Degradation Study of C.I. Reactive Yellow 145 by Advanced Oxidation Process

Tanveer Hussain Bokhari[1,*], Muhammad Kashif[1], Ijaz Ahmad Bhatti[2], Muhammad Zubair[1], Shahid Adeel[1],
Muhammad Yousaf[1], Matloob Ahmad[1], Munwar Iqbal[2], Muhammad Usman[1], Muhammad Zuber[3] and Asim Mansha[1]

[1]Department of Chemistry, Government College University, Faisalabad-38000, Pakistan
[2]Department of Chemistry and Biochemistry, Agriculture University, Faisalabad, Pakistan
[3]Department of Applied Chemistry, Government College University, Faisalabad-38000, Pakistan

*Corresponding author: E-mail: tanveer.bokhari@yahoo.com

Advance oxidation processes hold great promise for the degradation and mineralization of textile dye and effluent. The degradation of C.I reactive yellow 145 dye at different conditions was carried out in order to assess the effectiveness and feasibility of the combined UV/ H_2O_2 system for purification of water. The operating parameters such as hydrogen peroxide dose, pH value, UV exposure time and initial concentration of reactive yellow 145 dye were evaluated. The degradation efficiency increased nonlinearly with increasing UV light intensity and hydrogen peroxide dosage. The observation of obtained results clearly demonstrated the importance of choosing the optimum degradation parameters to obtain a high degradation rate, which was essential for any practical application of photo degradation process. The degradation of reactive yellow 145 observed up to 98 % for the optimized levels of operation variables. It has been concluded that this process can be used as an efficient and environmental friendly technique for effluent treatment of industrial wastewater containing dyes from textile industry. Development of this technology is of great importance as the existing technology in textile industry is not efficient for treating the wastewaters resulting in discharge of coloured water into rivers and public sewage system which is a health hazard.

Key Words: Reactive yellow, Azo dye, Advanced oxidation process, Ultraviolet radiation and hydrogen peroxide.

INTRODUCTION

Synthetic dyes have great importance in textile industry, paper, pulp manufacturing, cosmetic, food, biological stains, printing, pharmaceutical industries and laboratories. The waste from these industries causes the water bodies to become coloured and disturb the natural growth activity of aquatic life by blocking sunlight and re-oxygenation capacity of water. Azo dyes are found to have their passage to drinking water that is harmful to humans as some of these dyes are carcinogenic and mutagenic in nature. It is thus necessary to remove them from water bodies or treat them in different ways, minimizing their hazardous effect to aquatic life as well as the human life. Azo dyes are very stable to ultraviolet and visible light irradiation. Moreover, they are resistant to aerobic degradation[1] and can be reduced to potentially carcinogenic aromatic amines under anaerobic conditions or *in vivo*[2]. About 1-20 % of the total synthetic dyes in the world is lost during the dyeing process and is released in the textile effluents[3,4]. Chlorination and ozonation have been used for the removal of certain dyes but they work at slow rates, as well as have high operating costs[5]. There is a dire need to establish method(s) to treat and eliminate pollutants from water and wastewater.

Different approaches have been suggested to tackle the removal of dyes from aqueous solution. Among the widely used ones are the adsorption methods, biological degradation, coagulation processes and the ozone and hypochlorite treatment of dye waste effluents[6-8]. All these methods are either costly, inefficient or result in the production of secondary waste product. Among these methods some are nondestructive; they transfer organic compounds from one phase to another phase and cause secondary pollution problem and other needs chemicals, adsorbents, or catalysts resulting in high operating costs[9]. Recent progress on this frontier has led to study the feasibility of using advanced oxidation processes (AOP)[10]. Among the promising methods in this category, utilizes a reagent which is a mixture of H_2O_2 and Fe_2C, commonly known as the Fenton's reagent[11]. There are quite a few studies on the usage of this reagent with the aim to degrade a particular species under consideration[12-14]. Additionally, Fenton's reagent in the presence of UV radiation, a process called as photo-Fenton reaction, has also been studied and has shown promising results[15].

The purpose of the present study was degradation of reactive yellow 145 dye with the help of advanced oxidation process. Different parameters such as pH, doses of hydrogen

peroxide, time for degradation and dye concentration were evaluated during this study. The degradation efficiency was analyzed by using ultraviolet/visible spectrophotometer.

EXPERIMENTAL

Hydrogen peroxide was purchased from Fluka, Germany (35 % w/w), $K_2Cr_2O_7$, ferrous ammonium sulphate (FAS), NaOH and H_2SO_4 were purchased from Merck, Germany. All the chemicals were of analytical grade, double distilled water was used for the preparation of solutions. The authentic RY 145 dye (m.f.: $C_{28}H_{20}ClN_9O_{16}S_5Na_4$ and m.w.: 1026.25 g/Mol) was obtained from Harris dyes and chemical and used without further purification. The molecular structure of RY 145 is shown in Fig. 1.
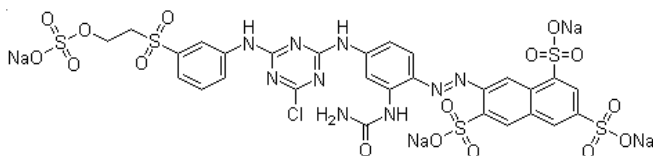

Fig. 1. Molecular structure of yellow ME2RL(C.I. reactive yellow 145)

Treatment of samples: The aqeous samples of dye were treated by batch UV photo reactor emitting radiation having wavelength of 254 nm, 180 watt intensity, in presence and in the absence of H_2O_2 for different time intervals 20-60 min. The combined effect of H_2O_2 and UV also studied by adding different concentration (2-10 mM) of H_2O_2 and UV irradiation time for the removal of colour substances as well as minimizing chemical oxygen demand (COD)[5]. Three concentration of dye solution of 50, 100 and 150 ppm were prepared form 1000 ppm stock solution in distilled water. The absorbance of different concentrations of dye solution was recorded and determined the λ_{max}[16]. Then 10 mL dye solution was taken into UV reactor and irradiated under various condition and optimized the operating variable for maximum dye degradation. After treatment, the absorbance were checked regularly for degradation determination at λ_{max}. Different concentration of dye and different percentages of hydrogen peroxide were used and the results were verified by applying T-test and by standard deviation, to check the significance of data[17].

Statistical analysis: The data obtained was analyzed statically to check the efficiency of method[18].

Decolorization of dye was measured by following formula[19]

$$\text{Decolorization (\%)} = \frac{\text{Initial ABS} * - \text{Final ABS} *}{\text{Initial ABS} *}$$

The standard deviation was found by the following formula[20].

$$\sigma = \sqrt{\frac{\Sigma(x - \bar{x})^2}{n}}$$

The verification of obtained results and standard deviation, the T-test was applied. The T-test is used for verification of our results. The formula of T-test is given below[21].

$$t = \frac{\bar{x} - \mu_0}{\frac{s}{\sqrt{n}}}$$

RESULTS AND DISCUSSION

It has been investigated that the bonding of azo compounds can be directly degraded by ultraviolet radiation, but this seems to be a slow process that could be significantly enhanced in the presence of hydrogen peroxide. By exposing to ultraviolet light, hydrogen peroxide is quickly dissociated, producing hydroxyl radicals, a non-selective and influential oxidant, which is accountable for the dye disintegration very quickly[22]. Although the degradation rate generally depends on the particular type of the dye, ultraviolet/hydrogen peroxide procedure can easily be applied to any industrial wastewater containing azo group (-N=N-). The process is optimized by the changing the parameters. The obtained results can be considered as a starting step to create the economical viability of the process, defining earlier the extent of destruction desirable for the next application of the wastewater. The choice of the method from different advanced oxidation processes's is dictated by the compromise between the economy and the desired final quality of the water[23]. Advanced oxidation process, ultraviolet/ hydrogen peroxide process has been proved to be the most influential method for degradation of dyes. Removal of dyes has been sensitive to the operational parameters. For photo destruction an optimum dose of hydrogen peroxide has been found to give a suitable rate constant, beyond the critical hydrogen peroxide dose the oxidation rate reached a maximum value[24]. Degradation of dye by photo-oxidative process in the ultraviolet/hydrogen peroxide proved to be a promising wastewater treatment technology. In the experiments, the important outcome was the finding of optimum hydrogen peroxide concentration in the ultraviolet/hydrogen peroxide system. Usually, by increasing the initial concentration of hydrogen peroxide, the decomposition rate of dye increased. But an optimum value of initial concentration is reached, at which the reaction rate is higher. If the concentration was overdosed with the optimum, the degradation rate decreased reversely[25].

It was observed through experimental results that the ultraviolet/hydrogen peroxide process proved to be a reasonable pretreatment method for degradation of dye wastewater from textile industries under the appropriate operating conditions such as pH, dye concentration, ultraviolet intensity and hydrogen peroxide concentration[26]. It was found that best degradation was obtained at low pH (acidic condition). Bleaching rate was increased when ultraviolet/hydrogen peroxide was also present, but the rate was slow when treated with ultraviolet radiation alone. The results showed that the decolorization mostly increases as the initial hydrogen peroxide concentration enhanced to some extant[27].

Maximum wavelength (λ_{max}): Maximum wavelength was determined with the help of double beam spectrophotometer (Cecil CE 7200, Germany). The solution was taken in sample cell scanned the spectrophotometer though the visible range (800-350 nm) of light. The highest peak obtained illustrates the maximum light that is absorbed[28]. Before treatment, the maximum wavelength obtained for reactive yellow 145 is approximately 418 nm. λ_{max} for different concentrations is shown in Fig. 2.

Effect of hydrogen peroxide dose: The effect of hydrogen peroxide dosage (ranging from 0.03-0.07 mL) on the degradation
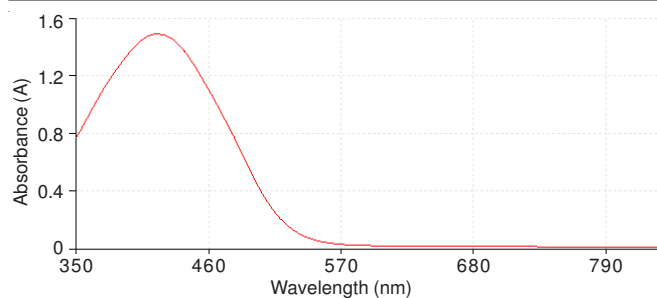
Fig. 2. λ_{max} of 150 ppm solution of reactive yellow 145

was analyzed by stabilizing all other conditions of the reaction and only altering the hydrogen peroxide doses[29]. The conditions of the treatment experiment were ultraviolet power 24 Watt, dye concentration 50 ppm, 100 ppm and 150 ppm, reaction time 1 h, pH 3.0 and volume of the dye solution 10 mL. The results from the irradiation of the C.I. reactive yellow 145 dye using different concentrations of hydrogen peroxide had shown that the colour removal efficiency was increased with increasing hydrogen peroxide concentration (Fig. 3). If the concentration was overdosed with the optimum, the degradation rate decreased reversely[25]. Degradation by addition of hydrogen peroxide was due to increase in the hydroxyl radical concentration[30]. At low concentration hydrogen peroxide is not able to generate enough hydroxyl radicals and the removal rate is limited. At high hydrogen peroxide concentration hydrogen peroxide acts as a hydroxyl radical quencher consequently lowering the hydroxyl radical concentration[31].
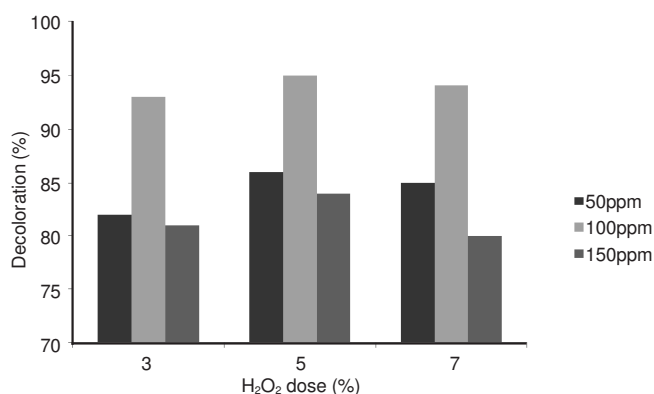

Fig. 3. Comparison of % decolorization of reactive yellow 145 50, 100 and 150 ppm at different dose of hydrogen peroxide
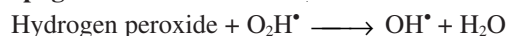
With increasing hydrogen peroxide concentration more hydroxyl radicals are available to attack the aromatic rings and the rate of reaction increases and above 5 % hydrogen peroxide of dye solution (0.05 mL), hydroxyl radical ($OH^{\bullet}$) efficiently reacts with hydrogen peroxide and produces $HO_2^{\bullet}$. Because $HO_2^{\bullet}$ radicals are less reactive than $OH^{\bullet}$, increasing $HO_2^{\bullet}$ results in negligible contribution in the dye destruction[32].

Following chain reaction usually takes place while using hydrogen peroxide as an oxidizing agent in the presence of ultraviolet light[33].
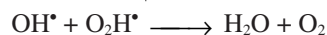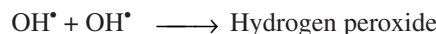
Initiation:

$$OH^{\bullet} + \text{Hydrogen peroxide} \longrightarrow HO_2^{\bullet} + H_2O$$

Propagation:

$$\text{Hydrogen peroxide} + O_2H^{\bullet} \longrightarrow OH^{\bullet} + H_2O$$

Termination:

$$OH^{\bullet} + OH^{\bullet} \longrightarrow \text{Hydrogen peroxide}$$

$$O_2H^{\bullet} + O_2H^{\bullet} \longrightarrow \text{Hydrogen peroxide} + O_2$$

$$OH^{\bullet} + O_2H^{\bullet} \longrightarrow H_2O + O_2$$

In addition, the $OH^{\bullet}$ radicals generated at a high local concentration would readily dimerize to hydrogen peroxide. Therefore, it should be important to optimize the applied dose of hydrogen peroxide in order to maximize the performance of the ultraviolet/hydrogen peroxide process and minimize the treatment cost. The optimum dose for this experiment is 0.05 cm^3 (5 wt %), whereas above this dose the decolorization efficiency goes on decreasing. Effect of hydrogen peroxide doses is shown with the help of Fig. 2. The 5 % hydrogen peroxide concentration by weight was found to very effective point for degradation of dye (> 95 % degradation) in the ultraviolet/hydrogen peroxide reactor.

Effect of pH on dye aqueous solution degradation: The dye aqueous discharged form industry has different pH values, so, the optimization is very important for degradation of dye and the pH effect on the degradation was carried out at pH ranges form 3-11. It was found, degradation of dye was increased by decreasing the pH (Fig. 4). The maximum degradation was found[34] at pH 3. It was found that effective dye decolorization correspond to at dependent upon the pH of the solution. The rate of C.I. reactive yellow 145 degradation was faster in acidic pH than in neutral or alkaline system, because under acidic pH, $OH^{\bullet}$ found to be predominant reactive oxidant and under alkaline pH, OH formed by reaction of hydroxyl radicals with hydrogen peroxide. These hydroperoxyl radicals don't have as high oxidizing power as $OH^{\bullet}$.
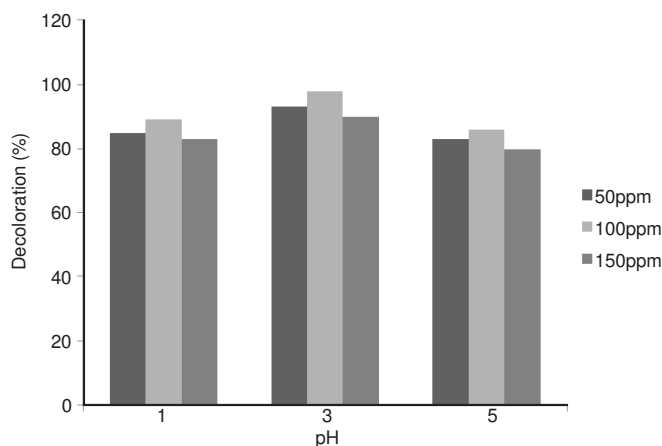

Fig. 4. Comparison of % decolorization of reactive yellow 145 50, 100 and 150 ppm at different pH values

Effect of initial dye concentration on degradation: It was seen that the photo-oxidation efficiency was lessened as initial dye concentration increased and hydrogen peroxide concentration was kept same. This might be due to the molar extinction coefficient of the dye is very high and as a result, the solution became deceptive to ultraviolet radiation[35]. For investigation of the effect of initial dye concentration on the dye decolorization, the initial dye concentration was varied by keeping the other variable same. It was found that the initial

rate increased with increase in initial dye concentration from but decreased when the initial dye concentration was greater than 100 ppm[36]. The obtained results have indicated that the photodegradation rate of C.I. reactive yellow 145 was enhanced (Fig. 5).
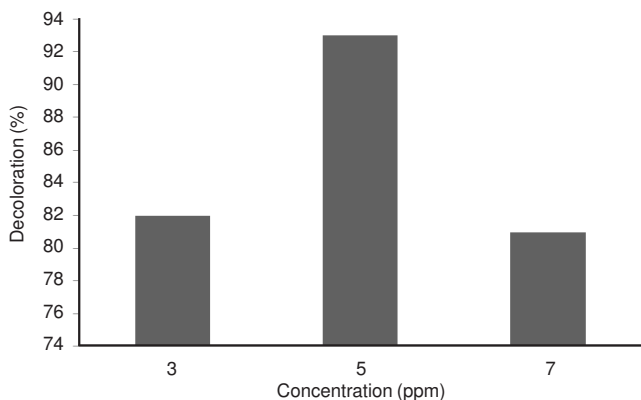

Fig. 5.   Comparison of % decoloration of reactive yellow 145 50, 100 and 150 ppm

Effect of ultraviolet intensity on dye degradation: The effect of ultraviolet light power on the decolorization of C.I RY 145 dye was also investigated. Ultraviolet light irradiates H_2O_2 to degrade dye very quickly because the concentration of OH radical increased. The colour removal rate increased with incrementing ultraviolet light power which may be the reason that ultraviolet light resulted higher OH radical generation[26]. The concentration of dye against time for experiments was carried out with ultraviolet radiation. The loss in colour of sample can be related to the production of hydroxyl radicals, which acts as a powerful oxidizing agent. The pH measurement at the end of the ultraviolet/hydrogen peroxide process showed that the dye solution became slightly acidic and remained constant after 1 h of irradiation. This may be due to the production of organic and inorganic acid anions[35]. The effect of different ultraviolet light intensity on the degradation rate of dye was observed and the degradation of dye was greatly accelerated by increase of ultraviolet intensity, indicating that ultraviolet light had an important impact on the degradation of dye (Fig. 6).
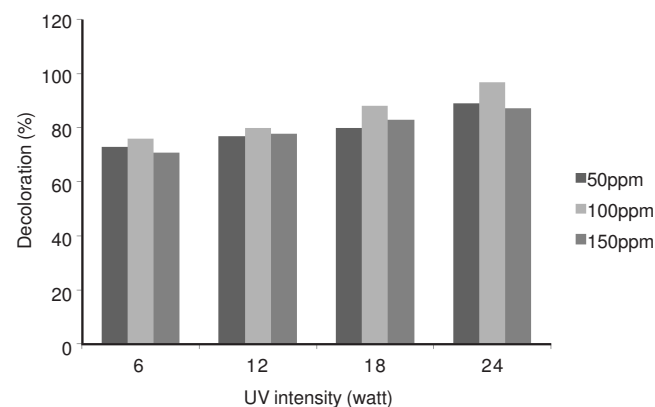

Fig. 6.   Comparison of % decolorization of reactive yellow 145 50, 100 and 150 ppm at different UV intensity

Effect of reaction time on dye degradation: The degradation of C.I reactive yellow 145 dye at different reaction times

has been carried out. It was observed that the reaction rate was fast at the initial stage and almost 65 % C.I reactive yellow 145 was removed within 10 min and 98 % of C.I. reactive yellow 145 removal took place within 1 h. No further notable degradation of dye was observed by extending the reaction time. This can be attributed to the relative high concentrations[29]. As the oxidation reactions proceeded, it gave rise to the appearance of a series of intermediates whose competitive effect inhibited the degradation of dye. Based on the result, the reaction time for the ultraviolet/hydrogen peroxide oxidation of C.I reactive yellow 145 in batch reactor was determined to be 1 h for evaluating other parameters and after 1 h irradiation the degradation was very slow and non significant response was observed. Effect of time on decolorization process is summarized in Fig. 7. UV-spectra of degraded dye is shown in Fig. 8.
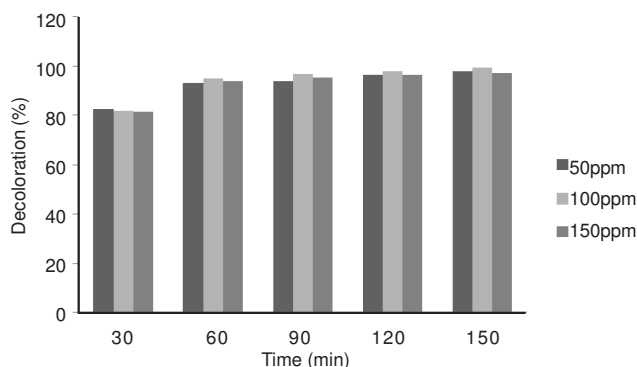

Fig. 7.   Comparison of % decolorization of reactive yellow 145 50, 100 and 150 ppm at different interval of time
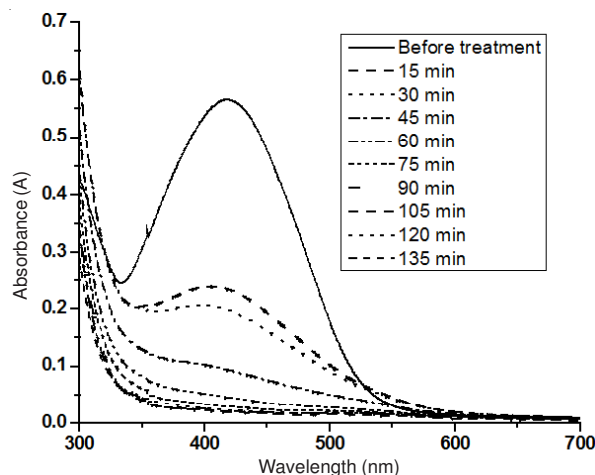

Fig. 8.   UV spectra of degraded reactive yellow 145 from 15-135 min at Shaking speed = 100 rpm, UV intensity = 24 watt, pH = 3 and H_2O_2 = 5 % in solution

Effect of shaking speed on degradation: Shaking speed has very little effect on degradation rate. But as the shaking speed is increased, the degradation also increases. This increase was very small. This is due to the fact that as the shaking speed increases, the molecules in the solution are in continuous motion and the chance of collision of molecules is increased. As the collision increases, rate of reaction also increases. So degradation rate is increased by increasing the shaking speed (Fig. 9).
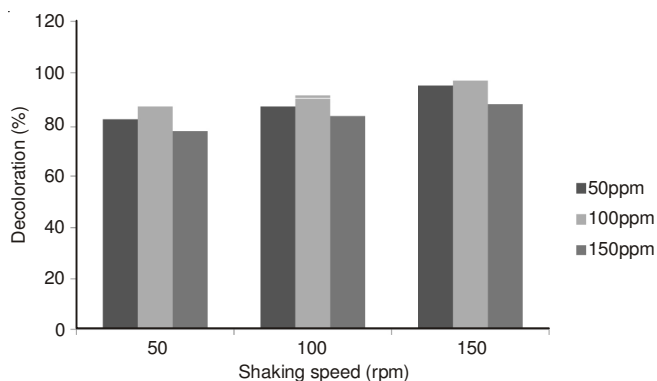
Fig. 9. Comparison of % decolorization of reactive yellow 145 50, 100 and 150 ppm at different shaking speed

Conclusion

The aqueous containing C.I reactive yellow 145 dye using ultraviolet/hydrogen peroxide treatment was investigated. The conditions like ultraviolet, hydrogen peroxide, time, pH and concentration was optimized to get maximum degradation of dye under optimized conditions. The optimal design was used for optimization in combination response surface methodology. The photo-oxidation of C.I. reactive yellow 145 dye was monitored spectrophotometerically. The dye decolorization found to be dependent on its concentration, amount of hydrogen peroxide, time of irradiation and pH of the solution. Dye decolorization increased with increasing hydrogen peroxide concentration and decreases with decreasing dye concentration. It was found that the response of C.I. reactive yellow 145 dye degradation was very sensitive to the independent factors of dye concentration, hydrogen peroxide concentration, shaking speed pH and reaction time. Hydrogen peroxide had efficiently catalyzed the degradation of dye in the presence of light. The degradation dye was found very high by using ultraviolet light source. The hydrogen peroxide enhanced the decomposition dye at moderate level. The results showed that the ultraviolet in the presence of hydrogen peroxide can be used for the degradation of textile dyes. The oxidative degradation of C.I. reactive yellow 145 in the ultraviolet/hydrogen peroxide process proved to be a promising wastewater treatment technology. It was found that approximately 99 % decolorization have been obtained when 5 % hydrogen peroxide of 100 ppm solution was irradiated with 24 W ultraviolet power at pH 3.0 for 1 h.

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