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Investigation of the treatability of essential oil industry wastewater using Fenton oxidation process

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ABSTRACT

Lavender essential oil is one of the most common essentials oils and contributes significantly to the global market as it is used in many fields. Accordingly, the production of it in Turkey has shown remarkable improvement in recent years. Lavender essential oil production is carried out by steam distillation and generates high-strength wastewater. Since the discharge to natural environments without treatment causes various problems, the treatment of this wastewater using various treatment technologies is mandatory. In the present study, the treatability of lavender essential oil production wastewater (LOPW) by Fenton process was investigated. For this purpose, laboratory scale experimental studies were conducted to examine the effects of various basic operational parameters on the performance of Fenton oxidation. Under the optimal conditions (pH = 4.0, H_2O_2 = 88 mM, Fe^{2+} = 54 mM and H_2O_2/Fe^{2+} molar ratio = 1.62), a chemical oxygen demand (COD) removal efficiency as high as 81% was achieved. Under the same conditions, the highest color removal efficiencies were found to be 92% for Pt-Co, 94% for spectral absorption coefficient. The results suggest that Fenton process can be applied as a pretreatment process to improve COD and color removal from LOPW.

Keywords: Advanced oxidation; COD removal; Fenton process; Industrial wastewater; Lavender essential oil production wastewater; Spectral absorption coefficient

1. Introduction

Essential oils are natural products that can be isolated from medicinal and aromatic plants [1]. Lavender essential oil is one of the best-known essential oils in the world. It has been used since ancient times for its carminative, sedative and antidepressant properties [2], and it has a wide range of applications in the cosmetics, perfume, pharmaceutical, and food industries and as well as its use in, aromatherapy as a relaxant [3]. Due to the commercial and industrial importance of lavender essential oil, the demand for this oil is increasing day by day in the world. In Turkey also, interest in lavender and lavender oil production has increased in the last decade and lavender oil has become commercially popular. Lavender was produced on less than 50 ha of land before 2000, but this is approaching 700 ha today [4]. Accordingly, the number of enterprises active in this sector is also increasing.

Lavender essential oil is traditionally obtained by steam distillation from lavender flowers (*Lavandula angustifolia*) [1]. The process is carried out in distillation vessels with a capacity of 500–1000 kg. Lavender flowers and water are placed in the distillation vessels with, 500 kg of lavender flowers per liter of water, and steam is supplied under pressure to the vessels. The steam extracts the oil droplets and passes them to a cooling system. At the end of this process, besides lavender oil, which is of commercial importance, wastewater is also produced. This wastewater has an intense color and a high organic load. It is estimated that small scale enterprises in Turkey generate 8 m^3/d of wastewater. Since these enterprises are seasonally operated, the wastewater is generated only during lavender season from June to September. This wastewater has a high organic load [a considerable chemical oxygen demand (COD) level] and color, and is discharged without any treatment, causing various environmental problems such as polluting surface and groundwater, damaging aquatic life, and reducing soil fertility. In addition, discharge of this wastewater to the sewage system and sending it to domestic wastewater treatment plants can lead to various technical and environmental risks. Therefore, these enterprises must implement a process to reduce organic load and color before discharging their industrial wastewater. Many processes have been applied for the treatment of industrial wastewater. Biological treatment processes are environmentally friendly and cost effective methods which are used in the treatment of industrial wastewater containing high organic loads and colors. However, these treatment processes are not recommended for this type of seasonally produced wastewater [5], since they require longer times to remove pollutants [6]. In addition, these treatment methods are not effective in removing the recalcitrant organic pollutants found in industrial wastewater. Studies have indicated that the organic content and refractory character of essential oil industry wastewaters pose a challenge for biological treatment and a pre-treatment process should be used [7]. Furthermore, other conventional treatment technologies such as coagulation, flocculation or adsorption also enable the transfer of pollutants from only one phase to the other [8].

Advanced oxidation processes (AOPs) are efficacious methods of removing color and breaking down organic pollutants in various industrial wastewaters. AOPs produce a large amount of hydroxyl radicals, strong oxidants that can ensure complete mineralization of organics to CO_2, water and inorganic components [9,10]. Among AOPs, Fenton oxidation is one of the most widely applied methods and it has been proven in the treatment of various industrial wastewaters such as in the cosmetics [11], olive oil [12], tannery [6], textile [13], pulp and paper [14] and, distillery [15] industries.

Fenton oxidation provides the production of hydroxyl radicals which have high oxidizing capacity by reactions of ferrous ions and hydrogen peroxide at an acidic pH [Eq. (1)].

The hydroxyl radicals formed are extremely effective at breaking down any recalcitrant organic pollutants in a short time [Eq. (2)] [12,16].

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

$$\mathrm{HO}^{\bullet} + \mathrm{RH} \rightarrow \mathrm{H_2O} + \mathrm{R}^{\bullet} \tag{2}$$

In addition, the Fenton process offers a number of advantages such as simplicity, easy applicability, non-toxicity and high organic removal rates [14]. However, this process has some drawbacks such as the high costs (handling, transportation and storage) of reagents (especially H_2O_2) and excessive sludge formation [17].

Studies on the treatment of essential oil industry wastewater are very scarce. Avsar et al. [5] investigated the applications of electrocoagulation and Fenton processes in treatment of rose processing wastewater. In a case study conducted by Sigma group in Spain, a treatment process consisting of coagulation–flocculation, DAF and biological treatment was used for the fragrance and essential oils industry wastewater, and COD removal of 97% was achieved [7]. Heydari et al. [18] evaluated the pollutants removal performance (COD, phenol, oil and grease and turbidity) and biogas production from the up-flow anaerobic sludge blanket reactor treating synthetic spearmint essential oil wastewater (SEOW). However, to the authors' knowledge, no studies on the treatment of lavender essential oil production wastewater (LOPW) have been reported in the literature yet and therefore this study will be the first. The aim of the present study was to investigate the efficiency of the Fenton oxidation process for the removal of organic compounds and color from LOPW. In this context, the effects of basic operating parameters such as reaction time, initial pH, hydrogen peroxide and ferrous ion concentration and, H_2O_2/Fe^{2+} molar ratio on the reaction were investigated and optimum values were determined.

2. Materials and methods

2.1. Wastewater characteristics

LOPW was taken from the distillation vessels of a factory for the production of rose and other essential oils located in Isparta, Turkey. The factory works mainly as a rose processing plant. However, after the rose processing season, the distillation tanks used for rose processing are employed for lavender essential oil production in lavender season (June to September). The LOPW was stored in a refrigerator at 4°C to avoid microbial growth before it was used in these studies. The raw wastewater had a COD of 1,650 mg/L, a color of 930 Pt-Co and pH of 5.1. The characteristics of LOPW are shown in Table 1.

2.2. Chemicals and analytical methods

All chemicals used in the research, including ferrous sulphate heptahydrate ($FeSO_4·7H_2O$, content ≥ 99%), hydrogen peroxide (H_2O_2, 30% w/w), sodium hydroxide (NaOH) and sulfuric acid (H_2SO_4) and sodium sulfite (Na_2SO_3) were purchased from Merck. All the chemicals were of analytical grade. Deionized water was used in all experiments.

All the analyses were carried out in accordance with the Standard Methods for Examination of Water and wastewater [19] and replicated twice. The pH and conductivity

Table 1
Characteristics of lavender essential oil production wastewater

Parameters	Values
pH	5.11
Conductivity (µS/cm)	280 µS/cm
Oil and grease (mg/L)	50
COD (mg/L)	1,650
Color (465 nm (as Pt-Co))	930
SAC_{436} (m^{-1})	28.66
SAC_{525} (m^{-1})	14.19
SAC_{620} (m^{-1})	6.92

were measured by WTW Multi 340i, Germany. The COD was determined by the reactor digestion method for COD in a range of 100–1,500 mg/L by using a HACH DR 5000. Residual H_2O_2 concentration was determined by the iodometric titration method.

Platinum-cobalt (Pt-Co) color parameter is used in the discharge of colored wastewater to the receiving environment in Turkey. Besides, spectral absorption coefficient (SAC) measurement is preferred instead of Pt-Co in this type of wastewater [20,21] in that the color tones moves away from the Pt-Co standard and the results obtained can be misleading, especially in the measurement of colored wastewater. The color measurements were determined with two different scales, Pt-Co and SAC, by using a spectrophotometer (Hach Lange DR-5000), therefore. Pt-Co measurements were performed at 465 nm. For the SAC parameters, the measured absorbance values at 436 (yellow), 525 (red) and 620 nm (blue) were converted to SAC values according to the following equation [22]:

$$\text{SAC} = \frac{A_\lambda}{d} \times 1{,}000 \tag{3}$$

where A_λ is the absorbance at wavelength λ nm and d, the path length of the cell (mm) and the SAC unit is m^{-1}.

2.3. Experimental procedure

A number of preliminary tests were conducted to determine the concentration of factors such as ferrous ion and H_2O_2 which influence the efficiency of the Fenton process now that LOPW was the first studied wastewater in the literature. For this purpose, experiments were carried out with combinations of different ferrous ion and H_2O_2 doses based on the doses used in the treatment of various industrial wastewater in the literature. After determining the dose ranges to be used, the effects of reaction time, pH, H_2O_2 and ferrous ion concentrations on color and COD removal were investigated. Firstly, the optimum reaction time was determined by applying the Fenton process to wastewater at reaction time varying from 10 to 90 min (rapid mixing for the first 5 min of each and slow mixing for the remaining part). The reaction time is reported to be in the range 5–90 min in the literature [23,24]. Experiments were carried out for $H_2O_2/Fe^{2+} = 3.24$ (118 mM H_2O_2 and 36 mM Fe^{2+}) and $H_2O_2/Fe^{2+} = 0.54$ (29 mM H_2O_2 and 54 mM Fe^{2+}) at pH 4. Then, the optimum pH value was determined with experiments in the pH range from 2.5 to 6 at 88 mM H_2O_2 concentration and 54 mM ferrous ion concentration. To determine the effect of H_2O_2 concentration on COD and color removal, H_2O_2 doses between 15–147 mM at a dose of 54 mM ferrous ion concentration were used. Finally, the optimum ferrous ion concentration was determined by using 88 mM H_2O_2 and 18–72 mM ferrous ion concentration. All experiments were performed at room temperature (22°C–25°C) by using the jar test method with six beakers. Each experiment was executed with a 400 mL sample of wastewater with COD of 1,650 mg/L and 930 Pt-Co color. Initially, the pH of the wastewater was adjusted by using 6 N NaOH and/or 3 N H_2SO_4, after which the required amounts of $FeSO_4·7H_2O$ and H_2O_2 were added. All samples were mixed at specified period of time. Subsequently, the samples were set aside for 2 h for precipitation following pH adjustment (7.5–8) with 6N NaOH to stop the reaction and to allow the precipitation in the form of iron(III) hydroxide of the ferric ions in the environment. After 2 h, the supernatant was withdrawn for COD and color analyses [25]. To prevent interference of the residual H_2O_2 in COD measurements and to terminate the reaction, the excess of H_2O_2 was removed by adding sodium sulfite (Na_2SO_3) prior to the COD determination. The added Na_2SO_3 to quench residual H_2O_2 was calculated based on the concentration of remaining H_2O_2 and the stoichiometry between Na_2SO_3 and H_2O_2 (3.7 mg/L Na_2SO_3 for 1 mg/L H_2O_2) [26]. Prior to the measurement of color, the samples were filtered through a filter paper with a pore size of 0.45 μm. All the conducted experiments were carried out in duplicate.

3. Results and discussion

3.1. Effect of the reaction time

To determine the effect of reaction time, experiments were carried out using two H_2O_2/Fe^{2+} molar ratios: 3.24 and 0.54 at pH 4.0. COD removal vs. time at different H_2O_2/Fe^{2+} molar ratios are presented in Fig. 1A. As seen from Fig. 1A, the oxidation reactions occurred quickly and 78% and 64% COD removal were obtained for molar ratios of $H_2O_2/Fe^{2+} = 3.24$ and 0.54, respectively even in the first 10 min. After 10 min the oxidation reactions slowed down and 81% and 69% COD removal was observed at 60 min reaction time and at molar ratio of $H_2O_2/Fe^{2+} = 3.24$ and 0.54, respectively. It can be seen from the same figure that the highest COD removal was achieved at the $H_2O_2/Fe^{2+} = 3.24$ molar ratio. This is evidence that less OH radicals are produced due to the insufficient concentration of H_2O_2 in the environment for the formation of OH radicals in the ratio of $H_2O_2/Fe^{2+} = 0.54$ compared to 3.24.

The decrease in color as Pt-Co, SAC_{436}, SAC_{525} and SAC_{620} with time for two different H_2O_2/Fe^{2+} molar ratios is shown in Fig. 1B. It can be seen that by increasing the reaction time from 10 to 60 min, the color removal efficiency as Pt-Co could be enhanced from 57% to 75% for the molar ratio of $H_2O_2/Fe^{2+} = 0.54$, and from 75% to 86% for a molar ratio of $H_2O_2/Fe^{2+} = 3.24$. Additionally, SAC measurements were in accord with the Pt-Co results, and the color removal as SAC_{436}, SAC_{525} and SAC_{620} was 84%, 91% and 98% for a molar ratio of $H_2O_2/Fe^{2+} = 3.24$ in 60 min (Fig. 1B). Similarly, the color removal efficiencies obtained for a molar ratio of $H_2O_2/Fe^{2+} = 0.54$ and a reaction period of 60 min were 72% for SAC_{436}, 75% for SAC_{525} and 72% for SAC_{620}. However, when the reaction time was increased from 60 to 90 min, the color removal efficiencies (Pt-Co and SAC) increased only slightly. Therefore, an appropriate reaction time for treatment of LOPW was determined as 60 min and a reaction time of 60 min was used in all subsequent experiments. This result is compatible with the required oxidation time determined for other wastewater [24,27].

3.2. Effect of initial pH

pH is a determining factor in the concentration of ferrous ions, the stability and concentration of H_2O_2, and hence the rate of production of OH radicals in Fenton processes [28].

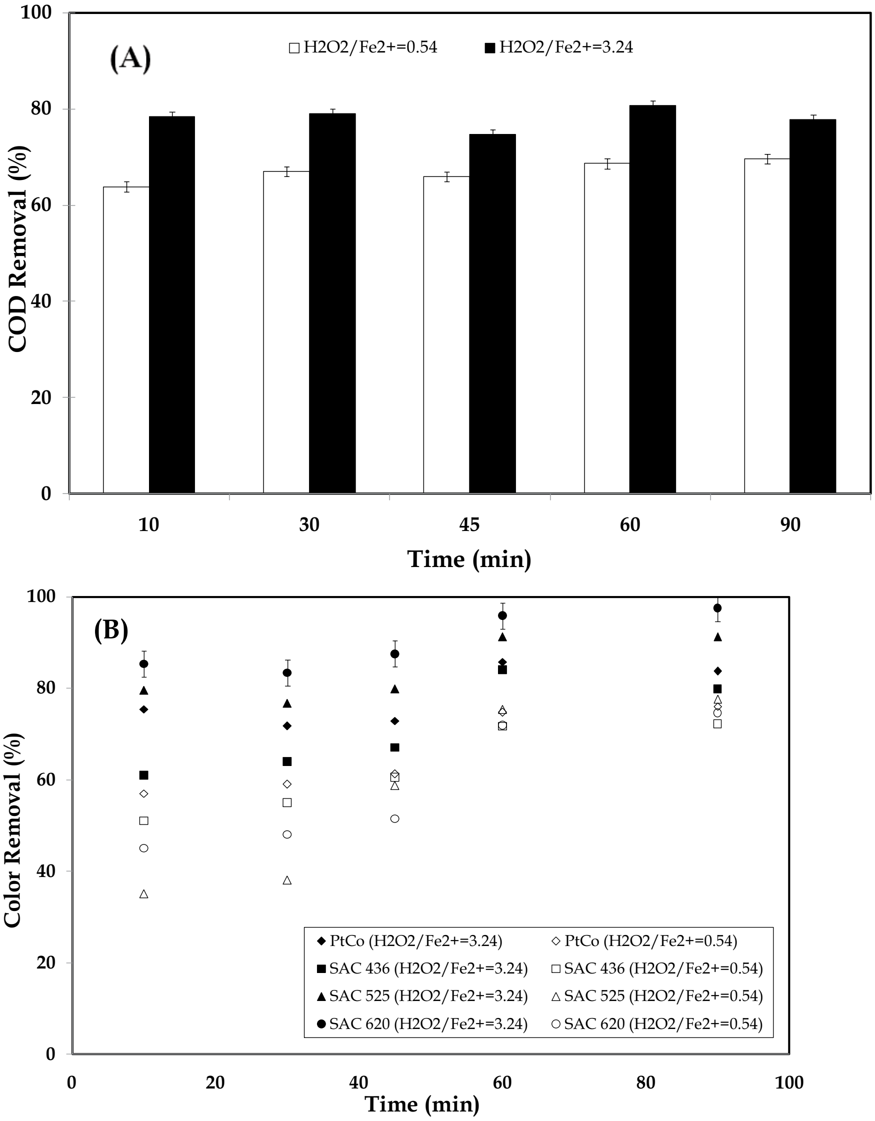

Fig. 1. Effect of time on COD removal (A) and color removal (B) at different H_2O_2/Fe^{2+} molar ratios (pH = 4.0; H_2O_2/Fe^{2+} = 0.54 (29 mM H_2O_2 and 54 mM Fe^{2+}); H_2O_2/Fe^{2+} = 3.24 (118 mM H_2O_2 and 36 mM Fe^{2+})).

For this reason, the experiments to determine the effective wastewater pH in the treatment of LOPW by the Fenton process were carried out for a 60 min reaction time at different pH values ranging from 2.5 to 6.0 at a constant loading of ferrous ions and H_2O_2. The constant loading for optimization of the pH was 54 mM Fe^{2+} and 88 mM H_2O_2. COD removals obtained from the experiments as a function of pH are depicted in Fig. 2A.

As seen in Fig. 2A, the COD removal efficiencies obtained in the pH range of 2.5–4.0 are almost the same, and high removal efficiencies were obtained in acidic conditions. This result was expected because the Fenton process is effective in strict acidic conditions. However, at pH values higher than 4.0, COD removal efficiency was adversely affected by increasing pH value. COD removal at pH 4.0 was 80%, but it decreased to 72% at pH 6.0. This behavior can be explained by the formation of ferric oxyhydroxide precipitates at higher pH values, which react more slowly with H_2O_2 than dissolved ferric ions and hinders the reaction between ferric ions and H_2O_2 [29,30]. In addition, in such conditions, the stability of H_2O_2 decreases and it easily decomposes to oxygen and water instead of reactive species [31]. For all these reasons, fewer OH radicals are produced, and thus the removal efficiency of the process decreases.

The effect of pH on color removal performance in terms of the Pt-Co, SAC_{436}, SAC_{525}, SAC_{620} parameters is presented in Fig. 2B. As seen from Fig. 2B, the color removal efficiencies increased with increasing pH between pH 2.5 and 4.0 and reached a maximum at pH 4.0. Studies in the literature show that acidic conditions are suitable for color removal [32]. At pH above 4.0, color removal efficiencies exhibited a trend similar to COD removal and decreased with increasing pH value. Color removal efficiency as Pt-Co decreased from 89% to 61% with a change of pH value from 4.0 to 6.0.

Similarly, at pH 6.0, color removals for SAC parameters were smaller compared to results at pH 4.0. The maximum

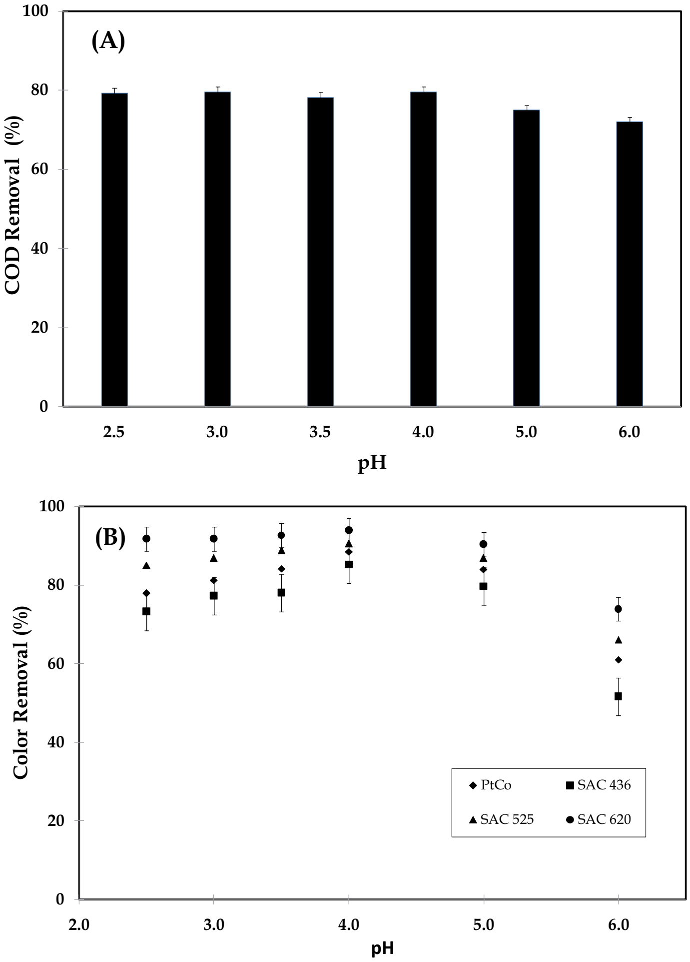

Fig. 2. Effect of pH on removal of COD (A) and color (B) from LOPW by Fenton oxidation. H_2O_2 concentration = 88 mM; ferrous ion concentration = 54 mM; reaction time = 60 min).

color removal efficiencies were 89%, 85%, 91%, 94% for Pt-Co, SAC_{436}, SAC_{525} and SAC_{620}, respectively, and were obtained at pH 4.0.

Consequently, pH 4.0, which resulted in the highest COD and color removals, was determined as the optimum pH value. Although no cost analysis was performed, it can be said that pH 4.0 is more suitable in terms of operating cost since it requires less acid addition than pH 3.0. Similarly, the maximum COD and color removal from carpet dyeing wastewater by Fenton oxidation was achieved at pH 4.0 by Kumar et al. [23]. Similarly, and in a study conducted by Üstün et al. [20] the highest yield was obtained at pH 4.0 by Fenton oxidation. However, the optimum pH for the removal of pollutants in the Fenton oxidation process is reported to be 3.0 in a majority of studies [24,33]. For this reason, it was found appropriate to use pH 3.0 and pH 4.0 as the initial pH throughout all the rest of the experiments in order to compare with the studies in the literature.

3.3. *Effect of initial H_2O_2 concentration*

In Fenton processes, H_2O_2 is the main source of OH radicals which oxidize organic compounds and it greatly affects the removal of pollutants. In addition, since the amount of H_2O_2 used constitutes one of the major operational costs of the Fenton process, the H_2O_2 concentration needs to be optimized. In the H_2O_2 optimization experiments carried out for this purpose, ferrous ion concentration was constant held at 54 mM, while H_2O_2 concentration was varied between 15 and 147 mM. The effect of different H_2O_2 concentrations (15, 29, 59, 88, 118 and 147 mM) on COD removal from LOPW wastewater is shown in Fig. 3A. COD removal efficiencies were enhanced with increasing H_2O_2 concentrations as a result of the generation of a larger amount of OH radicals. By increasing H_2O_2 concentration from 15 to 147 mM, COD removal efficiency increased from 56% to 83% and from 55% to 88% for pH 3.0 and pH 4.0, respectively. However, there was no significant improvement in COD removal at H_2O_2 concentrations higher than 88 mM for either pH value. Similar observations were reported in studies on the treatment of different industrial wastewaters [12,34]. For example, Mert et al. [12] determined that the optimum H_2O_2 concentration for Fenton oxidation in the treatment of olive oil wastewater was 100 mM. In a study applying Fenton process for the treatment of rose essential oil wastewater, 8,325 mg/L (245 mM) H_2O_2 were used to obtain 65.7%

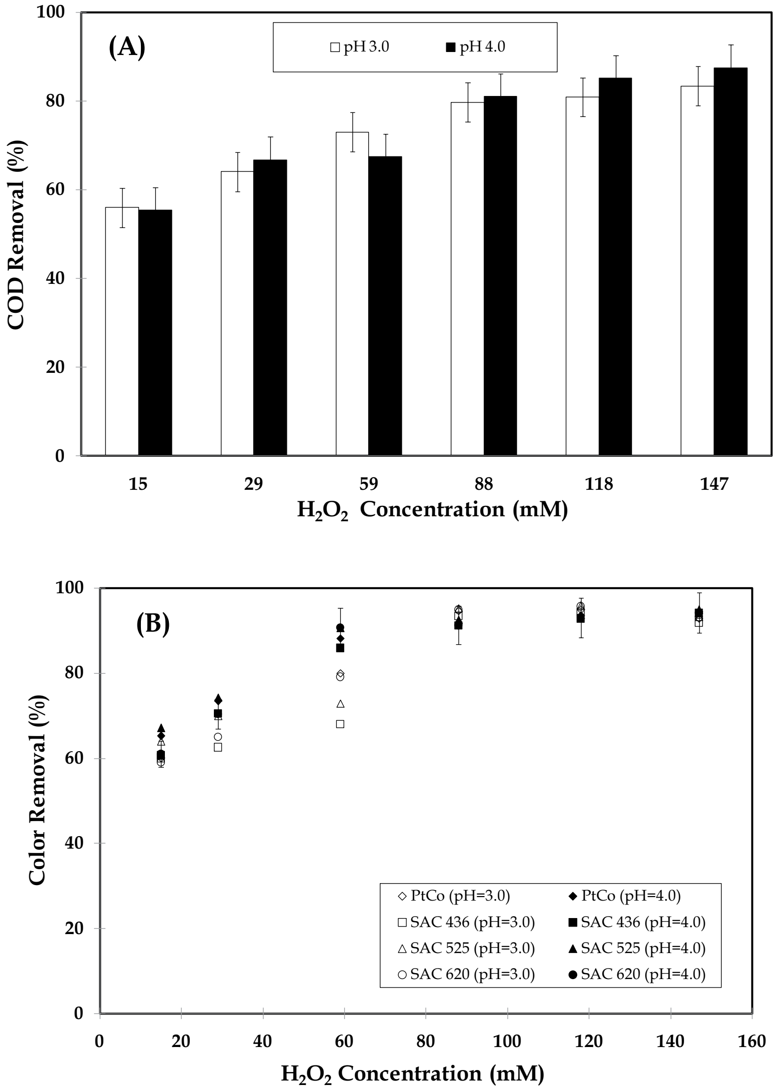

Fig. 3. Effect of H_2O_2 concentration on removal of COD (A) and color (B) from LOPW by Fenton oxidation (pH = 3.0 and pH = 4.0; ferrous ion concentration = 54 mM; reaction time = 60 min).

COD removal [5]. However, it should not be ignored that rose processing wastewater contains higher amounts of organic matter (1,650 mg/L COD) than LOPW.

Fig. 3B depicts the removal of color (as SAC and Pt-Co parameters) at different H_2O_2 concentrations (15, 29, 59, 88, 118 and 147 mM). As shown in Fig. 3B, color removal efficiency was increased by increasing the H_2O_2 concentration from 15 to 88 mM. At pH 3.0, color removal efficiencies were 95% for Pt-Co, 93% for SAC_{436}, 95% for SAC_{525}, and 95% for SAC_{620} when using 88 mM H_2O_2. Similarly, at pH 4.0, over 90% color removal efficiency was obtained for all color parameters (for Pt-Co scale and SAC). However, a H_2O_2 concentration higher than 88 mM did not lead to higher color removal. In fact, when the concentration of H_2O_2 was increased from 88 to 147 mM, color removal decreased slightly from 95% to 93% for Pt-Co, from 93% to 92% for SAC_{436}, from 95% to 93% for SAC_{525}, and from 95% to 92% for SAC_{620} at pH 3.0. Similar trends were observed at pH 4.0. This slight decrease stems from excess H_2O_2 acting as an inhibitor for OH radicals. After a certain concentration, excess H_2O_2 reacts with OH radicals in competition with organic pollutants, producing hydroperoxyl radicals with a lower oxidation potential than the OH radical and lowering oxidation efficiency [35].

In this study, the highest removal efficiency in terms of both color removal and COD removal was obtained when the concentration of 88 mM H_2O_2, in other words, the H_2O_2/COD ratio was 1.818. The studies published on Fenton oxidation have stated the H_2O_2/COD ratios to be used in Fenton processes should be determined according to the stoichiometric ratio between COD and H_2O_2 (1 g of COD requires 2.125 g of H_2O_2) [11,36]. In the light of this information, it can be said that the H_2O_2/COD ratio in our study is close to the stoichiometric ratio and is within the ranges accepted in the literature. For this reason, 88 mM H_2O_2 concentration was determined as the optimum H_2O_2 dose for COD and color removal, based on the experimental results and literature information, and this value was used in subsequent experiments.

3.4. Effect of ferrous ion concentration and H_2O_2/Fe^{2+} molar ratio

As is known, iron acts as a catalyst for the decomposition of H_2O_2 and provides the formation of OH radicals in the Fenton process. However, the addition of too much ferrous ions causes a scavenging effect and diminishes the efficiency of the process. In addition, an increase in the ferrous ion concentration increases the amount of iron sludge formed after the process, by increasing sludge treatment cost. For this reason, the ferrous ion concentration needs to be optimized in Fenton processes. In this set of experiments, the H_2O_2 concentration was kept constant at 88 mM while the ferrous ion concentration was varied from 18 to 72 mM. Fig. 4A represents the COD removal efficiencies under different ferrous ion concentrations (18–72 mM) and a constant H_2O_2 concentration of 88 mM. As can be seen from the figure, COD removal efficiencies varied between 69% and 80% at pH 3.0, depending on the ferrous ion concentration, and increased with an increase of ferrous ion concentration. Similarly, at pH 4.0, COD removal efficiencies increased from 74% to 81% with an increase in the ferrous ion concentration from 18 to 54 mM. This is due to the formation of more OH radicals with the increase in the concentration of ferrous ions, which catalyze H_2O_2 decomposition. On the other hand, no significant increment in COD removal was observed at either pH value since H_2O_2 was restricted to producing more OH radicals after a 54 mM ferrous ion concentration [23]. Maximum COD removal efficiencies were acquired at a ferrous ion concentration of 54 mM, and were 80% and 81% for pH 3.0 and pH 4.0 respectively.

In addition to the amount of H_2O_2 and ferrous ions, the ratio of H_2O_2/Fe^{2+} also plays an important role in the production of sufficient OH radicals. It can be seen from Fig. 4A that low H_2O_2/Fe^{2+} molar ratios provided higher treatment efficiencies. COD and color removal efficiency increased

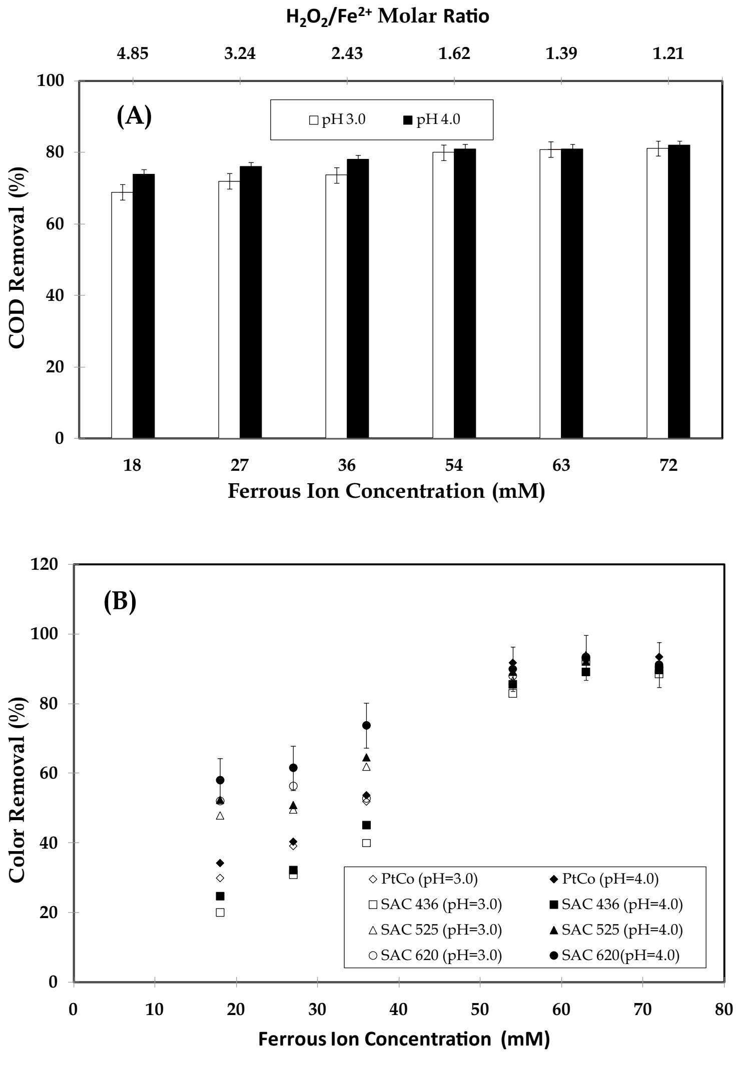

Fig. 4. Effect of ferrous ion concentration on removal of COD (A) and color (B) from LOPW by Fenton oxidation (pH = 3.0 and pH = 4.0, H_2O_2 concentration = 88 mM, reaction time = 60 min).

with a H_2O_2/Fe^{2+} molar ratio decreasing from 4.85 to 1.62 and then remaining stable. For example at pH 3.0, while 68% COD removal was achieved at the molar ratio of H_2O_2/Fe^{2+} = 4.85, 80% COD removal was achieved at the molar ratio of H_2O_2/Fe^{2+} = 1.62. At higher H_2O_2/Fe^{2+} molar ratios, the amounts of ferrous ions in the environment decreases. Therefore, the removal efficiencies have decreased due to insufficient formation of OH radicals as ferrous ions react less with H_2O_2 [37].

The color removal efficiencies (Pt-Co and SAC parameters) as a function the ferrous ion concentration is illustrated in Fig. 4B. As can be seen from the figure, it is obvious that ferrous ion concentration significantly influences not only COD removal but also color removal. The color removal efficiencies enhanced dramatically with increasing ferrous ion concentration, and 30% and 34% color removal efficiency (for Pt-Co) was obtained at a ferrous ion concentration of 18 mM, while 86% and 92% removal efficiencies were achieved at a ferrous ion concentration of 54 mM for pH 3.0 and pH 4.0 respectively. Additionally, similar trends were observed in all SAC parameters (for 436, 525 and 620 nm) and removal efficiencies of above 80% were obtained at a 54 mM ferrous ion concentration for both pH values. For example, at pH 4.0, the removal efficiency obtained for SAC_{436} was 86% while it was 90% for SAC_{620}. In the light of the results mentioned above, it can be seen that the optimal ferrous ion concentration was 54 mM for both color and COD removal.

Based on the results, the optimum ratios of H_2O_2/Fe^{2+} molar ratio for the treatment of LOPW by the Fenton process was 1.62. A wide range of molar ratios has been reported in the literature depending on the type of wastewater and the organic load in the wastewater. The ratio found in this study was similar to the optimum ratio reported by Abedinzadeh et al. [14] and Beng et al. [38].

Due to the complex nature of the Fenton process and wastewater, it is difficult to describe the degradation mechanism of an organic compound by Fenton's reagent. Many studies on the removal of organic matter in various wastewater in Fenton systems indicate that OH radicals are the main active oxidant in the degradation of organic pollutants [17,39]. Although the Fenton system involves many reactions, a simplified, possible mechanism for degradation of organic pollutants in LOPW by OH radicals can be proposed, including the following steps. In the first-step of the system, H_2O_2 is rapidly decomposed by the catalyst ferrous ions, forming a strong oxidizing radical OH. In the next step, the OH radicals formed attack the target organic pollutants and provide oxidation.

3.5. Kinetic modeling

In terms of modeling the kinetic data for COD and color removal by Fenton oxidation, various kinetic models including first-order, second-order and Behnajady–Modirshahla–Ghanbery (BMG) reaction kinetics were evaluated. The first-order, second-order and BMG kinetic models can be represented by the following equations:

- First-order kinetic model

$$C_t = C_0 \times e^{-k_1 t} \tag{4}$$

- Second-order kinetic model

$$\frac{1}{C_t} = \frac{1}{C_0} + k_2 t \tag{5}$$

- BMG kinetic model

$$\frac{C_t}{C_0} = 1 - \frac{t}{m + bt} \tag{6}$$

where C is the COD or color concentration at time t (min); C_0 is initial concentration of COD or color; k_1 and k_2 are the first and second-order rate constants, respectively; and b and m are constants relating to relating to reaction kinetics and oxidation capacities [27,28].

The kinetic parameters and correlation coefficients for first, second-order kinetic model and BMG kinetic model are summarized in Table 2. As shown in Table 2, the correlation coefficients (R^2) for first-order kinetic model were higher than those of the second-order model and BMG kinetic models. In addition, in the first-order kinetic model, higher k_1 constants were obtained with H_2O_2/Fe^{2+} 3.24 molar ratio compared to H_2O_2/Fe^{2+} 0.54 molar ratio. The correlation coefficients calculated for the first-order kinetic model ranged from 0.81 to 0.97. Therefore, it is possible to say

Table 2
Kinetic parameters and correlation coefficients for COD, SAC_{436}, SAC_{525}, and SAC_{620}, removal by Fenton oxidation

H_2O_2/Fe^{2+}		First-order kinetic model		Second-order kinetic model		BMG kinetic model		
		k_1 (min^{-1})	R^2	k_2 (L/mg min)	R^2	m (min)	b	R^2
0.54	COD	0.002	0.849	0.000004	0.860	2.469	1.416	0.740
	SAC_{436}	0.007	0.890	0.00075	0.840	11.86	1.265	0.700
	SAC_{525}	0.015	0.880	0.00294	0.790	31.63	0.942	0.820
	SAC_{620}	0.011	0.815	0.004	0.710	21.24	1.147	0.640
3.24	COD	0.004	0.970	0.000013	0.960	2.314	1.198	0.840
	SAC_{436}	0.008	0.940	0.001	0.840	11.86	1.265	0.700
	SAC_{525}	0.016	0.880	0.012	0.720	6.14	1.034	0.690
	SAC_{620}	0.028	0.9	0.098	0.62	4.801	0.981	0.65

that COD and color removal with the Fenton process from LOPW follows the first-order kinetic model.

4. Conclusions

Lavender essential oil production wastewater has high organic load (1,650 mg/L COD) and dark brown color (930 Pt-Co). A small-sized enterprise in Turkey seasonally produces an average of 8 m^3/d of wastewater. Enterprises producing lavender oil do not have treatment plants to treat this wastewater. These wastewaters are discharged directly and cause significant environmental problems. These environmental problems highlight the disposal of the aforementioned wastewater among the burning issues. Since the wastewater is produced seasonally, it may be more effective to use a treatment technology that can be intermittently applied in the treatment of wastewater.

In this study, which is a first for the treatment of LOPW, the Fenton oxidation process was applied. The performance of the Fenton oxidation process in the treatment of this wastewater was investigated in terms of COD and color removal. According to the results, the process required a short contact time of 60 min for effective COD and color removal. The best results for both COD and color removal were obtained at pH 4.0, with a concentration of 88 mM H_2O_2 and a 54 mM ferrous ion concentration and a H_2O_2/Fe^{2+} molar ratio of 1.62. A fairly high COD removal (80%) was achieved in optimum conditions and the COD value of the treated water was reduced to 330 mg/L. The color levels of the wastewater were significantly decreased from 930 Pt-Co to about 70 Pt-Co levels. In conclusion, Fenton oxidation was successfully applied for the removal of both COD and color from LOPW. The process is recommended as an effective pretreatment method as well as being easily applicable to the treatment of such wastewater. However, the degradation of organic matter by the Fenton process may lead to the formation of by-products which require further investigation for a better understanding of the process. In addition, the by-products formed may have a greater hazard than the target pollutant. For this reason, in further studies, it is extremely important to determine the oxidation by-products that may occur during oxidation of LOPW under the best conditions. Moreover, not only treatment of wastewater, but also recovery of substances from wastewater can be an alternative approach. After a more comprehensive characterization of the wastewater, the recovery of valuable compounds (such as phenolic compounds) from the plant extract to the wastewater can also be focused.

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