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Photo-degradation of monoazo dye blue 13 using advanced oxidation process

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ABSTRACT

The high energy radiation overcome the bonding of solute in a solution and H_2O_2 acts as an oxidizing agent and generates a free radical in the solution which results in photo-degradation by converting the solute in to simple form and resultantly, colored substance under the effect of photo-degradation becomes colorless. The photo-degradation of monoazo dye Blue 13 in an aqueous solution was investigated using a laboratory scale UV lamp in the presence of H_2O_2 and for maximum degradation of dye, the independent parameter UV power, UV exposure time, pH and H_2O_2 concentration were optimized. It was found that neither UV in the presence of H_2O_2 is able to degrade Blue 13 under optimum condition. The results revealed that the use of both UV and H_2O_2 have pronounced effect on the discoloration of dyes which could be used for management of textile effluents contain waste dyes.

Capsule Summary: Photo-degradation of monoazo dye blue 13 was investigated and advanced oxidation process showed promising efficiency for the treatment of dye as a function of pH and hydrogen peroxide.

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INTRODUCTION

Azo dyeing is a technique in which an insoluble azoic dye is produced directly onto or within the fibre. This is achieved by treating a fiber with both diazoic and coupling components. With suitable adjustment of dye bath conditions the two components of fiber and dye react to produce the required insoluble azo dye color. This technique of dyeing is unique, in that the final color is controlled by the choice of the diazoic and coupling components (Al-Kadsai and Guan, 2005; Muneer et al., 2012). But the azo dyes are found carcinogenic and now banned by World Health Organization, but traditionally azo dyes are being used in our dye industry now a day.

The main problem is the waste water of these dying industries which is disposed off into streams or rivers without any treatment and it not only affect humanity but also the marine life (Manzoor et al., 2013; Ullah et al., 2013). It is the need of time to invent such a method of treatment that degrade the azo groups in water so that they become other small basic molecule and do not harm the nature cycle. In the mean while the water we use will also become safer. The pH value is negative logarithm of hydrogen ion concentration, and has a value of 7 at 25 ^{0}C in pure water. The presence of alkali or acid may increase or decrease the pH (Alaton, 2003; Aleboyeg et al., 2005; Islam et al., 2014).

Although pH usually has no direct impact on consumers, it is one of the most important operational water quality parameter. Careful attention of pH control is necessary at all stage of water treatment to ensure satisfactory water clarification and disinfection. pH measurement in water provides a mean of classification of other characteristics or behavior such as corrosive activity or the inter linked factors controlling biological function in body (Ghandour et al., 1985). The structure of C.I Blue 13 Dye is given below

MATERIAL AND METHODS

Chemicals

The commercial CI Blue 13 dye was taken from a local supplier named Haris Dyes and Chemicals Faisalabad and no further purification was done to assure the real conditions at which the dye industry works and the water residual should contain same kind of impurities as it is on commercial scale. Hydrogen peroxide (H2O2) used was 35% V/V. The pH of dye solution was maintained by using dilute HCl (0.1M) and NaOH (0.1M) to the required value.

Effect of pH

The pH of each sample was determined by using pH meter (InoLab, wtw series, 720). The pH meter was calibrated by using standard buffer solutions (pH= 10.00 and 7.00) prior to determine the pH of samples. The pH of the samples was measured before and after the UV irradiation.

Determination of maximum wavelength λ_{max}

The maximum wavelength of the dye was determined by using HITACHI U-2800 double beam spectrophotometer. The dye solution was introduced into the sample cell and then spectrophotometer was scanned through all the visible range (780-380nm) of light. The peak of the graph plotted by spectrophotometer shows the wavelength at which the maximum light was absorbed by the sample.

Measurement of absorbance of each sample at λ_{max}

To determine the absorbance of each dye sample at λmax by using spectrophotometer, each solution was scanned at the λmax of CI Blue 13. The spectrophotometer was calibrated by using the distilled water in both reference and sample cells and then absorbance of dye sample at λmax was measured by introducing the dye solution into sample cell instead of distilled water.

Effect of UV light Intensity

To see how the UV light intensity effects the photo-degradation three UV-A tube rods all 6 W and of 254nm were used in UV reactor. Switching on 1, 2 or 3 rods simultaneously 6, 12 and 18 W intensity of UV-A light of 254nm was obtained. In this way the effect of UV light intensity (6, 12, 18 W) was determined by switching on 1, 2 or 3 rods respectively.

RESULTS AND DISCUSSION

The dye sample was analyzed for pH, and colour intensity before and after treatment with UV, H2O2 and UV/H2O2 and response of dye degradation are shown in Fig. 1 and 2. It was revealed from the data that the absorbance of the dye sample was 1.028 at λmax 568nm. After treatment it was observed that there was 0.49-2.43% discoloration when treated with the UV radiation of 6W for different interval of time respectively. Then by changing the UV radiation intensity to 12W, there was 0.88-4.86% discoloration in the dye solution. Bby changing the UV radiation intensity to 18 W, 1.26-7.30% discoloration in dye solution was observed. Similarly, in case of H_2O_2 used alone, 1.46-7.00% discoloration was observed with different concentration of H_2O_2 respectively. But when a combination of H_2O_2 and UV radiation is used, the discoloration jumps to 17.41-34.24% at 6W UV radiation intensity with different concentration of H_2O_2 and different interval of irradiation time. Similarly, 34.82-66.47% discoloration was observed when 12W UV radiation intensity with different concentration of H_2O_2 and different interval of time is used. Hence, discoloration reaches to 52.24-99.71% when 18 W UV radiation intensity with different concentration of H_2O_2 and different interval of time is used.

It is clear from the results that direct UV photolysis of 254 nm cannot cause a considerable discoloration of the dye by promoting the dye molecules to an excited state. This may be attributed that molecules in exited state have a very short lifetime; they return to the ground state or decompose to yield different molecules (Andreozzi et al., 2000). During this process hydroxyl radical generates, which can destruct the azo group present in the dyes as well as oxidation which cause mineralization and degradation of dye structure.

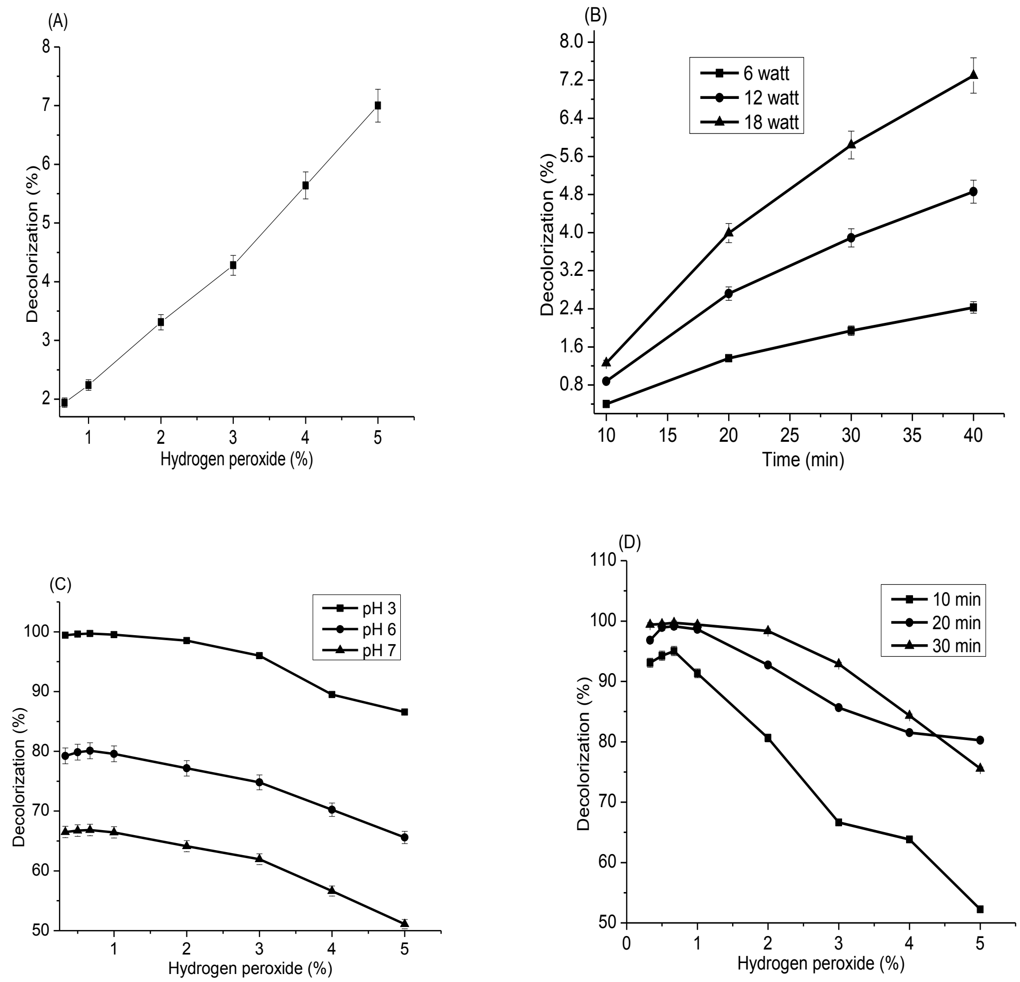

Fig. 1: Degradation of blue 13 at different hydrogen peroxide concentration, pHs and UV exposure time

The hydroxyl radicals are short-lived and are highly reactive species that react non-selectively with organic matter present in wastewater. These radicals oxidize organic compounds producing organic radicals, which are highly reactive and undergo further oxidation (Basfar and Rahim, 2002). The pH of the sample was 7.86. The sample was treated with H_2O_2 and again pH was observed. The measurement of the sample pH before and after treatment showed that the pH difference was almost negligible i.e. pH was decreased slightly8 which was due to the formation of acids in response of dye degradation and resultantly pH of solution may decrease. For finding the optimum pH conditioned, three different pH parameters in UV radiation for 40 minutes were compared and interpreted. It was observed that at pH 7.86, maximum discoloration (99.708%) occurs by using 0.67% H_2O_2 and 18W intensity of UV light. While keeping the same parameters at pH 6 the discoloration rate was > 90% and at pH 9 the discoloration rate was 80%, respectively (Iqbal et al., 2014).

Effect of H_2O_2 dosage: The effect of H_2O_2 dosage on the discoloration efficiency was investigated, while stabilizing all other conditions of the reaction. It can be seen that the discoloration efficiency first increases with increasing H_2O_2 dose up to a certain point, and then starts to decrease. In the discoloration of C.I. black 5 the same behavior has been reported previously. This behavior is due to the fact that H_2O_2 is a scavenger for hydroxyl radicals according to the reaction given in the following equation (Bilal et al., 2014).

Initiation:

$OH^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O$

Propagation:

$H_2O_2 + O_2H^{\bullet} \rightarrow OH^{\bullet} + H_2O$

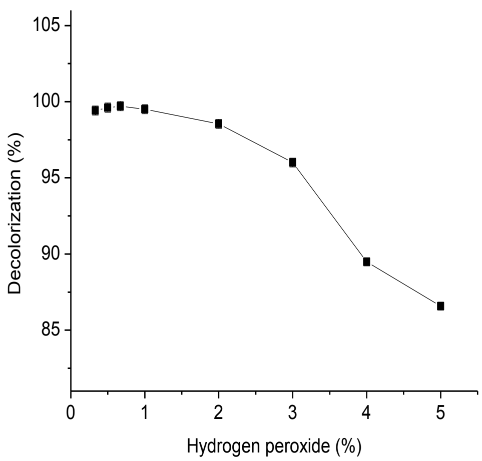

Fig. 2: Degradation of blue 13 at different hydrogen peroxide concentration, pHs (7.86) and UV exposure time (30 min), UV intensity (18 watt)

Termination:
$OH^{\bullet} + OH^{\bullet} \rightarrow H_2O_2$
$O_2H^{\bullet} + O_2H^{\bullet} \rightarrow H2O2 + O_2$
$OH^{\bullet} + O_2H^{\bullet} \rightarrow H_2O + O_2$
When enough H2O2 is present in the solution, it starts to compete with the dye for reaction with hydroxyl radicals. Since $HO^{\bullet}{}_2$ is less reactive than the $OH^{\bullet}$ radical. An increased level of H_2O_2 has a diminishing effect on the reaction rate10. In addition, the $OH^{\bullet}$ radicals generated at a high local concentration will readily dimerize to H_2O_2. Therefore, it is important to optimize the applied dose of H_2O_2 to maximize the performance of the UV/H_2O_2 process and minimize the treatment cost. The optimum dose of H_2O_2 for this experiment is 0.67% where the discoloration efficiency reached 99.70%, whereas above this dose the discoloration efficiency goes on decreasing and reaches to 86.57% when 5% H_2O_2 was used. The H_2O_2 concentration is an important parameter to adjust and control the discoloration of dyes in the UV/H_2O_2 reactor. Degradation of the color is due to the hydroxyl radicals generated upon photolysis of H_2O_2. Several studies have proposed different reaction mechanisms for this photolysis. It is widely accepted that the main interaction between H_2O_2 with UV radiation and free radicals are well represented by the above reactions (Aleboyeh et al., 2005).

Effect of UV intensity

The effect of the UV radiation intensity on the discoloration efficiency was also studied, by treating the samples in (6, 12 & 18W) UV chamber. The results have shown that UV radiation intensity enhanced the dye degradation non significantly which may be due the unavailability of hydroxyl radicals. At low UV radiation intensity, the rate of photolysis of H2O2 into hydroxyl radical (H_2O_2 hv $\rightarrow 2^{\bullet}OH$) is reduced12.

The results have shown 99.70% discoloration at 18W UV, 66.47% at 12W and 33.23% at 6W UV radiation intensity. So we can see that the maximum discoloration is
obtained at 18W intensity, and subsequently rate of discoloration is going to decrease with decrease in UV irradiation13. It is clear from the results that maximum discoloration was obtained at 0.67% H_2O_2 dosage. From the above discussed results we can conclude that the discoloration efficiency is directly proportional to the intensity of applied UV light and H_2O_2 concentration14.

Effect of pH on discoloration efficiency

The effect of pH on the discoloration efficiency of the blue dye solution was studied by stabilizing all the other conditions and only varying the pH of the dye solution. At the original pH (pH=7.86) conditions of the dye solution, removal efficiency was 99.70%, while increasing the pH (e.g. pH 9) of the dye solution, led to a decrease in the dye removal efficiency to 94.50%. So it can be concluded that the pH increase leads to a decrease in the discoloration efficiency. In the same way, decreasing the pH (e.g. pH 6) of the dye solution, led to a decrease in the dye removal efficiency to 92.14%. From the above results it is concluded that the discoloration efficiency decrease when the pH of the dye solution either increased or decreased.

Effect of time on discoloration efficiency

UV exposure time also has a significant effect on the discoloration of the dye. Greater the exposure time higher was the discoloration of the dye solution (Iqbal et al., 2014). It means that the discoloration of dye solution is directly proportional to the exposure time of UV radiation. It is well known that when the hydroxyl radicals produced in the initiation step, they shift the dye molecules to the exited state and the dye molecules destroy due to breakage of the Azo bond. The UV radiations continuously take the dye molecules to the exited state, and the hydroxyl group destroys them on reaching the ground state again. If a dye solution remains more time in UV chamber, it means that more dye molecules are destroyed, which means the more discoloration and more water purification can occur.

CONCLUSIONS

The dye CI-13 blue showed higher discoloration i.e. 99.70% at 0.67% H_2O_2 using 18 W intensity of UV light for 40 min at 7.86 pH. Overall, it was observed that dye solution could be degraded effectively; however, the optimization of independent variable such as UV intensity, UV exposure time, initial pH and H_2O_2 concentration is compulsory. By optimizing the variable, complete degradation of dye can be achieved and photo-catalytic technique could be used successfully for the management of textile effluents contains waste dyes.

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