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Research Article

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Treatment of the azo dye in the solution by fenton-SBR process

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ABSTRACT

Treatment of dye wastewater was experimentally investigated in this study. A combined Fenton-SBR system was employed to treat dye C.I. Acid Black 1 wastewater. With the optimal Fenton conditions: $[dye]_0$=50mg/L, pH=3.50, $[H_2O_2]$=0.5mM, and $[Fe^{2+}]_0$=0.025mM, and 25□, the degradation efficiency of C.I. Acid Black 1 in solution reached 96.8%. The hydraulic retention time (HRT) in SBR unit has no more important effect on the degradation efficiency of dye C.I. Acid Black 1 in solution. Under the best operating conditions, 99% removal of dye C.I. Acid Black 1 in solution by Fenton-SBR process was achieved.

Keywords: Fenton-SBR; C.I. Acid Black 1; Degradation efficiency

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INTRODUCTION

The textile industry consumes large amounts of water in the dyeing and finishing processes. Generally, the generated effluents are characterized by presenting low metal and suspended solid contents, high temperature, alkaline pH in most situations, high chemical oxygen demand (COD), and the presence of chlorinated organic compounds, surfactants and intense colour [1]. As the discharge of this type of wastewater, without any treatment, generates negative environmental impacts in the receiving water bodies, it is necessary to find treatment techniques efficient enough to remove those pollutants. Alternative solutions to the conventional treatment have been reported, including electrochemical treatment, ozonation, advanced oxidation processes and combined processes have been recently reviewed [2].

Advanced oxidation processes have been offering promise for wastewater treatment because they are able to oxidise a wide range of compounds that are otherwise difficult to degrade. Among advanced oxidation processes, oxidation using Fenton's reagent is an attractive treatment for the effective decolourisation and degradation of textile wastewater because of its low cost, the lack of toxicity of the reagents, the absence of mass transfer limitation due to its homogeneous catalytic nature and the simplicity of the technology[3].

The Fenton system uses ferrous ions to react with hydrogen peroxide, producing hydroxyl radicals with powerful oxidising ability to degrade organic pollutants(R) as shown in Eqs.(1)-(4)[4].

$$H_2O_2 + Fe^{2+} \rightarrow OH^{\bullet} + OH^{-} + Fe^{3+} \quad (1)$$

$$OH^{\bullet} + RH \rightarrow R^{\bullet} + H_2O \quad (2)$$

$$R^{\bullet} + Fe^{3+} \rightarrow R^{+} + Fe^{2+} \quad (3)$$

$$Fe^{2+} + OH^{\bullet} \rightarrow Fe^{3+} + OH^{-} \quad (4)$$

Many investigations have been conducted into the decolourisation of textile wastewater using Fenton oxidation[5-8].

Sequencing batch reactor (SBR) is a wastewater treatment process based on the principles of the activated sludge process. SBR has been successfully employed in the treatment of both municipal and industrial wastewater and it can be considered suitable for biological system modelling at laboratory scale because of the small volumes of effluent that can handle and because of the good control it offers[9]. Combined Fenton-SBR process has been reported to be effective in treatment of recalcitrant wastewater [10-14]. In our previous work, degradation of dye using Fenton and photo-Fenton was studied [15].

The goal of this paper is to examine the effect of operating conditions of the Fenton pretreatment of the azo dye wastewater. Then, the combined Fenton-SBR treatment of the azo dye wastewater was also examined. Effects of Fenton treated wastewater characteristics under different Fenton operating conditions and SBR hydraulic retention time (HRT) on SBR and combined process efficiency were also evaluated.

EXPERIMENTAL SECTION

2.1 Materials

A commercial azo dye, C.I. Acid Black 1, was used in this study. Fig.1 depicts the chemical structure[16]. $FeSO_4 \cdot 7H_2O$, H_2O_2 (30%w/w) were analytical grade and were used without further treatment. The de-ionized and doubly distilled water was used. pH of the solutions was adjusted using HNO_3 and NaOH solutions.

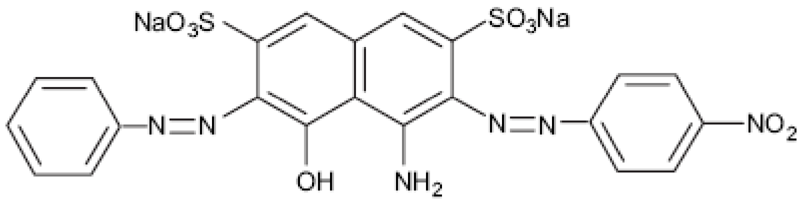

Fig.1 Chemical structure of C.I. Acid Black 1

2.2 Experimental setup and procedure

2.2.1 Fenton process

The experiments were conducted using a 2.5L Pyrex reactor with 2L of the C.I. Acid Black 1 wastewater. The required amount of $FeSO_4 \cdot 7H_2O$ was added to the dye wastewater and mixed by a magnetic stirrer to ensure complete homogeneity during reaction. Thereafter, necessary amount of hydrogen peroxide was added to the mixture with simultaneous adjustment to the required pH value by (1+1) H_2SO_4. The reaction time at which hydrogen peroxide was added to the mixture was considered the beginning of the beginning of the experiment. The reaction was allowed to continue for the required time. Thereafter, pH in the solution was increased to above 10 for iron precipitation and decomposing residual H_2O_2 with 10% NaOH[17]. Precipitated iron was separated from the reactor and the supernatant was used to feed the SBR after pH adjustment to 7.0. Samples were taken and filtered through a 0.45μm membrane syringe filter for determination.

2.2.2 SBR reactor

The operating liquid volume of the 2L SBR was 1.5L and depth 20cm. The reactor was equipped with an aquarium pump and air diffuser to keep DO above 3mg/L, and stirring plate and stirrer bar (200 rpm) for mixing. Feeding and decanting were performed using two peristaltic pumps. The cycle period was divided into five phases: filling (0.25h), aeration (variable), settling (1.25 h), decant (0.25 h) and idle (0.25 h). The cycle was repeated 6-9 times as necessary to allow cell acclimation and to obtain repetitive results. The SBR was inoculated with 200mL of sludge from the aeration tank of a wastewater treatment plant in Shaoxing City. The concentration of mixed liquor suspended solids in the SBR was maintained at 4000 mg/L by extracting excess sludge.

2.3 Analytical methods

The UV-vis spectra of C.I. Acid Black 1 were recorded from 200 to 800nm using a UV/Vis spectrophotometer with a spectrometric quartz cell. The maximum absorbance wavelength of C.I. Acid Black 1 was found at 618nm. In the whole reaction process, it was found that the measure of concentration of C.I. Acid Black 1 is not interfered by the degradation products. Therefore, the concentration of C.I. Acid Black 1 in reaction mixture at different reaction times was determined by measuring the absorption intensity of solution at 618nm and using a calibration curve. In order to decrease the experimental error, the sampling and measurement of the absorbance of reaction solutions were finished in 1 minute [18].

The degradation efficiency of C.I. Acid Black 1 was defined as follows:

$$\text{Degradation efficiency} = \left(1 - \frac{C_t}{C_0}\right) \times 100\% \quad (5)$$

Where C_0 is the initial concentration of C.I. Acid Black 1, and C_t is the concentration of C.I. Acid Black 1 at reaction time t (minute).

RESULTS AND DISCUSSION

3.1 Fenton pretreatment

3.1.1 Effect of pH

The effect of pH on the decolorization of C.I. Acid Black 1 by Fenton processes is studied in the pH range of 2.50-5.00 and the results are shown in Fig.2.

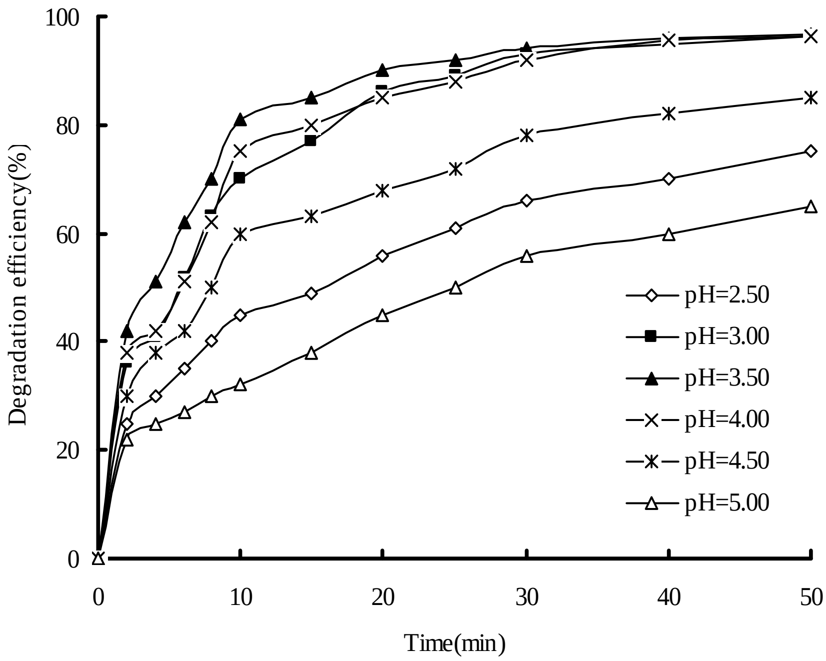

Fig.2 Effect of initial pH on the decolorization of an azo dye C.I. Acid Black 1 during Fenton oxidation. Experimental conditions: $[dye]_0$=50mg/L, $[H_2O_2]_0$=0.5mM, $[Fe^{2+}]_0$=0.025mM, and temperature=298 K

The results indicated that the degradation of C.I. Acid Black 1 was significantly influenced by the pH of the solution and the best decolorization efficiency was obtained at about 3.50. Many studies have revealed that the solution pH can dramatically influence the degradation of synthetic dyes in water by Fenton oxidation and the optimal solution pH values were achieved at range 3.00-4.00 [19, 20]. At low pH(below 3.00), the reaction could be slowed down because hydrogen peroxide can stay stable probably solvating a proton to form an oxonium ion (e.g. $H_3O_2^+$). An oxonium ion makes hydrogen peroxide electrophilic to enhance its stability and presumably to reduce substantially the reactivity with ferrous ion. At the same time, the formed complex species $[Fe(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{3+}$ also react more slowly with hydrogen peroxide. In addition, the scavenging effect of the $HO^{\bullet}$ radical by H^+ is severe. On the other hand, at high pH(above 4.00), the oxidatio efficiency rapidly decreased, not only by decomposition of hydrogen peroxide, but also by deactivation of a ferrous catalyst with the formation of ferric hydroxide complexes leading to a reduction of $HO^{\bullet}$ radical [20-22]. Herein, a suitable initial pH for the decolorization of C.I. Acid Black 1 by Fenton oxidation process was recommended as 3.50.

3.1.2 Effect of the initial H_2O_2 concentration

Fig.3 shows the relationship between the degradation of dye and the initial concentration of H_2O_2 in the Fenton oxidation processes.

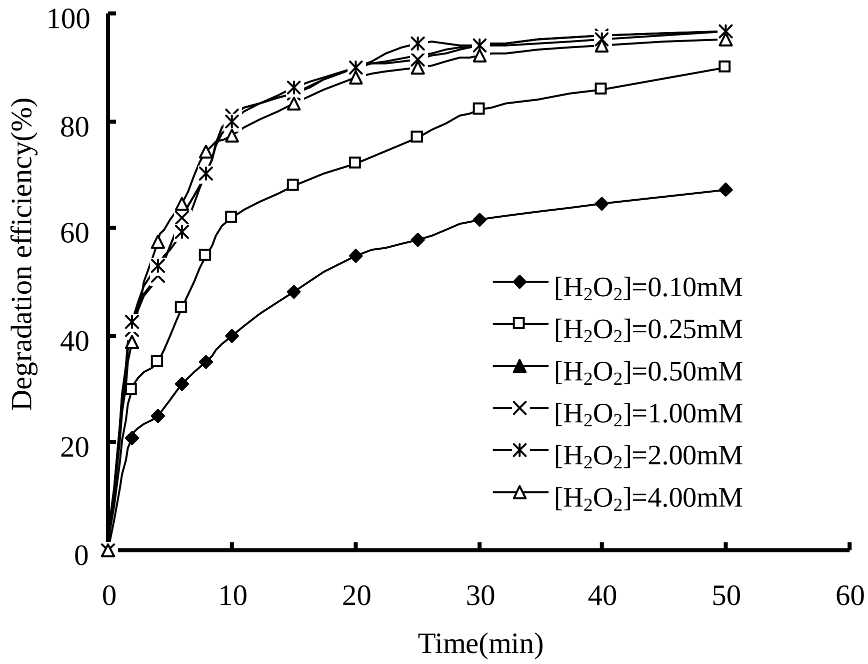

Fig.3 Effect of initial H_2O_2 on the decolorization of an azo dye C.I. Acid Black 1 during Fenton oxidation. Experimental conditions: $[dye]_0$=50mg/L, pH=3.50, $[Fe^{2+}]_0$=0.025mM, and temperature=298 K

As it can be seen, the effect of increasing the concentration of H_2O_2 from 0.1mM to 0.5mM was positive for the degradation of C.I. Acid Black 1. This is due to the oxidation power of Fenton process which was imporved with increasing $HO^{\bullet}$ radical amount in solution obtained from the decomposition of increasing hydrogen peroxide. Further increase from 0.5mM to 4.0mM causes no significant change in decolorization. This may be explained by the fact that at a higher H_2O_2 concentration scavenging of $HO^{\bullet}$ radicals will occur, which can be expressed by the Eqs.(12)[23]:

$$HO_2^{\bullet} + HO^{\bullet} \rightarrow H_2O + O_2 \qquad (12)$$

According to the results above, the optimal hydrogen peroxide concentration for the most effective degradation of 50mg/L C.I. Acid Black 1 is about 0.5mM.

3.1.3 Effect of the initial Fe^{2+} concentration

The effect of the initial Fe^{2+} concentration on the decolorization of C.I. Acid Black 1 has been studied. The results are shown in Fig.4.

From Fig.4, it can be seen that the decolorization efficiency of the C.I. Acid Black 1 increases with increasing initial Fe^{2+} concentration. Although, the increase is from 0.025mM to 0.10mM, it is very soft. It may be explained by the redox reactions since $HO^{\bullet}$ radicals may be scavenged by the reaction with the hydrogen peroxide or with another Fe^{2+} molecule as below. The lower degradation capacity of Fe^{2+} at small concentration is probably due to the lowest $HO^{\bullet}$ radicals production abailable for oxidation[17]. The optimum dosage of Fe^{2+} is 0.025mM.

3.1.4 Effect of the initial C.I. Acid Black 1 concentration

The effect of initial C.I. Acid Black 1 concentration on the Fenton oxidation process was investigated, since pollutant concentration is an important parameter in wastewater treatment. Fig.5 shows the influence of the concentration on dye degradation in Fenton reactions.

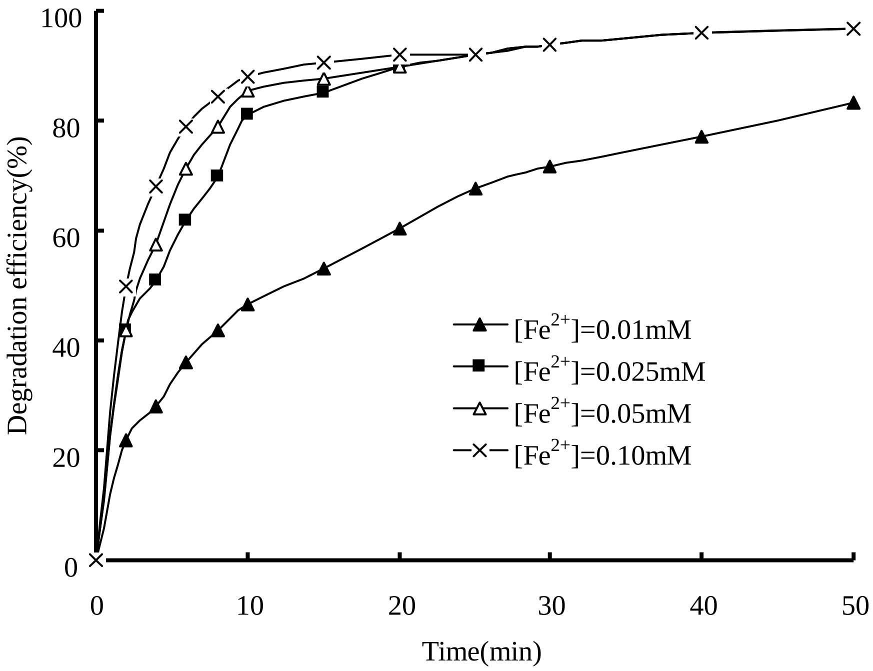

Fig.4 Effect of initial Fe^{2+} concentration on the decolorization of an azo dye C.I. Acid Black 1 during Fenton oxidation. Experimental conditions: $[dye]_0$=50mg/L, pH=3.50, $[H_2O_2]_0$=0.5mM, and temperature=298 K

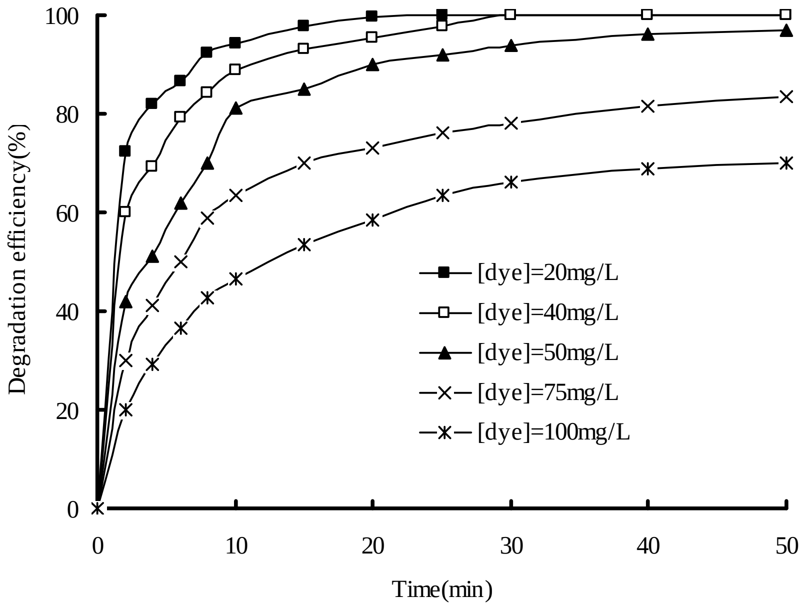

Fig.5 Effect of initial dye concentration on the decolorization of an azo dye C.I. Acid Black 1 during Fenton oxidation. Experimental conditions: $[Fe^{2+}]_0$=0.025mM, pH=3.50, $[H_2O_2]_0$=0.5mM, and temperature=298 K

It can be seen that the decolorization efficiency of C.I. Acid Black 1 was decreased with the increasing concentration of C.I. Acid Black 1. As increasing of the C.I. Acid Black 1 concentration from 20mg/L to 100mg/L, the decolorization efficiency of C.I. Acid Black 1 within 10min of reaction decreased from 94.2% to 46.5%. This is due to that a relative lower concentration of $HO^{\bullet}$ results from the increasing concentration of C.I. Acid Black 1 but the same dosage of H_2O_2 and Fe^{2+}, which led to a decreasing of the decolorization efficiency of C.I. Acid Black 1.

3.2 Combined Fenton-SBR treatment

The SBR process was employee as a following treatment step for wastewater from Fenton process. Under the optimal conditions, such as $[dye]_0$=50mg/L, pH=3.50, $[H_2O_2]$=0.5mM, and $[Fe^{2+}]_0$=0.025mM, and 25□, the degradation efficiency of C.I. Acid Black 1 from Fenton process reached 96.8%. The pH in the solution was around 6.5.

3.2.1 Effect of cycle period on perfoumance of SBR
In order to examine the effect of cycle period on SBR performance, HRT was varied in the range 12h-48h. The SBR was operated for 30days respectively at HRT of 12, 24, 36 and 48h, and was fed with wastewater pretreated under the Fenton process. Fig.6 shows the SBR efficiency in terms of the degradation efficiency of C.I. Acid Black 1 at HRT of 12, 24, 36 and 48h.

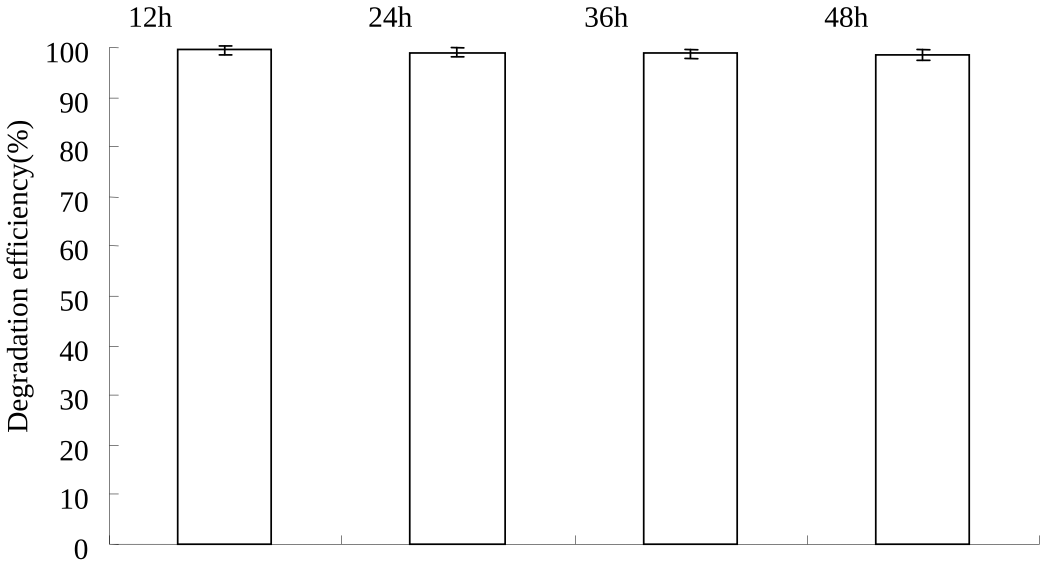

Fig.6 SBR efficiency in terms of the degradation efficiency of C.I. Acid Black 1 at HRT of 12, 24, 36 and 48h

No remarkable improvement in SBR efficiency was observed due to HRT increase from 12h to 48h. This indicated that most substrated degradation occurred during the first 12h and a smaller portion was degraded in rest of the retention time. So, it was decided to operate the SBR at HRT of 12h in subsequent.

3.2.2 Combined Fenton-SBR treatment
The combined Fenton-SBR treatment was operated at HRT of 12h and the cycle was repeated 6times to obtain repetitive results. Fig.7 dipicted the degradation efficiency of C.I. Acid Black 1 variation with aeration time. The degradation of C.I. Acid Black 1 was complete in 12h and kept the same level along with the treatment time increased.

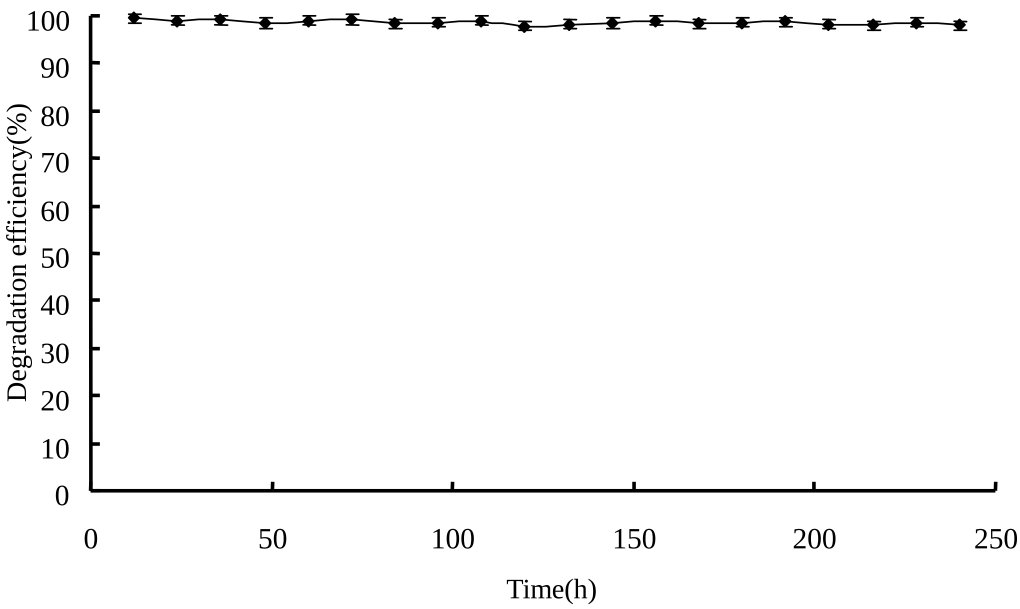

Fig.7 Performance of the combined Fenton-SBR treatment

CONCLUSION

(1) The pH, [Fe^{2+}] , [dye] and [H_2O_2] have an important effect on the degradation of dye with the Fenton process. Under the optimum conditions, such as, $[dye]_0$=50mg/L, pH=3.50, [H_2O_2]=0.5mM, and $[Fe^{2+}]_0$=0.025mM, and 25, the degradation efficiency of C.I. Acid Black 1 with Fenton process reached 96.8%.
(2) HRT had no remarkable improvement in SBR efficiency.
(3) Combined Fenton-SBR is an effective process for treatment of C.I. Acid Black 1 in solution.

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REFERENCES

[1] SDR Carmen; MM Luis; ARB Rui, *J. Hazard. Mater.*, **2009**, 172, 1551-1559.
[2] A Chiavola, *Water Environ. Res.*, **2008**, 80(10), 1538-1563.
[3] A Gutowska; J Kaluzna-Czaplinska; WK Jozwiak, *Dyes Pigments*, **2007**, 74, 41-46.
[4] SB Wang, *Dyes Pigments*, **2008**, 76, 714-720.
[5] JH Sun; SP Sun; GL Wang; LP Qiao, *Dyes Pigments*, **2007**, 74, 647-652.
[6] YH Huang; YF Huang; PS Chang; CY Chen, *J. Hazard. Mater.*, **2008**, 154, 655-662.
[7] M Tamal; D Dalia; M Subhasis, *J. Hazard. Mater.*, **2010**, 180, 204-211.
[8] TH Kim; C Park; JM Yang; S Kim, *J. Hazard. Mater.*, **2004**, 112, 95-103.
[9] J García-Montańo; F Torrades; JA García-Hortal, *J. Hazard. Mater.*, **2006**, 134, 220-229.
[10] SE Emad; C Malay, *J. Hazard. Mater.*, **2011**, 192, 1418-1426.
[11] JS Cuo; AA Abdulhussain; YP Chen, *J. Hazard. Mater.*, **2010**, 178, 699-705.
[12] WW Ben; ZM Qiang; X Pan, *Water Res.*, **2009**, 43, 4392-4402.
[13] J Li; ZK Luan; L Yu, *Biores. Techn*., **2011**, 102, 10319-10326.
[14] A Christensen; DG. Mirat; G Temesgen, *Water Res.*, **2009**, 43, 3910-3921.
[15] MQ Qiu; CC Huang, *Desalin. Water Treat.*, **2010**, 24, 1-5.
[16] SB Wang, *Dyes Pigments*, **2008**, 76, 714-720.
[17] I Talinli; GK Anderson, *Water Res.*, **1992**, 26, 107-110.
[18] SL Marco; AP José, *Dyes Pigments*, **2006**, 71, 236-244.
[19] JH Sun; SP Sun; GL Wang; LP Qiao, *Dyes Pigments*, **2007**, 74, 647-652.
[20] SB Wang, *Dyes Pigments*, **2008**, 76, 714-720.
[21] J Feng; X Hu; PL Yue, *Water Res.*, **2006**, 40, 641-646.
[22] MM Hassan; CJ Hawkyard, *J. Chem. Technol. Biotechnol.*, **2002**, 77(7), 834-841.
[23] M Muruganandham; M Swaminathan, *Dyes Pigments*, **2004**, 63(3), 315-321.