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Determination of the efficiency of fenton-like process in the presence of zero-valent catalyst: Reactive dye degradation

Filiz Nuran Acar[1]*, Salih Bingöl[1], İbrahim Cengiz[2]

[1] Atatürk University, Faculty of Engineering, Department of Environmental Engineering, 25100, Erzurum, Türkiye

[2] Atatürk University, Faculty of Applied Sciences, Department of Emergency Medical Services and Disaster Management, 25100, Erzurum, Türkiye

Abstract

In this study, the removability of azo group Reactive Red 2 (RR2) dye from aqueous solution was investigated in the presence of zero-valent iron with a Fenton-like process based on color and Chemical Oxygen Demand (COD) parameters. The effects of pH, zero-valent iron, and hydrogen peroxide (H_2O_2) concentrations on color and COD removal were investigated. The optimum color and COD removal conditions were determined as pH 3, ZVI = 0.1g/L, and H_2O_2 = 150mg/L. Under optimum conditions, at initial RR2 values of 10, 30, 50, 70, 100, 150, and 200 mg/L, color removal ranged from 100% to 95%, and COD removal ranged from 97.98% to 65.67%. The increase in RR2 concentration has a negative effect, mainly on COD removal. Kinetic evaluations were made by examining the efficiency of the process against time at different dyestuff concentrations at a constant temperature of 20°C under the most suitable process conditions for both color and COD removal. Pseudo-first-order, pseudo-second-order, and Behnajady-Modirshahla-Ghanbery kinetic models were applied to the color and COD removal results. At concentrations of 100, 150, 200 mg/L RR2 in the BMG model, the coefficient of determination for color was calculated in the range of 0.9984-1, while for COD it was determined in the range of 0.9935–0.9987. The results from kinetic calculations showed that the Fenton-like reaction fits the Behnajady-Modirshahla-Ghanbery model. This process can be considered a feasible advanced oxidation process, particularly for color removal, as it is inexpensive, easily accessible, and environmentally friendly.

Keywords: Advanced oxidation processes, fenton-like process, zero valent iron, reactive dye, reaction kinetics

1. Introduction

Increasing environmental pollution due to technological and industrial developments reveals the need for careful protection of aquatic environments. Today, the environment is more threatened by the impact of new and non-biodegradable resistant organics than by readily biodegradable pollutants in the natural environment. Synthetic dyestuffs used in textiles, cosmetics, leather, paper, and food are essential to resistant organics [1,2]. Over 10,000 different dyestuffs and pigments are used in various industries worldwide, and it is estimated that over 7×10^5 tons of synthetic dyestuffs are produced annually [3–5]. Of these synthetic dyes produced, 56% are textile dyes, 23.5% are pigments, 14% are paper dyes, and 6.5% are other dyes [5]. The textile industry is one of the largest producers of wastewater due to the large quantities of water used in dyeing processes [5]. It is estimated that about 300,000 tons of textile dyestuffs are discharged each year [5,6]. Depending on the class of dyestuff, up to 2% loss of dyestuff can occur in basic dyes and up to 50% in reactive dyes during the textile dyeing process.

The most essential characteristic of wastewater containing dyes is that it is highly colored. For this reason, color is usually the first pollutant parameter recognized in wastewater, directly indicating that the water is contaminated [5]. In natural aquatic environments, colored wastewater can degrade the appearance and inhibit photosynthesis by reducing light transmission [7]. In addition, dyestuffs are persistent in receiving environments because they are difficult to degrade due to their strong bond structure and high stability against light, temperature, water, soap,

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***Author of correspondence:** facar@atauni.edu.tr
Tel: +90 (442) 231 4802 **Fax:** n/a

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detergents, and other bleaches [4,8]. Therefore, they have harmful effects on all living things. Dyestuffs are known to cause symptoms such as rhinitis, allergies, occupational asthma, and dermatitis in humans, as well as carcinogenic, mutagenic, and teratogenic effects [8,9].

Conventional biological treatment processes are inadequate to remove these effects [10]. Therefore, Advanced Oxidation Processes (AOP) are preferred for removing resistant compounds such as dyestuffs from wastewater [11–13]. AOP includes a variety of treatment methods that have been evolving for about 50 years, from the 1970s to the present. These can be grouped as photolysis-based processes, ozone-based processes, hydroxyl radical production processes, sulfate radical production, thermal processes, and high-energy processes [14]. One of the processes in which hydroxyl radical production is achieved is the Fenton reaction. Henry John Horstman Fenton first performed the Fenton reaction in 1894 [15]. This oxidation reaction is based on producing strong oxidative hydroxyl ($OH^\bullet$) radicals in acidic conditions with divalent iron ions of hydrogen peroxide. $OH^\bullet$ radicals are highly reactive, aggressive, and powerful oxidants due to their high standard potentials of 2.8 V in acidic media and 1.55 V in basic media against a standard hydrogen electrode and rapidly and non-selectively convert a significant fraction of resistant contaminants in the water medium to CO_2 and H_2O [12,15,16]. In the Fenton process, the following equations are generally realized in the production of $OH^\bullet$ radical [17].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^\bullet + OH^- \tag{1}$$

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

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^- + H^+ \tag{3}$$

$$Fe^{3+} + HO_2^\bullet \rightarrow Fe^{2+} + O_2 + H^+ \tag{4}$$

$$H_2O_2 + OH^\bullet \rightarrow H_2O + HO_2^\bullet \tag{5}$$

The performance of Fenton-like processes that generate hydroxyl radicals as an alternative to the classical Fenton process is also considerable. In Fenton-like processes, instead of divalent iron, trivalent [18,19] zero valent iron (ZVI) [20] or various nanomaterials are used as catalysts [21–24]. ZVI is an environmentally friendly reducing agent. ZVI particles, which are used as catalysts in Fenton-like processes, have attracted wide attention primarily due to their cheapness, easy availability, and effectiveness in removing pollutants [25]. In the Fenton-like reaction in the presence of ZVI, Fe^{2+} ions are produced by first etching the surface of ZVI under acidic conditions. Then, $OH^\bullet$ radical production is realized in the presence of H_2O_2. This step is the classical Fenton reaction. Then the surface of the ZVI reduces Fe^{3+} ions to Fe^{2+} ions. The reactions are as follows [3,26]:

$$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2 \tag{6}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^\bullet + OH^- \tag{1}$$

$$2Fe^{3+} + Fe^0 \rightarrow 3Fe^{2+} \tag{7}$$

The ZVI Fenton-like process has several advantages over the classical Fenton process. These are preventing unnecessary anion loading to aquatic environments with the use of ZVI, using less ZVI compared to the iron used in the classical Fenton process, faster recycling of ferric iron on the iron surface, controlling the risk of release of toxic intermediates, and producing a non-toxic end product [3,27].

Many studies in the literature focus on different aspects of the ZVI-Fenton-like process. In a study investigating the removal of Rhodamine B using a Fenton-like process based on zero-valent iron, the optimal conditions were found to be pH 4, ZVI 9 mM, H_2O_2 8 mM, and RhB concentration 0.1; complete color removal was achieved within a 30-minute reaction time, while total organic carbon removal reached 63% within a 120-minute reaction time [28]. COD removal from desulfurization wastewater was investigated using a ZVI Fenton-like process and chemical precipitation method. Optimal conditions were determined to be a reaction time of 1 hour, H_2O_2 dosage of 33.3 mg/L, iron dosage of 0.075 g/L, pH 4.5–6.5, and a reaction temperature of 35 °C. It has been reported that the ZVI Fenton-like process is a good alternative for the treatment of desulfurization wastewater from coal-fired power plants [29]. The use of pyrite, ilmenite, vanadium titano-magnetite (VTM), ZVI, and zero-valent copper (ZVC) as Fenton-like catalysts for the removal of imidacloprid has been investigated. It has been reported that ZVI showed the highest activity among recyclable solid catalysts, with iron corrosion dissolution and a removal rate of 96.8% [30]. In a study investigating the simultaneous removal of thallium and organic matter from aqueous solutions using a ZVI-Fenton-like process, Tl and TOC removal rates of 99% and 80%, respectively, were achieved under optimal conditions. Five sequential cyclic tests using Fe^0 as a catalyst resulted in stable and efficient treatment performance. Therefore, it has been reported that the ZVI-supported Fenton-like process is promising for the removal of Tl and organic matter from wastewater [31]. The performance of Fe^0/peroxymonosulfate (PMS), Fe^0/peroxydisulfate (PDS), and Fe^0/H_2O_2 was compared for the treatment of oil-based drilling cuttings containing petroleum hydrocarbons.

Table 1. Experimental conditions for the Fenton-like process

Parameters	Variable conditions	Fixed conditions
pH	2, 3, 4, 5, 6	C_o=50 mg/L, COD_o = 44.47 mg/L, ZVI = 0.1 g/L, H_2O_2 = 100 mg/L, T = 20ºC, t = 20 min.
ZVI (g/L)	0.05; 0.1; 0.2; 0.3; 0.4; 0.5	C_o=100 mg/L, COD_o = 90.41 mg/L, pH =3, H_2O_2 = 100 mg/L, T = 20ºC, t=20 min.
H_2O_2 (mg/L)	50, 100, 150, 200, 250, 300	C_o=200 mg/L, COD_o = 193.81 mg/L, pH=3, ZVI = 0.1 g/L, T = 20ºC, t =20 min.
RR2 (mg/L)	10, 30, 50, 70, 100, 150, 200 (COD: 18.34; 36.52; 44.47; 55.04; 90.41; 147.16; 193.81)	pH = 3, ZVI= 0.1 g/L, H_2O_2 =150mg/L, T = 20 °C, t =20 min.

It was reported that all three processes were effective in removing straight-chain alkanes and that the degradation capacity decreased in the order Fe^0/H_2O_2 > Fe^0/PMS > Fe^0/PDS [32]. In another study, it was reported that drugs were degraded with a ZVI-Fenton-like process for secondary urban wastewater treatment at pH 4, and a significant portion of bacteria was removed. It has been reported that ZVI-Fenton at pH 4 is an effective treatment method against chemical (primary pollutants and intermediate products) and microbiological pollutants [33]. In a study conducted on the removal of ibuprofen and phenol using ZVI-Fenton, it was reported that both ibuprofen and phenol could be degraded under similar conditions. It was reported that the ZVI-Fenton process could be applied to pollutant mixtures [34].

In this study, the aim was to investigate the removal of Reactive Red 2, one of the reactive dyestuffs frequently used in textile dyeing processes, from aqueous solution by the Fenton-like process based on hydroxyl radical production. In order to achieve color and COD removal with effective efficiency, different experimental conditions were created, and the most suitable process conditions were determined. Reaction kinetics was tested with three different kinetic models.

2. Materials and methods

2.1. Materials

Reactive Red 2 (RR2) ($C_{19}H_{10}C_{l2}N_6Na_2O_7S_2$) was used as the dye. RR2 was obtained from Sigma-Aldrich. The molecular weight of the azo group RR2 is 615.34 g/mol, and its chemical structure is given in Fig. 1.

Hydrogen peroxide (H_2O_2) used as an oxidant in the Fenton-like reaction is 30% Riedel-de Haën brand. H_2O_2 stock solution was prepared with distilled water, diluted, and used in the experiments at desired concentrations. Zero-valent iron (ZVI) was used as a catalyst. ZVI has a particle size of 10 µm and was obtained from Merck.

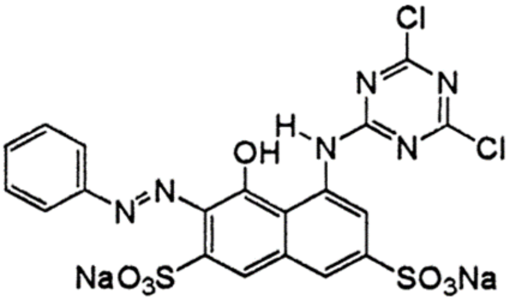

Figure 1. Chemical structure of Reactive Red 2 dyestuff.

2.2. Experimental setup and procedures

Fenton-like oxidation experiments were carried out in a batch reactor. First, a stock solution containing RR2 dyestuff was prepared. The stock solution was diluted, and solutions at desired concentrations were prepared and used in the experiments. For the dilute solutions taken into 250 mL bottles, pH adjustments were made first, and then the bottle was placed on a magnetic stirrer with a temperature probe. The catalyst and H_2O_2 were added to the solution at the desired dosages, respectively, and the experiment was started. The total running time was 20 minutes with three minutes of fast stirring and 17 minutes of slow stirring. Stirring speeds were 200 rpm for fast stirring and 80 rpm for slow stirring. After 20 minutes, the solution was neutralized and kept for 2 hours. Color and COD analyses were performed on the experimental samples to determine the effectiveness of Fenton-like processes in dyestuff removal. Experimental conditions are given in Table 1.

2.3. Analyses

After each test, the sample to be analyzed was passed through a membrane filter (0.45 µm), and then color and COD were measured. In the 400–1000 nm range, the peak wavelength detected in the visible region for RR2 dyestuff was 537 nm as a result of spectrum analysis. Color analysis was performed spectrophotometrically at the relevant wavelength. COD measurements were read spectrophotometrically at 600 nm wavelength according to Standard Methods [35] after heating at 148 °C for 2 hours in a thermoreactor.

Table 2. Removal efficiency and kinetic calculation equations

Removal efficiency	
Color removal efficiency = $\frac{C_0-C_t}{C_0}$ x 100 (1)	Co: Initial dye concentration Ct: concentration of dye in the solution at time t
COD removal efficiency = $\frac{COD_0-COD_t}{COD_0}$ x 100 (2)	CODo: Initial COD concentration CODt: COD concentration in solution at time t
Kinetic Calculations	
Pseudo-first order kinetic model [36] $\ln C_t = \ln C_0 - k_1 t$ (3)	t: Time Ct: concentration of dye in the solution at time t Co: Initial dye concentration k1: Pseudo-first order kinetic rate constant
Pseudo-second-order kinetic model [36] $\frac{1}{C_t} = \frac{1}{C_0} + k_2\, t$ (4)	t: Time Ct: concentration of dye in the solution at time t Co: Initial dye concentration k2: Pseudo-second order kinetic rate constant
BMG kinetic model [37] $\frac{t}{1-(C_t/C_0)} = m + bt$ (5)	m ve b: kinetic constants The constants m and b are usually defined as 1/m and 1/b, respectively. 1/m is related to pollutant removal, 1/b to oxidation capacity.

2.4. Theory

Equations and explanations for all calculations of the study are given in Table 2.

3. Results

3.1. Effect of pH

Fenton processes are strongly dependent on the pH of the solution, and it is the most critical parameter affecting the oxidation capacity [16]. In the experiments to determine the effect of pH on the Fenton-like reaction, the studies were carried out in the pH 2–6 range. The color removal results of the experiments carried out at 50 mg/L RR2 initial dyestuff concentration, 20 °C temperature, 0.1 g/L ZVI, and 100 mg/L H_2O_2 concentration are shown in Fig. 2. At the end of 20 minutes, 100% color removal efficiency was achieved at pH 2 and 3, and the color disappeared completely. In this experiment, the fact that the efficiency obtained at pH 2 was the same as pH 3 can be attributed to the low initial concentration of RR2. Significant decreases in decolorization were observed with increasing pH. The results obtained at pH 4, 5, and 6 were 68%, 28%, and 24%, respectively.

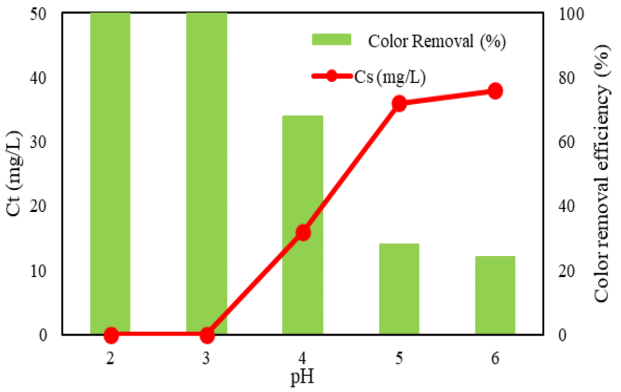

Figure 2. Effect of pH on color removal (C_o = 50 mg/L, ZVI = 0.1 g/L, H_2O_2 = 100mg/L, T=20 °C, t=20 min.).

The results of the effect of pH on COD under the same experimental conditions are as shown in Fig. 3. Although a high COD removal of 87.90% was achieved at pH 2, the highest COD removal was obtained at pH 3. At pH 3, the COD value decreased to 2.52 mg/L, which corresponds to an efficiency of 94.33%. The COD removal efficiencies obtained at pH 4, 5, and 6 are 21.90%, 11.02% and 10.19%, respectively. These results show that the efficiency of the Fenton-like reaction decreases with increasing pH. Fenton and Fenton-like reactions are maximized at low pH values. In many studies, the optimum pH value was found to be 3, mostly independent of the properties of the pollutant [3,38–40].

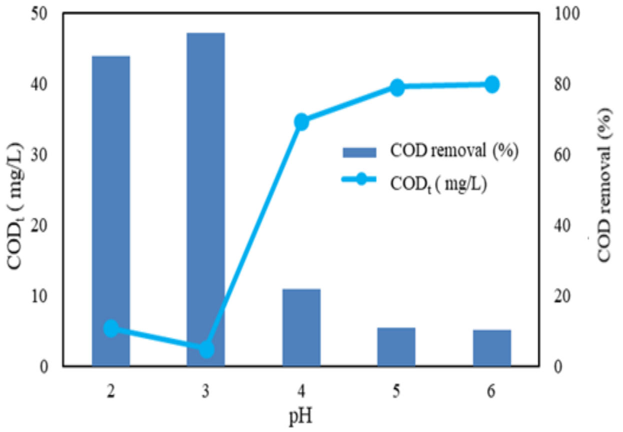

Figure 3. Effect of pH on COD removal (C_o = 50 mg/L, COD_o = 44.47 mg/L, ZVI= 0.1 g/L, H_2O_2=100mg/L, T=20 °C, t=20 min.)

These results obtained from color and COD removal can be explained theoretically as follows [41,42]: In Fenton reactions, when pH is lower than 3, complex iron compounds $[Fe(H_2O)_6]^{2+}$, $[Fe(H_2O)_6]^{3+}$, and $[Fe(H_2O)_5OH]^{2+}$ are formed, which react more slowly with H_2O_2. Thus, as mentioned in reactions 2 and 8, the reaction slows down and the oxidation capacity decreases.

$$\mathrm{Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + OH^{\bullet} + H_2O} \qquad (8)$$

In addition to the situation described in reaction 8, at pH <3, the formation of the oxonium ion (H_3O_2), which increases the stability of H_2O_2 and limits the production of the OH• radical, causes the reaction to slow down, as expressed by reactions 3 and 9.

$$\mathrm{R^{\bullet} + H_2O_2 \rightarrow ROH + OH^{\bullet}} \qquad (9)$$

The formation of the H_3O_2 ion occurs in the presence of high H^+ ions as described in reaction 10.

$$\mathrm{H_2O_2 + H^+ \rightarrow H_3O_2} \qquad (10)$$

If the pH increases, the formation of the OH• radical decreases as the iron in the medium is consumed by precipitation as $Fe(OH)_3$, and the production of Fe^{2+} from Fe^{3+} stops after precipitation (Reaction 11).

$$\mathrm{Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3} \qquad (11)$$

Another reason for the decrease in OH• radical formation with increasing pH is the increase in the rate of self-degradation of H_2O_2, as indicated in reaction 12.

$$\mathrm{H_2O_2 \rightarrow 2H_2O + O_2} \qquad (12)$$

3.2. The effect of ZVI

The effect of the amount of ZVI on the process was investigated for different ZVI concentrations at pH 3, which is considered to be optimum, at a constant concentration of 100 mg/L H_2O_2. The initial RR2 dyestuff concentration in these experiments was 100 mg/L. ZVI concentrations were 0.05 g/L, 0.1 g/L, 0.2 g/L, 0.3 g/L, 0.4 g/L, and 0.5 g/L. Fig. 4 shows the results of color removal. At 0.1 g/L ZVI concentration, RR2 concentration decreased to 2 mg/L at the end of the reaction period. This result shows the highest color removal efficiency with a value of 98%. Although the highest efficiency was obtained with ZVI at this concentration, the decolorization efficiencies obtained for other ZVI concentrations were also quite high. For other ZVI concentrations of 0.05 g/L, 0.2 g/L, 0.3 g/L, 0.4 g/L, and 0.5 g/L, the color removal efficiencies for RR2 dyestuff were 97%, 97%, 96%, 96%, 96%, and 95%, respectively.

The results of COD removal are given in Fig. 5, and approximate results were obtained with high efficiencies at all ZVI concentrations. From the lowest ZVI concentration to the highest, values of 92.45%, 93%, 93%, 90.38%, 90.19%, 89.28%, and 87.03% were recorded, respectively. At 0.1 g/L ZVI concentration, the COD concentration decreased from 90.41 mg/L to 5.49 mg/L with 93.93% efficiency. Since the highest efficiency was obtained at the same ZVI concentration in the color removal results, 0.1 g/L was considered the most suitable ZVI dose. Fu et al. (2010) found that 95.5%, 96.75%, 96.80%, and 97.05% color removal was achieved with 0.1, 0.2, 0.3, and 0.4 g/L ZVI doses used for the degradation of Acid Red 73 dyestuff at pH 3 by the Fenton-like process, and the color removal efficiencies obtained are very close to each other [3]. Moon et al. (2011) reported in their study that they removed Orange II dyestuff from aqueous media by the Fenton-like process using synthesized nano ZVI (nZVI). They investigated the removal of Orange II from aqueous media by a Fenton-like process. In their studies conducted at pH 3, 30% and 53% decolorization was achieved at 5 and 10 mg/L nZVI doses, respectively, while decolorization was 95% at 20 mg/L nZVI dose with increasing nZVI. Since there was no significant increase in decolorization efficiency when the nZVI dose was increased to 40, 60, 80, and 100 mg/L, they determined the appropriate catalyst dose as 20 mg/L [39]. Zhang et al. (2017) reported that the highest norfloxacin removal at 10, 50, 100, 500, and 1000 mg/L nZVI doses was observed at a 100 mg/L nZVI dose in norfloxacin degradation in nZVI synthesized by the Fenton-like process [40].

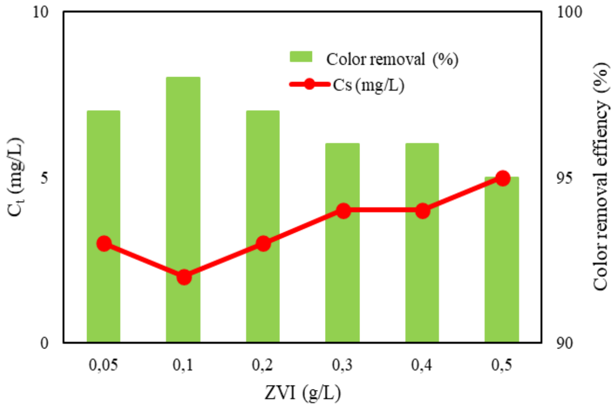

Figure 4. Effect of ZVI on color removal (C_o =100 mg/L, pH=3, H_2O_2 = 100mg/L, T = 20 °C, t = 20 min.).

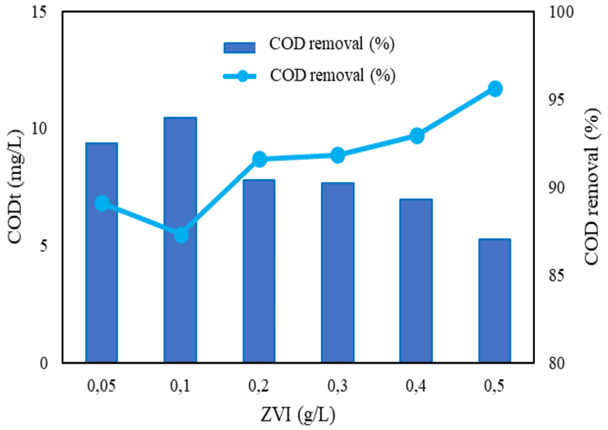

Figure 5. Effect of ZVI on COD removal (C_o=100 mg/L, pH=3, H_2O_2=100 mg/L, T=20 °C, t=20 min.).

The amount of ZVI used in the Fenton-like process is essential for initiating catalytic activity and generating the OH• radical. The increase in the catalyst dose can increase the removal rate of pollutants from wastewater. However, the catalyst cannot be added without any limitations. Excessive addition of catalyst to the solution results in an increase in catalyst cost and the formation of excessive volumes of sludge after treatment [43]. In addition, the catalyst has a scavenging effect on the OH• radical at high concentration. Therefore, the reaction is negatively affected [43,44]. At low catalyst concentrations, fewer OH• radicals are formed in the environment, and an effective reaction does not occur [44,45]. Another study emphasized that high iron ion concentration has little effect on oxidation capacity, but decreasing iron ion concentration is more important to initiate the oxidation reaction [46]. Considering all these reasons, it is obvious that it is necessary to determine the optimum dose for ZVI concentration.

3.3. Effect of H_2O_2

In the Fenton-like process, the concentration of H_2O_2 in solution is critical since the production of the OH• radical under catalysis occurs by H_2O_2 degradation. Therefore, the optimum H_2O_2 dosage should be determined experimentally. Insufficient H_2O_2 dosage means less production of the OH• radical. In contrast, high H_2O_2 dosage should not be preferred. The most important reason for this is that the presence of excessive amounts of H_2O_2 has a scavenging effect on the OH• radical as expressed in Reaction 5 [43]. The effect of H_2O_2 was studied at 50, 100, 150, 200, 250, and 300 mg/L H_2O_2 concentrations at pH and ZVI doses determined as optimum. In this study, RR2 concentration was increased to 200 mg/L to observe the effect of H_2O_2 on decolorization more clearly. The results of color removal are given in Fig. 6. At the end of 20 minutes, it is seen that the color removal increases with the increase of H_2O_2. This increase reached the highest level at 250 mg/L H_2O_2 concentration, but the color removal decreased to 97.5% at 300 mg/L H_2O_2 concentration. As can be seen from the figure, the lowest efficiency was obtained at 50 mg/L H_2O_2 concentration with 87.5%. At 250 mg/L H_2O_2, RR2 dyestuff concentration decreased from 200 mg/L to 3 mg/L; the highest color removal was 98.5%. At 150 mg/L H_2O_2 concentration, the color removal was 95%.

As shown in Fig. 7, The highest COD removal was achieved at 250 mg/L H_2O_2 concentration with an efficiency of 79.04%, and the COD value decreased from 193.81 mg/L to 40.63 mg/L. The lowest COD removal efficiency was 55.98% at the lowest H_2O_2 dose of 50 mg/L, and the highest efficiency was 70.55% at the highest H_2O_2 dose of 300 mg/L.

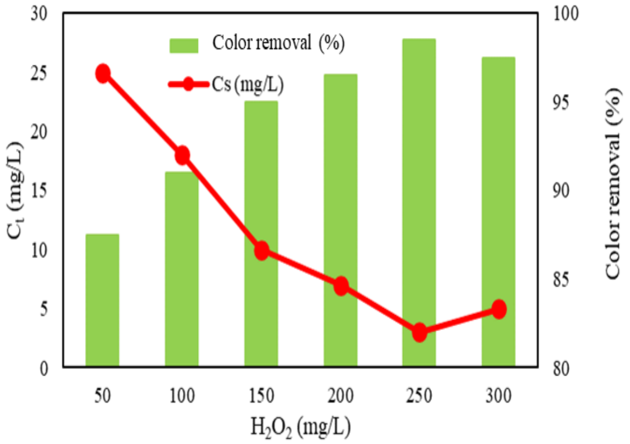

Figure 6. Effect of H_2O_2 on color removal (C_o=200 mg/L, pH=3, ZVI=0.1 g/L, T=20 °C, t=20 min.)

In decolorization, since the yield obtained at 150 mg/L H_2O_2 concentration was close to the yield obtained with 250 mg/L H_2O_2 concentration, 150 mg/L H_2O_2 was determined as the appropriate amount of oxidant. In this assumption, other effects of H_2O_2 overdose were also considered. These effects can be listed as the negative effects of excess H_2O_2 on the activation of microorganisms in case the Fenton-like process is used as pre-treatment before biological treatment, an increase in the cost of H_2O_2, and an increase in the discharge standards of the treated water in terms of COD, although there is no harm to the environment [43].

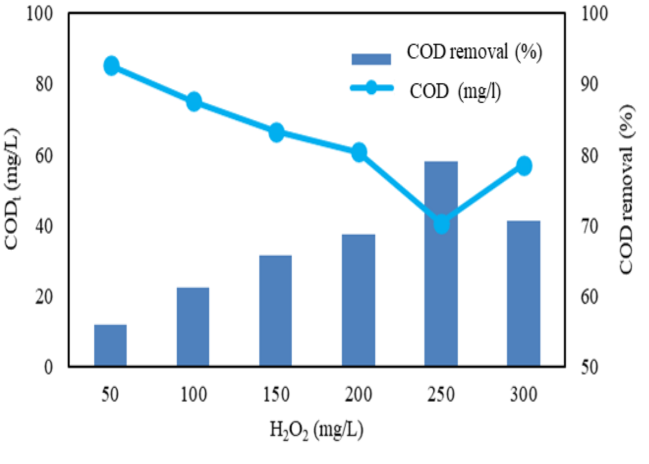

Figure 7. Effect of H_2O_2 on COD removal (C_o = 200 mg/L, COD_o = 193.81 mg/L, pH = 3, ZVI = 0.1 g/L, T=20 °C, t=20 min.)

3.4. Effect of the initial concentration of RR2

Initial pollutant concentration values directly affect the efficiency of treatment processes. This study investigated the performance of the Fenton-like reaction at low and high RR2 concentrations. In the study carried out at 20 °C, the initial concentrations of RR2 determined were 10, 30, 50, 70, 100, 150, and 200 mg/L. Optimum conditions were applied for other process parameters. Fig. 8 shows the color and COD removal efficiencies after 20 minutes for different RR2 initial values.

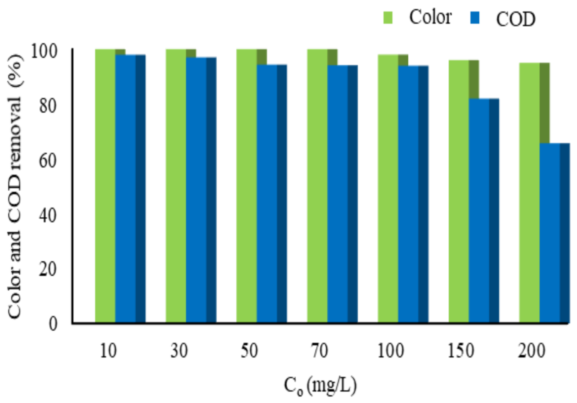

Figure 8. Effect of different initial RR2 concentrations on color and COD removal (pH=3, ZVI = 0.1g/L, H_2O_2=150mg/L).

Effective results were obtained at all RR2 initial concentration values for color removal. There is no significant decrease in color removal efficiency with increasing RR2 concentration. 100% color removal was achieved at 10, 30, 50, and 70 mg/L RR2 initial concentrations. At 100, 150, and 200 mg/L RR2 initial concentrations, 98%, 96%, and 95% color removal was achieved, respectively. These results indicate that the Fenton-like reaction in the presence of ZVI is highly efficient for high dyestuff concentrations in color removal under appropriate process conditions. COD removal efficiency decreased with increasing RR2 concentration. However, there was no significant decrease in COD removal up to 150 mg/L RR2 concentration. It was determined that the Fenton-like process provided a highly efficient removal of 10-100 mg/L RR2 initial concentrations. When COD and color removal were compared, it was observed that COD removal reached values close to color removal efficiencies up to 150 mg/L RR2 concentration. For example, at initial RR2 concentrations of 10 mg/L and 100 mg/L, COD removal was 97.98% and 93.93%, respectively. However, the decreases in COD removal efficiency were more significant at 150 and 200 mg/L RR2 concentrations. At 200 mg/L RR2 concentration, COD removal was 65.67%.

3.5. Kinetic calculations

The color and COD concentrations remaining in the solution according to the experimental studies carried out against time at different RR2 initial concentrations under optimum conditions for color and COD removal are shown in Fig. 9 and Fig. 10. Kinetic calculations were made using these data. Kinetic calculations were performed for RR2 concentrations of 100, 150, and 200 mg/L due to the rapid reaction in the first minutes at low RR2 concentrations and the lack of data over time.

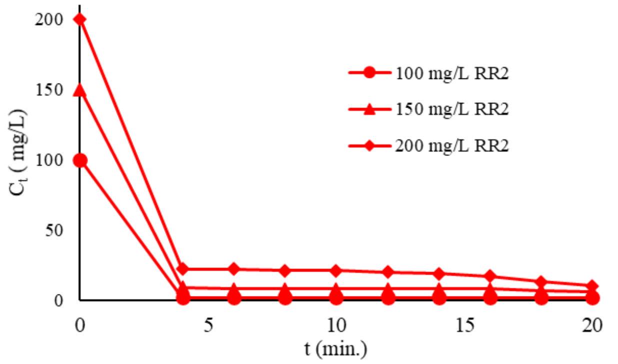

Figure 9. Effect of dyestuff initial concentrations on color and COD removal (pH=3, ZVI= 0.1g/L, H_2O_2=150 mg/L, T=20 °C).

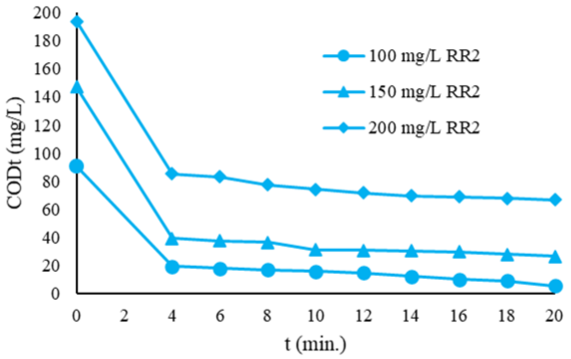

Figure 10. Effect of dyestuff initial concentrations on COD removal (pH=3, ZVI=0.1 g/L, H_2O_2=150mg/L, T=20 °C)

Pseudo-first order kinetics, pseudo-second order kinetics, and Behnajady-Modirshahla-Ghanbary kinetics models were used for kinetic evaluations. In the pseudo-first-order kinetic model, the reaction rate constant was calculated from the slope of the line obtained from lnC_o/C_t values versus t time values. In the pseudo-second-order kinetic model, the reaction rate constant was obtained from the slope of the line formed by $1/C_t$ values versus t. In the BMG kinetic model, where $t/\,[1-(C_t/C_o)]$ values were used against t time data, m and b constants were determined. The results of the equations and kinetic constants obtained by applying the kinetic models are given in Table 3. The results showed that the BMG model was the most appropriate kinetic model with high correlation coefficients for color and COD.The constants m and b, which are extreme values in the BMG kinetic model, can be determined by the following equation [37,47].

$$\frac{\frac{dCt}{Co}}{dt} = \frac{-m}{(m+bt)^2} \tag{6}$$

If the duration t is very short or close to zero, the equation is expressed as follows:

$$\frac{\frac{dCt}{Co}}{dt} = \frac{-1}{m} \tag{7}$$

This is the expression of the initial removal rate of the dyestuff. A high value of 1/m indicates that the pollutant is removed rapidly at the beginning of the reaction. The value 1/b represents the theoretical maximum pollutant removal fraction when t tends to infinity. This explains the maximum oxidation capacity of the Fenton-like process, which the following equation can express.

$$\frac{1}{b} = 1 - \frac{Ct \rightarrow \propto}{Co} \tag{8}$$

Tunç et al. (2012) conducted a study to determine the optimum experimental conditions for removing Acid Red 66 and Direct Blue 71 dyes from aqueous media. They applied pseudo-first-order kinetics, pseudo-second-order kinetics, and BMG kinetics models for the experimental results obtained from this study. They stated that the BMG model is more appropriate [47]. Similarly, Ertugay & Acar (2013, 2017), Basic Blue 9 and Direct Blue 71, and Bayar & Erdoğan (2019) stated that the kinetic results with Reactive Red 45 azo dyestuff in the Fenton process are based on the BMG kinetic model [48–50]. Apart from dyestuffs, it was stated that the BMG kinetic model is the most appropriate model for the removal of Lactate, one of the organic pollutants, by the Fenton process [51] and Paraquat, a water-soluble herbicide, by the Fenton-like process [52].

Various kinetic models have been adopted in Fenton-based oxidation processes. Although zero, first, and second-order kinetic models are widely used, they are insufficient to explain a series of reactions that develop rapidly at first and then slowly in Fenton oxidation. Although the species involved in the reaction are $HO^\bullet$ radicals in the initial stage, the reaction rate decreases over time due to the absence of $HO_2^\bullet$ radicals. Additionally, the formation of $HO{\cdot}2$ radicals, which have a lower oxidation potential than HO^* radicals, is another reason for the slow phase. Therefore, the Behnajady-Modirshahla-Ghanbary (BMG) kinetic model helps explain two-stage Fenton reactions [53,54].

4. Conclusion

The removal of RR2 dyestuff in aqueous media by the Fenton-like oxidation reaction in the presence of ZVI was investigated. The results obtained for the color and COD removal of the Fenton-like process at 20^oC constant temperature for a 20-minute reaction time can be listed as follows:

The pH study achieved 100% color removal at pH 2 and 3 for an initial concentration of 50 mg/L RR2. Significant reductions in color removal were recorded at pH values higher than pH 3, and the lowest efficiency of 24% was determined at pH 6. In COD removal, pH was found to be effective on the results. While COD removal was 94.33% at pH 3, it was realized as 10.19% at pH 6. The most suitable pH value for RR2 removal was accepted as 3.

The effect of ZVI concentration was investigated in the range of 0.05–0.5 g/L ZVI dose, 100 mg/L RR2 initial concentration, 100 mg/L H_2O_2 concentration, and pH 3. The highest efficiency of 98% for color and 93.33% for COD was achieved in the presence of 0.1 g/L ZVI, and this value was considered as the most appropriate ZVI dose.

The effect of H_2O_2 concentration was studied in the 50–300 mg/L H_2O_2 range, with 200 mg/L RR2 concentration at the optimum pH and ZVI dose. Although the highest removal for both color and COD was observed at 250 mg/L H_2O_2 concentration, since H_2O_2 consumption was not high and high removal efficiencies were obtained at 150 mg/L H_2O_2, it was decided that the most suitable H_2O_2 concentration was 150 mg/L.

Under optimum conditions, at initial RR2 values of 10, 30, 50, 70, 100, 150, and 200 mg/L, color removal

Table 3. Kinetic equations and parameters for color and COD removal

	Color				**COD**			
			Pseudo-First Order Kinetics					
Co		**k_1 (min^{-1})**	**R^2**			**k_1 (min^{-1})**	**R^2**	
100	y = -0.0991x + 4.1916	0.1143	0.3506		y = -0.1030x + 3.8451	0.1030	0.8143	
150	y = -0.0976x + 3.3961	0.0976	0.4390		y = -0.0601x + 4.2649	0.0601	0.5943	
200	y = -0.0991x + 4.1916	0.0991	0.6194		y = -0.0386x + 4.8122	0.0386	0.6065	
			Pseudo-Second Order Kinetics					
Co		**k_2 ($Lmg^{-1}min^{-1}$)**	**R^2**			**k_2 ($Lmg^{-1}min^{-1}$)**	**R^2**	
100	y = 0.0143x + 0.2964	0.0143	0.3506		y = -0.0065x + 0.0087	0.0065	0.8189	
150	y = 0.0051x + 0.0627	0.0051	0.6111		y = -0.0012x + 0.0161	0.0012	0.7754	
200	y= 0.0034x + 0.0163	0.0034	0.8046		y = -0.0004x + 0.0086	0.0004	0.7233	
			BMG Kinetics					
Co		**1/ b**	**1/ m**	**R^2**		**1/b**	**1/ m**	**R^2**
100	y = 1.0204x + 8E-15	0.9800	1.25e+14	1.0000	y = 1.0677x + 0.9004	0.9366	1.1106	0.9935
150	y = 1.0459x + 0.0732	0.9561	13.6612	0.9999	y = 1.2117x + 0.5433	0.8263	1.8406	0.9987
200	y = 1.0602x + 0.3443	0.9432	2.9044	0.9984	y = 1.4933x + 0.9748	0.6696	1.0258	0.9978

ranged from 100% to 95%, and COD removal ranged from 97.98% to 65.67%. The results show that the increase in RR2 concentration has a negative effect mostly on COD removal. Kinetic studies showed that the BMG model is suitable for both color and COD parameters for RR2 degradation by the Fenton-like process.

The Fenton-like process in the presence of ZVI gave highly effective color and COD removal results in a very short reaction time. This process is a remarkably advanced oxidation process, especially in color removal, with the use of ZVI, which is cheap, easily available, and considered environmentally friendly.

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