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Investigation of water decolorization by Fenton oxidation process in batch and continuous systems

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ABSTRACT

Nowadays, advanced oxidation methods such as Fenton and modified Fenton processes draw considerable attention to dye removal in textile wastewater. In Fenton process, low concentrations of Fe^{+2} and H_2O_2 solutions are used and these Fenton reagents generate $OH^{\cdot}$ radicals including high oxidation potential. The Fenton process, in which non-toxic and harmless reagents are applied at low concentrations, is very useful for decolorization of wastewater since it is very effective and less polluting. In this study, decolorization of the water samples containing azo dyes like Acid Red 88 (AR 88) was performed by Fenton oxidation process on a laboratory-scale setup. The aqueous solutions prepared by AR 88 dye were used for effective decolorization by Fenton oxidation method in batch process under various reaction conditions. By this method, the effects of solution temperature, pH, stirring speed, and concentration on the decolorization of the samples were investigated. The decolorization reaction kinetics of AR 88 dye was also determined in the batch system. Then, the Fenton oxidation experiments were carried out in the continuous system under the optimum conditions of stirring rate = 250 rpm; pH 2; $[H_2O_2] = 1.0$ mM; $[Fe^{2+}] = 0.1$ mM; azo dye concentration [AR 88] = 0.12 mM; and $T = 30$ °C. These optimum conditions were determined in the batch system studies. The efficiency of decolorization for both systems was about 99% and the decolorization kinetics of the water samples containing AR 88 dye was found as the second-order. The experimental results also showed that the Fenton's reagent was effective for the degradation of AR 88 dye using H_2O_2 and Fe^{2+} solutions at low concentrations.

Keywords: Fenton process; Oxidation; Textile dyes; Wastewater; Decolorization

1. Introduction

Synthetic dyes are used extensively by several industries including textile dyeing, paper, and plastic materials production. The wastewater originated from textile and dye industries cause serious environmental problems since the organic pollutants and non-biodegradability of the pollutants damage the ecological balance [1]. Color is one of the most obvious indicators of wastewater pollution. This type of

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wastewater causes colorization of aquatic life with its color prevents sunlight to be spread in any aquatic medium; moreover, decreases the oxygenation capacity of aquatic media. Additionally, azo dyes in the effluents have health risks due to their cancerogenic and toxic structures [2,3]. Nowadays, the advanced oxidation processes using ozone, titanium dioxide (TiO_2), ultraviolet (UV) light, and Fenton's reagent (H_2O_2 and ferrous ion) have received the considerable attention as the effective pretreatment processes of less biodegradable wastewater [4]. Azo dyes constitute the largest class of dyes and are widely used in a variety of industries from textile to cosmetics [2]. There are about 30 different kinds of dyes, used in textile industry, based on their chemical structure and type of chromospheres (Fig. 1). Anthraquinone and phthalocyanine are the most widespread among the groups of azo dyes including the –N=N– groups [5].

Decolorization of wastewater is one of the significant problems as the dye is visible even at low concentrations. Most of the dyes are found to be resistant to conventional treatment processes such as activated sludge [3]. Various treatment methods have been developed to remove azo dyes from wastewater. Among these technologies, Fenton oxidation processes are effective to degrade a wide range of azo dyes. Fenton process is an advanced homogeneous catalytic oxidation process using a mixture of hydrogen peroxide and ferrous ions. Compared with other oxidation processes, Fenton's reagent is relatively inexpensive and the process is easy to operate and maintain. Consequently, many studies have been reported about the treatment of wastewater containing azo dyes, and decolorization by homogeneous Fenton's reagent generate $OH^{\cdot}$ radicals with high oxidation potential. They can oxidize many types of chemicals [6–8]. The main disadvantage of the Fenton process is that ferrous ions are consumed more rapidly than they are regenerated [9,10]. Therefore, higher ferrous ion dosage is needed to keep the moderate hydroxyl radicals production. This results in a large amount of ferric hydroxide sludge during the neutralization stage of the Fenton process which requires additional separation processes and disposal [11,12].

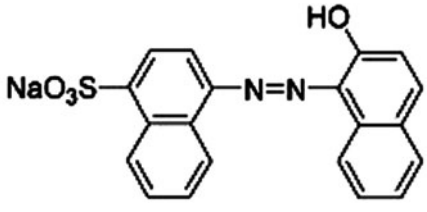

Fig. 1. Chemical structure of AR 88 ($C_{20}H_{13}N_2O_4SNa$) (Molecular weight = 400.33 g mol^{-1} and solubility = 116 g l^{-1} at 30 °C).

In this study, the decolorization of water containing AR 88 by Fenton oxidation and its kinetics were investigated in the batch system. Decolorization of the aqueous solutions was also studied in the continuous system under the optimum process conditions.

2. Materials and methods

The chemicals, $FeSO_47H_2O$: MW = 278 g mol^{-1}, H_2O_2: 1.13 g ml^{-1} (35%), H_2SO_4: 1.84 g ml^{-1}, NaOH: MW = 40 g mol^{-1}, used in this study, were reagent grade Merck products. Acid Red 88 (AR 88): MW = 400.38 g mol^{-1}, the textile dye with the molecular formula $C_{20}H_{13}N_2O_4SNa$, was provided by Burboya Co., Bursa, Turkey. The synthetic wastewater samples to be used in the experiments were prepared using AR 88. This azo dye was specifically chosen as it is used commercially in textile industries in Turkey and mostly found in the textile wastewater. The residual dye concentration was measured by the 6105 UV–vis spectrophotometer at wavelength of 500 nm. Decolorization of the water samples containing AR 88 was investigated using the Fenton oxidation process. In this study, the aqueous solutions prepared by AR 88 dye were decolorized by Fenton process in the batch system and the optimum pH, temperature, Fe ions concentration, hydrogen peroxide concentration, and dye concentration values were determined for effective discoloration. Then, Fenton process was applied in the continuous system.

Chemical oxidation of AR 88 in the batch system was carried out in a 500-ml beaker filled with 200 ml of the AR 88 solution under various conditions. In a typical run, the pH of the solution has been adjusted to the desired pH value. After stabilization of the temperature and pH, the catalyst solution was added to the medium. The reaction was started immediately when the required amount of H_2O_2 was added. All experiments were carried out under constant stirring and temperature conditions. Thereafter, the samples were withdrawn periodically and analyzed using a UV–vis spectrophotometer.

3. Results and discussion

In the homogeneous Fenton oxidation process, Fe^{+2} and H_2O_2 are used in low concentrations and these Fenton reagents generate $OH^{\cdot}$ radicals containing high oxidation potential for the organic pollutants. Thus, the generation rate and total amount of $OH^{\cdot}$ both play an important role in the degradation of pollutants

[13]. The Fenton process is a very effective and less polluting method, in which non-toxic and harmless reagents are used at low concentrations.

3.1. Effect of temperature

The effect of temperature on the decolorization of the aqueous solutions containing AR 88 dye was investigated in the temperature range between 20 and 50°C. The results indicated that the decolorization of AR 88 was not affected significantly by increasing the temperature of the solution. Fig. 2 shows that the decolorization progressed quickly within first 15 min of the reaction. In all cases, decolorization efficiency above 99% was reached in 60 min of reaction time. The optimum temperature value for this study was 30°C with 99.4% decolorization efficiency.

3.2. Effect of pH

The pH is a very important parameter for decolorization in the homogeneous Fenton oxidation process (Table 1). As known, the optimal pH value for the decolorization of water containing azo dyes is approximately from 2.0 to 4.0. Furthermore, at a higher initial pH value, the iron is precipitated as iron hydroxide during the homogeneous Fenton oxidation reaction. The pH of the solution decreases with the formation of organic acids by the oxidation process. In this study, the effect of pH was investigated by ranging the values of pH from 1.5 to 4.0. As expected, the decolorization of the water samples containing AR 88 was significantly affected by the pH of the solution and the maximum efficiency was reached when pH equals 2 (Fig. 3). According to the results of this study, the pH of the solution has a significant effect in the Fenton oxidation processes, and the Fenton oxidation efficiency was decreased with increasing alkalinity. There may be two causes of this behavior: first, H_2O_2 is not stable in alkaline solution; second, the formation of the ferric hydroxide complexes leads to a reduction of $OH^{\cdot}$ radicals [1].

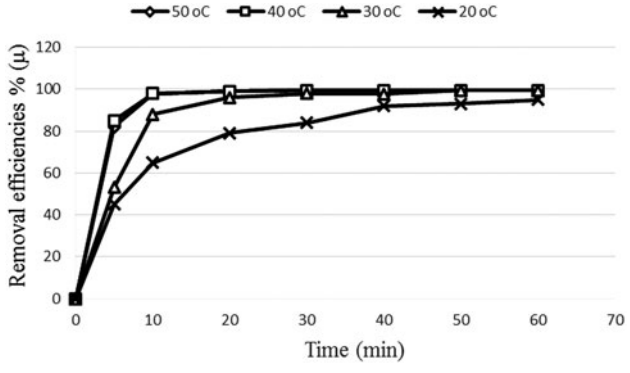

Fig. 2. The effect of temperature on decolorization (pH 2, $[H_2O_2]$ = 1.0 mM, [AR 88] = 0.12 mM, $[Fe^{2+}]$ = 0.1 mM, stirring speed = 250 rpm).

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

The effect of the Fe^{2+} catalyst concentration on the decolorization was investigated. The catalyst concentration affects the Fenton reaction significantly. Therefore, a series of experiments were performed to investigate the impact of the catalyst concentration on the decolorization efficiency of the water samples containing AR 88 by varying the catalyst concentration from 0.025 to 0.20 mM. The decolorization efficiency increased with the increasing Fe^{2+} catalyst concentration, and it increased to 99.4% at the optimum Fe^{2+} concentration of 0.1 mM in 60 min of reaction time (Fig. 4). As it can be seen in the figure, increasing the catalyst concentration above this optimum value does not increase the decolorization efficiency. This situation is in line with the above-mentioned study. Based on this study, the use of a much higher Fe^{2+} catalyst concentration could lead to the self-scavenging of $OH^{\cdot}$ radicals by Fe^{2+}. Moreover, it also induced a decrease in the degradation rate [4].

3.4. Effect of the concentration of H_2O_2

The effect of H_2O_2 concentration on the decolorization of the water samples containing AR 88 dye was investigated by ranging the values of H_2O_2 concentration from 0.025 to 0.20 mM. The decolorization efficiency increased by the increased concentration of H_2O_2 up to 1.0 mM and the decolorization efficiency reached 99.4% within 60 min of reaction time (Fig. 5). The decolorization rate increased by the increase in H_2O_2 concentration and the yield reached 99.4% more quickly. However, at low concentrations, H_2O_2 could not generate enough $OH^{\cdot}$ radicals, and the oxidation rate decreases. The oxidation mechanism can be shown as follows:

$$H_2O_2 + OH^{\cdot} \rightarrow HO_2\cdot + H_2O \quad (1)$$

$$H_2O_2 + OH_2\cdot \rightarrow OH\cdot + O_2 + H_2O \quad (2)$$

$$HO_2\cdot + OH\cdot \rightarrow H_2O + O_2 \quad (3)$$

Therefore, the addition of a higher H_2O_2 concentration does not improve the degradation. This situation

Table 1
Optimization of the effective parameters on the decolorization study

T (°C)	μ	pH	μ	$[H_2O_2]$ (mM)	μ	$[Fe^{2+}]$ (mM)	μ	[AR 88] (mM)	μ	rpm	μ
20	88.2	1.5	78.7	0.025	34.6	0.025	48.7	*0.12*	*99.4*	100	97.4
30	*99.4*	*2.0*	*99.4*	0.125	79.0	0.050	92.3	0.14	77.5	*250*	*99.4*
40	99.4	2.5	93.8	0.250	82.8	*0.100*	*99.4*	0.16	65.3	375	98.6
50	99.4	3.0	89.8	0.500	92.0	0.200	99.6	0.20	54.5	500	98.4
		3.5	86.4	*1.000*	*99.4*			0.45	24.2		
		4.0	79.9	1.500	99.5						
				2.500	99.6						

Note: μ—Removal efficiencies (%).

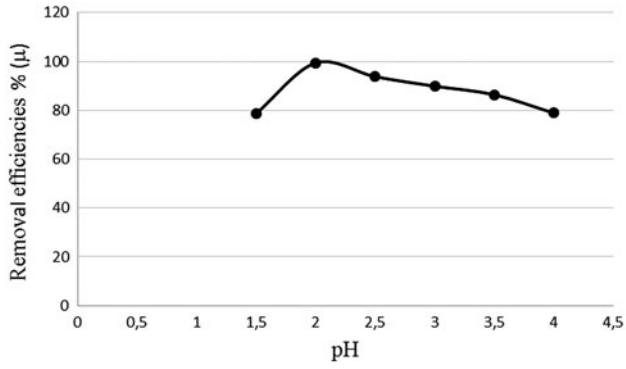

Fig. 3. The effect of initial pH on decolorization (T = 30°C, $[H_2O_2]$ = 1.0 mM, [AR 88] = 0.12 mM, $[Fe^{2+}]$ = 0.1 mM, stirring speed = 250 rpm).

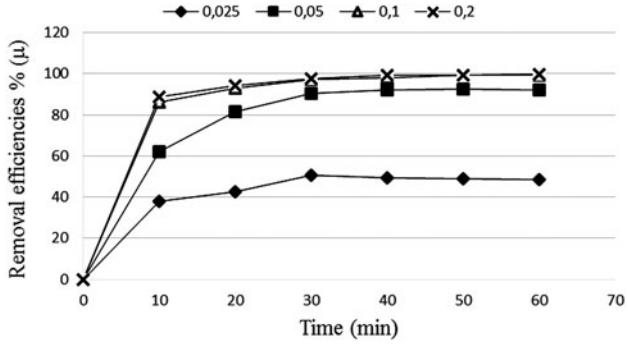

Fig. 4. The effect of catalyst concentration (Fe^{2+}) on decolorization efficiency (T = 30°C, pH 2, $[H_2O_2]$ = 1.0 mM, [AR 88] = 0.12 mM, stirring speed = 250 rpm).

was also reported and explained in the previous literature. The reason of this might be the generation of hydroperoxyl radicals ($HO_2^{\cdot}$) in the presence of an excess of H_2O_2. Although $HO_2^{\cdot}$ promotes radical chain reactions and is an effective oxidant itself, its

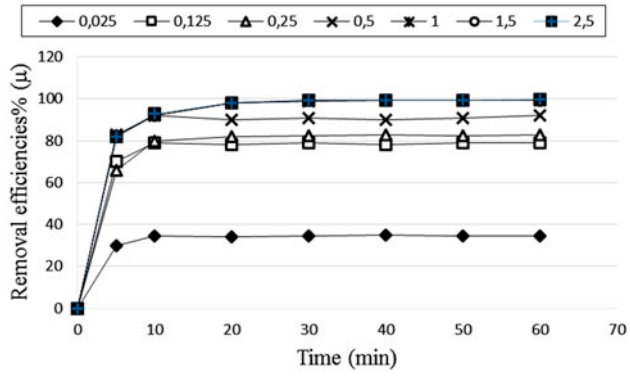

Fig. 5. The effect of H_2O_2 concentration on decolorization (T = 30°C, pH 2, [AR 88] = 0.12 mM, $[Fe^{2+}]$ = 0.1 mM, stirring speed = 250 rpm).

oxidation potential is much lower than that of $OH^{\cdot}$. The hydroperoxyl radicals are much less reactive and do not contribute to the oxidative degradation of organic substrates which occur only by reaction with $OH^{\cdot}$ [1,4].

3.5. Effect of the initial concentration of the AR 88 dye

The effect of initial concentration of AR 88 on the removal of dye was investigated by ranging the values of initial concentration from 0.12 to 0.45 mM (42–157 mg lt^{-1}). The initial concentration was adjusted based on the concentration of textile industry wastewater in Turkey. The effect of the initial dye concentration on the removal of AR 88 is shown in Fig. 6. The decolorization efficiency of 99.4% was achieved within 60 min for the initial dye concentration of 0.12 mM. As expected, the AR 88 decolorization efficiency increased by the decrease in the initial concentration of the solution but the amount of removal for all concentrations was approximately stayed at the same value.

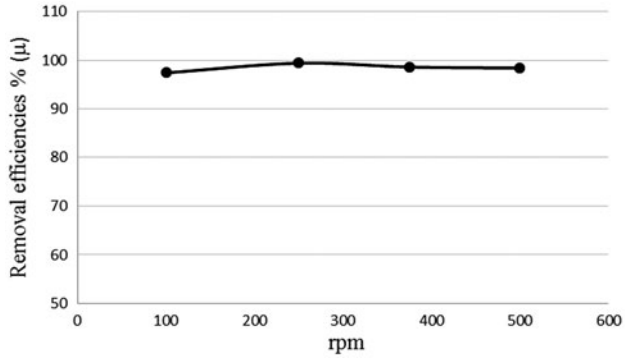

Fig. 6. The effect of stirring speed on decolorization (T = 30°C, pH 2, $[H_2O_2]$ = 1.0 mM, [AR 88] = 0.12 mM, $[Fe^{2+}]$ = 0.1 mM).

3.6. Effect of stirring rate

The effect of stirring rate on the decolorization of solution was investigated. The reactions were conducted in the range of 100–500 rpm. Fig. 7 shows that the effect of stirring rate on the decolorization increased up to 250 rpm and then the decolorization efficiency did not increase significantly. The optimum stirring rate was found to be 250 rpm.

3.7. Kinetics study

The same procedures as those applied in the investigations of the kinetics of homogeneous Fenton reaction were used in this study. The aqueous samples were taken from the solution periodically, and the concentration of the residual dye was measured by the 6105 UV–vis spectrophotometer at wavelength of 500 nm. The ratio of $[Fe^{2+}]$:$[H_2O_2]$ is very important in Fenton oxidation since it is well known that it has a significant effect on the reaction rate. The temperature was kept constant throughout the experiment and the

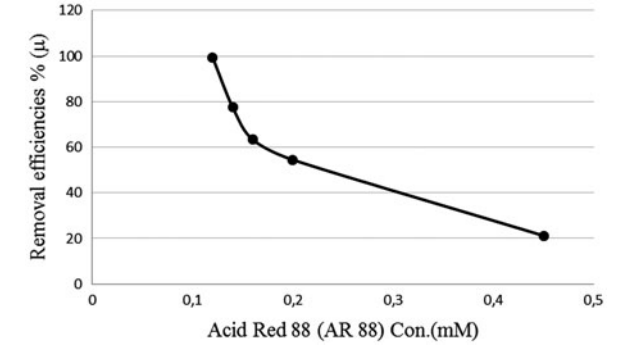

Fig. 7. The effect of initial AR 88 dye concentration on decolorization efficiency (T = 30°C, pH 2, $[H_2O_2]$ = 1.0 mM, $[Fe^{2+}]$ = 0.1 mM, stirring speed = 250 rpm).

obtained data under the optimum conditions were tested for the appropriate reaction order as follows (Eqs. (4)–(6)):

Zero-order reaction kinetics:

$$-\frac{dCi}{dt} = k_0 Cc_0 = k_{0.0} \Rightarrow C_0 - C_{ti} = k_{0.0}t \Rightarrow C_{ti} = C_0 - k_{0.0}t \quad (4)$$

First-order reaction kinetics:

$$-\frac{dCi}{dt} = k_1 Cc_0 Ci = k_{1.1} Ci \Rightarrow -\ln\frac{C_{ti}}{C_0} = k_{1.1}t \Rightarrow C_{ti} = C_0 e^{-k_{1.1}t} \quad (5)$$

Second-order reaction kinetics:

$$-\frac{dCi}{dt} = k_2 Cc_0 Ci^2 = k_{2.2} Ci^2 \Rightarrow \frac{1}{C_{ti}} - \frac{1}{C_0} = k_{2.2}t \Rightarrow \frac{1}{C_{ti}} = \frac{1}{C_0} + k_{2.2}t \quad (6)$$

Here, C_0 (mg lt^{-1}) is the initial concentration; C_{ti} (mg lt^{-1}) is the concentration of AR 88 at any time; k_0, k_1, and k_2 represent the apparent kinetics rate constants of zero-, first-, and second-order reaction kinetics, respectively; $k_{0.0}$, $k_{1.1}$, and $k_{2.2}$ represent the modified rate constants formed by multiplication of the initial constant catalyst concentration (Cc_0; mg lt^{-1}) with the rate constants; and t is the reaction time [13–16]. In the present study, it can be concluded that the decolorization by Fenton oxidation fits the second-order reaction kinetics. The apparent kinetic rate constant, $k_{2.2}$, of the decolorization was found to be 0.4822 lt mg^{-1} min^{-1} at the optimum conditions of [AR 88] = 0.12 mM, $[H_2O_2]$ = 1.0 mM, catalyst concentration = 0.1 mM, pH 2.0, and T=30°C.

3.8. Decolorization study in continuous system

Decolorization of water containing AR 88 by Fenton oxidation in continuous system was investigated for different flow rates (1.0, 1.5 and 2.0 ml min^{-1}) under the optimum process conditions determined in the batch studies which are: stirring rate = 250 rpm, pH 2, and T = 30°C. For continuous decolorization, 5.0 l (AR 88 (0.12 mM) + H_2O_2 (1.0 mM)) the mixture solution with the pH value adjusted to 2 and 500 ml of Fe^{2+} (0.1 mM) catalyst solutions were fed into the reactor (volume = 1,000 ml) separately. The highest decolorization efficiency was achieved as 99.4% at 1.5 ml min^{-1} feed rate of mixture solution (Fig. 8).

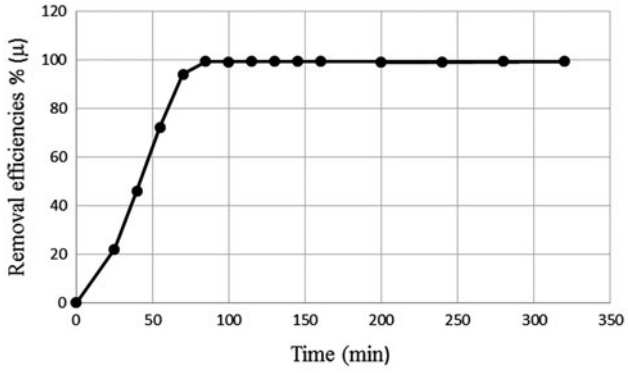

Fig. 8. Water decolorization by Fenton oxidation process in continuous system ($T = 30$ ℃, pH 2, stirring speed = 250 rpm, Feed rate = 1.5 ml min^{-1}).

4. Conclusion

The decolorization of aqueous solutions containing AR 88 was investigated and the optimum conditions were determined as follows: stirring rate = 250 rpm, pH 2, $[H_2O_2] = 1.0$ mM, $[Fe^{2+}] = 0.1$ mM, azo dye initial concentration (AR 88) = 0.12 mM, and $T = 30$ ℃. A Fenton reagent ratio of $[Fe^{2+}]:[H_2O_2] = (0.1:1)$ gave the best degree of decolorization for both batch and continuous systems (99.4%). Under these optimum conditions, it was concluded that the Fenton process was an effective method for the decolorization. It can also be concluded that the decolorization of AR 88 by Fenton oxidation fits the second-order reaction kinetics and the rate constant value was 0.4822 lt mg^{-1} min^{-1}. The obtained results may provide the theoretical basis and technical support for the possible applications of the continuous flow systems in the industrial wastewater treatment.

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