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Decolorization and mineralization of C.I. Acid Yellow 23 by Fenton and photo-Fenton processes

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Abstract

The degradation of azo dye C.I. Acid Yellow 23 (AY23) by Fenton and photo-Fenton processes was investigated. The degradation rate is strongly dependent on the pH, initial concentrations of the dye, Fe^{2+}, H_2O_2 and UV light intensity. The effect of these parameters has been studied and the optimum operational conditions of these two processes were found. The optimum conditions were obtained at $pH = 3$ for the H_2O_2/Fe^{2+} and $UV/H_2O_2/Fe^{2+}$ systems. The photo-Fenton process proved to be the most efficient and occurs at a much higher oxidation rate than Fenton process and allows achieving 90% degradation of aromatic content of AY23 in about 10 min of reaction time.

Keywords: Advanced oxidation processes (AOPs); Photo-Fenton; Fenton; C.I. Acid Yellow 23; Photooxidation; Decolorization

1. Introduction

Synthetic dyes are the major industrial pollutants and water contaminants [1,2]. Textile wastewater introduces intensive color and toxicity to aquatic systems [3] which is mostly non-biodegradable and resistant to destruction by physico-chemical treatment methods [4].

Due to the variability of the organic dyes and the resultant waste solution it is difficult to treat this kind of wastewater using traditional biochemical treatment process and coagulation treatment process is inadequate. 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 [5].

Advanced oxidation processes (AOPs) have attracted wide interests in wastewater treatment since the 1990s. In principle, AOPs are based on the generation of hydroxyl radicals in water, which are highly reactive and nonselective oxidants being able to oxidize organic compounds particularly unsaturated organic compounds such as azo dyes. Among AOPs, two of the most important processes to generate hydroxyl radicals are using the Fenton and photo-Fenton (Fe^{2+}/H_2O_2 and $Fe^{2+}/H_2O_2/UV$) systems [6].

Fenton's reagent, a mixture of ferrous (Fe^{2+}) ion and hydrogen peroxide which produces hydroxyl radicals (Eq. (1)), has been used extensively for oxidation of organic matter in water, and to reduce the chemical oxygen demand (COD) and total organic carbon (TOC) content [7]. Kang et al. [8] reported that the Fenton process could be adopted rapidly in a textile wastewater treatment system, without the need for reconstructing the existing coagulation unit. The only change in operating the process will be the addition of H_2O_2 and Fe^{2+} as well as pH adjustment. The use of Fe^{2+}/H_2O_2 as an oxidant for wastewater treatment is attractive since iron is highly abundant and non-toxic, and a 30% hydrogen peroxide aqueous solution is easy to handle and environmentally not harmful.

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

The rate of organic pollutant degradation could be increased by irradiation of Fenton with UV light (photo-Fenton process). UV light leads not only to the formation of additional hydroxyl radicals but also to recycling of ferrous catalyst by reduction of Fe^{3+}. In this way, the concentration of Fe^{2+} is increased and the overall reaction is accelerated. Among the AOPs, the oxidation using Fenton's reagent and photo-Fenton's reagent has been found to be a promising and attractive treatment method for the effective decolorization and degradation of dyes. Malik and Saha [5] reported that the removal rate is strongly dependent on the initial concentration of the dye, Fe^{2+} and H_2O_2. Muruganandham and Swaminathan [9] have carried out studies where similar results were obtained; they suggested a pH of 3 is the optimum pH for Fenton and photo-Fenton processes.

In the present study the optimal conditions of experimental parameters for the removal of AY23 have been determined which is extensively used in textile, foodstuff and pharmaceutical industries.

2. Experimental

2.1. Material

Acid Yellow 23 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 H_2SO_4 were products of Merck (Germany). Ferrous sulphate heptahydrate ($FeSO_4 \cdot 7H_2O$) used as a source of Fe^{2+} was purchased from Fluka (Switzerland).

2.2. Procedures

2.2.1. Fenton process

The experiments were carried out in a batch mode. Dye solution of 40 $mg\,l^{-1}$ was adjusted to $pH = 3.0 \pm 0.1$ using 1 N NaOH or 1 N H_2SO_4. A known amount of H_2O_2 and $FeSO_4$ were added to 500 ml of the solution. A magnetic stirrer provided continuous mixing.

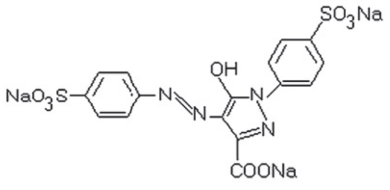
Name	Chemical Structure	λ_{max}(nm)
C.I. Acid Yellow 23		428

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

2.2.2. Photo-Fenton process

All experiments were carried out in a batch photoreactor. The radiation source was a low pressure mercury UV lamp (30 W, UV–C, $\lambda_{max} = 254$ nm, manufactured by Philips, Holland), which was placed above a batch photoreactor of 0.5 L volume. The incident UV light intensity was measured by a Lux-UV–IR meter (Leybold Co.). In each experiment, a known amount of H_2O_2 and $FeSO_4$ were added to 500 ml of the solution and a magnetic stirrer was used in order to achieve a homogeneous mixture.

2.3. Analytical methods

The pH of the solution was measured by using METTLER TOLEDO (MP 220) digital pH meter. Sample solutions were withdrawn at certain time intervals for spectrophotometric analysis. The decolorization and mineralization of AY23 were measured with UV–vis spectrophotometer (Ultrospec 2000, Biotech Pharmacia, England) at 428 and 254 nm. Calibration plot based on Beer–Lambert's law was established by relating the absorbance to the concentration. The absorbance at 428 nm is due to the color of the dye solution and it is used to monitor the decolorization of the dye. The absorbance at 254 nm represents the aromatic content of AY23 and absorbance decrease at 254 nm indicates the degradation of the aromatic part of the dye. Mineralization was monitored by chemical oxygen demand (COD) measurement. COD was measured by the dichromate reflux method. The effect of each parameter was studied by fixing the values of other parameters.

3. Results and discussion

3.1. Effect of pH

The pH value affects the oxidation of organic substances both directly and indirectly. The Fenton and photo-Fenton reactions are strongly pH dependent. The pH value influences the generation of hydroxyl radicals and thus the oxidation efficiency. Figs. 2 and 3 show the effect of the initial pH value during the use of the Fenton and photo-Fenton processes. A maximum decolorization of 97.4% at 20 min was obtained in Fe^{2+}/H_2O_2 process at pH = 3 and decolorization of

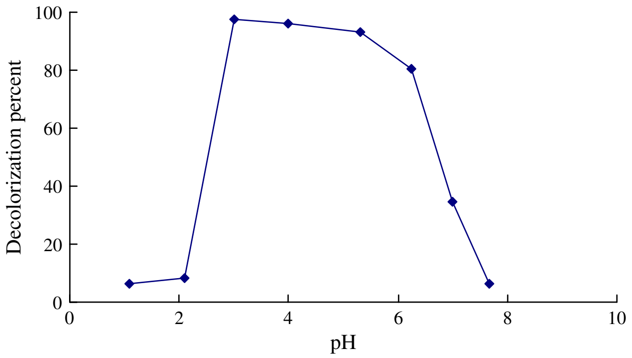


Fig. 2. Effect of pH on the decolorization of AY23 by Fenton process. $[AY23]_0 = 40\ mg\,l^{-1}$, $[H_2O_2]_0 = 500\ mg\,l^{-1}$, $[Fe^{2+}]_0 = 0.07$ mmol.

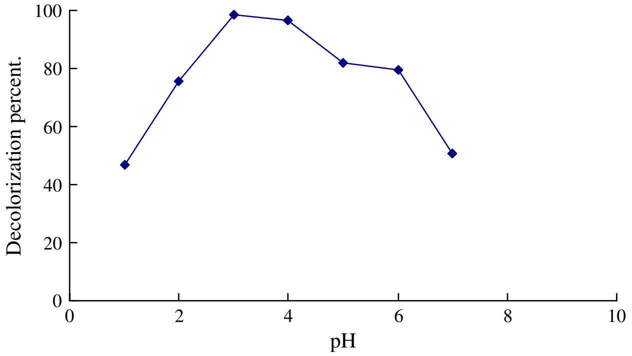


Fig. 3. Effect of pH on the decolorization of AY23 by photo-Fenton process. $[AY23]_0 = 40$ mg l^{-1}, $[H_2O_2]_0 = 500$ mg l^{-1}, $[Fe^{2+}]_0 = 0.05$ mmol, $I_0 = 30.3$ W m^{-2}.

99.68% at 5 min was obtained in UV/Fe^{2+}/H_2O_2 process at the same pH value. It can be seen from Figs. 2 and 3 that the removal efficiency increases from 6.3% to 97.4% in Fenton process after 20 min and from 47.03% to 98.68% in photo-Fenton process after 5 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% and 98.68% to 50.85% for Fenton and photo-Fenton processes, respectively. These results are in agreement with those reported in previous studies [10]. At a pH above 4, the decolorization strongly decreases because iron starts to precipitate as hydroxide. Additionally, the oxidation potential of hydroxyl radical was known to decrease with increasing pH and at a pH below 2, hydrogen peroxide can stay stable, probably solvating a proton to form an axonium ion (H_3O^+). An axonium ion makes hydrogen peroxide electrophilic to enhance its stability and presumably to reduce substantially the reactivity with ferrous ion [11,12]. Therefore, the amount of hydroxyl radicals would decrease and as a result the removal efficiency decreases.

3.2. Effect of the initial H_2O_2 concentration

Figs. 4 and 5 show the relationship between decolorization percentage of the dye and initial concentration of H_2O_2 for Fenton and photo-Fenton processes, respectively. The results indicate that the decolorization of AY23 was increased by increasing the concentration of H_2O_2. This can be explained by the effect of the additionally produced hydroxyl radicals. With increasing H_2O_2 concentration from 50 mg l^{-1} to 500 mg l^{-1} for Fenton process and 700 mg l^{-1} for photo-Fenton process, the decolorization percentage increases but above these ranges improvement was not obvious. This may be due to recombination of hydroxyl radicals and also hydroxyl radicals reaction with H_2O_2, contributing to the $^{\bullet}OH$ scavenging capacity (Eqs. (2)–(4)) [11].

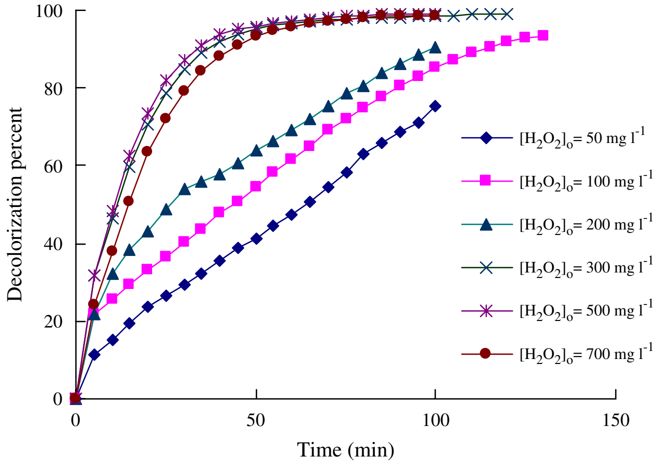


Fig. 4. Effect of the initial concentration of H_2O_2 in Fenton process. $[AY23]_0 = 40$ mg l^{-1}, $[Fe^{2+}]_0 = 0.05$ mmol, pH = 3.

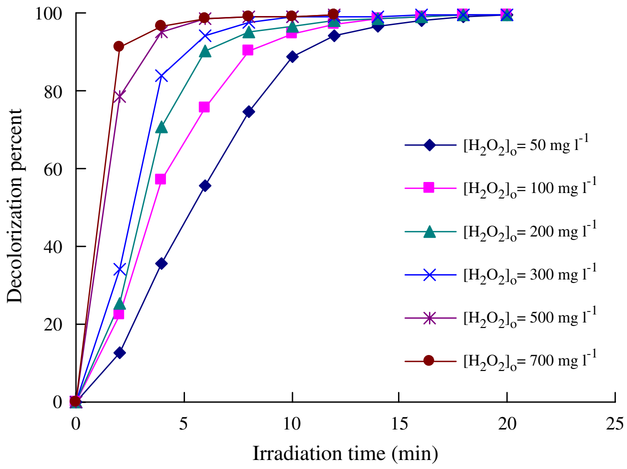


Fig. 5. Effect of the initial concentration of H_2O_2 in photo-Fenton process. $[AY23]_0 = 40$ mg l^{-1}, $[Fe^{2+}]_0 = 0.05$ mmol, pH = 3, $I_0 = 30.3$ W m^{-2}.

$$H_2O_2 + {}^{\bullet}OH \rightarrow H_2O + HO_2^{\bullet} \tag{2}$$

$$HO_2^{\bullet} + {}^{\bullet}OH \rightarrow H_2O + O_2 \tag{3}$$

$$^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2 \tag{4}$$

It can be postulated that H_2O_2 should be added at an optimum concentration to achieve the best degradation; hence 500 mg l^{-1} and 700 mg l^{-1} of H_2O_2 concentrations appear to be an optimum dosage for 40 mg l^{-1} of AY23 in Fenton and photo-Fenton processes, respectively.

3.3. Effect of Fe^{2+} concentration

Iron in its ferrous and ferric forms acts as a photo-catalyst and requires a working pH below 4.0 [13]. Amount of ferrous ion is one of the main parameters to influence the Fenton and photo-Fenton processes. In this study, various concentrations of Fe^{2+} were applied to obtain its optimal original concentration. The results for Fenton and photo-Fenton processes are shown in Figs. 6 and 7.

From the experimental results shown in Figs. 6 and 7 it can be seen that decolorization rate of AY23 distinctly increased with the increasing amount of Fe^{2+}. Addition of Fe^{2+} above 0.1 mmol in this process did not affect the decolorization rate. The decolorization percentage of AY23 began to decrease when the concentration of Fe^{2+} was higher than 0.1 mmol. It is known that Fe^{2+} had a catalytic decomposition effect on

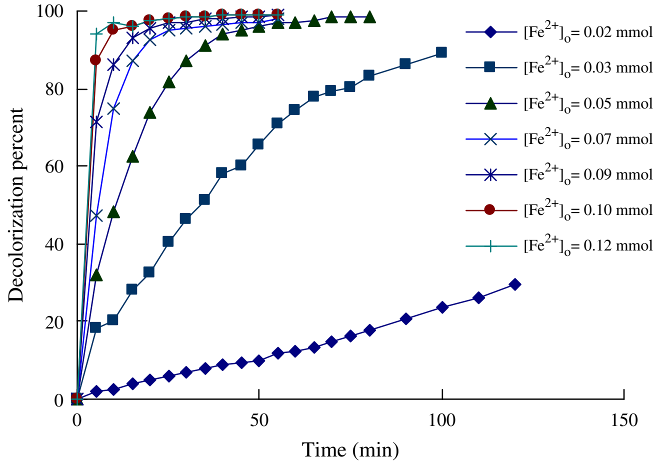


Fig. 6. Effect of the initial concentration of Fe^{2+} in Fenton process. $[AY23]_0 = 40\ mg\ l^{-1}$, $[H_2O_2]_0 = 500\ mg\ l^{-1}$, pH = 3.

H_2O_2. When Fe^{2+} concentration is increased, the catalytic effect also accordingly increases and when its concentration was higher, a great amount of Fe^{3+} was produced. Fe^{3+} undergoes a reaction with hydroxyl ions to form $Fe(OH)^{2+}$ which has strong absorption and as a result the strength of UV light would decrease (Eqs. (5)–(7)) [10,12].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{-}OH + {}^{\bullet}OH \tag{5}$$

$$Fe^{3+} + {}^{-}OH \rightarrow Fe(OH)^{2+} \leftrightarrow Fe^{2+} + {}^{\bullet}OH \tag{6}$$

$$Fe(OH)^{2+} + h\nu \rightarrow {}^{\bullet}OH + Fe^{2+} \tag{7}$$

3.4. Effect of the UV light intensity

The effect of UV light intensity on the decolorization of AY23 in photo-Fenton process was investigated by varying the UV light intensity from $8.6\ W\ m^{-2}$ to $45.3\ W\ m^{-2}$ and is depicted in Fig. 8. Within 2 min of increasing UV light intensity from $8.6\ W\ m^{-2}$ to $45.3\ W\ m^{-2}$ the decolorization increases from 57.34% to 96%. In this process UV light intensity is mainly used for photolysis of H_2O_2 and photo reduction of ferric ion to ferrous ion [9]. The enhancement of removal is due to the increase in hydroxyl radical formation. The rate of photolysis of H_2O_2 depends directly on the incident light intensity. At low UV light intensity the photolysis of H_2O_2 is limited, but at high UV light intensity more hydroxyl radicals are produced upon photodissociation of H_2O_2, hence removal rate increases.

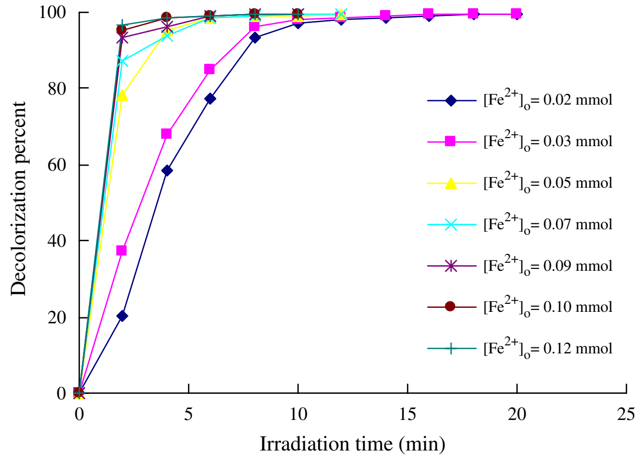


Fig. 7. Effect of the initial concentration of Fe^{2+} in photo-Fenton process. $[AY23]_0 = 40\ mg\ l^{-1}$, $[H_2O_2]_0 = 500\ mg\ l^{-1}$, pH = 3, $I_0 = 30.3\ W\ m^{-2}$.

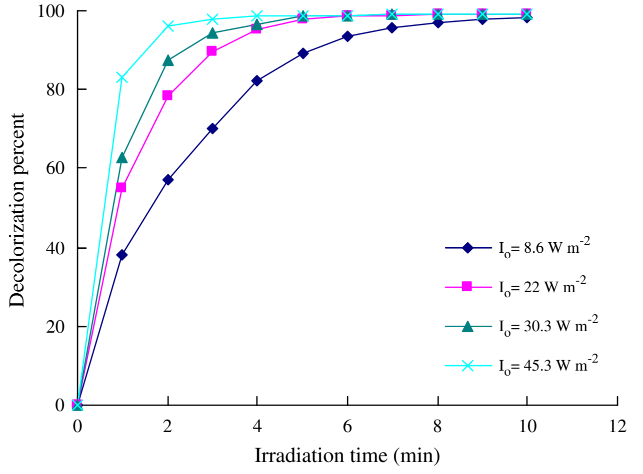


Fig. 8. Effect of UV light intensity in photo-Fenton process. $[AY23]_0 = 40\ mg\ l^{-1}$, $[H_2O_2]_0 = 500\ mg\ l^{-1}$, $[Fe^{2+}]_0 = 0.05$ mmol, pH = 3.

3.5. Effect of initial AY23 concentration

It is important from an application point of view to study the dependence of removal efficiency on the initial concentration of the dye. Therefore, the effect of dye concentration on the decolorization efficiency was investigated at different concentrations of AY23 and presented in Figs. 9 and 10. For

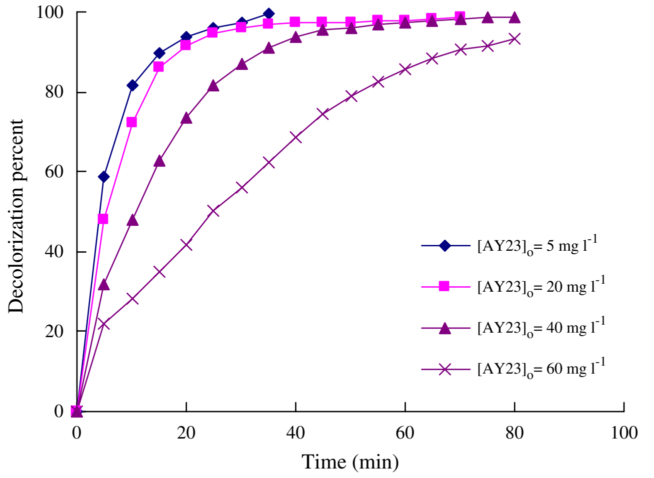


Fig. 9. Effect of the initial concentration of AY23 in Fenton process. $[H_2O_2]_0 = 500\ mg\ l^{-1}$, $[Fe^{2+}]_0 = 0.05$ mmol, pH = 3.

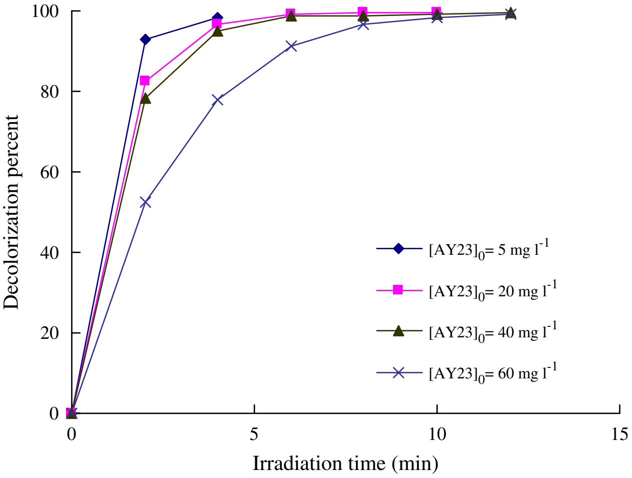


Fig. 10. Effect of the initial concentration of AY23 in photo-Fenton process. $[H_2O_2]_0 = 500\ mg\ l^{-1}$, $[Fe^{2+}]_0 = 0.05$ mmol, pH = 3, $I_0 = 30.3\ W\ m^{-2}$.

Fenton and photo-Fenton processes it was observed that the decolorization decreases with increasing the initial concentration of the dye. The presumed reason is that when the initial concentration of the dye is increased, the hydroxyl radical concentrations remain constant for all dye molecules and hence the removal rate decreases. Once the concentration of the dye is increased, it also causes the dye molecules to absorb light and photons never reach the photo-catalyst surface, thus the photodegradation efficiency decreases [4].

3.6. Effect of NaCl

Our study also examined the effect of NaCl which is generally found in textile waste stream, on the decolorization of AY23. In the absence of salt, the dye decolorization was 97% in less than 60 min and 10 min for Fenton and photo-Fenton processes, respectively. The addition of NaCl ($250\ mg\ l^{-1}$) to the dye solution caused only a 2% decrease in decolorization percentage. Addition of NaCl does not affect the removal rate significantly. The small decrease in the removal efficiency is due to the scavenging effect of chloride ion (Eqs. (8) and (9)) [3], and also increasing the amount of the salt did not reduce the decolorization rate considerably.

$$Cl^- + {}^{\bullet}OH \rightarrow HOCl^{\bullet -} \tag{8}$$

$$HOCl^{\bullet -} + H^+ \rightarrow {}^{\bullet}Cl + H_2O \tag{9}$$

3.7. Degradation of aromatic content and mineralization of AY23

Decolorization of the dye does not mean that it has been completely oxidized into CO_2 and H_2O. This is because in most cases, reaction intermediates are formed in solution during the degradation of the dye. In our case adjacent aromatic ring structure is one of the intermediates. Some of them are long-lived and can be more toxic than the original dye to aquatic life as reported by many researchers [6]. Therefore, in this study after the optimum operating conditions such as pH, initial concentration of the dye, Fe^{2+}, H_2O_2 and UV light intensity were found, the degradation of aromatic content and mineralization of AY23 were investigated. The experimental results in Fig. 11 showed that the degradation percentage of aromatic content of AY23 in the photo-Fenton process occurs at a much higher oxidation rate than Fenton process and allows achieving 90% degradation in about 10 min of reaction time. In addition, it is also found that decolorization of azo dye undergoes a faster reaction rate than aromatic content degradation.

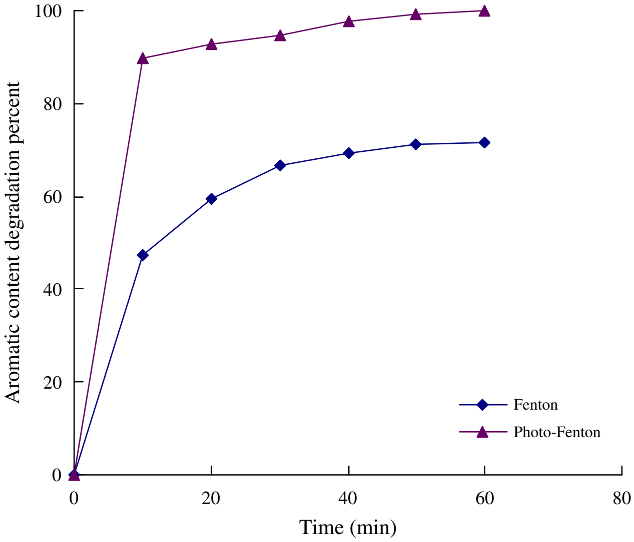


Fig. 11. Aromatic content degradation for Fenton and photo-Fenton processes. $[AY23]_0 = 40\ mg\ l^{-1}$, $[H_2O_2]_0 = 500\ mg\ l^{-1}$, $[Fe^{2+}]_0 = 0.05$ mmol, pH = 3, $I_0 = 30.3\ W\ m^{-2}$.

COD values have been related to the total concentration of organics in the solution and the decrease of COD reflects the degree of mineralization. It is important to measure the COD of the dye solution after the oxidative degradation in order to verify whether the dye is actually mineralized. The experiments for photo-Fenton process showed that 94.3% reduction of COD occurred for 60 min of irradiation time. Fig. 12 shows three decreasing trends of COD, decolorization and aromatic content degradation as the photo-Fenton oxidation proceeds. It appears that the photo-Fenton process is more beneficial for decolorization rather than for degradation and COD removal. These results show that the measurement of 254 nm absorbance cannot exactly reflect the actual content of the solution.

4. Conclusions

The results showed that Fenton and photo-Fenton processes are powerful methods for decolorization of AY23, but photo-Fenton process is more efficient. The results indicate that the degree of decolorization of AY23 was obviously affected by the initial concentration of the dye, Fe^{2+}, H_2O_2, and value of pH. The optimum conditions for the decolorization of

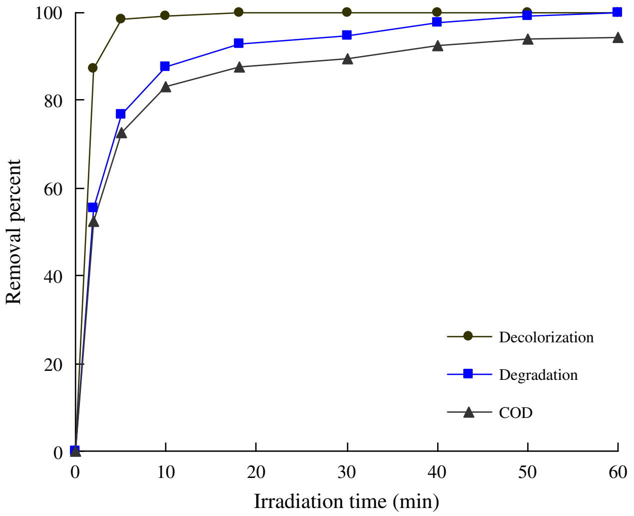


Fig. 12. Removal percentage of COD, decolorization and degradation for photo-Fenton process. $[AY23]_0 = 40\ mg\ l^{-1}$, $[H_2O_2]_0 = 500\ mg\ l^{-1}$, $[Fe^{2+}]_0 = 0.05$ mmol, pH = 3, $I_0 = 30.3\ W\ m^{-2}$.

AY23 in Fenton and photo-Fenton processes were observed at pH = 3.0, with an initial Fe^{2+} concentration of 0.1 mmol and an initial H_2O_2 concentration of $500\ mg\ l^{-1}$ for Fenton process and $700\ mg\ l^{-1}$ for photo-Fenton process with a dye concentration of $40\ mg\ l^{-1}$.

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