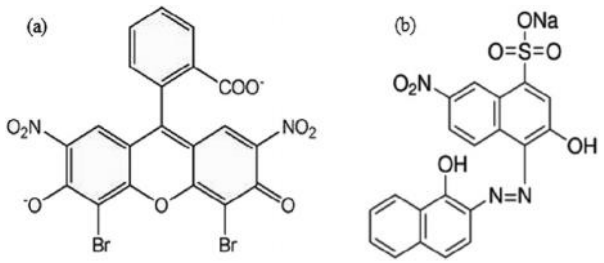

Fig. 1 Chemical structures of (a) Eosin blue and (b) Eriochrome black T

MATERIAL AND METHODS

Synthesis of Photocatalyst

$BiVO_4$ is prepared by room temperature solid-state metathesis synthesis reported elsewhere. Stoichiometric amounts of BiOCl (Loba Chemie PVT. Ltd) and $NaVO_3$ (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 bye product NaCl and the residue is dried at 80ºC in an air oven. The dried powder is subjected to phase identification, mcrostructural 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 (λ= 1.54059 Å), 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

Photo catalytic activity of $BiVO_4$ was evaluated in terms of degradation of Eosin blue (EB) and Eriochrome blck-T (EBT) under visible light. 100 mg of the catalyst was dispersed in 100ml EB/EBT aqueous solution (10 mg/L for EB and 20mg/L for EBT) 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 (Schimadzu). The extent of photodegradation was calculated using the following equation

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

where A_0 and A_t correspond to the initial absorbance and absorbance at time 't' respectively.

Photoluminescence studies

50 mg $BiVO_4$ catalyst is added to the beaker containing 100 ml of terpthalic acid (TPA) solution (0.25 mmol L^{-1} in 1mmol L^{-1} NaOH solution) and 10 µm H_2O_2. 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 flourometer (Flouromax 4) with the excitation wavelength of 315 nm.

RESULTS AND DISCUSSION

$BiVO_4$ occurs in three different crystalline modifications – tetragonal Zircon, tetragonal Scheelite and monoclinic Scheleite. Despite the coordination around Vanadium being the same in all three polymorphic forms, only monoclinic $BiVO_4$ is reported to exhibit visible light photo catalytic activity. X-ray diffraction pattern of sample prepared from room temperature solid-state metathesis reaction between BiOCl and $NaVO_3$ after grinding and washing is shown in Figure 2. All the experimentally observed diffraction peaks could be indexed to monoclic $BiVO_4$ of JCPDS File No. 75-2480. Absence of unidentified extra peaks due to any possible contamination indicates that the sample under study is phase pure monoclinic $BiVO_4$. Micro structural investigation of the sample revealed particle size in the µm region as seen in Figure 3. SEM image of the sample did not show any characteristic texture.

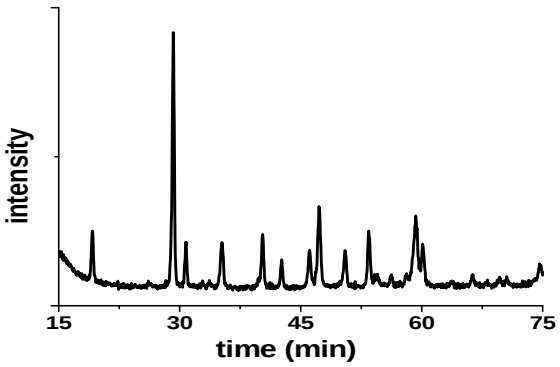

Fig.2. X-ray diffraction pattern of BiOCl+$NaVO_3$ mixture in 1:1 mole ratio after grinding and washing

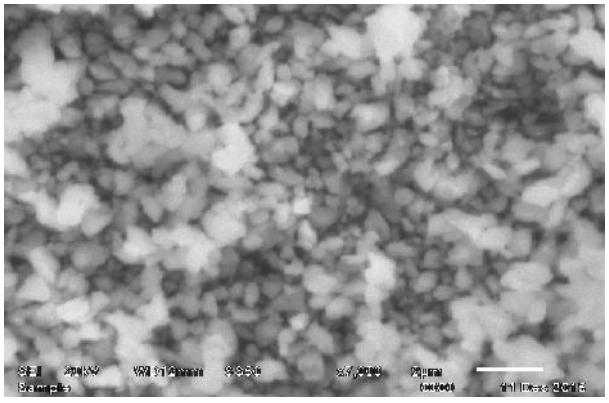

Fig. 3 SEM image of $BiVO_4$ Photocatalyst.

Photo catalytic degradation of Eosin Blue (EB) has been reported using ZnO nano palates under U.V light (Ye *et al*., 2006), nano porous SnO_2 under UV light (Chen *et al*., 2014), and Nd, N, S –tri doped TiO_2 decorated on single walled carbon nano tubes under visible light (Mamba *et al*., 2015). Figure 4 depicts temporal variation of spectral contours as a function of irradiation time for EB aqueous solution, EB+H_2O_2, EB + $BiVO_4$, and EB + $BiVO_4$ + H_2O_2. From the figure it can be seen that EB shows characteristic absorption at max = 517nm and under goes photolysis to an extent of 32% for irradiation up to 120 min (Fig.4a). In presence of H_2O_2, EB underwent photo degradation to a significant extent of 56% for the same irradiation time as above (Fig.4b). In presence of $BiVO_4$, EB showed the same 55% photo degradation for 120 min of irradiation (Fig.4c). However, in presence of both $BiVO_4$ and H_2O_2, absorption intensity of EB rapidly decreased to zero indicating that EB is completely photo degraded for the same 120 min of irradiation (Fig. 4d). The above results indicate a synergetic effect between $BiVO_4$ and H_2O_2 in effecting photo degradation of EB.

Erichrome Black-T (EBT) a water soluble azo dye is widely used as an indicator in complexometric titrations and for the determination of hardness of water (Jeffery *et al*.,). EBT is also used for the determination of rare earths and nucleic acids (Gettar *et al*., 1999 and Zhou *et al*., 2011). It causes eye, skin, respiratory tract and gastrointestinal irritation. Remediation of EBT was reported in terms of adsorption (Dave *et al*., 2011), bio-sorption (Barka.*et al*., 2011), and photo catalytic degradation using zirconium phosphate (Panwar *et al*., 2008), Ni^{2+} exchanged zeolite P (Nezamzadeh-Ejhieh *et al*., 2010), TiO_2 nano particles (Sushil Kumar *et al*., 2016), nano scale Ni structures (Kalwar *et al*., 2014), Zn doped TiO_2 (Singla *et al*., 2014), Ag_2O/TiON (Hussain. *et al*., 2013), ZnO nano particles (Iraj and Azar, 2014) $K_2Zn_3[FeCN_6]^{2-}$ (Jassal *et al*., 2015), super paramagnetic Fe_2O_3 nano particles (Esther Leena Preethi *et al*., 2015), and TiO_2 decorated carbon nano tubes (Mamba *et al*., 2015). Variation of UV-visible spectral intensities as a function of irradiation time for EBT aqueous solution, EBT + H_2O_2, EBT + $BiVO_4$, and EBT + $BiVO_4$ + H_2O_2 are shown in Figure 5.

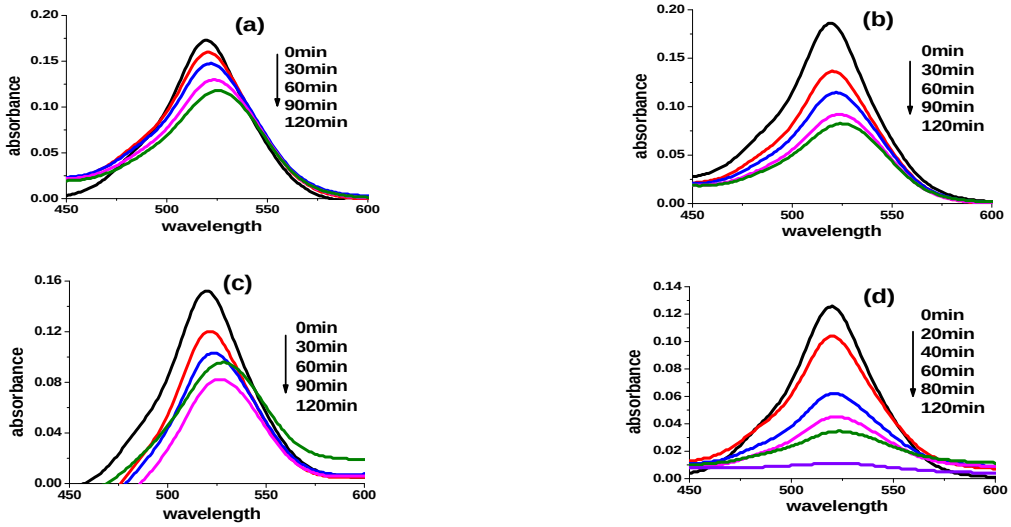

Fig.4 U.V-visible spectra of (a) EB aqueous solution, (b) EB+H_2O_2, (c) EB+$BiVO_4$ and (d) EB+H_2O_2+$BiVO_4$ as a function of irradiation time (EB-10ppm, $BiVO_4$-100mg, H_2O_2-10µm)

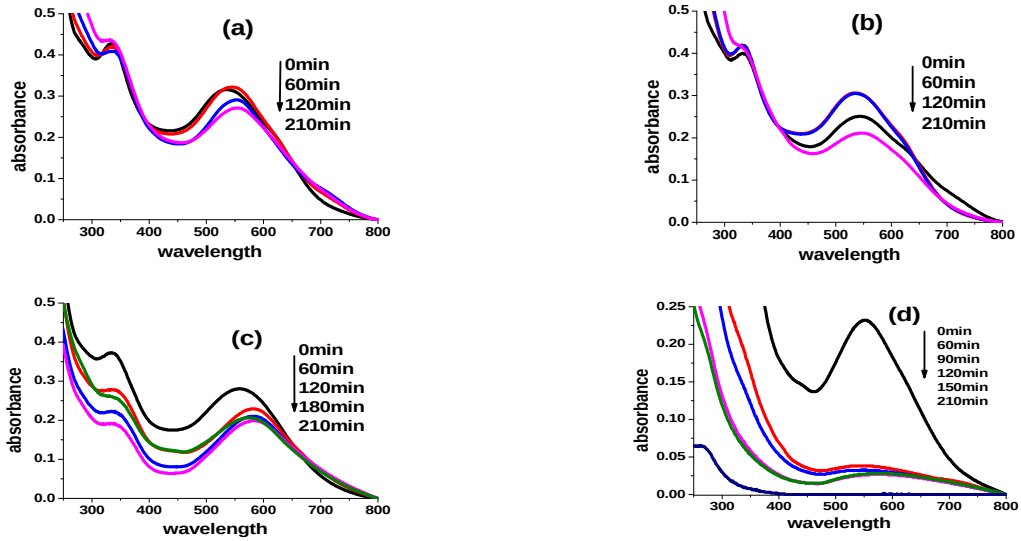

Fig.5. U.V-visible spectra of (a) EBT aqueous solution, (b) EBT+H_2O_2, (c) EBT+$BiVO_4$ and (d) EBT+H_2O_2+$BiVO_4$ as a function of irradiation time (EBT-20ppm, $BiVO_4$-100mg, H_2O_2-10µm)

It can be seen from Fig.5a, EBT exhibits a characteristic absorption at max = 550 nm. EBT undergoes very little photolysis for irradiation of 120 min. EBT in presence of H_2O_2 shows photo degradation to an extent of 33% for120 min of irradiation (Fig.5b). EBT in presence of $BiVO_4$ also show photo degradation to the same extent of 33% (Fig. 5c). However, in presence of both $BiVO_4$ and H_2O_2, absorption intensity of EBT steadily decreased and complete photo degradation is achieved for 210 min of irradiation (Fig. 5d).

The enhanced photo degradation observed in EB and EBT in presence of $BiVO_4$ and H_2O_2 can be ascribed to synergetic effect between these two which generates more OH free radicals that cause disintegration of dye structures. Possible mechanism involved is shown below:

$BiVO_4 + h\upsilon \rightarrow e^-_{CB}(BiVO_4) + h^+_{vB}(BiVO_4)$ ——— (i)

$e^-_{CB}(BiVO_4) + DNP/TNP \rightarrow$ Reduced dye ——— (ii)

$e^-_{CB}(BiVO_4) + H_2O_2 \rightarrow {}^{\cdot}OH + {}^-OH$ ——— (iii)

$h^+_{VB}(BiVO_4) + {}^-OH \rightarrow {}^{\cdot}OH$ ——— (iv)

$DNP/TNP + {}^{\cdot}OH \rightarrow$ degradation products ——— (v)

Rapid formation of ˙OH free radicals through steps (iii) and (iv) is the important in accumulation of more ·OH free radicals which are used for disintegration of both EB and EBT. In order to confirm the generation ·OH free radicals during irradiation of $BiVO_4$ in presence of H_2O_2 photolumiscence spectroscopy is used with Terpthalic acid (TPA) as a probe molecule. TPA combines preferentially with ·OH to form hydroxy terpthalic acid (HTPA) which shows a characteristic luminescence peak at 419nm. Fig. 6 depicts photoluminescence spectra for $BiVO_4$ +TPA with and without H_2O_2 prior to and after irradiation. Intense luminescence peak after irradiation confirms formation of ·OH free radicals due to irradiation in presence of H_2O_2.

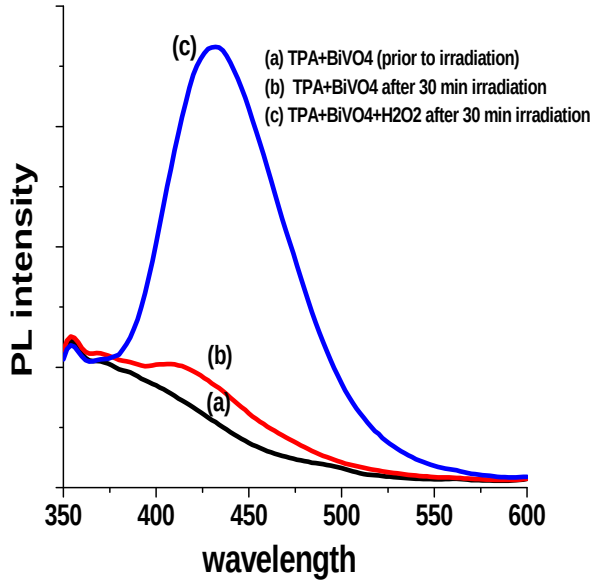

Fig.6 Photoluminescence spectra of TPA solution containing $BiVO_4$ in presence and in absence of H_2O_2 before and after irradiation for 30 min.

Plots of ln (C_t/C_0) vs time for the degradation of EB and EBT under different conditions are shown in Fig. 7. Rate constants calculated from respective slopes are given in Table 1.

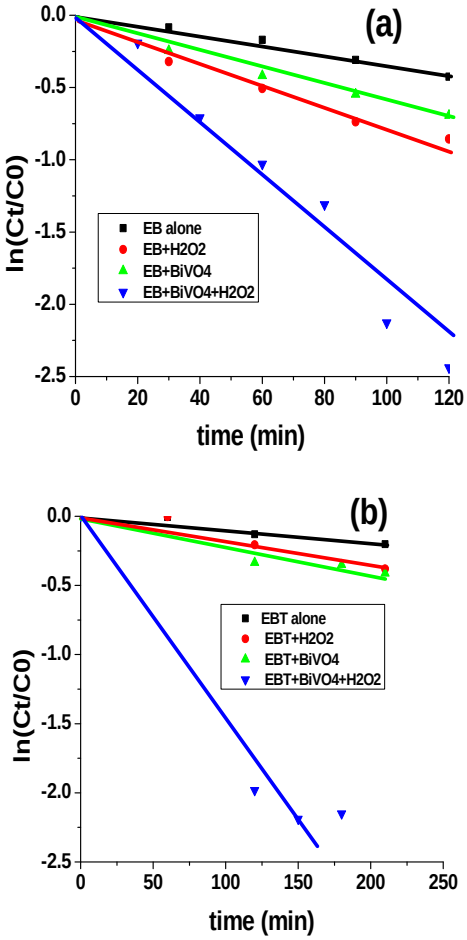

Fig. 7 Plot of lnCt/C0 vs time for photodegradation study of (a) EB and (b) EBT

Table 1 Calculated rate constants for photodegradation of Dye, Dye+H_2O_2, Dye+$BiVO_4$ and Dye+H_2O_2+$BiVO_4$

Photodegradation of	Rate constant K (min)	Photodegradation of	Rate constant K (min)
EB	3.0×10^{-5}	EBT	-
EB +H_2O_2	6.0×10^{-5}	EBT +H_2O_2	-
EB +$BiVO_4$	5.0×10^{-5}	EBT +$BiVO_4$	1.0×10^{-5}
EB +$BiVO_4$+H_2O_2	1.6×10^{-4}	EBT +$BiVO_4$+H_2O_2	6.0×10^{-5}

From the above results it may be concluded that both EB and EBT can be successfully photodegraded under visible light using monoclinic $BiVO_4$ as photocatalyst in presence of external oxidant H_2O_2.

CONCLUSION

Photo catalytic degradation of Eosin Blue and Eriochrome Black-T is studied under visible light irradiation using H_2O_2 sensitized monoclinic $BiVO_4$. Synergetic effect between $BiVO_4$ and H_2O_2 led to generation of more ˙OH free radicals. Complete degradation of Eosin Blue and Eriochrome Black-T occurred in 120 and 210 min respectively.

References

Barka. N., Abdennouri. M., Makhfouk. M.E.L. 2011. Removal of methylene blue and eriochrome black T from aqueous solutions by biosorption on Scolymus hispanicus L.: kinetics, equilibrium and thermodynamics, J. Taiwan Inst. Chem. Eng. 42, 320–326.

Chang. X., Yu. G., Huang. J., Li. Z., Zhu. S., Yu. P., Cheng. Ch., Deng. S., Ji. G. 2010. Enhancement of photocatalytic activity over $NaBiO_3$/BiOCl composite prepared by an in situ formation strategy, Catalysis Today, 153, 193-199.

Chen. W., Sun. F., Zhu. Z., Min. Z., Li. W. 2014. Nanoporous SnO_2 prepared by a photochemical strategy: Controlling of specific area and photocatalytic activity in degradation of dye pollutants, Microporous and Mesoporous Mater. 186, 65-72.

Dave. P.N., Kaur. S., Khosla. E. 2011. Removal of eriochrome black-T by adsorption on to eucalyptus bark using green technology, Indian J. Chem. Technol. 18, 53–60.

Esther Leena Preethi. M., Anitha Priya. J., Thiriveni. S. 2015. Solar light driven degradation of eriochrome black T by photocatalysis, IOSR J. Appl. Chem. 8, 55-62.

Gettar. R.T., Gautier. E.A., Servant. R.E., Batistoni. D.A. 1999. Eriochrome Black T as a post-column reagent for the ion chromatographic determination of rare earths, J. Chromatogr. A, 855, 111–119.

Hussain. S.T., Rashid, Anjum. D., Siddiqa. A., Badshah. A. 2013. Synthesis of visible light driven cobalt tailored Ag_2O/TiON nano photocatalysts by riverse micelle processing for degradation of Eriochrome black T, Mater. Res. Bull. 48, 705-714.

Iraj. K., Azar. S. 2014. Photocatalytic degradation of Eriochrome black T dye using ZnO nanoparticles, Mater. Lett. 120, 267-270.

Jassal. V., Shanker. U., Kaith. B.S., Shankar. S. 2015. Green synthesis of potassium zinc hexacyanoferrate nanocubes and their potential application in photocatalytic degradation of organic dyes, RSC Adv. 5, 26141-26149.

Jeffery. G. H., Bassett. J., Mendham. J., Denney. R C. Text book of Quantitative Analysis, 5th Edition.

Kalwar. N.H., Sirajuddin, Ali Soomro. R., Hussain Sherazi. S.T., Richard Hallam. K., Khaskeli. A.R. Inter. J. Metals. http://dx.doi.org/10.1155/2014/126103.

Li. H., Li. K., Wang. H. 2009. Hydrothermal synthesis and photocatalytic properties of bismuth molybdate materials, Mater. Chem. Phys. 116, 134-142.

Mamba. G., Mbianda. X.Y., Mishra. A.K. 2015. Enhanced visible light photocatalytic degradation of eriochrome black T and eosin blue shade in water using tridoped titania decorated on SWCNTs and MWCNTs: Effect of the type of carbon nanotube, Mater. Chem. Phys. 149-150, 734-742.

Martínez-de la Cruz. A., Obregón Alfaro. S. 2010. Synthesis and characterization of γ-Bi_2MoO_6 prepared by co-precipitation: Photoassisted degradation of organic dyes under vis-irradiation, J. Molecular Catal. A: Chem. 320, 85–91.

Martínez-de la Cruz. A., Garcia Perez. U.M. 2010. Photocatalytic properties of $BiVO_4$ prepared by the co-precipitation method: Degradation of rhodamine B and possible reaction mechanisms under visible irradiation, Mater. Res. Bulletin. 45, 135-141.

Montini. T., Gombac. V., Hameed. A., Felisari. L., Adami. G., Fornasiero. P. 2010. Synthesis, characterization and photocatalytic performance of transition metal tungstates, Chem. Phys. Lett. 498, 113-119.

Nezamzadeh-Ejhieh. A., Khorsandi. M. 2010. Heterogeneous photodecolorization of eriochrome black T using Ni/P zeolite catalyst, Desalination. 262, 79-85.

Panwar. O.P., Kumar. A., Paliwal. M., Ameta. R., Ameta. S.C. 2008. Use of zirconium phosphate as photocatalyst in photobleaching of some dyes, Bull. Catal. Soc. India. 7, 105–110.

Prasada Rao. A.V., Umabala. A.M., Suresh. P. 2015. Non-TiO_2 Based Photocatalysts for Remediation of Hazardous Organic Pollutants under Green Technology-Present Status: A Review, J. Aplicble. Chem. 4(4), 1145-1172,

Singla. P., Sharma. M., Pandey. O.P., Singh. K. 2014. Photocatalytic degradation of azo dyes using Zn-doped and undoped TiO_2 nanoparticles, Appl. Phys. A. 116, 371-378.

Suresh. P., Umabala. A.M., Prasada Rao. A.V. 2015. Rapid sun light degradation of Rhodamine-B, Methylene blue, Methyl orange, Congo red and their binary mixtures using suprastoichiometric Bi-Molybdate, Inter. J. Eng. Apli. Sci. 2, 42-46.

Suresh. P., Sujana Kumari. U., Siva Rao. T., Prasada Rao. A.V. 2014. Rapid Visible Light Photo Catalytic Degradation of Eosin Y, Congo Red and Methyl Orange with $Fe_2Mo_3O_{12}$ and MoO_3, J. Aplicble. Chem. 3, 2047-2054.

Sushil Kumar. K., Swathi. S., Ahmad. U., Mehta. S.K. 2013. Photocatalytic degradation of Eriochrome black T dye using well-crystalline anatase TiO_2 nanoparticles, 581, 392-397.

Tang. J., Zou. Z., Ye. J. 2007. Efficient Photocatalysis on $BaBiO_3$ Driven by Visible Light, J. Physical Chem. C. 111, 12779-12785.

Umabala. A.M. 2015. Effective visible light photo degradation of nitrobenzene using $BiVO_4$ prepared by room temperature solid-state metathesis, Inter. J. Sci. Res. 4, 1521-1524.

Umabala. A.M. 2015. Effective visible light photodegradation of ortho and para- nitrophenols using $BiVO_4$, Inter. J. Eng. Apli. Sci. 2, 122-125.

Umabala. A.M., Suresh. P., Prasada Rao. A.V. 2016. Visible light photocatalytic degradation of acetophenone using H_2O_2 sensitized $BiVO_4$, Inter. J.Curr. Res. Chem. Pharm. Sci. 3, 10-15.

Umabala. A.M., Suresh. P., Prasada Rao. A.V. 2016. Effective visible light photocatalytic degradation of Brilliant green using H_2O_2 sensitized $BiVO_4$, Der Pharma chem. 8, 61-66.

Ye. Ch., Bando. Y., Shen. G., Golberg. D. 2006. Thickness-dependent photocatalytic performance of ZnO nanoplatelets, J. Phys. Chem. B, 110, 15146-15151.

Yi-Hsien. B.L., Jian Xun. W., Jia-Shi. L., Wen-Hsin. Ch., Wan-Yu. L., Chiing-Chang. Ch. 2011. Synthesis, photocatalytic activities and degradation mechanism of Bi_2WO_6 toward crystal violet dye, Catalysis Today, 174, 148-159.

Zhou. H., Wu. X., Meng. F., Yang. J., Wang. M. 2011. Nucleic acids determination using the complex of eriochrome black T and silver nanoparticles in a resonance light scattering technique, Spectro chim. Acta Part A Mol. Biomol. Spectrosc. 78, 681–686.

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