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REMOVAL OF ACID RED 44 DYE FROM ITS LIQUID WASTE UNDER WIDE PHOTOCATALYTIC CONDITIONS

Asmaa M. Raslan[a*], Omima K. Houssin[b]
(a) Dept. of Chem. Fac. of Science (Girls), Al-Azhar University.*
(b) Dept. of Chem. Fac. of Science (Girls), Al-Azhar University.

ABSTRACT

The homogeneous photocatalytic oxidation of Acid Red 44 (AR44) with Fenton (Fe^{2+}/H_2O_2), photo-Fenton, ($Fe^{2+}/H_2O_2/UV$), and Fenton-like (Fe^{3+}/H_2O_2), photo-Fenton-like ($Fe^{3+}/H_2O_2/UV$) had been investigated in aqueous solution $[H_2O_2] = 5.0x10^{-2}$ M and $[AR44] = 1.0x10^{-5}$M, $7.0x10^{-5}$ M and at pH = 3.0. However, decolorization exhibited different rates for the two systems. The degradation rate in Fenton and photo-Fenton oxidation was much faster than that of the Fenton-like and photo-Fenton-like reaction in the initial stages.

The effects of operating parameters are also investigated, such as: $Fe^{2+}$and Fe^{3+} concentrations, initial dye concentration, and H_2O_2 concentration and light intensity.

Decolorization of model wastewater was rather successful using Fe^{2+} or Fe^{3+}. In the case of Fenton and photo-Fenton oxidation, the extent of degradation was 96%, 99% after 175, 66 minutes respectively, when the Fe^{2+} ion concentration was $\leq 1 x 10^{-4}$ M. When the Fe^{2+} ion concentration was $>1.0 x 10^{-4}$ M, the extent of dye degradation was 100%, 100% after 25, 20 mints, respectively. For Fenton-like and photo-Fenton-like oxidation, if the Fe^{3+} ion concentration was $\leq 1.0xl0^{-4}$ M, dye degradation was only 97%, 97% after 200,158 minutes, respectively. However, the extent of degradation was 98%, 99% after 64, 38 minutes, respectively at a Fe^{3+} ion concentration $1.0x10^{-4}$ M.

KEYWORDS: *Acid Red 44 dye, Liquid waste & Photocatalytic condition*

INTRODUCTION

Various industries such as textiles, paint and varnishes, ink, plastics, pulp and paper and cosmetics use different types of organic dyes and dye intermediates. About 15% of the dyes produced throughout the world are lost during synthesis and processing with wastewater [1, 2]. Such colored dye effluents pose a major threat to the surrounding ecosystem. Some of the dyes are extremely toxic [3].

The increased public concern with these dyes and the stringent international environmental standards (ISO 14001) have prompted the need to develop novel treatment methods for converting these organic dyes to harmless compounds [4]. Dye effluents can be treated by biological methods, flocculation, and reverse osmosis, adsorption on activated charcoal, chemical oxidation methods and advanced oxidation processes [5]. Biological methods have been proved to be ineffective [6-8]. Flocculation, reverse osmosis and adsorption methods transfer the pollutants to other media, thus causing secondary pollution [9, 10].

Chemical oxidation methods are not cost effective [11]. Advanced organic processes have been used to treat various organic pollutants during the last two decades. Advanced Oxidation Processes (AOPs) based on the generation of very reactive species such as hydroxyl radicals (°OH) that oxidize a broad range of organic pollutants quickly and non-selectively [12].Homogenous catalysts (Fenton, Fenton like, photo Fenton and photo-Fenton like reagent's) are widely used. The Fenton reaction is a widely used and studied catalytic process based on an electron transfer between H_2O_2 and a metal acting as a homogeneous catalyst [13]. The major advantage of Fenton process is that the reagent components are safe to handle and environmentally benign [14]. Fenton oxidation has been applied for the decolorization of effluents from textile dyeing process and dye manufacturing process. Compared to other oxidation processes, such as UV/H_2O_2 process, costs of Fenton oxidation are quite low [15, 16]. The reaction of H_2O_2 with ferric (Fe^{3+}) iron in acidic aqueous solutions which is among the most common homogeneous systems and potential sources hydroxyl radicals generation. Iron III-catalyzed H_2O_2 decomposition known as the Fenton like's reaction, provides an alternative way of oxidizing recalcitrant and/or toxic organic compounds present in most industrial wastewaters [17, 18]. Photo-Fenton is known to be able to improve the efficiency of dark Fenton or Fenton-like reagents, respectively, by means of the interaction of radiation (UV or Vis) with Fenton's reagent [19, 20].Considering the above mentioned facts, the aim of the this work was to remove C.I. Acid Red 44 dye by using UV photolysis in the presence of homogeneous photocatalyst (Fenton, Fenton like, photo- Fenton and photo-Fenton-like)

EXPERIMENTAL

II.1. Materials and methods

C.I. Acid Red 44 (AR44) was purchased from Aldrich Company and was used as received without further purification. Hydrogen peroxide (30% W/W,), Ferrous sulphate heptahydrate, Ferric sulphate were obtained from Merck. Double distilled water was used for all studies. The pH is adjusted to the desired values with HCl and NaOH obtained from Merck. The basic structure of AR44 is depicted in Fig.1.

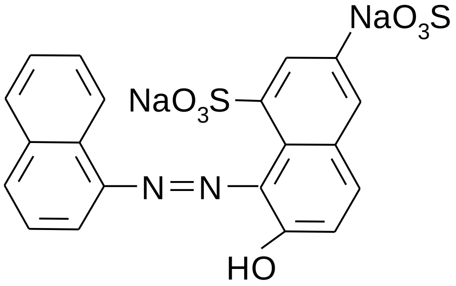

Fig.1.Structure of Acid Red 44 (AR44)

II.2. Instrumental techniques

The instrument used for the study was batch glass reactor equipped with a magnetic stirrer. The light source is low pressure mercury lamp (254 nm 2 lamp each of 4 watt), UV-9200 UV- VIS spectrophotometer, Multimeter; WTW (Wissenshaftlich-Technische Werkstatten GmbH) InoLab Multi Lev11, ba 12237de; Germany.

II.3. Photoreactor and light source

All experiments were carried out in a 500 ml thermostated batch glass reactor where the reaction solution was directly irradiated with a low pressure mercury lamp (254 nm 2 lamp each of 4 watt). The incident light flux of the low pressure Hg lamps (λ=254 nm) was determined by uranyl oxalate actinometry [21]. During all experiments, the reaction solution was vigorously mixed from the reactor bottom by means of a magnetic stirrer at 400 rpm to provide effective mixing and aeration of the reaction solution. The (dark) Fenton, Fenton- like experiments were conducted in the same beaker except that the UV-light source was not turned on for these experiments.

RESULTS AND DISCUSSION

III.2. Removal of AR44 by Fenton and Fenton like processes:

III.2.1. Effect of Fe^{2+} and Fe^{3+} concentration

The influence of iron concentrations ($[Fe^{2+}]$ = $[Fe^{3+}]$ =1.0 x $l0^{-5}$- 5.0 x $l0^{-3}$ M,), at pH 3.0 on the effectiveness of Fenton process for AR44 degradation in both Fenton and Fenton-like reactions expressed as color removal is illustrated in Figs.2-5 and Tables 1,2 , respectively. The concentration of hydrogen peroxide is fixed as 5.0x10^{-2} M and two dye concentrations are used (1.0x10^{-5} and 7. 0x10^{-5} M)

During the Fenton reaction, ferrous ions can quickly react with H_2O_2 to produce hydroxyl radicals and ferric ions (k = 70 M^{-1} S^{-1}, [22]), which will then be reduced by the dye to ferrous ions again. Meanwhile, ferric ions can also react with H_2O_2, producing hydroperoxide radicals which cause a second decomposition process for the dye according to (Eqs.1 and 2).

$H_2O_2 + Fe^{2+} \longrightarrow Fe^{3+} + HO^{-} + {}^{o}OH$ (1)

$H_2O_2+Fe^{3+} \longrightarrow Fe(OOH)^{2+}+H^{+} \longleftrightarrow Fe^{2+} + HO^{o}_2 + H^{+}$ (2)

In Fenton-like reaction, ferric ions react with H_2O_2 to produce ferrous ions at very slow rate (k=0.001 -0.01 M^{-1} s^{-1}, [22]); few ferrous ions can be formed and thus induce the Fenton reaction. Therefore, only one process with Fe^{3+}/H_2O_2 reaction will dominate (Eqs.3 and 4).

$Fe^{3+}+H_2O_2 \longrightarrow Fe(HO_2)^{2+}+H^{+}$

$, K = 2.9 \text{ x } 10^{-3}\ M^{-1}s^{-1}$ (3)

$Fe(HO_2)^{2+} \longrightarrow Fe^{2+} + HO^{o}_2$

$, k = 2.7 \text{ x } 10^{-3}\ M^{-1}s^{-1}$ (4)

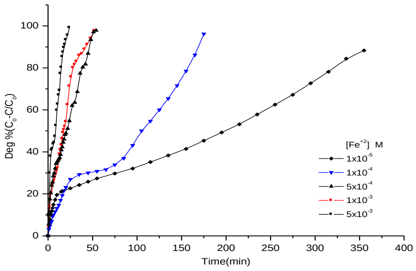

Fig.2.The degradation degree of different initial concentrations of Fe^{2+} in presence of 5.0 x10^{-2} M H_2O_2, [AR44] =1.0x10^{-5} M in Fenton process and pH 3.0.

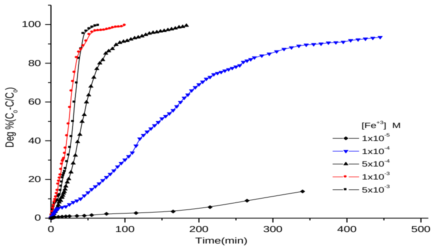

Fig.3.The degradation degree of different initial concentrations of Fe^{2+}in presence of 5.0 x10^{-2} M H_2O_2, [AR44] =7.0x10^{-5} M in Fenton process at pH 3.0.

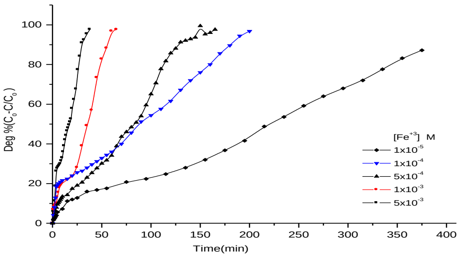

Fig.4.The degradation degree of different initial concentrations of Fe^{3+}in presence of 5.0 x10^{-2} M H_2O_2, [AR44] =1.0x10^{-5} M in Fenton-like process at pH 3.0.

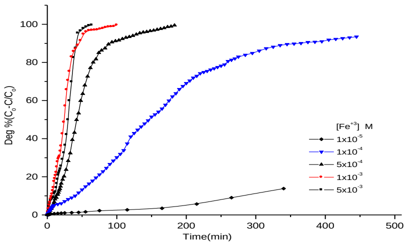

Fig.5.The degradation degree of different initial concentrations of Fe^{3+}in presence of 5.0 x10^{-2} M H_2O_2, [AR44] =7.0x10^{-5} M in Fenton-like process and pH 3.0.

Table 1.The values of *k* (min^{-1}) at λ_{max}(510nm) for the different concentrations of Fe^{2+} and obtained correlation coefficients for [AR44]=1.0x10^{-5} M ,7.0x10^{-5} M in presence of 5.0x10^{-2} M H_2O_2 in dark and pH 3 .0.

[Fe^{2+}] x10^3 M	[AR44]=1.0x10^5 M		[AR44]=7.0x10^5 M	
	k (min^{-1}) x10^3	r	*k* (min^{-1}) x10^3	r
0.01	3.75	0.980	0.14	0.998
0.10	6.99	0.970	3.25	0.980
50	49.0	0.927	54.2	0.992
1.00	55.42	0.976	57.94	0.974
5.0	107.96	0.968	98.54	0.987

Table 2.The values of *k* (min^{-1}) at λ_{max}(510nm) for the different concentrations of Fe^{3+} and obtained correlation coefficients for [AR44]=1.0x10^{-5} M ,7.0x10^{-5} M in presence of 5.0x10^{-2} M H_2O_2 in dark and pH 3 .0.

[Fe^{3+}] x10^3 M	[AR44]=1.0x10^5 M		[AR44]=7.0x10^5 M	
	k (min^{-1}) x10^3	r	*k* (min^{-1}) x10^3	r
0.01	2.79	0.991	0.355	0.963
0.10	8.53	0.977	6.06	0.993
50	8.57	0.976	22.83	0.988
1.00	26.79	0.934	47.24	0.960
5.0	52.76	0.919	58.24	0.966

III.2.2. Effect of AR44 initial concentration

The influence of the [AR44] was examined in this study, in the concentration range l.0xl0^{-5} - 9.0xl0^{-5} M, at constant concentrations of [Fe^{2+}] , [Fe^{3+}] and H_2O_2 , ([Fe^{2+}]=[Fe^{3+}]= l.0xl0^{-3} M and [H_2O_2]= 5.0xl0^{-2} M, respectively) at pH=3.0 and the solution was irradiated with UV light.Figs. 6, 7 and Table 3.

The increase of initial dye concentration decreases the efficiency of degradation of AR44. The obtained results demonstrate that dark Fenton degradation is faster for diluted solution of AR44 dye. The obtained results demonstrate that photodegradation is faster for diluted solution of AR44 dye.

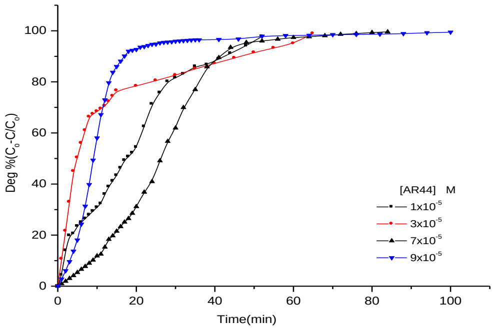

Fig.6.The degradation degree of different initial concentrations of AR44 in presence of 5.0 x10^{-2} M H_2O_2, [Fe^{2+}] =1.0x10^{-3} M in Fenton process at pH 3.0.

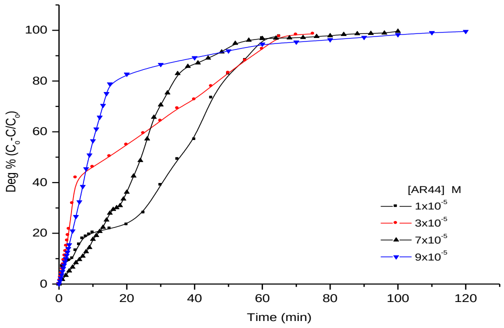

Fig.7.The degradation degree of on different initial concentrations of AR44 in presence of 5.0 x10^{-2} M H_2O_2, [Fe^{3+}] =1.0x10^{-3} M in Fenton-like process at pH 3.0.

Table 3.The values of *k* (min^{-1}) at λ_{max}(510nm) for different concentrations of AR44 and obtained correlation coefficients of $[Fe^{2+}]= [Fe^{3+}]=1.0x10^{-3}$ M in presence of $5.0x10^{-2}$ M H_2O_2 in dark and pH 3 .0.

[AR44] x10^5 M	$[Fe^{2+}]=1.0x10^3$M		$[Fe^{3+}]=1.0x10^3$ M	
	k (min^{-1}) x10^3	r	*k* (min^{-1}) x10^3	r
1.00	55.74	0.975	49.41	0.981
3.00	54.77	0.943	47.88	0.987
7.00	55.42	0.960	44.75	0.979
9.00	46.21	0.973	43.56	0.989

III.2.3.Effect of H_2O_2 initial concentration

Form Figs. 8, 9 and Table 4. The results indicate that the degradation of the dye increased with increasing H_2O_2 concentration. Several investigations have reported an optimal peroxide concentration in the Fenton oxidation of dyes [23, 24], unreacted H_2O_2 will act as a scavenger of °OH and produces a less potent perhydroxyl radical, resulting in less dye degradation.

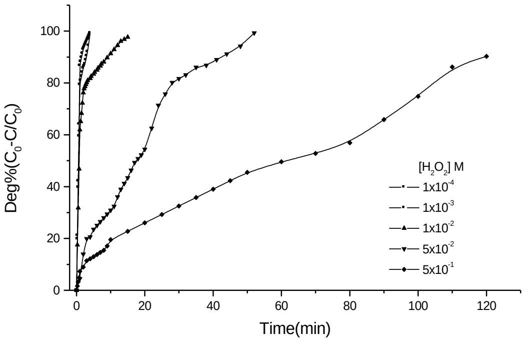

Fig.8.The degradation degree of [AR44] =$1.0x10^{-5}$ M with different initial concentrations of H_2O_2 in presence of $[Fe^{2+}]$ = 1.0 x10^{-3} M, in Fenton process and pH 3.0.

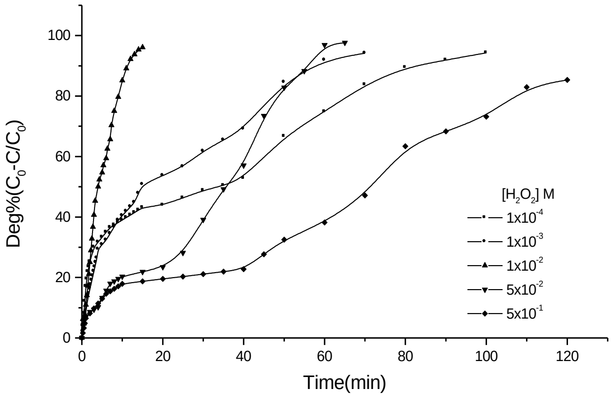

Fig.9.The degradation degree of [AR44] =$1.0x10^{-5}$ M with different initial concentrations of H_2O_2 in presence of $[Fe^{3+}]$ = 1.0 x10^{-3} M, in Fenton-like process and pH 3.0.

Table 4. The values of k (min^{-1}) at λ_{max}(510nm) for different concentrations of H_2O_2 and obtained correlation coefficients of [AR44]=1.0x10^{-5} M in presence of [Fe^{2+}]= [Fe^{3+}]=1.0x10^{-3} M in dark and pH 3 .0.

[H_2O_2] x10^2 M	[Fe^{2+}]=1.0x10^{3}M		[Fe^{3+}]=1.0x10^3 M	
	k (min^{-1}) x10^3	r	k (min^{-1}) x10^3	r
0.01	882.7	0.965	26.97	0.975
0.1	1175.25	0.972	38.73	0.982
1.00	274.74	0.952	195.85	0.990
5.00	55.42	0.975	17.52	0.956
50	11.74	0.992	8.34	0.909

III.2.4. Photo-Fenton and photo-Fenton like processes:

III.2.4.1. Effect of ferrous and ferric dosage

Amount of ferrous and ferric ions are one of the main parameters to influence the photo Fenton and photo Fenton- like processes. The effect of addition of Fe^{2+} and Fe^{3+} ([Fe^{2+}] = [Fe^{3+}] = 0.01 – 5x 10^{-3} M) at pH = 3.0 on the degradation of AR44 ([AR44] = 1.0x10^{-5} and 7x10^{-5} M) has been studied. The results are shown in Figs. 10-13 and the calculated pseudo first order rate constants and degree of degradation is given in Tables 5, 6.

The decolorization of the dye is mainly due to the hydroxyl radical generated by chemical and photochemical reactions (Eqs.5 and 6) respectively

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{o}OH$ (5) (5)

$H_2O_2 + h\nu \longrightarrow 2{}^{o}OH$ (6)

Moreover, the positive effect of irradiation on the degradation rate include the photoreduction of Fe^{3+} to Fe^{2+} ions, which produce new ºOH radicals with H_2O_2 according to the following mechanism [25,26].

$Fe^{3+} + H_2O_2 + h\nu \rightarrow Fe^{2+} + {}^{o}OH + H^+$ (7)

$HO^{o}_2 + H_2O_2 \longrightarrow {}^{o}OH + H_2O + O_2$ (8)

More hydroxyl radicals are produced with the increase in the concentration of Fe^{2+} and Fe^{3+} [27].

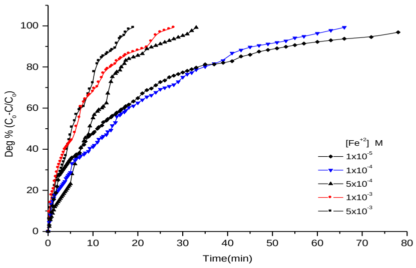

Fig.10.The degradation degree of different initial concentrations of Fe^{2+}in presence of 5.0 x10^{-2} M H_2O_2, [AR44] =1.0x10^{-5} M in photo-Fenton process and pH 3.0.

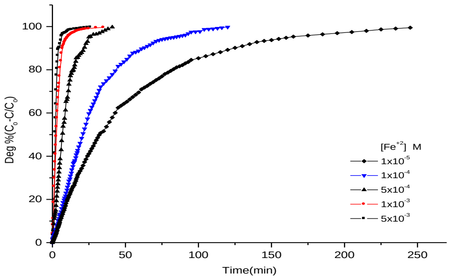

Fig.11.The degradation degree of different initial concentrations of Fe^{2+}in presence of 5.0 $x10^{-2}$ M H_2O_2 and [AR44] =$7.0x10^{-5}$M, in photo-Fenton process and pH 3.0.

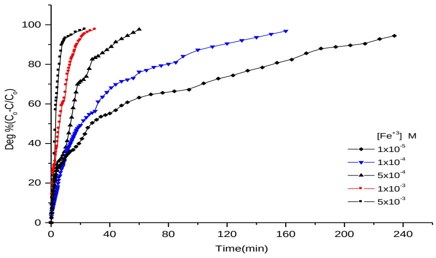

Fig.12.The degradation degree of different initial concentrations of Fe^{3+}in presence of 5.0 $x10^{-2}$ M H_2O_2 and [AR44] =$1.0x10^{-5}$ M in photo-Fenton like process and pH 3.0.

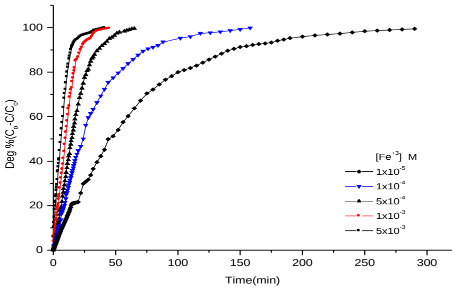

Fig.13.The degradation degree of different initial concentrations of Fe^{3+}in presence of 5.0 $x10^{-2}$ M H_2O_2 and [AR44] =$7.0x10^{-5}$ M, in photo-Fenton like process and pH 3.0.

Table 5.The values of *k* (min^{-1}) at λ_{max}(510nm) for the different concentrations of Fe^{2+} and obtained correlation coefficients for [AR44]=$1.0x10^{-5}$ M ,$7.0x10^{-5}$ M in presence of $5.0x10^{-2}$ M H_2O_2 in photo-Fenton process and pH 3.0

[Fe^{2+}] $x10^3$ M	[AR44]=$1.0x10^5$ M		[AR44]=$7.0x10^5$ M	
	k (min^{-1}) $x10^3$	r	*k* (min^{-1}) $x10^3$	r
0.01	18.91	0.998	18.82	0.998
0.10	36.54	0.998	37.78	0.997
50	112.24	0.997	112.24	0.997
1.00	273.79	0.986	233.03	0.970
5.0	436.5	0.973	385.15	0.963

Table 6. The values of *k* (min^{-1}) at λ_{max}(510nm) for the different concentrations of Fe^{3+} and obtained correlation coefficients for [AR44]=1.0x10^{-5} M ,7.0x10^{-5} M in presence of 5.0x10^{-2} M H_2O_2 in photo-Fenton-like process and pH 3.0

[Fe^{3+}] x10^3 M	[AR44]=1.0x10^5 M		[AR44]=7.0x10^5 M	
	k (min^{-1}) x10^3	r	*k* (min^{-1}) x10^3	r
0.01	12.14	0.974	15.88	0.999
0.10	22.62	0.985	30.24	0.999
50	95.41	0.995	61.77	0.993
1.00	116.54	0.988	108.02	0.993
5.0	152.88	0.985	137.68	0.990

III.2.5. Effect of initial AR44 concentration

Photochemical processes are strongly dependent on solution absorption once penetration of light can be strongly limited in high absorption solutions such as dyes [28].

Therefore, influence of the [AR44] on its photo-Fenton and photo-Fenton like degradation was examined in this study, in the concentration range l.0 – 9.0x10^{-5} M, at constant concentrations of [Fe^{2+}] , [Fe^{3+}] and H_2O_2, ([Fe^{2+}] = [Fe^{3+}] = 1.0xI0^{-3} and [H_2O_2] = 5.0x10^{-2} M, respectively) at pH =3.0 and the solution was irradiated with UV. The degree of degradation of different time intervals for irradiation of different [AR44] in presence of photo- Fenton and photo- Fenton- like are presented in Figs. 14- 15. Large degree of removal is observed in both processes. This is due to fast reaction of Fe^{2+} or Fe^{3+} with the H_2O_2 producing hydroxyl radicals. Data in (Table 7) show that the degradation rate increases with the decrease in the dye concentration. At high dye concentration, a significant amount of UV light of 257 nm may be absorbed by dye molecules and this reduces the absorbance of UV light by the catalyst. The increase in dye concentration also decreases the path length of photon entering this solution. It should be pointed out that even at a high initial concentration of AR44 (3.0-9.0 x 10^{-5} M), about 99% of removal can be achieved after 100 and 120 min for Fenton and Fenton like reactions, respectively. This indicates that Fenton and Fenton-like catalysts can also work well at a high initial concentration of AR44.

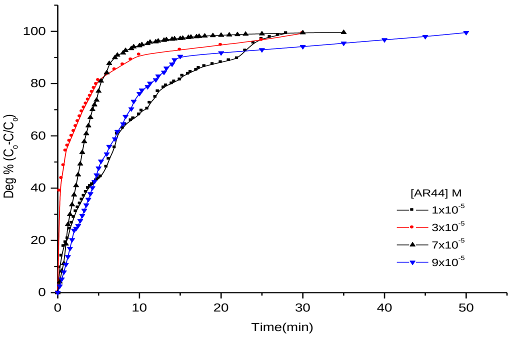

Fig.14.The degradation degree of different initial concentrations of AR44 in presence of 5.0 x10^{-2} M H_2O_2 and [Fe^{2+}] =1.0x10^{-3} M in photo-Fenton process and pH 3.0.

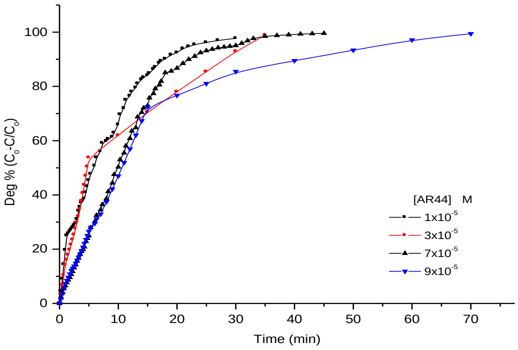

Fig.15.The degradation degree of different initial concentrations of AR44 in presence of 5.0 x10^{-2} M H_2O_2 and $[Fe^{3+}]$ =1.0x10^{-3} M, in photo-Fenton- like process and pH 3.0.

Table 7.The values of *k* (min^{-1}) at λ_{max}(510nm) for different concentrations of AR44 and obtained correlation coefficients of $[Fe^{2+}]$= $[Fe^{3+}]$=1.0x10^{-3} M in presence of 5.0x10^{-2} M H_2O_2 in photo-Fenton and photo-Fenton- like process and pH 3.0

[AR44] x10^{5} M	$[Fe^{2+}]$=1.0x10^{3}M		$[Fe^{3+}]$=1.0x10^{3} M	
	k (min^{-1}) x10^{3}	r	*k* (min^{-1}) x10^{3}	r
1.00	273.79	0.986	126.91	0.996
3.00	147.36	0.994	120.64	0.961
7.00	142.16	0.996	94.0	0.987
9.00	108.02	0.996	69.65	0.989

III.2.6. Effect of H_2O_2 initial concentration:

Initial concentration of H_2O_2 plays an important role in the photo- Fenton processes. The effect of addition of H_2O_2 (0.01- 50x10^{-2} M) on the photodegradation of AR44 for photo- Fenton and photo-Fenton like processes are shown in Figs.16,17 at day concentrations of 1.0 and 7.0x10^{-5} M and pH = 3.0. Addition of H_2O_2 up to a concentration of 1.0x10^{-3} M increases the photodegradation rate constants (Figs. 16, 17). However, high H_2O_2 concentrations (H_2O_2> 1.0x10^{-3}M) lead to decrease of the AR44 removal rate. The increase in the photodegradation is due to the increase in hydroxyl radical concentration by the addition of H_2O_2. But at high dosage of H_2O_2 the decrease is due to the hydroxyl radical scavenging effect of H_2O_2 (Eqs.9-11) [29, 27]. Moreover, the effect of a high H_2O_2 concentration can be attributed to the fact that it is competing with AR44 for °OH radicals, thus decreasing their steady-state concentration and AR44 oxidation rate.

$H_2O_2 + {}^\circ OH \rightarrow H_2O + HO^\circ_2$ (9)
$HO^\circ_2 + {}^\circ OH \rightarrow H_2O + O_2$ (10)
${}^\circ OH + {}^\circ OH \rightarrow H_2O_2$ (11)
The calculated rate constants are given in Table 8.

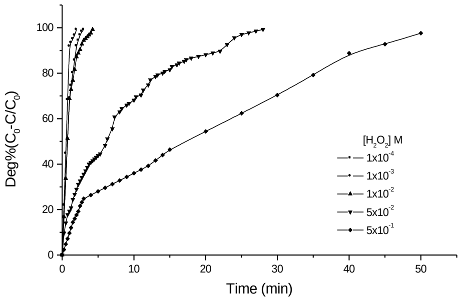

Fig.16.The degradation degree of different initial concentrations of H_2O_2 in presence of [AR44] $=1.0x10^{-5}$M, [Fe^{2+}] $=1.0x10^{-3}$M, in photo-Fenton process and pH 3.0.

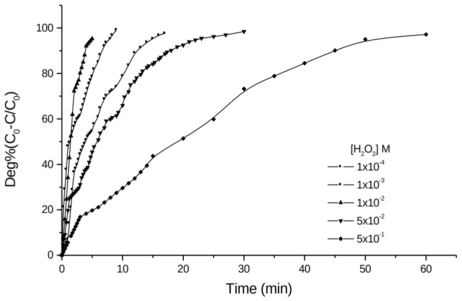

Fig.17.The degradation degree of different initial concentrations of H_2O_2 in presence of [AR44] $=1.0x10^{-5}$M, [Fe^{3+}] $=1.0x10^{-3}$M, in photo-Fenton like process and pH 3.0.

Table 8.The values of k (min^{-1}) at λ_{max}(510nm) for different concentrations of H_2O_2 and obtained correlation coefficients of [AR44]=$1.0x10^{-5}$ M in presence of [Fe^{2+}]= [Fe^{3+}]=$1.0x10^{-3}$ M in photo-Fenton and photo-Fenton-like process and pH 3.0

[H_2O_2] $x10^2$ M	[Fe^{2+}]=$1.0x10^3$M		[Fe^{3+}]=$1.0x10^3$ M	
	k (min^{-1}) $x10^3$	r	k (min^{-1}) $x10^3$	r
0.01	1368.51	0.983	188.97	0.984
0.1	2140.83	0.980	353.82	0.971
1.00	976.99	0.988	586.45	0.994
5.00	273.79	0.986	126.91	0.996
50	46.26	0.965	42.02	0.988

III. 1. 3.4. Effect of light intensity

In photo-Fenton process, UV light is mainly used for **(i)** photolysis of H_2O_2 and **(ii)** photoreduction of ferric ion to ferrous ion. [27]. Hence, the influence of UV light intensity on the degradation of the dye has been investigated. The light intensity is adjusted by changing the distance between the lamps and the reaction cell (10 cm and 20 cm) and the number of lamps (1 and 2 UV lamps).The AR44 concentrations are $1.0x10^{-5}$ M and 7.0x $10^{-5}$and H_2O_2 concentration is $5.0x10^{-2}$ M and [Fe^{2+}]=[Fe^{3+}]=$5.0x10^{-3}$ M at pH = 3.0.The results are shown in Figs.(18-21) and Tables (9,10).Increase of light intensity increases the degradation of AR44. This increase in degradation is due to increase production of hydroxyl radical; at low light intensity the rates of photolysis of H_2O_2 and photoreduction of Fe^{3+} are reduced.

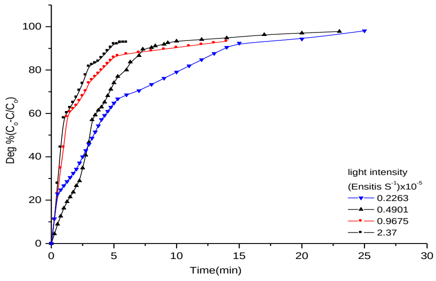

Fig.18.The degradation degree of AR44 at different light intensity in presence of 1.0x10^{-5} M AR44, 5.0 x10^{-2} M H_2O_2, 5.0x10^{-3} M Fe^{2+} , in photo -Fenton process and pH 3.0.

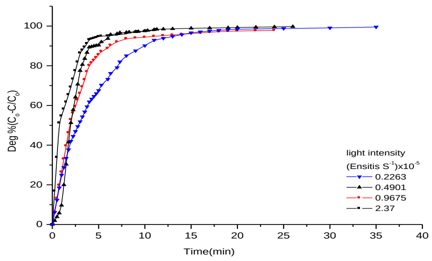

Fig.19.The degradation degree of AR44 at different light intensity in presence of 7.0x10^{-5} M AR44, 5.0 x10^{-2} M H_2O_2,5.0x10^{-3} M Fe^{2+} in photo -Fenton process and pH 3.0.

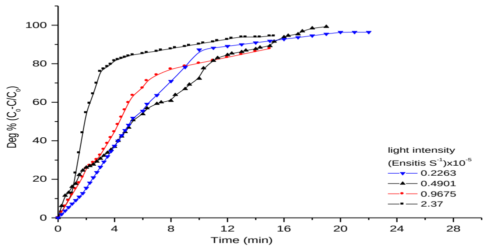

Fig.20.The degradation degree of AR44 at different light intensity in presence of 1.0x10-5 M AR44, in photo -Fenton-like process and pH 3.0,+5.0 x10-2 M H2O2, 5.0x10-3 M Fe3

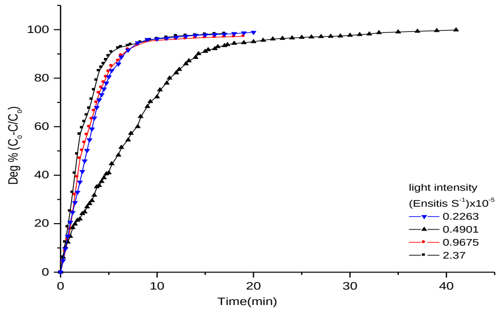

Fig.21.The degradation degree of AR44 at different light intensity in presence of 7.0x10^{-5} M AR44, 5.0 x10^{-2} M H_2O_2, 5.0x10^{-3} M Fe^{3+}, in photo-Fenton like process and pH 3.0**.**

Table 9.The values of *k* (min^{-1}) at λ_{max}(510nm) at different light intensity and obtained correlation coefficients for AR44 in presence of [AR44]=1.0x10^{-5} M ,7.0x10^{-5} M,[Fe^{2+}]=1.0x10^{-3} M 5.0x10^{-2} M, H_2O_2 in photo-Fenton process and pH 3.0.

Light intensity (μ Einteins s^{-1})x10^{5}	[AR44]=1.0x10^{5} M		[AR44]=7.0x10^{5} M	
	k (min^{-1}) x10^{3}	r	*k* (min^{-1}) x10^{3}	r
0.2263	230.63	0.999	204.08	0.994
0.4901	436.65	0.973	385.15	0.960
0.9675	480.15	0.982	436.36	0.987
2.37	536.83	0.982	430.57	0.960

Table 10.The values of *k* (min^{-1}) at λ_{max}(510nm) at different light intensity and obtained correlation coefficients for AR44 in presence of [AR44]=1.0x10^{-5} M ,7.0x10^{-5} M,[Fe^{3+}]=1.0x10^{-3} M 5.0x10^{-2} M, H_2O_2 in photo-Fenton-like process and pH 3.0.

Light intensity (μ Einteins s^{-1})x10^{5}	[AR44]=1.0x10^{5} M		[AR44]=7.0x10^{5} M	
	k (min^{-1}) x10^{3}	r	*k* (min^{-1}) x10^{3}	r
0.2263	161.99	0.992	74.58	0.981
0.4901	258.01	0.978	137.68	0.990
0.9675	339.96	0.997	174.0	0.987
2.37	418.19	0.984	401.16	0.989

CONCLUSIONS

The degradation rate in Fenton oxidation was much faster than that of the Fenton-like reaction in the initial stages. The effect of operating parameters is also investigated, such as: Fe^{2+}and Fe^{3+} concentrations, initial dye concentration, and H_2O_2 concentration and light intensity. In the case of Fenton oxidation, the extent of degradation was 96% after 175 mints when the Fe^{2+} ion concentration was $\leq$ 1 x 10^{-4} M. When the Fe^{2+} ion concentration was >1.0 x 10^{-4} M, the extent of dye degradation was 100% after 25 min. For Fenton-like oxidation, if the Fe^{3+} ion concentration was $\leq$ 1xl0^{-4} M, dye degradation was only 97% after 200 mints. By contrast, the extent of degradation was 99% after 64 mints at an Fe^{3+} ion concentration 1.0x10^{-4} M the results indicate that the degradation of the dye increase with increasing H_2O_2 concentration (([dye] = 1.0x10^{-5} and 7.0x10^{-5} M and [Fe^{2+}] = [Fe^{3+}] = (1.0x10^{-5} -5.0x10^{-3} M), at pH =3.0). When the H_2O_2 concentration increased to 1.0 x 10^{-3} M, 90% decolourisation could be achieved after 1 h in the Fenton reaction.

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