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Incorporating Submerged MBR in Conventional Activated Sludge Process for Municipal Wastewater Treatment: A Feasibility and Performance Assessment

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Abstract

A pilot-scale submerged membrane bioreactor (MBR) was incorporated in a conventional activated sludge (CAS) process for more than 100 days in order to assess the feasibility and performance on the municipal wastewater treatment. After a stabilization period of 50 days, the MBR unit was operated under various temperatures (21 ± 4°C), mixed liquor suspended solids (MLSS) concentrations (14000 ± 1800 mg L^{-1}), and different aeration intensities (3 to 6 m^3 h^{-1}). No significant deterioration in membrane flux was observed while operating with high biomass concentration. From the results, the removal of total suspended solids (TSS), chemical oxygen demand (COD), total phosphorus (TP) were enhanced using MBR. However, due to some limiting operational conditions, the total nitrogen (TN) removal was less efficient in MBR than in CAS. The MBR unit was 100% effective in removing E. coli and enterococcus, as well as noroviruses and adenovirus, making it more efficient than CAS. Also, the removal of most of the trace organic compounds (TrOCs) including personal care products, pharmaceuticals, steroid hormones and perfluorinated compounds were enhanced after the incorporation of MBR to CAS, as well as for many heavy metals in MBR.

Keywords: Membrane bioreactor; Wastewater treatment plant; Microbiological contaminations; Emerging pollutants; Water quality indices

Introduction

Municipal wastewater reclamation is a promising process to relieve growing pressure on global water resource. Nonetheless, municipal wastewater and even the reclaimed waters can have potential human health issues and ecosystem threats due to the presence of trace contaminants and pathogenic impurities [1]. Adequate treatment of municipal wastewater is needed to achieve high quality reclaimed water and to reduce health and ecological hazards [2]. For example, pharmaceutically active compounds (PhACs) which indicate overgrowing portion of trace organic contaminants (TrOCs) in the urban aquatic environment, after human consumption, reach to wastewater treatment plant (WWTP) in metabolised and/or unmetabolised form. Therefore, the municipal wastewater treatment plants (WWTPs), based on the conventional activated sludge (CAS) process, are not efficient enough to remove several emerging pollutants [3]. Also, legislation for reclaimed municipal wastewater reuse is very demanding concerning effluent quality and health safety [4]. Among the most promising wastewater treatment processes, Membrane bioreactors (MBRs) seem to be able to satisfy more stringent regulations for sustainable water reclamation and use [5].

MBRs have emerged in the field of wastewater treatment processes as one of the best alternatives to the CAS processes due to some enhanced characteristics including small spatial requirements, higher effluent quality and low sludge productions [6]. In fact, MBR process, which couples biological-activated sludge process and membrane filtration to separate treated effluent from mixed liquor, has become state-of-art in wastewater treatment and becoming increasingly applied [7]. Furthermore, Membrane-based bioreactors can remove microbiological pathogens, thus avoiding extensive and costly disinfection processes and also the threats possibly coming from disinfection by-products. High biomass concentration acclimatization in the bioreactor is possible by operating MBR at very high SRTs without manifest difficulties [2]. Indeed, the high biomass concentrations and long SRTs can offer favorable conditions for more efficient biodegradation of refractory organic micropollutants. The potential presence and growing concerns of TrOCs such as pharmaceutical and personal care products (PPCPs), steroid hormones, pesticides and heavy metals in the aquatic environment enforced many researches into their fate in wastewater treatment processes [8].

Nonetheless, MBR possess some major limitations including high capital investment and high energy requirements [9]. Also, membrane fouling leads to a decline in permeate flux, hence needing more frequent membrane cleaning followed by membrane replacement which increases operating costs [5]. Although the cost of the membrane modules is declining, the capital investment for building MBR plant remains higher. The use of anti-fouling strategies adopted to the system for maintaining sustainable permeate flux, high operational costs can be associated. Still, operational optimization including intermittent aeration, regular chemical cleanings, operation at sub-critical flux, membrane relaxation can compensate overall operation and maintenance costs [10].

The main objective of the study was to incorporate the MBR pilot unit in CAS process to assess the feasibility and performance in the real wastewater treatment. The removal efficiencies of several pollution enhanced by the incorporation of MBR unit in CAS process were studied. First, the influence of sludge characteristics (MLSS

concentrations) on membrane hydraulic performance (membrane flux) of MBR unit based on mixed liquor temperature variations were investigated. Second, the comparative removal efficiencies between MBR unit and CAS process regarding TSS, COD, nutrients, fecal bacteria, human-enteric viruses and emerging micropollutants (TrOCs and heavy metals) were studied.

Material and Methods

Experimental set-up

A pilot scale submerged MBR unit with an effective working volume of 4.26 m^3 was constructed (ARTAS Ltd.,Turkey) and located at Kenkäveronniemi Wastewater Treatment Plant (WWTP) in Mikkeli, Southern Savonia region, Finland as shown in Figure 1. The MBR unit was designed to treat 3 m^3 of wastewater per day. The full-scale Kenkäveronniemi WWTP (Conventional Activated Sludge process) consisted of typical treatment facilities including coarse screening, sand and grit removal chamber, primary sedimentation tanks, aerobic bioreactors, secondary sedimentation tanks and disinfection process. Three compartments: anaerobic tank, nitrification tank and membrane tank were designed to ensure the removal of pollution levels in the wastewater. The wastewater was fed to anaerobic tank and then transferred to the nitrification and membrane tank. Aeration to the nitrification and membrane tank, primarily to maintain microbiological activities and to enhance oxidation of nitrogenous and carbonaceous substances, was provided through the air diffusers by using two air blowers (each capacity 6 m^3 h^{-1} at 300-400 mbar). Also, the membrane fouling was controlled physically by providing cross-flow aeration for the scouring of the membrane modules and adopting intermittent suction cycle. The submerged flat-sheet membrane units (0.4 µm pore size), with total of 16 m^2 surface area (KUBOTA Corporation, Japan), were used for the solid-liquid separation. The permeate pump (Thomas, Germany) was operated in an intermittent suction mode with a cycle of 9 min ON and 1 min OFF. For in-situ cleaning of membranes, the clean-in-place (CIP) tank was also installed and connected with Sodium hypochlorite (NaOCl) and Citric acid dosing tanks. Additionally, the automation system (Siemens, Germany) was equipped with the pilot unit to control the MBR process. The characteristics of raw municipal wastewater are given in Table 1.

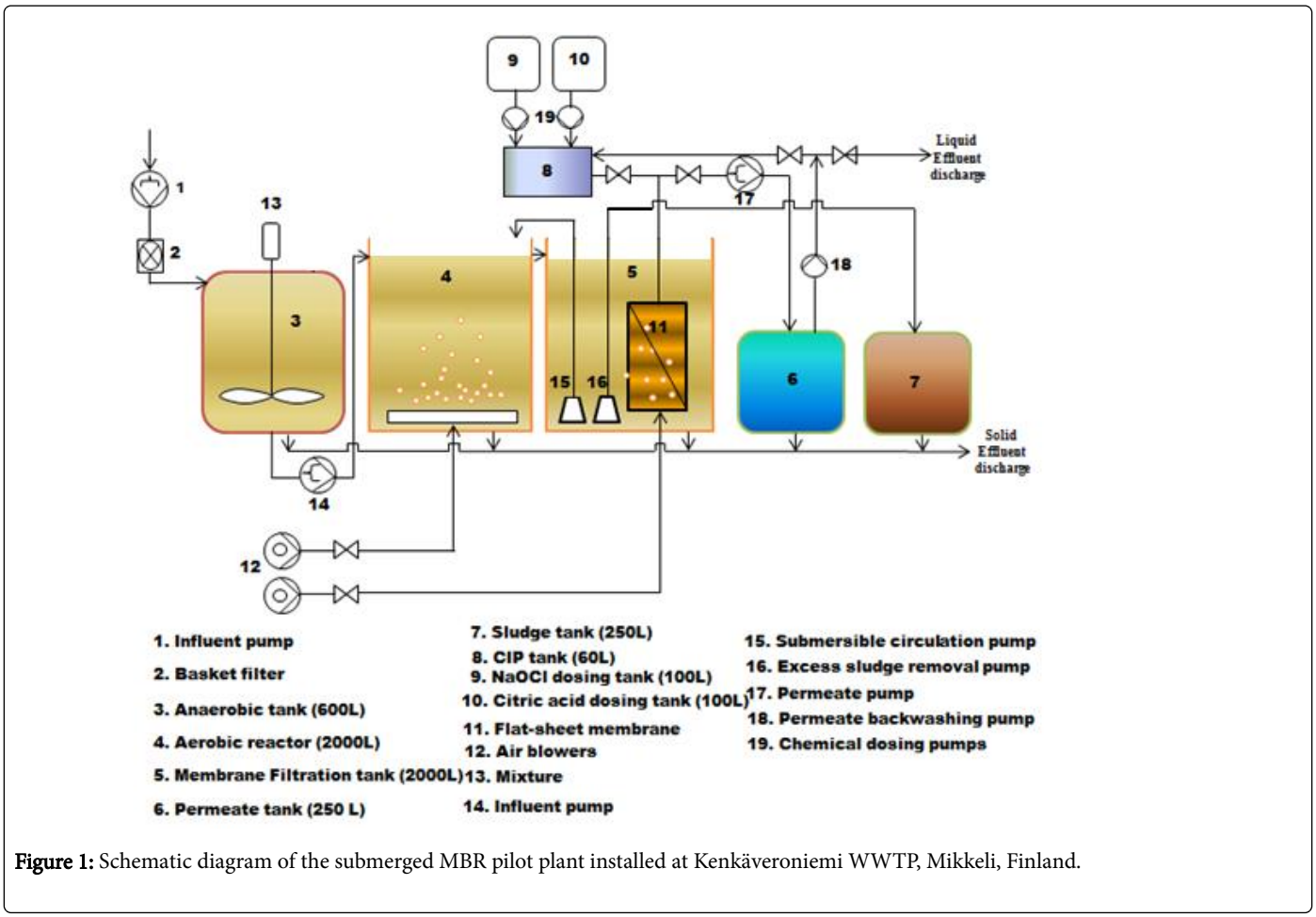

Figure 1: Schematic diagram of the submerged MBR pilot plant installed at Kenkäveroniemi WWTP, Mikkeli, Finland.

Operating conditions

The MBR unit was operated for more than 100 days (starting from April 2014 and continued till end of July 2014). In practice, the incorporation of MBR pilot into the conventional process of the local wastewater treatment plant was carried out by feeding the unit with activated sludge from the aeration tank of the full-scale CAS process (mean initial suspended solids concentration of 3100-5200 mg L^{-1}) after screening through a 3 mm screen. Therefore, since a fully mature sludge was used as influent to the pilot plant, a relatively low solid retention time (SRT) of about 6 days was maintained by removing highly concentrated mixed liquor (approximately 600 L day^{-1}) from the

system. The amount of this daily removal of sludge was experimentally estimated during the start-up phase and then applied in order to avoid the accumulation of excess solids within the bioreactors and maintain a lower retention time.

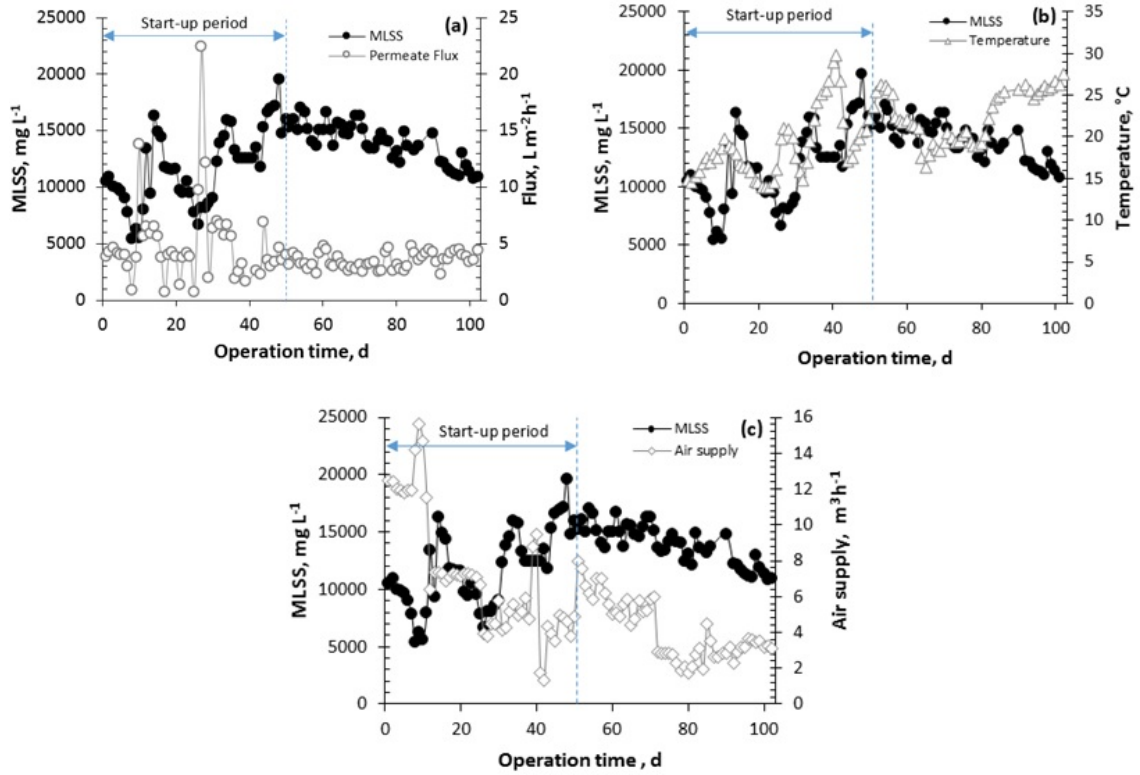

Figure 2: Effects of MLSS concentration and (a) permeate flux; (b) sludge temperature; and (c) air supply on MBR operation.

The system was operated at constant flux of (3.8 ± 1) L m^{-2} h^{-1}. As the main aeration tank of CAS was continuously fed with Ca $(OH)_2$, no additional buffer was injected to the MBR process, thus pH value spontaneously evolved between 4.7 and 6.5 during the experiment. The operating conditions of MBR pilot unit and full-scale CAS are summarized in Table 2.

Sampling and analytical methods

The effluents from both MBR unit and CAS process were sampled once a week and analyzed for TSS, COD, TN, TP, Ammonia nitrate (NO_3-N) and Ammonia nitrogen (NH_4-N). The grab samples for MLSS concentration of both aerobic and membrane tanks were collected and analyzed on daily basis. The Norovirus (GI and GII) and Adenovirus were sampled and analyzed using real-time polymerase chain reaction (qPCR) assay method. Also, samples were collected for TrOCs and analyzed by solid-phase extraction succeeded by ultra-performance liquid chromatography mass spectrometry (UPLC-MS). All these analyses were performed according to Standard Methods [11]. Total amount of E. coli and Enterococcus in the effluents of MBR and CAS were analyzed by using Enterolert® and Colilert® methods. The analysis of heavy metals was conducted with an inductively coupled plasma-optical emission spectrometer (ICP-OES, model iCAP 6300, Thermo Electron Corporation, USA) [12]. Moreover, membrane hydraulic performance, pH, DO, aeration intensity and temperature were obtained by using direct online measurements via automation system over experimental period. The experimental protocol acquired for the study is as shown in Table 3.

Results and Discussion

Effects of key parameters on MBR operation

The steady-state condition of the MBR process was reached approximately after the 50 days of the pilot operation as indicated in Figures 2a-2c. The stability of the process was defined based on the evolution of steady membrane flux and the nearly stable MLSS concentration of the system. Indeed, frequent malfunctioning in automation system delayed the process stability. From this point, a relatively stable permeate flux was maintained at 3.8 ± 1 L m^{-2} h^{-1} for the rest of the investigation operation. For the MLSS concentration, it was highly oscillating from 5000 mg L^{-1} to 19000 mg L^{-1} before the steady-state. After the start-up period, however, it remained at 14800 ± 1100 mg L^{-1}, as shown in Figure 2a. The trans-membrane pressure measured across the membrane was found to be 1.85 ± 0.2 kPa, and therefore transmitting low permeability drop during the experimental period. Schwarz et al. [13] reported that membrane flux continues to decline when MLSS increases significantly as high as 10000 to 15000 mg L^{-1}. However, the membrane flux was not found to be deteriorated with high biomass concentration in this study. Due to the complex interactions in the system, the correlations between mixed liquor characteristics and hydraulic membrane performance are difficult to establish [14].

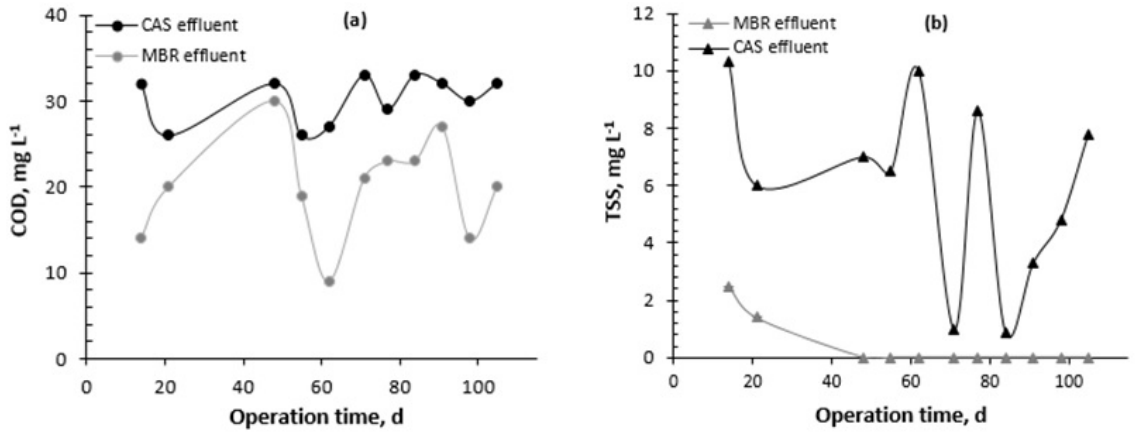

Figure 3: Concentrations of (a) COD; and (b) TSS in MBR and CAS effluents.

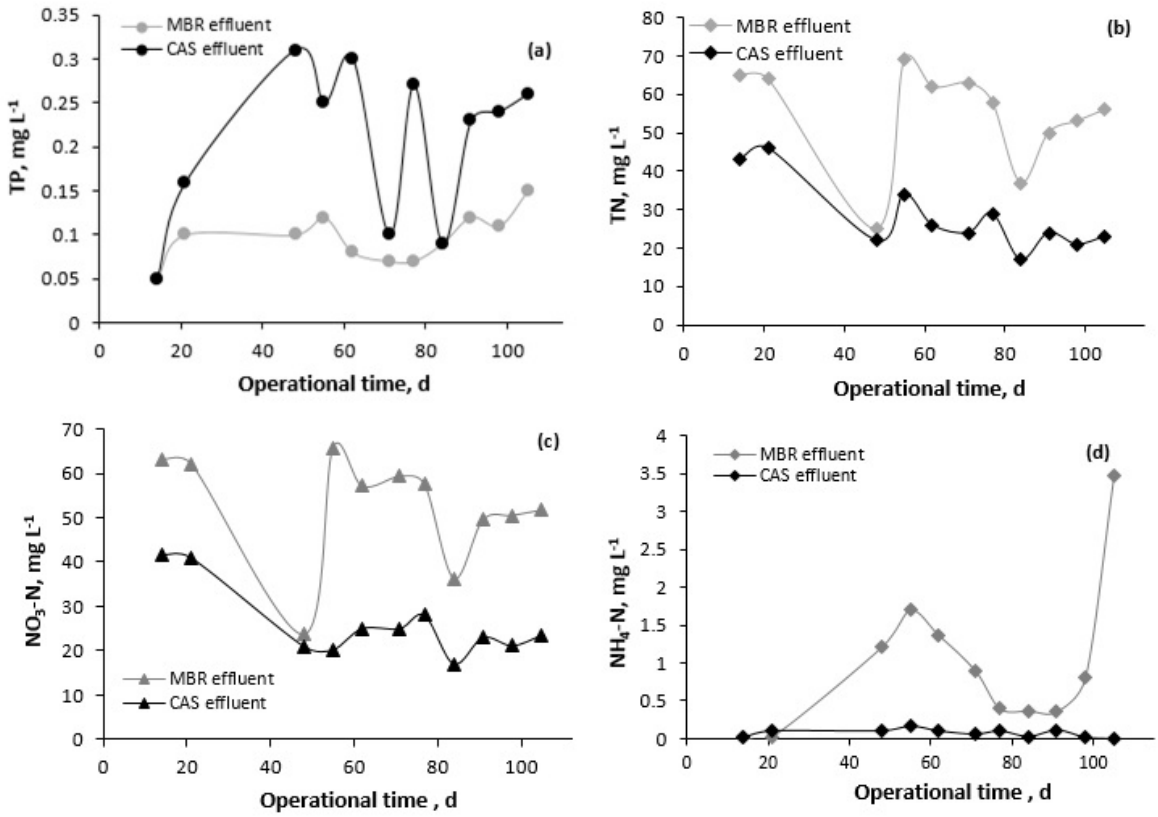

Figure 4: Concentrations of (a) Total phosphorus (TP); (b) Total nitrogen (TN); (c) Nitrate- nitrogen (NO_3-N); and (d) Ammonium – nitrogen (NH_4-N) in MBR and CAS effluents.

The sludge temperature was around 21 ± 2.5°C from day 51 till day 80 (beginning of June to end of June 2014) as shown in Figure 2b. So, the temperature of sludge in bioreactors was relatively low till day 80, which corresponds to the still-cold spring season in Finland. However, a gradual rise in the sludge temperature from 20°C to 27°C was observed from day 81 till day 100 (beginning of July to end of July 2014). The incoming wastewater temperature to the WWTP was recorded between 9°C and 16°C during the experiment. As the incoming wastewater temperature increased gradually in the beginning of summer, the sludge temperature inside MBR process raised too. About 3 to 5 degrees of temperature rise in mixed liquor was found due to continuous aeration in the main oxidation tank and within

MBR unit. The MLSS concentration was nearly stable during day 51 to day 80 at 14800 ± 1100 mg L^{-1}. Thus, at low process temperature, MLSS concentration was almost stable. However, the MLSS concentration started declining from day 81 (15800 mg L^{-1}) to day 100 (10800 mg L^{-1}). As the hydraulic parameters (such as SRT, HRT, flux) were maintained approximately constant, the decreasing trend of MLSS concentrations after day 81 might be attributed to the decreasing viscosity due to gradual temperature increased of the mixed liquor. The influence of sludge viscosity on MLSS concentration or vice-versa is also reported by other researchers [15-17]. Indeed, increase in the sludge temperature enhances rapid growth of microorganisms and thus biodegradation, however, the shorter sludge age maintained during the experiment might have effected on sludge rheology and microbial community. The growth of microorganisms is decreased and the microbial flocs with filamentous organisms are more dispersed and weaker at shorter SRT [18,19]. The aeration intensity was maintained at 6.0 ± 1.0 m^3 h^{-1} from day 51 to day 71 as shown in Figure 2c. The dissolved oxygen (DO) concentration was maintained at about 2.0 mg L^{-1} inside the bioreactors over entire period of operation. The oxygen transfer efficiency can be inhibited by high MLSS concentration in MBRs, which requires higher coarse bubble aeration intensity to maintain certain DO concentration [16]. From day 72 up to day 100 of operation, the aeration intensity was practically decreased to 3.0 ± 1.0 m^3 h^{-1}. Thus, the aeration intensity was optimized almost up to half of the initial concentration, however, no significant fouling was observed. These results can be attributed to the low flux operation, which emphasizes slow fouling effects. In the previous study, Thanh et al. [20] reported a less fouling effect in low flux (3.8 L m^{-2} h^{-1}) lab-scale MBR when treating a high strength leachate.

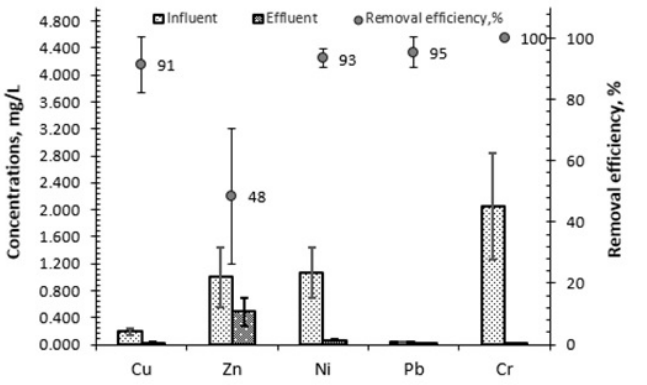

Figure 5: Concentrations of selected heavy metals in the influent and permeate of MBR unit and corresponding removal efficiencies.

Comparative Permeate Quality

Removal of COD and TSS

The concentrations of COD and TSS measured in the effluents of MBR and CAS processes over experimental period are shown in Figures 3a and 3b. The average TSS concentrations of about 0.4 mg L^{-1} and 6.0 mg L^{-1} were measured in the effluents of MBR and CAS, respectively. The MBR effluent was found almost free of TSS with concentrations of <1 mg L^{-1} confirming the excellent solids removal of MBR systems, which is in agreement with other studies [21,22]. Likewise, the average COD concentration of MBR effluent was approximately 20 mg L^{-1}, whereas 30 mg L^{-1} was measured in CAS effluent. Most of the organic matters were already degraded in the CAS oxidation ditch. Nonetheless, the incorporation of MBR seems to further improve the removal efficiency of COD.

A high and stable COD removal can be achieved with higher MLSS concentration which can decompose more organic compounds as compared to CAS processes [23]. In this work, despite shorter SRT, the MLSS concentration was always higher (14000 ± 1800 mg L^{-1}), which might have attributed to the improved COD removal. It is also reported that the interception ability of membranes plays an important role in highly stable removal of the particulate (suspended and colloidal) COD, representing a large fraction of total COD in municipal wastewaters [24].

Removal of nutrients (TP and TN)

Enhanced biological phosphorus removal (EBPR) was expected during MBR process. In Figure 4a, the average TP concentrations in the effluents of MBR and CAS processes were close to 0.1 mg L^{-1} and 0.2 mg L^{-1}, respectively, thus showing improved removal inside the MBR process. The removal of phosphorus depends on the amount of excess sludge wasting in which the soluble phosphorus (ortho-phosphate) is bounded to the biomass and removed as luxury uptake. Thus, maintaining relatively shorter SRT by discharging a large amount of excess sludge can have better advantage for phosphorus removal compared to longer SRT operation [23]. The removal of TP in the MBR process could be attributed to polyphosphate accumulating organisms (PAOs), whose growth is favored in MBRs [25]. During EMBR process, polyphosphate decomposes and, thus orthophosphate (PO_4) is released by the aid of PAOs under anaerobic conditions. Under the aerobic conditions, released PO_4 is used for the synthesis of new PAO cells and excess is stored as polyphosphate (known as the luxury uptake of phosphorus) and simultaneously removed with waste sludge [26]. The TP concentration in MBR effluents was found almost steady (0.096 ± 0.01 mg L^{-1}) from the beginning to the end of the experiment, even though no chemicals were added to the MBR pilot plant to enhance adsorption or coagulation processes.

The total nitrogen (TN) is the sum of organic-nitrogen, ammonia nitrogen (NH_4-N), NO_2-N and NO_3-N. The average TN concentration was measured about 55 mg L^{-1} and 28 mg L^{-1}, respectively in MBR and CAS effluents as shown in Figure 4b. The mixed liquor entering the MBR unit might contain high NO_2-N and NO_3-N along with residual NH_4-N. However, due to insufficient promotion of biological conditions related to short SRT, reduced pH and hypothetically a low residual NH_4-N and carbon (dissolved CO_2) content in substrate, the nitrification process was found to be inhibited in MBR unit during this study. Thus, average ammonia (NH_4-N) concentration in the MBR effluent was 0.97 ± 1.0 mg L^{-1}, whereas relatively low and stable of 0.07 ± 0.1 mg L^{-1} was measured in CAS effluent as shown in Figures 4c and 4d. Proper growth of nitrifiers needs at least 10 days of SRT to perform biological decomposition of nitrogenous matters [26]. Similarly, the concentrations of NO_3-N were measured 53 ± 12 mg L^{-1} and 26 ± 8 mg L^{-1} in the effluents of MBR and CAS, respectively. The presences of high concentrations of NO_3-N were attributed to the increase of TN concentrations in the MBR than in CAS effluents. The reduction of NO_3-N to gaseous nitrogen would have been possible if provided with appropriate anoxic conditions in MBR unit, which then should enhance the overall nitrification efficiency. Furthermore, pH in the MBR process was estimated at 5.36 ± 0.4 during the pilot operation. This tendency was expected due to the formation of acidity (H^+)

during the oxidation of NH_4-N in main process oxidation ditch, from which the MBR unit was fed. In MBRs, nitrification rate slows down at a pH below 7.0 and decreases to less than 50% of maximum value under pH 5.0 [27].

Parameter	Units	Raw water	
		Range	Mean ± SD
pH	Unitless	6.9 -7.4	7.21 ± 0.1
COD	mg L^{-1}	520 - 850	611.8 ± 126
TSS	mg L^{-1}	220 - 730	417.5 ± 163
TP	mg L^{-1}	5.8 - 15	9.80 ± 2.0
TN	mg L^{-1}	44 - 68	58.33 ± 6.0
NH_4-N	mg L^{-1}	31 - 48	42.83 ± 5.0
Temperature	°C	9-16	11.07 ± 2.0

Table 1: Characteristics of raw municipal wastewater

Removal of microbiological contaminations (bacteria and viruses)

Escherichia coli (*E. coli*) and enterococcus were taken as fecal bacterial indicators, whereas noroviruses (GI and GII) and adenoviruses were selected as human viruses, and the concentrations in the effluents of MBR and CAS processes (before disinfection) are as shown in Tables 4a and 4b. The bacterial indicators and human viruses were enumerated as most probable number (MPN) 100 mL^{-1} and genomic copies (GC) mL^{-1} of sampling solution, respectively.

Parameters	MBR	CAS
Operational period, days	>100	
Flux, L m^{-2} h^{-1}	3.8 ± 1 , Constant flux mode	
Solid Retention Time (SRT), days	6	28 ± 3
Hydraulic retention time (HRT), h	38	4 – 8 up to 12
MLSS concentration, mg L^{-1}	14000 ± 1800	3100 - 5200
Temperature, °C	21 ± 4	08-18
Dissolved Oxygen (DO), mg L^{-1}	2.0 ± 1	02-03
pH	4.5 - 6.0	6.7 – 7.3
Intermittent filtration cycle	9 min ON / 1 min OFF	

Table 2: Operating conditions of submerged MBR pilot unit and full-scale CAS

No traces of E. coli were found in the MBR permeate as shown in Table 4a. However, 22800 ± 16800 MPN/100 mL of *E. coli* were found in the CAS permeate sampled from secondary clarifier. Likewise, Enterococcus in the MBR effluent was found to be almost zero, whereas 3400 ± 1300 MPN/100 mL was measured in CAS effluent. However, during test 3, about 20 MPN/100 mL of Enterococcus was found due to the contamination of permeate tank by the return sludge from excess sludge removal line. Furthermore, no traces of human norovirus (GI and GII) and adenovirus were detected in the MBR effluent. However, significant concentrations were found in CAS effluent as shown in Table 4b.

Parameters	Material flow			
	MBR effluent	CAS effluent	MBR sludge	MBR inflow (sludge)
MLSS			✓	
COD	✓	✓		
SS	✓	✓		
TP	✓	✓		
PO_4-P	✓	✓		
TN	✓	✓		
NO_3-N	✓	✓		
NH_4-N	✓	✓		
E-Coli	✓	✓		
Enterococcus	✓	✓		
Viruses	✓	✓		
Heavy Metals	✓			✓
TrOCs	✓[a]	✓[a]		
Remarks	Weekly	Weekly	Daily	Weekly
[a]sampling done once				

Table 3: Experimental protocol

Based on the experimental results, excellent reduction of both bacterial and viral indicators was found in the MBR effluent as compared to CAS. Almost up to 100% elimination of pathogens was achieved by MBR system. Marti et al. [28] reported that the bacterial indicators removal occurs in MBR process due to membrane size exclusion, but the retention of viral indicators is highly dependent on the formation of irremovable fouling (conditioned by the TMP). As very low TMP values were observed, therefore no irremovable fouling of membranes was expected. Thus, the significant removal of viruses might be attributed to the probable adsorption or absorption of viruses on or within the biological flocs around the membrane surface. The rejection of human enteric viruses is not related to TMP, but their adsorption to MLSS plays a crucial role in the removal by MBR [29]. Also, due to the development of a thin dynamic layer of foulants on the membrane surface during the process operation, the microfiltration membrane pore size is further reduced and behaves like UF membranes. In general, the removal of pathogen by membrane processes is achieved by size exclusion, and is dependent on the properties of pathogens, physiochemical properties of membrane, and the solution environment [30].

Removal of heavy metals

The heavy metals concentrations in the influent (sludge) and permeate of the MBR unit were analyzed during the experimental

period. The concentrations of selected heavy metals including Cr, Ni, Pb, Cu, Zn and corresponding removal efficiencies are shown in Figure 5.

Samplings/ Indicators	MBR effluent		CAS effluent	
	Escherichia Coli (MPN/10ml)	*Enterococcus* (MPN/100ml)	*Escherichia Coli* (MPN/100 ml)	*Enterococcus* (MPN/100 ml)
1	<1	<1	23820	3790
2	<1	<1	11700	3300
3	<1	20	51700	5500
4	<1	<1	14000	2600
5	<1	<1	12900	1900

Table 4a: Removal of bacterial indicators in MBR and CAS in aqueous phase.

Sampligs/ Indicaors	MBR effluent			CAS effluent		
	Norovirus GI (GC/ml)	Norovirus GII (GC/ml)	Adenovirus (GC/ml)	NorovirusGI (GC/ml)	Norovirus GII(GC/ml)	Adenovirus (GC/ml)
1	a	a	a	>4	7	8
2	b	b	b	>6	9	>5
3	b	b	b	>1	>5	8
[a]Under Detection Limit (0.4 to 0.6 GC/mL); [b]Not detected.						

Table 4b: Removal of viral indicators in MBR and CAS in aqueous phase.

The concentrations of Cr and Pb in the treated effluents were close to zero. Cu and Ni concentrations were measured ranging from 0.02 mg L^{-1} to 0.06 mg L^{-1}. Similarly, Zn concentration was found about 0.49 mg L^{-1}. The concentrations of all the metals were compared with [31] recommended limits for reclaimed water and found always satisfying. The removal efficiencies for Cr, Pb, Ni, Cu, and Zn were achieved 99.9% ± 0.1%, 95% ± 5%, 93% ± 3%, 91% ± 9% and 48% ± 22%, respectively. Therefore, the metal removal efficiency achieved in the MBR system followed the sequence Cr>Pb>Ni>Cu>Zn. Similar tendency of metal removal was also reported by Katsou et al. [32], where it was concluded that the heavy metals were removed through various processes including precipitation of metals inside the biological reactor, Biosorption on sludge flocs and retention of the insoluble metal species by microfiltration membranes.

Category	Name	Initial concentration (ng L^{-1})	Chemical formula
Pharmaceuticals	Ibuprofen	3000	$C_{13}H_{18}O_2$
	Diclofenac	760	$C_{14}H_{11}Cl_2NO_2$
	Ketoprofen	330	$C_{16}H_{14}O_3$
	Naproxen	3900	$C_{14}H_{14}O_3$
	Sulfamethoxazole	220	$C_{10}H_{11}N_3O_3S$
	Doxycycline	380	$C_{22}H_{24}N_2O_8$
	Hydrocortisone	320	$C_{21}H_{30}O_5$
	Enalapril	190	$C_{20}H_{28}N_2O_5$
	Entacapone	90	$C_{14}H_{15}N_3O_5$
	Bezafibrate	190	$C_{19}H_{20}ClNO_4$
	Fluoxetine	40	$C_{17}H_{18}F_3NO$
	Hydrochlorothiazide	2300	$C_7H_8ClN_3O_4S_2$
	Methotrexate	170	$C_{20}H_{22}N_8O_5$
	Cyclophosphamide	10	$C_7H_{15}Cl_2N_2O_2P$
	warfarin	50	$C_{19}H_{16}O_4$
	Atenolol	530	$C_{14}H_{22}N_2O_3$
	Metoprolol	1400	$C_{15}H_{25}NO_3$
	Furosemide	3200	$C_{12}H_{11}ClN_2O_5S$
	Metronidazole	290	$C_6H_9N_3O_3$
	Tetracycline	3900	$C_{22}H_{24}N_2O_8$
Steroid hormones	Estradiol	50	$C_{18}H_{24}O_2$
	Estriol (E3)	140	$C_{18}H_{24}O_3$
	Estrone (E1)	120	$C_{18}H_{22}O_2$
	Testosterone	33	$C_{19}H_{28}O_2$

Perfluorinated Chemicals (PFCs)	Perfluorooctane sulfonate (PFOS)	13	$C_8HF_{17}O_3S$
	Perfluorooctanoic acid (PFOA)	5	$C_8HF_{15}O_2$

Table 5: Category, name, initial concentrations and chemical formula of TrOCs in this study

Moreover, the different removal efficiencies discussed above can also be explained by the solubilization of the selected heavy metals from the sludge to the liquid phase. Indeed, metals solubilize at different pH: the solubilization of Zn and Ni initiates at pH 6-6.5, whereas Cr, Pb and Cu require lower pH of 2-3 to start solubilizing [33,34]. The pH evolution of MBR process during pilot operation shows a pH varying from 4.7 to 6.5, which is consistent with the relatively high Zn concentration of 0.49 mg L^{-1}, and thus with the lower removal efficiency measured (about 48%). Conversely, the solubilization of Cr, Pb and Cu was probably less significant due to low pH required. Indeed, these metals were supposed to be retained within the sludge in the solid phase.

Furthermore, it is known that metals can be found in the sludge in several forms such as exchangeable, reducing, oxidizable and residual fractions [34]. Even though heavy metals fractions are highly related to the sludge characteristics, metal considered and the nature of treatment applied [12]. It is generally accepted that Cr, Pb, Ni and to some extent Cu are present in oxidizable and residual fractions, which are in the most stable forms in sludge. On the contrary, Zn is the most unstable metal since it is majorly present in exchangeable and reducible fractions, which are usually called "unstable forms" [12]. Aforesaid statements can be correlated to this work in which low removal efficiency of Zn and higher efficiencies of Cr, Cu, Pb and Ni removal were measured. Therefore, in addition to the solubilization profiles discussed earlier, these observations can be partially attributed to the unstable form of Zn in opposition to the stable forms of Cr, Cu, Pb and Ni. Higher concentrations of unstable Zn were detected in the MBR permeate (solubilized Zn not retained by the membrane), whereas stable Cr, Cu, Pb and Ni were retained in the biomass. Moreover, the metals concentrations were not analyzed from sludge retained in/or wasted in MBR process during this work.

Fate of trace organic compounds (TrOC): Pharmaceutical and personal care products (PPCPs), steroidal hormones, perfluorinated compounds (PFCs)

The occurrence and fate of selected 26 emerging TrOCs were investigated as listed in Table 5. The concentrations of each individual compounds in the effluents of MBR and CAS in aqueous phases are presented in Figure 6.

A significant variation in the removal of TrOCs was observed. Most of the pharmaceutically active TrOCs including ibuprofen, doxycycline, hydrocortisone, enalapril, entacapone, fluoxetine and methotrexate were found to be lower and even below detection limits both in MBR and CAS effluents. TrOCs removal efficiency of both (MBR and CAS) treatment processes are more often found similar and very high [35]. However, the concentrations of TrOCs such as ketoprofen, diclofenac, naproxen, bezafibrate, cyclophosphamide, warfarin, atenolol, furosemide, metronidazole and tetracycline were removed significantly in MBR effluents (5 to 300 ng L^{-1}) than in CAS effluents (13 to 2100 ng L^{-1}). Similarly, concentrations of sulfamethoxazole and hydrochlorothiazide in the effluents of MBR and CAS were about (53 ng L^{-1} and 1700 ng L^{-1}) and (73 ng L^{-1} and 2000 ng L^{-1}), respectively. An average metoprolol concentration of 1100 ng L^{-1} was achieved in MBR than 1200 ng L^{-1} in CAS effluent, thus being the lowest effectively removed TrOC. Therefore, considering above results, to some extent, MBR is prominently effective than CAS. However, the degradation pathways of TrOCs and their intermediates analysis are still largely unknown [36]. The concentrations of atenolol, sulfamethoxazole, ketoprofen, naproxen, ibuprofen, diclofenac, estradiol, estrone, estriol and testosterone found in MBR permeate in this study are lower than or similar to the work performed by Trinh et al. [37]. Ibuprofen, doxycycline, hydrocortisone, enalapril, entacapone, fluoxetine and methotrexate were found to be removed efficiently in both CAS and MBR with effluent concentration ranging from <10 to 30 ng L^{-1}, whereas naproxen, ketoprofen, bezafibrate and metronidazole were removed better in MBR than in CAS. These results are in agreement with previous studies [38]. The concentration of diclofenac, which is in the watch list of substances in EU that requires environmental monitoring in the member states [39], was found about 160 ng L^{-1} and 830 ng L^{-1} in MBR and CAS effluents, respectively, which are consistent with previous studies [37,38]. Thus, the removal of diclofenac in MBR was enhanced than in CAS. The concentrations of four steroid hormones including estradiol, estriol (E3), estrone (E1) and testosterone were measured below limit of detection (<1 to <50 ng L^{-1}) in both MBR and CAS effluents. These compounds hold hydrophobicity (log D>3), thus are supposed to be removed majorly via biotransformation as explained by Trinh et al. [37]. Conversely, the concentrations of two PFCs including PFOA and PFOS, were found to be more in effluents of both the treatment plants than in source. Both PFCs are the stable end products resulting from the degradation of precursor substances through variety transformations. Due to their complex chemical structure, PFCs are extremely recalcitrant compounds, thus not susceptible for biodegradation easily [35].

The fate of TrOCs removal during CAS or MBR process depends on physicochemical characteristics of compounds, operational conditions and their degradation pathways undergoing biological processes [40]. The removal of TrOCs in CAS process is a complex activity which involves both sorption (adsorption and absorption) and biodegradation. In typical MBR processes, as the MLSS concentrations and mean-cell retention time are much higher than in CAS, sorption has been suggested as the major removal mechanism for the removal of TrOCs. The sorption of a TrOCs into the activated sludge can be assessed by evaluating Log D (effective octanol-water partitioning co-efficient) value of the compound at given pH. The removal of very hydrophobic (Log D>3.2) compounds is dominated probably due to sorption to the activated sludge, thus shows high removal efficiency. However, for the hydrophilic TrOCs (Log D<3.2), the removal efficiency is influenced mostly due to their intrinsic biodegradability other than sorption mechanism [40,41]. In this study, moderate to highly hydrophobic pharmaceutical TrOCs were removed more effectively in MBR than in CAS. MBRs operating at higher biomass concentrations provide better formation of bacterial flocs, which can assimilate persistent TrOCs. This phenomenon can be attributed to enhanced mass-transfer conditions favored by smaller flocs and the presence of free-living bacteria. Thus, the biomass characteristics are crucial for biodegradation and sorption of TrOCs in MBRs more than in CAS [40]. In the present study, higher removal of certain TrOCs in MBRs than in CAS can be attributed partially to the operation of MBR under relatively high MLSS concentration. Certain molecular features

and physicochemical properties of TrOCs can be used to qualitatively predict the rate of removal during MBR treatment [41]. Moreover, pH of mixed liquor also effects the removal of TrOCs, which influences both physiology of microorganisms and the solubility of micropollutants in wastewater [40]. The removal efficiencies of ionisable trace organics including ibuprofen, ketoprofen, sulfamethoxazole and diclofenac is highly dependent on pH of sludge, in fact at an acidic pH, high removal of these compounds exist [40,42], which explains in part the TrOCs removal data of this study.

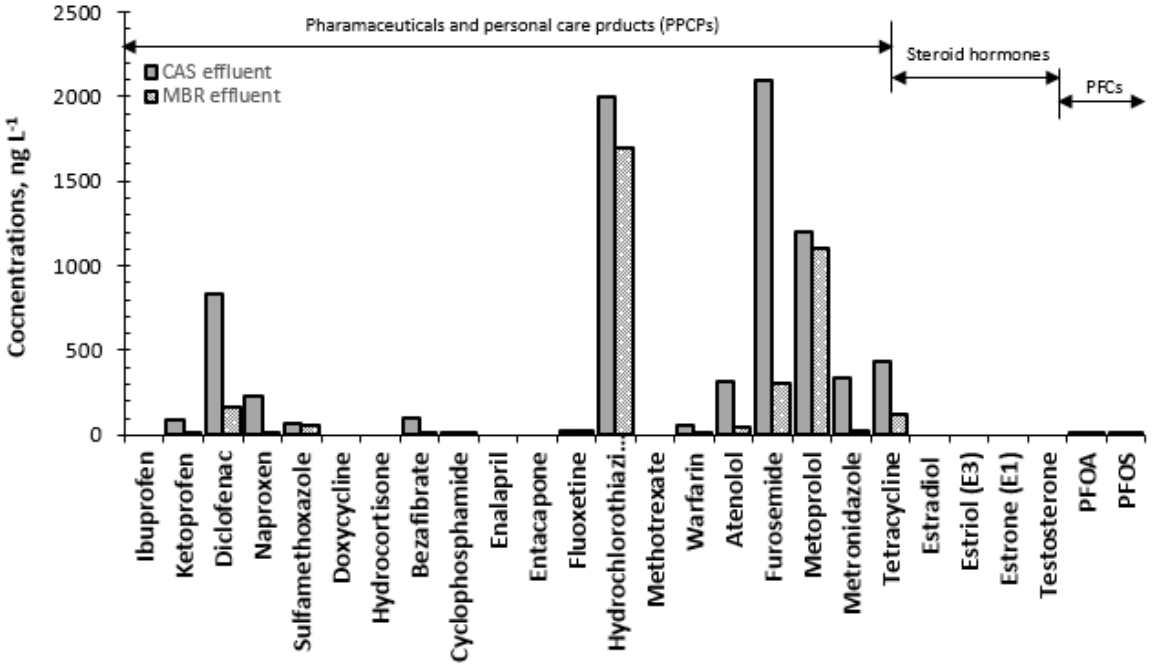

Figure 6: Concentrations of selected TrOCs in MBR and CAS effluents. The compounds with concentrations below detection limit in the effluents are missed (blank) in the figure.

Conclusion

The MBR pilot was incorporated in CAS process, by loading it with activated sludge from aeration tank, in order to assess the feasibility and performance of such integrated process with respect to pollutants and nutrients removal. The MBR operational parameters including MLSS, temperature and aeration intensity were studied, and it was found that under moderate temperature and higher MLSS concentration operation, no significant deterioration of membrane flux was observed. Moreover, aeration intensity was lowered approximately to half capacity without indicative membrane fouling. Significant reduction in the concentrations of TSS, COD, and TP was achieved in the effluents of MBR, more than in CAS, highlighting the promising performance of MBR for the removal of solids, organic and inorganic pollutants. However, less efficient removal of TN inside MBR was noticed due to insufficient promotion of biological nitrification/denitrification. Almost 100% elimination of E. coli, enterococcus and human enteric viruses including noroviruses (GI and GII) and adenoviruses was achieved in MBR, which is a better performance than CAS alone. Furthermore, most of 26 tested TrOCs were better removed when the MBR was incorporate, in comparison with CAS. However, PFCs were not degraded easily during the treatment processes, probably due to their complex chemical structure. On the other hand, and for the case of MBR incorporation, the removal of heavy metals including Cr, Pb, Ni, Cu and Zn was 99.9% ± 0.01%, 95% ± 10%, 93% ± 3%, 91% ± 12% and 48% ± 22%, respectively. Thus, the heavy metals removal efficiencies achieved in the MBR system followed the sequence Cr>Pb>Ni>Cu>Zn.

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