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Original Research

Efficient Removal and Conditions Optimization of Textile Dyes Using UV/TiO_2 Based Advanced Oxidation Process

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Abstract

Textile and other dye house effluents from different industries have many worst effects on aquatic as well as non-aquatic life. The present work was carried out for the conditions optimization of degradation of Allura Red AC dye. This was done by UV treatment and examining the effects of different parameters on degradation i.e. pH, concentration of the dye, temperature, radiation exposure time and concentration of TiO_2. The efficiency of the treatment was monitored by checking the highest degradation value, parameters of water quality such as chemical oxygen demand (COD), biological oxygen demand (BOD) and toxicity. The end products of degradation of dye were checked out by UV/visible spectrophotometer, Fourier transform- infra red (FT-IR) and gas chromatography-mass spectrometry (GC-MS) techniques. From the results, it was concluded that the degradation efficiency was in the order UV/H_2O_2/TiO_2> UV/H_2O_2> UV alone. Furthermore, it was also concluded that UV/H_2O_2/TiO_2 could be implemented on industrial scale for the removal of the toxic pollutants from industrial effluents.

Keywords: degradation, dyes, water quality, advanced oxidation process, environmental remediation

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Introduction

Dyes are organic compounds which are not easily degradable by ordinary methods. The reason behind the increased pollution by dyes is due to their extensive use in all industries ranging from textile to food. Their extensive uses have made them the major environmental pollutants [1, 2]. Almost all dyes have complex structural arrangement as well as they are much more stable than other molecules. That's why they are not easy to degrade to the permitted limits of environmental limits [3-5]. The recent era is an industrialized one, where many industries like paper, textile, food and cosmetics are using a variety of dyes to impose color to their products. Thus, discharging the wide range of pollutants in the environment cause many carcinogenic issues worldwide as well as creating problems with ground water. Azo dyes are being used extensively in all industries like paper, paint, food, drugs and textile. They can be identified by the azo group (-N=N-) or chromophores present in them which causes the presence of color. When this azo group is made to break, then their color is vanished. The removal of their color is due to the damaging of conjugation present in azo dyes [6]. Azo dyes are banned by world health organization (WHO) due to their carcinogenic side effects. Traditionally, these dyes are being used extensively in industries now a day. The dye Allura red is from the class of azo dyes which is extensively used in food and cosmetic industries worldwide. The main problem is the untreated wastewater of these dying industries having harmful effects on human activities as well as on marine life [7]. Textile and other industries are found to use large number of dyes and as a result they excrete very large amount of toxic waste in the water stream which not only affect the main stream of water supply but also have effects on the environment [4, 8]. Dyes are very complex and stable compounds. Therefore, their removal from wastewater is a difficult task and cannot be done by ordinary conventional treatments like mechanical screening, biological treatment, simple and bio-filtration [9]. Irradiation process is one of the most appropriate processes for the degradation of organic pollutants. In these processes UV or gamma radiations alone or with H_2O_2 or coupled with a catalyst show promising effects on degrading these carcinogenic and toxic compounds. This radiation process is called as advanced oxidation processes (AOPs). Intensity and exposure time of pollutants to the radiations depend mainly on the type of pollutants, their structure as well as the reactivity to produce the end products. Many other parameters like pH, concentration of dye and oxidizing agent (H_2O_2) and temperature also have direct effect on the degradation efficiency of the process [10, 11]. AOPs have become very important process for the treatment of dye wastewater. Another benefit of this process is that it produces significantly almost harmless end products as compared to the other traditional and classical treatment methods. The techniques which fall in AOPs are UV degradation process, gamma radiation treatment, Fenton and Photo-Fenton processes etc. The other available processes for degradation of dyes such as adsorption and coagulation are less effective due to the fact that they only turn the pollutant from on phase to another leaving it non-degraded and harmful [12]. All radiations processes for the treatment of pollutants (dyes) are classes of AOPs. The main mechanism of the work of these processes is to generate and then utilize a very strong and non-selectively reactive oxidizing agent such as hydroxyl group (·OH) for degradation of dyes to less toxic or non-toxic by products. Radiation processes are getting more significance in AOPs as they generate same amount of oxidizing (·OH and H_2O_2) as well as reducing agents (e_{aq}^- and H·). That is why these techniques are getting more attraction of scientists for the removal of industrial dyes and other pollutants [13]. The formation of this oxidizing agent can be elaborated by the following equations [9, 14].

$$H_2O_2 + hv\ (254\ nm) \rightarrow 2OH\cdot$$

The propagation step will be as follow:

$$H_2O_2 + OH\cdot \rightarrow OH_2\cdot + H_2O$$
$$H_2O_2 + H_2O \rightarrow OH_2\cdot OH + O_2$$

The termination step will be given as:

$$H_2O_2 + O_2 \rightarrow 2OH_2\cdot$$
$$H_2O_2 \rightarrow 2OH\cdot$$

The present work was carried out for the radiation degradation of Allura Red (AC) dye which is used in industries, especially food industries. The degradation of dye was done by UV alone, UV/H_2O_2 and then UV/H_2O_2/TiO_2 to evaluate the best degradation parameters by monitoring the water quality like COD, BOD and toxicity which are noted before and after each treatment. The end products after degradation were examined by FT-IR and GC-MS.

Materials and Methods

Allura Red (AC) dye was kindly supplied by Harris dyes and Chemicals Faisalabad and was used without purifying it further. Pure hydrogen peroxide (H_2O_2) was used. TiO_2 was used as catalyst. 1000 ppm stock solution of dye was prepared and then it was diluted to 50, 100 and 150 ppm concentrations separately. To study the effect of different parameters on degradation, the concentrations were varied such as for H_2O_2 (0.3 mL, 0.6 mL, 0.9 mL) and TiO_2 (0.2 g, 0.4 g, 0.6 g).

The solutions of Allura Red AC dye were treated with UV reactor with radiation of 254 nm and 144 watts' intensity. This process was repeated for all the sets of samples. The absorbance of each sample was noted before and after UV treatment at 502 nm which is λ_{max} of the dye solution. The relative effect of UV and $H_2O_2$and UV/H_2O_2/TiO_2 was evaluated by studying the parameter effects of different concentration of H_2O_2 and TiO_2. Percentage degradation was calculated by following formula:

$$\text{Degradation (\%)} = 1- C_0/C_i \times 100$$

Where, C_0 is absorbance of sample calculated before UV treatment and C_i is absorbance of sample calculated after UV treatment.

Fourier Transform Infrared Spectroscopy (FT-IR)

This technique was used to monitor the end products of degraded sample by applying it before and after UV radiation treatment at Central Hi-Tech Lab Govt. College University Faisalabad. Before UV treatment, the sample was analyzed by FT-IR and it was noticed that organic pollutant functional groups were present in UV region. The degraded sample was processed before the final FT-IR and it was extracted by acetone or chloroform as an organic phase by solvent extraction method. The sample was evaporated and the organic phase was concentrated and kept safe for further FT-IR treatment. FT-IR is a quick and appropriate technique not only due to find the functional groups present in the specific region but also due to its non-destructive behavior towards the model compound without changing its nature and without the necessity of any chemical species [15].

Gas Chromatography Mass Spectrometry (GC-MS)

Gas chromatography mass spectrometry (GC-MS) was performed at central Hi-Tech Lab Govt. College University Faisalabad. GC-MS was done to check the end products of the degraded sample. Before the treatment of GC-MS the irradiated sample was extracted by an organic phase (acetone). The organic phase was retained and kept for further treatment of GC-MS. The carrier gas (helium) was inert in nature. The graph obtained by GC-MS was evaluated on the basis of mass/charge ratio of the fragments generated by the degradation. The proposed degradation pathway of the dye is given in Fig. 1.

Removal of Hydrogen Peroxide

After the treatment of the samples, hydrogen peroxide was removed for further tests like toxicity. Removal of hydrogen peroxide is very important from irradiated samples. MnO_2 was added to the samples. This reaction was carried out for the time period of 60 minutes. After the completion of this reaction the sample was filtered and subjected to the toxicity tests.

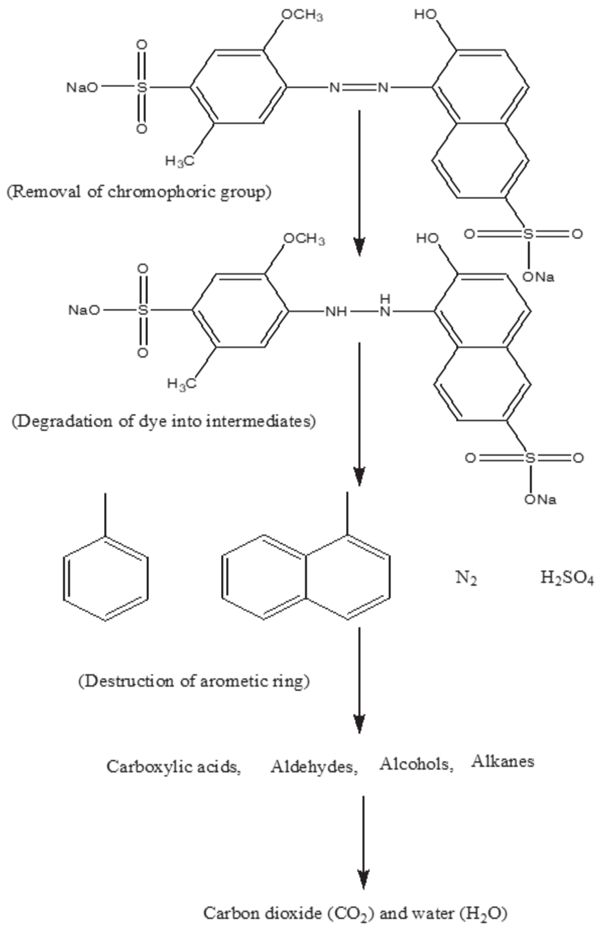

Fig. 1. Proposed pathway of degradation of Allura Red (AC) dye.

Results and Discussion

The main objective of the research work was to optimize the conditions for degradation of Allura Red dye solutions by UV radiation alone and with H_2O_2 and TiO_2. This method of degradation converts the dye molecule to less or non-toxic and environmentally acceptable by products. The end products of the degradation process were examined by UV/vis spectrophotometer, GC-MS, and FT-IR. The best degraded samples were marked for optimization of the experimental conditions. The samples collected from best degraded model samples were then subjected for checking different parameters such as pH, COD, BOD and toxicity. The operational factors affecting the degradation efficiency such as pH, dye concentration, concentration of H_2O_2, time were studied [16, 17].

Effect of pH

The data collected for pH of Allura Red dye indicated that the solutions of dye were slightly acidic in nature.

The pH measured for samples 50, 100, 150 ppm before UV treatment was 5.43, 6.18 and 6.27 respectively. When these solutions of dye were subjected to UV light then a slight change was observed in pH. The values for UV treated samples were 5.43, 6.63 and 5.48 for 30 min UV treatment, 5.39, 6.13 and 6.20 for 45 min UV treatment, 6.87, 6.81 and 6.75 for 60 min UV treatment for 50, 100 and 150 ppm solutions respectively. When these dye solutions were treated with UV/H_2O_2 there was an observation of decrease in pH that was 5.22, 4.71 and 4.61 for 30 min UV treatment, 4.59, 4.55 and 4.50 for 45 min UV treatment, 6.23, 6.18 and 6.08 for 60 min for 50, 100 and 150 ppm dye solutions respectively as shown in Fig. 2.

The pH of samples is increased due to the formation of low molecular weight carboxylic acids on degradation of dye molecules when OH radical reacts with organic molecules (dye molecules). The pH starts to decrease first and then become stable as at the end of degradation CO_2 and H_2O is formed. Similar results were examined by [18] which considerably explained that a slight change was observed in the dye solutions when UV treatment was carried out. Fig. 2 shows the effect of pH on % degradation of Allura Red dye.

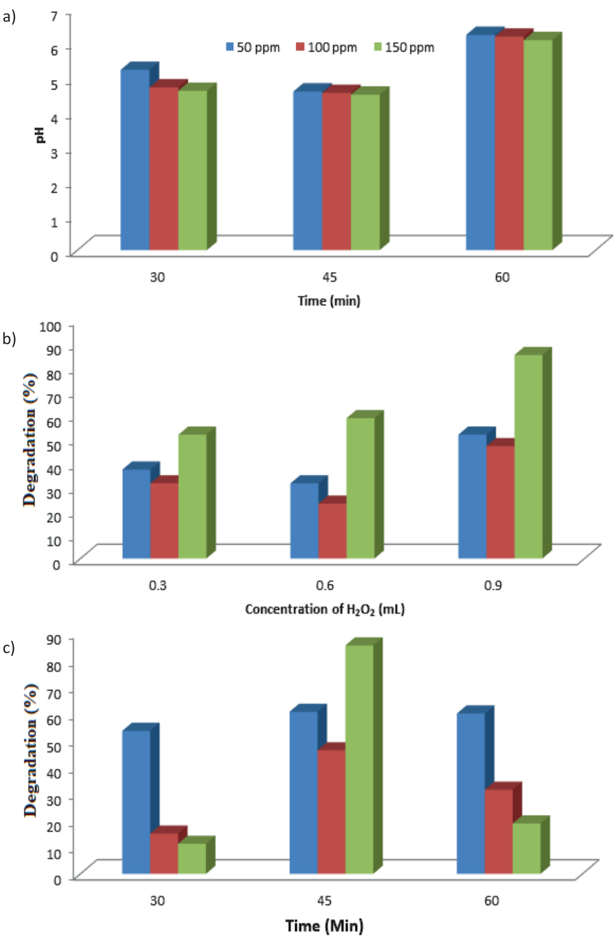

Fig. 2. Effects of a) UV/H_2O_2 on pH, b) H_2O_2 on degradation and c) time on degradation of different concentrations of Allura Red dye.

Effect of Dye Concentration

By keeping in mind, the importance of applications, it is very important to know the effect of initial dye concentration on the removal efficiency. The effect of initial concentration of Allura Red dye was monitored by evaluating the percent degradation of different concentration of dye i.e. 50, 100 and 150 ppm keeping other parameters like H_2O_2 and TiO_2constant. Table 1 show that the degradation of Allura Red dye decreased as concentration increased.

Effect of H_2O_2

Hydrogen peroxide is a strong oxidizing agent and it produced hydroxyl radical, when exposed to UV light source, which further reacted with dye molecule and caused the breakdown of organic dye molecule. The results obtained show that the maximum degradation occurred at 0.9 mL of H_2O_2 out of the selected concentrations 0.3, 0.6 and 0.9 mL. This indicated that by increasing the concentration of H_2O_2 the degradation of dye increased up to certain extent and then stopped because of the formation of low molecular weight smaller molecules. Fig. 2 clearly shows the effect of concentration of H_2O_2 on degradation of dye.

Effect of Time

Degradation of 150 ppm solution of Allura Red dye with 0.9 mL H_2O_2 was carried out at different time interval to check the effect of time on degradation efficiency. It was noted that at start the degradation increased up to 45 min and then decreased. This showed that the optimum time for best degradation was 45 min. As the degradation efficiency increased up to 45 min and then decreased. This was due to the formation of end products which then further reacts with each other after long interval of time and they increased the absorbance of the sample. Fig. 2 shows the effect time on the degradation of all three concentrations (50 ppm, 100 ppm, 150 ppm). After the results obtained from

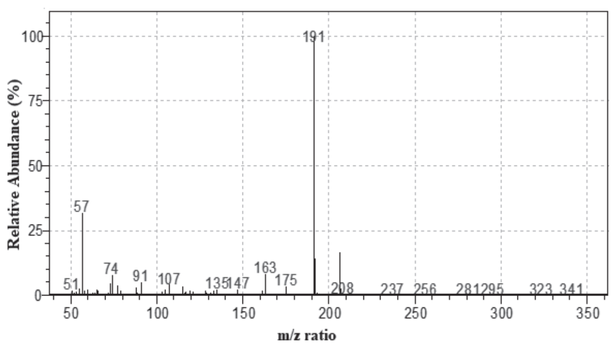

Fig. 3. GCMS Spectra showing the fragments of degraded sample of Allura Red dye.

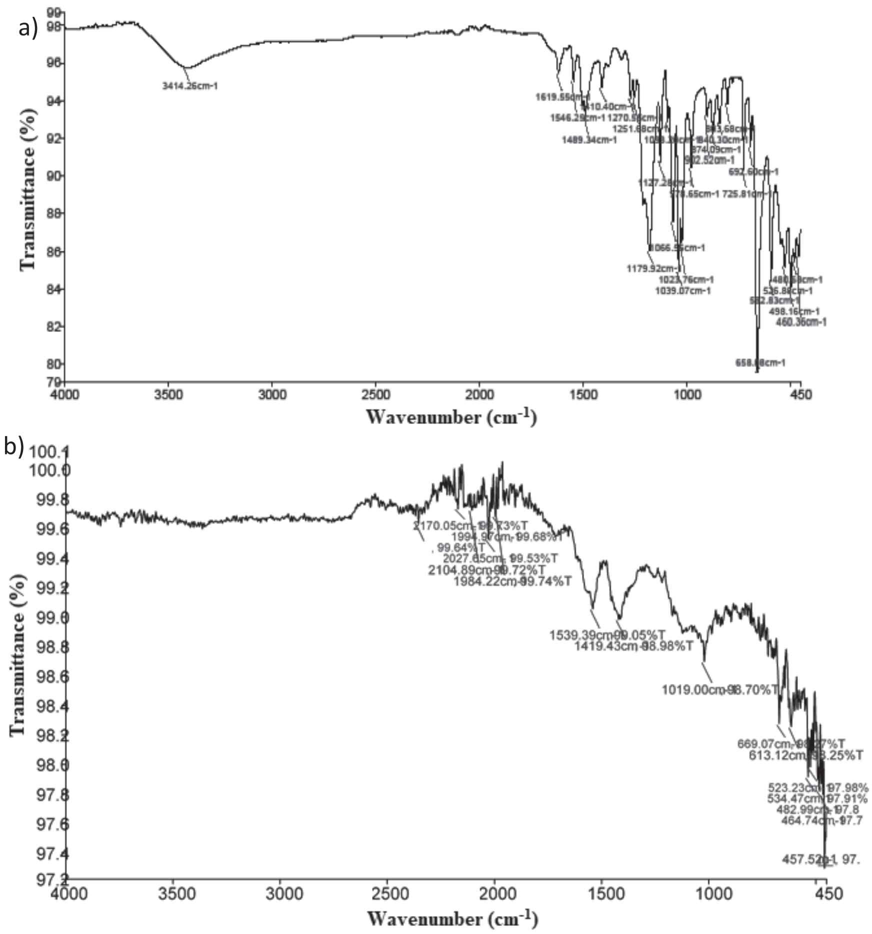

Fig. 4. FT-IR spectra illustrating the presence of various functional groups of Allura Red dye a) before UV treatment and b) degraded sample after UV treatment.

UV/vis spectrophotometer, COD, DO and toxicity analysis, it was necessary to confirm that either our sample was degraded or not, GC-MS studies were carried out. Samples treated by UV were then studied under the light of GC-MS results which clearly indicated that dye molecules were completely destroyed (Fig. 3). This was confirmed by the formation of H_2O, CO_2 and other low molecular weight aliphatic acids. Fig. 4 shows the FT-IR spectra before the degradation of dye. When dye was irradiated different functional groups disappear as a result of chemical reactions and appearance of some new functionalities [19, 20]. The FTIR of Allura Red dye has shown different vibration peaks at 3300 cm^{-1} for N-H stretching due to secondary amine that shows one band, 1669 cm^{-1} for C=N stretching, 1587 cm^{-1} N-H bending, 1350 cm^{-1} for C-N stretching, 1280 cm^{-1} C-N stretching due to primary amine, 1336 cm^{-1} C-N stretching due to diarylether, 1475 cm^{-1}, 1504 cm^{-1}, 1574 cm^{-1} for C=C stretching less than 1600cm^{-1} due to attachment of conjugated group with it and 3 to 4 band must be expected if aliphatic group is attached with it. After the irradiation process the dye sample was degraded and the effects of degradation was recorded in the spectra by the appearance and disappearance of different functional groups [21-22].

Conclusions

UV treatment has been conducted for the degradation of Allura Red (AC) dye. In UV treatment 50, 100, 150 ppm solutions were prepared. Firstly, UV alone then UV/H_2O_2 was applied to check degradation efficiency followed by $UV/H_2O_2/TiO_2$ for degrading the dye samples. During these two treatments, hydroxyl radicals of high activity were produced by the exposure of H_2O_2 to UV. The samples were found highly polluted before the treatment. After these treatments, pH, COD, BOD and toxicity of dye solutions were examined. It was noted that almost all the parameters were within the allowed limits by environmental protection agency (EPA) Pakistan. These treatments were found to be most efficient due to effective degradation of the pollutants. The treated wastewater can be reused by industries and hence play an important role in the economy of the country.

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Conflict of Interest

The authors declare no conflict of interest.

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