

Application of Photo-Fenton System (UV/ H₂O₂/ Fe²⁺) for Efficient Decolorization of Azo-Dye Acid Yellow 17 in Aqueous Solution

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ABSTRACT: *Herein we report, the robustness of UV/H₂O₂/Fe²⁺ system for efficient decolorization of azo-dye Acid Yellow (AY17) solution. It has been found that 88% AY17 decolorized by UV/H₂O₂/Fe²⁺ system in 25 minutes under the following optimized conditions; [dye] = 0.14 mM, [H₂O₂] = 1.0 mM, [Fe²⁺] = 0.09 mM, stirring velocity = 100 rpm, and pH = 3.0. The decolorization of AY17 by UV/H₂O₂/Fe²⁺ system exhibit second order reaction kinetics. Thermodynamic parameters, activation enthalpy, ΔH^* , (13.76 kJ/mol^l) and entropy ΔS^* , (0.034686 J/K) of the dye decolorization were also determined. It was ascertained that electrolytes such as HCO₃⁻, CO₃²⁻, Cl⁻ and SO₄²⁻ decrease the decolorization efficiency by scavenging the hydroxyl radical generation in the dye solution. Finally, the AY17 decolorization in the tap water sample by UV/H₂O₂/Fe²⁺ system was also examined.*

KEYWORDS: *Azo dye; Oxidative degradation; UV/H₂O₂/Fe²⁺; Optimum conditions; Second-order kinetics.*

INTRODUCTION

Dyes from textile industry are not only harmful to aquatic life, but also carcinogenic and mutagenic to human beings [1, 2]. Even though, a small amount (ca. 1 mg/L) of these dyes in water are not acceptable [3]. The presences of these dyes in aquatic system absorb and reflect the sunlight. Hence, increase the growth of bacteria and affect photosynthesis [4].

The removal of these dyes from industrial effluents is an important problem throughout the world [5]. Several

processes are used for the effective removal of dyes from industrial effluents. These include, adsorption, reverse osmosis, carbon adsorption, flocculation and activated sludge processes[6–8]. Naghizadeh and his co-worker used modified chitosan in the presence of hydrogen peroxide as adsorbent for removal of reactive blue 29 dye [6, 7]. Similarly, nanoparticles of montmorillonite were also used as adsorbent for removal of several dyes [8]. For the last decades, the most advantageous processes

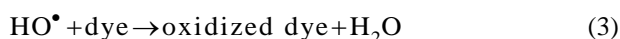
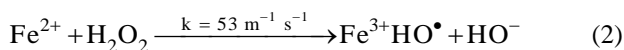
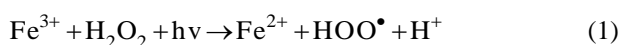
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used for the effective removal of dyes from waste water were Advanced Oxidation Processes (AOPs) also called advanced oxidation reduction Technologies. These methods include the use of gamma irradiation, Fenton process, Fenton-like process, photo-Fenton process, photo-Fenton-like process, UV/PMS/Fe²⁺ process, UV/PMS/Fe³⁺ process, UV/PS/Fe²⁺, UV/PS/Fe³⁺ process, ozonation, homogeneous and heterogeneous catalysis, electrolysis, and electro Fenton processes etc. [9–12]. Among the above mentioned AOPs, Photo-Fenton process was widely used [13, 14]. Mechanism for photo-Fenton process, involving the production of hydroxyl radical from hydrogen peroxide can be described through the following Eqs. (1-3) [15].



Ozen et al. [16, 17] has demonstrated the mechanism of azo dyes degradation by hydroxyl radical ($\bullet\text{OH}$). They proposed that degradation of azo dyes may occur *via* C–N and N–N bond breaking subsequent $\bullet\text{OH}$ addition to the (-N=N-) chromophore group.

Among the several textile dyes, the azo group (-N=N-) containing dyes contribute about 70% of annual total dye consumption [18]. Moreover, these dyes have stable aromatic structure and synthetic origin. Thus, they are more difficult to degrade [19]. One example of azo dyes is Acid yellow 17. The azo group in Acid yellow 17 is attached to aromatic ring having SO₃H and OH groups Fig.1.

Although, The AY17 dye was removed by various possesses such as biosorption, activate carbon adsorption and by ozonation [20–22]. To the best of our knowledge, none of the studies are presented in the literature regarding the removal of AY17 by UV/H₂O₂/Fe²⁺ system. Therefore, this study demonstrates kinetics, thermodynamics, and optimization of the reaction conditions (such as pH, concentration of H₂O₂, Fe²⁺ and dye etc.), for the decolorization of AY17 solution by UV/H₂O₂/Fe²⁺ system.

EXPERIMENTAL SECTION

Material and Method

AY17 dye (60 % dye content) was purchased from Acros Organics, Belgium. While, hydrogen peroxide (H₂O₂, 30 % w/w), ferrous sulfate (FeSO₄.7H₂O, 99.5%),

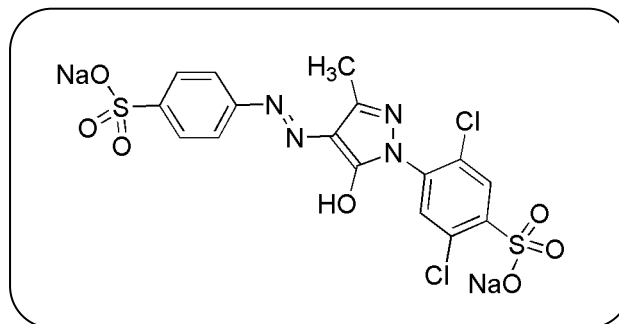


Fig. 1: Molecular structure of AY-17 azo dye.

sodium sulfate (Na₂SO₄, 98%), sulfuric acid (H₂SO₄, 97%), sodium bicarbonate (NaHCO₃, 99%), sodium chloride (NaCl, 99%), and sodium carbonate (Na₂CO₃, 98%) from Sigma Aldrich were used without further purification.

Decolorization of AY17 by UV/H₂O₂/Fe²⁺ system was carried out in 50 ml beakers at constant temperature in thermostat under continuous stirring. The pH of the solution was adjusted using a dilute solution of NaOH and H₂SO₄. All experiments are carried out at room temperature (25 °C).

Instruments

Photolysis of AY17 in of dye solution was performed with 254 nm UV radiation using low pressure Hg-UV lamp (PENRAY, USA) as a source of radiation. The photochemical assembly was enclosed in a wooden box. A magnetic stirrer was used for stirring the sample to achieve a uniform dose rate of UV irradiation over AY17 dye solution. Pyrex glass beaker having 50 cm² area was used for UV irradiation of dye sample solutions. The oxidative decolorization of AY17 dye was monitored by Lambda 650 UV-Visible spectrophotometer manufactured by PerkinElmer.

In the present study UV-Visible spectrophotometer (PerkinElmer, Model: Lambda-650, UK) was used for the quantitative analysis. The UV-visible spectrophotometer was used to measure the absorbance of acid yellow 17 dye solution. The absorbance depends on the concentration of analyte i.e. acid yellow 17 dye. UV-visible spectrophotometer has photomultiplier detector and two lamps i.e., one mercury and one deuterium lamp. It works in the wave length range from 190 - 900 nm.

For the photolysis of aqueous solution of AY 17 dye, a photochemical apparatus fitted with a 4 W low pressure

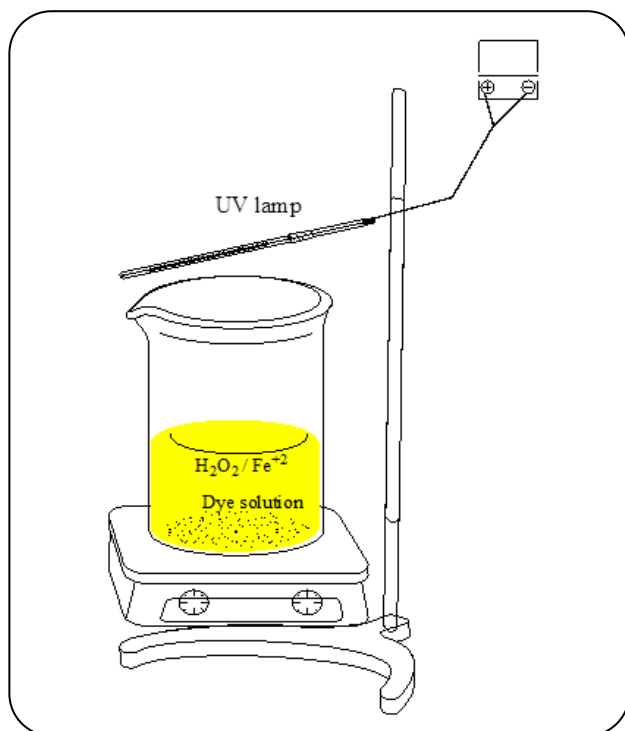


Fig. 2: Experimental Setup for decolorization of AY17 through H₂O₂/Fe²⁺/ UV system

Hg-UV lamp (PENRAY, USA) was used. The wave length of the light emitted by Hg-UV lamp was 254 nm. The lamp was enclosed in wooden box. A magnetic stirrer was used for stirring the sample to achieve homogenous flow of UV radiation through solution. The area of Pyrex glass beaker was 50 cm² which was used for sample solution for UV radiation treatment (Fig. 2).

Gas chromatography-mass spectrometry (GC-MS)

GC-MS analysis was performed using a HP-6890 series GC equipped with a HP-5973 mass spectrometry for identification of intermediates of AY 17 dye which produced during the oxidation. With the help of HP-5MS capillary column (30 m x 0.25 mm x 0.25 μm), separation of the sample components was achieved. Mass spectra was obtained by the electron-impact mode (EI) at 70 eV, using scan mode (50-500 m/z) under these conditions: purge time = 1 min, purge flow = 26.5 mL/min and pressure = 7.63 psi. GC-MS information was compared with NIST mass spectra library for identification of unknown compounds. The conditions used for the analysis of AY 17 on GC-MS system are given in Table 1.

RESULTS AND DISCUSSION

Selection of Efficient AOP for Oxidative Degradation of Dye

Several AOPs such as UV, UV/Fe²⁺, UV/H₂O₂ and UV/Fe²⁺/H₂O₂ process were checked for decolorization of dye solution (Fig. 3a). It was observed that these systems decolorized AY-17 dye up to 2 % (UV), 3 % (UV/Fe²⁺), 5% (UV/H₂O₂), and 88% (UV/Fe²⁺/H₂O₂) in 25 minutes, respectively. It was assessed that UV/Fe²⁺/H₂O₂ system decolorized AY17 more efficiently. Therefore, UV/Fe²⁺/H₂O₂ system was further employed for decolorization of AY17. The reason for such a high decolorization efficiency might be explained in term of large number of hydroxyl radical (•OH) generation by UV/Fe²⁺/H₂O₂ system [15, 23].

Effect of the pH on AY17 decolorization

The effect of initial pH is a very important parameter in photo-Fenton process. The value of pH has a crucial effect on oxidation potential of hydroxyl radical, because the pH value have a reciprocal relation to oxidation potential [24]. To find the optimal pH for decolorization of AY17 dye by UV/ H₂O₂/Fe²⁺ system, solutions of AY17 having initial pH of 2.0, 3.0, 6.0, and 8.0 were decolorized by UV/ H₂O₂/Fe²⁺ system as shown in Fig. 4a. It was found that maximum decolorization efficiency (88%) were achieved at pH 3 [8] which could be described by correlating the relative stability (with pH) of various ferric ion species [25]. Similarly, Fenton and Fenton like processes, photo-Fenton process also have maximum catalytic activity at pH = 3. The generation of hydroxyl radical depends on the pH of solution, which results the decolorization of Ay 17 solution [9, 26]. At pH 3.0, Fe³⁺ ions exist as [FeOH]²⁺, convert into Fe²⁺ ion and •OH upon UV irradiation. Hence, generation of both species (Fe²⁺ and •OH) favored the dye decolorization process (Eq. (4)).



Furthermore, the high decolorization efficiency at pH 3.0 may also due to the fast decomposition of •OH and H₂O₂ [27]. The low decolorization efficiency at pH 2.0 was due to the existence of Fe³⁺ as [Fe(H₂O)₆]³⁺, which slowly regenerated into [Fe(H₂O)₆]²⁺. The other reason for low decolorization efficiency at pH 2.0 was the conversion of H₂O₂ to more stable oxonium ion (H₃O₂⁺) which was less reactivity toward the Fe²⁺ ion (Eq. (2)) [28, 29].

Table 1: Operating conditions for GC-MS analysis of AY 17 dye.

Items	Conditions	
Injector	Split-state	split less
	Temperature (K)	483 K
	SPME extraction time (min)	2
	SPME desorption time (min)	1
Oven	Temperature program	323 K (4 min) to 423 K at 278 K /min, 423 K to 523 K (5 min) at 281 K/min
Carrier Gas	Gas	Helium
	Flow rate (mL/min)	1.5
Detector	GC-MS	
	Ion source temperature	503 K
	Quadrupole temperature	423
	Electron energy	70 eV
	Scan range (m/z)	50-500

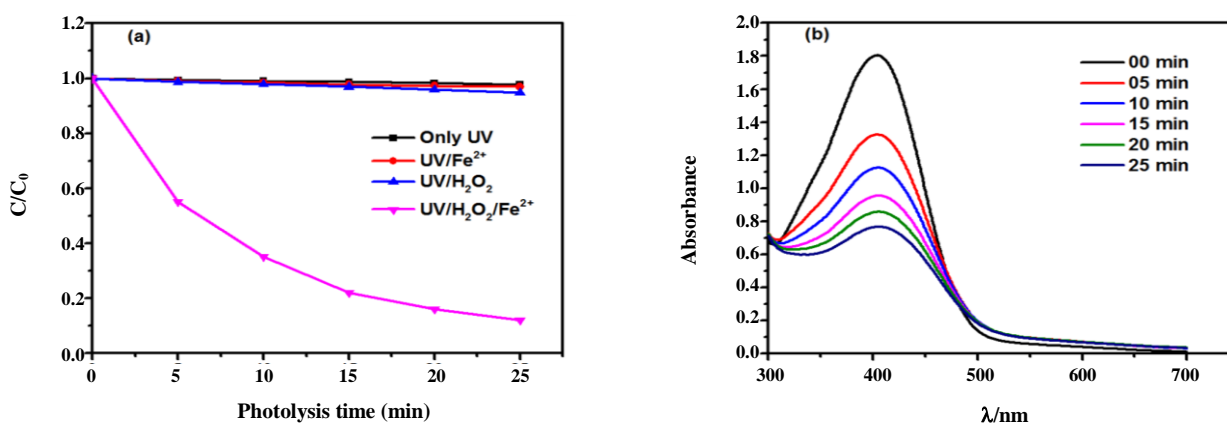


Fig. 3: (a) C/C_0 vs Photolysis time (t) plot for selection of suitable AOP for efficient decolorization of AY17 dye. (b) Absorbance spectra of AY17 dye during at various time interval in the presence of UV/ H₂O₂/Fe²⁺ system, other experimental conditions: $[AY17]_0 = 0.14$ mM, $[H_2O_2]_0 = 1.00$ mM, $[Fe^{2+}] = 0.09$ mM, pH = 3.0, $T = 298$ K.

At high pH > 3 the decolorization decreased due to the precipitation of iron as derivative of hydroxide, reducing ferrous availability and the radiation transmission. Another possible reason at high pH the auto decomposition and dissociation of hydrogen peroxide [24]. At pH 8 the degradation of AY17 decreased due to the deactivation of $\bullet OH$ by its fast reaction with HO_2^- [30]. The present studies is in correlation with literature [9, 10, 30].

Effect of H₂O₂ concentration on AY17 decolorization

The effect of initial H₂O₂ concentration on the decolorization was shown in Fig. 4b. It was observed that

decolorization of dye increased with (up to a certain limit, i.e. 1mM) concentration of H₂O₂. The increased in degradation was due to the fact, that high concentration of H₂O₂, increased the $\bullet OH$ radical generation which oxidized AY17 dye more efficiently (eq. 5) [31, 32].



The decreased in the dye decolorization at high conc. of H₂O₂ (i.e. above 1.00 mM to 1.50 mM) may due to the scavenging of $\bullet OH$ radical by H₂O₂. Dimerization of $\bullet OH$ radical or peroxy radical (HO₂ \bullet) formed in reaction pathway may also inhibit the degradation of dye (Eqs. (6-10)) [20, 33].

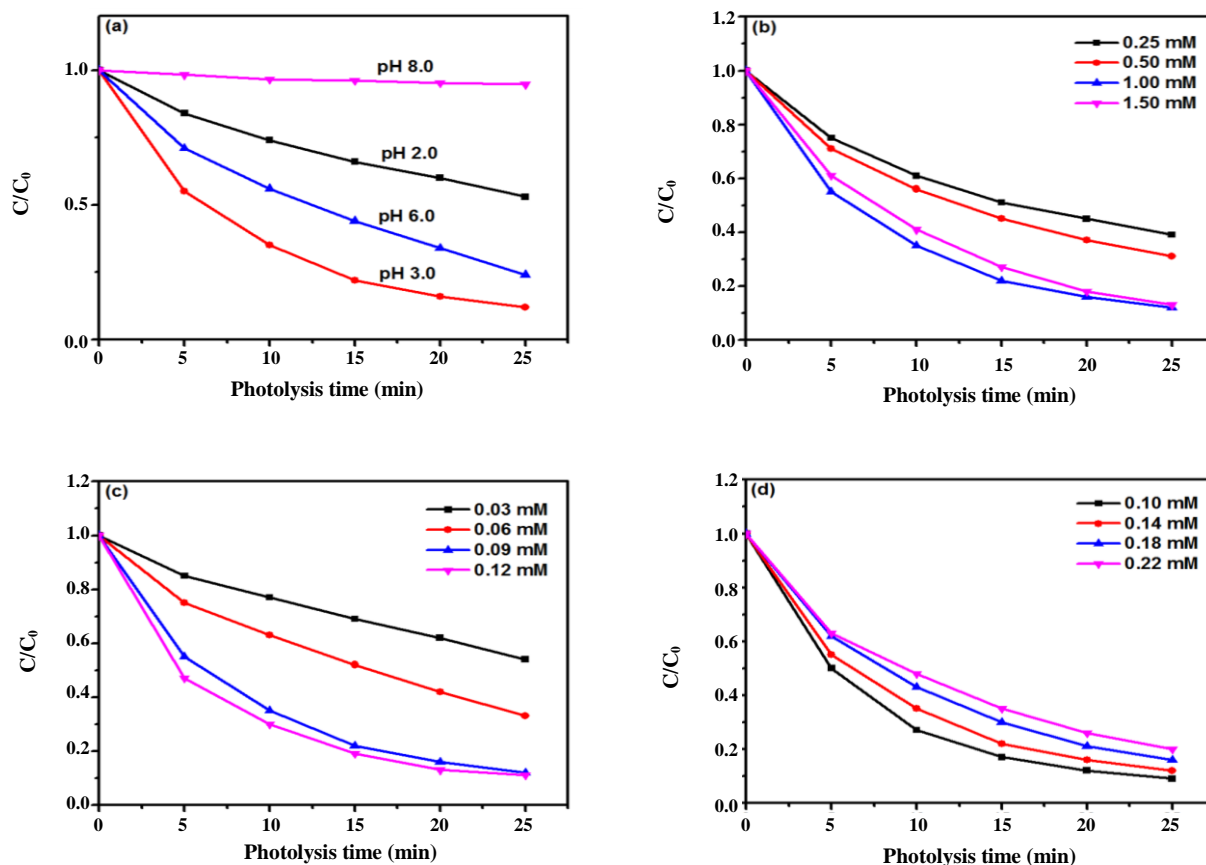
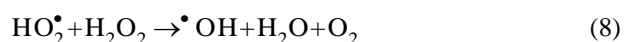
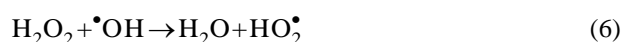


Fig. 4: C/C_0 vs Photolysis time (t) plot showing effect of various conditions on decolorization of AY17: (a) pH, (b) H₂O₂, (c) Fe²⁺, (d) concentration of dye. The optimized conditions were determined as: pH = 3.0, [H₂O₂]₀ = 1.00 mM, [AY 17]₀ = 0.14 mM and [Fe²⁺]₀ = 0.09 mM



Effect of Fe²⁺ concentration on AY17 decolorization

Optimizing the Fe²⁺ concentration is an important parameter in decolorization of dye solution. Because the concentration of Fe²⁺ may affect the yield of $\bullet\text{OH}$ radical as shown in eq. 3. Similarly, high concentration (more than optimum) of Fe²⁺ can also scavenge the hydroxyl radical $\bullet\text{OH}$ [34]. Therefore, the effect of various Fe²⁺ conc. on the AY 17 decolorization was monitored (Fig. 4c).

It was observed that in the absence of Fe²⁺, the dye solution did not decolorize efficiently, however, in the presence of Fe²⁺ (0.03 to 0.09 mM) the decolorization efficiently improved. It was also noted that further increase in Fe²⁺ concentration (i.e. more than 0.09 mM) decrease the decolorization efficiency which may be explained in term of scavenging of hydroxyl radical $\bullet\text{OH}$ by Fe³⁺ ion [35]. The molar ratio Fe²⁺ to H₂O₂ used was 1.11 which are correlation with literature [11].

Effect of AY17 dye concentration on decolorization

The concentration of AY 17 was varied from 0.1 mM to 0.22 mM to find the optimum concentration of AY17 for high decolorization efficiency. It was ascertained that the extent of decolorization efficiency decreases from 91% to 80% as conc. of dye increased (Fig. 4d). The plausible explanation for the decrease in dye decolorization efficiency with an increase in dye

concentration may be due to the low penetration of photon entering the solution because of the inner filter effect as high concentration makes more impermeable to UV radiation [30]. The second reason is that when the concentration of AY 17 dye increased, the number of AY 17 dye molecules increased. But the numbers of hydroxyl radical remain the same, when the concentration of Fe^{2+} and H_2O_2 remain unchanged. It was also observed that when the concentration of AY 17 dye increased the rate of decolorization reaction increased while rate constant of decolorization decreased (see next section). This phenomenon can be explained by the fact that when the AY 17 dye concentration is low the hydroxyl radical is trapped by hydrogen peroxide, but at high concentration of AY 17 dye this trapping becomes negligible [36]. The results achieved in this study concur with our previous study [9, 10].

Effect of stirring on AY17 decolorization

Effect of stirring on decolorization of dye solution by UV/ $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ system was also checked. During Stirring velocity studies other parameters such as $\text{pH} = 3$, temperature = 298 K, concentration of AY 17, Fe^{2+} and H_2O_2 were 0.14, 0.09 and 1 mM, respectively. A series of dye solutions under optimized condition were stirred with velocity of 0, 100, and 200 and, 400 rpm (Fig. 5). Maximum decolorization was attained at 100 rpm. These results can be described in term of influence of stirring velocity on mass transfer characteristics of the chemical species as well as an increase in ambition of gases (such as O_2 and CO_2) into solutions [37]. The CO_2 might be dissolved in dye solution through HCO_3^- and CO_3^{2-} ion formation due to high stirring velocity, eq. (11 & 12). The complexes of ferrous ions follow various reactions (13-16) which the decreased decolorization kinetic. These ions HCO_3^- CO_3^{2-} trapped the hydroxyl radical through the following reaction Eqs. (17, 18) [38]. However, on the other hand the aspiration of O_2 in the reaction mixture increases the efficiency and kinetic of decolorization by producing $\cdot\text{OH}$ radical through reactions shown by Eqs. (19-21) [39, 40]. These diverse effects are competitive and the compromise between these two leads to optimal speed of stirring about 100 rpm.

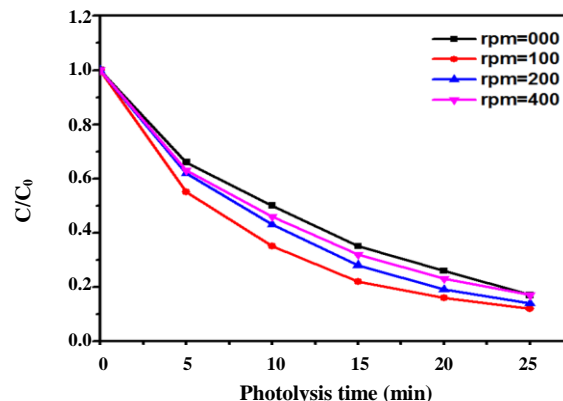
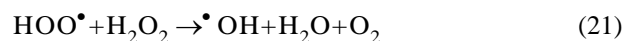
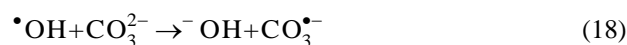
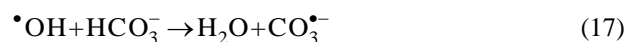
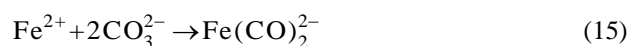
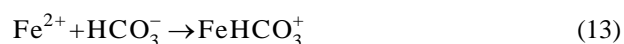


Fig. 5: C/C^0 vs Photolysis time (t) plot representing the effect of Stirring velocity on the decolorization of AY17 dye Reaction conditions: $[\text{AY 17}]_0 = 0.14 \text{ mM}$, $[\text{Fe}^{2+}]_0 = 0.09 \text{ mM}$, $[\text{H}_2\text{O}_2]_0 = 1.0 \text{ mM}$, $\text{pH} = 3.0$.



Effect CO_3^{2-} and HCO_3^- on AY17 decolorization

Sodium carbonate and bicarbonate are usually used in dyeing process for adjusting pH and for fixing of dye on fabrics and fastening of dyeing process [41]. Due to heavy use of these salts the concentration of the aquatic environment the carbonate and bicarbonate usually found in the range of 1.0 – 5.0 mM [42]. It affected the dye decolorization induced by UV/ $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ system. Hence, the effect of these anion on dye decolorization was checked by adding certain amount of CO_3^{2-} and HCO_3^- in dye solution containing optimum concentration of H_2O_2 and Fe^{2+} (Figs. 6a and 6b).

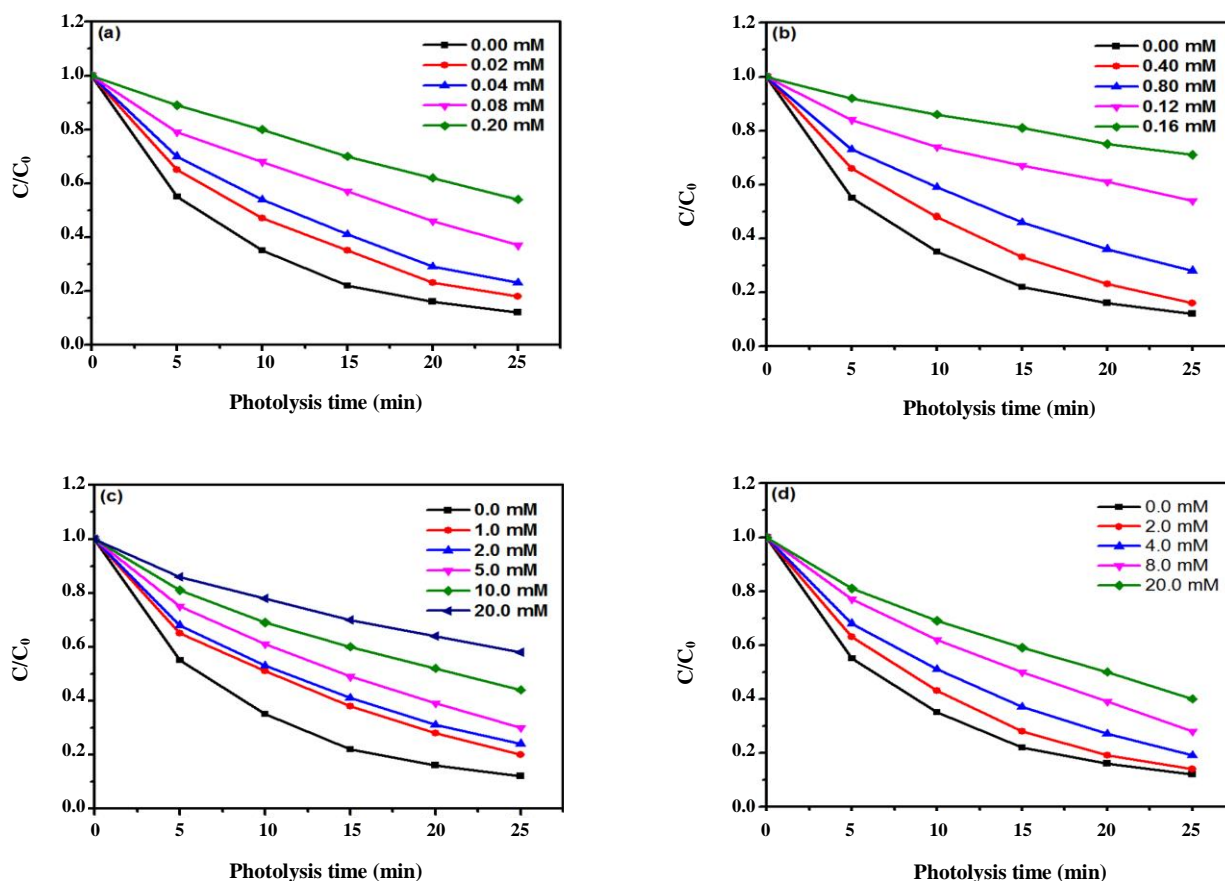
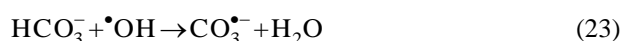
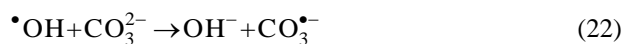


Fig. 6: C/C_0 vs Photolysis time (t) plot showing effect of various Anions on AY17 dye decolorization on: (a) carbonate, CO_3^{2-} , (b) bicarbonate, HCO_3^- , (c) Chloride, Cl^- (d) sulfate, SO_4^- . Other reaction conditions: $[\text{AY } 17]_0 = 0.14 \text{ mM}$, $[\text{Fe}^{2+}]_0 = 0.09 \text{ mM}$, $[\text{H}_2\text{O}_2]_0 = 1.0 \text{ mM}$.

To study the effect of carbonate ion, various initial concentration of CO_3^{2-} such as 0.02, 0.04, 0.08 and 0.2 mM were used. It was observed that the decolorization decreased from 88% to 82%, 77%, 63%, and 46%, with addition of 0.02, 0.04, 0.08 and 0.2 mM CO_3^{2-} , respectively (Fig. 6a). The rate of degradation of AY17 decreased due to the presence of carbonate ion which scavenges the hydroxyl radical $\bullet\text{OH}$, although, producing radical, $\text{CO}_3^{\bullet-}$ but is less reactive than hydroxyl radical as given in eq. 22. Due to this scavenging of hydroxyl radical the number of hydroxyl radical in solution decreased and as a result the degradation percentage decreased.

The Fig. 6b shows that the percent degradation decreased when the conc. of bicarbonate ion increased. In case of HCO_3^- , an abrupt decrease in decolorization efficiency from 88% to 29%. The decrease in percent degradation was due to the scavenging of hydroxyl radical by bicarbonate ion, as shown in Eq. (23). When

bicarbonate ion is attacked by hydroxyl radical it forms $\text{CO}_3^{\bullet-}$ radical which is less reactive than hydroxyl radical [43]. As a result, the concentration of hydroxyl radical decreased and hence the percent degradation of the dye also decreased.

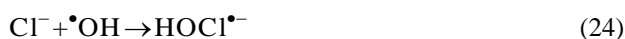


Effect of Cl^- and SO_4^- on AY17 decolorization

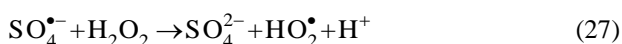
The presence of inorganic anion such as Cl^- and SO_4^{2-} in wastewater has also a considerable effect on the decolorization rate. The decolorization rate was enormously decreased due to the presence of these anions.

Various conc. of SO_4^- and Cl^- ions were added in solution of dye to study the effect of these anions (Figs. 5c & d). It was noted that in case of Cl^- , the decreased in

decolorization was due to the scavenging of hydroxyl radical by chloride (eq. 24-26) [44, 45]



While in case of SO_4^{2-} , the decrease in efficiency of decolorization decreased with addition of sulfate ion concentration was due to the scavenging of hydroxyl radical by sulfate ion Eq. (27-28, 21, 22). In scavenging reactions HO_2^{\bullet} and $\text{SO}_4^{\bullet-}$ radical are formed along with sulfate radical. Secondary radical HO_2^{\bullet} and $\text{SO}_4^{\bullet-}$ are less reactive than hydroxyl radical, as a result the decolorization of AY 17 dye decreased. The second reason for decreasing decolorization was due to the formation of iron-sulfate complexes such as FeSO_4 , FeSO_4^+ , and $\text{Fe}(\text{OH})_2$ Eqs. ((29-32)). Due to formation of these species the availability of Fe^{2+} become lessor for catalyzing the hydroxyl radical formation.



Determination of AY17 decolorization Kinetic

In the present study zero, first, and second order kinetic was applied to study the decolorization of AY17 by UV/ $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ system (Eqs. (33-35)). [46, 47].

$$A_t = A_0 - k_0 t \quad (\text{Zeroth-order}) \quad (33)$$

$$\ln A_t = \ln A_0 - k_1 t \quad (\text{First-order}) \quad (34)$$

$$1/A_t = 1/A_0 + k_2 t \quad (\text{Second order}) \quad (35)$$

Where A_t is absorbance of AY17 at time t , A_0 is the initial absorbance (absorbance at time $t = 0$ min) of the dye, and k_0 , k_1 and k_2 were the zero, first and second order kinetic constant. The slope of the straight-line equation

(Eqs. (27-29)) were used to calculate rate constants, of zero, first and second order reaction kinetics. The following equation was applied for half-life determination, zero, first and second order kinetic (Eqs. (36-38)).

$$t_{1/2} = A_0 / 2k_0 \quad (\text{Zeroth-order}) \quad (36)$$

$$t_{1/2} = \ln 2 / k_1 \quad (\text{First-order}) \quad (37)$$

$$t_{1/2} = 1 / k_2 [A_0] \quad (\text{Second-order}) \quad (38)$$

It was observed that the Second-order kinetic gives much better R^2 value than zero and first order kinetic (Table 2). Moreover, the values of half-life calculated through first-order kinetic model were closely related to experimental values. Thus, in the present study it was concluded that the decolorization of AY17 by UV/ $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ system follows Second-order kinetic (Eq. (39))

$$\text{rate}_{\text{AY17}} = k[\text{AY17}][\text{OH}] \quad (39)$$

Although, the decolorization of dye follow second order kinetics. However, the decolorization rate as a function of dye concentration was investigated using Pseudo-first-order kinetics (Fig. 7). It was found that k_{app} (apparent pseudo-first-order rate constant) decreased with an increase in the initial concentration of AY17 dye (Table 3). The decrease in k_{app} with an increase in dye concentration may be due to the involvement of parallel reaction of byproduct with hydroxyl radical [33].

Effect of Temperature on AY17 decolorization

The effect of temperature on the decolorization of AY17 dye solutions was also investigated. Solutions of dye were decolorized under optimized conditions (0.14 mM dye, 1 mM H_2O_2 , 0.09 mM Fe^{2+}) at various temperatures of 298, 308, and 318K (Fig. 8). It was observed that both efficiency and the rate of decolorization increased with temperature. The increased in decolorization efficiency with temperature could be explained in term of enhancement of a $\bullet\text{OH}$ radical generation. It was suggested that at high temperature the conc. of $[\text{FeOH}]^{2+}$ may increase, which results an increased in photo-production of Fe^{2+} from $[\text{FeOH}]^{2+}$ as mentioned previously by eq. 4. [48, 49].

The energy of activation was calculated from the slope of the straight-line eqn. (40). The entropy and enthalpy of activation was also obtained using eq. (41).

Table 2: The kinetic data for decolorization of AY17 by UV/H₂O₂/Fe²⁺ system.

T (K)	Zero-order kinetics			First-order kinetics			Second-order kinetics		
	k ₀ ^a (A/min)	t _{1/2} (min)	R ²	k ₁ (min) ⁻¹	t _{1/2}	R ²	k ₂ ^a (A. min) ⁻¹	t _{1/2}	R ²
298	0.042	15.55	0.80	0.085	8.15	0.98	0.228	3.36	0.96
308	0.043	16.34	0.55	0.094	7.37	0.82	0.323	2.20	0.97
318	0.042	16.62	0.51	0.097	7.14	0.78	0.372	1.93	0.95

a) The unit of k₀ and k₂ are in term of absorbance

Table 3: Decolorization efficiency and rate constant (k_{app}) of AY17 dye using Pseudo first-order kinetics at pH 3 using UV/H₂O₂/Fe²⁺ system.

[Fe ²⁺] ₀ (mM)	[H ₂ O ₂] ₀ (mM)	[AY 17] ₀ (mM)	k _{app} 10 ⁻² (min) ⁻¹	R ²	% Decolorization
0.09	1.0	0.10	10.585	0.99	91
0.09	1.0	0.14	9.171	0.99	88
0.09	1.0	0.18	7.736	0.99	84
0.09	1.0	0.22	6.741	0.99	80

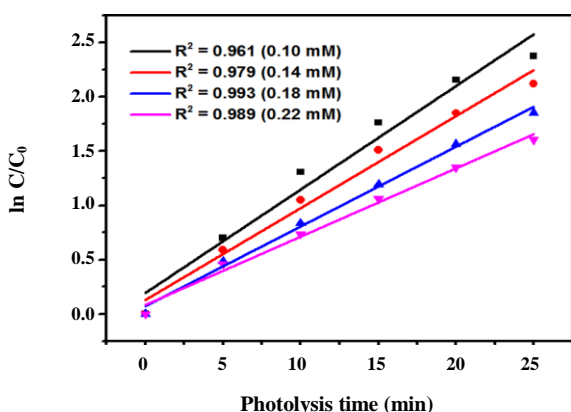


Fig. 7: $\ln C_0/C$ vs time plot at various concentration of AY17 dye. Experimental conditions: [AY 17]₀ = 0.1, 0.14, 0.18 and 0.22 mM, [H₂O₂]₀ = 1.0 mM, [Fe³⁺]₀ = 0.09 mM.

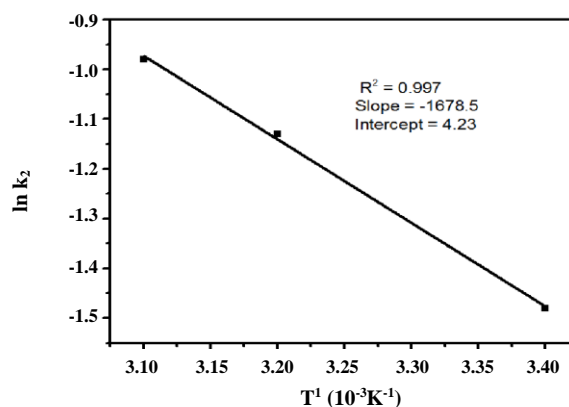


Fig. 8: $\ln k_2$ vs T^{-1} plot representing the effect of temperature on the degradation of Acid yellow 17 dye. Experimental condition: [H₂O₂] = 1.0 mM; [AY 17]₀ = 0.14 mM; [Fe²⁺]₀ = 0.09 mM; pH = 3.0. Temperature = 298, 308 and 318K.

$$\ln k_2 = \ln A - E_a / RT \quad (40)$$

$$\ln k_2 = \Delta S^* / R - \Delta H^* / RT \quad (41)$$

Where, k_2 represent the second-order rate constant, T, is temperature of solution in K, A is the Arrhenius constant, R is the ideal gas constant (0.0082 kJ/mol.K) and E_a minimum activation energy that are required by reactants for proceeding oxidation reaction. For determination of ΔH^* and ΔS^* a graph was plotted between $\ln k_2$ vs. $1/T$.

From the slope and intercept ΔS^* and ΔH^* were calculated by using eq. 35. The ΔH^* value is used to make out the nature of photo-Fenton oxidation reaction. When the value of ΔH^* is positive the reaction is endothermic, on other hand negative value ΔH^* indicates that the process is exothermic. In our case the ΔH^* value is positive, so the photo-Fenton oxidation process is endothermic process. The value of ΔS^* calculated from the intercept of figure have positive value, which indicates that the randomness of reaction increased in UV/H₂O₂/Fe²⁺

Table 4: Thermodynamic parameters for the decolorization of AY17 dye by UV/H₂O₂/Fe²⁺ system.

T(K)	ln(k ₂)	ΔH* (kJ/mol)	E _a (kJ/mol)	ΔS* (kJ/mol)
298	-1.48	13.76	13.76	0.034686
308	-1.13			
318	-0.98			

process. The thermodynamic parameters are given in Table 4. Our study is supported by literature [50].

Decolorization of AY 17 dye in tape water sample by UV/H₂O₂/Fe²⁺ system

The Decolorization of AY 17 in real in tape water was also examined (Fig. 9). It was determined that the efficiency of decolorization of dye in tape water was quite low (i.e. 43%) as compared to ideal one (88%). The reason for such a low degradation was the presence of certain amount of •OH scavenger's anions such as CO₃²⁻ (0.25 mM), HCO₃⁻ (2.58 mM), Cl⁻ (2.35 mM), and SO₄²⁻ (0.5 mM) in tape water sample [51].

Identification of degradation products and possible degradation pathway

GC-MS analysis of AY 17 solutions which was treated with UV/H₂O₂/Fe²⁺ process showed the formation of 9 degradation intermediates (Fig. 10). The structures of degradation intermediate were obtained from their degree of protonation, chemical formula and m/z value. During UV/H₂O₂/Fe²⁺ process the degradation intermediates are formed (due to the involvement of •OH and •H radicals). It was inferred that •OH radical addition may cause substitution and electron transfer reaction while •H radical may have favored elimination reaction. The GC spectrum resolved that the major degradation product, DP3, was obtained at retention time of 2.75 and 3.06 min with relative abundance was 100 percent. The degradation product at retention time 1.65 with relative abundance 20% were proposed to be DP2. Other degradation product with relative low abundance (~10 %) at retention time of 4.56, 6.03 and 7.46 min were proposed to DP7, DP8, and DP9, respectively. Similarly, degradation products with extremely less relative abundance (<<10%) were also observed.

CONCLUSIONS

It was concluded that the UV/H₂O₂/Fe²⁺ was an efficient system for decolorization of AY17 dye in aqueous medium.

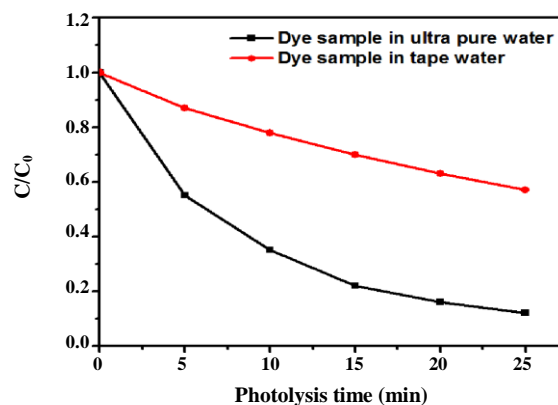


Fig. 9: C/C⁰ vs Photolysis time (t) plot. For decolorization of AY17 dye by UV/H₂O₂/Fe²⁺ system in real and ideal solutions
Reaction conditions: [AY 17]₀ = 0.14 mM, [Fe²⁺]₀ = 0.09 mM, [H₂O₂]₀ = 1.0mM, pH= 3.0, T = 298 K.

The optimum conditions for maximum decolorization of AY 17 dye were adjusted. These conditions were the pH (~ 3) of the solution, concentration of Fe²⁺ (~ 0.09 mM), concentration of H₂O₂ (~1.0 mM), concentration of dye (0.14 mM), and stirring velocity (~100 rpm) of the solution. The efficiency of decolorization of dye solution was found to be increased with temperature. Various anions such as CO₃²⁻, HCO₃⁻, Cl⁻ and SO₄²⁻ decreased the decolorization efficiency. The decolorization of AY 17 dye by UV/H₂O₂/Fe²⁺ system followed the *Second-order* kinetics. Photolysis and UV/oxidant did not show efficient results. The decolorization of AY 17 by UV/H₂O₂/Fe²⁺ process increases with increase of temperature. The activation energy and entropy of activation were calculated. The decolorization process is endothermic process. The rate constant at different initial concentration of AY 17 dye decreased with increasing AY 17 concentration. The UV/H₂O₂/Fe²⁺ shows efficient results for both model and tape water solutions.

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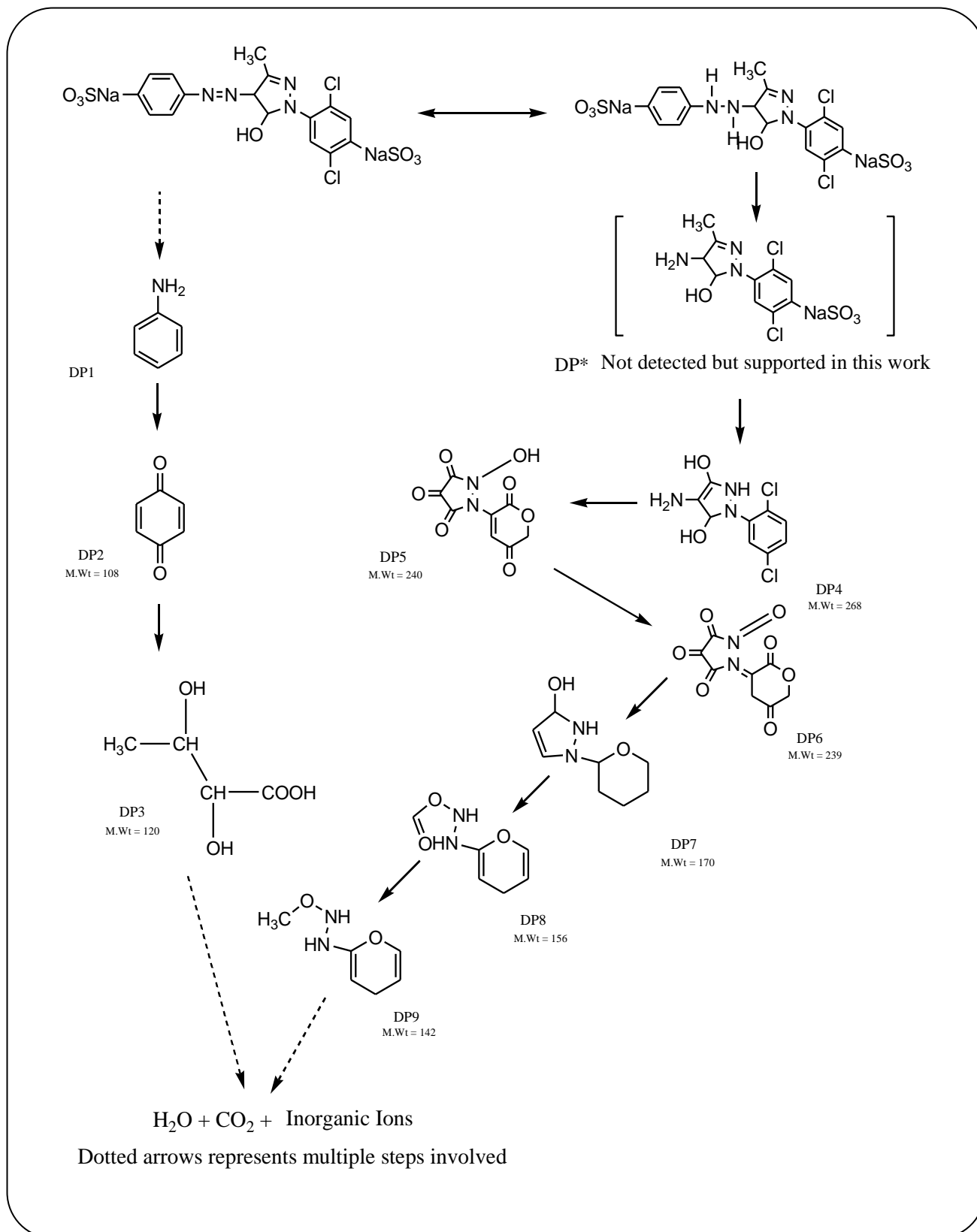


Fig. 10: Proposed degradation pathway of AY 17 dye by photo-Fenton process.

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