Short Communication

Photocatalytic degradation of disperse dye Violet-26 using TiO₂ and ZnO nanomaterials and process variable optimization

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ABSTRACT

The degradation of disperse V-26 in solution using UV, UV/H₂O₂, UV/H₂O₂/TiO₂ and UV/H₂O₂/ZnO were investigated. The impacts of various key parameters i.e. initial pH, concentration of hydrogen peroxide (H₂O₂) dose and the dye concentration effect on degradation were studied. The maximum degradation of 93% was optimized using UV/H₂O₂/TiO₂ at pH 3 in 60 min. Fourier transform infrared spectroscopy (FTIR) and gas chromatography-mass spectrometry (GC-MS) were applied to check the products obtained after complete degradation. The removal of peaks of certain groups present in dye molecule assured the maximum degradation of dispersive V-26. In biological treatment, cytotoxicity reduction and Ames test were used to check the toxicity level of products. Certain water parameters i.e. dissolved oxygen (DO), chemical oxygen demand (COD) and biological oxygen demand (BOD) were also performed to ensure the maximum degradation of DV-26. DO was increased up to 82%. The COD and BOD were reduced considerably owing to the treatment of disperse dye Violet 26 at optimum settings of process variables. The degradation of disperse dye V-26 with UV/H₂O₂/ZnO was 90.1% which increased up to 93% with the alternative photo-catalyst UV/H₂O₂/TiO₂.

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1. Introduction

The application of dyes and synthetic dyes, which covers almost all areas of life is constantly increasing and developing in many branches i.e. leather tanning industry, textile industry, food technology, paper production, pharmaceuticals and hair colorings [1]. The unwanted effluents which directly produce from unspent dyes are generally discharged without any further treatment [2]. This dyes effluent has major effect on the change of color of water even at low concentrations [3]. Moreover, usage of dyes significantly disperse dyes has been increased from 1970s [4]. Dyes are basically classified according to process of dyeing. The common classes of dyes include acid dyes, reactive dyes and disperse dyes. Reactive and acid dyes are water soluble. Reactive dyes are employed for cotton while acid dyes are used for wool, nylon, silk and some modified acrylic textiles. Finally, disperse dyes are generally partially soluble in water and used for polyester fibers. They are less water soluble, hence solubility can be increased with the mixing of disperse dye with some water miscible organic solvents. They are largely applied as dispersion in the textile dyeing process [5–7].

Among all the commercial dyes the disperse dyes constitute a major part involved in a vast range of processes in the different industries. The presence of azo group (N=N) attached to two substituents is very important characteristic of disperse dyes [8]. Owing to the toxicity of disperse dyes and massive mass production property lead to the requirement of developing new techniques. The difficulty in treating textile wastewater containing disperse dyes is the insufficient of biological processes [9–11]. Disperse dyes are among the persisting class of dyes due to recalcitrant nature and non-biodegradable behavior [12]. In the environmental fraternity the treatment of dye containing wastewater is considered very challenging due to this reason. Oxidation is the best known and most applied treatment to destroy the structure of dyes. In present years, the usage of advanced oxidation processes (AOP’s) have gained much interest especially with UV–H₂O₂ based system [13–15] which is very good technique to enhance the degradation of dyes. Furthermore, H₂O₂ decomposes into water and oxygen, hence it is known as friendly oxidant. Presence of ozone in water may arises some difficulties and serious problems [16]. These problems and issues can be resolved and avoided by oxidation with H₂O₂ stimulated with UV light. This recent work is basically focused to check the comparable photo-catalytic activity of ZnO and TiO₂ towards disperse dye degradation. TiO₂ and ZnO which are known as semiconductor photocatalyst photo-catalyst have been mostly applied to degrade destructive organic pollutants [17–20] into inorganic compounds like CO₂, HCl and water [21–25]. TiO₂ and ZnO are often used as catalytic agents since these semiconductors possess great properties like low cost, greater stability, zero toxicity and high efficiency. TiO₂ semiconductor photo-catalyst has advantage over ZnO due to its stability under different varying conditions, greater availability of radicals production, and its easy access and economic cost [9,10,26,27].

The present study aims to examine the ultraviolet radiation with hydrogen peroxide, hydrogen peroxide/TiO₂ and hydrogen peroxide/ZnO to degrade the disperse V-26 (Fig 1a, Table 1) and to produce compounds such as CO₂ and H₂O. The efficiency of process was gauged on the basis of dye degradation, toxicity reduction and water quality improvement. FTIR and GC–MS analysis was also performed to assure the degradation of end products of disperse V-26.

2. Material and methods

All the chemicals and reagents used in this study were of analytical grade. The molecular structure of commercial C.I. disperse V-26 (C₃₆H₂₃N₂O₄, MW: 422.43 g/mol) is shown in Fig. 1. The dye was taken from Khawaja & Company Dyes and Chemicals Faisalabad with no further purification. TiO₂ particles were prepared from Degussa (P25). TiO₂-P25, hydrogen peroxide and ZnO was purchased from Sigma Aldrich. The pH of the disperse V-26 solutions was adjusted by using dilute HCl (0.1M) and NaOH (0.1M). Disperse V-26 in their aqueous solution was subjected to UV/H₂O₂/TiO₂ and UV/H₂O₂/ZnO treatment and was examined using spectrophotometer (Cecil 7200). To prepare the disperse dye V-26 samples, distilled water was used. Various parameters including concentration of photo-catalysts, concentration of dye, UV dosage, pH, H₂O₂ were optimized to check the efficiency of photo-catalytic degradation process.

2.1 Irradiation of samples and analysis of disperse V-26 dye

The experiments for degradation using photo-catalytic techniques were performed by stuffing different concentrations (50 mg/L, 100 mg/L, 150 mg/L) of the stock solution (1000 mg/L) of given disperse dye solutions in the UV chamber. UV reactor was used having following specifications (wavelength 254 nm, power 144 W and shaker speed 120 rpm). Absorbance of all samples is noted at λmax 641 nm before and after treatments. In these concerned experiments, the solution of disperse V-26 was stirred by magnetic stirrer in the presence of TiO₂ and ZnO in the absence of light for 60 min to extent the adsorption equilibrium before UV radiation treatment. Millipore membrane with pore size 0.45 μm was used to filter the solutions of disperse dye V-26, and calibration curve method was significantly used to determine the UV–vis absorbance characteristics by UV–vis spectrophotometer in the University of Agriculture, Faisalabad (UAF). The percentage degradation was calculated by applying formula:

\[ \% \text{Degradation} = 100 \times \left( \frac{C_0 - C}{C_0} \right) \]
Where $C_0 =$ initial concentration of dye solution, $C =$ concentration of dye solution after photo irradiation.

2.2. Toxicological tests and water evaluation parameters

Elimination of $H_2O_2$ from irradiated samples was very necessary to avoid its toxic impact. For this purpose, addition of minor quantities of $MnO_2 (\leq 1 \text{mg/mL})$ was made to lessen the impact of $H_2O_2$. After a given reaction time of 45 min. the solution was clarified and uncovered to the toxicity tests such as hemolytic and Ames test. Hemolytic test was performed for cytotoxicity results, while Ames test is used to assess the mutagenicity of tested samples. All the tests were performed at the Biochemistry Laboratory, Department of Biochemistry, UAF, Pakistan. Cytotoxicity assay was evaluated by performing hemolytic experiments against human red blood cells (RBCs). Triton X-100 was used as positive control. To check the mutagenic prospective of chemical compounds the biological assay like Ames test was performed. A positive test shows the carcinogenic nature of chemical, since cancer is frequently related to mutation. However, a number of false-positives and false-negatives are known. The test serves as a quick and advantageous assay to evaluate the carcinogenic nature of a compound.

The determination of the DO was done from Hi-Tech Lab UAF, Pakistan. The samples were taken before and after irradiations and also with additional parameters like $H_2O_2$ and $TiO_2$ and ZnO. For COD determination the complete oxidation of the organic matter should be done. The test for the determination of COD was done by dichromate ($K_2Cr_2O_7$) method. The reduction of the COD values depends upon a number of the factors. The addition of the hydrogen peroxide, ZnO and $TiO_2$ also increased the reduction of the COD.

In the BOD the oxygen used by the bacteria is calculated by comparison of amount of oxygen left behind after five days with the initial oxygen amount which was a known quantity [28]. The amount of dissolved oxygen at room temperature is about $8 \text{mg/L}$. The BOD was calculated by previously reported methods.

$$\text{BOD} = (\text{BOD observed}) - (\text{Fraction seed}) \times (\text{BOD of seed})$$

3. Results and discussion

3.1. Effect of dye concentration and irradiation time

To design the model of numerous initial dye concentrations is for the basic purpose of inserting the impact of initial dye concentration to the degradation equation. Various concen-
3.2. Effect of pH

The effect of pH on the rate of degradation of different concentrations of disperse V-26 (50 ppm, 100 ppm, 150 ppm) at different pH values of 3, 5, 7, and 9 was checked. pH plays a significant role in the discoloration of dyes by H₂O₂/UV with different photo-catalyst (ZnO, TiO₂) process. In this study TiO₂ showed more catalytic activity under UV light irradiation than ZnO, that is why H₂O₂/UV/TiO₂ plays a significant role in degradation efficiency. Degradation and discoloration process is more effective in an acidic medium [32]. Increasing the pH from 3 to 9 led to a noticeable decrease in degradation efficiency from 92% to 95% as reference [33] demonstrated. At basic pH the reduction in efficiency can be observed because of the fact that a large part of H₂O₂ is utilized for the breakdown of alkalis forming oxygen and water rather than producing hydroxyl radicals under UV radiation. Moreover, at higher pH values, the H₂O₂/UV/TiO₂ process is very sensitive to the scavenging effect of carbonate [34]. Hence the instant concentration of hydroxyl radical decreases causing efficiency decrease. Temperature does not have any significant effect on discoloration of the dyes. Fig. 2b Shows the effect of pH on degradation efficiency of disperse V-26.
3.3. Effect of hydrogen peroxide

The impacts of H₂O₂ concentration on disperse V-26 degradation under H₂O₂/UV was also investigated in the range of 0.3-0.9 mL/L and the result is shown in Fig. 3. In the absence of H₂O₂ the value of %age degradation was 63.1 % but this value was suddenly increased up to 82.7 % by the addition of hydrogen peroxide (0.9 mL) with H₂O₂/UV. By increasing H₂O₂ concentration the degradation efficacy was increased. This is due to photo irradiation of H₂O₂ to diminish OH⁻ and the ability of H₂O₂ for trapping electrons. In the process of radiolysis, production of hydroxyl radicals (·OH) favors the oxidative degradation of dyes and this phenomenon can be more enhanced in the presence of H₂O₂ [35]. Results are given below which clearly show that in the absence of electron acceptor such as H₂O₂ decomposition of disperse V-26 decreases by increasing the dye concentration exhibiting the reason of intense color by increasing concentration. While adding the H₂O₂ the degradation pattern suddenly increased.

3.4. Effect of TiO₂, ZnO photo-catalysts dose

In order to get maximum degradation efficiency of disperse V-26, various concentrations of two photo-catalyst TiO₂ (0.2 g, 0.4 g, 0.6 g) and ZnO (0.2 g, 0.4 g, 0.6 g) were used (Fig. 4) while keeping all other parameters constant. Maximum degradation efficacy (93 %) was achieved with H₂O₂/UV/TiO₂ as compared to H₂O₂/UV/ZnO, which was (90.1 %). The decrease in the degradation efficacy was attributed to the reference [27], which clearly indicated the enhanced TiO₂ catalytic activity under UV light. The energy band gap of TiO₂ is 3.2 eV as compared to energy band gap of ZnO, which is 3.3 eV. TiO₂ is preferred over ZnO due to its stability under various conditions, its easy availability, non-toxic nature and its low cost results are demonstrated in Fig. 6.
3.5. Water quality parameters

In water or liquids, gaseous, free and non-bonded oxygen refers as dissolved oxygen. The sample solution of 50 ppm with addition of 0.9 mL H$_2$O$_2$ + 0.6 g TiO$_2$ and 0.9 mL H$_2$O$_2$ + 0.6 g ZnO was checked for DO, COD and BOD analysis. The DO values increased up to a significant rate after treatment which is the clear indication of degradation of dispersive V-26. (Fig. 5) shows the comparison in the values of DO in mg/L before and after treatment with different parameters. Before treatment the DO value was 2.01 mg/L which suddenly increased up to 3.25 mg/L with 0.9 mL H$_2$O$_2$ + 0.6 g ZnO and
Fig. 6 – (a, b) FTIR bands of dispersive dye V-26 before and after UV irradiation and (c) GC–MS profile of disperse violet 26 treated by UV in the presence of H₂O₂ and TiO₂.

Further increase up to 5.15 mg/L with 0.9 mL H₂O₂ + 0.6 g TiO₂. The BOD values before irradiation were 585 mg/L, 490 mg/L and 375 mg/L. Hydrogen peroxide showed a major role in BOD reduction. After irradiation these values were reduced to 315 mg/L, 205 mg/L and 105 mg/L shown in Fig. 5b. BOD reduction was up to 82.3 % in presence of H₂O₂ because hydrogen peroxide interacts with aqueous electron and hydrogen radical and may scavenge these species. Actually oxidative degradation of dyes occurs by hydroxyl radicals generated during radiolysis and is facilitated in the presence of hydrogen peroxide [35]. This result is strongly proved by comparing the BOD values already reported in the literature. For example, the initial AR and AY solutions had BOD values equal to 400, 330 mg/L, respectively. The UV irradiation caused a decrease in the BOD of the two dye solutions. The reduction in BOD values from 400 to 120 mg/L and from 330 to 80 mg/L respectively occurred in the presence of H₂O₂ [36]. After irradiation the values of COD reduced to a significant rate due to breakdown of
organic matter. It was thought that the hydrogen peroxide may decrease the COD to a significant value but practically it was noted that the value of COD increased by addition of hydrogen peroxide. The 50 ppm solution of disperse V-26 has COD value 925.895 mg/L before irradiation and was decreased to 515.146 mg/L for 50 ppm + 0.9 mL H₂O₂ + 0.6 g ZnO. Further decrease up to 397.34 mg/L was observed (Fig. 5c). The COD values of disperse V-26 were strongly recommended by giving a comparison of these values with the already reported COD values of two dyes in literature [37–42].

3.6 FTIR and GC–MS analysis

FTIR was used for un-treated and treated samples to identify the degraded end products. FTIR spectrometer (U-2001, Shimadzu, Japan) at HI-TECH lab Government College University Faisalabad (GCUF) was used in the range of 4000–400 cm⁻¹ for analysis. Spectrum of un-treated sample showed different vibrational peaks due to different functional groups present in disperse V-26. Spectrum of treated sample of sample dye has shown great variation by breakage of different functional groups and destruction of aromatic rings. After irradiation with UV/H₂O₂/TiO₂, the characteristics bands of dye molecule were vanished, which showed clear indication of destruction of DV-26 [43]. Results are demonstrated in Fig. 6. To assure the results obtained after UV irradiation treatment, toxicity profiling and water parameters analysis, the treated sample was further subjected for gas chromatography–mass spectroscopy (GC–MS). The GC–MS was performed for maximum degraded DV-26 sample treated with UV in the presence of H₂O₂ and TiO₂. The GC–MS analysis clearly indicates the complete breakdown of disperse violet 26 into lower molecular weight inorganic compounds and ions as well i.e. (H₂O, CO₂, NO₃- etc). The GC–MS spectrum is shown in (Fig. 6c).
3.7. Toxicological tests (Hemolysis, Ames)

Hemolysis is caused by microbes and other parasites like the plasmodium falciparum, hence known as infectious disease [44]. The cytotoxicity parameter was observed for untreated and treated samples of dispersive V-26. The cytotoxicity of un-irradiated 50 ppm was 16.1 % and it was reduced to 10.3 % when irradiated with UV radiation. Further reduction up to 7.6 % was noticed with the addition of photo-catalyst (TiO2). The Hydrogen peroxide and photo-catalyst TiO2 also showed a major effect on the reduction of cytotoxicity of the disperse V-26 (Fig. 7a). Ames test was performed to evaluate the mutagenic nature of DV-26. 50 ppm solution of disperse violet-26 was analyzed before and after UV irradiation for the mutagenicity using TA98 and TA100 strains, which are very sensitive to frame-shift and base-substitution mutagens respectively [45–47]. The disperse V-26 solution contained the mutagenicity about 8 (91.6 %) and 6 (88.5 %) before irradiation. The 50 ppm solution was irradiated by UV radiations and mutagenicity was reduced to a significant rate as 2 (98.9 %) and 2 (98.9 %) plates were affected by dye solution which is a clear evidence of reduction in the mutagenicity due to hydrogen peroxide. It was known that the UV radiation was not considered to be effective in the reduction of mutagenicity but with addition of hydrogen peroxide the mutagenicity was reduced to maximum level (Fig. 7b).

4. Conclusions

The degradation of disperse V-26 was done using UV/H2O2 assisted with various photo-catalysts (ZnO, TiO2). The photocatalytic method was found more efficient for the degradation of DV-26. Because of the high catalytic effect, greater stability and non-toxic nature of TiO2 photo-catalyst, the degradation was achieved up to 93 % with UV/H2O2/TiO2. The energy band gap of TiO2 (3.2 eV) is less than energy band gap of ZnO (3.3 eV) which makes it more efficient photo-catalyst and comparable to ZnO. Toxic effect of disperse dye V-26 was decreased by toxicity profiling tests (Hemolysis, Ames). The decrease in the toxicity of DV-26 assured the degradation of dye. The DO, COD and BOD were also improved significantly as a result of UV/H2O2/TiO2 treatment for DV-26. The physico-analytical techniques like FTIR and GC–MS were also performed to check the degradation of disperse dye V-26 and the removal of certain peaks in the molecule of dye confirmed the degradation of dye.

Conflicts of interest

The authors declare no conflicts of interest.

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