Desalination and Water Treatment
www.deswater.com

doi:10.5004/dwt.2017.20355

73 (2017) 281–288
April

Treatment of synthetic dye wastewater by using Fe/CuO particles prepared by co-precipitation: parametric and kinetic studies

Yeliz Asci*, Merve Cam

Eskisehir Osmangazi University, Faculty of Engineering and Architecture, Department of Chemical Engineering, Meselik Campus, Eskisehir, Turkey, Tel. +90 222 2393750;3644, email: yelizbal@ogu.edu.tr, yelizbal26@gmail.com (Y. Asci), merveecam@gmail.com (M. Cam)

Received 27 June 2016; Accepted 16 November 2016

ABSTRACT

In this study, decolorization of the synthetic wastewater containing Reactive Yellow 15 (RY15) by means of the heterogeneous Fenton process was investigated. Primarily, the Fe/CuO catalyst was prepared by co-precipitation method and characterized by BET and SEM-EDX analyses. The prepared catalyst was used in the Fenton tests. The effects of the amount of the catalyst, pH of the solution, hydrogen peroxide (H_2O_2) concentration, dye concentration, temperature and reaction time on the process were studied and the optimum conditions were determined. The decolorization efficiency of 98% was obtained under the optimum conditions (pH = 2, amount of catalyst = 4.0 g/L, temperature = 30°C, H_2O_2 concentration = 50 mM, time = 60 min). The decolorization kinetics of RY15 was also investigated. It was determined that the decolorization of RY15 obeyed the zero-order kinetics. Finally, reusability of the catalyst was investigated. The results show that the Fe/CuO catalyst is useful for the heterogeneous Fenton systems.

Keywords: Wastewater treatment; Reactive Yellow 15; Fe/CuO catalyst; Heterogeneous Fenton; Oxidation; Kinetics

1. Introduction

Wastewater generated in the textile industry contains azo dyes which cause catastrophic environmental problems [1]. The azo dyes are ones which contain one or more azo groups (–N=N–) linked to an aromatic chain and constitute the most commonly used dyes in the textile industry. Additionally, these dyes are most problematic pollutants of wastewaters coming from the textile industry [2]. This is because they have a complicated and stable molecular structure. Therefore, it is difficult to eliminate these dyes from water by any conventional physical, chemical and biological treatment methods [3,4].

The advanced oxidation processes (AOPs) have gained much attention recently in the treatment of various types of wastewater [5]. AOPs are useful alternative technologies that do not generate wastes in treatment of waste water containing dyes [6,7]. Among such AOPs, the Fenton reagent oxidation is a process in which an iron and hydrogen peroxide mixture is used. In this process, Fe(II)/Fe(III) reacts with hydrogen peroxide in an acidic medium and creates OH^- radicals having a high oxidation potential. These radicals decompose any organic pollutants and remove the dye from wastewater [8–10]. Despite such advantages of the Fenton process, its major drawback is the necessity to work in acidic pH levels. As a result of precipitation of the iron in high pH levels in aqueous environment, the ferric catalyst decomposes and looses its activity [11]. Additionally, removal of the precipitated sludge is expensive and cause a further pollution [12,13]. Due to drawbacks of this Fenton process, recently the heterogeneous catalysts, in which Fe ions are immobilized on the solid support, are developed by various techniques such as impregnation, coprecipitation, etc. [11,14,15]. In the coprecipitation procedure; (i) one or more metals are precipitated together with the support or precursor; (ii) instead of adding iron ion (Fe^{2+} or Fe^{3+})

---

*Corresponding author.

Presented at Desalination for the Environment: Clean Water and Energy, Rome, Italy, 22–26 May 2016

precursors, the commonly used salts such as $FeSO_4·7H_2O$, $FeCl_3$ or $Fe(NO_3)_3·9H_2O$ are utilized; (iii) a uniform distribution on a molecular scale of the different active species in the final catalyst could be attained; (iv) a very high metal loading of up to 80% can be reached [16–18]. The Fe–Ce–O [16], Fe_3O_4 [19], $ZnFe_2O_4$ [20], Fe_2O_3–SiO_2 [21] and $Fe_{3-x}Cr_xO_4$ [22] catalysts have been part of the vast investigation about the Fe ions immobilized on the solid support by coprecipitation. In this study, we used the Fe-supported CuO catalyst prepared by co-precipitation for decolorization of Reactive Yellow 15 (RY15).

Recently, CuO draws attention due to its various useful properties [23]. The CuO nanostructures have already been used in various applications such as gas sensors, bio-sensors, nanofluids, photodetectors, energetic materials (EMs), field emissions, supercapacitors, nanowires, nanotubes, ribbons, nanoplates, hollow microspheres and disks [23,24]. Copper(II) oxide particles, besides many other applications, are promising materials for heterogeneous catalysis because of their high catalytic activity, nontoxicity, low-cost, production facility, and availability [23]. For instance, Xie et al. investigated the heterogeneous Fenton-like oxidation of Acid Brilliant Scarlet 3R azo dye by CuO/SiO_2 catalyst [25]. Kim et al. reported the use of ultrasound in heterogeneous Fenton-like system over supported copper catalysts for degradation of p-chlorophenol [26]. Pan et al. also studied the degradation of p-nitrophenol using CuO/Al_2O_3 as a Fenton-like catalyst under microwave irradiation [27].

The present work encompasses the decolorization of RY15 by using the above-mentioned catalyst (Fe/CuO) that was not studied previously. The effects of parameters such as amount of catalyst, hydrogen peroxide concentration, pH, initial dye concentration and temperature on decolorization were investigated and the optimum conditions were determined. The kinetics of decolorization was also investigated.

2. Materials and methods

2.1. Materials

The azo dye Reactive Yellow 15 (RY15) was purchased from the Burboya Co. (Bursa, Turkey). The molecular formula and molecular weight of RY15 is $C_{20}H_{20}N_4Na_2O_{11}S_3$ and 634.57 g/mol, respectively. The reactive dyes (acid, reactive, disperse, vat, metal complex, mordant, direct, basic and sulphur) are mostly used ones among azo dyes. Furthermore, these dyes are the most problematic pollutants of textile wastewaters. Therefore, the azo dye Reactive Yellow 15 (RY15) was selected in this study. Hydrogen peroxide (30% w/w) and $Fe(NO_3)_3·9H_2O$ were supplied by Sigma-Aldrich Co. (Germany). CuO (Acros organics) (97%) was purchased from Thermo Fisher Scientific (Belgium). All chemicals were used without further treatment.

2.2. Preparation of catalyst

The 8.0 wt.%. Fe/CuO catalyst was prepared with co-precipitation method as follows: 5.8 g $Fe(NO_3)_3·9H_2O$ and 4.2 g CuO salts were dissolved in 100 ml of distilled water. Then, this solution was heated to 65°C in the magnetic stirrer at 300 rpm. The pH of the mixed solution was adjusted to 9 by addition of NH_4OH at speed of 10 mL/min. In the next step, the solution was aged for two hours at 300 rpm and 65°C. After aging, precipitate was washed three or four times with ethanol and dried in the oven at 100°C for one night. Finally, after the precipitate was granulated, it was calcined in an oven at 600°C for one hour in air atmosphere.

2.3. Characterization of catalyst

Surface morphology of the Fe/CuO was determined by scanning electron microscopy (Model SEM-JEOL JSM 5600LV). The chemical composition of Fe/CuO was defined by the Energy Dispersive Spectrometry (EDX) using the same instrument with SEM with an E2V Electronics device. The specific surface area (SSA) of the catalyst was also calculated by the BET (Brunauer, Emmett and Teller) theory using a Quantochrome Autosorb 1-C device.

2.4. Catalytic activity measurements

A 1 g portion of RY15 was solved in 1 L pure water, a stock dye solution was prepared and the tests were carried out by using this solution. The Fenton tests were conducted as follows: 25 mL sample was taken from 50 mg/L of prepared dye solution, and pH was adjusted by H_2SO_4 and NaOH solutions. 0.1 g catalyst was added into the solution with adjusted pH. After the catalyst was added, 50 mM H_2O_2 was added into the mixture, and the solution was placed in the water bath set at 30°C. After the time determined for the reaction was over, a 5 mL sample was taken from the solution in the water bath, and centrifuged for 5 min at 4000 rpm. After it was centrifuged, the absorbance value of the solution was read at a wavelength of 413 nm at the upper phase in the UV-spectrophotometer (Shimadzu, model UV-120-01). The decolorization efficiency was found by determining the concentration difference before and after the reaction.

All tests were conducted by changing any parameter and keeping others constant. The effect of loaded iron amount on the catalyst was investigated by varying the amount between 4 and 12 weight percentage. The other parameters were studied in the following ranges of variation: for the effect of catalyst amount, from 0.4 to 20 g/L; for the effect of solution pH, from 1.5 to 8.0; for the effect of H_2O_2 concentration, from 5.0 to 100 mM; for the effect of RY concentration, from 50 to 200 mg/L; and for the effect of temperature, from 20°C to 45°C.

3. Results and discussion

3.1. Characterization of catalyst

The SEM image of the 8.0 wt.%. Fe/CuO is shown in Fig. 1. As seen in Fig. 1, the small size Fe particles have a homogeneous dispersion on CuO crystals. Fig. 2 shows the EDX spectra. The EDX analyses revealed that the iron amount of the Fe/CuO catalyst is 28.6 wt.% (Table 1). The surface area of the catalyst was also defined by BET analy-

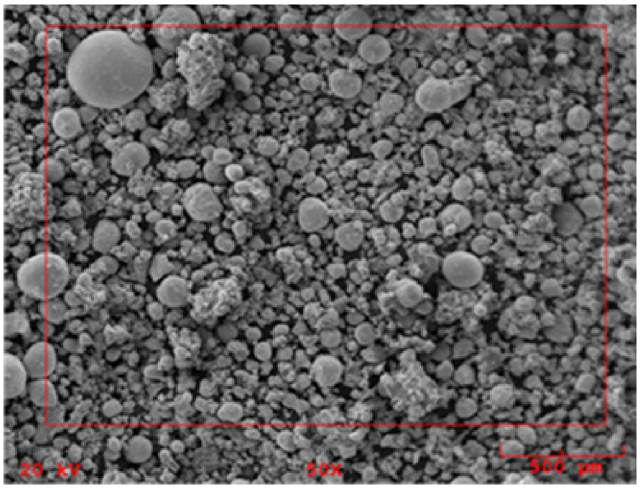

Fig. 1. SEM image of 8.0 wt.% Fe/CuO catalyst (magnification 50X).

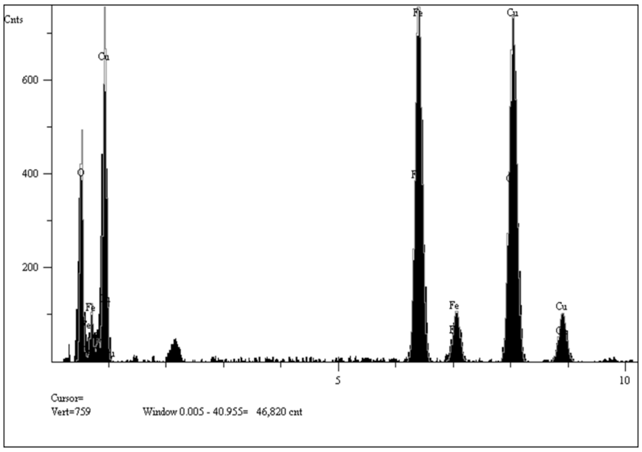

Fig. 2. EDX spectra of 8.0 wt.% Fe/CuO catalyst.

Table 1
EDX elemental analysis of 8.0 wt.% Fe/CuO catalyst

Percentage compositions	
Fe	28.62
Cu	58.72
O	12.66

sis. According to the results of the analysis, it is found that the surface area of the catalyst is 15 m^2/g. Low surface area observation is believed to be caused by the calcination step in which porosity is achieved. A similar result (low surface area) was also obtained by Tian et al. [28].

3.2. Effect of the iron amount loaded on the catalyst on the decolorization of RY15

The effect of iron loading of CuO has been investigated employing different ferrous ion concentrations. The catalysts prepared with Fe weight percentages of 4.0, 8.0, and 12 were used for the decolorization of RY15 at 30°C. Percentage iron loaded on the catalyst for decolorization of RY15 increases from 4.0 wt.% to 8.0 wt.% and then reduces. Hence, under these experimental conditions, 8.0 wt.% of Fe were found to be optimum for efficient removal of RY15. This may be explained as follows: An increase in the amount of the iron loaded on the catalyst increase the number of the active iron centers on the surface of the catalyst. This allows formation of more OH^- radicals [29]. But, higher iron concentration reduces the oxidation potential of the formed OH^- radicals and causes a decrease in the decolorization efficiency [5]. The same observation was reported by Hassan and Hameed for the decolorization of Reactive Blue 4 dye by a heterogeneous Fenton-like process using Fe-ball clay [30].

3.3. Effect of catalyst dosage on the decolorization of RY15

Amount of the catalyst affects the heterogenous Fenton reactions considerably. Therefore, the effect of the amount of catalyst on the decolorization efficiency of RY15 was investigated by using the catalyst dosages between 0.4 and 20 g/L. The decolorization increased from 46 to 98.3% with the increase in the dosage of catalyst from 0.4 to 4.0 g/L within 180 min, and when the catalyst dosage increased from 4.0 to 20 g/L, the decolorization efficiency decreased to 96.8% (Fig. 3). Therefore, the optimal catalyst dosage was selected as 4.0 g/L for the decolorization of 50 mg/L RY15. This behavior may be due to the inhibition effect shown by excess iron ions that act as scavengers as shown by Eq. (1) as it has been widely observed in Fenton processes as mentioned in the previous section [15].

$$Fe^{2+} + \cdot OH \rightarrow Fe^{3+} + OH^- \tag{1}$$

3.4. Effect of pH on the decolorization of the dye RY15

The pH is an important parameter in the Fenton process. It affects directly the mechanism of dye oxidation since a change in pH of the solution causes a variation of the concentration of Fe [31]. The tests were conducted at a pH value of 1.5 to 8.0 to determine an optimum pH (Fig. 4). The results showed that the dye decolorization was affected considerably by pH of the solution. As seen in Fig. 4, as pH increases from 1.5 to 2.0, the decolorization of RY15 increased and it reached the maximum value of 98% at pH = 2. If pH is above 2, the decolorization efficiency decreases since the Fe cations are leached at lower pH values [32]. Moreover, the need for lower pH may be due to the increased oxidant formation, i.e., the hydroxyl radical. In addition, at lower pH values, the catalyst surface is positively charged and this facilitates the adsorption of the negatively charged dye and hence enhances the decolorization [21]. On the other hand, unlike the conventional homogenous Fenton process, 83% decolorization is obtained even at pH values above 6. Consequently, because iron is immobilized on the surface of the catalyst in the heterogeneous system, the precipitation of iron hydroxide is prevented and this enables to work at higher pH values [29]. In Table 2, some other results that have been reported using heterogeneous catalysts for decolorization of the different azo dyes at high pH values are compared [12,21,30,33,34]. As seen in the Table 2, other studies could not obtain good decolorization at pH ≥ 5.

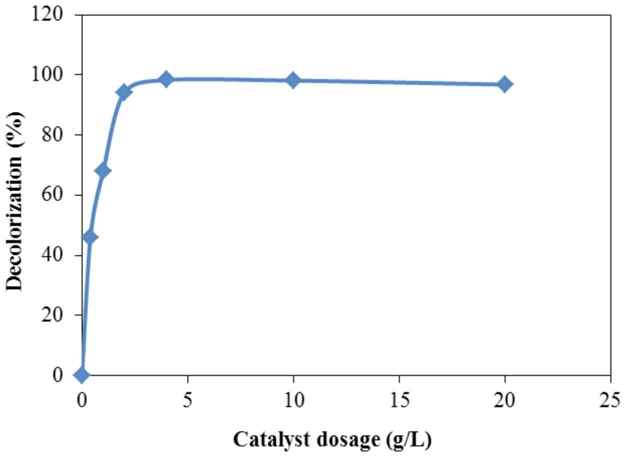

Fig. 3. Effect of dosage of catalyst on the decolorization of RY15 ([RY15] = 50 mg/L, [H_2O_2] = 50 mM, 8.0 wt.% of Fe/CuO, pH = 2, time = 180 min, temperature = 30°C, and stirring speed = 140 rpm).

3.5. Effect of temperature on the decolorization of RY15

The tests were conducted at temperatures of 20°C, 25°C, 30°C, 40°C and 45°C to investigate the effect of the reaction temperature on decolorization of RY15. When the temperature increases from 20°C to 30°C, the decolorization efficiency of RY15 increases from 94% to 98%. This is because the higher temperature increased the reaction rate between hydrogen peroxide and catalyst, and the generation rate of the hydroxyl radical increased simultaneously [12]. However, when the temperature increases from 30°C to 45°C, the decolorization efficiency decreases (Fig. 5). It can be possible that hydrogen peroxide may undergo self decomposition at high temperature [35]. Ayodele et al. also reported that H_2O_2 has become thermally decomposed into H_2O and O_2, and is subjected to a scavenging effect at high temperature [15]. Additionally, high working temperature has some disadvantage that both of the investment and operational costs would be high to increase the wastewater's temperature [35]. Therefore, the tests were conducted at an optimum temperature of 30°C.

3.6. Effect of H_2O_2 concentration on the decolorization of RY15

The effect of the hydrogen peroxide concentration on the RY15 removal efficiency using Fe/CuO catalyst is shown in

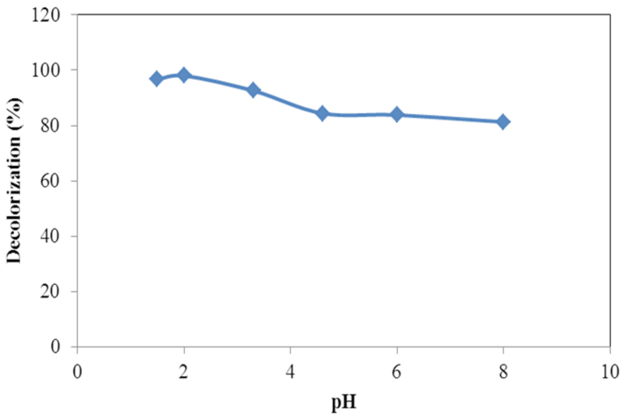

Fig. 4. Effect of pH on the decolorization of RY15([RY15] = 50 mg/L, [H_2O_2] = 50 mM, dosage of catalyst = 4.0 g/L with 8.0 wt.% of Fe/CuO, time = 60 min, temperature = 30°C, and stirring speed = 140 rpm).

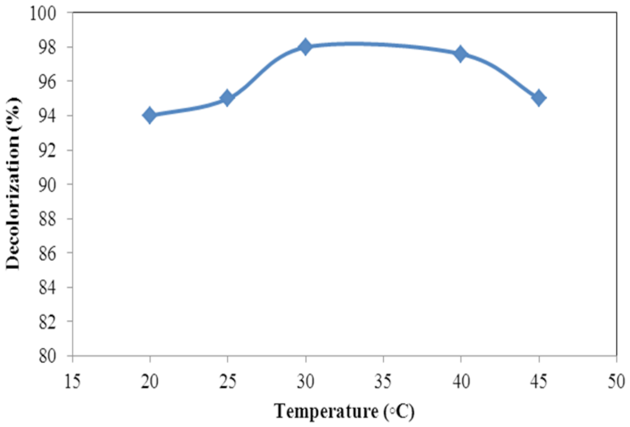

Fig. 5. Effect of temperature on the decolorization of RY15 ([RY15] = 50 mg/L, [H_2O_2] = 50 mM, dosage of catalyst = 4.0 g/L with 8.0 wt.% of Fe/CuO, pH = 2, time = 60 min, and stirring speed = 140 rpm).

Table 2
Dye removal efficiencies (%) of various heterogeneous catalysts

Dye type	Catalyst type	pH	Time	Removal efficiency (%)	References
Rhodamine B	Graphite tailings	7.0	60	58	[12]
Methyl orange	Fe_2O_3–SiO_2	6.0	20	46	[21]
Reactive blue 4	Fe-ball clay	5.0	60	68	[30]
Rhodamine 6G	CuFeZSM-5 zeolite	6.5	60	30	[33]
Methylene blue	$LiFe(WO_4)_2$	7.0	60	79	[34]
Reactive yellow 15	Fe/CuO	8.0	60	81	Our study

Fig. 6. Apparently, as the H_2O_2 concentration increased from 5.0 to 50 mM, the decolorization increased from 91% to 98% within 60 min. However, the removal efficiency decreased as the H_2O_2 concentration became greater than 50 mM. Further increase in the hydrogen peroxide concentration in the aqueous phase does not increase the formation of hydroxyl radicals since the excess of hydrogen peroxide reacts with hydroxyl radical to generate hydroperoxy radical ($HO_2\cdot$) which is a scavenger for hydroxyl radical through Eqs. (2) and (3) [12,31,36].

$$H_2O_2 + HO\cdot \rightarrow H_2O + HO_2\cdot \tag{2}$$

$$HO_2\cdot + HO\cdot \rightarrow H_2O + O_2 \tag{3}$$

Furthermore, the reactivity and oxidation potential (1.7 eV) of hydroperoxy radical ($HO_2\cdot$) is much lower than that of hydroxyl radical (2.8 eV) [15]. As a result, the hydroperoxy radicals do not contribute to the oxidative degradation of organic substrates, which occur only by reaction with OH. [32]. This trend is in conformity with the established trend in the literature [37,38]. Therefore, from the experimental results, a suitable H_2O_2 concentration of 50 mM was selected.

3.7. Effect of dye concentration on the decolorization of RY15

The effect of the initial dye concentration was investigated for 50, 100 and 200 mg/L dye concentrations and at temperatures of 25°C and 30°C, and the results are shown in Fig. 7. As seen, the decolorization efficiency decreases as the initial dye concentration increases at both temperatures. As increasing of the RY15 concentration from 50 to 200 mg/L, the decolorization efficiency of RY15 decreased from 95% to 85%, from 98.1% to 96.0% for 25°C and 30°C, respectively, within 60 min of reaction. This behavior is characteristic of advanced oxidation processes [12]. Its reason is that, when the dye concentration increases, OH^- concentration remains unchanged [39]. In addition, the higher concentration of RY15 would consume more HO· radical, so the effect would be reduced with the increase of the initial concentration of RY15 [12]. The similar observation was reported by Tekbas et al. [40] for the decolorization of Reactive Orange 16 dye by a Fenton process using zeolite catalyst.

3.8. The reuse tests

The reuse tests were performed in order to evaluate the activity of the catalyst after three consecutive cycles. The catalysts were used in three consecutive cycles using fresh solutions at optimum conditions (50 mg/L dye concentration, pH 2.0, 30°C, 50 mM H_2O_2 and 4.0 g/L catalyst dosage with 8.0 wt.% of Fe/CuO). In each test, the catalyst was filtered and separated and then washed several times by deionized water and dried overnight at 110°C. The results showed that the activity of the catalyst decreased gradually during three successive runs. About 98% RY15 removal takes place at 60 min in the first run. In the second run, 88.6% of dyes were removed at 60 min. The third run gave 86% dye removal. The decrease in efficiency is considered to be caused by this initial activity decrease due to small amounts of iron leached from catalyst surface [30]. These values are compatible with those measured in some other work published [13,30,33,40].

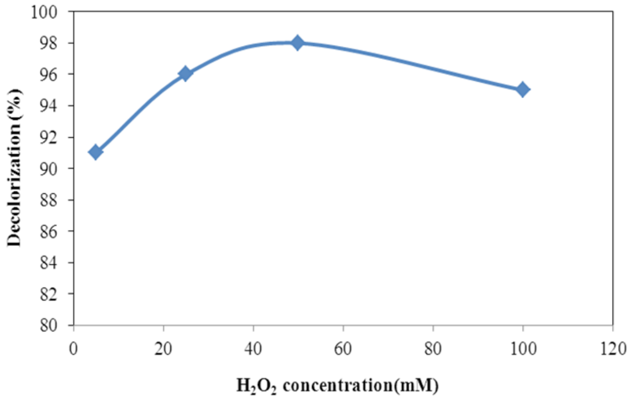

Fig. 6. Effect of H_2O_2 concentration on the decolorization of RY15([RY15] = 50 mg/L, dosage of catalyst = 4.0 g/L with 8.0 wt.% of Fe/CuO, pH = 2, time = 60 min, temperature = 30°C, and stirring speed = 140 rpm).

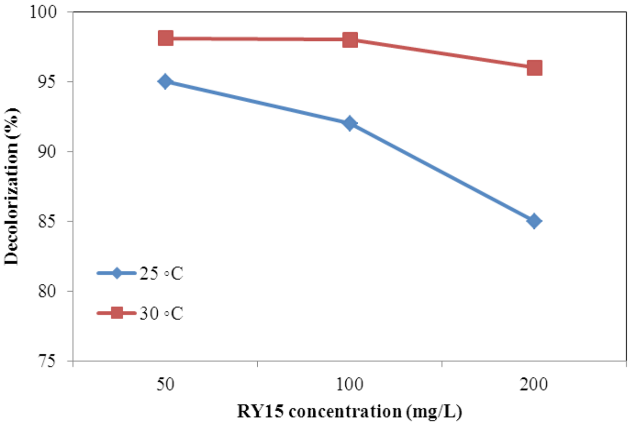

Fig. 7. Effect of initial dye concentration on the decolorization of RY15([H_2O_2] = 50 mM, dosage of catalyst = 4.0 g/L with 8.0 wt.% of Fe/CuO, pH = 2, time = 60 min, temperature = 30°C, and stirring speed = 140 rpm).

3.9. Effect of time and kinetic studies

Fig. 8 shows the effect of reaction time on the removal of RY15. As shown in Fig. 8, the percentage of dye removal abruptly increased up to 30 min (96.8%). However, the removal increased from 30 to 60 min at a slower rate and it was almost constant after 60 min (98%). It can be seen that it took about 30 min for RY15 removal to reach the equilibrium conditions. But, 60 min of contact time was required to reach a satisfactory equilibrium. Therefore, the following batch tests were conducted for the investigation of the influences of pH, initial dye and H_2O_2 concentrations and temperature for 60 min.

The decolorization kinetics of RY15 for a heterogeneous Fenton reaction were also investigated. The individual expressions were presented as equations given below [39,41]:

Zero-order reaction kinetics:

$$-\frac{dC}{dt} = k_0 \tag{4}$$

First-order reaction kinetics:

$$-\frac{dC}{dt} = k_1 C \tag{5}$$

Second-order reaction kinetics:

$$-\frac{dC}{dt} = k_2 C^2 \tag{6}$$

where C is the concentration of RY15; k_0, k_1, and k_2 represent the apparent kinetic rate constants of zero-, first-, and second-order reaction kinetics, respectively, and t is the reaction time.

By integrating Eqs. (4)–(6), the following equations could be obtained [Eqs. (7)–(9)]:

$$C_t = C_0 - k_0 t \tag{7}$$

$$C_t = C_0 e^{-k_1 t} \tag{8}$$

$$1/C_t = 1/C_0 + k_2 t \tag{9}$$

where C_0 is the initial concentration of the dye and C_t is the concentration of the dye at time t.

The plots of linear form of the zero-, first-, and second-order reaction kinetics for the RY15 removal were obtained at the temperature of 30°C. The kinetic parameters are summarized in Table 3. Comparing the regression coefficients (R^2) obtained, the zero-order reaction kinetics best described the decolorization of the RY15 via Fenton process (Table 3 and Fig. 9). At the same time the calculated values of C_o closely approximated the measured experimental values for zero-order kinetic model. In the present study, it can be concluded that the decolorization of RY15 by Fenton oxidation fits the zero-order reaction kinetics of the type: the apparent kinetic rate constant, k_0, of the decolorization of RY15 was found to be 1.5086 mg/L min^{-1} at the conditions of [RY15] = 50 mg/L, [H_2O_2] = 50 mM, pH = 2.0, and 30°C.

4. Conclusion

This paper presents the results of a detailed study on decolorization of RY15 from the synthetic wastewater by using Fe/CuO catalyst. In this study, the effect of the amount of the catalyst, pH, H_2O_2 concentration, initial dye concentration, temperature and reaction time on the heterogeneous Fenton process were investigated. The best reaction conditions were found as pH = 2.0, H_2O_2 concentration

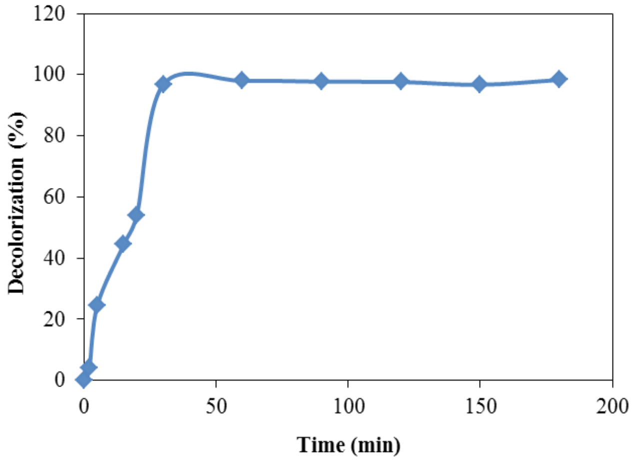

Fig. 8. Effect of reaction time on the decolorization of RY15([RY15] 50 mg/L, [H_2O_2] = 50 mM, dosage of catalyst = 4.0 g/L with 8.0 wt.% of Fe/CuO, pH = 2, temperature = 30°C, and stirring speed = 140 rpm).

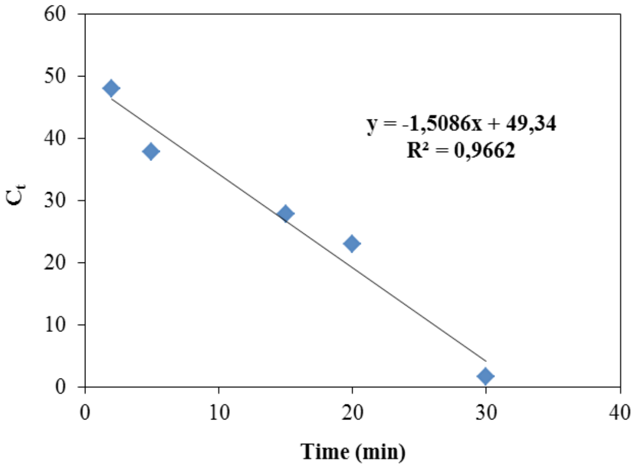

Fig. 9. Linearized zero-order kinetic plot for the decolorization of RY15 by Fenton oxidation.

Table 3
The kinetic constants for the decolorization of RY15 by Fenton oxidation at 30°C

Zero-order kinetic			First-order kinetic			Second-order kinetic		
k_0 (mg /L min^{-1})	C_o (mg/L)	R^2	k_1 (min^{-1})	C_o (mg/L)	R^2	k_2 (L/mg min^{-1})	C_o (mg/L)	R^2
1.5036	49.34	0.966	0.1074	83.850	0.774	0.0187	–8.53	0.619

= 50 mM, amount of the catalyst = 4.0 g/L, Fe amount loaded on the catalyst = 8.0 wt.%, dye concentration = 50 mg/L, time = 60 min and temperature = 30°C. Under these conditions, 98% decolorization efficiency was obtained. It was determined that the decolorization kinetics of RY15 complied with zero-degree. More importantly, it is seen that Fe/CuO catalyst has a better stability and reusability. Finally, it may be said that, because this catalyst never generates the iron hydroxide sludge and may work at wide pH range, the drawbacks of the homogeneous Fenton process are overcome.

Acknowledgment

The authors wish to thank Eskisehir Osmangazi University Scientific Research Projects Commission for partially supporting this study financially (Project No.201415F10).

References

[1] H. Ghodbane, O. Hamdaoui, Decolorization of antraquinonic dye, C.I. Acid Blue 25, in aqueous solution by direct UV irradiation, UV/H_2O_2 and UV/Fe(II) processes, Chem. Eng. J., 160 (2010) 226–231.

[2] M.S. Lucas, J.A. Peres, Decolorization of the azo dye Reactive Black 5 by Fenton and photo-Fenton oxidation, Dyes Pigm., 71 (2006) 236–244.

[3] N. Modirshahla, M.A. Behnajady, F. Ghanbary, Decolorization and mineralization of C.I. Acid Yellow 23 by Fenton and photo-Fenton processes, Dyes Pigm., 73 (2007) 305–310.

[4] J-H. Suna, S-H. Shia, Y-F. Leea, S-P. Sun, Fenton oxidative decolorization of the azo dye Direct Blue 15 in aqueous solution, Chem. Eng. J., 155 (2009) 680–683.

[5] B.H. Hameed, T.W. Lee, Degradation of malachite green in aqueous solution by Fenton process, J. Hazard. Mater., 164 (2009) 468–472.

[6] J-H. Sun, S-P. Sun, G-L. Wang, L-P. Qiao, Degradation of azo dye Amido black 10B in aqueous solution by Fenton oxidation process, Dyes Pigm., 74 (2007) 647–652.

[7] A.N. Soon, B.H. Hameed, Heterogeneous catalytic treatment of synthetic dyes in aqueous media using Fenton and photo-assisted Fenton process, Desalination, 269 (2011) 1–16.

[8] C.S.D. Rodrigues, L.M. Madeira, R.A.R. Boaventura, Optimization of the azo dye Procion Red H-EXL degradation by Fenton's reagent using experimental design, J. Hazard. Mater., 164 (2009) 987–994.

[9] M. Jonstrup, M. Punzi, B. Mattiasson, Comparison of anaerobic pre-treatment and aerobic post-treatment coupled to photo-Fenton oxidation for degradation of azo dyes, J. Photochem. Photobiol., A 224 (2011) 55–61.

[10] R. Liu, H.M. Chiu, C.-S. Shiau, R.Y-L. Yeh , Y.-T. Hung, Degradation and sludge production of textile dyes by Fenton and photo-Fenton processes, Dyes Pigm., 73 (2007) 1–6.

[11] F.L.Y. Lam, X. Hu, A high performance bimetallic catalyst for photo-Fenton oxidation of Orange II over a wide pH range, Catal. Commun., 8 (2007) 2125–2129.

[12] B. Cuiping, G. Wenqi, F. Dexin, X. Mob, Z. Qi, C. Shaohua, G. Zhongxue, Z. Yanshui, Natural graphite tailings as heterogeneous Fenton catalyst for the decolorization of rhodamine B, Chem. Eng. J., 197 (2012) 306–313.

[13] B. Muthukumari, K. Selvam, I. Muthuvel, M. Swaminathan, Photoassisted hetero-Fenton mineralisation of azo dyes by Fe(II)-Al_2O_3 catalyst, Chem. Eng. J., 153 (2009) 9–15.

[14] J. Feng, X. Hu, P.L. Yue, Effect of initial solution pH on the degradation of Orange II using clay-based Fe nanocomposites as heterogeneous photo-Fenton catalyst, Water Res., 40 (2006) 641–646.

[15] O.B. Ayodele, J.K. Lim, B.H. Hameed, Pillared montmorillonite supported ferric oxalate as heterogeneous photo-Fenton catalyst for degradation of amoxicillin, Appl. Catal., A 413–414 (2012) 301–309.

[16] A.F. Rossi, N. Amaral-Silva, R.C. Martins, R.M. Quinta-Ferreira, Heterogeneous Fenton using ceria based catalysts: effects of the calcination temperature in the process efficiency, Appl. Catal. B, 111–112 (2012) 254–263.

[17] S. Rojas, ICP-CSIC, Preparation of catalysts, Heterogeneous catalysts, (2013).

[18] F. Pinna, Supported metal catalysts preparation, Catal. Today, 41 (1998) 129–137.

[19] W. Wang, Y. Liu, T. Li, M. Zhou, Heterogeneous Fenton catalytic degradation of phenol based on controlled release of magnetic nanoparticles, Chem. Eng. J., 242 (2014) 1–9.

[20] H. Lee, J.C. Jung, H. Kim, Y.-M. Chung, T.J. Kim, S.J. Lee, S.-H. Oh, Y.S. Kim, I.K. Song, Catal. Lett., 122 (2008) 281–286.

[21] N. Panda, H. Sahoo, S. Mohapatra, Decolourization of Methyl Orange using Fenton-like mesoporous Fe_2O_3–SiO_2 composite, J. Hazard. Mater., 185 (2011) 359–365.

[22] X. Liang, Y. Zhonga, H. Hea, P. Yuan, J. Zhu, S. Zhu, Z. Jiang, The application of chromium substituted magnetite as heterogeneous Fenton catalyst for the degradation of aqueous cationic and anionic dyes, Chem. Eng. J., 191 (2012) 177–184.

[23] A. Angı, D. Sanlı, C. Erkey, Ö. Birer, Catalytic activity of copper (II) oxide prepared via ultrasound assisted Fenton-like reaction, Ultrason. Sonochem., 21 (2014) 854–859.

[24] Q. Zhang, K. Zhang, D. Xu, G. Yang, H. Huang, F. Nie, C. Liu, S. Yang, CuO nanostructures: Synthesis, characterization, growth mechanisms, fundamental properties, and applications, Prog. Mater. Sci., 60 (2014) 208–337.

[25] F. Xie, J. Zhong, L. Wang, K. Wang, D.X. Hua, Degradation of acid scarlet 3R with CuO/SiO_2 hollow sphere catalyst, IOP Conf. Series: Mater. Sci. Eng., 87 (2015) 012039.

[26] J.K. Kim, F. Martinez, I.S. Metcalfe, The beneficial role of use of ultrasound in heterogeneous Fenton-like system over supported copper catalysts for degradation of p-chlorophenol, Catal. Today, 124 (2007) 224–231.

[27] W. Pan, G. Zhang, T. Zhenga, P. Wang, Degradation of p-nitrophenol using CuO/Al_2O_3 as a Fenton-like catalyst under microwave irradiation, RSC Adv. 5 (2015) 27043–27051.

[28] H.S. Tian, Y.T. Tu, D.S. Chen, X Chen, Y. Xiong, Degradation of Acid Orange II at neutral pH using $Fe_2(MoO_4)_3$ as a heterogeneous Fenton-like catalyst, Chem. Eng. J., 169 (2011) 31–37.

[29] R. Idel-aouad, M. Valiente, A. Yaacoubi, B. Tanouti, M. López-Mesas, Rapid decolourization and mineralization of the azo dye C.I. Acid Red 14 by heterogeneous Fenton reaction, J. Hazard. Mater., 186 (2011) 745–750.

[30] H. Hassan, B.H. Hameed, Fe–clay as effective heterogeneous Fenton catalyst for the decolorization of Reactive Blue 4, Chem. Eng. J., 171 (2011) 912–918.

[31] C. Bouasla, M.E-H. Samar, F. Ismail, Degradation of methyl violet 6B dye by the Fenton process, Desalination, 254 (2010) 35–41.

[32] Y. Aşçı, Decolorization of Direct Orange 26 by Heterogeneous Fenton Oxidation, Desalin. Water Treat., 51 (2013) 7612–7620.

[33] M. Dükkancı, G. Gündüz, S. Yılmaz, R.V. Prihod'ko, Heterogeneous Fenton-like degradation of Rhodamine 6G in water using CuFeZSM-5 zeolite catalyst prepared by hydrothermal synthesis, J. Hazard. Mater., 181 (2010) 343–350.

[34] F. Ji, C. Li, J. Zhang, L. Deng, Efficient decolorization of dye pollutants with $LiFe(WO_4)_2$ as a reusable heterogeneous Fenton-like catalyst, Desalination, 269 (2011) 284–290.

[35] M. Karatas, Y.A. Argun, M.E. Argun, Decolorization of antraquinonic dye, Reactive Blue 114 from synthetic wastewater by Fenton process: Kinetics and thermodynamics, J. Ind. Eng. Chem., 18 (2012) 1058–1062.

[36] T.L.P. Dantas, V.P. Mendonca, H.J. Jos´e, A.E. Rodrigues, R.F.P.M. Moreira, Treatment of textile wastewater by heterogeneous Fenton process using a new composite Fe_2O_3/carbon, Chem. Eng. J., 118 (2006) 77–82.

[37] N.K. Daud, B.H. Hameed, Fenton-like oxidation of reactive black 5 solution using iron–Montmorillonite K10 catalyst, J. Hazard. Mater., 176 (2010) 1118–1121.

[38] S-P. Sun, C.-J. Li, J.-H. Sun, S.-H. Shi, M.-H. Fan, Q. Zhou, Decolorization of an azo dye Orange G in aqueous solution by Fenton oxidation process: effect of system parameters and kinetic study, J. Hazard. Mater., 161 (2009) 1052–1057.

[39] N. Ertugay, F.N. Acar, Removal of COD and color from Direct Blue 71 azo dye wastewater by Fenton's oxidation: kinetic study, Arab. J. Chem. doi: 10.1016/j.arabjc.2013.02.009.

[40] M. Tekbas, H.C. Yatmaz, N. Bektas, Heterogeneous photo Fenton oxidation of reactive azo dye solutions using iron exchanged zeolite as a catalyst, Micropor. Mesopor. Mat., 115 (2008) 594–602.

[41] N.K. Daud, U.G. Akpan, B.H. Hameed, Decolorization of Sunzol Black DN conc. in aqueous solution by Fenton oxidation process: effect of system parameters and kinetic study, Desal. Water Treat., 37 (2012) 1–7.