

A kinetic model for the decolorization of C.I. Acid Yellow 23 by Fenton process

M.A. Behnajady*, N. Modirshahla, F. Ghanbary

Department of Applied Chemistry, Islamic Azad University, Tabriz Branch, P.O. Box 1655, Tabriz, Islamic Republic of Iran

Received 8 November 2006; received in revised form 3 February 2007; accepted 5 February 2007

Available online 12 February 2007

Abstract

The decolorization of azo dye C.I. Acid Yellow 23 (AY23) by Fenton process was investigated. The decolorization rate is strongly dependent on the initial concentrations of the Fe^{2+} and H_2O_2 . The optimum operational conditions were obtained at pH 3.

A kinetic model has been developed to predict the decolorization of AY23 at different operational conditions by Fenton process. The model allows to simulate the system behavior involving the influence of hydrogen peroxide, Fe(II) and dye concentrations.

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Keywords: Advanced oxidation processes (AOPs); Fenton; C.I. Acid Yellow 23; Kinetic model

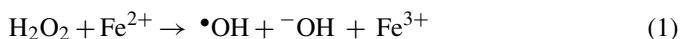
1. Introduction

Synthetic dyes are the major industrial pollutants and water contaminants [1–3]. Wastewater from textile, paper, and some other industries contain residual dyes, which are not readily biodegradable. Azo dyes, the largest class of synthetic dyes used in food industries, are characterized by the presence of one or more azo bonds ($-\text{N}=\text{N}-$) in association with one or more aromatic systems, which may also carry sulfonic acid groups. One of them is Tartrazine or C.I. Acid Yellow 23 an azo dye present in thousands of foods and drugs. Many studies indicate that these dyes are toxic or carcinogenic. If these colorants come into contact along with certain drugs in the human body they can induce allergic and asthmatic reactions in sensitive people. An additional difficulty is that, when present, these dyes are not normally removed by conventional wastewater treatment systems. Therefore, the employment of these dyes must be controlled and the effluents must be treated before being released into the aquatic and terrestrial environment [4].

There are several methods used to decolorize the textile wastewater, but they cannot be effectively applied for all dyes [5]. Activated carbon adsorption process for the removal of dyes is an accepted practice, but the cost of treatment is high. Ozone

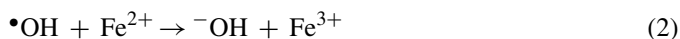
and hypochlorite oxidations are effective decolorization methods, but they are not desirable because of the high cost of the equipments, operating costs and the secondary pollution arising from the residual chlorine [6].

Recently, chemical treatment methods, based on the generation of hydroxyl radicals, known as advanced oxidation processes (AOPs) has been developed [7]. It is one of the potential alternatives to decolorize and to reduce recalcitrant wastewater loads from textile dyeing and finishing effluents. This process implies generation and subsequent reaction of hydroxyl radicals, which are the most powerful oxidizing species after fluorine [8]. Among these processes, the oxidation using Fenton's reagent has proven a promising and attractive treatment method for the effective decolorization and degradation of dyes [9].



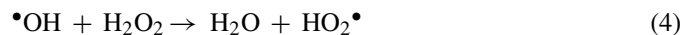
The Fenton system uses ferrous ions to react with hydrogen peroxide, producing hydroxyl radicals with powerful oxidizing abilities to degrade certain toxic contaminants [10].

Hydroxyl radicals may react with ferrous ions to form ferric ions or react with organics:

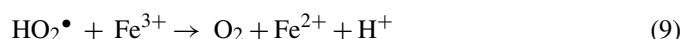
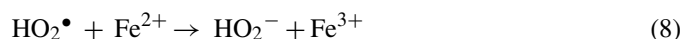


* Corresponding author. Tel.: +98 411 3320198; fax: +98 411 3313922.
E-mail address: behnajady@iaut.ac.ir (M.A. Behnajady).

Hydroxyl radicals can also react with hydrogen peroxide to produce other radicals, and may also combine with each other to produce hydrogen peroxide, which are shown below [10]:



Ferrous ions and radicals are produced during the reactions. The reactions are shown in Eqs. (6)–(9) [10]:



The reaction rate in Eq. (6) is much slower than that of Eq. (1). It can be derived that ferrous ions are consumed quickly, but reproduced slowly [10]. Consequently, the oxidation rate of organic compounds is fast when large amount of ferrous ions are present because large amount of hydroxyl radicals are produced. However, the Fenton reaction may slow down due to the slow ferrous ion production. Gallard and De Laat [11] suggested that the Fenton's oxidation process (FOP) should be a simple first-order reaction, while Guedes et al. [12] believes that it should be a second-order reaction. Because the information regarding the kinetic study of the removal of AY23 by Fenton's oxidation is still limited, the use of hydrogen peroxide with iron salt to degrade AY23 at various concentrations of Fe(II) and H₂O₂ was investigated in this study. A mathematical model was also derived to predict the reaction kinetics and process performance under various reaction conditions in water.

2. Experimental

2.1. Materials

AY23 was obtained from Acros (USA) and used without further purification. Fig. 1 shows the chemical structure of this dye. Hydrogen peroxide solution (30%, w/w), NaOH and H₂SO₄ were products of Merck (Germany). Ferrous sulfate heptahydrate (FeSO₄·7H₂O) was used as a source of Fe²⁺ and purchased from Fluka (Switzerland).

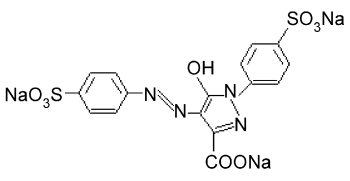
Name	Chemical Structure	λ_{max} (nm)
Acid Yellow 23		428

Fig. 1. Chemical structure and absorption maxima of AY23.

2.2. Analytical methods

The pH of the solution is measured by using METTLER TOLEDO (MP 220) digital pH meter. The glassware was covered with aluminum foil during the tests to minimize the exposure of samples to light, in order to prevent any unwanted side reactions. Sample solutions were withdrawn at certain time intervals for spectrophotometric analyses. Calibration plot based on Beer–Lambert's law was established by relating the absorbance to the concentration.

3. Results and discussion

3.1. Effect of pH

The pH value affects the oxidation of organic substances both directly and indirectly. The Fenton reaction is strongly pH dependent. The pH value influences the generation of hydroxyl radicals and thus the oxidation efficiency. Fig. 2 shows the effect of the initial pH value during the use of the Fenton process. A maximum degradation of 97.4% at 20 min was obtained in Fe²⁺/H₂O₂ process at pH 3. It can be seen from Fig. 2 that the removal efficiency increases from 6.3% to 97.4% in Fenton process after 20 min as a consequence of increasing pH of the solution from 1 to 3. On the other hand increasing pH value from 3 to 7 decreases the color removal from 97.4% to 6.1% for FOP. These results are in agreement with those reported in previous studies [13].

3.2. The effect of Fe(II) and H₂O₂ concentrations and ratios on AY23 decolorization

Iron in its ferrous and ferric forms acts as a photo-catalyst and requires a working pH below 4.0 [14]. To investigate the effect of catalyst, [Fe(II)] and [H₂O₂] were used in terms of [Fe(II)]:[H₂O₂] ratios (FH). The initial concentrations of Fe(II) used in this study were 8.37, 13.95, 19.53, 25.11 and 33.40 mg l⁻¹, and the FH ratios were set at 0.016, 0.028, 0.039, 0.05 and 0.067 and the concentration of H₂O₂ was kept constant at 500 mg l⁻¹. The initial concentrations of H₂O₂ used in this study were 50, 100, 200, 500 and 700 mg l⁻¹, and the FH ratios were set at 0.0199, 0.0279, 0.06975, 0.1395 and 0.279 and the

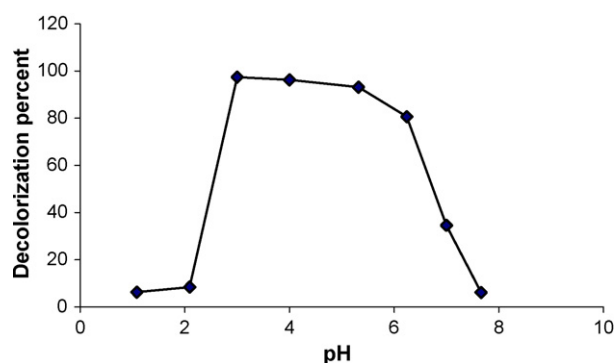


Fig. 2. Effect of pH on the decolorization of AY23 by Fenton process. [AY23]₀ = 40 mg l⁻¹, [H₂O₂]₀ = 500 mg l⁻¹, and [Fe²⁺]₀ = 19.53 mg l⁻¹.

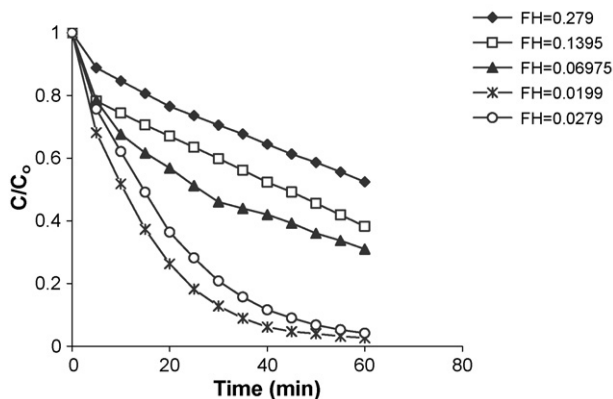


Fig. 3. The decolorization curves of the AY23 by FOP in various FH ratios. $[AY23]_0 = 40 \text{ mg l}^{-1}$, $[Fe^{2+}]_0 = 13.95 \text{ mg l}^{-1}$, $[H_2O_2]_0 = 50, 100, 200, 500$ and 700 mg l^{-1} .

concentration of Fe(II) was fixed at 13.95 mg l^{-1} . The results of a series of decay curves conducted under the above conditions were summarized and shown in Figs. 3 and 4. In general, the higher $[Fe(II)]$ or $[H_2O_2]$, the faster and more complete the decay of AY23. A rapid initial AY23 decay was observed in the first 5 min, followed by a much slower retardation stage, which was likely due to the depletion of oxidants in the solution. The fast reactive-stage was initiated by the hydroxyl radical ($\bullet OH$) resulting from the reactions between Fe^{2+} and H_2O_2 (Eq. (1)). In this stage, hydrogen peroxide was consumed vigorously due to the catalytic formation of $\bullet OH$. In addition the Fe^{3+} produced from the FOP might also react with H_2O_2 to form weaker radicals (such as $\bullet OOH$), which further reduced the amount of hydrogen peroxide in the solution [15]. As the $[H_2O_2]$ gradually is lowered to a trivial level, the retardation stage would be initiated, where the low amount of oxidant in the solution became the limiting factor. A number of researchers have previously suggested that the FOP should be a simple first-order reaction, while others believe that it should be a second-order reaction [15]. In this study a simpler and more accurate model to forecast FOP has been proposed.

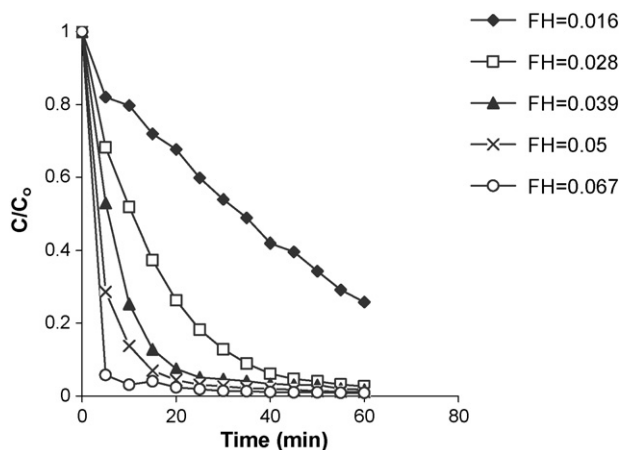


Fig. 4. The decolorization curves of the AY23 by FOP in various FH ratios. $[AY23]_0 = 40 \text{ mg l}^{-1}$, $[H_2O_2]_0 = 500 \text{ mg l}^{-1}$, $[Fe^{2+}]_0 = 8.37, 13.95, 19.53, 25.11$ and 33.40 mg l^{-1} .

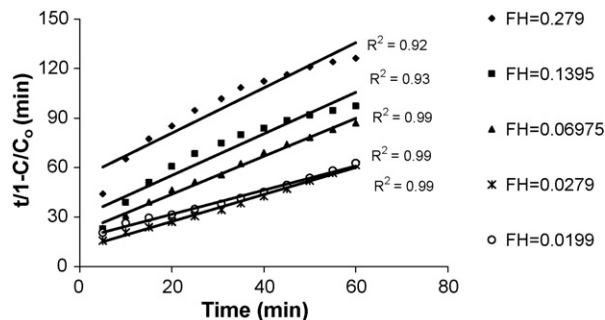


Fig. 5. The plot of $t/(1 - C/C_0)$ vs. t in FOP. $[AY23]_0 = 40 \text{ mg l}^{-1}$, $[Fe^{2+}]_0 = 13.95 \text{ mg l}^{-1}$, $[H_2O_2]_0 = 50, 100, 200, 500$ and 700 mg l^{-1} .

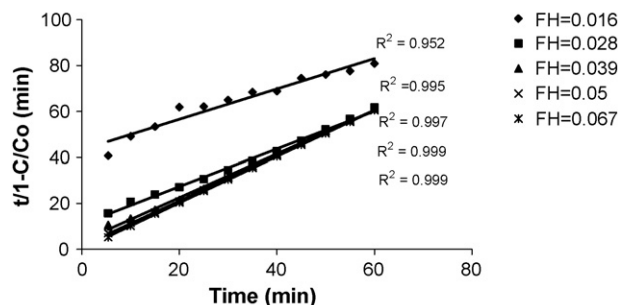


Fig. 6. The plot of $t/(1 - C/C_0)$ vs. t in FOP. $[AY23]_0 = 40 \text{ mg l}^{-1}$, $[H_2O_2]_0 = 500 \text{ mg l}^{-1}$, $[Fe^{2+}]_0 = 8.37, 13.95, 19.53, 25.11$ and 33.40 mg l^{-1} .

3.3. Kinetic model for AY23 decolorization with FOP

To fully utilize the results in real applications, a mathematical model was derived in this study to simulate the reaction kinetics, as shown in Eq. (10):

$$\frac{C}{C_0} = 1 - \frac{t}{m + bt} \quad (10)$$

where C is the AY23 concentration at time t (min), and C_0 is the initial concentration of AY23 at time $t=0$, and b and m are two characteristic constants relating to the reaction kinetics and oxidation capacities that will be discussed later. To solve the constants Eq. (10) can be linearized:

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

By plotting $t/(1 - C/C_0)$ versus t (Figs. 5 and 6), a straight line with an intercept of m and a slope of b was obtained and the results are listed in Tables 1 and 2. The corresponding regression

Table 1

The constants m and b for decolorization of AY23 (40 mg l^{-1}) in the presence of Fe^{2+} (13.95 mg l^{-1}) at different H_2O_2 concentrations (50, 100, 200, 300, 500 and 700 mg l^{-1})

FH	m	b
0.0199	17.255	0.7284
0.0279	11.078	0.8165
0.0697	20.984	1.1493
0.1395	30.293	1.255
0.279	53.842	1.361

Table 2

The constants m and b for decolorization of AY23 (40 mg l^{-1}) in the presence of H_2O_2 (500 mg l^{-1}) at different Fe^{2+} concentrations (8.37, 13.95, 19.53, 25.11 and 33.40)

FH	m	b
0.016	43.449	0.6596
0.028	11.081	0.8165
0.039	3.6918	0.9471
0.05	1.587	0.9811
0.067	0.3942	1.002

results with very high r^2 ranging from 0.92 to 1.00 were observed indicating that the AY23 decay kinetics was well described by the suggested model in Eq. (10). It is worthwhile to further analyze the two characteristic constants (m and b) and rationalize the model. For describing the reaction kinetics, the model was plotted in Fig. 7, where the corresponding physical meanings of m and b were therefore inspected by examining two extreme cases in Eq. (10). On the other hand, the terms m and b can be determined by taking the derivation of Eq. (10) to give:

$$\frac{dC/C_0}{dt} = \frac{-m}{(m + bt)^2} \quad (12)$$

when t is very short or approaching zero, the slope at the original can be resolved as:

$$\frac{dC/C_0}{dt} = -\frac{1}{m} \quad (13)$$

and its physical meaning is the initial AY23 removal rate in the process. Therefore the higher $1/m$ shows the faster initial decay rate of AY23. When t is long and approaching infinity, the reciprocal of constant b is the theoretical maximum AY23 removal fraction, which is equal to the maximum oxidation capacity of FOP at the end of the reaction:

$$\frac{1}{b} = 1 - \frac{C_{t \rightarrow \infty}}{C_0} \quad (14)$$

To quantify these two constants, it was found that m and b can be correlated to the FH ratios, and the results are shown in Figs. 8 and 9, where the correlations can be formulated in the following equations:

$$\log\left(\frac{1}{b}\right) = N_{\log(1/b)} \log \text{FH} + I_{\log(1/b)} \quad (15)$$

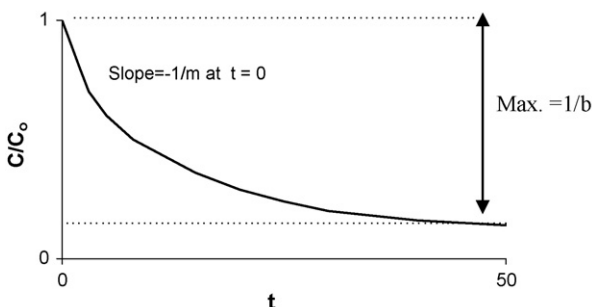


Fig. 7. The linear form of the model used for describing the reaction kinetics.

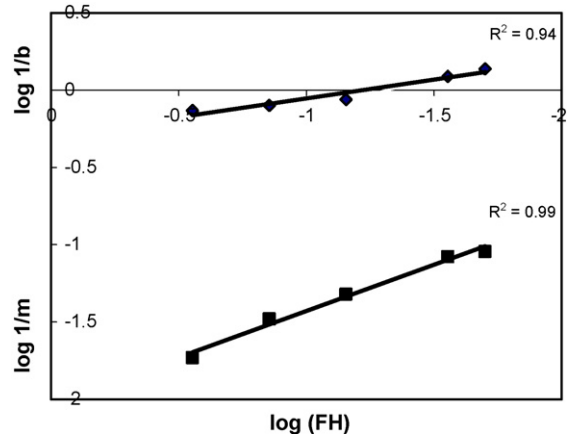


Fig. 8. Correlations of FH ratios with maximum oxidation capacity ($1/b$) and initial decay ($1/m$). $[\text{AY23}]_0 = 40 \text{ mg l}^{-1}$, $[\text{Fe}^{2+}]_0 = 13.95 \text{ mg l}^{-1}$, $[\text{H}_2\text{O}_2]_0 = 50, 100, 200, 500$ and 700 mg l^{-1} .

$$\log\left(\frac{1}{m}\right) = N_{\log(1/m)} \log \text{FH} + I_{\log(1/m)} \quad (16)$$

which

$$b = \frac{1}{10^{N_{\log(1/b)} \log \text{FH} + I_{\log(1/b)}}} \quad (17)$$

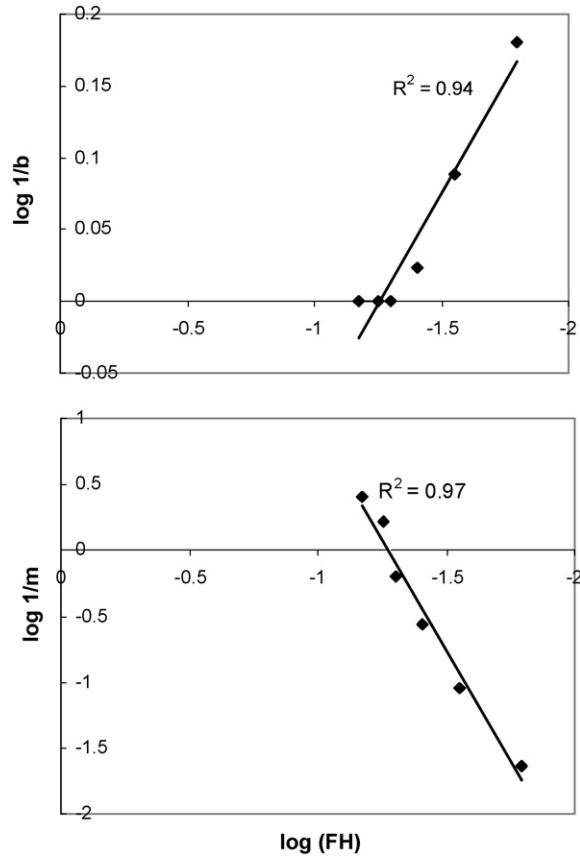


Fig. 9. Correlations of FH ratios with maximum oxidation capacity ($1/b$) and initial decay ($1/m$). $[\text{AY23}]_0 = 40 \text{ mg l}^{-1}$, $[\text{H}_2\text{O}_2]_0 = 500 \text{ mg l}^{-1}$, $[\text{Fe}^{2+}]_0 = 8.37, 13.95, 19.53, 25.11$ and 33.40 mg l^{-1} .

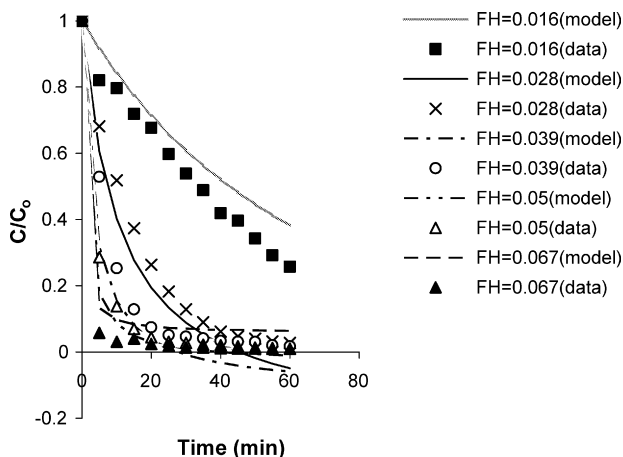


Fig. 10. Prediction of AY23 concentration by the proposed model in FOP. $[AY23]_0 = 40 \text{ mg l}^{-1}$, $[Fe^{2+}]_0 = 13.95 \text{ mg l}^{-1}$, $[H_2O_2]_0 = 50, 100, 200, 500$ and 700 mg l^{-1} .

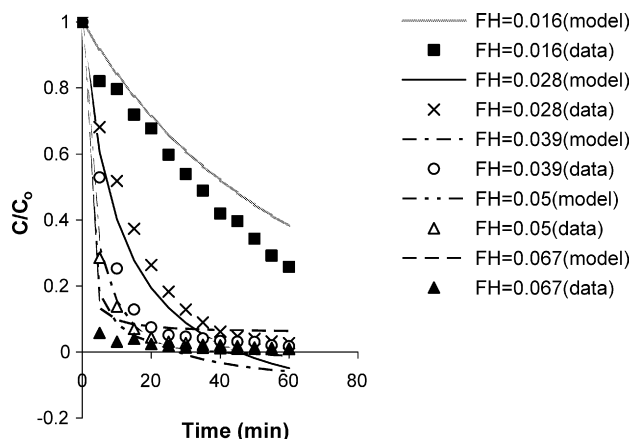


Fig. 11. Prediction of AY23 concentration by the proposed model in FOP. $[AY23]_0 = 40 \text{ mg l}^{-1}$, $[H_2O_2]_0 = 500 \text{ mg l}^{-1}$, $[Fe^{2+}]_0 = 8.37, 13.95, 19.53, 25.11$ and 33.40 mg l^{-1} .

$$m = \frac{1}{10^{N \log(1/m)} \log FH + I \log(1/m)} \quad (18)$$

where N is the slope and I is the intercept of each equation. It is very interesting to note that the $1/b$ and $1/m$ are inversely proportional to the FH ratios: the higher the FH values, the lower the $1/b$ and $1/m$.

By substituting Eqs. (17) and (18) into Eq. (10), we obtain:

$$\frac{C}{C_0} = 1 - \frac{t}{(1/10^{N \log(1/m)} \log FH + I \log(1/m)) + (1/10^{N \log(1/b)} \log FH + I \log(1/b))t} \quad (19)$$

For evaluation of Eq. (19) to predict of C/C_0 at different FH ratios, a comparison between experimental and calculated C/C_0 for decolorization of AY23 with FOP was shown in Figs. 10 and 11. From these plots, it can be seen that the results obtained from the model were in good agreement with the experimental data.

4. Conclusions

The results showed that FOP is a powerful method for decolorization of AY23. A mathematical model has been derived successfully to describe the reaction kinetics at various reaction conditions. The corresponding parameters involved in this model have been identified as the initial AY23 decay rate and the final oxidation capacity. The optimum conditions for the decolorization of AY23 in FOP were observed at pH 3. From the results, as high as 98% of AY23 can be decolorized by 13.95 mg l^{-1} ferrous ions and $500 \text{ mg l}^{-1} H_2O_2$. Therefore, the use of FOP to decolorize AY23 is practicable, but an accurate evaluation of doses is important to achieve a proper performance.

Acknowledgement

The authors would like to thank Islamic Azad university of Tabriz branch for financial supports.

References

- [1] D.H. Brown, H.R. Hitz, L. Schafer, The assessment of the possible inhibitory effect of dye stuffs on aerobic wastewater, *Chemosphere* 10 (1981) 245–261.
- [2] A.A. Vaidya, K.V. Datye, Environmental pollution during chemical processing of synthetic fibers, *Colourage* 14 (1982) 3–10.
- [3] N. Modirshahla, M.A. Behnajady, F. Ghanbary, Decolorization and mineralization of C.I. Acid Yellow 23 by Fenton and photo-Fenton processes, *Dyes Pigments* 73 (2007) 305–310.
- [4] E.P. Chagas, L.R. Durrant, Decolorization of azo dyes by *Phanerochate chrysosporium* and *Pleurotus sajorcaju*, *Enzyme Microbial Technol.* 29 (2001) 473–477.
- [5] M. Neamtu, A. Yediler, I. Siminiceanu, M. Macoveanu, A. Kettrup, Decolorization of disperse red 354 azo dye in water by several oxidation processes—a comparative study, *Dyes Pigments* 60 (2004) 61–68.
- [6] P.K. Malik, S.K. Saha, Oxidation of direct dyes with hydrogen peroxide using ferrous ion catalyst, *Sep. Purif. Technol.* 31 (2003) 241–250.
- [7] M. Perez, F. Torrades, X. Domenech, Fenton and photo-Fenton oxidation of textile effluents, *J. Peral Water Res.* 36 (2002) 2703–2710.
- [8] O. Legrini, E. Oliveros, A.M. Braum, Photochemical process for water treatment, *Chem. Rev.* 93 (1993) 671–678.
- [9] M.C. Lu, J.N. Chen, C.P. Chang, Oxidation of dichlorvos with hydrogen peroxide using ferrous ion as catalyst, *J. Hazard. Mater. B* 65 (1999) 277–288.
- [10] E. Chamarro, A. Marco, S. Esplugas, Use of Fenton reagent to improve organic chemical biodegradability, *Water Res.* 35 (2001) 1047–1051.
- [11] H. Gallard, T. De Laat, Kinetics of oxidation of chlorobenzenes and phenyl-ureas by $Fe(II)/H_2O_2$ and $Fe(III)/H_2O_2$, *Chemosphere* 42 (2001) 405–413.
- [12] A.M. Guedes, L.M. Madeira, R.A. Boaventura, C.A. Costa, Fenton oxidation of cork cooking wastewater—overall kinetic analysis, *Water Res.* 37 (2003) 3061–3069.
- [13] M.P. Titus, V.G. Molina, M.A. Banos, J. Gimenez, S. Esplugas, Degradation of chlorophenols by means of advanced oxidation processes: a general review, *Appl. Catal. B* 47 (2004) 219–256.
- [14] X. Xu, W. Zhao, Y. Huang, D. Wang, 2-Chlorophenol oxidation kinetic by photo-assisted Fenton process, *J. Environ. Sci.* 15 (2003) 475–481.
- [15] W. Chu, C.Y. Kwan, K.H. Chan, C. Calvin, An unconventional approach to studying the reaction kinetics of the Fenton's oxidation of 2,4-dichlorophenoxyacetic acid, *Chemosphere* 57 (2004) 1165–1171.