Color and chemical oxygen demand removal using homogeneous and heterogeneous Fenton oxidation of sugar industry wastewater

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ABSTRACT

In this study, color and chemical oxygen demand (COD) removal efficiencies from sugar industry wastewater were compared by applying homogeneous and heterogeneous Fenton oxidation processes. The parameters effecting the oxidation process such as iron ion concentration, catalyst amount, hydrogen peroxide concentration, pH, temperature and reaction time were examined and optimum experimental conditions were determined. Synthesized $Fe(III)/SnO_2$ was used as catalyst in the heterogeneous Fenton process. It was aimed to eliminate the iron-containing sludge formation, which was the disadvantage of the homogeneous Fenton process, by the heterogeneous Fenton process. Under the optimum conditions, in the homogeneous Fenton process 81% color and 70% COD removal efficiency and in the heterogeneous Fenton process 94% color and 80% COD removal efficiency were achieved. Finally, a cost analysis was made. The cost analysis result showed that the heterogeneous Fenton was more economical. These results showed that the heterogeneous Fenton method is more suitable for sugar industry wastewater treatment.

Keywords: Sugar industry wastewater; Color and chemical oxygen demand removal; Fenton process; Cost analysis

1. Introduction

The sugar industry has an important role among other food industries in the world due to its effects on human nutrition and health, and its contribution to the development of countries in terms of industry and economy. Although the sugar industry is generally not considered to be among the industries that cause the damage to the environment, these operating can cause serious organic pollutants if they are not operated with care and attention to the environment [1,2]. A large volume of waste is generated during sugar production and this waste contains a high amount of pollution load, especially in terms of suspended solids, organic matter and press sludge, pulp and air pollutants [3,4].

During sugar production, an average of 1,500–2,000 m³ of water is consumed per 100 tons of beets. The wastewater from a sugar factory that processes 2,000 tons of beets a day has the same pollution as the wastewater of a city with a population of 200,000–300,000. Wastewater generated in sugar factories during beet transport and beet washing has high organic pollution due to the soil and sugar of damaged beets (chemical oxygen demand (COD) value varies between 5,000–20,000 mg/L). In addition, the water discharged during the crystallization process in evaporation and vacuum boilers has a high amount of ammonia and BOD value [5,6].
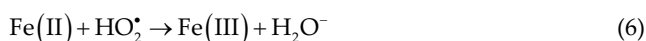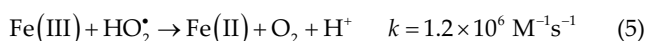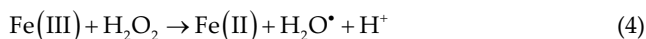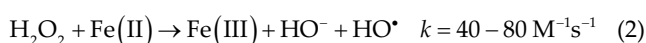
Generally, physico-chemical and biological (aerobic and anaerobic) treatment methods are used in the treatment of wastewater of the sugar industry [7–10]. Sugar industry wastewater contains high amounts of pollutants and biological treatment methods are insufficient to break down these pollutants. That is, the brown color and other impurities in the biologically treated wastewater remain due to the repolymerization of substances such as melanin's, melanoidins

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and caramels that are not removed during the biodegradation process, and can reduce its reuse. Moreover, high molecular weight-colored impurities have antimicrobial and cytotoxic properties and thus biological treatment alone cannot separate them [11].

Also, physicochemical methods (coagulation–flocculation, filtration, activated carbon adsorption, stripping with air) are not preferred because of the transfer of pollutants from one environment to another. Advanced oxidation processes (AOPs) have gained importance in recent years as highly effective methods in the treatment of such pollutants. AOPs is a method based on the formation of a highly effective hydroxyl radical (2.8 eV), the hydroxyl radical formed can transform toxic and persistent organic materials into harmless end products. The hydroxyl radical enters the oxidation reaction without separating any organic matter. It provides complete mineralization of organic pollutants under appropriate reaction conditions and the formation of end products such as CO_2 and H_2O [12–18].

The mechanism of the Fenton process can be expressed as stated in Eqs. (1)–(8) [19–23].

$$AOPS + \text{organic pollutants}$$
$$\rightarrow CO_2 + H_2O + \text{inorganic ions} \tag{1}$$

$$H_2O_2 + Fe(II) \rightarrow Fe(III) + HO^- + HO^\bullet \quad k = 40 - 80 \ M^{-1}s^{-1} \tag{2}$$

$$RH + HO^\bullet \rightarrow R^\bullet + H_2O \tag{3}$$

$$Fe(III) + H_2O_2 \rightarrow Fe(II) + H_2O^\bullet + H^+ \tag{4}$$

$$Fe(III) + HO_2^\bullet \rightarrow Fe(II) + O_2 + H^+ \quad k = 1.2 \times 10^6 \ M^{-1}s^{-1} \tag{5}$$

$$Fe(II) + HO_2^\bullet \rightarrow Fe(III) + H_2O^- \tag{6}$$

$$HO^\bullet + H_2O_2 \rightarrow H_2O + HO_2^\bullet \tag{7}$$

$$HO^\bullet + Fe(II) \rightarrow Fe(III) + OH^- \tag{8}$$
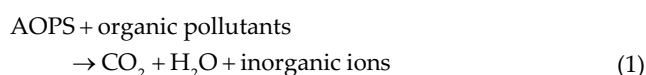
The advantages of the Fenton process are listed below [24,25].

- Iron salts and hydrogen peroxide are non-toxic, cheap and easy to find;
- No energy is required to activate the hydrogen peroxide since the Fenton reaction takes place at atmospheric pressure and room temperature;
- Simple equipment, inexpensive method and easy implementation;
- High removal efficiency of toxic and non-biodegradable organic compounds;
- No mass transfer limitation due to its homogeneous catalytic structure.

The disadvantages of Fenton reaction, such as occurring at low pH, iron ions cannot being reused, relatively long reaction time compared to other advanced oxidation processes, and catalytic sludge formation, can be eliminated by heterogeneous Fenton processes [26,27].

Advanced oxidation processes using semiconductors are called heterogeneous Fenton oxidation processes. The catalysts both generate hydroxyl radicals from hydrogen peroxide and prevent waste ferric oxide sludge formation. The catalysts can be easily recovered after the reaction and can be actively used in other processes [28,29]. Metal oxide catalysts are generally used as semiconductors in photocatalytic degradation systems. Metal oxide semiconductors have more positive valence band potentials compared to other semiconductors [30,31]. Therefore, metal oxide semiconductors form spaces with high oxidation potentials and in this way they can oxidize almost all chemical substances [32].

In recent studies, various metal oxides have been used as catalysts in sugar industry wastewater treatment. Some metal oxides are such as $NiCo_2O_4$ [33], NiO and Co_3O_4 [34], $FeMoO_4$ [35], CuO, ZnO, FeO and MnO [36], TiO_2-SiO_2 [37], Fe/ZnO_2 [38], Fe/MnO_2 and Fe/SnO_2 [39]. Among them, SnO_2 as a support in catalyst attracted attention due to its high activity and hydrothermal stability. SnO_2 has high oxidation potentials (3.6 eV) and can therefore oxidize all kinds of organic compounds [40,41]. In addition, compared to other semiconductor materials, SnO_2 is frequently used as a catalyst in advanced oxidation processes due to its non-toxicity, economical and easy use [42].

Because of these mentioned properties of SnO_2, we preferred it in this study as catalytic support. Also, although metal oxides have been widely used as catalysts and as catalytic supports, to the best of our knowledge, the use of SnO_2 metal oxide as a heterogeneous Fenton catalyst are limited in literature. In this study, the iron ions were immobilized on the SnO_2 surface by co-precipitation procedure. The advantage of immobilizing the iron ions on the SnO_2 support is: the ferrous ion is part of the crystal system of oxides. This feature enhances the stability of the catalyst towards the splitting of H_2O_2, and thus the leaching of ferrous ions from the catalyst is reduced [20]. The decrease in leaching of iron ensures that iron is released to the environment as much as needed, this prevents both Fe pollution in the water and prevents the formation of iron oxide sludge, providing the opportunity to work at higher pH. In this context, in this study, homogeneous Fenton and heterogeneous Fenton processes were applied for the treatment of sugar industry wastewater and treatment efficiencies were compared. $Fe(III)/SnO_2$ catalyst containing 8% (w/w) iron ions was synthesized as a catalyst in the heterogeneous Fenton process. The effects of parameters such as iron ion concentration, amount of catalyst, hydrogen peroxide concentration, pH, temperature and reaction time on removal were researched and optimum conditions were determined.

2. Materials and methods

2.1. Sugar industry wastewater

Sugar industry wastewater was used in experimental studies. Sugar industry wastewater was supplied from Ankara Sugar Factory in Turkey. This wastewater has been taken from the raw wastewater entering the treatment plant. The characteristic of wastewater are presented in Table 1. The parameters of sugar industry wastewater were determined according to "Standard Methods for the Examination of Water and Wastewater".

2.2. Chemicals

Hydrogen peroxide (H_2O_2) (Sigma-Aldrich, St. Louis, MO 63103, USA) of 30% by weight was used in all oxidation processes. Iron(II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) (Merck, Darmstadt, Germany) was used in the homogeneous Fenton process experiments. Sodium hydroxide (NaOH) (Sigma-Aldrich, St. Louis, MO 63103, USA) and sulfuric acid (H_2SO_4) (Merck, Darmstadt, Germany) were used to adjust the pH of the samples. Iron(III) nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$) (Sigma-Aldrich, St. Louis, MO 63103, USA), tin(IV) oxide (SnO_2) (Merck, Darmstadt, Germany) and ammonium hydroxide (NH_4OH) (Sigma-Aldrich, St. Louis, MO 63103, USA) were used in catalyst synthesis.

2.3. Catalyst

Fe(III)/SnO_2 catalyst containing 8% (w/w) of iron ions was prepared to be used in the heterogeneous Fenton process. First, $Fe(NO_3)_3 \cdot 9H_2O$ and SnO_2 were dissolved in 100 mL of distilled water. Then, the temperature was brought to 65°C by stirring in a magnetic stirrer. The pH was adjusted to 9 by adding NH_4OH (26%) dropwise to the solution. It was stirred at 65°C and 300 rpm for 2 h. The precipitate obtained was filtered and dried in an oven at 105°C for 24 h. Then it was kept in the ash furnace at 600°C for 1 h [38,39]. Also, the characterization of this catalyst was made in detail in our previous publication [39].

2.4. Homogeneous Fenton process

First, the pH value of a certain volume of wastewater sample was adjusted to the desired value with 2M H_2SO_4. $FeSO_4 \cdot 7H_2O$ solution at desired concentrations was added to the pH adjusted samples. The Fenton reaction was started by adding hydrogen peroxide at the desired concentration. The samples prepared in 100 mL flasks were kept in a shaking water bath at a constant temperature for a certain time. At the end of the certain test period, the pH of the samples was brought to the range of 8–9 by using 2 M NaOH. As a result of the operations carried out, the above clear solution was taken, the filtration process was carried out and the necessary analyzes were made.

2.5. Heterogeneous Fenton process

First of all, the pH of the wastewater sample was adjusted to the desired value. The determined amount of catalyst was added to the pH adjusted solution. Then H_2O_2 solution was added. The prepared mixture was kept in the shaking water bath at a constant temperature for a certain time. At the end of the reaction period, the pH was brought to the range of 8–9. The solution was filtered and necessary analyzes were made.

2.6. Color analysis

In color analysis, the maximum wavelength and absorbance values of the wastewater sample were determined by scanning the wavelength range of 320–900 nm in the spectrophotometer. Color removal efficiency was calculated by measuring 349 nm wavelength for sugar industry wastewater.

2.7. COD analysis

In the COD analysis, Hach Lange DR 3900 (Königsweg 10, D-14163 Berlin, Germany) branded 13 mm diameter COD test kits were used. The 2 mL of sample was placed into the kits and kept in Hach Lange LT200 brand thermoreactor at 148°C for 2 h. Then, the COD removal efficiency was calculated by making measurements in the spectrophotometer.

3. Results and discussion

3.1. Effect of the Fe(II) concentration on homogeneous Fenton process and effect of the catalyst amount on heterogeneous Fenton process

In experimental studies, the effect of Fe(II) concentration on color and COD removals were investigated for the homogeneous Fenton process. The effect of the amount of Fe(III)/SnO_2 catalyst in the heterogeneous Fenton process was investigated. The results were represented in Figs. 1 and 2. In the experimental studies of the homogeneous Fenton process, other parameters (such as pH, hydrogen peroxide concentration, temperature, reaction time) were kept
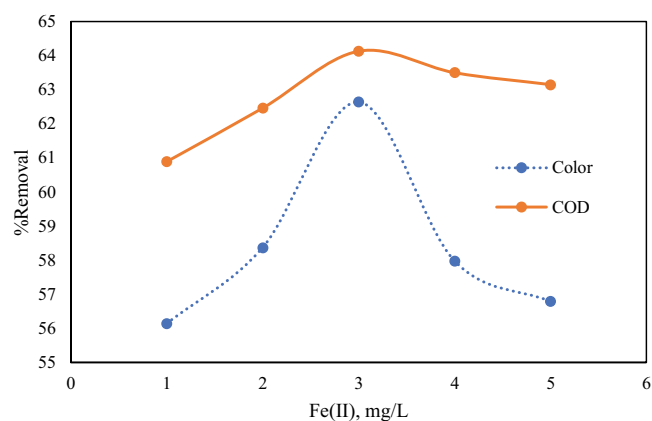
Table 1
Parameters of wastewater used in the experiments

Parameter	Value
Chemical oxygen demand, mg/L	4,480
Color, abs	2.02
Total suspended solids, mg/L	158
Total volatile suspended solids, mg/L	114
Total nitrogen, mg/L	49
Phosphate, mg/L	2.1
pH	7.6
Collapsible sludge volume, mL/L	0.1
Volatile organic acid, Mg·HAC/L	2,278
Calcium, mg/L	867
Temperature, °C	13.1

Fig. 1. Effect of the Fe(II) concentration on homogeneous Fenton process (pH = 2, H_2O_2 = 200 mg/L, T = 30°C, t = 120 min).

constant and the iron concentration was changed at 50, 100, 200, 300 and 400 mg/L values. In the heterogeneous Fenton process, studies were carried out at the amount of 1, 2, 4, 6 and 8 g/L catalyst.

When Fig. 1 is examined; it was observed that as the iron ion concentration increased, the color and COD removal efficiency increased, and the COD removal rate remained constant above a certain concentration and the color removal efficiency decreased. The highest COD and color removal results were obtained at a Fe(II) concentration of 200 mg/L. By evaluating all these results, the optimum Fe(II) concentration was determined as 200 mg/L. As seen in Fig. 2 in the heterogeneous Fenton process, as the amount of catalyst increased, the color and COD removal efficiency increased. After 6 g/L of catalyst amount, a slight decrease in color and COD removal was observed. Therefore, the optimum amount of catalyst was determined as 6 g/L.

In both processes, an inverse trend is observed after the optimum amount of catalyst. The reason for this can be explained as follows: iron ion concentration is one of the important parameters in Fenton processes as it enables the generation of hydroxyl radicals. The iron ion catalyzes hydrogen peroxide to generate hydroxyl radicals. In general, if the concentration of iron ions increases, the reaction rate increases as a significant amount of hydroxyl radicals are produced in a short time [43]. Above a certain concentration of iron ions, the reaction rate decreases and the concentration of dissolved or suspended iron ions increases. The reason for this is the scavenging effect at high concentrations of iron ions, so the reaction of iron ions with hydroxyl radicals [44]. The ferric ions formed react with hydrogen peroxide and form $HO_2^{\bullet}$ with less oxidizing ability. On the other hand, a high increase in iron ion concentration results in the formation of insoluble ferric oxohydroxides [45,46].

$$HO^{\bullet} + Fe(II) + H^{+} \rightarrow Fe(III) + H_2O \tag{9}$$

$$Fe(III) + H_2O_2 \rightarrow Fe(II) + HO_2^{\bullet} + H^{+} \tag{10}$$

$$Fe(III) + H_2O_2 \rightarrow Fe\text{-}OOH^{2+} + H^{+} \quad k = 0.001 - 0.01\,M^{-1}s^{-1} \tag{11}$$

In addition, as shown in Figs. 1 and 2, when the homogeneous Fenton process and heterogeneous Fenton are compared, a very high yield was obtained in heterogeneous Fenton. We can explain this as follows. Since Fe is immobilized on the support in heterogeneous Fenton, Fe is used as needed in the reaction and the remainder remains on the catalyst surface. Therefore, the scavenging effect of the dissolved Fe ions remaining in the environment is reduced.

3.2. Effect of the pH on homogeneous and heterogeneous Fenton processes

Experiments to determine the pH effect were carried out at constant hydrogen peroxide concentration, temperature and reaction time. pH values were changed as 1, 5, 2, 3, 4 and 5. Advanced oxidation processes are significantly effected by the pH value. The precipitation of iron ion at high pH values causes it to lose its activity. Therefore, the oxidation process is more efficient in acidic conditions. As the iron ion is more active in acidic conditions, more hydroxyl radicals are produced. However, when the pH is too low, the rate at which iron ions generate hydroxyl radicals decreases. Therefore, working at the most appropriate pH value will increase process efficiency [47–49].

As Fig. 3 is examined, the maximum color and COD removal efficiency for the homogeneous Fenton process were achieved at pH = 2 as 62.3% and 64.2%, respectively. After pH = 2 value, a decrease in color and COD removal efficiency from wastewater were observed. Therefore, the optimum pH value was determined as 2. As can be seen from the figure, the higher color and COD removal efficiency were obtained in the heterogeneous Fenton process compared to the homogeneous Fenton process. The color and COD removal efficiency increased up to pH = 3 and then decreased slightly. The maximum color (92.6%) and COD (75.1%) removal efficiency were attained at pH=3. However, unlike the homogeneous Fenton process, 89.6% of color removal was still obtained, even when the pH was as high as 5.0. In the literature Gamaralalage et al. [50], Vilardi et al. [51], Rodrigues
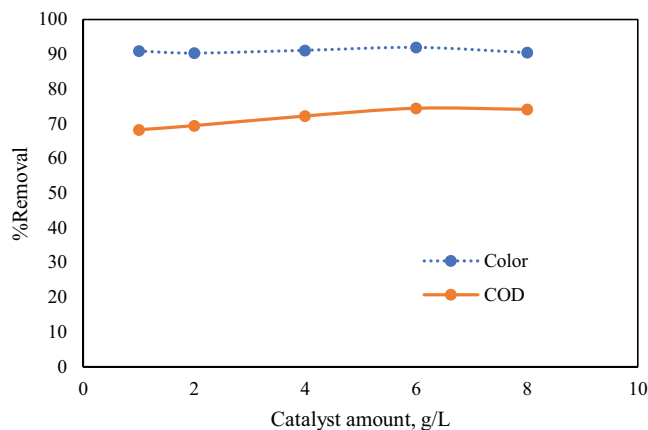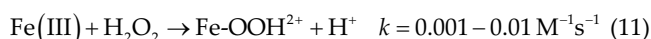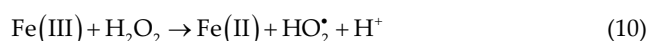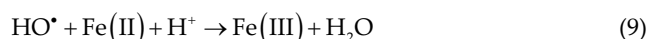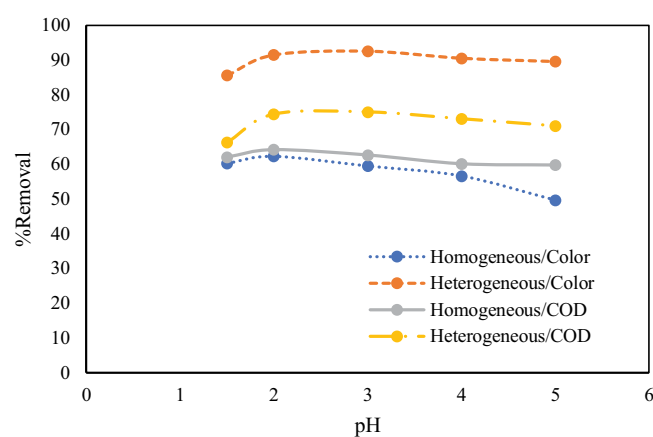
Fig. 2. Effect of the catalyst amount on heterogeneous Fenton process (pH = 2, H_2O_2 = 200 mg/L, T = 30°C, t = 120 min).

Fig. 3. Effect of the pH on homogeneous and heterogeneous Fenton processes (Fe(II) = 200 mg/L, H_2O_2 = 200 mg/L, T = 30°C, t = 120 min for homogeneous Fenton process; m = 6 g/L, H_2O_2 = 200 mg/L, T = 30°C, t = 120 min for heterogeneous Fenton process).

et al. [52] and Rajesh et al. [53] have reported the optimum pH value as 3 in their experimental studies.

In Fenton process, iron ions are unstable at high pH values and these ions are converted into colloidal ferric form. They produce hydroxo complexes without forming a hydroxyl radical. Hydrogen peroxide and iron ions are more stable in the pH range of 2–4. In acidic conditions, the reaction of iron ions with hydrogen peroxide occurs more easily and more hydroxyl radicals are produced [48]. In the pH range of 2–3, ferric species $Fe(OH)_2^+$ reach the highest percentage, thus ensuring maximum system reactivity. Under these conditions, the breakdown efficiency of H_2O_2 increases with the dominant activity of $Fe(OH)_2^+$ ions. When the pH is below 2, excess hydrogen ions scavenge the $OH^•$ radicals (Eq. (12)). Therefore, the removal efficiency decreases [48]. Also, H_2O_2 is stabilized by excess hydrogen ions in form of oxonium according to Eq. (13). Oxonium is a stable and electrophilic form whose reactivity is low for the reaction with iron to generate hydroxyl radical [54].

$$^•OH + H^+ + e^- \rightarrow H_2O \tag{12}$$

$$H_2O_2 + H^+ \rightarrow H_3O_2^+ \tag{13}$$

At high pH values, iron ions are unstable and can easily form ferric ions. When the pH is higher than 4.0, the activity of the Fenton reagent is reduced due to the presence of passive iron oxyhydroxides and the formation of ferric hydroxide precipitate. When pH is higher than 9.0, ferric hydroxy complexes form to $Fe(OH)_4^-$. Also, hydrogen peroxide is unstable at high pH values. Hydrogen peroxide decomposes to give off oxygen and water and lose its oxidative ability [46,55–57].

The heterogeneous Fenton process prevents all the disadvantages as follows. At a higher initial pH, the iron is precipitated as iron hydroxide; but in this case, because Fe(III) is immobilized on the surface of the catalyst, the precipitation is avoided [58]. As a result, this allows working in a wider pH range, unlike the homogeneous Fenton process.
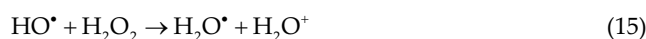
3.3. Effect of the H_2O_2 concentration on homogeneous and heterogeneous Fenton processes

In order to examine the effect of hydrogen peroxide concentration on homogeneous and heterogeneous Fenton processes; experiments were conducted at five different concentrations of hydrogen peroxide such as 50, 100, 200, 300 and 400 mg/L under the optimum conditions previously determined. Experimental results are represented in Fig. 4.

Hydrogen peroxide is an important parameter for oxidation reactions since it is the source of hydroxyl radicals. Generally, the removal efficiency increases with increasing hydrogen peroxide concentration. However, the increase in hydrogen peroxide concentration was a negative impact. That is, when the oxidant concentration is high, recombination of hydroxyl radicals can be occur and generated H_2O_2 (Eq. 14) [23,59].

$$OH + {}^•OH \rightarrow H_2O_2 \qquad k = 5.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1} \tag{14}$$
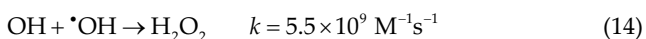
On the other hand, the presence of excessive hydrogen peroxide in the environment also causes the reaction of hydrogen peroxide with hydroxyl radicals. As a result perhydroxyl radicals ($H_2O^•$) are formed, which are less reactive than the hydroxyl radical. This situation inhibits the oxidation reaction and causes a decrease in removal efficiency [21,60–61].

$$HO^• + H_2O_2 \rightarrow H_2O^• + H_2O^+ \tag{15}$$

$$H_2O^• + HO^• \rightarrow O_2 + H_2O \tag{16}$$

$$Fe(II) + HO^• \rightarrow Fe(III) + OH^- \qquad k = 3.2 \times 10^8 \text{ M}^{-1}\text{s}^{-1} \tag{17}$$

When Fig. 4 is examined, it is seen that the efficiency of color and COD removal from wastewater increased with the increasing concentration of hydrogen peroxide in both homogeneous Fenton and heterogeneous Fenton processes. In the homogeneous Fenton process, when the hydrogen peroxide concentration increased from 100 to 300 mg/L, the color and COD removal efficiency increased and decreased after 300 mg/L. The maximum color (68.7%) and COD (65.8%) removal efficiency were achieved at 300 mg/L hydrogen peroxide concentration. In the heterogeneous Fenton process, the maximum color and COD removal efficiency were acquired at 100 mg/L hydrogen peroxide concentration, and then removal efficiency remained constant. In the heterogeneous Fenton process, color and COD removal efficiency were attained at a hydrogen peroxide concentration of 100 mg/L as 93.2% and 77.5%, respectively. According to the experimental results, higher color and COD removal efficiency were reached in the heterogeneous Fenton process compared to the homogeneous Fenton process. However, the hydrogen peroxide concentration determined optimally in the homogeneous Fenton process was 3 times the heterogeneous Fenton process. In other words, higher removal efficiency was obtained at lower hydrogen peroxide concentration in the heterogeneous Fenton process. In
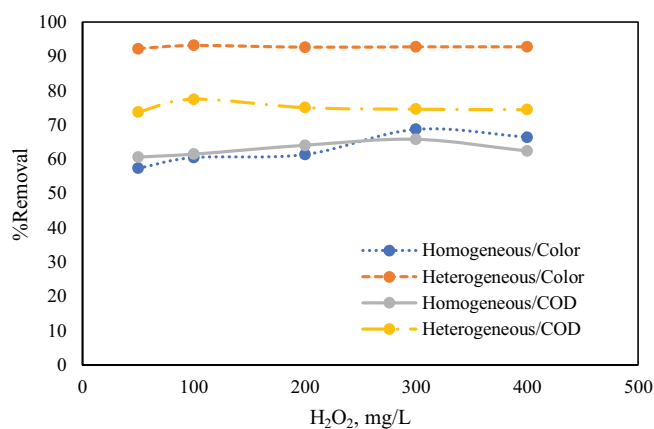
Fig. 4. Effect of the H_2O_2 concentration on homogeneous and heterogeneous Fenton processes (Fe(II) = 200 mg/L, pH = 2, T = 30°C, t = 120 min for homogeneous Fenton process; m = 6 g/L, pH = 3, T = 30°C, t = 120 min for heterogeneous Fenton process).

the heterogeneous Fenton process, the oxidation reaction occurs at the active sites on the catalyst surface. The catalyst retains its ability to generate hydroxyl radicals from hydrogen peroxide and generates more hydroxyl radicals [62].

3.4. Effect of the temperature on homogeneous and heterogeneous Fenton processes

The effect of temperature on homogeneous Fenton and heterogeneous Fenton processes was investigated by carried out experiments at 25°C, 30°C, 35°C, 40°C and 50°C. The experimental studies were performed in the determined optimum conditions such as Fe(II) and H_2O_2 concentrations, catalyst amount and pH.

The temperature effects the catalytic oxidation reaction rate in Fenton processes and thus the conversion time of hydrogen peroxide. Therefore, removal efficiency increases with increasing temperature. But at the same time, high temperature causes of hydrogen peroxide to decompose into oxygen and water, reducing its utilization rate [63,64].

As presented in Fig. 5, a decrease in color and COD removal efficiency were observed at temperatures above 35°C for both processes. The optimum temperature for the homogeneous Fenton process was determined as 35°C. Demir-Duz et al. [65] and Arzate-Salgado et al. [66] reported the optimum temperature as 30°C in their studies. According to the experimental results of heterogeneous Fenton process, 93.2% color and 77.6% COD removal efficiency were acquired at 30°C. Zhao et al. [67] and Exposito et al. [44] carried out their experimental studies at 30°C as the optimum temperature. As can be seen in the figure, there was no significant change in the efficiency of heterogeneous Fenton process when the temperature increased from 25°C to 50°C. Since there is a small increase in 30°C, the optimum temperature was taken as 30°C. However, the fact that there is no significant increase or decrease in yield with temperature is an important advantage for the heterogeneous Fenton process over the homogeneous Fenton process. This indicates that it is possible to work with
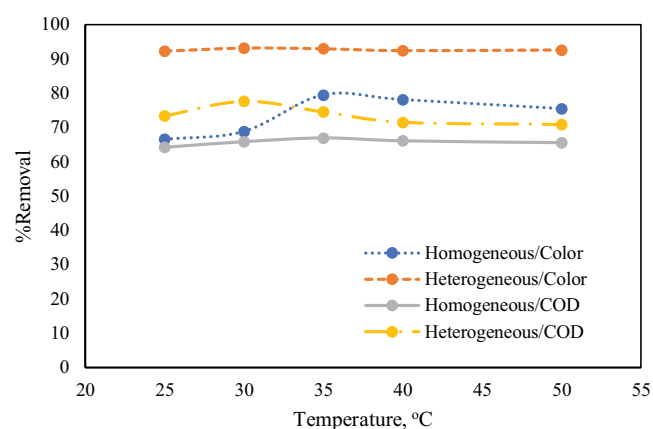
heterogeneous Fenton at low temperatures. Low temperature means low energy. This reduces operating costs.

3.5. Effect of the reaction time on homogeneous and heterogeneous Fenton processes

The reaction time is an important parameter in the formation of hydroxyl radicals and removal of pollution in wastewater. Advanced oxidation processes provide higher removal at lower reaction times compared to other methods [68]. In order to determine the optimum reaction time in the homogeneous Fenton and heterogeneous Fenton process, studies have been carried out at different times. The data obtained by conducting experiments for reaction times of 5, 10, 15, 30, 45, 60, 90, 120, 150, 180 and 240 min are presented in Fig. 6.

Considering the results reported in Fig. 6, it is seen that the color removal starts after 15 min in the homogeneous Fenton process. The COD removal efficiency increased from the 5th minute and remained constant after the 90th min. The maximum color (80.7%) and COD (69.5%) removal efficiency were reached in 90 min reaction time. In the experimental results, it was observed that high color and COD removal efficiency were attained from the first minutes for the heterogeneous Fenton process. According to Fig. 6, it was observed that there was a decrease in removal efficiency from this moment when the efficiency reached the highest level in 45 min reaction time. Therefore, the optimum reaction time has been determined as 45 min. The color and COD removal efficiency were acquired as 93.6% and 79.8%, respectively, at a reaction time of 45 min.

In the heterogeneous Fenton process, higher color and COD removal was achieved at a lower reaction time compared to the homogeneous Fenton process. This can be explained by the pore size, total pore volume and surface area of the catalyst used in the heterogeneous Fenton process. Active sites on the catalyst surface allow oxidation reactions to occur faster. Thus, higher wastewater treatment is achieved at low reaction times.

Fig. 5. Effect of the temperature on homogeneous and heterogeneous Fenton processes (Fe(II) = 200 mg/L, pH = 2, H_2O_2 = 300 mg/L, t = 120 min for homogeneous Fenton process; m = 6 g/L, pH = 3, H_2O_2 = 100 mg/L, t = 120 min for heterogeneous Fenton process).
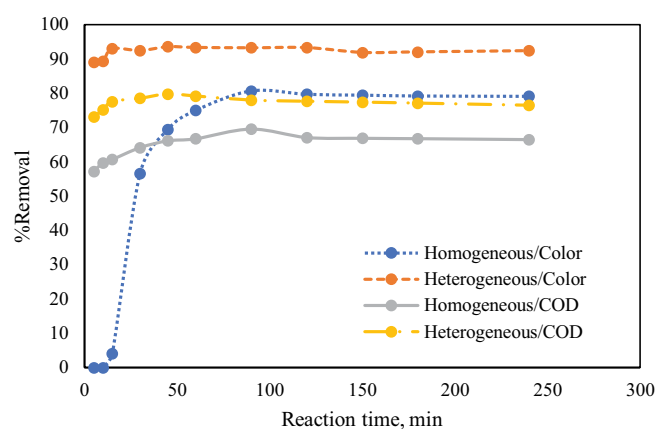

Fig. 6. Effect of the reaction time on homogeneous and heterogeneous Fenton processes (Fe(II) = 200 mg/L, pH = 2, H_2O_2 = 300 mg/L, T = 35°C for homogeneous Fenton process; m = 6 g/L, pH = 3, H_2O_2 = 100 mg/L, T = 30°C for heterogeneous Fenton process).

Table 2
Comparison of experimental results of sugar industry wastewater

Process	Optimum experimental conditions						Removal	
	Fe(II)	Catalyst amount	pH	H_2O_2	T	Reaction time	Color	Chemical oxygen demand
Homogeneous Fenton	200 mg/L	–	2	300 mg/L	35°C	90 min	81%	70%
Heterogeneous Fenton	–	6 g/L	3	100 mg/L	30°C	45 min	94%	80%

Table 3
Comparison the results of sugar industry wastewater treatment studies in the literature

Process	Color removal, %	Chemical oxygen demand removal, %	References
Electrochemical treatment	86	84	[3]
Electrochemical treatment	–	80.74	[5]
Thermal treatment	89.6	84.2	[35]
Photocatalysis	85.02	80.3	[69]
Electrochemical treatment	–	60	[70]
Nanofiltration	–	78	[71]
Electrocoagulation	89	85	[72]
Electrochemical treatment	–	79.66	[73]
Homogeneous Fenton	81	70	In this study
Heterogeneous Fenton	94	80	In this study

Table 4
Cost calculation of homogeneous Fenton and heterogeneous Fenton processes (Euro/50 mL)

Process	Fe^{+2}, Fe^{+3}	H_2O_2	SnO_2	Electrical energy	Total (Euro)/1 L
Homogeneous Fenton	0.058	0.00116		0.234	5.86
Heterogeneous Fenton	0.019	0.00116	0.042	0.117	3.58

The optimum conditions determined by experimental studies are presented in Table 2. In the heterogeneous Fenton process, higher color and COD removal efficiencies were obtained in a shorter reaction time. The comparison the results of sugar industry wastewater treatment studies in the literature are also shown in Table 3. It is concluded that homogeneous and heterogeneous Fenton processes provide effective removal when compared to the processes in the literature.

3.6. Cost analysis

While performing the cost analysis, separate calculations were made for homogeneous Fenton and heterogeneous Fenton. Cost calculations were made using the optimum values of Fe^{+2} and H_2O_2 concentrations determined for homogeneous Fenton and heterogeneous Fenton processes. In addition, the energy consumed by the water bath is also included in the calculations. The cost of large-scale projects can be determined in advance by making cost analysis of low-scale projects or laboratory studies. In this way, the importance of cost analysis is very great. For this reason, it is aimed to choose the most suitable process by calculating the cost of all inputs used in both systems. The price of the chemicals used in the cost analysis, the price of $FeSO_4 \cdot 7H_2O$ is 59.35 Euro/1 kg, the price of H_2O_2 is 77.2 Euro/500 mL, the price of $Fe(NO_3)_3 \cdot 9H_2O$ is 110 Euro/1 kg, and the price of SnO_2 is 667 Euro/2 kg (Merck, 2023). The amounts of H_2SO_4, NaOH and NH_4OH used in pH adjustment were neglected because they were very low. The unit price of electricity is 2.22 TL (0.078 Euros) for 1 kWh (July 2023). The water bath is 230 V and 8.7 A. Accordingly, the cost calculation is given in Table 4 [74].

As can be seen in the table, chemical costs are very close to each other when both processes are compared. The energy cost was lower in heterogeneous Fenton because the reaction time was shorter. Therefore, it can be said that heterogeneous Fenton is more economical. In addition, the catalysts used in heterogeneous Fenton processes have the ability to be used repeatedly. This will further reduce the cost. The important disadvantage of the homogeneous Fenton process is also the generation of iron-containing sludge waste. The removal of sludge waste increases costs for businesses. As a result, it can be said that heterogeneous Fenton is more advantageous.

4. Conclusions

In this study, homogeneous Fenton and heterogeneous Fenton processes were compared for the treatment of

sugar industry wastewater. The wastewater were obtained from Ankara Sugar Factory in Turkey. The parameters effecting the oxidation reaction such as iron ion concentration, catalyst amount, hydrogen peroxide concentration, pH, temperature and reaction time were investigated. In the heterogeneous Fenton process, $Fe(III)/SnO_2$ was synthesized and used as a catalyst. Under optimum conditions, 81% color and 70% COD removal efficiency were obtained in the homogeneous Fenton process. In the heterogeneous Fenton process, color and COD removal efficiency were achieved as 94% and 80%, respectively. When the two methods were compared, in the heterogeneous Fenton process, higher color and COD removal efficiency were attained at lower hydrogen peroxide concentration and shorter reaction time. The reasons for this can be stated as follows: in the heterogeneous Fenton process, the oxidation reaction performs place at the catalyst surface. Supported by metal oxides, the catalyst creates a large surface area and provides active sites that enable more hydroxyl radical generation. Iron oxide sludge and catalyst loss do not occur because iron is immobile in the structure and pores of the catalyst. This also allows removal in the higher pH range. That is, 90% color removal was obtained even at pH = 5 in heterogeneous Fenton. In addition, its ability to work at high pH is important for the continuation of aquatic life. Acidic conditions will endanger living things. The result of the cost analysis also showed that heterogeneous Fenton is more economical. This result shows that heterogeneous Fenton is more advantageous than homogeneous Fenton in every aspect.

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