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Anaerobic treatment of ozonated membrane concentrate

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ABSTRACT

A concentrate stream is generated by the application of nanofiltration (NF) membranes in wastewater reuse. Due to the high concentrations of pollutants, disposal of NF concentrates is an important problem. In this study, ozonation and anaerobic treatment processes were performed to treat cotton dyeing textile mill wastewater NF concentrate. After ozonation, the concentration of biochemical oxygen demand (BOD_5) increased while dissolved chemical oxygen demand (DCOD) decreased. Thus, biodegradability of the concentrate was increased by the ozonation process. The average removal efficiencies of DCOD, BOD_5, and sulfate (SO_4^{2-}) in the anaerobic process were achieved about 72, 76, and 68%, respectively. These results indicated that the combination of ozonation and anaerobic treatment showed a remarkable performance for the removal of pollutants from NF concentrate.

Keywords: Anaerobic treatment; Membrane concentrate; Ozone; Textile wastewater

1. Introduction

Textile industry is one of the most important industries in Turkey. In Turkey, textile industry has shown a continuous, huge development over the years. The textile sector is Turkey's largest manufacturing industry and the largest export sector, and also has a very important position in the world. Turkey's textile industry remains important to the economy. Turkey ranks sixth in the world's exports of clothing, with 3.5% of the total global apparel trade, and the second largest supplier to the European Union, after China [1].

According to the Turkish Statistical Institute reports for the year 2008, within the whole Turkish manufacturing sector, textile industry is responsible for 15% of water consumption, which makes it the second largest industrial water consumer. In 2008, textile industry consumed 191.5 million m^3 of water [2]. Textile processes such as dyeing, bleaching, and finishing generally consume high quantity of water and produce large volumes of wastewater. For examples, nearly 40–250 and 2.5–125 m^3/ton product water was consumed in dying and bleaching process, respectively [3]. Washing and rinsing processes also contribute to textile wastewater generation. Textile wastewater is characterized mainly by strong color and high concentrations of organic and inorganic pollutants [4–6], and may cause

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serious environmental problems if it is discharged without proper treatment. Physical, chemical, and biological methods can be used to treat textile wastewater. Conventional treatment processes such as coagulation, flocculation, aerobic, and anaerobic treatment have been commonly used for the removal of pollutants from the textile wastewater [5,7]. However, these treatment processes usually do not produce high-quality effluent for discharge or reuse purposes [8]. Following conventional treatment, advanced treatment methods such as membrane process are required for the treatment of textile wastewater to meet discharge limits and reuse in industry [9–11]. During the membrane treatment, two streams are generated. The effluent stream is discharged or reused, while the concentrate stream includes highly intensive pollutants, which should be treated before disposing. Due to the increase in environmental awareness and the new restrictions in regulations, treatment of membrane concentrate has recently gained increasing attention [12,13].

Because of the difficulty of concentrate stream treatment and fouling problem in membrane process, pretreatment process including ozonation, biological treatment, or reverse osmosis is needed. A major limitation in membrane filtration of wastewater effluent during wastewater reclamation/reuse is significant reduction in permeate flux caused by membrane fouling. In the operation of a membrane system, membrane fouling is dependent on many parameters, for example, membrane characteristics, source (feed) water characteristics, and hydraulic conditions of the system [14]. It is known that ozone is a strong oxidant which is able to form a more powerful, non-selective hydroxyl radical at high pH values. Because of this high oxidation potential, ozone can effectively break down the double bonds of dye chromophores as well as other functional groups such as the complex aromatic rings of dyes [15]. In the literature, the ozonation process has been suggested as a potential alternative for decolorization and improvement of biological degradation of textile effluents [12–16]. Ozone is an extremely strong oxidant ($E^\circ = 2.07$ V) and reacts rapidly with most of the organic compounds either directly or via radicals formed in a reaction chain as OH radicals [12]. Numerous studies have been carried out by nanofiltration (NF) membrane to treat textile wastewater. For example, Gozálvez-Zafrilla et al. [17] conducted studies on biologically treated wastewater from the textile using NF90, NF200, and NF270 membranes. They found that textile wastewater was effectively treated with these types of NF membranes [17]. Similarly, Alcaina-Miranda et al. [18] studied treated textile wastewater using NF270 and NF Duraslick. The authors reported that NF was a success method to treat textile wastewater [18].

However, very few studies have been performed for the treatment of membrane concentrate [9]. In this study, textile wastewater from a cotton dyeing mill was treated by NF270 membrane. The concentrate from NF270 membrane was further treated by the combination of ozonation and anaerobic degradation. Firstly, the effect of ozonation conditions on the distribution of organic contents of NF270 concentrate was investigated and optimized. Then, the performance of anaerobic degradation of ozonated concentrate was evaluated on the removal of organic pollutants.

2. Materials and methods

2.1. Wastewater

Wastewater samples were taken from a cotton dyeing textile mill in Istanbul, Turkey. On the basis of waste and wastewater generation, the textile mills can be classified into two main groups: first one, dry processing mills and second one, wet processing mills. In the dry processing mills, mainly solid waste is generated due to the rejection of cotton. In the other group, desizing, scouring, bleaching, mercerizing, dyeing, printing, and finishing are the main processes [19]. The most polluted processes in the mill are bleaching and dyeing. Thus, bleaching and dyeing wastewaters are segregated from others such as washing, rinsing, etc. The characteristics of bleaching and dyeing wastewaters are shown in Table 1. As shown in Table 1, bleaching wastewater and dyeing wastewater can be characterized by highly polluted industrial discharges in terms of pollutant concentrations (i.e. SO_4^{2-}). The ratio of $COD/(SO_4^{2-})$ should be over 2 to produce methane [20]. For this reason, the optimum mixture was predetermined according to the specific proportions of bleaching (80%) and dyeing wastewaters (20%), and biochemical methane potentials of the tested mixtures. The characteristics of mixed wastewater are also shown in Table 1. All samples were kept at 4°C in a refrigerated room prior to any analysis.

2.2. Experimental setup

The present advanced oxidation treatment method consisted of a 5-μm cartridge filter, a ultrafiltration membrane (UP150) with a pore size of 0.04 μm (or 150 kDa), and a NF membrane (NF270) with an average pore size of 0.80 nm. UP150 (Microdyn-Nadir GmbH, Wiesbaden, Germany) and NF270 (Dow Film Tech, Minneapolis, MN) membranes were operated at constant 2.5 and

Table 1
Characterization of textile wastewater

Parameter	Unit	Bleaching wastewater	Dyeing wastewater	Mixed wastewater	NF270 concentrate
Conductivity	mS/cm	8.80–10.52	5.79–10.37	8.98–10.52	13.72
pH	–	8.80–10.52	8.77–10.81	8.79–10.53	8.80–10.5
DCOD	mg/L	1,970–2,877	700–1,155	1,750–2,530	3,000–4,300
BOD_5	mg/L	120–888	75–203	110–740	345- 2,303
SO_4^{2-}	mg/L	61–301	1,077–1,490	265–425	395–580
Suspended Solids	mg/L	2,222–5,180	989–5,986	2,188–4,218	6,618–12,200

5.0 bar transmembrane pressures (TMP), respectively. The main characteristics of NF270 concentrate are shown in Table 1.

Experimental scheme of ozonation and anaerobic treatment is depicted in Fig. 1. Ozone setup consisted of ozonator generator (Sander Laboratory Ozonizer 300.5), a reaction column having 20 cm diameter with 102 cm height, and 2% potassium iodide (KI) bottles. The height of the liquid inside the column was kept at 50 cm. Dried air was supplied to the ozonator and a needle valve was placed before the column to control the dried air-flow rate. Excess ozone was captured in a 2% potassium iodide (KI) bottle.

The fermentor system (Electrolab) consisted of a bioreactor, a control panel, and a cooling system (Fig. 2). The bioreactor had a 6-L total capacity and a

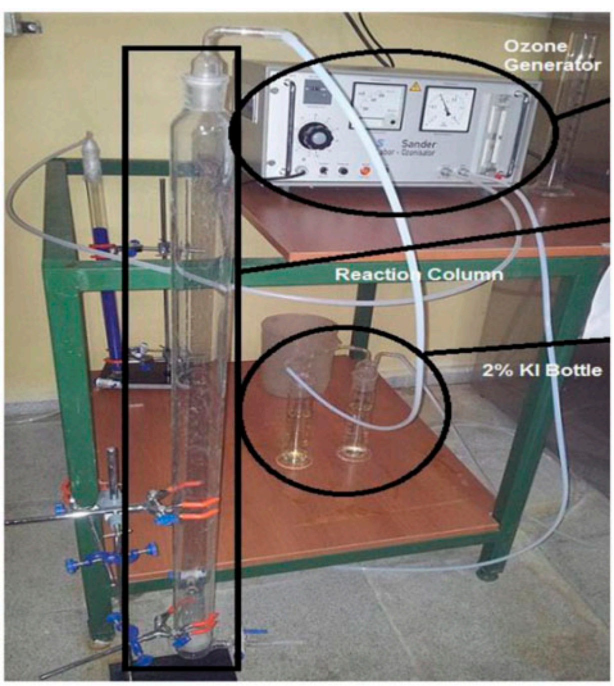

Fig. 1. Photograph of the ozone setup.

Fig. 2. Photograph of the anaerobic fermenter.

5-L working volume. It was inoculated with 500 mL of actively digesting granular sludge obtained from an ongoing mesophilic anaerobic treatment plant treating paper-cardboard wastewater. Prior to seeding, total solids (TS) content of the granular sludge was determined about 326.6 g/L. The volatile solids (VS) content of the sludge was found to be 36% of TS. During the anaerobic treatment, pH was automatically adjusted to 7.0 by the gradual addition of NaOH or H_3PO_4 reagents (Merck Chemical Corp.). The fermentor system was operated in continuously fed mode at mesophilic conditions, and the temperature was controlled at 37˚C. Moreover, oxidation and reduction potential (ORP) value was also automatically monitored and continuously controlled during the experimental period. The above parameters were kept automatically monitored by using specific digital ion analysis probes (Fig. 3).

Fig. 3. Photograph of pH, ORP, and temperature probes connected to the fermentor system.

2.3. Analytical procedure

Dissolved chemical oxygen demand (DCOD) was measured after samples were passed from 0.22-μm filter. DCOD was analyzed by closed reflux colorimetric method according to Standard Method (SM) number of 5220D [21]. Five-day biochemical oxygen demand (BOD_5) was determined by SM-5210B method [21]. Particulate and dissolved organic content of organic matter were defined using 0.05-μm (MP005) pore-sized membrane. SO_4^{2-} was measured using a double-beam UV–vis spectrophotometer (Shimadzu UV-1800) with 1 nm of resolution in accordance with SM 4500E [21]. pH and conductivity were analyzed using a multimeter (Thermo Orion 5 star). The amount of feed and off-gas ozone collected in the 2% KI bottles were determined by the iodometric titration procedure (SM 420). Deionized water used in the experiments was supplied from a purification system (Meck Millipore Direct-Q 3, 5, 8 Ultrapure Water Systems). Stability of the treatment process and components of wastewater samples were monitored in Environmental Engineering Laboratory at Yildiz Technical University in Istanbul, Turkey.

3. Results and discussion

3.1. Ozonation

Ozonation was optimized by increasing the applied ozone dose from 109 to 250 mg/(L.min), and the operation time from 5 to 15 min. As can be seen in Fig. 4, amounts of the generated ozone (mg) increased with the increasing of time from 5 to 15 min and air-flow rate from 20 to 50 L/min.

Diavalent ions and organic matter with molecular weight of >400 Da can be removed by NF270 membrane. Forty-seven percent COD of mixed textile wastewater was lower than 100 Da [22]. In this study, COD concentration increased nearly by 41%. Changes in parameters of NF270 membrane concentrate at different ozonation conditions are given in Table 2. The results indicated that increasing the air-flow rate over time did not increase the applied ozone dose expressed in mg/(L.min) accordingly. DCOD decreased from 3,425 to 2,000 mg/L, while BOD_5 increased from 300 to 932 mg/L with an applied ozone dose of 130 mg/(Lmin). The increase in BOD_5 showed that the ozonation enhanced the biodegradability of the concentrate by converting the non-biodegradable organics to biodegradable forms. Similar results have been reported during the ozonation of different waste streams [13,23–26]. The experimental results showed that the amount of ozone leaving the reactor was found to be higher than the amount of ozone used in the reactor with an ozonation time of more than 10 min. Thus, the optimum ozonation time was judged to be 10 min for the present case. Moreover, the value of the dry air-flow rate used for ozone generation was determined to be lower than 30 L dry air/h due to excessive foam formation in the ozonation column. Considering the above-mentioned facts, the highest increase in BOD_5 was obtained with the air-flow rate of 20 L air/h at 10 min without any operating problem.

3.2. Anaerobic treatment

The ratio of COD/BOD_5 should be lower than 2 to use aerobic biological treatment process. As seen in

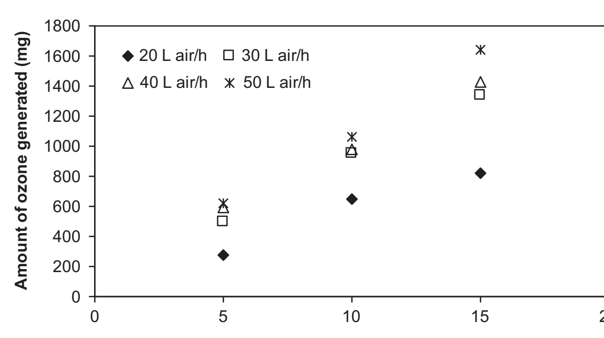

Fig. 4. The amount of ozone generated at different ozone dose and reaction time (volume of wastewater sample = 500 mL).

Table 2
The variations of pollutant parameters after ozonation

Wastewater parameters	Unit	WW[a]	Applied ozone dose, mg/(Lmin) 112	130	109	198	190	178	238	196	191	250	213	218
	Production time, min		5	10	15	5	10	15	5	10	15	5	10	15
Conductivity	ms/cm	8.98	8.9	8.9	9.0	8.7	8.6	8.9	9.1	9.1	9.0	8.7	8.6	9.0
pH	–	8.44	8.3	8.1	8.3	8.2	8.2	7.8	7.5	7.4	7.4	7.5	7.2	7.1
DCOD	mg/L	3,425	3,200	3,125	2,800	3,100	2,950	2,575	2,700	2,300	2,000	2,675	2,400	2,175
BOD_5	mg/L	300	868	932	748	870	819	846	820	816	944	700	814	800

[a]Raw wastewater.

Table 1, the ratio is generally higher than 2 and aerobic treatment may not be suitable for the treatment of the NF concentrate. Thus, anaerobic fermenter was used to remove organic matter from ozonated membrane concentrate.

Hydraulic retention time in the anaerobic fermenter was kept at 10 d. pH, ORP, and temperature were automatically controlled by a control panel. pH and temperature were adjusted to 7.0 and 37˚C, respectively. The adjustment of pH was automatically performed by the use of 3 N NaOH and 5 N H_3PO_4. At the first stage, nitrogen gas was purged to ensure anaerobic conditions in the reactor. ORP was −350 mV at the initial stage and decreased to −400 mV during the following bioreactor operation.

The performance of anaerobic fermenter was evaluated by monitoring the DCOD, BOD_5, and SO_4^{2-}. At the initial stage, DCOD removal efficiency was around 40%, while it increased to 76% on day 9. During the rest of the monitoring period, DCOD removal efficiencies fluctuated between 37% and 84%, with an average value of 64 (±9.7)%. The average DCOD removal efficiency (39%) at the initial stage (days 1–8) increased about two folds on day 9. According to the experimental period (days 10–50) performed after the observation of the first peak value (76%), the increase in the initial stage DCOD removal efficiency was determined to be about 1.6 folds (Fig. 5).

Change in BOD_5 had a similar pattern as DCOD. Removal efficiency of BOD_5 was low at the initial stage and changed between 12 and 31%. The efficiency increased after day 10 and reached 90% on day 16. Then, BOD_5 removal efficiencies varied between 50 and 89%, with an average value of 72 (±13)%. The results showed that the average BOD_5 removal efficiency (28%) at the initial stage (days 1–14) increased about 3.2 folds on day 16. On the basis of the analyses conducted on days 18–50, the increase in the initial stage BOD_5 removal efficiency was determined to be about 2.6 folds (Fig. 6).

The removal efficiencies of SO_4^{2-} were around 40% at the initial stage, while the highest efficiency was 84% on day 13 and varied between 54 and 83% in the following days, with an average value of 75 (±6.9)%. During the operational period, the results indicated that the average SO_4^{2-} removal efficiency (41%) at the initial stage (days 1–12) increased about 2.1 folds on day 13. Based on the experiments conducted on days 14–50, the increase in the initial stage ${SO_4}^{2-}$ removal efficiency was determined to be about 1.8 folds (Fig. 7).

During the anaerobic treatment, products of acidification phase can be used by both methanogenic and sulfate-reducing bacteria. Typical equations for the sulfate reduction under anaerobic conditions are given below:

$$SO_4^{2-} + CH_3COOH + 2H^+ \rightarrow HS^- + 2HCO_3^- + 3H^+ \quad (1)$$

$$2SO_4^{2-} + 19H^+ + 16e^- \rightarrow H_2S + HS^- + 8H_2O \quad (2)$$

According to the equations, reduction of 1 mg SO_4^{2-} consumes 0.63 mg acetic acid or 0.667 mg COD. As seen in Table 1, DCOD concentration was between 3,000 and 4,300 mg/L and approximately 2,520 mg/L of this DCOD was removed. This indicated that a small quantity of DCOD corresponding to 310 mg COD was used through SO_4^{2-} as an electron acceptor. The rest of DCOD was removed by the other anaerobic bacteria. It is observed that the anaerobic system may be used to remove both non-biodegradable part of organics and sulfate.

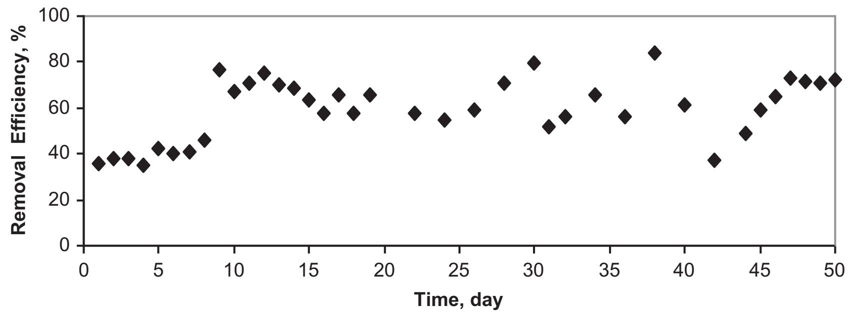

Fig. 5. Removal efficiency of DCOD.

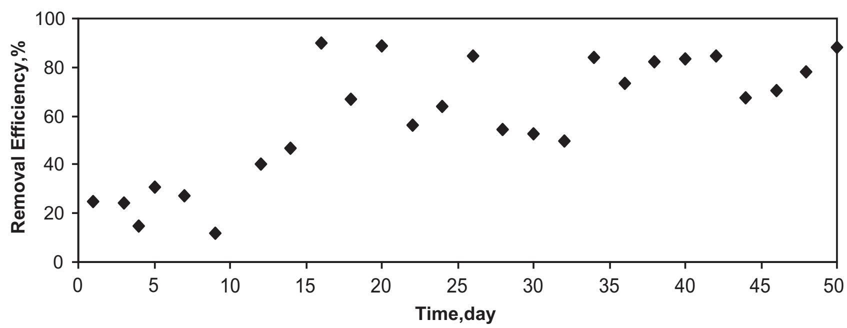

Fig. 6. Removal efficiency of BOD_5.

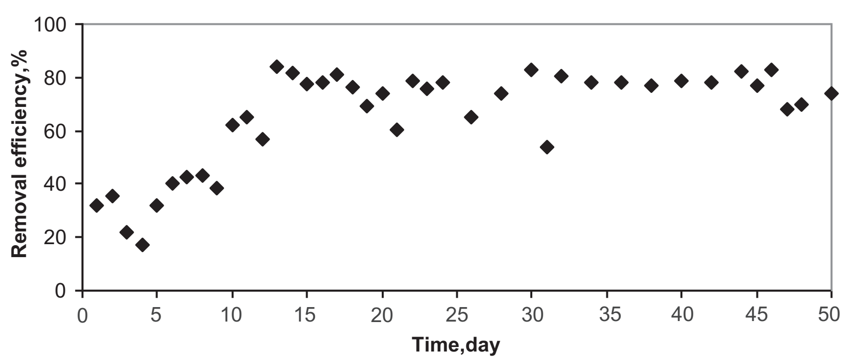

Fig. 7. Removal efficiency of SO_4^{2-}.

4. Conclusions

This work deals with the anaerobic treatability of ozonated membrane concentrate from textile wastewater. Biodegradability of the membrane concentrate was almost three times increased by the ozonation. Removal efficiencies of DCOD, BOD_5, and SO_4^{2-} were lower than 50% in the first 10 days, while others increased to over 80%. These results indicated that the membrane concentrate from textile wastewater can be effectively treated with the combination of ozonation and anaerobic treatment. This study proved that ozonation could be performed before the biological treatment and NF membranes could be successfully used to treat textile wastewater. Finally, considering the remarkable performance of the proposed treatment method, it is believed that comparison of the effects of ozone and NF membranes on the treatment of different wastewater types might be worthy of investigation by future studies.

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