Removal of Congo Red by photochemical treatment using photo-Fenton reagent

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ABSTRACT

Oxidation by photo-Fenton reaction is an economically feasible process for degradation of a variety of hazardous pollutants in wastewater from dyeing and printing industries. Oxidation of Congo Red (CR) using photo-Fenton reagent has been carried out under ambient condition. The effect of different parameters like the concentration of Fe²⁺, initial concentration of (CR) dye, pH, hydrogen peroxide are studied and optimal condition are reported. The photo-Fenton degradation process was monitored by HPLC and UV-visible spectroscopy.

KEYWORDS

Advanced oxidation processes (AOPs);
Congo red;
Dye degradation;
Fenton’s reagent.

INTRODUCTION

Synthetic dyes are present in many spheres of our everyday life and their application are continuously growing, e.g., in various branches of the textile industry, of the leather tanning industry, in paper production, in food technology, in agricultural research, in light harvesting arrays, in photo electrochemical.

Cells, and in hair colorings. Moreover synthetic dyes have been employed for the control of the efficacy of sewage and wastewater treatment, etc[1-5]. Dyes make our world beautiful, but they bring pollution. Wastewaters originating from dyes production and application industries pose a major threat to surrounding ecosystems, because of their toxicity and potentially carcinogenic nature[6-8]. The removal of these dyes from the wastewater is a great challenge for the related industries, since they are persistent in nature and difficult to destroy by ordinary treatment methods, especially in ppm and ppb concentrations. The traditional methods of removing these dyes by various processes like carbon adsorption, activated sludge treatment, membrane filtration, flocculation and reverse osmosis are inefficient, and has further disadvantage of secondary pollution. These processes transfer pollutants from one phase to another phase. Ozone and hypochlorite oxidation are efficient decolorizing methods, but they are very expensive and tedious processes. Further secondary pollution arising from residual chlorine adds to the problem[9].

In recent years, innovative technologies such as the Advanced Oxidation Processes (AOPs) have emerged for the destruction of organic compounds[10]. Some systems e.g. UV-H₂O₂ and UV-O₃ are widely known and are in practical use also[11,12]. Another treatment method using the Fenton reaction[13], utilizes hydroxyl radicals produced interaction of H₂O₂ with ferrous salts.

Fe²⁺ + H₂O₂ → Fe³⁺ + OH⁻ + OH⁻ (1)

In the dark, this reaction is stopped after complete conversion of Fe²⁺-H₂O₂. It has also been found that illumination of the Fe²⁺-Fe³⁺-H₂O₂ system increases
the rate of degradation of many organic substances, e.g. nitrophenol, nitrobenzen, anisole and di-n-butyl-ortho-phosphate. The reasons for the rate enhancement of degradation on irradiation include the photoreduction of Fe$^{3+}$ ion back to Fe$^{2+}$ ions, which produce new $\cdot$OH radicals with H$_2$O$_2$ as shown above or according to the following mechanism:

$$\text{Fe}^{3+} + \text{H}_2\text{O}_2 + \text{hv} \rightarrow \text{Fe}^{2+} + \cdot\text{OH} + \text{H}^+ \quad (2)$$

The direct photolysis of H$_2$O$_2$ also generates $\cdot$OH radicals.

$$\text{H}_2\text{O}_2 + \text{hv} \rightarrow 2\cdot\text{OH} \quad (3)$$

**EXPERIMENTAL PROCEDURES**

**Materials**

Sample of diazo dye Congo Red (CR) was obtained from Aldrich. The molecular formula of Congo Red is C$_{32}$H$_{22}$N$_6$O$_6$S$_2$Na$_2$ and formula weight is 697. The structure of the congo red is shown in Figure 1.

Other reagents namely, hydrogen peroxide (35% W/V), FeSO$_4$·7H$_2$O, HCl and NaOH were of A.R. grade (from Merck).

**Degradation procedure**

Photo-Fenton reaction were carried out at room temperature using in a circular pyrex glass cell volume 75 ml, the photochemical degradation of CR dye were studied taking 60 ml of 25 mg/l of dye and 5 ml of different concentration of FeSO$_4$.7H$_2$O, H$_2$O$_2$. The reaction mixture was translate to the photo reactor and was irradiated with deuterium lamp. In attempt to determine the effect of Fe$^{2+}$ concentration on photo-Fenton reactions the amount of Fe$^{2+}$ added was changed between 50-350 mg/l while 35% H$_2$O$_2$, 25 mg/l for dye and pH was kept constant. Then to determine the effect of H$_2$O$_2$ concentration on photo-Fenton reaction the amount of H$_2$O$_2$ added changed between (35% to 25%) while 350 mg/l Fe$^{2+}$, 25 mg/l for CR dye and pH was kept constant. The effect of initial dye concentration was also investigated between 10-100 mg/l when H$_2$O$_2$ concentration, Fe$^{2+}$ 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 H$_2$O$_2$ 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 Fe$^{2+}$ 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 Shimatzu spectrophotometer. The color and decolorization ratios were measured with spectrophotometric technique and calculated according to the literatures. This was done by monitoring the absorbance change at $\lambda_{max}$ of maximum peaks for each dye. The estimation of decolorization degree (DD%) was done according to the relation:

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

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

**RESULTS AND DISCUSSION**

**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 CR dye were recorded in term of change in intensity of characteristics peaks. Figure 2 shows the UV-V is spectra of 10 ppm of Congo red.

**Effect of pH on Fenton process**

The influence of pH on the decolorization was investigated by keeping the Fe$^{2+}$ concentration and oxi-
dant 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\(^{[19,20]}\). 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\(^{[21]}\). 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(H\(_2\)O)\(_6\)]\(^{2+}\), which reacts more slowly with peroxide compared to that of
Figure 5: Effect of $\text{H}_2\text{O}_2$ concentration on the degradation percentage of CR dye in presence of 300mg/l Fe$^{2+}$ at pH=3

Figure 6: Effect of initial dye concentration (CR) at optimum condition [Fe$^{2+}$]=200mg/l and [H2O2]=300 mg/l and pH=3

Figure 7: Decolorization of CR dye during the course of reaction

$[\text{Fe(OH)}(\text{H}_2\text{O})_5]^{2+}$. In addition, the peroxide gets solvated in the presence of high concentration of H$^+$ ions to form stable oxonium ion $[\text{H}_3\text{O}_2]^+$. An oxonium ion makes peroxide electrophilic to enhance its stability and
presumably substantially reduce the reactivity with Fe\textsuperscript{2+} 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 CR dye. During this determination, pH was adjusted between (2-6) and the efficiencies of color removal were followed. Maximum percentage color removal were obtained at pH 3.0 for Congo red (Figure 3).

**Effect of initial Fe\textsuperscript{2+} concentration**

Dye degradation efficiency by photo Fenton process is influenced by the concentration of Fe\textsuperscript{2+} ions which catalyze hydrogen peroxide decomposition resulting in OH\textsuperscript{-} radical production and consequently the degradation of organic molecule as previously referred in equations (1-3). According to the literature\textsuperscript{22} increasing ferrous salt concentration, degradation rate of organic compound also increases, certain level where further addition of iron becomes inefficient. The effect of Fe\textsuperscript{2+} concentration on color removal was examined by changing the Fe\textsuperscript{2+} concentration between 25-300 mgl\textsuperscript{-1}, while keeping the concentration of H\textsubscript{2}O\textsubscript{2}, pH and dye concentration constant [H\textsubscript{2}O\textsubscript{2}]=100mg l\textsuperscript{-1}, 25 mg l\textsuperscript{-1} for each dye, pH=3.0. (Figure 4) show that as Fe\textsuperscript{2+} doses were increased from 25-200mg l\textsuperscript{-1}, the removal % increased from 60% to 91% 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\textsubscript{2}O\textsubscript{2} becomes the limiting factor for further
Effect of initial H$_2$O$_2$ 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$^{25,26}$. 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 determine the optimum H$_2$O$_2$ dose, studies were activated at constant Fe$^{2+}$ dosage as 300 mg/l for CR dye at pH=3.0, 25 mg/l concentration dye at varied dosages of H$_2$O$_2$ from 100-300 mg/l. The better removal efficiencies obtained at 300 mg/l. (Figure 5)

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 Figure 6. The degradation percentage in each time increased with CR 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$^{27,28}$.

Decolourization of dye during the course of reaction

Figure (7) depicts that as the reaction time increases, peak 497nm of CR disappear gradually and degradation was complete after 180 minutes for CR 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.

HPLC chromatographic analysis

The photo- Fenton degradation process was monitored by HPLC chromatogram for (CR) dye degradation. Figure 8 illustrated the HPLC chromatogram and showed the absorbance peak, which appeared at retention time of 16.59 minutes for (CR) before irradiation, and after irradiation the intensity of the peaks are gradually decreased with irradiation time increased.

A new absorbance peaks are appear after one hour of irradiation with retention time (5.09, 14.98 min) as shown in Figure 8 Irradiation time of three hours show that no HPLC peaks were detected (using optimum initial concentration of CR dye 25mg/l). These results are in a good agreement with results obtained from the UV Visible spectrum.

CONCLUSION

Photo-fenton reaction is capable of oxidizing dyes like Congo red into colourless degradation products. Degradation of dyes by photo –Fenton as oxidizing agent may open new avenues for the treatment of waste water from dyeing, printing and textile industries. The treated waste water may be used for cooling, cleaning, waste land irrigation etc., which is not possible otherwise with coloured water.

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