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Investigation of different treatment strategies such as membrane filtration and Fenton processes in the treatment of dairy industry wastewater

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ABSTRACT

This study investigated the treatability of dairy industry wastewaters by using the Fenton process and membrane bioreactors. Firstly, the effects of the Fenton process on the reaction time, pH, Fe^{2+} and H_2O_2 concentrations on chemical oxygen demand (COD) and total organic carbon (TOC) removal were determined to evaluate the treatment of dairy industry wastewater. According to the results obtained, the optimum reaction time, pH, Fe^{2+} and H_2O_2 concentrations were found to be 60 min, pH 3, 1 g/L, 1.5 g/L, respectively, while the COD and TOC removal efficiencies were 87% and 75%. Secondly, biological treatability of wastewater in membrane bioreactors was investigated. The input water COD concentrations of 0.6–2 g/L, sludge age values of 3 h to 10 d and different hydraulic waiting processes were studied. Loading was made to the system at 5 kg COD/m^3d, and later, loading was increased up to 17 kg COD/m^3d based on the input water COD values. After treatment with membrane bioreactors, the COD removal efficiency varied between 95%–98%. As the output water concentrations obtained as a result of the study satisfied the discharge limits, the applied biological treatment and advanced oxidation methods were completed successfully.

Keywords: Dairy wastewater; Elimination; Fenton process; Membrane bioreactor

1. Introduction

With the increase in the consumption of foods such as milk and cheese linked to the rapid increase in the population of Turkey, water pollution and environmental pollution originating from these dairy facilities have increased considerably. Due to the high pollution load of dairy industry wastewaters, discharge of untreated/partly treated wastewaters from dairy processing industries into receiving bodies leads to significant environmental problems [1]. The dairy and dairy product industry encompasses the production of products such as raw milk, drinking milk, yogurt and Aryan (a drink made out of yogurt, water and salt), butter, cheese, ice-cream and milk powder [2]. Wastewaters coming from the dairy industry consist of clean waters from heating and cooling systems, domestic wastewaters, wastewaters coming from cleaning of facilities and equipment, and whey. In the dairy industry, ~0.2–10 L of wastewater is produced per liter of processed milk [3]. The dairy industry produces strong wastewaters characterized by high biochemical oxygen demand (BOD) and chemical oxygen demand (COD) concentrations, dissolved or suspended solids including oil and grease, ammonia or nutrients such as minerals and phosphate compounds [4].

For the purpose of treating wastewaters from the dairy industry, very different systems have been developed in various countries around the world. These may be listed as biological treatment (aerobic, anaerobic, trickling filter), chemical treatment field treatment and membrane technologies. Changes observed in the amount and characteristics of wastewaters make it difficult to biologically treat wastewaters originating from this industry. For this, advanced

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oxidation processes (AOP) are used to reduce the organic load and toxicity, especially before biological treatment [5]. Membrane bioreactors (MBR), ozonation and AOPs were presented as promising technologies for the removal and/or degradation of polar, permanent pollutants. MBR technology combines activated sludge and the biological degradation process with membrane filtration and direct solid-liquid separation. Membrane bioreactors have significant advantages such as the provision of effective solid-liquid separation, ability to provide high-quality output water, smaller facility sizes and low rates of sludge production. Usage of micro- or ultrafiltration technology (pore sizes of 0.05–0.4 mm) in MBR systems allows complete physical confinement of bacterial flocks in the bioreactor and all suspended solids [6]. The treatment efficiency is affected by factors such as the parameter to be removed, the chemical substance that is used, retention time and stirring rate, and the amount of sludge to be formed may be more or less based on the type of chemical substance [7].

In recent years, chemical treatment methods known as AOP involving the production of hydroxyl radicals have been applied successfully for degradation or removal of resistant pollutants depending on the high oxidative power of the OH^- radical. Among AOPs, the Fenton process is a catalytic method that is prevalently used today which is based on the production of hydroxyl radicals (OH^-) from hydrogen peroxide with iron ions that behave as homogenous catalysts in acidic environments. The Fenton process generally involves 4 states of pH adjustment, oxidation reaction, neutralization–coagulation and precipitation. There are studies in the literature showing the successful use of AOPs regarding paper industry wastewaters [8], tannery wastewaters [9] and drug industry wastewaters [10].

In general, the optimum H_2O_2/Fe^{2+} mole ratio recommended for Fenton treatment is between 10 and 40 [11]. While the hydrogen peroxide dosage is important to obtain the best degradation efficiency, the concentration of iron ions is important for the reaction kinetics. Furthermore, the excess of either of these compounds may reduce the degradation efficiency as both H_2O_2 and Fe^{2+} can capture hydroxyl radicals as shown in Eqs. (1) and (2). The stoichiometric ratio of H_2O_2/Fe^{2+} is dependent on the physical-chemical properties of the wastewater. Likewise, the design of experiments is commonly used to optimize the process parameters and increase the quality of products by using engineering and statistics applications. Both H_2O_2 dose and Fe^{2+} concentration are two important factors that are effective on the Fenton process [12–14].

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

$$k = 63\ M^{-1}\ s^{-1}$$

$$H_2O_2 + Fe^{3+} \leftrightarrow H^+ + FeOOH_2^+ \tag{2}$$

Iron ions start the separation of H_2O_2, catalyze it and form hydroxyl radicals.

The produced Fe^{3+} may react with H_2O_2 and hydroperoxyl radicals in a Fenton-like process, and this leads to the re-formation of Fe^{2+}. The ferric ions that are formed separate hydrogen peroxide into water and oxygen by catalyzing it. Iron ions and radicals also form in the reactions (Eqs. (3) and (4)). Hydroxyl radicals ($^{\bullet}OH$) are effective in the degradation of organic chemicals because they are reactive electrophiles that rapidly and non-selectively react with electron-rich organic compounds (they prefer electrons). For this reason, AOPs are effective in the degradation of hazardous byproducts or several toxic and bio-resistant organic pollutants without producing much sludge. The Fenton reaction has a shorter reaction time than other advanced oxidation processes, and for this reason, the Fenton reactive is used when a higher COD removal is necessary. The reactions that occur during the Fenton process may be expressed as follows [13,14]:

$$H_2O_2 + OH^{\bullet} \rightarrow HO_2^{\bullet} + H_2O \tag{3}$$

$$k = 27 \times 10^7\ M^{-1}\ s^{-1}$$

$$OH^{\bullet} + Fe^{2+} \rightarrow Fe^{3+} + OH^- \tag{4}$$

$$k = 3\ 2 \times 10^8\ M^{-1}\ s^{-1}$$

Fenton treatment is prevalently applied for treatment of wastewaters that cannot be biologically degraded. The efficiency of the Fenton process is dependent on the properties of the wastewater, pH values, H_2O_2/Fe^{2+} concentrations and reaction time. The Fenton process uses iron ions to enter a reaction with hydrogen peroxide, and it creates hydroxyl radicals which are strong oxidizers to degrade some toxic pollutants [15].

In recent years, many studies involving AOPs have shown high efficiency in the treatment of some industrial wastewater. For this purpose, advanced oxidation methods such as LED-assisted electro-Fenton [16] photo-Fenton [17] heterogeneous sono-Fenton [18] are used in the treatment of many industrial wastewater.

Conventional biological treatment of dairy industry wastewaters is limited due to the presence of toxic pollutants and resistant organics. Among AOPs, the Fenton process may be effectively used to treat wastewaters. Although the Fenton process is commonly used in treating various industrial wastewaters, there are few studies in the literature about the treatment of wastewaters from the dairy industry by using the Fenton process. When advanced treatment methods are applied before biological treatment methods, they play a protective and burden-reducing role in biological treatment systems as they remove toxic or difficult to decompose substances from the environment. To decide upon suitable processes for the treatment of dairy industry wastewaters, wastewater characterization, treatability studies and usage and assessment of the optimum units and processes for wastewater treatment have been investigated. Membrane bioreactors are effective considering the wastewater quality for the treatment of dairy industry wastewaters with biological methods. As an alternative to conventional methods used in treatment plants, it is possible to increase the treatment efficiency by using a dual system (biological and chemical processes) in order to provide a safer discharge with technological methods. For this reason, by using membrane bioreactors and the Fenton process in this study, the aim was to determine the effects of different parameters on treatment efficiency and analyze the chemical and biological treatability of dairy industry wastewaters to optimize the operational conditions.

This study was carried out at the Van Yüzüncü Yıl University Engineering Faculty Research Laboratory in May 2020.

2. Material and method

The wastewater that was used in the experiments was obtained from a pilot milk factory located in Van Yüzüncü Yıl University, Turkey. The amount of wastewater from the facility varies between 2–3 m^3 wastewater/ton of processed milk per day (including the wastewater from the washing of milk cans, storage tanks, pasteurizers, cream separators, homogenizer, and cooling systems, tools, and other equipment in the bottling unit. Experiments regarding Fenton oxidation were carried out by using 500 mL of dairy industry wastewater in 1,000 mL Erlenmeyer flasks. In the Fenton process experiments, the pH was adjusted by adding dilute H_2SO_4 and NaOH. During the reaction time (60 min), the stirring process was achieved by using a jar test device branded Velp Scientifica, JLT6 (Italy). Afterwards, for solid–liquid separation, the specimens were centrifuged for 5 min at 5,000 rpm by using a Hettich Rotofix 32 A (Germany) device. COD, H_2O_2 and total organic carbon (TOC) analyses were conducted on specimens collected from the top phase. In the experiments with membrane bioreactors, activated sludge collected from the precipitation pond of the wastewater treatment facility was used. The collected sludge was loaded with the dairy industry wastewater as a carbon and energy source, and the aim was to achieve adaptation of the microorganisms to the wastewater. In the experiments, a Kerafol-brand cylindrical ceramic membrane module with a surface area of 1.5 m^2 was used. Its pore size was 200 nm. The ceramic membrane module had an outer diameter of 2.8 mm, inner diameter of 2.3 mm and 165 channels. The length of the ceramic membrane placed into a polymer housing was 315 mm. When the ceramic membrane that was used became clogged, it was back-washed by using pressurized air.

2.1. Dairy wastewater treatment methods

In this study, a series of experiments were carried out to provide COD and TOC removal from dairy industry wastewaters and to find the most appropriate treatment method. Firstly, the optimum operating conditions of the Fenton process were determined to assess the treatment status of dairy wastewater. In the Fenton process, $FeSO_4{\cdot}7H_2O$ and H_2O_2 were added sequentially, followed by fast mixing at 150 rpm for 5 min and slow mixing at 60 rpm for 57 min. In the determined time intervals, the pH of the obtained specimens was adjusted to the range of 7–8 with sodium hydroxide, and precipitation was facilitated. Secondly, the biological treatability of wastewater in membrane bioreactors was examined. For continuous trials in the membrane bioreactor that was used for continuous treatment of the wastewater, desired concentrations of wastewater were prepared inside a feeding tank with a volume of 50 L. Afterwards, continuous feeding was carried out at the desired flow rate with the help of a peristaltic pump to provide wastewater input. Air flow was adjusted with a flowmeter found on the line with the air pump. A level controller was used so that the volume of the fluid exiting the membrane module and the volume of the extracted sludge would be equal to the feeding flow rate. A cooling circulator was used to control the temperature inside the reactor. Additionally, the system was back-washed at the desired intervals by using a compressor in back-washing. All of these systems were controlled with an automation system.

Continuous trials were carried out by connecting the membrane unit to the system. The microorganisms were habituated to the wastewater under aerobic conditions. Hydraulic balance was achieved by equalizing the input and output flow rates in the reactor. The amount of water in the reactor would reduce if there was a higher flow rate of the treated water coming out of the membrane than the flow rate of the feed and its fluctuations. This problem was eliminated with a fluid level control system for the output flow rate to be equal to the input flow rate in the membrane. The volume of the reactor that was used in this study was 15 L, while the temperature of the activated sludge in the reactor was kept constant at 25°C with the help of a heat exchanger. Throughout the study, the pH of the activated sludge was continuously monitored and balanced at the value of pH 7. In the study, the wastewater was provided directly to the system with a peristaltic pump with adjustable flow. The study was begun by keeping the feed flow rate and input wastewater concentration constant and changing the sludge age as seen in Table 1.

2.2. Sample analysis

The H_2O_2 concentration was measured at 352 nm spectrophotometrically (WTW-6100 UV) [19]. To correct the intervention of H_2O_2 on COD, the equation developed by Talinli and Anderson was used [20]. The TOC concentration was determined by using Teledyne/Tekmar-TOC fusion. COD parameter measurements were made in compliance with the Standard Methods, and the "open reflux" titrimetric method was used [21]. The analytical method and units for the dairy industry wastewater parameters are shown in Table 2.

2.3. Wastewater resources and characterization

Determination of wastewater characterization is necessary for the design and operation of treatment plants and discharge units [22]. Conventional parameters were considered for the characterization of the dairy industry

Table 1
Parameters with effects on continuous treatment of wastewater investigated in the study and variation ranges

Parameter	Variation limits
Inlet water concentration (S_0)	600–2,000 mg/L
Hydraulic retention time (θ_h)	1–6 h
Volumetric organic load	5–17 kg COD m^3/d
Sludge age (θ_c)	3 h–10 d
Inlet water supply flow (Q_b)	25–300 mL/min

Table 2
Analytical method and unit of the dairy industry wastewater parameters

Parameter	Analytical method
COD, mg/L	Closed reflux method, titrimetric method
BOD, mg/L	Respirometric method
TSS, mg/L	Gravimetric method
SS, mg/L	Photometric method
pH	Potentiometric/pH prop
TN, mg/L	Catalytic thermal decomposition method
TP, mg/L	Spectrophotometric method
TOC, mg/L	TOC-L catalytic oxidation method

COD – chemical oxygen demand; BOD – biochemical oxygen demand; TSS – total suspended solids; SS – suspended solids; TN – total nitrogen; TP – total phosphorus.

Table 3
Properties and discharge limits of the dairy industry wastewater used in the study

Parameter	Values	Discharge limits (TWPCR)
TCOD	9,670	160
DCOD	4,225	–
PCOD	5,445	–
BOD	4,200	–
TSS	8,400	–
SS	4,050	–
pH	62	6–9
TN	52	–
TP	25	–
TOC	840	–

wastewaters (Table 3). Whether or not the COD removal efficiency obtained by chemical treatment satisfied the discharge criteria were determined based on the Turkish Water Pollution Control Regulation (TWPCR) [23]. The wastewater specimens were kept at 4°C until analysis, and they were analyzed at a laboratory accredited with the ISO 17025 quality system.

3. Results and discussion

The results obtained from the experiments were compared with the results obtained from different treatment processes applied to dairy industry wastewaters and are given in Table 4.

The treatment efficiency varied based on the chemical composition of the wastewater. It was seen that dairy industry wastewaters could be treated with high efficiency by biological treatment, and they could be treated to the level of about 85% with the Fenton process. While high efficiencies were obtained in long time periods with biological treatment, similar efficiencies could be obtained in minutes during oxidation studies. It was emphasized that the oxidation process increased biological treatability by increasing the BOD/COD ratio in studies where advanced oxidation and biological treatment were carried out together. The results obtained in this study were in agreement with the results in the literature. Characterization of dairy industry wastewaters containing high levels of organic pollutants caused by BOD, COD and other wastewater characteristics was similar to values found in other studies in the literature [30].

Table 4
Efficiency of different treatment processes for dairy industry wastewaters

Treatment process	BOD (%) removal	COD removal (%)	Reference
Fenton process	–	91	[24]
Electro-Fenton process	–	95.78	[25]
Membrane bioreactor		96	[26]
Activated sludge	–	71	[27]
Electrocoagulation	97.95	98.84	[28]
Coagulation/flocculation	–	92	[29]
This study	–	95–98	–

3.1. Fenton treatment of dairy wastewater

3.1.1. Effects of H_2O_2 dose on oxidation efficiency

To determine the effects of H_2O_2 dose on oxidation efficiency and determine the optimum H_2O_2 dose, experiments were conducted by keeping Fe^{2+}, pH and a temperature of 25°C constant and changing the H_2O_2 concentration. The effects of the H_2O_2 concentration were studied at 6 different values in the range of 0.5–4.3 g/L. Accordingly, the maximum efficiency was determined at a H_2O_2 dose of 3.5 g/L. The results are shown in Fig. 1. When the H_2O_2 dose increased above a certain value the effectiveness of OH radicals decreases according to the reaction given in Eq. (5), and the removal efficiency was reduced.

$$HO^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \quad (5)$$

In general, an increase in the H_2O_2 concentration leads to an increase in the degradation rate of pollutants [31,32]. However, using excessive amounts of H_2O_2 is not recommended as excess usage of H_2O_2 will provide a positive intervention for COD. Another negative effect of excess H_2O_2 concentrations is its radical scavenging effect on OH radicals [33,34].

3.1.2. Effects of Fe^{2+} dose on oxidation efficiency

The concentration of reactive substances used in the Fenton process plays an important role in the degradation of organic substances. As the Fe^{2+} concentration increases, the degradation speed of organic substances increases. However, an increase in the Fe^{2+} concentration leads to an increase in the amount of total dissolved iron ions, resulting in sludge formation in the solution. Thus, excess sludge formation should be avoided.

The effects of the Fe^{2+} concentration on COD and TOC removal efficiencies were studied at concentrations of 0.35, 0.5, 0.8, 1.0 and 4.3 g/L (Fig. 2). In the absence of Fe^{2+}, effective oxidation does not take place based on the Fenton reaction as there is no main factor to produce hydroxyl radicals in the environment.

High Fe^{2+} concentrations will lead to the consumption of OH radicals in the medium (radical scavenging effect), and in this way, the removal efficiency will decrease. Additionally, excess Fe^{2+} in the medium will lead to the transformation of H_2O_2 into the water by oxidation into Fe^{3+} (Eq. (6)) [35].

$$Fe^{2+} + H_2O_2 \rightarrow 2H^+ \rightarrow 2Fe^{2+} + H_2O \quad (6)$$

3.1.3. Effects of pH on oxidation efficiency

In the Fenton process, pH is one of the important parameters. pH varies in a narrow range of 2.0–5.0, and the highest removal efficiency is generally obtained at around pH 3 in the literature [36]. To determine the optimum pH value, the Fenton process was applied in the range of pH 2.0–7.0 by keeping the Fe^{2+} (1.5 g/L), H_2O_2 (1.5 g/L) and temperature (T = 25°C) constant (Fig. 3). The highest COD removal efficiency was obtained at pH 3. The lowest removal efficiency was obtained at pH 7.0. Similarly, Vinita et al. [37] found that the optimum pH was 3.5 in their study about the removal of chlorinated aliphatic organics.

Outside the optimum pH value range, oxidation ability decreases as a result of ferrous hydroxide complex formation and scavenging of •OH radicals with separation of H_2O_2. As $[Fe^{2+}(H_2O)]^{2+}$ forms at low pH values, a lower amount of hydroxyl radicals is created [38].

Mandal et al. [39] reported that pH had a significant effect on COD removal efficiency in the treatment of dye wastewaters, and the optimum pH range was 3–5.

According to Eq. (7) given below; the pH value must be acidic to produce the hydroxyl radical required for the oxidation of organic compounds (Eq. (7)) [40].

$$2Fe^{2+} + H_2O_2 + 2H^+ \rightarrow 2Fe^{3+} + 2H_2O \quad (7)$$

However, when the pH is too low (pH < 2.0), the reaction slows down due to the formation of complex iron species and the formation of the oxonium ion. Due to the scavenging of hydroxyl radicals of the H^+ ion at low pH, the removal rate is limited and the oxidation ability is reduced (Eqs. (8) and (9)) [18,41].

$$OH^{\bullet} + H^+ + e^- \rightarrow H_2O \quad (8)$$

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \quad (9)$$

3.1.4. Effects of reaction time on oxidation efficiency

The reaction time may vary based on the type of organic substance in the wastewater. The changes in the COD and TOC removal were observed at the optimum conditions (Fe^{2+} = 1.0 g/L, H_2O_2: 3.5 g/L and initial pH: 3) by collecting specimens at 15, 30, 60 and 90 min (Fig. 4). The maximum removal efficiencies for the COD and TOC parameters were reached at the 90th minute, with 70% TOC and 86% COD removal efficiencies obtained. There was no significant change in the removal efficiencies after a reaction time of 60 min. Therefore, 60 min could be taken as the most suitable reaction time based on the optimum conditions. It may be stated that as the amount of

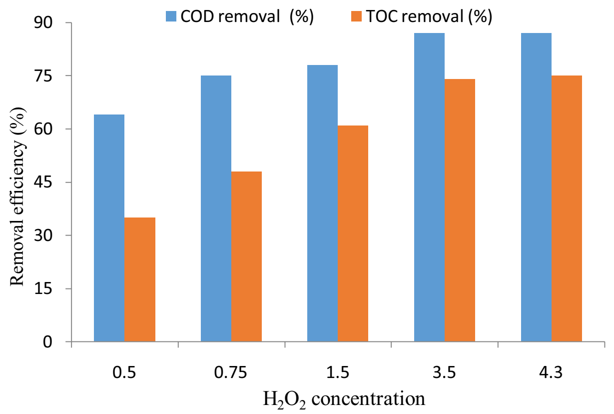

Fig. 1. Effects of different H_2O_2 doses on COD and TOC removal efficiencies (pH = 3; Fe^{2+} = 1 g/L; T = 25°C).

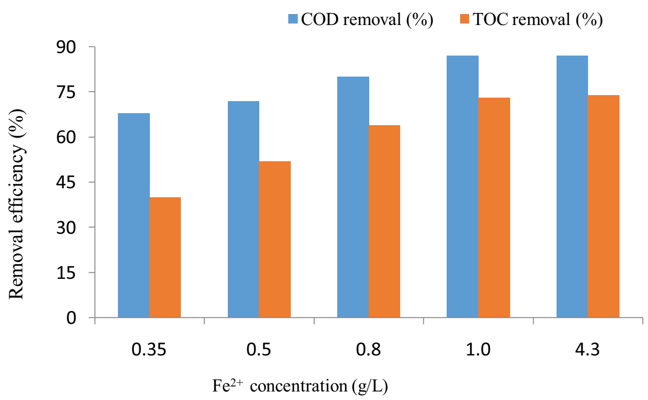

Fig. 2. Effects of different Fe^{2+} doses on COD and TOC removal efficiencies (pH = 3; H_2O_2 = 3.5 g/L; T = 25°C).

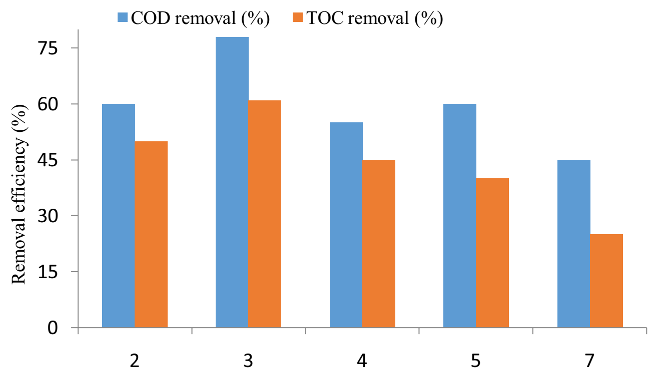

Fig. 3. Effects of different pH values on COD and TOC removal efficiencies (H_2O_2 = 1.5 g/L; Fe^{2+} = 1.5 g/L; T = 25°C).

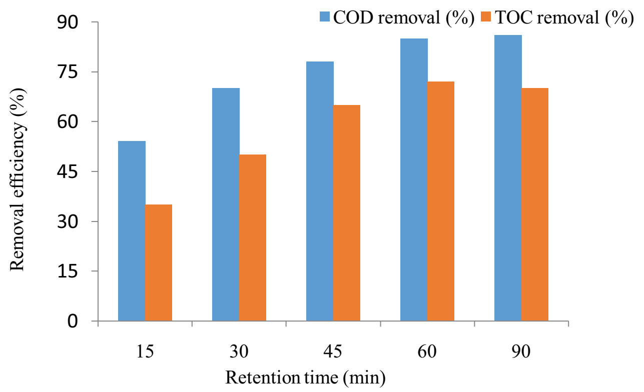

Fig. 4. Effects of reaction time on COD and TOC removal efficiencies (H_2O_2 = 1.5 g/L; Fe^{2+} = 1.5 g/L; T = 25°C).

H_2O_2 in the medium will decrease as a result of its reaction with Fe^{2+}, the reaction will not change much in times longer than 60 min. Some studies reported the reaction time for the Fenton process was between 30 min and 2 h [42]. The optimum reaction time was reported to 30 min in some studies where the electro-Fenton process was used [43].

3.2. Biological treatability with membrane bioreactors of dairy wastewater

3.2.1. Sludge age

During continuous trials, the sludge age was adjusted manually by removing part of the concentrated sludge from the reactor daily. This way, controlled experiments were conducted in the reactor at the desired sludge age.

3.2.2. Hydraulic retention time

The hydraulic retention time (HRT) was adjusted with the help of a wastewater feed pump. This pump was a peristaltic feed pump, and it was used to feed the desired flow rate of wastewater into the reactor. As the reactor volume was known, the hydraulic retention time could be easily determined by adjusting the feed flow rate.

In a study where dairy industry wastewaters were treated in aerobic conditions, the reactor volume was 25 L. COD, BOD_5, TKN and oil-grease removal efficiency were monitored. The COD of the treated dairy wastewater was 11,000 mg/L. HRT values of 3, 4, 6 and 8 d were studied. At a hydraulic retention time of 3 d and organic loading of 1,340 g BOD_5/m^3d, 87% COD removal efficiency was obtained. As a result of the study, high organic matter and N removal was obtained in the system, and it was stated that the system could be successfully used in treatment of dairy industry wastewaters [44].

For treatment of the dairy industry wastewater in the membrane bioreactor, the COD and BOD_5 removal efficiency increased with decreased organic load and increased hydraulic retention time. As a result of treating the dairy industry wastewater with a hydraulic retention time of 4 d and under an organic load of 0.6 kg BOD_5/m^3d, the discharge standard in the TWPCR was achieved in terms of the COD parameter. However, it was concluded that a longer hydraulic retention time is needed for more ammonium removal [45].

During the operational period of continuous treatment of dairy industry wastewaters in a jet loop membrane bioreactor, very high performance was obtained at retention times of 2.5–3.0 h. These times were sufficient even in cases were the loads were very high (>24 kg/m^3d). However, at times where the input COD was higher than 5,000 mg/L, the θ_h had to be kept in the range of 4–6 h. In the case of COD concentrations higher than 7,000 mg/L, high efficiency could be obtained when the θ_h values were in the range of 6–8 h. More than the high load values, high input water concentrations were effective on the hydraulic retention times in the system. During the study, the θ_c values were changed between 3 and 80 h. High performance was obtained in all cases at sludge ages of 8 h or higher [44].

3.2.3. Effects of different sludge ages on MBR performance

This study investigated how different sludge ages affect COD removal. In the study, experiments were carried out at input water COD concentrations of 600–2,000 mg/L, sludge ages between 3 h and 10 d and different hydraulic retention times, and Fig. 5 shows that stable outputs were obtained from the system. The mean total suspended solids (TSS) in the reactor was 2,000 mg/L. In the study, the treatment efficiency was determined by considering the COD parameter. The values that were obtained as a result of treatment were compared to the operational discharge limits, and decisions were made about whether or not the treatment efficiency was adequate.

As seen in Fig. 5, the sludge age was directly related to the membrane flux. Sludge was removed from the system with a flow rate equal to the difference between the flow rates of the feed and membrane output. At the moment when the sludge age was kept constant at 24 h, the COD treatment efficiency varied between 95% and 98%. Under the operational conditions at sludge age of 12 h, 90%–96% COD treatment efficiency was obtained.

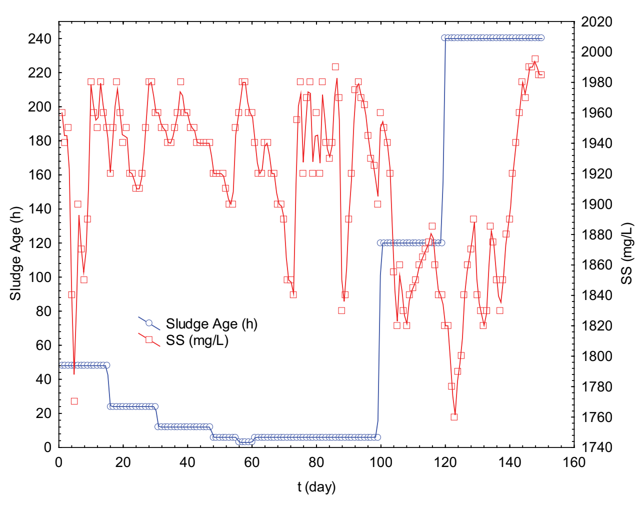

Fig. 5. Change in different sludge age values over time.

While operating at sludge age of 3 h, the COD treatment efficiency measured from the membrane output was in the range of 95%–98%.

In the study, high treatment efficiencies were obtained at high sludge concentrations. While the reaction speed in biological wastewater treatment is dependent on factors such as old-young biomass, it is directly related to the biomass concentration. Long sludge ages are preferred as they help reproduction of slow-multiplying microorganisms that can consume macromolecules such as polysaccharides, carbohydrates and proteins as substrates, increase the TSS concentration in the reactor, and therefore, reduce the reactor volume that is needed and the amount of sludge to be evacuated from the reactor. Several studies have observed that MBR systems show good performance in cases where the sludge age is 10 d or longer [6].

3.2.4. Effects of different hydraulic retention times on system performance

In the study, by keeping the sludge age constant at 3 h, trials were carried out with different hydraulic retention times for the wastewater with an input water concentration of 600 mg/L (Fig. 6). For a hydraulic retention time of 3 h, the load on the system was increased to 10 kg COD/m^3d. The COD removal efficiency was observed to be 80%. The load was increased up to 15 kg COD/m^3d at a hydraulic retention time of 2 h, and when the load was increased up to 17 kg COD/m^3d at a hydraulic retention time of 1 h, the treatment efficiency dropped to 70% as in Fig. 6.

It is understood that HRT should not be too long when control of membrane clogging and an economic design are desired. Studies with membrane bioreactors have recommended the optimum HRT value of 2 h [46]. Another study investigating the effects of HRT presented three MBR systems with HRT values of 10–12 h, 6–8 h and 4–5 h, and it was observed that the total COD removal efficiency was 94% in all three reactors. The slight reduction in the COD removal with decreased HRT was explained by substrate and dissolved oxygen transfer rate obstructed by high TSS concentration and sludge viscosity. It was claimed that low HRT causes excessive multiplication of filamentous bacteria, and this has a negative effect on the membrane flux [47].

3.2.5. Effects of different input water concentrations on output water performance

In the system operated with different sludge ages and hydraulic retention times, the best treatment efficiency was obtained at 3 h of sludge age and hydraulic retention time as a result of the trials. As seen in Fig. 7, when the input water concentration was increased to 1,800 mg/L at the same feed flow rate, there was an increase in the COD concentration, and the mean output COD concentration was determined as 100 mg/L. By increasing the input water COD value to 2,000 mg/L, there was an increase in the COD concentration, and the mean output COD concentration was determined as 150 mg/L. Fig. 7 shows that the system was very sensitive to hydraulic retention times.

In the study, wastewater that was subjected to pretreatment and had a concentration of 600 mg/L was introduced. Initially, the TSS content of the bioreactor became approximately 1,500 mg/L. By starting with 5 kg COD/m^3d organic loading in the system, occasional feeding was provided. As seen in Fig. 8, the COD loads given to the system varied in the range of 5–17 kg/m^3/d. Although there were large fluctuations in the loadings, stable outputs could be obtained from the membrane bioreactor system even at high loads. Fig. 8 shows that a COD removal efficiency of higher than 95% was achieved in almost all conditions.

4. Conclusions

This study, water pollution control regulations specified in the dairy industry wastewater discharge standards in Turkey to develop appropriate treatment system and for this purpose various treatment alternatives (Fenton process and membrane bioreactors) aimed to evaluate. Fenton processes and membrane bioreactors are suitable treatment technologies for the treatment of wastewaters with high permanent organic substance content. Therefore, the

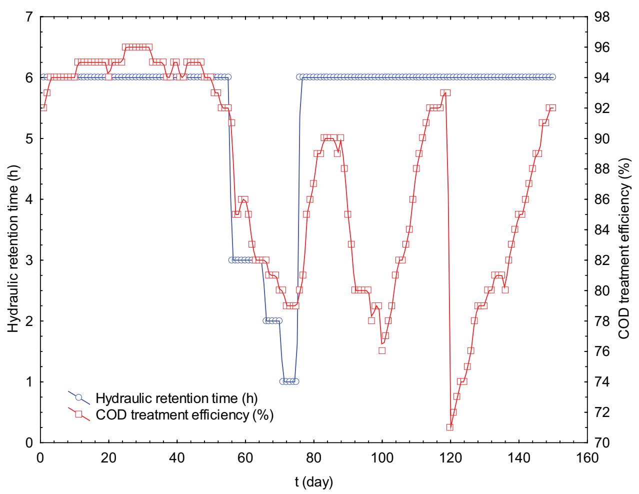

Fig. 6. Change in different hydraulic retention times over time.

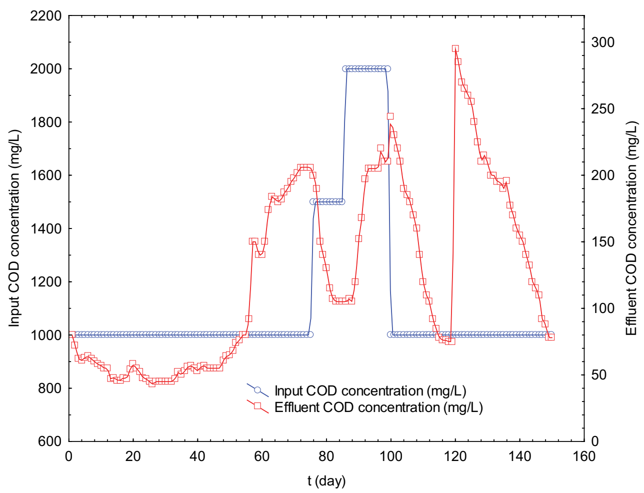

Fig. 7. Change in different input water concentrations over time.

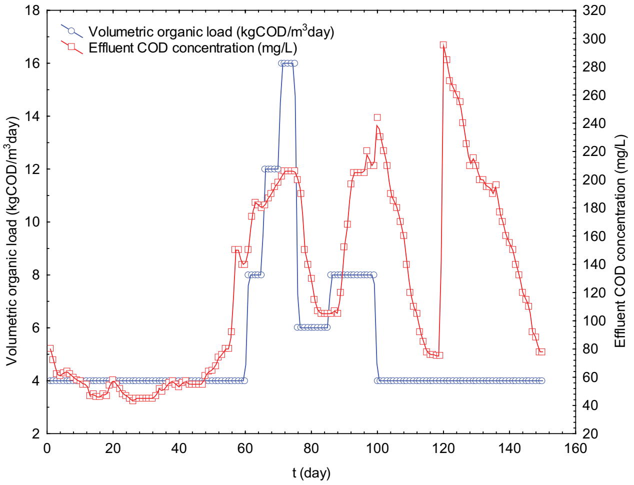

Fig. 8. Change in different volumetric organic loadings over time.

efficiency of the Fenton process and membrane bioreactors are considered separately due to the high COD and TOC content of the dairy industry. Using Fenton process, under the optimum values of initial H_2O_2 = 3.5 g/L, Fe^{2+} = 1 g/L, pH = 3, T = 25°C and reaction time of 60 min, the COD and TOC removal efficiencies were found to be 87% and 75%, respectively. The optimum conditions determined in the study were pH = 3, Fe^{2+}, H_2O_2 and a reaction time of 60 min. When these conditions were provided, >80% COD and >60% TOC removal efficiencies were obtained. In terms of the COD and TOC parameters, the output of the Fenton oxidation process satisfied the discharge standards in Turkey. Additionally, the wastewater obtained from the milk factory was subjected to pretreatment and treated biologically in membrane bioreactors in the study. Experiments were conducted at the input water COD concentrations of 600–2,000 mg/L, sludge ages of 3 h to 10 d and different hydraulic retention times. Higher than 95% COD removal efficiency was obtained in almost all conditions. During the trials, the TSS concentration varied between 1,800 and 2,000 mg/L. The sludge age and hydraulic retention time were selected as 3 h for biological treatment of dairy industry wastewater that was pretreated. As the output water concentrations obtained as a result of the study satisfied the operational discharge limits, it was observed that the biological treatment method for wastewater treatment was completed successfully. It has been observed that treatment plants consisting of a combination of chemical and biological processes are preferred in terms of operation and removal efficiency in enterprises with low wastewater flow.

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