UV/H₂O₂, UV/H₂O₂/SnO₂ and Fe/H₂O₂ based advanced oxidation processes for the degradation of disperse violet 63 in aqueous medium

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Abstract
The photodegradation of disperse violet 63 dye was investigated in aqueous solution using UV/H₂O₂, UV/H₂O₂/SnO₂ and Fenton reagent. The maximum decolorization was achieved in 60 min with 50 mg l⁻¹ of dye concentration. The suitability of each process depends upon dye concentration. The photo degradation is very effective at low dye concentration. The degradation percentage increased by enhancing initial amount of hydrogen peroxide and UV irradiation time. The influence of operational parameters like pH, H₂O₂ concentration, catalyst amount and dye concentration were investigated. After 60 min reaction time, the maximum decolorization of disperse violet 63 with UV/H₂O₂, UV/H₂O₂/SnO₂ and Fe/H₂O₂ was 81%, 92.7% and 96.4% respectively. The results indicated that Fenton process had more photocatalytic activity for degradation of disperse violet 63 dye than that of UV/H₂O₂ and UV/H₂O₂/SnO₂. After 60 min, the comparative decomposition order was Fe/H₂O₂ > UV/H₂O₂/SnO₂ > UV/H₂O₂. It may be concluded that Fenton process could possibly be used for the remediation of toxic pollutants from textile effluents.

1. Introduction
Now a days, the release of industrial sewages that contain organic dyes causes water pollution such as lakes and rivers [1–3]. The degradation of organic contaminants and dyes in wastewater has become the problem of environmental concern [4].

Among these organic pollutants, dyes are hazardous complexes. Major input of dyes into the atmosphere owing paper production, leather tanning, hair coloring, textile processing and food processing etc [5–7]. Dyes are toxic and potential contaminants. Therefore, the removal of hazardous and wastewater pollutants has achieved considerable attention. This leads to the severe environmental problems for the reason that of carcinogenicity, mutagenicity and toxicity of released organic dyes [8–13].

Dyes are complex organic molecules contained wastewater result in water contamination due to their high visibility level of 1 ppm in wastewater. It can affect the quantity of oxygen able to be used for biodegradation of microorganisms in water and diminish light dissemination that lead to decreased photosynthetic activity [14–16]. Some conventional treatment techniques such as chemical, biological and physical methods like coagulation, ozonation, chlorination, adsorption, bio-degradation, etc, have been used to havoc these dangerous compounds, but they have certain limitations.

On the other hand, advance oxidation process containing photo-catalyst is the verdant method [17, 18]. Among distinct treatment methods, the use of advance oxidation process (AOP) has obtained considerable attention owing to production of most influential oxidizing agent (OH, E° = 2.73 V) in sufficient extents to
attain effective degradation of target contaminants. Advanced oxidation process has become one of the promising technologies to treat organic contaminants in wastewater [19–21].

The main objective of this study was to evaluate the effect of different materials including UV/H₂O₂, UV/H₂O₂/SnO₂ and Fe/H₂O₂ based advanced oxidation processes for the degradation of disperse violet 63 in aqueous medium.

2. Material and methods

Disperse violet 63 dye was purchased from Harris dyes and chemical used without any further purification. Hydrogen peroxide (35% w/w) was purchased from Sigma-Aldrich (Germany). FeSO₄.7H₂O, HCl, SnO₂ and NaOH were obtained from Merck (Germany). Distilled water has been used to prepare different solutions. 0.1 M dilute HCl and 0.1 M NaOH was used to adjust the pH of the sample solutions. The molecular structure of disperse violet 63 is shown in figure 1.

2.1. Preparation of stock solution

1000 ppm stock solution of disperse violet 63 dye was prepared by dissolving 1 g of dye in 1000 mL distilled water. Dye solution was diluted by dilution method to prepare solutions of different concentration 50 ppm, 100 ppm and 150 ppm.

2.2. Treatment of samples

The samples of dye were exposed to treatment by batch UV photo reactor contained lamps of emitting UV radiations of 254 nm wavelength and 144 watts intensity. Then experiments were conducted under UV light. The continuous stirring of aqueous suspensions was insured using magnetic stirrer throughout the experiment. Then dye concentration in degraded samples was determined with a double beam spectrophotometer. Decolorization efficiency has been studied as follows (Eq. 1);

\[ \text{Decolorization efficiency} \% = \frac{C_0 - C}{C_0} \times 100 \]  (1)

Where \( C_0 \) is the concentration before irradiation and \( C \) is concentration after irradiation.

2.3. Determination of maximum wavelength (\( \lambda_{max} \))

Double beam spectrophotometer (Perkin Elmer) was used to determine the maximum wavelength of dye solution. It was observed that H₂O₂ had no effect. In the sample cell dye solution was added then scanned spectrophotometer through visible series (200–800 nm). The aqueous solution of dye indicated maximum absorption (\( \lambda_{max} \)) in visible zone at wavelengths of 482 nm for violet 63 dye (figure 2).

2.4. Measurement of absorbance

Absorbance of each dye solution was evaluated by double beam spectrophotometer. Each dye solution was scanned at maximum wavelength 482 nm. Distilled water was used in sample and reference cells to adjust the spectrophotometer and then dye solution was introduced into sample cell to measure absorbance of dye sample at maximum wavelength.
3. Results and discussion

3.1. Effect of H$_2$O$_2$ concentration

Table 1 shows the degradation of disperse violet 63 dye as a function of different process variables. The effect of H$_2$O$_2$ dose ranging from 3%–9% on degradation of disperse violet 63 dye was studied. It has been investigated that degradation percentage increases by enhancing initial amount of hydrogen peroxide to critical rate upon which it is maximal and further on it is restrained. When increased quantity of H$_2$O$_2$ is added to solution, then additional hydroxyl radicals are obtainable for oxidation of dye. As a result, there must be appropriate amount of H$_2$O$_2$ for the effective dyes removal [22–28]. Therefore, H$_2$O$_2$ should be introduced at an optimal concentration to obtain best degradation and the optimum concentration was 9% H$_2$O$_2$.

The ·OH radicals generated attack the disperse violet 63 framework at different positions like, unsaturation points. In several such attacks the disperse violet 63 get converted into CO$_2$ and hetero-atoms which are further mineralized [29–32]. Results showed that degradation rate of disperse violet 63 was enhanced due to hydrogen peroxide. (figure 3).

3.2. Effect of pH

pH is main key factor to study because dye containing industrial wastewater is discharged at different pH levels. The influence of pH on removal efficiency of disperse violet 63 dye was explored by adding incremental amounts of either diluted NaOH or HCl to dye solution in the presence of UV radiation. Results showed that removal efficiency was decreased with rise in pH exhibiting maximum removal efficiency at pH 3. After 60 min, 79.2% of dye was degraded at this pH. Therefore, the oxidation process was performed in acidic medium. The same results were found out by other researchers for several pollutants and dyes [33–36]. The effect of pH on degradation of dye is shown in figure 4.
3.3. Effect of dye concentration

The influence of this parameter on the decolorization was investigated by changing concentration over a range of 50 ppm to 150 ppm by keeping other parameters constant such as 144 W UV intensity, H₂O₂ dose 9% and catalyst dosage 0.3 g l⁻¹. Rate of degradation is related to production of hydroxyl radicals reacting with dye molecules. It has been observed that the availability of free OH radicals is not sufficient for photo-oxidation process when disperse violet 63 is present at high levels. It was experimented that by enhancing the initial concentration of dye, removal efficiency of dye decreased. These results are comparable with photo-oxidation of Reactive Red 2 and Direct Yellow 12 dyes that decreases with increase in initial dye concentration [31, 37]. The results are shown in (figure 5).

3.4. Effect of SnO₂ concentration

The influence of catalyst dosage on photodegradation of disperse violet 63 dye was examined by changing the amount of SnO₂ from 0.1 to 0.3 g l⁻¹ keeping all other parameters constant. Experiments conducted with different SnO₂ concentrations showed that the degradation rate increased with increase in catalyst loading. The enhancement of removal rate may be due to increase in the availability of active sites, which increases the
number of dye molecules absorbed and the increase in the density of particles in the area of illumination [38]. Results showed that maximum degradation is observed with 0.3 g of SnO2 catalyst dosage. The outcomes showed that degradation rate achieved for disperse violet 63 was 92.7% (figure 6).

3.5. Fenton process

Effect of Fenton reagent (Fe²⁺/H₂O₂) on degradation of disperse violet 63 dye was investigated. The concentration of different constituents in reaction mixture was; FeSO₄ = 80 mg and H₂O₂ = 0.9 ml. Fenton reagent was dissolved in reaction blend after temperature adjustment. Then hydrogen peroxide was added and started to stir for 1 h and then, degradation efficiency was measured. The Fe (II) dosage is used to catalyze the color removal within a shorter time [1, 39]. It was observed that maximum degradation rate for disperse violet 63 was 96.4% within 1 h (figure 7). These results are comparable with maximum efficiency of reactive red 198 and reactive blue 19 in Fenton reaction [1, 10, 40, 41].

Under the environmental scenario, the advanced oxidation processes are potential agents for the remediation of industrial effluents particularly dyes from textile units. These processes with different oxidation agents could possibly be used for removal of toxic pollutants [18, 19, 21, 35, 42, 43].

Figure 5. Effect of dye concentration on % degradation of disperse violet 63.

Figure 6. Effect of SnO₂ concentration on % degradation of disperse violet 63.
4. Conclusions

In this study, the obtained results show the effectiveness of AOPs in removing dyes, which resist other treatment methods. AOPs have become one of the promising technologies to treat organic contaminants in wastewater. The photocatalytic degradation of disperse violet 63 dye was investigated by using UV/H$_2$O$_2$, UV/H$_2$O$_2$/SnO$_2$ and Fe/H$_2$O$_2$ processes. The color removal of dye solution with Fenton reagent was greater than UV/H$_2$O$_2$ and UV/H$_2$O$_2$/SnO$_2$. The Fenton process can be used to treat dye in wastewater treatment plant. Results indicated that the Fenton process is very suitable alternative to UV/H$_2$O$_2$/SnO$_2$ and UV/H$_2$O$_2$. The data obtained showed that acidic pH is appropriate for disperse violet 63 photocatalytic degradation. We propose different reaction procedures in which the dye photolytic oxidation is proposed in solution by generated hydroxyl radicals.

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