



Treatment of Reactive Dyeing Wastewater by Different Advanced Oxidation Processes

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ABSTRACT

This study makes investigation the effectiveness of the photo-Fenton's reagents in treatment of reactive dyeing wastewater under different operational conditions, such as, different concentrations of reactive azo dye C.I.Reactive Red 12 (RR12), hydrogen peroxide [H₂O₂] concentrations and [Fe²⁺], [Fe³⁺] concentrations. Oxidation by photo-Fenton and photo-Fenton-like reactions is an economically feasible process for degradation of a variety of hazardous pollutants in wastewater from dyeing and printing industries. Results indicated that by increasing the initial concentration of H₂O₂, Fe²⁺ and Fe³⁺, the rate of (RR 12) decolorization was enhanced; however, the rate of (RR12) decolorization decreased with an increase in the initial concentration of RR 12. The decolorization rate of reactive dye in the presence of various advanced oxidation processes (AOPs) obeyed the following order : photo-Fenton > photo-Fenton-like > UV/H₂O₂ and the color removal was found also to depend on dye structure.

Keywords: reactive dye, photoFenton, photoFenton-like.

INTRODUCTION

The world is facing the challenge of purification of water and air resources. In spite of many uses, the organic compounds are toxic in nature and environmental contamination by these toxic chemicals is emerging as a serious global problem. Organic compounds containing industrial effluents from textile, dyeing and printing industries may cause skin cancer due to photosensitization and photodynamic damage. On the contrary, degradation products of these organic compounds are relatively less toxic and in some cases, these are almost harmless. Secondly, polluted water is of almost no use, but if these organic compounds are degraded to smaller fragments, then this treated water may be used for washing, cooling, irrigation and cleaning purposes[1]. One of the heavy metals that has been a major focus in water and waste water treatment is chromium and the hexavalent form of it has been considered to be more hazardous due to its carcinogenic properties [2]. Chromium has been considered as one of the toxic pollutants and because of its carcinogenic characteristics, it has become a serious health problem. Extensive use of chromium results in large quantities of chromium containing

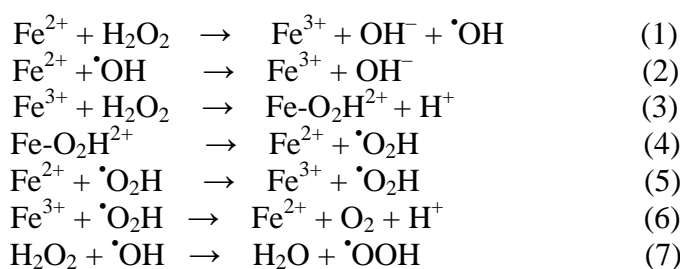
effluents which need sufficient treatments[3]. Various methods have been proposed for the treatments of wastewater containing nickel as well as copper in wastewater, such as chemical precipitation, reverse osmosis, ion exchange, electrolysis, adsorption and photocatalysis. Removal of Ni (II) and Cu (II) from wastewater can effectively remove by photocatalysis [4].

Commonly applied treatment methods for color removal from dye-contaminated effluents consist of various processes involving biological, physical and chemical decolorization methods [5].

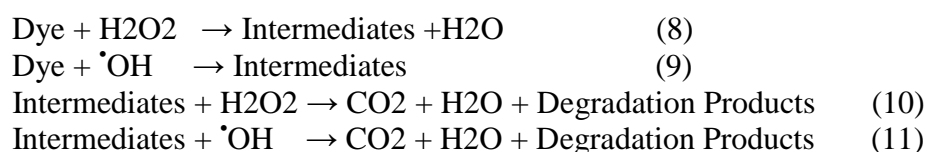
Conventional treatments of dye effluents include biological oxidation and adsorption. Although less expensive than other approaches, biological treatment is ineffective for decolorization because the dyes are toxic. Adsorption onto activated carbon transfers most of the contaminant from the wastewater to the solid phase. This method therefore requires further disposal of the sludge. In recent years, advanced oxidation processes (AOPs) and electrochemical methods have been developed to treat the contaminants of drinking water and industrial effluents. Advanced oxidation processes almost all are based on the generation of reactive species such as hydroxyl radicals ($\bullet\text{OH}$) which degrade a broad range of organic pollutants quickly and non-selectively. Although it is claimed that there are other species involved, the active species responsible for the destruction of contaminants in most cases seems to be the hydroxyl radical ($\bullet\text{OH}$) which is unstable and quite reactive. Due to the instability of $\bullet\text{OH}$ radical, it must be generated continuously "in situ" through chemical or photochemical reactions[6].

Common AOPs involve Fenton, Fenton-like, photo-Fenton's processes, ozonation, photo chemical and electrochemical oxidation, photolysis with H_2O_2 and O_3 , high voltage electrical discharge (corona) process, TiO_2 photocatalysis, radiolysis, wet oxidation, water solutions treatment by electronic beams or γ -beams and various combinations of these methods [7-11].

Compared with other oxidation processes, processes using Fenton type reagent are relatively cheap, easily operated and maintained [12]. Fenton process, one of the most effective processes for the removal of organic pollutants from aqueous solutions [13-15], involves the application of ferrous salts and hydrogen peroxide to produce hydroxyl radical according to the following scheme of reactions [16]:



Dye degradation :



When a Fenton-like reagent is used, the sequence of reaction begins with reaction (3). There are many bibliographic sources which report that Fenton reagent is more effective than Fenton-like reagent[17].

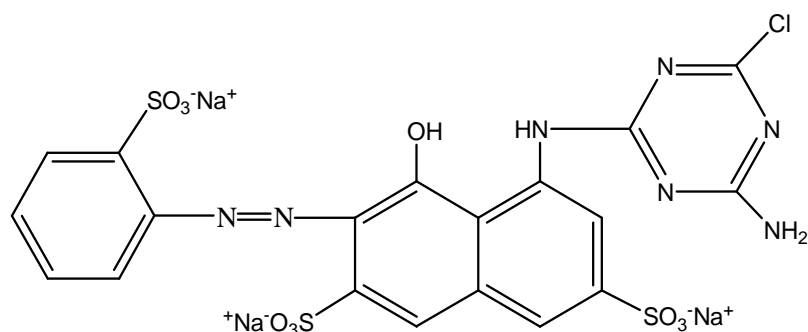
Due to slow dissociation rate in the dark, the generation of hydroxyl radicals was reduced. It is obvious that the most effective AOPs for treating dye solutions is a UV-enhanced $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ and $\text{H}_2\text{O}_2/\text{Fe}^{3+}$ solutions [18]. The high removal efficiencies of this method can be explained by the fact that oxidation reaction are coupled to coagulation occurring due to the presence of ferrous/ferric cations, thus these metallic ions play a double role as a catalyst and a coagulant in the process.

Moreover, in the Fenton process the hydrogen peroxide reacting with ferrous ions forms a strong oxidizing agent (hydroxyl radical), whose oxidation potential is higher than that of ozone (2.8 V compared to 2.07V). In Fenton-like reaction, ferric ions react with H_2O_2 to produce ferrous ions at very slow rate ($k = 0.001 - 0.01 \text{ M}^{-1}\text{s}^{-1}$) few ferrous ions can be formed and thus induce the Fenton reaction. Therefore, only one process with $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ reaction will dominate [19].

In this study, UV irradiated Fenton reagent (photo-Fenton process) and also UV irradiation Fenton-like reagent (photoFenton-like process) were applied for the minimization of organic content of colored synthetic wastewaters. Reactive azo dye, C. I Reactive Red 12 with azo chromophore was used as model organic pollutants. Investigations were carried out in order to establish optimal operating conditions, (pH, concentration of dye, concentration of H_2O_2 , and concentrations of Fe^{+2} and Fe^{+3} ions) for the degradation of study dye in model colored wastewaters.

MATERIALS AND METHODS

Series of experiments were conducted in order to find optimal conditions for study the photodegradation of reactive textile dye from wastewaters. The sample of reactive textile dye C. I. Reactive Red 12 (Cibacron BrilliantRed B-A) with azo chromophore from (CIBA Geigy), was used as model pollutant. Their structures is depicted below:



M. Wt = 697.998 gram

Other reagents namely, hydrogen peroxide (30% w/v), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$, NaOH and HCl were of grad from Merck. The effect of initial pH on treatment efficiency of azo dye was investigated. This was done with the pH range of 2-6 when initial concentration of Fe^{2+} or Fe^{3+} and H_2O_2 were $1 \times 10^{-5} \text{ M}$ and 10 Mm respectively, and at fixed dye concentration ($1 \times 10^{-5} \text{ M}$).

The photochemical degradation of RR 12 was studied to determine the effect of Fe^{+2} , Fe^{+3} and H_2O_2 concentrations on Fenton and Fenton-like treatment, the amount of Fe^{+2} and Fe^{+3} added was changed between 4×10^{-6} to $1 \times 10^{-4} \text{ M}$ when H_2O_2 concentration was kept constant at 10 Mm in presence of Fe^{2+} and 20 Mm in case of Fe^{3+} for dye under investigation. The amount of H_2O_2

added was changed between 2 and 50 mM when Fe^{2+} or Fe^{3+} concentration was kept constant at $2 \times 10^{-5} \text{ M}$ for the dyes. The effect of initial dye concentration was also investigated between 1×10^{-5} to $9 \times 10^{-5} \text{ M}$ when H_2O_2 concentration and Fe^{2+} or Fe^{3+} ion concentrations and pH were fixed. The optimum dosages, which gave better results in color removal, were selected based on the results of the preliminary experiments, and as shown in (Table 1). Firstly, the H_2O_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. Following the pH adjustment using a pH with 400 WMB7V lamp (Images H. Heal & Co. Ltd. Halifax England) high pressure Hg lamp, was used in order to stimulate day light, which is congenital for such photo-oxidation studies. All the measurements were performed at room temperature. The color and decolorization ratios were measured with spectrophotometric technique and calculated according to the literature [20]. This was done by monitoring the absorbance change at λ max of maximum peak for dye. The estimation of decolorization degree (DD%) was done according to the relation (12).

$$\text{DD}\% = \frac{A_0 - A_t}{A_0} \times 100$$

Where, A_0 is the initial intensity of color and A_t is the intensity of color at time t of the oxidation.

Table 1. Best conditions for degradation of C.I. Reactive Red 12 (RR 12) in Fenton and Fenton-like processes

Parameter	Range of parameter study	Fenton parameter concentration				Fenton-like parameter concentration			
		pH	[Fe^{2+}] M	[H_2O_2] mM	[Dye] M	pH	[Fe^{3+}] M	[H_2O_2] mM	[Dye] M
pH	2-6	-	2×10^{-5}	10	1×10^{-5}	-	2×10^{-5}	20	1×10^{-5}
[H_2O_2]	2-50 mM	2.85	2×10^{-5}	-	1×10^{-5}	2.85	2×10^{-5}	-	1×10^{-5}
[Fe^{2+}] or [Fe^{3+}]	4×10^{-6} - 1×10^{-4} M	2.85	-	10	1×10^{-5}	2.85	-	20	1×10^{-5}
[Dye]	1×10^{-5} - 9×10^{-5} M	2.85	2×10^{-5}	10	-	2.85	2×10^{-5}	20	-

RESULTS AND DISCUSSION

Effect of the H_2O_2 concentration

To determine the desired conditions of Fenton and Fenton-like processes for the decolorization of RR 12 dye, important variable such as effect dosage of H_2O_2 concentration on color removal efficiency was investigated. In order to investigate the effect of H_2O_2 concentration on the decolorization efficiency, experiments were conducted at different H_2O_2 concentrations from 2 mM to 50 mM with $2 \times 10^{-5} \text{ M}$ Fe^{2+} or Fe^{3+} solutions and pH 2.85. Fig.(1a,b) shows the relationship between the color removal % of dye and the initial concentration of H_2O_2 in the photo-Fenton and photo-Fenton-like processes. The objective of this evaluation is to select the effective operational concentration of H_2O_2 in photo-Fenton and photo-Fenton-like processes. The existing results as in Fig. (2a,b) show the relationship between the degradation degree (DD%) of dye and time in the photo-Fenton and photo-Fenton-like processes, the addition of H_2O_2 from 2 mM to 30 mM increases the decolorization of the dye from 84.04% to 99.74% at 55 min. The increase in the decolorization is due to the increase in hydroxyl radical concentration by addition of H_2O_2 . With further increasing of H_2O_2 concentration to 50 mM, degradation efficiency is decreasing due to the fact that at a higher H_2O_2 concentration scavenging of hydroxyl radicals will occur eq.(7) [21]. In the photo-Fenton-like process, the addition of H_2O_2 between 2 mM to 50 mM increases decolorization from 50.43% to 98% at 55min. Further increase causes no significant change in decolorization for photo-Fenton-like processes. As demonstrated from the results, the better color removal efficiency for RR 12 dye was obtained at concentration of 10

mM in photo-Fenton process and 20 mM H₂O₂ in photo-Fenton process see (Table 1). The effect of H₂O₂ concentration on the degradation rates of RR12 is shown in Fig.(3a,b). The degradation rates were increased by increasing the concentration of H₂O₂. This can be explained by the effect of additionally produced hydroxyl radicals.

With increasing H₂O₂ concentration from 2mM to 10mM for photo-Fenton processes, the rate constant increased but above this range the improvement was not obvious. This may be due to recombination of hydroxyl radicals and also hydroxyl radicals reaction with H₂O₂ contributing to the OH scavenging capacity [18, 22]. It can be postulated that H₂O₂ should be added at an optimum concentration to achieve the best degradation. Hence 10mM of H₂O₂ appears as an optimal dosage for photo-Fenton process and 20mM of H₂O₂ for photo-Fenton-like process as in Fig (1a,b).

Effect of pH

The reactive dye wastewaters have an alkaline pH, which leads to the precipitation of iron hydroxide, requiring preneutralisation. The redox potential of the system is also lower in an alkaline pH. Studies showed that the oxidation is rapid at the pH range 2-4, and the acidification of the waste water is necessary [23]. Therefore, in this work the best results were achieved at pH 2.85. Fenton oxidation is known as a highly pH dependent process since pH plays an important role in the mechanism of OH production in the Fenton's reaction [24]. At high pH (pH > 4), the generation of OH gets slower because of the formation of the ferric hydroxo complexes. The complexes would further form [Fe(OH)₄] when the pH value is higher than 9.0[25]. 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 this study, optimum pH value was determined for reactive dye (RR 12). During this determination, pH was adjusted between 2 and 6 and efficiencies of color removal (decolorization degree %) were observed . Maximum color removal efficiencies were obtained at pH 2.85 , for the dye in case photo-Fenton and photo-Fenton-like processes. At pH 2.85, [dye]=1X10⁻⁵M, [Fe⁺²]= [Fe⁺³] = 2X10⁻⁵ M , [H₂O₂]=10mM in photo-Fenton and 20mM in photo-Fenton-like , the color removal gives the best results compared with pH 6.0 , as shown in Fig. (4). The efficiencies of color removal (decolorization degree %) enhanced from 31.58 % at pH 6.0 to 99.74 % at pH 2.85 at the same time (55min) in photo-Fenton process , while in photo-Fenton – like process , color removal % increases from 29.0 % at pH 6.0 to 85.08% at pH 2.85 at the same time (55min). In highly acidic solutions (pH 2.0) the decolorization rates become significantly slower with decreasing pH while a similar behavior is also found in highly alkaline solutions[25].

Effect of initial dye concentration

The effect of the initial concentration of dye (RR 12) introduced in the reaction mixture on color removal for the dye was studied in both photo-Fenton and photo-Fenton – like processes. This was conducted at pH 2.85, 10mM H₂O₂ and [Fe⁺²] = 2X 10⁻⁵ M in photo- Fenton process and at pH 2.85, 20mM H₂O₂, [Fe⁺³]= 2X 10⁻⁵ M in photo-Fenton-like process . Dye concentrations were varied from 1 x 10⁻⁵ to 9X10⁻⁵M. The optimum dye concentrations were 1 x 10⁻⁵ M as shown in Fig.(5a,b). The color removal in photo- Fenton process reached 87.11% at 30 minute and further reached 99.74% at 55 min, while in photo-Fenton-like process the color removal reached 85.08 % at 55 minute and increased to 99.80% at 80 minute . The Fig.(5a,b) shows that with the increase in dye concentration, the time required for degradation also increases. At low concentration of dye, the percentage conversion is higher compared to that at higher concentration [26]. A quick oxidation during the first 30 minute in photo-Fenton process and 55 min in photo-Fenton-like process for RR12 was followed by a much slower reaction. At the

optimum conditions for the dye, the best dye concentration was equal to 1.0×10^{-5} M see in fig (6a,b) where the color removal% of dye decrease with increase the concentration of dye. The complete color removal for dye occur at 55min in photo-Fenton process, while at 80 min in photo-Fenton-like process. Further decrease in the dye decolorization in high concentrations of dye was probably due to the formation of dimmer molecules[27]through a sequence of reactions from single dye molecules. Decolorization of the dimmer molecule is more difficult, leading to the leveling off color removal. For photo-Fenton processes it was observed that the rate constant of degradation of RR12 decreased with increasing the initial dye concentrations. As an example Fig.(7a,b) shows, that at low concentration of RR12 the rate constant is higher compared to that at higher concentration. The presumed reason is that when the initial concentration of the dye increased, the hydroxyl radical concentration remained constant for all dyes molecules and hence the removal rate constant decreased [28,29].

Effect of initial Fe^{+2} concentration

Photooxidation of reactive dye pollutants (RR12) has been carried out in the presence of photo-Fenton reagent, in order to investigate the effect of Fe^{+2} concentration on the dye degradation, experiments were conducted at different Fe^{+2} concentration (4×10^{-6} M to 1×10^{-4} M) , fixed H_2O_2 concentration $[H_2O_2]= 10$ Mm, fixed pH 2.85 and fixed dye concentration $[dye]= 1 \times 10^{-5}$ M . Hydrogen peroxide catalysed the Fe^{+2} ions and decomposition to $\cdot OH$ radical which make the degradation of dye pollutants. According to the literature [30], increasing ferrous salt concentration, color removal% of organic compound also increases, to certain level where further addition of iron becomes inefficient [26]as shown in Fig (8). The existing results as in Fig. (9) show that as Fe^{+2} doses were increased from 4×10^{-6} to 2×10^{-5} M, the removal % increased from 59. 23% to 67.11% for RR 12 at 20 min. 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 [26]. A quick oxidation during the first 30minute (87.11%) for $[Fe^{2+}] = 2 \times 10^{-5}$ M and followed by a much slower reaction. At 55 minute complete removal occur. It can be hypothesised that in analogy to the oxidation with ozone, during the photo-Fenton process the substances which are easy to oxidize are also removed readily. The reactions which occur in the first step of the photo-Fenton process, a part from coagulation, are thus among those leading to modification of the structure of the dye, an observation which can be confirmed by the rapid decolorization of the solution at the outset of the process [18].

Effect of initial Fe^{3+} concentration

The effect of the initial concentration of Fe^{3+} introduced in the reaction mixture on color removal for the dye is presented in Fig.(10). Such effect is measured at pH 2.85, 1.0×10^{-5} M dye concentration and 20 mM H_2O_2 . The figure shows that a wide range of Fe^{3+} concentrations (4.0×10^{-6} M to 1.0×10^{-4} M) can be used. The optimal Fe^{3+} concentration for RR 12 was 1.0×10^{-4} M in photo-Fenton-like process as shown in Fig. (11). The color removal in photo-Fenton-like process was relative slow compared with effect of Fe^{2+} concentration where degradation efficiency of dye is increasing with increasing the concentration of Fe^{3+} concentration (4.0×10^{-6} M to 1.0×10^{-4} M) from 63.04 % to 89.42 % at 40 min and from 93.98 % to 99.21 at 70 min.

The kinetic model RR 12 distinctly increased with increasing the amount of Fe^{2+} and Fe^{3+} for photo-Fenton and photo-Fenton- like processes see Figs.(12a,b). In photo- Fenton process addition of Fe^{2+} from 4×10^{-6} M to 6×10^{-5} M increases rate constant of reaction for the dye. In photo-Fenton process the increase is to 2×10^{-5} M RR12 . In case of photo Fenton like for the dye the calculated rate constants increase to concentration of 1×10^{-4} M see Fig. 12. The rate

constant began to decrease above these concentrations range. It is known that the Fe^{2+} and Fe^{3+} have a catalytic decomposition effect on H_2O_2 [31,32]. When Fe^{2+} and Fe^{3+} increased the catalytic effect also increased. When the concentration of Fe^{2+} was higher, a great amount of Fe^{2+} exited easily in the form of $Fe(OH)_2$ in acidic environment [33] therefore, the decreases in the degradation rate occurred.

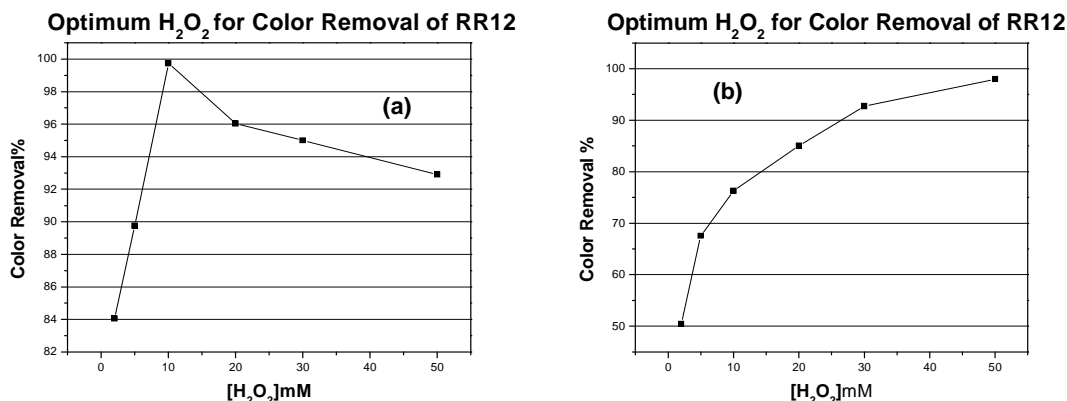


Figure 1. Effect of varying $[H_2O_2]$ ($pH = 2.85, [dye] = 1 \times 10^{-5} M, [Fe^{2+}] = [Fe^{3+}] = 2 \times 10^{-5} M$ and time removal=55min) on color removal in photo-Fenton(a) and photo-Fenton-like(b) processes.

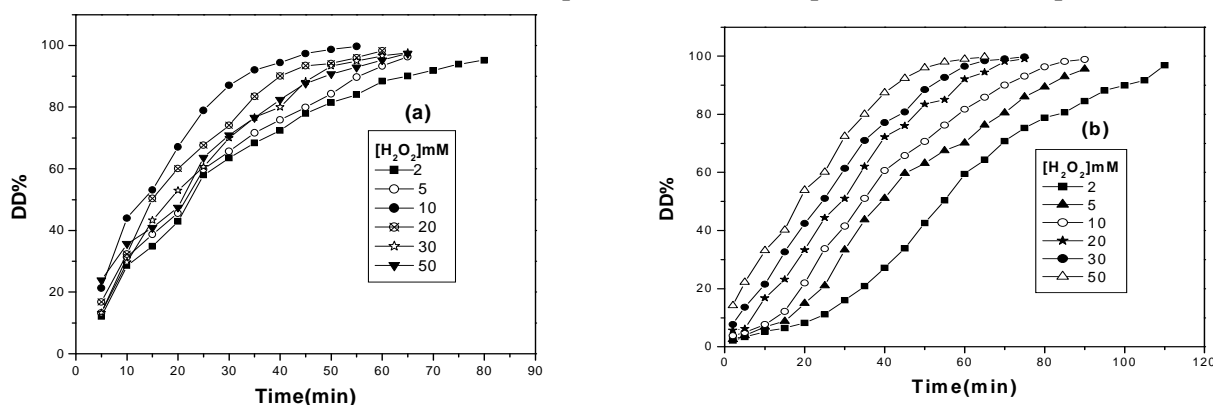


Figure 2. The degradation degree of $[RR\ 12] = 1.0 \times 10^{-5} M$ with different initial concentrations of H_2O_2 in presence of $[Fe^{2+}] = 2.0 \times 10^{-5} M$ in photo-Fenton (a) and $[Fe^{3+}] = 2.0 \times 10^{-5} M$ in photo-Fenton-like processes (b) at pH 2.85.

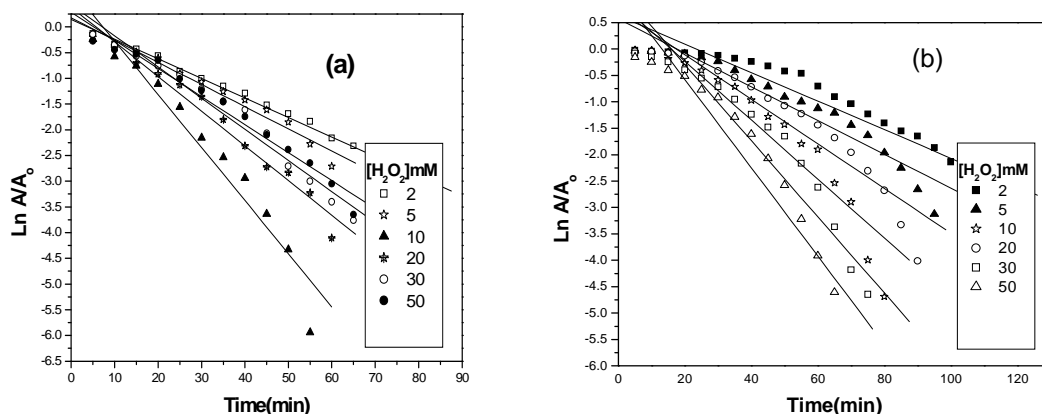


Figure 3. Kinetic of photo degradation of $[RR12] = 1.0 \times 10^{-5} M$ at different initial concentrations of H_2O_2 in presence of $[Fe^{2+}] = 2.0 \times 10^{-5} M$ in photo-Fenton Process(a) and $[Fe^{3+}] = 2.0 \times 10^{-5} M$ in photoFenton-like (b) at pH 2.85.

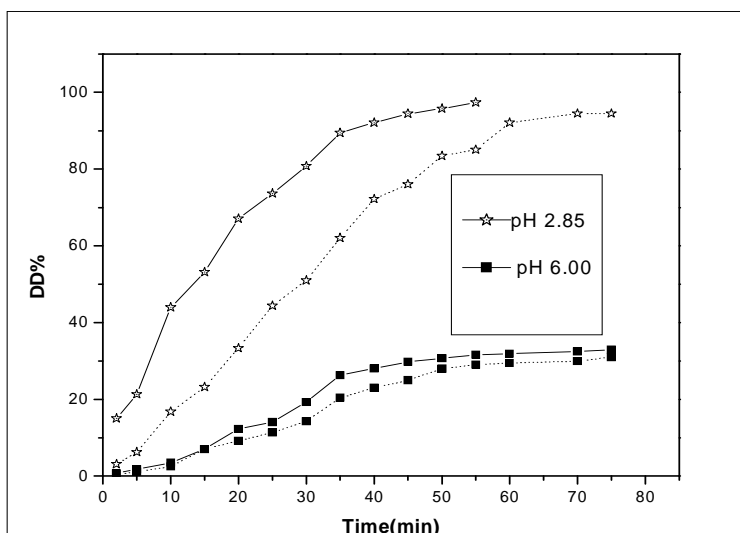


Figure 4. The degradation degree of $[RR12] = 1 \times 10^{-5} M$ at two different pH in presence of $[H_2O_2] = 10mM, [Fe^{2+}] = 2 \times 10^{-5} M$ in photo-Fenton (-) processes and $[H_2O_2] = 20mM, [Fe^{3+}] = 2 \times 10^{-5} M$ in photo-Fenton like (....) processes .

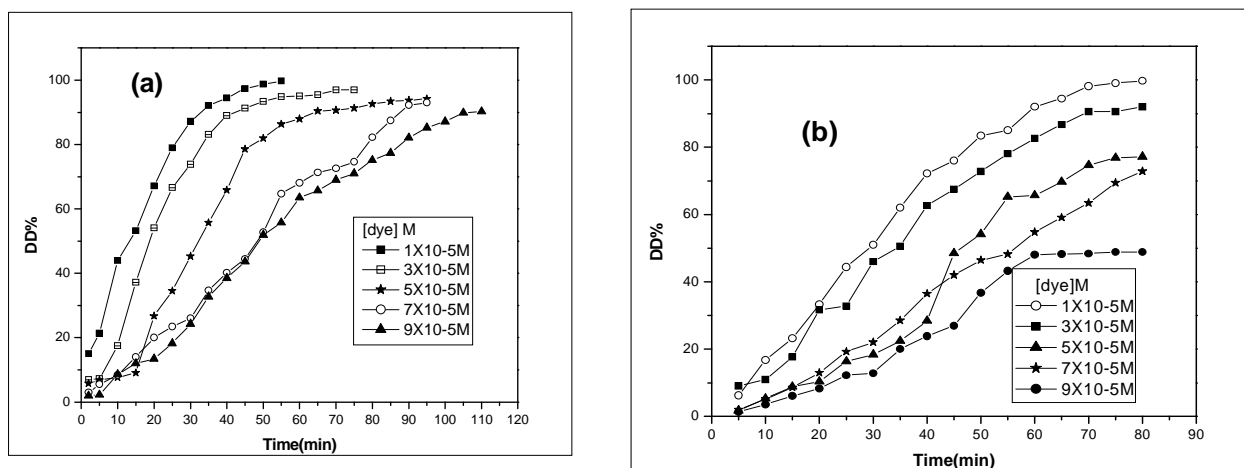


Figure 5. The degradation degree of different initial concentrations of $[RR12]$ in presence of $[H_2O_2] = 10mM, [Fe^{2+}] = 2 \times 10^{-5} M$, in photo-Fenton process (a) and in presence of $[H_2O_2] = 20mM, [Fe^{3+}] = 2 \times 10^{-5} M$, in photo-Fenton-like process (b) at pH 2.85 .

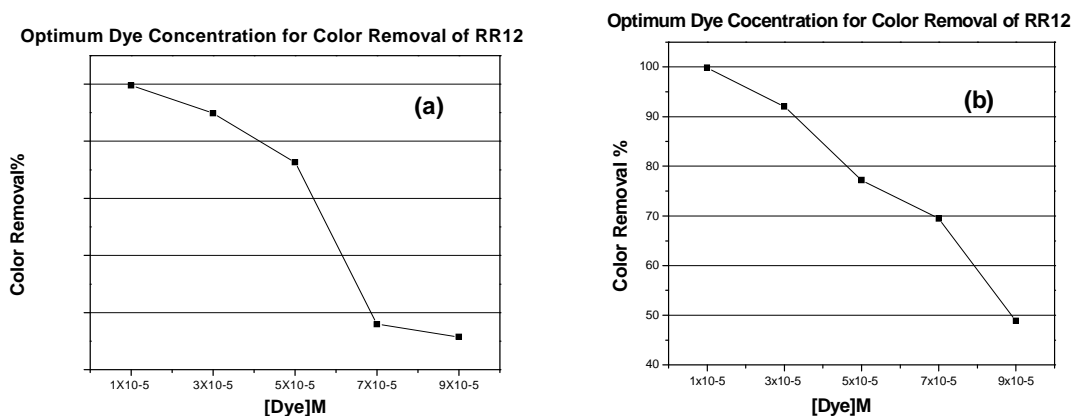


Figure 6. Effect of varying dye concentrations (pH = 2.85, $[Fe^{2+}] = [Fe^{3+}] = 2 \times 10^{-5} M, [H_2O_2] = 10mM$ and time removal=55min) on color removal in photo- Fenton process(a) and in photo- Fenton-like process(b).

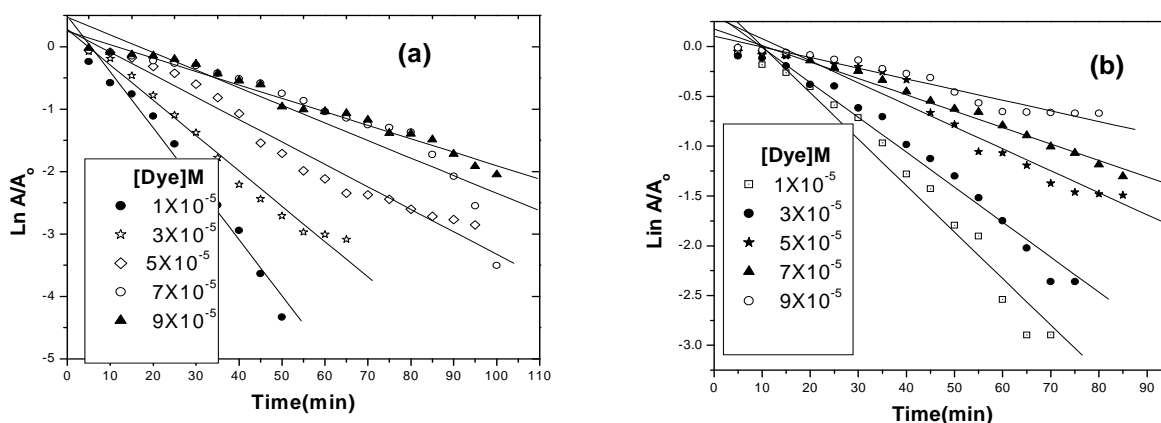


Figure 7. Kinetic of photodegradation of [RR12] at different initial concentrations in presence of $[Fe^{2+}]=[Fe^{3+}]=2 \times 10^{-5} M$ and $10mM H_2O_2$ in photo-Fenton process (a) and $20mM H_2O_2$ in photo-Fenton-like process (b) at pH 2.85.

Optimum Fe^{+2} for color removal of RR 12

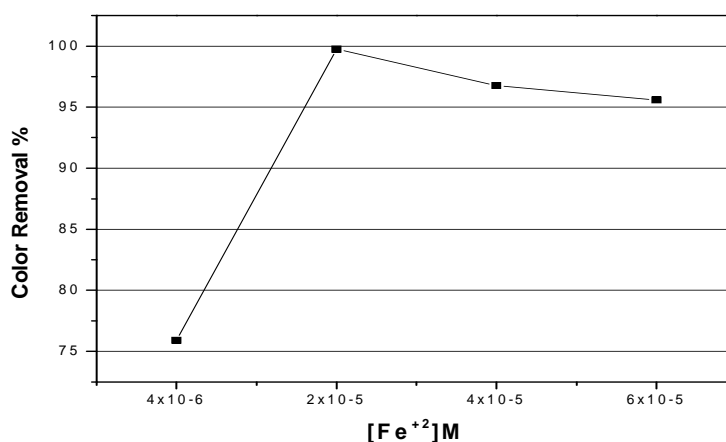


Figure 8. Effect of varying $[Fe^{+2}]$ (pH = 2.85, [dye]= $1 \times 10^{-5} M$, $[H_2O_2]= 10mM$ and time removal=55min) on color removal in photo- Fenton process.

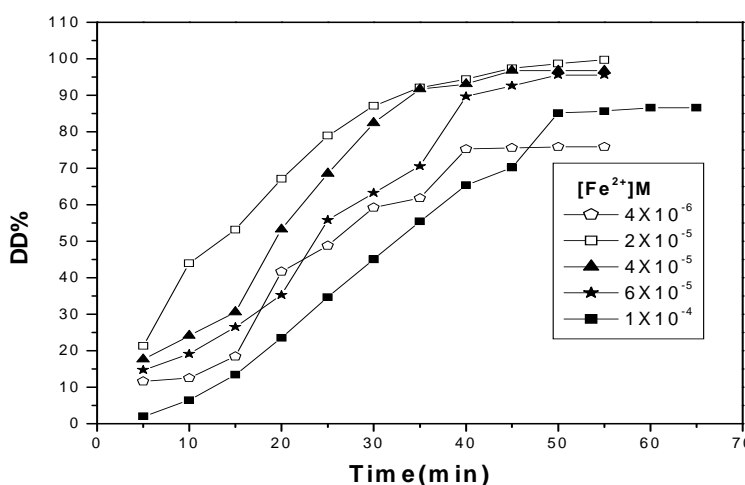


Figure 9. The degradation degree of $[RR 12] = 1.0 \times 10^{-5} M$ with different initial concentrations of Fe^{2+} in presence of $[H_2O_2] = 10mM$ in photo-Fenton process at pH 2.85.

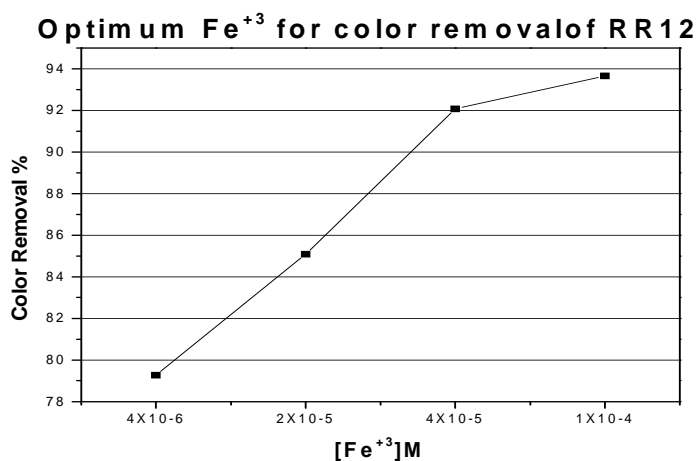


Figure 10. Effect of varying [Fe³⁺] (pH = 2.85, [dye] = 1x10⁻⁵M, [H₂O₂] = 20mM and time removal = 55min) on color removal in photo-Fenton-like process

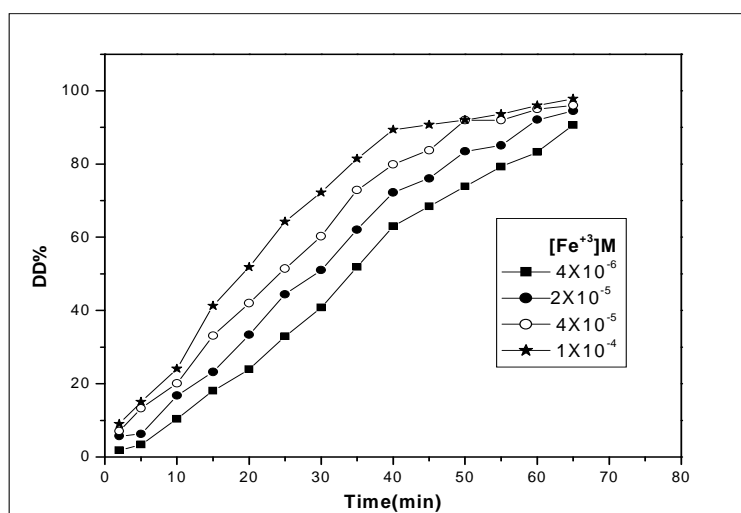


Figure 11. The degradation degree of [RR 12] = 1.0 x 10⁻⁵M with different initial concentrations of Fe³⁺ in presence of [H₂O₂] = 20 mM in photo-Fenton-like process at pH 2.85

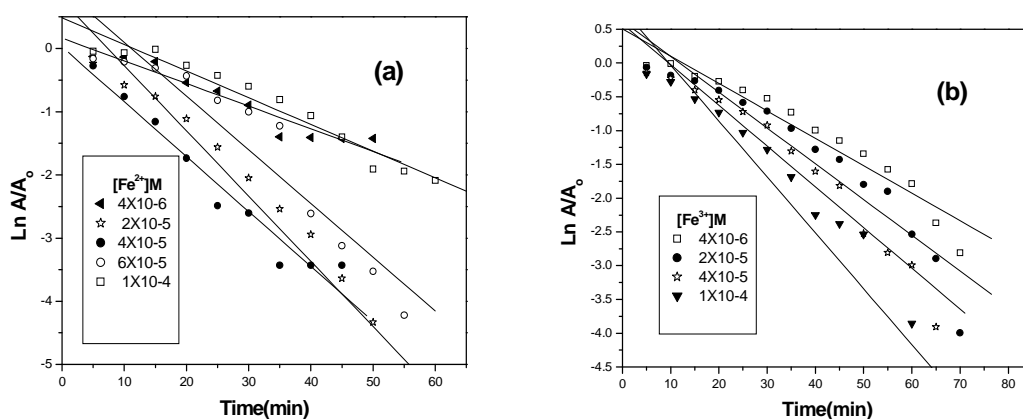


Figure 12. Kinetic of photo degradation of [RR12] = 1.0 x 10⁻⁵ M at different initial concentrations of [Fe²⁺] and [Fe³⁺] in presence of 10mM H₂O₂ in photo-Fenton process (a) and 20mM H₂O₂ in photo-Fenton-like (b) process at pH 2.85.

CONCLUSION

In this study, we assessed the possibility of different advanced oxidation processes (AOPs) for the reactive dye R R12 decolorization. The following conclusions can be drawn from this work :

- The results indicated, the decolorization degree of the reactive dye RR12 is strongly dependent on Fe^{2+} and Fe^{3+} ion concentrations, the H_2O_2 concentration, the initial dye concentration and the solution pH.
- Optimal operating conditions for each process were established.
- The degradation degree in presence of photo-Fenton process are more effective and faster than photo-Fenton-like process and other advanced oxidation processes in decolorization of RR12
- Degradation of dyes by different advanced oxidation processes 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, waste land irrigation etc., which is not possible otherwise with colored water.

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