

Factors Affecting the Kinetic Parameters Related to the Degradation of Direct Yellow 50 by Fenton and Photo-Fenton Processes

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ABSTRACT

In a laboratory study, photocatalytic degradation of the non-biodegradable azo dye Direct Yellow 50 (DY50) solutions by Fenton ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$) and photo-Fenton ($\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV}$) processes had been carried out. Batch experiments were conducted to determine optimal operating conditions expressed as color removal. A comparative study of these two processes was done including the following variables: pH, light intensity and initial concentrations of Fe^{2+} , H_2O_2 and DY50. The effect of these parameters had been studied and the optimum operational conditions of these two processes were found. The optimum conditions were obtained at pH 3, Fe^{2+} , H_2O_2 and DY50 concentrations of, 1.0 mM, 10 mM and 0.02 mM, respectively for the two systems. The photo-Fenton system proved to be the most efficient and occurs at a much higher oxidation rate than Fenton system and allows achieving 100% degradation of DY50 in 7 min of reaction time. The decoloration rate pseudo constants were calculated. The results of the study show that photo-Fenton process is an effective and economic treatment process for DY50 under acidic conditions by producing higher degradation efficiency in a relatively short radiation time compared to Fenton process. Electrical energy per order (EE/O) was proposed to assess the relative performance of each catalytic system used. It is found that EE/O decreases with increasing the value of k_{app} .

Key Words: Direct Dye, Fenton's process, Photo-Fenton's process, Kinetics, Electrical energy per order.

1. INTRODUCTION

Wastewaters from textile and dye industries are highly colored with considerable amount of auxiliary chemicals. Direct discharge of textile industry wastewater into the receiving media causes serious environmental pollution by imparting intensive color and toxicity to aquatic environment [1]. The azo-dyes, characterized by having an azo group consisting of two nitrogen atoms ($\text{N}=\text{N}$), are the largest class of dyes used in textile industry [2]. Azo-dyes are the most problematic pollutants of textile wastewaters since more than 15% of the textile dyes end up in the wastewater stream [3]. Apart from the aesthetic problems created when colored effluents reach the natural water currents, dyes strongly absorb sunlight, thus impeding the photosynthetic activity of aquatic plants and seriously threatening the whole ecosystem [4, 5].

Physical or chemical operations for the removal of dye pollutants, such as adsorption, chemical flocculation, electroflotation, reverse osmosis, ultrafiltration, coagulation or ion exchange have been used efficiently [6] although they are non-destructive, since they just transfer dissolved organic contaminants from wastewater phase to another phase that will have to be regenerated and post-treated by expensive operations [7]. Hence, there is considerable current interest in developing alternative and more cost-effective techniques. For that reasons, advanced oxidation processes (AOPs) have emerged as an important class of technologies for the oxidation of dyes into CO_2 , H_2O and inorganic ions, or biodegradable compounds [8].

Among AOPs, homogenous Fenton reaction ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) is one of the most important processes to generate hydroxyl radicals, $^{\circ}\text{OH}$ [9]. Oxidation power of Fenton reagent is due to the generation of hydroxyl radicals ($^{\circ}\text{OH}$) during the iron catalyzed decomposition of hydrogen peroxide in acid medium. The hydroxyl radicals with a high oxidation potential (2.8V) can completely destroy the pollutants in Fenton reagent treatments. Degradation of pollutants can be considerably improved by using UV radiation for the generation of additional hydroxyl radicals. Photo-Fenton ($\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV}$) treatment has been effectively used for degradation of recalcitrant pollutants [10, 11, 12]. However, the optimal operating conditions and reagent concentrations need to be determined in order to reduce the cost of photo-Fenton treatment and to improve the extent of dyestuff removal. In the light of literature studies, the major objective of this study is to investigate the effects of reagent concentrations (initial dyestuff, H_2O_2 , Fe^{2+} concentrations and pH) on dyestuff by the Fenton and photo-Fenton treatment

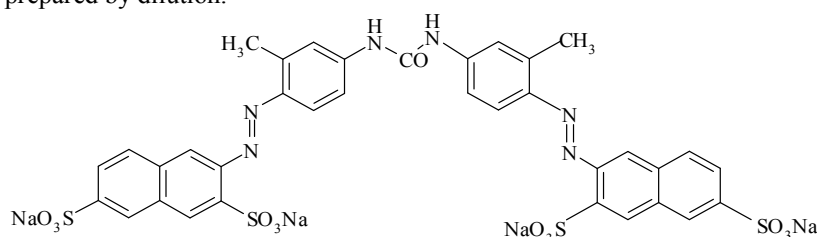
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studies reporting color removal. A typical azo-dye, Direct Yellow50 (DY50) was used as the dyestuff in aqueous solution. A comparative study of these two processes is done including the following variables: pH, light intensity and initial concentrations of Fe^{2+} , H_2O_2 and DY50. The effect of these parameters has been studied and the optimum operational conditions of these two processes were found. Electrical energy per order (EE/O) was proposed to assess the relative performance of each catalytic system used.

2. EXPERIMENTAL

2.1. Dye solutions:

A commercial azo dye (C.I. Direct Yellow 50 (DY50)) was obtained from Ciba-Geigy (Scheme 1). The dye was of commercial grade and used as received. 1.2×10^{-2} M stock solution of DY50 was prepared by dissolving 1.53 gm of the dye in 250 ml deionised water from which working solutions are prepared by dilution.



Scheme 1: C.I. Direct Yellow 50 (DY50)

2.2. Chemicals for pH adjustment

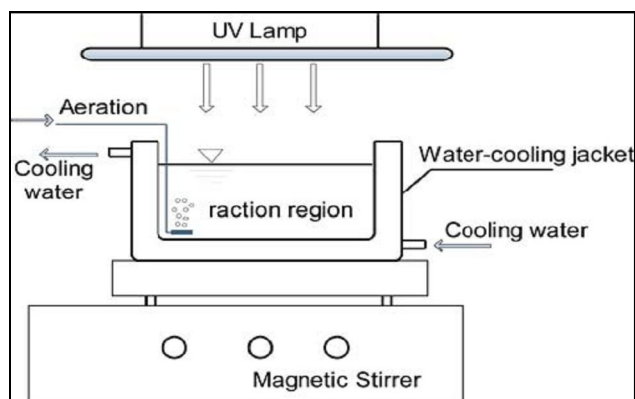
For the pH adjustment, concentrated reagent grade sulphuric acid and sodium hydroxide solutions (Panreac) were used. All solutions were prepared with deionised water obtained from a Millipore Milli-Q system.

2.3. Fenton's and photo-Fenton's oxidation reagent

The hydroxyl radical, $^{\circ}\text{OH}$, was generated in situ by the addition of the following reagents in aqueous media: hydrogen peroxide, H_2O_2 , Panreac, 33% w/v and ferrous sulphate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, Merck, 99.5%.

2.4. Batch photoreactor.

All experiments were conducted in a 500 ml thermostated batch glass reactor (Scheme 2) equipped with a magnetic stirrer. The light source was low pressure mercury lamp (2 lamps each of 4 watt) which basically emits at 254nm, used as artificial light source, when working under photo-Fenton's conditions. The reaction mixture inside the cell, consisting of 250 ml of dye sample and the precise amount of Fenton's reagent, was continuously stirred with a magnetic bar and the temperature fixed at the required level (298K). The intensity of the incident light, measured employing a uranyl actinometer (13, 14), was $0.226\text{--}2.371 \mu\text{Einstein} \times 10^{-5} \text{ s}^{-1}$. All experiments were carried out using 2 UV lamps each of 4 watt at distance 20 cm apart from the reaction mixture.



Scheme 2: Experimental setup for the photocatalytic dye degradation.

3. RESULTS AND DISCUSSION

3.1. Fenton's and photo-Fenton's reactions

3.1.1. Evaluation of kinetic parameters

The kinetics of Fenton reaction can be quite complex because of the larger number of steps involved [13, 15]. The general elementary rate law for reaction of a target organic compound (RH) can be written as follows:

$$-dC_{RH}/dt = k_{HO} k_{OH} C_{RH} + \sum K_{oxi} C_{oxi} C_{RH} \quad (1)$$

where oxi represents oxidants other than $^{\circ}OH$ that may be present, such as ferryl. Hydroxyl radical is usually regarded as the sole or most important reactive species. Then:

$$-dC_{RH}/dt = k_{HO} k_{OH} C_{RH} \quad (2)$$

Considering that the concentration of reactive species must reach quickly a stationary-state regimen during the process, and provided that k_{OH} can be considered constant, the rate law for the degradation process can be treated as being pseudo-first order, in terms of consumption of the target organic compound. We have

$$-dC_{RH}/dt = k_{app} C_{RH} \quad (3)$$

and, by integration, we obtain:

$$\ln C_{RH} = \ln C_{(RH)0} - k_{app} t \quad (4)$$

A plot of $\ln C_{RH}$ versus time generated a straight line with a negative slope. The slope of this line corresponds to the apparent rate constant value for the degradation of the organic target compound. In our case, we follow the rate of decolourization of the dye ($\lambda = 397$ for DY50). Consequently, Eq. 4 was converted to:

$$\ln C = \ln C_0 - k_{app} t \quad (5)$$

$$\ln C / \ln C_0 = -k_{app} t \quad (6) \text{ and}$$

$$t_{1/2} = 0.693/k \quad (7)$$

Color removal % is given by Eq. 8

$$\text{Color removal (\%)} = ((C_0 - C_t) / C_0) \times 100 \quad (8)$$

As indicated in several papers [16-20] decolourization kinetics of most dyes can be safely treated using a pseudo-first order rate law, based on the steady-state approximation. The following parameters were evaluated aiming to find the optimal conditions to promote the degradation of the dye: pH and concentrations of Fe^{2+} , H_2O_2 , and dye. The pH in the initial assays was defined as being 3, since it has been reported that Fenton's reactions occur efficiently at pH in a range between 2.9 and 3.5 [21-23].

3.1.2. Factors affecting the degradation of DY50

3.1.2.1. Effect of ferrous dosage

The concentration of Fe^{2+} is one of the critical parameters in Fenton and the photo-Fenton processes. In the present study, the influence of different iron concentrations ($[Fe^{2+}] = 0.01, 0.02, 0.05, 0.5, 1.0$ and 1.50 mM), at pH 3.0 on the effectiveness of Fenton and photo-Fenton processes expressed as color removal (Eq. 8) is illustrated in Figure 1. The concentration of hydrogen peroxide is fixed as 10 mM and dye concentrations is $[DY50] = 0.02$ mM. The calculated k_{app} and $t_{1/2}$ according to Eqs. 6 and 7 are given in Table 1.

Fenton's and photo-Fenton's reactions are AOPs where oxidant species are generated from hydrogen peroxide and Fe²⁺/Fe³⁺ as a catalytic couple. In Fenton's reaction [24], ferrous salts react with hydrogen peroxide to generate the hydroxyl radicals as follows (Eq.9):



Then, Fe³⁺ can be reduced by reaction with exceeding H₂O₂ to form again ferrous ion and more radicals. This second process is called Fenton's-like [25], is slower than Fenton's reaction and allows Fe²⁺ regeneration giving place to a catalytic mechanism (Eqs. 10-12):



The rate of contaminants degradation can be considerably increased via photochemical reaction in the photo-Fenton's process [25, 26]. In this case, the regeneration of Fe²⁺, with production of new HO[•] radicals, follows a photoreduction process (Eqs. 13 and 14):



Fenton's and photo-Fenton's type reactions offer successful pollutant removal with relatively low operational costs [27].

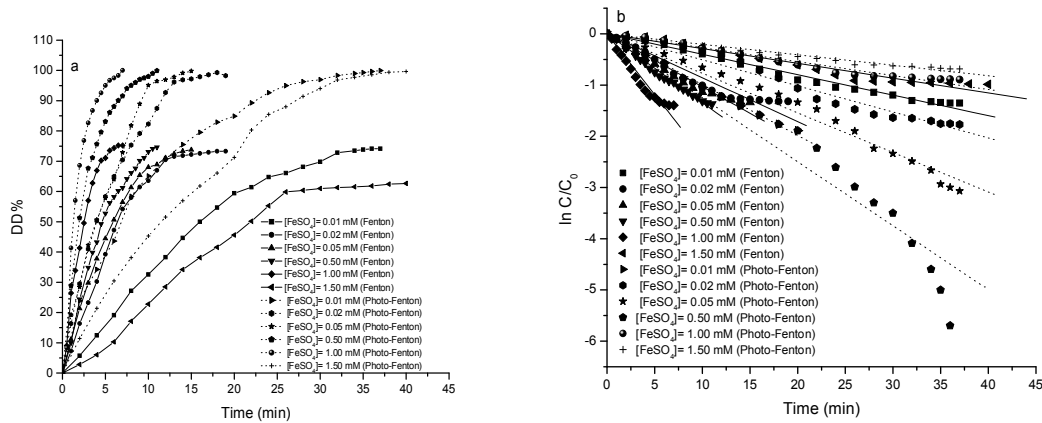


Figure 1: Effect of the initial Fe²⁺ concentrations on the degree of degradation (DD%), a) and the apparent rate constant (k_{app}), b) for the decolourization of DY50 ([DY50]=0.02mM [Fe²⁺]= 1.0 mM at pH = 3.0: (–) Fenton (----) photo-Fenton).

Table 1: The values of k (min⁻¹), t_{1/2} (min), R_{initial} (mol l⁻¹ min⁻¹) and EE/O (wKh) at different Fe²⁺ in presence of [DY50]=0.02mM M, 10 mM H₂O₂ and light intensity 0.9675 (μ Einteins s⁻¹)x10⁻⁵ at pH 3.0 for the photocatalytic degradation of DY50 in Fenton and photo-Fenton processes .

Fenton						Photo-Fenton				
[Fe ²⁺] mM	k _{app} x10 ³ (min ⁻¹)	t _{1/2} (min)	R _{initial} x10 ⁶ (k _{app} x C ₀) (mol l ⁻¹ min ⁻¹)	EE/O (wKh)	r	k _{app} x10 ³ (min ⁻¹)	t _{1/2} (min)	R _{initial} x10 ⁶ (k _{app} x C ₀) (mol l ⁻¹ min ⁻¹)	EE/O (kWh)	r
0.01	45.65	15.18	0.91	101.81	0.998	95.25	7.27	1.90	48.79	0.998
0.02	108.48	6.38	2.16	42.84	0.996	173.66	3.99	3.47	26.76	0.999
0.05	116.20	5.96	2.32	4.00	0.997	263.30	2.63	5.26	17.65	0.961
0.50	149.12	4.64	2.98	31.16	0.998	354.89	1.95	7.09	13.09	0.999
1.00	264.21	2.62	5.28	17.59	0.995	606.65	1.14	12.12	7.66	0.998
1.50	32.29	21.46	0.64	143.94	0.994	61.10	11.34	1.222	76.07	0.999

3. 1.2. 2. Effect of H₂O₂ concentration

Moreover, for a fixed Fe²⁺ concentration (1.0 mM), the following H₂O₂ concentrations were tested: 5.0, 10.0, 25.0, 50.0 and 75.0 mM. When the concentration of H₂O₂ increased from 5.0 mM to 10.0 mM, the removal of color increased. This could be explained by the effect of the hydroxyl radicals produced additionally. Thereafter a reverse trend was followed. Thus the H₂O₂ concentration was optimized to 10.0 mM for the removal of 0.02mM of the test compounds from water.

For DY50 decolourization, the best H₂O₂ concentration can be taken as 10.0 mM. At these conditions, the time needed to reduce to half the initial colour of the dye was t_{1/2} = 2.62 min with a k_{app} = 0.264min⁻¹ (color removal = 99.97 in 7 min, Figure 2). At these optimal conditions, the molar ratio H₂O₂/Fe(II) was 10.0. As we can see in the results shown in Figure 2, a further increase in oxidant concentration slows down the degradation process, because hydrogen peroxide in excess acts as hydroxyl-radical scavenger as shown by the following equation (Eq. 15) [28]:



Moreover, some competitive reactions could take place [29]:

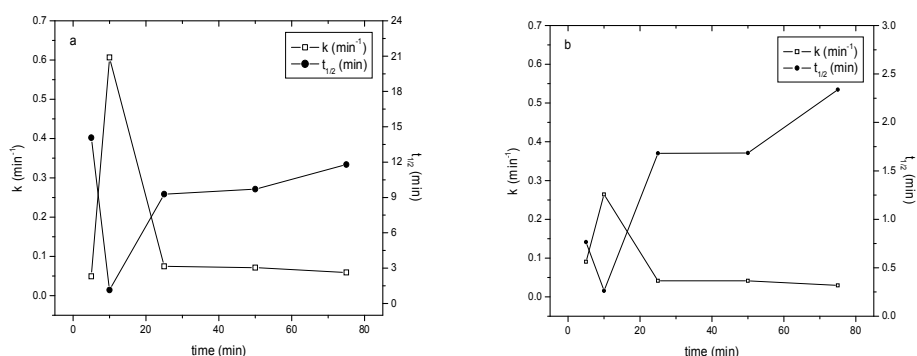


Figure 2: Effect of the initial H₂O₂ concentration on the apparent rate constant (k_{app}) and half-life time (t_{1/2}) for the decolourization of DY50 ([DY50]=0.02 mM, [Fe²⁺]= 1.0 mM at pH = 3.0: a) Fenton and b) photo-Fenton.

Table 2: The values of k (min⁻¹), t_{1/2} (min), R_{initial} (mol l⁻¹ min⁻¹) and EE/O (wKh) at different H₂O₂ concentrations in presence of [DY50] =0.02 mM, [Fe²⁺] = 1.0 mM, 10 mM H₂O₂ and light intensity 0.9675 (μ Einteins s⁻¹) x10⁻⁵ at pH 3.0 for the photocatalytic degradation of DY50 in Fenton and photo-Fenton processes.

Fenton						Photo-Fenton				
[H ₂ O ₂] mM	k _{app} x10 ³ (min ⁻¹)	t _{1/2} (min)	R _{initial} x10 ⁶ (k _{app} xC ₀) (mol l ⁻¹ min ⁻¹)	EE/O (wKh)	r	k _{app} x10 ³ (min ⁻¹)	t _{1/2} (min)	R _{initial} x10 ⁶ (k _{app} xC ₀) (mol l ⁻¹ min ⁻¹)	EE/O (kWh)	r
5	90.63	7.64	1.81	51.28	0.992	49.23	14.07	0.98	94.41	0.993
10	264.21	2.62	5.28	17.59	0.998	606.42	1.14	12.12	7.66	0.995
25	41.21	16.81	0.82	112.78	0.997	74.71	9.27	1.49	62.21	0.994
50	41.16	16.83	0.82	112.92	0.998	71.43	9.70	1.42	65.07	0.996
75	29.65	23.37	0.59	156.76	0.999	58.76	11.79	1.17	79.10	0.995

3. 1.2.3. Effect of pH

The pH value affects the oxidation of organic substances both directly and indirectly. The Fenton and photo-Fenton reactions are strongly pH dependent. The pH value influences the generation of hydroxyl radicals and thus the oxidation efficiency. The effect of pH on the rate of degradation of DY50 by Fenton and photo-Fenton processes is shown in Figure 3. This Figure shows that pH significantly influences the degradation of DY50. The experiments were carried out at pH within the range 1–7. In all this range, the degradation by photo-Fenton is higher than Fenton process. At low pH (1 and 2) we have a very low degradation both in Fenton and photo-Fenton processes. By increasing the pH to 3 we can obtain the highest rate constant for the two systems. These results are in agreement

with those reported in previous studies [30, 31]. The optimum pH was found to be about 3. The degradation decreased at pH values higher than 4, because iron precipitated as hydroxide, which resulted in a reduction in the transmission of the radiation (photo-Fenton) [32]. Additionally, the oxidation potential of hydroxyl radical was known to decrease with increasing pH [33]. Another reason for the inefficient degradation at pH > 3 is due to the dissociation and auto-decomposition of H₂O₂ [34]. For pH values below 3, the reaction of hydrogen peroxide with Fe²⁺ is seriously affected causing the reduction in hydroxyl radical production. The low degradation at pH 1 and 2 is also due to the hydroxyl radical scavenging of H⁺ ions (Eq. 17) [33].

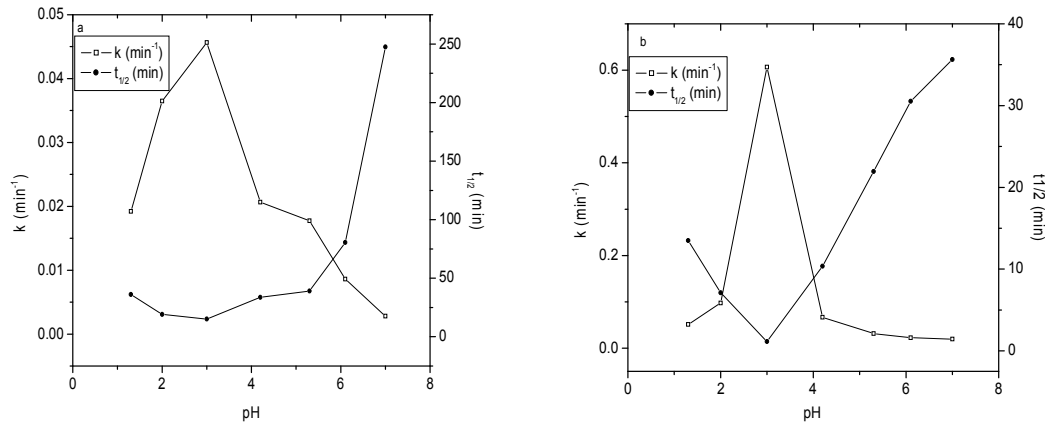


Figure 3: Effect of the initial pH on the apparent rate constant (k_{app}) and half-life time ($t_{1/2}$) for the decolorization of DY50 ($[\text{DY50}] = 0.02 \text{ mM}$, $[\text{Fe}^{2+}] = 1.0 \text{ mM}$, $10 \text{ mM H}_2\text{O}_2$: a) Fenton and b) photo-Fenton.

Table 3: The values of k (min^{-1}), $t_{1/2}$ (min), $R_{initial}$ ($\text{mol l}^{-1} \text{ min}^{-1}$) and EE/O (wKh) at different pH in presence of $[\text{DY50}] = 0.02 \text{ mM}$, $[\text{Fe}^{2+}] = 1.0 \text{ mM}$, $10 \text{ mM H}_2\text{O}_2$ and light intensity 0.9675 ($\mu \text{Einstein s}^{-1}$) $\times 10^{-5}$ for the photocatalytic degradation of DY50 in Fenton and photo-Fenton processes.

pH	Fenton					Photo-Fenton				
	$k_{app} \times 10^3$ (min^{-1})	$t_{1/2}$ (min)	$R_{initial} \times 10^6$ ($k_{app} \times C_0$) ($\text{mol l}^{-1} \text{ min}^{-1}$)	EE/O (wKh)	r	$k_{app} \times 10^3$ (min^{-1})	$t_{1/2}$ (min)	$R_{initial} \times 10^6$ ($k_{app} \times C_0$) ($\text{mol l}^{-1} \text{ min}^{-1}$)	EE/O (kWh)	r
1.3	19.21	36.07	0.38	241.95	0.981	51.32	13.50	1.02	90.56898	0.977
2.0	36.48	18.99	0.72	127.41	0.993	97.51	7.10	1.95	47.66691	0.997
3.0	45.65	15.18	0.91	101.81	0.997	606.42	1.14	12.12	7.664655	0.998
4.2	20.64	33.57	0.41	225.19	0.995	66.92	10.35	1.33	69.45607	0.999
5.3	17.75	39.04	0.35	261.85	0.998	31.57	21.95	0.63	147.2284	0.995
6.1	8.61	80.48	0.17	539.83	0.993	22.70	30.52	0.454	204.7577	0.999
7.0	2.80	247.50	0.05	1660.00	0.995	19.45	35.62	0.389	238.9717	0.999

3. 1.2.4. Effect of DY50 concentration

The influence of the concentrations of DY50 was examined in this study, in the concentration range 0.02mM- 0.50mM, at 1.0 mM of Fe²⁺ 10.0 mM H₂O₂ and pH=3.0 and the solution was irradiated with UV light (λ 254nm).

The increase of initial dye concentration in Fenton and photo-Fenton processes decreases the efficiency of degradation of DY50 (Figure 4).

Large degree of removal is observed in both processes. This is due to fast reaction of Fe²⁺ with the H₂O₂ producing hydroxyl radicals. Since azo bonds are more active, the diazo group of DY50 decolorization is due to the initial electrophilic cleavage of its chromophoric azo (-N=N-) bond attached to naphthalene ring [35]. Data in Table 4 shows that the photodegradation rate increases with the decreasing in the dye concentration. The obtained results demonstrate that photodegradation is faster for diluted solution of DY50 dye. Moreover, when the initial concentration of the DY50 increases, the hydroxyl radical concentrations remain constant for all dye molecules and hence the removal rate constant decreases.

Moreover, in photo-Fenton process at high dye concentration, a significant amount of UV light of 254 nm may be absorbed by dye molecules and this reduces the absorbance of UV light by the catalyst [36]. The increase in dye concentration also decreases the path length of photon entering the solution. Increasing the quantity of DY50 molecules per volume unit logically enhances the probability of collision between organic matter and oxidizing species, leading to an increase in the degradation rate. So the rise in its 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 molecules, the degradation rate slows down.

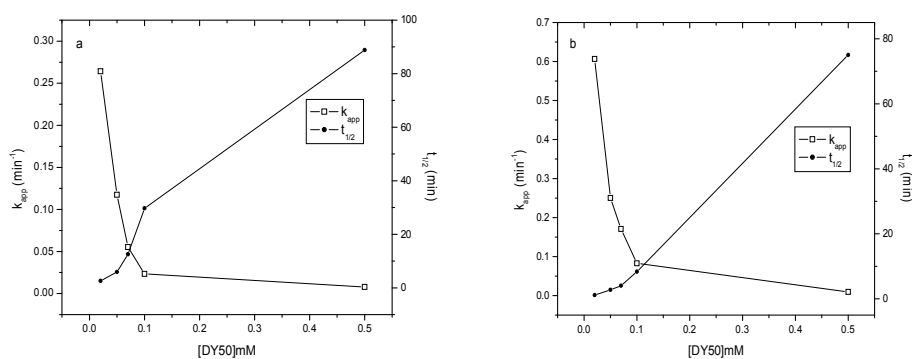


Figure 4: Effect of the initial DY50 concentrations on the apparent rate constant (k_{app}) and half-life time ($t_{1/2}$) for the decolourization of DY50 ($[DY50]=0.02\text{mM}$, $[\text{Fe}^{2+}]=1.0\text{ mM}$, $10\text{ mM H}_2\text{O}_2$: a) Fenton and b) photo-Fenton.

Table 4: The values of k (min^{-1}), $t_{1/2}$ (min), R_{initial} ($\text{mol l}^{-1} \text{min}^{-1}$) and EE/O (kWh) at different DY50 concentrations in presence of $[\text{Fe}^{2+}] = 1.0\text{ mM}$, $10\text{ mM H}_2\text{O}_2$ and light intensity 0.9675 ($\mu\text{Einteins s}^{-1}$) $\times 10^{-5}$ at pH 3.0 for the photocatalytic degradation of DY50 in Fenton and photo-Fenton processes.

[DY50] mM	Fenton					Photo-Fenton				
	$k_{app} \times 10^3$ (min^{-1})	$t_{1/2}$ (min)	$R_{\text{initial}} \times 10^6$ ($k_{app} \times C_0$) ($\text{mol l}^{-1} \text{min}^{-1}$)	EE/O (kWh)	r	$k_{app} \times 10^3$ (min^{-1})	$t_{1/2}$ (min)	$R_{\text{initial}} \times 10^6$ ($k_{app} \times C_0$) ($\text{mol l}^{-1} \text{min}^{-1}$)	EE/O (kWh)	r
0.02	264.21	2.62	5.28	17.59	0.995	606.42	1.14	12.10	7.66	0.998
0.05	117.41	5.90	5.87	39.58	0.998	250.15	2.77	12.53	18.58	0.999
0.07	55.36	12.51	3.87	83.95	0.994	170.66	4.06	11.92	27.23	0.998
0.10	23.30	29.74	2.33	199.48	0.996	82.84	8.36	8.23	56.10	0.997
0.50	7.80	88.84	3.90	595.89	0.999	9.24	75.00	4.66	503.03	0.998

3. 1.2.5. Effect of light intensity

Light intensity is critical parameter affecting photodegradation rate [37]. The influence of light intensity on the rate of DY50 degradation has been examined at constant dye concentration (0.02mM), and at 10mM H₂O₂ and pH = 3.0. Degradation experiments are carried out for the catalytic degradation of DY50 with different light intensities. 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 ($\lambda = 245\text{ nm}$)). The results obtained are presented in Figure 5 and Table 5. The results showed that the removal percent steadily increased with increasing the light intensity. The results also showed that the UV light intensity plays an important role in degradation of DY50 as cited previously [38]. This is due to effective role of light intensity in the formation of high amounts of $^{\circ}\text{OH}$. These results indicate that the removal efficiency is a function of light intensity.

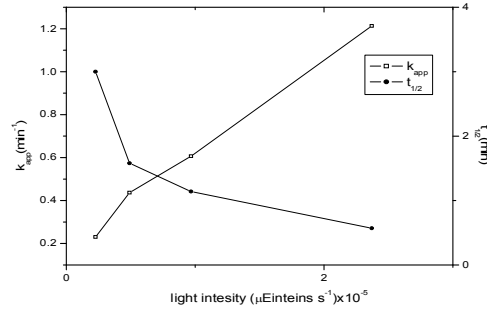


Figure 5: Effect of light intensity on the apparent rate constant (k_{app}) and half-life time ($t_{1/2}$) for the decolourization of DY50 ($[DY50]=0.02\text{mM}$, $[\text{Fe}^{2+}]=1.0\text{mM}$, $10\text{mM H}_2\text{O}_2$ and $\text{pH } 3$) for photo-Fenton.

Table 5: The values of k (min^{-1}), $t_{1/2}$ (min), R_{initial} ($\text{mol l}^{-1} \text{min}^{-1}$) and EE/O (kWh) at different light intensity in presence of $[\text{Fe}^{2+}] = 1.0\text{mM}$, 0.02mM DY50 and $10\text{mM H}_2\text{O}_2$ at $\text{pH } 3.0$ for the photocatalytic degradation of DY50 in photo-Fenton processes.

Light intensity ($\mu\text{Einteins s}^{-1}$) $\times 10^5$	$k_{app} \times 10^3$ (min^{-1})	$t_{1/2}$ (min)	Rinitial ($k_{app} \times C_0$) $\times 10^6$ ($\text{mol l}^{-1} \text{min}^{-1}$)	EE/O (kWh)	r
0.2263 ^a	230.63	3.00	4.61	20.15	0.993
0.4901 ^b	436.65	1.58	8.73	10.64	0.998
0.9675 ^c	606.42	1.14	12.12	7.66	0.995
2.3700 ^d	1212.84	0.57	24.25	3.83	0.992

^a one lamp at 20cm, ^b one lamp at 10 cm, ^c two lamps at 20 cm and ^d two lamps at 10 cm.

3.1.2.5. Efficiency of Photodegradation

The evaluation of the efficiency of photodegradation treatment processes is difficult because the reaction rate depends on many factors. Thus, there is need for a figure of merit that can be used to assess the relative performance of each system. As a figure of merit, the electrical energy per order (EE/O) has been proposed, defined as the electrical energy (in kilowatt hours) required to reduce the concentration of a pollutant by one order of magnitude in 1000 US gallons (3785 L) of water. The EE/O value may be calculated from the following equation ([39, 40, 41]:

$$EE/O = (P \times (t/60) \times 3782) / (V \times \log(C_0/C_t)) \quad (18)$$

where P is the lamp power (in kilowatts), t is the irradiation time (in minutes), V is the reactor volume (in litres) and C_0 and C_t are the initial and final concentrations over the irradiation time. The EE/O values are related to the first-order rate constant, k_{app} (per minute) by:

$$EE/O = (145.25 \times P) / (V \times k_{app}) \quad (19)$$

Data in tables 1-4 show that the value of EE/O (kWh) decreases with increasing the value of the k_{app} . Low values of EE/O are obtained at the best condition for degradation ($[\text{Fe}^{2+}] = 1.0\text{mM}$, $10.0\text{mM H}_2\text{O}_2$, $\text{pH} = 3.0$ and $[DY50] = 0.02\text{mM}$). This indicates that using optimum condition in degradation of dye relatively use low operational electric energy.

3. 1.2.6. Comparison of different Fenton's and photo-Fenton's processes

Although attempts to monitor colour removal were also carried out, the disappearance was too fast in presence of light. Light can play two different roles that will lead to an improvement of the reaction yields: (a) it drives photo-Fenton's reaction, producing extra hydroxyl radicals and the recovery of Fe^{2+} needed in Fenton's reaction. The photo-Fenton's reaction may involve photolysis of ferric ion (reaction (12)) or photolysis of Fe^{3+} complexes or any of their potential intermediates [42]. (b) It can drive ligand to metal charge transfer in the potentially photolabile complexes formed by Fe^{3+} and organic compounds, a process that has been well proven for the complexes formed between Fe^{3+} and the carboxylic acid moiety [43].

4. CONCLUSIONS

Treatment azo dye Direct Yellow 50 (DY50) solutions by Fenton ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$) and photo-Fenton ($\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV}$) processes led to complete decolourization. The catalytic effect of photo-Fenton process was found to be higher than Fenton process. The process of decolourization was adequately modelled using first-order kinetics and rate constants with respect to the two systems were obtained. The efficiency of the photodegradation of Direct Yellow 50 was assessed by determining the electrical energy per order (EE/O) for each catalytic system.

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