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DEGRADATION OF TEXTILE DYE FROM AQUEOUS SOLUTION BY USING MBIR DOWEX 11 PHOTOCATALYST

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ABSTRACT

Advanced oxidation processes (AOPs) have proved very effective in treatment of the various hazardous organic pollutants in water. The photocatalytic degradation of azo dye Direct Red 81 with UV/Visible/MBIR (Methylene Blue Immobilized Resin) Dowex 11 interface was investigated. Kinetic analysis indicates that the photodegradation rate of azo dye can usually be approximated as pseudo-first-order kinetics according to the Langmuir-Hinshelwood model. The degradation of dye depends on several parameters such as catalyst dose, concentration of dye, pH of the solution and light intensity. The mechanism of the photodegradation process under UV- Visible light illumination involves an electron excitation and generation of very active oxygenated species that attack the dye molecules leading to photodegradation. The dye solution could be completely decolorized and effectively mineralized, with average removal efficiency larger than 97% for a reaction time of 160 min.

Key Words: *Degradation, Decolorization, Efficiency, Direct Red 81, MBIR Dowex 11*

INTRODUCTION

The textile processing industry is putting a severe burden on the environment, through the release of heavily polluted wastewaters. The removal of the non-biodegradable organic chemicals is a crucial ecological problem. Azo dyes are an important class of synthetic organic compounds used in the textile industry and are therefore common industrial pollutants. Due to the stability of modern dyes, mostly azo dyes conventional biological treatment methods for industrial wastewater are ineffective resulting often in an intensively colored discharge from the treatment facilities. Heterogeneous photocatalysis, by semiconductor particles is a promising technology for the reduction of global environmental pollutants. Purification of wastewater of textile industries, paper industries, food industries, chemical industries, contain residual dyes which are not readily bio degradable is challenging for researchers and environmentalists. Adsorption and chemical coagulation are common techniques used in treatment of such wastewater. However these methods transfer dyes from liquid to solid phase and produces secondary pollution and requiring further treatment. About 1–20% of the total world production of dyes is lost during the dyeing process and is released in the textile effluents (Rafols and Barcelo, 1997; Houas et al., 2001). Recently there has been considerable interest in the utilization of advance oxidation processes (AOPs) for the complete destruction of dyes. AOPs are based on generation of reactive species such as hydroxyl radicals that oxidizes a broad range of organic pollutants quickly and non selectively (Das et al., 1999; Yang et al., 1998). Heterogeneous photocatalysis has emerged as an important destructive technology leading to the total mineralization of the organic pollutants including organic reactive dyes (Galindo et al., 2001; Khodja et al., 2001). AOPs such as Fenton and photo-Fenton catalytic reactions (Kuo, 1992; Kang et al., 2000), H₂O₂/UV processes (Ince and Gonenc, 1997) and TiO₂ mediated photo-catalysis (Vinodgopal and Kamat, 1996) have been studied under a broad range of experimental conditions in order to reduce the color and organic load of dye containing effluent waste waters. It is widely accepted that the anatase TiO₂ is a more efficient photocatalyst than the rutile TiO₂ because of the formers relatively high adsorptive affinity for organics and the superior hole-trapping ability (Linsebigler et al., 1995; Jung and Imaishi, 2001). (Akyol et al., 2004) was studied the photocatalytic transformation of Remazol Red by ZnO. (Pandurangan et al., 2001) carried out the photocatalytic degradation of textile dye, Basic yellow Auramine O by a batch process using ZnO as the catalyst and sunlight as the illuminant. Visible light sensitive photocatalysts have been developed by (Meena and Pachwarya, 2009; Pachwarya and Meena, 2011). The visible light photocatalyst is an impressive task in order to

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utilize the solar energy effectively. The present work investigates the influence of azo dye Direct Red 81 in presence of visible light induced methylene blue immobilized resin Dowex 11.

MATERIALS AND METHODS

Dye

Direct Red 81	=	Loba (Loba Chemicals India)
IUPAC Name	=	2-Naphthalenesulfonicacid, 7-(benzoylamino)hydroxy-3-[[4- [(4- sulfophenyl) azo] phenyl] azo]- disodium salt
Molecular Formula	=	C ₂₉ H ₁₉ N ₅ Na ₂ O ₈ S ₂
Molecular Weight	=	675.6
Solubility	=	Soluble in water
Appearance	=	Red
λ_{\max}	=	508 nm
Class	=	Azo

Structure of dye: Shown in Fig. 1.

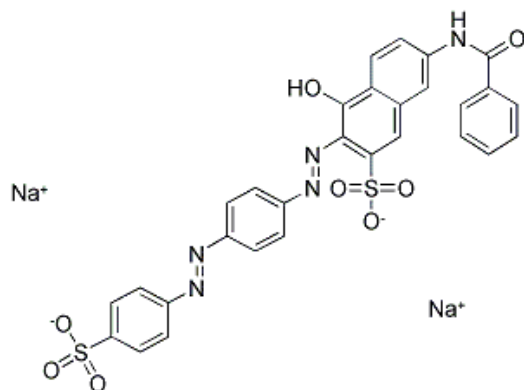
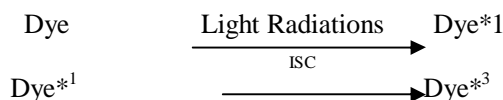


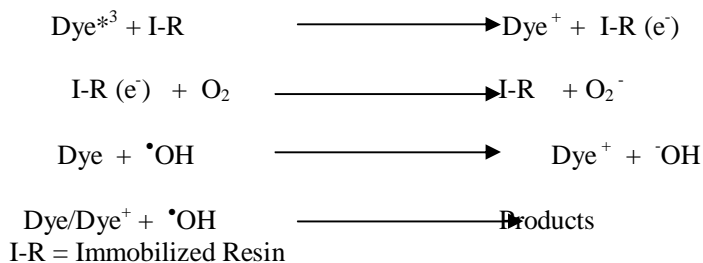
Figure 1: Structure of Direct Red 81

Photocatalytic studies and design of photoreaction chamber

We prepared photocatalyst by following materials Dowex 11 Resin 20-50 mesh (Sisco Chemicals, India Mumbai), methylene blue hydrate for Microscopy (Loba Chemicals India). For immobilization we prepare approximately M/1000 concentration solution of methylene blue in double distilled water and add Dowex-11 resin in this solution and shake well. After completing immobilization of methylene blue inside the pores of resin. All the process carried out in dark place. Then filter prepared resin from solution, wash this resin by double distilled water twice and used it as photocatalyst. Photochemical degradation experiments were carried out in glass reactor which containing solution of Direct Red 81 dye and photocatalyst. Solution of reactor is continuously stirred by magnetic stirrer during the experiment. The solution is illuminated by halogen lamp (Philips, India) above the reactor which emitted irradiation comparable to visible light. The intensity was measured by photometer (IL1400A). The lamp was surrounded with aluminium reflector in order to avoid loss of irradiation. pH of the solution was monitored by Fisher Scientific Acumen 50. The mechanism of the photo degradation process under UV-Visible light illumination involves an electron excitation and generation of very active oxygenated species that attack the dye molecules leading to photodegradation.



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The change in dye concentration is observed simply by Shimadzu-1600 UV/Visible spectrophotometer at $\lambda_{\text{max}} 508\text{nm}$. We shuck out 10 ml of solution by pipette at the 10 minute time interval, Filter the catalyst particles and calculate the removal efficiency (X %) of dye solution by this equation.

$$X \% = (C_i - C_t / C_i) \times 100$$

Where, C_i and C_t are optical densities of dye solution at initial time and at time t respectively. A schematic diagram of the set-up can be seen in Fig. 2.

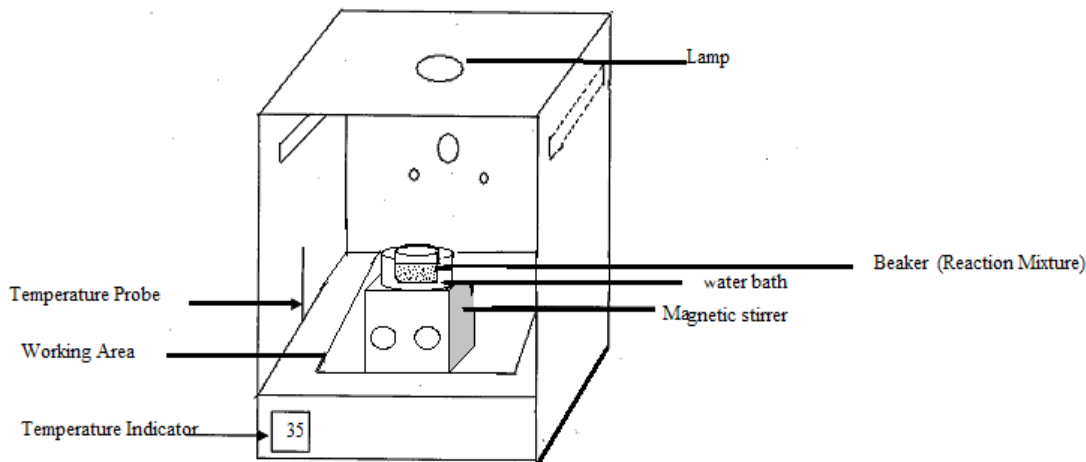


Figure 2: Experimental Set-up of Photochemical Reaction Chamber

RESULTS AND DISCUSSION

Kinetic Study

Photocatalytic degradation of Direct Red 81 was observed at $\lambda_{\text{max}} = 508 \text{ nm}$. The optimum condition was obtained at initial dye concentration: 40 mg/L, catalyst loading: 2gm/100ml, solution volume: 100ml, light intensity: 10.4 mWcm^{-2} , pH: 7.5 and temperature = 303 K. The plot of $1 + \log$ optical density versus exposure time is a straight line (Fig. 3). This indicates that the photocatalytic degradation of Direct Red 81 follows pseudo first-order kinetics (Behnajady et al., 2006; Ted Chang et al., 2000; Faisal et al., 2007). The rate constant (K) for the reaction was determined using the expression. Rate = K [Direct Red 81] K = 2.303 \times slope. The rate constant for this reaction is $1.44 \times 10^{-2} \text{ min}^{-1}$.

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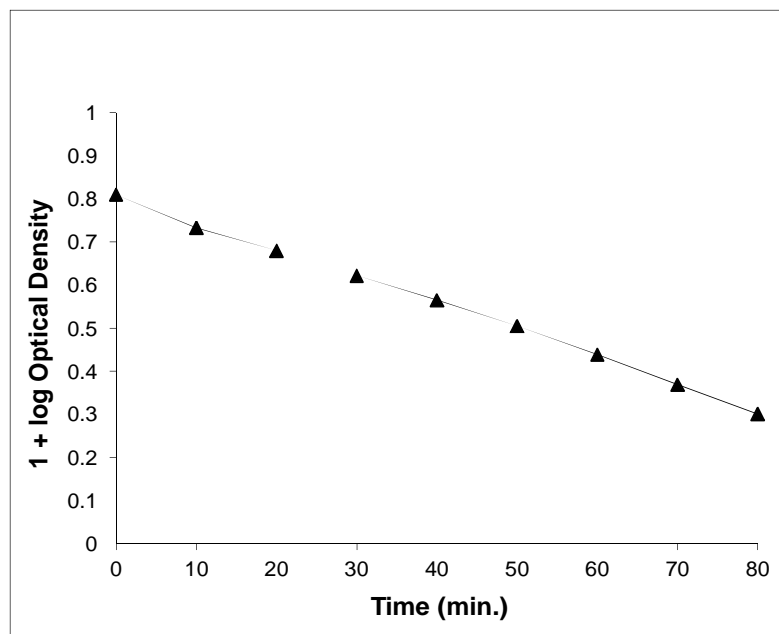


Figure 3: Kinetic study of Direct Red 81 photocatalyst system.

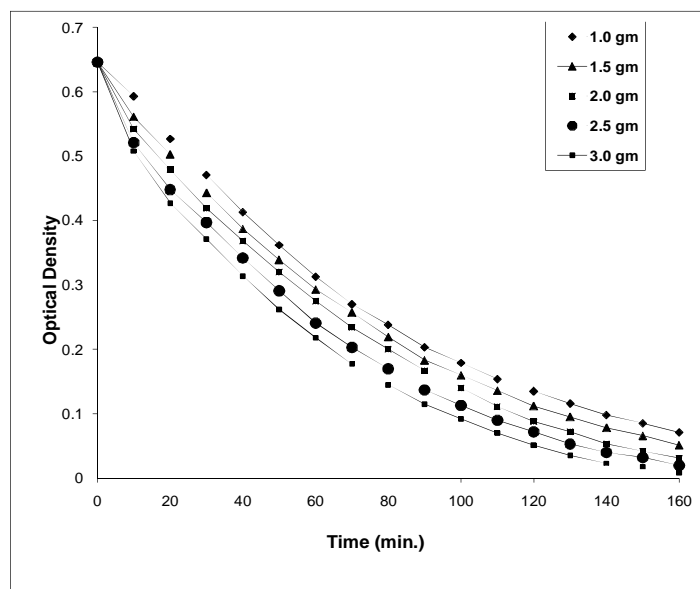


Figure 4: Effect of catalyst loading on optical density.

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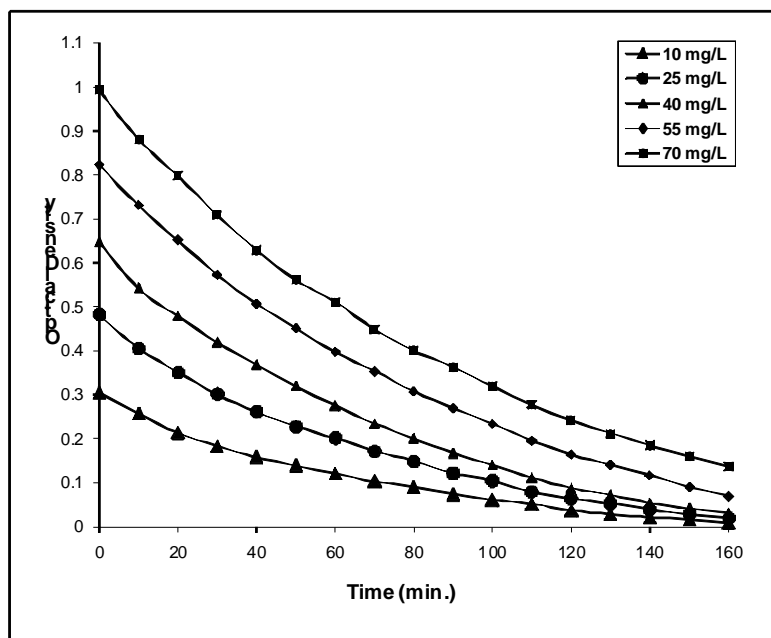


Figure 5: Effect of initial dye concentration on optical density.

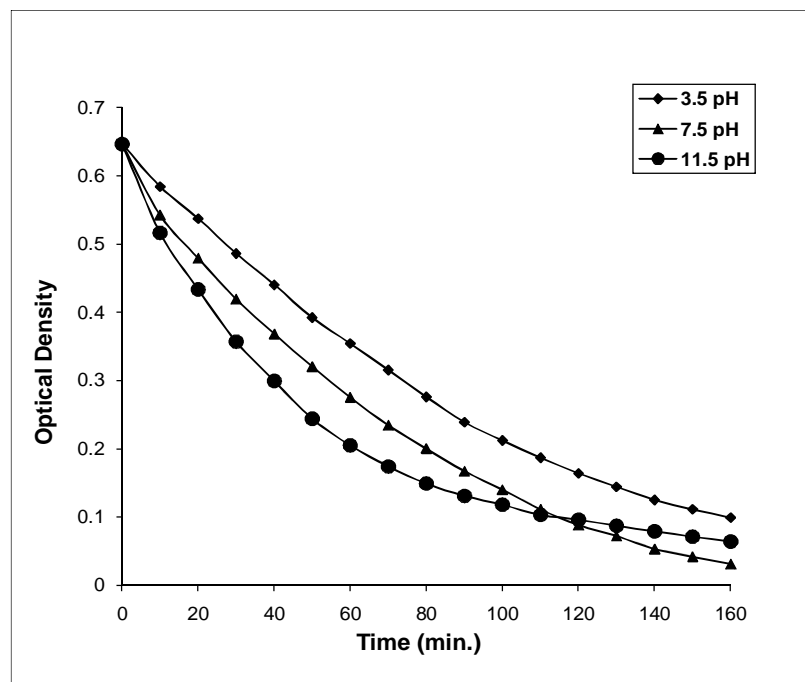


Figure 6: Effect of pH on optical density.

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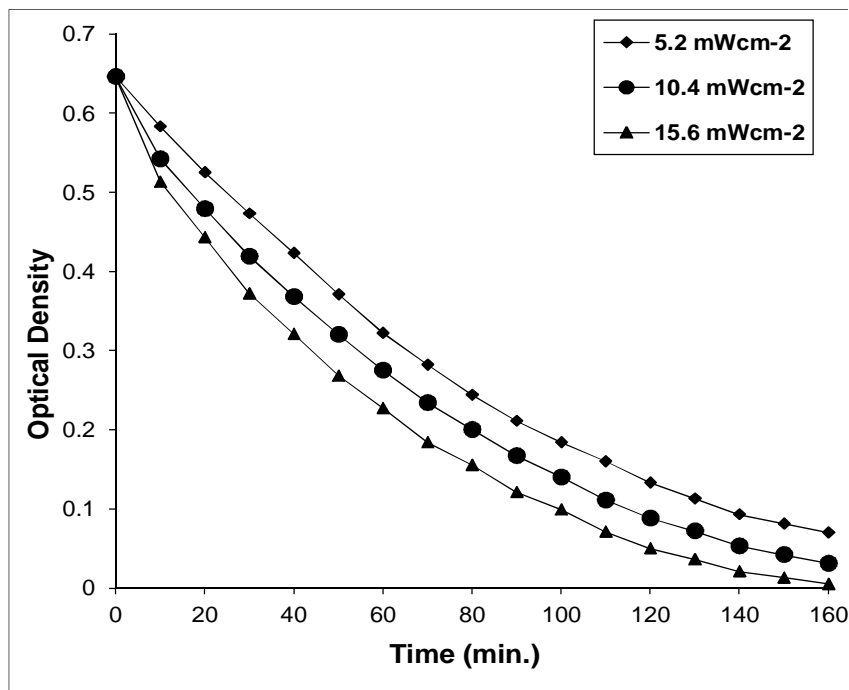


Figure 7: Effect of variation of light intensity on optical density.

Effect of Catalyst

The amount of the photocatalyst is most important parameter that affects the rate of photo catalytic degradation. We observe effect of variation in amount of photocatalyst from 1.0 to 3.0 gm/100ml and concentration of dye 40 mg/L, at constant pH 7.5 and light intensity 10.4mWcm⁻² (Fig. 4). On the rate of degradation we find out that as concentration of catalyst increases rate of degradation also increases. Increase in the rate of degradation with increase in amount of catalyst is due to availability of more catalyst surface area for absorption of quanta and interaction of molecules of reaction mixture with catalyst, resultant number of holes, hydroxyl radicals and super oxide ions (O₂⁻) are increase. These are principle oxidizing intermediate in advance oxidation process resultant increases degradation efficiency.

Effect of initial dye concentration

The effect of initial dye concentration on the optical density was studied by varying the concentration from 10mg/L to 70mg/L at constant photocatalyst (2.0gm/100ml), pH 7.5 and light intensity 10.4mWcm⁻² (Fig. 5). The concentration of dye increases the rate of degradation decreases. This effect may be caused by following reason-

The dye concentration increase number of photons reach to catalyst surface decrease resultant less number of catalyst molecules undergoes excitation and due to this effect rate of formation hydroxyl radicals and super oxide ions (O₂⁻) is decreases so rate of degradation efficiency is also decrease.

The surface area of catalyst is fixed so as the concentration of dye increases rate of degradation decreases because limited number of dye molecules attached at the active site of the catalyst and remaining dye molecules persist in solution until earlier attached molecule is degraded and number of active side of catalyst also decreases due to less availability of photons for excitation of catalyst molecules. Competitions between dye molecules to attach active site also effect rate of degradation. At higher concentration number of dye molecule also high so more will be the competition for attachment to active site of catalyst between the dye molecule and resultant reduce the rate of degradation efficiency.

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Effect of pH

We observe effect of pH variation from 3.5 to 11.5 (photocatalyst 2.0gm/100ml, dye concentration 40 mg/L, light intensity 10.4 mWcm⁻²) on optical density of dye molecules is very interesting. The results shows (Fig. 6) that rate of degradation is very low in high acidic pH range lower than pH 3.5. As well as pH increases rate of degradation also increases when pH reaches to basic range the rate of degradation increases fast, in pH range 7.5 to 9 very good rate of degradation. On further increase pH the rate of degradation also start to decrease after pH range 10 or above rate of degradation is less and continually decreases as pH increases. So we conclude that rate of degradation in basic medium is higher than acidic medium. The increase in rate of photocatalytic degradation may be due to more availability of ⁻OH ions in pH range 7.5 to 9 will generate more [•]OH radicals by combining with the holes which are formed due to electronic excitation in catalyst. Formation of hydroxyl radicals is more responsible for the photocatalytic degradation than super oxide ions (O₂⁻). At higher pH the rate of degradation decreases. This effect may cause due to competition between ⁻OH groups to attach active site of catalyst, so rate of attachment of ⁻OH group decreases. Resultant formation of hydroxyl radicals ([•]OH) decreases by this reason rate of degradation also decreases.

Effect of light intensity

Light intensity is most important factor which affects the rate of degradation. We find out that as light intensity increases from 5.2 to 15.6 mWcm⁻² (photocatalyst 2.0gm/100ml, dye concentration 40 mg/L, pH 7.5) the rate of degradation of dye molecules also increases up to some extent after it no change observe in rate of degradation. This change in rate of degradation of dye molecules by variation in light intensity as light intensity increases number of photons increases to reach the catalyst surface so number excited catalyst molecules increases and resultant increase the number of holes, hydroxyl radicals and super oxide ions (O₂⁻) and rate of degradation of dye molecules increase. We observe that after some extent of increase in light intensity there is no effect on rate of degradation on further increases in light intensity. This may cause that maximum number of photons which required for excitation are available in fix range irradiating light intensity after it if we further increase light intensity no any considerable change observed in rate of degradation because there is no requirement of more photons for excitation. Because all catalyst molecules become active (excited) in fix light intensity range after it we increase light intensity to any range, the rate of degradation remains unchanged (Fig. 7).

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REFERENCES

- Akyol A, Yatmaz HC and Bayramoglu M (2004). Photocatalytic Decolorization of Remazol Red RR in Aqueous ZnO Suspensions. *Applied Catalysis B: Environmental*, **54** (1) 19-24.
- Behnajady MA, Modirshahla N and Hamzavi R (2006). Kinetic Study on Photocatalytic Degradation of C.I Acid Yellow 23 by ZnO Photocatalyst. *Journal of Hazardous Materials*, **133** (1-3) 226-232.
- Das S, Kamat PV, Padmaja, Stephen S and Madison A (1999). Free Radical Induced Oxidation of the Azo Dye Acid Yellow 9: Kinetics and Reaction Mechanism. *Journal Chemistry Soc Perkins Trans* **2**, 1219-1223.
- Faisal M, Abu Tariq M and Muneer M (2007). Photocatalysed Degradation of Selected Dyes in UV-irradiation Aqueous Suspension of titania. *Dyes and Pigments*, **72** (2) 233-239.
- Galindo C, Jacques P and Kalt A (2001). Photochemical and Photocatalytic Degradation of an Indigoid Dye: a case Study of Acid Blue 74 (AB74). *Journal of Photochemistry and Photobiology A: Chemistry*, **141**, 47-53.
- Houas A, Lachheb H, Ksibi M, Elaloui E, Guillard C and Hermann JM (2001). Photocatalytic degradation pathway of methylene blue in water. *Applied Catalysis B: Environmental*, **31** (2) 145-157.

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- Ince NH and Gonenc DT (1997).** Treatability of a Textile Azo Dye by UV/H₂O₂. *Environmental Technology*, **18** (2) 179–185.
- Jung SC and Imaishi N (2001).** Preparation, crystal structure, and Photocatalytic activity of TiO₂ films by chemical vapor deposition. *Journal of Chemical Engineering*, **18** (6) 867-872.
- Kang SF, Liao CH and Po ST (2000).** Decolorization of Textile Wastewater by Photo- Fenton Oxidation Technology. *Chemosphere*, **41** (8) 1287–1295.
- Khodja AA, Sehili T, Pilichowski JF and Boule P (2001).** Photocatalytic Degradation of 2-phenylphenol on TiO₂ and ZnO in Aqueous Suspensions. *Journal of Photochemistry and Photobiology A: Chemistry*, **141** (2-3) 231-239.
- Kuo WG (1992).** Decolorizing dye wastewater with Fenton's reagent. *Water Research*, **26** (7) 881-886.
- Linsebigler AL, Lu GQ and Yates JT (1995).** Photocatalysis on TiO₂ surfaces: principles, mechanisms, and selected results. *Chem Rev*, **95** (3) 735-758.
- Meena RC and Pachwarya Rambabu (2009).** Photocatalytic degradation of model textile azo dyes in textile wastewater using methylene blue immobilized resin Dowex-11. *Journal of Scientific and Industrial Research*, **68**, 730-734.
- Pachwarya RB and Meena RC (2011).** Degradation of Azo dyes ponceau S, S-IV from the wastewater of textile industries in a new photocatalytic reactor with high efficiency using recently developed photocatalyst MBIRD-11. *Energy Sources, Part A*, **33** (18) 1651-1660.
- Pandurangan A, Kamala P, Uma S, Palanichamy M and Murugesan V (2001).** Degradation of basic yellow auramine O-A textile dye by semiconductor photocatalysis. *Indian Journal Chemical Technology*, **8** (6) 496-499.
- Rafols C and Barcelo D (1997).** Determination of mono- and disulphonated azo dyes by liquid chromatography–atmospheric pressure ionization mass spectrometry. *Journal Chromatography A*, **777** (1) 177–192.
- Ted Chang H, Wu Nan-Min and Zhu Wat Faqing (2000).** Kinetic Model for Photocatalytic Degradation of Organic Contaminants in a Thin-film TiO₂ Catalyst. *Water Research* **34** (2) 407-416.
- Vinodgopal K and Kamat PV (1996).** Combine electrochemistry with Photocatalysis. *Chemtech*, **26** (4) 18–22.
- Yang Y, Wyatt DT and Bahorsky M (1998).** Decolorization of dyes using UV/H₂O₂ photochemical oxidation. *Textile Chemist and Colorist*, **30** (4) 27-35.