

Impact of UV/TiO₂/H₂O₂ on Degradation of Disperse Red F₃BS

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The object of this work was to establish methods for the treatment of dye disperse red F₃BS using UV radiation in the presence of H₂O₂ and TiO₂. The degradation was monitored through UV/visible, FTIR and GC-MS techniques. The efficiency of advanced oxidation processes was evaluated on the basis of extent of degradation, improvement of water quality parameters and cytotoxicity reduction. The toxicities were determined through allium cepa and shrimptest. The independent variables such as radiation dose, catalysts concentration, exposure time, pH, temperature, *etc.* were optimized for maximum degradation of dyes. The advanced oxidation processes showed promising efficiency for the degradation of pollutants and it was observed that γ -irradiation in the presence of H₂O₂ was more efficient for the degradation of toxic residues, improvement in water quality parameters and toxicity reduction as compared to UV/TiO₂/H₂O₂ treatment. From the results, it is also concluded that the advanced oxidation processes such as UV/TiO₂/H₂O₂ could be successfully used for the treatment of industrial wastewater contain dyes at commercial scale because the water quality parameters values fall within the permissible limits recommended by the international environmental agencies.

Keywords: Disperse red F₃BS, UV radiation, TiO₂, H₂O₂, Degradation.

INTRODUCTION

Pollution has become a problematic issue for the environment. From last few decades, there is a growing concern of toxic pollution due to their harmful effect on living organisms. The water bodies serve as temporary or final receptors of diverse variety of contaminants, which consequently are contaminating the watersheds and adjoining territories^{1,2}. The rapid industrialization is a major concern and a severe threat to the survival of living organisms which is jeopardizing the ecological balance³. As a result of exposure to contaminated water containing toxic agent, negative impact ranging from cytotoxicity to mutagenicity in various model have been documented well⁴⁻⁶. Among the damages caused by chemical agents to exposed organisms, genotoxic and mutagenic effects have shown to be worrying, which can lead to several health problems and also affect future generations due to inheritable alterations in genetic material⁷. Toxicants screening in environmental samples using method *in vitro* are reliable to measure the extent of pollution load and this biological assessment is compulsory for effluent monitoring, discharged from industries before being mixed with water bodies^{8,9}.

Dyes are the substances which are soluble in water can be transported easily in the water cycle¹⁰⁻¹² and they are detected

at long distances from their sources of discharge^{13,14}. Disposal of industrial effluents into fresh water bodies disturbs water quality parameters which are necessary to sustain aquatic life^{15,16}. If the safety of wastewater discharged from industries is assured by industrialists or by pollution control boards, then treated industrial wastewater may be potentially used for fish production, irrigation for non-edible cash crop, aquaculture and for many other such types of multifarious uses¹⁷⁻¹⁹.

In this regard, there are several methods being in practice for the treatment of industrial wastewater²⁰⁻²⁷. The radiation treatment methods has been emerged as very effective technology for the degradation and mineralization of pollutants, which can be employed as; O₃, O₃-UV, H₂O₂-UV, O₃-H₂O₂, TiO₂-UV, Fe²⁺-H₂O₂, γ - and electron beam irradiation which are named as advanced oxidation processes^{28,29}.

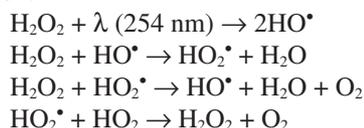
Advanced oxidation processes (AOPs) were used to convert the constituents of dye pollutant into simple, relatively harmless and inorganic molecules. To achieve this goal, oxidants *i.e.* compound or species that are electron donors are utilized. The main aim of advanced oxidation processes is to produce hydroxyl radicals (HO^{*}) which is very powerful oxidant, highly reactive, short lived and relatively non selective

electrophilic oxidizing agent and degrade the organic compound efficiently^{30,31}.

The HO[•] can be generated by both photochemical processes *e.g.*, UV radiation in combination with O₃, H₂O₂ or a photosensitizer natural organic matter and nonphotochemical processes *e.g.* electron beam irradiation, O₃, in combination with H₂O₂ or Fenton's reagent.

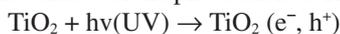
The production of e⁻_{aq}, H[•] and OH[•] upon irradiation in water makes it an effective process for the removal of pollutants. The most reactive species are the oxidizing OH[•] the reducing species such as e⁻_{aq} and H[•] also interact with pollutants present in wastewater³²⁻³⁵. The degradation of pollutants depends on different factors, such as types of radiation, absorbed dose, dose rate, pollutant concentration, oxidant concentration and synergistic effects of radiation³⁶⁻³⁸.

Photolysis is defined as the use of radiant energy without the presence of any catalyst to irradiate a polluted aqueous solution. The formation of reactive oxygen species and radicals lead to the degradation of the targeted compound³⁹. Generation of HO[•] by UV photolysis from H₂O₂, can be described by the following equations⁴⁰.



However, high concentrations of H₂O₂ may scavenge the HO[•] make the process less effective⁴¹ so, for effective treatment, there is a need to optimize the conditions.

The photoexcitation of TiO₂ particles promotes an electron from the valence band to the conduction band, generating an electron/hole pair. Both reductive and oxidative processes can occur at or near the surface of the photo excited TiO₂ particle⁴².



The photogenerated hole has the potential to oxidize several substrates by electron transfer.

In the present work the radiation induced degradation of disperse red F₃BS dye which is used in textiles. Treatment is carried out UV/H₂O₂/TiO₂ on the basis of water quality parameter dissolved oxygen (DO), biological oxygen demand (BOD) and chemical oxygen demand (COD) were determined before and after treatment. Radiolytic end products were analyzed using Fourier transform infrared (FTIR) and Gas chromatography- mass spectrometry (GC-MS).

EXPERIMENTAL

The disperse red F₃BS as shown in Fig. 1 is provided by Harris Dyes and Chemical (PVT) limited, Faisalabad, Pakistan. The dye was used without purification while hydrogen peroxide was purchased from Fluke, Germany. Titanium dioxide (TiO₂) and demineralized distilled water was used for preparation of dye solutions.

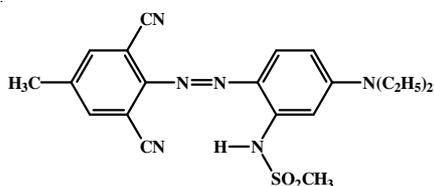


Fig. 1. Structural formula of disperse red F₃BS

Treatment of samples: The aqueous solutions of model compounds were also treated by batch UV photo reactor emitting radiation having wavelength of 254 nm, 44 watt intensity in the presence of TiO₂ and H₂O₂. Double beam spectrophotometer (CECIL CE 7200) was calibrated by using K₂Cr₂O₇ standard solutions. 1 mL of concentrated sulphuric acid (98 %) was mixed in 100 mL doubly distilled water. 3.5 mL of this acidic solution was taken and 5.5 mg of potassium dichromate was dissolved in it. The final volume was made to 50 mL in a volumetric flask by triply distilled water. The concentration of dichromate ions in this solution were 1.87 × 10⁻⁴ M. The absorption spectrum of this solution was analyzed from 200 nm to 500 nm wavelength range. The absorbance of two maximum and two minimum were compared with reported values. The combined effect of H₂O₂ and UV was studied by adding different concentration of H₂O₂ and UV irradiation.

Gas chromatography-mass spectrometry (GC-MS): Gas chromatography-mass spectrometer 6890 N Agilent, (Japan) with DB-5 column was used at Pakistan Council for Scientific and Industrial Research (PCSIR) Lahore. The operating software was Chem. station. Gas chromatography-mass spectrometric (GC-MS) analyses were carried out after treatment in order to identify the degraded products. Before analysis, the aqueous irradiated samples were extracted with acetone. The organic phase were decanted and then dehydrated by MgSO₄ for 24 h. The organic phases were then concentrated and stored for analysis. The GC system (Agilent Technologies 6890N) with DB-5 capillary column coupled to MS detector through EI interface was used for this study. The carrier gas was helium. The mass/charge measurement of fragments was determined by Chem. station Software. The identified compounds were then compared with software library.

Dissolved oxygen (DO) meter: Digital DO meter (Lovibond Senso Direct 150) was used for the measurement of dissolved oxygen in the samples.

Fourier transform infrared spectrophotometer: Fourier transform infrared spectrometry (FTIR) was used before and after treatments in order to identify their degraded end products. Before treatment the sample was subjected to analysis using FTIR spectrophotometer (U-2001, Shimadzu, Japan) at PCSIR Laboratories complex Lahore. Prior to analysis of irradiated samples, the aqueous irradiated samples were extracted with acetone. The organic phase were decanted and then dehydrated by MgSO₄ for 24 h. The organic phases was concentrated and stored for FTIR analysis.

Toxicological test

H₂O₂ removal from treated sample: To avoid the H₂O₂ toxic effect, it was important to eliminate it from irradiated solutions. To remove H₂O₂, small amounts of MnO₂ (< 1 mg/mL) were added to the solutions. After a reaction time of 1 h, the solution was filtered and subjected to the toxicity tests such as *A. cepa*, haemolytic, brine shrimp and ames bioassays. The *A. cepa*, brine shrimp and haemolytic test are used for cytotoxicity, while Ames test is used to evaluate the mutagenicity of tested samples.

Allium cepa root macro-analysis test: The root initiation and growth assessment was done using the procedure of

modified *Allium cepa* test. The bases of the bulbs were gently scrapped and root primordial were exposed to sample solution. The bulbs were planted directly on the effluents and their dilution without an initial rooting over water. All petroleum industrial wastewater and their dilution experiments were seeded in five replicates. Ultra-pure water was used as a negative control and 4×10^{-4} M of methyl methane sulfonate (MMS) Sigma-Aldrich, was used as a positive control.

Shrimp test: To check the effect of phenolic compounds on the living organisms like shrimps (*Artemiafranciscana*) shrimp test was done. These shrimps were exposed to the phenolic compounds to check the toxicity effect. Ultra-pure water was used as a negative control and 4×10^{-4} M of methyl methane sulfonate (MMS) Sigma-Aldrich, was used as a positive control.

RESULTS AND DISCUSSION

The aim of this work was to establish treatment methods for dyes degradation by advance oxidation process using radiation treatment *via* UV/ $\text{TiO}_2/\text{H}_2\text{O}_2$ and $\gamma/\text{H}_2\text{O}_2$. The advance oxidation process converts toxic organic pollutants to less toxic and environmental friendly products. The end products were analyzed by using UV/visible spectrophotometer, Fourier transform infrared spectroscopy and gas chromatography-mass spectroscopy (GC-MS). Model results were benchmarked to experimental data for optimization of treatment conditions. The samples collected were subjected to analyze the parameters such as pH, COD and TOC before and after treatment.

λ_{max} Determination: The aqueous solution of disperse red F_3BS showed maximum absorption (λ_{max}) in the visible region at wavelength of 5835 nm. Advance oxidation process by using UV in combination with H_2O and TiO_2 as well as γ -radiation in the presence of TiO_2 were carried out was carried out for the treatment of dye solutions having concentrations 50, 100 and 150 ppm as a model system. The effect of different operational parameters such as exposure time, pH and concentration range of H_2O_2 has been studied. The standard curve of dye can be seen in Fig. 2.

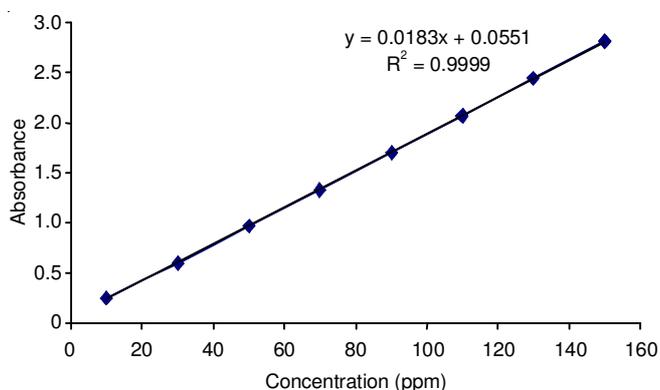


Fig. 2. Standard curve for aqueous solution of disperse red F_3BS , effect of H_2O_2 concentration in combination with ultra violet radiations on degradation of disperse red F_3BS

Fig. 3 showed the effect of H_2O_2 on degradation of disperse red F_3BS . Results showed that maximum degradation occurred

on 5 % H_2O_2 . It can be observed that the degradation increases with increasing concentration of hydrogen peroxide up to a point where it reaches a maximum and then starts decreasing. The combine effect of coupling the UV radiations with H_2O_2 were carried out for disperse red F_3BS solutions ranging from 50 to 150 ppm. The treatments were performed and optimized conditions were selected on basis of results. The UV radiation and different concentrations of H_2O_2 range from 3 to 7 % (Fig. 3). The result showed that when the UV radiation interacts with H_2O_2 the hemolytic degradation of H_2O_2 occurred resulted into the formation of two hydroxyl radicals that interact with molecules and break down of molecule occurred and intermediates, the final products were low molecular weight aliphatic acids as well as the CO_2 and H_2O_2 . It is evident from results that degradation is easily achieved as comparative COD reduction, due to the fact that the degradation obtained when big molecules are broken down to the smaller one but reduction COD occurred when small organic molecules further break.

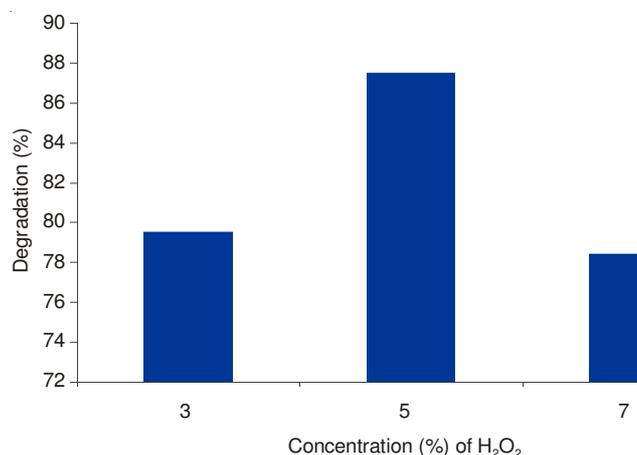


Fig. 3. Effect of H_2O_2 concentration on degradation of disperse red F_3BS

Degradation of disperse red F_3BS at different time:

Degradation of disperse red F_3BS with 5 % H_2O_2 at different reaction time has been carried out. It was observed that the reaction rate was average at the initial stage and almost 41.66 % disperse red F_3BS was removed within 90 min and 83.33 % disperse red F_3BS degradation took place within 90 min. No further notable degradation of sample was observed by extending the reaction time. This can be attributed to the relative high concentration. Experiments were carried out at different time intervals (30, 60 and 90) min. Results are given in Fig. 4 and showed that as time increased the efficiency of degrading sample increase upto 80 min. After 90 min the degradation efficiency was decrease. Optimum time for disperse red F_3BS is 90 min. After this time efficiency was decreased because when maximum level of degradation achieved then degraded product to combined and increase the absorbance.

pH of disperse red F_3BS solution after treatment: The pH results are shown in Fig. 5 which showed that as pH increased, the efficiency of degrading disperse red F_3BS decreased as well. Before treatment the solution was lightly basic and after treatment pH reduces significantly. From the results it is highlighted that the disperse red F_3BS molecules

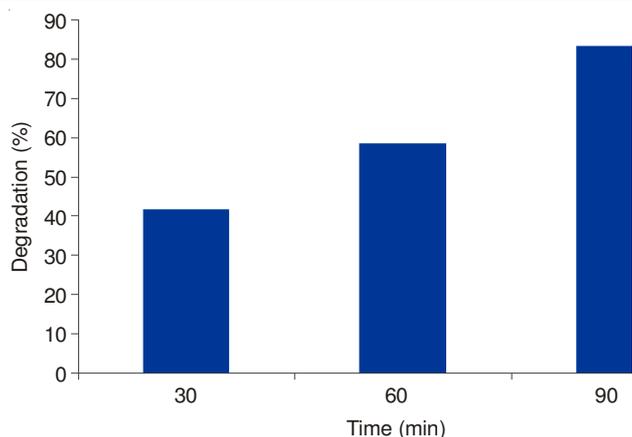


Fig. 4. Degradation of disperse red F₃BS at different time

are broken down to small fragments with the effect of UV/H₂O₂ and the possible products may be low molecular weight carboxylic acids. However the change in pH is an important parameter to justify the rationale behind the radiation treatment of samples. The pH value decreased after the radiation treatment as the organic molecule are broken down to simpler low molecular weight carboxylic acid, but after a certain dose the pH value stabilized and no further decrease was observed since further treatment may result into the formation of CO₂ and H₂O when OH[•] react with organic molecules. It is also concluded that maximum degradation occurred in the range of 5.2-5.9 pH and acidic pH favors the degradation process. Hence, pH favors the degradation process because acidic pH facilitates the OH radical and prevented to form OH₂[•] radical. Degradation decrease when OH₂[•] radical formed during reaction. Where in case of basic pH, bubbles produced in quartz cell and absorbance increase due to reaction with cell in basic media.

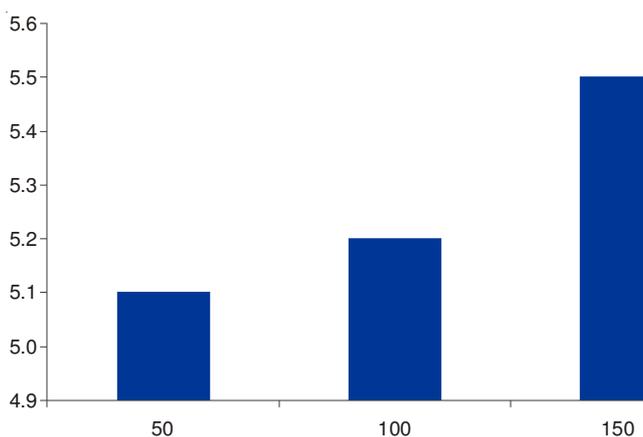


Fig. 5. pH for disperse red F₃BS after treatment

GC-MS studies of treated disperse red F₃BS aqueous solution: For the confirmation of results of UV/visible spectrophotometer and COD analyses, the treated samples were subjected to analyze by gas chromatography couples with mass spectrometry (GC-MS). The GC-MS profile clearly indicated that molecule has been completely broken down into CO₂ and H₂O or the fragments of low molecular weight which were determined by GC-MS system. The profile of disperse red

F₃BS for UV is shown in Fig. 6. Gas chromatographic-mass spectrometric study was also performed of sample treated with UV in the presence of H₂O₂ and TiO₂. When dye solution treated by UV radiation in the presence of H₂O₂ and TiO₂, the radiolytic end product were acidic units (acetic acid and other lower molecular carboxylic acids), which indicated that the dye was completely degraded in the presence of TiO₂ in addition to H₂O₂.

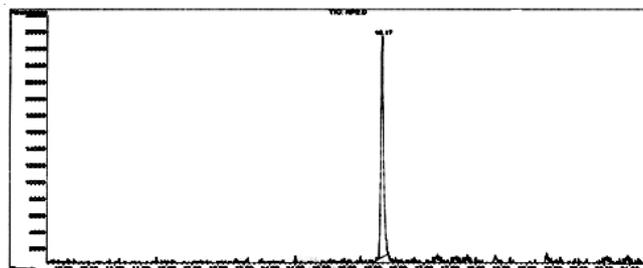


Fig. 6. GC-MS profile of disperse red F₃BS solution treated by UV in the presence of H₂O₂ and TiO₂

FTIR Studies of treated disperse red F₃BS aqueous solution: FTIR spectrum of irradiated solution by UV showed disappearance of peaks after treatment of dye solution treated by UV/H₂O₂/TiO₂. The FTIR profile of dye solution before treatment showed specific vibration peaks at 3800 cm⁻¹ (background peaks), 3700-3500 cm⁻¹ (OH str, free), 3600-3200 cm⁻¹ (OH str), 2915.16 cm⁻¹ (-CH stretch vibration), 1638.15 cm⁻¹ (vibration for alkenes with C=C stretching), 1460.39 cm⁻¹ (for alkanes with C-H deformation), 1381.08 cm⁻¹ (OH in plane), 1248.49 cm⁻¹ (C-C-OH str), 1099.80 cm⁻¹ (C-O Str vibration), 947.75 cm⁻¹ (for benzene ring with three adjacent H atoms, C-H deformation). The major peaks observed before treatment disappeared after treatment and some new peaks appeared after treatment which correspond to the end product detected. The FTIR spectrum of treated samples clearly indicates that disperse red F₃BS molecules have been degraded, which support the assumption that OH[•] bring about the chain oxidation reaction to break down complex molecule into simpler compounds. Therefore, our findings that reduction in COD and decrease of pH of the solution revealed the degradation of the disperse red F₃BS.

Conclusion

Advanced oxidation processes are proficient to treat pollutants, resistant to conventional methods. The advanced oxidation process by using TiO₂/UV/H₂O₂ has been carried out for treatment of model dyes.

The selected dyes were model systems were disperse red F₃BS commonly used in textile sector. The aqueous solutions having concentration 50, 100 and 150 ppm were subjected to treatment. The treatments involve the γ -radiation with H₂O₂ and UV in the presence of H₂O₂ and TiO₂. The powerful oxidants such as hydroxyl radicals generated during the treatment, degrade the dyes nonselectively by means of chain oxidation process and resultantly dye degradation and mineralization achieved satisfactorily. From the GC-MS analyses, it was revealed that the treatment has degraded the molecule into small fragment and upon further treatment the intermediates

also converted into simple compounds. The treatments using H₂O₂ and UV/H₂O₂/TiO₂ was improved the water quality parameters such as COD and BOD and values lies within the permissible limit recommended by environmental protection agency. This treatment degrade as well as eliminate the pollutants rather than transfer from one phase to other phase, no need for extra man power, eliminate the need of chemical addition repeatedly.

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