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Long-term operation of a pilot scale anaerobic membrane bioreactor (AnMBR) for the treatment of municipal wastewater under psychrophilic conditions

J. Gouveia [a], F. Plaza [b], G. Garralon [b], F. Fdz-Polanco [a], M. Peña [a,*]

[a] Department of Chemical Engineering and Environmental Technology, School of Industrial Engineering, Dr. Mergelina s/n, 47011, University of Valladolid, Valladolid, Spain
[b] CADAGUA. Gran via 45, Bilbao, Spain

HIGHLIGHTS

- Viability of AnMBR at psychrophilic conditions for treating municipal wastewater.
- Effluent with high quality (100–120 mg O_2/L) at HRT of 7 h.
- The membrane permits the biodegradation of slowly biodegradable matter.
- SMY depends on the recirculation between the membrane module and the UASB reactor.
- Long-term reliability and operability of the AnMBR technology.

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ABSTRACT

The performance of a pilot scale anaerobic membrane bioreactor (AnMBR), comprising an upflow anaerobic sludge blanket (UASB) reactor coupled to an external ultrafiltration membrane treating municipal wastewater at 18 ± 2 °C, was evaluated over three years of stable operation. The reactor was inoculated with a mesophilic inoculum without acclimation. The AnMBR supported a tCOD removal efficiency of 87 ± 1% at hydraulic retention time (HRT) of 7 h, operating at a volumetric loading rate (VLR) of between 2 and 2.5 kg tCOD/m^3 d, reaching effluent tCOD concentrations of 100–120 mg/L and BOD_5 concentrations of 35–50 mg O_2/L. Specific methane yield varied from 0.18 to 0.23 Nm^3 CH_4/kg $COD_{removed}$ depending on the recirculation between the membrane module and the UASB reactor. The permeate flow rate, using cycles of 15 s backwash, 7.5 min filtration, and continuous biogas sparging (40–60 m/h), ranged from 10 to 14 Lm^2/h with trans-membrane pressure (TMP) values of 400–550 mbar.

1. Introduction

Municipal wastewater is the most common type of wastewater, characterized by low organic strength and high particulate organic matter content (Ozgun et al., 2013a). The activated sludge process is the most widely used to treat this wastewater (Rittmann and McCarty, 2001; Metcalf and Eddy, 2003). However, this treatment presents some clear disadvantages when compared to anaerobic treatment, such as its high cost of aeration and the generation of large amounts of residual sludge. Thus, the main conceptual limitation of the activated sludge process is the high biomass yield that implies the use of energy (O_2) to transform biodegradable dissolved or suspended organic matter into settleable microorganisms that are often partially converted into biogas using anaerobic digestion.

In contrast, anaerobic processes, which are widely used for industrial wastewater treatment, have clear advantages such as a significantly lower generation of excess sludge and the conversion of organic matter into valuable biogas without energy consumption (Baek and Pagilla, 2006; Lin et al., 2013; Smith et al., 2012; van Lier et al., 2001). Therefore, the anaerobic process could be an attractive treatment for municipal wastewater in order to reduce sludge production and to optimize energy use. Nevertheless, the advantages of anaerobic treatment are not clear in the case of municipal wastewater, especially in cold weather (Baek and Pagilla, 2006; van Lier et al., 2001). Anaerobic processes strongly depend on operational temperature and therefore the heating of the large volume of municipal wastewater makes

* Corresponding author.
E-mail addresses: jgouveia@iq.uva.es (J. Gouveia), ggl@cadagua.es (G. Garralon), ffp@iq.uva.es (F. Fdz-Polanco), pena@iq.uva.es (M. Peña).

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mesophilic anaerobic treatment economically unviable in cold or temperate countries. There are numerous examples of Upflow Anaerobic Sludge Blanket (UASB) reactor treating municipal wastewater in tropical countries, and the results obtained showed the feasibility of this system at an ambient temperature of around 20–35 °C (Chernicharo and Machado, 1998; Wiegant, 2001). The low strength of municipal wastewater, together with the slow growth rate of methanogens at temperatures of below 20 °C, would entail high reactor volume as a result of the high residence times to avoid cell washout (Baek and Pagilla, 2006; Lin et al., 2013; Smith et al., 2012; van Lier et al., 2001). In addition, the hydrolysis of particulate matter into dissolved molecules becomes the rate-limiting step, which results in the accumulation of suspended solids (SS) in the reactor, and a decrease in both organic matter conversion efficiency and methanogenic activity (Lettinga et al., 2001; Martinez-Sosa et al., 2011). Conventional anaerobic technologies such as UASB and the expended granule sludge blanket (EGSB), based on biofilms or granules with good settling characteristics are adequate for retaining the biomass inside the reactor during the treatment of high strength wastewater under mesophilic conditions. However, when operating at temperatures in the psychrophilic range, these technologies are not sufficient to maintain the high concentration of active biomass, which is the compulsory condition required for the treatment of low strength wastewaters. In this context, the success of the anaerobic technology for municipal wastewater at low temperature depends on the complete separation of HRT and solid retention time (SRT) (Ho and Sung, 2010). The use of micro or ultrafiltration membranes allows the biomass to be completely retained, irrespective of their settling characteristics. Hence, membrane technology combined with anaerobic biological processes, known as the anaerobic membrane bioreactor (AnMBR), seems in theory to offer very attractive possibilities for the treatment of municipal wastewater at psychrophilic temperature (Ozgun et al., 2013a; Smith et al., 2013). Nevertheless, there are still critical technical–economic limitations that hinder the widespread implementation of AnMBRs, such as low operational fluxes, rapid membrane fouling and their high capital and operational costs (Kocadagistan and Topcu, 2007; Ozgun et al., 2013a). Fortunately, membrane acquisition and/or replacement costs have decreased significantly over the past decade due to a decline in membrane module costs (Santos et al., 2011). However, despite the aforementioned constraints, AnMBR has been identified as a key technology for the treatment of municipal wastewater, whose treatment performance is seemingly dependent on the chosen process configuration (Liao et al., 2006). To date, completely stirred tank anaerobic reactors (CSTR), UASB reactors and EGSB reactors have been investigated in combination with micro and ultrafiltration membranes. However, the optimal process configuration, i.e. anaerobic bioreactor type and the coupling of the bioreactor with the membrane module, needs to be determined. In this context, despite several studies having been conducted to date on municipal sewage treatment in anaerobic membrane reactors, the number of long-term studies carried out under psychrophilic conditions on a pilot scale is scarce (Lin et al., 2013; Ozgun et al., 2013a; Shin et al., 2014).

The aim of this work was to experimentally assess the long term feasibility of the treatment of municipal wastewater under psychrophilic conditions (18 ± 2 °C) in a pilot scale AnMBR consisting of an UASB reactor coupled with an ultrafiltration membrane unit. The operability of the membrane, the influence of the HRT, the volumetric loading rate (VLR), the effect of the membrane on the treatment of municipal wastewater and the recirculation rate between UASB and the membrane module on the effluent quality was investigated.

2. Methods

2.1. Pilot plant configuration

Fig. 1 shows the experimental pilot plant set up. The pilot plant consisted of a rotatory sieve (defender TR-40/25 Toro Wastewater Equipment Industries), a circular primary settler (with a total volume of 25 L and HRT between 1 and 3 h) followed by a UASB reactor coupled to an external submerged membrane module. The volume of the UASB was 160 L and the volume of the membrane unit 150 L. Both modules were equipped with biogas, temperature and pressure meters. Both the UASB reactor and membrane module were operated at T = 18 ± 2 °C. The characteristics of the tubular ultrafiltration membrane module (ZW-10 Zenon, GE) were as follows: mean pore size 0.045 μm and filtration area 0.93 m^2. The settler, the UASB reactor and the membrane module were placed in a room provided with an air-conditioning system, in order to maintain the temperature of the UASB reactor at 18 °C during both winter and summer time.

To control membrane fouling and to maintain the trans-membrane pressure (TMP), biogas sparging, relaxation time and permeate back-flush were used. In the first period (day 1–328), the standard operation cycle was fixed at 1 min back-flush, 5 s of relaxation time, and 30 min filtration followed by 5 s of relaxation time. During the second period (day 329–1371), the cycle was reduced to 15 s back-flush, 5 s of relaxation time, 7.5 min filtration, and 5 s of relaxation time. The biogas was continuously sparged through a coarse bubble diffuser located at the bottom of the hollow fibers, with a superficial velocity of 25 m/h in period I and of

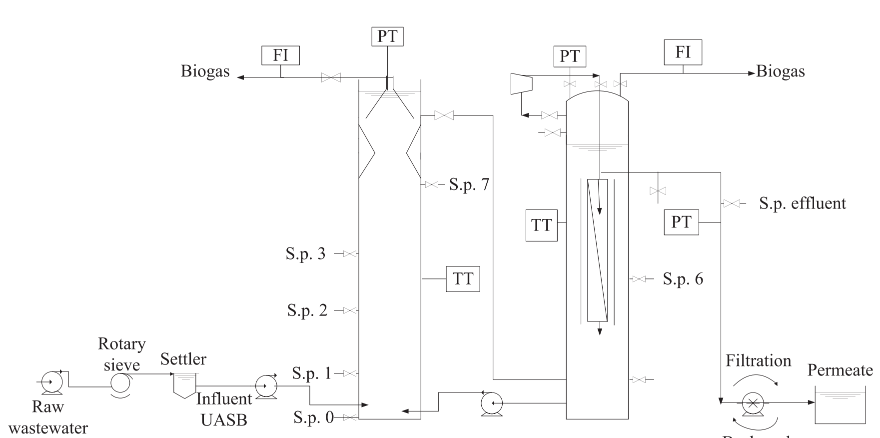

Fig. 1. AnMBR pilot plant flow scheme (FI – flow-rate indicator; PT – pressure transmit; TT – temperature transmit; S.p. – sampling point).

40–60 m/h during period II. Temperature and pressure filtration were stored online using data acquisition technology.

The effluent of the UASB reactor was conducted by gravity to the bottom of the membrane module. The system was operated with different recirculation flow rates from the membrane module to the UASB reactor (day 1–1014) in order to ensure good contact between the biomass and the wastewater, to control the concentration of solids in the effluent of the UASB and to minimize solid concentration in the membrane module. The superficial velocity in the UASB was maintained between 0.15 and 0.45 m/h. From day 1015–1371, the AnMBR was operated without recirculation from the membrane module to the UASB reactor and the superficial velocity in the UASB was maintained at 0.2–0.3 m/h.

2.2. Inoculum and feed wastewater

The UASB reactor was inoculated with 60 L of sludge from a mesophilic (35 °C) anaerobic sludge pilot digester without previous acclimatization to psychrophilic conditions. The initial concentration of sludge in the UASB was around 10 g/L of TSS (total suspended solid). After ten months of operation, the reactor was reinoculated with 43 L of non-acclimated sludge from a mesophilic digester (flocculent sludge) of the wastewater treatment plant (WWTP) of Valladolid with 51.4 g TSS/L. The pilot plant was continuously fed with the raw municipal wastewater from the city of Valladolid drawn from a nearby sewer.

2.3. Chemical assays and sampling

Liquid samples were taken twice a week from each of the elements of the plant to monitor the process performance, sampling points (S.p.) 0, 1, 2, 3, 7, 6 and effluent, as shown in Fig. 1. Alkalinity, tCOD, sCOD, total solids (TS), volatile solids (VS), total suspended solids (TSS), volatile suspended solids (VSS), biological oxygen demand (BOD_5), total nitrogen (N-TKN) and ammonia nitrogen ($N\text{-}NH_4^+$) were determined according to the Standard methods for examination of water and wastewater (APHA et al., 2005). sCOD was determined following sample filtration through 0.45 μm. The concentrations of volatile fatty acids (VFAs) were determined by gas chromatography using Agilent 7820A GC-FID equipped with a G4513A autosampler and a Chromosorb WAW packed column (2 m × 1/8″ × 2.1 mm SS) (10% SP 1000, 1% H_3PO_4, WAW 100/120) (Teknokroma, Spain). The injector, oven and detector temperatures were 375 °C, 130 °C and 350 °C, respectively. N_2 was used as the carrier gas at 45 mL min^{-1}. Nitrate nitrogen (NO_3^--N), nitrite nitrogen (NO_2^--N), chloride (Cl^-), sulfate (SO_4^{2-}) and soluble phosphorus ($P\text{-}PO_4^{3-}$) concentrations were analyzed by HPLC–IC using a Waters 515 HPLC pump (Waters, Milford, USA), coupled with an ion conductivity detector (Waters 432, Milford, USA), and equipped with an IC-Pak Anion Guard-Pak column (Waters, Milford, USA), and an IC-Pak Anion HC (150 mm × 4.6 mm) column (Waters, Milford, USA). Biogas composition was analyzed using a gas chromatograph (Varian CP-3800, Palo Alto, CA, USA) coupled with a thermal conductivity detector and equipped with a CP-Molsieve 5A (15 m × 0.53 mm × 15 μm) and a CP-Pora BOND Q (25 m × 0.53 mm × 15 μm) columns. The injector, oven and detector temperatures were 150 °C, 40 °C and 175 °C, respectively. Helium was used as the carrier gas at 13.7 mL/min.

2.4. Biochemical methane potential assay

Biochemical methane potential (BMP) tests were carried out in triplicate to assess the biodegradability of the accumulated material in the membrane module. The BMP tests were conducted directly using the suspension from the membrane module, with the concentrated sludge obtained after centrifuging the suspension at 10,000 rpm for 10 min, and the supernatant obtained. A control test without substrate was included. All the experiments were carried out under mesophilic conditions in a thermostatic room (35.1 ± 0.3 °C) and were subjected to continuous agitation in an orbital shaker. The anaerobic inoculum used was obtained from a pilot sludge digester and pre-incubated for two days (35.1 ± 0.3 °C) in order to minimize its residual biodegradable organic matter content. Serum bottles of 120 mL volume were used in the BMP tests, with a reaction volume of 60 mL in order to have enough headspace for biogas accumulation. The substrate/inoculum ratio selected was 0.4 g VS/g VS. The pH of the substrate/inoculum mixture was measured to ensure optimum biological activity and the bottles were gassed with He and sealed immediately using rubber septa and aluminum crimp caps. Biogas production was estimated by measuring the pressure in the headspace of the bottles and the biogas composition. The specific methane yield (SMY), mL CH_4/g VS_{fed} was calculated by dividing the methane production associated with the substrate (after having subtracted the production due to inoculum) by the quantity of volatile solids of substrate at the beginning of the test. The theoretical methane production was calculated assuming that 350 L of methane was generated per kg of COD removed.

3. Results and discussion

The UASB reactor was continuously fed with municipal wastewater after pre-treatment in a rotary sieve (1 mm mesh) and primary sedimentation. The main wastewater characteristics fed to the UASB reactor are listed in Table 1. There is a significant variation in the tCOD of the municipal wastewater during the entire period of operation. The particulate COD fed to the UASB reactor represented around 30–46% of the tCOD. Ammonium nitrogen and phosphate concentrations in the influent were 71 ± 14 and 10 ± 2 mg/L, respectively.

3.1. Removal efficiency of COD

The AnMBR was operated by gradually increasing the VLR via a decrease in the HRT of the UASB reactor. Fig. 2 shows the removal efficiencies of tCOD, VLR (calculated considering only the volume of the UASB reactor) and tCOD of the influent and effluent of the AnMBR. Table 2 summarizes the steady state results obtained for the different HRTs tested. The HRT varied between 17 and 11 h during the period with recirculation and between 13 and 7 h during the period without recirculation. The results showed that, the total removal efficiency was similar regardless of the HRT and VLR tested, probably due to the presence of the membrane. The total removal efficiency obtained was higher than 80%, with tCOD values in the effluent ranging from 110 to 125 mg O_2/L in both periods. During the period with recirculation, the HRT was decreased to 11 h. Under this operational condition and with a

Table 1
Presettled wastewater characteristics fed to the UASB reactor (average values).

Parameter	Influent (mg/L)
tCOD	892 ± 271
sCOD	501 ± 165
$tBOD_5$	573 ± 233
$sBOD_5$	335 ± 31
TSS	123 ± 35
VSS	110 ± 30
N-TKN	92 ± 12
$N\text{-}NH_4^+$	71 ± 14
$P\text{-}PO_4$	10 ± 2
SO_4^{2-}	47 ± 25

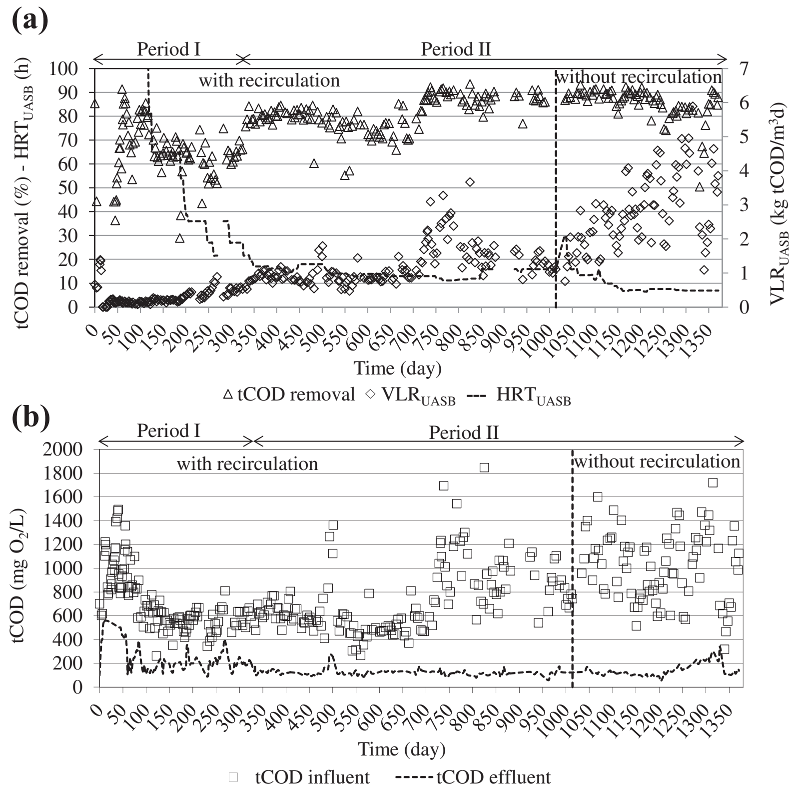

Fig. 2. (a) Evolution of tCOD removal efficiency of the AnMBR, VLR and HRT of UASB reactor. (b) Evolution of tCOD in the influent and effluent of AnMBR during the entire period of operation.

Table 2
Principal parameters of operation of AnMBR, (average values).

Time (d)	HRT_{UASB} (h)	VLR ($gCOD/L_{UASB}$ d)	F/M ($gCOD/gVS_{UASB}$ d)	tCOD effluent (mg/L)	BOD_5 effluent (mg/L)	Biogas (L/d)	Total removal efficiency % tCOD
353–381(*)	17.1	0.95 ± 0.09	0.065 ± 0.013	138 ± 11.3	52.5 ± 9.8	29.5 ± 4.6	79.7 ± 1.9
384–416(*)	16.1	0.91 ± 0.13	0.086 ± 0.008	119 ± 10.7	30.3 ± 4.2	29 ± 4.8	80.9 ± 2.5
517–553(*)	14.1	0.81 ± 0.18	0.089 ± 0.007	114 ± 15.2	34 ± 3	23.1 ± 3.3	75.1 ± 7.4
557–584(*)	13.2	0.84 ± 0.28	0.085 ± 0.010	111 ± 16.6	33 ± 1	18.6 ± 4.7	74.2 ± 7.9
620–720(*)	13.0	0.98 ± 0.21	0.083 ± 0.010	132 ± 12.7	47.1 ± 3.3	22 ± 8.7	76 ± 5.2
720–748(*)	13.0	1.91 ± 0.51	0.146 ± 0.046	121 ± 20.5	47 ± 9.5	69.1 ± 14	88.5 ± 2.7
766–789(*)	11.2	2.61 ± 0.39	0.173 ± 0.016	121 ± 12.9	36 ± 5.7	127.6 ± 46	90.1 ± 1.2
1063–1095(–)	13.4	2.00 ± 0.43	0.127 ± 0.026	115 ± 13.3	43.7 ± 5.1	83.4 ± 17.4	89.5 ± 1.8
1109–1137(–)	10.0	2.73 ± 0.19	0.157 ± 0.057	117 ± 6.6	39.8 ± 7.9	91.5 ± 18.6	89.8 ± 1.2
1216–1273(–)	7.6	3.20 ± 0.90	0.38 ± 0.136	160 ± 22.3	64.1 ± 12.9	90.8 ± 10.5	82.9 ± 4.8
1298–1327(–)	7.0	4.70 ± 0.62	0.322 ± 0.079	226 ± 13.5	122 ± 1.4	85.7 ± 12.4	82.6 ± 1
1328–1354(–)	7.0	2.2 ± 0.85	0.261 ± 0.140	122 ± 36	42 ± 11.5	59.8 ± 14.9	72.9 ± 7.8
1355–1371(–)	7.0	3.94 ± 0.45	0.206 ± 0.085	140 ± 7.4	46 ± 16.7	63.8 ± 15.7	88.6 ± 2.2

(*) with recirculation, (–) without recirculation.

VLR of 2.61 kg $tCOD/m^3$ d, a tCOD removal efficiency of 90.1 ± 1.2%, an effluent tCOD of 121 ± 12.9 mg O_2/L and an effluent BOD_5 of 36 ± 5.7 mg O_2/L were obtained. The HRT was decreased to 7 h when operating without recirculation from the membrane module to the UASB reactor, and, even at such a low HRT, good quality effluent was obtained under a VLR of 2.2 kg COD/m^3 d; the tCOD of the effluent was 122 ± 36 mg O_2/L. However, when the VLR increased at a constant HRT of 7 h, the tCOD removal efficiency of the AnMBR clearly decreased. During the last period with a HRT of 7 h and VLRs above 4 kg COD/m^3 d, a continuous increase in the tCOD of the effluent was observed, reaching effluent tCOD values of 125–250 mg O_2/L and effluent BOD_5 of 40–125 mg O_2/L at VLRs of 4.5–5.5 kg COD/m^3 d (Fig. 2).

The mean value of total VFA in the effluent at a VLR of 2–2.5 kg COD/m^3 d was 21.2 ± 14.6 mg/L (composed of acetic, propionic, butyric acid at 68.5 ± 48.4%, 15.2 ± 9.5%, and 16.3 ± 11.1%, respectively). VLRs of 3.5–4.5 kg COD/m^3 d resulted in an increase of VFA, with effluent VFA concentrations of 47.2 ± 33.4 mg/L.

The results obtained confirmed that AnMBR treating municipal wastewater at psychrophilic temperature (18 ± 2 °C) achieved effluent tCOD values below the legal discharge limit at HRT of 7–10 h and VLRs of 2.5 kg $tCOD/m^3$ d. Similar tCOD removal efficiencies were obtained by Martinez-Sosa et al. (2012), working at 20 ± 1 °C with higher HRT (17.76–26.4 h) but lower VLRs (0.4–0.9 kg COD/m^3 d). Likewise, Smith et al. (2013) also obtained similar COD removal (92 ± 5%) at 15 ± 1 °C, with a VLR of 0.66 kg COD/m^3 d and an HRT of 16 h when working with synthetic wastewater, however with municipal wastewater the COD removal efficiency averaged 69 ± 10%. Gao et al. (2014), working with municipal wastewater at three temperatures (35 °C, 25 °C and 15 °C) with volumetric loading rates between 1.2 and 1.44 g COD/L d and a HRT of 6 h, reported a decrease in COD removal efficiency in correspondence with temperature, ranging from 74% to 67% and 51%, respectively.

3.2. Start up and sludge granulation

The UASB reactor was inoculated with sludge from a mesophilic pilot plant anaerobic digester operating at a SRT of 20 days, fed with primary and secondary sludge from the WWTP of Burgos (Spain) (Period I). After ten months of operation at low temperature with VLR lower than 0.5 kg COD/m^3 d, the removal efficiency remained below 60%. The reactor was re-inoculated with sludge from a mesophilic digester from the WWTP of Valladolid (Spain), which allowed the VLR to be increased and supported higher organic matter removal efficiencies (period II). However, this increase in VLR had to be conducted slowly. Hence, a period of six months was needed to reduce the HRT down to 13 h while maintaining the effluent tCOD at 100–120 mg O_2/L. In this work, the first inoculation and the re-inoculation were performed without acclimation to psychrophilic conditions, thus entailing long startup periods. Sludge adaptation in the experimental system from mesophilic to psychrophilic conditions involved the loss of active biomass, which, together with the low strength wastewater, was probably responsible for the slow process start up. This period could be reduced in correspondence with a more efficient acclimation to the psychrophilic conditions, by gradually decreasing the temperature. In the work carried out by Gao et al. (2014), Giménez et al. (2012), Martinez-Sosa et al. (2012) and Pretel et al. (2014) the startup was carried out at mesophilic conditions and the temperature was decreased stepwise (around 35 °C, 25 °C, 20 °C). Bae et al. (2014) indicate that the results reported were obtained after an acclimation period of 225 days at 25 °C. Also, Shin et al. (2014) working without temperature control (8–30 °C), started the reactor during the winter period, reported higher COD removal after full acclimation during the following spring and summer. Moreover, Smith et al. (2013) reported, by comparing bacterial and archaeal microbial communities in the AnMBR after 275 days of inoculation, and in three different inocula, using pyrosequencing to target 16S rRNA genes, that those mesophilic inocula are suitable for seeding psychrophilic AnMBR treating low strength wastewater.

In the present work, granulation of the biomass was observed approximately eight months after re-inoculation, despite the reactor being operated with low superficial rates (0.15–0.25 m/h). The presence of the membrane might have contributed to sludge granulation, as it prevented the loss of inorganic material, promoting the formation of granules. These granules remained during the rest of the reactor's operation, co-existing with filamentous bacteria. The color of the granules was black during the entire period of operation, and the size was between 1 and 2.5 mm. Controversy still exists in literature regarding the factors affecting anaerobic biomass granulation during the treatment of municipal wastewater (Aiyuk et al., 2006). In some cases, the need to add sugars to facilitate the formation of granules has been reported (Mergaert et al., 1992), and in other cases granulation did not occur in the presence of sugars. Liu et al. (2012), by working in the range of temperature between 27 and 30 °C and with relation Food/Microorganisms (F/M) of 0.1–3.8 g COD/g SSd, attributed granulation to the high F/M ratio. Aiyuk and Verstraete (2004), working at 33 °C, with a VLR between 1 and 2 kg COD/m^3 d and HRT of 4, 8 and 10 h reported loss of granular sludge integrity, while other authors (Ghangrekar et al., 2005) reported granulation at VLRs in the range of 2.0–4.5 kg COD/m^3 d. Abbasi and Abbasi (2012) recently analyzed the influence of key operational parameters affecting sludge granulation and granule stability in UASB reactors. They conclude that it is as yet not possible to give a precise recipe adequate for all substrates and reactor operations conditions.

3.3. Solids concentration in the UASB reactor and membrane module

The concentration of VS was measured at different heights within the UASB reactor, S.p. 0, 1, 2, 3 and 7. The variations observed were directly related to the changes in the superficial rate. The concentration of VS at the bottom (S.p. 0) of the reactor ranged from 39 to 45 g VS/L, from 7 to 11 g VS/L at the middle height (S.p. 1, 2, 3) and from 1 to 8 g VS/L below the tree phase separator (S.p. 7). Considering the individual volume of each zone, the amount of VS estimated in the UASB remained at 1630–2300 g VS throughout the AnMBR operation. The VS concentration in the central zone of the membrane module also remained constant at 5.95 ± 2.04 g/L. No biomass wastage was carried out in the UASB reactor, except for the sampling associated to the monitoring of the different parameters. Purging of solids from the membrane module was carried out during cleaning operation. The total amount of VS wasted from the AnMBR accounted for 0.5 kg/year due to the sampling and 2.2 kg VS/year due to wastage from the membrane module. This represented a negligible growth of the biomass based on the removal of tCOD recorded. Shin et al. (2014), using a pilot scale anaerobic fluidized membrane bioreactor (AFMBR) treating municipal wastewater without temperature control (9–30 °C), obtained a biosolid production average of 0.051 g VSS/g $COD_{removed}$ independently of the temperature, with a wasting ratio of 1%. The difference observed in the biosolid production could be due to the different solid concentration in the bulk liquid in the membrane module, and different SRT. Bae et al. (2014), using synthetic wastewater at 25 °C in an AFMBR, obtained a sludge production rate of 0.003 g VSS/g $COD_{removed}$ with a wasting ratio around 0.8–0.5%. Nevertheless Pretel et al. (2014) reported a sludge production rate of 0.16 TSS/kg $COD_{removed}$, 0.43 TSS/kg $COD_{removed}$ and 0.55 TSS/kg $COD_{removed}$ at the respective temperatures of 33 °C, 22 °C and 17 °C and SRT of 70 days, 38 days and 30 days, working with a semi-industrial AnMBR plant treating sulfate-rich urban wastewater.

3.4. Biogas composition in the UASB reactor and in the membrane module

Biogas production and biogas composition were periodically measured in the UASB reactor and in the membrane module separately. No significant difference in the biogas composition was observed during the operation with and without recirculation. However, the composition of biogas was slightly different between the UASB reactor and the membrane module. The values of the biogas composition in both periods in the UASB reactor were: CO_2 = 7–12%, H_2S = 0.25–0.37%, N_2 = 5–12% and CH_4 = 80–83%, while in the membrane module biogas was composed of CO_2 = 9–13%, H_2S = 0.1–0.3%, N_2 = 2–6.5% and CH_4 = 83–86%. These results of biogas composition recorded in the UASB reactor were similar to those reported by Elmitwalli et al. (2002) working with an anaerobic filter + an anaerobic hybrid, at 13 °C and to the results of Alvarez et al. (2008) working with a hydrolytic upflow sludge bed and UASB at 21–14 °C treating municipal wastewater. Martinez-Sosa et al. (2012) working with an integrated anaerobic fluidized-bed membrane bioreactor at 20 °C with municipal wastewater supplemented with glucose also sowed around 80% of methane in the biogas. Giménez et al. (2012) reported a biogas composition (mean values) of CO_2 = 4.4%, H_2S = 1.3%, N_2 = 48.6% and CH_4 = 45.7% working in a semi-industrial SAnMBR treating sulfate-rich urban wastewater at 20 °C.

The high values of N_2 in the present study, and low values of CO_2, were associated with the low total alkalinity of the wastewater, which ranged from 450–550 mg $CaCO_3$/L, whereas total alkalinity in the UASB reactor remained at 450–700 mg $CaCO_3$/L.

The composition of CH_4 was 2–3 percentage points higher in the membrane module than in the UASB reactor. This can be attributed to the higher temperature in the membrane module (1.5–2 °C) than in the UASB reactor due to the turbulence in the membrane, both contributing to the desorption of the dissolved methane. Moreover, the contribution of the membrane module's biogas production to the total biogas produced was different with or without recirculation. During process operation with recirculation, the biogas from the membrane module represented 26.4% of the total biogas production. However, the biogas production of the membrane module represented 13.7% of the total production during process operation without recirculation. This difference was attributed to the greater amount of liquid flowing to the membrane module during the recirculation period and subjected to the higher turbulence of the membrane module that facilitated the desorption of the dissolved methane in the module. Therefore the membrane operation conditions, at a high rate of biogas sparging, facilitated the recovery of the methane from the AnMBR, which otherwise would be dissolved in the effluent in the UASB reactor due to the low operation temperatures. Thus, the membrane contributed to the reduction of methane dissolved in the effluent of the AnMBR. In this context, Giménez et al. (2012) reported that the biogas-assisted mixing avoided super-saturation and guaranteed the minimum concentration of dissolved methane at the effluent, (i.e. the saturation concentration).

3.5. Specific methane yield

The specific methane yield was calculated from the total production and composition of biogas (UASB reactor and membrane module) and tCOD removed (difference between the tCOD fed to the UASB reactor and tCOD of permeate). The specific methane production obtained throughout the operation of the AnMBR was 0.199 Nm^3 CH_4/kg $tCOD_{removed}$. The SMY was low compared with the theoretical value (0.35 Nm^3 CH_4/kg COD), which was attributed to the fact that not all particulate material retained by the membrane was biodegraded. In AnMBRs, together with the biological removal, a physical removal of particulate matter occurs due to the presence of the membrane, which does not contribute to the production of methane. Hence, a detailed analysis of each operation period reveals differences in the SMY. The SMY during the recirculation period obtained was 0.235 Nm^3 CH_4/kg $tCOD_{removed}$, which compares positively with the 0.187 Nm^3 CH_4/kg $tCOD_{removed}$ obtained without recirculation. This higher productivity (25.6%) could be attributed to the partial biodegradation of the slowly biodegradable particulate COD that accumulated in the system. The recirculation of the suspension from the membrane module to the UASB reactor permitted a better contact between the biomass and the particulate COD. Therefore, the membrane contributed to the increase in the specific production of methane. The particulate COD, in conventional UASB reactors operated at low temperature, leaving the reactor without significant treatment, with higher HRT being needed, in order to obtain an effluent quality similar to that obtained in the present study. The SMY obtained in this work were in accordance with values reported in literature. The SMP obtained by Ozgun et al. (2013b), in an UASB reactor working at 25 ± 2 °C and fed with synthetic wastewater, was 0.13 Nm^3 CH_4/kg $COD_{removed}$ and 0.11 Nm^3 CH_4/kg $COD_{removed}$ at an upflow velocity of 1.2 m/h and 0.6 m/h, respectively. Gao et al. (2014) obtained a SMY of 0.19 L CH_4/g $COD_{removed}$, 0.19 L CH_4/g $COD_{removed}$, and 0.14 L CH_4/g $COD_{removed}$ working at temperature of 35 °C, 25 °C and 15 °C respectively, with municipal wastewater. Martinez-Sosa et al. (2012) using an AnSMBR treating low-strength wastewater for 90 days under psychrophilic conditions (20 °C) obtained an average SMY of 0.24 Nm^3 CH_4/kg $COD_{removed}$. The authors indicated that, even considering the theoretical methane dissolved, calculated according to Henry's law, in the biogas balance, the yield obtained around 0.29 L CH_4/g $COD_{removed}$, which was still lower than the theoretical value and indicated that particulate or soluble organics were not completely degraded, but physically retained by the membrane.

3.6. Nitrogen and phosphorus removal

The N-TKN and N-NH_4^+ were determined in the soluble phase of the influent and effluent of the UASB reactor, inside the membrane module and at the effluent from the membrane (Fig. 3). Most of the N-TKN in the residual wastewater was present in the form of N-NH_4^+, (≈75.45 ± 0.95% of the total N-TKN). There was no significant increase in the concentration of N-NH_4^+ in the effluent of the AnMBR as a result of the treatment process (79.84 ± 2.2% of the total N-TKN). However, N-TKN accumulated within the membrane module. The concentration of soluble N-TKN and N-NH_4^+ gradually increased up to 213.58 and 104.02 mg/L, respectively, in the membrane module. This increase in nitrogen content throughout the operation of the AnMBR could be due both to the hydrolysis of the accumulated particulate organic matter and also to the cell decay. Phosphorous concentration underwent a similar trend, with no significant difference between the concentration of P at the soluble phase of the influent and effluent of the AnMBR being

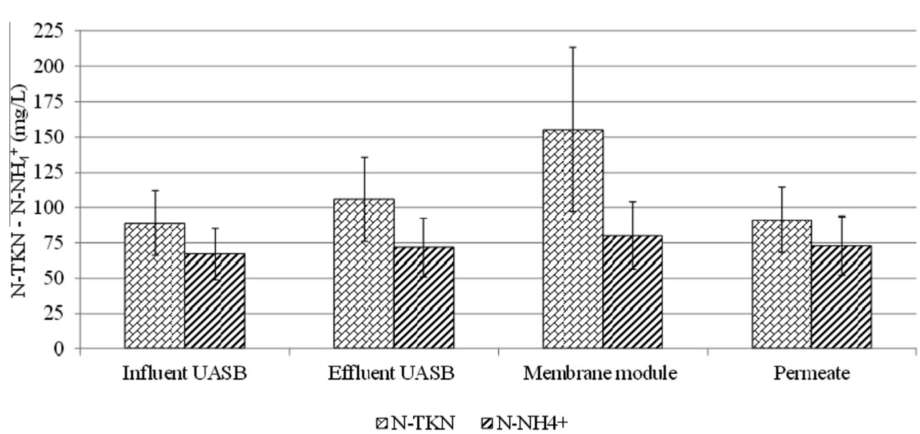

Fig. 3. N-TKN, N-NH_4^+ concentration in the AnMBR (mean values) during the entire period of operation.

recorded. A build-up in P concentration was also recorded inside the soluble phase of the membrane module up to 23.8 ± 14.6 mg P-PO_4/L. This predictably low removal of nitrogen and phosphorus in the AnMBR could be beneficial if the effluent is to be used for agriculture or irrigation purpose. Lin et al. (2013) suggested that the forward osmosis membrane process could provide another perspective to resolve this challenge, since the FO process can almost totally reject N and P contaminants. In this respect, an increase in TNK and NH_4^+ concentration in the membrane module was observed by Chen et al. (2014), in a FO-AnMBR at 25 °C treating synthetic wastewater, achieving nearly 100% total phosphorus removal and 62% N-NH_4^+ removal.

3.7. Accumulation of particulate COD

One of the fundamental effects of the functioning membrane was the accumulation of particulate COD inside the system. Fig. 4 shows a clear difference between the values of sCOD inside the membrane module and the tCOD in the AnMBR effluent. This difference, caused by the different porous diameter of lab filter for sCOD (0.45 μm) and the membrane (0.045 μm), generates a very high quality effluent, and the subsequent accumulation in the membrane module of non-biodegradable matter and the slowly biodegradable particulate COD. The sCOD in the membrane module increased up to 4000 and 6000 mg/L during the period with recirculation and without recirculation, respectively, while the tCOD in the effluent remained at 100–120 mg/L. The particulate COD in the range of 0.45–0.045 μm is slowly biodegradable and non-settleable at low temperatures due both to its size and to the high turbulence existing in the central zone of the membrane module. This accumulation increased with the increase of the VLR and depended on the content of particulate matter of the wastewater. In fact, the higher values of sCOD corresponded to VLR ranging from 3.5 to 5 kg COD/m^3 d. The decrease in accumulated COD values was due either to the purging of the membrane module or to the cleaning of the membrane. This accumulation of particulate//colloidal material was also reported in recent literature, independently of the use of micro or ultrafiltration membranes. Bae et al. (2014) working with synthetic wastewater at 25 °C in an anaerobic fluidized membrane bioreactor, using a PVDF membrane with a pore size of 0.1 μm, reported that the sCOD of the bulk liquid was 10–26 times higher than that of the permeate. Martinez-Sosa et al. (2012) also concluded that organic compounds were not completely degraded, but physically retained by the membrane. Moreover Shin et al. (2014) suggests that the limiting steps in organic degradation at low temperature are the hydrolysis of VSS and colloidal materials rather than methanogenesis.

3.8. Biochemical methane potential assay of accumulated particulate matter

To facilitate membrane filtration and to reduce the fouling, several purges of the membrane module were carried out in order to eliminate accumulated material. The purges were carried out every time the membrane module was chemically cleaned. Every time, the volume purged was around 145 L and the amount of volatile solids purged was 1 kg (mean value). The BMP from the accumulated material in the membrane module was carried out in order to determine the mesophilic anaerobic biodegradability, envisaging a process configuration where the solids wasted (purges) from the anaerobic membrane module at psychrophilic temperature could be further stabilized in a mesophilic anaerobic digester. The specific methane yield by day 17 was 417.65 mL CH_4/g VS_{fed} for the suspension, 390.21 mL CH_4/g VS_{fed} for the concentrated solid and 166.93 mL CH_4/g VS_{fed} for the supernatant. Thus, the mesophilic biodegradability of this particulate organic matter present in the suspension, in the concentrated sludge and in the supernatant was 56.81%, 38.84% and 28.30%, respectively.

3.9. Membrane behavior

Fig. 5 illustrates the performance of the membrane throughout the operation of the AnMBR. Biogas was continuously sparged (coarse bubbles) at the bottom of the hollow fibbers with a superficial velocity (u_g) of 23 m/h. During period I, the low solid concentration (<0.5 g/L) and the low flux resulted in a low TMP (50 mbar). Nevertheless, solid concentration inside the membrane module increased up to 5–7 g VSS/L during period II, which together with the increase in the permeate flow, entailed a significant increase in the TMP and a subsequent increase in u_g to 40–60 m/h. The filtration cycle was then decreased to 7.5 min filtration, 15 s backflush and 10 s of relaxation time in order to maintain the TMP and to reduce membrane fouling. The membrane module operated at high fluxes of permeate, 14–15 L/m^2 h (recirculation period) and 10–12 L/m^2 h (without recirculation), which resulted in TMPs ranging from 500 to 550 mbar (Fig. 5), with specific gas demand per membrane area of between 0.4–1 Nm^3/m^2 h. During the last stage of the work, the permeate flow along the cycle was inconstant, decreasing slightly at around 1–2%. The permeate fluxes

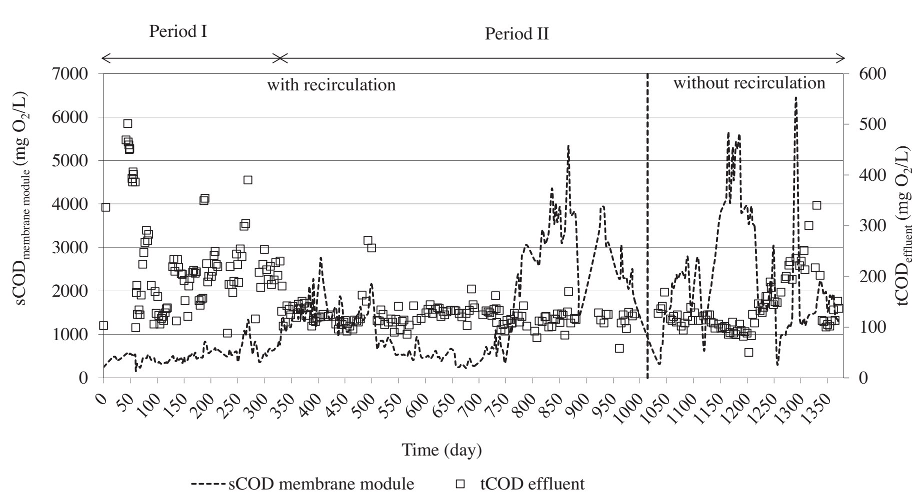

Fig. 4. Evolution of sCOD accumulation in the membrane module and $tCOD_{effluent}$ during the entire period of operation.

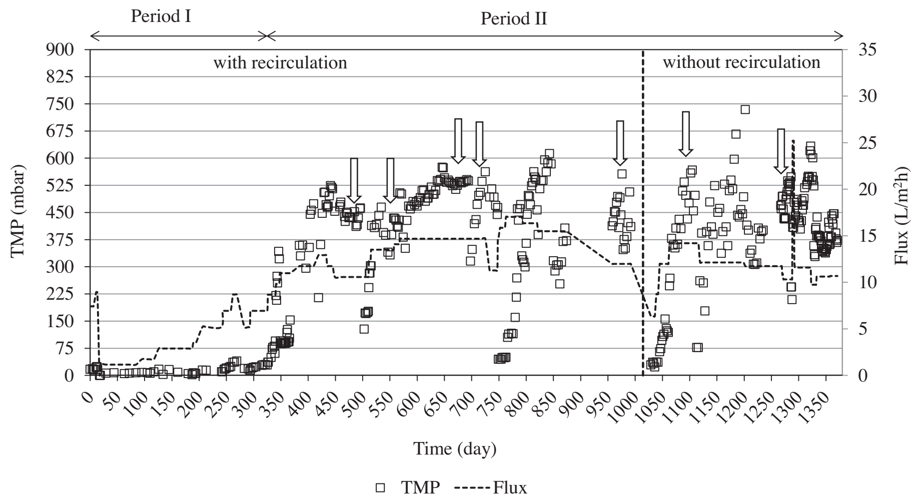

Fig. 5. Evolution of TMP and permeate flux during the entire period of operation (arrows indicate the chemical cleaning).

obtained are higher than those reported in literature, considering the long-term operation of the membrane. Smith et al. (2012) reported, in a recent review, sub-critical fluxes values of 7, 10 and 17 L/m^2 h, depending on operation conditions, solid concentration, SRT, and the methodology followed to control the fouling. Nevertheless, these fluxes are still low compared with those obtained in the aerobic membrane bioreactor (Lin et al., 2013; Smith et al., 2012). Robles et al. (2012) also reported a high flux of around 13–10 L/m^2 h, with solid concentrations of between 10 and 25 g/L, and temperatures in the range of 33–20 °C with an average specific gas demand per membrane area of 0.23 Nm^3/m^2 h.

In the present study, the membrane was chemically cleaned seven times, throughout the operation period. This represents a cleaning session approximately every six months of operation. The cleaning was carried out using 1000 ppm of NaClO for between 4 and 6 h and at room temperature. After these cleaning periods, the permeability reached a value of 0.128 L/m^2 h mbar, representing a recovery of 61.4% of the initial permeability. Physical deterioration of the fibers was not observed during the long-term operation of the AnMBR. Lin et al. (2013) reported that the typical cleaning protocol used in AnMBRs comprised a weekly clean in place, and a cleaning out of place using 1000 mg/L NaClO and 2000 mg/L citric acid, conducted twice yearly. Nevertheless, in the present study only chemical cleaning out place was carried out. Shin et al. (2014), working with a pilot scale anaerobic fluidized membrane bioreactor (AFMBR), used only the scouring effect of the fluidized GAC and relaxation, to prevent fouling. Their AFMBR operated continuously for 485 days at net fluxes of 4.1–7.1 L/m^2 h, and no chemical cleaning was carried out during the entire period. Although the authors suggested that, the chemical cleaning of the membrane would have been desirable once quarterly. Nevertheless, Robles et al. (2012) reported that, no chemical cleaning was conducted during system operating for more than one year.

The behavior obtained in the present study demonstrate the long-term reliability and operability of the AnMBR technology for treating municipal wastewater in psychrophilic conditions. The quality of the effluent, free from solids and mineralized nutrients, makes it suitable for irrigation or agricultural purposes, or for nutrient recovery. Nevertheless more research should be conducted on dissolved methane losses in the effluent, the optimum SRT in the AnMBR, and the optimal operation protocol in order to increase the permeate flux and the economic feasibility of the AnMBR.

4. Conclusions

The results obtained for the long-term operation show the feasibility of the AnMBR technology for the treatment of municipal wastewater at psychrophilic temperature. Operating at VLR between 2 and 2.5 kg tCOD/m^3 d and HRT of 7 h, the tCOD removal efficiencies obtained were 87 ± 1%, reaching values of tCOD in the effluent of 100–120 mg O_2/L. The specific methane yield obtained was 0.18 and 0.23 Nm^3 CH_4/kg $COD_{removed}$ depending on the recirculation between the membrane module and the UASB reactor. The membrane operated with flux of between 10 and 14 L/m^2 h during the three years of stable operation, requiring chemical cleaning every six months.

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