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Decolorization of Direct Orange 26 by heterogeneous Fenton oxidation

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ABSTRACT

In this work, the decolorization of Direct Orange 26 (DO26) was conducted using Fe(III)-sepiolite catalyst in the presence of hydrogen peroxide (H_2O_2) in a batch process. The catalyst was prepared by ion exchange. All experiments were performed on a laboratory-scale setup. The effects of different parameters such as solution pH, catalyst concentration, initial concentration of H_2O_2 and DO26, stirring speed on the decolorization efficiency of the process were studied. The best reaction conditions were found to be an initial pH of 2.0 when the concentration of catalyst was 1.5 g/L with $[H_2O_2]_o$ of 35 mM, $[DO26]_o$ of 40 mg/L, and a stirring speed of 250 rpm at a temperature of 25˚C. Under optimal conditions, a 98% decolorization efficiency of DO26 was achieved within 60 min of the reaction. The kinetics of decolorization of DO26 followed second-order reaction kinetics. Stability and reuse of the catalyst were also tested. This catalyst successfully overcomes the two problems faced by the heterogeneous Fenton process. The catalyst is reusable and the high effectivity of the catalyst in a wide range of pH.

Keywords: Direct Orange 26; Oxidation; Heterogeneous Fenton; Catalyst

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1. Introduction

Pollution of water by dyes is a serious problem in developed countries. Approximately, 1–10% or more of dyes are discharged into waste streams without treatment by the textile industry worldwide. The effluents from the textile dyeing industry contain many organic pollutants and are a serious environmental hazard because of their lasting color, high chemical oxygen demand, and nonbiodegradability [1]. Therefore, the removal of dyes from waste water is a challenge for the affected industries.

In recent years, advanced oxidation processes using ozone, titanium dioxide (TiO_2), ultraviolet (UV) light, and Fenton's reagent (H_2O_2 and ferrous ion) have received considerable attention as effective pretreatment processes of less biodegradable wastewater [2]. Among them, the homogeneous Fenton process is one of the most practical advanced oxidation technologies available due to its generation of hydroxyl radicals that can oxidize many types of chemicals [3]. Therefore, many studies have been performed on obtaining the optimal conditions to achieve the best efficiency [4–7].

Even though the homogeneous Fenton reaction is very powerful in the degradation of organic compounds, its disadvantage is the requirement to remove Fe ions from water after wastewater treatment [8]. To overcome this drawback, heterogeneous catalysts were used as an alternative to conventional homogeneous catalysts.

In heterogeneous solid catalysts, the iron ions are "immobilized" on the solid supports or within the structure and in the pore/interlayer of the catalysts. As a result, the catalysts can maintain their ability to generate hydroxyl radicals from hydrogen peroxide, and iron hydroxide precipitation is prevented. In addition to showing limited leaching of iron ions, the catalysts can easily be recovered after the reaction and remain active during successive operations [9]. Unlike the homogeneous Fenton reaction, in which strict control of the pH to approximately 2.0–3.0 is required for a good catalytic performance, immobilized Fenton catalytic systems provide the possibility of working in a wider pH range [10].

Several authors have studied different types of iron catalyst immobilized on an inorganic support: zeolite [11,12], clay [13,14], activated carbon [15,16], alumina [17,18], and fly ash [19] for synthetic dye removal.

The use of clays as catalysts for Fenton-like reactions is a promising alternative because they are abundant in nature and, when combined with the functionality of iron, they can easily be customized for specific applications [20]. The wide usefulness of clay minerals is essentially a result of their high specific surface area, high chemical and mechanical stabilities, and a variety of surface and structural properties [10]. Among these clays, sepiolite, which forms an important group of clay minerals, is a hydrous magnesium silicate characterized by its fibrous morphology and intracrystalline channels. It is a nonswelling, lightweight, porous clay with a large specific surface area (more than 200 m^2/g). Unlike other clays, the individual particles of sepiolite have a needle-like morphology, and currently, sepiolite has received considerable attention because of its sorptive, rheological, and catalytic properties and its structural morphology; therefore, the use of sepiolitic clays is expanding. Moreover, the abundance and availability of sepiolite mineral reserves as a raw material source and its relatively low cost guarantee its continued utilization in the future. Most of the world's sepiolite reserves are found in Turkey [21–24].

Although clay materials have been widely used as catalysts and as catalytic supports, to the best of our knowledge, the use of sepiolite clay as a Fenton catalyst has not yet been reported. The goal of this work was to investigate the applicability of Fe(III)–sepiolite clay as a heterogeneous Fenton catalyst for the decolorization of DO26 dye as a model pollutant. The effects of operating conditions, such as catalyst concentration, hydrogen peroxide concentration, initial pH, initial dye concentration, and stirring speed, on color removal were investigated. Finally, the kinetics of dye decolorization were discussed.

2. Materials and methods

2.1. Materials

The azo dye Direct Orange 26 (DO26) was obtained from Burboya Co. Textile Industry, Bursa, Turkey, at 45% of purity and was used without further purification. This dye was specifically selected for this study because it has been commercially important and commonly used in textile industries. The main characteristics of DO26 are presented in Table 1. Hydrogen peroxide (30%, w/w) and $Fe(NO_3)_3 \cdot 9H_2O$ were obtained from Sigma-Aldrich. All chemicals were analytical-grade reagents and were used as received without further purification. Deionized water was used in the present work. The solid material used as the heterogeneous catalyst was a natural clay without pretreatment supplied from sepiolite mines of the Eskisehir region of Turkey.

2.2. Preparation of the catalyst

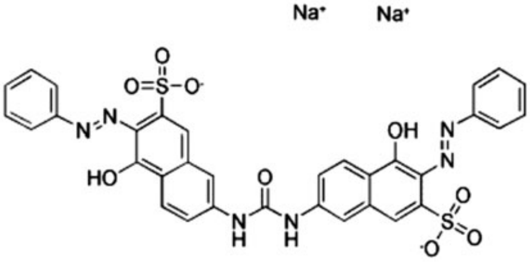
After washing and drying, the selected 0.038–0.053 mm-sized sepiolite was prepared through a cation exchange process as follows: 10 g sepiolite and 100 mL of 1 g/L $Fe(NO_3)_3 \cdot 9H_2O$ solution were mixed and shaken at 175 rpm for 6 h at 55°C [25]. The samples were washed with deionized water and dried at 105°C.

2.3. Characterization of catalyst

Scanning electron microscopy (Model SEM-JEOL JSM 5600LV) was used to study the surface morphology of the sepiolite and Fe(III)-sepiolite.

Energy Dispersive Spectrometry (EDX) was performed to determine the chemical composition in the

Table 1
Characteristics of DO26



Molecular formula	$C_{33}H_{22}N_6Na_2O_9S_2$
Formula weight	756.67
Colour	Orange
λ_{max} (nm)	494.5

sepiolite and Fe(III)-sepiolite using the same instrument with SEM with an E2 V Electronics.

2.4. Experimental procedure

Chemical oxidation of DO26 was carried out in batch mode, using a beaker filled with 250 mL of the DO26 solution at a given concentration. In a typical run, the pH of the DO26 solution has been adjusted to the desired pH value by NaOH or H_2SO_4. After stabilization of the temperature and pH, the powder catalyst (Fe(III)-sepiolite) was added to the DO26 solution. The beginning of the reaction was considered when the required amount of H_2O_2 was added. All experiments were carried out under constant stirring to ensure good dispersion of the catalyst. Thereafter, samples were withdrawn periodically and centrifuged to remove suspended particles for 5 min and analyzed using a UV–vis spectrophotometer (Shimadzu, model UV-120-01).

2.5. Analytical methods

The maximum absorbance wavelength (λ_{max}) of DO26 was found to be 494.5 nm using a UV–vis spectrophotometer (Thermo Electron Corporation, model Helios Aquamate). The concentration of dye in the reaction mixture at different reaction times was determined by measuring the absorption intensity at $\lambda_{max} = 494.5$ nm from a calibration curve. Prior to the measurement, a calibration curve was obtained using the standard DO26 solution with known concentrations. The decolorization efficiency of DO26 is defined as follows:

$$\text{Decolorization efficiency}\,(\%) = \frac{(C_0 - C_t)}{C_0} \times 100 \qquad (1)$$

where C_0 and C_t are the concentrations (mg/L) of the dye at time 0 and t, respectively [26,27].

3. Results and discussion

3.1. Characterization of catalyst

SEM images of the sepiolite and Fe(III)-sepiolite are shown in Fig. 1(a) and (b). a visible change of the surface morphology in the Fe(III)-loaded sepiolite can be seen from the figure. Sepiolite (Fig. 1(a)) shows a more uniform particle size distribution with relatively smooth surfaces, while that of Fe(III)-sepiolite (Fig. 2(b)) shows the formation of irregular flaky morphology with random orientation. Such a flaky appearance was attributed to the pillaring and reduction in certain amorphous regions, originally associated with raw sepiolite clay [28].

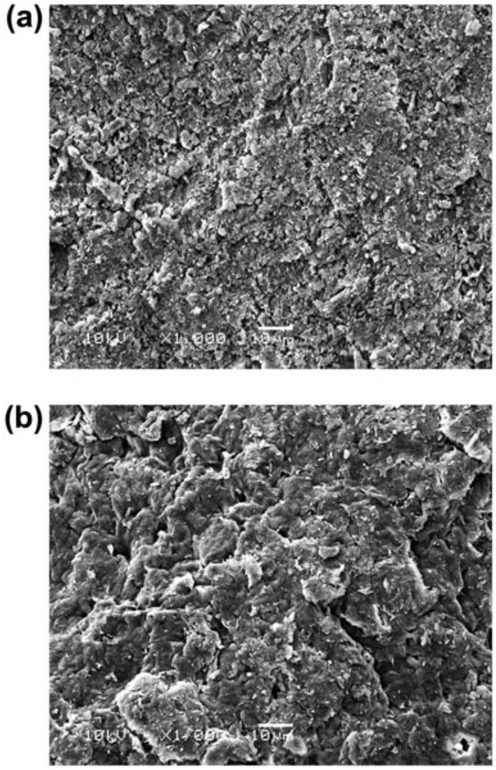


Fig. 1. SEM images of (a) sepiolite and (b) Fe(III)-sepiolite (magnification 1,000×).

Table 2 and Fig. 2(a) and (b) show the elemental analysis and EDX spectra, respectively. The EDX analyses revealed that the iron concentration of the Fe(III)-sepiolite catalyst is 0.380 wt.%, while it is 0.084 wt.% in the sepiolite. The determined iron contents of the Fe(III)-sepiolite catalyst varied slightly; this may be due to the high hydration degree of solid at the stages of the preparation procedure, thus making difficult to obtain the targeted iron contents.

3.2. Effect of pH

The effect of pH was investigated by varying the pH from 2.0 to 6.0 and is shown in Fig. 3. The results indicated that the decolorization of dye was significantly influenced by the pH of the solution. The optimum pH value for the decolorization of dye was pH 2.0 with 97.5% decolorization of the dye within 60 min of reaction.

The pH plays an important role in the nature of Fenton processes, and it was reported that the Fenton oxidation efficiency decreases with increasing alkalinity. There may be two causes of this behavior:

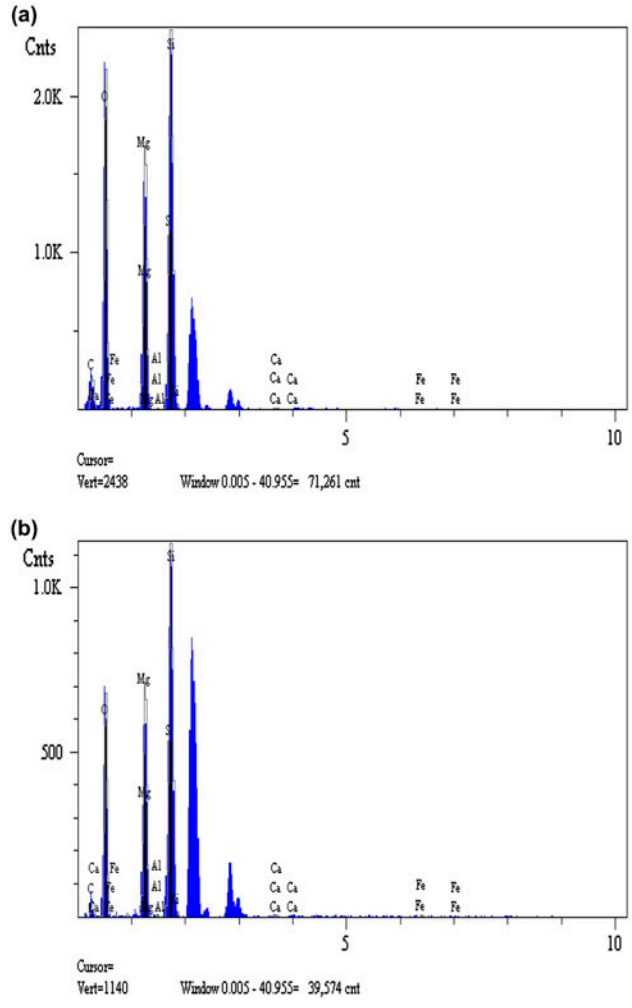


Fig. 2. EDX spectra of (a) sepiolite and (b) Fe(III)-sepiolite.

Table 2
EDX elemental analysis of sepiolite and Fe(III)-sepiolite samples

Sample	Percentage compositions (%)						
	O_2	Si	Al	Fe	Ca	Mg	C
Sepiolite	49.48	20.90	0.08	0.084	0.16	14.09	15.21
Fe(III)-sepiolite	44.22	27.22	0.17	0.380	0.23	15.79	11.99

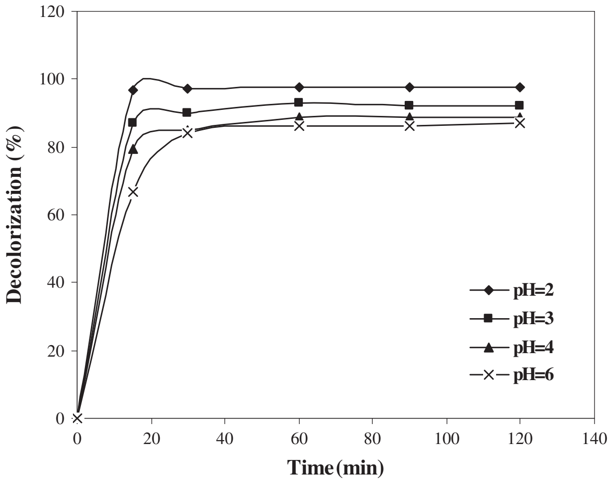


Fig. 3. Effect of pH on the decolorization of DO26 ($[DO26]_o = 40$ mg/L, $[H_2O_2] = 35$ mM, concentration of catalyst: 2.0 g/L, temperature = 25°C, and stirring speed = 250 rpm).

first, H_2O_2 is not stable in alkaline solution. Second, the formation of ferric hydroxide complexes leads to a reduction of OH radicals [1]. Additionally, it was reported that the leaching of Fe cations from the catalyst was enhanced at lower pH values [25]. However, unlike the conventional Fenton process, 86.2% of color removal was still obtained after a 60 min reaction, even when the initial pH was as high as 6.0; the heterogeneous Fenton process could perform effectively with Fe(III)-sepiolite as the catalyst. In homogeneous systems (Fe(III)/H_2O_2), it is known that the optimal value of the pH for the azo dye degradation is approximately 3.0–4.0. As the degradation proceeds, the formation of organic acids leads to a drop in the pH of the solution. At a higher initial pH, the iron is precipitated as iron hydroxide; but in this case, because Fe(III) is immobilized on the surface of the catalyst, the precipitation is avoided, resulting in a significant advantage over the homogeneous Fenton reaction [26].

3.3. Effect of the concentration of the catalyst

The influence of the catalyst concentration on the decolorization efficiency over time is presented in Fig. 4. The catalyst concentration markedly influences the heterogeneous Fenton reactions. Therefore, a series of experiments was carried out to investigate the influence of the catalyst concentration on the decolorization efficiency of DO26 by varying the amount of catalyst from 0.1 to 3.0 g/L. Decolorization of the dye with H_2O_2 only also was carried out and the decolorization was found as 13% at 60 min. The decolorization increased from 56.70 to 98.06% with the increase in concentration of catalyst from 0.1 to 1.5 g/L within 60 min, and when the catalyst concentration increased from 1.5 to 3.0 g/L, the decolorization efficiency decreased to 97.5%.

This phenomenon can be attributed to the fact that the increase in the amount of Fe(III)-sepiolite increases the presence of active sites on the catalyst surface and the free hydroxyl radical generation [26,29]. The

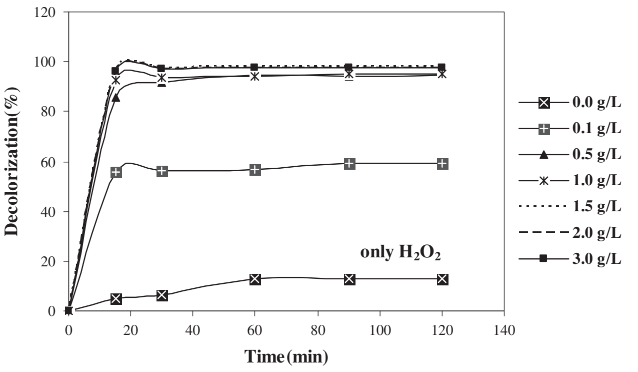


Fig. 4. Effect of concentration of catalyst on the decolorization of DO26 (pH = 2, $[DO26]_o = 40$ mg/L, $[H_2O_2] = 35$ mM, temperature = 25℃, and stirring speed = 250 rpm).

same observation was reported by Daud et al. [27] for the decolorization of Acid Red 1 dye by a heterogeneous Fenton-like process using Fe-Montmorillanite K10 catalyst. Many studies reported in the literature have revealed that the use of a much higher concentration of Fe could lead to the self-scavenging of $^{\bullet}OH$ radicals by Fe and induce a decrease in the degradation rate of pollutants [2]. In present study, 1.5 g/L was considered to be a suitable catalyst concentration for the decolorization of DO26.

3.4. Effect of the concentration of H_2O_2

The influence of the hydrogen peroxide concentration on the DO26 dye removal efficiency using Fe(III)-sepiolite is shown in Fig. 5. Apparently, as the H_2O_2 concentration increases from 5 to 35 mM, the decolorization increased from 85.68 to 96.47% within 15 min. However, the increasing rate of the removal efficiency slowed down gradually as the H_2O_2 concentration became greater than 35 mM. At low concentrations, H_2O_2 could not generate enough OH, and the oxidation rate was slow. The increase of the H_2O_2 led to an increase in the reaction rate as more radicals were formed. However, at higher H_2O_2 concentrations, the scavenging of $^{\bullet}OH$ radicals will occur:

$$H_2O_2 + OH^{\bullet} \rightarrow HO_2^{\bullet} + H_2O \qquad (2)$$

$$H_2O_2 + OH_2^{\bullet} \rightarrow OH^{\bullet} + O_2 + H_2O \qquad (3)$$

$$HO_2^{\bullet} + OH^{\bullet} \rightarrow H_2O + O_2 \qquad (4)$$

Thus, the addition of a higher concentration of H_2O_2 did not improve the degradation. This could be because hydroperoxyl radicals ($HO_2^{\bullet}$) were generated in the presence of an excess of H_2O_2. Although HO_2 promotes radical chain reactions and is an effective oxidant itself, its oxidation potential is much lower than that of $OH^{\bullet}$. The hydroperoxyl radicals are much less reactive and do not contribute to the oxidative degradation of organic substrates, which occur only by reaction with $OH^{\bullet}$ [1,2]. Therefore, from the experimental results, a suitable H_2O_2 concentration of 35 mM was selected.

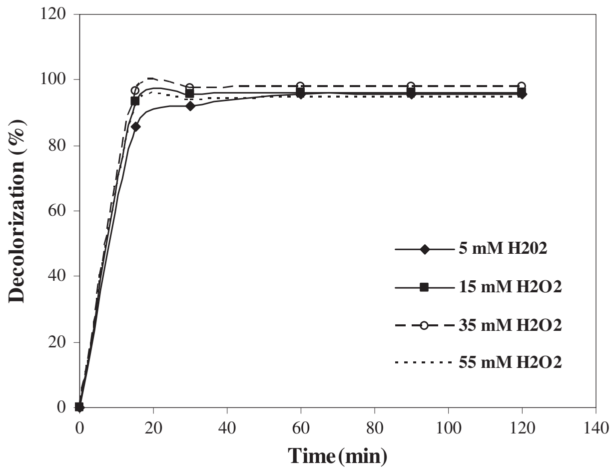


Fig. 5. Effect of the concentration of H_2O_2 on the decolorization of DO26 (pH = 2, $[DO26]_o = 40$ mg/L, concentration of catalyst = 1.5 g/L, temperature = 25℃, and stirring speed = 250 rpm).

3.5. Effect of the initial concentration of the dye

The concentration range chosen for the present study was that usually found in textile industry

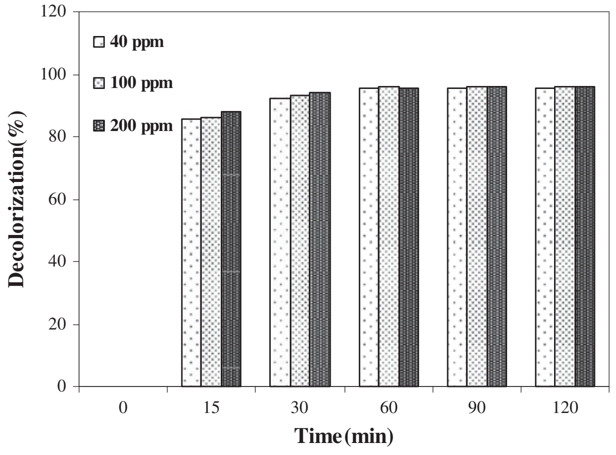


Fig. 6. Effect of the initial concentration of DO26 on the decolorization of DO26 (pH = 2, concentration of catalyst = 1.5 g/L, $[H_2O_2] = 5$ mM, temperature = 25℃, and stirring speed = 250 rpm).

wastewaters, between 40 and 200 mg/L. The influence of the initial dye concentration is shown in Fig. 6. Surprisingly, the DO26 decolorization efficiency was increased with the increase in the concentration of dye, and the color removal efficiencies achieved at 15 min were 85.68, 86.05, and 87.93% for the initial dye concentrations of 40, 100, and 200 mg/L, respectively. After 60 min of contact time, the decolorization efficiency increased to 95–96% for all concentrations. This phenomenon can be explained. Because the lifetime of hydroxyl radicals is very short (only a few nanoseconds), they can only react where they are formed. Increasing the quantity of DO26 molecules per volume unit logically enhances the probability of collision between organic matter and oxidizing species, leading to an increase in the degradation efficiency [27,30,31].

3.6. Effect of stirring speed

To study the effect of the string speed on the decolorization of DO26, the reactions were conducted at 140 and 250 rpm. Fig. 7 shows that an increase of stirring speed from 140 to 250 rpm improved the decolorization from 84.43 to 96.47% within 15 min of reaction, and after 90 min, the decolorization efficiencies were 92.5 and 98.06% for 140 and 250 rpm, respectively. This result was obtained because the mixture was more homogeneous at the high stirring speed, and the higher stirring speed increased the chance of contact of the reaction system with DO26 molecules [29]. Herein, 250 rpm was considered to be a suitable stirring speed for the decolorization of DO26.

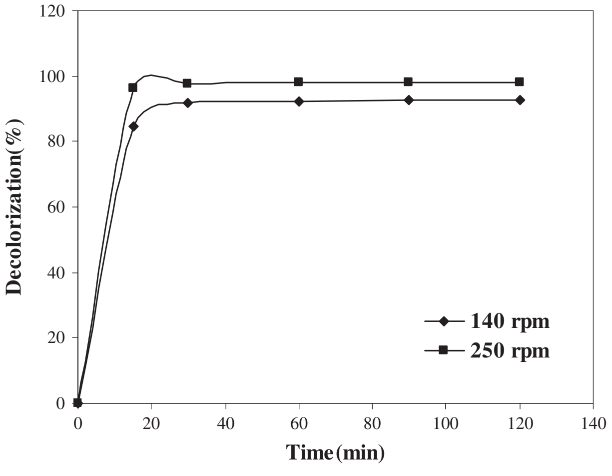


Fig. 7. Effect of stirring speed on the decolorization of DO26 (pH = 2, $[DO26]_o$ = 40 mg/L, $[H_2O_2]$ = 35 mM, concentration of catalyst = 1.5 g/L, and temperature = 25˚C).

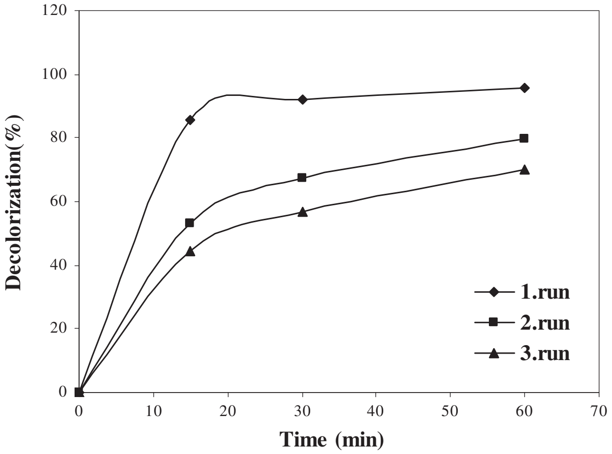


Fig. 8. Reuse of the catalyst for three consecutive runs (pH = 2, $[DO26]_o$ = 40 mg/L, $[H_2O_2]$ = 5 mM, concentration of catalyst = 1.5 g/L, and temperature = 25˚C).

3.7. Stability and reuse of catalyst, leaching test

It is necessary to investigate the stability and reusability of the catalyst due to economic and environmental reasons. Catalyst with reusability will reduce the cost of wastewater treatment. From environmental point of view, iron ions leached from catalyst could cause a secondary pollution in the environment [28]. Therefore, the reuse and leaching tests were performed to observe the possibility of Fe(III)-sepiolite catalyst reuse. The catalyst was used in three consecutive experiments. Between each experiment, the catalyst was removed by filtration and then washed with deionized water for several times and dried at 105˚C over night. It is obvious that the initial activity decreased gradually during successive runs Fig. 8. About 96% DO26 removal takes place at 60 min in the first run. In the second run, 80% of dye was removed at 60 min. Third run gave 70% dye removal. The decrease in efficiency may be due to leaching of Fe in each run [32]. Amount of Fe leached for the decolorization of DO26 in each run was measured using Atomic absorption spectrometer and the results are presented in Table 3. The leaching of Fe ions decreases in each run and, after the second run, the leaching is quite small compared with the effluent discharge standard which is 3 mg/L, and therefore leached iron concentrations are negligible, moreover it shows that catalysis performance is mainly based on heterogeneous effects of the catalyst [26,33].

Fe-ion leaching decreases with increase in pH (Table 4). The leaching phenomenon of metal catalyst is usually dependent on the pH environment. The leaching is higher at acidic condition (pH 2) and it is low at pH 4 and 6. It is observed that the leached

Table 3
Amount of Fe(III) ion leached from the catalyst for three consecutive runs (mg/L). (pH = 2, $[DO26]_o = 40$ mg/L, $[H_2O_2] = 5$ mM, concentration of catalyst = 1.5 g/L, and temperature = 25℃)

Time (min)	1. run	2. run	3. run
15	6.896	0.752	0.308
30	8.188	0.990	0.377
60	8.541	1.117	0.431

Table 4
Amount of Fe(III) ion leached for the different pHs (mg/L). ($[DO26]_o = 40$ mg/L, $[H_2O_2] = 5$ mM, concentration of catalyst = 1.5 g/L, and temperature = 25℃)

Time (min)	pH = 2	pH = 4	pH = 6
15	6.896	0.431	0.047
30	8.188	0.545	0.137
60	8.541	0.589	0.169

metal concentration is minimum at 15 min and pH 6 with the level of 0.047 mg/L. Finally, it can be said that catalyst is reusable but the efficiency of it decreases gradually due to low amounts of leached Fe ions.

3.8. Kinetics study

The decolorization kinetics of DO26 for a heterogeneous Fenton reaction were studied under various reaction conditions. The data were then regressed for the zero-, first-, and second-order reaction kinetics (Eqs. (5)–(7)).

Zero-order reaction kinetics:

$$\frac{dC}{dt} = -k_0 \tag{5}$$

First-order reaction kinetics:

$$\frac{dC}{dt} = -k_1 C \tag{6}$$

Second-order reaction kinetics:

$$\frac{dC}{dt} = -k_2 C^2 \tag{7}$$

where C is the concentration of DO26; k_0, k_1, and k_2 represent the apparent kinetics rate constants of zero-, first-, and second-order reaction kinetics, respectively; and t is the reaction time. By integrating the Eqs. (5)–(7), the following equations could be obtained (Eqs. (8)–(10)):

$$C_t = C_0 - k_0 t \tag{8}$$

$$C_t = C_0 e^{-k_1 t} \tag{9}$$

$$1/C_t = 1/C_0 + k_2 t \tag{10}$$

where C_0 is the initial concentration of the dye and C_t is the concentration of the dye at time t [34–36].

Regression analysis based on the zero-, first-, and second-order reaction kinetics for the decolorization of DO26 in oxidation process was conducted and the results were shown in Table 5. Comparing the

Table 5
The zero-, first-, and second-order kinetic rate constants for the decolorization of DO26 at different reaction conditions

pH	$[DO26]_o$ mg/L	$[H_2O_2]_o$ mM	[Catalyst] g/L	Stirring speed, rpm	Zero-order k_o (mg min/L)	R^2	First-order k_1 (1/min)	R^2	Second-order, k_2 (L min/mg)	R^2
3.0	40	35	2.0	250	0.507	0.518	0.038	0.669	0.005	0.902
4.0	40	35	2.0	250	0.490	0.548	0.031	0.696	0.003	0.890
6.0	40	35	2.0	250	0.502	0.632	0.031	0.776	0.002	0.875
2.0	40	5	1.5	250	0.529	0.550	0.047	0.797	0.008	0.998
2.0	100	5	1.5	250	1.331	0.497	0.060	0.719	0.009	0.990
2.0	200	5	1.5	250	2.659	0.478	0.068	0.637	0.009	0.923
2.0	40	15	1.5	250	0.517	0.487	0.045	0.582	0.009	0.741
2.0	40	35	1.5	250	0.526	0.479	0.055	0.590	0.019	0.845
2.0	40	55	1.5	250	0.512	0.492	0.041	0.600	0.007	0.814
2.0	40	35	0.5	250	0.521	0.541	0.043	0.749	0.006	0.971
2.0	40	35	1.0	250	0.506	0.481	0.039	0.544	0.006	0.687
2.0	40	35	3.0	250	0.523	0.478	0.052	0.568	0.015	0.779
2.0	40	35	1.5	140	0.510	0.530	0.038	0.672	0.004	0.828

regression coefficients (R^2) obtained, Table 5 shows the values of the regression coefficients for: (a) zero order is in the range of 0.478–0.632; (b) first order is in the range of 0.544–0.797; and (c) second order is in the range of 0.687–0.998. These results indicate that the second-order reaction kinetics best described the decolorization of the DO26 via Fenton process. In the present study, it can be concluded that the decolorization of DO26 by Fenton oxidation fits the second-order reaction kinetic of the type: the apparent kinetic rate constant, k_2, of the decolorization of DO26 was found to be 0.0019 L/mg min at an optimal condition of [DO26] = 40 mg/L, [H_2O_2] = 35 mM, catalyst concentration = 1.5 g/L, pH = 2.0, and 25˚C.

4. Conclusion

The heterogeneous Fenton process using Fe(III)-sepiolite provides good performance in the decolorization treatment of DO26 in aqueous solution. The heterogeneous Fenton oxidation process was evaluated by examining pH, H_2O_2 concentration, catalyst concentration, initial dye concentration, stirring speed, and reaction time. The optimal operational parameters were found to be a pH of 2.0, a 35 mM H_2O_2 concentration, a 1.5 g/L catalyst concentration, and a temperature of 25˚C for a dye concentration of 40 mg/L. Under these conditions, the decolorization process led to 98% decolorization of DO26 within 60 min. Other advantages of the heterogeneous system are the lack of generation of any solid waste (a significant disadvantage of the homogeneous Fenton process), the short contact time needed between the catalyst and the solution, and the high effectivity of the catalyst in a wide range of pH values.

The catalyst is reusable but the efficiency of the used catalyst is less than the fresh catalyst. The decrease in efficiency of the used catalyst is due to leaching Fe ion from the catalyst. Based on the results, catalyst is found to be a viable and reusable catalyst for the treatment of dye wastewater. Above all, the process is economical because of the availability of the raw material (sepiolite) employed.

References

[1] 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.

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

[3] N. Masomboon, C.W. Chen, J. Anotai, M.C. Lu, A statistical experimental design to determine o-toluidine degradation by the photo-Fenton process, Chem. Eng. J. 159 (2010) 116–122.

[4] 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.

[5] C.L. Hsueh, Y.H. Huang, C.C. Wang, C.Y. Chen, Degradation of azo dyes using low iron concentration of Fenton and Fenton-like system, Chemosphere 58 (2005) 1409–1414.

[6] J.H. Sun, S.H. Shia, Y.F. Lee, S.P. Sun, Fenton oxidative decolorization of the azo dye direct blue 15 in aqueous solution, Chem. Eng. J. 155 (2009) 680–683.

[7] 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.

[8] 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.

[9] 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.

[10] F. Martınez, G. Calleja, J.A. Melero, R. Molina, Heterogeneous photo-Fenton degradation of phenolic aqueous solutions over iron-containing SBA-15 catalyst, Appl. Catal. B 60 (2005) 181–190.

[11] M. Neamtu, C. Zaharia, C. Catrinescu, A. Yediler, M. Macoveanu, A. Kettrup, Fe exchanged Y zeolite as catalyst for wet peroxide oxidation of reactive azo dye Procion Marine H-EXL, Appl. Catal. B 48 (2004) 287–294.

[12] M. Neamtu, C. Catrineseu, A. Kettrup, Effect of dealumination of iron(III)-exchanged Y zeolites on oxidation of Reactive Yellow 84 azo dye in the presence of hydrogen peroxide, Appl. Catal. B 51 (2004) 149–157.

[13] M.A. De León, J. Castiglioni, J. Bussi, M. Sergio, Catalytic activity of an iron-pillared montmorillonitic clay mineral in heterogeneous photo-Fenton process, Catal. Today 133–135 (2008) 600–605.

[14] J. Feng, X. Hu, P.L. Yue, H.Y. Zhu, G.Q. Lu, A novel laponite clay-based Fe nanocomposite and its photo-catalytic activity in photo-assisted degradation of Orange II, Chem. Eng. Sci. 58 (2003) 679–685.

[15] J.H. Ramirez, F.J. Maldonado-Hódar, A.F. Pérez-Cadenas, C. Moreno-Castilla, C.A. Costa, L.M. Madeira, Azo-dye Orange II degradation by heterogeneous Fentonlike reaction using carbon-Fe catalysts, Appl. Catal. B 75 (2007) 312–323.

[16] F. Duarte, F.J. Maldonado-Hódar, A.F. Pérez-Cadenas, L.M. Madeira, Fenton-like degradation of azo-dye Orange II catalyzed by transition metals on carbon aerogels, Appl. Catal. B 851 (2009) 39–147.

[17] C.L. Hsueh, Y.H. Huang, C.C. Wang, C.Y. Chen, Photoassisted fenton degradation of nonbiodegradable azo-dye (Reactive Black 5) over a novel supported iron oxide catalyst at neutral pH, J. Mol. Catal. Chem. 245 (2006) 78–86.

[18] C.L. Hsueh, Y.H. Huang, C.Y. Chen, Novel activated alumina-supported iron oxide-composite as a heterogeneous catalyst for photooxidative degradation of reactive black 5, J. Hazard. Mater. 129 (2006) 228–233.

[19] Y.L. Song, J.T. Li, Degradation of C.I. Direct Black 168 from aqueous solution by fly ash/H_2O_2 combining ultrasound, Ultrason. Sonochem. 16 (2009) 440–444.

[20] 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.

[21] M. Alkan, O. Demirbas, S. Çelikçapa, M. Dogan, Sorption of acid red 57 from aqueous solution onto sepiolite, J. Hazard. Mater. B 116 (2004) 135–145.

[22] M. Doğan, A. Türkyilmaz, M. Alkan, Ö. Demirbaş, Adsorption of copper (II) ions onto sepiolite and electrokinetic properties, Desalination 238 (2009) 257–270.

[23] M. Doğan, Y. Turhan, M. Alkan, H. Namli, P. Turan, Ö. Demirbaş, Functionalized sepiolite for heavy metal ions adsorption, Desalination 230 (2008) 248–268.

[24] Ö. Gök, A.S. Özcan, A. Özcan, Adsorption kinetics of naphthalene onto organo-sepiolite from aqueous solutions, Desalination 220 (2008) 96–107.

[25] M. Tekbas, H.C. Yatmaz, N. Bektas, Heterogeneous photo-Fenton oxidation of reactive azo dye solutions using iron exchanged zeolite as a catalyst, Microporous Mesoporous Mater. 115 (2008) 594–602.

[26] R. Idel-aouad, M. Valiente, A. Yaacoubi, B. Tanouti, M.L. 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.

[27] N.K. Daud, M.A. Ahmad, B.H. Hameed, Decolorization of acid red 1 dye solution by Fenton-like process using Fe-Montmorillonite K10 catalyst, Chem. Eng. J. 165 (2010) 111–116.

[28] 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) 111–116.

[29] B. Cuiping, G. Wenqi, F. Dexin, X. Mo, 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.

[30] N.K. Daud, B.H. Hameed, Decolorization of acid red 1 by Fenton-like process using rice husk ash-based catalyst, J. Hazard. Mater. 176 (2010) 938–944.

[31] M.B. Kasiri, A.R. Khataee, Photooxidative decolorization of two organic dyes with different chemical structures by UV/H_2O_2 process: Experimental design, Desalination 270 (2011) 151–159.

[32] 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.

[33] 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.

[34] S.P. Sun, C.J. Li, J.H. Sun, S.H. Shi, M.H. Fan, Z. Qi, 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.

[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] 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, Desalin. Water Treat. 37 (2012) 1–7.