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Kinetic investigation of the oxidative decolorization of Direct Green 28 and Direct Blue 78 by hydrogen peroxide

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Abstract

Environmentally, H_2O_2 is a friendly oxidant. It is used in the current work to oxidize and decolorize two of the direct dyes that fulfill an outstanding demand. These dyes are C. I. Direct Green 28 (14155), **I**, and C. I. Direct Blue 78 (34200), **II**. This work may help in solving some of the environmental problems that are faced during the treatment of the wastewater stream of textile and dyeing fabrics. The oxidation of **I** does not occur in acidic medium. The reaction is slow in neutral medium. The reaction rate increases with pH till it reaches a maximum at 10.17. The oxidation of **I** is characterized by an autocatalytic behaviour. The oxidation of **II** does not take place in alkaline medium. The reaction was carried out in acidic phosphate buffer medium at pH = 5.0 in the presence of Cu (**II**) as a catalyst. The oxidation reaction of **I** showed a first order kinetics for [H_2O_2] and zero-order kinetics for [Dye]. The oxidation reaction of **II** showed a first order kinetics for both [dye] and [Cu (II)] and a zero-order kinetics for [H_2O_2]. The Cu (II)-catalyzed oxidation reaction of **II** showed an autocatalytic behaviour in acidic phosphate/citric acid buffer medium and the reaction rate reaches a maximum at pH = 4.15.

This study provides evidence that there is only but one fingerprint acquired by the reaction of each dye from its beginning at $t \rightarrow 0$ passing by the uncatalyzed and autocatalyzed stages. The kinetic and activation parameters of the oxidative decolorization of I and II were deduced. The oxidation reaction of both dyes was entropy controlled. A reaction mechanism of the oxidation of each dye was proposed.

Keywords: C. I. Direct Green 28; C. I. Direct Blue 78; Hydrogen peroxide; Autoxidation; Kinetics; Mechanism

1. Introduction

Optimizing procedures for the treatment of dye-containing wastewater is an enormous task, made extremely complex by the thousands of dyestuffs commercially available around the world. The effective elimination of colored effluents originating from the textile and related industries has become an important problem to the textile dyer and finisher as to meet the new discharge limit values [1]. One of the promising ways of the chemical treatment of the wastewater is the oxidation process. Many dyes may be effectively decolorized using chemical oxidizing agents such as chlorine in the form of liquid or gas. Ozone is a more powerful oxidant than chlorine and it is used for oxidizing dye wastewater [1].

Environmentally, H_2O_2 is a friendly oxidant [2,3]. The kinetics of the oxidation of the direct dye Durazol Blue 8G with H_2O_2 was studied spectrophotometrically in different media. An induction period was observed at the early stages of the reaction. The slowness of the oxidation reaction of Durazol blue 8G was a precursor of an autocatalytic behaviour [4].

Most of the direct dyes are sulphonated azo compounds. In the current work, the oxidative

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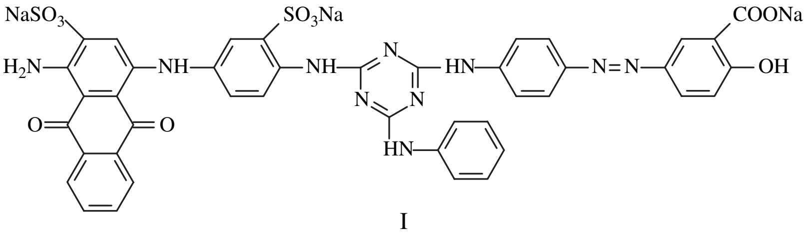
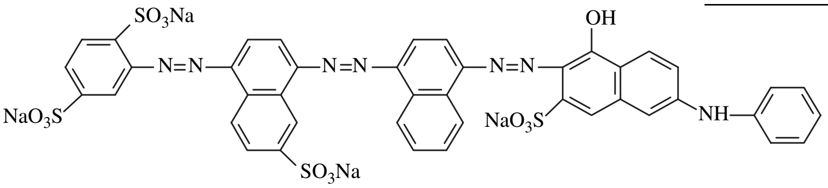
decolorization of two important direct dyes is to be investigated kinetically. One of them is C. I. Direct Green 28, 14155, Chlorantine Fast Green 5GLL; **I**. It is a monoazo dye. It has the structure [5]



I

C. I. Direct Green 28 (14155)
(ε = 14400 L mol^{-1} cm^{-1})

The other one is C. I. Direct Blue 78, 34200, Chlorantine Fast Blue 4GL; **II**. It is a trisazo dye. It has the structure [5]



II

C. I. Direct Blue 78 (34200)
(ε = 10850 L mol^{-1} cm^{-1})

Critical search of literature provided little information on the chemical oxidation of these dyes, **I** and **II**. The current work aims at studying the kinetics and the mechanism of the oxidative decolorization of **I** and **II** by H_2O_2. This work may solve a great ecological problem concerning the color removal of both dyes in the wastewater stream in dyeing and textile fabrics.

2. Experimental

2.1. Materials

The dyes **I** and **II**; (Aldrich) were used as received. Their stock solutions were prepared in doubly distilled H_2O and were diluted to the desired concentrations. H_2O_2 (30% volume, stabilizing free) was obtained from Winlab (England). The exact concentration of a freshly prepared H_2O_2 solution was determined with standard $KMnO_4$ solution [6]. Other chemicals were of analytical reagent grade and were used without further purification.

2.2. Measurements

Kinetic runs were carried out under pseudo first order conditions with respect to [dye]. The change in the absorbance of **I** and **II** was monitored spectrophotometrically. The measurements were performed in a 1-cm cell on Shimadzu 2100 S UV/Vis spectrophotometer. The cell holder temperature was held constant electronically by the aid of an attached Shimadzu temperature controller. The oxidation reaction of I with H_2O_2 does neither occur in aqueous acidic medium nor at pH below 7.0. The oxidation reaction of I was carried out in neutral and alkaline phosphate buffer solutions in the pH 8.0–11.55 range where a few drops of NaOH solution were added to attain higher pH values [2,4].

On the contrary, the oxidation reaction of **II** with H_2O_2 does neither occur in neutral medium nor in alkaline buffer solutions. The oxidation reaction of **II** was carried out in acidic phosphate buffer solution (pH = 5.0) in the presence of Cu (II) as a catalyst. Also, the reaction was carried out in Na_2HPO_4/citric acid buffer solutions in the pH 2.3–6.0 range in the presence of Cu (II). The primary salt effect of the reaction medium was kept constant.

3. Results and discussion

The spectrum of **I** in phosphate buffer solution (pH = 8.0) exhibits two bands at $\lambda_{max} = 620$ and

668 nm. The decay of the absorbance of I at $\lambda_{max} = 620$ nm was monitored at 45 °C (Fig. 1).

When Cu (II) was added to the dye II in a phosphate buffer solution of pH = 5.0, the λ_{max} changed from 602 nm to 598 nm, and the absorbance, A_o (at zero time) changed from 1.665 to 1.7274, respectively. This is due to the reaction between the dye II and Cu (II) as shown in Fig. 2. This figure illustrates the decay of the absorbance of II at $\lambda_{max} = 598$ nm in a phosphate buffer solution (pH = 5.0) at 40 °C. From Fig. 2 and from the fact that the absorbance is an additive property, the $[Cu^{2+}]$ that has been combined with the dye II was equal to 5.75×10^{-6} M. This represents 1% of the original concentration of the Cu^{2+} (6.67×10^{-4} M) in the reaction medium. This means that 99% of the Cu (II) remained unreacted with the dye and had the opportunity to combine with H_2O_2 (0.5 M) to form $Cu^{2+}(H_2O_2)$ as shown later in the reaction mechanism. The existence of the *o*-hydroxyazo group in the dye facilitates the proton transfer between the oxygen and the β-nitrogen. The latter is slightly more electronegative than the α-nitrogen because the oxygen ortho to the α-nitrogen tends to draw electrons from the α-nitrogen. The interaction between the azo group and cupric ion, as in the case of sunset yellow, should be with the β-nitrogen and leads to a 1:1 dye–Cu (II) complex with the liberation of a hydrogen ion per dye molecule [7–9]. Also, the six-membered ring formed by the interaction of the β-nitrogen with cupric ion is more stable than a five-membered ring would be [8]. When sunset yellow combined with cupric ion a shift in the visible absorption spectrum occurred [9]. The same phenomenon was also found with the dye (II), which means the formation of a dye–Cu (II) complex. The determination of the stoichiometry of the dye (II)–Cu (II) complex was beyond the scope of the current work. The absorbance, $A = f(t)$ curve of the oxidation reaction of I in phosphate buffer medium of pH = 8.0 has a sigmoid character with a point of inflection, x_{inf} which is typical of autocatalytic reactions (Fig. 3) and it is practically equal to half the initial dye concentration, i.e. $x_{inf} = a/2$ [10]. The time (t_{inf}) corresponding to x_{inf} as well as the maximum velocity, V_{max} have been determined (Table 1), [4,10,11]. The reaction proceeds with an induction period during which the product–catalyst accumulates. This means that a low rate of the reaction in its initial period, followed by rapid growth of the product yield in the successive period due to the increase in the amount of the catalyst have been observed [12]. Thus, each curve has been analyzed into two linear parts representing the slow uncatalyzed reaction and the fast autocatalyzed one [4]. The pseudo zero-order kinetic equation:

$$A = A_o - k_o t \qquad (1)$$

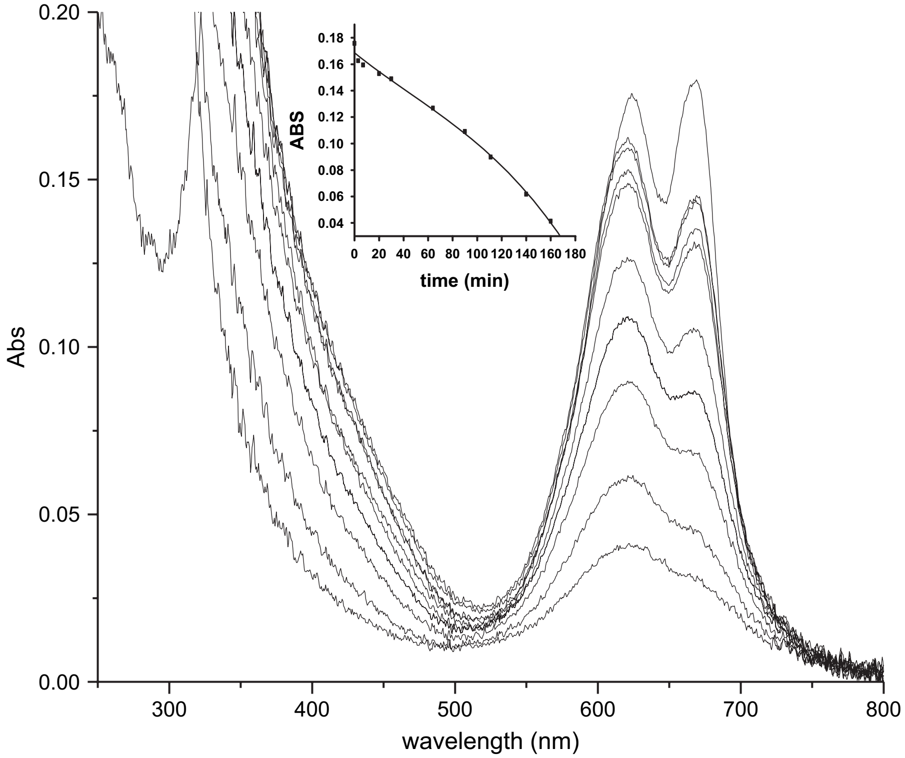


Fig. 1. Time sequence of the decrease in the absorbance band at $\lambda_{max} = 620$ nm for the oxidation of Direct Green 28 (1.0×10^{-5} M) with 0.5 M H_2O_2 in phosphate buffer solution (pH = 8.0) at 45 °C.

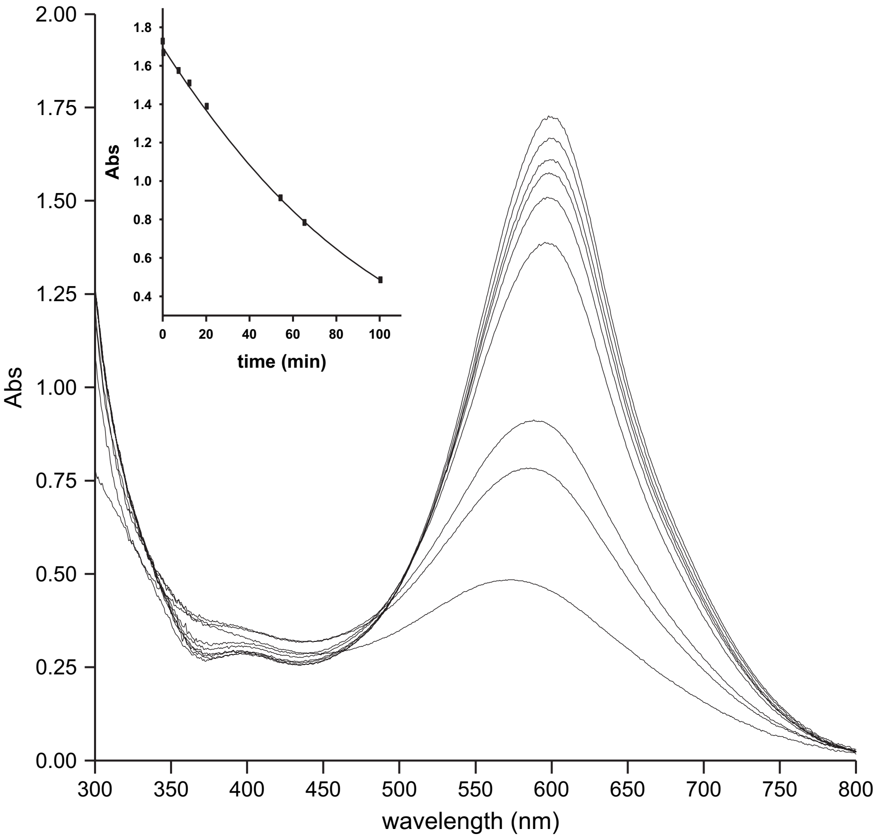


Fig. 2. Time sequence of the decrease in the absorbance band at $\lambda_{max} = 598$ nm for the oxidation of Direct Blue 78 (1.67×10^{-4} M) with 0.5 M H_2O_2 in presence of 6.67×10^{-4} M Cu (II) ion in phosphate buffer solution (pH = 5.0) at 40 °C. Dye in phosphate buffer solution at $\lambda_{max} = 602$ nm and $A_o = 1.665$. Dye + Cu (II) ion in phosphate buffer solution at $\lambda_{max} = 598$ nm and $A_o = 1.7274$.

has been applied to both linear parts, where A_o is the initial absorbance of the substrate (**I**) at zero time, A the absorbance of the substrate at time t and k_o is the observed rate constant. This means that the order with respect to the [I] is equal to zero, and

$$k_o = k[H_2O_2] \tag{2}$$

where k is the specific rate constant. In the case of the autocatalyzed reaction, Eq. (2) becomes

$${}_{o}k_{c} = k_c[H_2O_2] \tag{3}$$

where ${}_{o}k_{c}$ and k_c are the observed and the specific rate constants, respectively. From Eqs. (2) and (3) it was found that the order with respect to $[H_2O_2]$ is unity. Hence, the values of k and k_c at a given temperature can be directly determined from Eqs. (2) and (3), respectively. Moreover, the initial rate, V_o and the order as a function of the initial concentration with respect to H_2O_2 and the dye at time tending to zero ($t \to 0$) were also determined. This was done by determining the initial absorbance change $(dA/dt)_o$ from the intercept of (dA/dt) vs. absorbance curves [2,4]. The order at $t \to 0$ was the same with respect to [I] and $[H_2O_2]$ and was found to be equal to unity. This means that the order as a function of the initial concentration of I was greater than that as a function of time (zero-order). This is an indication of the autocatalytic

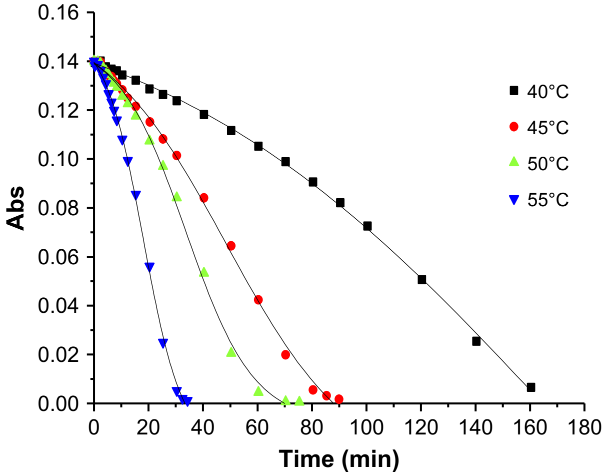


Fig. 3. Typical illustration of the relationship between absorbance and time for the oxidation reaction of Direct Green 28 (1.0×10^{-5} M) with 0.5 M H_2O_2 in phosphate buffer solution (pH = 8.0) at different temperatures.

Table 1
Kinetic parameters of the oxidation of Direct Green 28 with H_2O_2 in various media, at $t \rightarrow 0$, for uncatalyzed and autocatalyzed reactions

Medium	pH	t (°C)	$k'_o \times 10^4$ ($L\,mol^{-1}\,s^{-1}$)	$V_o \times 10^9$ ($M\,s^{-1}$)	$k_o \times 10^5$ ($M\,s^{-1}$)	$k \times 10^5$ (s^{-1})	${}_ok_c \times 10^5$ ($M\,s^{-1}$)	$k_c \times 10^5$ (s^{-1})	$x_{inf} \times 10^6$ (M)	t_{inf} (min)	$V_{max} \times 10^9$ ($M\,s^{-1}$)
Phosphate buffer	8.0	40	1.42	0.71	0.91	1.82	1.80	3.60	2.29	136.98	2.54
		45	3.08	1.54	2.17	4.33	3.29	6.57	4.72	48.37	4.56
		50	5.08	2.54	2.70	5.40	5.14	10.28	4.90	33.72	7.14
		55	6.76	3.98	4.75	9.50	9.78	19.56	4.65	18.11	13.58
Phosphate buffer + 2%(w/w) *t*-butanol	8.0	50	1.78	0.89	15.6[a]	31.20[b]					
		55	2.54	1.27	24.1[a]	48.20[b]					
Phosphate buffer	7.0	40	1.06	0.53	0.83	1.65	1.17	2.33	2.15	191.15	1.62
		45	1.56	0.78	1.20	2.40	1.70	3.39	5.10	88.65	2.36
		50	2.44	1.22	1.80	3.60	2.77	5.53	3.24	67.94	3.84
		55	3.82	1.91	2.57	5.14	4.71	9.43	3.86	39.39	6.55
2×10^{-3} M NaOH solution		55	2.60	1.30	3.78	7.60	9.30	18.60	5.73	23.30	12.90

[a] $k_o = s^{-1}$.
[b] $k = L\,mol^{-1}\,s^{-1}$.

behaviour [4,8]. Thus, the rate equation at $t \rightarrow 0$ can be written down as follows

$$V_o = k'_o[\mathbf{I}][H_2O_2] \tag{4}$$

where, k'_o is the initial rate constant at $t \rightarrow 0$. The values of k'_o and V_o for the oxidation reaction of I at $t \rightarrow 0$, k_o and k for the uncatalyzed reaction, ${}_ok_c$ and k_c, x_{inf}, t_{inf}, and V_{max} for the autocatalyzed oxidation reaction are collected in Table 1

The pseudo first order kinetic equation

$$\ln A = \ln A_o - k_o t \tag{5}$$

has been applied for the oxidation of the dye II with H_2O_2 in the presence of Cu^{2+} in acidic phosphate buffer solution (pH = 5.0), Fig. 4. This means that the order with respect to [II] is equal to unity. The value of k_o was deduced and was found to increase with increasing $[Cu^{2+}]$. The order with respect to $[Cu^{2+}]$ was found to be equal to unity. The value of k_o was independent of $[H_2O_2]$. This means that the order with respect to $[H_2O_2]$ was equal to zero. Hence,

$$k_o = k\left[Cu^{2+}\right] \tag{6}$$

The value of the specific rate constant, k, of the reaction can be determined at a given temperature from Eq. (6). Thus, the rate equation can be written down as follows

$$V = k[\mathrm{II}]\left[Cu^{2+}\right] \tag{7}$$

This means that the reaction follows a second-order kinetics, first order with respect to each of [II] and $[Cu^{2+}]$.

The order as a function of the initial concentration of II, i.e. order at $t \rightarrow 0$ ($n_{t\rightarrow 0}$) is equal to [11]

$$n_{t\rightarrow 0} = \frac{\ln\left(V'_o/V_o\right)}{\ln\left(a'/a\right)} \tag{8}$$

As an example, the initial rate at $t \rightarrow 0$ (V_o) corresponding to the initial dye concentration, a (1.67×10^{-4} M) was equal to 1.04×10^{-7} $M\,s^{-1}$ at 55 °C. The initial rate at $t \rightarrow 0$ (V'_o) corresponding to the initial dye concentration, a'(2.33×10^{-4} M) was equal to 1.1×10^{-7} $M\,s^{-1}$ at 55 °C. By substitution of the corresponding values in Eq. (8), the value of $n_{t\rightarrow 0}$ with respect to [II] was equal to 0.17 which is almost equal to zero. This

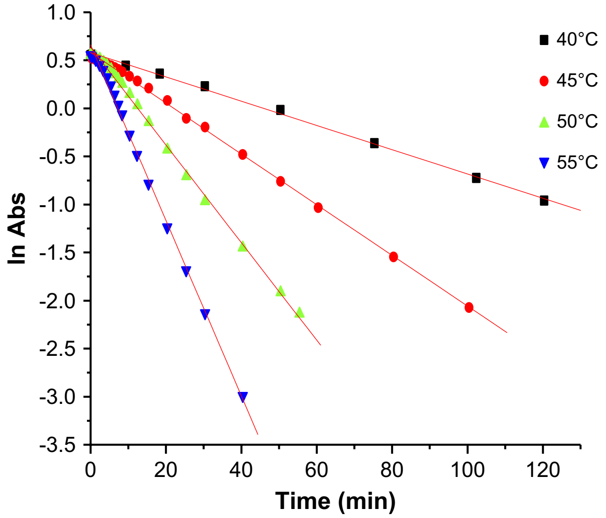


Fig. 4. Typical illustration of the relationship between absorbance and time for the oxidation reaction of Direct Blue 78 (1.67×10^{-4} M) with 0.5 M H_2O_2 in the presence of Cu^{2+} (6.67×10^{-4} M) in phosphate buffer solution (pH = 5.0) at different temperatures.

means that the order as a function of the initial concentration of the dye II was equal to zero, and was smaller than that as a function of time (unity, Eq. (7)). This provides evidence that an intermediate is formed during the reaction which causes an inhibition of the reaction rate [11]. The values of k_o and k for the oxidation of II are found in Table 3.

The activation energy, E was determined by applying Arrhenius equation. The change in the free energy of the activation, $\Delta G^{\#}$ was evaluated from Eyring's equation [10]

$$k = \frac{k_b T}{h} e^{-\Delta G^{\#}/RT} \tag{9}$$

where k_b is the Boltzmann's constant and h is the Planck's constant.

The change in the enthalpy of activation $\Delta H^{\#}$ was deduced from the relationship [10]

$$\Delta H^{\#} = E - RT \tag{10}$$

The change in the entropy of activation was determined from the relationship [10]

$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#} \tag{11}$$

All activation parameters of the oxidation of both dyes I and II are collected in Tables 2 and 3, respectively.

The Cu^{2+}-catalyzed oxidation reaction of II has the greatest rate. This is obvious from the great value of the specific rate constant, k, as well as from the great positive value of $\Delta S^{\#}$ ($+83.3\ J\ mol^{-1}\ deg^{-1}$), Table 3. However, the reaction is specified by a high value of E (108.4 kJ/mol). This provides evidence that the oxidation reaction of II is entropy controlled. The same conclusion is drawn to the other dye I. The greater the value of $\Delta S^{\#}$, the greater is the probability of the formation of the activated complex. A value of $\Delta S^{\#}$ of $+10.6\ J\ mol^{-1}\ deg^{-1}$ was found for the oxidation reaction of I at $t \to 0$ (Table 2). This means that the reaction was very fast in this period with a higher probability of the formation of the activated complex, I (HO_2^-).

The values of the kinetic parameters of the oxidation of I in a phosphate buffer medium of pH 8.0 were greater than those in a medium of pH 7.0. Moreover, the reaction rate at 55 °C increased in the following sequence: $pH = 7.0 <$ NaOH solution (2.0×10^{-3} M) $< pH = 8.0$ (Table 1). However, the values of k_o' and V_o at 55 °C in phosphate buffer solution of pH 7.0 are greater than those in 2.0×10^{-3} M NaOH solution. This is due to the greater induction period that has been observed with NaOH solution.

The formation of radicals during the autocatalytic oxidation process of I was investigated using 2% (w/w) *t*-butanol in a phosphate buffer solution ($pH = 8.0$) at 50 °C and 55 °C, Table 1. From this table, it is clear that the existence of *t*-butanol rendered the reaction mechanism more facile; following a first order kinetics with respect to [I] without exhibition of any autocatalytic behaviour. In the presence of *t*-butanol the solution became more viscous rendering the diffusion of the dye molecule and the active intermediate less facile. This may affect the rate-determining step (r.d.s.) of the reaction.

In the case of the dye (II) 6% (w/w) *t*-butanol was used in phosphate buffer solution ($pH = 5.0$) at 50 °C, Table 3. It is clear that the reaction rate was hindered in the presence of *t*-butanol.

The effect of pH on the rate constant of the oxidation of I was studied using constant concentration of all participants at 45 °C. The pH was varied from 8.0 to 11.5 using phosphate buffer solutions. The rate constants, k_o', k_o and ${}_ok_c$ of the reaction at $t \to 0$,

Table 2
Activation parameters of the oxidation of Direct Green 28 with H_2O_2 in different media at $t \to 0$, for uncatalyzed and for autocatalyzed reactions

Medium	pH	Activation parameters (kJ/mol)[a]	$t \to 0$	Uncatalyzed reaction	Autocatalyzed reaction
Phosphate buffer	8.0	E	106.1	95.6	96.7
		$\Delta H^{\#}$	103.4	92.9	94.0
		$\Delta G^{\#}$	100.0	105.4	103.7
		$\Delta S^{\#}$	+10.6	−39.0	−30.3
Phosphate buffer + 2%(w/w) *t*-butanol	8.0	E	64.7	76.7	
		$\Delta H^{\#}$	62.0	74.0	
		$\Delta G^{\#}$	104.9	103.2	
		$\Delta S^{\#}$	−138.0	−89.7	
Phosphate buffer	7.0	E	73.9	64.1	73.7
		$\Delta H^{\#}$	71.0	61.4	70.0
		$\Delta G^{\#}$	101.2	106.5	105.3
		$\Delta S^{\#}$	−94.2	−140.7	−107.0

[a] $\Delta S^{\#}$: $J\ mol^{-1}\ deg^{-1}$.

Table 3
Kinetic and activation parameters of the oxidation of Direct Blue 78 (1.67×10^{-4} M) with 0.5 M H_2O_2 in the presence of Cu^{2+} (6.67×10^{-4} M) in phosphate buffer solution (pH = 5.0)

t (°C)	$k_o \times 10^4$ (s^{-1})	k ($M^{-1} s^{-1}$)	E (kJ/mol)	$\Delta H^{\#}$ (kJ/mol)	$\Delta G^{\#}$ (kJ/mol)	$\Delta S^{\#}$ ($J mol^{-1} deg^{-1}$)
40	2.105	0.316	108.4	105.7	79.0	83.3
45	4.397	0.659				
50	8.472	1.270				
55	15.207	2.280				
50 (in presence of *t*-butanol)	2.295	0.344				

uncatalyzed reaction and autocatalyzed reaction, respectively, were plotted vs. pH (Fig. 5). Generally, the rate constant increased with increasing pH until reaching a maximum at pH = 10.17 and then decreased with increasing pH till the latter reached a value of 10.5. A sharp decrease was observed for the reaction at $t \rightarrow 0$. The rate constant of the uncatalyzed and autocatalyzed reactions slightly increased until a pH of 11.07 then reached a constant value till a pH = 11.55. For the reaction at $t \rightarrow 0$ a considerable increase in the rate constant was observed when the pH changed from 10.5 to 11.07 and then the rate constant remained unchanged until a pH of 11.55.

Also, in the case of the same dye I, the effect of NaOH concentration on the rate constant was investigated at 55 °C. At $t \rightarrow 0$ and for the uncatalyzed and autocatalyzed reactions the rate constant increased with increasing [NaOH] until reaching a maximum value at [NaOH] of 1.73×10^{-3} M. After that the rate constant decreased gradually. A sharp decrease of the rate constant with increasing [NaOH] was observed in the case of the reaction at $t \rightarrow 0$.

The isokinetic relationship between $\Delta H^{\#}$ and $\Delta S^{\#}$ of the autocatalytic oxidation reaction of I with H_2O_2 in phosphate buffer media of pH 7.0 and 8.0 has been investigated. The isokinetic temperature, β was found to be equal to 287.3 K which is below the average experimental temperature (320.5 K) indicating that the reaction is entropy controlled. This result provides evidence that the oxidation reaction of I by H_2O_2 in phosphate buffer solutions of pH 7.0 and 8.0 at $t \rightarrow 0$, for uncatalyzed and autocatalyzed processes followed one mechanism, i.e. the same r.d.s.

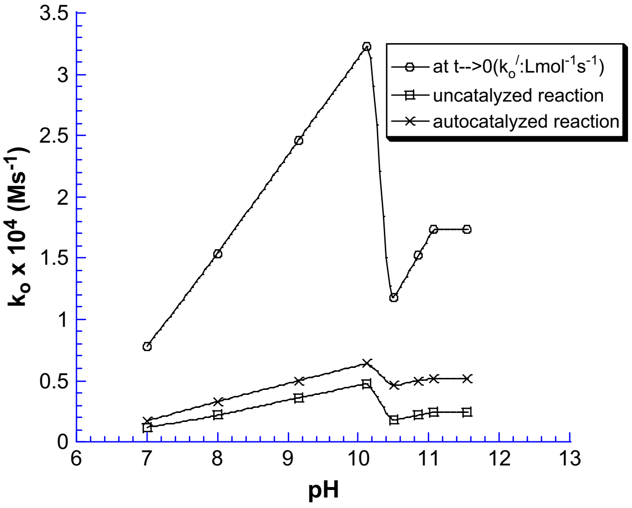


Fig. 5. A plot of the observed rate constant, k_o ($M s^{-1}$) vs. pH (phosphate buffer) for the oxidation reaction of Direct Green 28 (1.0×10^{-5} M) with 0.5 M H_2O_2 at 45 °C.

According to the above experimental findings and explanations the following mechanism is proposed for the autocatalyzed oxidation reaction of I with H_2O_2 in phosphate buffer solution of pH 7.0 and 8.0 in the absence of *t*-butanol

$$H_2O_2 \xrightarrow{k_1} HO_2^- + H^+ \qquad (12)$$

$$I + HO_2^- \xrightarrow{k_2} I(HO_2^-) \qquad (13)$$

$$I(HO_2^-) + I \xrightarrow[\text{slow}]{k_3} I_2(HO^{\bullet -}_2) \qquad (14)$$

$$I_2(HO^{\bullet -}_2) + H_2O_2 \xrightarrow[\text{fast}]{k_4} I{\cdot}O^{\bullet} + I\left(HO^-\right) + \frac{1}{2}O_2 + H_2O \qquad (15)$$

$$I\left(HO^-\right) + H_2O_2 \xrightarrow{k_5} I{\cdot}O^{\bullet} + HO^- + H_2O \qquad (16)$$

$$H^+ + OH^- \rightarrow H_2O \qquad (17)$$

$$I{\cdot}O^{\bullet} + {}^{\bullet}O{\cdot}I \rightarrow I_2O_2 \qquad (18)$$

The rate equation can be written down in terms of the slow step (r.d.s.), Eq. (14), as follows

$$V = k_3[I(HO_2^-)][I]. \qquad (19)$$

Applying the steady-state approximation principle for HO_2^- and $I(HO_2^-)$, then the rate equation (19) becomes

$$V = k_1[H_2O_2] \qquad (20)$$

This is in good agreement with the experimental findings that the reaction follows a first order kinetics with respect to $[H_2O_2]$ and a zero-order kinetics with respect to the [I].

The reaction between the intermediate $I_2(HO_2^{\cdot -})$ and the original reactant (H_2O_2) yields not only the stable product but also two or several molecules of active intermediates. This renders the kinetics of autocatalysis and branched chain reactions to be closely related [4,10,13].

On the other hand, in the presence of the radical scavenger (*t*-butanol) the oxidation reaction of I followed another mechanism which can be proposed as follows

$$H_2O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HO_2^- + H^+ \tag{21}$$

$$I + HO_2^- \xrightarrow{k_2} I(HO_2^-) \tag{22}$$

$$I_2(HO_2^-) + H_2O_2 \xrightarrow[\text{slow}]{k_3} I{\cdot}O + \frac{1}{2}O_2 + OH^- + H_2O \tag{23}$$

$$H^+ + OH^- \rightarrow H_2O$$

The rate equation can be written down in terms of the slow r.d.s. (Eq. (23)) as follows

$$V = k_3[I(HO_2^-)][H_2O_2] \tag{24}$$

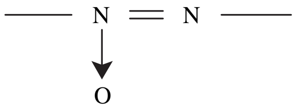
Applying the steady-state approximation principle for $I(HO_2^-)$, then the rate equation (24) becomes

$$V = K_1k_2[I][H_2O_2]/[H^+] \tag{25}$$

where, $K_1 = k_1/k_{-1} = [HO_2^-][H^+]/[H_2O_2]$.

This is in a good agreement with the experimental findings that the reaction in the presence of *t*-butanol follows a first order kinetics with respect to each of [I] and $[H_2O_2]$. From Eq. (25) it is clear that the reaction rate is inversely proportional to the $[H^+]$.

For the oxidation reaction in the presence of *t*-butanol the order with respect to the [I] at $t \rightarrow 0$ as well as in the bulk of the reaction was the same and was equal to unity. This means that the order as a function of the initial concentration of I and that as a function of time were the same (unity). In this case the autocatalytic behaviour of the oxidation reaction disappears. Formation of the azoxy product in Eq. (23),



$$—N{=}N— \quad (N \rightarrow O)$$

which is represented by (I. O), has been previously reported for the oxidation of azo-containing compounds, e.g. 4-(phenylazo) diphenylamine and tartrazine [14,15].

It is noteworthy to mention that the triazinyl ring in the dye I acts as a “chromophoric block” in separating the conjugated systems of the anthraquinone and azo chromophores by the interpolation of two adjacent single bonds [5].

Even more interesting is that the effect of pH on the rate constant of the oxidation reaction of II was studied at 55 °C. Na_2HPO_4/citric acid buffer solution in the pH 2.3–6.0 range was used. The primary salt effect of the reaction solution was kept constant. In this buffer medium the reaction showed an autocatalytic behaviour which was absent in the phosphate buffer medium (pH = 5.0). The existence of the induction period in the phosphate/citric acid buffer medium provides evidence of the slowness of the reaction in its first stage. In this case the reaction at $t \rightarrow 0$ was more slower than that in the phosphate buffer medium at pH = 5.0. The value of V_o in the latter medium with a dye concentration of 1.67×10^{-4} M was equal to 1.04×10^{-7} M s^{-1} at 55 °C. This is greater than the maximum value of V_o (2.68×10^{-8} M s^{-1}) in the phosphate/citric acid buffer medium at 55 °C, Table 4. In this table it is clear that all kinetic parameters, V_o, k_o, k, ${}_ok_c$, k_c and V_{max} increased with increasing pH until reaching a maximum value at pH = 4.15 and then decreased gradually. The variation of the observed rate constants k_o and ${}_ok_c$ with pH is shown in Fig. 6. The variation of V_o with pH also showed the same criterion, Fig. 7. In Figs. 6 and 7, the maximum values of k_o, ${}_ok_c$ and V_o were obtained at pH = 4.15 where the

Table 4
Effect of pH on the kinetic parameters at $t \rightarrow 0$, for uncatalyzed and autocatalyzed oxidation reactions of Direct Blue 78 (1.67×10^{-4} M) with 0.5 M H_2O_2 in the presence of Cu^{2+} (6.67×10^{-4} M) in phosphate/citric acid buffer solution at 55 °C

pH	$V_o \times 10^8$ (M s^{-1})	$k_o \times 10^4$ (M s^{-1})	k (s^{-1})	${}_ok_c \times 10^4$ (M s^{-1})	k_c (s^{-1})	$x_{inf} \times 10^5$ (M)	t_{inf} (min)	$V_{max} \times 10^4$ (M s^{-1})
2.3	1.32	1.44	0.216	8.74	1.31	9.48	26.23	1.21
2.7	2.15	2.03	0.304	10.83	1.62	9.09	21.67	1.50
3.13	2.33	2.60	0.390	12.20	1.83	9.35	17.11	1.69
4.15	2.68	3.00	0.450	14.20	2.13	9.22	16.48	1.96
4.57	1.75	2.11	0.316	10.89	1.63	9.74	17.64	1.50
5.34	1.61	1.17	0.175	9.73	1.46	10.50	17.18	1.35
6.00	1.50	1.00	0.150	8.86	1.33	10.27	18.79	1.22

oxidation potential of the system Cu^{2+}/Cu^{+} has its greatest value (standard value = +0.17 V).

Michaelis–Menten plot of $1/V$ vs. 1/[dye] was linear passing through the origin (Fig. 8) indicating the absence of a complex between the oxidant (H_2O_2) and the substrate (II), [16]. Accordingly, the following mechanism can be proposed for the oxidation reaction of II with H_2O_2 in the presence of Cu^{2+} in phosphate buffer medium of pH = 5.0.

$$\mathrm{II} + Cu^{2+} \xrightarrow{k_1} \mathrm{II}{\cdot}Cu^{2+} \tag{26}$$

$$\mathrm{II}{\cdot}Cu^{2+} + H_2O_2 \xrightarrow{k_2} \mathrm{II}{\cdot}Cu^{2+}(H_2O_2) \tag{27}$$

$$Cu^{2+} + H_2O_2 \xrightarrow{k_3} Cu^{2+}(H_2O_2) \tag{28}$$

$$\mathrm{II}{\cdot}Cu^{2+}(H_2O_2) \xrightarrow[\text{slow}]{k_4} \mathrm{II}{\cdot}Cu^{+}(HO^{\bullet}_2) + H^{+} \tag{29}$$

$$\begin{aligned}\mathrm{II}{\cdot}Cu^{+}(HO^{\bullet}_2) + Cu^{2+}(H_2O_2) &\xrightarrow{k_5} \mathrm{II}{\cdot}O + Cu^{+}({}^{\bullet}OH)\\ &+ \frac{1}{2}O_2 + H_2O + Cu^{2+}\end{aligned} \tag{30}$$

$$Cu^{+}({}^{\bullet}OH) \xrightarrow{k_6} Cu^{2+} + OH^{-} \tag{31}$$

$$H^{+} + OH^{-} \rightarrow H_2O$$

The rate equation can be written down in terms of the slow step, i.e. the r.d.s. (Eq. (29)) as follows

$$V = k_4[\mathrm{II}{\cdot}Cu^{2+}(H_2O_2)] \tag{32}$$

Applying the steady-state approximation principle for $\mathrm{II}{\cdot}Cu^{2+}(H_2O_2)$, then the rate equation (32) becomes

$$V = k_1[\mathrm{II}][Cu^{2+}] \tag{33}$$

This is in good agreement with the experimental findings that the reaction followed a first order kinetics with respect to each of [II] and $[Cu^{2+}]$ and a zero-order kinetics with respect to $[H_2O_2]$. According to Michaelis–Menten plot (Fig. 8) the reaction mechanism indicates that there is no direct combination between H_2O_2 and the dye molecule II. At the end of the reaction the catalyst (Cu^{2+}) has been regenerated (Eqs. (30) and (31)).

In Eq. (30) the azoxy product (II·O) has been formed. This is the case of the oxidation of the azo compounds [14,15].

4. Conclusion

The oxidation reaction of I is very slow in neutral medium and does not occur in acidic medium. This is because in acidic medium, no perhydroxyl ions (HO_2^-) are set free and the oxidation process does not take place. In alkaline medium the hydroxyl ions neutralize the hydrogen ions, thereby promoting the liberation of the active perhydroxyl ions.

The oxidation reaction of II does not take place in alkaline medium. The reaction was carried out in acidic phosphate buffer medium at pH = 5.0 in the presence of Cu^{2+} as a catalyst. The reaction showed a first order kinetics for both [dye] and $[Cu^{2+}]$ and a zero-order kinetics for $[H_2O_2]$. The oxidation

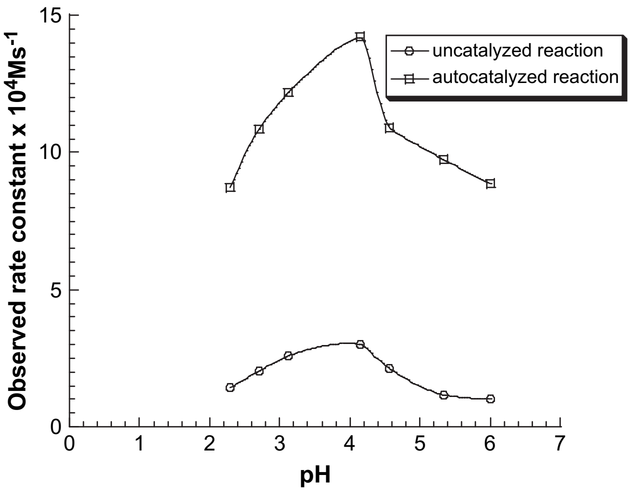


Fig. 6. Effect of pH on k_o (uncatalyzed) and ${}_{o}k_c$ (autocatalyzed) for the oxidation reaction of Direct Blue 78 (1.67×10^{-4} M) with 0.5 M H_2O_2 in the presence of Cu^{2+} (6.67×10^{-4} M) at 55 °C.

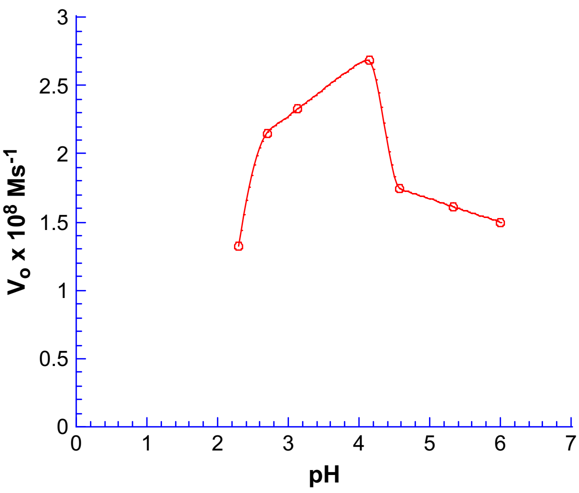


Fig. 7. Effect of pH on the initial reaction rate V_o at $t \rightarrow 0$ for the oxidation reaction of Direct Blue 78 (1.67×10^{-4} M) with 0.5 M H_2O_2 in the presence of Cu^{2+} (6.67×10^{-4} M) at 55 °C.

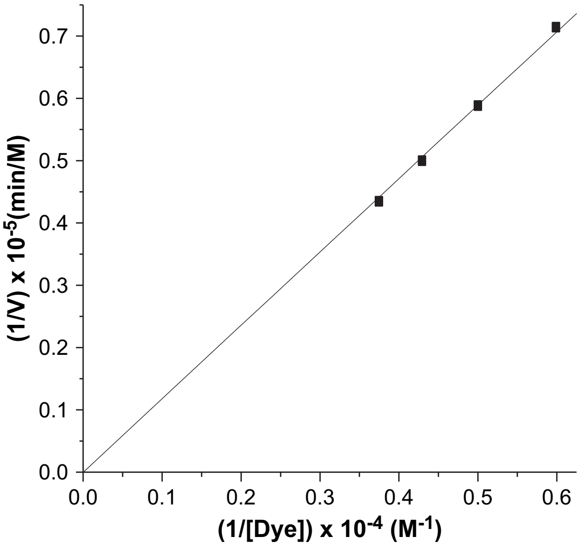


Fig. 8. Representation of Michaelis–Menten plot of $1/V$ vs. 1/[dye] for the oxidation reaction of Direct Blue 78 with 0.5 M H_2O_2 in the presence of Cu^{2+} (6.67×10^{-4} M) in phosphate buffer solution (pH = 5.0) at 55 °C.

reaction of I on the contrary showed a zero and a first order kinetics with respect to [dye] and [H_2O_2], respectively.

After the oxidation of both dyes I and II, their colors disappeared. The study of the effect of pH on the observed rate constant at different stages of the autocatalyzed oxidation reaction is of great importance. This study revealed the optimum reaction conditions and provided evidence that there is only but one fingerprint acquired by the reaction of each dye from its beginning at $t \rightarrow 0$ passing by the uncatalyzed and autocatalyzed stages, Figs. 5–7. The optimum conditions for the oxidative decolorization of I are working in phosphate buffer medium at pH = 10.12 and in 1.73×10^{-3} M NaOH solution. The optimum condition for the Cu^{2+}-catalyzed color removal of II is working in acidic phosphate/citric acid buffer medium at pH = 4.15.

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