

Degradation of Textile Dyes Ponceau-S and Sudan IV Using Recently Developed Photocatalyst, Immobilized Resin Dowex-11

R.C. Meena, Ram Babu Pachwarya, Vijay Kumar Meena and Shakuntla Arya
Department of Chemistry, Jai Narain Vyas University, Jodhpur (Raj.), 342001, India

Abstract: Problem statement: In present study, we selected a model dyes Ponceau S and Sudan IV, to test a recently developed photo catalyst methylene blue immobilized resin dowex-11. **Approach:** This is a light-activated process that has been successfully applied to remove organic and inorganic dyes of textile industries. **Results:** The reactor, made of glass slides (tubes) coated with a thin-film of methylene blue immobilized resin dowex-11 with the help of a suitable and non-reactive adhesive. Dye solution was continues recycles from reactor for 3 h in a recirculation mode under various conditions (with/without catalyst, with/without light radiation, variation in catalyst amount, dyes concentration, light intensities and pH). **Conclusion:** The ponceau S and sudan-IV, removal efficiency was evaluated using UV/Visible spectrophotometer at $\lambda_{\max} = 514 \pm 2$ nm Ponceau S and $\lambda_{\max} = 520$ nm respectively removal efficiency results (99%) after 3 h at pH 9) showed that new photo catalyst, methylene blue immobilized resin dowex-11 provided a promising technology to improve the quality of effluent from textile wastewater treatment plants.

Key words: Photocatalysis, methylene blue immobilized resin dowex-11, ponceau S, Sudan IV, degradation

INTRODUCTION

Wastewater of textile industries can not treated successfully by conventional treatment methods and presently used methods gives low quality water not suitable to use for domestic utilization. The presence of organic dyes in textile wastewater- these dyes are synthetic and non-biodegradable so, biological treatment of wastewater alone is usually not effective waters may result in poor water quality.

Heller^[1] pointed out that, all the extensive Knowledge that was gained during the development of semiconductor photo electrochemistry during the 1970s and 1980s greatly assist the development of photo catalysis process. Ever since 1977, when Frank and bard^[2,3] first examined the possibilities of using TiO₂ to decompose cyanide in water, there has been increasing interest in environmental applications Treatment plants have applied additional processes, like coagulation, or adsorption for the removal of the contaminants^[4-6]. However, these processes simply transfer pollutants from their water matrix into bio-solids, rather than completely eliminating these chemicals. For this reason, photocatalysis using Methylene blue Immobilized Resin Dowex-11 photo catalyst has been studied as an alternative to conventional processes. Heterogeneous

photocatalysis is a process by which the irradiation of a metal oxide semiconductor produces photo-excited electrons (e) and positively charged holes (h⁺). The photo-excitation of semiconductor particles, by means of light with a higher energy than the electronic band gap energy of the semiconductor, generates excess electrons in the Conduction Band (e CB) and an electron vacancy in the valence band (h⁺ VB). Although several semiconductors exist, (TiO₂) is the most widely used catalyst, mainly because of its photo stability, non-toxicity, low cost and water insolubility under most environmental conditions^[7]. In recent years, (TiO₂) photocatalysis has been successfully applied to remove organic and inorganic pollutants^[8], to inactivate microorganisms^[9] and to control disinfection by-product formation^[10,11]. TiO₂ photocatalysis was found to be effective for the destruction of a wide variety of environmental contaminants present in water and wastewater, this technology has not yet been successfully commercialized in past because of the costs and problems connected to the separation of TiO₂ particles from the suspension after treatment. In order to solve this problem, supported photo catalysts have been developed^[12-19], in particular, titanium powder has been immobilized on supports transparent to UV/VIS radiation. Unfortunately, the surface area of active

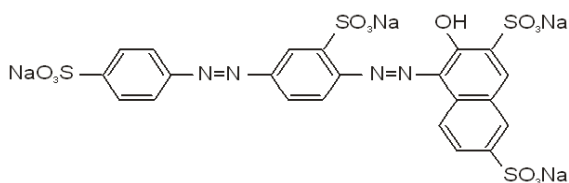
Corresponding Author: R.C. Meena, Department of Chemistry, Jai Narain Vyas University, Jodhpur (Rajasthan), 342001 India
Tel: 91-291-2431915/09414249584

catalyst exposed to solution is lower in supported systems than in suspended systems, reducing the catalytic activity. In this study, ponceau S and Sudan IV, were chosen as a model dye to test a novel photocatalytic reactor. The reactor, containing Methylene blue Immobilized Resin Dowex-11 thin film coated on glass slides (tubes) using adhesive for fixation of Methylene blue Immobilized Resin Dowex-11 on slide/tubes/cylinder surface. Adhesive must non reactive with solution and catalyst. Solution is irradiated by visible light for 3 h in a recirculation mode, under various conditions (with/without catalyst, with/without UV/VIS radiation, different amount of catalyst, different dye concentration, different light intensities, different pH conditions, effect of dissolve oxygen percentage. Ponceau S, (S-IV) degradation was tracked by measuring transparency of solution with the help of UV/Visible spectrophotometer. We also measured pH, dissolved oxygen and temperature.

Aim of the present study is to gain attention of researchers toward utilization of solar energy for Degradation of dye pollutants by Photo catalyst and find out new photo catalyst for different applications. A new developed cheap and better photo catalyst and new developed reactor and its applicability. The potential of degradation of (ponceau S and Sudan IV, are Azo dyes used as model compounds for experiment) dyes by (methylene immobilized resin dowex-11) catalyst is better and this catalyst and reactor study well in dim light also. We apply it in different condition and find out the effect of different parameters on rate of degradation. These parameters are (1) variation in catalyst loading, (2) variation in dye concentration, (3) variation in pH, (4) variation in light intensity, (5) effect of dissolve oxygen. All the sets are observed for more then 3 h.

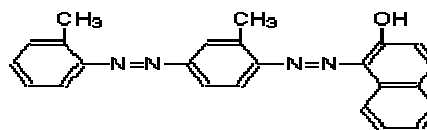
MATERIALS AND METHODS

Ponceau S, (Loba Chemicals India), Molecular Formula = $C_{22}H_{12}N_4O_{13}S_4Na_4$
Molecular Weight = 760.57, $\lambda_{max} = 514 \pm 2$ nm Class = Azo Dye



Sudan-IV = Loba (Loba Chemicals India) Molecular Formula: = $C_{24}H_{20}N_4O$

Molecular Weight: = 380.449, $\lambda_{max} = 520$ nm, Class = Azo Dye



Photocatalyst:

Used chemicals: We prepare Photo catalyst by following materials Dowex-11 Resin 20-50 mesh (Sisco Chemicals India Mumbai), Methylene blue hydrate for microscopy, (Loba Chemicals India).

Preparation of photo catalyst: 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. Put this mixture for 3 days for complete immobilization of methylene blue in side the pores of resin. All the process is carried out in dark place. After three days we can filter methylene blue immobilized resin from solution, wash this resin by double distilled water twice and used it as photo catalyst.

Role of methylene blue: Methylene blue is photosensitized dye. When molecule of methylene blue immobilized in pores of resin (fill in pores of resin). Methylene blue is photosensitized dye and becomes excited by absorbing photons of light radiations. In first electronic excitation, electron transfers into singlet state and through Inter System Crossing (ISC) electron can transfer to triplet state of methylene blue. Further inter molecule electronic interaction occurs between resin, methylene blue and solution mixture and resultant is formation of holes, hydroxyl radicals and supra oxide ions (o^-), these are highly oxidative in nature.

Analytical methods: The change in dye concentration is observed simply by Shimadzu-160 UV/Visible spectrophotometer. We suck out 10 mL of solution by pipette at the time interval of 15 min. and observe changes in percentage transparency of dye solution. Dissolved oxygen and temperature as well as pH (Fisher Scientific Acumen 50) were monitored during the experiments. Irradiation intensity was measured using a photometer (IL 1400A).

The reactor system: A Photocatalytic Reactor (PCR) was used to study the degradation of azo dyes Ponceau S and Sudan IV. The system consisted of the PCR, a 1 L open reservoir equipped with a stirrer to ensure complete mixing and a peristaltic pump to force the solution from the reservoir to the reactor.

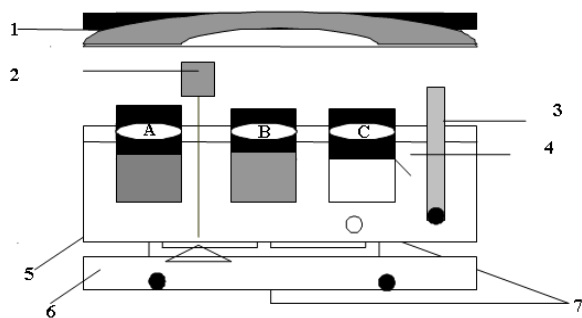


Fig. 1: Schematic diagram of the experimental setup: (1) Light lamp, (2) Stirrer, (3) Thermometer, (4) Glass reactor (beaker), (5) Water bath, (6) Magnetic stirrer. Beaker coated with Methylene Blue immobilized resin dowex-11 by non reactive adhesive (A) Dye solution without catalyst coated reactor shows no change in color (B) Shows (degradation of dye molecules) change in color by the action of photo catalyst (C), solution become colorless this shows the complete degradation occurs by the action of methylene blue immobilized resin dowex-11 (20-50 mesh) in 3 h irradiation time duration. (7) Reactor pump and connecting glass tube slides

The PCR was made of 3-9 glass or more slide/tubes/cylinder with different amount of catalyst coating. Reactor height is 30 cm and glass tubes, beakers were choosing because this kind of system is UV/Vis light transparent and easy modals. Each glass tubes had an inner diameter of 50 mm, an outer diameter of 90 mm, Water was divided among the 3 or more glass tubes/cylinder and forced to follow a fixed route inside each tube before leaving the reactor, resulting in increased irradiation time. Tungsten lamp of 200 watt, is used, the intensity of radiation is of 10.4 mW cm^{-2} . All experiments were performed at room temperature. Detailed reactor set up shown in Fig. 1.

RESULTS

Effect of catalyst: The amount of the photo catalyst affects the rate of photo catalytic degradation. We observe effect of variation in amount of photo catalyst on the rate of degradation at constant pH 7.5. 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, result is that number of holes,

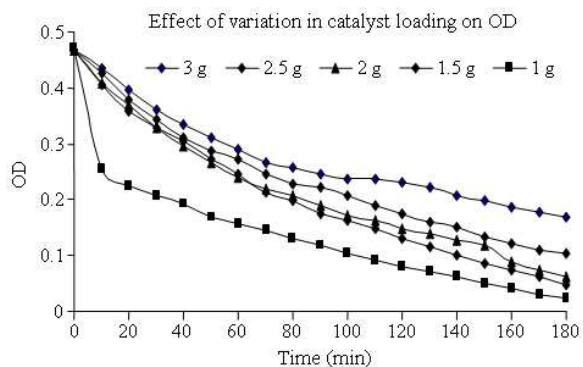


Fig. 2: Effect of catalyst loading on photo catalytic degradation (Temperature: 303 K, solution volume: 400 mL, initial dye concentration: 40 mg L^{-1} , pH 7.5, UV/visible lamp: 10.4 mW cm^{-2})

hydroxyl radicals and supra oxide ions (o^-) are increased. These are principle oxidizing intermediate in advance oxidation process and increases the rate of degradation. Effect catalyst loading on rate of degradation is graphically shown in Fig. 2.

Effect of initial dye concentration: We observe the effect of change in dye concentration on photo catalytic degradation and find out that as concentration of dye increases the rate of degradation decreases. This effect may be caused due to following reason:

- As the concentration of dye increases number of photons reaching to catalyst surface decreases result is that less number of catalyst molecules undergoes excitation and due to this effect rate of formation of holes, hydroxyl radicals and supra oxide ions (o^-) is decreased so rate of degradation also decreased
- Catalyst surface area is fixed so as the concentration of dye increases rate of degradation decreases because limited number of dye molecules attach at the active site of the catalyst and remaining dye molecules persist in solution until earlier attached molecules are degraded and number of active site of catalyst also decreases due less availability of photons for excitation of catalyst molecules. Competitions between dye molecules to attach to the active site also effect rate of degradation. At higher concentration number of dye molecules are also high so more will be the competition for attachment to active site of catalyst between the dye molecules and result is reduction in the rate of degradation

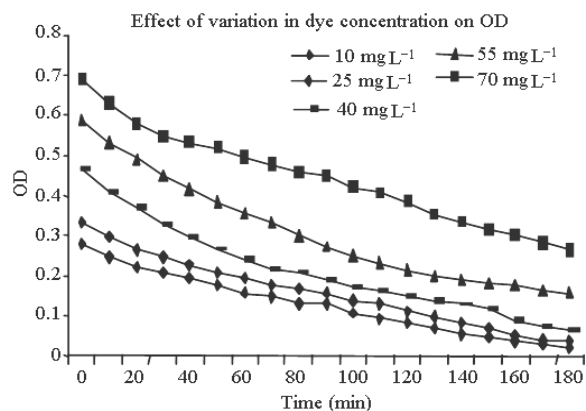


Fig. 3: Effect of initial dye concentration on degradation (Temperature: 303 K, solution volume: 400 mL, pH 7.5, UV/visible lamp: 10.4 mW cm⁻²)

Effect of change in dye concentration is shown graphically in Fig. 3.

Effect of pH: We observed that effect of pH on rate of degradation of dye molecules is very interesting. The results shows that rate of degradation is very low in high acidic pH range, if pH is lower than 3.5 rate of degradation is very less, as pH increases rate of degradation also increases when pH reaches to basic range the rate of degradation increases fast, in pH range 7.5-9 rate of degradation is very good. On further increasing pH the rate of degradation also start to decrease after pH range 10 or above rate of degradation is less and decreases as pH increases. So we conclude that rate of degradation in basic medium is higher than acidic medium. The increase in rate of photo catalytic degradation may be due to the more availability of ⁻OH ions in pH range 7.5-9 which will generate more ⁻OH radicals by combining with the holes which are formed due to electronic excitation in catalyst. Formation of hydroxyl radicals are responsible more for the photo catalytic degradation than supra oxide (⁻o). At higher pH the rate of degradation decreases. This effect is due to competition between ⁻OH groups to attach to the active site of catalyst, so rate of attachment of ⁻OH group decreases. Result is that formation of hydroxyl radicals (OH) decreases and due to this reason rate of degradation also decreases. Graphical representation of pH effect is shown in Fig. 4.

Effect of light intensity: We observe the effect of light intensity on rate of degradation. We find out that as light intensity increases the rate of degradation of dye molecules also increases up to certain extent and after it no changes are observed in rate of degradation.

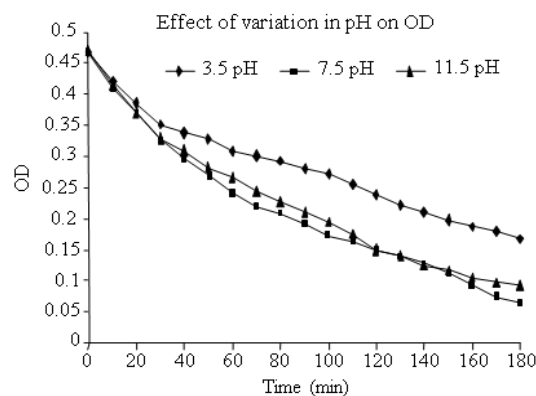


Fig. 4: Effect of pH on degradation (Temperature: 303 K, solution volume: 400 mL, initial dye concentration: 40 mg L⁻¹, UV lamp: 10.4 mW cm⁻²)

These changes in rate of degradation of dye molecules by variation in light intensity is due to the reason that as light intensity increases number of photons reaching the catalyst surface also increases so number of excited catalyst molecules increases and result is increase in the number of holes, hydroxyl radicals and Supra oxide ions (⁻o) and rate of degradation of dye molecules also increases.

We observe that after some extent of increase in light intensity there is no effect on rate of degradation on further increase in light intensity. The cause is that maximum numbers of photons which are required for excitation are available in fix range irradiating light intensity and after it if we further increase light intensity no considerable changes are 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 if we increase light intensity to any range, the rate of degradation remains unchanged.

Graphical representation of light intensity variation is shown in Fig. 5.

Effect of dissolved oxygen on rate of degradation:

We observed the effect of Dissolved oxygen on rate of degradation, as dissolved oxygen increase in dye solution rate of degradation also increase. We observed that when oxygen gas is passed through reaction mixture the rate of degradation increases but when Nitrogen or any other non reacting gas is passed through this solution no effect is observed on rate of degradation. This effect is may be due to more availability of oxygen for formation of supra oxide (⁻o) and hydroxyl radical. These are highly oxidative in nature and increase the rate of degradation of dye molecules.

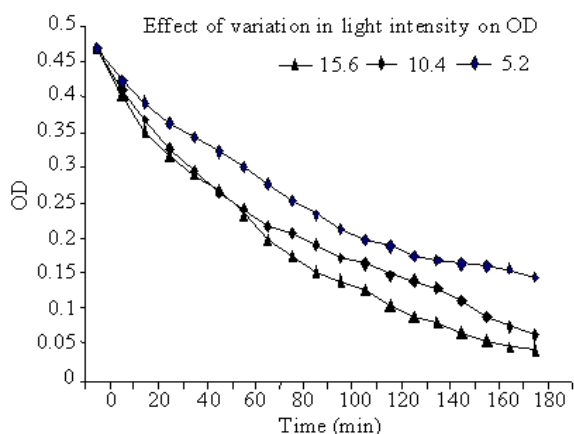


Fig. 5: Effect of variation of light intensity on degradation (Temperature: 303 K, solution volume: 400 mL, initial dye concentration: 40 mg L⁻¹, pH 7.5)

DISCUSSION

Probable chemical reaction of this degradation: Methylene Blue Immobilize Resin Dowex-11. This is newly developed photo catalyst. The dye immobilize in porosity of resin is methylene blue. Methylene blue is photo sensitive in nature, when light radiation is irradiated on due surface due to its electrons transfer from Valance Band (VB) to Conduction Band (CB) and through Intersystem Crossing (ISC) electron reach in to triplet state of methylene blue. After it intermolecular electronic transition start between resin, methylene blue dye molecules, water molecules, amido black dye molecules and dissolved oxygen, resultant through chain process, holes, hydroxyl radicals and Supra oxide ions (o^-) are produced and these are highly oxidizing in nature, by the action of holes, hydroxyl radicals and Supra oxide ions (o^-) on Azo dyes, are transformed in simple organic compounds like CO_2 , H_2O , SO_2 and N_2 . The main factors influencing the photo catalytic degradation of Azo dyes is variation in catalyst loading, variation in concentration of dye, variation in pH of the solution, variation in light intensity, variation in dissolve oxygen.

The generation of holes, hydroxyl radicals and Supra oxide ions (o^-) can be explained better with the help of proposed diagram. This proposed diagram shows the action of photo catalyst and process of generation of oxidative intermediates.

Photo catalysis shows in Fig. 6.

Photo catalysis action: Figure 6 Shows the Process of generation of holes, hydroxyl radicals and Supra oxide ions (o^-). These possess highly oxidative characteristic.

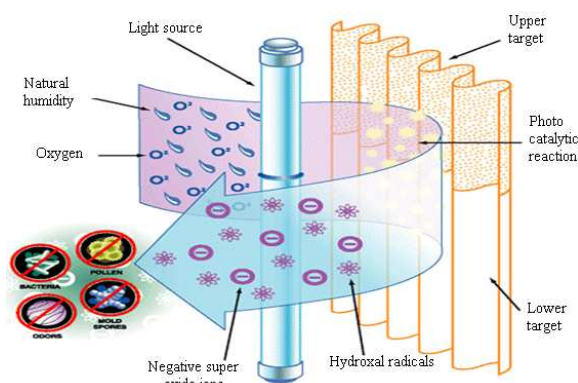


Fig. 6: Shows the process of generation of holes, hydroxyl radicals and Supra oxide ions (o^-). These possess highly oxidative characteristic

DISCUSSION

Ponceau S, (S-IV) photocatalytic degradation and absorbance behavior Photocatalytic destruction of the Ponceau S, (S-IV) solution was measured using UV/Vis spectrophotometer at $\lambda_{\text{Max}} = 620 \pm 4$ nm Ponceau S and (S-IV) $\lambda_{\text{Max}} = 520$. Experiment was conducted at pH 9 for 3h. Transparency of dye solutions were increases by 24, 40, 48, 85, 95 and 99% after 30 min, 1, 1.5 and 2, 2.5 and 3 h respectively. The increase in transparency is likely due to the degradation of the Ponceau S, (S-IV). The temperature was almost constant during the experiments (30°C), while the dissolved oxygen concentration ranged from 6.0 to 6.9 mg L⁻¹ (71-82% saturation). The highest removal rate of Ponceau S, (S-IV) is observed at pH 9. In The First 24 h experiment, the reactor operated with uncoated cylinder tubes or slides and the 200 watt UV/Visible light. During this experiment, no variation in transparency was detected. Next, the Methylene blue Immobilized Resin Dowex-11 thin-film was fixed on reactor cylinders/ tubes/slides and the reactor operated with the UV/VIS light for 3 h. During this time, significant variation in transparency was observed. Thus, the removal of Ponceau S, (S-IV) detected on (pH 9) can only be a result of photocatalysis and not a result of adsorption on the methylene blue Immobilized Resin Dowex-11 surface.

The Ponceau S, (S-IV) removal was completely inhibited below pH 2.5 and at pH 9, almost dye degraded and 99% transparency indicated fast rate of degradation of dyes. This represents higher removal efficiency than reported in previous studies with dyes utilizing visible radiation in aqueous suspensions of TiO_2 and dyes/Azo dyes. In this study positive results shows the removal of dyes and recover (99%)

transparent water from textile industries wastewater containing non biodegradable dyes mostly azo dyes. Successful degradation of dyes Ponceau S, (S-IV) using an immobilized Methylene blue Immobilized Resin Dowex-11 is achieved. The Ponceau S, (S-IV) removal amounted to 40 and 85% after 1h and 2 h, respectively at pH 9 and 99% after 3 h at pH 9. The Ponceau S, (S-IV) removal was due to photocatalytic degradation. The exposure of the reactor to UV/VIS radiation may be useful to both mineralize organic compounds adsorbed on the catalyst and to activate the catalyst. The results obtained using the photo-reactor after UV/VIS radiation exposure suggest that longer exposure time may improve both fouling removal and catalyst activation. Effect of These parameters on the rate of degradation are (1) variation in catalyst loading, (2) variation in dye concentration, (3) variation in pH, (4) variation in light intensity, (5) effect of dissolve oxygen. All the sets are observed for more then 3 h.

CONCLUSION

This study focused on the evaluation of Ponceau S, (S-IV)) removal by means of a novel photocatalytic reactor with thin-film of Methylene blue immobilized resin dowex-11 prepared. The system operated in a recirculation mode under various conditions (with/without catalyst, with/without UV/VIS radiation, different amount of catalyst, different dye concentration, different light intensities, different pH conditions, different dissolve oxygen percentage). Changes in transparency of solutions from dark colored non-transparent solution to 99% transparent solution shows success of experimental set up of instrument with applying Methylene blue Immobilized Resin Dowex-11 photo catalyst. These results show that new reactor set up using Methylene blue Immobilized Resin Dowex-11 photocatalysis provides a promising technology to improve the quality of effluent from textile wastewater treatment plants. After long observation we conclude that this photo catalyst (Methylene Blue immobilized Resin Dowex-11) with new reactor has good potential of degradation of Azo dyes/dyes into simple molecules and purify textile effluent (wastewater) which contains large amount of non fixed dyes mostly Azo dyes. These Azo dyes are non bio degradable.

We observe the effect of different parameters given in order:

- Effect of variation in dye concentration: As concentration of dye increases the rate of degradation of dye deceases

- Variation in amount of catalyst: As concentration of catalyst increases the rate of degradation of dye molecules also increases
- Variation in pH: In acidic range of pH the rate of degradation is very less as pH increases rate of degradation also increases and between pH ranges 7.5-9 rate of degradation is faster on further increase in pH the rate of degradation decreases
- Variation in light intensity: On increasing light intensity the rate of degradation of dye molecules increases up to certain limit after it there is no further changes in the rate of degradation
- Effect of dissolved oxygen: Rate of degradation increases up to some extent on increasing the dissolved oxygen in dye solution

ACKNOWLEDGEMENT

The researchers are thankful to the UGC, New Delhi for financial assistance and Head of the Department for providing necessary facilities.

REFERENCES

1. Heller, A., 1981. Conversion of sunlight into electrical power and photo assisted electrolysis of water in photo electrochemical cells. *Accounts Chem. Res.*, 14: 154-162. DOI: 10.1021/ar00065a004
2. Frank, S.N. and A.J. Bard, 1977. Heterogeneous photocatalytic oxidation of cyanide ion in aqueous solutions at titanium dioxide powder. *J. Am. Chem. Soc.*, 99: 303- 304. DOI: 10.1021/ja00443a081
3. Frank, S.N. and A.J. Bard, 1977. Heterogeneous photo catalytic oxidation of cyanide and sulfite in aqueous solutions at semiconductor powders. *J. Phys. Chem.*, 81: 1484-1488. DOI: 10.1021/j100530a011
4. Georgiou, D., A. Aivazidis, J. Hatiras and K. Gimouhopoulos, 2003. Treatment of cotton textile wastewater using lime and ferrous sulfate. *Water Res.*, 37: 2248-2250. DOI: 10.1016/S0043-1354(02)00481-5
5. Petrova, S.P. and P.A. Stoychev, 2003. Ultrafiltration purification of waters contaminated with bifunctional reactive dyes. *Desalination*, 154: 247-252. <http://cat.inist.fr/?aModele=afficheN&cpsidt=14674521>
6. Faria, P.C.C., J.J.M. Órfão and M.F.R. Pereira, 2004. A adsorption of anionic and cationic dyes on activated carbons with different surface chemistries. *Water Res.*, 38: 2043-2052. <http://cat.inist.fr/?aModele=afficheN&cpsidt=15674285>

7. Carneiro, P.A., M.E. Oslugi, J.J. Sene, M.A. Anderson and M.V.B. Zanoni, 2004. Evaluation of color removal and degradation of reactive textile azo dyes on nanoporous TiO₂ thin-film electrodes. *Electrochim. Acta*, 49: 3807-3820. <http://cat.inist.fr/?aModele=afficheN&cpsid=15936792>
8. Aguado, M.A., M.A. Anderson and C.G. Hill, 1994. Influence of light intensity and properties on the photocatalytic degradation of formic acid over TiO₂ ceramic membranes. *J. Mol. Catal.*, 89: 165-178. <http://cat.inist.fr/?aModele=afficheN&cpsid=4159991>
9. Rincón, A.G. and C. Pulgarin, 2004. Effect of pH, inorganic ions, organic matter and H₂O₂ on *E. coli* K12 photocatalytic inactivation by TiO₂: Implications in solar water disinfection. *Applied Catal. B: Environ.*, 51: 283-302. <http://infoscience.epfl.ch/record/55600>
10. Bekbolet, M., C.S. Uyguner, H. Selcuk, L. Rizzo, A.D. Nikolaou, S. Meric and V. Belgiorno, 2005. Application of oxidative removal of NOM to drinking water and formation of disinfection by-products. *Desalination*, 176: 155-166. <http://cat.inist.fr/?aModele=afficheN&cpsid=16941549>
11. Houas, A., H. Lachheb, M. Ksibi, E. Elaloui, C. Guillard and J.M. Hermann, 2001. Photocatalytic degradation pathway of Methylene blue, in water. *Applied Catal. B: Environ.*, 31: 145-157. DOI: 10.1016/S0926-3373(00)00276-9
12. Özkan, A., M.H. Özkan, R. Gürkan, M. Akçay and M. Sökmen, 2004. Photocatalytic degradation of a textile azo dyes, Sirius Gelb GC on TiO₂ or Ag-TiO₂ particles in the absence and presence of UV/VIS irradiation: The effects of some inorganic anions on the photocatalysis. *J. Photochem. Photobiol. A: Chem.*, 163: 29-35. DOI: 10.1016/S1010-6030(03)00426-X
13. Chester, G., M. Anderson, H. Read and S. Esplugas, 1993. A jacketed annular membrane photocatalytic reactor for wastewater treatment: Degradation of formic acid and atrazine. *J. Photochem. Photobiol. A: Chem.*, 71: 291-297. <http://cat.inist.fr/?aModele=afficheN&cpsid=4808607>
14. Franke, R. and C. Franke, 1999. Model reactor for photocatalytic degradation of persistent chemicals in ponds and waste water. *Chemosphere*, 39: 2651-2659. DOI: 10.1016/S0045-6535(99)00200-3
15. Ling, C.M., A.R. Mohamed and S. Bhatia, 2004. Performance of photocatalytic reactors using immobilized TiO₂ film for the degradation of phenol and methylene blue dyes present in water stream. *Chemosphere*, 57: 547-554. DOI: 10.1016/j.chemosphere.2004.07.011
16. Anderson, M.A., M.J. Giesemann and X. Quynin, 1988. Titania and alumina ceramic membranes. *J. Membrane Sci.*, 39: 243-258.
17. Matsuo, S., N. Sakaguchi, K. Yamada, T. Matsuo and H. Wakita, 2004. Role in photocatalysis and coordination structure of metal ions adsorbed on titanium dioxide particles: a comparison between lanthanide and ions. *Applied Surface Sci.*, 228: 233-244. DOI: 10.1016/j.apsusc.2004.01.015
18. Guillard, C., H. Lachheb, A. Houas, M. Ksibi, E. Elaloui and J.M. Hermann, 2003. Influence of chemical structure of dyes, of pH and of inorganic salts on their photocatalytic degradation by TiO₂: comparison of the efficiency of powder and supported TiO₂. *J. Photochem. Photobiol. A: Chem.*, 158: 27-36. DOI: 10.1016/S1010-6030(03)00016-9
19. Lachheb, H., E. Puzenat, A. Houas, M. Ksibi, E. Elaloui, C. Guillard and J.M. Hermann, 2002. Photocatalytic degradation of various types of dyes (Alizarin S, crocein orange G, methyl red, congo red, methylene blue) in water by UV/VIS-irradiated titania. *Applied Catal. B: Environ.*, 39: 75-90. DOI: 10.1016/S0926-3373(02)00078-4