



Effective degradation of C.I. Acid Red 73 by advanced Fenton process

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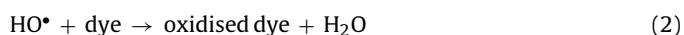
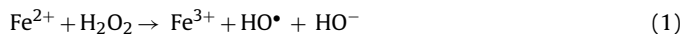
ABSTRACT

The degradation of C.I. Acid Red 73 (AR 73) was investigated by advanced Fenton process based on zero-valent iron and hydrogen peroxide. The effect of zero-valent iron dosage, hydrogen peroxide concentration, initial pH, initial dye concentration, mixing rate and temperature on the degradation of AR 73 was studied. The results showed that AR 73 removal efficiency increased with the increase of zero-valent iron addition, hydrogen peroxide concentration, mixing rate and temperature, but decreased with the increase of initial pH value. The residual concentration of AR 73 was only 6.4 mg/L after 30 min treatment at optimum conditions for 200.0 mg/L AR 73 initial concentration. And advanced Fenton process can partly remove COD values of AR 73. The activation energy of the degradation reaction is 31.98 kJ/mol.

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1. Introduction

Dyes are the important sources of water pollution and their degradation products may be carcinogens and toxic to mammals [1]. About a half of global production of synthetic textile dyes (7×10^5 t per year) are classified into azo compounds that have the chromophore of $-N=N-$ unit in their molecular structure [2]. Various treatment methods, such as coagulation and flocculation [3], adsorption [4], electrochemical treatment [5], advanced oxidation processes (AOPs) [6,7], etc. have been investigated to remove azo dyes from the wastewater. Among these technologies, AOPs are successfully applied for the treatment of dye wastewater. Among the AOPs, Fenton process is particularly attractive and effective to degrade a wide range of azo dyes [8,9]. The classical Fenton process is characterized by the reaction of aqueous ferrous ions with hydrogen peroxide to generate hydroxyl radicals which can oxidise organic pollutants (such as dye) in solution.



In Fenton process, ferrous ions and hydrogen peroxide are added and huge quantities of ferric salts need to be disposed of after Fenton reaction is complete [10].

Recently, a great deal of interest has developed in the degradation of azo dyes by zero-valent iron (ZVI) [11,12]. The merits of ZVI for dye decolorization are low toxicity, low cost, easy operation, low

iron concentration in effluent and no further treatment demand. In acidic conditions, the surface of the ZVI corrodes and generates in situ ferrous ions, which can lead to Fenton reactions in the presence of hydrogen peroxide (Eq. (3), (1) and (2)). The ZVI surface can then reduce the ferric ions down to ferrous ions (Eq. (4)). This process is named as advanced Fenton process (AFP) [13]. AFP has several advantages over conventional Fenton's process. Firstly, the implementation of ZVI instead of iron salts results in the avoidance of unnecessary loading of aquatic system with counter anions [14]. Secondly, the concentration of ferrous and ferric ions in wastewater treated by AFP is significantly lower in comparison to the classical Fenton's process that utilizes iron salts [15]. Thirdly, the faster recycling of ferric iron at the iron surface occurs through the Eq. (4) [16].



There are some reports on AFP combined with other techniques to degrade azo dye, such as photo degradation [17] and ultrasonic irradiation [18]. However, the degradation of azo dye by AFP alone is scarce. Therefore, in this study, an azo dye, Acid Red 73 (AR 73), was first selected as the model dye to test the treatment efficiency of AFP. The effects of operating conditions, such as ZVI dosage, initial concentrations of hydrogen peroxide and dye, initial pH, mixing rate and temperature on AR 73 degradation were investigated. The degradation of AR 73 in terms of COD removal was also explored. The goal was to use these results to gain insight into the mechanism of the reaction between AR 73 and AFP. Findings of this study will be useful in treating azo dye wastewater.

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Nomenclature

ZVI	zero-valent iron
AR 73	Acid Red 73
C.I.	Color Index
AOPs	advanced oxidation processes
AFP	advanced Fenton process
C_0	the initial concentration of AR 73 (mg/L)
C_t	the concentration of dye at time t (mg/L)
k_1	the pseudo first order rate constant (min^{-1})
t	the time of reaction (min)
E_a	Arrhenius activation energy (kJ/mol)
A_0	the Arrhenius factor
R	the gas constant (8.314J/(mol K))
T	the solution temperature (T)

2. Material and methods

2.1. Materials

AR 73 was obtained from China Dyestuffs Chemicals and directly used without further purification. The characteristics and chemical structure of AR 73 are shown in Table 1 and Fig. 1, respectively. The ZVI (analytical grade, 99% purity, 200 meshes) was obtained from Tianjin Fuchen Chemical reagents factory. Other reagents used were of analytical grade.

2.2. Analytical apparatus and methods

The pH values of the solution were determined using a PHS-25 digital-display pH meter (Shanghai Weiye Instrument Factory, China). The dye solution in bottles is mixed in a water-bathing constant temperature vibrator (Jintan Fuhua Instrument Co., Ltd., China). The residual dye concentration was determined by a 3101PC spectrophotometer at the maximum absorbance wavelength (509 nm) of AR 73. COD was determined by the closed reflux titrimetric method (Standard Methods 5520C) with dichromate solution as the oxidant in strong acid media, according to Standard Methods for Examination of Water and Wastewater [19].

2.3. Batch decolorization experiments

According to other decolorization experiments by ZVI [12,18], the batch decolorization experiments are designed as follows. A

Table 1
Characteristics of AR 73.

Azo dye	C.I. Acid Red 73
Formula	$\text{C}_{22}\text{H}_{14}\text{N}_4\text{Na}_2\text{O}_7\text{S}_2$
λ_{max} (nm)	509
MW (g mol^{-1})	556.49
C.I.	27,290

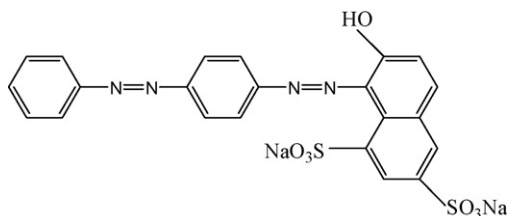


Fig. 1. Chemical structure of AR 73.

series of 500 mL conical flasks with plane bottom containing 200 mL 200.0 mg/L AR 73 solution was prepared. Various amounts of ZVI and H_2O_2 were added into these flasks to yield solid/liquid ratios of 0, 0.1, 0.2, 0.3 and 0.4 g/L, or H_2O_2 concentration of 0, 1.0, 2.0, 2.5 and 3.0 mM. The pH values were adjusted to the desired levels from pH 2.0 to 5.0 using H_2SO_4 (0.5 M) or NaOH (0.5 M). The dyes in flasks were mixed in the water-bathing constant temperature vibrator at a speed of 100 rpm and temperature of $20 \pm 2^\circ\text{C}$. At preselected time intervals, samples were withdrawn and filtrated through a $0.45 \mu\text{m}$ membrane filter immediately, and then the supernatant was analyzed. The dye concentration was quantified based on sample absorbance using a 3101PC spectrophotometer and previously prepared calibration curves according to the Lambert–Beer's law. Throughout the whole process, pH values were not readjusted and no buffer solution was added. The following parameters, concentrations of ZVI and hydrogen peroxide, solution pH, mixing rate and temperature, were evaluated. The initial AR 73 concentration for all assays was 200.0 mg/L, except for the assays which tested the effect of the initial AR 73 concentration on the decolorization.

3. Results and discussion

3.1. Effect of ZVI dosage on the decolorization of AR 73

In order to investigate the effect of ZVI addition on dye decolorization, five different iron powder additions (0, 0.1, 0.2, 0.3 and 0.4 g/L) were tested when H_2O_2 concentration was 2 mM at initial pH 3.0. As can be seen from Fig. 2, the residual concentration decreased promptly at the first 15 min, and then nearly unchanged from 15 to 30 min. So in the next operation in AFP, 30 min was selected as reaction time. The residual concentration was 181.6 mg/L after 30 min when ZVI concentration was 0 g/L, i.e., only 9.2% color was removed when H_2O_2 alone was used. The addition of iron powder would improve color removal efficiently in the presence of H_2O_2 and the residual AR 73 concentration significantly decreased with the increase of ZVI dosage. After 30 min, the residual concentration of AR 73 was 9.0, 6.5, 6.4 and 5.9 mg/L at ZVI concentration of 0.1, 0.2, 0.3 and 0.4 g/L. It is because that more dosage of ZVI provides substantially more surface active sites to accelerate the initial reaction resulting in more iron ions collided with azo dye molecules to remove color. However, the decolorization efficiency would increase less when iron powder addition was higher than 0.3 g/L. To save the ZVI dosage, 0.3 g/L ZVI dosage was selected in

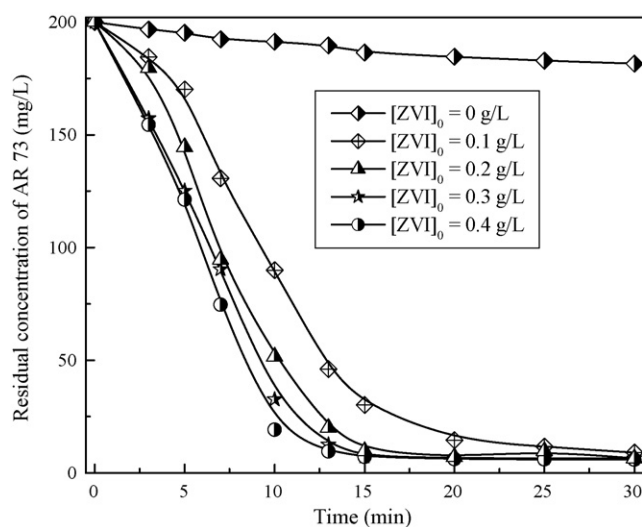
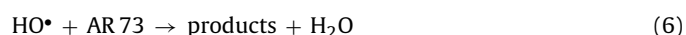
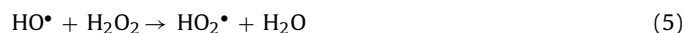


Fig. 2. Effect of ZVI dosage on the residual concentration of AR 73 ($C_0 = 200.0 \text{ mg/L}$, $[\text{H}_2\text{O}_2]_0 = 2.0 \text{ mM}$, mixing rate = 100 rpm, $T = 20 \pm 2^\circ\text{C}$, pH 3.0).

the next experiments. And as illustrated in Fig. 2, despite different decolorization efficiency was achieved at different ZVI addition, the residual concentration was nearly the same after 30 min as a result of the same hydrogen peroxide concentration.

3.2. Effect of initial H_2O_2 concentration on the decolorization of AR 73

Fig. 3 displays decolorization of AR 73 at different H_2O_2 concentrations when ZVI addition is 0.3 g/L at initial pH value 3.0. ZVI could not effectively decolorize AR 73 in the absence of hydrogen peroxide. When hydrogen peroxide concentration increased from 0 to 2.5 mM, AR 73 concentration decreased rapidly in the initial period of the reaction, and then it would slow down and level off. It is because ZVI was dissolved in acid solution producing ferrous ions, the ferrous ions would react with hydrogen peroxide to generate hydroxyl radicals. And the generation of hydroxyl radicals was dependent on hydrogen peroxide concentration. Consequently, the residual concentration decreased with the increase of hydrogen peroxide concentration. However, when hydrogen peroxide concentration increased from 2.5 to 3.0 mM, the AR 73 concentration was almost unchanged. This is possibly due to the competition between hydrogen peroxide and AR 73 for hydroxyl radicals [20] (Eq. (5) and (6)).



3.3. Effect of initial solution pH values on the decolorization of AR 73

The actual dye wastewater has a wide range of initial pH values, and the solution pH is an important operating parameter affecting AR 73 removal efficiency in AFP. The surface of ZVI generates Fe^{2+} in solutions in acid conditions, which is presented as Eq. (3). According to Nernst equation, the reduction potential for Fe^{2+}/Fe decreases with a decrease of the H^+ concentration and thus the initial pH values can affect the degradation of AR 73 in AFP.

The effect of pH value on the AR 73 decolorization was assessed at four initial pH values, 2.0, 3.0, 4.0 and 5.0 (Fig. 4). After reaction, the final pH values were 2.01, 3.03, 4.20 and 6.04, respectively. From Fig. 4, solution initial pH value remarkably influenced the color removal. The residual concentration of AR 73 was much lower at

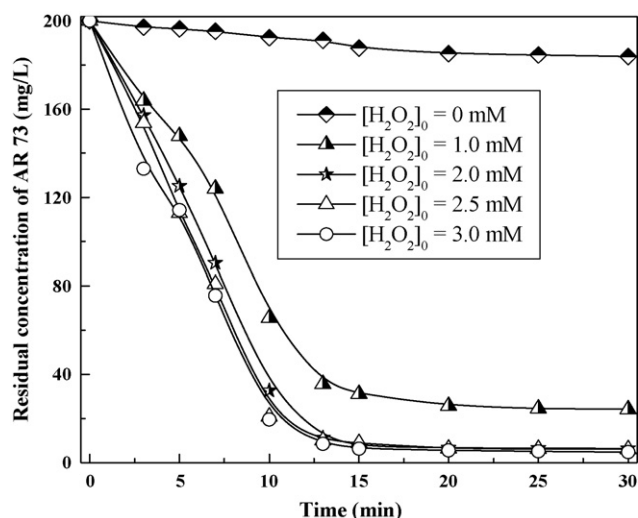


Fig. 3. Effect of H_2O_2 concentration on the decolorization of AR 73 ($C_0 = 200.0$ mg/L, $[ZVI]_0 = 0.3$ g/L, mixing rate = 100 rpm, $T = 20 \pm 2^\circ C$ at initial pH 3.0).

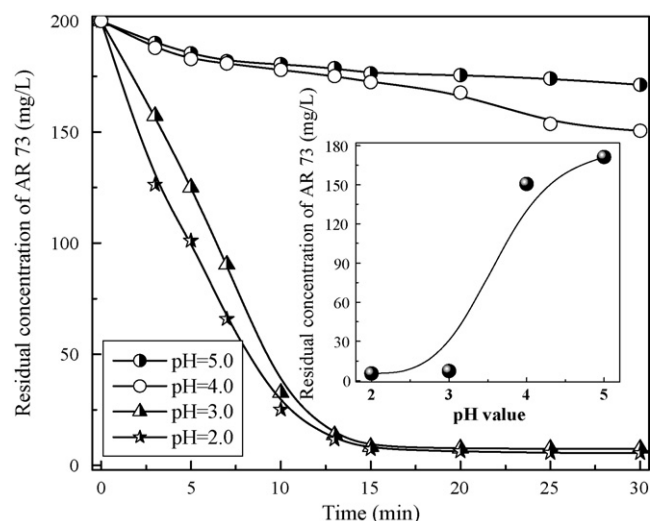


Fig. 4. Effect of initial pH value on the residual concentration of AR 73 ($C_0 = 200.0$ mg/L, $[ZVI]_0 = 0.3$ g/L, $[H_2O_2]_0 = 2.0$ mM, mixing rate = 100 rpm and $T = 20 \pm 2^\circ C$). Inset: relationship of pH value and residual AR 73 concentration at 30 min.

initial solution pH of 2.0 and 3.0 compared to pH of 4.0 and 5.0. When pH was 3, the residual concentration was only 6.4 mg/L after 30 min treatment. However, when pH rose to 5.0, the residual concentration was 171.3 mg/L after 30 min. This happens because ZVI is easily dissolved in acid conditions and hence produces Fe^{2+} ions, and the produced ferrous ions react with hydrogen peroxide to generate hydroxyl radicals. With pH values increased, in the presence of hydroxyl ions, Fe^{2+} ions originating from the ZVI can form ferrous hydroxide precipitates on the surface of ZVI, occupying the reactive sites and thus hindering the reaction process. And the results agree with previous reports on the ZVI transformation of dyes [17,18]. Therefore optimized pH value for conducting the AFP experiments is found to be 3.0.

3.4. Effect of initial dye concentrations on the decolorization of AR 73

Initial concentration of dyes is an important parameter in practical application. The effects of initial dye concentrations (100.0, 200.0 and 300.0 mg/L) on decolorization efficiencies of AR 73 were evaluated at 2.0 mM H_2O_2 and 0.3 g/L ZVI at pH 3.0. Color removal is generally assumed to be a first order reaction with respect to dye concentration by AFP, assuming HO^\bullet concentration to remain constant due to the hypothesis of a pseudo steady-state concentration of hydroxyl radicals [20]. The differential equation can be presented as follows [21,22]:

$$\frac{dC_t}{dt} = -k_1 C_t \quad (7)$$

and the following equation can be obtained [23]

$$C_t = C_0 e^{-k_1 t} \quad (8)$$

where C_t is the concentration of dye at time t (mg/L), C_0 is the initial concentration (mg/L), k_1 is the pseudo first order rate constant (min^{-1}), and t is the time of reaction (min).

As the initial dye concentration increases from 100.0 to 300.0 mg/L, the rate constant decreases from 0.1571 to 0.0765 min^{-1} . As also shown in Fig. 5, the color removal efficiency gradually decreased with an increase in the initial concentration. After 30 min reaction time, the color removal percentage was 97.0%, 96.8% and 89.8% at initial dye concentrations of 100.0, 200.0 and 300.0 mg/L, respectively. This is due to non-availability of

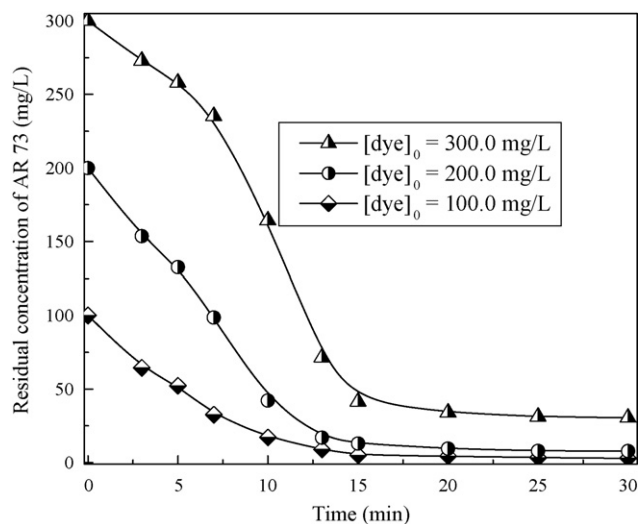


Fig. 5. Effect of initial concentration on AR 73 residual concentration in AFP ($[ZVI]_0 = 0.3$ g/L, $[H_2O_2]_0 = 2.0$ mM, mixing rate = 100 rpm, $T = 20 \pm 2$ °C at pH 3.0).

sufficient number of hydroxyl radicals. The presumed reason is that when the initial concentration of AR 73 is increased, the HO^\bullet concentration is not increased correspondingly. At the concentration of 100.0 mg/L, the generated HO^\bullet was not exhausted. And at 300.0 mg/L, HO^\bullet became exhausted. However, the results in Fig. 5 also show that under the present experimental conditions, the higher the concentration, the more the dye decolorized in 30 min (according to $C_0 \times$ decolorization efficiency). This happens because increase in concentration enhances the interaction between the dye and HO^\bullet .

3.5. Effect of mixing rate on the decolorization of AR 73

In order to evaluate the effect of mixing rate on the AR 73 decolorization in AFP, a series of decolorization assays were conducted with a vibrator at the mixing rates of 0 (without agitation), 25, 60, 100 and 140 rpm. Fig. 6 shows that as the mixing rate increased, the AR 73 residual concentration obviously decreased, i.e. the AR 73 decolorization efficiency increases with increasing mixing rate. For the experiment conducted without agitation, it is noticed a high residual AR 73 concentration, 166.3 mg/L. The residual concentra-

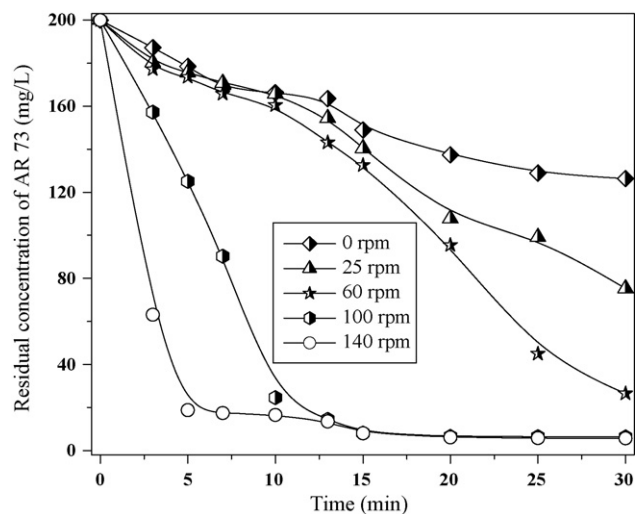


Fig. 6. Effect of mixing rate (rpm) on the AR 73 residual concentration ($C_0 = 200.0$ mg/L, $[ZVI]_0 = 0.3$ g/L, $[H_2O_2]_0 = 2.0$ mM, $T = 20 \pm 2$ °C at pH 3.0).

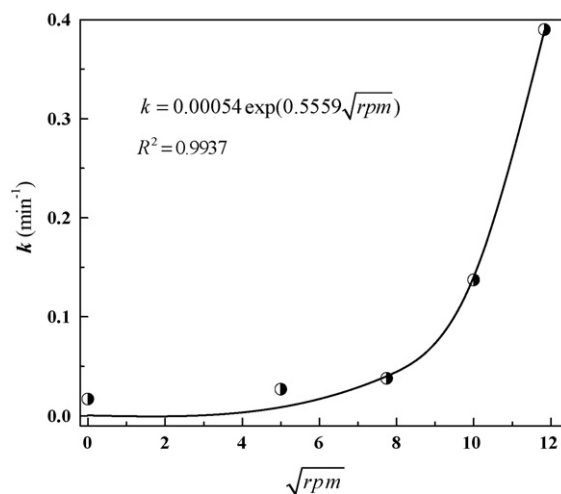


Fig. 7. Non-linear regression fit of rate constant data as a function of the square root of mixing rate (rpm).

tion decreases with the increase of the mixing rate. For example, at 10 min, the residual concentration of AR 73 was 165.8, 160.4, 24.7 and 16.5 mg/L with the mixing rate of 25, 60, 100 and 140 rpm, respectively.

Many studies have concluded that ZVI transformation reactions are mass transfer limited [24]. A criterion for whether or not the process is mass transfer limited is the dependence of the reaction rate constant on the mixing rate [25]. Increasing mixing rate decreases the mass resistance and increases the mobility of the system. To clarify the influence that mass transport had on the kinetics in AFP, the rate constants have been plotted vs. mixing rate in Fig. 7. From the figure, the decolorization rate followed a non-linear pattern with respect to the square root of the mixing speed, which is different from the report by several researchers [26–28], consistent with the results by Epiloto et al. [24]. The data of the present study can be described by an exponential function. Nam and Tratnyek [27] stated that deviation from linearity of the decolorization rate vs. the square root of the mixing rate is likely due to inefficient mixing by the shaker at or below 60 rpm.

3.6. Effect of temperature on the decolorization of AR 73

The effect of temperature on the AR 73 decolorization kinetics was evaluated at 20, 30 and 40 °C. According to $C = C_0 e^{-k_1 t}$, three regression lines can be obtained (Fig. 8). It is observed that the temperature has a strong effect on the AR 73 removal. The dye removal efficiency increased with the increasing of temperature due to the increment in the pseudo first order rate constants (k was 0.1348, 0.2133 and 0.3118 min^{-1} at 20, 30 and 40 °C, respectively). The rate constants increment is attributed to increased corrosion rates and collisions between the dye and hydroxyl radicals.

The rate constant k at different temperature was then applied to estimate the activation energy of the AR 73 by the Arrhenius equation [29,30].

$$\ln k = -\frac{E_a}{RT} + \ln A_0 \quad (9)$$

where E_a is the Arrhenius activation energy (kJ/mol), A_0 is the Arrhenius factor, R is the gas constant (8.314 J/(mol K)) and T is the solution temperature. The slope of the plot of $\ln k$ vs. $1/T$ (Inset) was used to evaluate E_a and the value of E_a was found to be 31.98 kJ/mol.

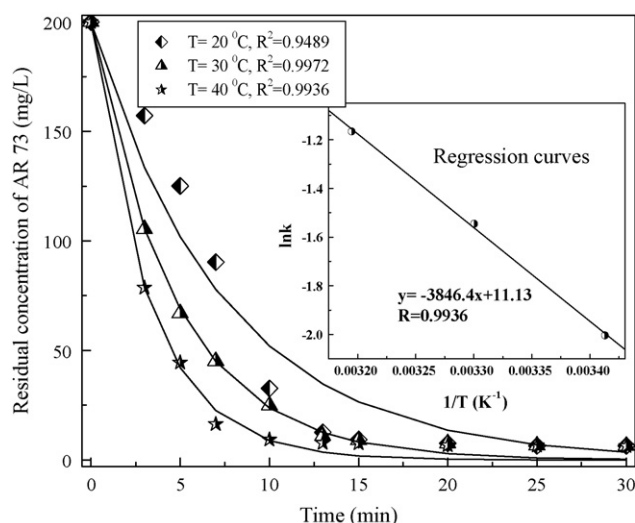


Fig. 8. Effect of temperature on AR 73 residual concentration ($C_0 = 200.0$ mg/L, $[ZVI]_0 = 0.3$ g/L, $[H_2O_2]_0 = 2.0$ mM, mixing rate = 100 rpm, pH 3.0). Inset: relationship of observed rate constant and temperature.

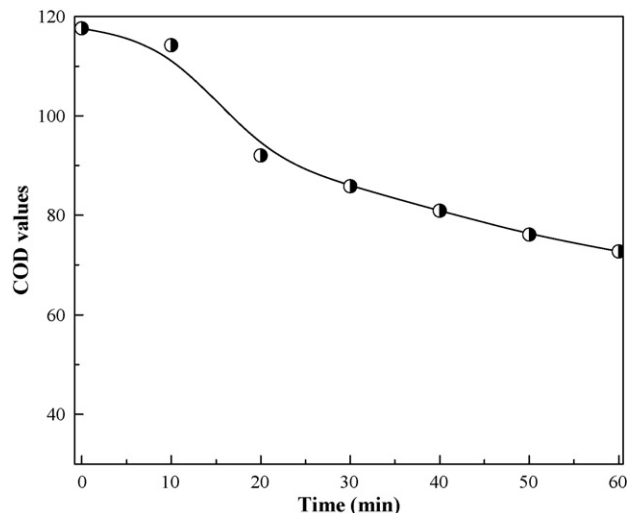


Fig. 9. COD removal at different time ($C_0 = 200.0$ mg/L, $[ZVI]_0 = 0.3$ g/L, $[H_2O_2]_0 = 2.0$ mM and mixing rate = 100 rpm at pH 3.0).

3.7. COD removal

As above discussed, over 96.8% decolorization efficiency was achieved after 30 min for 200.0 mg/L AR 73 wastewater at optimum conditions. As is known, complete decolorization of dye does not mean that the dye is completely degraded, so the degradation of AR 73 in terms of COD removal was also investigated. As can be seen from Fig. 9, COD values decreased with time. The initial COD of 200.0 mg/L AR 73 was 117.6 mg/L, after treatment by AFP for 30 and 60 min, the COD values decreased to 85.8 and 72.7 mg/L, i.e., 27.0% and 38.2% COD was removed, respectively. This is because that the intermediate products of AR 73 by AFP are difficult to oxidise, and complete oxidation may proceed in a longer time.

4. Conclusions

In this work, AFP alone was applied to degrade AR 73 synthetic wastewater. Parameters affecting the removal of AR 73 by AFP were investigated. Results showed that the AFP could remove AR 73 effectively. At the optimal experimental conditions

($[H_2O_2]_0 = 2.0$ mM, $[ZVI]_0 = 0.3$ g/L, pH 3.0, mixing rate = 100 rpm and at $\pm 20 \pm 2$ °C), the residual concentration of AR 73 was only 6.4 mg/L after 30 min treatment for 200.0 mg/L AR 73 initial concentration, and the decolorization efficiency attained 96.8%. The removal efficiency of AR 73 increased with the increase of hydrogen peroxide and ZVI concentration, temperature and mixing rate, but decreased with the increase of initial pH value and initial dye concentration. This study demonstrates that AFP alone (without combined other degradation technologies) can effectively degrade azo dye from wastewater. AFP approaches a simple, economical and environmentally friendly technology for the degradation of azo dye.

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