

Comparative Study of Oxidation of Some Azo Dyes by Different Advanced Oxidation Processes: Fenton, Fenton-Like, Photo-Fenton and Photo-Fenton-Like

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Abstract: This study makes a comparison between Fenton, Fenton-like, photo-Fenton and photo-Fenton-like treatment methods to investigate the removal of two acid dyes. The two selected acid dyes are C.I. Acid Orange 8 (AO8) and C.I. Acid Red 17 (AR17). These were chosen as model organic contaminants. The effect of operating parameters, such as amount of Fenton's reagent (H_2O_2 and Fe^{2+}) and Fenton's-like reagent (H_2O_2 and Fe^{3+}), hydrogen peroxide concentration, the two azo dyes concentration and the solution pH have been studied. Results indicated that simultaneous utilization of UV irradiation with Fenton's and Fenton's-like reagent increase the degradation degree (DD%) of (AO8) and (AR17). The dyes quickly lose their color, indicating that the dissolved organics have been oxidized. The dye degradation is dependent upon, concentrations of Fenton's and Fenton's-like reagents, H_2O_2 concentration, dyes concentration and the solution pH. Decolorization efficiency observed in the order of photo-Fenton>photo-Fenton-like>Fenton>Fenton-like for the two azo dyes. The color removal was found also to depend on the dye structure. Mono sulphonic azo dye (AO8) was degraded faster than disulphonic azo dye (AR17). The results indicated that the treatment of the two azo dyes with four advanced oxidation processes (AOPs) were efficient at optimum conditions. [Journal of American Science. 2010, 6(10):128-142]. (ISSN: 1545-1003).

Keywords : Advanced oxidation processes (AOPs); Azo dyes; Dye degradation; Fenton's reagent; Fenton's-like reagent

1. 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]. A part from the aesthetic problems relating to colored effluent, dyes also strongly absorb sunlight, thus impeding the photosynthetic activity of aquatic plants and seriously threatening the whole ecosystem[9]. So there is a clear need to treat dye wastewater prior to discharge into the effluent. Most of pollutants, except color, can be reduced by chemical, physical or biological methods. Therefore, the color problem of some textile wastewater caused by the residual dyes

during the dyeing process needs more effort to be studied and investigated [10,11].

Conventional treatment methods in the textile dyeing industry for color removal include coagulation/flocculation, and activated carbon adsorption[12,13]. Both coagulation and adsorption generate large amounts of sludge and waste which need further treatment for disposal. Biotreatment is still considered as an appropriate method for meeting discharge standard but it still remains a color problem. Also, ozonation[14] effectively decolorizes dyes but does not remove COD well and may produce exhausted ozone in the water and thereby, increase the cost of treatment.

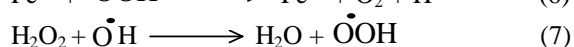
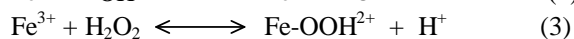
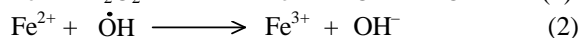
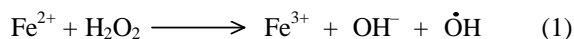
The limitations of conventional wastewater treatment methods can be overcome by the application of the so-called advanced oxidation processes (AOPs)[15] defined by Glaze *et al.* [16], which present a potential alternative to decolorize and to reduce recalcitrant colored wastewater loads[15]. AOPs are based on the generation of very reactive species such as [17] hydroxyl radicals ($\text{OH}\cdot$), which have a very strong oxidative potential [$E^\circ=+2.80\text{v}$], second only to fluorine. Hydroxyl radicals rapidly and nonselectively oxidize a broad range of organic

pollutants[18]. Common AOPs involve Fenton, Fenton-like, photo-Fenton 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 [19-23].

Fenton's oxidation, one of the 'oldest' AOPs, is relatively cheap, easily operated and maintained[9,24-27]. It has the advantages of both coagulation and catalytic oxidation, as well as being able to generate oxygen in water. Fenton and photo-Fenton type processes have proven to yield very good results either for complete mineralization of azo dyes results in the cleavage of the nitrogen double bond or for their transformation into less complex structures that are more easily biodegradable[28-30].

The Fenton reagents involve the application of ferrous ions to react with hydrogen peroxide producing hydroxyl radicals ($\dot{\text{O}}\text{H}$) with powerful oxidizing ability to degrade organic pollutants [6]. The Fenton reagent has been known for more than a century and has proved to be a powerful oxidant. The mechanism of the Fenton reaction is still under intense and controversial discussion. Generation of $\dot{\text{O}}\text{H}$ radicals by the dark reaction of H_2O_2 with ferrous salt has been the subject of numerous studies during the last decade [26]. This method seems to decolorize dyes with a variety of molecular structures.

The general mechanism using Fenton reagents, via which the hydroxyl radicals are produced, is a number of cyclic reactions, which utilize the Fe^{2+} or Fe^{3+} ions as a catalyst to decompose the H_2O_2 . These ions are regenerated in their original state at the end of the cyclic reactions according to the following scheme of reactions [31]:



More than 25 reactions occur, several involving the dye molecule, but the above seven are the most significant involving ions and radicals. 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 [32]. The above sequence of reactions begins very quickly if there is an abundant supply of H_2O_2 and dye. In cases, though, where reactants are in small concentrations ($<10 - 25 \text{ mg/L H}_2\text{O}_2$), the use of Fe^{2+} is more effective [33].

This reaction scheme is very attractive because Fe^{2+} or Fe^{3+} ions reagents are inexpensive, while H_2O_2 is also relatively inexpensive and is environmentally safe. Two disadvantages of the method are: the highly to moderately acidic environment (pH 2-5) which has to be used, and the need to recover the Fe^{2+} or Fe^{3+} ions at the end of the treatment. Major potential applications of this method are in the treatment of effluents from the textile industry, as well as from the cosmetic, pesticide and detergent producing industries [33].

Due to its 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 [15]. 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).

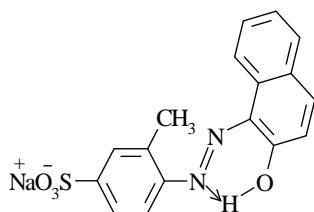
In Fenton-like reaction, ferric ions react with H_2O_2 to produce ferrous ions at very slow rate ($k = 0.001 - 0.01 \text{ M}^{-1}\text{s}^{-1}$) few ferrous ions can be formed and thus induce the Fenton reaction. Therefore, only one process with $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ reaction will dominate[34].

The aim of this study is to examine in detail the effect of major system parameters on the decolorization kinetics and compare the decolorization kinetics of the two dyes (C.I. Acid Orange 8 and C.I. Acid Red 17). The parameters, which are examined separately, are the concentration of Fe^{2+} (Fenton process), Fe^{3+} (Fenton-like process), the concentration of H_2O_2 , the initial dye concentration and the solution pH. In addition, for comparative reasons, the effect of the use of UV irradiated Fenton reagent (photo-Fenton process) and also UV irradiation Fenton-like reagent (photo-

Fenton-like process) on the decolorization kinetics of the two azo dyes are also examined.

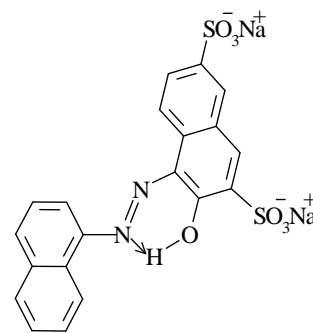
2. Experimental

Samples of acid textile dyes C.I. Acid Orange 8 (monosulphonic acid dye), were obtained from (ciba clayton limited, Manchester, England], and C.I. Acid Red 17 (disulphonic acid dye) from (ICI, Chemical Limited Imperial Industries). Their structures are depicted below.



C.I. Acid Orange 8

(Mol. wt. 364.360 g and λ_{\max} 490 nm)



C.I. Acid Red 17

(Mol. wt. 502.436 g and λ_{\max} 518 nm)

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

In an attempt to determine the effect of Fe^{2+} , Fe^{3+} and H_2O_2 concentrations on Fenton's and Fenton's-like treatment, the amount of Fe^{2+} and Fe^{3+} added was changed between 5×10^{-6} to 1×10^{-4} M when H_2O_2 concentration was kept constant at 10mM for Acid Orange 8 and 5,2 mM for Acid Red 17 in Fenton and Fenton-like process respectively. 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 1×10^{-5} M for the two dyes. The effect of initial dye concentration was also investigated between 1×10^{-5} to 1×10^{-4} 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-

meter, the Fe^{2+} or Fe^{3+} ions were quickly added to the dye solution. At various intervals, samples were quickly withdrawn for spectrometric analysis in case of before and after UV irradiation. The absorption spectra of the prepared solutions were recorded using Perkin Elmer-lambda spectrophotometer model 201 (Germany). Irradiation used with microsol light fastness tester equipped with a pre-stable timer and water color jacket (BS 1006 UK-TN) filed

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 photooxidation 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 [35]. 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 (8).

$$\text{DD}\% = \frac{A_i - A_t}{A_i} \times 100 \quad (8)$$

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

3. Results and Discussion

3.1. Fenton and photo-Fenton processes

3.1.1. Effect of initial Fe^{2+} concentration

Dye degradation efficiency by Fenton process is influenced by the concentration of Fe^{2+} ions which catalyze hydrogen peroxide decomposition resulting in $\cdot\text{OH}$ radical production and consequently the degradation of organic molecule. According to the literature [6], increasing ferrous salt concentration, degradation rate of organic compound also increases, to certain level where further addition of iron becomes inefficient [16].

The effect of Fe^{2+} concentration on color removal was examined by changing the Fe^{2+} concentration between 5×10^{-6} to 1×10^{-4} M while keeping the concentration of H_2O_2 , pH and dyes concentration constant ($[\text{H}_2\text{O}_2] = 10 \text{ mM}$ for Acid Orange 8 and 5 mM for Acid Red 17, pH 3.0 and $[\text{dye}] = 1 \times 10^{-5}$ M). Fig. 1a & b show that as Fe^{2+} doses were increased from 5×10^{-6} to 5×10^{-5} M, the removal % increased from 10% to 75% for Acid Orange 8 and from 15% to 65% for Acid Red 17 at 30 minute. Hence, it can be said that higher ferrous doses lead to the generation of more $\dot{\text{O}}\text{H}$ 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 $\dot{\text{O}}\text{H}$ generation [16].

The existing results show that the system, when operated with a source of UV light at the same conditions for the two dyes, can be optimal for complete textile wastewater decolorization and mineralization. The best experimental results for the photo-Fenton process proved the following: the removal of color was accomplished at two different rates. A quick oxidation during the first 10 and 23 min (85%) for Acid Orange 8 ($[\text{Fe}^{2+}] = 2 \times 10^{-5}$ M and Acid Red 17 $[\text{Fe}^{2+}] = 1 \times 10^{-5}$ M) respectively followed by a much slower reaction. At 47 minute complete removal occur for Acid Orange 8, while at 60 minute 95% (decolorization degree) for Acid Red 17. 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 [15].

3.1.2. Effect of the 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 $\dot{\text{O}}\text{H}$ radicals eq.(7) when it is present in higher concentration [36]. The result is the formation of perhydroxyl radicals which are significantly less

reactive species than hydroxyl radicals and thus directly influence the efficiency of dye degradation. During the determination of optimum H_2O_2 dose, studies were conducted at constant Fe^{2+} dosage as 1.0×10^{-5} M, at pH 3.0 and dye concentrations 1.0×10^{-5} M for the two dyes. Varied dosages of H_2O_2 from 2mM to 50 mM were applied, see Table (1). Efficiencies of color removal of Acid Orange 8 in Fenton and photo-Fenton processes at varied dosages of H_2O_2 and constant concentration of Fe^{2+} are illustrated in Fig. 2 as an example. The same results are obtained in case of Acid Red 17. The results showed that the color removal efficiencies for Fenton is 10mM H_2O_2 and about 38% color removal at 45 minute while the better removal efficiencies were reached with the photo-Fenton process to 100% at 27 minute by using the same dosage of H_2O_2 (10mM). The better removal efficiency for Acid Red 17 was 5mM for both Fenton and photo Fenton processes at the same conditions.

3.1.3. Effect of initial dye concentration

The effect of initial dyes concentration (Acid Orange 8 and Acid Red 17) on the decolorization degree at the optimum pH, Fenton reagent concentration and H_2O_2 dosage, were studied in both Fenton and photo-Fenton processes see (Table 1). As an example, Dyes concentrations were varied from 1×10^{-5} M, to 1×10^{-4} M (Fig. 3) for Acid Orange 8. Fig. 3 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 [16]. A quick oxidation during the first 15 minute for Acid Orange 8 was followed by a much slower reaction for the photo-Fenton process. At the optimum conditions for the two dyes, the best dye concentration was equal to 1.0×10^{-5} M. The color removal for Acid Orange 8 and Acid Red 17 are 85.5% and 71% at 50 minute for Fenton processes while, the removal are 98.5% and 83% at 50 minute for photo-Fenton process for the two dyes respectively. Further decrease in the dye decolorization in high concentrations of dye was probably due to the formation of dimmer molecules[37] through a sequence of reactions from single dye molecules. Decolorization of the dimmer molecule is more difficult, leading to the leveling off color removal.

3.1.4. Effect of initial pH

Fenton oxidation is known as a highly pH dependent process since pH plays an important role in the mechanism of $\dot{\text{O}}\text{H}$ production in the Fenton's reaction [29]. At high pH ($\text{pH} > 4$), the generation of $\dot{\text{O}}\text{H}$ gets slower because of the formation of the ferric

hydroxo complexes. The complexes would further form $[\text{Fe}(\text{OH})_4]$ when the pH value is higher than 9.0 [38]. On the other hand, at very low pH values (<2.0) hydrogen ions acts as $\dot{\text{O}}\text{H}$ radical-scavengers. The reaction is slowed down due to the formation of complex species $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$, which reacts more slowly with peroxide compared to that of $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$. 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 reduces the reactivity with Fe^{2+} ion [32]. Therefore, the initial pH value has to be in the acidic range (2-4) to generate the maximum amount of $\dot{\text{O}}\text{H}$ to oxidize organic compounds [39]. In this study, optimum pH value was determined for two acid dyes (Acid Orange 8 and Acid Red 17). During this determination, pH was adjusted between 2 and 6 and efficiencies of color removal (decolorization degree % (DD%)) were observed. Maximum color removal efficiencies were obtained at pH 3.0, for the two dyes and in case of Fenton and photo-Fenton processes. At pH 3.0 $[\text{dye}] = 1 \times 10^{-5}$ M, $[\text{Fe}^{2+}] = 1 \times 10^{-5}$ M and $[\text{H}_2\text{O}_2] = 10$ mM, the color removal gives the best results compared with the other pH's. In Fenton processes 23% and 19% for AO 8 and AR 17 respectively were observed at 27 minute. This result was enhanced to 100% and 83% at the same time for the two dyes respectively by using the photo-Fenton process under the described experimental conditions.

3.2. Fenton-like and photo-Fenton-like processes

3.2.1. 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 two dyes is presented in Fig. 4a,b. Such effect is measured at pH 3.0, 1.0×10^{-5} M dyes concentration and 10mM H_2O_2 for Acid Orange 8 and 2mM H_2O_2 for Acid Red 17. The figure shows that a wide range of Fe^{3+} concentrations (5.0×10^{-6} M to 1.0×10^{-4} M) can be used. The optimal Fe^{3+} concentration for Acid Orange 8 was 1.0×10^{-4} M in both Fenton-like and photo-Fenton-like process. The color removal in Fenton-like process was fast where (90%) was reached at the first 27 minute while 96% was reached at 60 minute. In photo-Fenton-like process the removal reached 91% at 15 minute and reached 96.5% at 60 minute. The optimum Fe^{3+} concentration was 1×10^{-4} M for Acid Red 17 in both Fenton-like and photo-Fenton-like processes and the same behavior was observed. Photo-Fenton-like process enhances only the color removal at first 12 minute (98% removal) and increases slightly to 99% at 55 minute.

3.2.2. Effect of H_2O_2 concentration

Concentration of H_2O_2 plays a more crucial role in the overall efficiency of the degradation processes. Usually it has been observed that the percentage degradation of the pollutant increases with an increase in the dosage of H_2O_2 [24, 27, 28], but excess quantities are not recommended [40]. During the determination of optimum H_2O_2 dose, studies were conducted at constant Fe^{3+} dose as 1.0×10^{-5} M, at pH 3.0 and dyes concentration 1.0×10^{-5} M. Varied dosage of H_2O_2 from 2mM to 50 mM were applied. As demonstrated from the results, the better color removal efficiencies for Acid Orange 8 and Acid Red 17 were obtained at concentration of 10mM and 2mM H_2O_2 respectively see (Table 1). The colour removal for Fenton-like process reached 30% at 60 minute and was enhanced to reach 96% at 60 minute for Acid Orange 8 in photo-Fenton-like process. On the other hand color removal in Acid Red 17, reached 35% at 60 minute and was enhanced to reach 85% at the same time by photo-Fenton-like process.

3.2.3. Effect of initial dye concentration

It has been found 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 [16]. The effect of the initial concentration of dyes introduced in the reaction mixture on color removal for the two dyes was studied. This was conducted at pH 3.0, 10mM H_2O_2 for Acid Orange 8 and 2mM H_2O_2 for Acid Red 17 and 1×10^{-4} M Fe^{3+} for Acid Orange 8 and Acid Red 17. Dye concentrations were varied from 1×10^{-5} to 1×10^{-4} M see (Table 1). The optimum dye concentrations were 1×10^{-5} M for the two dyes. The color removal in Fenton-like process reached 91% at 30 minute and further reached 96% at 60 minute, while in photo-Fenton-like process the color removal reached 90% at 10 minute and increased to 96% at 60 minute for Acid Orange 8. In case of Acid Red 17 efficiency of color removal reached 85% at 30 minute, while in photo-Fenton-like process the color removal reached 97.5% at 12 minute and increased to 99% at 55 minute.

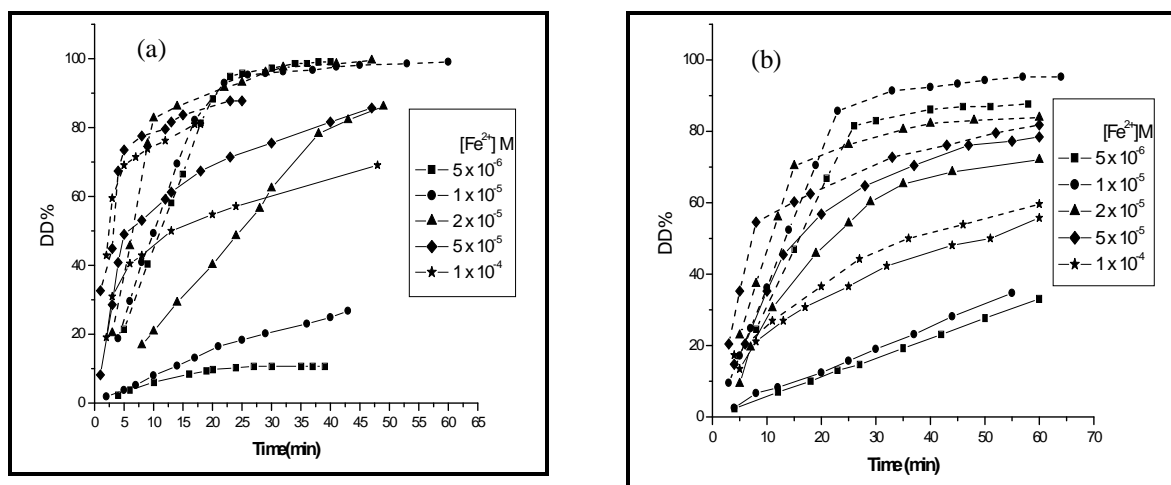


Fig. (1): The degradation degree of (a) [AO8] and (b) [AR 17] = 1.0×10^{-5} M with different initial concentrations of Fe^{2+} in presence of $[\text{H}_2\text{O}_2] = 10\text{mM}$ for (AO 8) and 5mM for (AR 17) in Fenton (–) and photo-Fenton (---) processes at pH3.0 .

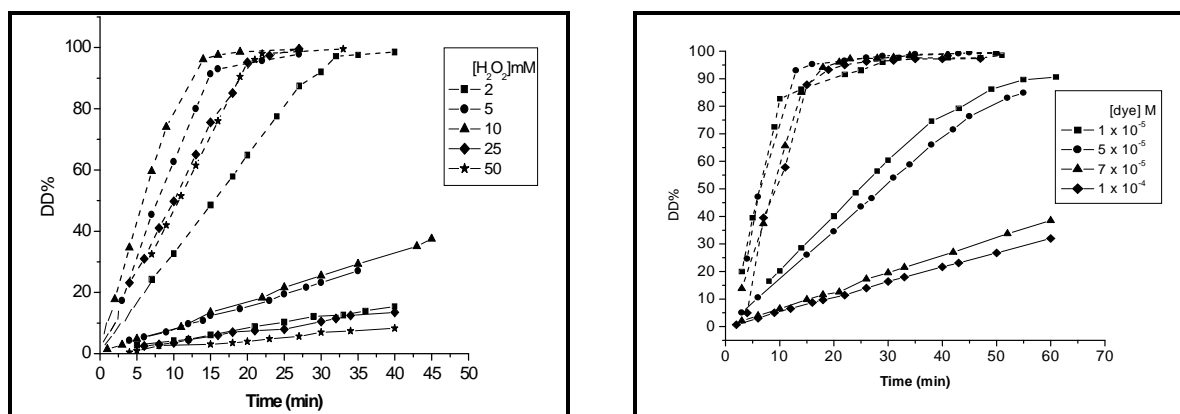


Fig. (2): The degradation degree of [AO 8] = 1.0×10^{-5} M with different initial concentrations of H_2O_2 in presence of $[\text{Fe}^{2+}] = 1.0 \times 10^{-5}$ M, in Fenton (–) and photo-Fenton (---) processes at pH 3.0.

Fig. (3): The degradation degree of different initial concentrations of (AO8) in presence of $[\text{H}_2\text{O}_2] = 10\text{mM}$, $[\text{Fe}^{2+}] = 2 \times 10^{-5}$ M, in Fenton (–) and photo-Fenton(---) processes at pH 3.0 .

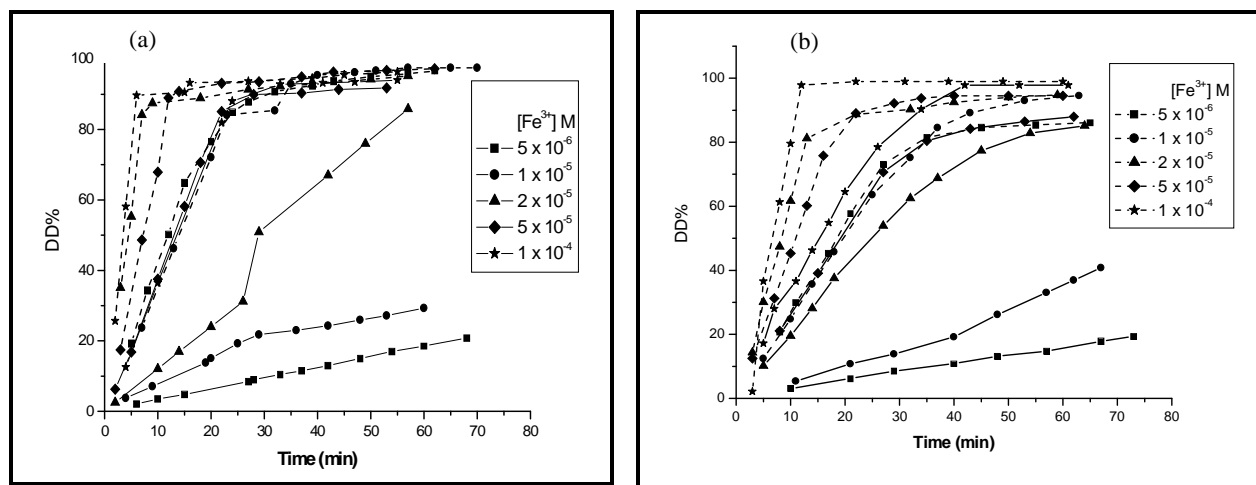


Fig. (4): The degradation degree of (a) [AO8] and (b) [AR17] = 1.0×10^{-5} M with different initial concentrations of Fe^{3+} in presence of $[H_2O_2] = 10$ mM for AO8 and 2mM for AR17 in Fenton-like (—) and photo-Fenton-like (----) processes at pH 3.0.

Table (1) Optimum parameter concentrations for C.I. Acid Orange 8 and C.I. Acid Red 17 in Fenton and Fenton-like Processes.

Parameter	Range of parameter study	C.I. Acid Orange 8								C.I. Acid Red 17							
		Fenton's- parameter Conc.				Fenton's-like parameter Conc.				Fenton's- parameter Conc.				Fenton's-like parameter Conc.			
		pH	$[Fe^{2+}]$ M	$[H_2O_2]$ mM	[Dye] M	pH	$[Fe^{3+}]$ M	$[H_2O_2]$ mM	[Dye] M	pH	$[Fe^{2+}]$ M	$[H_2O_2]$ mM	[Dye] M	pH	$[Fe^{3+}]$ M	$[H_2O_2]$ mM	[Dye] M
pH	2 – 6	-	1×10^{-5}	10	1×10^{-5}	-	1×10^{-5}	10	1×10^{-5}	-	1×10^{-5}	10	1×10^{-5}	-	1×10^{-5}	10	1×10^{-5}
H_2O_2 Conc.	2 – 50 mM	3	1×10^{-5}	-	1×10^{-5}	3	1×10^{-5}	-	1×10^{-5}	3	1×10^{-5}	-	1×10^{-5}	3	1×10^{-5}	-	1×10^{-5}
Fe^{2+} or Fe^{3+} Conc.	5×10^{-6} – 1×10^{-4} M	3	-	10	1×10^{-5}	3	-	10	1×10^{-5}	3	-	5	1×10^{-5}	3	-	2	1×10^{-5}
Dye Conc.	1×10^{-5} – 1×10^{-4} M	3	5×10^{-5}	10	-	3	1×10^{-4}	10	-	3	5×10^{-5}	5	-	3	1×10^{-4}	2	-

3.2.4. Effect of initial pH

The dependence of the decolorization degree on the solution pH is similar for the two dyes examined in both Fenton-like and photo-Fenton-like processes. 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 [38]. The optimal pH was 3.0 for both two dyes. In Fenton-like process the decolorisation degree for Acid Orange 8 and Acid Red 17 reached 26% and 20% respectively at 50 minute and was enhanced to 95% and 93% at the same time for photo-Fenton-like process. In photo-Fenton like process color removal reached 90% and 84% at the first 27 minute for Acid Orange 8 and Acid Red 17 respectively see Fig. 5.

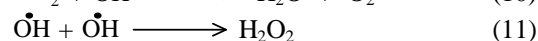
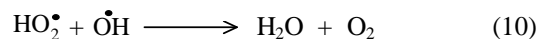
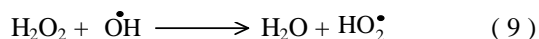
3.3. Degradation kinetics

3.3.1. $\text{Fe}^{2+} + \text{Fe}^{3+}$ concentration

The kinetic model of Acid Red 17 and the degradation rates of Acid Orange 8 and Acid Red 17 distinctly increased with increasing the amount of Fe^{2+} for Fenton and photo-Fenton processes see Figs. 6 and 7a,b. In Fenton process addition of Fe^{2+} from $5 \times 10^{-6}\text{M}$ to $5 \times 10^{-5}\text{M}$ increases rate constant of reaction for the two dyes. In photo-Fenton process the increase is to $2 \times 10^{-5}\text{M}$ for Acid Orange 8 and $1 \times 10^{-5}\text{M}$ for Acid Red 17. In case of Fenton like and photo Fenton like for the two dyes the calculated rate constants increase to concentration of $1 \times 10^{-4}\text{M}$ see Fig. 8a,b. 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 [33,41]. 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 $\text{Fe}(\text{OH})_2$ in acidic environment [42] therefore, the decreases in the degradation rate occurred.

3.3.2. H_2O_2 concentration

The effect of H_2O_2 concentration on the degradation rates of Acid Orange 8 is shown in Fig. 9. The degradation rates were increased by increasing the concentration of H_2O_2 . This can be explained by the effect of additionally produced hydroxyl radicals. With increasing H_2O_2 concentration from 2mM to 10mM for Fenton and 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 H_2O_2 contributing to the $\dot{\text{O}}\text{H}$ scavenging capacity (Eqs. 9-11) [15, 43].



It can be postulated that H_2O_2 should be added at an optimum concentration to achieve the best degradation. Hence 10mM of H_2O_2 appears as an optimal dosage for Fenton and photo-Fenton processes in case of Acid Orange 8 as an example.

3.3.3. Dye concentration

For Fenton and photo-Fenton processes it was observed that the rate constant of degradation of Acid Orange 8 and Acid Red 17 decreased with increasing the initial dye concentrations. As an example Fig. 10 shows, that at low concentration of Acid Orange 8, 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 [9,44].

3.3.4. pH.

The highest rate constant values were obtained for the two systems for Acid Orange 8 and Acid Red 17 when increasing the pH to 3.0. Fig. 11 shows that, the results are in agreement with those reported in previous studies [41].

3.4. Comparison with Fenton, Fenton-like, photo-Fenton and photo-Fenton-like processes for Acid Orange 8 and Acid Red 17.

Fig. 12 presents a comparison between the Fenton, Fenton-like, photo-Fenton and photo-Fenton-like processes for the two dyes. In these process, the Fe^{2+} and Fe^{3+} concentration is the same and equal to $1.0 \times 10^{-5}\text{M}$, in presence of 10mM H_2O_2 and pH 3.0. The concentration of the two dyes is the same in all experiments ($1.0 \times 10^{-5}\text{M}$). Fig. 12, shows that the use of Fenton reagent is effective than the use of Fenton-like reagent for both dyes. This is due to reaction sequence (1) through (7). Use of a Fenton-like reagent necessitates additional steps, reactions (3) and (4), in order to produce Fe^{2+} . This must then react with H_2O_2 to produce hydroxyl radicals.

Regarding decolorization efficiency after 30 minute reaction time, the Fenton and Fenton-like for the two dyes achieve nearly identical decolorization efficiencies. When the time increased the decolorization efficiencies increased rapidly the order of color removal for the two dyes in Fenton and Fenton-like processes.

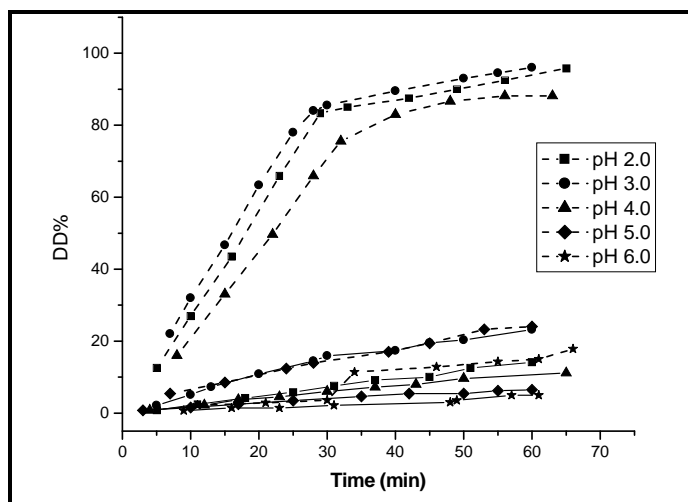


Fig. (5): The degradation degree of Acid Red 17 at different pH in presence of $[\text{dye}] = 1 \times 10^{-5} \text{M}$, $[\text{H}_2\text{O}_2] = 10 \text{mM}$ and $[\text{Fe}^{3+}] = 1 \times 10^{-5} \text{M}$ in Fenton-like (---) and photo-Fenton like (—) processes.

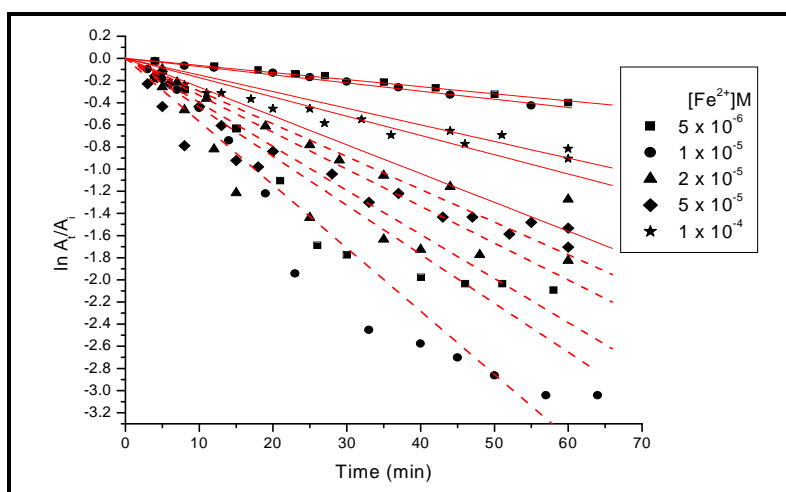


Fig. (6): Kinetic of photodegradation of $[\text{AR17}] = 1.0 \times 10^{-5} \text{M}$ at different initial concentrations of Fe^{2+} in presence of $[\text{H}_2\text{O}_2] = 5 \text{mM}$ in Fenton (---) and photo-Fenton (—) processes at pH 3.0.

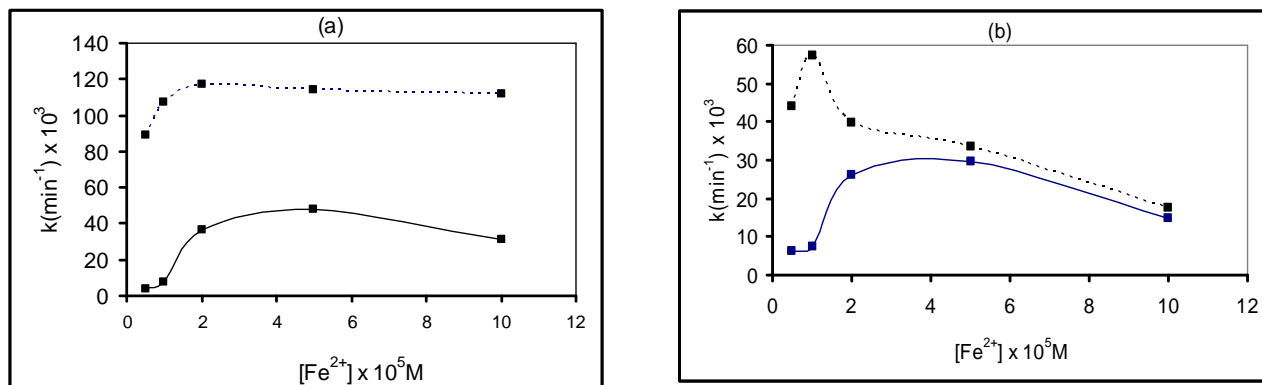


Fig. (7): Plot of $k(\text{min}^{-1})$ vs. $[\text{Fe}^{2+}]$ in presence of $[\text{H}_2\text{O}_2]=10\text{mM}$ for (AO8) and 5mM for (AR 17), (a) (AO8) and (b) $[\text{AR 17}] = 1.0 \times 10^{-5}\text{M}$ at pH3.0 in Fenton (—) and photo-Fenton (---) processes.

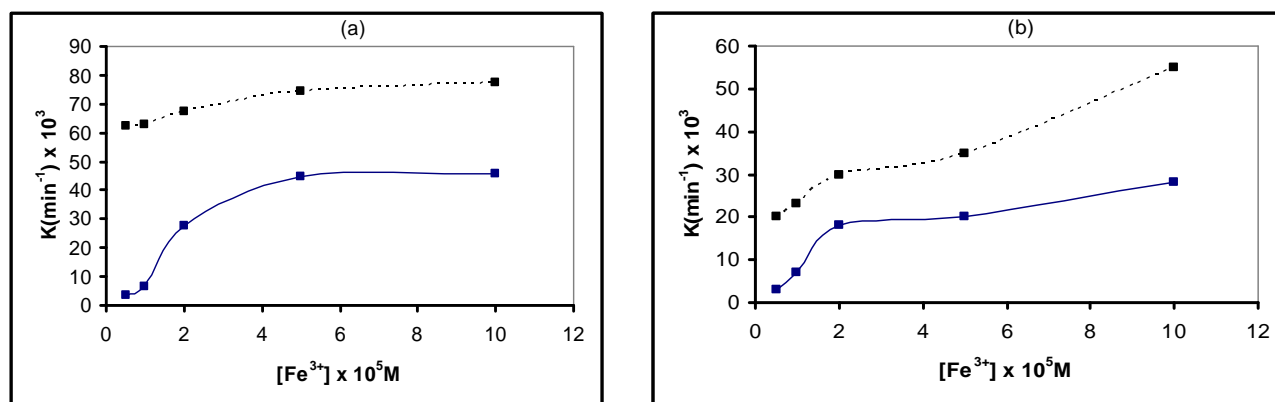


Fig. (8): Plot of $k(\text{min}^{-1})$ vs. $[\text{Fe}^{3+}]$ in presence of $[\text{H}_2\text{O}_2]=10\text{mM}$ for (AO8) and 2mM for (AR17), (a) [AO8] and (b) $[\text{AR17}] = 1.0 \times 10^{-5}\text{M}$ at pH3.0 in Fenton-like (—) and photo-Fenton-like (---) processes

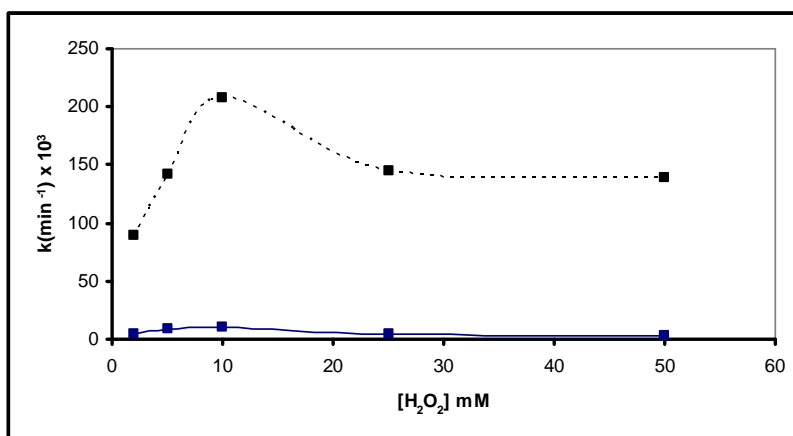


Fig. (9): Plot of $k(\text{min}^{-1})$ vs. $[\text{H}_2\text{O}_2]$ in presence of $[\text{Fe}^{2+}]=1.0 \times 10^{-5}\text{M}$, $[\text{AO8}]=1.0 \times 10^{-5}\text{M}$ at pH 3.0 in Fenton (—) and photo-Fenton (---) processes.

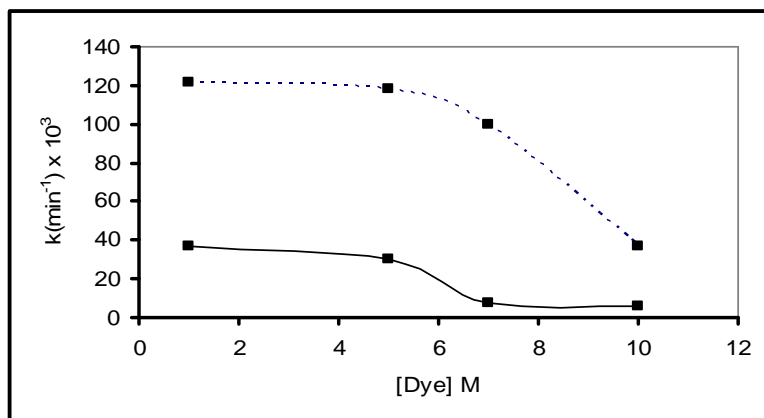


Fig. (10): Plot of $k(\text{min}^{-1})$ vs. [dye] in presence of $[\text{H}_2\text{O}_2] = 10\text{mM}$, $[\text{Fe}^{2+}] = 2 \times 10^{-5}\text{M}$ at pH 3.0 in Fenton (—) and photo-Fenton (---) processes.

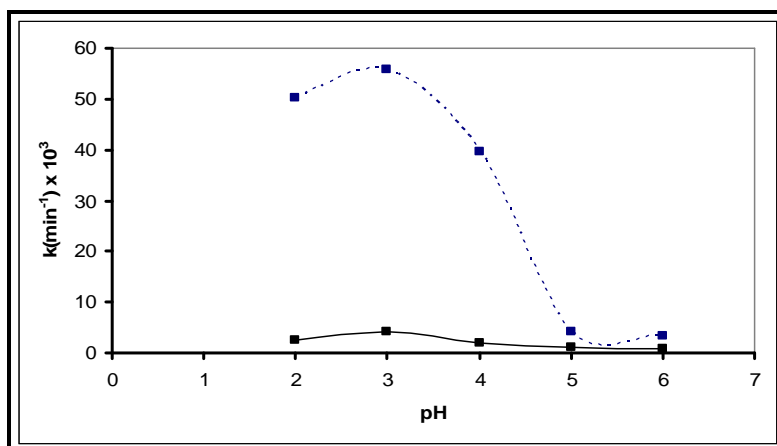


Fig. (11): Plot of $k(\text{min}^{-1})$ vs. pH in presence of $[\text{H}_2\text{O}_2] = 10\text{mM}$, $[\text{Fe}^{3+}] = 1 \times 10^{-5}\text{M}$ and $[\text{AR 17}] = 1 \times 10^{-5}\text{M}$ in Fenton like (—) and photo-Fenton like (---) processes.

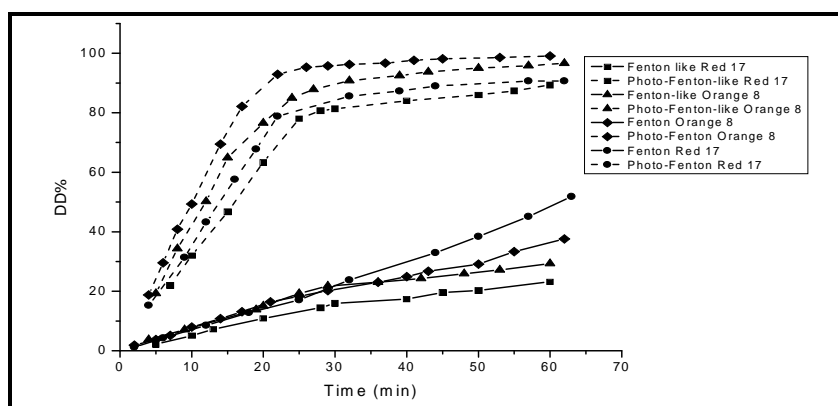


Fig. (12): The degradation degree of [AO 8] and [AR17] = $1.0 \times 10^{-5}\text{M}$ in (-) Fenton, Fenton-like, (---) photo Fenton and photo-Fenton-like processes $[\text{Fe}^{2+}] = [\text{Fe}^{3+}] = [1.0 \times 10^{-5}\text{M}]$ in presence of $[\text{H}_2\text{O}_2] = 10\text{mM}$ and pH 3.0.

Fenton-like (Red 17) < Fenton-like (Orange 8) < Fenton (Red 17) < Fenton (Orange 8) at 30 minute.

Fig. 12 shows also a comparison between the photo-Fenton and photo-Fenton-like process for both dyes (UV-irradiated-Fenton and Fenton-like reagent). Runs were made at the same previous conditions. From Fig. 12, it can be concluded that, the color removal appeared faster at the first 25 minutes as follows, 78%, 82%, 86%, 95% for photo-Fenton-like (Red 17), photo-Fenton (Red 17), photo-Fenton-like (Orange 8) and photo-Fenton (Orange 8), and increased to 88%, 91%, 96% and 99.5% respectively at 60 minutes. The order of color removal of the two dyes in photo-Fenton-like and photo-Fenton is as follows:

Photo-Fenton-like [Red 17] < photo-Fenton (Red 17) < photo-Fenton-like (Orange 8) < photo-Fenton (Orange 8) at 60 minute. The degradation rates for the four advanced oxidation processes of Acid Orange 8 and Acid Red 17 are presented in Fig. 13.

From the previous experiments, it seems that, the best conditions for degradation of Acid Orange 8 in Fenton, Fenton-like, photo-Fenton and photo-Fenton-like processes are as represented in Fig. 14a. The degradation degree for Acid Orange 8 enhances from 33% see (Fig. 12) to 90% see Fig. 14 at 55 minutes in Fenton process for Acid Orange 8. This is due to use of optimal Fe^{2+} concentration [$5.0 \times 10^{-5} \text{ M}$] see (Table 2).

In Fenton-like process the color removal was 28% and enhanced to 93% at 55 minutes, due to use of $[\text{Fe}^{3+}] = 1 \times 10^{-4} \text{ M}$ ions as shown in Table (2). UV irradiation-Fenton and Fenton-like reagent for Acid Orange 8 showed remarkable enhancement at the first 10 minutes. The degradation degree was 49% at the first 10 minutes and was enhanced to reach 83% when optimum condition was used of $[\text{Fe}^{2+}] = 2 \times 10^{-5} \text{ M}$. It then further increased to 99% at 55 minutes for photo-Fenton process. Also, similar behavior was observed in photo-Fenton-like process in presence of optimum condition $[\text{Fe}^{3+}] = 1 \times 10^{-4} \text{ M}$, where the degradation started fast and reached 96% at 55 minutes. Similar behavior was observed with Acid Red 17 in presence of optimum condition as seen in Fig. 14b and Table 3.

Table (2). Best conditions for degradation of Acid Orange 8 in Fenton, photo-Fenton, Fenton-like and photo-Fenton-like processes.

Processes Factors	Fenton	Photo-Fenton	Fenton-like	Photo-Fenton like
H_2O_2 Conc.	10mM	10mM	10mM	10mM
Fe^{2+} or Fe^{3+} Conc.	$5 \times 10^{-5} \text{ M}$	$2 \times 10^{-5} \text{ M}$	$1 \times 10^{-4} \text{ M}$	$2 \times 10^{-5} \text{ M}$
Dye Conc.	$1 \times 10^{-5} \text{ M}$	$1 \times 10^{-5} \text{ M}$	$1 \times 10^{-5} \text{ M}$	$1 \times 10^{-5} \text{ M}$
pH	3	3	3	3

Table (3). Best conditions for degradation of Acid Red 17 in Fenton, photo-Fenton, Fenton-like and photo-Fenton-like processes.

Processes Factors	Fenton	Photo-Fenton	Fenton-like	Photo-Fenton like
H_2O_2 Conc.	5mM	5mM	2mM	2mM
Fe^{2+} or Fe^{3+} Conc.	5×10^{-5}	1×10^{-5}	1×10^{-4}	1×10^{-4}
Dye Conc.	1×10^{-5}	1×10^{-5}	1×10^{-5}	1×10^{-5}
pH	3	3	3	3

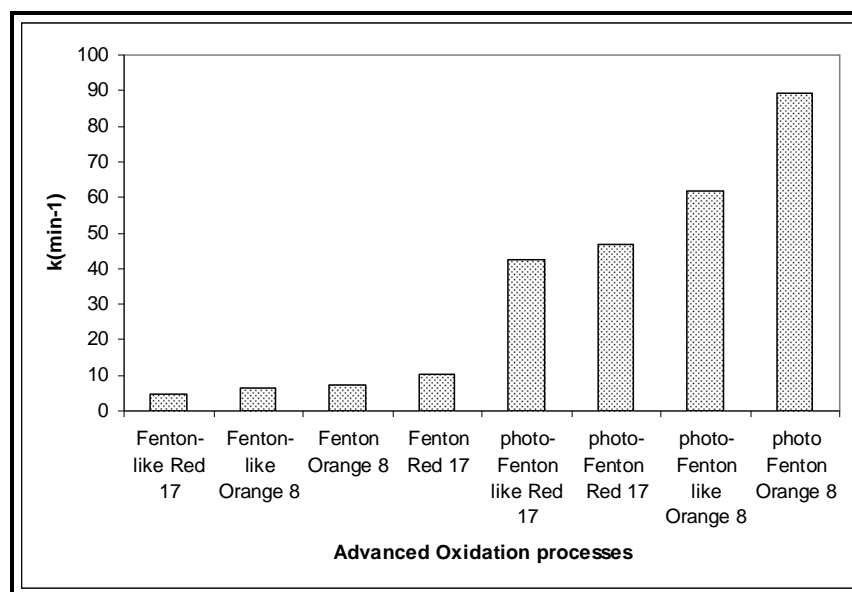


Fig. (13): Plot of $k(\text{min}^{-1})$ vs. four advanced oxidation processes of [AO8] and [AR17] = $1 \times 10^{-5}\text{M}$, $[\text{Fe}^{2+}]$, $[\text{Fe}^{3+}] = 1 \times 10^{-5}\text{M}$, $[\text{H}_2\text{O}_2] = 10\text{mM}$ and pH 3.0.

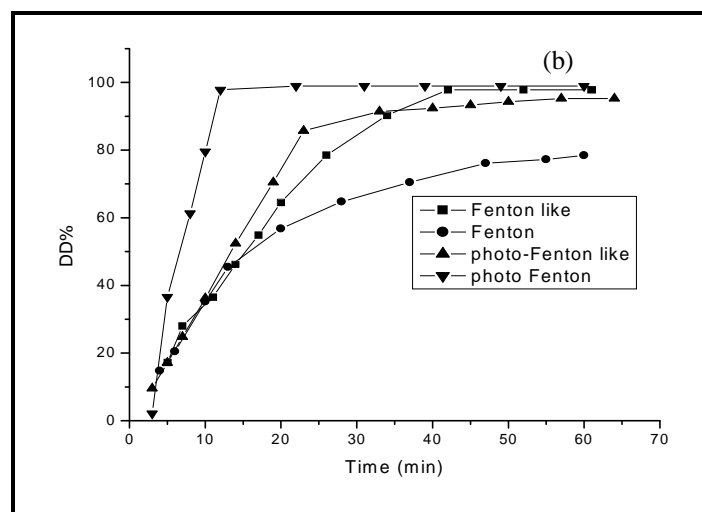
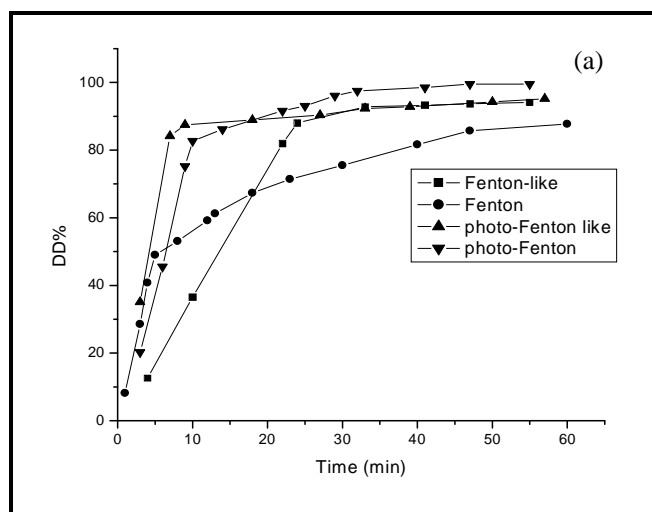


Fig. (14): The degradation degree of (a) (AO 8) and (b) (AR17) at the best conditions in Fenton, Photo-Fenton, Fenton-like and Photo-Fenton-like processes

4. Conclusion

Four advanced oxidation processes were used, for degradation of the two azo dyes Acid Orange 8 and Acid Red 17. These were comparatively examined. Based on the above results, it can be concluded that, the decolorization degree of the two azo dyes 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

(DD%) for Acid Orange 8 at optimum conditions in Fenton, Fenton-like, photo-Fenton and photo-Fenton-like processes were 89%, 93%, 99.5% and 96% at 55 minutes respectively. On the other hand the degradation degree for Acid Red 17 at optimum conditions in the same previous processes were 78%, 98%, 95% and 99% respectively at 55 minutes. From these results, it can be concluded that the four advanced oxidation processes were effective in color removal for the two azo dyes when optimal conditions were used.

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