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Degradation of patent blue V dye using modified photocatalytic reactor based on solar and UV irradiations

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ABSTRACT

The pollution effects caused by coloured wastewater streams due to the presence of biorefractory dyes are significant, directing the need for a concentrated effort for development of efficient treatment schemes. The present work reports the investigations related to the treatment of patent blue V containing wastewater using modified photocatalytic reactor providing the understanding into the effect of various process parameters and intensification using additives. Comparison of obtained results with natural (solar radiation) and artificial (fluorescent lamp, 11 W) sources confirmed the efficient treatment using the artificial source as expected though significant extent of degradation was also obtained based on the use of solar light. Modifications based on the use of glass coating at the interior of the reactor for possible enhanced utilization of the incident energy showed better degradation efficacy. The removal efficacy was also observed to be dependent on the operating parameters viz. initial concentration and pH with maximum extent of degradation being obtained at initial concentration of 10 ppm and pH of 2.5. Using optimized conditions, the maximum extent of degradation obtained in the present work for different approaches was 86.4% for UV/TiO_2, 64.7% for solar/TiO_2, 68.4% for UV/ZnO, 59.0% for solar/ZnO, 92.8% for UV/H_2O_2, 72.1% for solar/H_2O_2, 81.56% for UV/ferrous sulphate and 66.22% for solar/ferrous sulphate. UV irradiation with modified glass surface photoreactor has been established to be best degradation approach for the removal of patent blue V dye from the wastewater and use of different additives can help in enhancing the extent of degradation. The work has also showed the ways to improve the extent of degradation using solar-based treatment which can be very useful, especially in developing tropical countries like India.

Keywords: Patent blue V removal; UV irradiation; Solar light; Modified photoreactor; Degradation; Additives

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1. Introduction

Wastewater generated from textiles, wood finishing, paper and printing industries as well as leather and cosmetics industries are well known [1] to contain considerable amount of suspended solids, chlorinated organics, surfactant, heavy metals and most importantly dyes which impart obnoxious colour to the effluent. The coloured wastewater streams create significant problems considering both general appearance and toxicity to micro-organisms as well as reduce the availability of oxygen to the aquatic plants. A very small amount of dye in water is visible and it affects the penetration of light reducing the photosynthesis in aquatic plants affecting their growth due to the lower levels of dissolved oxygen. There are many structural varieties of dyes and pigments such as direct, reactive, acidic, basic, disperse, azo, diazo, anthraquinone-based and metal complex dyes [2–4]. Over 700,000 tons of approximately 10,000 types of dyes and pigments are produced annually worldwide. From this amount, about 20% appear as industrial effluents during the textile dyeing and finishing processes creating significant concerns and load on the effluent treatment facilities [5]. Many of these dyes find their way into the environment and also exhibit a high resistance to natural degradation facilities (sunlight, soil, bacteria, etc.) creating significant environmental issues. Considering these adverse effects, it has become necessary for industries to use efficient treatment techniques to decolorize the effluents before disposal into the water bodies. Many physical and chemical methods, such as coagulation, precipitation, floatation, chemical oxidation, solvent extraction, etc., have been tried in order to remove colour from wastewater [6–9]. These conventional approaches have not been very successful due to the fact that dyes are stable to conventional oxidizing agents. Also the treatment costs associated with some of the techniques such as solvent extraction and chemical oxidation are significant.

Advanced oxidation processes (AOPs) have also been explored for effective decolourization of dyes [10] and reported as an alternative to more conventionally applied adsorption and coagulation, which are considered as non-destructive as they merely transfer the dye from liquid to solid form of waste. AOP utilizes the strong oxidizing species such as OH radicals produced *in situ*, which causes a sequence of reactions thereafter to break down the macromolecules into smaller and less harmful intermediates. There are various methods such as cavitation, UV/H_2O_2, UV/Fenton, etc. through which OH radicals can be produced; although the use of artificial and natural energy-based photochemical degradation of several organic pollutants including dyes has been widely reported [11–13]. As documented in the literature [12,13] the intensity and distribution of light inside the reactor has a strong effect on the reaction rate. The above facts have attracted the interest of several researchers [14–17] to develop methodologies for improvements in the photocatalytic reactors with subsequent application for the oxidation of many organic pollutants present in aqueous systems [18,19]. It is important to understand here that a lot of work is indeed performed using different photocatalysis-based treatment approaches, but still the full commercial scale installations are lacking, which may be attributed partly to higher costs associated with the more commonly used UV-based irradiation, which has also been claimed as efficient at laboratory-scale operations. Another major problem is lack of uniform distribution of the incident light. The present work tries to address both these problems with experiments based on solar irradiations and modified reactor design.

Different photocatalysts have been applied for wastewater treatment applications including TiO_2, CuO, ZnO, etc. for different pollutants [20,21] though the work related to comparison of the different catalysts for the patent blue V dyes is lacking. It is important to establish the optimum loading for the specific dyes so as to avoid the problems of absorption and scattering of incident light by the catalyst. In the case of homogeneous photolysis operations involving the use of hydrogen peroxide and/or photo-Fenton reactions [22], scattering effects due to the presence of heterogeneous phase is not important and hence part of the current work also involved understanding the effect of addition of hydrogen peroxide and $FeSO_4$.

The study is aimed at developing a simple, efficient and economic way of degrading patent blue V usually present in textile wastewater effluents with specific reference to Indian context. Patent blue used as the model pollutant has a dark blue colour. Patent blue is an acidic dye and has a wide spread use in cosmetics, textiles, detergents and also as food additive [23]. Another important objective of the work was also to design an efficient photoreactor which can trap maximum amount of incident light energy so as to give efficient degradation of patent blue V. Initially, the efficacy of the conventional reactor has been compared with the modified reactor coated with borosilicate glass mirrors. Typically, the incident light can be absorbed, transmitted and emitted from the solution or the walls of the reactor. It is estimated that the amount of energy incident in the dye solution remains fixed in both cases, but the use of glass coating helps in transmitting the reflected energy back to the solution. Subsequently detailed experiments were performed to establish the effect of the type of the catalyst and type of source of irradiation. Comparison between the solar and UV irradiations has also been presented along with the intensification studies based on the use of different combination treatment approaches. The novelty of the current work is in terms of using modified photocatalytic reactor with glass coating inside the reactor and comparison of the different hybrid approaches for the treatment of patent blue dye.

2. Materials and methods

2.1. Materials

Patent blue (C.I. No. 45160; dark blue colour; molecular formula: $C_{27}H_{31}N_2NaO_7S_2$; molecular weight: 582.67 g/mol; IUPAC name: Bis [hydrogen [4-[4-(diethylamino)-5′-hydroxy-2′,4′-disulphonatobenzhydrylidene] cyclohexa-2,5-dien-1-ylidene] diethyl ammonium) was obtained from Loba Chem. Pvt. Ltd, Mumbai, India. The chemical structure of the dye has been depicted in Fig. 1. Ferrous sulphate ($FeSO_4$), zinc oxide (ZnO), hydrogen peroxide ($H_2O_{2)}$ and titanium dioxide (TiO_2) were obtained from Merck Specialties Pvt. Ltd, Mumbai, India. Dilute solutions of different chemicals with required concentrations were prepared using demineralised water freshly prepared in the laboratory. All the chemicals used for experimental studies were as received from the supplier.

2.2. Equipment and procedure

The actual image of photocatalytic reactor used for the experiments involving UV and solar irradiations is shown in Fig. 2. The cylindrical reactor was made up of polyacrylic material having dimensions 45 cm × 45 cm × 5 cm (*l* × *b* × *h*) with top portion of the reactor equipped with ports for sampling and stirring.

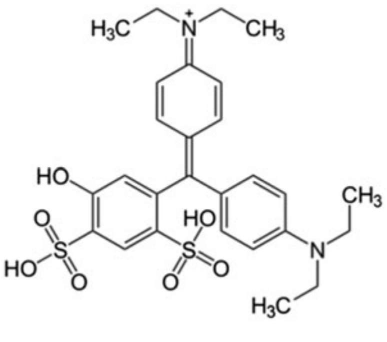

Fig. 1. Molecular structure of patent blue V.

The UV irradiation was carried out using three 11 W fluorescent lamps arranged in triangular fashion. The inside wall of the reactor was coated with borosilicate glass having thickness 4 mm for enhanced utilization of the incident energy. During the photolysis experiments, dye solution containing the appropriate quantity of the photocatalyst powder was stirred using agitators for obtaining the uniform suspension of catalyst in the solution. After specific time intervals, samples (20 mL volume) were withdrawn using suitable aliquots and analysed after filtration. Experiments were also performed using a normal reactor in absence of any glass coating to establish the degree of improvement in the modified photoreactor. In the case of solar photocatalysis, experiments were performed at ambient temperature using solar light as the energy source for catalyst excitation. The reactor assembly was the same as that used for UV-based experiments and continuous mechanical agitation was also used to ensure uniform mixing.

The aqueous dye solution (2.5 L volume) was introduced into the reactor and this operating volume was kept constant in all the sets of experiments. The catalyst was added to the solution at desired loadings and equilibrium was allowed to be established so as to eliminate any effects of adsorption on the catalyst surface. The suspension was exposed to the irradiations for 180 min. The effect of initial dye concentration (10–30 ppm) and pH (2.5–12.5) was also investigated to obtain the optimum conditions, which have been then used in the further experiments involving the combined approaches. The range of catalyst loading considered for experiments related to understanding the effect of catalyst was 0.2–1.2 g/L. The separation of solid particles from the solution was performed using simple filtration with the help of whatmann's filter paper for two times and then concentration of patent blue was measured using UV–vis spectrophotometer (ChemitoSpectrascan UV 2600 double beam) with analysis at the wavelength of $\lambda = 675$ nm. The performance of the process was assessed in terms of extent of degradation [24] quantified using the following equation:

$$\text{Extent of degradation } (\%) = \frac{C_0 - C}{C} \times 100 \tag{1}$$

where C_0 is the initial concentration of dye and C is the concentration of dye at the specific time interval.

All the experiments were repeated at least two times to check the reproducibility and average values

Fig. 2. Experimental set-up for photocatalysis experiments based on UV and solar irradiation.

have been reported in the discussion. Error bars have also been shown to depict the variation, which was within 2% of the reported average value.

2.3. Adsorption studies

Patent blue V solution was prepared with an initial concentration in the range of 5–50 ppm using demineralized water and subjected to adsorption studies. The solution was agitated for predetermined time with stirring at 200 rpm. The solution was analysed for patent blue V concentration using UV–vis spectrophotometer at regular intervals of time. The patent blue V removal was quantized in terms of adsorption capacity ($q_{e)}$ and extent of adsorption [25]:

$$q_e = \frac{(C_0 - C)}{w} \times V \tag{2}$$

$$\text{Extent of adsorption} = \frac{(C_0 - C)}{C_0} \times 100 \tag{3}$$

where C_0 and C are the initial and concentration at given time, respectively. V is the volume of the solution (L) and w is the amount of dye adsorbent used (g).

The obtained results for the adsorption of dye on the two catalysts used in the work (TiO_2 and ZnO) with respect to time have been shown in Figs. 3 and 4. From the figure, it has been observed that the percentage adsorption of the patent blue V dye on solid surface was 8 and 7% only for the case of TiO_2 and ZnO, respectively. The dye is adsorbed onto the catalyst surface until adsorption–desorption equilibrium is reached. From the results, it was noticed that the adsorption/desorption equilibrium of patent blue V dye at different initial concentration was reached in about 30 min, after which the concentration remained constant. During the actual photocatalysis experiments, equilibrated samples were used to establish the true extent of degradation obtained due to the use of irradiations.

3. Results and discussion

3.1. Comparison of conventional and modified photocatalytic reactor

Initially, degradation of patent blue V has been studied in the conventional and modified photocatalytic

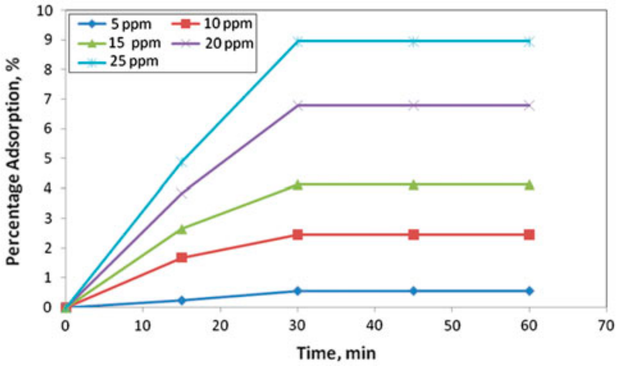

Fig. 3. Adsoprtion studies over TiO_2 catalyst surface.

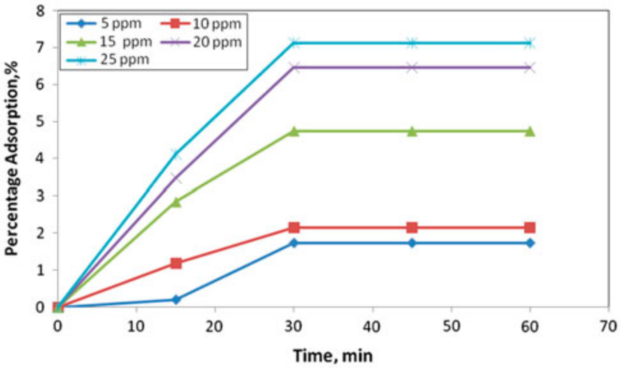

Fig. 4. Adsoprtion studies over ZnO catalyst surface.

reactor to establish the improvement obtained due to the modifications in the reactor. The obtained results have been depicted in Fig. 5, where the variation in the extent of degradation has been shown as a function of the initial concentration. It can be clearly seen from the figure that use of the glass coating is advantageous in enhancing the light utilization resulting in higher extents of degradation of patent blue V. Almost, four times higher degradation was obtained using modified photocatalytic reactor with glass coating as compared to the conventional photocatalytic reactor. The maximum extent of degradation as 41.5% was obtained using modified reactor under UV irradiation and 35.8% degradation was obtained under solar irradiation. Higher degradation using glass-coated reactor is attributed to the enhanced utilization of incident energy. The incident light can be absorbed, transmitted and emitted from the dye solution in the reactor. It is estimated that the amount of energy incident in the dye solution remains fixed in both cases, but the use of glass coating helps in transmitting the reflected energy back to the solution. Also glass coating helps in enhanced reflections into the solution resulting in higher extent of degradation. As enhanced extent of degradation was obtained using the modified reactor, it has been used for a detailed parameter optimization study and also for comparing the effect of using hybrid approaches for process intensification.

3.2. Effect of initial concentration

Initial dye concentration is one of the very important parameters in deciding the treatment efficiency in any wastewater treatment approach. The experiments related to effect of initial concentration have been performed for three approaches of using irradiation only, combination of irradiation with hydrogen peroxide and heterogeneous system based on the use of photocatalyst as titanium dioxide. The range of initial dye concentration has been kept the same in all the three cases as 10–30 ppm and the obtained results have been given in Fig. 6. It can be seen from the figure that the extent of degradation was higher at lower concentration of dye and hence lower initial concentration, specifically 10 ppm, has been selected in the further studies. The obtained results can be attributed to the fact that the at higher concentrations of dye solution, the penetration of photons into the solution decreases due to the filter effect making the solution less permeable to UV/solar radiation. Consequently, the generation of the hydroxyl radicals decreases at higher concentration of the dye and hence lower extent of decolorization is observed at higher loadings.

The observed trends in terms of variation with initial concentration were similar for the combination of irradiation with TiO_2 at 1 g/L catalyst loading using two irradiation sources though the actual values of the extent of degradation were higher in the presence of catalyst and for the use of UV irradiations. Quantitatively speaking, the extent of degradation of patent blue V decreased from 96.6 to 76.6% for UV/TiO_2 with an increase in the initial concentration from 10 to 30 ppm and from 94.7 to 74.9% for the case of solar/TiO_2. For all the cases, the degradation values were higher as compared to that obtained without using catalyst (extent of degradation is over the range of 10–40%). This can be attributed to the fact that the large quantity of photons are generated by photoexcitation of the TiO_2 species which can easily come in contact with a sufficient amount of patent blue V molecules, giving a higher extent of degradation as compared to that obtained for the case of without using any catalyst. However, at higher concentration of

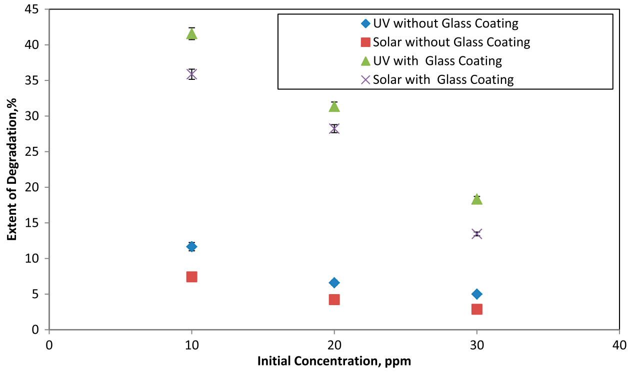

Fig. 5. Effect of initial concentration on removal of patent blue V using general and modified photoreactor under UV and solar irradiation (pH 2.5).

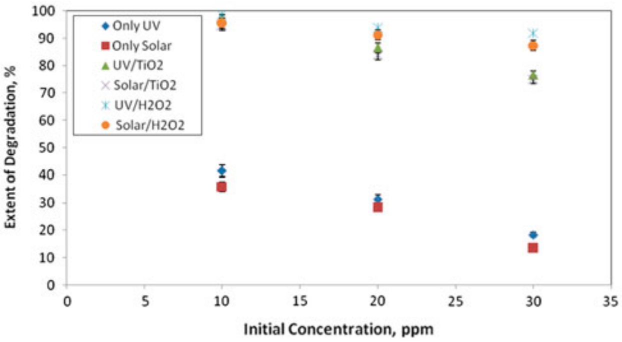

Fig. 6. Effect of initial concentration on removal of patent blue V using UV and solar irradiation with and without TiO_2/H_2O_2 (pH 2.5; catalyst loading = 1 g/L).

patent blue, it should be noted that the surface area of the TiO_2 catalyst should be sufficiently high to adsorb maximum quantum of dye molecules for degradation. This suggests that as the initial concentration of the dye increases, the requirement of catalyst surface needed for the degradation also increases. Since illumination time and amount of catalyst are constant, the OH radical (primary oxidant) formed on the surface of TiO_2 is also constant (on a lower side than that required for giving sufficient degradation at enhanced loading), which results in a decrease in the extent of degradation at higher initial concentration of dye.

Similar results have also been observed in the case of H_2O_2 addition in the dye solution when the experiments were carried out at different initial concentration of patent blue over the range of 10–30 ppm using UV/solar irradiation. The extent of degradation decreased as initial concentration increased at same loading of H_2O_2. For this case, the maximum extent of degradation obtained was at 10 ppm initial concentration of dye as 98.3% for UV/H_2O_2 and 95.5% for the case of solar/H_2O_2. The observed trends can be attributed to similar mechanisms related to the quantum of hydroxyl radicals formed as explained in details for the case of photolysis and combination of irradiation with photocatalyst.

3.3. Effect of pH

The effect of pH on the photocatalytic degradation of patent blue V has been studied using representative pH in the three conditions, i.e. acidic, basic and neutral. The influence of pH has been investigated for both the irradiation sources at optimum dye concentration of 10 ppm with the addition of solid catalyst (TiO_2) and hydrogen peroxide. The desired pH level was achieved by the addition of concentrated H_2SO_4 and 1 N NaOH to the solution as required. The obtained results have been given in Fig. 7.

For the case of H_2O_2-based degradation, it has been observed that degradation of patent blue V was more favourable in acidic conditions as compared to neutral and basic conditions. At pH 2.5, the maximum degradation as 96.7% was obtained for the UV/H_2O_2 process and 86.1% degradation was obtained for the solar/H_2O_2 treatment. The obtained results can be explained on the basis of higher oxidation capacity as well as the ease of generation of hydroxyl radicals under acidic conditions. Under alkaline conditions, the dissociation reaction of hydrogen peroxide is hampered and hence there is a possibility of scavenging of the free radicals by the non-dissociated H_2O_2. Overall the availability of hydroxyl radicals is hampered thereby reducing the extent of degradation under alkaline conditions. The results are consistent with those reported by Daneshvar et al. [26], who studied the degradation of Rhodamine B under UV/H_2O_2 treatment and reported that at pH 2, maximum extent of colour removal as 90% was obtained.

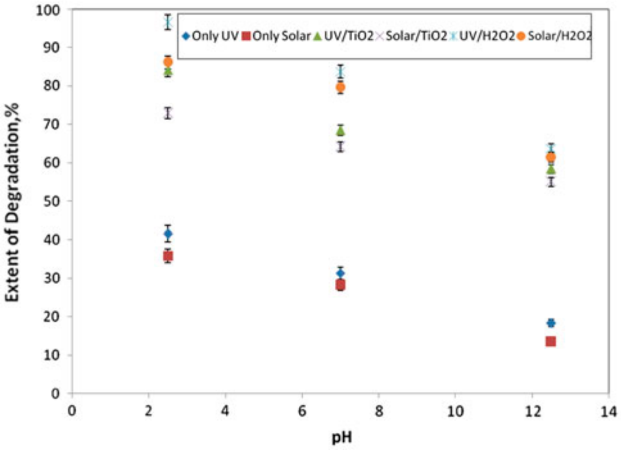

Fig. 7. Effect of pH on removal of patent blue V using UV and solar irradiation with and without catalyst (concentration = 10 ppm; catalyst loading = 1 g/L).

In the case of TiO_2-based photocatalysis, it was observed that the photocatalytic removal of dye is lower as compared to combination with H_2O_2 at catalyst loading of 1 g/L. The maximum degradation of patent blue v obtained was 84.1% for UV-assisted process and 72.8% for solar-based degradation obtained at 1 g/L TiO_2 catalyst loading at operating pH of 2.5. Again maximum extent of degradation was obtained under the acidic conditions. The effect of pH in the case of photocatalytic degradation is mainly based on two counteracting mechanisms of effect on the catalyst in terms of zero point charge of catalyst coupled with agglomeration effects and the oxidation capacity of free radicals. In the present case, TiO_2-particle agglomeration was not observed and hence enhanced oxidation potential of hydroxyl radicals under acidic conditions resulted in higher extents of degradation. The enhanced rate of degradation with a decrease in pH can also be explained on the basis of zero point charge of TiO_2. The adsorption of molecules at the metal sites is followed by the dissociation of OH^- groups leading to the formation of metal-hydroxyl complexes [27]. Due to the amphoteric behaviour of most metal hydroxides, the following two equilibria are considered:

$$\text{M–OH} + \text{H}^+ \rightarrow \text{M–OH}_2^+ \tag{4}$$

$$\text{M–OH} \rightarrow \text{M–O}^- + \text{H}^+ \tag{5}$$

The zero point charge [28] for TiO_2 is 6.8. TiO_2 surface is positively charged in acidic media ($pH < 6.8$), whereas it is negatively charged under alkaline condition ($pH > 6.8$). At low pH, electrostatic interactions between the positive catalyst surface and dye anions lead to strong adsorption of the latter on the metal oxide leading to higher rates of degradation. Credence to the obtained results can also be obtained based on literature illustrations. Mengyue et al. [29] reported that TiO_2 was the most active photocatalyst for the degradation of monocrotophos in the acidic conditions particularly at pH of 2. Khokhawala and Gogate [30] also reported that the possibility of bond breakage is favoured under acidic conditions based on the favoured state of molecules.

3.4. Comparison of degradation of patent blue using UV/H_2O_2 and UV/TiO_2 treatment approach

Presence of hydrogen peroxide or titanium dioxide under UV/solar irradiation results in the intensification in the formation of the highly reactive hydroxyl radicals which can bring about the decolourization. Experiments have been carried out using two different irradiation sources, i.e. fluorescent lamp (three each of 11 W) and natural solar radiations. The obtained results for degradation of patent blue V using different approaches as solar alone, UV alone, TiO_2 with UV/solar irradiation and hydrogen peroxide with UV/solar irradiation at initial concentration of patent blue V as 10 ppm and pH of 2.5 have been depicted in Fig. 8.

It can be seen from the figure that the extent of degradation was minimum for the treatment approach involving only irradiation without any addition of catalyst, i.e. hydrogen peroxide or TiO_2. Also, the extent of degradation was slightly higher using UV than solar irradiation attributed to the light intensity and higher exposed volume based on the use of 3 UV lamps in close vicinity. Further, the extent of degradation of dye increased when the UV irradiation-based degradation was supported by the presence of H_2O_2 (1 g/L) or TiO_2 (1 g/L). The extent of increase was higher for the UV irradiations as compared to solar irradiations. Maximum degradation of 92.8% was obtained using UV/H_2O_2 and 72.1% degradation was obtained using solar/H_2O_2. The degradation of the dye in UV/H_2O_2 process is the result of the reaction of hydroxyl radicals generated upon photolysis of hydrogen peroxide which exhibits a high oxidation potential ($E_0 = 2.8$ V) [31] and can bring about oxidation of organic compounds through sequential hydroxylation–dehydrogenation breakdown steps [32]. In the case of UV/TiO_2, enhanced degradation is attributed to the dissociation reaction of H_2O molecules generating active free radicals. The degradation of the dye using UV/TiO_2 (96.6%) was marginally higher than the UV/H_2O_2 process.

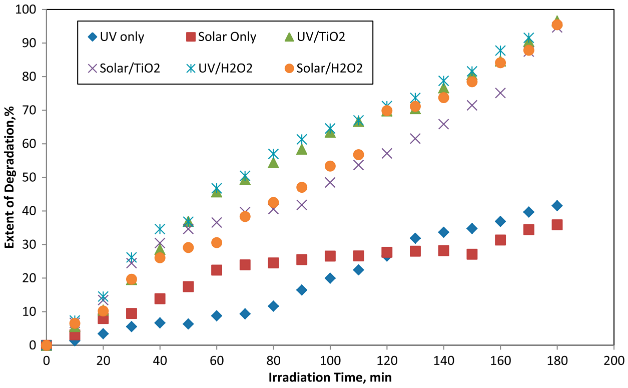

Fig. 8. Comparison of catalysts for removal of patent blue V using UV and solar irradiation (pH 2.5; concentration = 10 ppm; catalyst loading = 1 g/L).

The photocatalytic decolorization of dyes was found to follow pseudo-first-order kinetics based on the integral method of analysis. At low initial dye concentrations, the rate expression can be given by the following equation:

$$\frac{-\mathrm{d}[c]}{\mathrm{d}t} = k'[c] \tag{6}$$

where k' is the pseudo-first-order rate constant. The dye can be adsorbed on the TiO_2 surface initially until equilibrium is reached and hence the equilibrium concentration of the dye in the solution was taken as the initial dye concentration for kinetic analysis. Integration of equation (6) with the limit of $C = C_0$ at $t = 0$ where C_0 is the equilibrium concentration gives the following equation:

$$\ln\frac{C_0}{C} = k't \tag{7}$$

where C is the residual concentration at any given time t. A plot of $\ln C_0/C$ vs. t has been shown in Fig. 9. The obtained value of rate constant for UV/TiO_2 process was $9.99 \times 10^{-3}\ \text{min}^{-1}$ and for solar/TiO_2, the rate constant was $5.3 \times 10^{-3}\ \text{min}^{-1}$. Similarly the rate constants for UV/H_2O_2 and solar/H_2O_2 process were 8.63×10^{-3} and $6.2 \times 10^{-3}\ \text{min}^{-1}$, respectively.

3.5. Effect of H_2O_2 loading

The loading of hydrogen peroxide is one of the important factors affecting the degradation both from environmental as well as economical point of view. In order to avoid the use of excess hydrogen peroxide, which can add to both cost as well as COD if unutilized in the treatment, it is essential to establish the optimum loading for efficient treatment. The obtained results for the effect of addition of H_2O_2 over the range of 0.2–1.2 g/L on degradation of patent blue V (10 ppm initial concentration and pH of 2.5) have been given in Fig. 10. It has been observed that extent of degradation increased with an increase in the concentration of H_2O_2 till an optimum loading of 1%. Above 1% loading, the extent of degradation decreased with an increase in the hydrogen peroxide loading. Quantitatively, addition of H_2O_2 from 0.2 to 1 g/L increased the extent of degradation from 36.5 to 98.3% for the UV irradiation and from 31.8 to 95.4% for solar irradiation-based approach. Further increase in the H_2O_2 loading above 1 g/L, decreased the extent of degradation to 83.6% for UV-based approach and 61.5% for solar-based approach. The observed results can be attributed to the enhanced production of free radicals initially due to the dissociation of hydrogen peroxide, but above the optimum loading, residual hydrogen peroxide acts as a scavenger of the generated free radicals thereby decreasing the extent of degradation. The enhanced generation of hydroxyl radicals (mainly reaction (8)), which can attack the patent blue V molecule and the existence of optimum loading can be explained on the basis of series of reactions as given below:

$$H_2O_2 + h\gamma \rightarrow 2OH^{\cdot} \tag{8}$$

$$H_2O_2 + OH^{\cdot} \rightarrow HO_2^{\cdot} + H_2O \tag{9}$$

$$OH^{\cdot} + HO_2^{\cdot} \rightarrow H_2O + O_2 \tag{10}$$

$$OH^{\cdot} + OH^{\cdot} \rightarrow H_2O_2 \tag{11}$$

$$HO_2^{\cdot} + HO_2^{\cdot} \rightarrow H_2O_2 + O_2 \tag{12}$$

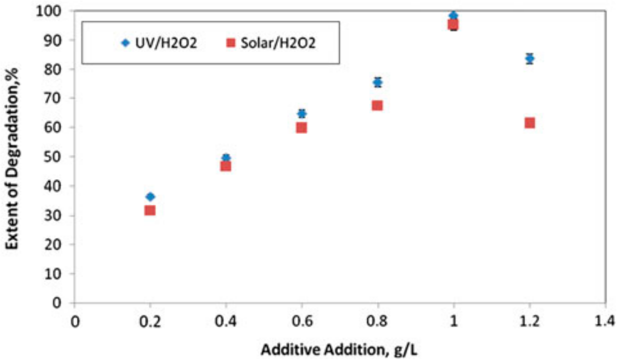

Fig. 10. Effect of H_2O_2 on removal of patent blue V using UV and solar irradiation (pH 2.5; concentration = 10 ppm).

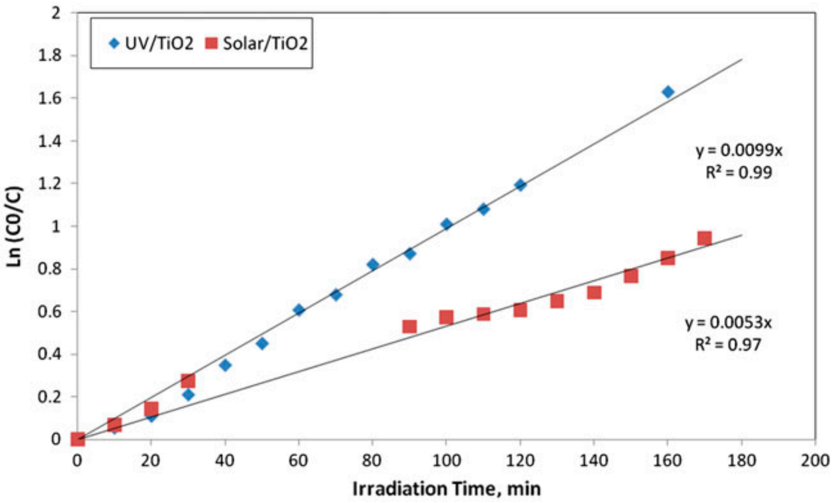

Fig. 9. Kinetic rate constant for TiO_2-based degradation of patent blue using UV and solar irradiation (pH 2.5; concentration = 10 ppm; catalyst loading = 1 g/L).

Above the optimum loading of 1%, the hydroxyl radical dominantly reacts with H_2O_2 and produces $HO_2^{\bullet}$ (Eq. (9)); also $OH^{\bullet}$ radicals generated at high concentration react with $HO_2^{\bullet}$ (Eq. (10)) or dimerize into H_2O_2 (Eq. (11)) [33,34]. Due to all these reactions consuming the generated hydroxyl radicals and due to the fact that the $HO_2^{\bullet}$ radicals are less reactive than $OH^{\bullet}$, there is a overall decrease in the extent of removal of dye. Hence, 1 g/L loading of H_2O_2 appears to be the optimum for the degradation of patent blue V.

3.6. Effect of catalyst loading and type of catalyst

A series of experiments were also carried out to investigate the optimum catalyst loading for the UV/photocatalyst approach as well as understand the effect of type of catalyst by varying the amount of two different metal catalysts, i.e. TiO_2 and ZnO over the concentration range of 0.2–1.2 g/L. The obtained results for the variation in the extent of degradation of dye at initial concentration of 10 ppm and pH of 2.5 for the case of TiO_2 and ZnO have been shown in Figs. 11 and 12, respectively. It can be seen from the figure that extent of degradation generally increases with the use of photocatalyst for both the cases and enhanced catalyst loading till an optimum value favours degradation. The maximum extent of degradation of patent blue in the presence of optimum loading of TiO_2 catalyst as 1 g/L was 96.6% for the UV-based approach and 94.7% for the solar irradiation-based treatment. For the case of ZnO catalyst, at similar loading of 1 g/L, the extent of degradation was 68.4% for UV and 59.0% for the solar irradiation-based treatments. The observed results can be attributed to the fact that the presence of catalyst, i.e. TiO_2 and ZnO enhances the dissociation of H_2O molecules to increase the number of free radicals generated, thereby increasing the rate of degradation of the organic compound. The higher destruction of patent blue V using TiO_2 than ZnO may be explained on the basis of higher activity of the TiO_2 catalyst as well as enhanced surface area available for the reaction. With an increase in the catalyst loading up to 1 g/L, more active surface area is available for enhanced dissociation and hence the rate of decolorization of dye increases. Above this optimum loading, increase in the turbidity of the solution reduces the light transmission through the solution. It should be also noted here that the particle–particle interaction becomes significant as the number of particles in the solution increases, which reduces the site density for surface holes and electrons and hence the extent of degradation decreases.

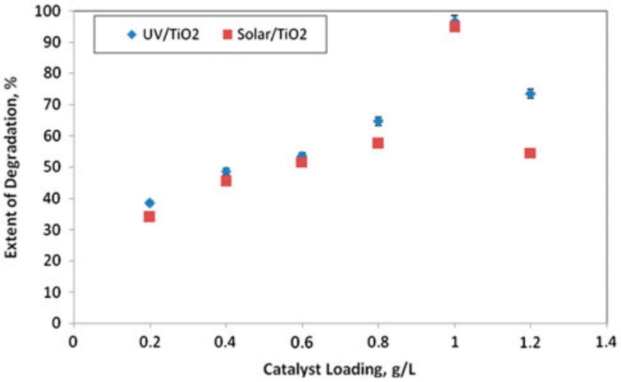

Fig. 11. Effect of titanium oxide loading on removal of patent blue V using UV and solar irradiation (pH 2.5; concentration = 10 ppm; catalyst loading = 0.2–1.2 g/L).

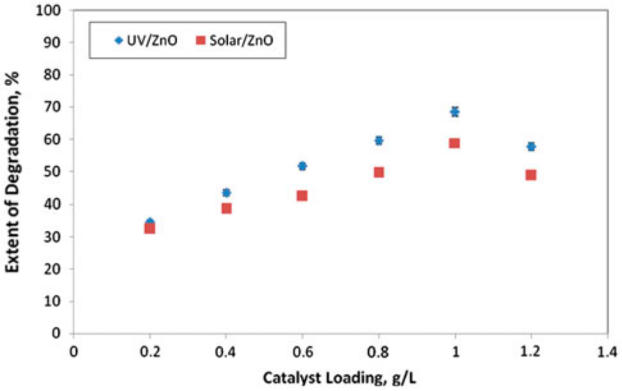

Fig. 12. Effect of zinc oxide loading on removal of patent blue V using UV and solar irradiation (pH 2.5; concentration = 10 ppm; catalyst loading = 0.2–1.2 g/L).

The results obtained in this work, are in good agreement with reported trends in the literature [28,34,35]. Kansal et al. [35] studied the effect of catalyst loading by performing experiments over the catalyst loading range of 0.25–2.0 g/L for dye solutions containing methyl orange and rhodamine 6G at initial concentration of 25 mg/L and natural pH (6.4 for methyl orange and 5.97 for rhodamine 6G). It has been reported that the initial rates of degradation increased significantly with an increase in the catalyst loading from 0.25 to 1.0 g/L and any further increase led to almost no change in the rate of decolorization. The initial increase in the rate of degradation was attributed to the increase in the total active surface area giving enhanced availability of active sites for the reaction [36]. Beyond the optimum loading, due to an increase in turbidity of the suspension with high dose of photocatalyst, there is a decrease in penetration of

UV light and hence photo-activated volume decreases [37] leading to lower rates of degradation.

3.7. Effect of combination with ferrous sulphate

Studies were also performed to understand the effect of introducing ferrous sulphate on the removal of patent blue V under UV as well as solar irradiation at optimum pH of 2.5 and dye concentration of 10 ppm. The ferrous sulphate loading was varied over the range of 0.2–0.8 g/L. Fig. 13 depicts the obtained results for patent blue V removal where it can be observed that the extent of dye removal increases with an increase in the loading of ferrous sulphate and the maximum removal of dye was observed at 0.8 g/L of additive loading in both the cases viz. solar/ferrous sulphate (66.22%) and UV/ferrous sulphate (81.56%). This can be attributed to the promotion of production of oxidizing species due to the presence of ferrous sulphate. In the aqueous medium, in the presence of solar or UV irradiation, splitting of $FeSO_4$ to ferrous ion (Fe^{2+}) and sulphate ion (SO_4^{2-}) occurs (reaction (13)). Reaction of sulphate ion and water molecule produces hydroxyl radicals in the presence of irradiations (reaction (14)) which thereby expedite the removal of patent blue V. During the treatment, hydrogen peroxide is also formed *in situ* (reaction (15)), which reacts with ferrous ions generating additional hydroxyl radicals (reaction (16)) also intensifying the extent of dye removal. The enhancement in generation of oxidizing species and destruction of dye can be shown by following reaction mechanisms:

$$FeSO_4 \rightarrow Fe^{2+} + SO_4^{2-} \quad (13)$$

$$SO_4^{2-} + H_2O \rightarrow HSO_4^- + HO^{\bullet} \quad (14)$$

$$HSO_4^- + HO^{\bullet} \rightarrow H_2O_2 + SO_3^{2-} \quad (15)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO^{\bullet} \quad (16)$$

The results presented in the work can also be confirmed by similar results presented in our earlier work [38] for removal of patent blue V using the air bubble-induced oxidation technique. It is also important to note that optimal additive loading is beneficial for intensification [39], which can be attributed to the fact that for higher $FeSO_4$ loading than optimal concentration, the solution becomes saturated with ferrous ions and self-quenching of hydroxyl radical occurs giving lower extent of degradation.

3.8. Mineralization study

The products from the oxidation of dye are typically some intermediates which on continued treatment results in the formation of CO_2 and H_2O, which can be established as complete mineralization. It is important to establish the reduction in the COD as these intermediates are expected to be aromatic compounds, which also accounts for the COD of the solution. Barka et al. [40] established the decomposition pathway based on the identification of the reaction intermediates in details using HPLC/MS and reported that several stages as hydroxylation, desulfonation, deamination, dealkylation and dehydroxylation were dominating the degradation. The extent of mineralization of patent blue V dye was also studied in the present work and the obtained results have been given in Fig. 14. The obtained percentage change in COD for solar and UV alone was only 16 and 26%, respectively. A higher extent of COD removal was

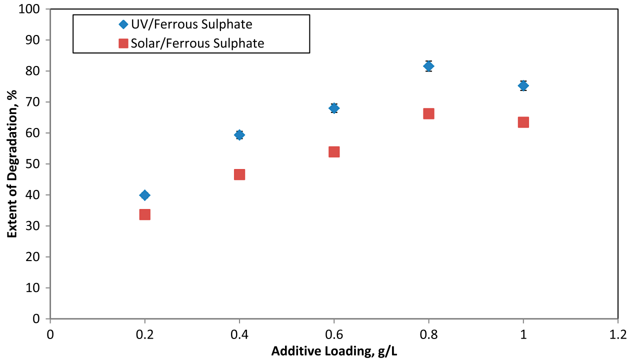

Fig. 13. Effect of addition of ferrous sulphate on removal of patent blue V using UV and solar irradiation (pH 2.5; concentration = 10 ppm; catalyst loading = 0.2–1 g/L).

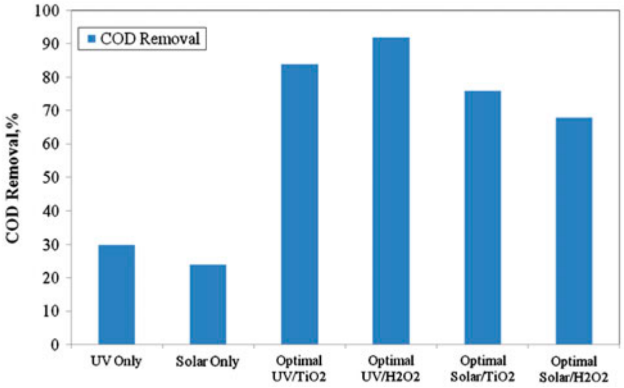

Fig. 14. Percentage reduction of COD using modified photocatalytic reactor.

obtained when experiments were carried out with TiO_2 or hydrogen peroxide under UV/solar irradiation. The obtained COD removal was 84 and 76% for the UV/TiO_2 and solar/TiO_2 approaches, whereas the COD removal for hydrogen peroxide in combination with UV and solar irradiation was 92 and 68%, respectively, at constant initial dye concentration of 10 ppm and pH as 2.5. It can be established that the COD removal followed the same trend as the removal of the parent compound.

4. Conclusions

The present work has conclusively established that patent blue V, an acidic dye, can be effectively removed from water using light irradiation-based treatment strategies involving the use of additives and can be intensified using modifications in the reactor. Following important design related information can be established from the results:

(1) The modifications in terms of the use of glass coating on the inner walls of the reactor resulted in significant improvement in the extent of degradation as compared to the conventional reactor.
(2) Lower initial concentration and acidic conditions were found to be favourable for the degradation of patent blue V.
(3) Presence of TiO_2 and H_2O_2 plays a favourable role in enhancing the degradation of the patent blue V using modified photocatalytic reactor.
(4) The maximum degradation of patent blue V was obtained using H_2O_2 in combination with UV irradiations followed by the combination of UV with TiO_2 catalyst.
(5) In the case of two metal oxides used in the work viz. TiO_2 and ZnO, TiO_2 was found to be more effective as compared to ZnO due to the higher band gap and large oxidation potential.
(6) Amongst all the treatment approaches, the maximum degradation as 98.3% was obtained for the UV/H_2O_2 process under modified photocatalytic reactor, i.e. with glass coating.
(7) The mineralization studies also confirmed that maximum COD removal as 92% was also obtained using the UV/H_2O_2 treatment.

Overall, it can be said that light irradiation-based treatment strategies holds good promise for degradation of patent blue and the extent of degradation can be maximized based on the use of modified reactor and by the use of intensifying additives.

References

[1] M. Neamtu, I. Siminiceanu, A. Yediler, A. Kettrup, Kinetics of decolorization and mineralization of reactive azo dyes in aqueous solution by the UV/H_2O_2 oxidation, Dyes Pigm. 53 (2002) 93–99.
[2] H. Zollinger, Color Chemistry: Syntheses, Properties and Applications of organic dyes and pigments, New York, NY, VCH Publisher, 1991, pp. 185–195.
[3] M.R. Alcantra, D. Daltin, Textile chemistry, Quim Nova 19 (1996) 320–330.
[4] C.C. Guaratini, M.V.B. Zanoni, Textile chemistry, Quim. Nova 23 (2000) 71–78.
[5] İ. Arslan, I.A. Balcioglu, T. Tuhkanen, Oxidative treatment of simulated dyehouse effluent by uv and near-UV light assisted Fenton's reagent, Chemosphere 39 (1999) 2767–2783.
[6] T.F. Robinson, G. McMullan, R. Marchant, P. Nigam, Remediation of dyes in textile effluent: A critical review on current treatment technologies with a proposed alternative, Bioresour. Technol. 77 (2001) 247–255.
[7] P.P. Zamora, A. Kunz, S.G. Moraes, R. Pelegrini, P.C. Moleiro, J. Reyes, N. Duran, Degradation of reactive dyes I. A comparative study of ozonation, enzymatic and photochemical processes, Chemosphere 38 (1999) 835–852.
[8] S. Ledakowicz, M. Solecka, R. Zylla, Biodegradation, decolourisation and detoxification of textile wastewater enhanced by advanced oxidation processes, J. Biotechnol. 89 (2001) 175–184.
[9] D. Georgiou, P. Melidis, A. Aivasidis, K. Gimouhopoulos, Degradation of azo-reactive dyes by ultraviolet radiation in the presence of hydrogen peroxide, Dyes Pigm. 52 (2002) 69–78.
[10] A. Aleboyeh, H. Aleboyeh, Y. Moussa, Decolorisation of Acid Blue 74 by ultraviolet/H_2O_2, Environ. Chem. Lett. 1 (2003) 161–164.
[11] V. Augugliaro, C. Baiocchi, A.B. Bianco Prevot, E.G. García-López, V. Loddo, S. Malato, G. Marcí, L. Palmisano, M. Pazzi, E. Pramauro, Azo-dyes photocatalytic degradation in aqueous suspension of TiO_2 under solar irradiation, Chemosphere 49 (2002) 1223–1230.
[12] O.M. Alfano, M.I. Cabrera, A.E. Cassano, Photocatalytic reactions involving hydroxyl radical attack, J. Catal. 172 (1997) 370–379.
[13] C. Turchi, D. Ollis, Photocatalytic degradation of organic water contaminants: Mechanisms involving hydroxyl radical attack, J. Catal. 122 (1990) 178–192.
[14] C.A. Martín, G. Sgalari, F. Santarelli, Photocatalytic processes using solar radiation. Modeling of photodegradation of contaminants in polluted waters, Ind. Eng. Chem. Res. 38 (1999) 2940–2946.
[15] M. Pasquali, F. Santarelli, J.F. Porter, P.-L. Yue, Radiative transfer in photocatalytic systems, AIChE J. 42 (1996) 532–537.
[16] R.J. Brandi, O.M. Alfano, A.E. Cassano, Rigorous model and experimental verification of the radiation field in a flat-plate solar collector simulator employed for photocatalytic reactions, Chem. Eng. Sci. 54 (1999) 2817–2827.
[17] D. Curcó, J. Giménez, A. Addardak, S. Cervera-March, S. Esplugas, Effects of radiation absorption and catalyst concentration on the photocatalytic degradation of pollutants, Catal. Today 76 (2002) 177–188.

[18] M. Schiavello, Photocatalysis and Environment. Trends and Applications, Nato Asi Series, Kluwer Academic Publishers, Dordrecht. 1988, pp. 65–95.

[19] A. Fujishima, K. Hashimoto, T. Watanabe, TiO_2 Photocatalysis: Fundamentals and Applications, Bkc Inc, Tokyo, 1999, pp. 120–145.

[20] M.I. Cabrera, O.M. Alfano, A.E. Cassano, Absorption and scattering coefficients of titanium dioxide particulate suspensions in water, J. Phys. Chem. 100 (1996) 20043–20050.

[21] M. Salaices, B. Serrano, H.I. de Lasa, Experimental evaluation of photon absorption in an aqueous TiO_2 slurry reactor, Chem. Eng. J. 90 (2002) 219–229.

[22] G.H. Rossetti, E.D. Albizzati, O.M. Alfano, Modeling of a flat-plate solar reactor. Degradation of formic acid by the photo-Fenton reaction, Sol. Energy 77 (2004) 461–470.

[23] St. Louis, Biochemicals and Reagents for Life Science Research, Sigma, MO, 2002, pp. 749–755.

[24] A. Giwa, P.O. Nkeonye, K.A. Bello, E.G. Kolawole, Solar photocatalytic degradation of Reactive Yellow 81 and Reactive Violet 1 in aqueous solution containing semiconductor oxides, Int. J. Appl. Sci. Technol. 2 (2012) 90–105.

[25] R.R. Gonte, K. Balasubramanian, J.D. Mumbrekar, Porous and cross-linked cellulose beads for toxic metal ion removal: HG(II) ions, J. Polym. 2013 (2013) Article ID 309136, 9 pages, doi: 10.1155/2013/309136.

[26] N. Daneshvar, D. Salari, A.R. Khataee, Photocatalytic degradation of azo dye acid red 14 in water: Investigation of the effect of operational parameters, J. Photochem. Photobiol., A 157 (2003) 111–116.

[27] W. Stumm, J.J. Morgan, Aquatic Chemistry, Wiley, New York, NY, 1981, pp. 1–88.

[28] S. Sakthivel, B. Neppolian, M.V. Shankar, B. Arabindoo, M. Palanichamy, V. Murugesan, Solar photocatalytic degradation of azo dye: Comparison of photocatalytic efficiency of ZnO and TiO_2, Sol. Energy Mater. Sol. Cells 77 (2003) 65–82.

[29] Z. Mengyue, C. Shifu, T. Yaowu, Photocatalytic degradation of organophosphorus pesticides using thin films of TiO_2, J. Chem. Technol. Biotechnol. 64 (1995) 339–344.

[30] I. Khokhawala, P.R. Gogate, Degradation of phenol using a combination of ultrasonic and UV irradiations at pilot scale operation, Ultrason. Sonochem. 17 (2010) 833–838.

[31] L.C. Juang, D.H. Tseng, J.F. Lee, Photolytic mechanism of monochlorobenzene in an aqueous UV/H_2O_2 system, Chemosphere 36 (1998) 1187–1199.

[32] R. Andreozzi, V. Caprio, A. Insola, R. Marotta, Advanced oxidation processes (AOP) for water purification and recovery, Catal. Today 53 (1999) 51–59.

[33] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals in aqueous solution, J. Phys. Chem. 17 (1988) 513–886.

[34] K. Sehested, O.L. Rasmussen, H. Fricke, Rate constants of OH with HO_2, O_2^-, and $H_2O_2^+$ from hydrogen peroxide formation in pulse-irradiated oxygenated water, J. Phys. Chem. 72 (1968) 626–631.

[35] S.K. Kansal, M. Singh, D. Sud, Studies on photodegradation of two commercial dyes in aqueous phase using different photocatalysts, J. Hazard. Mater. 141 (2006) 581–590.

[36] R.W. Matthews, Purification of water with near—UV. Illuminated suspensions of titanium dioxide, Water Res. 24 (1990) 653–660.

[37] M.S. Gonçalves, A.M. Oliveira-Campos, E.M. Pinto, P.M. Plasência, M.J.R. Queiroz, Photochemical treatment of solutions of azo dyes containing TiO_2, Chemosphere 39 (1999) 781–786.

[38] D.D. Mahale, N.N. Patil, D.S. Zodge, P.D. Gaikwad, B.S. Banerjee, K.N. Bawankar, A.V. Mohod, P.R. Gogate, Removal of patent blue V dye using air bubble-induced oxidation based on small glass balls: Intensification studies, Desalin. Water Treat. (ahead-of-print) (2015) 1–10.

[39] A.A. Pradhan, P.R. Gogate, Degradation of p-nitrophenol using acoustic cavitation and Fenton chemistry, J. Hazard. Mater. 173 (2010) 517–522.

[40] N. Barka, S. Qourzal, A. Assabbane, A. Nounah, Y. Ait-Ichou, Photocatalytic degradation of patent blue V by supported TiO_2: Kinetics, mineralization, and reaction pathway, Chem. Eng. Commun. 198 (2011) 1233–1243.