Comparative efficiencies of the degradation of C.I. Mordant Orange 1 using UV/H2O2, Fenton, and photo-Fenton processes

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Abstract: The kinetics of the photo degradation of C.I. Mordant Orange 1 imparted by UV/H_2O_2, Fenton and photo Fenton process were investigated. Negligible effects were observed in the presence of either UV light or H_2O_2 alone. As expected the Fenton-mediated degradation occurred much faster than the photolytic process. Photo Fenton showed higher in treatment efficiency than that of Fenton process. The effects of dye concentrations, H_2O_2 concentration, pH values and the presence of Fe^{2+} concentration on the degradation rate constant were also studied. The rate constant of dye degradation that occurred in both the phtolytic as well as in the Fenton and photo-Fenton processes was found to pseudo first-order kinetics. [Nature and Science 2010;8(10):8-15]. (ISSN: 1545-0740).

Keywords: C.I. Mordant Orange 1, Degradation, Kinetic, UV/H_2O_2 , Fenton, photo-Fenton processes.

1. Introduction

Hydrogen peroxide is increasingly favored as an environmentally acceptable bleaching agent both in domestic and industrial situations[1,2]. The combination of H_2O_2 as a bleaching agent, and solar or UV radiation for photochemical degradation of textile dyes without using solid catalyst as titanium, iron, or manganese oxides, were the main objectives of many studies, H_2O_2 is a safe, efficient and easy to use chemical oxidant suitable for wide usage on concentration prevention. Discovered by Thenard in 1818, it was first used to reduce odor in waste water treatment plants, and from then on , it became widely employed in waster water treatment[3]. However, since H_2O_2 itself is not an excellent oxidant for many organic pollutants, it must be combined with UV light, salts of particular metals or ozone to produce the desired degradation results.

Many different types of synthetic dyes such as azo, vat, nitre, indigo, etc., are widely used for different purposes in paper and pulp rnanufacturing, plastics, printing and textile industry[4-5]. The effluent from these industries, when it contains substantial amounts of such dyes, causes not only coloration of water, but also poses a threat to aquatic life[6] furthermore; their presence in drinking water constitutes a potential human health hazard[7,8]. It is therefore essential either to remove the dyes from water or to treat them in such a way so as to minimize their effects on the environment and also to decolorize the water.

Different approaches have been suggested to remove dyes from aqueous solution including adsorption, biological degradation, coagulation, advanced oxidation processes (AOP), photo-Fenton reaction, ozone treatment and hypochlorite treatment[9-16]. A very simple approach which can be commonly utilized is- the photolytic oxidation of such solutions. In many cases, this method is readily applicable due to the UV content of sunlight. On the other hand, the degradation of dye using Fenton's reagent has been reported in the literature and has shown promising results[17-19]. In this paper, we wanted to examine the relative efficiencies of two different AOP methods, namely UV/H_2O_2 and Fenton's for the degradation of the Alizaration yellow G dye, C.I. Mordant Orange 1 many of the parameters that affect dye degradation rate, such as dye concentration. H_2O_2 concentration, and pH were also evaluated. Since many electrolytes are present in dye effluent, the kinetics of dye degradation in both the presence and absence of various ions were determined[20,21].

2. Materials and Methods

2.1. Reagents

C.I. Mordant Orange 1 (Fig. 1) was procured from CIBA-GEIGY (Switzerland) and was used as received distilled water was used for all dye solutions. Hydrogen peroxide (35%) was obtained from merck and ferrous sulphate heptahydrate (98%) was obtained from Merck.
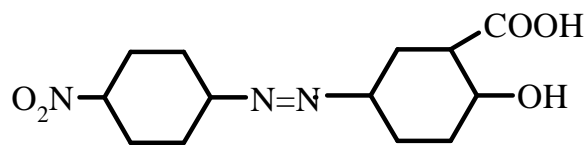

Fig. (1) C.I. Mordant Orange 1 Mol. Wt. 287.00 g/mol

2.2. Apparatuses

2.2.1. UV-visible spectroscopy

The absorption spectra are recorded with

UV-9200 UV-Vis spectrophotometer. The absorbance of solutions measured at $_{max}$ (485 nm) with using a 1cm quartz cell.

2.2.2. Batch type photoreactor

All experiments are conducted in a 500 ml thermostated bath glass reactor equipped with a magnetic stirrer. The light source is low pressure mercury lamp (254 nm 2 lamp each of 4 watt).

2.2.3. pH measurements

The pH values of the solutions are adjusted using Multimeter; WTW (Wissenshaftlich-Technische werkstatten GmbH) Imbolab Multi Lev 11, ba 12237 de Germany.

2.3. Preparation of solutions
2.3.1. Preparation of dye solutions

5.0×10^{-3}M stock solution of C.I. Mordant Orange 1 is prepared by dissolving 1.435gm of the dye in 1000 ml bi-distilled water from which working solutions are prepared (0.3-7.0×10^{-5}M) by dilution.

2.3.2. Preparation of H_2O_2 solutions

Different concentrations of H_2O_2 are freshly prepared (1.0, 2.0, 10.0, 30.0, 50.0, 70.0, mM). The concentrations of H_2O_2 are large excess in comparison to dye solutions, so that H_2O_2 concentration can be considered constant during the whole experiments.

2.3.3. Preparation of Fe^{2+} solution

1.0×10^{-2} M freshly prepared stock solutions of $FeSO_4$. $7 H_2O$ are prepared and different concentrations (5.0×10^{-6},1.0, 3.0, 5.0,7.0×10^{-5}M) are prepared by dilution.

2.4. Homogenous photodegradation

The experiments are carried out in a bath-type photoreactor. H_2O_2, Fenton ($Fe^{2+} + H_2O_2$) are acted as photocatalyst and UV light as illuminating light source. Reaction system is setup by adding the photocatalysts into 250ml dye solutions prepared in appropriate concentrations using bi-distilled water. The dye solutions are stirred and 5 ml samples are withdrawn at regular time intervals and the dye concentrations are measured spectrophotometrically.

3. Results and Discussion
3.1. Photocatalytic degradation with H_2O_2
3.1.1. Effect of initial dye concentration

The effect of different concentrations of C.I. Mordant Orange 1 (0.3-7.0×10^{-5}M) in presence of 30.0mM H_2O_2 and pH 3.0 are studies. Initially, a large degree of removal is observed. This is due to fast decomposition of H_2O_2 producing the hydroxyl

radicals. Moreover, dcoloriaztion of dye is mainly due to hydroxyl radicals generated. Azo bonds are more active and C.I. Mordant Orange 1 mountain one azo bond and dcolorization of dye is sue to the initial electrophilic cleavage of its chromophoric azo (–N=N–) bond attached to naphthalene ring[22].

The values of photodegradation Pseudo-first-order rate constant for different concentrations of C.I. Mordant Orange 1 calcualted from the linear plots of ln A/A_o against irradiation time[23] and the results of k are given in Table (1).

Table (1) :Values of K (min^{-1}) for the different concentration of the dye in presence of 30.0mM H_2O_2 and pH 3.0 .

Concentration of dye M	K min^{-1} x10^{-2}	R
0.30×10^{-5}	13.410	0.991
0.50	14.019	0.993
1.0	17.809	0.996
2.0	12.647	0.967
3.0	10.000	0.977
5.0	7.648	0.985
7.0	5.8954	0.995

Taking into account that, the life-time of hydroxyl radical is very short (only few nanoseconds), they can only react where they are formed[24]. Increasing the quantity of C.I. Mordant Orange 1 molecules per volume unit logically enhance the probability of collision between organic matter and oxidizing species, leading to an increase in the degradation rate so that a rise in concentration induces an inner filter effect, i.e., incident light would largely be wasted for dye excitation rather than for the hydroxyl radical precursor excitation. Consequently, the solution becomes more and more impermeable to UV radiation. As the rate of hydrogen peroxide photolysis directly depends on the fraction of incident light absorbed by H_2O_2 molecules, the degradation rate slows down.

3.1.2. Effect of initial pH

To study the effect of pH on photodegradation experiments are conducted for 1.0×10^{-5}M C.I. Mordant Orange 1 in presence of 30.0 mM H_2O_2 at different initial pH values (2.03-8.15). The calculated pseudo first-order rate constants and the values of K are given in Table (2)

Table (2) : Values of K (min^{-1}) for pH in presence of 1.0×10^{-5}M C.I. Mordant orange 1, 30.0 mM H_2O_2 .

pH	K min^{-1} x10^{-2}	R

| 2.03	5.243	0.957
3.00	8.112	0.932
4.00	6.210	0.961
5.10	4.250	0.952
7.09	3.198	0.960
8.15	2.609	0.981

The results show that high degradation rate constant values are observed at pH 3.00. The alkaline medium, hydrogen peroxide undergoes decomposition leading to dioxgen and water rather than producing Hydroxyl radicals under UV irradiation[25]. Therefore the instantaneous concentration in $°OH$ is lower than that as expected. The base-catalyzed decomposition involves the HO_2^- anion: the conjugated base of H_2O_2 reacts with a non dissociated molecule of H_2O_2 according to the (eq. 1).

$$HO_2^- + H_2O_2 \longrightarrow H_2O + O_2 + {}^-OH \quad (1)$$
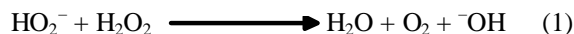
Furthermore, the deactivation of ${}^\bullet OH$ is greater when the pH of the solution is high (alkaline media), i.e. its expected that the reaction of $°OH$ with H_2O^- being approximately 100 time faster than its reaction with H_2O_2[26].

$${}^\bullet OH + HO_2^- \longrightarrow H_2O + O_2^{\bullet -} \quad (2)$$
$$H_2O_2 + {}^\bullet OH \longrightarrow H_2O + HO_2^- \quad (3)$$
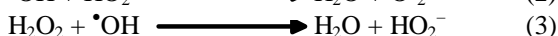
The reactivity of HO_2^- and or its basic from $O_2^{\bullet -}$ with organic compounds is very weak. They preferentially disproportionate producing some hydrogen peroxide and oxygen, according to the equation.

$$HO_2^\bullet + O_2^{\bullet -} + H_2 \longrightarrow H_2O_2 + O_2 + OH \quad (4)$$
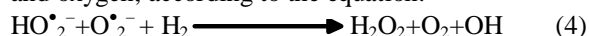
On the whole, the results demonstrate that it is very important to set a suitable pH in order to optimize the operating conditions.

3.1.3.   Effect of initial H_2O_2 dose on photo degradation .

The effect of varying the initial H_2O_2 dose (1.0 – 70.0 mM) for C.I. Mordant Orange 1 concentration 1.0 x 10^{-5} and at pH 3.0 for the application of the UV/H_2O_2 initiated degradation of dye effluent, it was necessary to initially change both the initial dye concentration and hydrogen peroxide concentration so as to optimize the conditions of maximum degradation.

Experiments were carried out in the presence of either UV light or H_2O_2 alone: neither of these treatments had an effect on the absorption maxima of the dye solution and imparted no degradation. However degradation of the dye occurred when it was subjected to UV light in the presence of H_2O_2, presumably due to the production of hydroxyl radicals, as shown below:

$$H_2O_2 + h\nu \longrightarrow 2OH^\bullet \quad (5)$$
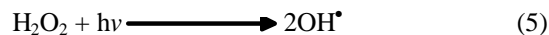
The hydroxyl radicals can in turn react with the dyes and lead to dye degradation.

$${}^\bullet OH + Dye \longrightarrow {}^\bullet Dye + H_2O \quad (6)$$
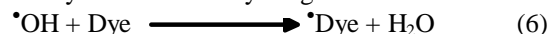
Further reactions in solution can then take place as a part of the overall scheme:

$${}^\bullet Dye + O_2 \longrightarrow Dye{-}O_2^\bullet \quad (7)$$
$$2\, Dye{-}O_2^\bullet \longrightarrow 2Dye{-}O^\bullet + O_2 \quad (8)$$
$$Dye{-}O^\bullet + O_2 \longrightarrow HO_2^\bullet + products \quad (9)$$

Additionally the peroxy radicals can also further react with the dye as follows:

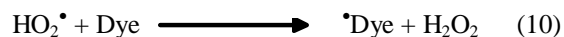$$HO_2^\bullet + Dye \longrightarrow {}^\bullet Dye + H_2O_2 \quad (10)$$

Table (3) shows the effect of increasing hydrogen peroxide concentrations on degradation rate with the most rapid degradation occurring at the highest H_2O_2 concentration tested. However, it can be seen that the apparent rate seemed to be reaching at higher H_2O_2 concentrations. For example, doubling the H_2O_2 concentration from (1.0, 70.0 mM). This can be explained to be due to the self – to quenching reaction of ${}^\bullet OH$ radicals with H_2O_2.
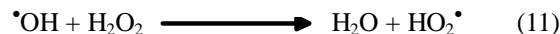
$${}^\bullet OH + H_2O_2 \longrightarrow H_2O + HO_2^\bullet \quad (11)$$

Table (3) : Values of K (min^{-1}) for the different concentration of the H_2O_2 in presence of 1.0×10^{-5} M C.I. Mordant orange 1 and pH 3.0.

H_2O_2 mM	K min^{-1} x10^{-2}	R
1.00	0.0598	0.996
2.00	0.09184	0.996
10.00	0.2625	0.942
30.00	0.6432	0.956
50.00	0.4502	0.943
70.00	0.3200	0.956

Therefore, 30.0 mM was selected as the optimum concentration of H_2O_2 for subsequent study. Similarly, the initial concentration of the dye affected the degradation of the dye; Table (1) shows that as the dye concentration increased, an almost linear decrease in the degradation rate of the dye observed[27]. However, as we were unable to find an optimum concentration of C.I. Mordant Orange 1 that would give the best degradation of the dye, it therefore appeared that the apparent decoloriton rate was independent of dye concentration in the range of $0.3\text{-}7.0 \times 10^{-5}$ mM.

Examination of the effect of pH on dye degradation revealed that dye decoloraiton was affected on pH 3.0. In order to optimize the

Fenton-mediated degradation of C.I. Mordant Orange 1 the concentrations of dye, hydrogen peroxide and Fe^{2+} were varied results are summarized Table (4-7) and Figs. (2a-5a).

3.2.: Fenton and photo-Fenton processes
        The Fenton's reagent involves reaction of ferrous ions with hydrogen peroxide to produce hydroxyl radicals, which are strong oxidizing reagents that react with the dye solution and degrade it[28].

$$H_2O_2 + Fe^{2+} \longrightarrow \ ^{\bullet}OH + OH^- + Fe^{3+} \quad (12)$$

        The hydroxyl radical propagates the reaction by reacting with the organic dye to produce further radicals, which can then react in many different steps.

$$^{\bullet}OH + + Dye \longrightarrow H_2O + \ Dye^{\bullet} \quad (13)$$

$$Dye^{\bullet} + H_2O_2 \longrightarrow Dye–OH + HO^{\bullet} \quad (14)$$

        Additionally many other reaction are also possible, which include the radical-radical reaction or the reaction of the OH radical with H_2O_2.

$$^{\bullet}OH + \ ^{\bullet}OH \longrightarrow H_2O_2 \quad (15)$$

        The peroxide radicals ($HO_2^{\bullet}$) produced in the above case can further oxidize other species present in the solution[19].

$$HO_2^{\bullet} + Fe^{2+} \longrightarrow O_2 + Fe^{3+} + H^+ \quad (16)$$
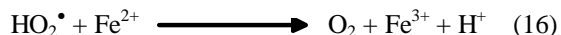
        The rapid deplection of H_2O_2 that is often observed with Fenton's reagents it probably due to the combined reactions (12-16). However, since reaction(13) has the highest rate constant, it is responsible for the degradation of the dye. Also, it is possible for Fe^{2+} to be auto regenerated in this system, and act as a catalyst(14).

$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} H^+ + HO_2^{\bullet} \quad (17)$$
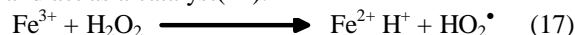
        Once can see from Table (4) that the rate C.I. Mordant Orange 1 degradation in the Fenton process was proportional to the amount of H_2O_2. This can be explained on the basis that   at higher concentrations of H_2O_2, more OH radicals are available which can degrade more dye molecule. Similarly, at a fixed concentration of H_2O_2, the extent of dye degradation decreased with increasing concentration of the dye solution (Table 5). Lastly, Table (6) shows that as the amount of the Fe^{2+} increased, the apparent rate of dye degradation increased proportionally, presumably because of more OH radicals being generated.

        It seems that unlike the photolytic process, the Fenton-mediated degradation of C.I. Mordant Orange 1 and H_2O_2 concentrations. Lastly Table (7) shows that as pH: 3.0 the apparent rate of dye degradation is large but on increase the values of pH apparent rate is decrease. The photo-Fenton (Fe^{2+}/UV) system is widely known Apos and is practical use[29]. The results are shown in Tables (4-7), and Figs. (2b-5b) illustrate that C.I. Mordant Orange 1 decolourization was excellent for photo-Fenton process instead of Fenton process. Due to the restriction of the power of UV-light used. The treatment efficiency improved slightly for dye waste water by photo-Fenton process. All pH values also dropped to acidic condition[30].

Table (4) : Effect of H_2O_2 concentration on C.I. Mordant orange 1 degradation in the Fenton, photo–Fenton processes .

Concentration of H_2O_2 mM	pH	Concentration of dye M	Concentration of Fe^{2+} M	Fenton		Photo-Fenton	
				$K \ min^{-1} \ x10^{-2}$	R	$K \ min^{-1} \ x \ 10^{-2}$	R
2.00				36.702	0.952	47.23	0.976
10.00				42.660	0.993	56.27	0.982
30.00	3.00	$10^{-5} \times 1.00$	$10^{-5} \times 3.00$	48.010	0.989	59.40	0.909
50.00				41.000	0.986	50.11	0.956
70.00				37.112	0.992	47.21	0.990

**Table (5) : Effect C.I. Mordant orange 1 concentration on its degradation in the Fenton, Photo-Fenton Processes.**

Concentration of dye M	Concentration of H_2O_2 mM	pH	Concentration of Fe^{2+} M	Fenton		Photo-Fenton	
				$K \ min^{-1} \ x10^{-2}$	R	$K \ min^{-1} \ x10^{-2}$	R
1.00×10^{-5}				16.67	0.952	35.72	0.986
3.00	30.00	3.00	$10^{-5} \times 3.00$	15.84	0.954	28.16	0.994
5.00				13.66	0.964	20.90	0.996
7.00				5.51	0.990	8.44	0.943

Table (6) : Effect of Fe^{2+} concentration on C.I.   Mordant orange 1 degradation in the Fenton, photo-Fenton processes.

Concentration of Fe^{2+} M	Concentration of H$_2$O$_2$	pH	Concentration of dye	Fenton		Photo-Fenton	
				K min^{-1} x 10^{-2}	R	K min^{-1} x 10^{-2}	R
10^{-6}×5.00				1.034	0.959	2.66	
10^{-5}×1.00				4.239	0.972	7.14	0.996
3.00	30.00	3.00	10^{-5}×1.00	25.081	0.989	36.040	0.972
5.00				13.721	0.953	20.66	
7.00				7.174	0.983	11.09	

Table (7) : Effect of pH on C.I.   Mordant orange 1 degradation in the Fenton, photo-Fenton processes .

pH	Concentration of H$_2$O$_2$ mM	Concentration of dye M	Concentration of Fe^{2+} M	Fenton		Photo-Fenton	
				K min^{-1} x10^{-2}	R	K min^{-1} x10^{-2}	R
3.00				14.227	0.988	19.723	0.980
4.00	30.00	10^{-5}×1.00	10^{-5}×3.00	9.261	0.981	11.166	0.969
5.00				5.130	0.973	8.589	0.996
7.00				2.810	0.984	5.634	0.973
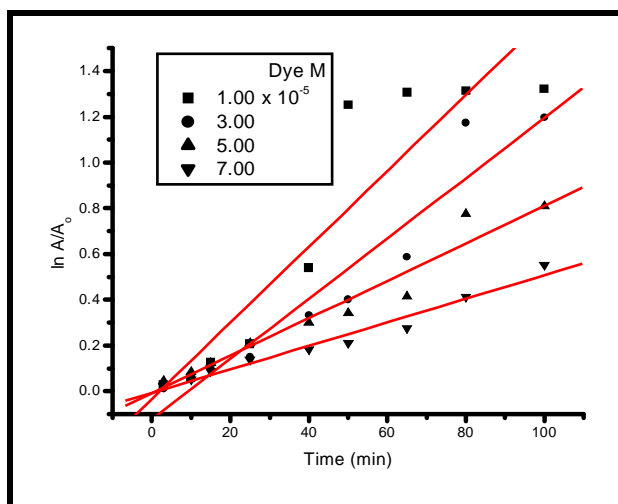
Fig. (2a) Kinetic of photodegradation of Fe^{2+} 3.0 x 10^{-5} at different initial concentrations of C.I. Mordant orange 1 in presence of 30.00 mM H$_2$O$_2$ in Fenton process and pH: 3.00.
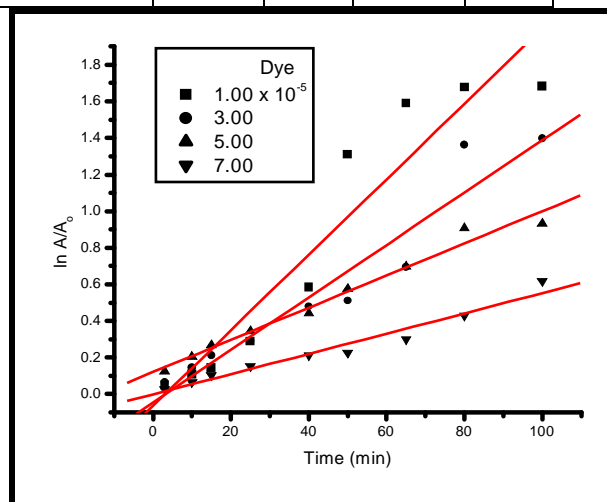
Fig. (2b) Kinetic of photodegradation of Fe^{2+} 3.0 x 10^{-5} at different initial concentrations of C.I. Mordant orange 1 in presence of 30.00 mM H$_2$O$_2$ in photo-Fenton process and pH: 3.00.
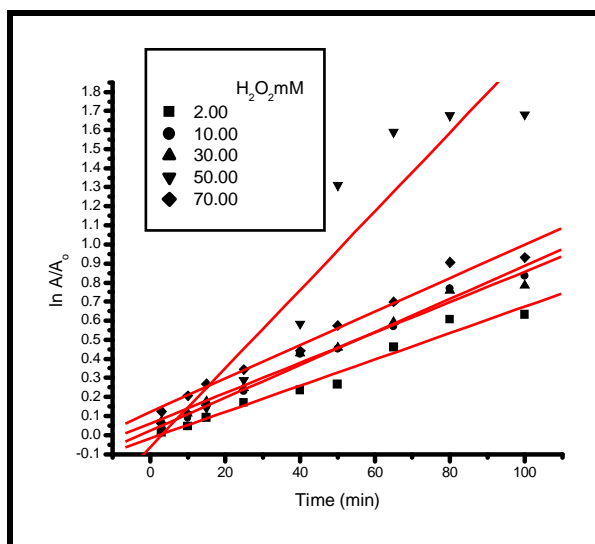
Fig. (3a): Kinetic of photodegradation of C.I. Mordant Orange 1 1.0 x 10^{-5} M at different initial concentrations of H_2O_2 in presence of Fe^{2+}: 3.0 x 10^{-5} in Fenton process and pH: 3.00.
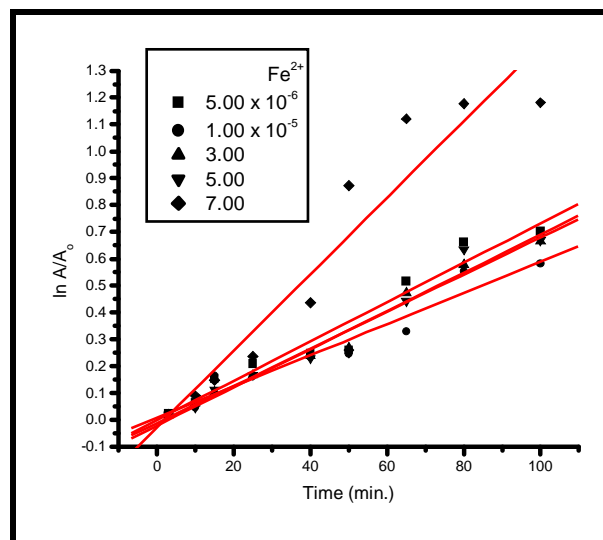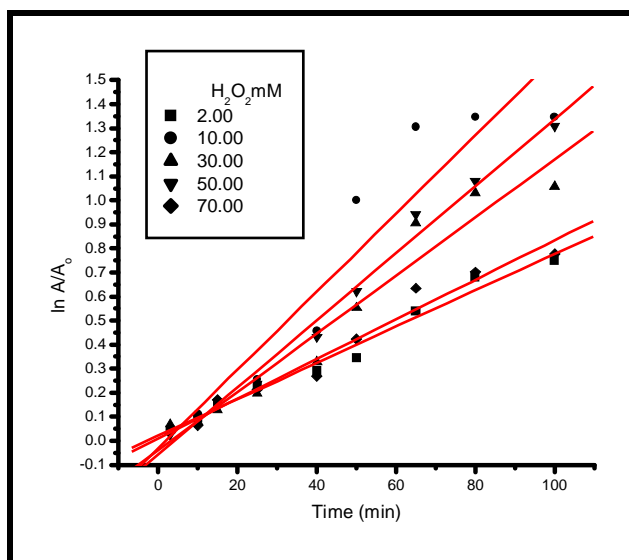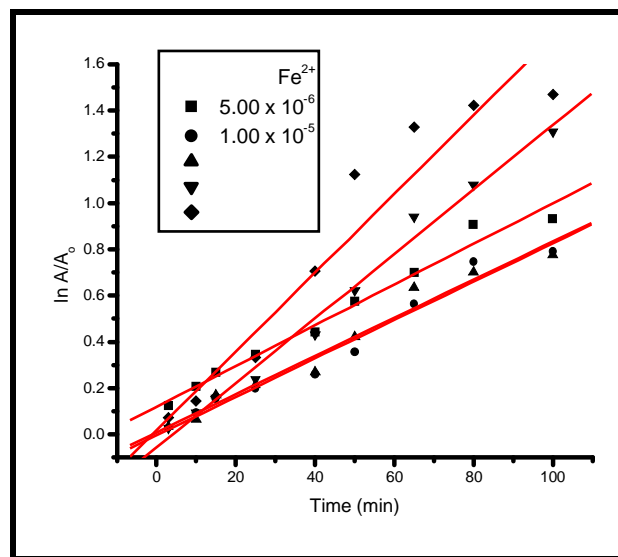

Fig. (4a): Kinetic of photodegradation of C.I. Mordant Orange 1 1.0 x 10^{-5} M at different initial concentrations of Fe^{2+} in presence of 30.00 mM H_2O_2 Fenton process and pH: 3.00.

Fig. (3b): Kinetic of photodegradation of C.I. Mordant Orange 1 1.0 x 10^{-5} M at different initial concentrations of H_2O_2 in presence of Fe^{2+}: 3.0 x 10^{-5} in Photo-Fenton process and pH: 3.00.

Fig. (4b): Kinetic of photodegradation of C.I. Mordant Orange 1 1.0 x 10^{-5} M at different initial concentrations of Fe^{2+} in presence of 30.00 mM H_2O_2 photo-Fenton process and pH: 3.00.
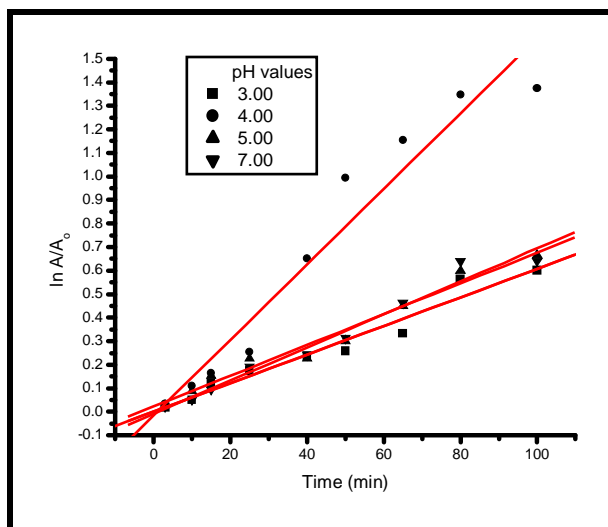
Fig. (5a): Kinetic of photodegradation of C.I. Mordant Orange 1 1.0 x 10^{-5} M at different initial concentrations of pH values in presence of 30.00 mM H$_2$O$_2$ Fenton process and Fe^{2+} 3.0 x 10^{-5} M
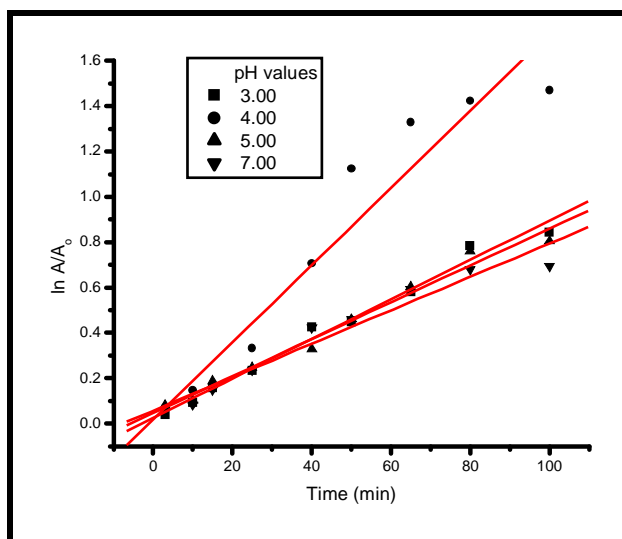

Fig. (5b): Kinetic of photodegradation of C.I. Mordant Orange 1 1.0 x 10^{-5} M at different initial concentrations of pH values in presence of 30.00 mM H$_2$O$_2$ Photo-Fenton process and Fe^{2+} 3.0 x 10^{-5} M.

5. Conclusions

- The results obtained showed that H$_2$O$_2$/UV system could be efficiently used to degrade the C.I. Mordant Orange 1.
- Photodegradation efficiency of dye was negligible when photolysis was carried out in the absence of H$_2$O$_2$ and UV light.

- The results indicated that the degree of degradation of C.I. Mordant Orange 1 was obviously affected by pH value and the amount. The optimum amount of Photocatalyst at pH: 3.0 and 30.0mM and at dye concentration of 1.0 x 10^{-5}M.
- It was observed that using of Fe^{2+} as a photocatalyst it increased the rate of degradation. The plot of ln A/A$_o$ dye versus irradiation time for C.I. Mordant Orange 1 was linear which showed that the photodegradation reaction obeys the pseudo-first-order kinetics reaction.
- The results show that the rate of reaction "k" min^{-1} in photo-Fenton large than Fenton.

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