

DEGRADATION STUDIES OF RHODAMINE B IN THE PRESENCE OF UV/H₂O₂ /Fe²⁺

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Abstract: The photo-oxidation of Rhodamine B was carried out in the presence of H₂O₂/ Fe²⁺ ion using UV light. The effects of dye concentration, pH, H₂O₂ dose and Fe²⁺ dose. These parameters strongly influenced the degradation of the dye. As expected, the increase of initial dye concentration decreased the percentage decoloration. Likewise increasing H₂O₂, Fe²⁺ concentration also increased the dye decoloration up to a certain limit after which it starts decreasing. The optimum operating conditions of the method were found to be [Dye] = 10mg/l; [H₂O₂] = 300mg/l; [Fe²⁺] = 250 mg/l at pH 2. Under these conditions, a maximum of 92% decoloration of the dye was achieved. The actual breakdown of the dye was confirmed using HPLC analyses.

Keywords: Rhodamine B; Degradation; Decoloration; UV/H₂O₂/Fe²⁺

I. INTRODUCTION

The relationship of industrial activity an environmental pollution is a serious topic and matter of great concern in modern times. Wastewater discharge from industrial units is a large problem for conventional treatment plants in the entire world. The release of these wastewaters in natural environments is not only hazardous to aquatic life but also in many cases mutagenic to humans ^(1,2) Many efforts have been devoted to develop technologies that are able to minimize the hazardous effects caused by industrial activities.

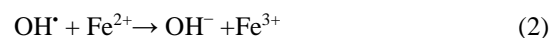
Numerous chemicals such as dyes are extensively employed to impart color to various industrial products. There are many kinds of dye available in the market. Based on their chemical structure or chromophores, 20 to 30 different groups of dyes can be classified. Anthraquinone, phthalocyanine, tri arylmethane and azo dyes are quantitatively the most important groups. The azo dyes, characterized by having an azo group consisting of two nitrogen atoms, are the largest class of dyes used in textile industry ⁽³⁾. Within the azo dyes one can have a wide types of dyes, namely acid, reactive, disperse, vat, metal complex, mordant, direct, basic and sulphur dyes.

Among these, the most used are the reactive azo dyes. Additionally, these dyes are the most problematic pollutants of textile waste waters. This fact occurs because after the reactive dyeing process is finished, more than 15% of the textile dyes is lost in wastewater stream during dye in operation ⁽⁴⁾. Dyestuffs wastewater can be removed by chemical and physical methods including adsorption, photocatalytic oxidation ^(5,6) coagulation-flocculation and electrochemical methods ⁽⁷⁾. In recent years, advanced oxidation processes (AOPs) have been intensively investigated for the treatment of waters and waste waters. AOPs, defined as processes generating hydroxyl radicals (OH[•]), are considered to be

promising alternatives to conventional processes due to their efficiency in oxidizing a great variety of organic contaminants ⁽⁸⁾. The Fenton and photo-Fenton systems have been widely applied in the treatment of non biodegradable wastewater in the field of AOPs ^(9,10). Oxidation with Fenton's reagent is based on ferrous ion and hydrogen peroxide, and exploits the reactivity of the hydroxyl radicals produced in acidic solution by the catalytic decomposition of H₂O₂. ⁽¹¹⁾



Hydroxyl radicals may be scavenged by reaction with another Fe²⁺:



Fenton reagent appears to be a very powerful oxidizing agent. Besides, the process is simple and non-expensive, taking place at low temperatures and at atmospheric pressure. ⁽¹²⁾ The chemical sare readily available at moderate cost and there is no need for special equipment. In photo-Fenton process in addition to the above reactions the formation of hydroxyl radical also occurs by the following reactions (Eq. (3)). ⁽¹³⁾



The rate of organic pollutant degradation could be increased by irradiation of Fenton with UV or visible light (photo-Fenton process). The illumination leads not only to the formation of additional hydroxyl radicals but also to recycling of ferrous catalyst by reduction of Fe³⁺. In this way, the concentration of Fe²⁺ is increased and the overall reaction is accelerated. Among the AOPs, the oxidation using Fenton's reagent and photo-Fenton's

Reagent has been found to be a promising and attractive treatment method for the effective degradation of dyes.

II. EXPERIMENTAL PROCEDURES

A. Materials

Rhodamine B (CI name Basic violet 10) was obtained from Fluka and used as such. Deionized water was used to make the dye solutions of desired concentration. The molecular formula of Rhodamine B C₂₈H₃₁ClN₂O₃ is and formula weight is 479.02 g/mol. The structure of the Rhodamine B ⁽¹⁴⁾ is shown in Fig.1

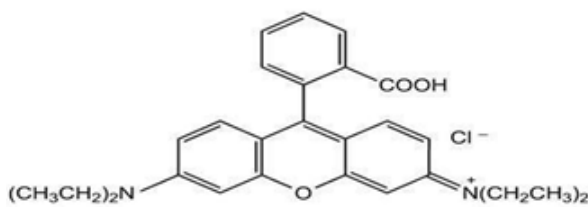


Figure1: Structure of Rhodamine B dye

Other reagents namely, hydrogen peroxide (35% W/V), FeSO₄·7H₂O, HCl and NaOH were of A.R. grade (from Merck)

B. Degradation Procedure

Photo-Fenton reaction were carried out at room temperature using in a circular pyrex glass cell volume 75ml, the photochemical degradation of Rh B dye were studied taking 60 ml of 25 mg l⁻¹ of dye and 5ml of different concentration of FeSO₄·7H₂O and H₂O₂. The reaction mixture was translate to the photo reactor and was irradiated with deuterium lamp.

In attempt to determine the effect of Fe²⁺ concentration on photo-Fenton reactions the amount of Fe²⁺ added was changed between 50-350 mg/l while 35% H₂O₂, 25mg l⁻¹ for dye and pH was kept constant. Then to determine the effect of H₂O₂ concentration on photo-Fenton reaction the amount of H₂O₂ added changed between (35% to 25%) while 300 mg l⁻¹ Fe²⁺, 25 mg l⁻¹ for Rh B dye and pH was kept constant. The effect of initial dye concentration was also investigated between 10-100mg l⁻¹ when H₂O₂ concentrations; Fe²⁺ concentration and pH were fixed from above experiments. The optimum dosages, which gave better results in color removal, were selected based on the results of the preliminary experiments. Firstly, the H₂O₂ was added to the dye solution and then the pH was adjusted to the desired value by the addition of a few drops of either HCl or NaOH solutions. Following the pH adjustment using pH-meter, the Fe²⁺ were quickly added to the dye solution.

At various intervals, samples were quickly withdrawn for spectrometric analysis before and after UV irradiation. The absorption spectra of the prepared solutions were recorded using Shematzu spectrophotometer. The color and decolorization ratios were measured with spectro-photometric technique and calculated according to the literatures⁽¹⁵⁾. This was done by monitoring the absorbance change at λ_{max} of maximum peaks for each dye. The estimation of decolorization degree (DD %) was done according to the relation:

$$DD\% = \frac{A_i - A_t}{A_i} \times 100$$

Where, A_i is the initial intensity of color and A_t is the intensity of color at t time of the degradation.

III. RESULTS AND DISCUSSION

A. UV-VIS spectra of CR dyes.

The photo-Fenton oxidation experiments were followed for decolorization photo-Fenton oxidation experiments using UV-VIS spectra and the decolorization of dye was recorded in term of change in intensity of characteristics peaks. Fig.2 shows the UV-V spectra of 10ppm of Rhodamine B.

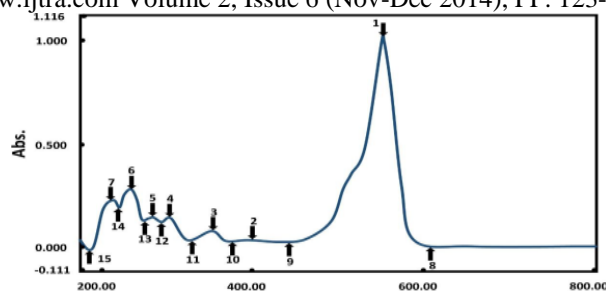


Figure 2: UV-Visible absorption spectrum for Rhodamine B dye 10 mg l-1.

B. Effect of pH on Fenton process

The influence of pH on the decolorization was investigated by keeping the Fe²⁺ concentration and oxidant concentration constant, pH of the solution is an important parameter for oxidation of pollutants in Fenton's reaction, Kang *et al.* reported that the photo-Fenton process is more effective under acidic conditions, and higher pH values are reported to be unsatisfactory for the oxidation of organic pollutants^(16, 17). At pH more than 4, the generation of OH· gets slower because of the formation of the ferric hydroxo complex. The complex would further form [Fe(OH)₄] when the pH value is higher than 9.0⁽¹⁸⁾. On the other hand at very low pH values (<2.0) hydrogen ions acts as OH· radical-scavengers. The reaction is slowed down due to the formation of complex species [Fe(H₂O)₆]²⁺, which reacts more slowly with peroxide compared to that of [Fe(OH)(H₂O)₅]²⁺. In addition, the peroxide gets solvated in the presence of high concentration of H⁺ ions to form stable oxonium ion [H₃O₂]⁺. An oxonium ion makes peroxide electrophilic to enhance its stability and presumably substantially reduce the reactivity with Fe²⁺ ion. Therefore, the initial pH value has to be in the acidic range (2-4) to generate the maximum amount of OH· to oxidize organic compounds (In this study, optimum pH value was determined for RhB dye. During this determination, pH was adjusted between (2-6) and the efficiencies of color removal were followed. Maximum percentage color removal was obtained at pH 2.0 for Rhodamine B (Fig.3).

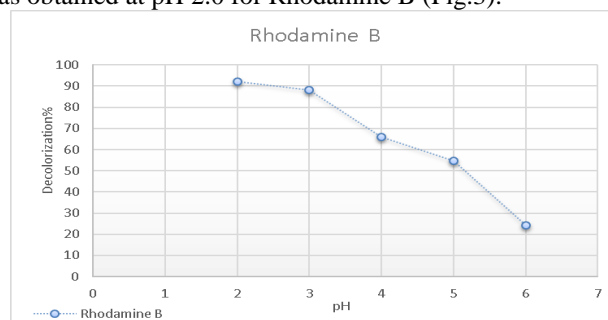


Figure: 3 Effect of pH on the decolorization percentage (DD%) of Rhodamine B dye at (25mg l⁻¹), [H₂O₂: FeSO₄]=100: 100 mg l⁻¹

C. Effect of initial Fe²⁺ concentration

Dye degradation efficiency by photo Fenton process is influenced by the concentration of Fe²⁺ ions which catalyze hydrogen peroxide decomposition resulting in OH· radical production and consequently the degradation of organic molecule as previously referred in equations (1-3). According to the literature⁽¹⁹⁾ increasing ferrous salt concentration, degradation rate of organic compound also increases certain

level where further addition of iron becomes inefficient. The effect of Fe^{2+} concentration on color removal was examined by changing the Fe^{2+} concentration between 25-300 $mg\ l^{-1}$, while keeping the concentration of H_2O_2 , pH and dye concentration constant [H_2O_2]=100 $mg\ l^{-1}$, 25 $mg\ l^{-1}$ for each dye, pH=2.0. (Fig.4) show that as Fe^{2+} doses were increased from 25-250 $mg\ l^{-1}$, the removal % increased from 11% to 92% at 270 minutes. Hence, it can be said that higher ferrous doses lead to the generation of more OH radicals. It also shows that higher ferrous doses not only make the redox reaction complete but also cause coagulation resulting in improved removal. At higher doses, the efficiency decrease indicating that H_2O_2 becomes the limiting factor for further OH generation.^(20,21)

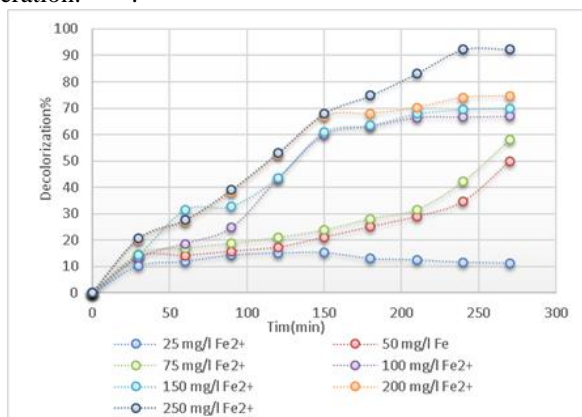


Fig.4- Effect of Fe^{+2} concentration on the degradation degree of Rh B dye in presence of 100 $mg\ l^{-1}$ H_2O_2 and pH=2

D. Effect of initial H_2O_2 concentration

Concentration of hydrogen peroxide is one of the operating parameters that significantly influence the final mineralization extent. With further increasing hydrogen peroxide concentration degradation efficiency also increases with the achievement of certain optimal Fenton reagent ratio. With further increasing of hydrogen peroxide concentration, degradation efficiency is decreasing due to the scavenging nature of hydrogen peroxide towards OH radical eq. (1-3) when it is present in higher concentration^(22, 23). As a result the formation of perhydroxyl radical are significantly less reactive species than hydroxyl radicals and thus it directly influence the efficiency of dye hydration. To determinate the optimum H_2O_2 dose, studies were activated at constant Fe^{2+} dosage as 250 $mg\ l^{-1}$ for Rh B dye at pH=2.0, 25 $mg\ l^{-1}$ concentration dye at varied dosages of H_2O_2 from 100-300 $mg\ l^{-1}$. The better removal efficiencies obtained at 300 $mg\ l^{-1}$. (Fig.5)

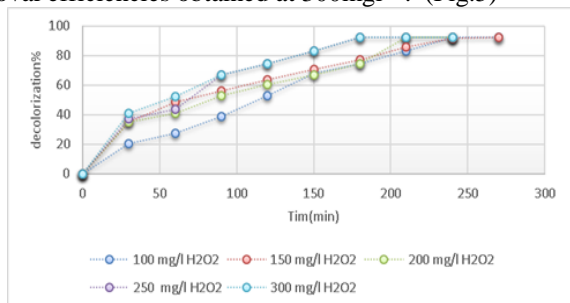


Figure: 5 Effect of H_2O_2 concentration on the degradation percentage of Rh B dye in presence of 250 $mg\ l^{-1}$ Fe^{+2} at pH=2

E. Effect of the initial dye concentration

Initial concentration of the dye plays a major role and has a significant influence on the degradation rate as a shown in Fig.6. the degradation percentage in each time increased with Rh B dye concentrations decreased and reach the highest value (92.2), this observed in the rate can be explained in the following way: (i) as the dye concentration is increased the rate of generation of hydroxyl radicals will not increase proportionally, (ii) high dye concentration can reduce the UV. Light penetration in to the depth of the solution which decreases the rate of generation of hydroxyl radicals; (iii) due to insufficient availability of oxidizing agent the degradation rate may further decrease; (iv) at high dye concentration Fe^{+2} ions gets shielded from absorbing UV light resulting in the abrupt termination of photo oxidation reaction; (v) there may be other reactions initiated at high concentration of the dye like dimerization, complex formation etc., which further complicates the reaction mechanism^(24,25).

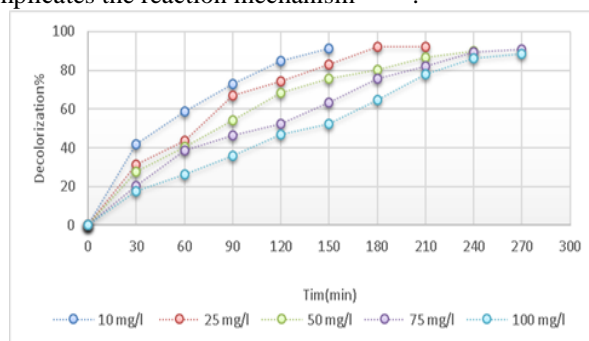


Figure 6: Effect of initial dye concentration (RhB) at optimum condition [Fe^{+2}]=250 $mg\ l^{-1}$ and [H_2O_2]=300 $mg\ l^{-1}$ and pH=2.

F. Decolourization of dye during the course of reaction

Figure (7) depicts that as the reaction time increases, peak 553nm of Rh B disappear gradually and degradation was complete after 180 minutes for Rh B dye. It indicates that the main chromophores in the original dye solution are destroyed with the Photo-Fenton reaction and proves that the dyes were fully decomposed in the system.

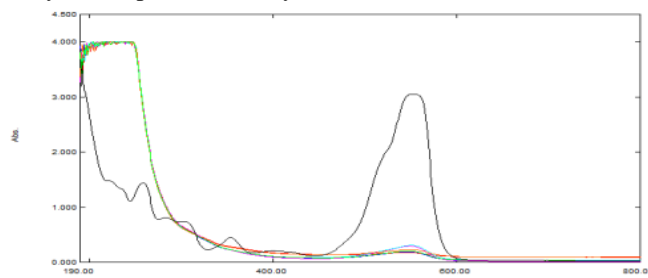


Figure 7: Decolorization of RhB dye during the course of reaction.

G. HPLC Chromatographic Analysis

The photo- Fenton degradation process was monitored by HPLC chromatogram for (Rh B) dye degradation. Fig. 8 illustrated the HPLC chromatogram and showed the absorbance peak, which appeared at retention time of 11.96 minutes for (Rh B) before irradiation, and after irradiation the intensity of this peak are gradually decreased with irradiation time increased.

A new absorbance peaks are appear after one hour of irradiation with retention time (9.52, 8.57 min) as shown in Fig. 8 Irradiation time of three hours show that no HPLC peaks were detected (using optimum initial concentration of Rh B dye 25mg^l⁻¹). These results are in a good agreement with results obtained from the UV Visible spectrum.

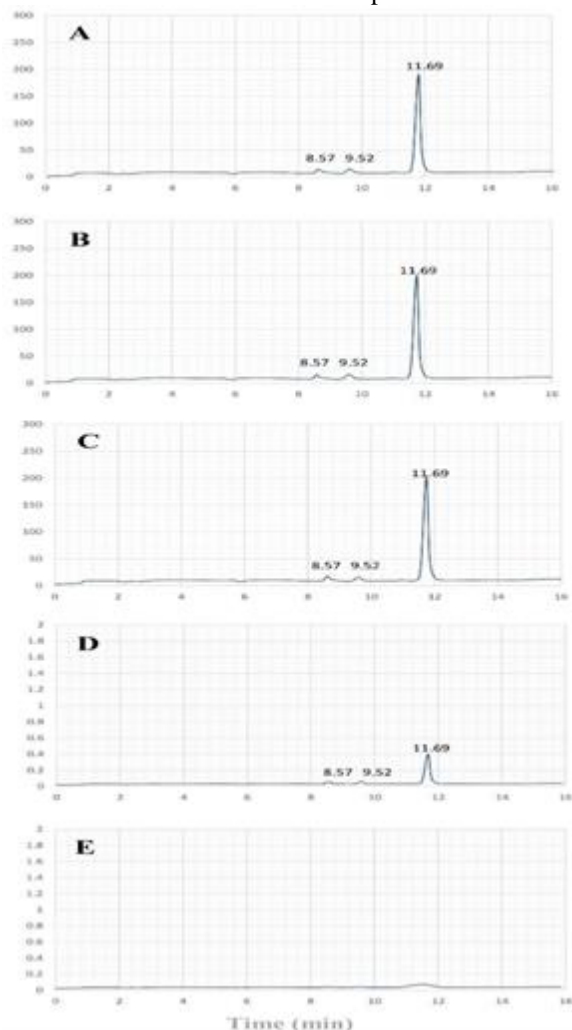


Figure 8: HPLC chromatogram of RhB dye (A) before photodegradation (B) after 60 min. (C) after 120 min. (D) after 180 min (E) after 240min. Initial dye concentration is 25mg^l⁻¹ [Fe²⁺]=250mg^l⁻¹, and H₂O₂=300mg^l⁻¹, pH=2

IV. CONCLUSION

The results showed that photo-Fenton processes are a powerful method for degradation of Rhodamine B. The degradation rate and percentage were influenced by the initial concentration of the Rhodamine B, the pH of solution, and the amount of hydrogen peroxide and iron salt. The optimum conditions for the degradation of Rhodamine B in photo-Fenton processes were observed at pH 2, 300 mg/l of Fe²⁺, 250mg/l of H₂O₂ with 25 mg/l dye concentration. The advantages of the photo-Fenton process as an oxidative treatment are low cost, rapid degradation, and simple handling. Therefore, H₂O₂/Fe²⁺/UV system would be applied to wastewater treatment works as a new developing methodology for reducing levels of other dyes, especially in countries with abundant solar light.

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