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Performances of a submerged anaerobic membrane bioreactor (AnMBR) for latex serum treatment

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ABSTRACT

This paper focused on anaerobic membrane bioreactor (AnMBR) performances when treating latex serum at two organic-loading rates (OLR), 8.1 and 12.7 kg COD m^{-3} d^{-1} and imposed solids retention time (SRT) and hydraulic retention time (HRT), 30 and 2 d, respectively. Results pointed out the determining role of the membrane barrier in AnMBR to improve chemical oxygen demand (COD) removal efficiency reaching 86 and 73.5% for OLR of 8.1 and 12.7 kg COD m^{-3} d^{-1}, respectively. The degradation of COD in the anaerobic metabolism induced some biogas production, notably methane with a methane yield coefficient close to 0.22 and 0.24 NL $gCOD_{removed}^{-1}$. In the experiment carried out in AnMBR, membrane fouling was mainly due to the structuring of cake deposit on the membrane surface, and this deposit appeared reversible by water rinsing. The analyses of rinsing solutions corresponding to cake detachment pointed out carbohydrates as the major component of fouling material whatever the OLR studied. Scanning electron microscopy analyses revealed a higher thickness of deposit when working at higher OLR, and atomic force microscopy (AFM) analyses showed a lower roughness relating to a more compact structure in the same conditions of higher OLR.

Keywords: Anaerobic membrane bioreactor; Anaerobic digestion; Membrane fouling; Latex serum; Cake deposit analyses

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1. Introduction

Latex is a major Thai rubber industry. The raw latex material for downstream industries (gloves, condoms, balloons, etc.) is obtained by centrifuging field latex. A by-product of this concentration step is skim latex presenting a low dry rubber content (DRC < 5%). To recover latex particles from skim latex, a physical–chemical process including sulphuric acid coagulation and flotation is generally developed, but it also produces a by-product called latex serum showing high acid content with low-pH effluent values (3.6–4.8) and high sulphate contamination [1,2]. A large volume of such latex serum is still considered as wastewater and conventionally rejected in large pond systems [3,4]. Because of high COD concentrations in such serum effluents, biological activities appear in ponds and quickly generate negative environmental impacts such as bad odours, due to the high level of sulphide content, and possible contaminations of ground and surface water [1,4]. Even if these systems are inexpensive and have relatively high efficiency for organic load reduction, their high footprint and possible environmental pollution limit their application.

Another way of latex serum valorization is the production of biogas by the anaerobic digestion of biodegradable organic matter present in serum effluent. Anaerobic processes are then proposed to treat serum effluent, but the significant presence of H_2S in biogas due to acid conditioning in the conventional coagulated skim latex processes inhibit the digestion process, which gives a lower organics removal efficiency and limited biogas use due to corrosion problems in combustion engines [2]. Even though it is a low-cost operation with high removal efficiency and biogas production as a useful energy source, concentrated latex factory owners have little interest in such anaerobic solutions [2].

According to the wide use of membrane technologies to separate and concentrate food products, some studies were developed to analyse the interest of membrane processes for directly separating rubber particles from skim latex suspension without the addition of acid [5,6]. The serum permeate would then be free from any acid contamination, and such a technique of separation appears as an environmentally friendly process, with the possibility of recovering valuable by-products from latex serum. Moreover, latex serum obtained without any sulphuric acid addition can appear as a promising approach by allowing serum fermentation with low H_2S content in biogas.

Because the conventional anaerobic process still encounters some difficulties of biomass washout inducing poor treatment performances and poor effluent quality [7], anaerobic (immersed) membrane bioreactor (AnMBR) including a final liquid–solid separation step on porous membranes offers relevant solutions by ensuring a total biomass retention according to the low cut-off of the membrane barrier [8]. Then, it is possible to maintain a high solids retention time (SRT) even when operating at low hydraulic retention time (HRT). Such conditions, high SRT, short HRT, offer stable biological performances and minimize reactor volumes [9]. Furthermore, it offers efficiency of effluent quality in terms of COD, suspended solids and pathogen counts in the final effluent [10]. Such AnMBRs have been applied for the treatment of various wastewaters such as brewery wastewater, artificial wastewater and sauerkraut brine, food wastewater, slaughterhouse wastewater, cheese whey, landfill leachate and municipal wastewater [8,11,12]. Nevertheless, the application of AnMBR is still restricted and limited due to membrane fouling phenomena. Indeed the biological suspension in submerged anaerobic membrane bioreactor (AnMBR) appears to have high concentrations of suspended solids and soluble polymeric substances (EPS). Such compounds are retained due to the membrane selectivity and their accumulation onto the membrane surface and in the membrane pores, drastically modifying the membrane permeability and obliging frequent chemical regeneration of membranes. The operations with too long SRT and too short HRT are not being suggested for submerged AnMBR applications due to the risk of negative effects on membrane fouling [13]. Intermittent filtration, backwashing and gas injections are simple operating techniques to minimize fouling [14–16]. Some pilot studies of such processes have been published for flat sheet (FS) membranes. However, there have been fewer pilot-scale studies of the hollow fibre (HF) configuration [17].

Thus, the objective of this study focused on the performance of an AnMBR equipped with a submerged HF membrane module when treating latex serum. The AnMBR performances were evaluated according to the fermentation step (COD removal and biogas production) and the membrane fouling dynamic for two different organic-loading rates (OLR) of 8.1 and 12.7 kg COD m^{-3} d^{-1}.

2. Materials and methods

2.1. AnMBR set-up

The AnMBR unit was set up as shown in Fig. 1. The system consisted of the association of two reactors in series, reactor 1 as an anaerobic reactor and reactor 2 as a separation step tank, presenting the same

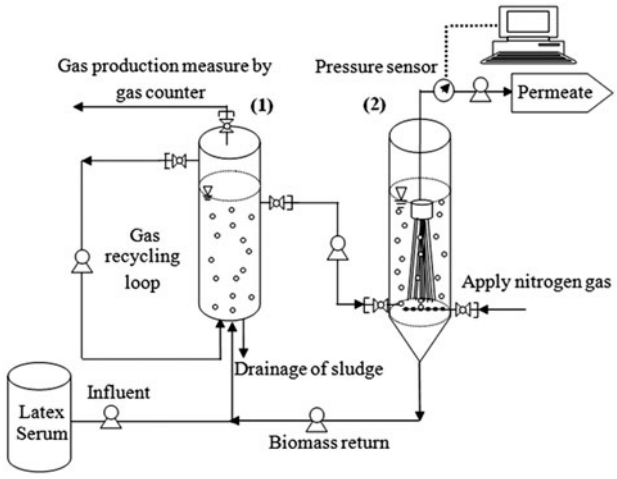

Fig. 1. Schematic diagram of AnMBR set-up.
Notes: (1) Anaerobic reactor and (2) Membrane reactor.

volume (6 L). This configuration of 2 reactors in series was chosen to favour better management of both operations. The biological system in reactor 1 was not disrupted by the membrane cleaning steps (no modification of the mixing intensity or no entrance of chemical reagents, for example), the immersion of the membrane module in a specific tank allowed some better controls of shear stresses by specific gas dispersion around the membrane module, of suspended solids concentration in this specific tank and even of cleaning in place, if necessary [18]. For both OLR, the experiment was carried out during two successive periods. During the first "start-up" period, reactor 2 was only functioning as a settling step. During the second period, after day 75, reactor 2 was equipped with a submerged HF membrane module (Shanghai Jofur Advanced Materials Co. Ltd, China) whose characteristics are given in Table 1.

Intermittent operation and its sequencing were imposed on each reactor during both periods:

(1) Reactor 1 presented a one hour cycle with 3 periods: (i) first period of 10 min for feeding with serum effluent, (ii) 15 min of mixing, realized by recycling a fraction of produced biogas at an instantaneous injection flow rate of 0.2 NL min^{-1}, (iii) 35 min of settling to decrease the sludge concentration in the supernatant of this reactor.
(2) Simultaneous to the feeding period, reactor 1 supernatant was extracted by overloading and sent towards reactor 2. During the start-up period (till day 75), reactor 2 worked as a settler. The settled sludge was recycled towards the anaerobic reactor during each feeding period of 10 min in each hour at an average flow rate of 9 L d^{-1} corresponding to an average daily recycle ratio equal to 150% in comparison with the daily influent flow rate. The settled water was recovered by overloading from reactor 2, and it corresponded to the treated water.

When the system worked as an AnMBR (from day 75 to day 128), reactor 2 was equipped with submerged membranes (Table 1). The filtration was then carried out for 4 min in each 5-min period (operated in a cycle of 4 min-on and 1 min-off). To ensure an easy control of gas injection in this laboratory-scale reactor, nitrogen gas was injected (1 L min^{-1}) in place of biogas at the bottom of the membrane module during filtration time to induce turbulence close to the membrane surface (of course biogas should be chosen for practical applications [19]). The recirculation of sludge between the membrane tank and the anaerobic reactor was operated as indicated for the start-up period. Permeate was considered as the treated water. The instantaneous permeate flux during filtration time was 5.83 L m^{-2} h^{-1}, and the net permeate flux was equal to 4.66 L m^{-2} h (taking into account the period of no filtration). The common working conditions for the start-up period and AnMBR period are given in Table 2.

2.2. Experimental conditions

The system was initially seeded by anaerobic sludge coming from the anaerobic digestion plant of a

Table 1
HF membrane characteristics

Characteristics	Content/Values
Type	Hollow fibre
Membrane material	PVDF
Membrane diameter (mm, inner/outer)	0.7/1.3
Total filtration area (m^2)	0.05
Mean pore size (μm)	0.1
Hydraulic resistance of cleaned membrane (m^{-1}) to water (27°C)	4.2×10^{11}

Table 2
Operating conditions for start-up (day 0–day 75) and AnMBR period (day 75 to day 128)

Conditions	Values
Total working volume (V, L)	12
Hydraulic retention time (HRT, d)	2
Solids retention time (SRT, d)	30
Temperature; ambient temperature (°C)	30 ± 2
$COD_{influent}$ (g L^{-1})	16.2 or 25.4
OLR (kg COD m^{-3} d^{-1})	8.1 or 12.7

latex factory, Songkhla province, South Thailand. The feed solution was a latex serum obtained from skim latex filtration (0.22-μm membrane cut-off). The characteristics of this feed latex serum are given in Table 3.

This initial latex serum was a light yellow coloured solution with low turbidity (the absence of particular fraction due to its recovery by porous membrane filtration). It presents a high concentration of soluble organic matter (COD > 25 g L^{-1}) and ammonia nitrogen (ammonia nitrogen > 1 g L^{-1}). Such a high ammonia nitrogen concentration was due to the addition of ammonia solution to stabilize initial recovered field latex suspension, it could induce inhibition of biological activity as it was reported when its concentration reached a level of 1.5–3.0 g L^{-1} [20–22]. However, due to the regulation of pH close to a neutral range in this study (Table 3), ammonia nitrogen concentration had never exceeded 0.5 and 0.9 g L^{-1} for OLR at 8.1 and 12.7 kg COD m^{-3} d^{-1}, respectively. The COD/BOD_5 ratio, equal to 2.13, confirmed the significant degree of biodegradability of such an effluent.

The experimental set-up was operated under two successive OLRs of 8.1 and 12.7 kg COD m^{-3} d^{-1}. Each OLR experiment lasted 128 d based on the two periods, start-up period and AnMBR period, as described in Section 2.1. For each OLR experiment, the initial sludge concentration in bioreactors was started up at 10 gVSS L^{-1} and pH was maintained in the range of 6.8–7.2 by sodium hydroxide (1 N) addition. During the AnMBR period (from day 75 to day 128), the filtration was operated by using a peristaltic pump connected to the permeate side of the membrane module. A pressure sensor was located in the permeate line in order to measure transmembrane pressure (TMP) as the difference between pressure in AnMBR (1 atm) and the pressure upstream from the permeate pump. A computer with Lab-View application was connected to a data acquisition card (National Instruments, Austin, USA).

The biogas production was evaluated by gas counter measurement directly connected to the headspace of the reactor. Biogas composition was analysed by gas chromatography (GC) (Agilent7890 A) as indicated by Thongmak et al. [23].

2.3. Identification of membrane fouling origin during AnMBR period

A membrane-cleaning procedure was carried out as soon as the TMP value reached a level close to 25 kPa, a value often considered as critical to avoid deposit compression and difficulty for the regeneration of membrane permeability [14,15]. The hydraulic resistance of fouled membrane was calculated by using Darcy's law:

$$R_{total} = TMP/\mu \cdot J \quad (1)$$

where R_{total} is the total filtration resistance (m^{-1}), TMP is TMP (Pa), μ is the dynamic viscosity (Pa s measured at 27.5 ± 1°C in cleaning conditions), J is the permeate flux (m^3 m^{-2} s^{-1}).

As supposed by the resistance in series model [16,24], the fouled membrane resistance R_{total} was considered as the sum of the initial clean membrane hydraulic resistance R_m, resistance due to cake deposit R_{cake}, resistance due to pore blocking $R_{pore\ blocking}$ and resistance due to adsorption of molecules onto the membrane surface and internal pore wall $R_{adsorption}$ as follows:

$$R_{total} = R_m + R_{cake} + R_{pore\ blocking} + R_{adsorption} \quad (2)$$

The cake deposit R_{cake} was considered as a reversible part of fouling when rinsing the membrane with

Table 3
Latex serum characteristics used for the two different OLR at 8.1 and 12.7 kg COD m^{-3} d^{-1}

Parameters	OLR ≈ 8.1 kg COD m^{-3} d^{-1}	OLR ≈ 12.7 kg COD m^{-3} d^{-1}
SCOD (g L^{-1})	16.2 ± 0.4	25.4 ± 0.2
BOD_5 (g L^{-1})	7.6 ± 0.4	10.9 ±0.5
Ammonia nitrogen (g L^{-1})	0.5 ± 0.03	0.9 ± 0.05
pH	7 ± 0.2	7 ± 0.2

distilled water, $R_{\text{pore blocking}}$ was considered as reversible fouling when backwashing was carried out and $R_{\text{adsorption}}$ was supposed reversible only when practising chemical cleaning.

When the TMP reached 25 kPa, the fouled membrane module was extracted from the AnMBR unit and replaced by a new cleaned one. The membrane cleaning procedure was then carried out consisting of three steps as follows:

(1) The fouled membrane module was rinsed with distilled water to remove compounds attached on the membrane surface. Distilled water was then filtered with the rinsed membrane to calculate its resistance after rinsing, R_{rinsing}.
(2) Backwashing was then carried out for 2hrs with distilled water to remove any compounds mechanically blocking the pores. Distilled water was then filtered with the backwashed membrane to calculate its resistance after backwashing, $R_{\text{backwashing}}$.
(3) Chemical cleaning was used in the final step. Membranes were then soaked successively in a 0.5 v/v % sodium hydroxide solution, 0.5 v/v % of sodium hypochlorite solution, and 0.5 v/v % of hydrochloric acid solution (2 h for each solution). R_{chemical} was then obtained after filtering distilled water. If the chemical cleaning was sufficient, the final membrane resistance R_{chemical} would have to be equal to the intrinsic membrane resistance R_{m}.

The specific hydraulic resistances due to each fouling origin can be expressed and calculated, respectively, as follows:

$$R_{\text{cake}} = R_{\text{total}} - R_{\text{rinsing}} \quad (3)$$

$$R_{\text{pore blocking}} = R_{\text{rinsing}} - R_{\text{backwashing}} \quad (4)$$

$$R_{\text{adsorption}} = R_{\text{backwashing}} - R_{\text{m}} \quad (5)$$

2.4. Analytical methods

2.4.1. Conventional criteria to quantify biological performances

The concentrations of chemical oxygen demand (COD), total volatile suspended solid (TVSS), total suspended solids (TSS) were measured as indicated in the Standard Methods [25]. COD in supernatant was analysed after about 30 min of sample settling.

2.4.2. Soluble and bound EPS extraction

The rinsing water recovered from fouled membrane cleaning was (i) centrifuged for about 30 min at 2,360×*g*. The supernatant from centrifugation was filtrated through a membrane with a mean pore size 0.45 μm, and thus, the permeate contains the soluble microbial products (SMP) fractions, (ii) heated for 10 min at 80˚C and this step was followed by the same centrifugation and filtration steps, and the permeate contains the soluble and bound EPS fractions [13,14]. Bound EPS was deduced as EPS fractions minus SMP fractions.

The SMP and bound EPS were characterized through protein and carbohydrate concentrations by the colorimetric method [26,27], which used bovine serum albumin (BSA) as protein and glucose as carbohydrates standards, respectively.

2.4.3. Fourier transform infrared (FTIR) spectroscopy

FTIR spectroscopy (EQUINOX 55, Bruker, Germany) and in house method, referring to WI-RES-FTIR-001, were employed to identify the functional groups of organic foulants. The wave number of spectra was calculated from an average of 32 scans and recorded covering a range from 4,000 to 400 cm^{-1} at a resolution of 4 cm^{-1}. The analyses were carried out on cleaning solutions recovered and placed in a dryer at 105˚C for 24 h to obtain dry foulants. Potassium bromide (KBr) pellets containing 0.50% (dry powder) of the sample were prepared and examined in the FTIR spectrophotometer [28].

2.4.4. Scanning electron microscopy, energy dispersive X-ray spectroscopy

Small pieces of clean and fouled membrane were cut to obtain membrane samples. These samples were fixed with 2.5% gluteraldehyde in a 0.1 M phosphate buffer solution (pH 7.2) for about 2 h. After that, each fixed sample was washed with a buffer solution three times for about 10 min per each washing. This sample was then dehydrated with a series of graded ethanol solutions (50, 70, 80, 90%, and three rounds of 100%) before mounting onto stub and coating. The coated sample was analysed by Scanning electron microscopy (SEM) (Quanta400, FEI: SEM). Furthermore, SEM coupled with energy dispersive X-ray (EDX) spectroscopy was used to detect the inorganic components of foulants [15,29].

2.4.5. Atomic force microscopy

The fouled membrane surface was analysed by atomic force microscopy (AFM) analysis (Nanosurf®, easyScan 2). The surface roughness of the cake layer on the fouled membrane was presented in terms of AFM image, the mean roughness (R_a) and root mean square roughness (R_{rms}) of the surface.

2.5. Kinetic coefficients

The experiment data for both OLRs were used to calculate some kinetic coefficients. Their values were deduced by using common relations as follows:

(1) COD removal rate (kg $COD_{removed}$ m^{-3} d^{-1}).

$$R_{COD\ removal} = (COD_{inf} - COD_{eff})/HRT \quad (6)$$

where COD_{inf} and COD_{eff} are the COD concentration (kg COD m^{-3}) in latex serum and treated water respectively, and HRT the hydraulic retention time (d).

(2) Daily biogas production (NL biogas $_{produced}$ d^{-1}) was deduced from the experiment.
(3) Methane yield coefficient (NL CH_4 $gCOD_{removed}^{-1}$).

$$Y_m = (\text{Biogas production} \times CH_4)/[(COD_{inf} - COD_{eff}) \times Q] \quad (7)$$

where biogas production is the daily biogas production, $\%CH_4$ is the percentage of methane in produced biogas and Q the daily average flow rate (L d^{-1}) of influent injected in the bioreactor.

(4) Biomass growth rate (kg $MLVSS_{produced}$ m^{-3} d^{-1}).

$$R_X = (\Delta X/\Delta t) + [(Q_{extracted} \times X)/V] \quad (8)$$

where ΔX (kg MLVSS m^{-3}) is the daily variation of the mixed liquor volatile suspended solid concentration in the reactor, Δt corresponds to a period of 1 d, $Q_{extracted}$ is the daily flow rate (m^3 d^{-1}) of sludge extraction from the bioreactor, X (kg MLVSS m^{-3}) the mixed liquor volatile suspended solid concentration in the reactor and V (m^3) the reactor volume.

(5) Biomass maximum growth rate (d^{-1}).

$$\mu_{apparent} = R_X/X \quad (9)$$

(6) Bioconversion yield coefficient (kg $MLVSS_{produced}$ kg $COD_{removed}^{-1}$).

$$Y_{obs} = R_X/R_{CODremoval} \quad (10)$$

3. Results and discussion

3.1. Biological performances of AnMBR

Fig. 2 presents the evolutions of COD in supernatant and permeate and the biogas production. COD in treated water was represented by (i) COD in supernatant during the start-up period, and (ii) COD in permeate when AnMBR was working.

During the start-up period, the COD in supernatant progressively decreased until it reached levels close to 4.3 and 11.9 gCOD L^{-1} for OLR of 8.1 and 12.7 kg COD m^{-3} d^{-1}, respectively. According to influent COD concentration, the corresponding COD removal efficiency was about 71 ± 5 and 50 ± 5%, respectively. In steady-state conditions, the average biogas production was then close to 20.5 ± 1.8 and 26.6 ± 3.9 NL d^{-1} (0.29 ± 0.03 and 0.31 ± 0.04 NL $biogas_{produced}$ $gCOD_{removed}^{-1}$) for OLR of 8.1 and 12.7 kg COD m^{-3} d^{-1}, with a methane percentage in biogas close to 60% what corresponded to an average methane yield coefficient close to 0.17 ± 0.02 and 0.19 ± 0.03 NL CH_4 $gCOD_{removed}^{-1}$, respectively.

When the membrane module was immersed in reactor 2, the largest soluble organic compounds and all biomass and suspended solids were then retained inside bioreactors by the membrane selectivity, and system performances were improved. COD concentration in permeate was equal to 2.3 and 6.7 gCOD L^{-1} for OLR of 8.1 and 12.7 kg COD m^{-3} d^{-1} respectively, which corresponded to 86 ± 2 and 73 ± 2% of COD removal efficiency. The VFA concentration in treated water was found in the ranges of 0.82 ± 0.11 $g_{equivalent\ acetate}$ L^{-1} and 2.10 ± 0.22 $g_{equivalent\ acetate}$ L^{-1} for OLR of 8.1 and 12.7 kg COD m^{-3} d^{-1}, respectively. No significant difference was observed in treated water when the filtration on membranes occurred. The concentration of VFA appeared 2.5 times higher when OLR increase was only 50%. Such VFA concentrations significantly contributed to the high level of soluble COD in treated water with the probable presence of hard soluble COD coming from influent or biomass activity (by-products of metabolism). Such high VFA concentrations, notably for the highest OLR, point out an insufficient contact time for the methanogenesis step [30], and that VFA accumulation had a negative effect on biogas production [31]. A significant difference of COD concentration could be observed between

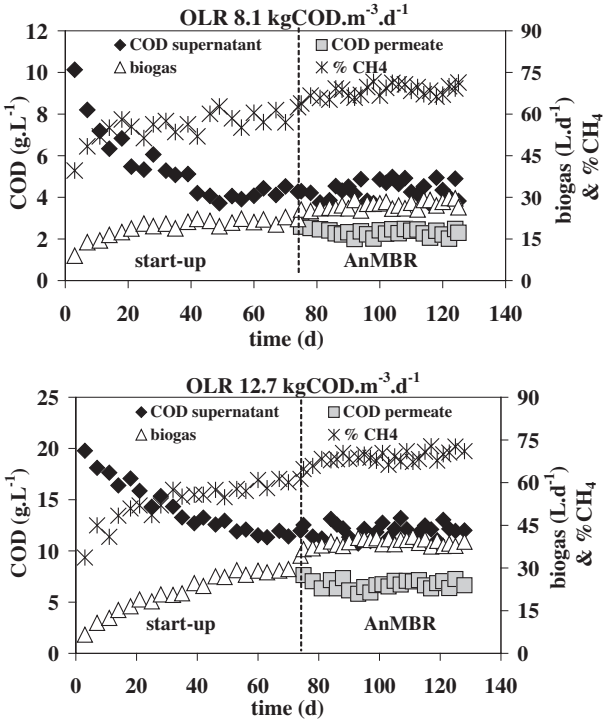

Fig. 2. Evolutions of COD concentration in supernatant and permeate, biogas production and the percentage of CH_4 in the produced biogas for the two OLRs.

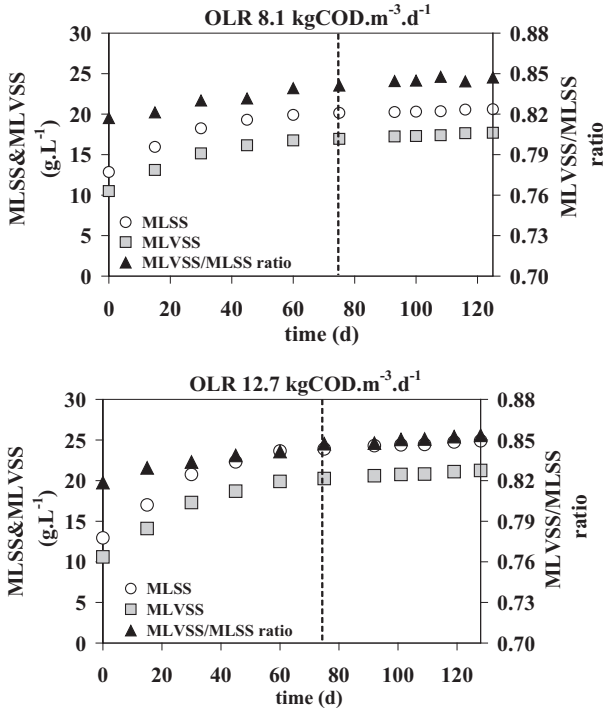

Fig. 3. Evolutions of MLSS, MLVSS concentrations and MLVSS/MLSS ratios with time.

supernatant obtained in the start-up period and permeate obtained in the presence of membranes. It points out (i) the role of the membrane barrier on treated water quality by stopping nonsettleable suspended fractions, and (ii) because of this membrane selectivity, numerous organic compounds accumulate inside the reactor with an increase in their retention time, favourable to their biodegradation, and the improvement of COD removal and biogas production by an increase in the biogas production to 27.2 ± 1.4 and 38.9 ± 1.2 NL d^{-1} (0.33 ± 0.02 and 0.35 ± 0.01 NL $biogas_{produced}$ $gCOD_{removed}{}^{-1}$) with methane content in biogas close to 65% corresponding to the methane yield coefficient to 0.22 ± 0.01 and 0.24 ± 0.01 NL $gCOD_{removed}{}^{-1}$.

Fig. 3 presents the evolutions of MLSS and MLVSS concentration in bioreactors and MLVSS/MLSS ratios during experiments. Because influent was only composed of soluble organic and mineral fractions (the latex serum was recovered by micro-filtration of skim latex and did not contain any suspended solids), the modification of suspended solids concentration in the reactor can be supposed due to biomass activity (biomass growth and lysis with the formation of new cells, biopolymers, bound EPS, fragments of lysed cells). During the start-up period, a progressive increase in MLSS and MLVSS concentrations could be observed until reaching levels close to 20 and 17 g L^{-1} and 25 and 20 for OLR of 8.1 and 12.7 kg COD m^{-3} d^{-1}, respectively. These increases corresponded to biomass activity mainly linked to COD conversion until reaching steady state conditions. The set-up of membranes in reactor 2 induced a slight increase in these criteria.

Some kinetic criteria were then deduced from experimental results, their calculated values are given in Table 4. As expected, the COD removal rate, MLVSS production and biogas production increased with applied OLR. The results of Rincón et al. [32] demonstrated that the rate of COD removal increased linearly with OLR increase. The methane yield coefficient showed a slight increase when OLR increased, while Y_{obs} was not affected by OLR modification, and it also shows the interest of anaerobic process presenting a relatively low sludge production (in comparison with aerobic process). The obtained methane yield (0.22 and 0.24 NL CH_4 $gCOD_{removed}{}^{-1}$ for OLR of 8.1 and 12.7 kg COD m^{-3} d^{-1}), can be compared with results (0.11 and 0.24 NL CH_4 $gCOD_{removed}{}^{-1}$, corresponding to OLR of about 2.9 and 5.2 kg COD m^{-3} d^{-1}) obtained with a UASB system [33], when treating a mixture of wash water combined

Table 4
Kinetic coefficients calculated from experimental data for both OLRs for the start-up period (first 75 d) and AnMBR period (from day 75 to day 128)

	OLR ≈ 8.1 kg COD m^{-3} d^{-1}		OLR ≈ 12.7 kg COD m^{-3} d^{-1}	
Criteria	Start-up	AnMBR	Start-up	AnMBR
COD removal rate (kg $COD_{removed}$ m^{-3} d^{-1})	5.8 ± 0.5	6.9 ± 0.2	6.4 ± 0.6	9.3 ± 0.3
Biogas production (NL $biogas_{produced}$ d^{-1})	20.5 ± 1.8	27.2 ± 1.4	26.6 ± 3.9	38.9 ± 1.2
Methane yield coefficient (NL CH_4 $gCOD_{removed}^{-1}$)	0.17 ± 0.02	0.22 ± 0.01	0.19 ± 0.03	0.24 ± 0.01
Biomass growth rate (kg $MLVSS_{produced}$ m^{-3} d^{-1})	0.58 ± 0.02	0.58 ± 0.01	0.69 ± 0.03	0.71 ± 0.01
Biomass maximum growth rate $\mu_{apparent}$ (d^{-1})	0.04 ± 0.01	0.03 ± 0.001	0.04 ± 0.01	0.03 ± 0.004
Bioconversion yield coefficient Y_{obs} (kg $MLVSS_{produced}$ kg $COD_{removed}^{-1}$)	0.10 ± 0.01	0.08 ± 0.001	0.11 ± 0.03	0.08 ± 0.002

with rubber skim wastewater coming from H_2SO_4 coagulation, and with wash water combined with polymer-treated wastewater. As a comparison, the methane yield obtained when treating slaughterhouse wastewater treatment with AnMBR [34] was in the range of 0.2 and 0.31 NL CH_4 $gCOD_{removed}^{-1}$ under the operating conditions of HRT 1.66–3.33 d, with a progressive increase of methane yield with increasing HRT.

3.2. Performance of filtration

After the immersion of the membrane module in reactor 2, the evolutions of TMP with time were measured and results are presented in Fig. 4 for both OLRs. As soon as TMP was close to 25 kPa, the membrane module was taken out from the reactor to be cleaned and the fouling was characterized as indicated in Sections 2.3 and 2.4.

The dynamic of TMP evolution was similar for both OLRs even though the concentration of MLSS and the difference of COD in supernatant and permeate were significantly higher when working at the highest OLR.

Before reaching 25 kPa, the TMP evolutions could be differentiated in two periods as often observed in submerged membrane bioreactors [15], (i) a slow TMP increase followed by (ii) a rapid TMP increase. The slow TMP evolution can be explained by the choice of sub-critical conditions of filtration, the slow TMP means that slow fouling occurred; Ognier et al. [35] explained such an evolution by adsorption or mechanisms involving some local build-up of deposits adhering strongly to the membrane material. The rapid increase was often explained by a progressive accumulation of colloids and biofilm development onto the membrane surface and pores that drastically modified membrane permeability and deposit porosity [29,35,36]. A higher OLR did not result in faster membrane fouling, Birima et al. [37] pointed out that due to local shear and fluctuation of liquid flow from bubbles and fibre movement, depositions of large particles on the membrane surface could be prevented.

3.3. Characterization of fouling

3.3.1. Main origin of fouling

During a period of 53 d, membranes were taken off 5 times from the reactors and cleaned according to the specific procedure described in the materials and methods section. The different hydraulic resistances were then calculated at each cleaning step. Results showed for both OLRs that the resistance caused by cake formation ($1.73 \pm 0.06 \times 10^{13}$ and $1.86 \pm 0.04 \times 10^{13}$ m^{-1},

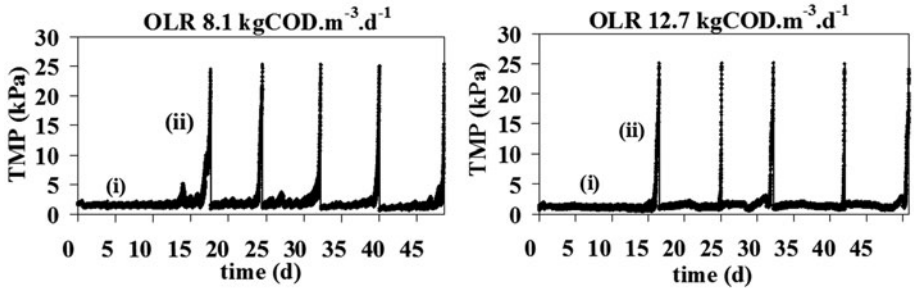

Fig. 4. TMP variations vs. time at different OLRs.

Table 5
Protein and carbohydrate concentrations in SMP and bound EPS

Parameter		OLR ≈ 8.1 kg COD m^{-3} d^{-1}	OLR ≈ 12.7 kg COD m^{-3} d^{-1}
SMP	Proteins (mg L^{-1})	17.8 ± 7.4	20.6 ± 5.5
	Carbohydrates (mg L^{-1})	185.2 ± 95	214.4 ± 93.8
Bound EPS	Proteins (mg L^{-1})	9 ± 5.7	12 ± 9.9
	Carbohydrates (mg L^{-1})	123.6 ± 45.2	134 ± 64.1

respectively) represented more than 95% of the total resistance. External cake deposits appeared then as the main origin of fouling, while pore blocking and adsorption appeared negligible. Such results were also previously noticed when working with a submerged AnMBR [15], probably linked to the high suspended solids concentration developed in such reactors that induces a quick accumulation of particles onto the membrane surface, despite shear stresses and fibre movement caused by gas bubbling close to the membrane surface [38]. No significant differences of hydraulic resistance were observed between each cleaning operation, even if slightly higher peaks could be observed for higher OLR. Results of Birima et al. [37] also reported that higher OLR did not result in faster membrane fouling.

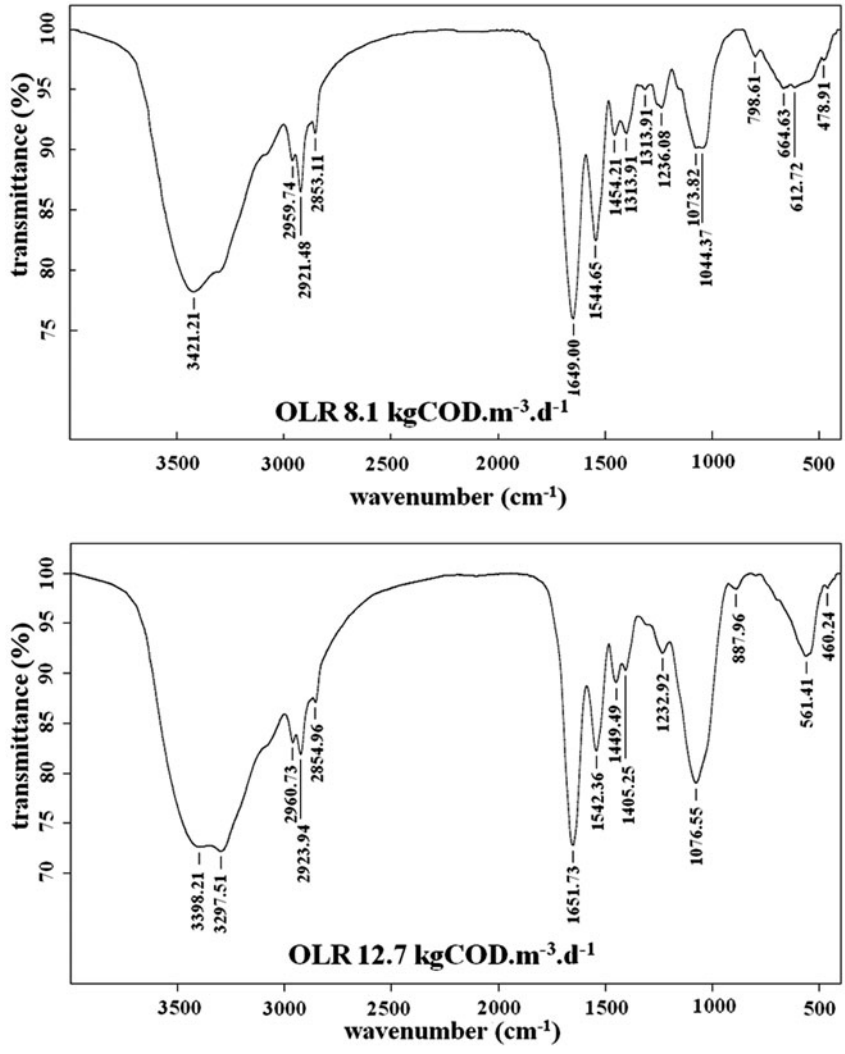

Fig. 5. FTIR spectra of fouled membrane surface.

3.3.2. Determination of SMP and bound EPS in deposit

The concentrations of SMP and bound EPS in rinsing water were measured at the end of each test as shown in Table 5. Carbohydrates were the major component of both SMP and EPS in both conditions; they impacted more on membrane fouling than proteins. Such observations were also noticed by Cern-Vivas et al. [14], indicating that carbohydrates SMP and carbohydrates EPS, rather than proteins, were the major factors affecting membrane fouling, and Dvořák et al. [39] showing that the majority of SMP components retained by the membrane were carbohydrates. In this study, it was noticed that the concentrations of SMP and bound EPS in deposit tended to increase with filtration runs. It agreed with previous research showing SMP concentrations in permeate were lower than in supernatants and meaning that SMPs were accumulated inside the MBR [40].

3.3.3. FTIR

Fig. 5 presents results of FTIR analyses and their spectra for both OLRs. A broad peak near 3,421 cm^{-1} indicates the presence of hydroxyl functional group (O–H stretching) [29], with the possibility of being polysaccharides due to a significant number of hydroxyl functional groups appearing at broad adsorption peaks above 3,000 cm^{-1} wavenumber [41]. In addition peaks in the range of 1,075–1,000 cm^{-1} are associated with C–O bonds from alcohol associated with polysaccharides [42]. A peak in the region of 3,000–2,850 cm^{-1} is due to the C–H bonds in the alkanes class [43,44]. Two sharp peaks around 1,700–1,600 cm^{-1} and 1,600–1,500 cm^{-1} correspond to proteins, namely amides I and II, and a peak in the range of 1,310–1,200 cm^{-1} corresponds to the presence of amide III [45]. Peaks near 1,454 cm^{-1} imply the possible presence of CH_2 group [44]. Peaks of 1,399 and 1,405 cm^{-1} indicate the presence of COO– group, attributed to amino acids [45]. The region of 960–875 cm^{-1} (O–H) and 850–750 cm^{-1} (N–H) correspond to carboxylic acid and amide [42], and at a wavenumber of 760–610 cm^{-1} (O–H) is attributed to carboxylic groups and COOH deformation [46]. Such results confirm that proteins and polysaccharides were the main components of cake layer on the membrane surface as reported by Kim and Jang [43]. If the peaks distribution appears similar for both OLR, higher absorbance was found for the highest OLR, indicating greater production.

3.3.4. SEM-EDX

Fig. 6 shows the SEM images of fouled and cleaned membranes, acquired before and after

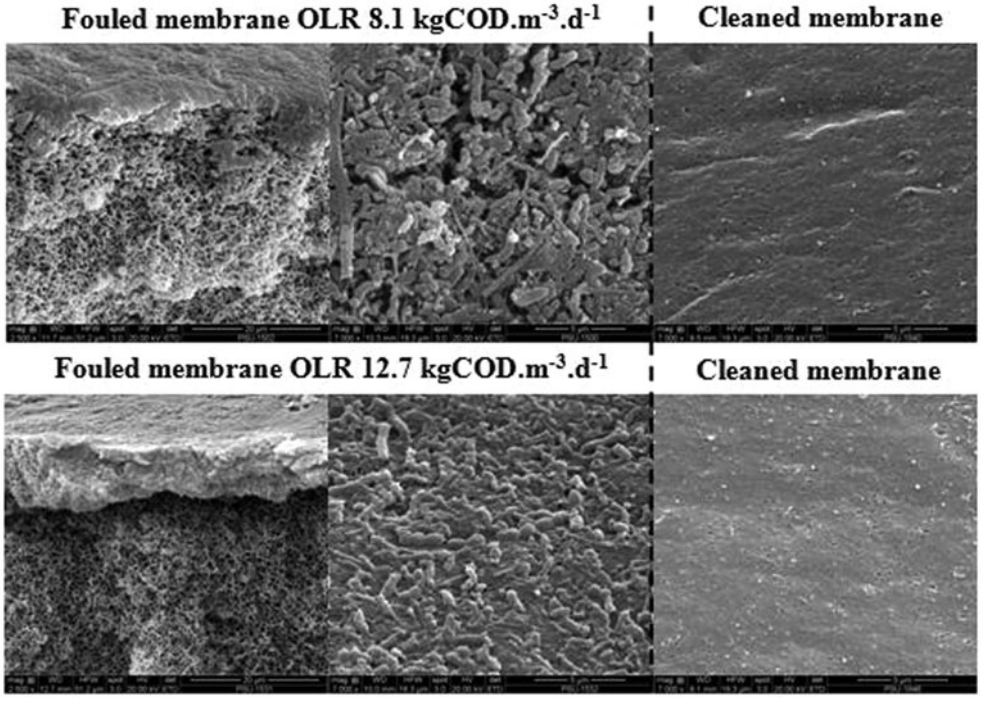

Fig. 6. SEM photographies of fouled and cleaned membrane surfaces.

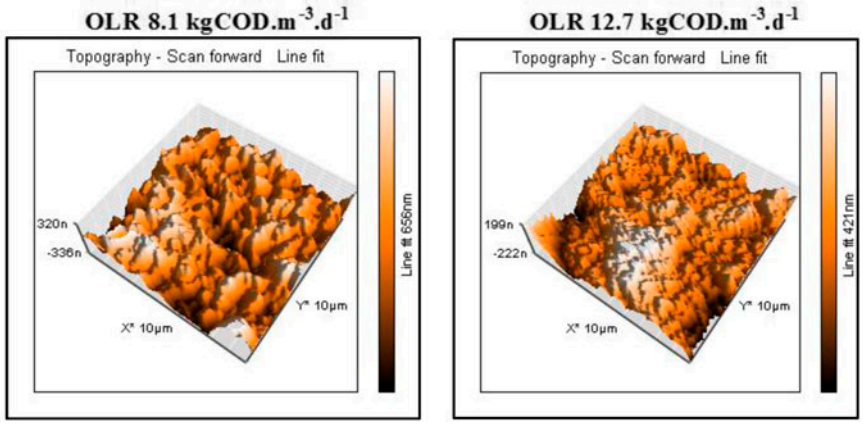

Fig. 7. AFM images of fouled membrane surface.

chemical cleaning. The fouled membrane was covered with a slime layer containing bacteria cells. The cleaned membrane shows the relevance of the chemical cleaning since no apparent fouling or particles accumulation can be observed on membrane surface. Fig. 6 reveals a higher thickness of deposit when working at the highest OLR. The cross section of fouled membrane presented a fouling layer of approximately 2.56–5.13 µm and 5.13–10.26 µm for OLR ≈ 8.1 kg COD m^{-3} d^{-1} and OLR ≈ 12.7 kg COD m^{-3} d^{-1}, respectively.

EDX analysis points out the main compounds detected on the membrane surface. C, O, and F are the main components in the case of a new membrane. The presence of Mg, Na, P, Al, Si, Zn, and Ca appeared in the fouled membrane surface. They were contained in the latex serum [47] and are well known as contributors to fouling layer formation; the inorganic precipitation coupled with the organic foulants further induced the cake layer formation [15,29]. However, membrane cleaning eliminated the majority of these compounds accumulated by filtration.

3.3.5. Atomic force microscopy

If the SEM method allows an evaluation of the cake layer thickness, the AFM method gives an average value of the external roughness. Fig. 7 shows AFM images of cake layer structure. The value of root mean square roughness (R_{rms}) was identified at around 129.8 and 77.82 nm, and the mean roughness (R_a) was 100.20 and 58.92 nm at an OLR of about 8.1 and 12.7 kg COD m^{-3} d^{-1}, respectively. In this study, higher OLR showed a higher thickness of cake deposit but a lower roughness related to a more compact structure as indicated by Shui-li et al. [48]. Nevertheless, such differences had no apparent impact on the TMP evolution dynamic. The roughness of the layer can then be an important indicator of the layer permeability; a low value of roughness can contribute to minimize the entrance of fouling materials inside the biofilm and compensate then the negative effect of a thicker layer notably when working under low TMP.

4. Conclusions

The performances of an AnMBR were analysed according to (i) the removal of organic matter and the production of biogas, and (ii) the dynamic of membrane fouling when treating latex serum obtained from micro-porous filtration of a skim latex suspension without any acid addition. The systems were tested according to two OLR, 8.1 and 12.7 kg COD m^{-3} d^{-1}. Results confirmed the high level of degradability of latex serum with a COD removal efficiency equal to 86 and 73.5% and a methane yield coefficient generated close to 0.22 and 0.24 NL CH_4 $gCOD_{removed}^{-1}$ for OLR of 8.1 and 12.7 kg COD m^{-3} d^{-1}, respectively, with a final filtration on the microporous membrane. Cake deposits on the membrane surface played the main role in fouling dynamics and the carbohydrates fraction appeared as the major component of cake deposit. AFM and SEM analyses showed that the highest OLR resulted in a more compact and thicker deposit than observed with the lowest OLR; nevertheless, no significant difference has been observed in TMP evolution with time, so thickness and compactness can be two antagonistic criteria to predict the evolution of layer permeability when filtering biological suspension in AnMBR.

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