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Decolorization of reactive orange 16 via ferrate(VI) oxidation assisted by sonication

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Abstract: The decolorization of azo dye C.I. reactive orange 16 (RO 16) via ferrate(VI) and sono-ferrate(VI) methods, which is the combination of the ferrate(VI) oxidation method with sonication, has been achieved in the present study. The influences of some important operating parameters, which are the initial pH, the concentration of potassium ferrate(VI) (K_2FeO_4) and the RO 16 dye, and ultrasonic density (for only the sono-ferrate(VI) method), on the color removal have been investigated. The optimum conditions have been determined as $pH = 7$ and $[K_2FeO_4] = 50 \text{ mg L}^{-1}$ for the individual ferrate(VI) oxidation method and $pH = 7$ and $[K_2FeO_4] = 50 \text{ mg L}^{-1}$ by direct sonication at 0.50 W mL^{-1} ultrasonic density and 20 kHz fixed frequency for the sono-ferrate(VI) method. The color removal efficiencies were 85% by ferrate(VI) method and 91% by sono-ferrate(VI) method. Kinetic studies were also performed for the decolorization of RO 16 under the optimized conditions at room temperature. It was seen that the oxidative decolorization of RO 16 via the sono-ferrate(VI) method happened more rapidly because of the production of OH^\bullet radical through sonication compared to the individual ferrate(VI) method.

Key words: Color removal, ferrate(VI), reactive orange 16, sono-ferrate(VI), ultrasound

1. Introduction

Huge amounts of synthetic dyes are used in many industries, such as dyestuffs, leather, tanning, and textiles. In the textile industry, it was estimated that approximately 10%–15% of total dyes utilized were lost during the dyeing processes and released into wastewater.¹ More than 60% of dyestuffs manufactured around the world are azo dyes,² which are recalcitrant, nonbiodegradable, carcinogenic, mutagenic, and toxic.³ Wastewaters that include azo dyes must be effectively treated to prevent possible harm to aquatic life, since they may contain different pollutants such as dyestuff with various structures and textile auxiliary materials such as surface active materials and polyvinyl alcohol utilized in sizing processes.⁴ Discharge of these kinds of colored wastewaters into the aquatic environment causes serious damage to the environment by indirectly blocking sunlight due to their intense colors and by decreasing the oxygenation capacity of the surface water. Additionally, they also result in aesthetic problems in the receiving medium to which they are discharged. Therefore, these kinds of wastewaters must be treated before their discharge.

Azo dyes cannot be biologically degraded in conventional aerobic biological treatment.⁵ Some physico-chemical treatment methods such as adsorption, coagulation, and electrocoagulation based on phase transfer

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also cannot decompose the dyestuff in the wastewaters. For these reasons, chemical oxidation methods have attracted much attention in recent years. In the literature, there are studies on the degradation of azo dyes by different oxidation methods such as conventional oxidation, the Fenton process, ozonation, ultraviolet light (UV)-H₂O₂, sonication, and advanced oxidation via ferrate(VI) due to their strong oxidation abilities. In the conventional oxidation of pollutants in waters and wastewaters, potassium permanganate is usually utilized as an effective oxidizing agent; however, its major disadvantage is that it is expensive. The Fenton process is a simple and very effective advanced oxidation method, and its reaction byproducts are nontoxic. Thus, the Fenton process can be a good alternative in removing pollutants mainly in soluble form in wastewaters, but it has two important disadvantages limiting its usage: 1) the Fenton process is a pH-dependent redox process that requires a strong acidic medium for an effective treatment; 2) as a result of treatment via the Fenton process, a significant amount of chemical sludge (which may also contain heavy metals and nonoxidized pollutants) is produced as a product, based on the amount and type of catalyst iron used in the process.⁶ Ozonation, UV-H₂O₂, and sonication are ecofriendly and effective oxidation processes. However, they need a large amount of electrical energy for effective removal of pollutants from wastewaters and thus their operating cost may be very high. When compared with other treatment alternatives, the capital costs of these processes, depending on the load and kind of pollutants and the flow rate to be treated, may also be too high. On the other hand, potassium ferrate(VI) has been investigated to remove various pollutants from waters and wastewaters in the last decade. It is found to be a strong oxidant in a wide pH range and an environmentally friendly oxidant with nontoxic byproducts (Fe(III)).⁷ Ferrate(VI) is a dual-function chemical reagent with excellent oxidation and coagulation ability.^{8,9} With these advantages, it is attracting growing attention as an emerging water and wastewater treatment method, but there are only a few studies on color removal via ferrate(VI). Li et al.⁹ investigated the oxidative color removal of azo dye orange II by potassium ferrate(VI) and potassium permanganate. In their comparative study, it was found that potassium ferrate(VI) is a more powerful oxidizing agent than potassium permanganate. In a similar study, Han et al.¹⁰ studied the effects of anions (which can be found in textile wastewaters) on the oxidative color removal of azo dye reactive brilliant red X-3B using potassium ferrate(VI) and potassium permanganate reagents. They proved that Cl⁻, SO₄³⁻, and NO₃⁻ anions improved the decolorization reactions, while CO₃⁻² and PO₄⁻³ anions inhibited them notably. In addition, Han et al.¹⁰ also showed that potassium ferrate(VI) is a more effective reagent at pH 4–9 than potassium permanganate, similar to the results of the study by Li et al.⁹

Sonication has also received increasing attention in recent years, particularly in the removal of toxic and hazardous compounds from contaminated water. Sonication is a method comprising the application of high-power ultrasonic irradiation onto the liquid medium. Its natural result is the formation of acoustic cavitation in the reaction medium. Acoustic cavitation is the sonochemical formation of microsized bubbles in the liquid medium and the collapse of these bubbles in microseconds.¹¹ Extraordinary conditions, namely hot spots of 5000 K and pressure of nearly 1000 bar, have occurred during the collapse of cavitation bubbles.¹² As a result of these extreme conditions, acoustic cavitation has two main mechanisms for the removal of pollutants in the solutions: 1) the production of strong free oxidizing radicals such as OH•, O•, N•, and H•; and 2) thermal decomposition of volatile hydrophobic compounds in the bubbles.¹³ Therefore, sonication, as an innovative advanced oxidation method, has been experienced by combining it with the Fenton process and ozone and hydrogen peroxide in order to improve the removal of different pollutants in contaminated waters. Although color removal from solutions using chemical oxidation via potassium ferrate(VI) and sonication individually

has been investigated under different conditions, improvement of the oxidation ability of potassium ferrate(VI) assisted by sonication (referred to as “sono-ferrate(VI)”) has not been studied in the literature. Therefore, the main aim of this study was to compare the individual and combined efficiencies of potassium ferrate(VI) oxidation and sonication with a fixed low ultrasonic frequency (20 kHz) for color removal from azo reactive orange 16 (RO 16) dye solutions. The influences of operating parameters such as initial pH, K_2FeO_4 dosage, RO 16 concentration, and sonication density ($W\text{ mL}^{-1}$) were investigated experimentally. In addition, kinetic analyses for color removal by both ferrate(VI) and sono-ferrate(VI) oxidation methods were performed in this study.

2. Results and discussion

2.1. Effect of initial pH on color removal

The initial pH of the reaction medium has an influence on color removal efficiency via ferrate(VI) due to its role in determining both the reactivity and stability of ferrate(VI), and by affecting the molecular structure of dyestuff.^{9,10,14} Hence, the effects of initial pH on color removal via ferrate(VI) and sono-ferrate(VI) methods were first tested in the pH range of 2–10. The experimental results of both methods are illustrated in Figure 1. The optimization experiments of initial pH were conducted by using an initial K_2FeO_4 concentration of 100 mg L^{-1} for both methods, as summarized in Table 1.

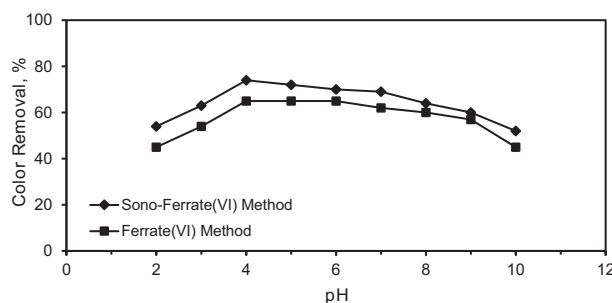


Figure 1. Effect of initial pH on color removal via ferrate(VI) and sono-ferrate(VI) methods.

As shown in Figure 1, maximum decolorization efficiency was obtained at pH 4 with both methods at the end of a 1-h oxidation period. At pH 4, decolorization of RO 16 was obtained by potassium ferrate at a rate of 66%, whereas it was obtained at a rate of 74% via the sono-ferrate oxidation method. Since the oxidizing power of the ferrate(VI) ions is higher in acidic media,^{15,16} efficiency of decolorization decreased with increasing pH from 4 to 9 at a negligible level. However, at pH of ≤ 3 and pH 10, decolorization efficiencies significantly decreased. At pH 2 and 3, 45% and 54% decolorization efficiencies were obtained with ferrate(VI) oxidation, respectively, while decolorization efficiencies were 51% and 61% via the sono-ferrate(VI) method, respectively. The reason for this result was that although ferrate(VI) was very strong as an oxidant at pH levels < 6 , it had a highly unstable character that resulted in self-decomposition with the production of Fe(III) and oxygen.^{9,10} At pH 10, on the other hand, decolorization efficiency was 45% by ferrate(VI) oxidation while it decreased to 50% with sono-ferrate(VI). The reason why these efficiencies decreased this much at pH 10 was that ferrate was chemically more stable at pH > 9 and thus had lower oxidant capacity.^{10,14} In other respects, as can be seen in Figure 1, the color removal efficiency of the sono-ferrate(VI) method was higher by as much as 4%–9% compared to the individual ferrate(VI) method, because hydroxyl radical ($OH\bullet$), known as the second strongest

Table 1. Reaction conditions for degradation of RO 16 via ferrate and sono-ferrate oxidation methods.

Affecting factors	Reaction conditions		
	Ranges	Other conditions for individual ferrate(VI) method	Other conditions for sono-ferrate(VI) method
Initial pH	2, 3, 4, 5, 6, 7, 8, 9, 10	[RO 16] = 100 mg L ⁻¹ , [K ₂ FeO ₄] = 20 mg L ⁻¹ , T = 24 °C, t = 60 min	[RO 16] = 100 mg L ⁻¹ , [K ₂ FeO ₄] = 20 mg L ⁻¹ , T = 24 °C, t = 60 min, ultrasonic density = 0.5 W mL ⁻¹
K ₂ FeO ₄ concentration, mg L ⁻¹	10, 20, 30, 40, 50, 60	[RO 16] = 100 mg L ⁻¹ , pH = 7, T = 24 °C, t = 60 min	[RO 16] = 100 mg L ⁻¹ , pH = 7, T = 24 °C, t = 60 min, ultrasonic density = 0.5 W mL ⁻¹
RO 16 dye concentration, mg L ⁻¹	50, 100, 150, 200	[K ₂ FeO ₄] = 50 mg L ⁻¹ , pH = 7, T = 24 °C, t = 60 min	[K ₂ FeO ₄] = 50 mg L ⁻¹ , pH = 7, T = 24 °C, t = 60 min, ultrasonic density = 0.5 W mL ⁻¹
Ultrasonic density, W mL ⁻¹ (only in the sono-ferrate method)	0, 0.25, 0.50, 1.00, 1.50, 2.00		[RO 16] = 100 mg L ⁻¹ , [K ₂ FeO ₄] = 50 mg L ⁻¹ , pH = 7, T = 24 °C, t = 60 min

oxidant in nature, was produced as a result of the reaction medium's exposure to sonication for a 1-h oxidation period (Eq. (1)).¹⁷⁻¹⁹ However, low production efficiency of OH• at the low ultrasonic frequency 20 kHz, at which sonication was carried out,^{11,20,21} limited the contribution of ultrasonic radiation in the sono-ferrate(VI) method to a negligible level. On the other hand, the lowest efficiency increases were obtained at pH 2 and 10 with the sono-assisted ferrate(VI) method because H⁺ ions in strong acidic medium as well as OH⁻ ions in strong basic medium indicated a radical scavenging effect against OH• radicals.^{22,23} As a result, it was observed that it had no significant effect on RO 16 decolorization at pH 4 and 9. At pH 7, 62% decolorization was obtained with ferrate(VI), whereas 69% decolorization efficiency was obtained with sono-ferrate(VI). Thus, optimum pH was determined as 7 and further optimization studies were carried out at pH 7.



2.2. Effect of K₂FeO₄ concentration on color removal

The dosage of potassium ferrate(VI) is one of the most important factors affecting both treatment cost and treatment efficiency. Since the amount of chemical sludge will increase as the dosage of potassium ferrate(VI) increases, sludge management and disposal lead to additional management problems in treatment plants. Moreover, increased amounts of chemical sludge lead to an increase in ferrate(VI)-sourced management costs of the oxidation process. For these reasons, optimization of potassium ferrate(VI) dosage is very important. Optimization of potassium ferrate(VI) was performed within the 10–60 mg L⁻¹ dosage range for both the ferrate(VI) and sono-ferrate(VI) methods for an oxidation period varying up to 1 h (Table 1). The results of experiments performed at pH 7 with 100 mg L⁻¹ RO 16 concentration are given in Figures 2a and 2b. As can be understood from Figures 2a and 2b, the decolorization efficiency always increased with increasing potassium ferrate(VI) dosage via both methods in accordance with Eqs. (2) and (3). This finding is consistent with the results of some studies in the literature.^{9,10,14} By increasing the dosage of potassium ferrate(VI) from 10 mg L⁻¹ to 50 mg L⁻¹, the efficiency increased from 46% to 85% just obtained with ferrate(VI) in a 1-h oxidation

period. In the sono-ferrate(VI) method, on the other hand, the decolorization efficiency increased from 52% to 91% with the increase in dosage from 10 mg L⁻¹ to 50 mg L⁻¹. There was a negligible increase in the decolorization performance of both oxidation methods in the end of the 1-h oxidation period by increasing the potassium ferrate(VI) dosage from 50 mg L⁻¹ to 60 mg L⁻¹. In oxidation experiments carried out with ferrate(VI) alone, it was observed that RO 16 decolorization was almost completed in the first 10 min due to consumption of ferrate(VI), a strong oxidant, in the reaction. In the sono-ferrate(VI) method, on the other hand, decolorization was very rapid in the first 10 min due to rapid consumption of ferrate(VI) in oxidation reactions; however, it was determined that decolorization was slowly increased in the remaining 50 min due to production of OH• radical caused by acoustic cavitation in the reaction medium (Eq. (1)).¹⁷⁻¹⁹ Since performing ultrasonic radiation at a low frequency (such as 20 kHz) limits the production amount of OH• radical in a reaction medium,^{11,20,21} it caused the efficiency increase in the sono-ferrate(VI) method (when all applied dosages were taken into consideration) at a limited rate such as 4%–9%. Therefore, the 50 mg L⁻¹ potassium ferrate dosage was found as the optimum dosage for both methods.

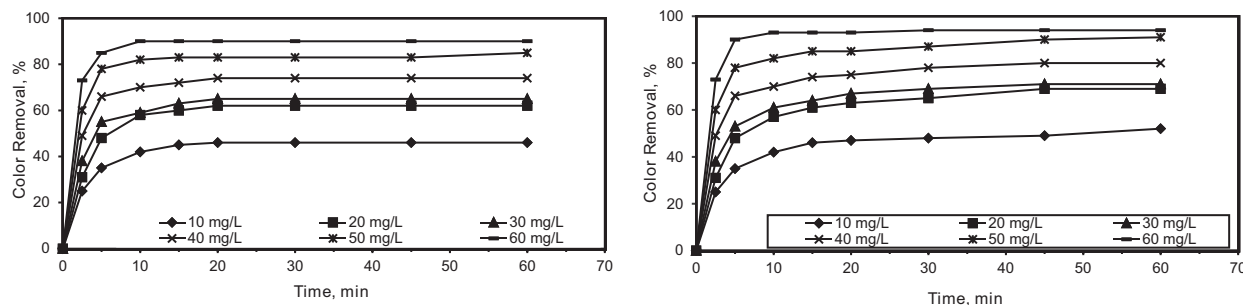
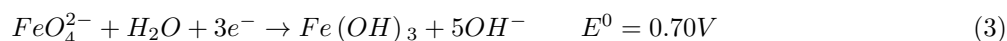


Figure 2. a) Effect of K₂FeO₄ concentration on color removal via ferrate(VI) method. b) Effect of K₂FeO₄ concentration on color removal via sono-ferrate(VI) method.



2.3. Effect of RO 16 concentration on color removal

The effect of RO 16 concentration on treatment efficiency of the ferrate(VI) and sono-ferrate(VI) methods was investigated with 50, 100, 150, and 200 mg L⁻¹ RO 16 concentrations, as presented in Table 1. For this reason, a series of experiments were performed at optimized pH 7 with 50 mg L⁻¹ potassium ferrate(VI) dosage for 1-h oxidation periods according to the previous optimization experiments. In the sono-ferrate(VI) method, ultrasonic radiation at 20 kHz frequency and 0.5 W mL⁻¹ density was added to these conditions. As shown in Figure 3, decreasing the dyestuff concentration from 100 mg L⁻¹ to 50 mg L⁻¹ increased the decolorization efficiencies of the ferrate(VI) and sono-ferrate(VI) methods from 83% and 88% to 96% and 99%, respectively. This increase in efficiency provided by the constant 50 mg L⁻¹ K₂FeO₄ concentration was caused by the excess presence of K₂FeO₄ in the reaction medium for adequate oxidation when the RO 16 concentration was decreased by half. On the other hand, increasing the RO 16 concentration to 150 and 200 mg L⁻¹ decreased the decolorization efficiencies to 67% and 58%, respectively, for the ferrate(VI) method, while it decreased to

71% and 62%, respectively, for the sono-ferrate(VI) method. This decrease in decolorization efficiency caused by increasing the concentration of RO 16 was because the 50 mg L⁻¹ concentration of K₂FeO₄ was insufficient. When compared to ferrate(VI), a negligible increase in the efficiency was provided by using the sono-ferrate(VI) method (Figure 3). This outcome is similar to the result of the study of Xu et al. performed on the degradation on azo dye brilliant red X-3B via composite ferrate solution.¹⁴

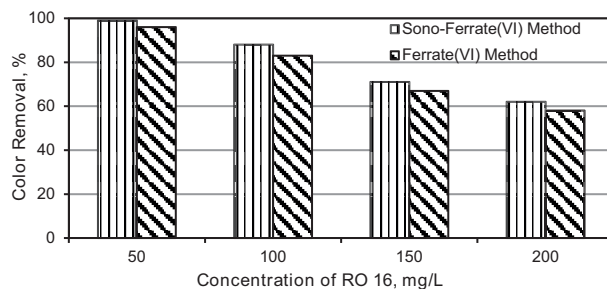


Figure 3. Effect of RO 16 concentration on color removal via ferrate(VI) and sono-ferrate(VI) methods.

2.4. Effect of ultrasonic density on color removal

The optimization of ultrasonic power is important, since it causes significant increase in both first capital and then also operating costs by using sonication processes for water and wastewater treatment. Within the scope of this study, ultrasonic power was optimized in terms of the ultrasonic density parameter, which is expressed as power applied per unit volume. The effect of ultrasonic density on efficiency was studied with 100 mL of RO 16 having 100 mg L⁻¹ concentration at pH 7 and with 50 mg L⁻¹ potassium ferrate(VI) dosage. Ultrasonic radiation, on the other hand, was investigated at 20 kHz constant frequency for a 1-h radiation period within the range of 0–2 W mL⁻¹ ultrasonic density. Experimental results are shown in Figure 4. While 85% decolorization efficiency was obtained in the case of not applying ultrasonic frequency (0 W mL⁻¹), decolorization always increased with the increase in ultrasonic density. While 91% efficiency was obtained with the 0.5 W mL⁻¹ ultrasonic density value of previous experiments, the efficiency was increased to 97% by increasing the ultrasonic density to 2 W mL⁻¹. Despite this increase in ultrasonic density, the reason for this limited efficiency in RO 16 decolorization was that the ultrasonic radiation was performed at a low ultrasonic frequency such as 20 kHz, at which the production of OH• was very low.^{17–19} The kinetic studies for the sono-ferrate(VI) oxidation method were carried out with an ultrasonic density of 0.50 W mL⁻¹.

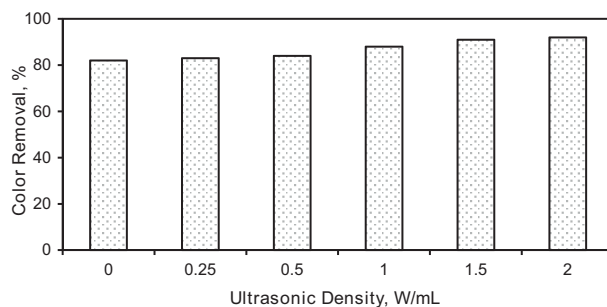


Figure 4. Effect of ultrasonic density on color removal via sono-ferrate(VI) method.

In addition, oxidation potential of sonication at 20 kHz frequency was experienced at 50 W mL⁻¹ power density for a 1-h period. It was determined that color removal efficiency of individual sonication was about 5%.

The reason for this result is that OH^\bullet production is very limited and so oxidation is not a dominant mechanism as a result of acoustic cavitation at the low ultrasonic frequency of 20 kHz.¹¹ However, the aim of this study is to improve the oxidation potential of ferrate(VI) oxidation by combining it with sonication, not to remove RO 16 via sonication alone.

2.5. Kinetic studies

The kinetic studies for RO 16 decolorization were carried out with 100 mg L^{-1} RO 16 concentration, 50 mg L^{-1} K_2FeO_4 concentration, and pH 7. In the sono-ferrate(VI) method, on the other hand, the ultrasonic radiation was carried out at 20 kHz frequency and 0.5 W mL^{-1} ultrasonic power density under the same conditions. As shown in Figure 5, decolorization was performed more rapidly and comparatively with higher efficiency than in the individual ferrate(VI) method due to the production of excessive oxidants such as OH^\bullet caused by acoustic cavitation in the sono-ferrate(VI) method.^{24,25} Moreover, it was determined that decolorization was carried out in two stages; these are a rapid oxidation stage in the first 10 min and then a slow oxidation stage in the remainder of the hour. In the first 10 min, the rate of decolorization obtained by the ferrate(VI) method compared to that obtained in the 1-h oxidation period was 89%, while it was 96% for the sono-ferrate(VI) method. The reason for this difference was the production of oxidant agents in the reaction medium even in limited amounts with 20 kHz frequency in the sono-ferrate(VI) method.¹¹ On the other hand, an individual sonication experiment was also performed in order to determine the effect of just ultrasonic radiation under the same experimental conditions. Approximately 5% decolorization was obtained with individual ultrasonic radiation in the oxidation experiments carried out at 0.50 W mL^{-1} power density without K_2FeO_4 . Thus, in the sono-ferrate(VI) method, it was determined that the dominating mechanism for RO 16 decolorization was ferrate(VI) oxidation. Combining sonication with ferrate(VI) oxidation increased the degradation rate and oxidation capacity of the sono-ferrate(VI) method. Similar results were obtained in the literature where sonication was applied together with other oxidation methods.²⁵

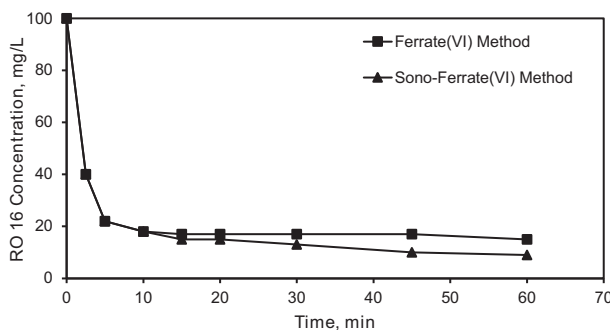


Figure 5. The decay curves for the decolorization of RO 16.

The zeroth, first, and second degree kinetic analysis of experimental data was carried out as given in Figure 5; however, it was determined that the data did not fit any of these methods. For this reason, the experimental data obtained after a 1-h oxidation period were applied with a new kinetic mathematical method^{3,24,26} as given in Eq. (4).

$$\frac{C_t}{C_0} = 1 - \left(\frac{t}{m + b \cdot t} \right) \quad (4)$$

Here, C_0 is the initial concentration of azo dye RO 16 (100 mg L^{-1}), C_t is the concentration at time t (mg L^{-1}), and b and m are the two dimensionless characteristic constants of the model relating to the initial removal rate and maximum oxidation capacities, respectively. In order to determine constants b and m , this equation can be linearized as follows (Eq. (5)):

$$\frac{t}{1 - (C_t/C_0)} = m + b \cdot t \quad (5)$$

The experimental data given in Figure 5 were applied to Eq. (5). The results are indicated in Figure 6, which is drawn as $t(1 - (C_t/C_0))^{-1}$ versus time for decolorization. In this figure, a straight line was obtained by plotting $t(1 - (C_t/C_0))^{-1}$ for the decolorization of RO 16 against oxidation time t , and m and b , the coefficients of Eq. (5), were obtained from the intercept and the slope of the line (Figure 6). For both methods, the b , m , and R^2 (determination coefficient) values obtained via the kinetic model are summarized in Table 2. The kinetic data obtained for RO 16 decolorization by both the ferrate(VI) and sono-ferrate(VI) methods were in accordance with the applied kinetic model and this can be shown by high correlation coefficients (R^2). Moreover, the b and m values indicated in Table 2 are proof of the higher oxidation capacity and higher oxidation rate of this novel hybrid method.

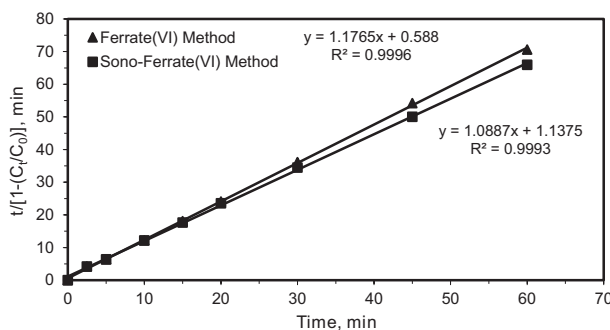


Figure 6. Relationship between $t/(1 - C_t/C_0)$ and oxidation time (t) for the decolorization of RO 16.

Table 2. The coefficients of determination and characteristic constants of the mathematical kinetic model.

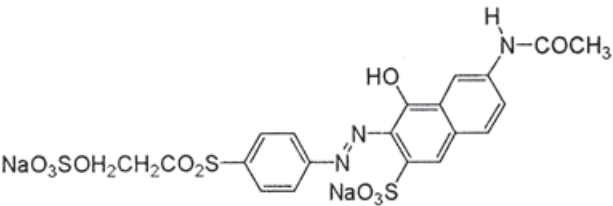
Parameters	Ferrate(VI) method			Sono-ferrate(VI) method		
	b	m	R^2	b	m	R^2
Decolorization	1.1765	0.588	0.9996	1.0887	1.1375	0.9993

3. Experimental

3.1. Materials

Reactive orange 16 (RO 16), used in this study, is a sulfonated reactive textile azo dye and was commercially purchased from a local supplier. It was utilized directly as received. The chemical characteristics of RO 16 are presented in Table 3. Potassium ferrate (K_2FeO_4) with $>90\%$ purity was bought from Sigma-Aldrich (Germany) and used as source of oxidizing agent ferrate(VI). All other chemicals were of analytical grade and supplied by Merck (Germany). All solutions were prepared using ultrapure water (MP MiniPure, Turkey).

Table 3. Chemical characteristics of reactive orange 16.

Parameters	Reactive orange 16
Chemical formula	C ₂₀ H ₁₇ N ₃ Na ₂ O ₁₁ S ₃
Chemical structure	
Molecular weight, g mol ⁻¹	617.54
Color index no.	17757
Chromophore Group	Single azo group
Maximum absorbance, λ _{max} , nm	493

3.2. Experimental method

Series of batch ferrate(VI) oxidation experiments were conducted at 500 mL⁻¹ working volume using a standard jar test apparatus (Mtops, South Korea) in order to investigate the influences of potassium ferrate(VI) (K₂FeO₄) concentration, initial pH, and RO 16 concentration on color removal at room temperature (24 ± 2 °C). Initial RO 16 concentration was kept constant at 50 mg L⁻¹ for all runs unless otherwise specified. H₂SO₄ and NaOH were utilized to adjust the initial pH in the range from 2 to 10 prior to the addition of K₂FeO₄. The pH measurements were carried out using a Hach Lange HQ 30d (Germany) single-input, multiparameter tool. It was assumed that the oxidation reaction started after the addition of K₂FeO₄ to the dye solution. The oxidation period was kept constant at 60 min. The mixing speed in this stage was set to 90 rpm. After the oxidation period, the solution pH was neutralized by addition of NaOH and H₂SO₄ to the reaction mixture. The reaction mixture was mixed to form and coagulate ferric iron (Fe(OH)₃) flocs at 30 rpm for 5 min. Later on, the solution was left standing in order to precipitate the flocs for 30 min. After 30 min of precipitation, 25 mL of sample was pipetted and filtered through a 0.45-μm pore sized membrane filter and filtrate was used for the UV-Vis spectrophotometric analyses after appropriate dilution.

The combination of ferrate(VI) with sonication was tested with 100 mL⁻¹ of the colored RO 16 solutions under the same conditions described above. However, the dye solution was sonicated by using an ultrasonic homogenizer during the 1-h oxidation stage, after the pH adjustment and addition of K₂FeO₄. Ultrasonic irradiation was performed by using an ultrasonic homogenizer (Bandelin, Germany) equipped with a titanium TT 13 probe in order to observe the effects of ultrasonic irradiation on the oxidative color removal performance of K₂FeO₄ in this novel combined method. The maximum ultrasonic power output of the sonicator was 200 W, while the ultrasonic frequency was constant at 20 kHz. The actual power was not measured during the experiments. During sonication applications, the reaction mixture was not mixed because of the vigorous turbulence effect of acoustic cavitation. Since the temperature of the dye solution rises inherently as a result of hot spots generated by acoustic cavitation, the temperature was not controlled in the sonication experiments and it was seen that the temperature rose to approximately 80 °C at 0.5 W mL⁻¹ ultrasonic density. In order to determine the influence of sonication on the removal of color from the RO 16 solution, experiments with individual ultrasound irradiation were also carried out at 0.5 W mL⁻¹ ultrasonic density for a 1-h sonication period. All experimental conditions are summarized in Table 1. All experiments were carried out in duplicate.

3.3. Analysis of samples

The residual RO 16 concentration was determined by measuring the absorbance value at the maximum wavelength (493 nm) of the RO 16 dye and computing the concentration from a calibration curve. A Thermo Aquamate UV-Visible spectrophotometer (USA) was employed for absorbance measurements using quartz cells of 1 cm in path length.

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