Desalination and Water Treatment
www.deswater.com
doi: 10.5004/dwt.2020.25076

180 (2020) 43–54
March

Assessment of a combined UASB and MBR process for treating wastewater from a seafood factory at different temperatures

Alvaro Silva-Teira[a,*], José Ramón Vázquez-Padín[b], Rubén Reif[b], Adrián Arias[a], Frank Rogalla[b], Juan Manuel Garrido[a]

[a]*Department of Chemical Engineering, School of Engineering, University of Santiago de Compostela. E- 15782. Santiago de Compostela, Spain, emails: alvaro.silva@usc.es (A. Silva-Teira), adrian.arias.bano@usc.es (A. Arias), juanmanuel.garrido@usc.es (J.M. Garrido)*
[b]*Trainasa/Aqualia (FCC Group), Puerto Rico 18–20. Office 7, E-36204, Vigo (Pontevedra), Spain, emails: jvazquezp@fcc.es (J.R. Vázquez-Padín), ruben.reif@gmail.com (R. Reif), frogalla@fcc.es (F. Rogalla)*

Received 27 April 2019; Accepted 22 October 2019

A B S T R A C T

A combined upflow anaerobic sludge blanket (UASB) and membrane bioreactor (MBR) bench-scale system was studied for treating wastewater generated in a seafood production facility. Hydraulic retention time in the UASB + MBR varied between 14 and 50 h. COD in the wastewater ranged between 500 and 3,000 mg/L. Despite the strong variability in the wastewater characteristics, the system was able to remove the organic carbon compounds and solids, stably complying in-force effluent discharge limits. This fact demonstrated the ability of the MBR post-treatment to polish the COD coming from the UASB reactor even when this methanogenic stage did not operate properly. Also, the effect of the temperature in the anaerobic UASB stage was evaluated, and organic removal rates up to 6 kgCOD/(m^3 d) and COD methanation percentages larger than 90% were obtained. The presence of quaternary ammonium compounds, which are used as biocides for cleaning in the production line, inhibited biological processes, especially in the anaerobic methanogenesis and nitrification stages.

Keywords: Anaerobic; MBR; QAC; Hybrid; Industrial wastewater

1. Introduction

The food, beverage and milk industries employed approximately 20 million people in rural and industrialized areas of the European Union in 2006 [1]. In recent decades, which saw annual increases in the added value greater than 500 MM€, policymakers have become concerned with the continued competitiveness of these sectors.

To improve the efficiency in these production processes, the European Commission has proposed strategies for reducing both the environmental impacts and the costs throughout this sector. Aligned with these goals, schemes focused on reducing the energy consumption and improving the performance of the water cycle, with the reuse of water being maximized, have been proposed. The wastewater treatment of the streams generated in these production processes must consider both of these aspects.

The wastewater (WW) generation in these production processes may vary from 2 to 40 L WW/kg of the obtained product [1], depending on the goods being manufactured and the efficiency of the process. To date, the industrial wastewater treatment plants (iWWTPs) installed in these facilities are mostly based on conventional activated sludge (CAS) systems, as a result of the large amount of knowledge available about them. The quality of the treated effluents has typically been a common concern in CAS systems. Thus, the wastewater should be post-treated to obtain a quality that

* Corresponding author.

will allow water reuse in the same factory. Another disadvantage of a CAS is the higher sludge production, and the larger aeration necessities in comparison with other systems as those based on a methanogenic treatment. Likewise, its larger area requirements compared with methanogenic or membrane bioreactors (MBRs) has been a critical issue in many factories, in which the enlargement of the production capacity has increased the amount of wastewater to be treated. In some cases, the expansion has not been feasible due to the bottleneck of land scarcity, limiting the use of CAS as a wastewater treatment system. Thus, in recent years, both MBR and anaerobic treatment technologies, which can handle larger organic loading rates, have been explored as alternatives [2,3]. The main costs of these treatments are associated with the energy demand, sludge management and chemical consumption [2], and these operating items may be reduced if new approaches are applied.

Anaerobic treatments degrade organic pollutants into methane-rich biogas in the total absence of oxygen. The lack of aeration strongly diminishes the energetic demand, and the expense of the anaerobic treatment in comparison with those of CAS systems. Furthermore, the obtained biogas can be profitably applied for energetic purposes, commonly through the internal conversion of this renewable fuel into electricity or heat, as is employed in many factories. The obtained biogas thus diminishes the demand for externally sourced natural gas, decreasing the operating expenses. Electric efficiencies up to 40% have been observed when working with modern combined heat and power gas engines [3]. However, if the biogas is directly converted into heat, the energetic performance can be as high as 83% [4]. Moreover, the sludge production in anaerobic systems is generally considerably lower than that generated in aerobic processes [5], impacting the sludge management costs. Nevertheless, anaerobic treatment only focuses on the chemical oxygen demand (COD) elimination; the quality of the effluent is lower, since solids and nutrients are not removed [6]. Over 2,200 anaerobic treatment systems were installed worldwide between 1981 and 2007 [3] for treating industrial wastewater. Among them, upflow anaerobic sludge blanket (UASB) reactors led the market in this period, representing over 50% of the installed systems.

MBRs completely retain the suspended solids in the system, since the pore size is lower than that of the solids [7,8]. Moreover, nitrogen removal is possible with some configurations of these systems [9,10]. For these reasons, remarkably high-quality effluents have been commonly obtained, and the MBR permeate can even be reused in the same factory, closing the water cycle. Possible uses of this recycled water include auxiliary applications, such as vehicle rinsing/washing, process water for cooling towers, and evaporative condensers. Nevertheless, due to legal and sanitary constraints, the use of reclaimed water is totally prohibited in those applications in which the treated water and edible goods would be in contact, such as the main production process. A further goal of this reuse is to diminish the water demands of the overall production process. However, the aeration requirements and sludge production in MBRs are much larger than those of anaerobic systems. The MBR market has grown in the last two decades [2,8], and it can now be considered a mature technology.

One of the main drawbacks of methanogenic UASB systems is the presence of solids, pathogens, organic carbon, and nutrients in the treated effluent. In this sense, coupling this anaerobic reactor in series to an aerobic MBR system, as a post-treatment to reduce the remaining organic carbon and solids, is considered a good strategy to obtain an effluent of reuse quality. Moreover, the in-series MBR guarantees the total retention of the biomass in the eventuality of a massive washout from the UASB. A patent of the University of Santiago de Compostela (ES2385002B2) includes both a UASB as a methanogenic reactor and an in series two-stage MBR as a polishing treatment. The patented system was intended to integrate the advantages of both anaerobic and aerobic systems, improving the quality of the anaerobically treated water and minimizing the energy required for the wastewater treatment. In the first stage, most of the organic carbon is converted to methane-rich biogas. In the second, after combining the flocculent and biofilm biomass, aerobic treatment is conducted to oxidize the remaining organic carbon, and to convert the ammonium coming from the anaerobic treatment into nitrate. Additionally, in the first stage of the MBR, an improvement of the flux through the membranes was expected by adding carriers on which the biofilm was developed. In this process, filtration specialized microorganisms were promoted. Buntner et al. [9] already assessed this system at the bench scale with dairy wastewater and obtained promising results. In this previous study, the temperature was maintained in the range of 17°C–25°C, and the methanation capacity was 70% on average. This anaerobic system was fed at an organic loading rate (OLR) ranging between 0.5 and 5 kg COD/(m^3 d) [9].

In this study, a combined UASB and MBR process that combines the advantages of anaerobic and MBR systems has been launched for treating seafood processing wastewaters. As of today, the proposed system has been proven neither in a real factory nor with real seafood wastewater. Thus, the main aim of this study was to demonstrate the feasibility of the above-explained combined UASB and MBR for treating this type of industrial wastewater. In the first UASB reactor, the degrading capacity of the methanogenic stage and its dependence with the temperature were assessed. The UASB effluent was fed to a second stage, a polishing aerobic MBR, in which the effluent quality and the filtration capacity were tracked and evaluated.

2. Materials and methods

2.1. Experimental setup

The study was carried out in a seafood processing factory located in Galicia (NW Spain). Squid, sole, cod, and hake are the raw materials employed in this facility.

A schematic of the combined UASB and MBR bench-scale system is shown in Fig. 1. The methanogenic treatment was conducted in a UASB reactor of 120 L. This system was provided with an external heating jacket for accurately controlling the reactor temperature. The MBR (56 L) was composed of two compartments. The first compartment (36 L) was stirred by aeration and is denoted as the biofilm compartment hereafter. In this compartment, biomass was present both in suspension and adhered onto carriers. A mixture of

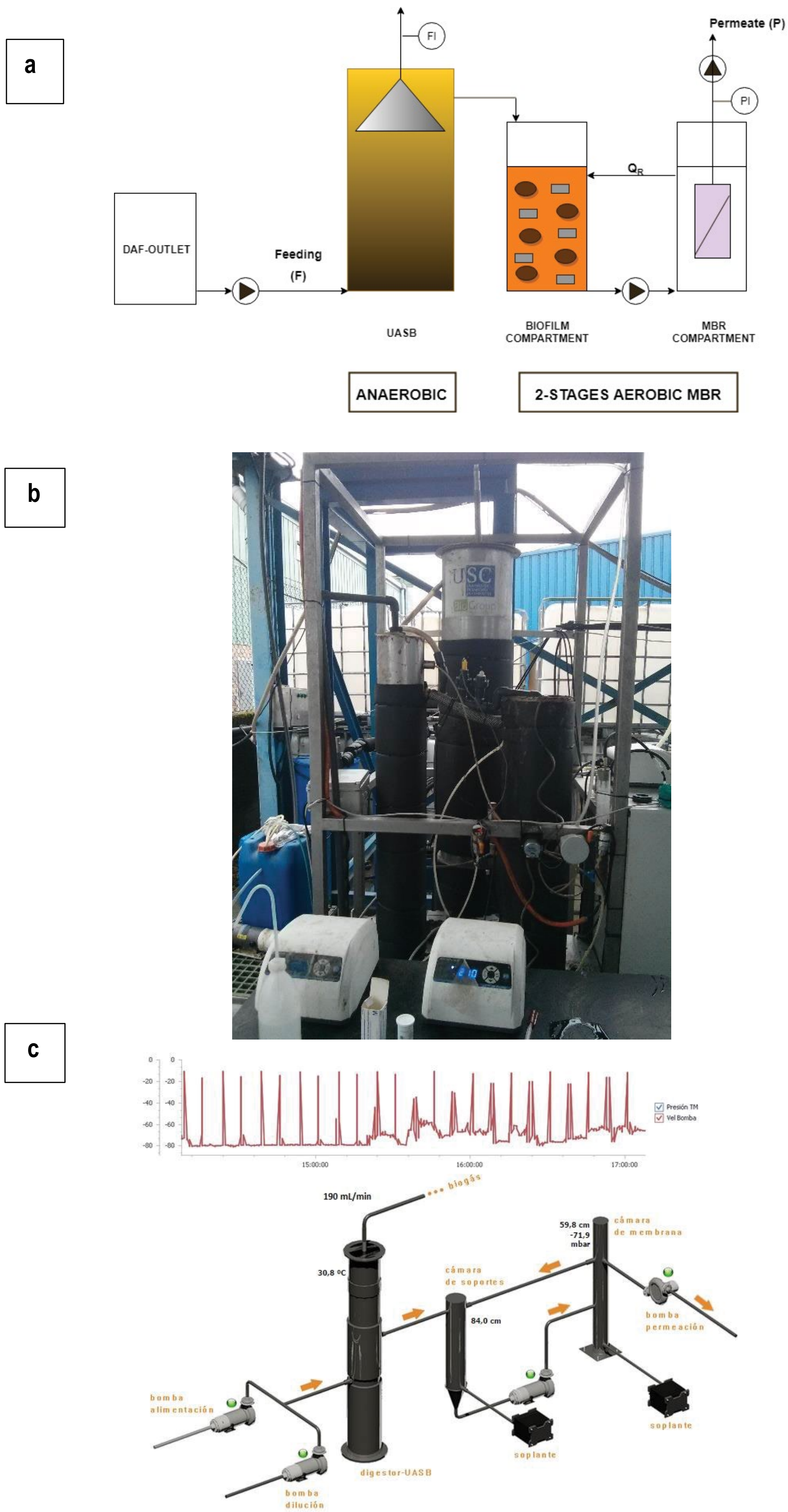

Fig. 1. (a) Schematic diagram of the three-stage UASB + MBR composed of an anaerobic stage (UASB) and an aerobic MBR consisting of a biofilm compartment and an MBR compartment where the membrane was located. (b) Picture of the bench-scale plant. (c) Supervisory Control and Data Acquisition System (SCADA) employed for tracking the continuous operation.

7 L (apparent volume) of foam (Levapor biocarrier; Levapor GmbH, Germany) and 2 L (apparent volume) of rigid carriers (Mutag BioChip; MultiUmweltechnologie AG, Germany) were used (Fig. 2). Both carriers occupied 26% of the apparent volume of the aerobic compartment.

The second aerated compartment (20 L), known as the membrane filtration compartment hereafter, contained an ultrafiltration hollow-fiber membrane (Zenon ZW-10) with an effective filtration surface of 0.9 m^2. The physical separation between the mixed liquor and permeate was achieved using a membrane with a pore diameter of 0.04 μm. The permeation cycle lasted 7.5 min, including 0.5 min of backwashing and 7 min of filtration. This compartment was aerated with a specific air demand (SAD_m) of 0.7 $m^3/(m^2\,h)$ to minimize membrane fouling. The operation of the system was monitored by a Programmable Logic Controller (PLC) (Allen Bradley Micrologix 1400) connected to a computer. The transmembrane pressure (TMP) data were measured with an analog pressure sensor (IFM Efector 500 PN 2009, Essen, Germany) and collected in the PC by an analog Micrologix PLC module.

To shorten the start-up period, the UASB was seeded with granular biomass collected from an expanded bed reactor located in a brewery and the MBR with screened activated sludge from a secondary treatment of a municipal wastewater treatment plant (WWTP). An internal recycle stream (R) was set up from the membrane filtration to the biofilm compartments of the MBR. R-value was defined according to Eq. (1) and the referred flows are depicted in Fig. 1:

$$R = \frac{Q_R}{F} \tag{1}$$

The R-value has been fixed at 2.2 within the experiments. The MBR was promptly purged when the total suspended solids (TSS) content increased above 8 g TSS/L, as recommended by Buntner et al. [9]. The mass of the TSS withdrawn was measured to estimate the overall biomass yield (Y_{OBS}). The characteristics of the wastewater generated and fed to the experimental setup are shown in Table 1.

2.2. Operational strategy

The system was operated for 305 d. Four different operating stages (Table 2) are distinguished according to the temperature at which the UASB was maintained. During the first stage, the temperature in the UASB reactor was initially not controlled (stage I), and it was operated in the range of 25°C–35°C in the remaining stages (from stages II to IV). The MBR was operated at ambient temperature during the

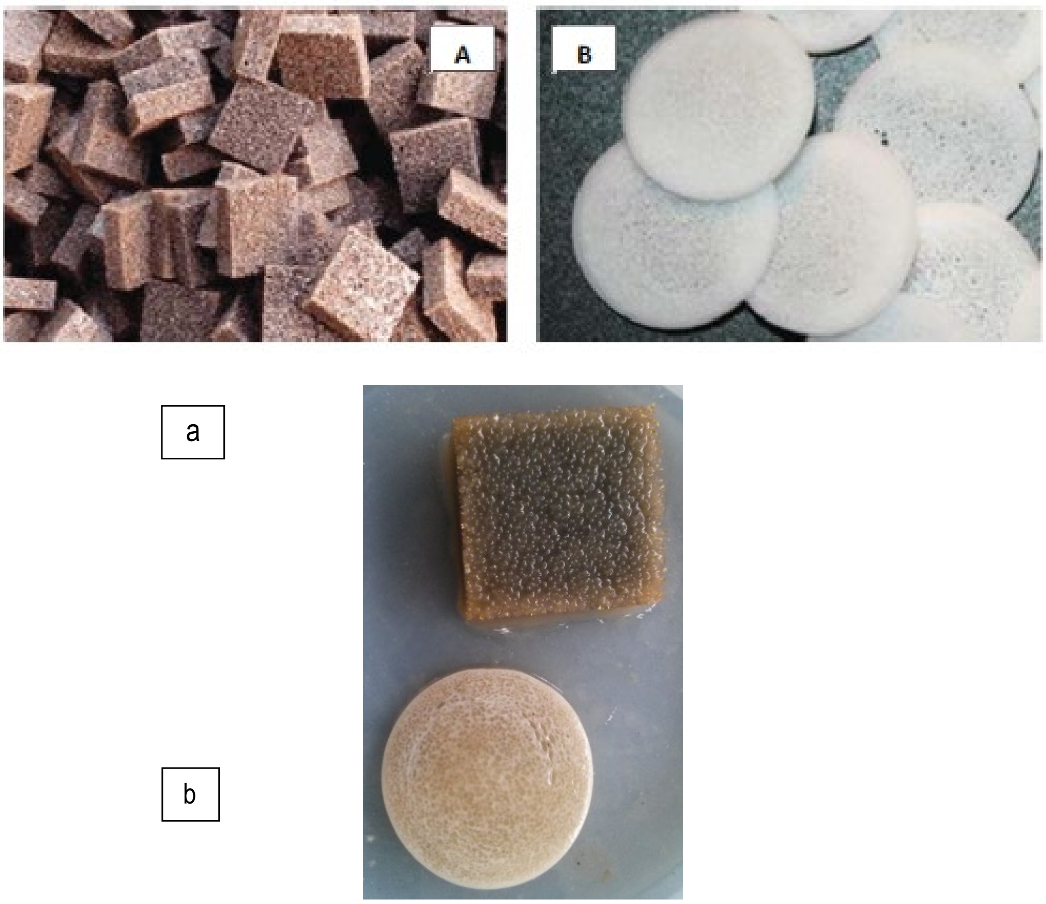

Fig. 2. Biomass carriers embedded in the MBR post-treatment. (a) Levapor biocarrier and (b) Mutag Biochip.

Table 1
Seafood wastewater characterization

Parameter	Average ± SD	Minimum	Maximum
COD_T (mg/L)	1,514 ± 668	308	3,008
COD_S (mg/L)	1,157 ± 455	280	2,156
TN (mg/L)	50 ± 23	12	99
TP (mg/L)	3 ± 2	1	13
TSS (mg/L)	215 ± 198	20	560
VSS (mg/L)	174 ± 274	16	448
pH	6.8 ± 0.9	4.3	8.6
Conductivity (mS/cm)	1.80 ± 0.38	1.21	2.32

SD: standard deviation.

Table 2
Operational strategy in the UASB system

Stage	Days of operation	Temperature UASB (°C)	Substrate (days)
I (Ambient)	0–131	17–25	Degreased
II	132–201	25	Degreased
III	202–254	30	Degreased (202–244)/Raw (245–254)
IV	255–305	35	Raw (255–288)/Degreased (289–305)

whole experimental period. Two different substrates were fed depending on the collection point of the current WWTP: (1) Raw wastewater: before the train of dissolved air flotation (DAF) vessels; (2) degreased wastewater: after the train of DAF vessels.

Table 2 summarizes the strategy of the stages, indicating the operational temperatures of the UASB system.

The anaerobic process can lead to a pH drop of the wastewater due to the low alkalinity of the wastewater used. Thus, an industrial-grade $Mg(OH)_2$ product with 80% $Mg(OH)_2$ (Magnesitas de Rubián S.A., Spain) was periodically added to the feed tank to increase the buffer capacity of the wastewater.

2.3. Analytical methods

The volatile suspended solids (VSS), total and soluble COD, nitrite, nitrate, and ammonium were determined according to the standard methods [11]. TP and TN were measured by using Hach Lange LCK (Germany) cuvette tests. The temperature and dissolved oxygen (DO) were measured with a multiparameter meter with a luminescent optical probe (Hach HQ40d IntelliCAL LDO101). A portable pH meter (Crison PH-25, Barcelona, Spain) was employed. The biogas production was measured by using a Milli GasCounter MGC-10 (Ritter, Germany), and its composition was measured in a gas chromatograph (HP 5890 Series II) with a Porapak Q 80/100 2 m × 1/8″ column SUPELCO (St. Louis, Missouri, US).. The biogas transportation from the factory to the Department of Chemical Engineering was conducted by means of Tedlar® bags.

The volatile fatty acids (VFAs) (including acetic, butyric, propionic, and valeric acids) were measured by a gas chromatograph (5890A by HP) equipped with a flame ionizer and an automatic injector (7673A by HP). The total organic carbon (TOC) was determined in a Shimadzu TOC-5000 TOC analyzer (Kyoto, Japan).

The colloidal biopolymer clusters (cBPC) were measured according to the procedure described by Sánchez et al. [12]. The cBPC is defined as a pool of colloidal organic matter in the liquid phase of the MBR sludge. It was measured as the difference between the TOC concentration present in a sample of the mixed liquor of the membrane compartment filtered through a 0.45 µm nitrocellulose filter and that measured in the permeate of a membrane with a pore size of 0.04 µm.

2.4. Nitrification activity tests

Assays to determine the specific nitrification rate of the biofilm compartment and suspended biomass were performed during the continuous operation. The flocculent and biofilm biomass were directly taken from the pilot plant. These samples were gently washed with phosphate buffer three times to remove the remaining oxidizable species. These assays were carried out in similar conditions to those present in the continuous operation for both suspended and attached biomass.

The biomass samples were continuously aerated, and ammonium was externally injected to assess the ammonium oxidizing capacity. The activity assay was run in a 500 mL vessel in the presence of phosphate buffer, ammonium (25 mgN/L) and sodium bicarbonate (42 mg $NaHCO_3$/L). Liquid-phase samples were taken every 45 min to analyze the evolution of the ammonium, nitrite, and nitrate concentrations. Tests were run at laboratory temperature at 20°C.

Table 3
Summary of the physico-chemical parameters collected during the continuous operation

	Influent	UASB effluent	MBR effluent
COD_T (mg/L)	1,514 ± 668	505 ± 475	55 ± 45
COD_S (mg/L)	1,157 ± 455	374 ± 322	55 ± 45
TN (mg/L)	50 ± 23	45 ± 25	27 ± 25
TP (mg/L)	3 ± 2	1 ± 1	2 ± 2
pH	6.9 ± 0.9	7.3 ± 0.6	–

2.5. Cake resistance

The resistance to filtration of the membrane filtration sludge was determined by a dead-end filterability test. The test was conducted at 25°C in a 180-mL pressurized cylinder (Amicon 8200®, Merck Millipore, Burlington, Massachusetts, US) using 0.2 μm flat sheet PVDF membrane filters (Durapore®; Merck Millipore, Burlington, Massachusetts, US). The cell was 100 mbar over-pressured by flushing with nitrogen gas. When the filtration was detected, a soft agitation was switched on, and the permeate was measured by weighing. The same procedure was performed with distilled water, activated sludge, and the colloidal fraction of the activated sludge. The Carman–Kozeny equation was employed to calculate the cake resistance (m^{-1}). Thus, the pressure reduction of the fluid flowing through the sludge cake was measured. The cake resistance was determined by considering the laminar flow of the fluid and taking into account that the filtration took place at constant pressure.

2.6. Anaerobic biodegradability batch assays

Biodegradability batch tests under anaerobic conditions were performed to determine the organic carbon content in the wastewater potentially broken down into methane-rich biogas. These tests were performed by employing the protocol published by Angelidaki et al. [13].

Wastewater from the current industrial WWTP was used as a substrate. Two different samples were taken as substrates, raw and degreased wastewaters. As an inoculum, an anaerobic granular biomass from a similar setup to the one employed for these experimental works fed with another substrate was used. The temperature, 37°C, and stirring velocity were controlled by an incubator.

3. Results and discussion

3.1. Biodegradability batch tests

Fig. 3 presents the evolution of the methane generated, normalized to the mass of the inoculum, as a function of time. Each series depicts either raw or degreased wastewater as collection points of the substrate in the current WWTP. Fig. 4 includes the overall extension of the methanation at the end of the test and 2 d after the beginning.

As it can be seen from Figs. 3 and 4, the raw and degreased wastewaters, respectively, behaved in different ways. When the raw substrate was fed, both the biodegradation rate at the beginning of the test and the overall extension of the obtained

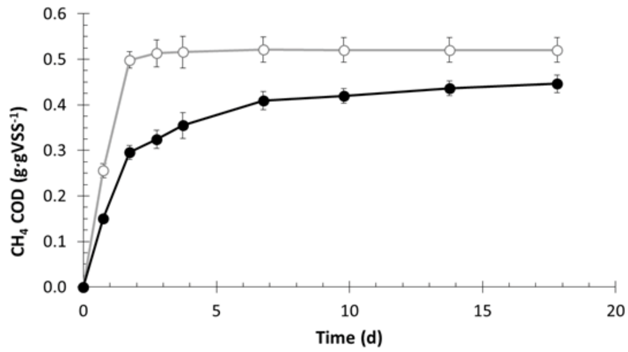

Fig. 3. Time evolution for the anaerobic biodegradability tests. Obtained methane per mass of inoculum for the substrates: (●) raw and (○) degreased wastewater.

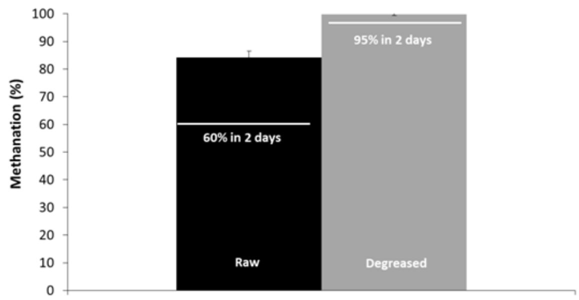

Fig. 4. Methanation percentage at the end of the biodegradability test (16 d) and after 2 d of experimentation. Degreased (●) and raw (●) substrates.

methane were lower than in the case of the degreased wastewater. In the case of the raw substrate, the overall methanation extension was up to 85%, reaching 60% in the first 48 h of the assay. When the degreased wastewater was the substrate, 98% of the carbon was transformed into methane and the 95% within the first 2 d. These differences are probably due to the higher concentration of fats in the raw substrate. The biodegradation complexity increased due to the presence of these large compounds, which made the hydrolysis a complex and slow process. On the other hand, these results indicate the high performance of the train of DAF vessels related to the separation of the difficultly-biodegradable compounds.

3.2. Overall performance of the combined UASB-MBR

The system was operated for 305 experimental days (Table 3). The total chemical organic demand (COD_T), soluble COD (COD_S), total nitrogen (TN), and total phosphorus (TP) in the wastewater fed to the first UASB system were 1,514 ± 668, 1,157 ± 455, 50 ± 23, and 3 ± 2 mg/L, respectively. The pH value in the influent was maintained at 6.9 ± 0.9. The average UASB effluent parameters were COD_T 505 ± 475, COD_S 374 ± 322, N–NH_4^+ 45 ± 25 mg/L, and P–PO_4^{3-} 1 ± 1 mg/L.

The anaerobic reactor was operated at the temperatures indicated in Table 2. The measured pH at the UASB outlet averaged 7.3 ± 0.6. The hydraulic retention time (HRT), referred to the UASB stage, ranged between 8 and 41 h.

The methanogenic treatment led to a COD_T removal of 63% ± 25% within the experimental stage. The average biogas production was 35–45 L/d, with a methane percentage of 71% ± 14%. The COD balance of the anaerobic reactor revealed that up to 90% of the total COD fed was methanized.

The effluent from the UASB was driven to the aerobic MBR post-treatment system. The TSS and VSS ranged between 4–28 and 4–24 g/L, respectively, in the biofilm and membrane filtration compartments. The average measured DO and pH in the biofilm compartment were 1.8 mg/L and 8.0 ± 0.4, respectively. The estimated biomass yield, referred to the combined UASB + MBR, was 0.18 kg VSS/kgCOD_T, similar to previously reported values [9,14] using the same process and for the treatment of other types of wastewater. In the permeate, the COD values were 55 ± 45 mg/L. The concentrations of TN and TP were 27 ± 25 and 2 ± 2 mg/L, respectively. The suspended solids were totally retained in the MBR due to the membrane's retention capacity. The achieved turbidity values were 1.1 ± 1.1 NTU in the permeate. With regard to the membrane performance, the net flux was maintained at 3–17 L/(m^2 h.). The TMP varied approximately 13–184 mbar, and the permeability values ranged between 37 and 462 L/(m^2 h bar).

3.3. *Impact of temperature on anaerobic stage*

Fig. 5 depicts the evolution of the COD fed, the effluent of the anaerobic UASB, and the COD concentration in the permeate. The temperature maintained in the anaerobic reactor was also monitored.

The main difference between Stage I (ambient temperature) and the other stages (Stages II, III, and IV) was the absence of a temperature control system in the UASB reactor.

Degreased wastewater was fed in Stage I. During the first 61 d, the measured temperature varied from 17°C to 25°C, and the anaerobic system worked as reported in other researches [15,16]. The observed COD removal efficiency of the UASB, 60%–80%, was in the range that was previously reported by other authors for similar wastewaters and concentrations. From day 61 onwards, significant daily ambient temperature changes were observed, which directly affected the performance of the anaerobic reactor. Differences between day and night of up to 15°C were detected in the facility in which the reactor was installed. This fact negatively impacted the stability of the anaerobic process, since temperature fluctuations typically have negative effects on both the microbial interactions and methanation performance of complex microbiological anaerobic processes [17,18]. Cha and Noike [19] studied the negative effect of rapid temperature changes in acidogenesis. There was found to be a dramatic decline in the number of acetate-utilizing methanogens, which in turn stopped the methanogenesis, when the temperature rapidly decreased by 5°C, especially at short HRTs of 6–12 h [19]. These stated HRT values were on the order of those observed in some periods of Stage I.

During Stages II and III, a higher degradation performance was observed. A decrease in the COD concentration was observed in the effluent of the UASB, as a consequence of the temperature rise in the methanogenic stage. Once the reactor was adapted to the new controlled temperature, stable COD concentrations were reached in the UASB effluent. COD values lower than 500 mg/L and below 250 mg/L were attained for Stages II and III, respectively. In the last days of Stage III, raw wastewater was fed without any negative impact in the methanogenic system.

In contraposition, a stable value of the COD effluent was not reached within Stage IV when the raw substrate was fed instead of degreased wastewater into the UASB reactor, even though there was a 5°C increase in the temperature set in the methanogenic reactor (Table 2). It was observed that the increased temperature in the methanogenic stage was still not capable of handling the complex raw wastewater. These results were according to the results of the biodegradability batch tests previously described (Figs. 3 and 4), which indicated a higher difficulty of anaerobically treating raw than degreased wastewater. Klaucans and Sams [20] reported a similar observation when dealing with wastewater from another food production factory. The codigestion of the separated fats and oils with primary sludges or scums has been a typical strategy followed in

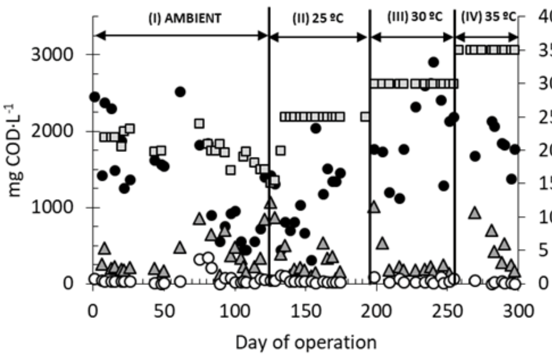

Fig. 5. Trends of the organic carbon concentration in the liquid streams. Daily trends of COD_T influent (●), UASB effluent (▲) and permeate (○). Secondary Y-axis: daily average temperature (■) in the experimental system. Indicated in the graph is the temperature status in the UASB reactor. Ambient makes reference to the period when the temperature in the anaerobic stage was not controlled.

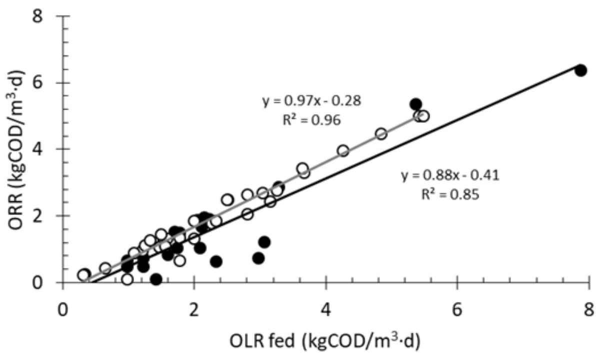

Fig. 6. Correlations between the feed organic loading rate (OLR) and ORR. Values corresponding to Stage I were drawn in black (●), and those corresponding to Stages II, III and IV were depicted in white (○). The linear correlation for Stage I was shown in black, and that for Stages II, III and IV is depicted in gray.

similar WWTPs [20]. This is due to the enzymes specialized for hydrolysis that are present in these primary sludges and scums. Hydrolysis has typically been the bottleneck in the anaerobic process when dealing with wastewaters rich in complex compounds such as fats, greases and oils. The contact of these substances with granular or attached biomass generally blocked the external layer of the biofilm, which impeded the mass transfer between the liquid phase and the biomass. In the medium term, this effect normally led to a gradual reduction in the degradation activity and ultimately the general failure of the biological system [21].

During the last days of Stage IV, the degreased wastewater feed was restored. As a consequence, a rapid increase in the performance of the methanogenic reactor was observed. This achievement was in accordance with the results of the anaerobic biodegradability assays (Figs. 3 and 4), which indicated a higher methanation capacity of degreased than raw wastewater.

The slope (Fig. 6) related to the set of values corresponding to Stages II, III, and IV was higher than the one corresponding to Stage I. Thus, it was confirmed that maintaining a constant temperature in the anaerobic stage positively affected the UASB stability [17,18].

Fig. 7 presents both the fed and removed OLR, and VFAs as acidification indicators.

During the first 60 d of operation, the COD removal capacity of the UASB was high, as indicated by Fig. 7. Moreover, the VFA values in the UASB effluent were always below 200 mgCOD/L, indicating that the methanogenesis was not the limiting stage in the overall anaerobic process. Hence, a removed OLR up to 3.5 kg COD/(m^3 d) was achieved, and the limits of the system were not attained, in line with other research [22].

Nonetheless, the COD concentration is only a function of the manufactured product and the type of goods produced in the factory. A sudden and severe COD increase in the wastewater was noted on day 61. As OLR is governed by both the inlet flow and the organic carbon concentration in the wastewater, such a rise in the COD in the influent resulted in feed OLR values as high as 8 kgCOD/(m^3 d), out of the advisable range for a methanogenic process at 15°C–25°C (Table 2) [22]. As a consequence, extremely high VFA values (Fig. 7) were detected. The VFA accumulation indicated that the biological process was stopped in acidogenesis; the methanogenesis was inhibited since the methanation percentages were as low as 3% in this period. Once the feed OLR decreased, the system quickly recovered to negligible VFA values. From day 85, negligible VFA concentrations were detected, and the COD inlet and removal varied within the expected ranges (Fig. 7), indicating that the overload period was overcome.

An intensive cleaning campaign was carried out in the factory for a short period, during which the production was stopped. For performing this task, cleaning and sterilizing products were used from days 93 to 105. These products included biocides, such as quaternary ammonium compounds (QAC) (9%) and glutaraldehyde (10%). A fraction of these biocides was present in the wastewater. Consequently, a VFA accumulation event was detected from day 120. QACs have a high affinity to adsorb onto biosolids, blocking organic carbon/biomass contact. The activity

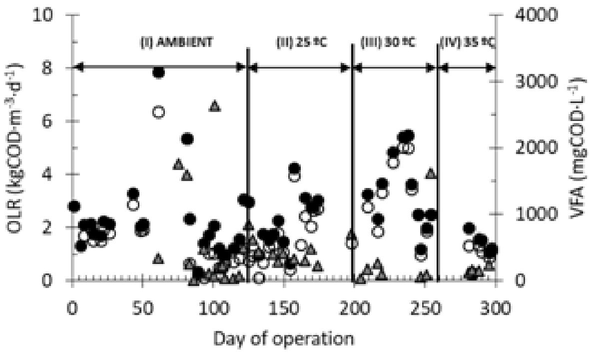

Fig. 7. Evolution of the organic loading rate (OLR), with all the streams and calculations referred to the UASB volume. Fed to the system (●), removed (○) and VFA (▲) observed in the effluent.

inhibition rates depended not only on the QAC concentration but also on the structures, acclimation and the presence of QAC-degrading communities [23]. As a consequence, the COD elimination was constrained, and a VFA concentration increase was detected (Fig. 7). This trend was also observed in another experimental prototype that was simultaneously run in the same factory and fed with the same wastewater. Both of them, as well as the current industrial WWTP, had been inhibited at the same time. Tezel et al. [23] deeply studied the effect of QACs in a methanogenic batch reactor. The anaerobic process stopped in acidogenesis, and there was a VFA accumulation when a threshold of 30 mg/L was passed. Accordingly, it can be estimated that the combined UASB and MBR system might have been fed with a minimum concentration of 30 mg QAC/L. Once the QACs were eliminated, the methanogens restored their activity 57 d later [23]. This indicates that a relatively long term is necessary for the methanogens to overcome the transient state caused by the presence of QACs. Hence, the inhibitory event observed from days 120 to 170 was probably due to the presence of a large amount of these biocides in the wastewater.

From day 128 onwards, the VFA concentrations started to decrease (Fig. 7), and the COD concentrations in the effluent were below 550 mg/L (Fig. 5). Additionally, setting the temperature to 25°C shortened the time required for the complete recovery of the anaerobic process, including methanogenesis. Once the system was restored, the temperature assessment on the anaerobic treatment continued. Buntner et al. [9] operated the same experimental setup, treating dairy wastewater with a slowly changing temperature of 17°C–24°C over 292 d, comparable temperatures to those included in Stage I. Despite this more favorable circumstance and the constant characteristics of the feed, values up to 4.2 kgCOD/(m^3 d) were eliminated. In the current experimental setup, similar removal rates were observed in the ambient temperature stage, even when operating under less favorable conditions such as more variable wastewater characteristics and daily changes in the temperature. van Lier et al. [6] included a summary of the expected values of the organic removal rate (ORR) when employing UASB reactors at 25°C with wastewater not including VFA and found similar values ranging between 4 and 8 kg COD/(m^3 d).

A comparison between the values observed during the first stage of the current study and those available in the literature indicates that the values collected in this research were in accordance with those previously published [15,16]. Ahn and Forster [24] studied the effect of temperature disturbances. A loss in the anaerobic reactor performance and a reduction in the effluent quality were noted when increasing or decreasing this parameter. This indicates that the stability of the temperature in an anaerobic system is crucial for maximizing its performance, as was also observed in the current study. Thus, a deep study of the anaerobic process was carried out once a temperature control system was installed.

Stages II, III, and IV are characterized by the temperature in the anaerobic UASB being controlled at 25°C, 30°C, and 35°C, respectively. Within the experiments, COD values below 250 mgCOD/L were observed in all samples, considering both the anaerobic methanation and the aerobic oxidation in the post-treatment. As a consequence, a removed OLR up to 5.1 kgCOD/(m^3 d) without detecting any acidification indicator and stable methanation percentages between 80% and 91% were collected. The only sample in which the VFA value was significant was the result of a temperature drop caused by a heating jacket malfunction. Similarly, Ahn and Forster [24] observed a sudden increase in the VFAs, especially acetic acid, when the temperature of the lab-scale digester rapidly switched from a stable 35°C to uncontrolled. This study also observed transient declines in the methane production when the temperature changed. van Lier et al. [6] reported removed OLR values up to 18 kgCOD/(m^3 d) under these conditions when feeding VFA-rich wastewaters at 30°C or, alternatively, when the UASB was set at 35°C with the absence of VFAs in the substrate feed. In this case, the large methanation percentages and such low COD concentrations in the UASB effluent indicated that the achieved removed OLR values were not limited by the capacity of the reactor. Moreover, in these stages, the VFA values were negligible. The COD concentration of the inlet wastewater and membrane filtration capacity are the limiting conditions.

The anaerobically treated effluents in the UASB can still be of low quality due to high levels of suspended solids and a high remaining COD fraction still [3]. Spanish law 5/2002, about industrial wastewater discharges in public sewerage systems, regulated the maximum COD to 1,600 mg/L and NH_4^+ to 60 mg/L when specific municipal regulations are not in force at the discharge point. Thus, this system coupled a polishing step in the aerobic MBR with the anaerobic UASB to produce a high-quality effluent.

In general, the results indicate that the presence of the temperature control (stages II, III, and IV) positively impacted the stability of the COD concentration in the UASB effluent.

3.4. Solids and nitrogen transformations in the MBR

The TSS showed a full and sustained elimination from the effluent due to the pore size, which retained all of the solid particles, similar to other research on MBRs [9,14,25]. Although the COD in the UASB effluent varied greatly (Fig. 5), the post-treatment was quite robust and could treat COD values up to 3,052 mgCOD/L, when the methanogenesis was inhibited on operating day 245. A permeate concentration averaging 55 ± 65 mgCOD/L was achieved, meeting the discharge limits applied to the factory.

Similarly, the solids production in the MBR has been strongly variable. The difference between the COD at the UASB outlet and that in the permeate acted as the driver for VSS generation in the MBR. The reported yields for the VSS generation in the MBR were between 0.2 and 0.4 kgVSS/kgCOD [5,10], depending on the applied solids retention time. As the permeate COD and observed overall biomass yield could be estimated as constant values, the biomass generation was changeable and strongly dependent on the anaerobic UASB performance. Solids management has been considered one of the major costs in wastewater treatment [2]. The less COD that needs to be removed aerobically, the cheaper is its associated cost, since the production rate is at least 10 times lower in the anaerobic processes in comparison with the aerobic process. A quantitative estimation has been performed, and the anaerobic and aerobic biomass yields are 0.03–0.18 [6] and 0.40–0.45 gVSS/$gCOD_{rem}$ [5], respectively. Taking into account these yields and the experimental concentrations of COD removed via either anaerobic or aerobic processes, the overall estimated solids production was 0.18 gVSS/$gCOD_{rem}$. In Stage I, the sludge generation rate doubled the value obtained in Stages II and III. Buntner et al. [9] reported an overall yield of 0.07 gVSS/COD_{rem} in a similar reactor and referred to the whole (UASB and MBR) system when operating with dairy wastewater. This reactor has been operated stably for 292 d in a temperature range of 17.5°C–24.5°C. A stable temperature is important to maintain an optimal internal state of the UASB, which enhances the performance. The UASB behavior governs the operational treatment costs since when more COD is anaerobically removed, (1) more biogas (profitable as an energy sources) is produced and (2) less solids are generated (with an associated management cost). The HRT of the whole UASB + MBR system of 14 and 50 h was similar to the HRT usually applied for CAS treatments. Nevertheless, the lower biomass generation and energy requirement of the proposed system diminished the operating expenses.

The nitrogen transformations in the MBR are tracked in Fig. 8.

During the first 50 d of operation, a large extension of the ammonium nitrification was observed. This extension

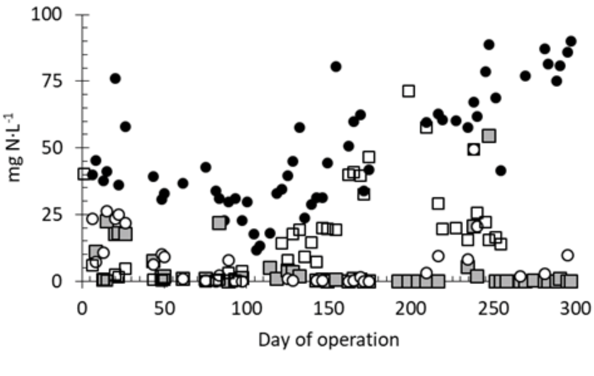

Fig. 8. Daily trends of nitrogen: as ammonium in the UASB outlet (●), as nitrate in the biofilm compartment (■), as nitrate in the permeate (○) and as ammonium in the permeate (□).

was also observed in a previous work employing the same system with dairy wastewater [12]. From day 50 onwards, the ammonium oxidizing capacity decreased. Two hypotheses were proposed for explaining this observation: (1) DO scarcity in both the biofilm and MBR compartments and (2) QAC presence in the post-treatment. On the one hand, DO was scarce in the biofilm compartment due to a massive concentration of VSS which consumed oxygen for its endogenous activities. This led to DO concentrations of 0.0–1.0 mg/L in the biofilm compartment from day 50 to 200. Afterward, higher values were obtained, up to 1.5–6.0 mg/L. Nevertheless, this reason may only explain the lack of nitrification in the biofilm compartment, since the DO concentration in the MBR was always higher than 3.0 mg/L due to the severe aeration demands of the membrane. For this reason, at least a fraction of the nitrification was expected in the MBR. The presence of QACs in the post-treatment could lead to a nitrification activity loss. This was suggested by Sarkar et al. [26], who studied the nitrification capacity losses in soils with concentrations of QACs as low as 50 mgQAC/kg soil. The QAC presence inhibited the nitrification capacity at concentrations significantly lower than the inhibitory thresholds for any other microbiological processes. Thus, this conclusion might explain the observations because the QACs might not have been washed out to non-inhibitory concentrations, unlike in the previous anaerobic process held in the UASB reactor. The nitrification capacity in the aerobic MBR was not recovered during the following 180 d of operation; it was only recovered in the last days of the experimental period, from day 200 onwards.

Nitrification batch assays were performed to elucidate the maximum nitrification capacity of the biomass taken from the MBR post-treatment. The average rates were as low as 3 mg $N–NO_3^-$/(L d), confirming the lack of nitrification detected in the continuous operation. Sarkar et al. [26] indicated the toxic effect of QACs to nitrifiers, especially if the formed bonds are irreversible. The high dissolved organic carbon (DOC) concentration in the mixed liquor could lead to competition for the DO, in which the heterotrophic biomass able to oxidize carbon competed in more favorable conditions than the autotrophic populations capable of oxidizing the ammonium present in the medium [5].

3.5. Membrane performance

During the start-up and first days of operation, the membrane behaved with remarkable permeability, 356 ± 80 L/(m^2 h bar), when the flux was in the range of 5–10 L/(m^2 h). Later, an increase in the flux of up to 14–17 L/(m^2 h) was observed. Once the lower values were restored, the permeability decrease did not stop. From day 61 to 135, an overall permeability decrease from the above-indicated values to below 100 L/(m^2 h bar) was observed. The fouling rate measured in this period was 1.13 mbar/d.

Apart from the excessive flux set by the permeate pump, the observed fouling indicators monitored by the cBPC were in the high range of 200 mgTOC/L [12]. Thus, the drop observed in this period was caused by the combined effect of two factors: (1) the above-mentioned unexpected sudden jump in the flux and (2) the extremely high cBPC values (Fig. 10) up to 600 mgTOC/L, in comparison with a maximum of 100 mgTOC/L observed by Sánchez et al. [12].

From day 97 onwards, five intensive chemical cleaning attempts were performed to try to recover the permeability. The permeability trends plotted in Fig. 9 indicate that this set of trials was unsuccessful, and no permeability recovery took place. This incapability of recovering the previous permeability by means of the intensive chemical cleanings indicated that this observed phenomenon can be described as irrecoverable fouling [7]. The fouling parameters were additionally investigated. In Fig. 10, the daily evolution of the cBPC is plotted.

As the cBPC were assigned as the colloidal fraction of the DOC of the sludge mixture in the liquid phase [12], the detected irrecoverable fouling can be caused by the high cBPC values, since the size of the colloidal particles was similar to the pore size of the membranes, and might block the pores, thereby diminishing the filtration capacity.

From day 135 onwards, coinciding with the applied temperature control, the permeability averaged 88 ± 18 L/(m^2 h bar). Unfortunately, these low values could not be increased because (1) the fouling that occurred was irrecoverable [7] and (2) the cBPC was not reduced to an adequate value, and a high fouling potential was maintained [12].

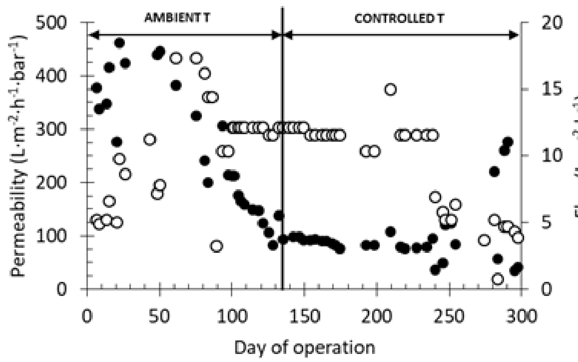

Fig. 9. Behavior of membrane parameters within the experimental period. On the main axis, the permeability (corrected to 20°C) was plotted (●). On the secondary axis, the evolution of the set flux (○) was depicted.

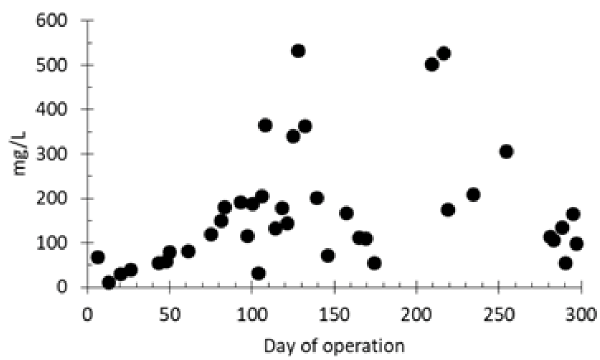

Fig. 10. Daily evolution of colloidal BPC (cBPC) within the experiments.

Cake resistance tests to measure the filtration capacity of the sludge were conducted, with a calculated value of 1.10×10^{12} m^{-1}. In this test, it was determined that about 35% of the overall resistance was a consequence of the colloidal fraction (3.90×10^{11} m^{-1}).

Other studies with a similar configuration to that employed in the current work and using the same model of membrane (Zenon ZW-10) reported improved efficiency indicators. Silva-Teira et al. [14] obtained a flux of 12–15 L/(m^2 h) and a permeability of 100–250 L/(m^2 h bar), and Buntner et al. [9] observed a flux of 13 ± 3 L/(m^2 h) and a permeability of 170 ± 75 L/(m^2 h bar).

In terms of the microbiological indicators in the permeate, the ultrafiltration membrane is considered one of the Best Available Technologies for providing a high-quality permeate. An effluent free of microbial indicators was expected based on another study [27] employing a similar pore size to that used in the current study. Although it was not in the scope of this work, no microbial indicators were expected in the effluent, and a complete compliance with Royal Decree 1620/2007 (Spanish Parliament) is expected. However, a further microbiological study is required to confirm this possibility. Once this study is undertaken, the treated water could be usable in the factory of origin for process and washing water or auxiliary water for cooling towers or evaporative condensers, among other purposes.

4. Conclusions

The use of a combined two-stage UASB and MBR system was used for treating an industrial wastewater stream generated in a seafood factory. The studied two-stage UASB + MBR was robust and reliable, and it has been shown to be capable of removing 94% ± 4% of the incoming COD and 100% of the TSS present in the wastewater during the experimental period. The combined system was capable of counteracting the COD overloads to the MBR polishing system, when the UASB efficiency diminished. The COD values present in the permeate always met the discharge limits of the factory.

The presence of biocides in the industrial wastewater stream in a concentration probably greater than 30 mg/L inhibited both the anaerobic treatment and nitrification process. The methanogenic phase was recovered in the anaerobic treatment after 50 d, but an irreversible nitrification decrease in the post-treatment was observed.

The temperature control and its stability over time are essential parameters for achieving the maximum removed OLR (6 kgCOD/m^3 d) at 30°C, corresponding to more than 90% of the feed OLR in the UASB system. The observed methanation percentages were greater than 90%. Under these conditions, larger removal performances could be achieved, since the OLR in the feed to the UASB was limited by the incoming wastewater COD concentration and the filtration capacity of the membrane.

Acknowledgments

This work was supported by the FEDER-Innterconecta Galicia 2013 ITC-20133118 (CDTI – Spanish Ministry of Economy and Competitiveness and Xunta de Galicia), co-funded by FEDER (EU). The authors from USC belong to the Competitive Research Group GRC/GPC2013-032 and to the Strategic Partnership CRETUS (AGRUP2015/02).

References

[1] European Commission, Integrated Pollution Prevention and Control: Food, Drink and Milk Industries, 228 (2006) 682.
[2] R. Iglesias, P. Simón, L. Moragas, A. Arce, I. Rodriguez-Roda, Comparison of full scale water reclamation technologies with an emphasis on membrane bioreactors, Water Sci. Technol., 75 (2017) 2562–2570.
[3] J. Van Lier, High-rate anaerobic wastewater treatment : diversifying from end-of the pipe treatment to resource oriented conversion techniques. Water Sci. Technol., 57 (2008) 1137–1148.
[4] R. Hakawati, B.M. Smyth, G. McCullough, F. De Rosa, D. Rooney, What is the most energy efficient route for biogas utilization: Heat, electricity or transport?, Appl. Energy, 206 (2017) 1076–1087.
[5] Metcalf&Eddy, G. Tchobanoglous, D. Stensel, R. Tsuchihashi, F. Burton, Wastewater Engineering, 5th ed., McGraw Hill, New York, 2014.
[6] J.B. Van Lier, N. Mahmoud, G. Zeeman, Anaerobic wastewater treatment, Environ. Sci. Technol., 20 (1986) 1200–1206.
[7] A. Drews, Membrane fouling in membrane bioreactors-characterisation, contradictions, cause and cures, J. Membr. Sci., 363 (2010) 1–28.
[8] S.J. Judd, The status of industrial and municipal effluent treatment with membrane bioreactor technology, Chem. Eng. J., 305 (2016) 37–45.
[9] D. Buntner, A. Sánchez, J.M. Garrido, Feasibility of combined UASB and MBR system in dairy wastewater treatment at ambient temperatures, Chem. Eng. J., 230 (2013) 475–481.
[10] A. Silva-Teira, J.R. Vázquez-Padín, R. Weiler, R. Fernández-González, F. Rogalla, J.M. Garrido, Performance of a hybrid membrane bioreactor treating a low strength and alkalinity wastewater, Process Biochem., 66 (2018) 176–182.
[11] E.W. Rice, R.B. Baird, A.D. Eaton, L.S. Clesceri, Standard Methods for the Examination of Water and Wastewater, 22nd ed., American Public Health Association, American Water Works Association, Water Environment Federation, 2012.
[12] A. Sánchez, D. Buntner, J.M. Garrido, Impact of methanogenic pre-treatment on the performance of an aerobic MBR system, Water Res., 47 (2013) 1229–1236.
[13] I. Angelidaki, J. Schmidt, L. Ellegaard, B. Ahring, An automatic system for simultaneous monitoring of gas evolution in multiple closed vessels, J. Microbiol. Methods, 33 (1998) 93–100.
[14] A. Silva-Teira, A. Sánchez, D. Buntner, L. Rodríguez-Hernández, J.M. Garrido, Removal of dissolved methane and nitrogen from anaerobically treated effluents at low temperature by MBR post-treatment, Chem. Eng. J., 326 (2017) 970–979.
[15] R.K. Dereli, M.E. Ersahin, H. Ozgun, I. Ozturk, D. Jeison, F. van der Zee, J.B. van Lier, Potentials of anaerobic membrane bioreactors to overcome treatment limitations induced by industrial wastewaters, Bioresour. Technol., 122 (2012) 160–170.
[16] G. Lettinga, S. Rebac, G. Zeeman, Challenge of psychrophilic anaerobic wastewater treatment, Trends Biotechnol., 19 (2001) 363–370.
[17] J. Kim, C. Lee, Response of a continuous anaerobic digester to temperature transitions: a critical range for restructuring the microbial community structure and function, Water Res., 89 (2016) 241–251.
[18] Q. Lin, J. De Vrieze, C. Li, J. Li, J. Li, M. Yao, P. Hedenec, H. Li, T. Li, J. Rui, J. Frouz, X. Li, Temperature regulates deterministic processes and the succession of microbial interactions in anaerobic digestion process, Water Res., 123 (2017) 134–143.
[19] G.C. Cha, T. Noike, Effect of rapid temperature change and HRT on anaerobic acidogenesis, Water Sci. Technol., 36 (1997) 247–253.
[20] E. Klaucans, K. Sams, Problems with fat, oil, and grease (FOG) in food industry wastewaters and recovered FOG recycling

methods using anaerobic co-digestion: a short review, Key Eng. Mater., 762 (2018) 61–68.
[21] L.A.S. Miranda, J.A.P. Henriques, L.O. Monteggia, A full-scale UASB reactor for treatment of pig and cattle slaughterhouse wastewater with a high oil and grease content, Braz. J. Chem. Eng., 22 (2005) 601–610.
[22] J.B. Lier, F.P. Zee, C.T.M.J. Frijters, M.E. Ersahin, Celebrating 40 years anaerobic sludge bed reactors for industrial waste-water treatment, Rev. Environ. Sci. Bio/Technol., 14 (2015) 681–702.
[23] U. Tezel, J.A. Pierson, S.G. Pavlostathis, Fate and effect of quaternary ammonium compounds on a mixed methanogenic culture, Water Res., 40 (2006) 3660–3668.
[24] J.-H. Ahn, C. Forster, The effect of temperature variations on the performance of mesophilic and thermophilic anaerobic filters treating a simulated papermill wastewater, Process Biochem., 37 (2002) 589–594.
[25] A. Sánchez, L. Rodriguez-Hernandez, D. Buntner, A.L. Esteban-García, I. Tejero, J.M. Garrido, Denitrification coupled with methane oxidation in a membrane bioreactor after methanogenic pre-treatment of wastewater, J. Chem. Technol. Biotechnol., 91 (2016) 2950–2958.
[26] B. Sarkar, M. Megharaj, Y. Xi, G. Krishnamurti, R. Naidu, Sorption of quaternary ammonium compounds in soils: implications to the soil microbial activities, J. Hazard. Mater., 184 (2010) 448–456.
[27] Á. Iglesias-Obelleiro, R. Fernández-González, J.M. Garrido-Fernández, Treatment of primary settled municipal wastewater in a pilot scale MBR, Desal. Wat. Treat., 44 (2012) 197–204..