KINETIC AND THERMODYNAMIC STUDY OF OXIDATIVE DEGRADATION OF ACID YELLOW 17 DYE BY FENTON-LIKE PROCESS: EFFECT OF HCO_3^-, CO_3^{2-}, Cl^- AND SO_4^{2-} ON DYE DEGRADATION

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ABSTRACT. We report here the degradation of AY-17 dye using Fenton-like process (H_2O_2/Fe^{3+}). The maximum degradation (83%) of AY17 dye is achieved at pH 3 in 60 min, with optimum concentrations of AY 17 (0.06 mM), H_2O_2 (0.9 mM), and Fe^{2+} (0.06 mM). The scavenging effects of HCO_3^-, CO_3^{2-}, Cl^- and SO_4^{2-} on dye degradation are also examined. The activation energy (E_a), activation enthalpy ($\triangle H^*$), and activation entropy ($\triangle S^*$) are calculated for the dye degradation using pseudo-first-order kinetics at various temperature.

KEY WORDS: Acid Yellow 17, H_2O_2/Fe^{3+}, Fenton-like process, Oxidative degradation, Scavenging effects

INTRODUCTION

The azo dyes are frequently used in textile industries due to its low energy consumption, easy utilization, high stability during washing and it presence in varieties of color. A huge amount of water is consumed by textile and dyeing industries. The resulting wastewater from these industries may contain reactive azo dyes and its intermediates. The direct discharge of these dyes-contaminated waste water (from these industries) to water bodies may produce a severe environmental problem. Even, a small quantity (1 mg/L) of these dyes might produce an adverse effect on environment. These dyes contaminated water might be harmful for both aquatic and human life, producing hazardous mutagenic or carcinogenic effect in human being [1, 2]. The discharge of dyes into water, depressed photosynthesis as well as respiration processes of aquatic system [3]. Hence, the treatment of water containing these hazardous pollutants is a major issue for environmental chemist [4–7]. Generally, these azo dyes are non-biodegradable in aerobic condition and convert to more toxic intermediate [8]. Various adsorbents and biosorbents have been used for removal of these dyes [9–11]. Ranjithkumar *et al.* [9] reported the use of activated carbon/Fe_2O_3 nanocomposite as adsorbent for removal of acid yellow 17. Similarly, Ashraf *et al.* [10] used a plant named *T. Angustata L*. and Gao *et al.* [11] used non-living aerobic granular sludge as biosorbent for removal of acid yellow 17 dye.

For the last two decades, AOPs have been playing an important role in the degradation of azo dyes [12–14]. In these processes high oxidizing agent •OH radical (having redox potential 2.8 V vs SHE) are used to oxidize the dyes. AOPs degraded complex structured dyes to smaller organic molecules or may completely oxidized it to CO_2 and H_2O [15, 16].

AOPs includes, Fenton, photo-Fenton, homogenous Fenton-like process, TiO_2/UV [17], ZnO/UV [18], ozonation [19], etc. Among them, Fenton process (Fe^{2+}/H_2O_2) is the commonly used for degradation of dyes and other organic pollutants. Because, it has many advantages: (1) it involves the breakdown of H_2O_2 into environmental friendly species such as O_2 and H_2O, (2) it is a non-toxic process [20], (3) and it is simple, it can be employed at STP and (4) and yield

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high efficiency [21]. Our group has already reported AY-17 dye removal by Fe^{2+}/H_2O_2 and $UV/Fe^{2+}/H_2O_2$ system [22, 23]. However, there are some disadvantages associated with these process [24]. To overcome these disadvantages, the modified Fenton processes were introduced − the Fe^{2+} were replaced with nano zero valent iron or Fe^{3+} [25, 26].

In the present study Fenton-like process, H_2O_2/Fe^{3+}, were used for degradation of AY 17 in aqueous medium. The optimum concentration of H_2O_2, Fe^{3+}, and AY 17 were determined for achieving high degradation efficiency. The effects of pH, temperature and various anions (CO_3^{2-}, HCO_3^-, Cl^- and SO_4^{2-}) on the efficiency of dye degradation were investigated. Kinetic study of dye degradation reaction was also carried out.

EXPERIMENTAL

Chemical and reagent

Acid Yellow 17 (dye content 60%) was obtained from Acros Organics. Hydrogen peroxide (30% w/w), ferric sulfate hepta hydrated, sodium carbonate, sodium sulfate, sulfuric acid, sodium chloride, hydrochloric acid, and sodium hydroxide analytical grade from Sigma Aldrich were used as received.

Experimental procedure

Ultra-pure water (resistivity ≥ 18.2 MΩ. cm), purify through Milli-Q® purification system was used for preparation of solutions. The UV-Vis spectra of AY 17 in a quartz cell (1 cm path length) were recorded in the range of 300-700 nm using a UV-visible spectrophotometer (Perkin Elmer, Model: Lambda-650, UK). All the experiments were performed in triplicate at room temperature. The pH of solutions was adjusted through pH meter; NeoMet ISTEC (Korea), using HCl and NaOH. Experiments were carried out in 50 mL beakers in thermostat of constant temperature. The experimental mixture is stirred by magnetic stirrer. In each experiment certain quantity of dye ferric ion (Fe^{3+}), and H_2O_2 were put in a volumetric flask and then diluted up to 50 ml by adding triply distilled water. The samples were instantly analyzed at fixed time intervals. The change in λ_{max} was monitored at consecutive time interval to study the course of the degradation process.

The change in concentration of AY 17 was determined from the absorbance intensity of reaction mixture (at 400 nm, ε = 12928 M^{-1} cm^{-1}) at various time intervals through the calibration plot. The absorption of reaction mixture and sampling were completed within one minute to minimize experimental error [27]. Percent degradation was calculated using Eq. (1).

$$\text{Percent Degradation (\%)} = \left(1 - \frac{C_t}{C_0}\right) \times 100\% \tag{1}$$

RESULTS AND DISCUSSION

Degradation of AY 17 by ferric ion (Fe^{3+}), hydrogen peroxide (H_2O_2), and Fenton-like process (H_2O_2/Fe^{3+}): selection of suitable system

The effect of various parameters on percent degradation of AY 17 was investigated (Figure 1). The maximum dye degradation was obtained in 60 minutes with optimal concentrations of H_2O_2 (0.9 mM), Fe^{3+} (0.06 mM), and AY 17 (0.06 mM) dye (see next sections). Foremost, AY 17 (0.06 mM) was degraded using individual H_2O_2 and Fe^{3+} systems and then Fenton like − H_2O_2 /Fe^{3+} system were applied. It was observed that the degradation of acid yellow 17 dye with Fe^{3+}, H_2O_2, and Fe^{3+}/H_2O_2 systems were about 3 %, 11 % and 83%, respectively in 60 minutes. The reason for low percent degradation of dye solutions through individual Fe^{3+} or H_2O_2 systems

were due to the low quantity of hydroxyl radical production because of the absence of an oxidizing agent, H_2O_2 (Fe^{3+} system) or catalyst, Fe^{3+} in (H_2O_2 system) while, high percent dye degradation in Fe^{3+}/ H_2O_2 system was due to production of large amount of hydroxyl radical ($^•OH$) because of the presence of both oxidizing and reducing species [28]. The general mechanism for hydroxyl radical ($^•OH$) generation is given by Eq. 2 and 3 [29].
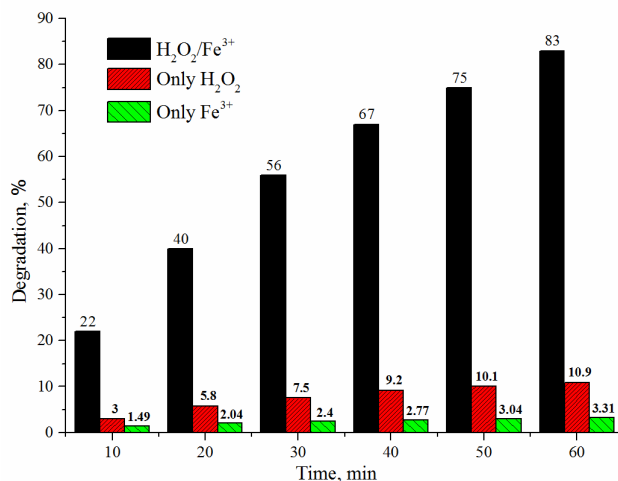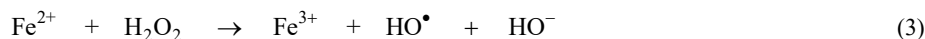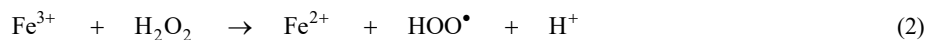
$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HOO^• + H^+ \tag{2}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^• + HO^- \tag{3}$$

Figure 1. Selection of suitable process for degradation of AY 17 dye: pH = 3.0, $[H_2O_2]_o$ = 0.9 mM, $[AY 17]_o = [Fe^{3+}]_o$ = 0.06 mM, T = 298 K.

Effect of pH dye degradation

As the pH plays an important role in the degradation of dye solution. Hence, dye solutions of pH 2.0, 3.0, 6.0, and 8.0 were degraded using Fenton-like process for 60 min. The initial concentration of acid yellow 17, H_2O_2 and ferric ion were taken as 0.06, 0.9, and 0.06 mM, for acid yellow 17, H_2O_2 and Fe^{3+}, respectively (Figure 2a). It was observed that highest percent degradation (83%) was achieved at pH 3.0. The reason for such a high degradation efficiency was the high production of hydroxyl radical ($^•OH$) by Fe^{3+} at pH 3.0 [30].

The low oxidative degradation of acid yellow 17 dye at pH 6.0 and 8.0 might be explained by several facts: Firstly, the formation of $Fe(OH)_3$ which has low catalytic properties in decomposition of hydrogen peroxide (H_2O_2) [31]. Secondly, the decrease in number of free iron species in solution because at high pH (6.0 and 8.0) precipitation of polymeric ferric oxy hydroxides occurred [32]. The activity of oxy hydroxides might be very low and it may hindered ferrous ion (Fe^{2+}) production for hydroxyl radical ($^•OH$) generation shown by Eq. 2 and 3 [33]. Another possibility for low oxidation was the formation of ferrous complexes, which also hindered the reaction of ferric ion (Fe^{3+}) with hydrogen peroxide [34]. Similarly, the low percent degradation of acid yellow 17 dye at pH ~ 2.0 was either due to the formation of iron complex species such as $[Fe(II)(H_2O)_6]^{2+})$ or scavenging of the hydroxyl ($^•OH$) radical hydronium ion (H_3O^+) at low pH [33, 35].

Effect of initial concentration of (H₂O₂)

The effect of H_2O_2 concentration over dye degradation was also checked. A series of 0.06 mM dye solutions containing various concentrations (i.e. 0.5, 0.6, 0.9 and 1.10 mM) of H_2O_2 and constant initial concentration of Fe^{3+} at pH 3 ware degraded to determine the initial optimum dose of H_2O_2 for maximum degradation of AY 17 (Figure 2b). The dye was oxidized through $^•OH$ radical produced *via* the reaction of hydrogen peroxide with Fe^{3+} (Fenton-like process). The mechanism for reaction of Fe^{3+} with H_2O_2 can be found elsewhere in literature [36–39].
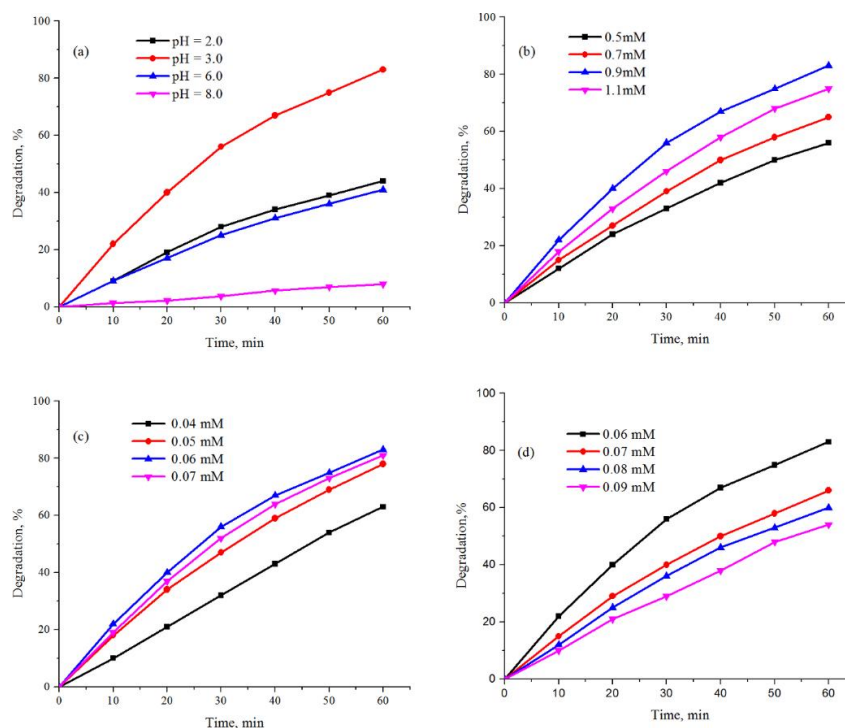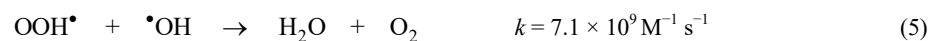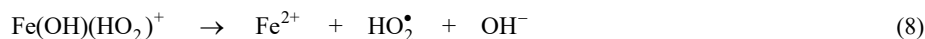

Figure 2. Effect of various conditions on % degradation of AY 17 by Fenton-like process: (a) pH, (b) H_2O_2, (c) Fe^{2+}, (d) concentration of dye. The optimized reaction conditions were determined as: $[H_2O_2]_o = 0.9$ mM, $[Fe^{2+}]_o = [AY\ 17]_o = 0.06$ mM, pH = 3.0.

It was observed that degradation of AY 17 dye increases with hydrogen peroxide concentration. Optimal concentration of H_2O_2 for high degradation (83%) was found to be 0.9 mM. it was also observed that further increase in H_2O_2 concentration decreased the percent degradation which might be due to scavenging of $^•OH$ radical by H_2O_2, hydroperoxy radical (OOH$^•$), form during H_2O_2/Fe^{3+} reaction or dimerization of hydroxyl radical ($^•OH$) with itself as given by equation (4-6) [37, 40].

$$H_2O_2 \ + \ ^•OH \ \rightarrow \ H_2O \ + \ OOH^• \qquad k = 2.7 \times 10^7\,M^{-1}\,s^{-1} \qquad (4)$$

$$OOH^• \ + \ ^•OH \ \rightarrow \ H_2O \ + \ O_2 \qquad k = 7.1 \times 10^9\,M^{-1}\,s^{-1} \qquad (5)$$

$$^•OH \ + \ ^•OH \ \rightarrow \ H_2O_2 \qquad\qquad k = 6.0 \times 10^9\,M^{-1}\,s^{-1} \qquad (6)$$

Effect of initial concentration of ferric ion (Fe^{3+})

As the production of $^\bullet$OH radicals by hydrogen peroxide is catalyzed by iron (Fe^{3+}), therefore, the optimum concentration of Fe^{3+} for maximum dye degradation was also determined at pH 3. Here, the initial concentration of dye (0.06 mM) and H_2O_2 (0.9 mM) were kept fixed. While concentration of Fe^{3+} was altered from 0.04 mM to 0.06 mM (Figure 2c). It was observed that the percent degradation of AY 17 dye increased from 63 % to 83 % upon increasing Fe^{3+} concentration. However, further increase in Fe^{3+} concentration decreased down the % degradation due to scavenging of $^\bullet$OH radical by Fe^{2+}. The ratio/proportion of H_2O_2:Fe^{3+} is also important in degradation of dye solution because it was reported that in H_2O_2/Fe^{3+} system the concentration of Fe^{2+} increased quickly and then attain "steady state'' with passage of time. In fact, the addition of Fe^{3+} to a system containing H_2O_2 lead to formation of Fe^{3+} peroxo complexes which convert into Fe^{2+} and $HO^\bullet_2$ Eq. (7-8) [33]. Hence, the scavenging of hydroxyl radical by hydrogen peroxide and Fe^{2+} depends on the molar ratio of H_2O_2 and Fe^{3+} [33].

$$Fe\text{-}OOH^{2+} \quad + \quad H_2O_2 \quad \rightarrow \quad Fe(OH)_2(HO_2)^+ \tag{7}$$

$$Fe(OH)(HO_2)^+ \quad \rightarrow \quad Fe^{2+} \quad + \quad HO^\bullet_2 \quad + \quad OH^- \tag{8}$$
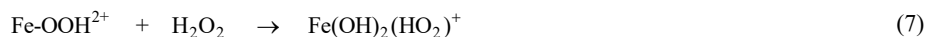
Dye concentration effect on degradation

The concentration of AY 17 dye is also important parameter which effects the percent degradation. Effect of initial concentration of dye on the degradation was shown in Figure 2d. By keeping the initial concentration of $[H_2O_2]$ = 0.90 mM and $[Fe^{3+}]$ = 0.06 mM, it was monitored that the percent degradation decreased from 83 % to 54 % upon increasing AY 17 concentrations which is in agreement with previous reports [41].

The high degradation of AY 17 at low concentration (0.06 mM) of dye was due to the frequent availability of hydroxyl ($^\bullet$OH) radical for low amount of dye molecule. Hence, the decreases in percent degradation (54 %) at comparatively high concentration (0.09 mM) of dye might be interpreted in term of the inadequate availability of hydroxyl radical for AY 17 molecules degradation [27].

Effect of CO_3^{2-} and HCO_3^- on the AY 17 percent degradation

A large amount of inorganic salts, like Na_2CO_3 and $NaHCO_3$ are commonly used in various dying process. The presence of these inorganic ions may affect the degradation of AY 17 dye. The influence of CO_3^{2-} and HCO_3^- on degradation of acid yellow 17 dye was investigated at pH 3. Figure 3 shows the degradation of dye solutions in presence of different concentrations of anions; HCO_3^- and CO_3^{2-}. It was observed that the presence of these ions has a negative effect on dye degradation. The percent degradation of AY 17 decreased from 83% to 66% in case of CO_3^{2-} while 70% in case of HCO_3^-. These results agree with literature [42]. These ions are much stable and do not form complexes with iron [43], hence, they are able to scavenge the hydroxyl radical ($^\bullet$OH) although another radical, $CO_3^{\bullet-}$, produced in the hydroxyl radical ($^\bullet$OH) scavenging reaction, but, it has much less reactivity than hydroxyl radical [44].

Effect of Cl^- and SO_4^{2-} on the AY 17 percent degradation

The effect of chloride (Cl^-) and sulfate (SO_4^{2-}) ions on dye degradation were investigated (Figure 4). It was noted that percent degradation diminished in the presence of these anions which is due to the scavenging of hydroxyl radical by these anions. The quenching ability of these anions also depends on the nature of these anions, concentration, and type of oxidant (i.e. H_2O_2) used for dye oxidation/degradation [45].

These anions also form stable complexes with Fe^{3+}/Fe^{2+}, therefore, the concentration of Fe^{3+}/Fe^{2+} decreased in the system which results decrease in hydroxyl radical formation.
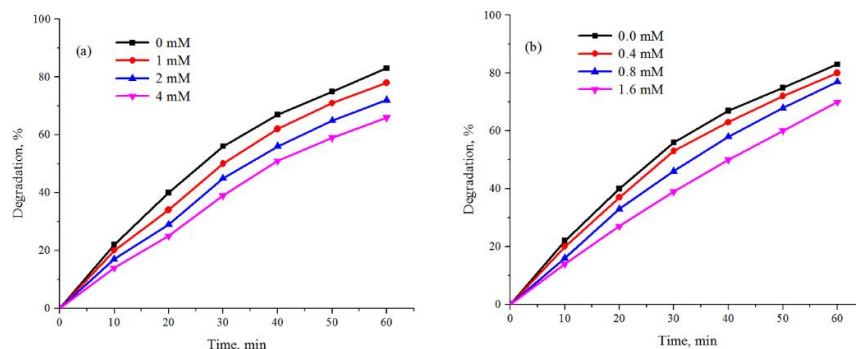

Figure 3. Effect of carbonate, CO_3^{2-} (a) and bicarbonate, HCO_3^{-} (b) ion on % degradation of acid yellow 17 dye in Fenton-like process. Other experimental condition: $[Fe^{3+}]_o = [AY\ 17]_o = 0.06$ mM, $[H_2O_2]_o = 0.9$ mM and pH = 3.0.
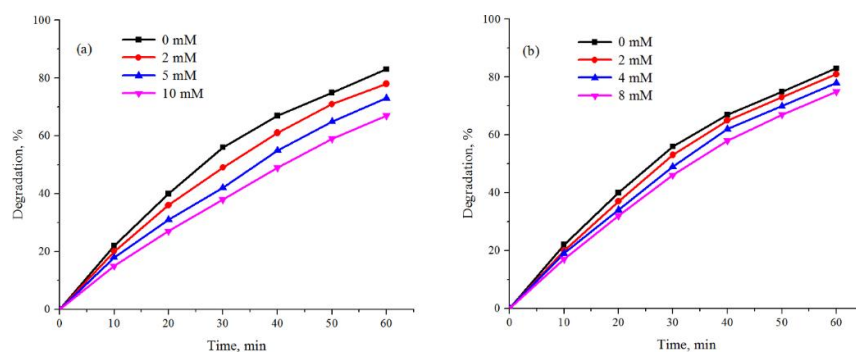

Figure 4. Effect Chloride, Cl^{-} (a) and sulfate, SO_4^{-} (b) ion on % degradation by Fenton-like process. Other experimental condition: $[H_2O_2]_o = 0.90$ mM, $[Fe^{3+}]_o = [AY\ 17] = 0.06$ mM, pH = 3.0 and temperature = 298 K.

Kinetic study

To examine the degradation kinetics of acid yellow 17 by Fenton-like process, the change in absorption as a function of time data were fitted in linear integrated equations derived for zero, first, second, pseudo-first and pseudo-second-order kinetic as shown by equations given in Table 1 [27, 46]. The rate constants were then calculated from the slope (in case of zero, first, second order) or intercept (in case of pseudo-second-order) of the plots (Table 2). By comparing R^2 of these plots, it was suggested that the degradation of AY 17 follows the pseudo-first-order because it have better R^2 value (0.95 or ~ 1). Similarly, half-lives were also calculated using half-life equations derived for zero, first, second, pseudo-first and pseudo-second-order kinetic and appeared in first right column of Table 1. It was ascertained that the half-life value calculated through pseudo-first-order kinetic equation were closely related to experimental

values. From these detail kinetic studies, it was concluded that the degradation of AY1 7 by Fenton-like process best fit in pseudo-first order kinetic of type.

$$r_{AY\,17} = k[AY17][OH] \approx k'[AY17] \qquad (9)$$

The pseudo-first-order rate constant for the degradation process of AY 17 by Fenton-like were found to be 0.0385, 0.0378 and 0.0426 at a temperature of 298, 308 and 318 K, respectively. These results have best correlation with previous literature [47].

Table 1. Integrated rate law along with half-life for various order of reaction [27, 46].

Order of Reaction Kinetic	Equation	Half life, min
Zeroth	$A_t = A_0 - k_0 t$	$A_0 / 2k_0$
First	$\ln A_t = \ln A_0 - k_0 t$	$\ln 2 / k_1$
Pseudo-first	$\log(A_t - A_e) = \log(A_0 - A_e) - k_1 t / 2.303$	$\ln 2 / k_1$
Second	$1/A_t = 1/A_0 + k_2 t$	$1/k_2[A_0]$
Pseudo-second	$t/A_t = 1/k_2 A_e^2 - (1/A_e) t$	$0.5A_0 A_e / k_2 (A_e - 0.5A_0)$

Table 2. The kinetic rate constants for degradation of AY 17 by Fenton-like process.

Order of kinetics	T/K	Rate constant, unit[a]	Half-life, min	R^2
Zero-order	298	207	36.7	0.95
	308	194	37.8	0.80
	318	181	39.6	0.70
First-order	298	375	23.8	0.99
	308	465	19.0	0.98
	318	504	17.7	0.95
Pseudo first-order	298	491	18.00	0.98
	308	517	18.34	0.98
	318	555	16.27	0.97
Second-order	298	833	13.16	0.90
	308	580	18.98	0.85
	318	176	6.31	0.90
Pseudo second-order	298	6580	1.71	0.84
	308	10562	1.07	0.77
	318	12566	0.81	0.81

[a]unit for zero order, first-order, and second-order, are M min⁻¹, min⁻¹, and M⁻¹.min, respectively.

Effect of temperature

The rate of chemical reaction, product yield and distribution critically depend upon the initial temperature of the system. In the present work the effect of temperature on rate of reaction and percent degradation were determined using temperatures range from 298 to 318 K (Figure 5a). It was recorded that rise in temperature not only increased percent degradation, but also the rate of reaction. This phenomenon might be explained in term of $^{\bullet}$OH generation as a function of temperature. It was suggested that the rise in temperature accelerates the reaction between H_2O_2 and Fe^{3+}, hence the generation of oxidizing species like $^{\bullet}$OH radical become improved [48, 49].
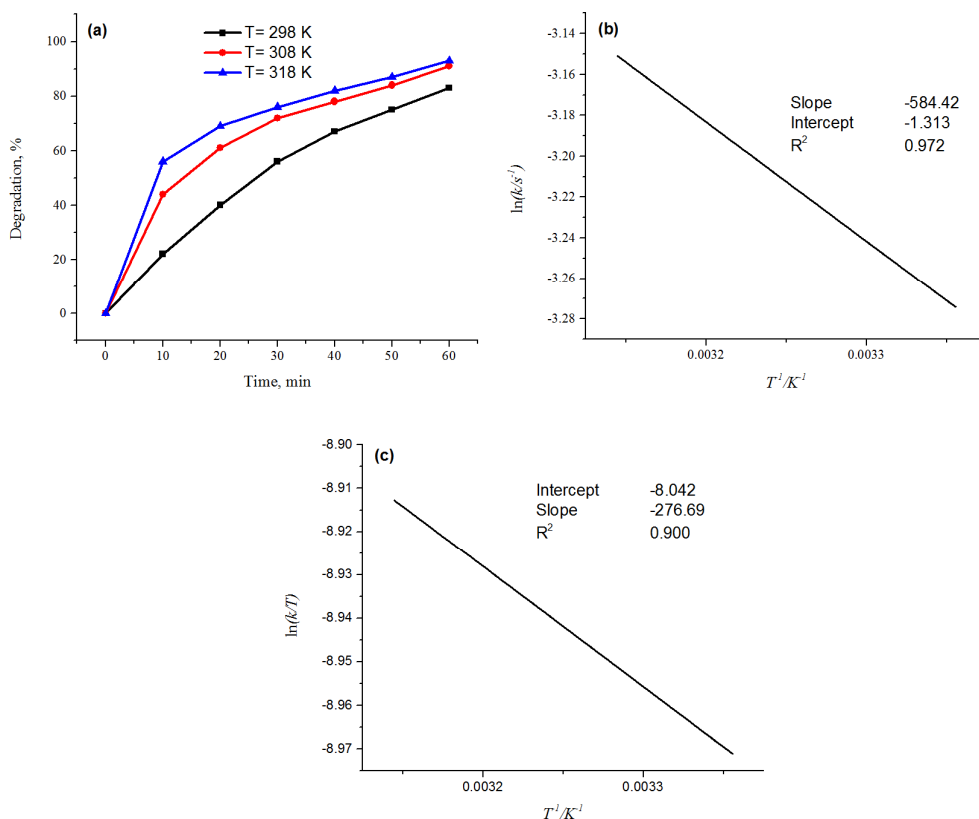
Figure 5. (a) Effect of initial temperature on % degradation of acid yellow 17 dye in Fenton-like process, (b) $\ln(k/s^{-1})$ *vs.* T^{-1}/K^{-1} plot, (c) $\ln(k/T)$ *vs.* T^{-1}/K^{-1} plot. Experimental condition: $[H_2O_2]_o = 0.90$ mM, $[Fe^{3+}]_o = [AY\ 17]_o = 0.06$ mM, pH = 3.0 and T = 298, 308 and 318 K.

The effect of temperature on the rate constant of the H_2O_2/Fe^{3+} system was determined by using eq. 10-11. The activation energy (Ea), enthalpy ($\triangle H^{\#}$), and entropy ($\triangle S^{\#}$) of activation of the H_2O_2/Fe^{3+} process was obtained by employing (see Figure 5 b and c)

$$\ln k = \ln A - \frac{E_a}{RT} \tag{10}$$

$$\ln \frac{k}{T} = \ln \frac{\kappa k_B}{h} + \frac{\Delta S^*}{R} - \frac{\Delta H^*}{R}\frac{1}{T} \tag{11}$$

Where slope = ΔH/R and intercept = $[\ln(kk_B/h)]+(\Delta S^{\#}/R)$, κ is usually taken as 1, R is universal gas constant, k_B is the Boltzmann constant and h is the Planck's constant. The thermodynamic parameters calculated through above equation (10 and 11) are collected in Table 4.

Table 4. Thermodynamic parameters for the degradation of AY 17 by Fenton-like oxidation *pseudo-first-order.*

E_a, kJmol^{-1}	ΔH^*, kJmol^{-1}	ΔS^*, kJ mol^{-1}K^{-1}
4.85	2.30	-0.264

Comparison between standard sample prepared in triply deionized water and natural water sample

A comparative study was performed between standard and natural water sample containing AY 17 dye. The result was shown in Figure 6 which clearly shows that the degradation is maximum in standard sample as compared to natural water sample. The aqueous mediums of natural water sample were further analyzed by ion chromatography (IC). It was found that certain anions such as HCO_3^- (0.298 mM), CO_3^{2-} (0.252 mM), SO_4^{2-} (0.5 mM), and Cl^- (0.335 mM) are present in aqueous medium therefore, the low degradation was due to the presence of these anions. As mentioned earlier, these anions act as scavengers of hydroxyl radical radicals. In natural water sample about 66% while in standard sample, 83% degradation achieved in 60 min. These results suggested that photo-Fenton-like process is relatively efficient method for the degradation of AY-17 in both natural and model sample [22].
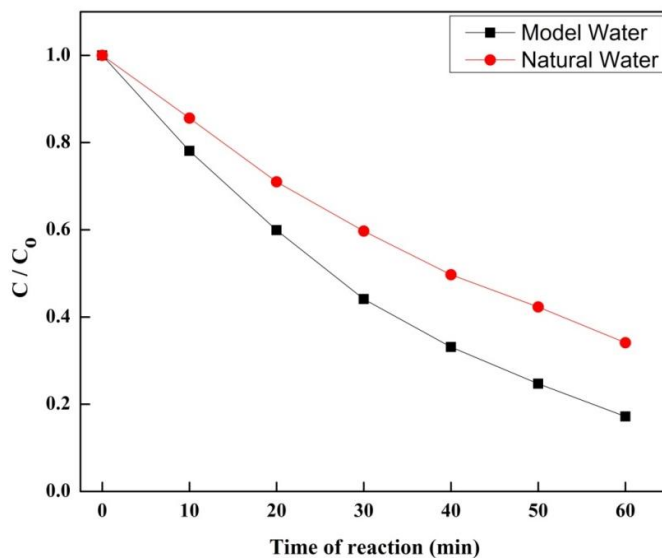

Figure 6. Effect of sulfate ions on degradation of AY 17 dye in Fenton-like process. Experimental condition: $[AY\ 17]_0 = [Fe^{3+}]_0 = 0.06$ mM, $[H_2O_2]_0 = 0.90$ mM, pH = 3.0, T = 298 K.

CONCLUSION

It was concluded that the Fenton-like process is simple and cost-effective method for degradation AY-17 dye. The percent degradation of AY-17 dye is found to be 66% and 83% in natural water sample and standard sample, respectively. The low degradation in natural water sample is due to scavenging of $^\bullet OH$ by various anions (CO_3^{2-} HCO_3^-, Cl^-, and SO_4^-), which

normally present in natural water sample. The rise in temperature also increases percent degradation of dye.

ACKNOWLEDGEMENT

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