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A comparative study of degradation of the azo dye C.I. Acid Blue 9 by Fenton and photo-Fenton oxidation

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ABSTRACT

A comparative study of degradation of the azo dye C.I. Acid Blue 9 in aqueous solution by Fenton and photo-Fenton oxidation processes has been carried out by the optimum conditions. Results indicate that the azo dye C.I. Acid Blue 9 can be effectively decolorized using two methods with a litter difference for optimal conditions, 97.7% and 98.12% respectively. However, in the mineralization removal of C.I. Acid Blue 9, with photo-Fenton oxidation process there is a significant increasement relatively to Fenton oxidation process. That is, although UV has little effect on dye degradation, it is particularly important in dye mineralization removal. In addition, the effect of relation $[H_2O_2]_0/[Fe^{2+}]_0$ and $[H_2O_2]_0/[dye]_0$ were also investigated. The results showed that a ratio $[H_2O_2]_0/[Fe^{2+}]_0$ ranged from 2.0 to 3.5 and a ratio $[H_2O_2]_0/[dye]_0$ of 7.0 are optimal operational conditions by Fenton and photo-Fenton oxidation processes.

Keywords: Comparative; Degradation; Mineralization; Fenton process; Photo-Fenton process; CI Acid Blue 9

1. Introduction

Azo dyes, which are difficult to be degraded biologically, are commonly found in the dye, textile and paper manufacturing wastewater. If these are not removed from the treated wastewater, a number of synthnetic azo dyes cause a formidable contamination of water, as color tends to persist even after the conventional treatment given to the wastewater. Color removal from industrial effluents has been a major concern in wastewater treatment. Moreover, the release of these wastewaters in natural environments is very problematic to aquatic life and mutagenic to human [1].

The effective decolorization methods are urgently required. Although numerous physical/chemical schemes, including coagulation, flocculation, adsorption and membrane filtration, have been used to decolorize textile effluents, these techniques suffer disadvantages of sludge generation, adsorbent regeneration and membrane fouling [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 decolorization and degradation of dyes 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 [3–5].

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) [6]

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

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

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

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

Many investigations have been conducted into the decolorization of dyes using Fenton oxidation [7–9].

Photo-Fenton, which is also a newly emerged AOP, has been applied to the treatment of dye stuffs [10–12,20]. In photo-Fenton process in addition to the above reactions the formation of hydroxyl radical also occurs by the following reactions:

$$H_2O_2 + UV \rightarrow HO^\bullet + HO^\bullet \quad (5)$$

$$Fe^{3+} + H_2O + UV \rightarrow HO^\bullet + Fe^{2+} + H^+ \quad (6)$$

The addition of UV to Fenton's process could be an interesting allied in dye decolorization due to its capacity to influence the direct formation of $HO^\bullet$ radicals [13].

The main objective of this study is to discuss about the degradation efficiency and the mineralization removal of the azo dye dye C.I. Acid Blue 9 in aqueous solution by Fenton and photo-Fenton oxidation processes. The influence of relation $[H_2O_2]_0/[Fe^{2+}]_0$ and $[H_2O_2]_0/[dye]_0$ on the degradation efficiency of C.I. Acid Blue 9 by Fenton and photo-Fenton oxidation process were also investigated.

2. Materials and methods

2.1. Reagents

A commercial azo dye, C.I. Acid Blue 9, was used in this study. It which belongs to acidic dyes group is soluble in cold water and methanol. It can be found in thousands of textile, foodstuff and pharmaceutical wastewaters. In addition, it is one of the components which can be used as an aquatic herbicide, in natural or manmade ponds, lakes, fountains, fish farms, and fish hatcheries, and may be applied by both professional applicators and homeowners. It is hazardous in case of ingestion, of kin contact, of eye contact, of inhalation. Fig. 1 depicts the chemical structure [14]. $FeSO_4{\cdot}7H_2O$, 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.

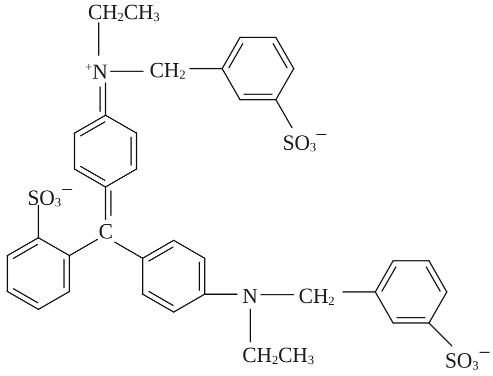

Fig. 1. Chemical structure of C.I. Acid Blue 9

2.2. Photoreactor

Photoreactor with diameter 10 cm and height 20 cm was supplied by NaDe Co., Ltd., P.R. of China. A 20 W low pressure mercury lamp was placed in a 50 mm diameter quartz tube and emits spectrum mainly at 253.7 nm. The lamp and tube were then immersed in the photoreactor cell with a light path of 80 mm. The reaction temperature was kept by using a thermostatically controlled outer water jacket. A magnetic stirrer was positioned at the bottom of reactor.

2.3. Experimental procedures

Fenton oxidation 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 operation was performed by taking an appropriate amount stock dye solution followed by the addition of ferrous ion and dilution with de-ionized water to 250 mL. pH of the solutions was adjusted using HNO_3 and NaOH solutions and was measured by a pH meter (PHS-3C). With the addition of H_2O_2, Fenton reaction is initiated. Samples were taken out from the beaker periodically using a pipette and were immediately analyzed.

Photo-Fenton oxidation experiments were conducted in a photoreactor. Each experimental run was performed by taking an appropriate amount stock dye solution followed by the addition of ferrous ion and dilution with de-ionized water to 250 mL. pH of the solutions was adjusted using HNO_3 and NaOH solutions and was measured by a pH meter (PHS-3C). Photo-Fenton reaction is initiated when the UV lamp is turned on.

2.4. Analytical methods

The UV–Vis spectra of C.I. Acid Blue 9 were recorded from 200 to 800 nm using a UV–Vis spectrophotometer with a spectrometric quartz cell. The maximum absorbance wavelength of C.I. Acid Blue 9 was found at 625 nm. In the whole reaction process, it was found that the measure of concentration of C.I. Acid Blue 9 is not interfered by the degradation products. Therefore, the concentration of C.I. Acid Blue 9 in reaction mixture at different reaction times was determined by measuring the absorption intensity of solution at 618 nm 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 min [15].

The degradation efficiency of C.I. Acid Blue 9 was defined as follows:

$$\text{Degradation efficiency} = \left(1 - \frac{C_t}{C_0}\right) \times 100\% \qquad (11)$$

where C_0 is the initial concentration of C.I. Acid Blue 9, and C_t is the concentration of C.I. Acid Blue 9 at reaction time t (minute).

Total organic carbon (TOC) in the aqueous solution was analyzed with an OI-Analytical 1010 analyzer. The TOC removal ratio is defined as follows:

$$\text{TOC removal ratio} = \left(1 - \frac{\text{TOC}_t}{\text{TOC}_0}\right) \times 100\%, \qquad (12)$$

where TOC_t and TOC_0 are the TOC values at reaction time t and 0, respectively.

3. Results and discussion

3.1. Comparison of degradation efficiency

To evaluate the degradation efficiency by Fenton oxidation and photo-Fenton oxidation and the benefit of each condition on the dye degradation efficiency, the tests were carried out under the following conditions: (a) H_2O_2, (b) UV, (c) UV+Fe^{2+}, (d) UV+H_2O_2, (e) Fe^{2+}+H_2O_2 (Fenton oxidation), (f) UV+Fe^{2+}+H_2O_2 (photo-Fenton oxidation). The results of degradation efficiency under above conditions are shown in Fig. 2. The experimental conditions are [dye] = 0.1 mmol/L, [Fe^{2+}] = 0.15 mmol/L, [H_2O_2] = 0.70 mmol/L, temperature = 20°C, pH = 4.5, UV lamp = 20 W.

As it can be seen , C.I. Acid Blue 9 is resistant to the oxidation from H_2O_2 alone. UV alone can remove dye color but at lower percentage. For Fenton process and photo-Fenton process, it was observed that the degradation efficiency of dye was more than other experimental conditions. The ranking of degradation efficiency of C.I. Acid Blue 9 was in the order of photo-Fenton oxidation>Fenton oxidation>UV+H_2O_2>UV+Fe^{2+}>UV>H_2O_2. From Fig. 1, it also indicated that the azo dye C.I. Acid Blue 9 can be effectively decolorized using two methods with a litter difference, 97.7% and 98.12%, respectively, for optimal conditions. The high degradation efficiency of the azo dye C.I. Acid Blue 9 by Fenton oxidation and photo-Fenton oxidation is due to the formation of more hydroxyl radical than the other processes. With the combination of UV and H_2O_2, the chemical bonds of dye compounds can be directly photolyzed by UV irradiation, but this is a slow process that can be substantially improved in the presence of H_2O_2 [16]. Adding Fe^{2+} to UV radiation improves the action of the UV wavelength on the dye decolorization. It is able to find the reason from Eqs. (5) and (6).

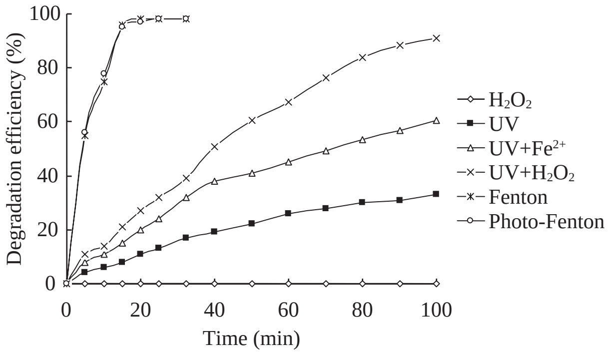

Fig. 2. Degradation efficiency of C.I. Acid Blue 9 under H_2O_2, UV, UV+Fe^{2+}, UV+ H_2O_2, Fenton oxidation and photo-Fenton oxidation respectively.

3.2. Effect of pH

The pH of the dye wastewater controls the production of hydroxyl free radical and the concentration of ferrous ions. Therefore, pH is an important parameter for Fenton and photo-Fenton processes. The effect of

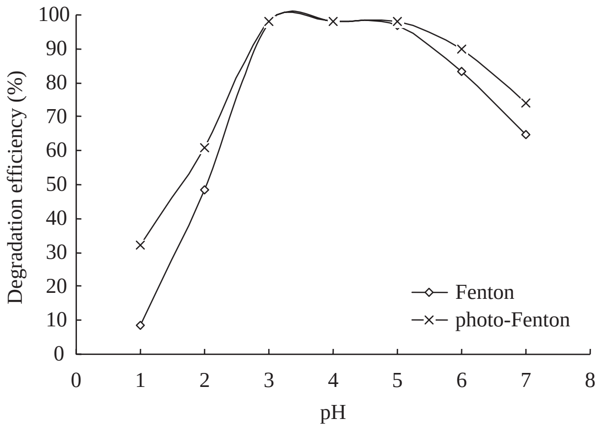

Fig. 3. Effect of pH on the degradation efficiency of C.I. Acid Blue 9 by Fenton and photo-Fenton process

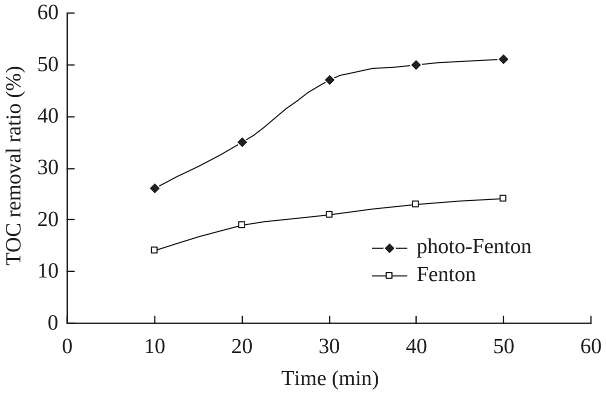

Fig. 4. A comparison of the TOC removal ratio of C.I. Acid Blue 9 by Fenton and photo-Fenton process.

initial pH on the treatment of dye solutions is shown in Fig. 3. The experimental conditions are [dye] = 0.1 mmol/L, $[Fe^{2+}] = 0.15$ mmol/L, $[H_2O_2] = 0.70$ mmol/L, temperature = 20°C, UV lamp = 20 W, reaction time = 50 min.

From Fig. 3, it indicates that pH significantly influences the degradation of C.I. Acid Blue 9. The optimum pH was found to be between 3.0 and 5.0 for the degradation of C.I. Acid Blue 9. It is in good agreement with early report [17]. At very low pH, the degradation efficiency was quite limited due to the hydroxyl free radical scavenging effects of H^+ ion [18]. When initial pH>5.0, the degradation efficiency rapidly decreased, not only by degradation of hydrogen peroxide but also by deactivation of a ferrous catalyst with the formation of ferric hydroxide complexes leading to a reduction of OH radical [19]. It is shown in Eq. (7).

$$^{\bullet}OH + H^+ + e^- \rightarrow H_2O \tag{7}$$

3.3. Mineralization study

It is known that reaction intermediates can form during the oxidation of the azo dye and some of them could be long-lived and even more toxic than their parent compounds. Therefore, it is necessary to understand the mineralization degree of the azo dye C.I. Acid Blue 9 to evaluate the degradation level applied by Fenton oxidation and photo-Fenton oxidation processes. Experimental conditions are [dye] = 0.1 mmol/L, $[H_2O_2] = 0.70$ mmol/L, $[Fe^{2+}] = 0.15$ mmol/L, temperature = 20°C, UV lamp = 20 W, pH = 4.5. TOC removal ratio of the azo dye C.I. Acid Blue 9 by Fenton oxidation and photo-Fenton oxidation processes is shown in Fig. 4.

From Fig. 4, it is evident that the TOC removal ratio in the photo-Fenton oxidation process is higher than Fenton oxidation process. It is possible to conclude that the UV is very useful to the mineralization removal. That is, although UV has little effect on dye degradation efficiency, it is particularly important in dye mineralization removal.

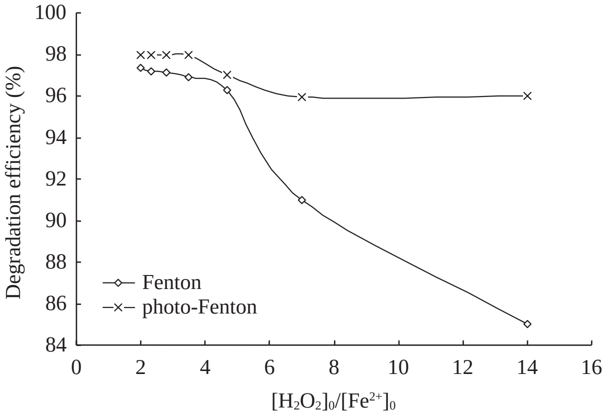

Fig. 5. Effect of initial $[H_2O_2]_0/[Fe^{2+}]_0$ ratio on dye degradation by Fenton and photo-Fenton processes.

3.4. Effect of relation $[H_2O_2]_0/[Fe^{2+}]_0$

To elucidate the role of initial concentration ratio of $[H_2O_2]_0/[Fe^{2+}]_0$ on the degradation of dye, a series of experiments were conducted with different $[Fe^{2+}]_0$ from 0.05 mM to 0.35 mM at fixed $[H_2O_2]_0 = 0.70$ mmol/L, $[Dye]_0 = 0.1$ mmol/L, temperature = 20°C, UV lamp = 20 W, reaction time = 50 min, pH = 4.5. Fig. 5 shows the effect of $[H_2O_2]_0/[Fe^{2+}]_0$ on the degradation of C.I. Acid Blue 9 by Fenton and photo-Fenton oxidation. The results indicated that the degradation of C.I. Acid Blue 9 is remarkably dependent on the initial $[H_2O_2]_0/[Fe^{2+}]_0$ ratio. At a low $[H_2O_2]_0/[Fe^{2+}]_0$ ratio, the degradation efficiency is high. The best ratio $[H_2O_2]_0/[Fe^{2+}]_0$ is from 2 to 3.5. This is because more $^{\bullet}OH$ radicals are produced with the increase of $[Fe^{2+}]$. The increase on the H_2O_2 dosage induces the OH scavenge, decreasing the oxidation effect. In the photo-Fenton process, this does not happen probably due to the UV that maintains the oxidation capacity.

3.5. Effect of relation $[H_2O_2]_0/[dye]_0$

To study the effect of initial concentration ratio $[H_2O_2]_0/[dye]_0$ on its degradation, the range 2–14 of the initial concentration ratio $[H_2O_2]_0/[dye]_0$ was investigated at fixed $[H_2O_2] = 0.70$ mmol/L, $[Fe^{2+}] = 0.15$ mmol/L, temperature = 20°C, UV lamp = 20 W, reaction time = 50 min, pH = 4.5. Fig. 6 shows the effect of initial $[H_2O_2]_0/[dye]_0$ ratio on dye degradation by Fenton and photo-Fenton processes. The results indicate that either for Fenton or for photo-Fenton processes, lower the $[H_2O_2]_0/[dye]_0$ ratio, lower is the

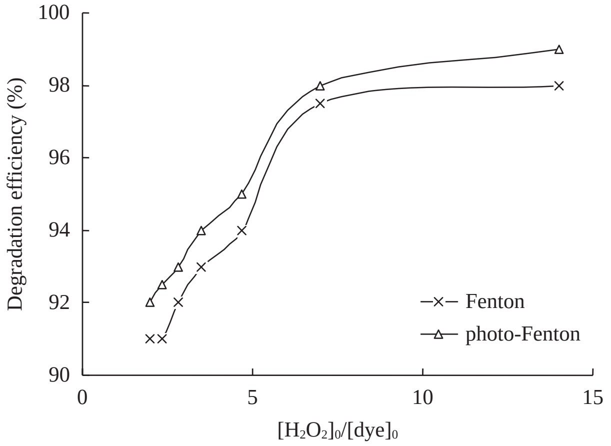

Fig. 6. Effect of initial $[H_2O_2]_0/[dye]_0$ ratio on dye degradation by Fenton and photo-Fenton processes.

degradation efficiency of C.I. Acid Blue 9. At the $[H_2O_2]_0/[dye]_0$ ratio of 7.0, the degradation efficiency is optimum. This is due to the fact that at higher H_2O_2 concentration, scavenging of OH radicals will occur increasing slowly the dye degradation.

4. Conclusions

Based on the results, the following conclusions can be drawn. pH is an important parameter for Fenton and photo-Fenton processes. The optimum pH was found to be between 3.0 and 5.0 for the degradation of C.I. Acid Blue 9 by Fenton and photo-Fenton processes. The azo dye C.I. Acid Blue 9 can be effectively decolorized using two methods with a litter difference, 97.7% and 98.12%, respectively, for optimal conditions. However, in the mineralization removal of C.I. Acid Blue 9, with photo-Fenton oxidation process there is a significant increasement relatively to Fenton oxidation process. That is, although UV has little effect on dye degradation, it is particularly important in dye mineralization removal. In addition, the effect of relation $[H_2O_2]_0/[Fe^{2+}]_0$ and $[H_2O_2]_0/[dye]_0$ were also investigated. The results showed that a ratio $[H_2O_2]_0/[Fe^{2+}]_0$ ranged from 2.0 to 3.5 and a ratio $[H_2O_2]_0/[dye]_0$ of 7.0 are optimal operational conditions by Fenton and photo-Fenton oxidation processes.

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