



# Performance of anaerobic membrane bioreactor treating landfill leachate

Kevser Cirik<sup>1</sup> · Serdar Gocer<sup>2</sup>

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## Abstract

**Background** Landfill leachate has been known as non-biodegradable/hardly—biodegradable wastewater, which contains significant amount of soluble organic and inorganic compounds. However, membrane bioreactor (MBR) technology have become a more viable treatment option for complex and recalcitrant compounds compared to activated sludge systems.

**Methods** This study aims at evaluating the performance of anaerobic membrane bioreactor (AnMBR) for the treatment of middle/old—aged landfill leachate (LFL). AnMBR was operated at different hydraulic retention times (HRTs) (48—12 h) and relaxation and backwashing (30 min—5 min, 5 min—0.5 min) periods. Additionally, Air stripping (pH 8, 24 g lime/L, 1.4 L/s air flow rate) as a pretreatment was evaluated prior to AnMBR.

**Results** Air stripping removed about 90%, 25%, and 64%  $\text{NH}_4^+$ , COD (Chemical Oxygen Demand) and color ( $\text{RES}_{620}$ ), respectively. The best results were obtained in combined air stripping—AnMBR operation corresponding to 95%, and 83% overall removals of color, and COD removals, respectively. Maximum methane yield and COD removal rate in AnMBR were 0.35 L methane/g COD<sub>removed</sub> and 5 gCOD removed /L.d, respectively.

**Conclusion** Pretreatment provided higher AnMBR flux that reached to 5.5LMH but increased fouling frequency due to the calcium precipitates in AnMBR which was verified with SEM—EDX analysis. Additionally, DEHP and DINP were not detected in permeate indicating AnMBR was successful for removing these micropollutants. This study showed that pretreatment clearly increased methane yield and COD removal rate.

**Keywords** Anaerobic membrane bioreactor · Landfill leachate · Air stripping · Micropollutants · Calcium

## Introduction

LFL is formed through decomposition of the waste and the percolation of water, which contains significant amount of soluble organic and inorganic compounds such as humic—type substances, heavy metals, ammonia—nitrogen, inorganic salts [1–3]. However, personal care products (PCPs), hormones, pharmaceuticals, halogenated hydrocarbons, pesticides, humic and folic acids are known as non biodegradable/hardly—biodegradable fraction of organic compounds in LFL [4–6]. Organic micropollutants, such as di—isononyl

phthalate (DINP) and di—(2—ethylhexyl phthalate) (DEHP) commonly found in LFL even if in micro levels, and due to the long half-lives they are highly persistent in the environment and also have estrogenic endocrine disrupting effects on intact organisms [7]. Thus, these contaminants adversely affect receiving environment and ground water resources and threats human health. As a result, a reliable treatment technology is essential to effectively remove contaminants from LFL and protect water bodies. In fact, leachate characteristics and composition vary significantly depending on its age (young—middle—old age LFL), which has an important effect on the selection of treatment technology [8]. To date, most studies on treatment of LFL focus on a wide range of physical, chemical, and biological processes. Middle and old age LFL contains mainly recalcitrant compounds and characterized by its low BOD/COD ratios (less than 0.2) and high ammonium concentration of around 2000 mg/L makes LFL even more complicated and requires a pretreatment prior to biological treatment system [9, 10]. In case of young LFL, biodegradable

✉ Kevser Cirik  
kcirik@ksu.edu.tr

<sup>1</sup> Department of Environmental Engineering, Kahramanmaraş Sutcu Imam University, 46100 Kahramanmaraş, Turkey

<sup>2</sup> Department of Environmental Engineering, Çukurova University, 01330 Adana, Turkey

organic fraction increases significantly making conventional biological treatment extensively employed method. However, treatment of middle age and old age LFL treatment requires the integration of suitable additional techniques. More recently, membrane bioreactor (MBR) technology, have become a more viable treatment option for complex and recalcitrant compounds compared to activated sludge systems [11]. MBR technology gained high popularity and importance because it offers several advantages in terms of excellent solid/liquid separation, high mixed liquor suspended solid (MLSS) concentration, high quality effluent, reduced sludge production and lower treatment costs. Although the application of MBR has grown worldwide, membrane fouling hinders MBR performance, and remains the most challenging issue affecting membrane separation processes. Fouling occurs due to the accumulation of material on the membrane surface; mainly microbial cells, and leads to an increase in TMP under constant flux operation and decrease in flux under constant pressure operation. Microbial cells grow on the membrane, producing polymeric substrates like proteins and polysaccharides known as SMP (soluble microbial products) and EPS (extracellular polymeric substrates) [12]. These substances have been proved to be the predominant cause of membrane fouling in MBRs [13–16].

To date, most studies on biological treatment of LFL focus on conventional system such as aerobic, anoxic, anaerobic treatment using upflow anaerobic sludge blanket (UASB) reactor etc. Additionally, many investigations have been carried out particularly with young LFL. In case of MBR systems, generally aerobic MBR systems have been operated that focus mainly on the reactor's performance in terms of organic matter and ammonia removal from the leachate at different operating conditions. There are limited studies related to anaerobic MBR and (to our knowledge) no study on the micropollutants removal from landfill leachate by AnMBR. Moreover, for most studies under AnMBR, the removal of only standard parameters such as COD, nitrogen, total organic carbon (TOC) etc. were reported and MBR performance parameters such as TMP, flux, fouling rate etc. were not included.

Thereby, we focused on the evaluation of submerged AnMBR in terms of AnMBR potential for reduction of organic strength and removal of micropollutants in middle/old age LFL. Additionally, a physico—chemical stage (air stripping) as pretreatment was investigated to remove ammonium ion prior to AnMBR. The objectives of this study were to: (i) determine the removal efficiencies of COD and color at varying hydraulic retention time (HRT) (2–0.5 d) (ii) evaluate effect of different relaxation and backwashing periods (iii) evaluate effect of pretreatment on membrane performance. The results of this study would help us in future studies aimed at use of AnMBRs in full—scale application for treatment of LFL.

## Methods

### Landfill leachate

Raw landfill leachate was collected from Kahramanmaraş (Turkey) sanitary landfill on—site. The total amounts waste deposited daily at the landfill were 815–830 t. The leachates collected in a lagoon before being discharged. Leachate was delivered 5 times per month to the laboratory from this lagoon and stored at 4 °C until used. The characteristic of landfill leachate was given in Table 1. The low biochemical oxygen demand (BOD)/COD ratio (0.1–0.3), the high pH value and the high concentrations of ammonia represents hard biodegradability.

### AnMBR design and operation

A laboratory—scale hollow fiber submerged AnMBR was used for this study. The AnMBR has an effective working volume of 4 L (wide: 14 cm, long: 37 cm, deep: 11 cm). Hollow fiber membrane module was created with P5S polypropylene membrane supplied from Zena Membranes Company (The Czech Republic) having a total surface area and pore size of 0.06 m<sup>2</sup> and 0.2 µm, respectively. Membrane module was submerged in the center of the AnMBR (Fig. 1).

At the base of the membrane module, a stainless steel tube diffuser was located and headspace biogas was recirculated at constant rate of 10 m<sup>3</sup>/m<sup>2</sup>.h by a gas recycle pump (Masterflex Console Drive, Model 7520—40, Thermo Fisher Scientific, USA) to provide mixing and to control fouling. The LFL was continuously pumped into the bottom of the bioreactor reactor using a peristaltic pump. To maintain a constant volume in AnMBR, the influent pumps were regulated with level sensors. Permeate was intermittently withdrawn using a peristaltic pump with different relaxation and backwashing (30 min—5 min, 5 min—0.5 min) periods according to experimental design. A magnetic stirrer (MS300HS, Misung Scientific Co., Seoul, Korea) was located at the bottom of the bioreactor to provide constant temperature at 35 ± 1 °C and necessary mixing of the sludge liquor. Oxidation—reduction potential (ORP) in the reactor was measured continuously using an ORP Meter (M 300, Mettler Toledo, Greifensee, Switzerland) equipped with a redox electrode. The trans—membrane pressure (TMP) of the system was continuously monitored. The outlet gas mixture port was directly connected to gas chromatograph (GC) equipment for methane measurement.

AnMBR was operated until TMP reached 900 mbars and then physical and/or chemical cleanings were applied. To remove cake layer by physically, sponge was used for scouring membrane surface. In case of chemical washing, membranes

**Table 1** Characteristics of Landfill leachate

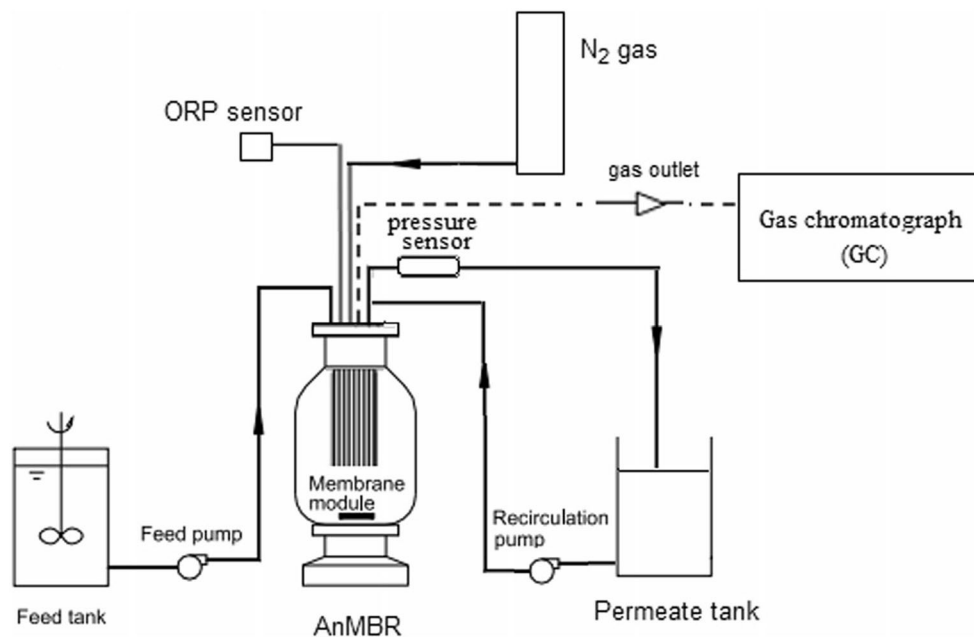
Parameter	Value	Parameter	Value
TOC(mg/L)	2254 ± 145	Sulfate (mg/L)	100 ± 50
COD(mg/L)	7014 ± 250	Copper (mg/L)	2.572 ± 0.6
BOD(mg/L)	1200 ± 300	Zinc(mg/L)	0.029 ± 0.01
NH <sub>4</sub> <sup>+</sup> (mg/L)	1000 ± 200	Iron (mg/L)	2.575 ± 0.5
Phosphorus (mg/L)	78 ± 10	Cadmium(mg/L)	0.001
NO <sub>2</sub> <sup>-</sup> (mg/L)	320 ± 20	Total chromium(mg/L)	0.254 ± 0.05
NO <sub>3</sub> <sup>-</sup> (mg/L)	670 ± 40	Lead(mg/L)	0.00025
TN (mg/L)	1600 ± 200	Mangan(mg/L)	0.1 ± 0.05
Color (Pt—Co)	6380 ± 300	Nickel(mg/L)	0.624 ± 0.1
Color (RES)	436 nm	TSS(mg/L)	1180 ± 100
	525 nm	VSS(mg/L)	830 ± 20
	620 nm	Phenol(mg/L)	18 ± 2
Sulfide (mg/L)	99 ± 6	Free Chlorine(mg/L)	0.6 ± 0.08
pH	8.2 ± 0.2	Calcium (Ca <sup>2+</sup> )	150 ± 15

were soaked in sodium hydroxide and nitric acid solution when there was a sharp increase in TMP.

The AnMBR was inoculated from a full—scale anaerobic digester located in Gaziantep, Turkey and acclimatized to wastewater for 20 days before AnMBR operation. The performance of AnMBR was evaluated for 150 days with five different periods (Table 2). The operational condition of AnMBR was changed after observing steady state operational conditions, which was decided when the measured effluent parameters fluctuated less than 10%. The MLSS concentration was kept at 6000 mg/L. The sludge was only drawn for the analytical purposes from AnMBR, which made a sludge residence time of almost 40 days.

The details of each period are shown in Table 2. Initially, the AnMBR was operated without air stripping, later the air—stripping unit was added to the experimental set—up. Batch mode air stripping stage was conducted at 24 g/L lime concentration (commercial hydrated) to adjust the pH of the leachate to 11. An air compressor coupled to bubble diffuser was used to fix air flow rate at 1.4 L/s.

In Period I, AnMBR was operated at 48h HRT and 30 min relaxation and 5 min backwashing periods. In this period, net flux was 0.5 LMH. Subsequent period (period II), net flux was increased to 1 LMH by lowering relaxation to 5 min with 0.5 min backwashing periods. Backwashing was performed from recirculation tank (Fig. 1). Later, HRT was reduced from



**Fig. 1** Schematic view of AnMBR

**Table 2** Operational conditions of AnMBR

Parameters	Periods				
	I	II	III	IV	V
Days	0–20	20–45	45–69	69–105	105–151
HRT (d)	48	48	24	24	12
Relaxation and backwashing period (min)	30–5	5–0.5	5–0.5	5–0.5	5–0.5
Air stripping as pretreatment	–	–	–	Lime addition Ca(OH) <sub>2</sub> (24 g/L)	Lime addition Ca(OH) <sub>2</sub> (24 g/L)
Net Flux (LMH)	0.5	1	1.5	2.5	5.5
Fouling rate (mbar/min)	0.008	0.014	0.059	0.073	0.1
Mean ORP (mV)	–417	–402	–377	–373	–383

48 h to 24 h at period III. In this period net flux was 1.5LMH. Finally, air stripping as pretreatment was applied prior to anaerobic treatment (Periods IV–V). In these periods, the performance of AnMBR was tested with pretreated leachate at different HRTs (24 h and 12 h). Sampling was performed three times a week for the measurement of NH<sub>4</sub><sup>+</sup>, COD, color, ORP, soluble microbial product (SMP), extracellular polymeric substance (EPS). Additionally, GC instrument was connected to outlet gas port of the reactor to provide methane gas sampling. Biogas recycling was eliminated during gas measurements. All assays were run in triplicate and the data illustrated in all figures are the mean values of the measurements for 3 cycles.

## Analytical methods

DOC, color, NH<sub>4</sub><sup>+</sup>, TN, ORP, flux, TMP, EPS and SMP were measured at regular time intervals. Influent, effluent (membrane permeate) and mixed liquor were regularly taken for analytical analysis. The samples were centrifuged at 9000 rpm for 10 min, and the supernatant was then analyzed for the measurement of TN, NH<sub>4</sub><sup>+</sup>–N, color, DOC, and COD concentrations. DOC and TN removal performances of MBR were evaluated the using a TOC–TN analyzer (Shimadzu TOC–VCPN/TNM–1, Kyoto, Japan. Anion and cation measurements were performed on ICS-5000 model ion chromatography instrument (Dionex, Sunnyvale, CA, USA) equipped with IonPac® AG9–HC guard and AS9HC analytical column. A mixture eluent containing 9 mM Na<sub>2</sub>CO<sub>3</sub> and 20 mM metanansulphonic acid ion chromatograph was passed through the device at a flow rate of 1 ml/min. All anions and cations were measured with a single injection. pH was measured by a pH meter (Thermo, Orion 4 Star, Indonesia). Color measurements were applied according to the standards of European Norm EN ISO 7887 at three different wavelengths, called 436 nm, 525 nm and 620 nm. These absorbance measurements were used to calculate the spectral adsorption coefficient (RES (λ) Eq. 2.1). A is the absorbance of the sample, d

is the optical path length of the cell (mm) and f is the conversion factor between mm and m, which is 1000.

$$\text{RES}(\lambda) = (A/d) \times f \quad (2.1)$$

Soluble microbial products (SMP) and extracellular polymeric substances (EPS) were extracted from the mixed liquor using heat treatment [17]. The mixed liquor was centrifuged for 30 min at 6000 rpm before the supernatant was collected and filtered through a 0.45 μm membrane. The filtered supernatant samples represented the concentration of SMP. The remaining sludge pellet was washed and re-suspended in saline water (5%NaCl). The sludge mixture was then diluted to its original volume. The NaCl solution for dilution was pre-heated to 80 °C for 1 h prior to recentrifugation under the same condition. The supernatant was collected and treated as EPS of the sludge. The total protein and carbohydrate contents of the SMP and EPS were determined using the modified Lowry method with bovine serum albumin (BSA) as the protein standard, and the Dubois phenol–sulphuric acid method with glucose as the standard, respectively [18, 19]. The absorbance of the various prepared samples was subsequently measured using a spectrophotometer (Chebios Optimum–One UV–VIS Spectrometer, Roma, Italy).

The analyses of soluble micropollutants in landfill leachate were determined by liquid–liquid extractions (LLE) using dichloromethane and detected with a GC–MS system (GC, Clarus 600 series, Perkin Elmer). Extraction procedure was adapted from Hu et al. [20]. The device was equipped with an Elite–5MS capillary column (60 m × 0.25 mm I.D × 0.25 μm df). Helium was used as carrier gas and the GC/MS condition for analyzing micropollutants was followed as described by Boonnorat et al. [21]. The selected micropollutants include DINP and DEHP. The standards of micropollutants were purchased from Sigma–Aldrich. In order to calibrate the mass detector, the calibration curves were prepared based on standard solutions in a concentration range from 0.5 to 10 ng/μL (LOQ of DINP and DEHP were 0.05 ng/L and 1 ng/L respectively). GC instrument (Agilent Technologies,

7820A GC system, China) equipped with Porapak Q and Molecular Sieve 5A columns was used to determine the concentrations of methane gases in outlet gas mixture. The methane was separated using a temperature program from 45 °C to 185 °C at a ramping rate of 20 °C/min and a thermal conductivity detector. Additionally, injection temperature was set to 250 °C.

Additionally, for the analyses of fouled membrane surfaces SEM—EDX analyses were conducted. Approximately 1 cm of the membrane fiber was removed from the module and fixed with 2.5% paraformaldehyde solution. The prepared samples were coated with gold and palladium mixture and scanned with scanning electron microscope (SEM, Carl Zeiss, EVO 50 model, Germany). Energy Diffuse X—ray (EDX, Bruker AXS Microanalysis GmbH, Germany) analyzer was also used to determine the inorganic composition of the fouled cake layer.

## Results and discussion

### Pretreatment performance

Pretreatment unit was performed as high ammonia concentration, especially in old/middle age LFL, reduces microbial activity, increases biomass loss and reduces the efficiency of conventional biological treatment. Wichitsathian et al. [22] observed a low nitrogen removal in aerobic MBR. When pretreatment was used, the nitrogen removal efficiency increased. They reported that the low NH<sub>3</sub>—N efficiency obtained in their study is a consequence of ammonia toxicity.

Air stripping performance is given in Table 3. High ammonia and color removals were obtained after 48 h reaction time corresponding to 90 and (25–82)% removal efficiencies, respectively. The average DOC removal efficiency obtained in this study was similar to that of Ferraz et al. [23] who observed about 20% DOC removal from old landfill leachate. Additionally, they reported removal of color (82%) and heavy metals (70–90%). Gotvajn et al. [24] used air stripping and obtained NH<sub>4</sub><sup>+</sup> and DOC removals of 80 and 42%, respectively.

**Table 3** Pretreatment performance of air—stripping

Parameters	Raw Leachate	Effluent	%Mean Removal
COD(mg/L)	6700 ± 150	4599 ± 200	26
DOC(mg/L)	2254 ± 145	1239 ± 120	45
TN (mg/L)	1598 ± 60	198 ± 45	87
NH <sub>4</sub> <sup>+</sup> (mg/L)	1873 ± 50	189 ± 43	90
Pt—Co	5256 ± 200	1020 ± 210	80
RES <sub>436</sub> (m <sup>-1</sup> )	203 ± 21	36 ± 10	82
RES <sub>525</sub> (m <sup>-1</sup> )	53 ± 5	19 ± 6	64
RES <sub>620</sub> (m <sup>-1</sup> )	12 ± 3	9 ± 2	25

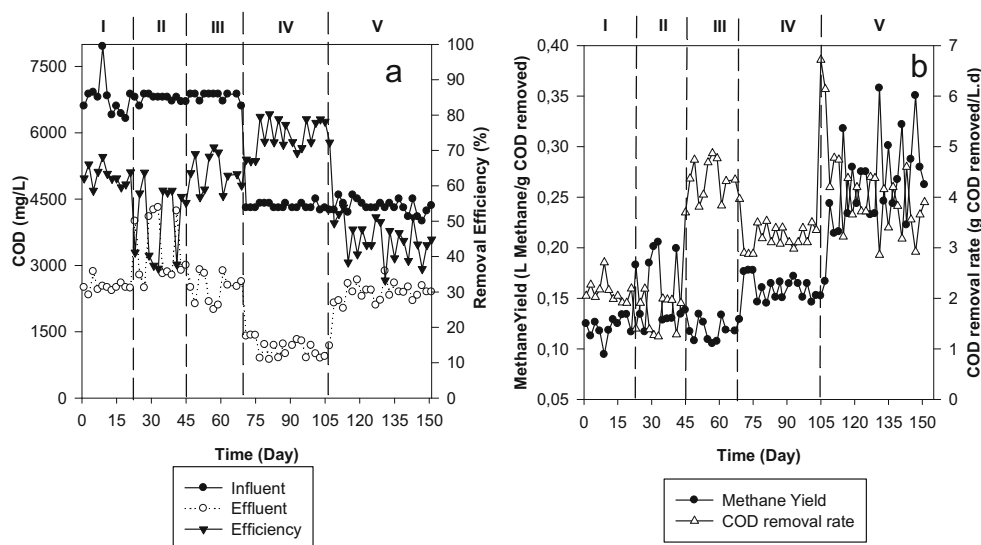
### AnMBR performance

#### COD removal and biogas production

Generally, positive ORP values represent aerobic media conditions while negative values reflect anaerobic environment conditions. During our study ORP values in AnMBR were between  $-300 \leq \text{ORP} \leq -450$  mV verifying anaerobic conditions.

The variations of COD concentrations and methane yield in the AnMBR is presented in Fig. 2. In the first period, continuously—fed AnMBR was operated at HRT of 48 h at 30 min relaxation and 5 min backwashing periods. COD removal efficiency was about 63% but decreased to about 50% with lowering relaxation to 5 min with 0.5 min backwashing at the second period (days 20—45), corresponding to effluent COD concentration of average 3300 mg/L. Decreasing relaxation and backwashing duration in period II did not represent better results in respect to COD removal, the net improvement was observed in period III with 63% removal efficiency when HRT was reduced to 24 h. In the following two periods (periods IV and V), pretreatment was performed prior to anaerobic treatment to evaluate AnMBR performance with and without air stripping (Fig. 2a). Air stripping and AnMBR achieved about 26% and 74% COD removal respectively; corresponding to 1100 mg/L permeate COD concentration and %83 overall removal efficiency (period IV). Later HRT of AnMBR was reduced to 12 h (period V). In this period, COD removal efficiency of AnMBR dropped to around 46%, which indicated that the HRT remained inadequate for microorganisms to oxidize the substrates in LFL. Setiadi and Fairus [25] achieved a low COD removal (31%) in the aerobic MBR treatment of old LFL with an initial BOD/COD ratio of around 0.17. Xie et al. [26] achieved higher COD removals with a pilot—scale anaerobic dynamic membrane bioreactor however, influent composed of young leachate and old leachate mixture, which has more biodegradability compared to our wastewater. Bohdziewicz at.al [27] achieved 45% COD removal in a pilot—scale anaerobic dynamic membrane bio reactor fed with a 75% (v/v) mixture of leachate and simulated wastewater. Similarly, Gotvajn et al. [24] also observed COD and BOD<sub>5</sub> removals as 80% and 90%, respectively, which was higher compared to our study; the reason was probably due to the dilution of LFL with simulated wastewater with a volumetric ratio of 0.3.

Figure 2b shows methane yield across COD removal rate during AnMBR operation. The first periods (period I-II, days 0–45) show about 0.15 L methane/g COD<sub>removed</sub> methane yield and 1.5 g COD<sub>removed</sub>/L.d COD removal rate. As expected COD removal rate increases linearly with the HRT decrease in Period III (Fig. B). Similar results were found in previously studies [28]. However, methane yield was stable but increased in Period.



**Fig. 2** COD removal performance and biogas production in AnMBR

IV when pretreatment was applied, corresponding to  $0.17 \text{ L methane/g COD}_{\text{removed}}$ . The decrease in HRT to 0.5 d in Period V, resulted in increasing COD removal rate and methane yield. Under optimized condition, AnMBR can convert up to 60% of the influent COD into methane, when COD equivalent of produced methane ( $4 \text{ g methane/g COD}$ ) was calculated. During our study, the pretreatment clearly increased methane yield and COD removal rate corresponding to maximum  $0.35 \text{ L methane/g COD}_{\text{removed}}$  and  $5 \text{ gCOD}_{\text{removed}}/\text{L.d}$ . (Period V). Xie et al. [29] examined the performance of a pilot-scale AnMBR treating young leachate and at a constant HRT of 7 days, and they obtained average 90% COD removal and  $0.46 \text{ L methane/g COD}_{\text{removed}}^{-1}$  biogas yield which was higher compared to our study. This was probably due to the landfill leachate age as they used younger LFL. Another study performed by Bohdziewicz et al. [27] examined the treatment efficiency of an AnMBR using old LFL diluted with synthetic wastewater. The authors reported biogas production at a leachate concentration of 20% by volume was  $0.45 \text{ L g COD}_{\text{removed}}^{-1} \text{ day}^{-1}$  which was 3.5 fold lower compared to our results, corresponding to  $1.6 \text{ L g COD}_{\text{removed}}^{-1} \text{ day}^{-1}$ .

### Color removal

Humic substances are refractory anionic macromolecules, comprised half of the total organic carbon in the raw leachate causing brown color of leachates. So far, color removal from LFL have been generally investigated by using chemical oxidation methods. In our study, biological color removal from old/young LFL was also investigated in respect to AnMBR performance.

Color removal performance of the pretreatment stage and AnMBR is represented in Table 4. Color values were recorded

at different color measurement methods. In periods I and II, similar removal efficiencies were obtained which were between 35–60%. Decreasing HRT adversely affected color removals corresponding to 20–35% (period III). Pretreatment improved biological color removal and generally, removals at 620 nm showed better results, which was reached to 98% at Period IV. Color removal efficiency of AnMBR was reduced by decreasing HRT to 12 h, corresponding to 4–40% removals (Table 4).

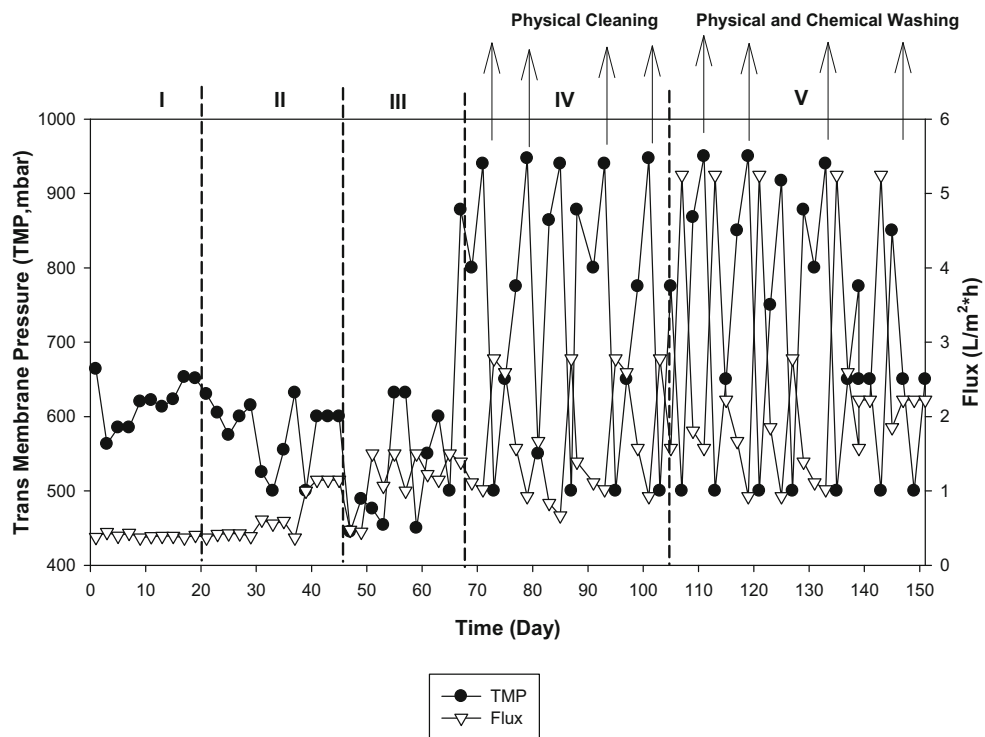
### TMP—Flux

Characterization of fouling during the operation of MBR in the present study was performed through monitoring of TMP. Figure 3 represents membrane flux and TMP profiles during AnMBR operation. During first three period, MBR was successfully operated without chemical cleaning but once in two weeks physically. In period I (days 1–20) very low flux was attained, corresponding to 0.5 LMH. The low net flux was probably due to the high relaxation period, thereby reducing total operation time. In period II, net flux was increased to 1LMH by lowering relaxation to 5 min with 0.5 min backwashing periods. Decreasing HRT resulted in higher fouling rate, which jumped to 0.059 mbar/min in days 45–69. Subsequent periods (periods IV and V) lime addition prior to anaerobic treatment was performed to evaluate AnMBR performance with and without air stripping in respect to membrane fouling.

Pretreatment in period IV allowed higher flux compared to previous periods, corresponding to 2.5 LMH. Although higher permeate flux was attained, AnMBR system experienced TMP fluctuation between 900 and 500 mbar and fouling rate was increased to 0.073 mbar/min, which was improved with physical and chemical cleaning. (period IV). At the last period

**Table 4** Color removal performance of the operating conditions

				AnMBR				
				Influent	Permeate	%removal		
Period I			RES <sub>436</sub>	203 m <sup>-1</sup>	116 m <sup>-1</sup>	35		
			RES <sub>525</sub>	53 m <sup>-1</sup>	37 m <sup>-1</sup>	44		
			RES <sub>620</sub>	12 m <sup>-1</sup>	13 m <sup>-1</sup>	60		
			Pt-Co	5256	3030	43		
Period II			RES <sub>436</sub>	203 m <sup>-1</sup>	107 m <sup>-1</sup>	44		
			RES <sub>525</sub>	53 m <sup>-1</sup>	38 m <sup>-1</sup>	60		
			RES <sub>620</sub>	12 m <sup>-1</sup>	20 m <sup>-1</sup>	57		
			Pt-Co	5256	2770	48		
Period III			RES <sub>436</sub>	203 m <sup>-1</sup>	80 m <sup>-1</sup>	22		
			RES <sub>525</sub>	53 m <sup>-1</sup>	29 m <sup>-1</sup>	25		
			RES <sub>620</sub>	12 m <sup>-1</sup>	12 m <sup>-1</sup>	32		
			Pt-Co	5830	2830	51		
				AnMBR				
				Permeate	Removal (%)	Overall removal (%)		
Period IV		Raw LFL	Pretreated LFL	%Removal				
		RES <sub>436</sub>	203	74	63	40 m <sup>-1</sup>	45	80
		RES <sub>525</sub>	53	19	64	3 m <sup>-1</sup>	84	94
		RES <sub>620</sub>	12	9	25	0.6 m <sup>-1</sup>	98	95
		Pt-Co	5256	1020	80	800	21	84
Period V		Raw LFL	Pretreated LFL	%Removal				
		RES <sub>436</sub>	203	74	63	74 m <sup>-1</sup>	43	63
		RES <sub>525</sub>	53	19	64	19 m <sup>-1</sup>	4	64
		RES <sub>620</sub>	12	9	25	6 m <sup>-1</sup>	4	50
		Pt-Co	5256	1020	80	600	41	88



**Fig. 3** TMP—flux profile during AnMBR operation

(days 105–155) a relatively high fouling rate and flux was observed when HRT was decreased to 12 h, corresponding to 0.1 mbar/min, and 5.5 LMH. These results were in accordance with previous studies that reported adverse effect of HRT reduction on fouling rate [30, 31]. However, in this period, frequency of physical and chemical cleaning was increased and AnMBR performance was decreased which matched by increased permeate COD concentrations (See Fig. 2a). Rapid fouling observed during periods IV and V was due to standard and intermediate pore blocking mechanisms, which caused increased TMP. The calcium concentration of AnMBR in periods I, II, and III was between 100 and 200 mg/L, however calcium concentration was increased to about 820 mg/L in periods IV, and V. The results suggest that high calcium content in AnMBR contributed to inorganic fouling by increasing the pore blocking resistance. As a result, pretreatment allowed higher flux compared to other periods performed without pretreatment step, the only adverse effect was increase of fouling rate, thereby cleaning frequency. This could be improved by adjusting initial lime concentration during pretreatment step. The color removal with pretreatment step, for example, was increased from 60 to 95%. As a result, pretreatment was enhanced AnMBR performance but lime concentration should take in consideration during air stripping process to eliminate TMP jumping and to decrease fouling frequency.

### SMP—EPS profile

The concentrations in terms of protein (EPS<sub>p</sub>, SMP<sub>p</sub>) and carbohydrate (EPS<sub>c</sub>, SMP<sub>c</sub>) were monitored every three days. The average results for each period are shown in Table 5. The most important biological pollutants in membrane—based processes include cell residues of biomass, complex nets formed by microbial cells, EPS and SMP biopolymers. Since EPS and SMP polymers are small in size, they can easily adhere to membrane surfaces and cause membrane fouling. In our study, carbohydrate was identified as the main foulant which was higher than

28–8 times more abundant than EPS (Table 5). SMP<sub>T</sub>/EPS<sub>T</sub> ratio was 28 in period I and increased to 22 in period III. Pretreatment decreased SMP<sub>T</sub>/EPS<sub>T</sub> ratio which was 9, and 8 in period IV and V, respectively.

Concentration of SMP<sub>c</sub> in effluents was a high fraction in all periods compared to SMP<sub>p</sub>, especially during period II as indicated in Table 5. Contrary to high concentration of SMP carbohydrates, SMP proteins in the effluent was found to be very low and it could be due to biomass decay as biodegradable substrate was limited. Moreover, composition of EPS (as protein and carbohydrate) was found to be relatively low and had similar values (Table 5). Lowering relaxation and backwashing periods caused increasing SMP content which was probably due to the breakage of sludge flocs and subsequent distribution of bacteria on membrane surface (period II). HRT decrease (period III) was responsible for increasing SMP and sludge deflocculation. Many reports indicated that high SMP concentration was one of major factors for membrane fouling [32–35].

However, there was no observed correlation between EPS—SMP concentration and membrane fouling (in this work). This behavior seems to be consistent with the findings of other researchers that also reported no association between EPS and fouling in MBRs [32, 36]. Contrary, many researchers reported that SMP concentration is positively correlated with membrane fouling [37, 38]. SMP was constantly lower in periods IV and V, due to cationic bridge between negatively charged biopolymers in sludge with Ca(OH)<sub>2</sub>. However, fouling rate was relatively increased compared to first three periods, which may be due to the inorganic fouling related to the calcium flocculants. Actually, calcium ion has different effects on membrane fouling depending on its concentrations. Normally, calcium ion increases bioflocculation and sludge stability thereby lowering fouling rate in MBRs [39]. Chen et al. [40] reported that calcium ion enrich membrane surface microorganism as well as EPS and promote biological flocculation. Kim and Jang [41] found that high

**Table 5** SMP—EPS values and fouling rate profile

SMP—EPS		Period I	Period II	Period III	Period IV	Period V
Supernatant SMP concentration (mg/L)	SMP <sub>C</sub>	92 ± 2	110 ± 3	164 ± 2	113 ± 11	93 ± 10
	SMP <sub>p</sub>	20 ± 2	23 ± 3	23 ± 2	17 ± 11	17 ± 10
	SMP <sub>T</sub>	115 ± 11	130 ± 10	185 ± 11	90 ± 6	120 ± 10
Permeate SMP concentration (mg/L)	SMP <sub>C</sub>	32	37	49	35	35
	SMP <sub>p</sub>	21	15	35	20	11
	SMP <sub>T</sub>	54 ± 5	52 ± 5	83 ± 7	39 ± 5	48 ± 5
EPS (mg/gMLVSS)	EPS <sub>C</sub>	2	3	5	8	11
	EPS <sub>p</sub>	2	2	2	2	2
	EPS <sub>T</sub>	4 ± 1	5 ± 1	8 ± 5	10 ± 2	14 ± 3
SMP rejection by membrane (%)		53	40	44	57	60
Fouling rate (mbar/min)		0.008	0.014	0.059	0.073	0.1



concentration of calcium is beneficial to membrane fouling. Arabi and Nakhla [42] investigated the impact of calcium concentration on membrane fouling and they found that 280 mg/L Ca(OH)<sub>2</sub> improved the membrane permeability, however calcium concentrations (at around 800 mg/L) resulted in substantial inorganic fouling of the membrane. Miao et al. [43] found the serious effect of Ca(OH)<sub>2</sub> on membrane fouling. The results obtained from our work suggest that inorganic fouling was more important than organic fouling, especially in periods IV and V where calcium ion concentration was high as 820 mg/L.

**SEM—EDX**

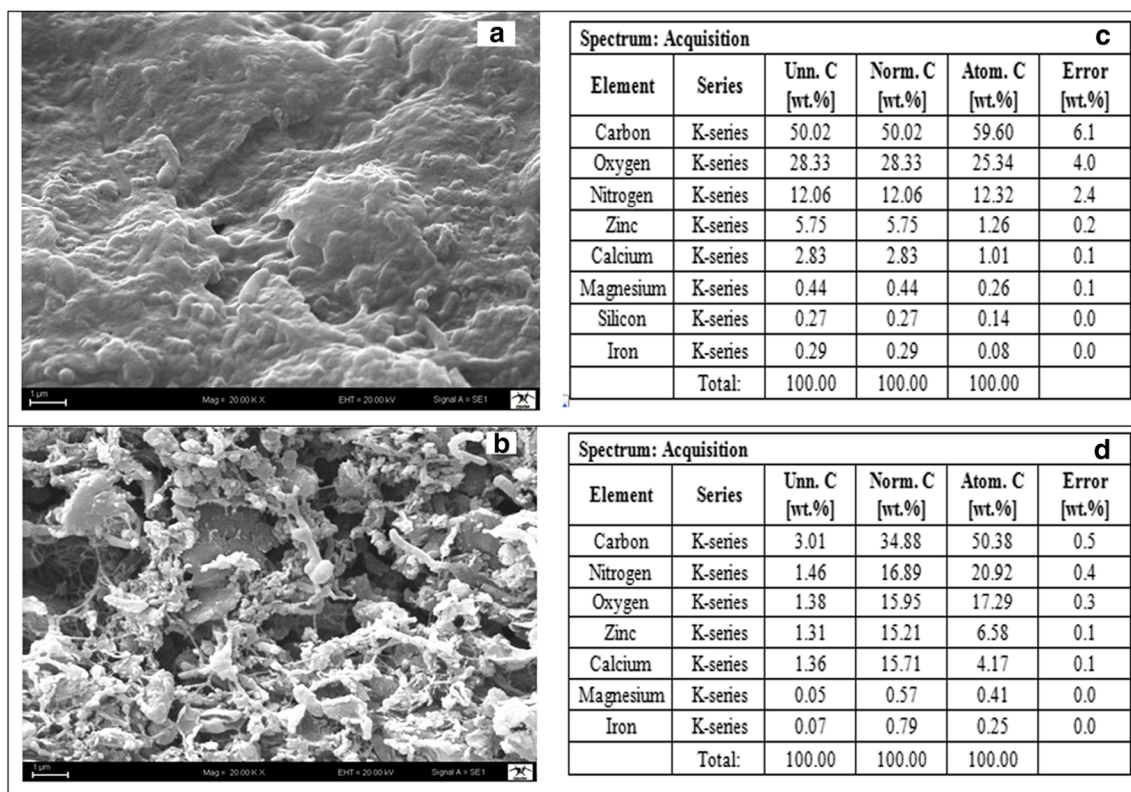
SEM images were taken to reveal the morphology of the membrane foulants. In Fig. 4, the SEM images showing the surfaces of the fouled membranes in Period III, and IV. Figure 4a shows the gel like cake layer have crests and valleys due to the microbial flocs indicating that biofouling occurred on the membrane surface. The surface of the fouled membrane in Fig. 4b, was significantly different from those of the fouled membrane in Fig. 4a, and it seems that cake layer was covered with Ca(OH)<sub>2</sub> precipitates and rod shaped bacteria.

In order to identify the chemical components of the cake layer, elemental analysis was also performed by EDX

analyzer. The elements of C, O, N, Zn, Ca, Mg, and Fe were detected as shown in Fig. 4. The relative content of C, O, and N were relatively high in both periods due to the microbial structure. However, relative content of the Ca(OH)<sub>2</sub> in period IV (15%) (Fig. 4d) is relatively higher than that in period III (2.83%) (Fig. 4c), which indicates more inorganics on the membrane surface in period IV, and cause inorganic fouling.

**Micropollutant removal**

In this study, occurrence and removal of DEHP and DINP were investigated in AnMBR as these micropollutants are commonly found in landfill leachate. Concentrations of DEHP and DINP in the raw leachate were detected within the range from 40 to 60 µg/L, and 5 to 15 µg/L, respectively. In our work, pretreatment contributed reducing of DEHP and DINP about 25% and 30%, respectively. The AnMBR performed well in respect to these contaminants in agreement with removals of COD, and TOC. Additionally, DINP and DEHP were not detected in AnMBR effluent during all periods as concentrations were below detection limit (LOQ of DINP and DEHP were 0.05 ng/L and 1 ng/L respectively). As a result, 100% removals were obtained in combined air stripping-AnMBR operation. Similarly, Yiping et al. [44] obtained high removal efficiencies of organic micropollutants in



**Fig. 4** SEM images and EDX analysis of membrane: (a) SEM image of fouled membrane(20kx) in Period III (without pretreatment), (b) SEM image of fouled membrane (20kx) in period IV (with pretreatment) (c)

EDX analysis of fouled membrane in Period III (without pretreatment), (d) EDX analysis of fouled membrane in Period IV (with pretreatment)

landfill leachate using combined anaerobic—MBR technology. They reported removal efficiencies of OCPs, 4—NP, and PAHs as 94, 77, and 59%, respectively. Fang et al. [45] achieved about 97.4% of DBP and about 98.8% of DEHP removal from landfill leachate by combined biodegradation-membrane processes.

## Conclusions

By continuously operating AnMBR fed with middle/old—aged LFL for around 150 days under different operational conditions, the AnMBR performance in terms of biological treatment of LFL and AnMBR performance was investigated.

The following conclusions are drawn based on the results of the study:

- Air stripping allowed high ammonia removal from LFL therefore increased biodegradability in AnMBR by eliminating ammonia toxicity.
- Pretreatment enhanced COD and color removal efficiencies in AnMBR. Color removal was jumped from 60% to 98%, and COD removal from 62% to 78%. The best results were obtained combined pretreatment-AnMBR operation corresponding to overall COD and color removals of 74% and 98%, respectively.
- Pretreatment lead to higher flux (5.5 LMH) and higher fouling rates (0.1 mbar/min) therefore increased the inorganic fouling due to the inorganic precipitates resulted from high calcium concentration (820 mg/L) in AnMBR. Thereby, Ca(OH)<sub>2</sub> concentration should take in consideration during air stripping process to eliminate TMP jumping and to decrease fouling frequency.
- AnMBR was effective in terms of DEHP and DINP removal.
- This study showed that pretreatment clearly increased methane yield and COD removal rate corresponding to maximum 0.35 L methane/g COD<sub>removed</sub> and 5 gCOD removed /L.d.

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## Compliance with ethical standards

**Conflict of interest** The authors declare no conflict of interest.

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