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Degradation of azo dye Amido black 10B in aqueous solution by Fenton oxidation process

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Abstract

The degradation of an azo dye Amido black 10B in aqueous solution by Fenton oxidation process has been investigated. The effects of different reaction parameters such as initial pH, the initial hydrogen peroxide concentration ($[H_2O_2]_0$), the initial ferrous concentration ($[Fe^{2+}]_0$), the initial Amido black 10B concentration ($[dye]_0$) and the temperature on the oxidative degradation of Amido black 10B have been assessed. The optimal reacting conditions were experimentally determined and it was found to be initial pH = 3.50, $[H_2O_2]_0 = 0.50$ mM, $[Fe^{2+}]_0 = 0.025$ mM for $[dye]_0 = 50$ mg/L at temperature = 25 °C. Under optimal conditions, 99.25% degradation efficiency of dye in aqueous solution was achieved after 60 min of reaction. The UV–vis spectral changes of Amido black 10B in aqueous solution during Fenton treatment process were studied. It was easier to destruct the azo linkage (–N=N–) group than to destruct the aromatic rings of Amido black 10B by Fenton oxidation. The experimental results showed that the Fenton oxidation process was an effective process for the degradation of azo dye Amido black 10B at low H_2O_2 and Fe^{2+} concentrations.

Keywords: Amido black 10B; Fenton process; Advanced oxidation technologies (AOTs); Hydroxyl radical; UV–vis spectra

1. Introduction

Azo dyes are widespread environmental pollutants associated with textile, cosmetic, food colorants, printing, and pharmaceutical industries. Yearly, 800,000 tonnes of dyes are produced in the world and about 50% of them are azo dyes [1]. Estimates indicate that approximately 10–15% of the synthetic textile dyes used are lost in waste streams during manufacturing or processing operations [2,3]. The effluents are strongly colored which not only created environmental and aesthetic problems, but also posed a great potential toxic threat to ecological and human health as most of these dyes are toxic and carcinogenic.

The strong electron-withdrawing character of the azo group stabilizes these aromatic pollutants against conversions by oxygenases. Therefore, azo dyes are not readily degraded under aerobic conditions [4,5]. Under anaerobic conditions, azo dyes are readily cleaved via a four electron reduction at the azo linkage generating aromatic amines. The aromatic amines cannot be regarded as environmentally safe end products as they are suspected to be carcinogens and mutagens [6–9]. Nowadays, various chemical and physical processes, such as elimination by adsorption onto activated carbon, coagulation by a chemical agent, ozone oxidation, hypochlorite oxidation, electrochemical method, etc. are applied for the treatment of dye waste effluents [10–12]. Nevertheless, these methods are usually non-destructive, inefficient, costly and resulted in the production of secondary waste products. Therefore, purification of azo dye wastewater is becoming a matter of great concern and it is necessary to develop novel and cost-effective technologies to treat azo dye wastewater.

Advanced oxidation technologies (AOTs) are innovative methods for water treatment and are extremely useful in the case of substances resistant to conventional technologies.

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AOTs are oxidation processes which generate hydroxyl radicals ($^{\bullet}OH$) that are very effective in degrading organic pollutants because of their strong oxidant power ($^{\bullet}OH + H^+ + e^- \rightarrow H_2O$; $E^0 = 2.80$ V) and nonselective species [13,14]. O_3/H_2O_2, O_3/UV, H_2O_2/UV, TiO_2/air/UV, Fe(II)/H_2O_2 (Fenton's reagent), Fe(III)/H_2O_2 (Fenton-like reaction), an oxidant (H_2O_2, O_3) and ultrasonic irradiation are the main types of AOTs that have been suggested in recent years [15–19]. Various combinations of them are employed for the complete mineralization of pollutants. Among these AOTs, Fenton's reagent is particularly attractive because of the low costs, the lack of toxicity of the reagents (i.e., Fe(II) and H_2O_2), the absence of mass transfer limitation due to its homogeneous catalytic nature and the simplicity of the technology [20]. Early studies have shown that the Fenton reaction is efficient in the degradation of organic compounds. The active species can be generated by the inter-reaction of hydrogen peroxide with ferrous and ferric ions according to Eqs. (1) and (2) [21,22], the $^{\bullet}OH$ radical can attack and initiate the oxidation of organic pollutant molecule (R) by several degradation mechanisms as shown below (Eqs.(3)–(5)) [23]:

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + {}^{\bullet}OH + H_2O \quad k_1 = 76\ M^{-1}\ s^{-1} \tag{1}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + {}^{\bullet}OOH + H^+ \quad k_2 = 0.01\text{–}0.02\ M^{-1}\ s^{-1} \tag{2}$$

$$^{\bullet}OH + RH \rightarrow H_2O + R^{\bullet} \quad k_3 = 10^7\text{–}10^{10}\ M^{-1}\ s^{-1} \tag{3}$$

$$R^{\bullet} + Fe^{3+} \rightarrow Fe^{2+} + R^+ \tag{4}$$

$$R^{\bullet} + H_2O_2 \rightarrow ROH + {}^{\bullet}OH \tag{5}$$

For economic degradation of dye wastewater by Fenton oxidation, there is a need to determine the optimal conditions of experimental parameters. The aim of the present work is to investigate the influence of various parameters on the degradation of a classical azo dye, called Amido black 10B, in aqueous solution by the Fenton oxidation process. The effects of pH, dosages of hydrogen peroxide and ferrous, the concentration of Amido black 10B and the temperature were examined. The optimal reacting conditions were evaluated. In addition, the UV–vis spectral changes of Amido black 10B in aqueous solution during Fenton treatment process were also studied.

2. Materials and methods

2.1. Reagents

Amido black 10B was obtained from Beijing Chemical Reagents Co. (Beijing, China), the molecular structure of it is displayed in Fig. 1. Hydrogen peroxide (30% w/w), ferrous sulfate ($FeSO_4 \cdot 7H_2O$), sulfuric acid and sodium hydroxide were all obtained from Shanghai Chemical Reagents Co. (Shanghai, China). All chemicals were of analytical grade and were used without any further purification. Deionized water was used throughout this study.

2.2. Experimental procedures

All experiments were carried out in 500 mL beakers, which were placed in a thermostat water bath with constant temperature and stirred by a magnetic stirrer. Each experimental run was performed by taking an appropriate amount of stock dye solution followed by the addition of ferrous ion and dilution with deionized water to 200 mL. Solution pH values were adjusted to the desired level using dilute sulfuric acid and sodium hydroxide, which were measured by a pH meter (PHS-3C). The reactions were initiated by adding hydrogen peroxide to the beaker. Samples were taken out from the beaker periodically using a pipette and were immediately analyzed and then returned back to the beaker. Each experiment was replicated three times or more.

2.3. Analytical methods

The UV–vis spectra of dye were recorded from 200 to 800 nm using a UV–vis spectrophotometer (Lambda 17, Perkin–Elmer) with a spectrometric quartz cell (1 cm path length). The maximum absorbance wavelength (λ_{max}) of Amido black 10B could be found at 618 nm from the spectra. Therefore, the concentration of the dye in the reaction mixture at different reaction times was determined by measuring the absorption intensity at $\lambda_{max} = 618$ nm and from a calibration curve. The degradation efficiency of Amido black 10B was defined as follows (Eq. (6)):

$$\text{Degradation efficiency}\ (\%) = (1 - C_t/C_0) \times 100\% \tag{6}$$

where C_0 is the initial concentration of Amido black 10B, and C_t is the concentration of Amido black 10B at reaction time t (min).

3. Results and discussion

3.1. Effect of pH

The pH of the solution is an important parameter for Fenton oxidation process, which controls the production rate of hydroxyl radical and the concentration of Fe^{2+}. It is also an

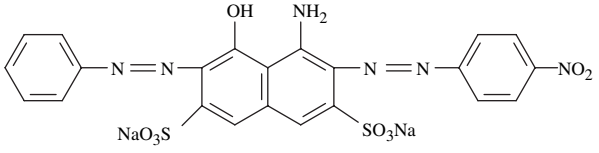

Fig. 1. Molecular structure of Amido black 10B.

important operational variable in actual wastewater treatment. In order to find the optimal pH of reaction mixture for the degradation of Amido black 10B in Fenton oxidation, a series of experiments were conducted at different pH values of 2.50, 3.00, 3.50, 4.00, 5.00, etc. The results are illustrated in Fig. 2. The results indicated that the degradation of Amido black 10B was significantly influenced by the pH of the solution and the optimal solution pH was observed 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 [19,24]. At low pH (below 3.00), the reaction according to Eqs. (1) and (2) could be slowed down because hydrogen peroxide can stay stable probably by solvating a proton to form an oxonium ion (e.g. $H_3O_2^+$, Eq. (7)). An oxonium ion makes hydrogen peroxide electrophilic to enhance its stability and presumably to reduce substantially the reactivity with ferrous ion [25]. 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 [26]. In addition, the scavenging effect of the $^{\bullet}OH$ radical by H^+ is severe (Eq. (8)) [27,28].

$$H_2O_2 + H^+ \rightarrow H_3O_2^+ \quad (7)$$

$$^{\bullet}OH + H^+ + e^- \rightarrow H_2O \quad (8)$$

On the other hand, in case of pH > 4.00, the oxidation 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 $^{\bullet}OH$ radical.

The measured final pH values after 60 min of reaction were 2.72 for an initial pH of 2.50, 3.13 for an initial pH of 3.00, 3.41 for an initial pH of 3.50, 3.81 for an initial pH of 4.00 and 4.38 for an initial pH of 5.00. The change in solution pH was related to the acidity of the intermediates produced during the degradation of Amido black 10B by Fenton oxidation. Similar phenomenon was reported by Feng et al. [27]. The drop in the final solution pH with initial pH values of 5.00, 4.00 and 3.50 may be due to the generation of HSO_4^- and NO_3^- and carboxylic acid during mineralization of Amido black 10B. The increase of the final solution pH with initial pH values of 3.00 and 2.50 may be due to the consumption of some H^+ by hydrogen peroxide according to Eq. (3) under a low pH condition.

Further experiments were conducted at an initial pH of 3.50, without adding any buffer for pH adjustments during the progress of the reaction.

3.2. Effect of the initial H_2O_2 concentration

Hydrogen peroxide plays the role of an oxidizing agent in Fenton oxidation process. The selection of an optimal hydrogen peroxide concentration for the degradation of Amido black 10B by Fenton oxidation is important from a practical point of view due to the cost of hydrogen peroxide. Fig. 3 shows the effect of initial H_2O_2 concentration ($[H_2O_2]_0$) on the degradation of Amido black 10B during Fenton treatment. As it can be seen, the effect of increasing $[H_2O_2]_0$ from 0.10 mM to 1.00 mM was first positive for the degradation of Amido black 10B. This is due to the oxidation power of Fenton process which was improved with increasing $^{\bullet}OH$ radical amount in solution obtained from the decomposition of increasing hydrogen peroxide. However, with continuous increasing of the $[H_2O_2]_0$ to 2.00 mM and 4.00 mM, the degradation rate of Amido black 10B reduced. This may be explained by the fact that the very reactive $^{\bullet}OH$ radical could be consumed by H_2O_2 and results in the generation of less reactive $^{\bullet}OOH$ radical (Eq. (9)) [21,22,29].

$$H_2O_2 + {}^{\bullet}OH \rightarrow {}^{\bullet}OOH + H_2O \quad k_9 = 2.7 \times 10^7\ M^{-1}\ s^{-1} \quad (9)$$

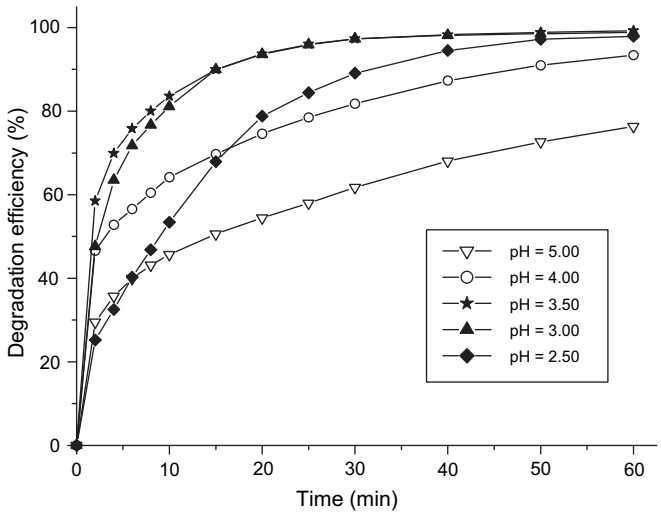

Fig. 2. Effect of pH on the degradation of Amido black 10B during Fenton oxidation treatment. Reaction conditions: $[dye]_0 = 50$ mg/L, $[H_2O_2]_0 = 0.50$ mM, $[Fe^{2+}]_0 = 0.025$ mM, and temperature = 25 ± 1 °C.

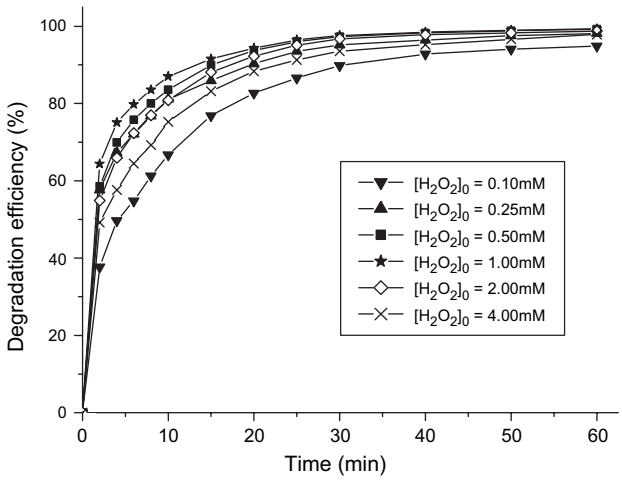

Fig. 3. Effect of initial H_2O_2 concentration on the degradation of Amido black 10B during Fenton oxidation treatment. Reaction conditions: $[dye]_0 = 50$ mg/L, $[Fe^{2+}]_0 = 0.025$ mM, pH = 3.50, and temperature = 25 ± 1 °C.

Thus in the condition of excess H_2O_2, which would become a scavenger of $^{\bullet}OH$ radical, and lead the degradation efficiency of Amido black 10B to decrease.

It is important to control the $[H_2O_2]_0$; the amount of hydrogen peroxide should be enough for the degradation of Amido black 10B, but a high concentration would be adverse to the degradation of dye and would increase the cost of the wastewater treatment. According to the results above, the optimal hydrogen peroxide concentration for the most effective degradation of 50 mg/L Amido black 10B is about 0.50–1.00 mM.

3.3. Effect of the initial Fe^{2+} concentration

To elucidate the role of initial concentration of Fe^{2+} ($[Fe^{2+}]_0$) on the degradation of Amido black 10B by Fenton oxidation, a series of experiments were conducted with different $[Fe^{2+}]_0$ from 0.01 mM to 0.10 mM. Fig. 4 shows the effect of $[Fe^{2+}]_0$ on the degradation of Amido black 10B by Fenton oxidation. The results indicated that the degradation of Amido black 10B is remarkably dependent on the $[Fe^{2+}]_0$ at fixed $[H_2O_2]_0$ and $[dye]_0$. At a low $[Fe^{2+}]_0$ (0.01 mM), the degradation efficiency was 86.92% after the 60 min reaction time. Both degradation efficiency and degradation rate were increased with increase of $[Fe^{2+}]_0$, the degradation efficiency being 97.35%, 98.57% and 98.89% after the 30 min reaction time with $[Fe^{2+}]_0$ of 0.025 mM, 0.05 mM and 0.10 mM, respectively. This is because more $^{\bullet}OH$ radicals are produced with the increase of $[Fe^{2+}]_0$ according to Eq. (1).

Considering the above-indicated results and the need to remove Fe after treatment, the optimal Fe^{2+} concentration was selected as 0.025 mM for the degradation of 50 mg/L Amido black 10B. Moreover, many studies have revealed that the use of a much higher concentration of Fe^{2+} could lead to the self-scavenging of $^{\bullet}OH$ radical by Fe^{2+} (Eq. (10)) [21,30] and induce the decrease in degradation rate of pollutants.

$$^{\bullet}OH + Fe^{2+} \rightarrow Fe^{3+} + OH^- \quad k_{10} = 4.3 \times 10^8\ M^{-1}\ s^{-1} \qquad (10)$$

3.4. Effect of the initial Amido black 10B concentration

To study the effect of initial Amido black 10B concentration ($[dye]_0$) on its degradation, the range 10–100 mg/L of $[dye]_0$ (which were the characteristic dye concentrations in wastewater from textile industry) was investigated. Fig. 5 shows the changes of Amido black 10B concentration with the reaction time. It was observed that lower the $[dye]_0$ (<50 mg/L), shorter is the reaction period needed to degrade Amido black 10B completely. At a higher $[dye]_0$ of 75 mg/L and 100 mg/L, the Amido black 10B concentration decreased quickly in the first 10 min and then slowed down as the time goes on. The degradation efficiencies were 69.25% and 52.41% after the 10 min reaction time. This is due to the fact that with constant $[H_2O_2]_0$ and $[Fe^{2+}]_0$, more hydrogen peroxide was consumed in the first 10 min because of a higher $[dye]_0$. After 10 min, the amount of hydrogen peroxide was smaller and the degradation of Amido black 10B slowed down significantly.

3.5. Effect of temperature

Temperature is critical to the reaction rate, the product yield and distribution. In order to determine the effect of reaction temperature on the degradation of Amido black 10B a series of experiments were conducted by varying temperature from 15 °C to 45 °C. The results are illustrated in Fig. 6. It can be seen that the temperature exerts a strong effect on the degradation rate of Amido black 10B and the degradation was accelerated by a rise in temperature. This is because higher temperature increased the reaction rate between hydrogen peroxide and any form of ferrous/ferric iron (chelated or not), thus increasing the rate of generation of oxidizing species such as $^{\bullet}OH$ radical or high-valence iron species.

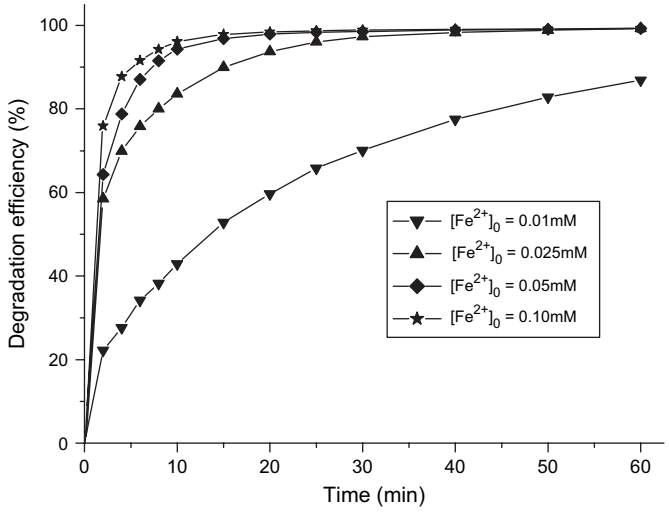

Fig. 4. Effect of initial Fe^{2+} concentration on the degradation of Amido black 10B during Fenton oxidation treatment. Reaction conditions: $[dye]_0 = 50$ mg/L, $[H_2O_2]_0 = 0.50$ mM, pH = 3.50, and temperature = 25 ± 1 °C.

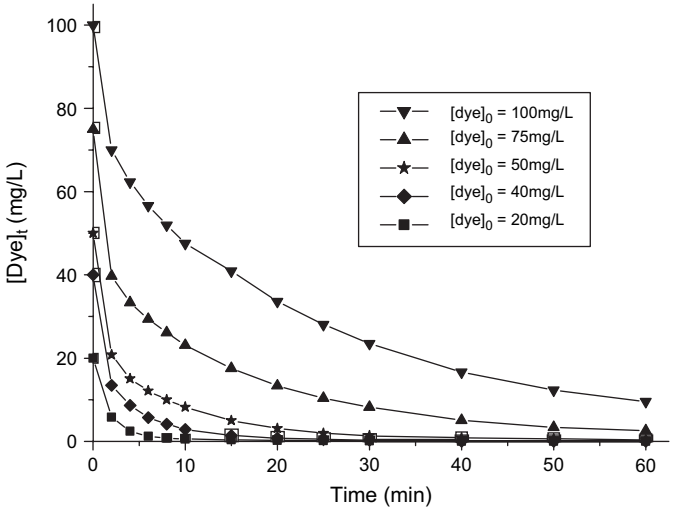

Fig. 5. Effect of initial Amido black 10B concentration on the degradation of dye during Fenton oxidation treatment. Reaction conditions: $[H_2O_2]_0 = 0.50$ mM, $[Fe^{2+}]_0 = 0.025$ mM, pH = 3.50, and temperature = 25 ± 1 °C.

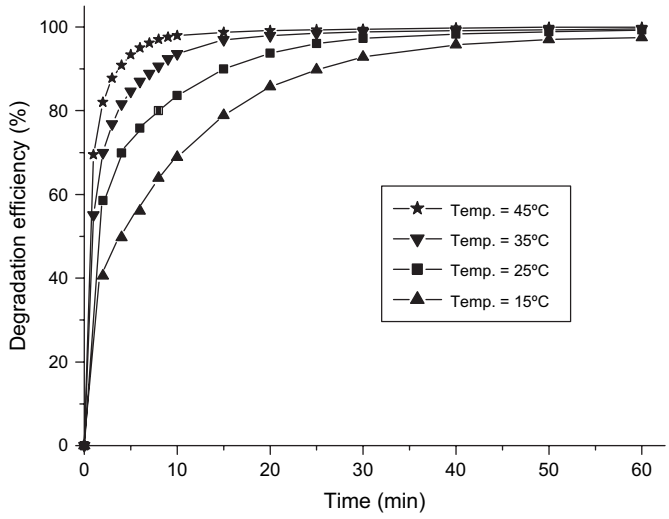

Fig. 6. Effect of temperature on the degradation of Amido black 10B during Fenton oxidation treatment. Reaction conditions: $[dye]_0 = 50$ mg/L, $[H_2O_2]_0 = 0.50$ mM, $[Fe^{2+}]_0 = 0.025$ mM, and pH = 3.50.

3.6. Spectral changes of Amido black 10B during Fenton oxidation process

The changes in the absorption spectra of Amido black 10B solution during the Fenton oxidation process at different reaction times are shown in Fig. 7. As can be seen from the spectra, before the treatment, the UV–vis spectrum of Amido black 10B was characterized by one main band in the visible region, with its maximum absorption at 618 nm, and by two bands in the ultraviolet region located at 226 nm and 318 nm. Different structural units and groups in the dye molecules have different absorbance peaks, the main conjugates of Amido black 10B include azo linkage (−N═N−), benzene ring and the naphthalene ring. The chromophore containing azo linkage has absorption in the visible region, while benzene ring and naphthalene ring has it in the ultraviolet region, and naphthalene ring's absorption wavelength is higher than that of the benzene ring [31]. So the peaks at 226 nm and 318 nm were ascribed to the absorption of the $\pi \rightarrow \pi^*$ transition related to the benzene ring and naphthalene ring bonded to the −N═N− group in the dye molecule. The peak at 618 nm was attributed to the absorption of the $n \rightarrow \pi^*$ transition related to the −N═N− group. It was clearly observed that the adsorption peak at 618 nm diminished very fast and nearly completely disappeared under 60 min of Fenton oxidation. This indicated a rapid degradation of Amido black 10B, a complete discolouration of 50 mg/L Amido black 10B can be achieved in 60 min in the presence of 0.5 mM H_2O_2 and 0.025 mM Fe^{2+}. The ultraviolet band at 318 nm was also observed to gradually diminish but at a lower rate than that of visible band, which indicated the destruction of the naphthalene rings.

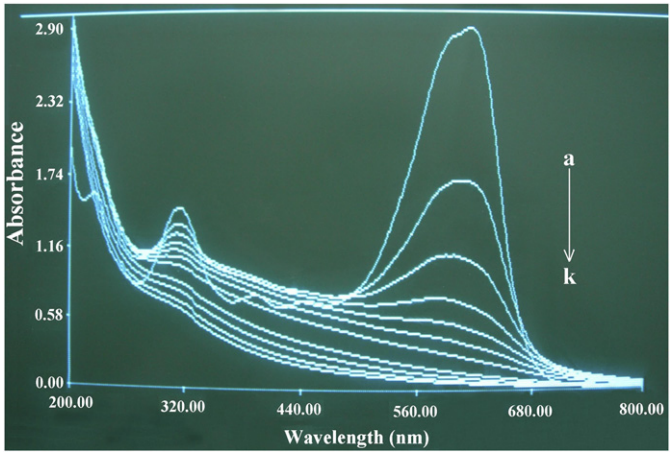

Fig. 7. UV–vis spectral changes of Amido black 10B during Fenton oxidation treatment ($a = 0$ min, $b = 1$ min, $c = 3$ min, $d = 6$ min, $e = 10$ min, $f = 15$ min, $g = 20$ min, $h = 30$ min, $i = 40$ min, $j = 50$ min, $k = 60$ min). Reaction conditions: $[dye]_0 = 50$ mg/L, $[H_2O_2]_0 = 0.50$ mM, $[Fe^{2+}]_0 = 0.025$ mM, pH = 3.50, and temperature = 25 ± 1 °C.

From the above-indicated results, it could be found that the discolouration of Amido black 10B is a fast process under Fenton oxidation, but the destruction of the aromatic rings is difficult. This is because the lowest energy absorption band is assigned to the $n \rightarrow \pi^*$ transition related to the −N═N− group [32]. Therefore, $^{\bullet}OH$ radical first attacks azo groups and opens −N═N− bonds, destructing the long conjugated π systems, and consequently causing discolouration.

4. Conclusions

Treatment of simulated wastewater containing azo dye Amido black 10B using Fenton oxidation process has been taken into consideration in the present study. Based on the experimental results presented above, it has been found that the solution pH, the initial H_2O_2 concentration, the initial Fe^{2+} concentration, the initial dye concentration and the temperature are the main factors that have strong influences on the degradation of Amido black 10B by Fenton oxidation process. The optimal operation parameters for the Fenton oxidation of Amido black 10B were 0.50 mM $[H_2O_2]_0$, 0.025 mM $[Fe^{2+}]_0$ for 50 mg/L $[dye]_0$ at an initial pH of 3.50 with 25 °C temperature. Under these conditions, 99.25% degradation efficiency of dye in aqueous solution was achieved after 60 min of reaction. The UV–vis spectral changes of Amido black 10B in aqueous solution during Fenton treatment process showed that it was easier to destruct the −N═N− group than to destruct the aromatic rings of Amido black 10B. The experimental results clearly indicated that the Fenton oxidation process was an effective process for the degradation of azo dye Amido black 10B at low $[H_2O_2]_0$ and $[Fe^{2+}]_0$, which could be available for the treatment of practical dye containing wastewater to some extent.

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