SYNTHESIS AND APPALICATION OF MgZnSrO$_3$ NANO-PARTICLE TO THE PHOTOCATALYTIC DECOLOURIZATION OF VICTORIA BLUE B DYE (VBB)

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ABSTRACT

Dyes present in the textile wastewater require a suitable technique for their removal, due to their negative environmental and health effects. Although there are several ways to treat such wastewater, this study is focused on photocatalytic degradation on MgZnSrO$_3$ nano-catalyst. Victoria Blue B (VBB) dye was used for photocatalytic degradation studies at 15mg/L concentration. Colour degradation was monitored using UV-Vis spectroscopy. Maximum colour removal was observed for the dye. It is found that, degradation rate of VBB for MgZnSrO$_3$ (Urea) the degradation was found to be 93.33% at pH 4 in 120 minutes for 0.4g/100ml. Also the results revealed that, the degradation facility is directly bear upon by the concentration of dye solution.

Keywords: Photocatalyst, Degradation, Nano-particles, MgZnSrO$_3$, VBB

I.INTRODUCTION

Industrial dyes have been most commonly used due to their advantages such as better dyeing processing conditions and bright colour. Generally, Industrial dyes exhibit a wide range of different chemical structures, primarily based on substituted aromatic and heterocylic groups [1]. However, the release of these coloured wastewaters in the environment is a considerable source of non-aesthetic pollution and eutrophication [2]. It is well known that some of the industrial dyes and degradation products such as aromatic amines are highly carcinogenic [3]. Since these dyes are highly soluble in water, their removal from wastewater is difficult by conventional coagulation and activated sludge processes [4]. Recently, there has been a considerable interest in the utilization of advanced oxidation processes (AOPs) for the complete destruction of dyes [5]-[7]. Heterogeneous photocatalysis (one kind of AOPs) has been considered as a cost effective alternative for the purification of dye containing wastewater [8]. Moreover, recent studies have demonstrated that photocatalysis can be used to mineralize organic compounds or degrade dyes under UV irradiation [9]. Titanium dioxide (TiO$_2$) is one of the most preferable semiconductors for the photocatalytic process [10]. Photocatalysis, which is one of the Advanced Oxidation Processes, is a new method used to mineralize dye compounds [11] and also semiconducting material absorbs light energy more than or equal to its band gap, thereby generating holes and

electrons which further releases free-radicals in the system to oxidize the substrate. The resultant free-radicals are very efficient oxidizers of organic compounds [12] [13]. The photocatalytic oxidation technology is frequently used for the complete degradation of organic micro- pollutants (dyes) in water, utilizing sunlight and UV radiation as energy sources [14].

The main objective of the present investigation is to study the efficiency of newly synthesized Magnesium zinc Strontiate nano-particles in colour removal of VBB, an extensively used industrial dye. The effect of pH and the different dosage of Magnesium zinc Strontiate nano-particles were studied.

II.MATERIALS AND METHODS

2.1.Materials and Reagents

The chemicals used for the synthesis of $MgZnSrO_3$ are Magnesium nitrate $(Mg(NO_3)_2.4H_2O)$, Zinc nitrate $(Zn(NO_3)_2.6H_2O)$, Strontium Nitrate $Sr(NO_3)_2$ (99% AR) and Urea $(NH_2.CO.NH_2)$ (99.5% AR), are obtained from Hi-media chemicals Mumbai, and used without further purification. The VBB dye used for the photocatalytic study was purchased from Colourtex Limited, Surat, Gujarat. The structure of the dye is given in Fig 1.
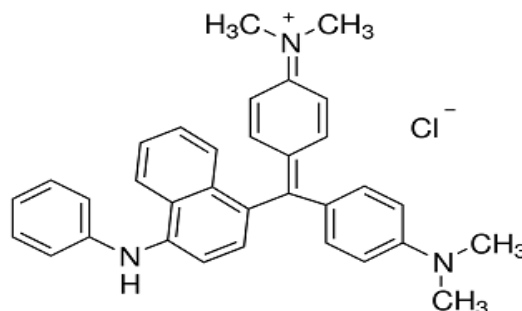

Fig 1: Chemical Structure of VBB dye

2.2.Synthesis of Magnesium Zinc Strontiate Nano-Particles

The Magnesium Zinc strontiate nano-particle was prepared by solution combustion method using procured Magnesium nitrate, zinc nitrate, Strontium Nitrate, and Urea has fuel. Stochiometric compositions of Magnesium nitrate (5.12g), zinc nitrate (5.94g), Strontium nitrate (4.23g) and Urea (6.05g) was taken in a silica crucible (with volume of 100 cm^3) using 20mL of distilled water. Crucible was then introduced into the muffle furnace for calcination which was preheated to 500°C. According to propellant chemistry the reaction is as follows;

$$2Mg(NO_3)_2 + 2Zn(NO_3)_2 + 2Sr(NO_3)_2 + 10NH_2CONH_2 \rightarrow 2MgZnSrO_3 + 20H_2O + 10CO_2$$
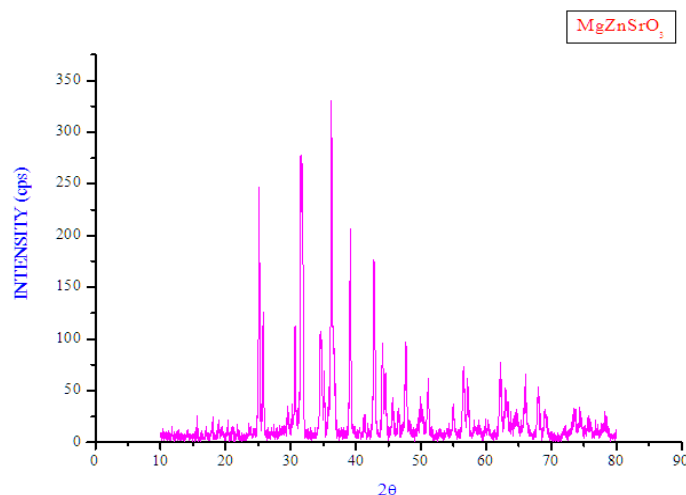
2.3 Characterization of Synthesized $MgZnSrO_3$ Nano-Particle

2.3.1.X-RAY Diffraction (XRD)

The XRD was performed by powder X-ray diffraction (Rigaku diffractometer) using Cu-Kα radiation (1.54 Å) in a θ-2θ configuration. The pattern obtained from the XRD analysis of the prepared $MgZnSrO_3$ nano-particle is presented in Figure 2. According to the Debye-Scherrer's formula $D = K\lambda/(\beta\ Cos\theta)$, where, K is the Scherrer's constant, λ the X-ray wavelength, β is the full width at half-maximum, and θ is the Bragg diffraction angle
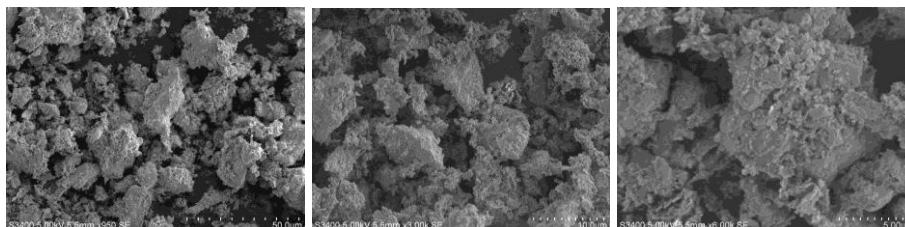
calculated using the Debye-Scherrer's formula. The average crystallite size of $MgZnSrO_3$ was found to be 33nm.

Fig 2: X-Ray diffraction of $MgZnSrO_3$ (urea)

2.3.2. Scanning Electron Micrograph (SEM)

Scanning Electron Microscope pictures have been taken for the $MgZnSrO_3$ nano-particles. The photographs revealed combination of cluster, Sharpe edge, and plate like structure and tube like structure morphology which looks like a colony. The enlarged image shows the uneven size and shape of the different nano-particles, which also revels the thick attachment of nano-particles over one another. (Fig. 3).

Fig 3: SEM Photograph of $MgZnSrO_3$ (Urea)
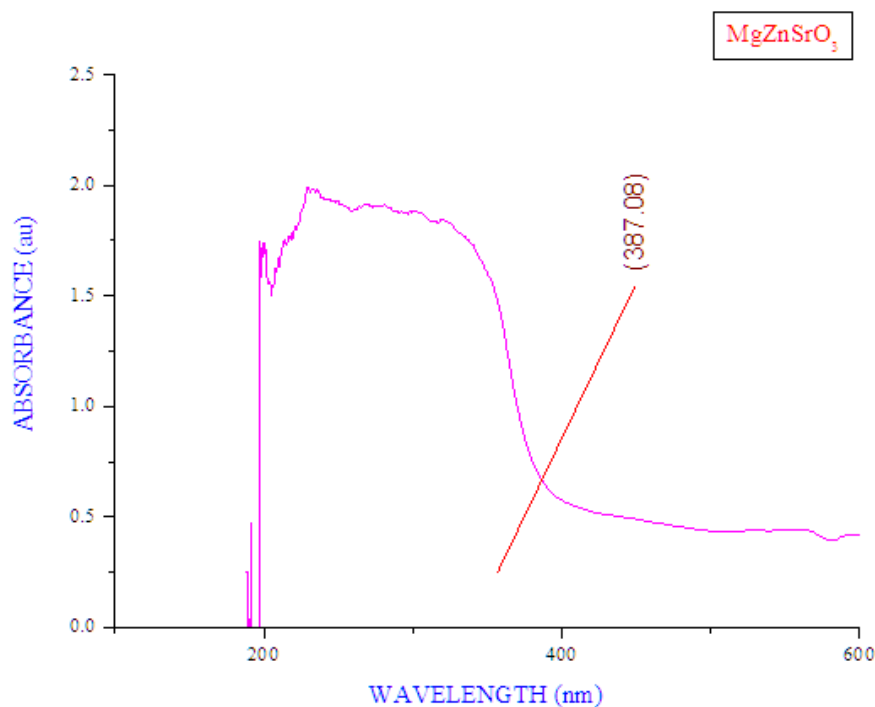
2.4. UV-Vis ABSORPTION SPECTROSCOPY

UV-Vis absorption spectra of as prepared $MgZnSrO_3$ were examined by using UV-Vis spectrophotometer of family Ocean Optics DH- 2000 by wavelength range from 200-800 nm at Research Laboratory, Department of Nanotechnology, Kuvempu University. According to the reflectance spectrum of $MgZnSrO_3$ photocatalyst the band edge was found to be at 387.08 nm and the band gap was calculated by Planck's equation as follows;

Band gap energy Eg = (h $\times$ C/λ); Where, h= Planks Constant; C= Velocity of light (Speed of light);

λ= Wavelength of light; h= 4.135×10^{-15} eV; C=3×10^8 m/s, λ= ---------$\times 10^{-9}$ nm;

Band gap energy (eV) = $4.135 \times 10^{-15} \times 3 \times 10^8 \times 10^9$; eV= (1240/ Wavelength (nm));

eV= (1240/ 387.08) = 3.2 eV

MgZnSrO₃

Fig. 4: UV-Vis absorption spectra of MgZnSrO$_3$ (Urea)

The band gap of MgZnSrO$_3$ is 3.2 eV. Hence band gap of the semiconductor is particle size dependent.

III. RESULT AND DISCUSSION

3.1 Experimental Procedure

The absorbance for the dye solution was determined by using the instrument UV-Vis spectrophotometer. λ_{max} of VBB was found to be 615nm. All the experiments were conducted under direct sunlight. A known concentration of dye solution was prepared by dissolving 0.015g of VBB dye in 1000ml double distilled water and investigated for its decolourization in the presence of MgZnSrO$_3$ nano-particle at different catalyst dosages and pH levels. After the experiments, the extent of decolourization was estimated by recording absorbance of the dye solution using UV-VIS spectrophotometer 169 in order to get the optimum catalyst dose. The experiments were repeated at different pH levels (from 2 to 11) for the 100ml of same standard dye solutions with the optimum catalyst dose.

The percentage of decolourization was calculated by using the equation,

$$\text{Decolourization} = (A_0 - A_t)/ A_0 \times 100$$

Where, A_0 is the initial absorbance of the dye solution

A_t is absorbance at time interval 't' i.e., after 120 minutes.

3.2.Mechanism of the Photocatalytic Degradation

$$MgZnSrO_3 + h\upsilon \rightarrow (e^-_{CB} + h^+_{VB}) \qquad \qquad \text{(Eq. 1)}$$

Step 1: Nano-particle molecules get excited and transfer electrons to the conduction band.

$$e^-_{CB} + O_2 \rightarrow O_2^{\bullet-} \qquad \qquad \text{(Eq. 2)}$$

Step 2: An electron in the conduction band of the nano-particles can reduce molecular oxygen and produce the super oxide radical.

$$H_2O + O_2^{\bullet-} \rightarrow OOH^{\bullet} + OH^{-} \qquad \text{(Eq. 3)}$$

$$2OOH^{\bullet} \rightarrow O_2 + H_2O_2 \qquad \text{(Eq. 4)}$$

$$O_2^{\bullet-} + VBB \rightarrow VBB\text{-}OO^{\bullet} \qquad \text{(Eq. 5)}$$

Step 3: Molecular oxygen, adsorbed on the surface of the photocatalysts prevents the hole-electron pair recombination process [15]. Recombination of hole-electron pair decreases the rate of photocatalytic degradation. This radical may form hydrogen peroxide or organic peroxide in the presence of oxygen and organic molecule.

$$O\ OH^{\bullet} + H_2O + e^{-}_{CB} \rightarrow H_2O_2 + OH^{-} \qquad \text{(Eq. 6)}$$

Step 4: Hydrogen peroxide can be generated in another path

$$H_2O_2 + e^{-}_{CB} \rightarrow OH^{\bullet} + OH^{-} \qquad \text{(Eq. 7)}$$

$$H_2O_2 + O_2^{\bullet-} \rightarrow OH^{\bullet} + OH^{-} + O_2 \qquad \text{(Eq. 8)}$$

Step 5: Hydrogen peroxide can form hydroxyl radicals which are powerful oxidizing agents.

$$OH^{\bullet} / O_2^{\bullet-} / MgZnSrO_3^{\bullet+} + VBB \rightarrow VBB \text{ degradation} \qquad \text{(Eq. 9)}$$
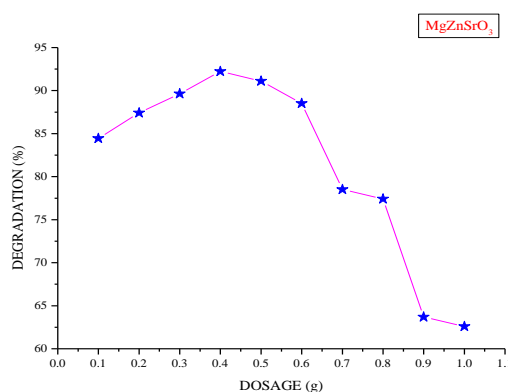
Step 6: The radicals produced are capable of attacking dye molecules and degrade them.

3.3. Effect of Catalyst Concentration on VBB

The effect of catalyst concentration on the photocatalytic degradation was studied over a range of the catalyst amount from 0.1 to 1g/100ml for VBB. The synthesized nano-particles have shown appreciable results. The $MgZnSrO_3$ (urea) with the nano-particle size 33 nm has shown 92.22% degradation. Since, the photodegradation was most effective at 0.4g/100ml in 120 minutes for $MgZnSrO_3$ (urea) nano-particle dosages showed in (Fig. 5) (Photo 1), further experiments were continued with same dosages.

The photocatalytic activity results in creating more number of H^{+} ions and e^{-CB} by generating $OH^{\bullet}$ radicals which act as the main oxidizing species. In this result, maximum degradation is mainly due to the availability of number active sites on the nano-particle surface and sunlight irradiation into the suspension, which is because of the increased scattering of light and screening effect. The more increase in the catalyst amount i.e., above 0.4g/100ml photocatalytic degradation is decreased by small extent. This is mainly because coincide of adsorption sites and also because of overcrowding owing to collision with ground state catalysts [16].

Fig. 5: Effect of catalyst concentration on VBB at 120 minutes [VBB=15 ppm, pH=7, $MgZnSrO_3$ (urea)]

Photo 1: Effect of catalyst concentration on VBB at 120 minutes [VBB=15 ppm, pH=7, MgZnSrO$_3$ (urea)]

3.4 Effect of pH oN VBB

In order to study the effect of pH on the degradation efficiency of MgZnSrO$_3$ (urea) as catalyst, the experiments were carried out at pH ranging from 2 to11. The results showed that pH significantly affected the degradation efficiency (Fig. 6) (Photo 2). The degradation rate of VBB for MgZnSrO$_3$ (urea) the degradation of the VBB was obtained from 71.11% to 93.33% from pH 2 to 4, similarly the degradation decreased to 65.59% at pH 11 in 120 minutes for 0.4g/100ml.

The maximum degradation rate for MgZnSrO$_3$ nano-particle was achieved at pH 4. More efficient formation of hydroxyl radicals was found to occur in acidic medium. Excess of hydroxyl anions increases the formation of OH$^\bullet$ radicals. These OH$^\bullet$ radicals are the main oxidizing species responsible for photocatalytic degradation [17].
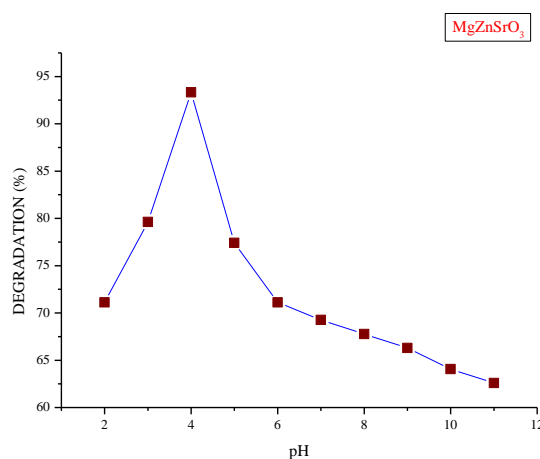

Fig. 6: Effect of pH on VBB at 120 minutes [VBB=15 ppm, MgZnSrO$_3$ (urea)]
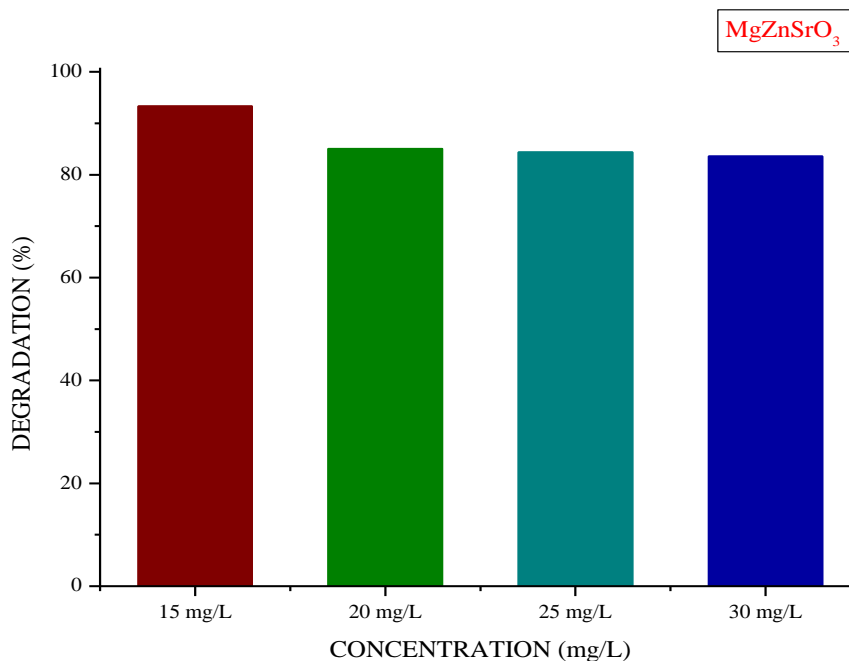

Photo 2: Effect of pH on VBB at 120 minutes [VBB=15 ppm, MgZnSrO$_3$ (urea)]

3.5. Effect of Initial Dye Concentration

The experiments were conducted to study the effect of initial dye concentration by varying the VBB concentration from 15, 20, 25 and 30 ppm respectively (Photo 3). The results obtained for MgZnSrO$_3$ (urea) is 93.33% for 15ppm, 85.07% for 20ppm, 84.39% for 25ppm and 83.60% for 30ppm respectively (Fig 7). These experiments illustrated that the degradation efficiency was directly affected by the concentration. The decrease in the degradation with an increase in dye concentration was ascribed to the equilibrium adsorption of dye on

the catalyst surface which results in a decrease in the active sites [18]. According to Beer Lambert law, as the initial dye concentration increases, the path length of photons entering the solution decreases. This results in the lower photon absorption of the catalyst particles, and consequently decrease photocatalytic reaction rate [19].
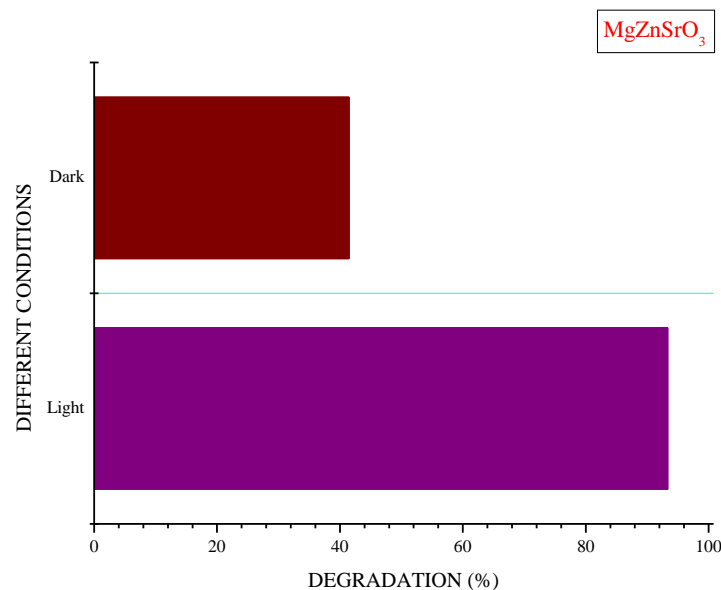

Fig 7: Effect of initial dye concentration on the photocatalytic degradation of VBB [MgZnSrO₃ (urea) g/pH=0.4/4 and VBB = (15, 20, 25 and 30) ppm]

Photo 3: Effect of initial dye concentration on the photocatalytic degradation of VBB [MgZnSrO₃ (urea) g/pH=0.4/4 and VBB = (15, 20, 25 and 30) ppm]

3.6.Effect of Sunlight Irradiation On VBB

The photocatalytic degradation of VBB dye (15mg/L) under two different experimental conditions were examined, *i.e.,* through sunlight alone, dye/dark/catalyst, and dye/sunlight/catalyst for the catalyst. VBB dye solution when exposed directly to the sunlight without the catalyst, the degradation was found to be zero during the entire experiments. The degradation rate was found to increase with increase in irradiation time, for dye/sunlight/ MgZnSrO₃ (urea) showed 93.33%, dye and for dye/dark/ MgZnSrO₃ (urea) 41.48% was recorded (Fig 8). These results clearly indicate that photodegradation occurs most efficiently in the presence of sunlight (Photo 4) [20] [21].

Fig. 8: Effect of sunlight irradiation with respect to Dark condition on photocatalytic degradation of VBB in 120 minutes

Photo 4: Effect of sunlight irradiation with respect to Dark condition on photocatalytic degradation of VBB in 120 minutes

IV.CONCLUSION

Photocatalysis is a very effective method for the degradation of azo dyes. In this study, Magnesium zinc strontiate nano-particles were synthesized and characterized by SEM and XRD studies. It was observed that the synthesized Magnesium zinc strontiate (average particle size 33nm) is photosensitive and effective in degrading selected industrial dye (VBB) in a short interval of time (120 minutes). From this experiment, we can conclude that the $MgZnSrO_3$ did in fact degrade the dye over short interval of time with the help of sunlight. Even though the result was achieved more than 93%, we still believe that if this experiment was done over a longer period of time that the concentration of the dyes would have been zero. This protocol developed may be employed effectively in the treatment of textile dye effluents which are hazardous to the environment.

V. ACKNOWLEDGEMENTS

REFERENCE

[1]. S Alahiane, S. Qourzal, M. El Ouardi, A. Abaamrane, A. Assabbane, Factors Influencing the Photocatalytic Degradation of Reactive Yellow 145 by TiO_2-Coated Non-Woven Fibers, American Journal of Analytical Chemistry, 5(8), 2014, 445-454.

[2]. I K Konstantinou, and T.A. Albanis, TiO_2-Assisted Photocatalytic Degradation of Azo Dyes in Aqueous Solution: Kinetic and Mechanistic Investigations: A Review, Applied Catalysis B: Environmental, 49(1), 2004, 1-14.

[3]. M Sangareswari, and M.M. Sundaram, Enhanced Photocatalytic Activity of Conducting Polypyrrole-TiO_2 Nanocomposite for Degradation of Organic Dyes under UV Light Irradiation, Journal of Nanoscience and Technology, 1(1), 2015, 9-12.

[4]. C Bhavya, K. Yogendra, and K.M. Mahadevan, A Study on the Synthesis, Characterization and Photocatalytic Activity of CaO Nanoparticle against Some Selected Azo Dyes, Indian Journal of Applied Research, 5(6), 2015, 361-365.

[5]. M S Mashkoura, A.F. Al-Kaimb, L.M. Ahmed, and F.H. Hussein, Zinc Oxide Assisted Photocatalytic Decolorization of Reactive Red 2 Dye. International Journal of Chemical Sciences, 9(1), 2011, 969-979.

[6]. K Maasoomeh, D. Nezameddin and S. Soodabeh, Heterogeneos Photocatalytic Decolorization of Brown NG by TiO_2-UV Process. Iranian Journal of Chemistry & Chemical Engineering, 29(3), 2010, 19-26.

[7]. E Chatzisymeon, C. Petrou, and D. Mantzavinos, Photocatalytic treatment of textile dye house effluents with simulated and natural solar light, Global Nest Journal, 15(1), 2013, 21-28.

[8]. J Grzechulska, and A.W. Morawski, Photocatalytic Decomposition of Azo-Dye Acid Black 1 in Water over Modified Titanium Dioxide, Applied Catalysis B: Environmental, 36(1), 2002, 45-51.

[9]. M Noorjahan, M.P. Reddy, V.D. Kumari, B. Lavedrine, P. Boule and M. Subrahmanyan, Photocatalytic Degradation of H-Acid over a Novel TiO_2 Thin Film Fixed Bed Reactor and in Aqueous Suspensions, Journal of Photochemistry and Photobiology A: Chemistry, 156(1-3), 2003, 179-187.

[10]. N Barka, S. Qourzal, A. Assabbane, A. Nounah, and Y. Ait-Ichou, Photocatalytic Degradation of an Azo Reactive Dye, Reactive Yellow 84, in Water Using an Industrial Titanium Dioxide Coated Media, Arabian Journal of Chemistry, 3(4), 2010, 279-283.

[11]. A Giwa, P.O. Nkeonye, K.A. Bello, E.G. Kolawole, and A.M.F.O. Campos, Solar Photocatalytic Degradation of Reactive Yellow 81 and Reactive Violet 1 in Aqueous Solution Containing Semiconductor Oxides, International Journal of Applied Science and Technology, 2(4), 2012, 90-105.

[12]. K Yogendra, Suneel Naik, K.M. Mahadevan, and N. Madhusudhana, A comparative study of Photocatalytic activities of two different synthesized ZnO composites against Coralene Red F3BS dye in presence of natural solar light, International Journal of Environmental Sciences and Research, 1(1), 2011, 11-15.

[13]. S Lodha, A. Jain, and P.B. Punjabi, A novel route for waste water treatment: Photocatalytic degradation of Rhodamine B, Arabian Journal of Chemistry, 4(4), 2011, 383-387.

[14]. M J Uddin, M.A. Islam, S.A. Haque, S. Hasan, M.S.A Amin, and M.M. Rahman, Preparation of nanostructured TiO2-based photocatalyst by controlling the calcining temperature and pH, International Nano Letters, 2(19), 2012, 1-10.

[15]. A Di-Paola, V. Augugliaro, L. Palmisano, G. Pantaleo, and E. Savinov, Heterogeneous photocatalytic degradation of nitrophenols, Journal of Photochemistry and Photobiology A: Chemistry, 155(1-3), 2003, 207-214.

[16]. A K Subramani, K. Byrappa, S. Ananda, K.M. Lokanatha Rai, C. Ranganathaiah, and M. Yoshimura, Photocatalytic degradation of indigo carmine dye using TiO_2 impregnated activated carbon, Bulletin of Materials Science, 30(1), 2007, 37-41.

[17]. C S Turchi, and D.F. Ollis, Photocatalytic Degradation of Organic Water Contaminants: Mechanisms Involving Hydroxyl Radical Attack, Journal of Catalysis, 122(1), 1990, 178-192.

[18]. V Mirkhani, S. Tangestaninejad, M. Moghadam, M.H. Habibi, and V. Rostami, A Photocatalytic Degradation of Azo Dyes Catalyzed by Ag Doped TiO_2 Photocatalyst, Journal of the Iranian Chemical Society, 6(3), 2009, 578-587.

[19]. K Byrappa, A.K. Subramani, S. Ananda, K.M. Lokanatha Rai, R. Dinesh, and M. Yoshimura, Photocatalytic degradation of Rhodamine B dye using hydrothermally synthesized ZnO, Bulletin of materials Science, 29(5), 2006, 433-438.

[20]. A Guillen Santiago, S.A. Mayen, G. Torres Delgado, R. Castanedo Perez, A. Maldonado, and M.L. De la Olvera, Photocatalytic degradation of Methylene blue using undoped and Ag doped TiO_2 thin films deposited by a sol gel process: Effect of the ageing time of the starting solution and the film thickness, Materials Science and Engineering B, 174(1-3), 2010, 84-87.

[21]. M Movahedi, A.R. Mahjoub, and S. Janitabar Darzi, Photodegradation of Congo Red in Aqueous Solution on ZnO as an Alternative Catalyst to TiO_2, Journal of the Iranian Chemical Society, 6(3), 2009, 570-577.