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COMPARISON OF TREATMENT EFFICIENCY AND MOLECULAR WEIGHT DISTRIBUTION OF MEMBRANE CONCENTRATE FROM TEXTILE WASTEWATER

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ABSTRACT

This study investigated the treatability and changes in molecular weight distributions (MWD) of membrane concentrate. Nanofiltration (NF) concentrate from textile wastewater was subjected sole anaerobic treatment (R1) and pre-ozonation (R2) plus anaerobic treatment. BOD_5, COD and TOC, color, sulphate and specific ultraviolet absorbtion at 254 nm ($SUVA_{254}$) were analysed. Pre-ozonation improved the biodegradability of the membrane concentrate. The low molecular weight (LMW) organics was an important reason for the overall biodegradability enhancement of the membrane concentrate. Color was caused mainly by matters with higher than MWD of 10 kDa and 80% of HMW organics were removed during anaerobic treatment. Nearly half of sulfate was lower than 0.5 kDa which indicates that sulfate hardly treated by NF membranes. $SUVA_{254}$ values after anaerobic treatment were generally higher than 2 l $mg^{-1}m^{-1}$ which indicates that membrane concentrate was in hydrophobic characteristics.

Keywords: anaerobic treatment, molecular weight distribution, nanofiltration concentrate, ozonation, textile industry

1. Introduction

Textile production represents an important industrial activitiy in Turkey and other developing countries. Wastewater from textile industry is characterized by intensive color and high concentrations of organic and inorganic pollutants (Sahinkaya *et al.,* 2008; Bes-Piá *et al.,* 2009). This may cause serious environmental problems if it is discharged without proper treatment. Various conventional treatment methods have been applied for the treatment of membrane concentrate from textile wastewater, however they are generally lack of effluent quality to meet discharge limits. On the other hand, advanced treatment methods such as membrane processes and ozone have been reported with higher treatment efficiencies for textile and other industrial wastewater (Shu *et al.*, 2005; Babursah *et al.,* 2006; Tahri *et al.,* 2012; Kurt *et al.,* 2012).

Nanofiltration (NF) membranes have been widely applied for the treatment of textile wastewater due to its capability of completely removal of organics and salts (Tahri *et al.*, 2012; Kurt *et al.*, 2012). During the NF treatment; membrane concentrate stream is generated with high concentration of pollutants (Badruzzaman *et al.,* 2009; Bes-Pia *et al.,* 2004). NF concentrate can be treated by the various treatment

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processes.Biological treatment technologies have been proven for the effectively degradation of organic pollutants at relatively low costs (Jarusutthirak and Amy, 2002; Yetilmezsoy, 2008) and can be used to treat NF concentrate. In particular, anaerobic treatment is an environmental friendly technology with its high treatment efficiency and rich energy content of biogas (Yetilmezsoy, 2008). Although textile industry has massive presence of organics, sulfate, and synthetic dyes, sulfate can be typically treated by biological anaerobic technologies. Also, Anaerobic biological processes are usually considered efficient and reliable due to several major advantages such as low sludge production and low energy requirement (Rasool and Lee, 2016; Rasool *et al.,* 2015). Although anaerobic treatment technologies are effective in removing of biodegradable organic compounds and suspendedsolids, they are unable to eliminate hardly refractoryorganic matters (Medeiros *et al.,* 2008). On the other hand, ozonation has been proven for the treatment of wastewater with high concentrations of pollutants and refractory organics (Kjeldsen *et al.,* 2002; Medeiros *et al.,* 2008). Advanced oxidation through ozonation can break the chemical structures of non-biodegradable organics. However, consumption of considerable amount of energy and chemicals during oxidation is the economic disadvantage of the process (Chen and Liu, 2006). Therefore, integration ofozonationintoanaerobic treatment may provide acost effective alternativefor the removal of organic pollutants (Medeiros *et al.,* 2008; Tahri *et al.,* 2012; Kurt *et al.,* 2012).

Application of treatment process changes the molecular weight (MW) of pollutants. Moreover, molecular weight distribution (MWD) analysis of pollutantscould providea deeply understanding of the performance of the treatment systems. Researcher have performed studies to determine the relationship between MWD and treatment performance. The results from biological treatment studies have indicated that low fractionated organics can be effectively removed by microorganisms (Kjeldsen *et al.,* 2002; Chen and Liu, 2006). Zhao *et al.,* (2012) and Campagna *et al.,* (2013), reported higher organic removal efficiency when the materials had a molecular weight less than 1 kDa, while Dulekgurgen *et al.,* (2006), obtained the highest treatment efficiency with less than 2 nm. On the other hand, high-molecular-organics could be effectively removed by chemical and physical processes. It has been proven that flocculation plus sedimentation is an effective option for the treatment of pollutants with molecular weights higher than 50 µm. For instance, Chian, (1977), applied chemical precipitationand obtained elevated removal efficiencies for high-molecular-weight particles (>5 kDa). Similarly, Uner *et al.,* (2006), studied the chemical treatability of textile finishing wastewater and reported 87% COD removal efficiency for particles with highmolecularweight (0.45 µm-100 kDa) compared to 57% removal efficiency for particles with lower MWs (<1 kDa). Furthermore, conventional filtration methods provided the removal of pollutants with MWs higher than 3 µm (Malpei *et al.,* 1997). In addition to organics, MWD analyses have been used for the evaluation of other pollution parameters. Ged and Boyer (2013) evaluated the MWD of phosphorus fractions of aquatic dissolved organic matter. The study conducted by Qian *et al.* (2013) revealed that colour is formed by organic matterswith MWs higher than 1 kDa. Researchers obtained higher colour removal by applying activated carbon adsorption/ozone process on molecules with a rangeof 1–10 kDa (Campagna *et al.*, 2013) Using MWD analysis, Zhao *et al.* (2012) applied NF and obtained 85% removal efficiency ofUV254 by >500 Da. These results indicates that molecular weight distribution (MWD) analysis has been widely used to evaluate deeply the treatment performance and determine the alternative methods. For example, if 90% of the COD is greater than 0.45 µm it means settling can be used on the other hand if MWD is less than 0,1 kDa settling is not proper treatment method for this type of wastewater.

Molecular weight distribution (MWD) analysis has gained increasing popularity in recent years since it contributes comprehensive evaluation on the treatment performance of the chose suitable processes. In the literature, researchers pointed that MW and particle size distributions, taking advantages of treatment technologies. The aim of the present study is to monitor the changes in MWD of pollutants in membrane concentrate from textile wastewater during ozonation and anaerobic treatment. Furthermore, this study is the new and rare study, which is about MWD of membrane concentrate wastewaters. Especially, it is the only study that has been applied on both ozonation and anaerobic treatment for the investigated MWD analysis.

2. Experimental

2.1. Pre-ozonation and anaerobic treatment process

Wastewater samples were taken from a cotton dyeing mill in Istanbul, Turkey. In the mill, wastewaters from bleaching and dyeing processes are mixed in an equalization tank. Membrane concentrate was obtained by sequential filtration of mixed wastewater through the 5 µm cartridge filter plus ultrafiltration (UF) and nanofiltration (NF) membranes. 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 NF270-2540 membrane (Cakmakci and Ozyaka, 2013). UP150 (Microdyn-Nadir GmbH, Wiesbaden, Germany) and NF membranes (Dow Film Tech, Minneapolis, MN) were operated at constant 2.5 and 5.0 bar transmembrane pressures (TMP), respectively. The characteristics of mixed wastewater and membrane concentrate were as shown in Table 1. Stability of the treatment process and components of wastewater samples were monitored at pilot scale in Environmental Engineering Laboratory at Yildiz Technical University in Istanbul, Turkey.

Table 1. Characterization of mixed textile wastewater and membrane concentrate.

Consitituent	Mixed wastewater	Concentrate
Color	NM	4.06 (436 nm)
		3.0 (525 nm)
		2.3 (620 nm)
Conductivity (mS cm^{-1})	18.98-38.52	36.7
UV_{254} (cm^{-1})	NM	12
pH	8.8-10.5	8.6
BOD (mg l^{-1})	110-740	640
COD (mg l^{-1})	1750-2530	3100
SO_4^{2-} (mg l^{-1})	265-3425	3620
NH_4^+-N (mg l^{-1})	NM	110
TOC (mg l^{-1})	NM	1086

NM: Not measured.

Experimental schemes of pre-ozonation and anaerobic treatment were as shown in Figure 1. Ozone set-up 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.

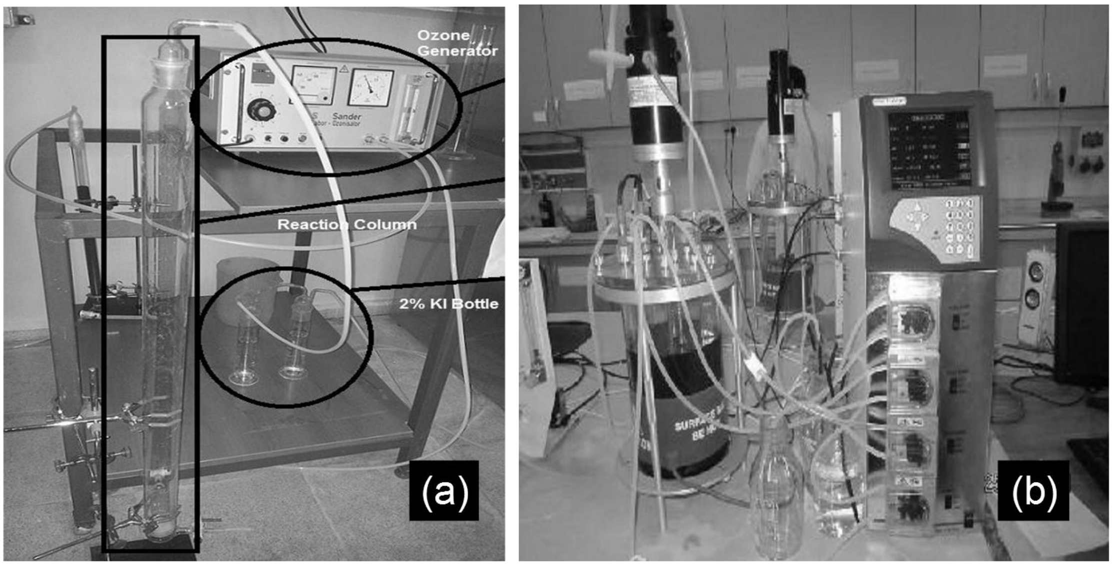


Figure 1. Flow diagram of sequential filtration

Dry air and oxygen dose capacities of the ozonator were 2 g h^{-1} and 4 g h^{-1}, respectively. 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 2% potassium iodide (KI) bottle.

Anaerobic treatment studies were performed by feeding the reactors with raw an pre-ozonated membrane concentrates. Reactor 1 was fed by raw membrane concentrate while Reactor 2 was fed through pre-ozonated membrane concentrate. The reactor system (Electrolab) consisted of a bioreactor, control panel and cooling system. The bioreactor had a 6 L total capacity and a 5 l of working volume. Reactors were continuously operated at 37 °C. Oxidation and reduction potential (ORP) value was automatically monitored along with pH during the experimental period. pH was kept constant around 6.9 by adding 3 N NaOH and 5 N H_3PO_4 solutions. Reactors were continuously mixed at 220 rpm and operated for nearly one year at a constant hydraulic retention time (HRT) of 10 days. Reactors were seeded by anaerobic sludge granules from an anaerobic treatment plant treating food industry wastewater. Total solids and the volatile suspended solids were analyzed 72.9 g l^{-1} and 57.0 g l^{-1}, respectively.

2.2. Molecular weight distribution analysis

Membrane separation method was used for molecular weight distribution (MWD) analysis. Separation experiments were performed by a stirred membrane cell (Amicon, Model 8400) with the diameter of 76 mm and effective membrane area of 41.8 cm^2. The membrane separation cell consisted of a methyl-methacrylate glass holder with total volume of 350 ml. Membrane concentrate samples were sequentially filtered through a MF and UF as shown in Figure 2. The pore size of MF membrane (Microdyn Nadir) was 0.05 µm while UF nominal molecular weight limits (NMWL) of UF membranes were in the range of 0.1 to 100 kDa (PALL and Spectrum Inc.). The characteristics of membranes can be seen Table 2.

Table 2. The characteristics of membranes

Membrane Material	Operating temperature (°C)	pH range	Nominal pore size	Nominal Molecular Weight (NMWL) (kDa)
PES	0-95	1-11	0.05 µm	-
PES	0-40	1-14	7.9 nm	100
PES	0-40	1-14	6.3 nm	50
PES	0-40	1-14	3.5 nm	10
PES	0-40	1-14	2 nm	1
CE	0-37	2-9	1.6 nm	0.5

PES: Polyethersulfone, CE: Cellulose Ester.

All membranes were soaked with deionized water to remove glycerin before filtration experiments. The sequential filtration experiments were performed until obtaining final permeate volume of 150 ml. During the filtration, the cell was pressurized with N_2 gas. Microfiltration was performed under 1 bar while operating pressures in UF filtration analyses were 2 bars for the ranges of 100-1 kDa and 4 bars for 0.5 and 0.1 kDa.

2.3. Analyses

All samples were kept at 4°C in a refrigerated room prior to any analysis. All characterization analysis were performed by following the instructions in Standard Methods (APHA, 2005). The chemical oxygen demand (COD) was analyzed using a closed reflux colorimetric method according to the standard method (SM) number of 5220D. The total organic carbon (TOC) was measured using a TOC analyzer (IL 550 TOC-TN analyzer, Hach Lange) and a related method (SM-5310B). Conductivity was measured using Thermo Scientific Orion 5-Star.The biochemical oxygen demand (BOD_5) was determined using the SM-5210B method. Ammonia (NH_4^+-N) was measured with a preliminary distillation method (SM-4500-A) using a semi-automatic distillatory (Velp Scientifica model UDK 132). Sulfate (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. Sulfate ion is then precipitated in an acetic acid medium with barium chloride ($BaCl_2$) so as to form barium sulfate ($BaSO_4$) crystals of uniform size. Light absorbance of the $BaSO_4$ suspension is measured by a photometer, and the SO_4^{-2} concentration is determined by comparison of the reading with a standard curve. UV_{254} and color were measured by using a double-beam UV-VIS spectrophotometer from Shimadzu (UV-1800) with a resolution of 1 nm. Specific ultraviolet absorption (SUVA) values were calculated by dividing UV_{254} to DOC to characterize the hydrophobic/hydrophilic degree of organics.

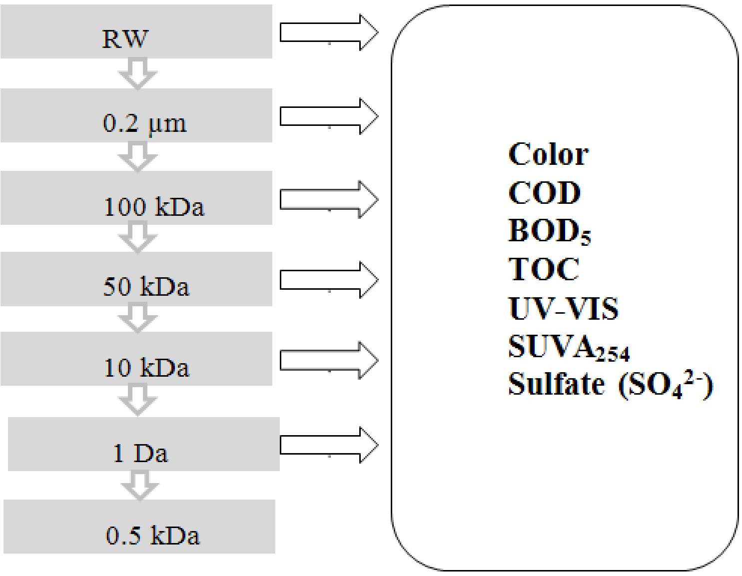


Figure 2. (a) Photograph of the ozone set-up, (b) Photograph of the anaerobic reactor

3. Results and discussions

3.1. Optimization of pre-ozonation

Optimum pre-ozonation conditions were determined by changing the air flow rates and ozonation duration. Optimization studies were performed at air flowrates of 20 L h^{-1}, 30 L $h^{-1}$and 40 L $h^{-1}$of air flow rates for 5 minutes, 10 minutes and 15 minutes. The maximum BOD_5 values (1250 mg l^{-1}) was obtained by 30 L air/h at 10 min. and Reactor 2 was fed with the this pre-ozonated membrane concentrate. Although the air flow and duration of ozonation were constant through the studies, effluent values fluctuated due to the changes in the characteristics of membrane concentrate wastewater. Although conductivity remained constant, pH decreased at the 8.2 during ozonation process. COD concentrations (3010 mg l^{-1}) decreased due to the mineralization of organic matters. Changes in parameters at different ozonation conditions are given in Table 3.

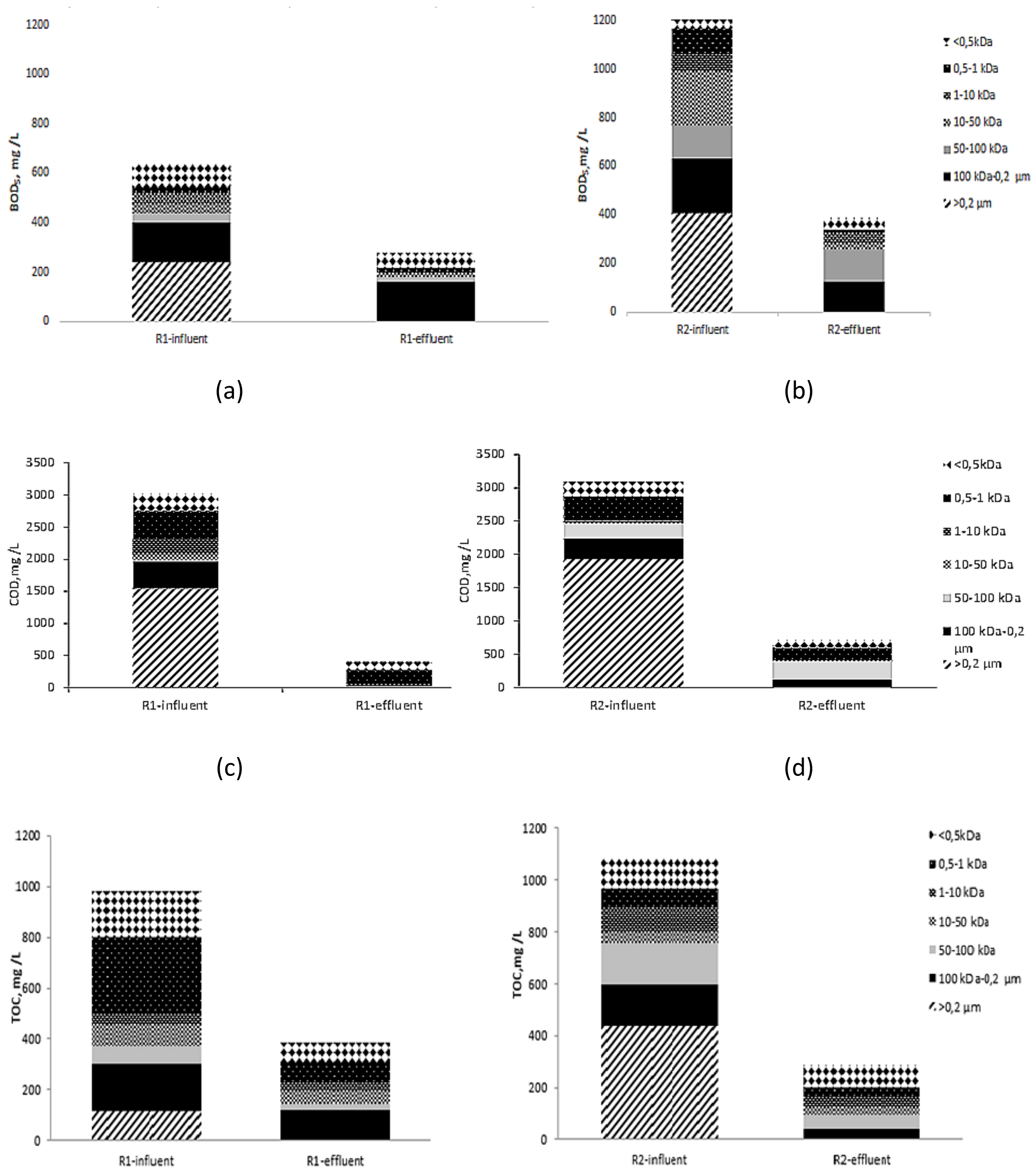
Table 3. The variations of pollutant parameters after ozonation

Ozone flow rate, l h^{-1}			20	20	20	30	30	30	40	40	40
Ozonation time, min			5	10	15	5	10	15	5	10	15
Wastewater parameters	Conductivity	mS cm^{-1}	8.98	8.9	8.9	9	8.7	8.6	8.9	9.1	9.1
	pH	-	8.44	8.3	8.1	8.3	8.2	8.2	7.8	7.5	7.4
	COD	mg l^{-1}	3425	3200	3125	2800	3010	2950	2575	2700	2300
	BOD_5	mg l^{-1}	300	868	932	748	1250	819	846	1000	816

3.2. Organic matter removal

Organic matter concentrations of raw membrane concentrate fed to Reactor 1 were 3100 mg COD l^{-1} and 640 mg BOD_5 l^{-1}, respectively. On the other hand, COD and BOD_5 values of pre-ozonated membrane concentrate were 3010 mg l^{-1} and 1250 mg l^{-1}, respectively. Removal efficiencies and MWDs of COD and

BOD_5 in both reactors were as shown in Figure 3a-3d. Influent BOD_5 values were 640 mg l^{-1} in Reactor 1 and 1250 mg l^{-1} in Reactor 2 which indicates that pre-ozonation increased biodegradable organics about 95%. After anaerobic treatment total BOD_5 removals were 57% in Reactor 1 and 70% in Reactor 2. Similarly, pre-ozonation slightly enhanced COD treatment efficiency which was 81% in Reactor 1 and 86% in Reactor 2, respectively.



(a) (b)

(c) (d)

(e) (f)

Figure 3. MW distributions of BOD_5 (a) R1 (b) R2, COD (c) R1 (d) R2, and TOC (e) R1 (f) R2

Comparison of BOD_5 fractions in the influents of reactors indicates that organics with MW of ≤ 0.5 kDa was 58% higher in the Reactor 1 influent while organics with MW of ≥0.2 µm was 18% higher in influent of Reactor 1. Similar molecular transformations with increase in biodegradability were reported by other researchers (Bijan and Mohseni, 2005; Medeiros *et al.,* 2008). In Reactor 1, COD and BOD_5 with MW of ≥0.2 µm were 51% and 38% at influent and they increased to 74% and 57%, respectively at the effluent.

At the same time the amount of the same fractions of BOD_5 increased from 18% to 32% in Reactor 2. Significant increase in the amount of higher BOD_5 fractions in both reactors was associated with bioaccumulation of small organic matters. During the anaerobic treatment, BOD_5 with MW less than 0.5 kDa increased from 16% to 21% in Reactor 1 and increased from 7% to 12% in Reactor 2.

On the other hand, the MWD of COD in both reactors indicated that considerable amount of higher molecular organics were converted to lower fractions during anaerobic degradation. Zhao *et al.*, (2012), reported the similar results and they were correlated this transformation with partial degradation (Zhao *et al.,* 2012). The amounts of BOD_5 within the range of 50-100 kDa and 10-50 kDa remained stable in Reactor 1 whereas former fraction increased from 11% to 35% and the later fraction decreased from 18% to 8% in Reactor 2. These results indicated that some of smaller biodegradable organics were converted to higher fractions during anaerobic treatment in Reactor 2. On the other hand, organics with MW of 0.5-1 kDa was 6% in the influentand all was completely degraded in the Reactor 1. It is noted that ozonation breaks down the structure of high MW organic matter into biodegradable compounds. At the same time, ozone also contributes to the conversion of certain organic materials to end products (Ulson de Souza *et al.,* 2010). For this reason, the changes in the COD and BOD after ozonation are expected to be different. Likewise, the obtained results in this study are different from each other. Baban *et al.*, (2003), also concluded that ozonation was found to have only slight effect on COD removal.

The BOD_5/COD ratio is widely used to evaluate the biodegradability of waste and biological treatment is more appropriate when the ratio is higher than 0.3 (Edzwald and Tobiason, 1999; Campagna *et al.,* 2013). Effects of pre-ozonation and anaerobic treatment on the biodegradability of membrane concentrate were investigated in detail. Although biodegradability in raw membrane concentrate was very low in all fractions, BOD_5/COD ratio steadily increased with the decreasing of fractions size. Comparison of BOD_5/COD values indicates that pre-ozonated membrane concentrate has almost two times higher biodegradability than raw membrane concentrate. Pre-ozonation improved biodegradability of membrane concentrate significantly and BOD_5/COD ratio increased from 0.21 to 0.40. Higher biodegradability ratios suggest that pre-ozonated membrane concentrate could be effectively treated by anaerobic processes. Researchers reported similar enhancement effect of pre-ozonation for various concentrates (Chian, 1977; Bijan and Mohseni, 2005; Dulekgurgen *et al.*, 2006; Tehrani-Bagha *et al.,* 2010; Campagna *et al.,* 2013).

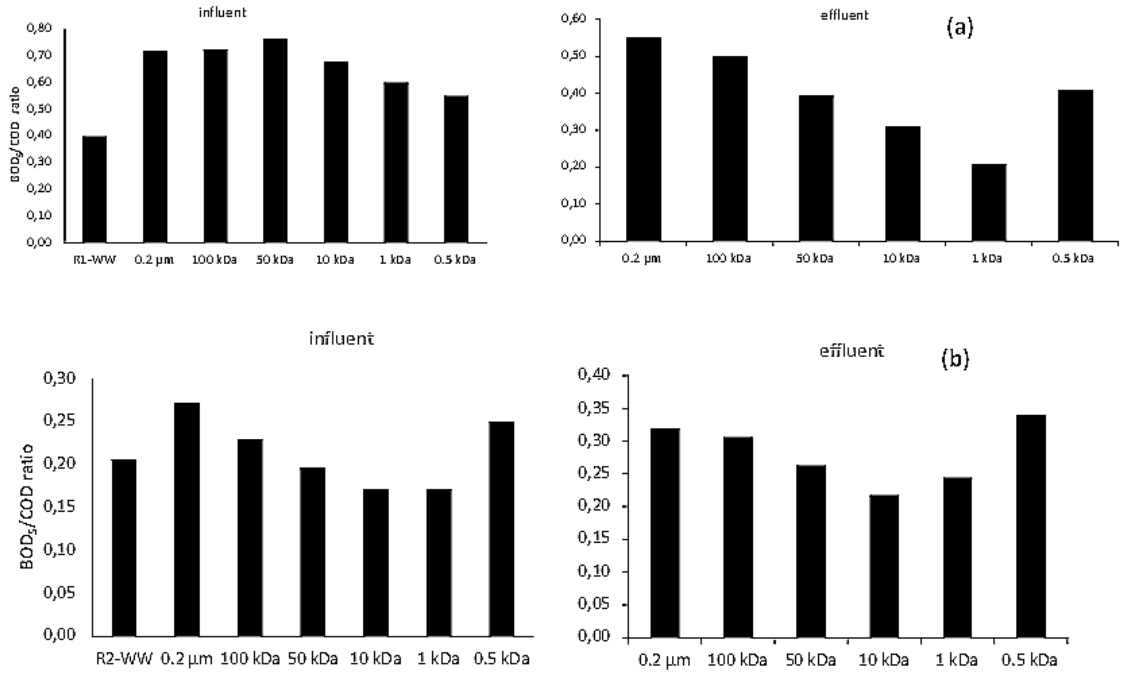


Figure 4. The ratio of BOD_5/COD (a) R1 (b) R2

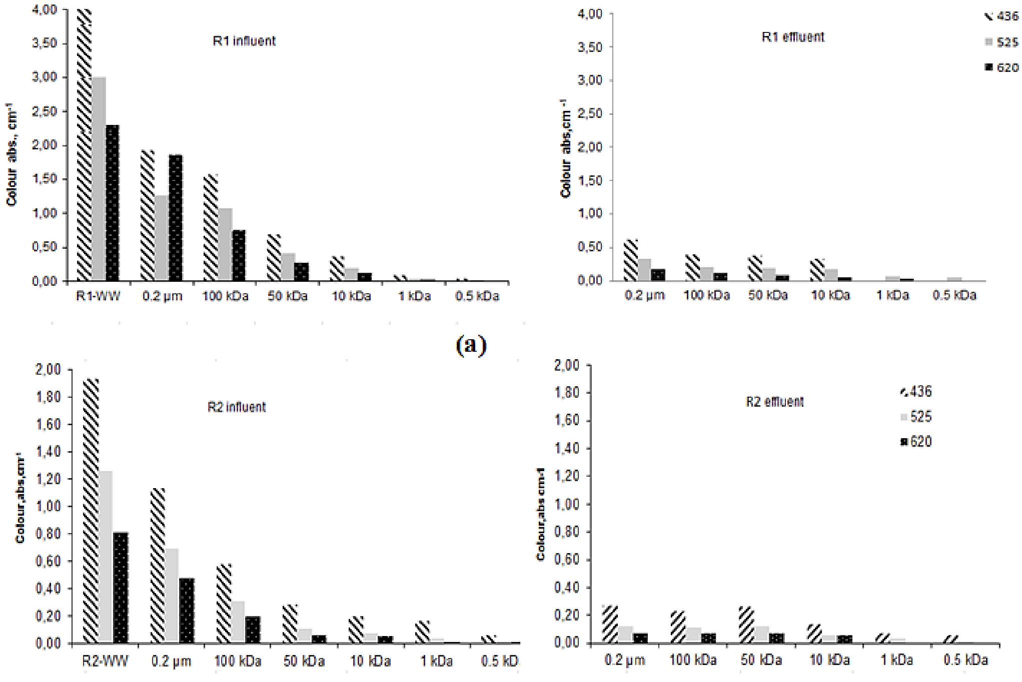
MWD analysis revealed controversial results in both reactors. BOD_5/COD ratios decreased from 0.76 to 0.39 at 50kDa, 0.68 to 0.31 at 10 kDa, 0.60 to 0.21 at 1 kDa, 0.55 to 0.41 at 0.5 kDa in Reactor 1 effluent (Figure 4). On the other hand, reverse relationship was observed between biodegradability and organic matter fractions in Reactor 2. BOD_5/COD ratio increased from 0.20 at 50 kDa, 0.17 at 10 kDa, 0.17 at 1 kDa and 0.25 at 0.5 kDa to 0.26, 0.22, 0.24 and 0.34, respectively. These values indicate that BOD_5/COD ratio steadily increased following anaerobic treatment due to the transformation of lower organics to higher fractions.

3.3. *Total organic carbon (TOC) removal*

MWD of TOC at influent and effluent of the reactors were shown as in Figure 3e and 3f. TOC removal efficiency was 64% in Reactor 1 while it was 73% in Reactor 2. Higher TOC removal in Reactor 2 was due to mineralization of organic compounds by pre-ozonation and conversion to CO_2. Similarly, Bijan *et al.* (2005) found that pre-ozonation enhanced TOC removal. Pre-ozonation also reacted with refractory compounds and converted them to biodegradable intermediates. Comparison of MWD in influent and effluent indicates that pre-ozonation removed the most of low molecular TOC while anaerobic treatment convertedhigher organics to lower fractions. TOC removal with MW of ≥2 µm was measured as 12% in the influent, and it was increased up to 31% in the effluent. This may be ascribed to the enhancement of higher molecular fractions during the anaerobic treatment. On the other hand, TOC removal with MW of ≥2 µm was determined to be about 40% in the raw membrane concentrate. Then it was decreased to 19% following pre-ozonation and anaerobic treatment. Similar effect of pre-ozonation on the transformation of TOC fractions was reported by other researchers (Bijan and Mohseni, 2005; Medeiros *et al.,* 2008; Tehrani-Bagha *et al.,* 2010). These results indicated that both sole anaerobic treatment and pre-ozonation plus anaerobic treatment converted lower materials into higher fractions.

3.4. *Color removal*

Color removal performances of pre-ozonation and anaerobic treatment were as shown in Figure 5. Color removal performances of two reactors were monitored by measuring at 436, 525 and 620 nm. Absorbance values at 436, 525 and 620 nm in the influent of Reactor 1 were 4.71, 3.93 and 2.84 cm^{-1} while those reduced to 1.23, 1.10 and 0.90 cm^{-1} in the effluent.



(a)

(b)

Figure 5. Color distribution of (a) R1 (b) R2

Comparison of the absorbance values at 436 nm in influent membrane concentrates clearly indicated pre-ozonation has significant effect on color removal. Similarly, absorbance values in Reactor 2 decreased from 1.93, 1.26 and 0.81 cm^{-1} to 0.55, 0.34 and 0.17 cm^{-1}, respectively. The changes in absorbance values indicated that color removal efficiencies were in the range of 68% to 74% in Reactor 1 and 72% to 79% in Reactor 2.

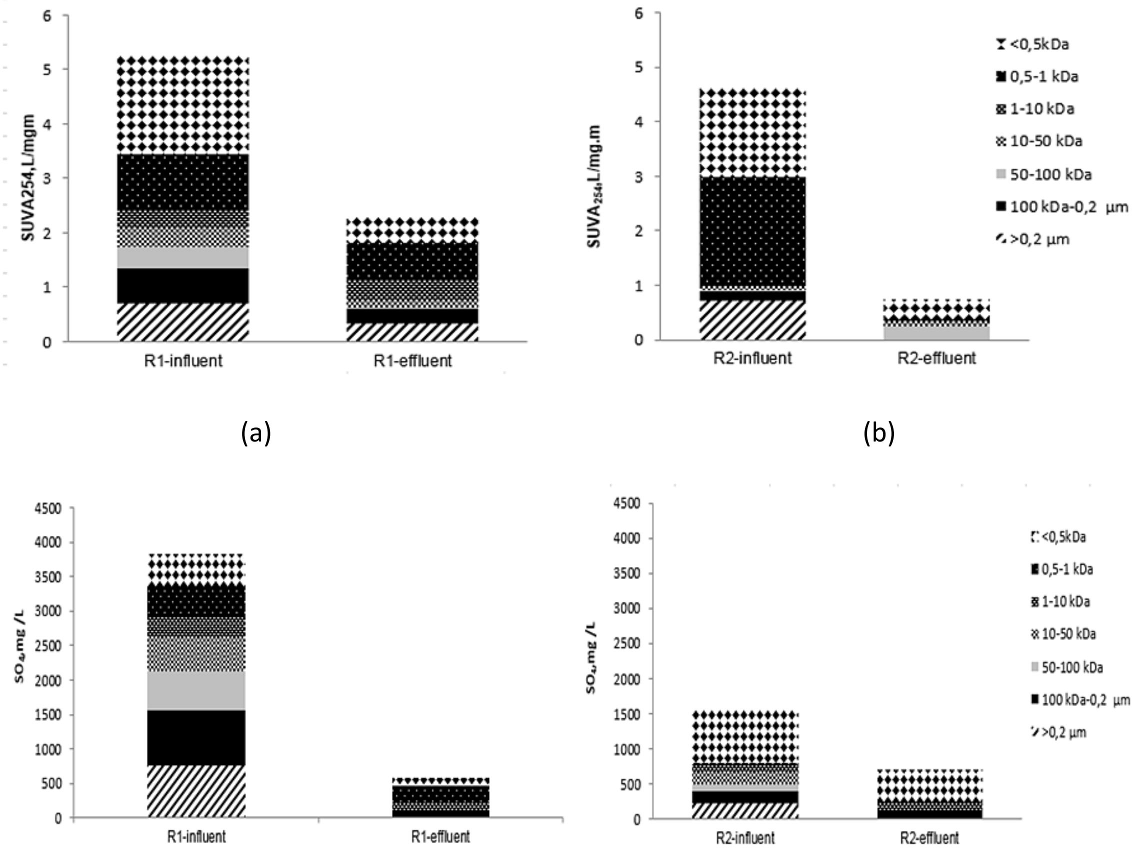
Transformation of organics during pre-ozonation and anaerobic treatment can be accurately monitored with MWD analysis. Percentages of color producing matters with MW of ≥0.2 µm increased from 14%, 24% and 19% at 436, 525 and 620 nm in influent of Reactor 1 to 50%, 70% and 80% in the effluent (Figure 5a). These significant changes during anaerobic treatment could be attributed due to the increase of higher molecular fractions by bio-coagulation of the smaller matters (Zhao *et al.,* 2012). Moreover, relative contributions of low molecular organics in color developmentconsiderably increased after anaerobic treatment. In contrast to Reactor 1, the contributions of matters withMW of ≥0.2 µm in color development decreased from 41%, 30% and 18% to 15%, 11% and 5% in Reactor 2 (Figure 7b). At the same time, color producing matters with MWof higher than 0.5 kDA at 436, 525 and 620 nm increased from 3.11%, 1.59% and 1.11% to 18.52%, 1.67% and 8.57%. Similar to Reactor 1, ratios of low molecular organics in color development in Reactor 2 increased. The increase in the contribution of low molecular organics could be associated with the partial degradation of large organics during anaerobic treatment.

3.5. Specific UV absorbance

Specific UV absorbance (SUVA) at 254 nm is related with the presence of aromatic organics (Dulekgurgen *et al.,* 2006). SUVA values ≥4 indicate that high MW organic matter is hydrophobic while SUVA<2 is the indicative of hydrophilic organics (Chian, 1977; Dulekgurgen *et al.,* 2006; Campagna *et al.,* 2013). Figure 6a and 6b shows the changes in SUVA values of reactors. SUVA removal efficiency was 57% in Reactor 1 while it was 84% in Reactor 2. SUVA with MW of higher than 0.2 µm was 13% in influent and it remained almost constant during anaerobic treatment. On the other hand, same SUVA fraction decreased from 16% in raw membrane concentrate to 1% after pre-ozonation plus anaerobic treatment in Reactor 2. The difference behaviors in both reactors indicate that hydrophobic organics were not treated during anaerobic treatment however pre-ozonationwas effective on the removal of hydrophobic organics. In Reactor 1, 34% of SUVA in influent was less than 0.5 kDa.In the influent and effluent of Reactor 2, 36% and 49% of SUVA values were less than 0.5 kDa while 13% and 1% of SUVA values were in the range of 100 kDa to 0.2 µm. According to these values, it can be concluded that SUVA was mostly composed of low molecular organics. Pre-ozonation has no significant effect on the MWD of SUVA, however, SUVA with low molecular organics increased after anaerobic treatment.

3.6. Sulfate (SO_4^{2-})

MWD of sulfate in the influent and effluent of reactors was as shown in Figure 6c and 6d. Total sulfate removal efficiencies were 55% in Reactor 1 and 62% in Reactor 2. Sulfate may be either in dissolved form or together with biomass. On the other hand, both sulfate and biomass with sulfate may be seperated by applying membrane separation. Since the molecular weight of sulfate in biomass may have high MW, they can be effectively removed by high-MW membranes. It was concluded that MW fractions ranging from 4.8 to 12.5 $\times 10^3$ Da showed wide variations in sulfate (Cifonell,1974). In another study, sulfate removal occurred in the anaerobic reactor, with efficiencies of 41% and 54%, However, sulfate removal must have predominantly occurred by reduction to sulfide, and followed by precipitation with metals under anaerobic conditions (Amaral *et al.,* 2014). Ratio of sulfate with MW ≥0.2 µm was 80% in influent of Reactor 1 and it decreased to 78% in effluent which shows that high molecular sulfate was removed slightly. On the other hand, sulfate with MW less than 0.5 kDa was 12%, and increased to 20% after anaerobic treatment. This increment was due to the conversion of higher molecular fractions into lower molecular through mineralization. In influent of Reactor 2, 14% of sulfate was higher than 0.2 µm and 49% was higher than 0.5 kDa. In general, half of sulfate was in low molecular fractions. 86% of sulfate in influent was less than 0.2 µm, and it decreased to 80% after anaerobic treatment. At the same time, sulfate <0.5 kDa was 49% in influent, and it increased to 66% after anaerobic treatment. Similar to other parameters, pre-ozonationand anaerobic treatment mineralized higher sulfate molecules and increased the lower fractions.



(a) (b)

(c) (d)

Figure 6. MW distributions of $SUVA_{254}$ (a) R1 (b) R2 and sulfate (c) R1 (d) R2

4. Conclusions

In the present study, molecular weight distribution (MWD) was analyzed during the treatment of raw and pre-ozonated membrane concentrate by anaerobic treatment. Pre-ozonation significantly improved the biodegradability (BOD_5/COD) of the concentrate. The difference between the COD values of the ozonated and non-ozonated concentrate was mainly the result of mineralization and increase in the oxidation state of organics during pre-ozonation.Increasing BOD_5, accompanied by decreasing COD, indicates that the biodegradability of the membrane concentrate improved. The production of LMW organics was an important reason for the overall biodegradability enhancement of the membrane concentrate. BOD_5 fractions for 50–100 kDa, 1–10 kDa and <0.5 kDa were 6, 6 and 16% in the influent and 7,7 and 21% in the effluent of Reactor 1. Similarly, 50–100 kDa, 1–0.10 kDa and <0.5 kDa were 11, 5 and 7% in the influent and 35, 10 and 12% in the effluent of Reactor 2. This means moleculer fractions were changed during the anaerobic treatment.

COD fractions for 50–100 kDa, 1–10 kDa and <0.5 kDa were 1, 8 and 8% in the influent and 3, 10 and 32% in the effluent of Reactor 1. Likewise, 50–100 kDa, 1–10 kDa and <0.5 kDa were 1, 7 and 7 % in the influent and 38, 13 and 15% in the effluent of Reactor 2. Color was caused mainly by matters with higher than MWD of higher 10 kDa and 80% of HMW organics were removed during anaerobic treatment. Most of TOC was composed of higher molecular materials and it can be effectively treated by membrane and coagulation. TOC fractions 50–100 kDa, 1–10 kDa and <0.5 kDa were 7, 5 and 19% for the influent and 7, 7 and 21% for the effluent of the of Reactor 1 respectively. Moreover, 50–100 kDa, 1–10 kDa and <0.5 kDa were 15, 9 and 11% for the influent, and 20, 13 and 30% for the effluent of Reactor 2 respectively.

SUVA values are generally higher than 2 L mg^{-1}m^{-1} which indicates that membrane concentrate is in hydrophobic characteristics. Coagulation and classical treatment methods can effectively applied for the treatment of concentrate. Half of sulfate was lower than 0.5 kDa which indicates that sulfate hardly treated by NF membranes which have higher MWCO than 500 Da. SO_4^2 fractions for 50–100 kDa, 1–10 kDa and <0.5 kDa were 15, 8 and 12% in the influent and 1,17 and 21 % in the effluent of Reactor 1. Similarly, 50–100 kDa, 1–0.10 kDa and <0.5 kDa were 7,6 and 49 % in the influent and 2, 11 and 66% in the effluent of Reactor 2. This means moleculer fractions were changed during anaerobic treatment. Pre-ozonation and anaerobic treatment mineralized higher sulfate molecules and increased the lower fractions.

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