



Laser-induced removal of a dye C.I. Acid Red 87 using n-type WO₃ semiconductor catalyst

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ABSTRACT

Water contamination by organic substances such as dyes is of great concern worldwide due to their utilization in many industrial processes and environmental concerns. To cater the needs for waste water treatment polluted with organic dyes, laser-induced photocatalytic process was investigated for removal of a dye derivative namely Acid Red 87 using n-type WO₃ semiconductor catalyst. The degradation was investigated in aqueous suspensions of tungsten oxide under different experimental conditions using laser instead of conventional UV lamp as an irradiation source. The degradation process was monitored by measuring the change in dye concentration as a function of laser irradiation time by employing UV spectroscopic analysis. The degradation of dye was studied by varying different parameters such as laser energy, reaction pH, substrate concentration, catalyst concentration, and in the presence of electron acceptors such as hydrogen peroxide (H₂O₂), and potassium bromate (KBrO₃). The degradation rates were found to be strongly dependent on all the above-mentioned parameters. Our experimental results revealed that the dye degradation process was very fast (within few minutes) under laser irradiation as compared to conventional setups using broad spectral lamps (hours or days) and this laser-induced photocatalytic degradation method could be an effective means to eliminate the pollutants present in liquid phase. The experience gained through this study could be beneficial for treatment of waste water contaminated with organic dyes and other organic pollutants.

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1. Introduction

Water contamination is caused by various sources such as industrial effluents, agricultural runoff and chemical spills. Industrial effluents contain several non-biodegradable substrates that can be harmful to the environment [1]. The industries like textiles, paint, varnishes, ink, plastics, pulp, paper, petrochemical and cosmetics use different types of organic matter, dyes and dye intermediates. These colored dye effluents pose a major threat to the water reservoirs and the surrounding ecosystem. The contaminated water with organic dyes could trigger many illnesses and not only harmful to humans but also to water living species (animals, plants, etc.). Some of the organic matter specifically dyes are highly toxic [2]. A substantial amount of dye-stuff is discharged into waste water during the dyeing process in the textile industry [3], which poses a major threat to the environment [3–6]. Due to these reasons, waste water contaminated with carcinogenic dyes has gained strong attention.

During the past two decades, photocatalytic processes using semiconductor metal oxides under UV and visible light illumination have been applied in the treatment of waste water pollutants. Various studies have been carried out for the removal of photo-stable dyes [7–20]. The mechanism constituting heterogeneous photocatalytic oxidation processes has been discussed extensively in the literature [21,22]. Briefly, when a semiconductor absorbs a photon of energy equal to or greater than its bandgap, an electron may be promoted from the valence band to the conduction band (e⁻cb) leaving behind an electron vacancy or “hole” in the valence band (h⁺vb). Once the charge separation is maintained, the electron and hole may migrate to the catalyst surface where they participate in redox reactions with sorbed species. Specially, h⁺vb may react with surface-bound H₂O or OH⁻ to produce the hydroxyl radical (OH•) and e⁻cb is picked up by electron accepting species to generate radical anion, as indicated below.



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SC—semiconductor, A—electron acceptor (generally dissolved oxygen).

It has been suggested that the hydroxyl radicals (OH^\bullet) and radical anions are the primary oxidizing species in the photocatalytic oxidation processes. These oxidative reactions would result in the bleaching of the dye. Alternatively, direct absorption of light by the dye, can lead to charge injection from the excited state of the dye to the conduction band of the semiconductor as summarized in the following equations:



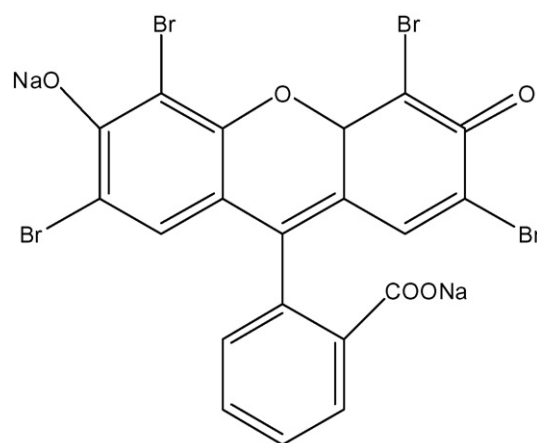
Earlier studies [7–20] have shown that heterogeneous photocatalytic oxidation processes can be used for removing coloring material from dye effluent in the presence of light. Acid Red 87 is the most widely used counterstain in routine staining of histological tissue sections (erythrocytes, collagen, epithelial cells, etc.) [23,24]. Several biological stains, such as Acid Red 87, auramine O, hematoxylin, rose bengal, etc. are widely used in biomedical research laboratories and also for diagnostic purposes. Some of these stains are known to be toxic or mutagenic for human and animals [25,26].

It is worth mentioning that all the previous work on removal of dyes from waste water using heterogeneous photocatalysis has been carried out with broad spectral radiation sources such as lamps and TiO_2 as a photocatalyst. Several problems are associated with the use of lamps emitting over broad spectral wavelength range. For example, the long term power stability due to over heating of lamps during the operation, low photonic efficiency, longer exposure time (h) for complete mineralization of pollutants are the major drawbacks associated with UV lamps as a source of irradiation.

Since laser light has unique properties like mono-chromaticity, high intensity, and low beam divergence, it is of great interest to use laser radiations as an excitation source to study the activity of photocatalysts. Due to these properties laser beam can transmit over long range in water and could expose a longer column which is not possible with broad spectral lamps which has high beam divergence and could not expose samples over a broad range. Due to these reasons, lasers are excellent tools to build a tandem facility [27]. However, the initial cost of laser-based systems will be much higher than lamp based systems.

The main objective of this study is not concerned with the economical aspects of laser application rather to test the concept how lasers are effective in removal of dyes as compared with the conventional setup using UV lamps as reported in the literature [28,29].

In the present study, special laser-based setup was developed at our laboratory to study the removal of dye from water using 355 nm laser radiations. The selection of 355 nm laser wavelength is based on the bandgap energy of the WO_3 which is around 440 nm. Hence the laser excitation energy is much higher than bandgap energy at 355 nm to pump appreciable amount of WO_3 . The unique features of our setup are that it is free of many logistics to overcome the obstacles such as heating of lamps, longer irradiation times, and low degradation rates, etc. associated with conventional photocatalytic setups using UV lamps. The photo-degradation study of a dye derivative Acid Red 87, xanthene tetrabromofluorescent dye, was carried out by using a locally synthesized WO_3 as photocatalyst in aqueous solution under a variety of experimental conditions in order to optimize the degradation. The chemical structure of the dye has been presented below:



Acid Red 87

2. Materials and methods

2.1. Chemicals

Acid Red 87 was obtained from BDH Chemicals Ltd. (minimum dye content ~88%). Tungsten oxide was used as a photocatalyst in all the studies. The WO_3 was prepared following the similar procedure described elsewhere [30]. A brief detail of the preparation method is as follows. For the synthesis of WO_3 , tungstic acid was heated for 7 h at 300°C (after which the sample color changes to yellow green and the temperature was further raised to 500°C at a slow rate of $10^\circ\text{C min}^{-1}$). The temperature was kept constant at 500°C for another 7 h after which the color became pale yellow which indicates the complete removal of water and oxygen from the synthesized WO_3 . The other chemicals used in this study such as H_2O_2 and KBrO_3 were obtained from Merck.

2.2. Procedure

Stock solutions of the dye containing desired concentrations were prepared in water. For irradiation experiments, 100 mL solution of desired concentration of the dye was taken into the reaction vessel and the required amount of photocatalyst was added and the solution was stirred for at least 15 min in the dark to allow equilibration of the system so that the loss of compound due to adsorption can be taken into account. The pH of the reaction mixture was adjusted by adding a dilute aqueous solution of HNO_3 or NaOH . The zero time reading was obtained from a blank solution kept in the dark but otherwise treated similar to the irradiated solution. Irradiations were carried out using a 355 nm wavelength high power laser beam generated from the third harmonic of the Spectra Physics Nd:YAG laser (Model GCR 250), with a pulse width of ~8 ns. In order to avoid the destructive effect of radiation, laser beam diameter was expanded to 1.0 cm. A schematic diagram of the experimental set-up is depicted in Fig. 1 and is described in detail in earlier publications [31–33]. Samples (2 mL) were collected before and at regular time intervals during the irradiation. The catalyst was removed through filtration before the UV analysis.

2.3. Analysis

The degradation was monitored by measuring the absorbance on a UV–vis spectrophotometer. The absorption maxima of the dye derivative has been found to be 517 nm. Therefore, the degradation of the dye was estimated at this wavelength as a function of irradiation time. For each experiment, the degradation rate for the

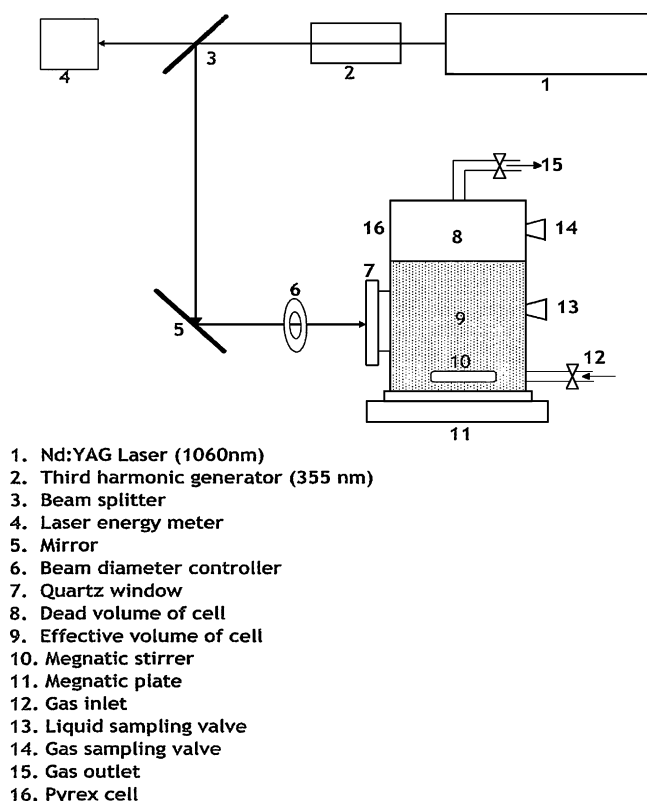


Fig. 1. A schematic diagram of the experimental setup applied for the removal of dye using laser-induced photocatalysis process.

decomposition of the model pollutant was calculated from the initial slope obtained by linear regression from a plot of the natural logarithm of absorbance of the dye as a function of irradiation time, i.e. first order degradation kinetics. It was calculated in terms of ($M \text{ min}^{-1}$).

3. Results and discussion

3.1. Photolysis of WO_3 suspensions containing Acid Red 87

Fig. 2 depicts typical UV absorption spectrum representing the trend of removal of Acid Red 87 dye for WO_3 at different times (0–12 min) under laser irradiation. It can be seen from Fig. 2 that ~95% degradation was achieved within very short laser exposure time (12 min) using 355 nm laser radiations. Initially, the degradation of the dye was found to be very fast and it became slower with the increase in irradiation time. This may be due to the fact that as oxidation proceeds, less and less of the surface of the WO_3 particle is covered as the pollutant is decomposed. Evidently, at total decomposition, the rate of degradation is zero and a decreased photocatalytic rate is to be expected with increasing irradiation time. Blank experiment was also carried out by irradiating the aqueous solution of the dye derivative in the absence of WO_3 , where ~20% degradation of the dye was observed.

In a previous study based on the photocatalytic removal of Acid Red 87 or Eosin Y using a 16 W UV lamp, it has been reported that only ~90% degradation of dye was observed even after 2 h irradiation [28]. Moreover, they removed 50 ppm dye concentration, while in the present study, ~95% degradation was achieved using 150 ppm within 12 min of laser irradiation using 100 mJ energy. In this study, it is proved experimentally that laser-based heterogeneous photocatalysis could be an efficient and effective method for waste water treatment for removal of dye derivatives as compared

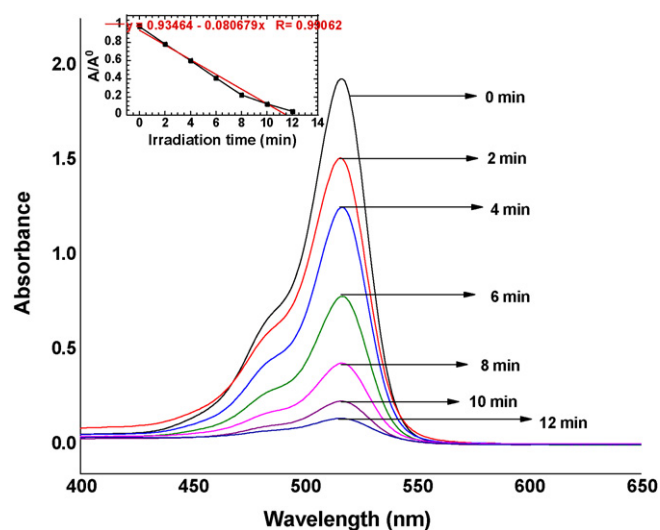


Fig. 2. Typical UV-vis spectra showing the change in absorption intensity as a function of laser exposure time for an aqueous solution of Acid Red 87 in presence of WO_3 . Experimental conditions: dye concentration = 0.25 mM, $V = 100 \text{ mL}$, $\text{pH} = 4.8$, $\text{WO}_3 = 2 \text{ g L}^{-1}$, laser energy = 100 mJ, laser exposure time = 12 min. (Inset) Change in absorption intensity as a function of irradiation time for an aqueous solution of Acid Red 87 in presence of WO_3 and curve fit data for the degradation kinetics.

to conventional UV lamp based methods reported in the literature in earlier publications.

For each experiment, the rate constant was calculated from the plot of natural logarithm of dye concentration as a function of irradiation time. The degradation rate for the decomposition of the dye under investigation was calculated using the formula [7,8] given below:

$$-d[A]/dt = kc^n$$

where A = absorbance, k = rate constant, c = concentration of the pollutant, n = order of reaction. A typical plot of A/A^0 versus time is depicted in figure inset of Fig. 2 for dye degradation. The least square fit, $R = 0.99$ and rate constant = 0.08 min^{-1} .

3.2. Effect of incident laser energy on degradation process

The effect of incident laser energy on the degradation of dye was investigated and the results obtained are presented in Table 1. It is obvious from the table that the degradation of the dye was significantly influenced by the laser energy and degradation was found to increase almost linearly with the increase in laser energy up to a certain energy level. When 150 mJ of laser energy was applied, maximum 95% degradation was recorded within 8 min of irradiation and a further increase in the laser energy was not found to be beneficial for the degradation of dye. This phenomenon may be explained in terms of the fact that when higher laser energy is employed, incident photon flux increases in the solution exciting more and more catalyst particles which, in turn, increases the degradation of the dye derivative. The dependency of photocatalytic property on the light intensity observed in this study followed similar trend as explained by Ollis et al. [34], in which, it was concluded that there is a linear relationship between the rate and the light intensity up to a certain level.

3.3. Effect of solution pH on the dye removal

The effect of solution pH of dye derivative was studied in the range of 3–13 and the values obtained are listed in Table 1. The photocatalytic degradation was found to decrease with the increase in reaction pH and the best result for photocatalytic degradation for

Table 1
Laser induced photocatalytic degradation of Acid Red 87 in aqueous suspensions of WO_3 under different experimental conditions.

Parameters	Degradation rates ($\times 10^{-3} \text{ M min}^{-1}$)
Energy (mJ)	
40.00	0.0075
70.00	0.0148
100.0	0.0378
130.0	0.0460
150.0	0.0501
180.0	0.0523
200.0	0.0529
Reaction pH	
3.10	0.0450
4.80	0.0378
7.20	0.0285
9.20	0.0250
12.3	0.0196
Substrate concentration (mM)	
0.10	0.0114
0.15	0.0167
0.25	0.0378
0.40	0.0293
Catalyst concentration (g L^{-1})	
0.50	0.0190
1.00	0.0378
2.00	0.0535
3.00	0.0715
4.00	0.0790
5.00	0.0805
6.00	0.0812
7.00	0.0809

dye was obtained at pH 3.2. This behavior is characteristic for many photocatalytic systems and similar results have been obtained by the photo-degradation of other dyes [35,36].

The interpretation of pH effect on the photocatalytic process is very difficult task because of its multiple roles such as electrostatic interactions between the semiconductor surface, solvent molecules, substrate and charged radicals formed during the reaction process. A possible explanation for the retardation of degradation rate with increasing reaction pH may be offered in terms of the surface charge of catalyst and its relation to the adsorption tendency of dye. In this study, it was found that the dye tend to adsorb slightly on the surface of catalyst more in acidic environment as compared to basic, i.e., the higher is the adsorption, the higher is the degradation. Fig. 3 depicts the trend of adsorption

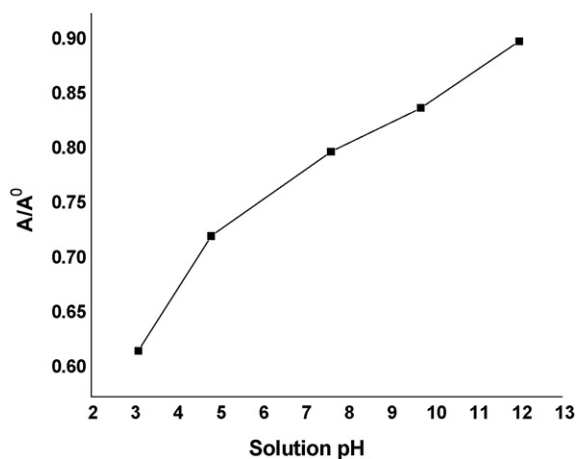


Fig. 3. Change in dye concentration as a function of pH after stirring the aqueous suspensions of dye in the dark, showing the adsorption of the dye on the surface of the photocatalyst.

versus the solution pH. The adsorption of the dye on the surface of photocatalyst was investigated by stirring the aqueous solution in the dark at different pH. After removing the catalyst, analysis of the samples with UV spectrophotometer indicates some loss of the compound as shown by the change in absorption intensity as a function of solution pH in Fig. 3.

Another possible reason for the different reaction rates at different pH values may be correlated to the generation of active hydroxyl radicals and occupancy of active sites of catalyst surface for the production of OH^\bullet radicals by formed intermediate products. Values of solution pH can alter the degradation route and lead the formation of different intermediate products [37]. Based on the photocatalytic mechanism, the active OH^\bullet radicals are produced on the surface of catalyst by the reaction of h^\bullet and adsorbed OH^- . During the course of photocatalytic reactions, formation of some negatively charged species (e.g., intermediate products) can occur and compete with OH^- for occupancy of catalyst surface. This competition reduces the possibility of adsorption of OH^- on the surface of catalyst which, in turn, affect the generation of active OH^\bullet thereby decreasing the efficiency of the process.

3.4. Effect of dye concentration on dye removal process

It is important both from mechanistic and application points of view to study the dependence of the photocatalytic reaction rate on the substrate concentrations. Hence, the influence of substrate concentration varying from 0.10 to 0.40 mM on the degradation rate of the dye derivative was studied. It can be accessed from Table 1 that the degradation rate increased with the increase in substrate concentration from 0.10 to 0.25 mM and a further increase in the concentrations of the substrate led to a decrease in the degradation rate. The decrease in degradation rate at higher concentration of the dye may be rationalized in terms of the fact that as the initial concentrations of the dye increases, the color of the irradiating mixture becomes more and more intense which prevents the penetration of light to the surface of the catalyst. The absorbance of the zero time samples versus the dye concentration were measured and found that the absorbance linearly increases with the increase in dye concentration that supports our observation that the color of the suspensions become more and more intense as the dye concentration increases. Hence, the generations of relative amount of reactive species on the surface of the catalyst do not increase as the intensity of light, illumination time and concentration of the catalyst are constant. Consequently, the degradation of the dye decreases as the dye concentration exceeds the optimum limit [38,39]. Another explanation could be that the light reaching the catalyst's particles is sufficient to activate active sites but the catalyst's active sites are not enough to convert the dye within the 10 min period of this type of experiments.

3.5. Effect of catalyst concentration on dye removal process

The effect of photocatalyst concentration on the degradation kinetics of Acid Red 87 was investigated employing different concentrations of WO_3 varying from 0.5 to 7 g L^{-1} (Table 1). As expected, the degradation rate for decomposition of the model compound under investigation was found to increase with the increase in catalyst concentration up to a certain catalyst loading (5 g L^{-1}) and reaches to saturation limit which is in agreement with a number of studies reported earlier [38,40,41]. At lower catalyst loading much of light may be transmitted through the solution. However, higher reaction rates at higher amount of catalyst loading may be explained in terms of complete utilization of incident photons striking on the catalyst surface and/or availability of active sites at the surface, i.e., higher adsorption of incident light can lead

the formation of high photoactivated volume in suspension thereby increasing the efficiency of the system.

Whether in static, slurry or dynamic flow reactors, the initial reaction rates were found to be directly proportional to catalyst concentration indicating a heterogeneous regime. However, it has been observed that above a certain concentration, the reaction rate levels off and becomes independent of the catalyst concentration. Daneshwar et al. [42], for instance, found that the optimum catalyst loading for the best degradation is 160 mg L^{-1} . In another study, on the other hand, the optimum catalyst concentration was found to be 1 g L^{-1} [40] and moreover, the effect of higher dose was not investigated. Many other examples could be presented here demonstrating the different optimum catalyst loading for the different investigations. Similarly, the nature of the organic molecules under investigation can also affect the optimum catalyst loading. In a recent study, for example, it has been found that the initial reaction rate increases with increase in catalyst concentration up to 5 g L^{-1} for the 1,2-diphenylhydrazine [41]. In contrast, under identical reaction conditions, the best degradation of benzidine was achieved at 2 g L^{-1} catalyst concentration and a further increase in catalyst concentration led a decrease in rate [41]. This limit, therefore, depends on the geometry and working conditions of the photoreactor, concentration and nature of organic contaminants, and a defined amount of catalyst in which all the particles, i.e. the entire surface exposed, are totally illuminated. When the catalyst concentration is very high, after traveling a certain distance on an optical path, turbidity impedes further penetration of light in the reactor lowering the efficiency of the system.

3.6. Effect of added electron acceptors on dye degradation

One practical problem in photocatalytic reactions using semiconductors is the undesired electron/hole recombination, which, in the absence of proper electron acceptor or donor, is extremely efficient and hence represents the major energy-wasting step thus limiting the achievable quantum yield. One strategy to inhibit electron-hole pair recombination is to add other (irreversible) electron acceptors to the reaction. They could have several different effects such as (1) to increase the number of trapped electrons and, consequently, avoid recombination, (2) to generate more radicals and other oxidizing species, (3) to increase the oxidation rate of intermediate compounds and (4) to avoid problems caused by low oxygen concentration. It is pertinent to mention here that in

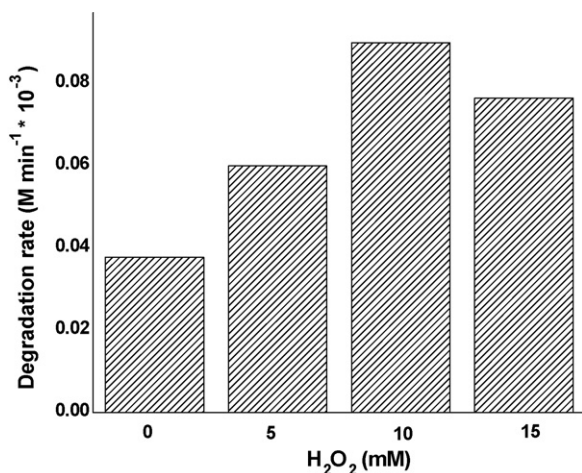


Fig. 4. Influence of hydrogen peroxide on the degradation rate for the decomposition of Acid Red 87. Experimental conditions: dye concentration = 0.25 mM , $V = 100 \text{ mL}$, $\text{pH} = 4.8$, $\text{WO}_3 = 1 \text{ g L}^{-1}$, laser energy = 100 mJ , $\text{H}_2\text{O}_2 = 5.0, 10.0,$ and 15.0 mM , laser exposure time = 10 min .

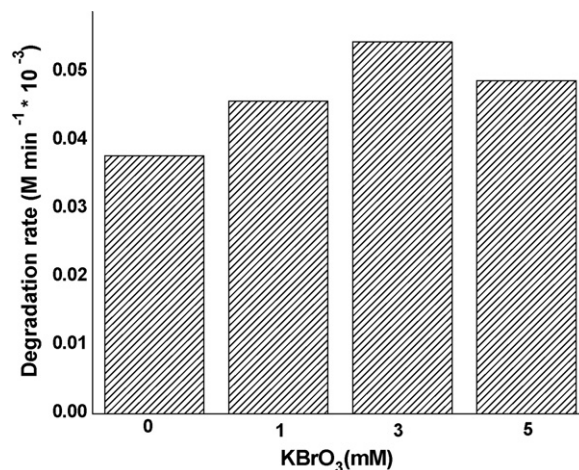
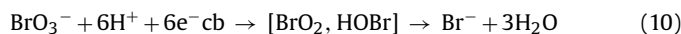
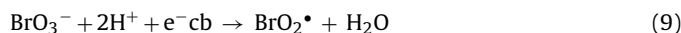
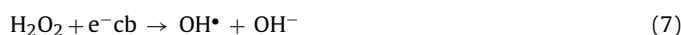


Fig. 5. Influence of potassium bromide on the degradation rate for the decomposition of Acid Red 87. Experimental conditions: dye concentration = 0.25 mM , $V = 100 \text{ mL}$, $\text{pH} = 4.8$, $\text{WO}_3 = 1 \text{ g L}^{-1}$, laser energy = 100 mJ , $\text{KBrO}_3 = 1.0, 3.0,$ and 5.0 mM , laser exposure time = 10 min .

highly toxic waste water where the degradation of organic pollutants is the major concern, the addition of additives to enhance the degradation rate may often be justified. In this connection, we have studied the effect of electron acceptors such as hydrogen peroxide, and bromate ions on the photocatalytic degradation of the model compound under investigation. The effect of H_2O_2 and KBrO_3 on the degradation of the dye under investigation has been illustrated in Figs. 4 and 5, respectively. These acceptors are known to generate hydroxyl radicals according to Eqs. (7)–(10):



The respective one-electron reduction potentials of different species are: $E(\text{H}_2\text{O}_2/\text{OH}^\bullet) = 800 \text{ mV}$, and $E(\text{BrO}_3^-/\text{BrO}_2^\bullet) = 1150 \text{ mV}$ [43]. From the thermodynamic point of view, H_2O_2 and KBrO_3 additives should therefore be efficient electron acceptors. As expected, the addition of these electron acceptors was found to accelerate the degradation of dye and after an optimal concentration the rate was decreased. The decrease in degradation rate may be due to the generation of secondary radical species which are less reactive than the OH^\bullet radicals. At higher concentration, for instance, it has been demonstrated that the reactive OH^\bullet radicals could be consumed by H_2O_2 and formation of less reactive OOH^\bullet takes place Eqs. (11) [44,45]:



The effect of H_2O_2 and KBrO_3 on the degradation of dye under identical conditions but in the absence of WO_3 was also investigated. The dye removal trend was found approximately similar as observed in the case of blank experiment which indicates that the presence of these additives in the absence of catalyst is not effective for the degradation of the dye. We also investigated the degradation of dye in presence of WO_3 and $\text{H}_2\text{O}_2/\text{KBrO}_3$ but in the absence of light where no noticeable loss of the dye was observed.

4. Conclusions

A linear dependence of dye degradation was found on the incident laser energy. Experimental results revealed that an acidic environment was highly favorable for the degradation of Acid

Red 87. The most appropriate dye concentration for the maximum degradation was found = 0.25 mM. A linear increase in dye degradation was observed with the increase in catalyst concentration. The maximum removal of dye was achieved using laser energy = 150 mJ and catalyst concentration = 5 g L⁻¹. The addition of electron acceptors such as H₂O₂ and KBrO₃ significantly enhanced the degradation process under investigation. This study clearly demonstrates that the laser-induced photocatalytic degradation method could be applied as an effective method to remove the organic pollutants present in waste water in shorter time durations as compared to conventional setups. The optimization of various operational parameters demonstrates the significance of selection of the optimum experimental conditions to obtain a high degradation rate. The removal of dye was achieved with a rate constant = 0.08 min⁻¹ which is quite high as compared with rates reported for conventional setups.

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References

- [1] O. Ligrini, E. Oliveros, A. Braun, Photochemical processes for water treatment, *Chem. Rev.* 93 (1993) 671–698.
- [2] I. Arsalan, I.A. Balcioglu, D.W. Bahnemann, Advanced chemical oxidation of reactive dyes in simulated dye house effluents by ferrioxalate-Fenton/UV-A and TiO₂/UV-A processes, *Dyes Pigments* 47 (2000) 207–218.
- [3] C.E. Searle, Chemical Carcinogenesis, ACS Monograph, American Chemical Society, Washington, DC, 1976.
- [4] C.T. Helmes, C.C. Sigman, Z.A. Fund, M.K. Thompson, M.K. Voeltz, M. Makie, et al., A study of azo and nitro dyes for the selection of candidates for carcinogen bioassay, *J. Environ. Sci. Health A* 19 (1984) 97–231.
- [5] M. Boeninger, Carcinogenicity and metabolism of azo dyes, especially those derived from benzidine, DHHS (NIOSH), Publication No. 80e119, July 1980.
- [6] J.J. Roxon, A.J. Ryan, S.E. Wright, Reduction of water soluble azo dyes by intestinal bacteria, *Food Cosmet. Toxicol.* 5 (1967) 367–369.
- [7] K. Vinodgopal, I. Bedja, S. Hotechandani, P.V. Kamat, Photocatalytic approach for the reductive decolorization of textile azo dyes in colloidal semiconductor suspensions, *Langmuir* 10 (1994) 1767–1771.
- [8] M. Muneer, R. Phillips, S. Das, Photocatalytic degradation of waste water pollutants: titanium dioxide-mediated oxidation of a textile dye, *Acid Blue 40*, *Res. Chem. Intermed.* 23 (1997) 233–246.
- [9] T. Takagishi, N. Katsuda, Photodegradation of dyes by spectro-irradiation, *Int. Conf. Exhib. AACTT* (1999) 358–366.
- [10] M. Qamar, C.R. Yoon, H.J. Oh, N.H. Lee, K. Park, D.H. Kim, K.S. Lee, W.J. Lee, S.J. Kim, Preparation and photocatalytic activity of nanotubes obtained from titanium dioxide, *Catal. Today* 131 (2008) 3–14.
- [11] M. Vautier, C. Guillard, J.M. Hermann, Photocatalytic degradation of dyes in water: case study of indigo and of indigo carmine, *J. Catal.* 20 (2001) 46–59.
- [12] Y. Xu, C.H. Langford, UV or visible-light-induced degradation of X3B on TiO₂ nanoparticles: the influence of adsorption, *Langmuir* 17 (2001) 897–902.
- [13] T.C.-K. Yang, Lin-Shu-Yin, W. Guo, T.-H. Chung, S.-F. Wang, S.H.-Y. Tsai, In situ studies of the photodegradation of a dye adsorbed on TiO₂ particles by the DRIFTS, *Adsorpt. Sci. Technol. Proc. Pac. Basin Conf.* 2 (2000) 683–687.
- [14] K. Hirano, E. Suzuki, A. Ishikawa, T. Moroi, H. Shiroishi, M. Kaneko, Sensitization of TiO₂ particles by dyes to achieve hydrogen evolution by visible light, *J. Photochem. Photobiol. A Chem.* 136 (2000) 157–161.
- [15] M.Sö. Kmen, A.Ö. Zkan, Decolourising textile wastewater with modified titania: the effects of inorganic anions on the photocatalysis, *J. Photochem. Photobiol. A Chem.* 147 (2002) 77–81.
- [16] M. Qamar, M. Muneer, Comparative photocatalytic study of two selected pesticide derivatives, indole-3-acetic acid and indole-3-butyric acid in aqueous suspensions of titanium dioxide, *J. Hazard. Mater.* B120 (2005) 219–227.
- [17] M.R. Sohrabi, M. Ghavami, Photocatalytic degradation of direct red 23 dye using UV/TiO₂: effect of operational parameters, *J. Hazard. Mater.* 153 (2008) 1235–1239.
- [18] M.A. Hasnat, M.M. Uddin, A.J.F. Samed, S.S. Alam, S. Hossain, Adsorption and photocatalytic decolorization of synthetic dye erythrosine on an anatase TiO₂ and ZnO surfaces, *J. Hazard. Mater.* 147 (2007) 471–477.
- [19] M. Mahalakshami, B. Arabindoo, M. Palanichamy, V. Murugesan, Photocatalytic degradation of carbofuran using semiconductor oxides, *J. Hazard. Mater.* 143 (2007) 240–245.
- [20] H.K. Singh, M. Saquib, M.M. Haque, M. Muneer, Heterogeneous photocatalysed degradation of uracil and 5-bromouracil in aqueous suspensions of titanium dioxide, *J. Hazard. Mater.* 142 (2007) 425–430.
- [21] C.S. Turchi, D.F. Ollis, Photocatalytic degradation of organic contaminants: mechanisms involving hydroxyl radical attack, *J. Catal.* 122 (1990) 178–185.
- [22] R.W. Mathews, S.R. McEvoy, Photocatalytic degradation of phenol in the presence of near-UV illuminated titanium dioxide, *J. Photochem. Photobiol. A Chem.* 64 (1992) 231–246.
- [23] F.L. Carson, *Histology, A Self-Instructional Text*, ASCP Press, Chicago, 1990.
- [24] C.F. Culling, R.T. Allison, W.T. Barr, *Cellular Pathology Technique*, 4th ed., Butterworths, 1985.
- [25] G. Lynn, E.B. Sansone, *Destruction of Hazardous Chemicals in the Laboratory*, 2nd ed., Wiley, New York, 1994.
- [26] *Sax's Dangerous Properties of Industrial Materials*, 8th ed., Van Nostrand-Reinhold, New York, 1992.
- [27] L.B. Isaac, E.B. Regina, P.H. Richard, R.H. Peter, High-average-power dye laser at Lawrence Livermore National Laboratory, *Appl. Opt.* 31 (1992) 6993–7006.
- [28] I. Poullos, E. Micropoulou, R. Panou, K. Kostopoulou, Photooxidation of Eosin Y in the presence of semiconducting oxides, *Appl. Catal. B Environ.* 41 (2003) 345–355.
- [29] S. Chakrabarty, B.K. Dutta, Photocatalytic degradation of model textile dyes in wastewater using ZnO as semiconductor catalyst, *J. Hazard. Mater. (B)* 112 (2004) 269–278.
- [30] A. Hameed, Ph.D. Thesis, King Fahd University of Petroleum and Minerals, Dhahran, Saudi-Arabia, 2005.
- [31] M.A. Gondal, M.N. Sayeed, A. Arfaj, Activity comparison of Fe₂O₃, NiO, WO₃ and TiO₂ semiconductor catalysts in phenol degradation by laser enhanced photocatalytic process, *Chem. Phys. Lett.* 445 (2007) 325–330.
- [32] M.A. Gondal, M.N. Sayeed, Z. Seddighi, Selective laser induced photo-catalytic removal of phenol from water using P-type NiO semiconductor catalyst, *J. Hazard. Mater.* 155 (2008) 83–89.
- [33] M.A. Gondal, M.N. Sayeed, Z.H. Yamani, A. Arfaj, Efficient removal of phenol from water using Fe₂O₃ semiconductor catalyst under UV laser irradiation, *J. Environ. Sci. Health Part A* 44 (2009) 515–521.
- [34] D.F. Ollis, E. Pelizzetti, N. Serpone, Photocatalyzed destruction of water contaminants, *Environ. Sci. Technol.* 25 (1991) 1522–1529.
- [35] H.R. Pouretedal, A. Norozi, M.H. Keshavarz, A. Semmani, Nanoparticles of zinc sulfide doped with manganese, nickel and copper as nanophotocatalyst in the degradation of organic dyes, *J. Hazard. Mater.* 162 (2009) 674–681.
- [36] T. Sauer, G.C. Neto, H.J. José, R.F.P.M. Moreira, Kinetics of photocatalytic degradation of reactive dyes in a TiO₂ slurry reactor, *J. Photochem. Photobiol. A Chem.* 149 (2002) 147–154.
- [37] C. Guillard, Photocatalytic degradation of butanoic acid Influence of its ionization state on the degradation pathway: comparison with O₃/UV process, *J. Photochem. Photobiol. A Chem.* 135 (2000) 65–75.
- [38] M. Qamar, M. Saquib, M. Muneer, Photocatalytic degradation of two selected dye derivatives, chromotrope 2B and amido black 10B, in aqueous suspensions of titanium dioxide, *Dyes Pigments* 65 (2005) 1–9.
- [39] M.A. Tariq, M. Faisal, M. Muneer, Semiconductor-mediated photocatalysed degradation of two selected azo dye derivatives, amaranth and bismarck brown in aqueous suspension, *J. Hazard. Mater.* 127 (2005) 172–179.
- [40] U. Stafford, K.A. Gray, P.V. Kamat, Photocatalytic degradation of 4-chlorophenol: the effects of varying TiO₂ concentration and light wavelength, *J. Catal.* 167 (1997) 25–32.
- [41] M. Muneer, H.K. Singh, D.W. Bahnemann, Semiconductor-mediated photocatalysed degradation of two selected priority organic pollutants, benzidine and 1,2-diphenylhydrazine, in aqueous suspension, *Chemosphere* 49 (2002) 193–203.
- [42] N. Daneshwar, M.H. Rasoulifard, A.R. Khataee, F. Hosseinzadeh, Removal of C.I. acid orange 7 from aqueous solution by UV irradiation in the presence of ZnO nanopowder, *J. Hazard. Mater.* 143 (2007) 95–101.
- [43] P. Wardman, Reduction potential of one-electron couples involving free radicals in aqueous solution, *J. Phys. Chem.* 18 (1989) 1637–1755.
- [44] N. Kang, D.S. Lee, J. Yoon, Kinetic modeling of Fenton oxidation of phenol and monochlorophenols, *Chemosphere* 47 (2002) 915–924.
- [45] M.W. Peterson, J.A. Turner, A.J. Nozik, Mechanistic studies of the photocatalytic behavior of titania: particles in a photoelectrochemical slurry cell and the relevance to photo-detoxification reactions, *J. Phys. Chem.* 95 (1991) 221–225.