International Journal of Engineering Science Invention (IJESI)
ISSN (Online): 2319 – 6734, ISSN (Print): 2319 – 6726
www.ijesi.org ||Volume 7 Issue 3 Ver. I || March 2018 || PP. 49-54

Heterogeneous Photocatalytic Degradation of Azure-A Dye By Highly Efficient Zno-Nano Photocatalyst In Presence Of Different Operational Parameters

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ABSTRACT: *Nowadays, environmental pollution is a critical problem of the world. In this paper, we report the successful synthesis of ZnO Nano photo catalyst by the precipitation method and their effective use as a photocatalyst for photo catalytic degradation of organic dye using safe and inexpensive visible light. Photo catalytic heterogeneous degradation is most effective method of purification of polluted water. Textile wastewater includes a large variety of dyes and chemicals additions that more the environmental challenge for textile industry not only as liquid waste but also in its chemical composition. Advanced oxidation processes hold great promise to provide alternative for better treatment and protection of environment pollution, in this paper the effect of different operational parameters such as, catalyst loading, initial dye concentration, pH variation, H_2O_2 and $K_2S_2O_8$ oxidants and effect of other commercial photo catalyst on the extent of Heterogeneous photo catalytic degradation rate have been investigated.*

KEYWORDS: *-ZnO particles, Azure-A dye, Heterogeneous photo degradation, visible light.*

Date of Submission: 16-02-2018 Date of acceptance: 03-03-2018

I. Introduction

The population growth with its enhanced need has led to many industrial developments and thus increases in water pollution. Textile industries use colored dyes that become a major source of environmental contamination, for surface and ground water contamination. Pollutants, the release of these colored effluents in to water bodies us harmful to the aquatic ecosystem and result in pollution, eutrophication and perturbations in aquatic life so that all these organic pollutants cause eye and skin problems, irritation of the digestive tract and may be severely harmful if swallowed**.**

Nanotechnology provides us ways to purify the air and water resources by utilizing Nano-ZnO semiconductor particles as photo catalyst. Nano-technology greatest structures that have excellent properties by controlling atoms and molecules on the nanometer scale by involving precise placements of individual atoms of the size around 0.1 – 100 nm [1-2].

Now a day's Nano-ZnO has been used as a photo catalyst for the photo catalytic degradation of organic dyes and pollutant's due to its compatibility with widely used photo catalyst. Nano-ZnO is a wide band gap group II-VI semiconductor. It has several distinct properties such as high electron mobility, good optical transparency, wide band gap (3.37eV) and room temperature photoluminescence which are favorable for solar energy application ZnO-Nano crystals have hexagonal wurtzite structure tetrahydrally coordinated O^{2-} and zn^{2+} ions arranged alternately along the C-axis, which is mostly used for photo catalytic studies. Photocatalytic process is completed through various reaction routes of oxidation and redaction reactions. These reactions involve photon adsorption from the light source by the photo catalyst such as Nano-ZnO, exciton generation and transfer to charge carriers to the respective band and interaction of charge carriers with the sensitized molecules. So now dyes it is used as more effective, inexpensive and nontoxic visible light semiconductor phtocatalyst for the degradation of a wide range of organic pollutants and synthetic dyes as compared to other photo catalyst [3, 4] In photochemical degradation of organic pollutants, the high reaction rate and mineralization rates in Nano-ZnO have been reported due to the sufficient quantity generation of hydroxyl hydroxyl radicals ($^{\cdot}OH$). The active species hydroxyl radical formed by the decomposition of water or by the reaction of the hole with the $^{-}$ OH, is an extremely strong and non-selective oxidant which leads to particle or complete mineralization of several organic pollutants.

$ZnO + hv_{(visible)} \longrightarrow ZnO(h^{+}_{VB} + e^{-}_{CB})$

$h^{+}_{VB} + {}^{-}OH \longrightarrow {}^{\bullet}OH$

${}^{\bullet}OH + \text{dye [AA]} \longrightarrow \text{degradation of (AA)}$

In this work practical application of wastewater treatment by using Nano-ZnO in presence of visible light there is a need to determine the optimal conditions of experimental variation for economic removal of the pollutants. Azure-A (AA) is an mostly used textile industry dye which possess lots of deleterious effects in this study Heterogeneous photo catalytic degradation of Azure A has been investigated utilizing ZnO NPs under different operational parameters in order to optimize the reaction condition for better and efficient heterogeneous photo catalysis in presence of visible light.

II. Experimental Procedure

Required chemicals

In this work the dye used Azure-A was analytical grade (Loba chemical). Zinc Nitrate ($Zn(No_3)_2$ and Sodium hydro oxide (NaOH) were obtained from Merck Co. (Germany) Ethanol (99%) was purchased from Aldrich Co.(England) H_2O_2, $K_2S_2O_8$, $FeCl_3$, Na_2CO_3were used standard grade. Purred distilled water was used throughout the investigation to prepare the solution.

Synthesis of Nano Zinc Oxide Particles

Synthesis of Nano ZnO catalyst

To prepare of Nano-ZnO in a typical experiment a 0.45 M aqueous solution of zinc nitrate (Zn $(No_3)_2.4H_2O$) and 0.9M aqueous solution of sodium hydroxide were prepared in distilled water. Then the beaker containing NaOH solution was heated at the temperature of about 55^0C. The Zn $(No_3)_2$ solutions were added drop vise slowly for 40 min to the above heated solution under high speed stirring. The beaker was sealed at this condition for 2 h. The precipitated Nano-Zno was cleaned with demonized water and ethanol then dried in air atmosphere at about 60^0C morphology of the sample was investigated using XRD, SEM and TEM [5].

Procedure of experiment and condition

During the photo catalytic degradation of different dye solution containing known concentration of dye solution and Nano Zinc Oxide put in a Pyrex vessel, after stirring for ten minutes, the slurry was placed in dark place for half an hour in the order to set up equilibrium between adsorption and desorption phenomenon of dye solution molecule onthe surface of Nano-ZnO photo calalyst. at this time the lamp was switched on to initiate the reaction. During the experiments 5ml of suspension were withdrawn at regular intervals and were immediately centrifuged at 3500vpm (revolution per minute) for 3 min. to completely remove of Nano-ZnO catalyst particles. The filtrates were analyzed by visible spectrophotometer (systronics 104, 106). The solution in the photo reactor will be thermo states by constant circulation of water to keep the temperature in the range of $30 + 0.3^0$C. The pH will be constantly monitored using a digital pH-meter. The pH of the reaction mixture will be adjusted by adding a dilute aqueous solution of HCl or NaOH. In this process all kinetic experiments the pseudo first order kinetic reaction with respect to dye were monitored at λmax, using spectrophotometer. Beer's law was valid for the measurement under the experimental conditions considered. Solution concentration, dye solution pH, intensity of dye, wavelength, catalyst loading of Nano-ZnO, effect of $K_2S_2O_8$ and H_2O_2on the role of reaction, solar light, relative catalytic efficiency of the Nano-ZnO wish other photo catalyst were investigated for their effects on the photo catalytic degradation performance and decolorization defined as -

$$Efficiency\ \% = \frac{Co - C}{Co} \times 100 \qquad (1)$$

Where C_o is the initial concentration of the dye solution before irradiation, C is the residual concentration of the dye solution after irradiation time [6].

III. Results And Discussion

a. Effect of initial dye solution concentration of Azure-A (AA)

The influence of initial dye solution (Azure-A) concentrations was investigated by varying the initial concentration from 1.5×10^{-5} mol^{-1} dm^{-3} to 7.5×10^{-5} mol^{-1} dm^{-3} at pH 10.2 and with Nano-ZnO catalyst amount 55mg/100 mL. Rate constant of [AA] dye solution is increased with increase in dye concentration (AA) from 1.5×10^{-5} mol^{-1} dm^{-3} to 4.5×10^{-5} mol^{-1} dm^{-3}. Rate constant has been found to be maximal at 4.5×10^{-5} mol^{-1} dm^{-3}(fig.1) the dye concentration influenced the extent of adsorption and rate of reaction at the surface of the Nano-ZnO photo catalyst. Increasing initial dye concentration (AA) would improve the rate of the liquid phase reaction and surface reaction as well and the adsorption of dye solution molecules on the Nano-ZnO photo catalyst surface hinders competitive adsorption of OH^- ions (hydroxyl ions), thus it lowers the formation rate of hydroxyl radicals (OH^-) and consequently it affected the rate of dye solution reaction [7].

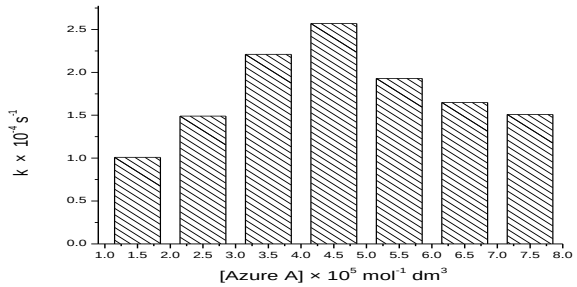

Fig1 : Effect of initial dye concentration variation of (AA)

b.Effect of Nano-ZnO photocatalyst amount

Heterogeneous photo catalysic degradation of Azure-A (AA) dye in the in this study the catalyst amount is has strong parameter photocatalytic photodegradation kinetics of [AA] dye. In order to determine the optimal amount of Nano-ZnO photocatalyst, concentrations a sequence of experiments were carried out using different concentration of Nano-ZnO photocatalyst varying from 25 mg /100mL to 95 mg /100mL at optimized pH 10.2. It has been investigated that as the concentration of catalyst amount increased from 25mg/100mL to 55 mg/100mL, the increase in the Nano-ZnO photocatalyst loading could be attributed to the fact that a larger quantity of photons were adsorbed, thus accelerating the process. The most efficient decomposition of Azure-A dye solution has been observed at photocatalyst amount 55 mg/100mL. Further increase of the Nano-ZnO concentration resulted in a decrease of rate of photodecoloration. On further increase in concentration all the molecules got adsorbed on Nano-ZnO photocatalyst thus no improvement was achieved on further adding more ZnO Photocatalyst amount. The decrease in efficiency, which is observed in the fig. 2might be due to an increase in capacity of the suspension and to an enhancement of the light reflectance, because of the excess of Nano-ZnO photocatalyst particles [8].

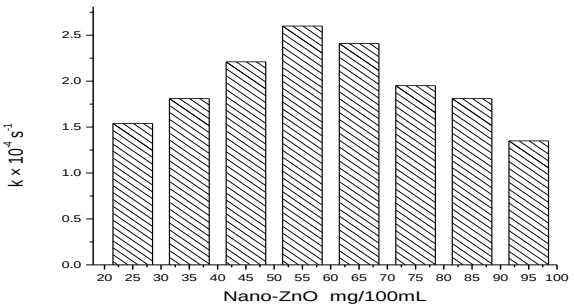

Fig. 2: Effect of Azure A amount catalyst variation of (AA)

c. Effect of Azure-A dye pH

The waste water from textile industries usually has large range of pH values pH plays an important role both in the characteristic of textile wastewater and generation of ($OH^{\cdot}$) hydroxyl radicals. The effect of pH on the rate of photo degradation has been investigated in the pH series 5.2 to 12.2 upon changing the pH, the surface hydroxyl group could undergo protonation and deprotonation according to the following reaction.

$$\text{Nano-ZnO } OH^{+} + H^{+} \longrightarrow \text{Nano-ZnO } H^{+} \quad (2)$$

$$\text{Nano-Zano } OH + OH^{-} \longrightarrow \text{Nano-ZnO}^{-} + H_2O \quad (3)$$

Bahnemann et al have reviewed that acid-base properties of the metal oxide surfaces could have considerable implications upon photo catalytic activity. The point of zero charge of the Nano-ZnO photo catalyst is at pH Thus the Nano-ZnO catalyst surface becomes positively charged in acidic media, whereas it is negatively charged under alkaline conditions. Since Azure-A dye is cationic dye, thus there was a poor adsorption in the acidic medium. Therefore, decrease in pH caused decrease in photo degradation rate. Higher pH favors electrostatic interactions between the negative Nano-ZnO photo catalyst surface and cationic dye led to strong adsorption and enhancing photo degradation rate. The optimal pH was observed at 10.2. The results obtained in (fig. 3) indicated that, at pH 10.2 a strong adsorption of the Azure-A dye on the Nano-ZnO catalyst particles was observed as a result of the electrostatic attraction of the negatively charged Nano-ZnO with the AA dye [9].

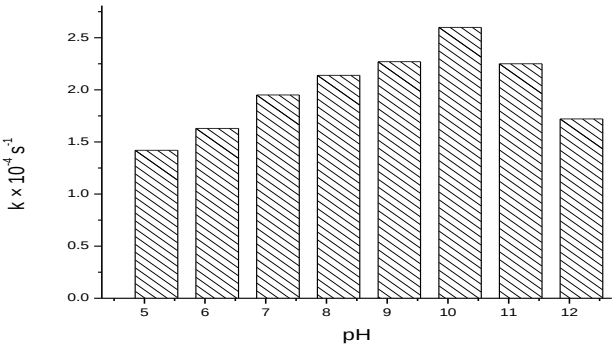

Fig. 3: Effect of Azure A pH

d. Effect of other photocatalysts

Heterogeneous photocatalysic degradation of Azure-A (AA). Experiments were performed with other photocatalysts such as Nano-ZnO,C-ZnO, TiO_2 and CdS. Generally, semiconductors having large band gaps are good photocatalysts. Band gap energy of Nano-ZnO, TiO_2 and BiOCl are larger than 3eV show strong activity. The conduction and valence band potentials of both ZnO and TiO_2 are larger than the corresponding redox potentials of H^+/H_2 and H_2O/O_2 and the photogenerated electron and hole can be separated efficiently. CdS with smaller band gaps show less activity since their conduction bands are much lower than that of Nano-ZnO,BiOCl and TiO_2. Electrons in these semiconductors rapidly fall into the hole thus showing reduced activity. It is observed that the activity of the photocatalyst get also affected by the particle size, crystallinity and amount of impurities present in the photocatalyst [10].

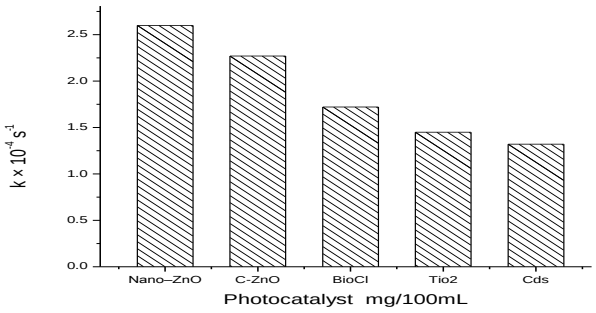

Fig. 4: Effect of other photocatalyst.

e. Effect of H_2O_2 and $K_2S_2O_8$ solution

The addition of other power oxidizing species such as H_2O_2 solution and $K_2S_2O_8$ solution to Nano-ZnO photo catalyst suspension is a well-known procedure and lead to an increase in the rate of photooxidation of Azure-A dye. The photo catalytic photo degradation has been studied at different H_2O_2 concentrations H_2O_2 is well-known to have two functions in the process of photo catalytic degradation. It accepts a photo generated election from the conduction band and it also forms $^{\cdot}OH$ radicals according to following equation.

$$H_2O_2 + e^- \longrightarrow OH + {}^{\bullet}OH \quad (4)$$

$$H_2O_2 + O_2^{\bullet-} \longrightarrow OH^- + {}^{\bullet}OH + O_2 \quad (5)$$

The rate of reaction has been found to be increased as the concentration of H_2O_2 solution increased and it reached to the optimum value at 10×10^{-5} mol^{-1} dm^{-3}. On further addition of H_2O_2 solution it decreased as the concentration of the H_2O_2 increased beyond the optimum because excess H_2O_2 might act as an $^{\cdot}OH$ scavenger and form peroxo compounds, which are detrimental to the photocatalytic action [11].

$$H_2O_2 + 2hv^+_{VB} \longrightarrow O_2 + 2H^+ \quad (6)$$

$$H_2O_2 + {}^{\bullet}OH \longrightarrow HO_2^{\bullet} + H_2O \quad (7)$$

$$^{\bullet}OH + {}^{\bullet}OH \longrightarrow H_2O + O_2 \quad (8)$$

The effect of persulphate ion on the photo catalytic degradation of dyes was investigated. The concentration of $K_2S_2O_8$ solution was 2×10^{-5} mol^{-1} dm^{-3} to 14×10^{-5} mol^{-1} dm^{-3}.The data have been presented in fig.(6). The percentage photo degradation of the dye increased with increasing amount of persulphate ion concentration. $K_2S_2O_8$ solution proved to be a beneficial oxidizing agent in photocatalytic detoxification since it generates $SO_4^{\cdot-}$ Oxidant as per reactions (9) and (10) utilizing the semiconductor generated electrons (e^-_{cb}).

$$S_2O_8^{2-} + e^-_{aq} \longrightarrow SO_4^{\cdot-} + SO_4^{2-} \quad (9)$$

$$S_2O_8^{2-} + e^-_{cb} \longrightarrow SO_4^{\cdot-} + SO_4^{2-} \quad (10)$$

This formation of hydroxyl radical and sulphate radical enhanced the photo degradation of dye molecules at faster rate. The optimum concentration has been found to be 10×10^{-5} mol^{-1} dm^{-3}. Above thus optimum concentration the rate constant values decreased due to the absorption of sulphate ions on the surface of Nano-ZnO deactivating a section of photo catalyst [12, 13].

$SO_4^{-\bullet} + e^-_{cb} \longrightarrow SO_4^{2-}$ (11)

$SO_4^{-\bullet} + H_2O \longrightarrow {}^{\bullet}OH + SO_4^{2-} + H^+$ (12)

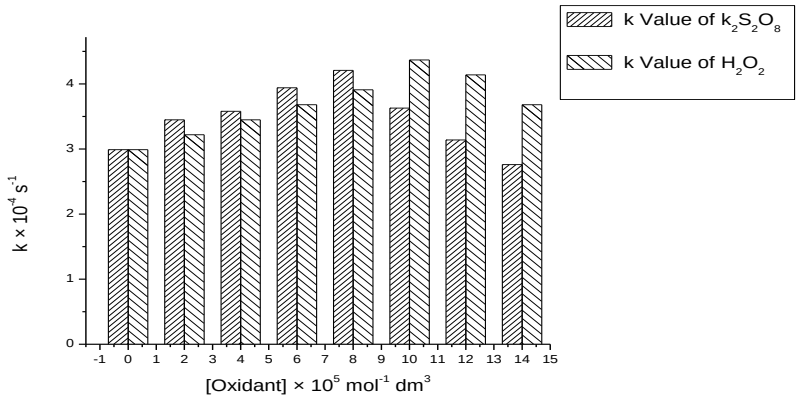

Fig. 6: Effect of oxidant H_2O_2 and $K_2S_2O_8$

f. Mechanism of Azure-A (AA) photocatalytic degradation

The photocatalyst Nano-ZnO is a wide band gap (3.2eV) semiconductor, corresponding to radiation in the near UV range. The use of high energy UV light is not only costly, but also can be hazardous. Therefore, the possible use of visible light has recently drawn attention. Organic pollutants like dyestuffs have the ability to absorb visible light. When dye molecules are adsorbed onto the surfaces of Nano-ZnO their translational mobility is considerably reduced and it extends the range of excitation energies of the semiconductors Nano-ZnO into visible region [14]. The visible light excites the dye molecules adsorbed on Nano-ZnO and subsequently inject electrons to conduction band (CB) of Nano-ZnO. While the CB acts as a mediator for transferring electrons from the dye molecule to substrate electron acceptors on Nano-ZnO surface, the valance band (VB) remains unaffected in a typical photosensitization. The conduction band election of Nano-ZnO is scavenged by O_2 molecule to form $O_2^{\bullet-}$ or more active radicals such as OH, these active oxygen species attack the cationic dye radical or dye molecule, leading to degradation followed by mineralization of organic pollutant (Azure A). Photosensitized degradation of organic dyes (AA) has been carried out on Nano-ZnO where the organic dye serves as both a sensitizer and a substrate to be degraded. Such type of electron transfer mechanism has been called a "photosensitizing oxidation." The mechanism of dye degradation under visible light irradiation can be described as following.

$AA + hv_{(visible)} \longrightarrow AA^*$ (13)

$AA^* + \text{Nano-ZnO} \longrightarrow AA^{\bullet+} + \text{Nano-ZnO}(e^-_{CB})$ (14)

$\text{Nano-ZnO}(e^-_{CB}) + O_2 \longrightarrow \text{Nano-ZnO} + O_2^{\bullet-}$ (15)

$O_2^{-\bullet} + H^+ \longrightarrow HO_2^{\bullet}$ (16)

$HO_2^{\bullet} + H^+ + \text{Nano-ZnO}(e^-_{CB}) \longrightarrow H_2O_2 + \text{Nano-ZnO}$ (17)

$O_2^{\bullet-} + 2H_2O \longrightarrow H_2O_2 + e^-$ (18)

$H_2O_2 + \text{Nano-ZnO}(e^-_{CB}) \longrightarrow {}^{\bullet}OH + OH^- + \text{Nano-ZnO}$ (19)

$AA^{\bullet+} + OH^- \longrightarrow AA + {}^{\bullet}OH$ (20)

$AA^{\bullet+} + O_2^{\bullet-} \longrightarrow \text{Degradation products}$ (21)

$AA^{\bullet+} + {}^{\bullet}OH \longrightarrow \text{Degradation products}$ (22)

This process of dye sensitization has an advantage in photo degradation of organic pollutants dye with visible light. Photosensitizing mechanism will help to improve the overall efficiency and make the heterogeneous photo degradation of textile dyes using solar light more feasible. The mechanism of Nano-ZnO photocatalyst particle is of very complex nature. Cationic dye radicals interact with $O_2^{\bullet-}$, $HO_2^{\bullet}$ Or${}^{\bullet}OH$ species to generate intermediates ultimately lead to the generation of degradation products. Hydroxyl radical (${}^{\bullet}OH$) being very strong oxidizing agent (standard oxidation potential 2.8 eV) mineralized dye to end product [15].

$AA\ (AA^{+\bullet}) + {}^{\bullet}OH \longrightarrow \text{Degradation products}$ (23)

As the photo degradation process with illumination of many unstable intermediate species which finally mineralized into CO_2, H_2O, NO_3^- and SO_4^{2-}.

IV. Conclusion

Heterogeneous photocatalytic degradation processes are most efficient method of purification of water pollution because of their simplicity. Low cost, case of controlling parameters and their high efficiency in degrading recalcitrant organic and inorganic substances in aqueous systems, and they are being increasingly utilized. It has been found Azure-A dye is readily and rapidly degraded in aqueous solution by Vis/ZnO NPs in relatively short time of about 80 min. after selection of desired operational parameters pH 10.2 ZnO NPs = 55mg/100ml. AA = $4.5 \times 10^{-5} mol^{-1} dm^{-3}$, $[H_2O_2] = 10 \times 10^{-5}\ mol^{-1}\ dm^{-3}$) . With addition of oxidants like H_2O_2 and K_2SO_8 into illuminated ZnO NPs suspension, a synergistic effect was observed leading to an enhancement of the process except of the excessive amount of H_2O_2 and K_2SO_8 which caused a decreased rate of reaction. Heterogeneous Photocatalysic degradation of AA with Vis/ZnO NPs system followed pseudo-first order reaction kinetics. The data presented in the paper clearly indicates that Vis/ZnO NPs, as an advanced oxidation process, is multipurpose, environmentally benign, easily adaptable and efficient treatment method for the water pollution.

Acknowledgement

Authors acknowledge supports, practical and laboratory facilities provided by Chemistry Department, Govt. Madhav Science P. G. College, Ujjain (M.P.) India.

Reference

[1]. Shrivastava, V.S., *Metallic and organic nanomaterials and their use in pollution control;A Review. Archives of Applied Science Research, 2 (82),*2010.
[2]. Yogendra, K.,Mahadevan, K.M.,Naik, S.,&Madhusudhana, N.,*Photocatalytic activity of synthetic ZnO composite against coralene red F3BS dye in presence of solar light. Int. J. of Envir. Sciences,1 (5)*2011.
[3]. Akyol, A.,&Bayramoglu, M., *Photocatalytic degradation of remazol red F_3B using ZnO catalyst. Journal of Hazardous Materials, 124,* 2005, (241).
[4]. Seyed-Dorraji, M.S.,Daneshvar, N.,&AberS., *Influence of inorganic oxidants and metal ions on photocatalytic activity of prepared zinc oxide nanocrystals.Global NEST Journal.,11,* 2009, (535).
[5]. Moghaddam, A. B., Nazari, T., Badraghi, J. &Kazemzad, M., *Synthesis of ZnO nanoparticles and electrodeposition of polypyrrole/ZnOnanocomposite film.Int. J.Electrochem. Sci., 4,* 2009, (247).
[6]. Pare, B., Swami, D., Qureshi, T.,*Photocatalytic degradation of environmental hazardous crystal violet dye using bismuth oxychloride as photocatalst. International Journal of Chemical Science.,9(3),*2011, 1183-1193.
[7]. Akyol, A., Bayramoglu, M., *Photocatalytic degradation of remazol red F_3B using ZnO catalyst.J. Hazard, Mater. B, 124,* 2005, (241).
[8]. Fujishima, A.A., Rao, T.N., and Tryk, D. A., *Titanium dioxide photocatalysis.J. photochem.Photobiol.CPhotochem.Rev., 1 (21),* 2002.
[9]. Davis, A.P., and Huang, C.P., *The removal of phenols from water by a photocatalytic oxidation process.Wat.Sci. Technol., 21,*1990, (455).
[10]. Kyriacou, G., Tzaoanas, K., and Poulios, I., *Decolarization and mineralization of hazardous brilliant cresyl blue dye.J.Environ. Sci Health A., 32,* 1997, (963).
[11]. Graetzel, C.K., Jirousek, M., and Graetzel, M.,*Decomposition of organophosphorous compounds on photoctivted TiO_2 surfaces. J.Mol. Catal.,60,*1990, (375).
[12]. Abdullah, M., Gary, K.C.L., and Matthews, R.W., *Effects of common inorganic anions on rates of photocatalytic oxidation of organic carbon over illuminated titanium dioxide. J. Phys. Chem., 94,* 1990, (6620).
[13]. Haarstrick, A., Kut, O.M., and heinzle, E.,*TiO_2-Assisteddegradation of environmentally relevant organic compounds in wastewater using a novel fluidized bed phoyoreactor.Environ. Sci. Technol, 30,*1996, (817).
[14]. Subramani,A.K.,Byrappa,K.,Ananda,S.,andLokanathaRai, M.K.,*Photocatalytic degradation of indigo caramine dye using TiO_2impregnated active carbon. Bull Mater. Sci., 30,* 2007, (37).
[15]. Pare, B., Swami, D., More P., Qureshi, T. and Thapak T.R.,*Mineralization of methylene violet dye dsing titanium dioxide in presence of visible light.International Journal of Chemical Science, 9(4),*2011, 1685-1697.

International Journal of Engineering Science Invention (IJESI) is UGC approved Journal with Sl. No. 3822, Journal no. 43302.

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