Fenton Oxidation Kinetics of Azo Dye Acid Light Yellow 2G Wastewater by Online Spectrophotometry

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ABSTRACT

The online spectrophotometric technique was adopted to monitor the degradation of simulated Acid Light Yellow 2G (ALY 2G) solution with the Fenton oxidation process, and the kinetic process was also discussed. The effects of the initial concentration of H_2O_2 and Fe_2SO_4, pH value, and initial dye concentration on the degradation process were studied. The results showed that the ALY 2G can be degraded by Fenton oxidation, and the colour removal rate of Acid Light Yellow 2G was 94.66% after 300 s when the concentration of simulated wastewater was 20 mg/L, the dosage of Fe^{2+} was 0.1 mmol/L, the dosage of H_2O_2 was 0.6 mmol/L, and the pH was 3. The degradation process was divided into two stages: the first stage, the degradation rate is very fast; in the second stage, with the extension of reaction time, the increase of decolourization rate decreases. The first stage of the reaction accords with the first-order kinetics, and the reaction rate constant K_{ap} is 0.04824 s^{-1}. The intrinsic reaction rate constant of ALY 2G and hydroxyl in aqueous solution in the Fenton oxidation method is 0.55×10^9 $M^{-1}s^{-1}$.

INTRODUCTION

Textile and dyeing industries are one of the most important chemical industries. However, many printing and dyeing plants produce large amounts of high chroma wastewater during the production process (Xu et al. 2015b). Many aromatic agents, metals and chlorides contained in wastewater are toxic to aquatic organisms, human beings and even affect biosphere (Laszlo & Erzsebet 2008). Every year, 12% of synthetic dyes are run off during the production process, resulting in dye-containing wastewater with high chroma and chemical oxygen demand (COD), low biochemical oxygen demand, oxidation resistance and difficult biodegradation (Xu et al. 2016). Therefore, the most critical problem in the dyeing industry is how to treat visible pollutants contained in dye wastewater (Lee et al. 2006) to meet the industry emission standards.

Advanced oxidation processes (AOPs) have great potential for degrading organic pollutants in industrial wastewater. This oxidation mechanism produces strong oxidants, such as hydroxyl radicals (Cheng et al. 2016), which have high activity and are non-selective for decomposing organic pollutants into CO_2, H_2O, and inorganic salts in the water environment (Inmaculada et al. 2015). Fenton oxidation ($Fe^{2+}/H_2O_2/H^+$)

has received the intensive attention in wastewater treatment due to its superior degradation efficiency, rapid reaction speed and moderate investment (Azizi et al. 2015). Under weak acidic conditions, Fe^{2+} is oxidized by H_2O_2 to form Fe^{3+}, hydroxyl (·OH) and OH^- (Xu et al. 2015a), which produces highly reactive ·OH to destroy the molecular structure of organic dyes, thus achieves the decolourization effect of dye wastewater. The spectrophotometer can record the mass concentration change of the dye (Gao et al. 2019a, Gao et al. 2019b, Sibel et al. 2012, Xu et al. 2018) and monitor the instantaneous state of the dye decolourization during the Fenton oxidation process. Therefore, the experimental results are real-time and reliable with a very minor error.

In the present study, azo dye Acid Light Yellow 2G was selected as the target pollutant. We studied the effect of initial Fe^{2+}, initial H_2O_2 concentration, initial pH value of the solution and different dye concentrations on the degradation of ALY 2G by the Fenton method. The decolourization kinetics performance of Fenton oxidation was studied based on the experimental data. The kinetic model of azo dye degradation with Fenton's reagent was established. In this study, the online spectrophotometric system was used to monitor the degradation of Acid Light Yellow 2G. The kinetic analysis
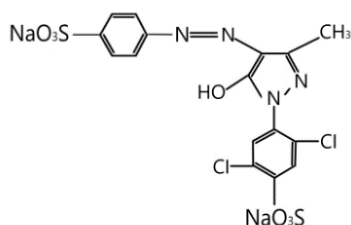
Fig. 1: Molecular structure of Acid Light Yellow 2G.

result was expected to provide basic experimental data for a deeper understanding of the Fenton oxidation process of wastewater containing ALY 2G dye.

MATERIALS AND METHODS

Chemical Reagents

The structure of Acid Light Yellow 2G is shown in Fig. 1. ALY 2G was purchased from Shijiazhuang Dyestuffs Company (China) and the ALY 2G solution was prepared by dissolving a requisite quantity of dye in ultrapure water. Ferrous sulphate ($FeSO_4 \cdot 7H_2O$) and hydrogen peroxide (H_2O_2) were purchased from Tianjin Damao Chemical Reagent Company, and sulfuric acid (H_2SO_4) from Modern Chemical Reagent Company. They were of reagent analytical grade.

Apparatus Set-up

The online spectrophotometric system is shown in Fig. 2. Reaction section (degradation device) includes a digital magnetic stirrer apparatus (Shanghai Instrument Company, China), and a 500 mL beaker. Optical measuring part contains UV-Vis spectrometer (UNICO 2802, Shanghai, China), cycle peristaltic pump and cuvette (1 mL). The recording unit is a computer with the monitoring frequency of 12 min^{-1} during the oxidation process.

Experimental Procedure

Fenton oxidation process was performed in a 500 mL vessel. With the role of a peristaltic pump, the simulated

dye wastewater was pumped into the cuvette of UV-Vis spectrophotometer. Absorbance at maximal absorption peak of dye was obtained by the spectrophotometer. The effects of $FeSO_4$ dosage, H_2O_2 dosage, initial pH, and initial dye concentration on the degradation of Acid Light Yellow 2G were studied by single-factor experiments.

Feasibility Analysis of Online Spectrophotometric Technique

Online spectrophotometry method was applied to analyze the decolourization of ALY 2G dye in the Fenton process. The UV-Vis spectra of ALY 2G, H_2SO_4, Fe^{2+}, and Fe^{3+} are presented in Fig. 3. Azo dye ALY 2G has a maximum adsorption peak of 402 nm, which does not vary with the addition of H_2SO_4, Fe^{2+} and Fe^{3+}. Therefore, during the experiment, online spectrophotometry can be used to monitor ALY 2G wavelength at 402 nm. The standard equations and standard curves for dye concentration (C) and absorbance (A) are given in Fig. 4. The relationship of the absorbance (A) at 402 nm against concentration (C) of ALY 2G is A = 0.0309C + 0.0015 (R^2 = 0.9998).
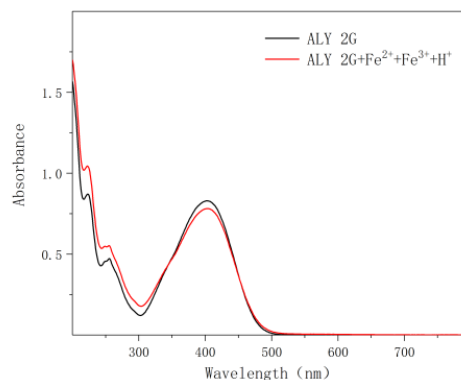

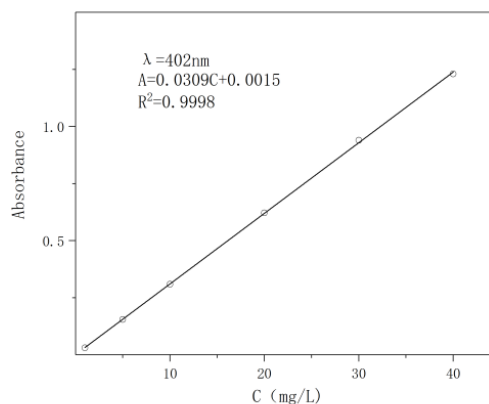Fig. 3: Comparison of dye UV-Vis spectra between dye and dye ($+H_2SO_4 + Fe^{2+} + Fe^{3+}$).
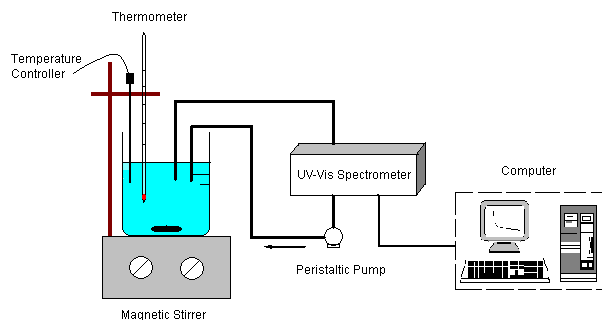

Fig. 4: Standard curve.

Fig. 2: Online spectrophotometric system.

RESULTS AND DISCUSSION

Single Factor Experiment

The effects of initial $FeSO_4$ dosage, initial H_2O_2 dosage, pH value, and initial dye concentration on chroma removal have been discussed. When the reaction time reaches 300 s, the decolourization rate of the dye was calculated. The colour removal rate (R) is defined as given in Eqs. 1. C_0 and C represent the initial and the instant concentrations of the dye with reaction time, respectively.

$$R = \frac{C_0 - C}{C_0} \times 100\% \qquad ...(1)$$

The effect of $FeSO_4$ dosage: The effect of different dosages of Fe^{2+} on the dye decolourization rate is shown in Fig. 5. Under the dye concentration of 20 mg/L, H_2O_2 dosage of 0.6 mmol/L and pH of 3 conditions, Fe^{2+} concentration ranged from 0.04 to 0.4 mmol/L (temperature kept at 25°C). It can be observed from Fig. 5 that different concentrations of Fe^{2+} have a great effect on colour removal. When the Fe^{2+} concentration is 0.04-0.1 mmol/L, the colour removal rate becomes higher and higher as Fe^{2+} concentration increases. The colour removal rate was 93.46% when Fe^{2+} concentration was 0.1 mmol/L. In addition, the colour removal rate of ALY 2G increased sharply in the first 30 s stage with the increase of Fe^{2+} concentration. After 30 seconds, the colour removal rate of ALY 2G dye did not increase, but the decolourization rate decreased slightly when the concentration ranges of dye changed from 0.2 to 0.4 mmol/L. This experimental result makes us known that excessive Fe^{2+} concentration is not beneficial to decolourization of ALY 2G among Fenton oxidation process. This reason is that because the excess ferrous ion competes with the dye molecules for the hydroxyl radical ·OH (Fe^{2+} + ·OH → Fe^{3+} + OH^-) (Xu et al. 2015b). Therefore, choosing an appropriate amount of Fe^{2+} can improve the degradation effect of the ALY 2G dye. We have chosen the initial Fe^{2+} concentration of 0.1 mmol/L

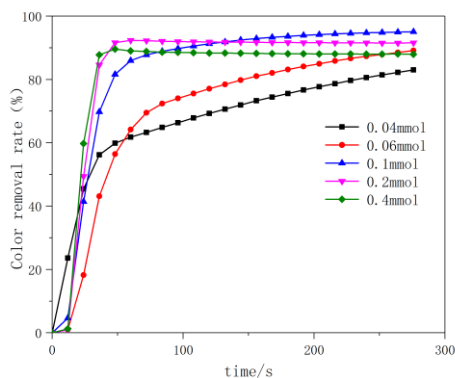as an optimum dosage for efficient decolourization to ALY 2G aqueous solutions.

The effect of initial H_2O_2 dosage: H_2O_2 is one of the very important factors affecting the degradation efficiency of dyes. The hydroxyl group can decompose the molecular structure of azo dyes, and then bleach ALY 2G dye wastewater. The hydroxyl group derives from H_2O_2. Fig. 6 displays the effect of the decolourization rate R of ALY 2G on various H_2O_2 concentrations. We can see from Fig. 6 that experimental monitoring in 300s, the decolourization trends of ALY 2G under 0.6, 3 and 6 mmol/L concentrations are very similar. The decolourization rate was 84.53% (lowest value) when H_2O_2 concentration was 0.18 mmol/L. When the H_2O_2 concentration was increased to 0.6 mmol/L, the dye decolourization rate reached 93.38%. However, when the H_2O_2 concentration was 12 mmol/L, the decolourization rate was relatively low (90.52%). The reason is that excess H_2O_2 will consume ·OH and compete with ALY 2G dye for hydroxyl radical ·OH (Eqs. 2-3). This process results in the production of the hydroperoxyl radical (·OOH as a scavenger of hydroxyl radical) and then decreases the colour removal rate of dye (Sehested et al. 2003, Xu et al. 2016). In brief, we choose 0.6 mmol/L as an optimum H_2O_2 concentration of the decolourization of ALY 2G in the Fenton oxidation process.

$$H_2O_2 + \cdot OH \rightarrow \cdot OOH + H_2O \qquad ...(2)$$
$$\cdot OH + \cdot OOH \rightarrow H_2O + O_2 \qquad ...(3)$$
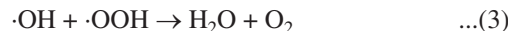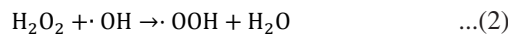
The effect of solution pH: The pH of the solution plays an important role in dye degradation for the Fenton process. The influence of pH value on the decomposition of ALY 2G is illustrated in Fig. 7. The change trends of decolourization rate with various pH value are consistent. The decolourization rate increases from 57.12% to 94.66% as the pH value increases from 1.5 to 3. However, when the pH value further increases to 4, the decolourization rate decreases to be 89.39%. At the lower pH value(<3) the ·OH is consumed by the excessive hydrogen ion (·OH + H^+ + e^- → H_2O), and
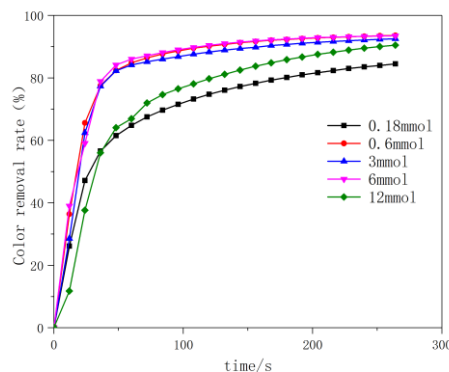
Fig. 5: Influence of initial Fe^{2+} concentration on dye removal.

Fig. 6: Influence of initial H_2O_2 concentration on dye removal.
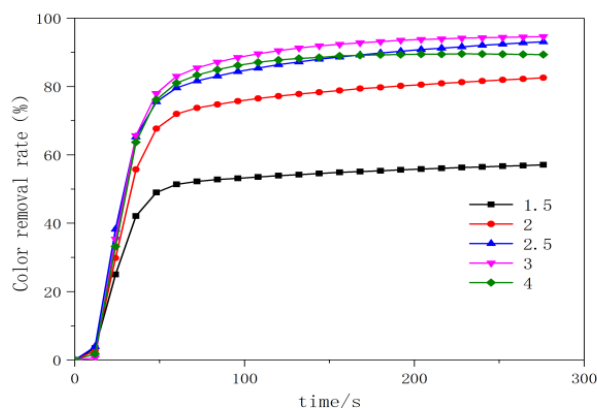
Fig. 7: Influence of initial pH on dye removal.

thus the decolourization rate is relatively small. When the solution (pH > 3), with the formation of the iron hydroxide complex, the hydrogen peroxide is decomposed and the ferrous ion catalyst is invalidated, which ultimately leads to a reduction in the oxidation ability of Fenton (Gao et al. 2014). Therefore, the pH value of 3 is considered to be the optimum value for the decolourization of azo dye ALY 2G in Fenton oxidation.

The effect of initial ALY 2G concentration: Fig. 8 shows the trend of the colour removal rate with various dye concentrations (conditions: $[Fe^{2+}]$ = 0.1 mmol/L, $[H_2O_2]$ = 0.6 mmol/L, and pH = 3). Although the initial concentrations of the dye ALY 2G were different (from 10 to 40 mg/L), the chroma removal rate of dye can all reach more than 90% and the difference of all removal rates is very small after 300s. Moreover, it can be seen that the reaction rate gradually decreases as increasing dye concentration between 50s and 150s. The reason for this is that as the initial concentration of the Acid Light Yellow 2G dye solution increases, the number of dye molecules in the solution increases, whereas the amount of ·OH in the solution does not increase, which leads to a decrease in the reaction rate.
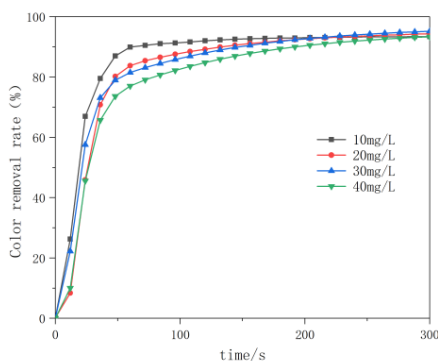

Fig. 8: Influence of initial dye concentration on dye removal.

Reaction Kinetic Fitting Analysis

Kinetic process analysis is helpful to understand the Fenton oxidation process. Acid Light Yellow 2G was decolourized successfully in the experimental process, and the first stage of decolourization was analysed by first-order kinetics (Gao et al. 2019b). The first-order kinetics calculation formula (Eqs. 4-5) is as follow:

$$\frac{dC}{dt} = K_{ap}t \qquad ...(4)$$

$$\ln\frac{C_0}{C_t} = K_{ap}t \qquad ...(5)$$

Where, t is the reaction time; C is the instant dye concentration; C_0 represents the initial dye concentration.

Figs. 9-12 show the changes of $\ln(C_0/C_t)$ with time under different initial Fe^{2+} concentrations, different H_2O_2 concentrations, different pH, and different dye concentrations, respectively. The linear fitting results of the relationship curve between $\ln(C_0/C_t)$ and time (t) are given in Table 1. The kinetic parameters are also listed in Table 1. The values of the kinetic parameters (the correlation coefficients R^2) are all above 0.94. It can be seen that the oxidation
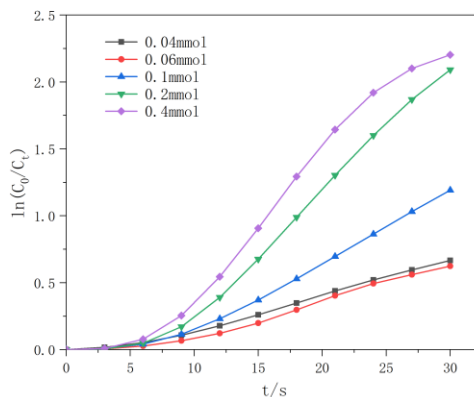

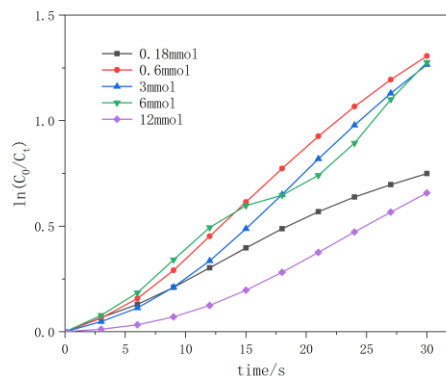Fig. 9: First-order kinetics of reactions in different Fe^{2+} concentrations.

Fig. 10: First-order kinetics of reactions in different H_2O_2 concentrations.
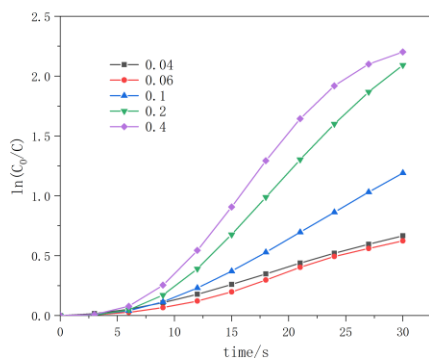
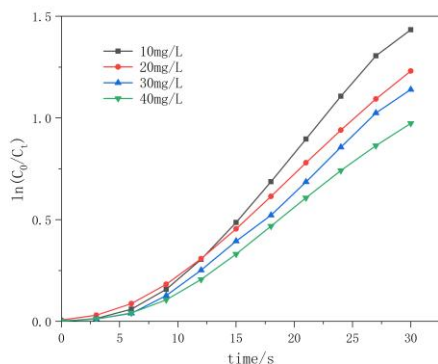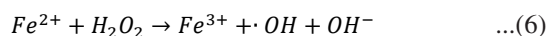Fig. 11: First-order kinetics of reactions in different pH.

Fig. 12: First-order kinetics of reactions in different dye concentrations.

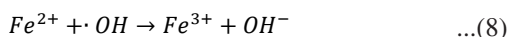process of Acid Light Yellow 2G by Fenton method accords with first-order kinetics.

First-order kinetics fitting is performed for the fast reaction stage. The fast stage of the Fenton oxidation process abides by first-order kinetics. Under the optimal reaction condition in Fenton oxidation, the correlation coefficient is 0.98 and the reaction rate K_{ap} is 0.04824 s^{-1}.
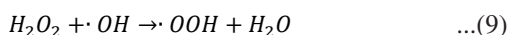
Kinetics Study

The Fenton oxidation method uses a catalyst Fe^{2+} and H_2O_2 to undergo a redox reaction to form a highly active ·OH which can decompose the molecular structure of organic dyes. The reaction mechanism can be expressed by (Eqs. 6-14) (D represents dye molecules) (Gao et al. 2014, Gao et al. 2019b, Kuši et al. 2006, Sibel et al. 2012, Sehested et al. 2003).
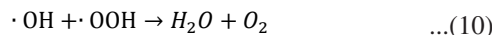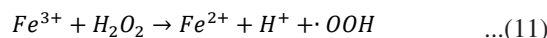
$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^- \qquad ...(6)$$
$$k_1 = 76 \ M^{-1}s^{-1}$$

$$D + \cdot OH \rightarrow D_{oxid} \qquad ...(7)$$

$$Fe^{2+} + \cdot OH \rightarrow Fe^{3+} + OH^- \qquad ...(8)$$
$$k_3 = 3.2 \times 10^8$$

$$H_2O_2 + \cdot OH \rightarrow \cdot OOH + H_2O \qquad ...(9)$$

$$k_4 = 4.5 \times 10^7$$

$$\cdot OH + \cdot OOH \rightarrow H_2O + O_2 \qquad ...(10)$$
$$k_5 = 6.6 \times 10^{11}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + \cdot OOH \qquad ...(11)$$
$$k_6 = 0.02 M^{-1}s^{-1}$$

The reaction rate of dye can be defined as:

$$-\frac{d[D]}{dt} = k_2[\cdot OH][D] \qquad ...(12)$$

According to the steady-state assumption, [·OH] can be obtained as follow:

$$\frac{d[\cdot OH]}{dt} = k_1[Fe^{2+}][H_2O_2] - k_2[\cdot OH][D] - k_3[Fe^{2+}][\cdot OH]$$
$$- k_4[H_2O_2][\cdot OH] - k_5[\cdot OH][\cdot OOH] = 0 \qquad ...(13)$$

$$-\frac{d[\cdot OOH]}{dt} = k_4[H_2O_2][\cdot OH] - k_5[\cdot OOH][\cdot OH] = 0 \ ...(14)$$

According to Eq. (14), we obtain:

$$k_5[\cdot OH][\cdot OOH] = k_4[H_2O_2][\cdot OH] \qquad ...(15)$$

According to Eqs. (13) and (15), we obtain:

$$\frac{d[\cdot OH]}{dt} = k_1[Fe^{2+}][H_2O_2] - k_2[\cdot OH][D] - k_3[Fe^{2+}][\cdot OH]$$
$$- 2k_4[H_2O_2][\cdot OH] = 0 \qquad ...(16)$$

$$[\cdot OH] = \frac{k_1[Fe^{2+}][H_2O_2]}{k_2[D] + k_3[Fe^{2+}] + 2k_4[H_2O_2]} \qquad ...(17)$$

Combined Eqs. (12) with (17), we obtained:

$$-\frac{d[D]}{dt} = \frac{k_1k_2[Fe^{2+}][H_2O_2][D]}{k_2[D] + k_3[Fe^{2+}] + 2k_4[H_2O_2]} \qquad ...(18)$$

Thus, Eq. (18) deduces to

$$\frac{[H_2O_2][D]}{-\frac{d[D]}{dt}} = \frac{[D]}{k_1[Fe^{2+}]} + \frac{k_3}{k_1k_2} + \frac{2k_4[H_2O_2]}{k_2k_1[Fe^{2+}]} \qquad ...(19)$$

By fitting the first-order kinetics to the oxidation reaction process in the last stage, the results show that the correlation coefficients are all above 0.95. It can be seen that the fast stage meets the first-order kinetics, so that:

$$-\frac{d[D]}{dt} = Kap[D] \qquad ...(20)$$

Combined Eqs. (19) with (20), we obtained:

$$\frac{[H_2O_2]}{Kap} = k[D]_0 + B \qquad ...(21)$$

$$B = \frac{k_3}{k_2k_1} + \frac{2k_4[H_2O_2]_0}{k_2k_1[Fe^{2+}]_0} \qquad ...(22)$$

The experimental results are shown in Fig. 13. $[H_2O_2]/K_{ap}$ has a good linear relationship with the dye concentration (R^2

Table 1: Degradation kinetics data.

FeSO$_4$ (mmol/L)	H$_2$O$_2$ (mmol/L)	pH	Dye concentration（mg/L）	First-order kinetics	
				K$_{ap}$	R^2
0.04	3	3	20	0.0239	0.98182
0.06	3	3	20	0.02298	0.95885
0.1	3	3	20	0.04236	0.95748
0.2	3	3	20	0.07708	0.95702
0.4	3	3	20	0.08617	0.96601
0.1	0.18	3	20	0.02634	0.99524
0.1	0.6	3	20	0.04658	0.99384
0.1	3	3	20	0.0448	0.98128
0.1	6	3	20	0.04107	0.98546
0.1	12	3	20	0.023	0.95326
0.1	0.6	1.5	20	0.02147	0.99136
0.1	0.6	2	20	0.03481	0.99652
0.1	0.6	2.5	20	0.0447	0.99558
0.1	0.6	3	20	0.04824	0.98836
0.1	0.6	4	20	0.04468	0.99148
0.1	0.6	3	10	0.05251	0.96378
0.1	0.6	3	20	0.03869	0.94459
0.1	0.6	3	30	0.04116	0.96418
0.1	0.6	3	40	0.03526	0.96477

= 0.97133). According to intercept B, the intrinsic reaction rate constant of the dye concentration and ·OH in the aqueous solution is obtained ($k_2 = 0.55 \times 10^9 M^{-1}S^{-1}$).

CONCLUSION

In this study, the degradation of the azo dye Acid Light Yellow 2G by Fenton method and its influence factors (initial dye concentration, initial solution Fe^{2+} concentration, initial H$_2$O$_2$ concentration, and initial pH value) were studied. The following conclusions can be made.
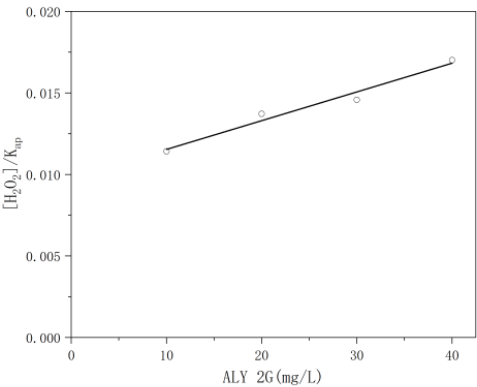

Fig. 13: Relationship between [H$_2$O$_2$]/K$_{ap}$ and [D]$_0$.

1. The online spectrophotometric method was used to monitor the absorbance of dye Acid Light Yellow 2G with Fenton oxidation. This technique is accurate, feasible and fast. The Fenton oxidation process can be divided into two stages: a rapid degradation stage (t < 30s) and a slow degradation phase (t >30s).

2. The best experimental conditions for degradation of dyes are that FeSO$_4$ is 0.1 mmol/L, H$_2$O$_2$ is 0.6 mmol/L, initial pH is 3, and when the dye concentration is 20 mg/L, the colour removal rate is 94.66%. Fenton oxidation process conforms to first-order reaction kinetics in the first stage. According to the formula K$_{ap}$ = ln (C$_0$/C$_t$), the first-order rate constant is the linear fitting slope. The reaction rate constant K$_{ap}$ is 0.04824 s^{-1} under the best experimental conditions.

3. During the Fenton oxidation process, the intrinsic reaction rate constant of the ALY 2G dye and ·OH in aqueous solution was ($k_2 = 0.55 \times 10^9 M^{-1}S^{-1}$).

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