



Kinetics Study of Fenton Degradation of Acid Yellow G by Online Spectrometry Technology

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ABSTRACT

The kinetics of Fenton degradation of azo dye Acid Yellow G by online spectrometry technology was studied in this research. The main influential parameters of Fenton process such as FeSO_4 dosage, H_2O_2 dosage, reaction temperature and pH were investigated and the optimum conditions were 20mg/L FeSO_4 , 50mg/L H_2O_2 , pH=3 and 38°C. Degradation kinetics analyses of acid yellow G were carried out for superior interpretation of Fenton process and the result indicated that the Behnjady-Modirshahla-Ghanbery (B-M-G) model is more applicable than the first or second order kinetics.

INTRODUCTION

Fenton process, including homogeneous or heterogeneous ones, is a kind of promising and efficient advanced oxidation technology which has aroused wide attention in the environmental contamination control field especially the aqueous issues over the latest decades (Li et al. 2012, Liou et al. 2003). As to the wastewater treatment, in common impression, dyeing or printing-related wastes are characterized as refractory, massive (one of the top 5 proportion of annual industrial total effluent amount) degradation task causing plenty of manual and economic expenditures (Guo et al. 2008), while the disposal efficiency is not as desirable as expected through the current wastewater treatment method (Modirshahla et al. 2007). Typically, the microbial treatment is capable of degrading high concentration contamination, though there is a requirement of steady input effluent amount and a proper pH value, moreover enough reaction capacity and period are necessary to ensure that all the treatment procedures can be carried out completely. The physical treatment mainly plays a prior or synergetic role in reality and in some special cases, ultrafiltration or reverse osmosis (Petricin et al. 2015) is applied for excellent removal or purification of yielding water with high energy cost.

Fenton process is a kind of sanitary, absolute and easily available method compared to other chemical treatments. During the reaction, hydroxyl radicals, which equip high oxidation potential (2.8eV) (Emmanuel et al. 2016) can be

generated to degrade the soluble contaminates to small inorganic molecules. Most refractory contaminates such as dyes (Almeida et al. 2015), explosives (Liou et al. 2003, Liou & Lu 2007), medicament (Alalm 2015) and other natural or artificial substances can be oxidized by this non-selective destructive power and meanwhile there is no appearance of toxic or troublesome second contamination.

Instead of off-line manipulation, online spectrometry shows advantages in convenient recording, integrated information and minor system error, therefore it was selected as the monitoring method providing more instant degradation information (Xu et al. 2008, Tunç et al. 2012).

MATERIALS AND METHODS

Device: Online spectrometry device (Xu et al. 2008, Tunç et al. 2012) is presented briefly in Fig. 1. The Fenton process takes place in the special glass container which has an interlayer for water bath heating by the super thermostatic water-circulating bath (501 Shanghai Instrument Manufacture) when there was a demand of temperature-control. Electronic stirrer (JJ-1 Tianjin Chemical Equipment Limited Company) was applied instead of magnetic one to guarantee the homogeneity of reaction solution and mostly the reaction part was fixed by an experimental iron stand. The simulated dyeing contamination was dissolved in deionized water and the emulsion tube was selected to conjoin each of the different parts. The peristaltic pump (HL-1D Shanghai In-

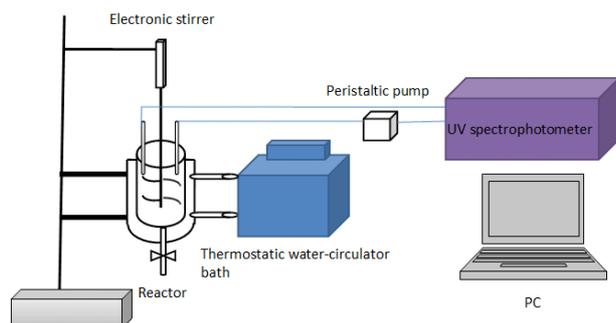


Fig. 1: Online spectrometric technology device.

strument Manufacture) was applied to drive the solution flowing in the whole circulatory system. Commuter (Lenovo laptop Y450) and UV-Vis spectrometer (SP-756PC Shanghai Spectrometric Instrument Limited Company) made up the online detecting section and successfully the instant absorbance of a simulated solution can be recorded and processed for degradation performance analysis.

Reagents: Acid yellow G (AY), which is a widely applied stuff in the present dyeing industry, was purchased from Tianjin Chemical Limited Corporation (China) with analytical purity. Chemically, AY has a nitrogen double bond and benzenes ring that contribute to its chemical stability. The chemical structure is given in Table 1 (Modirshahla et al. 2007). Ferric trichloride, hydrogen peroxide, hydrochloric acid and sodium hydroxide were also analytically pure and from the Tianjin Chemical Limited Corporation (China).

Procedure: First of all, the monitoring system was initialized in advance to ensure that all the degradation information can be recorded. The 200mL simulated dyeing wastewater (the pH of water sample has been adjusted properly already), ferrous ion and hydrogen peroxide were added into the reaction bath, strictly in sequence. Because the hydrogen peroxide can be decomposed by itself for irradiation or thermic reason and the generated radicals would react with target contaminate resulting system error. The each AY concentration of a single second in the simulated printing wastewater can be recorded in the selected experimental period 1400s and then be processed through the standard for-

Table 1: Chemical structure and absorption maxima of AY.

Name	Chemical Structure	λ_{\max} (nm)
Acid Yellow G		392

mula which is characterized as

$$A = 0.0333C \quad R^2 = 0.999$$

The removal of AY was defined as:

$$R = \frac{C_0 - C_i}{C_0} \times 100\% \quad \dots(1)$$

The C_0 , C_i were the concentration of AY at time 0 and i . The removal was effected by different ferrous ion, hydrogen peroxide dosages, various experimental temperature and solution pH values.

RESULTS AND DISCUSSION

The effect of pH: In terms of homogeneous Fenton process, an acid environment is a precondition because of the iron precipitation issue. And actually, the mentioned problem would show more obvious gradually, when the solution pH surpassed 5 due to the hydrolyzation of iron ions (eq. 2) (Xu et al. 2008). Meanwhile, more hydrogen peroxide can be decomposed at higher pH value environment. However, if the acidity of solution is too low, which is also an obstacle for excellent removal, because the hydrogen ion consuming hydroxyl radicals as a scavenger role (eq. 3). Therefore, a series pH values of 2, 3, 4, 5 and non-adjusted sample (the pH was theoretically assumed as 7) were selected to investigate a proper acidity of the AY contaminated wastewater in this research and the final removal efficiency is shown in Fig. 2.



What can be seen in the Fig. 2 is that the various pH values from 2 to 7 affected the removal efficiency, obviously and generally, the removal showed firstly ascending and then decreasing trend. As the former scavenged explanation of hydrogen ions, when the solution pH was 2, some radicals were consumed resulting to the deficiency in the removal and the final degradation percentage was about 40%. While compared to the strong acid environment, the non-adjusted water sample was the most deficient with only 20% removal more or less. In conclusion, pH 3 was the most appropriate in this experiment with the removal more than 90%.

The effect of temperature: The temperature is a non-negligible factor for the chemical reaction, especially the homogeneous aqueous reaction such as the Fenton process. Higher temperature could accelerate the velocity of molecular movement, in other words, the possibility of radicals and contamination collision was increased. Reflected to the apparent behaviour, the reaction rate constant or the state of final degradation can be improved which can be seen from the Fig. 3.

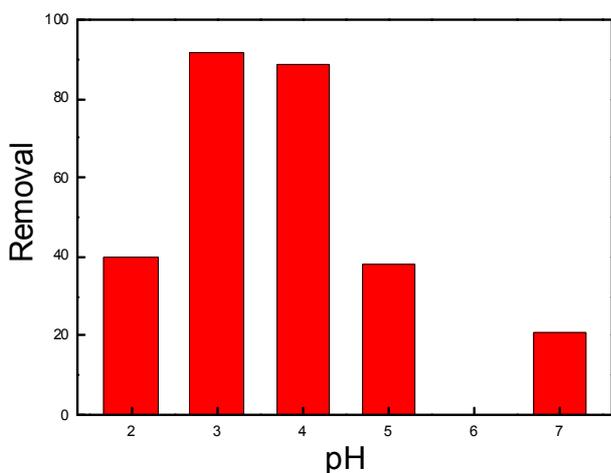


Fig. 2: The effect of different pH values on AY removal. (Experimental conditions: Initial AY concentration: 20mg/L, FeSO_4 :20mg/L, H_2O_2 :50mg/L).

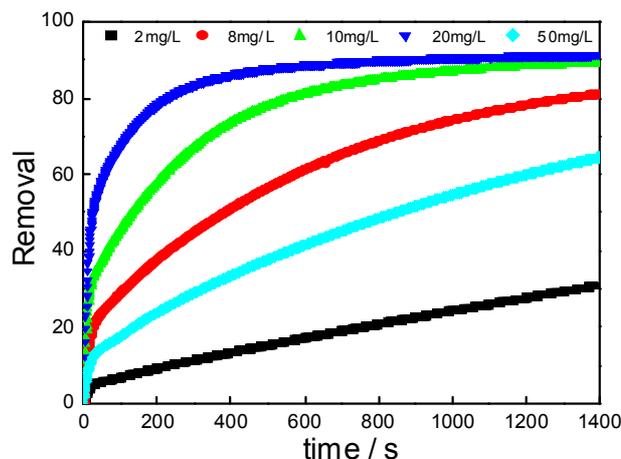


Fig. 4: The effect of different FeSO_4 concentrations on AY removal. (Experimental conditions: Initial AY concentration: 20mg/L, H_2O_2 :40mg/L, pH=4).

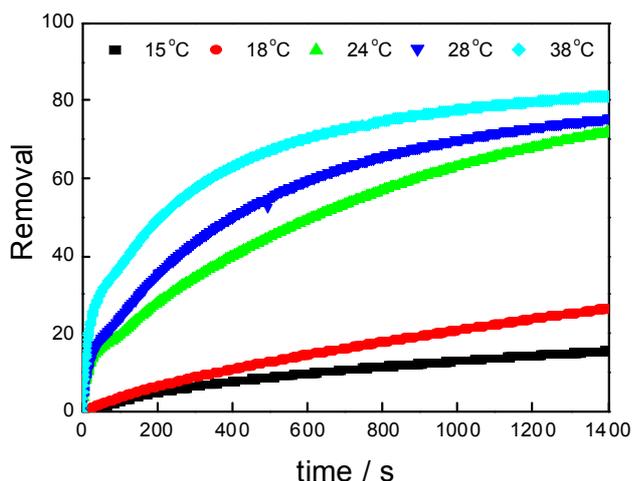


Fig. 3: The effect of different experimental temperatures on AY removal. (Experimental conditions: Initial AY concentration: 20mg/L, FeSO_4 :8mg/L, H_2O_2 :10mg/L, pH=4).

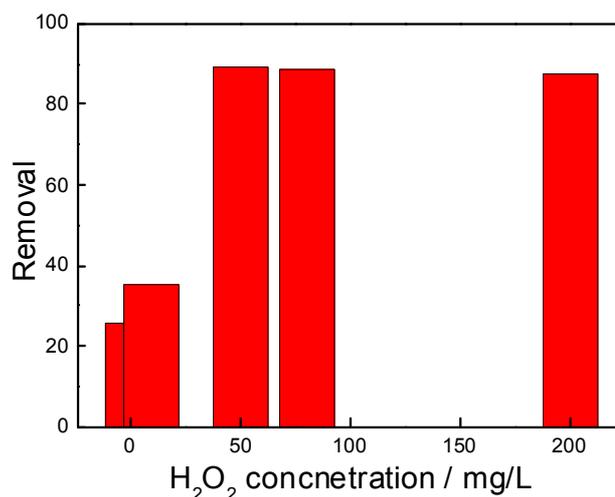


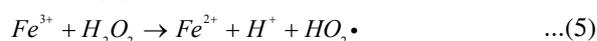
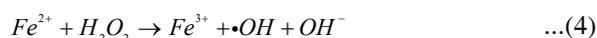
Fig. 5: The effect of different H_2O_2 concentrations on AY removal. (Experimental conditions: Initial AY concentration: 20mg/L, FeSO_4 :10mg/L, pH=4).

In the temperature experiment, the added ferrous ion and hydrogen peroxide amount were decreased deliberately to emphasize the role of temperature. It can be concluded that the decolorization of AY became more efficient along with the increase of selected temperature from 15°C to 38°C, correspondingly, the final removals were 10%, 25%, 65%, 75% and 85% respectively. About 75% improvement on final removal could be observed if the experimental temperature was raised 23°C. However, the side effect of higher temperature also existed that more hydrogen peroxide would be decomposed, radicals getting unstable and meanwhile the hydrolysis of iron ion can be enhanced as well, which led to

deficiency. Therefore, extra thermal application was good for the reaction in a proper temperature range, and as to Fenton process the indoor temperature is adequate for the Gibbs free energy of Fenton reaction is negative, which means the reaction can take place spontaneously in nature (Karatas et al. 2012).

The effect of Fenton reagent: Ferrous ion and hydrogen peroxide are the two cores of Fenton reagents and the amount of them was investigated completely in this research. Through the Fenton process mechanism, normally speaking, the iron ion takes redox in the Fenton basic reactions. In detail, ferrous ion catalysts added hydrogen peroxide to

generate hydroxyl radicals for contamination degradation (eq. 4). At the same time, the ferrous ion lost electron transforming to ferric ion. On the condition that the over dosed hydrogen peroxide could also react with the newborn ferric ion and ferrous ion to generate another radical named peroxy which equips the oxidized ability as well, however it is not so powerful as the hydroxyl radical (eq. 5). If the ferrous ion is excessive, the extra reactive ions would deoxidize hydroxyl radicals causing low efficiency (eq. 6). Therefore, various amounts of FeSO_4 2 mg/L, 8 mg/L, 10 mg/L, 20 mg/L, 50mg/L were applied for investigation of appropriate ferrous sulphate dosage.



The effect of ferrous sulphate concentration was presented in Fig. 4. First of all, the removal efficiency showed best at 20mg/L dosage, in detail, 80% removal can be reached at 200s and the final removal was over 90%. More added ferrous ion taking part in the Fenton process resulted superior degradation behaviour, because plenty of hydroxyl radicals generated and then oxidized with contamination. When the dosage of ferrous sulphate increased to 50mg/L, an obvious drop of about 30% in removal appeared because over-dosed iron ions scavenged the radical. Therefore, the ferrous ion dosage should be controlled under the 20mg/L in this experiment.

The other necessary component of Fenton reagent is hydrogen peroxide. Besides involving the eqs. 4-5, hydrogen peroxide could also scavenge the hydroxyl radical, generating peroxy radical to decrease the oxidization efficiency even more obvious at overdosed condition (eq. 7). Next, some hydroxyl radicals can be consumed by the hydroperoxy radical to generate water and oxygen (eq. 8).



In this study, various hydrogen peroxide dosages 1mg/L, 10mg/L, 50mg/L, 80mg/L, 200mg/L were selected for the investigation. What can be seen from Fig. 5 is that the degradation was poor at low hydrogen peroxide dosage like 1mg/L or 10mg/L with the corresponding removal as 25% and 35%. Plenty of radical resources for the Fenton reaction were provided by large amount of hydrogen peroxide although the side effect taking place at the same time. Even the hydrogen peroxide was superfluous, the radicals concentration still could keep high, since the Fenton process taking place primarily, therefore, the removal just appeared slight dropdown. In general, the best amount of hydrogen peroxide can be assumed as 50mg/L at which the removal kept high and saved the raw reagent.

Kinetics analysis: The kinetics analysis has been investigated by many Fenton-field researchers. Alalm et al. (2015) suggested that the Fenton degradation of pharmaceuticals fit the pseudo-first order kinetics and Li et al. (2012) revealed

Table 2: Kinetics fitting at different conditions (FeSO_4 mg/L, H_2O_2 mg/L, pH and $T^\circ\text{C}$). k_1 (s^{-1}), k_2 ($\text{L mg}^{-1}\text{s}^{-1}$) are the first and second order reaction constant respectively.

FeSO_4	H_2O_2	pH	T	First order		Second order		B-M-G model		
				k_1	R^2	k_2	R^2	m	b	R^2
2	40	4	24	0.00023	0.999	2.3E-4	0.999	191.06	5.78	0.905
8	40	4	24	0.00103	0.994	0.00103	0.994	74.97	1.56	0.982
10	40	4	24	0.00118	0.947	0.00118	0.947	46.21	1.20	0.990
20	40	4	24	0.00091	0.848	9.13E-4	0.848	43.39	1.03	0.989
50	40	4	24	0.00064	0.999	6.44E-4	0.999	149.49	2.14	0.976
10	1	4	24	1.95E-4	0.975	1.1E-5	0.982	1062.40	4.72	0.988
10	10	4	24	2.82E-4	0.993	1.73E-5	0.998	1156.49	2.34	0.963
10	50	4	24	0.00101	0.906	2.45E-4	0.970	30.56	1.19	0.986
10	80	4	24	0.00112	0.931	2.55E-4	0.984	31.07	1.25	0.975
10	200	4	24	0.00108	0.940	2.27E-4	0.989	28.90	1.28	0.962
20	50	2	24	3.89E-5	0.436	3.29E-6	0.500	62.98	1.87	0.956
20	50	3	24	6.90E-4	0.805	2.47E-4	0.909	24.86	1.05	0.977
20	50	4	24	5.79E-4	0.791	1.66E-4	0.891	23.44	1.10	0.987
20	50	5	24	3.50E-5	0.408	2.5E-6	0.427	27.24	2.53	0.989
20	50	7	24	5.64E-5	0.890	3.26E-6	0.903	86.31	5.21	0.977
8	10	4	15	0.00011	0.982	5.59E-6	0.986	2615.93	6.30	0.995
8	10	4	18	0.00021	0.997	1.17E-5	0.999	2772.08	1.99	0.955
8	10	4	24	0.00080	0.997	8.54E-5	0.996	106.59	1.95	0.976
8	10	4	28	0.00084	0.977	1.01E-4	0.999	98.21	1.67	0.984
8	10	4	38	0.00069	0.940	1.18E-4	0.988	54.61	1.34	0.986

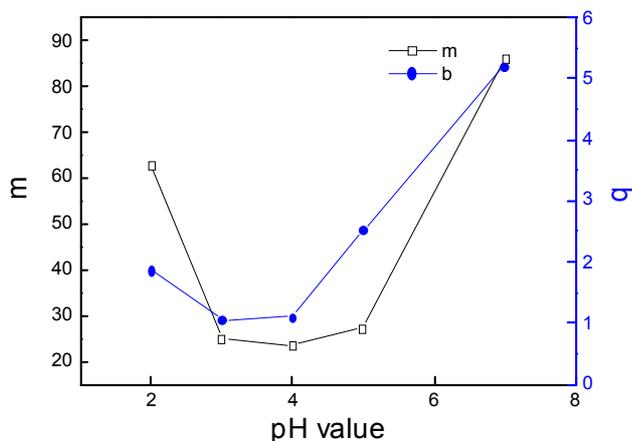


Fig. 6: The effect of various pH value on m and b constant.

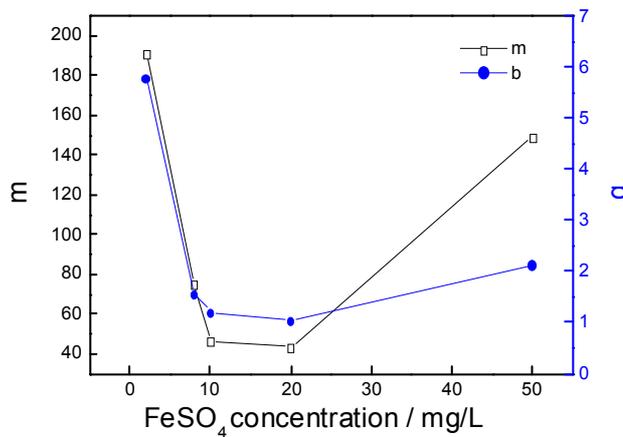


Fig. 8: The effect of various FeSO₄ dosages on m and b constant.

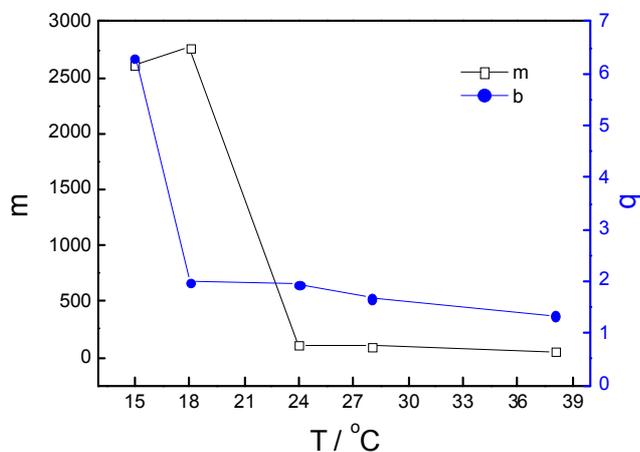


Fig. 7: The effect of various temperatures on m and b constant.

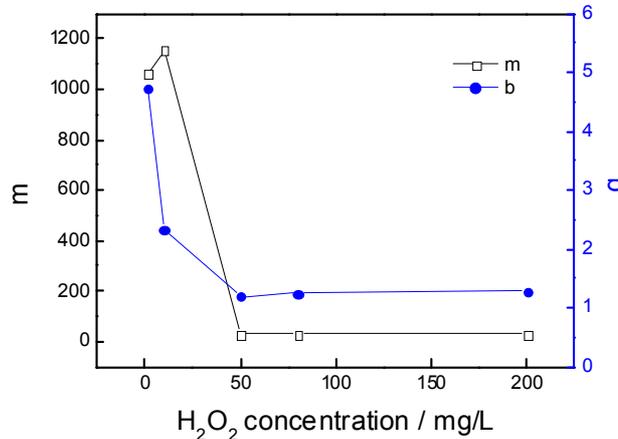


Fig. 9: The effect of various H₂O₂ dosages on m and b constant.

that the Fenton degradation of amoxicillin fit the first order kinetics. While, another researcher like Karatas et al. (2012) suggested that the Fenton degradation of Reactive Blue 114 fit the pseudo second order kinetics. Some researchers reported that a kind of hyperbola kinetics named B-M-G was used for describing Fenton degradation of dyes and the linear fitting result was perfect (Emmanuel et al. 2016, Tunç et al. 2012). In this study, the first order, second order kinetics and B-M-G model proposed by Behnajady et. al (2007) were applied for the kinetics analysis and the linear fitting results are presented in Table 2.

The first and second order kinetic formulas were followed as:

$$\ln \frac{C_i}{C_0} = k_1 t \quad \dots(9)$$

$$\frac{1}{C_i} - \frac{1}{C_0} = k_2 t \quad \dots(10)$$

The BMG model was characterized as:

$$\frac{C_i}{C_0} = 1 - \frac{t}{m + bt} \quad \dots(11)$$

$$\frac{m}{t} + b = \frac{C_0}{C_0 - C_i} \quad \dots(12)$$

The m, b are two constants in the model and C₀, C_i corresponds the AY concentration at initial and time i, k₁ and k₂ represent the reaction constant of first, second order kinetics.

The eq. 11 can be taken derivation:

$$\frac{d(C_i / C_0)}{dt} = \frac{-m}{(m + bt)^2} \quad \dots(13)$$

At the time zero, eq. 13 can be transformed to:

$$\frac{d(C_i / C_0)}{dt} = \frac{-1}{m} \quad \dots(14)$$

And if the time is infinite, the eq. 11 can simplified as:

$$\frac{C_i}{C_0} = 1 - \frac{1}{b} \quad \dots(15)$$

Then, the constant m and b possess the physical meaning that $1/m$ represents the degradation rate and b can be used for the justification of final degradation state. Since the condition that the value of correlation coefficient approaching to 1 represents the fitting is excellent. Generally based on the linear correlation data, most coefficients of the BMG model are higher than the other two kinetics and relatively approximated to 1. Therefore, the BMG model has an advantage in depicting the Fenton decolorization of AY at different experimental conditions as the best chemical model which can be seen from Figs. 6-9 intuitively.

In detail, at each optimum condition: 20mg/L FeSO_4 , 50mg/L H_2O_2 , pH of 3 and 38°C experimental temperature; the corresponding smallest m values are 43.39, 30.56, 24.86 and 54.61, respectively, in each group which imply that the degradation proceeded relative fastest under such conditions. Moreover, in the terms of the constant b , the corresponding values are 1.03, 1.19, 1.05 and 1.34 in each group, that means the target contamination has been removed most thoroughly, comparably.

CONCLUSION

The Fenton process of Acid Yellow G was investigated fully in this study. By the application of online spectrometric technology, momentary data can be recorded for more impressive interpretation of Fenton process. At 20mg/L FeSO_4 , 50mg/L H_2O_2 , pH=3 and 38°C condition, the degradation showed most efficient and the relative removal surpassing 90%. Lastly, two common first and second order kinetics as well as BMG model were used for Fenton kinetic analysis and the BMG model was proved to be more applicable in simulating the Acid Yellow G decolorization after linear fitting and data analysis.

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