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Removal of pharmaceuticals and organic matter from municipal wastewater using two-stage anaerobic fluidized membrane bioreactor

Kasturi Dutta [a], Ming-Yi Lee [a], Webber Wei-Po Lai [b], Chien Hsien Lee [c], Angela Yu-Chen Lin [b], Cheng-Fang Lin [b], Jih-Gaw Lin [a,*]

[a] Institute of Environmental Engineering, National Chiao Tung University, 1001 University Road, Hsinchu City 30010, Taiwan
[b] Graduate Institute of Environmental Engineering, National Taiwan University, Taiwan
[c] Sewer System Office, Construction and Planning Agency, Ministry of Interior, Room 403, No. 342, Sec. 2, Bade Rd., Songshan District, Taipei City 10556, Taiwan

HIGHLIGHTS

- Two-stage AFMBR was able to treat municipal wastewater at a minimum HRT of 1.28 h.
- COD and TSS removal efficiencies of 67% and 98%, respectively were achieved.
- 20 detected pharmaceuticals in municipal wastewater were effectively removed.
- GAC's scouring effect in AFMBR replaced any other membrane fouling control process.

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ABSTRACT

The aim of present study was to treat municipal wastewater in two-stage anaerobic fluidized membrane bioreactor (AFMBR) (anaerobic fluidized bed reactor (AFBR) followed by AFMBR) using granular activated carbon (GAC) as carrier medium in both stages. Approximately 95% COD removal efficiency could be obtained when the two-stage AFMBR was operated at total HRT of 5 h (2 h for AFBR and 3 h for AFMBR) and influent COD concentration of 250 mg/L. About 67% COD and 99% TSS removal efficiency could be achieved by the system treating the effluent from primary clarifier of municipal wastewater treatment plant, at HRT of 1.28 h and OLR of 5.65 kg COD/m^3 d. The system could also effectively remove twenty detected pharmaceuticals in raw wastewaters with removal efficiency in the range of 86–100% except for diclofenac (78%). No other membrane fouling control was required except scouring effect of GAC for flux of 16 LMH.

1. Introduction

With worldwide increasing pressures on existing water resources due to increase in human population and activity, reuse and conservation of water resources assumes a very high priority. Domestic wastewater is found to be a potential source of energy (McCarty et al., 2011). Anaerobic digestion of wastewater can produce methane gas, which can be used by methane-driven engine to generate electricity. Complete anaerobic treatment of domestic wastewater has the potential to achieve net energy production while meeting stringent effluent standards. An anaerobic fluidized bed reactor (AFBR) containing particulate media such as granular activated carbon (GAC) that is suspended in the reactor by the upward velocity of the fluid (with recirculation flow rate 1008 L/d) is widely used to treat low strength municipal wastewater (McCarty et al., 2011; Yoo et al., 2012). Wastewater treatment is effected by a biofilm attached to the media. The AFBR is particularly effective for low strength wastewaters as it has good mass transfer characteristics and can retain a high concentration of active microorganisms without organism washout at short detention times of minutes to a few hours. Damayanti et al. (2011) studied the effect of powdered active carbon (PAC), zeolite and Moringa oleifera on membrane fouling. They observed that at optimum dosage (8 g/L), PAC provided above 85% reduction in fouling rates during the short-term filtration and critical flux tests.

However, sometimes AFBR alone is not quite sufficient to meet stringent regulatory standards (McCarty et al., 2011) for effluent. Membrane bioreactor is found to be capable of producing high-quality effluent with small footprint and low suspended solids.

* Corresponding author. Tel.: +886 35722681; fax: +886 35725958.
E-mail address: jglin@mail.nctu.edu.tw (J.-G. Lin).

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Ho et al. (2007) studied the applicability of an anaerobic membrane bioreactor (AMBR) to treat low strength wastewater. High biological activity on the membrane surface caused high biofouling potential. Ho and Sung (2010) observed that the role of attached sludge on the membrane in AMBR as a biofilm for biological organic removal was minimal compared to suspended sludge. The main disadvantage of membrane bioreactor is high energy usage to reduce the fouling problem. Coupling of fluidized bed reactor with membrane reactor was found to potentially reduce the membrane energy cost (Kim et al., 2011). The use of carrier (GAC, PAC, Zeolite) in membrane reactor was reported to reduce fouling problem of membrane significantly (Ng et al., 2006). High removal efficiency >80% with production of biogas can be obtained by using the staged AFMBR. Initially the reactors are operated with synthetic wastewater containing mainly acetate, propionate and methanol (Kim et al., 2011). These substrates are easily degraded by methanogen bacteria and produce large amount of biogas. Kim et al. (2011) reported that fouling can be controlled if membranes are placed directly in contact with GAC in AFMBR. Energy recovery from that of the gaseous methane produced in the AFBR was sufficient to balance the energy requirement to operate whole system.

The occurrence of pharmaceuticals in aqueous environments has been documented in various studies because of their incomplete removal in municipal wastewater treatment (secondary treatment processes) and their potential risk to ecosystem and human health (Hirsch et al., 1999; Castiglioni et al., 2006; Lindberg et al., 2006; Gros et al., 2007). Lin et al. (2009) investigated 97 commonly used pharmaceuticals in the four Taiwanese wastewater treatment plants (WWTPs) and found that the significant amount of pharmaceuticals survived through the treatment processes and the removal efficiency varied greatly among the four WWTPs. Carballa et al. (2007b) demonstrated that 13 pharmaceuticals were removed to various degree in anaerobic digestion of sewage sludge collected from an sewage treatment plant (STP) in Spain. Pharmaceutical degradation in WWTPs was thought to depend greatly on the type of treatment units and operational parameters in the plants, as well as physicochemical properties of each individual target compounds.

In the present study the application of two-stage AFMBR system for treating the municipal wastewater at ambient temperature was investigated. The two-stage AFMBR system was started up with simulated municipal wastewater first and then fed with real municipal wastewater. Beside the evaluation of common effluent quality such as chemical oxygen demand (COD), soluble COD (sCOD), total suspended solids (TSS) and volatile suspended solids (VSS), the removal efficiencies of 20 commonly found pharmaceuticals observed in wastewater were also investigated.

2. Methods

2.1. Reactor design and set up

The schematic diagram of reactors AFBR-AFMBR (Firstek Scientific Co., Ltd.) is shown in Fig. 1. Both the reactors are identical in all aspects except membranes are installed in AFMBR. Reactors consisted of a glass tubular section of 40 mm internal diameter and 1000 mm height. Over this, an upper section of 180 mm internal

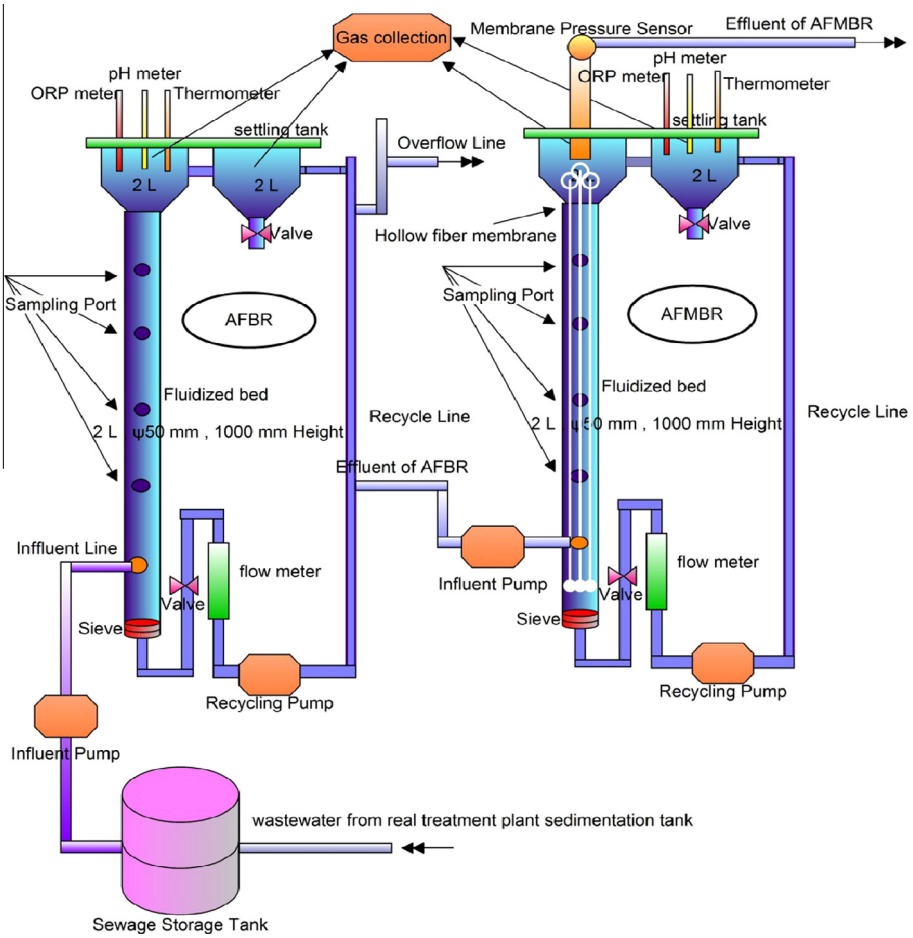

Fig. 1. Schematic diagram of AFBR-AFMBR.

diameter at the top with conical bottom and 200 mm length was mounted. Similar size settling tank with volume of 2 L, internal diameter of 180 mm and height of 200 mm was connected to the reactor to prevent the carryover of particulates to the recycle line. The sludge collected in the settler was recycled directly to the main reactor using silicone tubing. The column has five sampling ports located at 50, 250, 450 and 650 mm above the reactor bottom. Two reactors were connected with a silicon tube. A hollow fiber membrane module, consisting of twenty polyvinylidenefluoride (PVDF) membranes with 1.2 mm diameter, 105 cm long, pore size of <0.1 μm and total membrane surface area of 0.04 m^2 was installed inside the AFMBR. The effluent from AFBR delivered to AFMBR using peristaltic pump, which was automatically controlled to maintain constant water level in the reactor. The GAC used in this study was of 10–30 mesh size with specific surface area, bulk density and specific gravity of 500–1000 m^2/g, 0.85 and 2 g/cm^3, respectively. The AFBR and AFMBR were packed with GAC up to 25% and 50%, respectively and fluidized up to 50% and 100% of column height with upflow velocity of 91.7 and 116 m/h, respectively with the help of a magnetic pump for effluent recirculation. The two-stage AFMBR was operated under different modes with varying hydraulic retention time (HRT), influent COD, organic loading rate (OLR) and fluidization at ambient temperature.

2.2. Seed sludge and reactor operation strategy

A 400 mL of seed sludge (MLSS: 29,967 mg/L and MLVSS: 21,000 mg/L) from municipal wastewater treatment plant in Linkao Taiwan, was added to AFBR. The operating conditions for two-stage AFMBR system are presented in Table 1. The overall study was carried out in twelve different phases (phase I–XII). For first three phases (phase I–III, days 1–78), only first stage of the reactor system was operated under sequencing batch mode with intermittent feeding of simulated municipal wastewater (containing non-fat dry milk (NFDM): 830 mg/L, Na-acetate: 600 mg/L, yeast extract: 40 mg/L, KH_2PO_4: 44 mg/L, $KHCO_3$: 600 mg/L and NH_4Cl: 191 mg/L; with COD of about 1000 mg/L) for acclimation and biofilm formation (not shown in Table 1). After day 78 the reactor was operated under continuous mode with initial HRT of 8 h, influent COD concentration of 1000 mg/L and OLR of 3 kg/m^3 d. The AFMBR was connected with AFBR on day 160 (phase VI). The system was fed with effluent from primary clarifier from wastewater treatment plant located in Linkao from day 219 (phase VIII). The effluent from primary clarifier was collected, sieved through 10 μm filters before introducing in the AFBR and treated with different HRT and OLR.

2.3. Analytical methods

Total chemical oxygen demand (TCOD), soluble chemical oxygen demand (sCOD), 5 day Biological oxygen demand (BOD_5), Total suspended solids (TSS), Volatile suspended solids (VSS) and alkalinity of influent and effluent were measured twice or thrice per week according to the Standard Methods (APHA, 1998). Temperature, pH, and ORP were monitored online using probes installed inside the reactor system. Biogas production was measured daily from gas collection bag using a syringe.

2.4. Analysis of pharmaceuticals

2.4.1. Sample collection and pretreatment

The samples were collected from the influent of AFBR, effluent of AFBR and effluent of AFMBR in amber glass bottles and stored in ice-packed coolers. Four milliliters of 0.125 M EDTA-2Na were added to the bottles prior to sample collection. All the collected samples were filtered, then purified and concentrated by solid phase extraction (SPE). Detailed descriptions for sample preparation and SPE can be found in Supplementary Information, Text S1. The samples were then analyzed by liquid chromatography tandem mass spectrometry (LC–MS/MS).

2.4.2. LC–MS/MS Analysis

An Agilent 1200 module (Agilent Technologies, Palo Alto, CA, USA) coupled to a Sciex API 4000 quadrupole mass spectrometry (Applied Biosystems API 4000, Foster City, CA, USA) equipped with an electrospray ionization (ESI) interface was used. A binary gradient with a flow rate of 1.0 mL/min was used. The autosampler was operated at room temperature. Mass spectrometric measurements were carried out on a Sciex API 4000 (Applied Biosystems, Foster City, CA, USA) equipped with an ESI interface. Analyses were performed in positive mode for all pharmaceuticals except for ibuprofen, naproxen, ketoprofen and diclofenac, which were done in negative mode. Ions were acquired in multiple reaction monitoring (MRM) modes with a dwell time of 200 ms and unit mass resolution on both mass analyzers. Detailed descriptions for sample analysis can be found in Supplementary Text S1. The detailed LC

Table 1
Operating conditions for two-stage AFMBR.

Phase	Reactors	Influent COD (mg/L)	HRT (h)	Influent flow rate (L/h)	OLR (kg COD/m^3 d)	Upflow velocity (m/h)/expansion %
IV (79–92)	AFBR	1000	8	0.25	3	104 (67.7%)
V-1 (93–105)	AFBR	750	6	0.33	3	104 (67.7%)
V-2 (106–159)	AFBR	750	6	0.33	3	91.7 (50%)
VI (160–177)	AFBR	500	4	0.5	3	91.7 (50%)
	AFMBR	40–80	5.83	0.34	0.16–0.33	116 (100%)
VII (178–218)	AFBR	250	2	1	3	91.7 (50%)
	AFMBR	20–60	3	0.66	0.16–0.48	116 (100%)
Real sewage						
Phase	Days	Inf. COD (mg/L)	HRT (h)	Influent flow rate (L/h)	OLR (kg COD/m^3d)	Upflow velocity (m/h)/expansion %
VIII (219–246)	AFBR	38	1.55	1.29	0.58	91.7 (50%)
	AFMBR	25	2	1	0.3	116 (100%)
IX (247–257)	AFBR	70	1.55	1.29	1.08	91.7 (50%)
	AFMBR	25	2	1	0.3	116 (100%)
X (258–263)	AFBR	70	1.36	1.47	1.23	49 (40%)
	AFMBR	25	1.55	1.29	0.39	116 (100%)
XI (264–281)	AFBR	131.7	0.45	4.44	7	49 (40%)
	AFMBR	48.5	1.55	1.29	0.75	116 (100%)
XII (282–299)	AFBR	106	0.45	4.44	5.65	49 (40%)
	AFMBR	50	0.83	2.41	1.44	116 (100%)

gradients and mass spectrometer conditions of all pharmaceuticals and internal standards are described in Tables S1–S3.

Quantification was performed based on internal standard calibration using sulfamethazine-$^{13}C_6$, erythromycin-$^{13}C,d_3$, roxithromycin-d_7, ciprofloxacin-d_8, cephalexin-d_5 and ibuprofen-d_3. The linearity of calibration curves was estimated by fitting a linear mode, least-squares regression analysis ($y = a + bx$). The method detection limits (MDLs) were determined with the minimum concentration of analyte in the linear range with a signal-to noise ratio of $\geqslant$10:1. The recoveries, MDLs and linearity (regression coefficient) of investigated pharmaceuticals are shown in Table S4.

3. Results and discussion

3.1. Start-up of two-stage AFMBR using simulated municipal wastewater

The AFBR reactor operated under sequencing batch mode for initial 78 d (phase I–III). The reactor was fed with simulated municipal wastewater containing NFDM as main COD source. Fig. 2 shows the COD removal performance of AFBR in batch mode. The reactor performance was unstable in phase I (Fig. 2). The COD removal efficiency decreased and effluent COD concentration increased. At same time pH decreased below 6.5. It is well known that pH <6.5 inhibits the anaerobic microorganisms. To overcome this problem the duration of one batch was increased from 3 to 6 d in phase II. The COD removal efficiency recovered and reached about 95% at the end of phase II (Fig. 2). The duration of batch again reduced to 3 d in phase III, however the COD removal efficiency was maintained near to 95% (Fig. 2).

On day 79 (phase IV), the reactor operation mode was shifted from batch to continuous. The AFBR was operated from day 79 to 218 at different HRTs and influent COD concentrations (Table 1) with a constant OLR of 3 kg/m^3 d. The HRT of AFBR was shortened from 8 h (phase IV) to 2 h (phase VII) along with decrease in influent COD concentration from 1000 mg/L (phase IV) to 250 mg/L (phase VII) to simulate the real municipal wastewater. Fig. 3 shows the profiles of pH, temperature, ORP and alkalinity in AFBR during phase IV–VII. The ORP of the system was always maintained less than −400 mV, which confirmed the prevalence of anaerobic environment inside the reactor. The alkalinity of the system maintained about 1000 mg $CaCO_3$/L in phase V, but it reduced to about 800 mg $CaCO_3$/L in phase VII. The pH of the system maintained in between 7 and 7.5 throughout the operational period, which is favorable for anaerobic treatment. The temperature of the system varied from 20 to 25 °C during the reactor operation. It was reported that low temperature (<20 °C) can adversely affect the reactor performance with a decrease in COD removal efficiency for anaerobic treatment (Bergamo et al., 2009). The effluent COD decreased below 60 mg/L in phase VI and it was further lowered to 40 mg/L in phase VII as influent COD decreased from 500 to 250 mg/L, with COD removal efficiency more than 80%. The

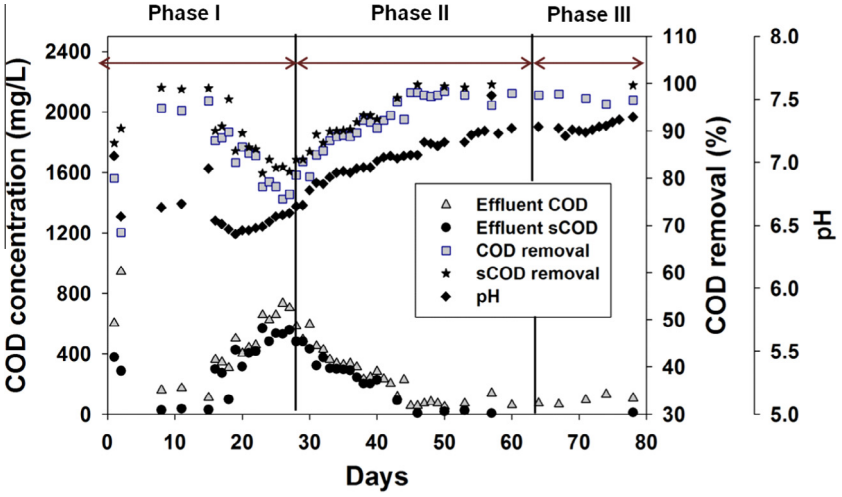

Fig. 2. COD removal performance of AFBR in batch mode.

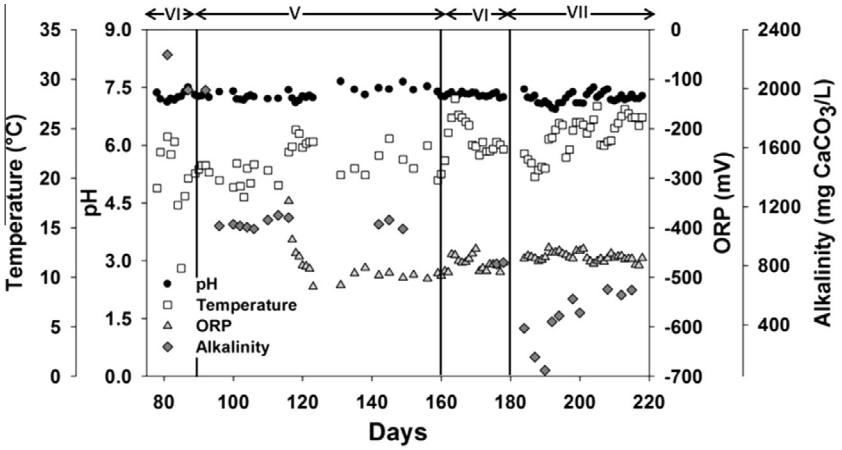

Fig. 3. Profiles of pH, temperature ORP and alkalinity of AFBR (phase VI–VII).

effluent sCOD concentration was also below 20 mg/L with removal efficiency of 95%. In the present study very low effluet COD (lower than aerobic system) can be achieved. In anaerobic CSTR, the minimum theoretically-achievable substrate concentration (S_{min}, the growth-equilibrium substrate concentration at which organism growth is just balanced by organism decay) can be very low (6.2 mg COD/L for acetate and 2.2 mg COD/L). Plug-flow operation can achieve effluent concentrations even lower than S_{min}. As AFBR operated in plugflow mode this can achieve such low effluent COD (Shin et al., 2012). The COD and sCOD removal efficiencies suggested that the AFBR reached steady state in phase VI and VII. The effluent TSS and VSS were found to be in the range of 8–25 mg/L and 6–20 mg/L, respectively. The change in fluidization level from 67% to 50% did not show any effect on COD removal performance of the reactor. Lower fluidization is preferred as it consumes less energy.

The AFMBR was connected to AFBR in phase VI on day 160. The effluent from AFBR was fed to AFMBR. The membrane flux in phase VI was 4.25 LMH (L/m^2 h) which was low. Therefore it was increased to 8.25 LMH in next phase (Fig. 4). The trans-membrane pressure (TMP) increased to 0.25 bar from day 184 to 188 in phase VII. This increase in TMP was possibly due to improper fluidization of GAC in AFMBR, which was rectified by adjusting the magnetic pump to increase the recirculation rate. This helped to run the reactor with a higher flux at 8.25 LMH and maintain a similar TMP of 0.15 bar (Fig. 4). The overall performance of two-stage AFMBR (in phase VII) treating simulated municipal wastewater is summarized in Table 2. The system could achieve high quality effluent with COD, sCOD, TSS and VSS concentration of 12.7, 11.5, 4 and 2.5 mg/L, respectively. The effluent TSS and VSS concentration was constantly below 10 mg/L. The biogas production was found to be 0.92 L/d (0.17 m^3/kg COD removed), which equivalent to 0.123 kWh of energy per m^3 of wastewater. The maximum energy required for operating the two-stage reactor system was calculated according to method described by Kim et al. (2011) and found to be 0.112 kWh/m^3 (Table S1). The results suggest that the energy required by the system can be met with the energy recovered from the wastewater treatment. The energy requirement can be further reduced by reduction of fluidization in AFBR.

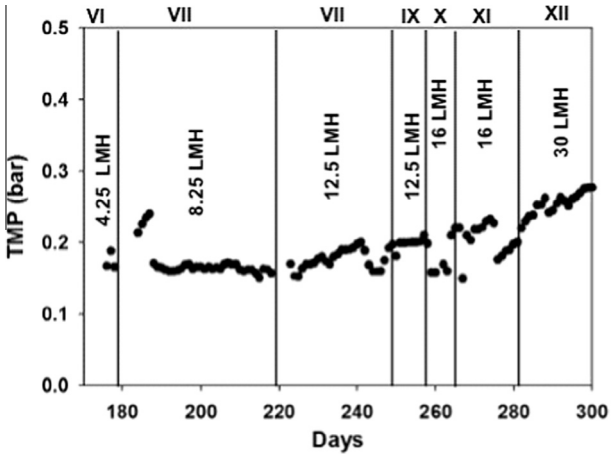

Fig. 4. Profiles of TMP in AFMBR.

3.2. Treatment of real sewage by two-stage AFMBR system

3.2.1. Removal of organics and solids

From day 219 onwards, the two-stage AFMBR was started to feed with real municipal wastewater. The total HRT of the reactor system further decreased gradually from 5 to 3.55, 2.91 and 2 up to 1.28 h in different phases. The details of reactor operating conditions are shown in Table 1. The overall reactor performance at different phases is shown in Table 3. The COD concentration of the influent varies from 38 to 132 mg/L at different phases (phase VIII–XII). The COD removal varied from 67% (phase XII) to 84.6% (phase XI). The low COD and sCOD removals at phase XII might be due to very low HRT (1.28 h) of the system. However, the effluent quality was still within the acceptable range with effluent COD and sCOD concentrations of 35 and 21 mg/L, respectively. The second stage of the reactor system AFMBR was reported to be a good polishing system as a post-treatment of anaerobic treatment system (Kim et al., 2011). In this study also, the AFMBR could produce high quality effluent. At low influent COD concentration the removal efficiencies of COD and sCOD were higher in AFMBR than AFBR (Table 3). The COD and sCOD removal efficiencies in AFMBR were found to be 28–60% and 30–52%, respectively. It was also observed that inspite of continuous decrease in HRT the reactor was stably maintained (Table 3). The gas production was not observed in these stages. This could be attributed to the presence of sulfate in wastewater (Table 3, measured in phase IX and X). The sulfate reducing bacteria compete with the methanogens, therefore when sulfate present in the influent wastewater the COD utilized by sulfate reducing bacteria rather than methanogens. As a result no/very less gas production could be observed (Shayegan et al., 2005; O'Reilly and Colleran, 2006).

The first stage of the reactor system, AFBR was able to remove most of the TSS and VSS from the wastewater. The removals of TSS and VSS by AFBR were 40–90% and 66–90%, respectively in different phases of operation. In previous reports no TSS and VSS removals could be observed by AFBR (Kim et al., 2011; Yoo et al., 2012). The high removal efficiency of AFBR could help to reduce the load in AFMBR, thus increase the durability of the membrane. The rest of the TSS and VSS were removed in AFMBR and the concentrations were reduced close to zero. In some phases the TSS and VSS concentration in the effluent was higher than zero. This may be due to same reason as described in the earlier section, which is the contamination of the effluent upon a long storage period.

Table 2
Performance of two-stage AFMBR in phase VII.

Parameter[a]	Influent	Effluent		Removal efficiency (%)		
		AFBR	AFMBR	AFBR	AFMBR	Overall
TCOD	240.0 ± 9.5	33.4 ± 15.1	12.7 ± 5.7	86.08	61.98	94.71
SCOD	215.5 ± 16.4	16.23 ± 4.7	11.5 ± 4.8	92.47	29.14	94.66
TSS	13	8	4	38.46	50	69
VSS	11	6	2.5	45.45	58.33	77
pH	7.3	7.23	7.1	–	–	–
Alk. as $CaCO_3$	422	446	426	–	–	–
Methane production[b]	0.92					

[a] Expressed in mg/L except pH.
[b] Expressed in L/d.

Table 3
Performance of two-stage AFMBR treating real sewage.

Parameter[a]	Influent	Effluent		Removal efficiency (%)		
		AFBR	AFMBR	AFBR	AFMBR	Overall
Phase VIII (219–246) total HRT: 3.55 h						
TCOD	38 ± 5.6	21 ± 6	10	44.7	52	74
SCOD	32 ± 2.8	16.6 ± 2.3	8 ± 2.8	48.12	52	75
TSS	7.5 ± 5	0.8	0.5	89	37.5	93.3
VSS	5.6 ± 4	0.8	0.5	86	37.5	91
pH		6.79	6.4			
Alk. as $CaCO_3$	100	117	127			
Phase IX (247–257) total HRT: 3.55 h						
TCOD	53 ± 30	29 ± 14	10 ± 0.4	45	65.5	81
SCOD	26 ± 16	20 ± 9	10 ± 0.8	23	50	61
BOD_5	17 ± 15	9.5 ± 0.7	0	44	100	100
TSS	8 ± 9	2.7 ± 1.5	0.7 ± 0.2	66.3	81.5	93.8
VSS	7 ± 7.7	2.3 ± 1.4	0.5 ± 0.3			
pH		6.64	6.4			
Alk. as $CaCO_3$						
Sulfate	45 ± 22	25 ± 15	21 ± 15			
Phase X (258–263) total HRT: 2.91 h						
TCOD	70	40.6	17	42	58	75
SCOD						
BOD_5	18	8	0	55.5	100	100
TSS	6.4 ± 1.13	3.8 ± 0.3	0	40.6	100	100
VSS	2.8 ± 0.6	0.6 ± 0.3	0	78.6	100	100
pH		6.7	6.4			
Alk. as $CaCO_3$	189 ± 8.8	167.5	126 ± 16			
Sulfate	43.7	42.2	35			
Phase XI (264–281) total HRT: 2 h						
TCOD	132 ± 75	52 ± 12.5	20.3 ± 5	60.6	61	84.6
SCOD						
BOD_5						
TSS	26.8 ± 18.7	5.5 ± 3.2	3.7 ± 2.6	79.5	32.7	86.2
VSS	19 ± 14.5	3 ± 1.3	1.53 ± 1.1	84.2	49	92
pH		6.8	6.5			
Alk. as $CaCO_3$	212.5 ± 13.4	205 ± 92	182.5 ± 12			
Phase XII (282–299) total HRT: 1.28 h						
TCOD	106 ± 33	49 ± 22	35 ± 10	54	28.6	67
SCOD	44 ± 10	30 ± 12	21 ± 13	32	30	52
TSS	35 ± 43	3.24 ± 1.25	0.6	91	81	98
VSS	29 ± 34	3 ± 1.3	0.3	90	90	99
pH		6.76	6.2			
Alk. as $CaCO_3$	169 ± 21	173 ± 73	191 ± 94			

[a] Expressed in mg/L except pH.

3.2.2. Effect of flux increase on AFMBR performance

In the present study the AFMBR (treating real municipal wastewater) was operated at different fluxes starting from 12.5 to 30 LMH which is the highest limit of the membrane flux. The corresponding OLR was varied from 0.3 to 1.44 kg/m^3 d. The AFMBR operated for total 139 days (59 days treating synthetic wastewater and rest 80 days treating real municipal wastewater). During the operation of AFMBR the membrane cleaning was obtained only by scouring effect of GAC, and no other physical or chemical methods were employed. Sometimes the longer operational period raised the TMP a little (from 0.15 to 0.2 bar), which could be brought down to previous value by relaxing the membrane for 1–2 h (Fig. 4). Therefore membrane relaxing was carried out at regular intervals and at the end of each phase. However, a continuous increase in TMP indicative of membrane fouling was observed during phase XII in which the membrane flux was maintained at its highest limit i.e. 30 LMH. At such high flux either the scouring effect of GAC may not be sufficient for membrane fouling control, or more regular membrane relaxing is required. The increase in OLR from 0.3 to 1.44 kg/m^3 d (phase VIII to phase XII) which was another possible reason for increase in TMP and higher fouling rate. Previously, Yoo et al. (2012) reported that the increase of flux to 14 LMH sharply increased the TMP. Instead of this TMP increase in phase XII the reactor performance was not much affected (Table 3). The maximum sustainable flux for the AFMBR system could not be detected as the flux was increased from 16 to 30 LMH. Further study needs to be carried out at different fluxes in between 16 and 30 LMH to find out the maximum sustainable flux for the system. However, the reactor performance was stable at 16 LMH, which is higher than the sustainable fluxes reported by others (9–10 LMH) (Berube et al., 2006; Vyrides and Stuckey, 2009; Huang et al., 2011; Martinez-Sosa et al., 2011; Yoo et al., 2012).

3.2.3. Occurrence and removals of pharmaceuticals

The occurrence of 26 commonly found pharmaceuticals in the influent (real municipal wastewater and effluent of the two-stage AFMBR and the overall reactor performance at different stages is shown in Table 4. Twenty target pharmaceuticals from various classes were detected in the influent; majority of the compounds were found to occur at the ng/L level with four drugs reached μg/L concentrations, including caffeine (3470 ng/L), cephalexin (2905 ng/L), acetaminophen (2695 ng/L) and ibuprofen (2500 ng/L). Results demonstrated that all target pharmaceuticals were largely removed in the two-stage AFMBR system and the removal efficiencies were higher in AFMBR than that of AFBR. Table 4 indicates that these pharmaceuticals were partly removed in the first stage (AFBR), and subsequently the second stage (AFMBR) was used for further polishing to remove the refractory compound residues. Biodegradation, sorption onto the GAC in the first and

Table 4
Removal of 26 pharmaceuticals in the AFBR-AFMBR system.

Pharmaceuticals	MDLs (ng/L)	Influent (ng/L)	Effluent (ng/L)		Removal efficiency (%)		
			AFBR	AFMBR	AFBR	AFMBR	Overall
Sulfonamide antibiotics							
Sulfadiazine	0.1	18.9 ± 2.1	11.4 ± 1.2	1.2 ± 0.1	39.7	89.5	93.7
Sulfamethoxazole	0.1	312 ± 34.6	201 ± 19.8	34.1 ± 2.9	35.5	83.0	89.1
Sulfathiazole	0.5	ND	ND	ND	–	–	–
Sulfamethazine	0.1	ND	ND	ND	–	–	–
Macrolides antibiotics							
Erythromycin-H_2O	0.1	319 ± 42.4	132 ± 19.1	43.9 ± 2.1	58.7	66.7	86.3
Clarithromycin	0.5	324 ± 6.4	140 ± 4.9	35.5 ± 2.1	56.9	74.6	89.0
Josamycin	0.5	ND	ND	ND	–	–	–
Roxithromycin	0.5	ND	ND	ND	–	–	–
Tylosin	1.0	ND	ND	ND	–	–	–
Quinolone antibiotics							
Nalidixic acid	0.25	5.7 ± 0.5	1.1 ± 0.3	ND	80.7	100	100
Flumequine	0.5	0.9 ± 0.0	0.9 ± 0.4	ND	0	100	100
Pipemidic acid	0.5	112 ± 0.7	5.9 ± 1.1	ND	94.5	100	100
Norfloxacin	0.5	ND	ND	ND	–	–	–
Ciprofloxacin	0.5	157 ± 20.5	16.6 ± 2.8	ND	89.4	100	100
Ofloxacin	0.5	417 ± 84.1	23.3 ± 0.8	1.1 ± 0.2	94.4	95.3	100
Cephalosporins antibiotics							
Cephalexin	0.5	2905 ± 530	884 ± 78.5	121 ± 9.9	69.6	86.3	95.8
Cephradine	0.5	51.2 ± 6.0	24.2 ± 1.1	3.3 ± 0.3	52.7	86.4	93.6
Other antibiotics							
Trimethoprim	0.1	15.9 ± 3.6	2.0 ± 0.3	ND	87.42	100	100
Psychiatric drugs							
Carbamazepine	0.1	24.8 ± 4.5	6.7 ± 0.2	0.9 ± 0.0	73.0	86.6	96.4
Psychostimulants							
Caffeine	0.1	3470 ± 56.6	460 ± 2.8	55.4 ± 4.1	86.7	88.0	98.4
Vasodilators							
Pentoxifylline	0.25	11.7 ± 1.1	1.5 ± 0.3	ND	87.2	100	100
NSAIDs							
Acetaminophen	0.1	2695 ± 21.2	330 ± 14.8	6.9 ± 0.2	87.8	97.9	100
Ibuprofen	5	2500 ± 127.3	1155 ± 21.2	228 ± 16.3	53.8	80.3	90.9
Naproxen	5	432 ± 6.4	96.0 ± 3.7	15.7 ± 1.8	77.8	83.7	96.4
Ketoprofen	5	30.4 ± 4.5	8.0 ± 0.4	ND	73.7	100	100
Diclofenac	1	57.8 ± 2.5	39.7 ± 2.2	12.6 ± 0.7	31.3	68.3	78.2

ND: not detected.

second stage may be involved in removing these pharmaceuticals to certain degree, and membrane filtration in the AFMBR is very likely to play a significant role in further polishing (Kim et al., 2011). However, future investigation to understand the detail removal mechanisms for each and specific pharmaceuticals are necessary. Despite the fact that caffeine, cephalexin and ibuprofen occurred at high concentration in the untreated wastewaters, similar to other wastewater treatment processes, they are mostly (>90%) removed. Nine compounds (nalidixic acid, flumequine, pipemidic acid, ciprofloxacin, ofloxacin, trimethoprim, pentoxifylline, acetaminophen and ketoprofen) were removed below detection limits while rest of the compounds has removal efficiency close to 90% except for that of diclofenac (78% removed). Previous work have also demonstrated the persistence of diclofenac through anaerobic digestion process; the reported removal were 0–69% (Carballa et al., 2007b; Lahti and Oikari, 2011). In addition, Kim et al. (2007) observed no degradation of diclofenac through a membrane bioreactor system.

Compared to the secondary wastewater treatment processes, this two-stage AFMBR system demonstrated a significant better removal for many groups of compounds. For example, carbamazepine and trimethoprim were known to survive through most of the secondary wastewater treatment (Ternes, 1998; Castiglioni et al., 2006; Carballa et al., 2007a; Lin et al., 2009); however, they were effectively removed in this work. Macrolide, quinolone and sulfonamide antibiotics have shown to have a wide range of treatment efficiencies in secondary wastewater treatment processes while they are 86–100% removed in this work. Karthikeyan and Meyer (2006) indicated 44–100% removal of erythromycin-H_2O in WWTPs. Lin et al. (2009) documented 0–56% and 0–99% for erythromycin-H_2O and clarithromycin, respectively; similarly, quinolones were 11–80% removed in four WWTPs in Taiwan. Many other works again showed lower and disparity in sulfonamide antibiotics removal (20–82%) (Ghosh et al., 2009; Lin et al., 2009; Radjenovic et al., 2009).

4. Conclusion

The two-stage AFMBR system employed for treating primary effluent of municipal wastewater at HRT of 1.28 h and OLR of 5.65, was able to produce an effluent with COD of 10 mg/L and BOD_5, TSS and VSS near to zero. In addition, this system demonstrated its effectiveness for removing various groups of commonly detected pharmaceuticals with removal efficiencies more than 90%. Biological processes, sorption onto the GAC and membrane filtration could each play a role in removing these pharmaceuticals. The scouring effect of GAC fluidization in AFMBR successfully replaced the need of any other membrane fouling control process.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biortech.2014.03.054.

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