Investigation of Operating Condition and Bio-fouling in Anaerobic Membrane Bioreactor for Biogas Production from Latex Serum

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ชื่อวิทยานิพนธ์ การศึกษาสภาวะของการเดินระบบและไบโอฟาวลิ่งในถังปฏิกรณ์ชีวภาพเมมเบรนแบบไร้อากาศสำหรับการผลิตก๊าซชีวภาพจากซีรัมน้ำยาง

ผู้เขียน นางสาวนฤมล ทองมาก

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บทคัดย่อ

วัตถุประสงค์ของงานวิจัยนี้สนใจศึกษาการบำบัดซีรัมน้ำยางโดยวิธีการแบบไร้อากาศเพื่อ (i) ลดความเข้มข้นสารอินทรีย์น้ำทิ้ง (ซีรัมน้ำยาง) และลดผลกระทบต่อสิ่งแวดล้อม (ii) ผลิตก๊าซชีวภาพและก๊าซมีเทนเป็นพลังงานทดแทน โดยซีรัมน้ำยางถูกนำกลับโดยการใช้ไมโครฟิลเตรชันทำให้เกิดการนำกลับส่วนของเนื้อยางจากหางน้ำยาง และเป็นการหลีกเลี่ยงการปรับสภาพหางน้ำยางด้วยการเติมกรดจับเนื้อยางซึ่งเป็นการยับยั้งขั้นตอนการหมักแบบไร้อากาศ

งานวิจัยนี้ได้ดำเนินการผ่าน 3 ชุดการทดลองคือ (i) เพื่อแยกส่วนของยางและซีรัมน้ำยางจากหางน้ำยางโดยการใช้ไมโครฟิลเตรชัน (ii) เพื่อวิเคราะห์ศักยภาพการเกิดก๊าซมีเทน (BMP) และการบำบัดแบบทีละครั้งในสภาวะไร้อากาศของซีรัมน้ำยาง(iii) เพื่อพัฒนาการใช้ระบบถังปฏิกรณ์ชีวภาพเมมเบรนแบบไร้อากาศ (AnMBR) สำหรับการบำบัดซีรัมน้ำยาง โดยลักษณะของยางที่ข้นขึ้นและซีรัมน้ำยางถูกวิเคราะห์ผ่านตัวแปรดังต่อไปนี้ ปริมาณของแข็งทั้งหมดในน้ำยาง (Total solids content, TSC) ปริมาณส่วนที่เป็นเนื้อยางทั้งหมดในน้ำยาง (Dry rubber content, DRC) กรดไขมันระเหยง่าย (Volatile fatty acids, VFA) ความเสถียรเชิงกลของน้ำยาง (Mechanical stability time, MST) ความต้องการออกซิเจนทางเคมี (Chemical oxygen demand, COD) ไนโตรเจนทั้งหมด Total kjeldahl nitrogen (TKN) ความเป็นกรด-ด่าง (pH) ความขุ่น (Turbidity) และ โปรตีน (Protein) ประสิทธิภาพของการทดสอบการเกิดก๊าซมีเทนและสภาวะไร้อากาศแบบทีละครั้งถูกวิเคราะห์ผ่านตัวแปรที่สำคัญเช่น COD pH การผลิตและองค์ประกอบของก๊าซชีวภาพ สำหรับประสิทธิภาพของระบบถังปฏิกรณ์ชีวภาพเมมเบรนแบบไร้อากาศถูกประเมินด้วยการวิเคราะห์ ความต้องการออกซิเจนทางเคมีที่ละลายน้ำได้ (Soluble chemical oxygen demand, SCOD) ปริมาณของแข็งแขวนลอยทั้งหมด (Total suspended solids, TSS) ของแข็งแขวนลอยระเหยง่าย (Volatile suspended solids, VSS) กรดไขมันระเหยง่าย (Volatile fatty acids, VFA)

ความเป็นด่าง (Alkalinity) การผลิตและองค์ประกอบของก๊าซชีวภาพ รวมถึงประเมินเรื่องการจำแนกลักษณะของฟาวลิ่ง

ผลการศึกษาของการใช้ไมโครฟิลเตรชัน (ขนาดรูกรอง 0.22 μm) กรองหางน้ำยาง พบว่ามีความเป็นไปได้ในการกักกันเนื้อยางให้คงอยู่ในระบบในส่วนของรีเทนเทต (เข้มข้นถึงร้อยละ 38 ของเนื้อยางแห้งด้วยค่าความเข้มข้นเชิงปริมาตรใกล้กับ 10) และนำกลับส่วนละลายน้ำคือซีรัมน้ำยาง (องค์ประกอบหลัก คือ คาร์โบไฮเดรต โปรตีน และกรดฮิวมิก) ในส่วนของเพอมิเอท ซีรัมน้ำยางเป็นสารละลายสีเหลืองใสมีค่าความเข้มข้นสารอินทรีย์ในรูป COD ประมาณ 30 $g.L^{-1}$ ด้วยค่าอัตราส่วน COD/BOD_5 เข้าใกล้ค่า 2 ซึ่งแสดงว่าซีรัมน้ำยางมีศักยภาพสูงในการย่อยสลายทางชีวภาพ

ผลการทดสอบศักยภาพการเกิดก๊าซมีเทนและการบำบัดแบบทีละครั้งในสภาวะไร้อากาศยืนยันศักยภาพที่สูงของซีรัมน้ำยางในการบำบัดด้วยวิธีทางชีวภาพแบบไร้อากาศ โดยมีประสิทธิภาพการบำบัด COD สูงกว่าร้อยละ 80 ค่าสัมประสิทธิ์มีเทนยีลด์อยู่ระหว่าง 0.27 ถึง 0.35 $NLCH_{4produced}.gCOD_{removed}^{-1}$ ซึ่งเป็นสิ่งที่ยืนยันข้อดีที่น่าสนใจของการบำบัดซีรัมน้ำยางด้วยวิธีแบบไร้อากาศนี้

ถังปฏิกรณ์ชีวภาพเมมเบรนแบบไร้อากาศที่ทำงานแบบกึ่งต่อเนื่องถูกติดตั้งทดสอบร่วมกับการแยกของแข็งแขวนลอยออกจากส่วนของน้ำโดยการกรองด้วยเมมเบรนชนิดรูพรุนในรูปแบบของระบบถังปฏิกรณ์ชีวภาพเมมเบรนแบบไร้อากาศ โดยสมรรถนะของระบบถูกวิเคราะห์ที่ค่าอัตราภาระบรรทุกสารอินทรีย์ 2 ค่าที่ต่างกัน (8.1 และ 12.7 kg $COD.m^{-3}.d^{-1}$) ค่าระยะเวลาเก็บกักรวม (HRT) และค่าระยะเวลาเก็บกักของแข็ง (SRT) ถูกกำหนดที่ 2 และ 30 วัน ตามลำดับ เมื่อถังปฏิกรณ์ชีวภาพติดตั้งร่วมกับชุดเมมเบรนแบบท่อกลวงเส้นใยจมตัว (ขนาดรูกรอง 0.1 μm) ซึ่งการกรองโดยชุดเมมเบรนดำเนินการด้วยเวลากรอง 4 นาทีต่อรอบการทำงาน 5 นาที โดยดำเนินการตามชุดการศึกษาที่ออกแบบและวิเคราะห์ผลของการเติมก๊าซที่ด้านล่างของชุดเมมเบรนเพื่อลดฟาวลิ่งของเมมเบรน ผลศึกษาแสดงให้เห็นว่าการใช้ก๊าซเติมเข้าไปส่งผลดีต่อการกรองตลอดช่วงเวลาเดินระบบ และผลการทดลองระบบถังปฏิกรณ์ชีวภาพเมมเบรนแบบไร้อากาศชี้ให้เห็นถึงผลที่ดีของการใช้เมมเบรนร่วมในถังปฏิกรณ์ชีวภาพแบบไร้อากาศเพื่อปรับปรุงประสิทธิภาพการบำบัดสารอินทรีย์ในรูป COD ที่ร้อยละ 86 และร้อยละ 73.5 สำหรับค่าอัตราภาระบรรทุกสารอินทรีย์ที่ 8.1 และ 12.7 kg $COD.m^{-3}.d^{-1}$ โดยค่าสัมประสิทธิ์มีเทนยีลด์ที่ได้อยู่ในช่วงระหว่าง 0.22 ถึง 0.24 $NLCH_{4produced}.gCOD_{removed}^{-1}$ ผลศึกษานี้นำไปสู่การนำศักยภาพของพลังงานทดแทนในรูปก๊าซมีเทนเพื่อผลิตกระแสไฟฟ้าได้ประมาณ 30 และ45 $kWh.m^{-3}$ เมื่อบำบัดซีรัมน้ำยางด้วยถังปฏิกรณ์ชีวภาพเมมเบรนแบบไร้อากาศ การวิเคราะห์ที่เฉพาะสำหรับการเกิดฟาวลิ่งของ

เมมเบรนในระบบถังปฏิกรณ์ชีวภาพเมมเบรนแบบไร้อากาศพบว่า รูปแบบฟาวลิ่งที่เด่นชัดเป็นการเกิดของชั้นเค้กสะสม อย่างไรก็ตามฟาวลิ่งลักษณะนี้เป็นแบบผันกลับได้เพียงใช้การล้างด้วยน้ำแบบต่อเนื่อง พบคาร์โบไฮเดรตปรากฏในชั้นฟาวแลนท์ไม่ว่าจะเดินระบบที่ค่าอัตราภาระบรรทุกสารอินทรีย์ที่ค่าใด การวิเคราะห์ด้วยเทคนิคกล้องจุลทรรศน์แรงอะตอม (Atomic Force Microscopy, AFM) และกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด (Scanning Electron Microscopy, SEM) ของตัวอย่างฟาวแลนท์บนเมมเบรนแสดงให้เห็นว่าชั้นสะสมที่ทำให้เกิดฟาวลิ่งมีความหนาและอัดแน่นมากเมื่อเดินระบบที่ค่าอัตราภาระบรรทุกสารอินทรีย์สูงสุด ทั้งนี้พลวัตของฟาวลิ่งที่พบนั้นไม่มีความแตกต่างกันของทั้งสองค่าอัตราภาระบรรทุกสารอินทรีย์ที่ศึกษา

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ABSTRACT

The aim of this research was to investigate the benefit of treating latex serum by anaerobic process to (i) decrease organic matter concentration in effluent and its environmental impact, and (ii) produce biogas and methane favouring an important energy recovery. Latex serum was proposed to be recovered by using micro-filtration for recovery of dry rubber content from skim latex suspension, avoiding the acidification step which was possible inhibitory step for anaerobic digestion.

Three main experiments were defined in this research (i) to separate rubber content and latex serum from skim latex suspension by using microfiltration, (ii) to analyse biochemical methane potential (BMP) and anaerobic sequencing batch test of such recovered latex serum, (iii) to develop anaerobic membrane bioreactor (AnMBR) for treatment of latex serum. The characteristics of concentrated latex suspension and latex serum were analyzed in terms of total solids content (TSC), dry rubber content (DRC), volatile fatty acids (VFA), mechanical stability time (MST), chemical oxygen demand (COD), total kjeldahl nitrogen (TKN), pH, turbidity and protein. The removal efficiency in BMP test and anaerobic sequencing batch test were measured according to COD, pH, biogas production and composition of biogas. The efficiency of AnMBR was analyzed by soluble chemical oxygen demand (SCOD), total suspended solids (TSS), volatile suspended solids (VSS), VFA, alkalinity, biogas production and its composition and membrane fouling characterisations were evaluated.

Result of microfiltration (0.22 μm pore size cut-off) of skim latex suspension showed the possibility to retain and concentrate rubber content in the

retentate phase (up to 38% of DRC with a volumetric concentration factor close to 10) and recover only the soluble fractions (mainly composed by carbohydrates, proteins and humic acids) in the permeate phase as latex serum. It appeared as a clear yellow solution and present COD concentration close to 30 $g.L^{-1}$, with a COD/BOD_5 ratio close to 2 confirming a high potential for biodegradability.

The results of BMP tests and anaerobic sequencing batch tests confirmed the high potential of latex serum to be treated by anaerobic process. The COD removal efficiency appeared higher than 80%. The methane yield coefficient was in the range 0.27 to 0.35 $NLCH_{4produced}.gCOD_{removed}^{-1}$. The important of COD removal and methane production capacity also proved the great interest of treating latex serum by anaerobic way.

A semi-continuous anaerobic reactor was then set-up in association with a final liquid-solid separation step by filtration on porous membrane forming the anaerobic membrane bioreactor (AnMBR). The performances of AnMBR were analysed for two different organic loading rates (OLR of 8.1 and 12.7 $kgCOD.m^{-3}.d^{-1}$), the hydraulic retention time (HRT) and the solid retention time (SRT) were fixed at 2 d and 30 d, respectively. When equipped with an immersed hollow fibre module (0.1 µm pore size), the filtration was carried out 4 min-on 1 min-off. The specific experiments were carried out to analyse the role of gas injection at the bottom of the hollow fibre membrane module to minimise membrane fouling. They showed the benefit of practising gas injection all along the filtration time. The results pointed out the positive role of the membrane barrier present in AnMBR to improve significantly the COD removal efficiency till reaching 86 and 73.5% levels for OLR of 8.1 and 12.7 $kgCOD.m^{-3}.d^{-1}$, respectively. The methane yield coefficient was found in the range of 0.22 to 0.24 $Nm^3CH_4.kgCOD_{removed}^{-1}$. These results induced a potential of energy recovery in the range of 30 and 45 $kWh.m^{-3}$ when treating latex serum by AnMBR. The specific analysis of membrane fouling in AnMBR showed the dominant of cake deposit, nevertheless this fouling appeared removable by only water rinsing. Carbohydrates appeared to be the major foulant compound whatever OLR. Atomic force microscopy (AFM) and scanning electron microscopy (SEM) analyses revealed a more compact and thick deposit of fouling when working at high OLR, even the dynamic of fouling did not appeared as significantly different for both studied OLRs.

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LIST OF ABBREVIATIONS

ABR	Anaerobic baffled reactor
AFM	Atomic force microscopy
ALK	Alkalinity
AnMBR	Anaerobic membrane bioreactor
ASBR	Anaerobic sequencing batch reactor
BMP	Biochemical methane potential
BOD	Biochemical oxygen demand
C	Carbohydrate
Ca	Calcium
CH_4	Methane
CO_2	Carbon dioxide
COD	Chemical oxygen demand
CUMAR	Cross-flow ultrafiltration membrane anaerobic reactor
DAP	Diammonium phosphate
DRC	Dry rubber content
EDX	Energy dispersive X-ray spectroscopy
EPS	Extracellular polymeric substances
F/M	Food to microorganisms ratio
FID	Flame ionization detector
FTIR	Fourier transform infrared
H_2SO_4	Sulfuric acid
HCl	Hydrochloric acid
HRT	Hydraulic retention time
J	Permeate flux
K	The maximum substrate utilization rate
MAS	Membrane anaerobic system
MBR	Membrane bioreactor
MCE	Mixed cellulose esters

LIST OF ABBREVIATIONS (continued)

MF	Microfiltration
Mg	Magnesium
MLSS	Mixed liquor suspended solids
MLVSS	Mixed liquor volatile suspended solids
MST	Mechanical stability time
MW	Molecular weight
MWCO	Molecular weight cut-off
N	Nitrogen
N_2	Nitrogen gas
NaOCl	Sodium hypochlorite
NaOH	Sodium hydroxide
NH_3-N	Ammonia nitrogen
OLR	Organic loading rates
P	Protein
PE	Polyethylene
PES	Polyethersulfone
PP	Polypropylene
PVDF	Polyvinylidene fluoride
R*	Specific hydraulic resistance
R_a	Mean roughness
R_{rms}	Root-mean-square roughness
SAMBR	Submerged anaerobic membrane reactor
SCOD	Soluble chemical oxygen demand
SDS	Sodium dodecyl sulfate
SEM	Scanning electron microscopy
SMP	Soluble microbial products
SO_4^{2-}	Sulfates
SRT	Solids retention time
SS	Suspended solids

LIST OF ABBREVIATIONS (continued)

STP	Standard temperature and pressure
S/X	Substrates to inoculums ratio
TCD	Thermal conductivity detector
TCOD	Total chemical oxygen demand
Temp.	Temperature
TKN	Total kjeldahl nitrogen
TMTD	Tetramethyl thiuram disulphide
TMP	Transmembrane pressure
TS	Total solids
TSC	Total solids content
TSS	Total suspended solids
UASB	Upflow anaerobic sludge blanket
UF	Ultrafiltration
VCF	Volumetric concentration factor
VFA	Volatile fatty acids
VSS	Volatile suspended solids
Y_{obs}	Bioconversion yield coefficient
ZnO	Zinc oxide
μ	Dynamic viscosity
$\mu_{apparent}$	Biomass maximum growth rate
μ_{max}	The maximum specific growth rate

CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

1.1 Rationale/problem statement

Para rubber or *Hevea brasiliensis* is the one of economic crops of Thailand and ASEAN (Association of South East Asian Nations). Thailand had about 35,483 km^2 of Para rubber plantations in 2013, mainly in the South of Thailand. Nowadays, Para rubber plantations are spreading in many areas of Thailand such as in the East, the Northeast and the North. The products from fresh latex can be classified under two categories; 1) use in the form of dry rubber by coagulation using formic acid such as smoked sheet rubber and dried sheet rubber and 2) use in the form of concentrated latex. In 2014, about 776 million kilogram of concentrated latex was produced from fresh latex. Domestic demand of concentrated latex for downstream latex industries was about 120 million kilogram. The concentrated latex is supplied to the downstream latex industries (gloves, condoms, balloons, etc.), while latex products from dry rubber are used for tires, rubber soles and machine parts and equipments (Rubber Research Institute of Thailand, 2011 and 2015).

Fresh latex (presenting a dry rubber content, DRC in the range of 25-45%) is subjected to centrifugation to extract the rubber content in a concentrated latex suspension to reach DRC of about 60% while the smallest latex particles are not completely extracted and remain with other soluble fractions in the supernatant of centrifugation that still contains a rubber content in the range of 4-8%, so called skim latex suspension. One of the characteristics of skim latex suspension is its high pH value, in a range of 9-11, due to the addition of ammonia and other chemicals (tetramethyl thiuram disulphide TMTD, zinc oxide ZnO, and diammonium phosphate DAP) in fresh latex suspension to avoid any fermentation and damaging of rubber content (Jawjit et al., 2015). Skim latex suspension can also be treated to recover the finest latex particles (2-10 times smaller than the average size of latex particles in concentrated latex suspension (Sridang et al., 2012)). By conventional way, the

recovery of such particles necessitates the use of a coagulation step by adding sulfuric acid (H_2SO_4) as coagulant (Tekasakul and Tekasakul, 2006; Jawjit et al., 2015). The final effluent of such treatment is then discharged as serum wastewater, about 20 $m^3_{effluent}.ton^{-1}$ of recovered skim rubber; it presents a low range of pH (3.0-4.0) due to the addition of acid (Danteravanich et al., 2002). The serum solution mainly contains soluble fractions such as proteins, sugars, carotenoids and organic and inorganic salts (Abrahama et al., 2009; Sakdapipanich and Rojruthai, 2014). The composition of discharged serum appears then as major causes of organic contamination in terms of chemical oxygen demand (COD = 15.2-38.8 $g.L^{-1}$), suspended solids (SS = 2.1-4.8 $g.L^{-1}$), total kjeldahl nitrogen (TKN = 1.6-3.3 $g.L^{-1}$) and sulfates (SO_4^{2-}= 8.5-11.0 $g.L^{-1}$) which occurred from sulfuric acid used in coagulation process. In addition, such high presence of sulfate in wastewater generates malodorous hydrogen sulfide gas as soon as anaerobic conditions occurred (Abraham et al., 2009; Nopthavon, 2010; Sulaiman et al., 2010).

If the wastewater treatment of concentrated latex is not properly carried out, the concentrated latex industry can be a major source of wastewater pollution affecting the environment and nearby communities. Concentrated latex wastewater is then the most important pollution source when compared with other rubber processing, due to its content (Mohammadi et al., 2010; Nguyen and Luong, 2012).

Some studies pointed out the potential benefit of membrane separation technology as an alternative method to treat skim latex suspension without needing acid addition (Devaraj and Zairossani, 2007; Veerasamy et al., 2008; Thongmak, 2009). This membrane separation step allows the retention of small latex particles in retentate of filtration and provides serum (filtrate phase) free from any acid contamination. Such treatment appears then as an environmental friendly processing and the valorisation of valuable by-products present in latex serum can then envisaged. For example, soluble organic matter can be converted to biogas by conventional anaerobic fermentation (Liu and Tay, 2002; George et al., 2004), except if serum still contains high sulfate content that is a major inhibitor of methanogenic populations (Chaiprapat et al., 2011; Wijekoon et al., 2011). To improve the functioning control of conventional anaerobic digester, notably by avoiding some

biomass washout, recent researches have presented the potential benefit of anaerobic membrane bioreactor (AnMBR) (Fuchs et al., 2003; He et al., 2005; Jeison and Lier, 2006; Kanai et al., 2010). Due to its specific capacity of biomass retention whatever the flocculation state of bacterial population, AnMBR can provide specific bacteria groups, which are slowly increased in the system and play a key role in the treatment efficiency and methane production (Ozgun et al., 2013). However, the application of AnMBR for wastewater treatment is still limited by membrane fouling phenomena causing flux decline, transmembrane pressure (TMP) increasing, and requirements of frequent membrane cleaning and replacement (Lin et al., 2013). Control and reduction of bio-fouling in AnMBR appear then as important strategies.

This research was then focused on the following new findings. The first idea was based on the recovery of rubber content from skim latex without acidification. Then because the rubber particles in skim latex appear close to micro particles, this research proposed to treat skim latex suspension by microfiltration (MF) for micro particles of rubber and soluble latex serum separation. The second idea was to analyze the methane potential of this latex serum obtained without acidification when developing anaerobic treatment. The third idea was to develop AnMBR to intensify the transformation of organic matter in latex serum for biogas production. The analysis of AnMBR performances including the identification and quantification of membrane fouling dynamics was investigated. Each of these three new concepts applied to latex serum treatment that was hardly in literature nowadays.

1.2 Theory and literature review

1.2.1 Fresh latex

The characteristic of fresh latex after being collected from the latex vessels of rubber trees is a milky white turbid fluid (a milky colloid) with particle sizes in the range of 0.05 to 5 microns, pH and viscosity in the range of 6.5-7.0 and 12-15 centipoises, respectively (viscosity of water is 1 centipoise at ambient temperature). Normally, ammonia is added to fresh latex after harvesting from plantations to prevent any fermentation and damaging of the rubber content. Fresh latex contains 25-45% of dry rubber content (DRC) and is composed of various non

rubber compounds (proteins, sugars, carbohydrates, etc.) depending on the age and species of the rubber tree and the season of tapping as shown in Table 1.1.

Table 1.1 Components of fresh latex.

Composition	Percent (by weight)			
	Morton (1987)	Blackley (1997)	White and De (2001)	Zhao et al. (2010)
Dry rubber content, DRC	36	33	30 - 40	30 - 40
Water	58.5	61 - 63.9	55 - 65	55 - 65
Protein	1.4	1 - 1.5	1 - 1.5	2 - 3
Sterol glycosides	-	-	-	0.1 - 0.5
Resin	-	1 - 2.5	1.5 - 3	1.5 - 3.5
Ash	-	0.1-1	-	0.5 - 1
Carbohydrate	1.6	1	0.8 - 1	1 - 2
Minerals	1.0	-	0.7 - 0.9	-
Neutral lipids	0.6	-	-	-
Glycolipids+phospholipids	-	-	-	-
Inorganic constituents	0.5	-	-	-
Others	0.4	-	-	-

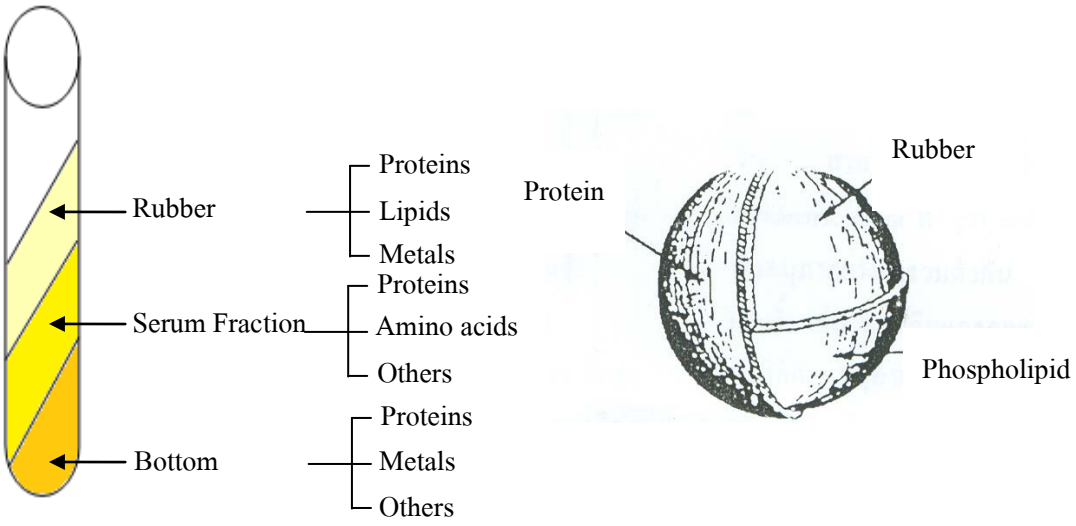
1.2.1.1 Composition of fresh latex

When high velocity centrifugation (12,000 up rpm) of fresh latex is practised, 3 fractions can be differentiated (Figure 1.1a), as follows:

1.2.1.1.1 Rubber phase

Rubber phase is about 30-36% by weight and it is found in the upper fraction of fresh latex separation. Rubber content is a hydrogen compound that has 5 atoms of carbon and 8 atoms of hydrogen. The chemical name and formula are poly-isoprene, $(C_5H_8)_n$, with n in the range of 2,000-5,000 units per molecule. These compounds are arranged in the pattern of cis-configuration, so called cis-1,4-poly-isoprene with a molecular weight reaching 1,000,000 daltons. The latex particle shape is spherical or pear-shaped, with a particle size between 0.05 to 5 microns. The

surface of the latex particle presents a negative charge, enclosed with protein and lipids as shown in Figure 1.1b.



(a) Separation of fresh latex through centrifugation at high rapidity about 12,000 up rpm (Sakdapipanich, 2010).

(b) Characteristic of latex particles (Blackley, 1996).

Figure 1.1 The composition of fresh latex and latex particles.

1.2.1.1.2 Serum phase

Serum phase or latex serum can be estimated at about 44-55% by weight of fresh latex. Latex serum is a clear solution. Latex serum has a density of approximately 1.02 $g.mL^{-1}$. It is composed of various substances such as 1) protein and amino acids where α-globulin, glutamic acid and aspartic acid are mostly found, 2) Carbohydrate with most of the sugar found being quebrachitol and containing a small amount of sucrose, glucose, galactose, fructose, raffinose and pentose, 3) Metal ion such as potassium (K), manganese (Mn), sodium (Na), calcium (Ca), copper (Cu), magnesium (Mg) and iron (Fe) depending on production process. Table 1.2 summarizes some characteristics of latex serum reported by previous research (Ahmad bin Ibbrahim, 1982).

Table 1.2 Characteristics of latex serum.

Characteristics	**Results of analysis**
pH	4.77
Total solids	42,550
Volatile solids	36,410
Suspended solids	2,850
COD	32,690
BOD	13,670
Total nitrogen	4,620
Ammonia nitrogen	3,430
Albuminoid nitrogen	755
Nitrate nitrogen	3
Nitrite nitrogen	1
Total sugars	500
Reducing sugars	409
Al	1.6
Ca	6.0
Cu	4.0
Fe	2.0
K	618
Mg	61
Mn	0.6
Na	11.0
P	61.0
Rb	3.0
Si	8.0

Remark: Units of all analysis results are $mg.L^{-1}$, except pH.

(Source: Ahmad bin Ibbrahim, 1982)

1.2.1.1.3 Bottom phase

The bottom phase is found in the under fraction, it is about 15-20% by weight of fresh latex. The main composition of this phase is lutoids particles. They consist of proteins, carbohydrates (sugar), acid and salts included inside particles (Sakdapipanich, 2010). The lutoids are spherical in shape, vary in size from 0.5-3 μm, and are bound by a single osmo-sensitive membrane about 8 nm thick (Mengumpun et al., 2008).

1.2.2 Trend of concentrated latex industry

Thailand is the top natural rubber producer and concentrated latex exporter in the world. Thailand's natural rubber production in 2014 was about 4.32 million tons with the growth rate up by 33%, compared with production in 2010. The top 4 products of natural rubber are rubber smoked sheet, standard Thai rubber, concentrated latex and compound, of which concentrated latex was about 18% of the total productions (Figure 1.2). The production capacity of concentrated latex was about 776,597 metric tons of Thailand’s, fresh latex production of which 119,762 metric tons was supplied for domestic use. The domestic demand of concentrated latex for downstream latex industries increased by about 46% from the years 2008 to 2014 (Rubber Research Institute of Thailand, 2015). Nowadays, Thailand has 101 concentrated latex factories supporting consumption demand. The number of concentrated latex factories in the Southern Thailand increased by about 22% from 55 factories in 2002 to 67 factories in 2011 (Danteravanich et al., 2002; Department of Industrial Works, 2011).

Concentrated latex is the raw material used to produce various rubber products such as gloves, condoms, balloons, nipples, foam products, scientific instruments, hose, etc. Table 1.3 shows the domestic demand of concentrated latex production by type of products from the years 2012 to 2014.

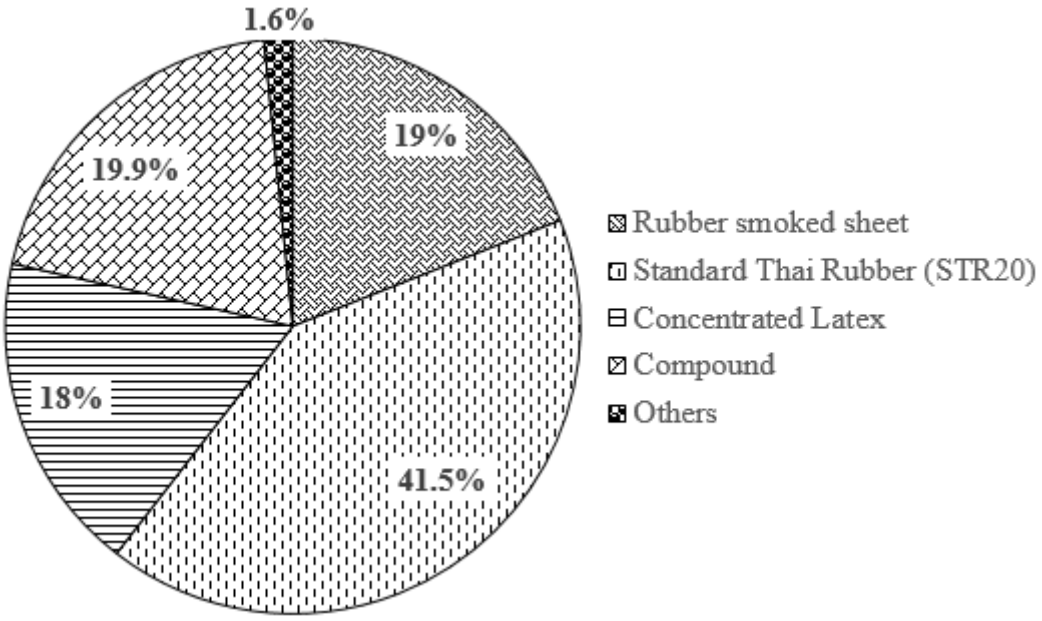


Figure 1.2 Thailand's natural rubber production by types in 2014.
(Adapted from: The Thai Rubber Association, 2015)

Table 1.3 The domestic demand of concentrated latex production by type of products.

Type of products	Year		
	2012	**2013**	**2014**
Gloves	66,381	69,645	58,865
Condoms	5,285	5,469	6,464
Foam products	262	233	234
Scientific instruments	684	841	952

Remark: All units are in metric tons
(Rubber Research Institute of Thailand, 2015)

1.2.3 Concentrated latex and skim latex production

Fresh latex is a raw material for producing concentrated latex (60% of DRC). Processing to obtain concentrated latex suspension can be achieved by evaporation, electro-decantation, creaming or centrifugation. The most common process in Thailand is centrifugation. It can be summarized by the following steps (Jawjit et al., 2015): 1) adding ammonia and TMTD/ZnO to preserve fresh latex properties, 2) Adding DAP (diammonium hydrogen phosphate) and leaving it one

night to precipitate magnesium (white sludge), 3) Feed fresh latex into centrifuge bowl, based on the principle that the latex particles have a density lower than serum phase (aqueous solution). After centrifugation, it can be separated into two portions as concentrated latex with 60% of DRC, and skim latex with 4-8% of DRC. Concentrated latex is stored and transferred to the customer while the residual phase, skim latex suspension, can also be treated to recover the smallest latex particles and produce skim rubber.

Skim latex suspension contains a low content of latex particles (in the range of 4-8% DRC), whose sizes are smaller (2-10 times) than the average latex particle present in concentrated latex suspension (Sridang et al., 2012). To recover latex particles in skim latex, a physic-chemical process is conventionally carried out (Tekasakul and Tekasakul, 2006; Jawjit et al., 2015), it includes a coagulation step by acidification with sulphuric acid addition (method accepted in Thailand) and a liquid-solid phase separation by flotation. The recovered latex particles are then used to produce skim crepe and skim block (rubber products of lower quality and lower cost).

The effluent, liquid phase, of this process is then discharged as serum wastewater Figure 1.3. Characteristics of such serum phases show the presence of a majority of biodegradable compounds (proteins, sugar and carbohydrate); such effluents should be then excellent substrates to carry out biological processes for their treatment. Conventionally, aerobic and anaerobic ponds are used to store and treat these effluents (Boonruangkhow, 2006). They present low kinetic rates and necessitate high hydraulic retention time and large area requirement. If the chosen organic loading rate is sufficiently low, the wastewater treatment can be efficient, in opposite, malodour and toxicity problems occur due to insufficient oxygen transfer throughout the pond volume. More recently the use of conventional intensive anaerobic treatment (UASB for example) was developed to favour biogas and energy recovering when treating such wastewaters (Nopthavon, 2010; Jawjit et al., 2010; Kongjan et al., 2014). Thought their evident benefit, such treatment let still some difficulties to control the process, reducing the treatment performances: longer start-up period to adapt bacterial populations to effluent characteristics and variability, residual coagulated rubber particles combined with granular sludge, biomass washout, and some malfunctioning notably due to the presence of high sulfate level in effluent due to sulphuric acid addition during acid coagulation step (Gerardi, 2003; Nguyen and Luong, 2012).

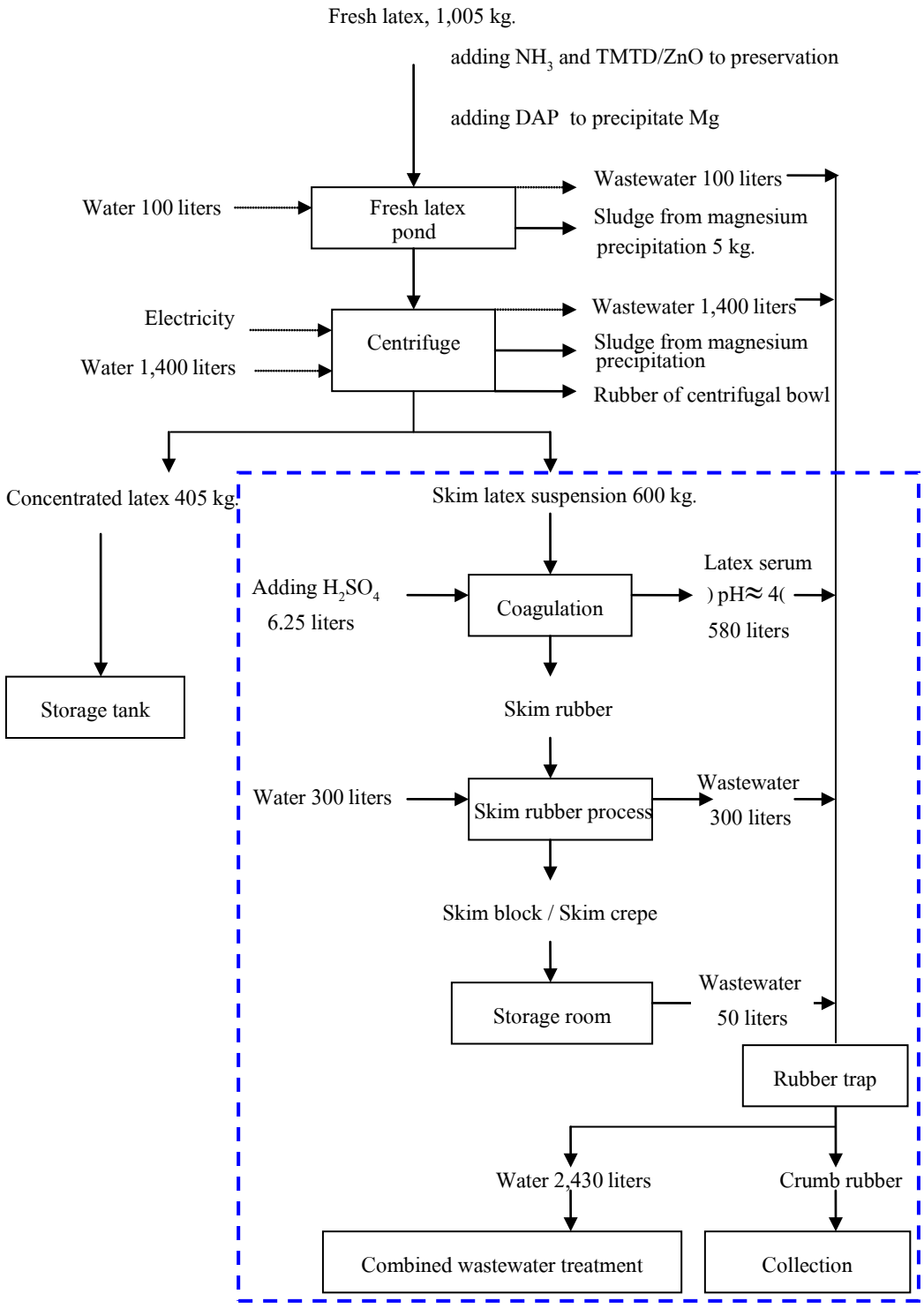


Figure 1.3 A schematic diagram of concentrated latex processing: Conventional process to recover latex particles from skim latex suspension.
(Pollution Control Department, 2005)

Therefore, it was important to propose new solutions able to overcome these disadvantages. This research was then focused on alternative processes based on membrane separation steps to favour (i) the rubber extraction of skim latex without any acid addition (Figure 1.4) and (ii) secure and enhance the anaerobic process to optimise biogas production from organic matter present in serum phase.

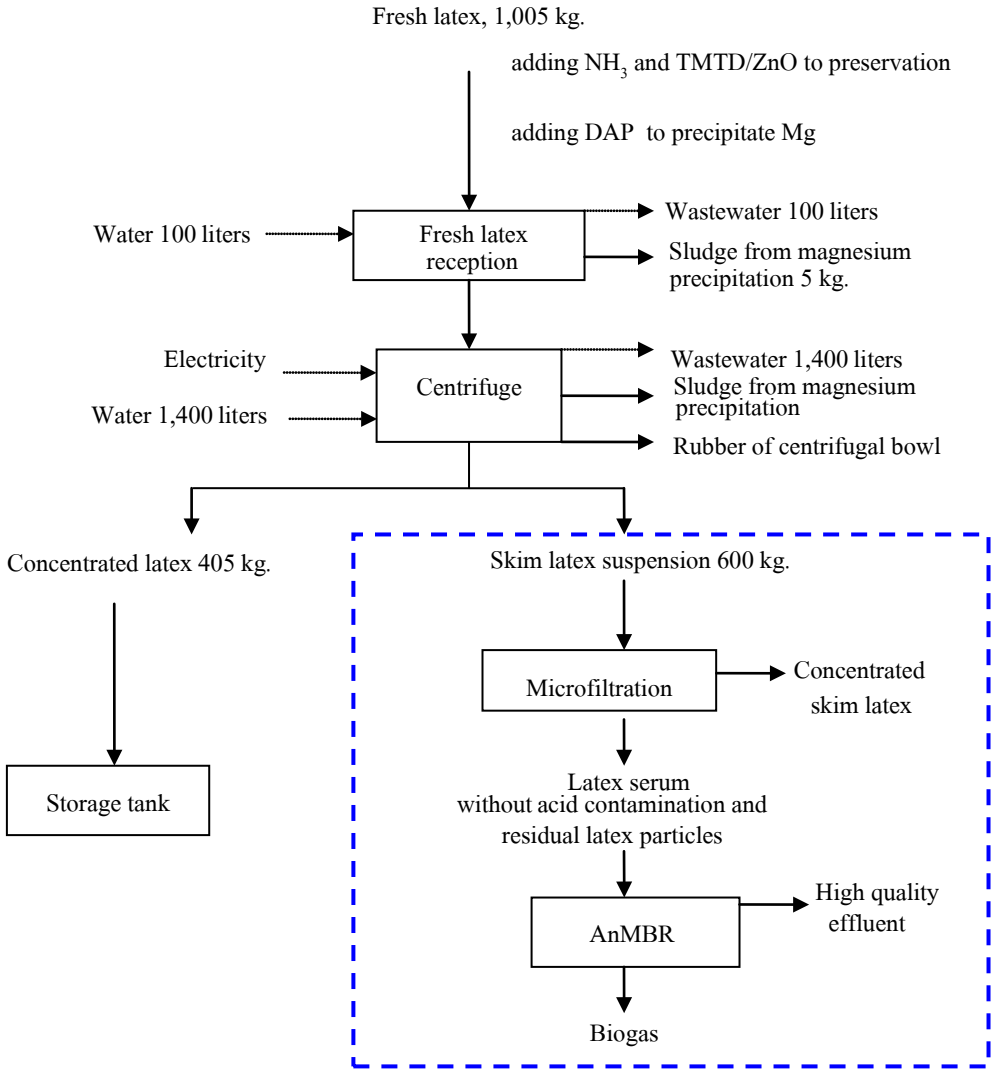


Figure 1.4 A schematic diagram of concentrated latex processing: Alternative processes based on membrane separation steps to recover latex particles from skim latex suspension without acid addition.
(Adapted from Pollution Control Department, 2005)

1.2.4 Serum and wastewater in the concentrated latex industry

In general, the concentrated latex production process can be divided in 2 steps, direct extraction from fresh latex and chemical extraction from skim latex (Figure 1.3) that generate 2 types of wastewater: wastewater discharged from (1) concentrated latex step and (2) skim rubber step. The flux generated by the former step is more important but as water is only coming from process cleaning it is less concentrated in pollutant than wastewater coming from the skim conditioning step. It can be noticed that the average quantity of wastewater generated from concentrated latex processing appears close to 4 $m^3.ton^{-1}$ of concentrated latex produced, while the average quantity of skim rubber processing wastewater is discharged at about 20-40 $m^3.ton^{-1}$ of skim rubber produced (Figure 1.3). The wastewater coming from skim rubber step composed by wastewater from cleaning process (with probably a composition closed to the composition of the cleaning water of the former step) and serum from coagulation process. The characteristics of combined wastewater (mixing of all wastewater including the serum phase, Figure 1.3 and serum are given in Table 1.4). The organic matter in serum phase confirmed the potential benefit to treat specifically this liquid phase to recover biogas for example and decrease significantly the pollutant concentration in the final effluent. These values also explain why wastewater coming from skim rubber process has been identified as the most important pollution source of latex industry regarding its low pH, its high content of organic substance and its potential to produce sulfide gas in absence of oxygen (Danteravanich et al., 2002; Vijayaraghavan et al., 2008; Kumlanghan et al., 2008; Abraham et al., 2009; Nopthavon, 2009; Sulaiman et al., 2010; Peiris, 2011).

Other ways of serum valorisation can also be envisaged. Latex serum can be an excellent substrate for the production of *Chlorella* whose growth rate was observed to be significantly higher when 1% of latex serum was applied in place of chemical fertilizer (Cheewasedtham, 2006). Leavings of latex serum can also be turned into fertilizers, according to its content, proteins, sugars, carotenoids and organic and inorganic salts (Abraham et al., 2009). Additionally, latex serum can be a source of value-added bio-chemicals such as industrial protein and quebrachitol (Veerasamy and Ismail, 2012) which is a raw material for drugs or cosmetics.

Table 1.4 Characteristics of wastewater from concentrated latex industry.

Parameters	Source of wastewater	
	Combined wastewater	**Serum (skim wastewater)**
pH	3.7-6.3	3.0-4.0
BOD	1.0-6.2	12.0-27.7
COD	2.0-8.8	15.2-38.8
TKN	0.3-0.7	1.6-3.3
SS	0.2-1.7	2.1-4.8
SO_4^{2-}	0.5-1.6	8.5-11.0

Remark: Unit of all parameters is $g.L^{-1}$, except pH.

(Danteravanich et al., 2002; Vijayaraghavan et al., 2008; Kumlanghan et al., 2008; Abraham et al., 2009; Nopthavon, 2009; Sulaiman et al., 2010; Peiris, 2011)

1.2.5 Latex wastewater treatment

Several technologies of wastewater treatment are applied in the rubber industry. The conventional technologies include physical treatment units, rubber traps for uncoagulated latex particle removal, and extensive biological treatment systems such as anaerobic-cum-facultative lagoon systems, anaerobic-cum-aerated lagoon systems, aerated lagoon systems and oxidation ditch systems which are based on biological treatment processes (Vijayaraghavan et al., 2008a; Vijayaraghavan et al., 2008b). More recently, intensive systems were developed to treat such effluents, aerobic systems as activated sludge process, and anaerobic systems to recover biogas and energy such as upflow anaerobic sludge blanket (UASB).

The stabilization ponds and aerated lagoons have been widely applied in concentrated latex factories (Mohammadi et al., 2010). The average removal efficiency of these treatments in terms of COD, SS, TKN and SO_4^{2-} were about 90%, 70%, 70% and 80% respectively. Though the percentage of organic removal in terms of COD was over 90%, the treated water still had a high organic effluent content which did not comply with the industrial effluent standards in Thailand (Danteravanich et al., 2002). Other treatment systems have also been implemented for

latex wastewater treatment such as activated sludge system (Leong et al., 2003; Thonglimp et al., 2005), electrochemical method (Vijayaraghavan et al., 2008a; Vijayaraghavan et al., 2008b), physicochemical treatment (Asia and Akporhonor, 2007), ultrasonic irradiation process (Ye et al., 2010), anaerobic reactor treatment process (Kumlanghan et al., 2008), upflow anaerobic sludge blanket (UASB) (Jawjit et al., 2010) and membrane filtration (Konieczny and Bodzek, 1996; Ersu et al., 2004; Sulaiman et al., 2010). Table 1.5 shows the wastewater treatment systems applied for the treatment of latex wastewater.

Table 1.5 Treatment systems of latex wastewater.

Type of systems	Conditions and efficiency	Disadvantages	References
Membrane filtration (Ultrafiltration : UF)	• Polyacrylonitrile and polysulfone membranes are suitable for the UF of latex wastewaters. • The effectiveness was within the range of 89.4-94.6% of TS and 86.3-94.2% of TOC when increasing the concentration of latex in wastewaters in the range of 9.4-18.6 $kg.m^{-3}$. • The operating condition was at T = 298 K, pressure ΔP = 0.20 MPa and cross-flow velocity U = 3.0 $m.s^{-1}$.	Gel layer on the membrane surface decreases the hydraulic permeability.	Konieczny and Bodzek (1996)
Activated sludge with anaerobic, aerobic systems and a rock bed filtration	• To upgrade the existing three aerated lagoons using two anaerobic waste stabilization ponds and the activated sludge plant coupled with anaerobic, aerobic systems and a rock bed filtration are recommended for effluent reuse and reclamation. • The removal efficiency after upgrading showed about 96% of BOD, 78% of COD and 94% of SS.	The rock bed filtration unit required flushing to overcome mosquito breeding and heavy algae growth inside the rock media.	Leong et al. (2003)

Table 1.5 Treatment systems of latex wastewater (continued).

Type of systems	Conditions and efficiency	Disadvantages	References
Membrane filtration (Ultrafiltration : UF)	• The feasibility study of using flat-sheet cellulose filter materials for latex rinse wastewater was investigated. • The average permeate flux of 27 $L.m^{-2}.hr^{-1}$ with an average TMP of 0.81 bar showed positively to remove total solids (TS) concentration from 3.8% to 20% from latex wastewater. • The turbidity of permeate ranged from 0.13-0.35 NTU. COD removals ranged from 69%-95% depending on the characteristics of the latex wastewater. TS removals were between 98%-99% with less than 0.6 $g.L^{-1}$ in permeates. • The pore blocking seemed to describe better the flux decline with time data as compared to the cake formation models.	Pore blocking within the membrane is main cause for fouling which requires chemical cleaning**.**	Ersu et al. (2004)
Activated sludge	• Concentrated latex wastewater was in the range of 3.1-3.9 $g.L^{-1}$ of BOD_5 and 5.6-7.6 $g.L^{-1}$ of COD. • The study was operated at OLR of 1.8 kg $BOD_5.m^{-3}.d^{-1}$, the F/M ratio of 0.4 day^{-1} and the HRT 2 days. • The result showed that the average BOD_5 and COD removal efficiency were 93.24% and 92.37%.	This condition was not satisfied because of filamentous organisms blooming.	Thonglimp et al. (2005)

Table 1.5 Treatment systems of latex wastewater (continued).

Type of systems	Conditions and efficiency	Disadvantages	References
Coagulation and flocculation and sand filtration	• Latex wastewater (influent ($g.L^{-1}$): BOD=2.6, COD=3.1, phosphate = 0.001) was treated at the optimum doses of alum (0.6 $g.L^{-1}$), iron (III) chloride (0.7 $g.L^{-1}$), lime (0.9 $g.L^{-1}$) and polyacrylamide (0.5 $g.L^{-1}$) followed by sand filtration bed. • The results showed almost complete removal of solid contents after filtration. High BOD, COD and phosphate reduction were in the range of 91-97%, 89-97% and 90-93%, respectively.	The coagulants increased the volume of solids and sludge concentration about 5-26%.	Asia and Akporhonor, (2007)
Anaerobic filter	• A cell-based biosensor system was designed for monitoring an anaerobic filter for treatment of high BOD levels in concentrated latex wastewater (influent ($g.L^{-1}$): BOD=6.3, COD= 8.8). • The performance of anaerobic filter was observed at a flow rate of 10 $mL.d^{-1}$, OLR 0.2 g $COD.L^{-1}.d^{-1}$ and HRT 50 days that gave the highest efficiency in COD and BOD removal. • The percentage of COD and BOD reduction was up to 97%. The BOD biosensor was successfully applied to off-line and on-line monitoring of the anaerobic reactor treatment process which could be also carried out with short analysis time.	The dilution factor of the on-line monitoring was limited by the tube size and the speed of the pump to only between 17 and 54 times. The effluent still did not meet the required standard value.	Kumlanghan et al. (2008)

Table 1.5 Treatment systems of latex wastewater (continued).

Type of systems	Conditions and efficiency	Disadvantages	References
Electrolytic (electrochemical method)	• An undivided electrolytic cell consisting of two sets of graphite as anode and stainless sheets as cathode was employed to generate hypochlorous acid which served as an oxidizing agent to destroy the organic matter in latex wastewater (influent: COD=3.8 $g.L^{-1}$). • A 90-min electrolysis period for the optimum operating conditions (an initial pH 4.5, sodium chloride content 3% and current density 74.5 $mA.cm^{-2}$), provided a good characteristics of the treated wastewater with a pH = 7.3, COD = 0.08 $g.L^{-1}$, BOD_5 = 0.06 $g.L^{-1}$, TOC = 0.05 $g.L^{-1}$, residual total chlorine 0.1 $g.L^{-1}$ and turbidity 17 NTU under the temperature 54^{o}C.	Treated wastewater had a high temperature and the excess chlorine concentration needed to be minimized before discharge.	Vijayaraghavan et al. (2008a)
Ultrasonic irradiation	• The characteristics of the raw rubber wastewater before ultrasonic irradiation was as follows: COD = 6.8 $g.L^{-1}$ and TSS = 1.5 $g.L^{-1}$. • The optimum conditions for maximum efficiency of the ultrasonic reactors were obtained at a power density of 0.024 $W.cm^{-3}$ after 90 min irradiation. • The highest reduction of COD and TSS values were about 91% and 76%.	Ultrasonic irradiation alone may not be suitable for completely treating complex wastewaters. The effluent could not meet the Malaysian wastewater standard.	Ye et al. (2010)

Table 1.5 Treatment systems of latex wastewater (continued).

Type of systems	Conditions and efficiency	Disadvantages	References
Two-stage UASB	• The optimum operating conditions were found at mesophilic condition (35 ^{o}C), HRT 24 hrs for acid tank and 48 hrs for UASB tank. pH values should be controlled at 7 to achieve high treatment performance. • The average removal efficiency of COD and SS were 81.08% and 94.22% while methane production was about 0.116 $LCH_4.gCOD_{removed}^{-1}$ (16.257-22.76 $m^3CH_4.d^{-1}$).	The inhibition from ammonia nitrogen (NH_3-N) on anaerobic bacteria was initially observed at 1.0 $g.L^{-1}$ NH_3-N while the strong inhibition was observed at 3.0 $g.L^{-1}$ NH_3-N. The residual coagulated rubber particles would combine with granular sludge, as a result, reducing the treatment performance.	Jawjit et al. (2010)
Membrane filtration (Membrane Bioreactor: MBR)	• The MBR was set up using flat sheet membranes with a total effective area of 0.2 m^2. A steady-state MLSS concentration was attained at 8.5 $g.L^{-1}$. • The optimum flux of the system for minimize fouling phenomena was obtained at 9 $L.m^{-2}.hr^{-1}$ while the optimum COD concentration was about 3.5 $g.L^{-1}$. The BOD_3 and COD removal efficiencies were 96.78% and 96.99%.	The membrane module required to clean or replace due to fouling.	Sulaiman et al. (2010)

The examples of latex wastewater treatment given in Table 1.5 can be compared to other industrial wastewater as presented in Table 1.6.

Table 1.6 Treatment systems of other industrial wastewater.

Types of wastewater	Conditions and efficiency	References
Palm oil mill effluent (POME)	• A modified anaerobic baffled bioreactor (MABR) was investigated under steady-state conditions from 3 to 10 days of hydraulic retention time. • The removal was in the ranges from 87.4 to 95.3% of COD and 44.1 to 91.3% of grease/oil. • Biogas production rate was 12.2–42.1 $L.d^{-1}$ and contained around 70% of methane on the average, corresponding to methane gas yield was from 0.32 to 0.42 l $LCH_4.g\ COD_{removed}^{-1}$.	Faisal and Unno (2001)
Palm oil mill effluent (POME)	• The upflow anaerobic sludge-fixed film (UASFF) reactor was developed to decrease the start-up period at low hydraulic retention time (HRT). • The reactor was working at HRT of 1.5 and 3 days and operating at 38 °C. The organic loading was gradually increased from 2.63 to 23.15 $gCOD.L^{-1}.d^{-1}$. • The size of granules increased from an initial pinpoint size to reach 2 mm within 20 days. • High chemical oxygen demand removals were achieved of 89 and 97% at HRT of 1.5 and 3 days, respectively. At the highest organic loading rate obtained methane yield of 0.346 $LCH_4.gCOD_{removed}^{-1}$.	Najafpour et al. (2006)

Table 1.6 Treatment systems of other industrial wastewater (continued).

Types of wastewater	Conditions and efficiency	References
Rice winery wastewater	• The anaerobic acidogenesis was used to study bio-hydrogen production from rice winery wastewater in an upflow reactor. • The experiment was conducted to investigate effects of HRT from 2 to 24hrs. (COD = 14-36 $gCOD.L^{-1}$, pH = 4.5-6 and temperature = 20-55°C). • The biogas produced under all test conditions was composed of mostly hydrogen (53-61%) and carbon dioxide (37-45%), but contained no detectable methane. • Specific hydrogen production rate increased with organic concentration in wastewater and temperature, but with a decrease in HRT. • An optimum hydrogen production rate of 9.33 $LH_2.gVSS^{-1}.d^{-1}$ was achieved at an HRT of 2 hrs, COD of 34 $g.L^{-1}$, pH 5.5 and 55°C. The hydrogen yield was in the range of 1.37-2.14 mol.mol-$hexose^{-1}$.	Yu et al. (2002)
Textile wastewater	• A fluidized bed reactor (FBR) with pumice as the support material was used to treat a real cotton textile wastewater. • The attached volatile solids level on the support material was 0.073 g VSS/g support material at the end of the 128-d start-up period. • Results for HRT of 24 hrs and OLR of 3 $kgCOD.m^{-3}.d^{-1}$ indicated the possibility of anaerobic treatment of textile wastewater with the supplementation of an external carbon source in the form of glucose (about 2 $g.L^{-1}$). The removals of COD, BOD_5 and color were found around 82%, 94% and 59%, respectively. • The increase of external carbon source to real textile wastewater did not improve the color removal efficiency of the anaerobic FBR reactor.	Şen and Demirer (2003)

Table 1.6 Treatment systems of other industrial wastewater (continued).

Types of wastewater	Conditions and efficiency	References
Poultry slaughterhouse wastewater	• Anaerobic fixed-film reactors with non-random support were used to study the poultry slaughterhouse wastewater treatment. • The system was carried out with two lab-scale reactors, one upflow and the other downflow, both reactors were operated at 35°C. • The COD removal efficiencies for OLR of 8 $kgCOD.m^{-3}.d^{-1}$ were found in the range of 85-95% and 55-75% when treating at the highest OLR (35 $kgCOD.m^{-3}.d^{-1}$). • Moreover, the reactor shows a quite stable performance when operating under stressed conditions, such as shock loads, very low hydraulic retention time or low temperature.	Pozo et al. (2000)
Soybean protein processing wastewater	• The treatment performance of soybean protein processing wastewater was investigated by using anaerobic baffled reactor (ABR) with four compartments. • The reactor was operated at 35 ± 1 °C with a constant HRT of 39.5 hrs and corresponding to OLR of 1.2, 3.0, 4.8 and 6.0 $kgCOD.m^{-3}.d^{-1}$. • The COD removal efficiencies were found 92-97% at OLR of 1.2-6.0 $kgCOD.m^{-3}.d^{-1}$. • Propionate and butyrate were found dominance in the 1^{st} compartment and acetate was dominated in the 2^{nd} compartment and decreased in the 3^{rd} and 4^{th} compartment. 93% of VFAs were removed in the 3^{rd} and 4^{th} compartments. • The highest H_2 yield was found in the 2^{nd} compartment, thereafter decreased from the 2^{nd} to 4^{th} which corresponded to the increased of the methane yield.	Zhu et al. (2008)

Table 1.6 Treatment systems of other industrial wastewater (continued).

Types of wastewater	Conditions and efficiency	References
Cassava wastewater	• The hydrogen production from cassava wastewater was investigated by using anaerobic sequencing batch reactors. The system was controlled at 37 °C. • Without nitrogen supplementation, the maximum hydrogen production performance in terms of specific hydrogen production rate (SHPR) (388 mL H_2.gVSS^{-1}.d^{-1} or 3800 mL H_2.L^{-1}.d^{-1}) and hydrogen yield (186 mL H_2.gCODremoved^{-1}) were obtained at a COD loading rate of 30 kg.m^{-3}.d^{-1} and 6 cycles per day. • In case of nitrogen supplementation, the COD:N ratio of 100:2.2 was found to provide a maximum specific hydrogen production rate of 524 mL H_2.gVSS^{-1}.d^{-1} and hydrogen yield of 438 mL H_2.gCODremoved^{-1}. Excess nitrogen led to decreased hydrogen production efficiency.	Sreethawong et al. (2010)
Pharmaceutical wastewater	• Up-flow anaerobic stage reactor (UASR) under various organic loading rates (OLR) was investigated to treat pharmaceutical wastewater. Reactor temperature was maintained at 37 °C • COD removal efficiency at low OLRs (0.43-1.86 kgCOD m^{-3}.d^{-1}) was found in the range of 70-75% and decreased to 45% when increasing the OLRs to 3.73 kgCOD.m^{-3}.d^{-1} by reducing the HRT (4-2 d). • The microbial community of the reactor stages was dominated by *Methanosaeta* and *Methanosarcina* when operated at low OLR (0.86-1.86 kgCOD.m^{-3}.d^{-1}) and high OLR (2.98-3.73 kgCOD.m^{-3}.d^{-1}), respectively.	Chelliapan et al. (2011)

1.2.6 Anaerobic wastewater treatment process

The anaerobic treatment is the most beneficial process when treating wastewater characterised by high concentration of biodegradable organic matter because its low intrinsic kinetics can be compensated by high biomass concentrations inside the reactor, such high biomass concentration appear as a limiting factor in aerobic process by inducing low oxygen transfer due to the suspension viscosity. Moreover anaerobic systems combine the removal of organic pollutants with the production of renewable energy in terms of methane present in produced biogas (Fezzani and Cheikh, 2008; Maya-Altamira et al., 2008). The anaerobic processes have then been widely applied for the treatment of various industrial wastewaters containing high concentration of biodegradable organic matter such as wastewater from dairies, breweries and slaughterhouses. Dairy wastewater is composed of higher concentrations of carbohydrates, proteins (casein) and lipids (Mohan et al., 2008) which are easily biodegradable and favour the growth of microorganisms (Ramasamy and Abbasi, 2000). The anaerobic processes could treat dairy wastewaters at organic loading rates (OLR) from 4 to 24 kg $COD.m^{-3}.d^{-1}$ and a high COD removal efficiencies, over 90%, can be reached when operating in anaerobic filter at moderate OLR, around 5-6 kg $COD.m^{-3}.d^{-1}$ (Omil et al., 2003).

Shao et al. (2008) studied the treatment of brewery wastewater in an anaerobic sequencing batch reactor (ASBR), pilot scale, and suggested that this technology was a potential alternative for brewery wastewater treatment. When OLR was operated between 1.5kg$COD.m^{-3}.d^{-1}$ and 5.0 kg$COD.m^{-3}.d^{-1}$ at HRT 1 day, the COD removal was more than 90%. The biogas production reached 0.48 $Nm^3.kg\ COD_{removed}^{-1}$ with a methane percentage varying between 50% and 80%.

Rajakumar et al. (2012) reported the performance of hybrid upflow anaerobic sludge blanket (HUASB) reactor for the treatment of poultry slaughterhouse wastewater. They observed that the OLR could load up to 19kg$COD.m^{-3}.d^{-1}$ achieving TCOD and SCOD removal efficiencies between 70-86% and 80-92%, respectively. The maximum methane yield was about 0.32 $Nm^3.kg\ COD_{removed}^{-1}$ at an OLR of 9.27kg$COD.m^{-3}.d^{-1}$ which is close to the theoretical methane yield (0.35 NL CH_4.g $COD_{removed}^{-1}$) and maximum methane content of about 72%.

In addition, anaerobic processes were widely developed to treat palm oil mill effluent (Alrawi et al., 2011), while, the stabilization ponds and aerated lagoons are generally used to treat concentrated latex wastewater in Southern Thailand (Vijayaraghavan et al., 2008). These later treatment systems need longer hydraulic retention time, require large spaces and have malodor problems (Sulaiman et al., 2010).

Enclosed anaerobic treatment systems have been promoted and implemented to solve these problems and to convert organic matter to biogas (Kumlanghan et al., 2008). Upflow anaerobic sludge blanket UASB system is one of the notable developments in anaerobic wastewater treatment but the start-up of UASB system is long as it depends on the formation of biomass granules (Boonsawang et al., 2008; Mohammadi et al., 2010). Borja et al. (1996) reported that granulation of the biomass in the acidogenic and methanogenic reactor of UASB was found after 80 days and 110 days, respectively, when treating palm oil mill effluent (POME). The granules in the methanogenic and acidogenic reactors were formed with different characteristics. The acidogenic granules were much more fragile, appeared less dense and had a much lower settling velocity which led easily to wash out from the reactor. Meanwhile, the methanogenic granules consisted of networks of long multicellular filaments, *Methanothrix* spp., with a diversity of rod and coccus bacteria entrapped in a dense matrix. Rajakumar et al. (2012) observed when treating poultry slaughterhouse wastewater using HUASB reactor that, at mesophilic conditions (29-35 ^{o}C), *Methanobacterium* and *Methanosaeta* bacteria were dominant at the end of reactor start-up period, whereas *Methanosarcina*, *Cocci* and *rods* were predominant at the end of treatment studies. The methane-forming bacteria had a slow growth rate and also low increase in their population. They were often washed out from the reactor and this could affect the stability of the system and then the specific biogas production rate (L CH_4.$gCOD_{removed}^{-1}$), the methane content in the biogas and the COD removal efficiency.

In fact anaerobic process is complex and a lot of operational conditions and physical, chemical and biological criteria can modify the kinetic rates and the bacteria equilibrium inside the reactor.

1.2.6.1 Anaerobic process and reaction

The anaerobic digestion is accomplished in four successive stages (Appels et al., 2008): hydrolysis, acidogenesis, acetogenesis and methanogenesis as shown in Figure 1.5. Microorganisms in each step of the anaerobic process belong to different groups working sequentially or in symbiosis. The products of each fermentation step become the substrates of the next bacterial group. The details of each step are described in Figure 1.6 (Gerardi, 2003, and Clisso, 2012). Generally the first and the fourth stages present the slowest kinetics rates. When the initial substrate is soluble, the former stage disappears and the anaerobic process begins with acidogenesis, methanogenesis is then the limiting step. Acetogenic and methanogenic populations are very sensitive to pH, it is then important to control acidogenesis and pH decrease to avoid any malfunctioning of the process.

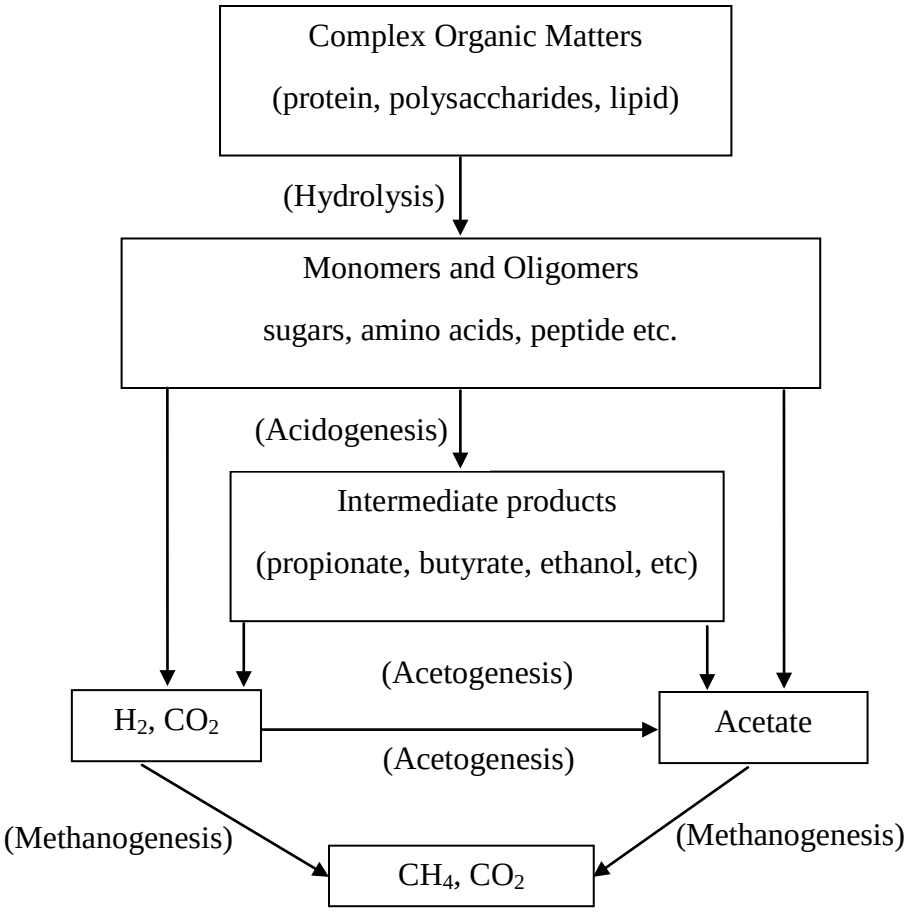


Figure 1.5 Degradation stages of anaerobic digestion process.
(Visvanathan and Abeynayaka, 2012)

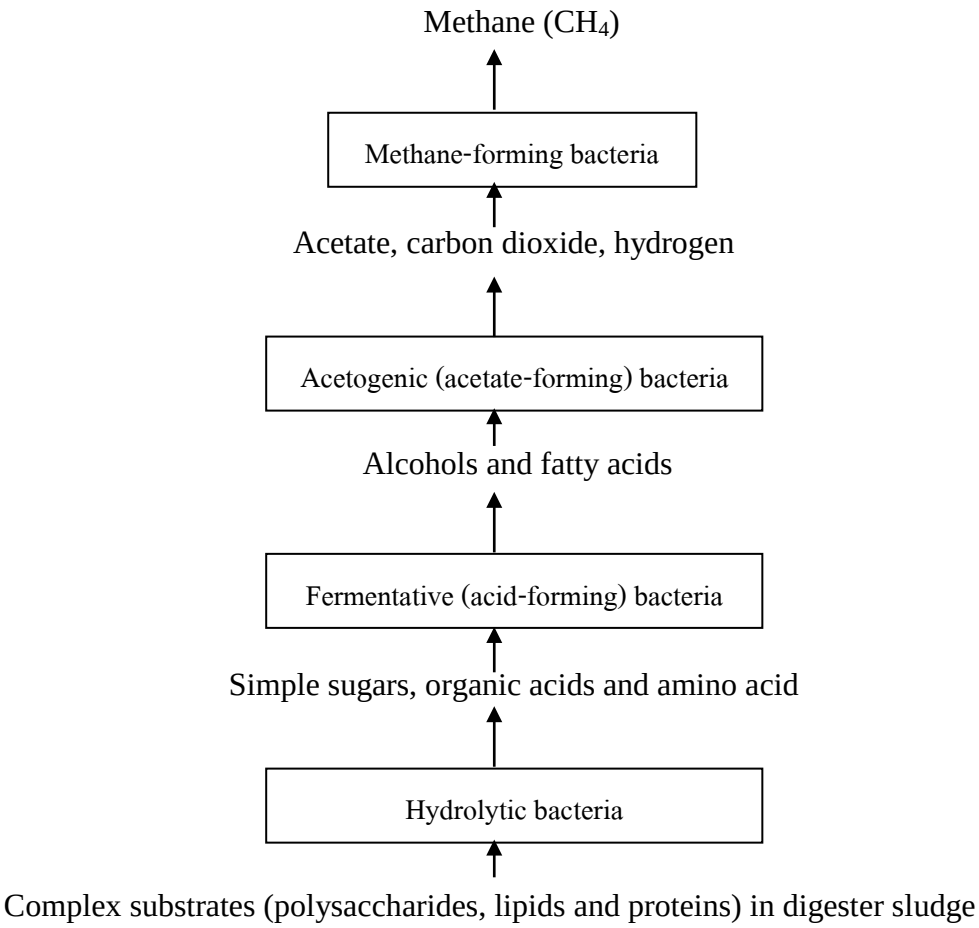


Figure 1.6 The degradation of compounds through step-by step biochemical reaction by a diversity of bacteria groups to methane (Gerardi, 2006).

1.2.6.1.1 Hydrolysis stage

Only soluble substrates can be adsorbed and degraded by bacteria. Hydrolysis is then necessary to solubilise complex substrates composed by insoluble compounds or large polymeric substances. Hydrolysis allows the breakage of complex compounds into simple and soluble substrates by hydrolytic bacteria groups:

- Complex carbohydrates are transformed into simple sugars.
- Complex lipids are transformed into fatty acids.
- Complex proteins are transformed into amino acids.

Hydrolytic bacteria consist of a consortium of Gram-positive, rod-shaped, facultative anaerobic bacteria and anaerobic bacteria that can break down insoluble/poorly soluble complex compounds into simple and soluble molecules.

An example of breakage of unique bonds undergoes hydrolysis reaction of an insoluble compound into a simple sugar, in this case, glucose as shown in equation 1.1 (Gerardi, 2003, 2006 and Waste-to-Energy Research and Technology Council, 2012).

$$C_6H_{10}O_4 + 2H_2O \rightarrow C_6H_{12}O_6 + 2H_2 \quad (1.1)$$

1.2.6.1.2 Acidogenesis stage

The soluble organic molecules generate by hydrolysis stage are further broken down into simpler molecules by acidogenic bacteria or acid-formers such as *Clostridium*, which convert simple sugars, fatty acids and amino acids to 1) organic acids such as acetate, butyrate, formate, lactate, propionate and succinate, 2) alcohols such as ethanol and methanol, 3) acetone, and 4) carbon dioxide, hydrogen and water. Acetate can be used directly by methane-forming bacteria, while carbon dioxide and hydrogen can be converted directly to acetate or methane. Glucose is converted to ethanol, propionate and acetic acid, respectively through acidogenesis reactions as shown in equation 1.2-1.4 for example (Gerardi, 2003, 2006 and Waste-to-Energy Research and Technology Council, 2012). If the pH is not controlled the acidogenic biomass tends to buffer itself and poor mixing leads to a decrease in acidogenic activity (Borja et al., 1996). A pH range of 5.7-6.0 for the acid reactor is recommended to provide a stable reaction and then the most favorable substrate could be utilized in the methane reactor (Cui et al., 2011).

$$C_6H_{12}O_6 \leftrightarrow 2CH_3CH_2OH + 2CO_2 \quad (1.2)$$

$$C_6H_{12}O_6 + 2H_2 \leftrightarrow 2CH_3CH_2COOH + 2H_2O \quad (1.3)$$

$$C_6H_{12}O_6 \rightarrow 3CH_3COOH \quad (1.4)$$

1.2.6.1.3 Acetogenesis stage

This stage transforms the products of the acidogenesis stage, which cannot be used directly as a substrate by methane-forming bacteria. The simple

molecules from the acidogenesis stage are further degraded to acetate through the activity of acetogenic or acetate-forming bacteria (Figure 1.7). Acetate is the major substrate obtained for methane production. The conversion of butyrate, propionate and ethanol are presented in equation 1.5-1.7 (Gerardi, 2003, 2006 and Waste-to-Energy Research and Technology Council, 2012).

$$CH_3CH_2CH_2COOH + 2H_2O \rightarrow 2CH_3COOH + 2H^+ \quad (1.5)$$

$$CH_3CH_2COOH + 2H_2O \rightarrow CH_3COOH + CO_2 + 3H_2 \quad (1.6)$$

$$CH_3CH_2OH + H_2O \rightarrow CH_3COOH + 2H_2 \quad (1.7)$$

1.2.6.1.4 Methanogenesis stage

In the final stage, acetate, hydrogen and carbon dioxide are converted to methane and carbon dioxide, which will be accomplished by methanogenic or methane-forming bacteria. This stage occurs through three basic biochemical reactions, which are achieved by three different groups of methane-forming bacteria as follows: 1) Acetate is split by acetoclastic methanogens to produce methane (equation 1.8). 2) Hydrogen and carbon dioxide is combined to produce methane by hydrogenotrophic methanogens (equation 1.9) and 3) the methyl ($-CH_3$) is removed from simple substrates to produce methane by methyltrophic methanogens (equation 1.10) (Gerardi, 2003, 2006 and Waste-to-Energy Research and Technology Council, 2012).

$$\text{Acetate} \xrightarrow{\text{acetoclastic methane-forming bacteria}} CH_4 + CO_2 \quad (1.8)$$

$$H_2 + CO_2 \xrightarrow{\text{hydrogenotrophic methane-forming bacteria}} CH_4 + 2H_2O \quad (1.9)$$

$$\text{Methanol} \xrightarrow{\text{methyltrophic methane-forming bacteria}} CH_4 + 2H_2O \quad (1.10)$$

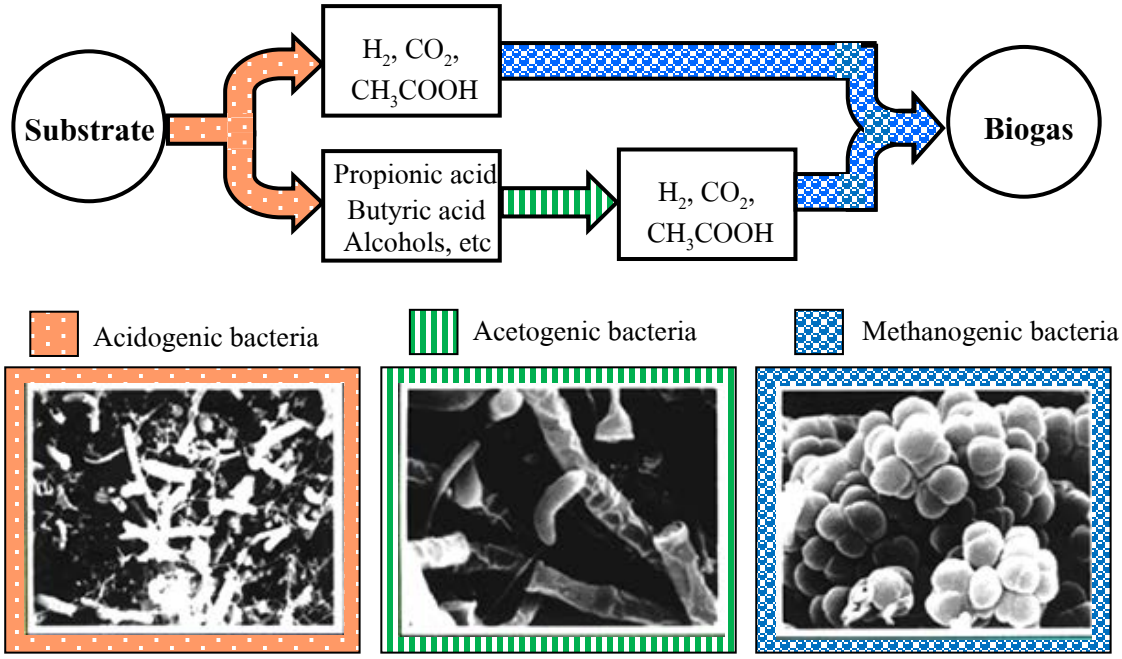


Figure 1.7 Schematic of the sequence of anaerobic methane generation from complex organic substances and scanning electron micrographs of individual microorganisms involved. (Waste-to-Energy Research and Technology Council, 2012).

1.2.6.2 Determining factors of anaerobic process control

1.2.6.2.1 Alkalinity and pH

The pH is a factor affecting enzymatic activity and digester performance. Sufficient alkalinity is necessary for pH control. Because alkalinity serves as a buffer to prevent rapid change in pH, the typical values of pH in anaerobic digesters are observed in the range 6.8-7.2, which occurs as volatile acids converting to methane and carbon dioxide. However, a pH within 7.0-7.2 is the recommended value for most anaerobic bacteria, including methane-forming bacteria. If pH values are below 6 or above 7, they are restrictive and rather toxic to methane-forming bacteria. A high level of alkalinity is required to maintain a constant pH using typical values of alkalinity in anaerobic digesters in a range of 2-4 g $CaCO_3.L^{-1}$. In addition, the ratio of volatile acid to alkalinity could be also maintained in the range 0.1-0.2 which is suitable for stable digestion and methanogenesis (Borja et al., 1996). A decrease of alkalinity could occur according to 1) an accumulation of organic acids due to methane-forming bacteria failing to convert the organic acids to methane, 2) a

slug discharge of organic acids to the anaerobic digester, or 3) the presence of wastes which could inhibit the activity of methane-forming bacteria (Gerardi, 2003).

1.2.6.2.2 Temperature

The optimum temperature for most methane-forming bacteria can be divided into two ranges, the mesophilic range from 30 to 35^{o}C and the thermophilic range from 50 to 60 ^{o}C. The methane-forming bacteria are inhibited at 40-50 ^{o}C. Digester performance falters somewhere near 42^{o}C, as this temperature represents the transition from mesophilic to thermophilic microorganisms. The minimum temperature should be maintained at 32 ^{o}C while the preferred temperature is 35^{o}C since most of methane-forming bacteria are mesophiles. The fluctuations of temperature in the anaerobic digester should be as small as possible (2-3 ^{o}C per day for mesophiles and less than 1 ^{o}C per day for thermophiles) since the methane-forming bacteria grow slowly, they are very sensitive to a small temperature change. The production of methane and methane-forming bacteria activity could be stopped within 12 hours when temperature increases 10 ^{o}C per day (Gerardi, 2003). The operating temperature could influence more methanogens than acidogens (Chou et al., 2004). Yilmaz et al. (2008) revealed the effect of temperature on the performance of anaerobic digestion, the report showed thermophilic digester at higher organic loadings and shorter retention times gave better performances than mesophilic digester and found VFA value higher in mesophilic digester effluent.

1.2.6.2.3 Mixing

Mixing of anaerobic digester increases the distribution of bacteria, substrate and nutrient throughout the digester as well as equalizing temperature. Mixing can be achieved by mechanical method, gas recirculation or sludge recirculation. Mechanical mixers are more effective than gas recirculation. However, they often became clogged or fouled with solids inside the digester. Sludge recirculation is often used when no mixing equipment is available. Mixing methods could be classified into two modes, 1) an intermediate mode with limited mixing and 2) a rapid mode with complete mixing but such mixing intensity causes some solids destruction and important energy requirements (Gerardi, 2003).

1.2.6.2.4 Nutrients

The nutrients can be grouped into two groups as macronutrients and micronutrients. Macronutrients, such as nitrogen and phosphorus, are required in relatively large quantities by all bacteria. Micronutrients, such as cobalt and nickel, are required in relatively small quantities by most bacteria and they are essential for methane-forming bacteria to convert acetate to methane. The quantity of substrate or COD of feeding is used to determine the amount of nitrogen and phosphorus. The general nutrient requirement is given by the ratios COD/N/P close to 600/7/1 or C/N close to 25/1 recommended for optimal biogas production (Gerardi, 2003). Nevertheless Ammary (2004) found an optimal ratio of COD/N/P approximately equal to 900/5/1.7, with a COD removal higher than 80%, for anaerobic treatment of olive mills wastewater. It has also been reported that the growth of cell showed severe decreases when concentration of nitrogen was less than 0.3 $g.L^{-1}$ (Singh et al., 1999)

1.2.6.2.5 Retention time

The solids retention time (SRT) and hydraulic retention time (HRT) are two significant parameters of an anaerobic digester. SRT is the residence time of biomass (solids) in the digester, while HRT is the residence time of the liquid (water and soluble compounds) in the digester.

Without any liquid-solid separation step in or downstream the digester, HRT is equal to SRT, then the classical values of HRT and SRT are in the range of 15 to 30 days, even more.

In opposite, when a liquid-solid separation step exists (fluidised granular bed or settling downstream the fermenter); SRT can be significantly different from HRT. A longer SRT operation advantages the presence of populations presenting a low growth rate, as methanogenic bacteria, and induces some better treatment performance and more biogas generation (Huang et al., 2011). Nevertheless to high value of SRT induce high biomass concentration inside the reactor and problems of mixing and mass transfer. The typical SRT values are in the range of 15 to 30 days. HRT is directly linked to the reactor volume (V) and organic loading rates (OLR); its increase induces a V increase and an OLR decrease. According to the

nature of influent HRT can be in the range of 1-2 days for the digestion of soluble and easily biodegradable molecule and more than 10 days for solid waste.

1.2.6.2.6 Toxic substances

Some inhibition of bacteria activity can be observed when the bacterial population is exposed to high concentration of substrate or when the population is not acclimated to the substrate yet, even when instantaneous functioning conditions are not in the optimal range for bacterial activity. Toxicity in an anaerobic digester may be acute when there is rapid exposure of bacteria to a relatively high concentration of toxic present in influent or suspension inside the reactor. The indicators of inhibition and toxicity are the disappearance of biogas production, rapid modification of pH, alkalinity and increasing in volatile fatty acid concentration inside the reactor. The three most common types of toxic substances are ammonia, hydrogen sulfide and heavy metals.

Ammonia concentration of more than 1.5 $g.L^{-1}$ at high pH may cause the failure of the digester, while free ammonia becomes toxic has an effect on digester failure when the ammonia concentration is above 3 $g.L^{-1}$. Singh et al. (1999) mentioned that high nitrogen concentration (1.0 $g.L^{-1}$) as NH_4 has resulted in inhibition of granule in UASB reactor.

Hydrogen sulfide is one of the most toxic compounds on anaerobic digesters. The formation of hydrogen sulfide occurs during the reduction of sulphate when degradation of organic compounds occurs in anaerobic conditions. Chen et al. (2008) mentioned the level of inhibitory sulfide was in the range of 0.1-0.8 $g.L^{-1}$ of dissolved sulfide or about 0.05-0.4 $g.L^{-1}$ for undissociated H_2S.

Heavy metal ions such as copper, nickel and zinc are very toxic to methane-forming bacteria even at relatively low concentrations. To reduce the toxicity of these ions several methods can be operated by precipitation, even as metal sulfides (approximately 0.002 $g.L^{-1}$ of ions are precipitated as metal sulfides by 0.001 $g.L^{-1}$ of sulfide). In addition, the cations or metal (Ca, Mg, K and Na) are toxic and significant enough to inhibit anaerobic bacteria activity at concentrations above 1.5 $g.L^{-1}$ (Gerardi, 2003) while Ahn et al. (2006) found that the performance of anaerobic digestion for treating swine wastewater increased with increasing of calcium

concentration until 3 $g.L^{-1}$ and an inhibitory effect on anaerobic digestion appeared in the range of 5-7 $g.L^{-1}$ of calcium concentration.

1.2.7 Anaerobic membrane bioreactor (AnMBR)

Except the presence of toxics, the stability of an anaerobic digester is mainly depending on the control of the acidogenic step which induces pH decreasing, accumulation of by-products (propionic acid…), bad flocculation of suspended population or bad granulation in UASB and of course bad degradation of organic matter and low biogas production.

When this step is under control, the weak point of anaerobic reactor is the maintenance of dispersed populations inside the reactor, notably the retention of slow-growth anaerobic microorganisms when operating at short HRT (Huang et al., 2011). Such a question can be solved by associating the bioreactor to a downstream separation step based on porous membrane filtration presenting a cut-off sufficiently low to retain any bacterial species whatever their state of flocculation/granulation. Such an association, fermenter and membrane separation step, defined the Anaerobic Membrane Bioreactor AnMBR.

Using such separation step allows a perfect differentiation of HRT and SRT (Huang et al., 2011). AnMBR appears then as a beneficial alternative technology.

AnMBR can maintain high SRT even when operating at a low HRT. A high SRT was excellent for the stable performance of the system, while a short HRT minimized the reactor volume (Fuchs et al., 2003; He et al., 2005; Kocadagistan and Topcu, 2007; Lew et al., 2009). Furthermore, it offered efficiency of effluent quality in terms of a solids-free final effluent, with pathogen and COD reduction (Vallero et al., 2005; Ho and Sung, 2010; Fang, 2010) and it does not require other post treatment steps if reuse or recycling was required (Lin et al., 2010).

Even though AnMBR system has many advantages, its application is still restricted by membrane fouling phenomena inducing TMP increase and flux decline.

1.2.7.1 AnMBR configuration

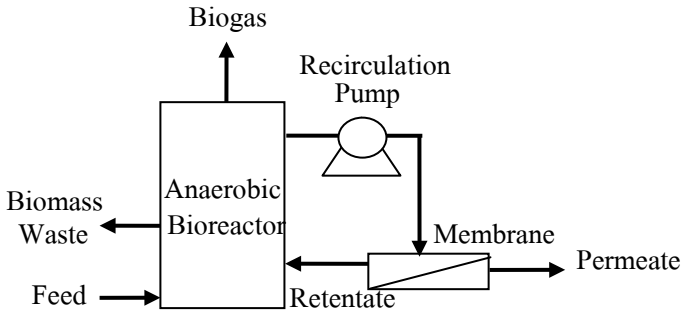
Anaerobic Membrane Bioreactor (AnMBR) is the combination of anaerobic reactor with membrane separation technology. The membrane unit can either be located in an external reactor (side-stream operation) or submerged in the reactor, as shown in Figure 1.8 (Jeison and Lier, 2007; Lew et al., 2009; Fang, 2010).

1.2.7.1.1 The side-stream configuration

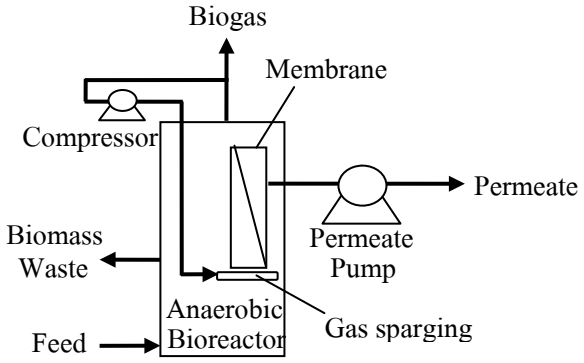
The membrane unit is situated externally to the anaerobic reactor which makes easy the membrane replacement and cleaning (Figure 1.8a). This configuration conventionally works in a cross flow mode with a high velocity of the suspension circulation inside the membrane module working in an in-out mode. A pump is used to recycle the suspension in a loop and provide sufficient cross-flow velocities (normally in the range 0.5-3 $m.s^{-1}$) to reduce external membrane fouling. According to the high level of shear stresses obtained by cross flow velocity, the filtration can be carried out under relatively high transmembrane pressure (TMP) (commonly between 0.5-2 bars). The energy requirements for suspension recycling can then appear prohibitive according to the filterability of the suspension, notably when treating wastewater by biological way. Moreover high cross flow velocities can induce some reduction or disruption of floc size increasing the deposition of small colloids on membrane surface and intensifying then the membrane fouling dynamic.

1.2.7.1.2 The submerged configuration

The membrane filtration unit is immersed inside the reactor; the membrane unit can either be immersed directly inside the anaerobic reactor (Figure 1.8b) or immersed in an external chamber (Figure 1.8c) as in side stream systems but the turbulence close to the membrane surface is not then obtained by direct circulation of the suspension but by gas injection under the membrane module. Such gas injection in place of suspension pumping allows a drastic decreasing of energy cost.

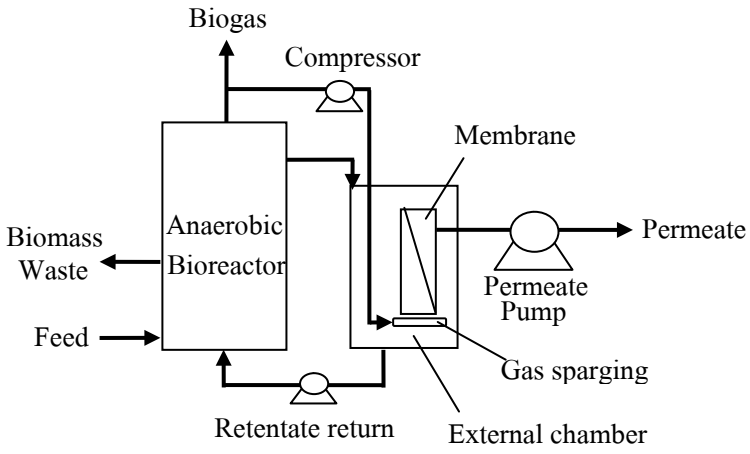


a) Side-stream configuration



b) Submerged membrane configuration

(the membrane immersed directly into anaerobic reactor)



c) Submerged membrane configuration

(the membrane immersed in an external chamber)

Figure 1.8 The membrane configuration of AnMBR application (Fang, 2010).

In case of immersed systems, the configuration presenting two separated chambers in series favours better management of operations. The biological system in chamber 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 (chamber 2) allows some better controls of (i) shear stresses by specific gas dispersion around the membrane module, (ii) suspended solids concentration in this specific tank and even (iii) cleaning in place, if necessary (Visvanathan and Abeynayaka, 2012). Such configurations function under low transmembrane pressure (less than 50 kPa) and do not necessitate any suspension circulation under high velocity, so the energy requirement remains significantly lower. Gas bubbles are injected locally to scour the membrane surface and limit accumulation of retained compounds onto the membrane surface.

1.2.7.2 Operating conditions

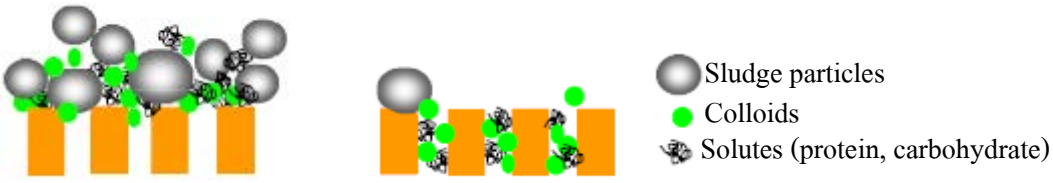
As conventional anaerobic processes, most of the AnMBR was operated in the mesophilic range (He et al., 2005; Vyrides and Stuckey, 2009; Zayen et al., 2010) or in the thermophilic range (Jeison and Lier, 2008; Wijekoon et al., 2011). Critical flux values were in the range 5-21 $L.m^{-2}.hr^{-1}$ under mesophilic conditions and in the range of 16-23 $L.m^{-2}.hr^{-1}$ under thermophilic conditions (Jeison and Lier, 2006). Operating conditions in AnMBR have been reported in several research, Skouteris et al. (2012) summarized HRT values ranged from a few hours (about 2 hrs.) to a few days (about 20 days), while SRT values ranged from a few days such as 18 days or 30 days till a year. Most researchers worked at high SRT values (higher than 150 days) due to longer SRT values resulted in the generation of greater quantities of biogas. However, Longer SRT also generates important increase of the suspension viscosity with problem of mixing and important flux decline (He et al., 2005).

1.2.7.3 Membrane fouling phenomena and control in membrane bioreactor

Membrane fouling is the main weak point in the application of membrane technology. Membrane fouling leads to permeate flux decline with time and/or a rapid increase of transmembrane pressure (TMP) generating frequent membrane cleaning and membrane lifetime reducing (Wu et al., 2010; Zhang et al., 2011). Membrane fouling can occur by different mechanisms as follows:

- Polarisation layer occurs by large soluble molecule accumulation close to the membrane surface.
- Cake layer formation occurs by particle deposition.
- Biofilm development appears when particles are composed by biomass flocs.
- Precipitation of inorganic matter appears when concentration of salts in the polarisation layer becomes higher than saturated concentration
- Pore clogging when particle sizes are in the range of pore diameter (Liu et al., 2003).
- Adsorption of small molecules by physic-chemical links onto the membrane surface including pore wall.

When developing Membrane Bioreactors, cake, biofilm formation and pore clogging generally appear as the dominant fouling phenomena as shown in Figure 1.9 (Meng et al., 2009).



a) cake layer b) pore blocking

Figure 1.9 Dominant membrane fouling origins in membrane bioreactors (Meng et al., 2009).

1.2.7.3.1 Classification of membrane fouling

1) Removable, irremovable and irreversible

According to the possibility or not to control membrane fouling, three types of membrane fouling can be differential as shown in Figure 1.10.

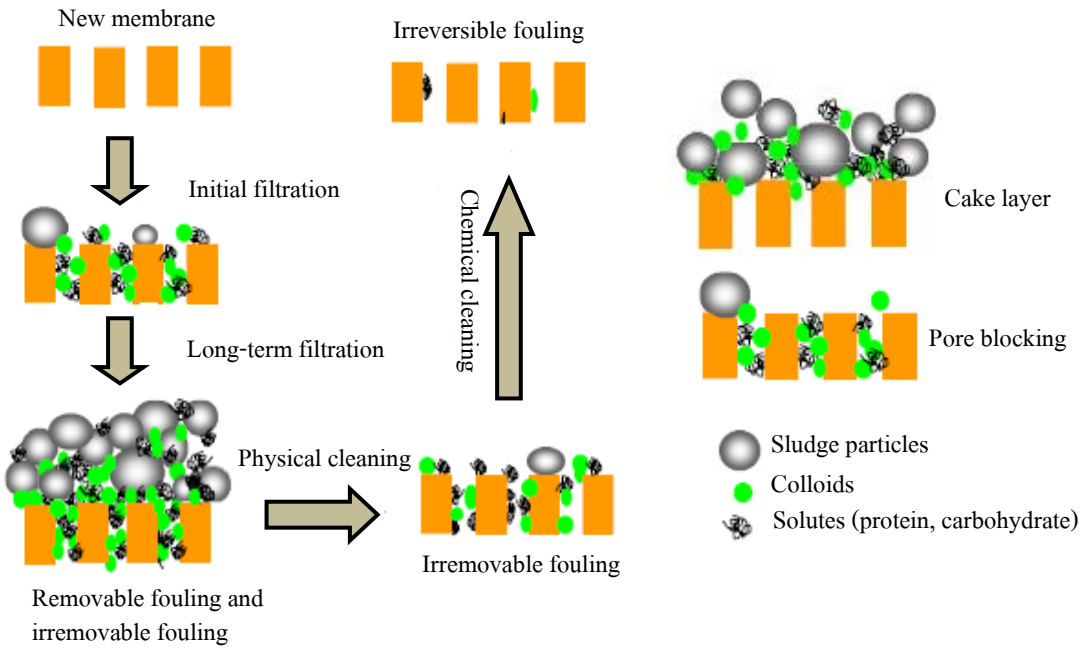


Figure 1.10 Schematic illustration of the formation and removal of removable and irremovable fouling in MBRs (Meng et al., 2009).

- **Removable fouling**

Removable fouling is caused by loosely attached foulants (i.e., sludge flocs and colloids deposit when they are larger than the membrane pores). In general, removable fouling is attributed to the formation of cake layer, which can be easily eliminated by a good implementation of physical cleaning (i.e., tangential filtration, relaxation and backwashing).

- **Irremovable fouling**

Irremovable fouling is caused by adsorption of foulants on the membrane surface or on the pore wall, including some precipitates of inorganic substances. Such a fouling can only be eliminated by chemical cleaning. Pore

blocking, generated by the mechanical retention of compounds presenting a size close to the pore size, can be removed by backwash or chemical cleaning; it can then be classified as removable or irremovable fouling according to the cleaning procedure.

- **Irreversible fouling**

Irreversible fouling is a permanent fouling which cannot be removed by any cleaning approaches; it causes a low permeability decline of membrane properties with time (Meng et al., 2009). Nevertheless, the lifetime of polymeric membranes used in MBRs should be close to 5 years, the lifetime of ceramic membranes must be largely over 10 years.

2) Bio-fouling, organic fouling, and inorganic fouling

The fouling components in MBRs can be classified into three major categories: bio-fouling, organic fouling, and inorganic fouling. The understanding of the formation of membrane foulants will help the proper selection and operation of fouling control.

- **Bio-fouling**

Bio-fouling is a main defect of a low pressure porous membrane such as microfiltration and ultrafiltration when treating wastewater. Most foulants (microbial flocs) in MBRs are much larger than the membrane pore size. Bio-fouling points to the deposition, growth and metabolism of bacteria cells or flocs on the membrane surface, which may begin with the deposition of individual cells or cell clusters on the membrane surface, afterwards the cells multiply and form a biocake layer. The important component on membrane surfaces of the formation of biological foulants and cake layer is soluble microbial products (SMP) and extracellular polymeric substances (EPS), which are secreted by bacteria. Several techniques have been implemented for understanding the floc/cell deposition process and the microstructure or architecture of the cake layer such as scanning electron microscopy (SEM), confocal laser scanning microscopy (CLSM), atomic force microscopy (AFM), and direct observation through the membrane (DOTM). Using microbiology methods such as polymerase chain reaction denaturing gradient gel electrophoresis (PCR–DGGE) and Fluorescence In Situ Hybridization (FISH) also succeeded in examining the microbial community structures and microbial colonization on the

membranes in MBRs. For the development of appropriate bio-fouling control strategies in the future, understanding the deposition behaviour of bioflocs/cells and mechanisms of cell attachment in MBRs is still an important study (Meng et al., 2009).

- **Organic fouling**

Organic fouling in MBRs is defined as the deposition of biopolymers (i.e., proteins and polysaccharides) on the membranes. The biopolymers are of a small size that can be deposited onto the membranes readily due to the permeate flow. They have lower back transport velocity due to lift forces in comparison to large particles (e.g., colloids and sludge flocs). The identification and characterization of organic fouling in MBRs can be investigated by Fourier transform infrared (FTIR) spectroscopy, solid state 13C-nuclear magnetic resonance (NMR) spectroscopy and high performance size exclusion chromatography (HP-SEC), which are efficient analytical methods. The major components of the biopolymers were identified as proteins and polysaccharides (Meng et al., 2009).

- **Inorganic fouling**

Inorganic fouling refers to chemical precipitation and biological precipitation as shown in Figure 1.11. Chemical precipitation occurs when the concentration of chemical species (cations and anions such as Ca^{2+}, Mg^{2+}, Al^{3+}, Fe^{3+}, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}, OH^-) in MBRs exceed the saturation concentrations due to concentration polarization. Concentration polarization phenomena will also lead to higher concentrations of retained salts on the membrane surface. The biopolymers contain ionisable groups such as COO^-, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}, OH^-, which caused biological precipitation in MBR (Meng et al., 2009).

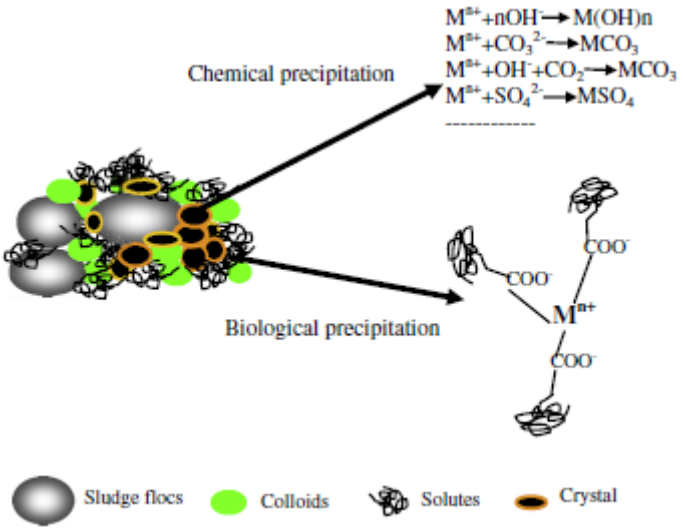


Figure1.11 Schematic illustration of the formation of inorganic fouling in MBRs (Meng et al., 2009).

1.2.7.3.2 Fouling factors

Several factors influence membrane fouling and they can be defined into four categories, i.e. membrane materials, feed water characteristics, biomass characteristics and operating conditions (Le-Clech et al., 2006; Meng et al., 2009; Wang et al., 2013a).

1) Membrane characteristics

- **Pore size and distribution**

The effects of pore size and distribution of pore size on membrane fouling are strongly related to the feed solution characteristics or in particular the particle size distribution. If pore size is larger than particle size, pore blocking and/or restriction is expected to occur. Therefore, the large pore membranes like microfiltration membrane (MF) would present higher fouling propensity compared to ultrafiltration membranes (UF). It is expected that smaller pore membranes would reject a wider range of materials while resulting cake layer features and higher resistance compared to large pore membranes. However, cake layer is more reversible and is more easily removed during the cleaning step than is fouling from internal pore clogging. The larger pore size membrane suffered in long-term performances due to the deposition of organic and inorganic materials onto and into the membrane pores, which is irremovable fouling (Le-Clech et al., 2006).

- **Porosity/roughness**

The rough membranes are more prone to the occurrence of fouling layers when compared to the smooth membranes. For example, in the research of Fang and Shi (2005), it was shown that the MF membranes with similar nominal pore sizes (polyvinylidene fluoride (PVDF), mixed cellulose esters (MCE) and polyethersulfone (PES) membranes) operated under the same conditions. The results showed different fouling behaviors among the membranes tested. The main characteristic of PVDF and MCE membrane fouling is cake formation. Meanwhile pore blocking was responsible for 86% of total hydraulic resistance when the PES membrane was used. The PVDF and MCE membranes showed a 50% lower fouling resistance than the PES membrane (Le-Clech et al., 2006).

- **Membrane and membrane module configuration**

The current trend design of membrane configuration in MBR favours the submerged over side-stream configurations in the majority of the studies dealing with domestic wastewater treatment. In submerged MBR processes, the membrane can be configured as vertical flat plates, vertical or horizontal hollow fine fibres (filtration from out-to-in) or, more rarely, as tubes (filtration from in-to-out). The hollow fibre modules are generally cheap for manufacturing and allow high membrane density in each module. Furthermore, they can tolerate vigorous backwashing while flat plate and tubular membranes may probably be easier to control fluid dynamics and distributions. However, the hollow fibres may be more prone to fouling and require more frequent washing and cleaning (Le-Clech et al., 2006; Lebegue et al., 2008).

- **Hydrophobicity**

Hydrophobicity is one of the significant factors, which affects membrane fouling. The hydrophobic membranes seem to have a more severe effect on membrane fouling than hydrophilic membranes, because of the hydrophobic interactions occurring between solutes, microbial cells and membrane material (Le-Clech et al., 2006).

- **Materials**

The majority of the membranes used in MBRs are polymeric-based, while ceramic membranes are not the preferred option for MBR applications due to

their high cost. A direct comparison between polyethylene (PE) and PVDF membranes clearly indicated that the latter led to a better prevention of irreversible fouling and PE membrane fouled more quickly (Le-Clech et al., 2006). Yamato et al. (2006) reported that PVDF membrane was superior to PE membrane in terms of irremovable fouling prevention in MBRs when used for the treatment of municipal wastewater (Meng et al., 2009). Additionally, Lin et al. (2009) mentioned that PVDF membranes had a longer durability and relatively lower fouling propensity when compared with other polymeric membranes.

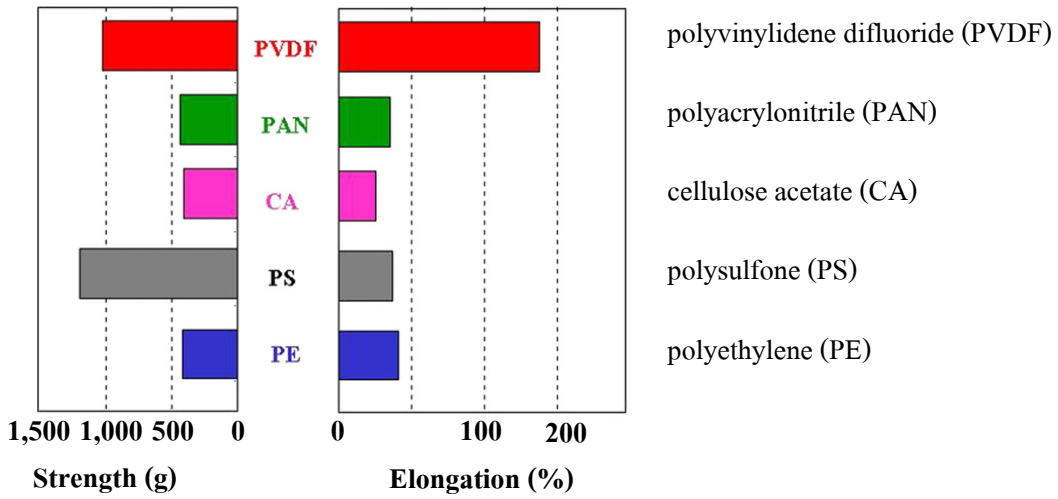


Figure 1.12 Summary of polymer properties (Judd and Judd, 2011).

Figure 1.12 shows polymer properties. The left-hand side of the figure measures the tensile strength of various membrane polymers at their breaking point. On the right, the per cent elongation before the fibre breaks provides a measure of flexibility, with PVDF combining strength and flexibility. Flexibility is required when air scouring of hollow fibre membranes is employed, producing lateral movement of the fibre (Judd and Judd, 2011).

2) Nature of feed and concentration

The effect of feed characteristics and composition is included in membrane fouling factors. For example, the impact of Calcium on membrane fouling in MBR found that a Calcium concentration of 0.28 $g.L^{-1}$ improved the membrane

permeability. This concentration was beneficial in controlling and improving bio-fouling due to binding and bridging EPS. While higher Calcium concentrations at around 0.83 $g.L^{-1}$ resulting in the decline of membrane permeability was the result of very high Calcium concentrations in the sludge that contributed to significant inorganic fouling. However, Calcium can reduce the carbohydrate EPS and protein EPS by around 60% of carbohydrate EPS and 30% of protein EPS, which shows that organic fouling was reduced in the presence of Calcium ions (Arabi and Nakhla, 2008). Afterwards, Arabi and Nakhla (2009) examined the influence of three influent Mg concentrations of 0.005, 0.021 and 0.096 $g.L^{-1}$ at a constant influent Calcium concentration of 1.7mM, corresponding to Mg/Ca ratios of 1/5, 1/1 and 5/1. In terms of membrane fouling rate, no differences were observed between Mg/Ca ratios of 1/5 and 1/1 but Mg/Ca ratio of 5/1 showed higher membrane permeability and lower fouling rates. This was due to Magnesium bridging of negatively charged biopolymers, thus enhancing bioflocculation, and decreasing membrane fouling.

3) Biomass characteristics

- **MLSS concentration**

MLSS concentration is the main foulant parameter which directly affects membrane fouling when working in supra-critical conditions (Field et al., 1995). The MLSS concentration at 30 $g.L^{-1}$ has a negative influence on the MBR hydraulic performances (higher TMP or lower flux). The concentration of MLSS at around 8 to 12 $g.L^{-1}$ did not appear to have significant effects on membrane fouling. More fouling is expected as the MLSS concentration increases above 15 $g.L^{-1}$ (Le-Clech et al., 2006).

- **Floc size**

Given the large size of the floc particles, compared to the pore size of the membrane generally used in MBR, are not expected to directly block pore entrances or floc deposit on the membrane surface due to drag forces resulting from the low/modest fluxes and the shear induced back transport phenomenon. However, independent of floc size, biological floc plays a major role in the formation of cake layer on the membrane surface (Le-Clech et al., 2006).

- **Extracellular polymeric substances (EPS)**

The EPS in either bound or soluble form is defined as the predominant factor of membrane fouling in MBRs. EPS have been found outside the bacterial cell surface and in the intercellular space of microbial aggregates, which consist of different classes of macromolecules such as polysaccharides, proteins, nucleic acids, (phosphor-) lipids and other polymeric compounds (Figure 1.13). In an anaerobic MBR, Fawehinmi et al. (2004) observed the relationship between specific resistance with eEPS (bound EPS) that was increased linearly, rising from 20 to 130 mg.gSS^{-1}. While, the result of chromatographs of eEPS solution revealed the molecular weight of proteins and carbohydrates in the range of 45-670 kDa and 0.5-1 kDa (Gorner et al., 2003). The presence of both proteins and carbohydrates around the biological cells was discussed and proposed as a key parameter in the floc formation, which had a significant role in MBR fouling (Le-Clech et al., 2006; Meng et al., 2009).

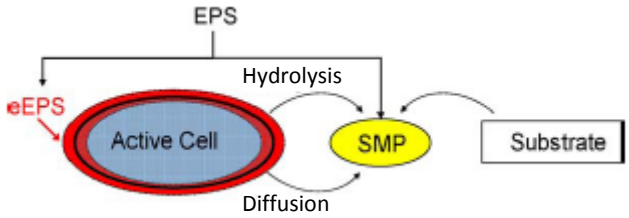


Figure 1.13 Simplified representation of EPS, eEPS and SMP (Le-Clech et al., 2006).

- **Soluble microbial products (SMP)**

SMP (soluble EPS) can be defined as the soluble cellular components or the pool of organic compounds that are released into solution during cell lysis, diffused through the cell membrane, are lost during synthesis or are excreted for some purpose (it occurs from substrate metabolism and biomass decay). SMP can adsorb on the membrane surface, block membrane pores and/or form a gel structure on the membrane surface during filtration where they provide a possible nutrient source for biofilm and a hydraulic resistance to permeate flow (Le-Clech et al., 2006; Meng et al., 2009; Ayral et al., 2009; Grelot et al., 2010; Lebegue et al., 2010).

4) Operating conditions

- **Tangential conditions**

External accumulation of compounds on the membrane surface, cake deposit and polarisation layer can be minimised by inducing local tangential shear stresses. Such shear stresses are induced by high local suspension circulation (side-stream MBRs) or gas injection in submerged MBRs. According to the ratio between tangential strength F_T and pressure filtration strength F_p, the separation is carried out in sub ($F_T > F_P$) or supra-critical flux ($F_T < F_P$) (Field et al., 1995). In sub-critical conditions, the main origin of fouling is linked to internal origin (pore blocking and adsorption of soluble compounds inside the pores). In supra-critical conditions, the main origin of fouling is external fouling mainly linked in MBRs to cake deposit and biofilm development. The critical conditions are very depending on suspension characteristics (biomass and EPS/SMP concentrations) and filtration conditions (TMP and permeate flux) (Tardieu et al., 1998; 1999; Sridang et al., 2006; Lebegue et al., 2009).

- **Solids retention time (SRT)**

In submerged anaerobic membrane bioreactor (SAnMBR) process, Huang et al. (2011) reported that a too short HRT, inducing important biomass activity (cell growth and EPS production), and too long SRT (causing notably important biomass concentrations in the suspension), generally induce important membrane fouling dynamic. For example, a HRT decreasing from 12 to 8 hrs induced a lower Carbohydrate/Protein (C/P) ratio in SAnMBR, which would contribute to a more severe membrane fouling.

1.2.7.4 Mitigation of fouling

Nevertheless, membrane fouling dynamic can be governed by improving or modifying the anti-fouling properties of the membrane. Some reports stated that operating the system under little fouling conditions and/or pre-treating the biomass suspension can limit fouling propensity (Le-Clech et al., 2006). Fouling control had been studied in different techniques, and physical or chemical cleaning was also widely used in membrane application as shown in Table 1.7.

Table 1.7 Techniques of fouling mitigation.

Fouling control	References
Injecting acidic feed, so-called "backfeeding" was applied to prevent membrane fouling caused by struvite ($MgNH_4PO_4 \cdot 6H_2O$) deposition in AnMBR, which could improve the membrane flux of the polymeric (polypropylene) membranes by approximately 100% compared to without the back feeding mode.	Choo et al. (2000)
Adding powdered activated carbon (PAC) could control the deposition of organics and fine colloids onto the polymeric membrane in AnMBR. The specific resistance values of the biomass cake mixed with PAC was twice lower than the cake without PAC. This technique increased the mean particle size of the biosolids from 7.5 to 20 μm. The PAC addition led to the reduction of the floc which attached to the bio-film, and reduction of the filamentous and soluble microbial products inside the reactor. However, its failing was extra operating and disposal cost.	Choo et al. (2000); Le-Clech et al. (2006); Vyrides and Stuckey (2009)
Modifying the membrane surface properties could reduce membrane fouling. A commercial polypropylene (PP) membrane changed the surface property from hydrophobic to hydrophilic by graft polymerization with a 2-hydroxyethyl methacrylate (HEMA) solution. The cake resistances were significantly reduced and thus the flux increased by about 35% when the degree of grafting was set up at about 70%.	Choo et al. (2000)
Intermittent operation such as an operational cycle of 10 min of filtration, followed by 30 sec of back-flush was highly efficient in removing the cake layer in mesophilic and thermophilic reactors.	Jeison and Lier (2006)

Table 1.7 Techniques of fouling mitigation (continued).

Fouling control	References
Biogas recirculation in AnMBR was used for sludge mixing and membrane scouring for cake formation control instead of air bubbling of aerobic submerged MBRs	Jeison and Lier (2006); Spagni et al. (2010)
Operating at a low flux of about 5-10 $L.m^{-2}.hr^{-1}$ was possible for stable operation achievement in an AnMBR during a period of 135 days without membrane cleaning.	Zhang et al. (2007)
An operational cycle of 4 min of filtration and 1 min of relaxation without backwash showed that relaxations had benefits due to no energy or permeate consumption.	Lin et al. (2009, 2010); Spagni et al. (2010)

1.2.7.5 Fouled membrane cleaning

Membrane cleaning can be defined as physical and chemical cleaning methods. Physical cleaning methods are very fast operations, which can be performed frequently and membrane units usually do not have to be taken off-line, while chemical cleaning methods are typically performed in intervals ranging from days to months and membrane units has to be taken off-line (Zhang et al., 2007). Chemical cleaning is more effective than physical cleaning for the removal of inorganic precipitation, which causes severe irremovable fouling. Chemical cleaning agents such as EDTA might efficiently remove inorganics on the membrane surface (Meng et al., 2009). The detail of each cleaning is concluded as follows:

1.2.7.5.1 Physical cleaning

Physical cleaning methods are usually applied by mechanical force to remove and dislocate foulants from the membrane surface. They include several techniques such as membrane relaxation, forward and reverse flushing, backwashing,

air flushing (also called air sparging, air scouring or air bubbling) and CO_2 back permeation (Wang et al., 2010). Mainly, membrane backwashing and membrane relaxation have been used as standard operating strategies to limit fouling (Le-Clech et al., 2006).

- **Backwashing** is where permeate is pumped backward through the membrane to the concentrate side. Backwashing can easily be applied with hollow fibre, capillary and tubular membranes, but not flat sheet membranes. The backwashing frequency, duration and flux are factors of backwashing design. For example, more frequent backwashing (200 sec filtration/15 sec backwashing) gave lower efficiency than less frequent, less frequent backwashing (600 sec filtration/45 sec backwashing) decreased the amount of irreversible fouling (Jiang et al., 2005). Generally, the hollow fibre and capillary membranes were backwashed at a lower flux (1-2 times filtration flux) but operated at a longer duration (0.5-2 min) while a higher flux (3-10 times filtration flux) with a shorter duration (8-20 sec) was also normally applied in tubular membranes backwashing (Jiang, 2007). Some positive experiments were also carried out with flat sheet membranes with periodic backawash (Grelot et al., 2010).

- **Membrane relaxation** is the periodic pause of filtration or non-continuous filtration. To increase the fouling removal efficiency during relaxation, air scouring can be applied. Relaxation of flat sheet and hollow fibre membranes operation was typically applied in the range of 1-2 min every 8-15 min of operation (Judd and Judd, 2006).

1.2.7.5.2 Chemical cleaning

Chemical cleaning is used to remove irremovable fouling. The optimal selection of the cleaning agent depends mainly on dominant compounds of foulant and has no harmful effect on membrane surface or membrane properties. The efficiency of chemical cleaning depended on a few factors that were necessary such as chemical concentration, contact time, temperature and TMP (Jiang, 2007). Most chemical cleaning agents are recommended by membrane manufacturers as shown in Table 1.8 and the most efficient chemical cleaning agents for a variety of targets are as follows:

1. Caustic solutions at high concentrations and high temperatures could break bonds between the membrane surface and the fouling material and help solubilize proteins. Sodium hydroxide (NaOH) and sodium hypochlorite (NaOCl) are the most often used to remove organic fouling (Jiang, 2007; Zhang et al., 2007).

2. Acid solutions are effective to remove precipitated salts and scalants such as citric acid and nitric acid.

3. EDTA can be used to enhance the solubility of metal ions such as manganese, calcium, magnesium, and iron. The removal of these divalent cations could break the interactions in metal-organic complexes (Zhang et al., 2007).

Table 1.8 Examples of intensive chemical cleaning protocols of four MBR suppliers (Judd and Judd, 2006).

Technology	Type	Chemical	Concentration (%)	Protocols
Mitsubishi	CIP	NaOCl	0.3	Backflow through membrane (2 hrs.) and soaking (2 hrs.)
Zenon	CIA	Citric acid	0.2	Backpulse and recirculate
		NaOCl	0.2	
Memcor	CIA	Citric acid	0.2-0.3	Recirculate through lumens, mixed liquors and in-tank air manifolds
		NaOCl	0.01	
Kubota	CIP	Citric acid	0.2	Backflow and soaking (2 hrs.)
		NaOCl	0.5	
		Oxalic acid	1	

Remark: CIP: Cleaning in place, without membrane tank draining; chemical solutions generally backflushed under gravity in-to-out.

CIA: Cleaning in air, where membrane tank is isolated and drained; module rinsed before soaking in cleaning solution and rinsed after soaking to remove excess reagent.

1.2.7.6 Anaerobic membrane bioreactor (AnMBR) for wastewater treatment

The application of membrane technology coupled with anaerobic reactor is becoming increasingly popular since it leads to increase in anaerobes without any washout from the system. This is essential for a successful anaerobic operation. AnMBR system can operate at a high SRT and short HRT. (Jeison and Lier, 2008; Vyrides and Stuckey, 2009; Lew et al., 2009; Ho and Sung, 2010). A high SRT is desirable for process stability while a short HRT minimizes the reactor volume and leads to reduce the capital cost of reactor (Fuch et al., 2003). The start-up of AnMBR is rather rapid. Acclimatization of the digester sludge of the cross-flow ultrafiltration membrane anaerobic reactor (CUMAR) system was completed after 40 days operation (Ince et al., 1997). AnMBR has typically been applied in the treatment of high strength and low strength wastewater (Table 1.9) such as brewery wastewater (Ince et al., 1997), slaughterhouse wastewater, artificial wastewater and sauerkraut brine (Fuchs et al., 2003), food wastewater (He et al., 2005), slaughterhouse wastewater (Saddoud and Sayadi, 2007), cheese whey (Saddoud et al., 2007), saline sewage wastewater (Vyrides and Stuckey, 2009), domestic wastewater (Lew et al., 2009), landfill leachate (Zayen et al., 2010), palm oil mill effluent (Abdurahman et al., 2011), municipal wastewater (Lin et al., 2011a), and so on.

Table 1.9 The application of AnMBR for wastewater treatment.

Types of wastewater/ Operating condition	Efficiency and Performance	References
Brewery wastewater TKN = 0.1-0.2 $g.L^{-1}$ BOD_5= 65-80 $g.L^{-1}$ COD = 80-90 $g.L^{-1}$ Ultrafiltation MWCO=200 kDa OLR=2.5 $kgCOD.m^{-3}.d^{-1}$ F/M=0.21 $kgCOD.kgVSS^{-1}.d^{-1}$ HRT = 2.5-3.2 days pH = 6.9-7.2 Temp. = 36±1 ^oC.	• This research studied the composition of the microbial population in cross-flow ultrafiltration anaerobic reactor. • The most dominant group of microbial population in the system of an initial study was *Methanococcus* followed by *Methanosarcina*, short rods, medium rods, filaments and long rods. *Methanococcus* species were revealed to be the most dominant group and then medium rods, short rods, *Methanosarcina*, long rods and filament species at the end of the study. • The removal efficiency was over 98% of COD and 99% of BOD_5. The methane content in biogas was obtained at an amount of about 80% in the digester.	Ince et al. (1997)
Food wastewater SS = 0.6-1 $g.L^{-1}$ COD = 2-15 $g.L^{-1}$ Ultrafiltration MWCO=20-70 kDa pH=7±0.2 Temp.=37±0.5^oC HRT=60 hr. SRT=50 days OLR<4.5 $kgCOD.m^{-3}.d^{-1}$	• The anaerobic membrane bioreactor (AMBR) was investigated for treating food wastewater by using ultrafiltration membranes. • The efficiency in terms of COD was in the range of 81-94% and the gas yield stabilized at 0.136 $m^3.kgCOD^{-1}$. • Membranes with the largest MWCO and roughest surface related to the highest flux decline and the lowest recoverable flux rate during long-term operations. • Membrane autopsy showed the formation of a thick bio-film layer on the membrane surfaces which caused a significant flux decline.	He et al. (2005)

Table 1.9 The application of AnMBR for wastewater treatment (continued).

Types of wastewater/ Operating condition	Efficiency and Performance	References
Artificial wastewater COD=9.7 $g.L^{-1}$ Slaughterhouse wastewater SS = 2.4-4.7 $g.L^{-1}$ COD = 5.8-20 $g.L^{-1}$ Sauerkraut brine COD = 40-64 $g.L^{-1}$ TKN =1.1-1.6 $g.L^{-1}$ Microfiltration Pore size=0.2µm HRT=1.2 days Temp.=30^{o}C	• Using a cross-flow membrane bioreactor for three different types of wastewater showed that the volumetric loading rate could attain to a maximum value of 20 $gCOD.L^{-1}.d^{-1}$ for artificial wastewater treatment, 8.6 $gCOD.L^{-1}.d^{-1}$ for sauerkraut brine wastewater and 6-8 $gCOD.L^{-1}.d^{-1}$ for animal slaughterhouse wastewater. • The performance of the system at a steady operating state was higher than 90% of COD removal for all wastewater. • The methane yields were between 0.17-0.30 $LCH_4.gCOD^{-1}$ for artificial wastewater, 0.20-0.34 $LCH_4.gCOD^{-1}$ for sauerkraut brine wastewater and 0.12-0.32 $LCH_4.gCOD^{-1}$ for animal slaughterhouse wastewater.	Fuchs et al. (2003)
Domestic wastewater COD=0.5 $g.L^{-1}$ Microfiltration Pore size=0.2 µm Backwash=3L of permeate for 5 sec. OLR=1.08, 2.16 and 4.32 $gCOD.L^{-1}.d^{-1}$ HRT=12,6 and 4.5 hr Temp.=25^{o}C	• The AnMBR was operated at different backwash frequencies (15, 30 and 60 min) and influent flux (3.75, 7.50 and 11.25 L.m-2.hr-1) on fouling amelioration. • The backwash frequency between 30-60 min showed the best condition for energy savings and fouling amelioration. • The performance of reactor gave a constant COD removal of 88% and an accumulation of 350 mgTSS.L-1.d-1 in the reactor. • A mix of 0.1 M NaOH and 1% H2O2 interspersed with 1% HCl gave the best cleaning process, with a recovery of 75%.	Lew et al. (2009)

Table 1.9 The application of AnMBR for wastewater treatment (continued).

Types of wastewater/ Operating condition	Efficiency and Performance	References
Slaughterhouse wastewater Protein=1.90-3.2 $g.L^{-1}$ BOD_5=3.5-8 $g.L^{-1}$ SCOD=5.4-15.5 $g.L^{-1}$ TCOD=7.1-20.4 $g.L^{-1}$ Ultrafiltration MWCO=100 kDa OLR=4.37-13.27 $kgTCOD.m^{-3}.d^{-1}$ HRT=1.66-3.33 days	• This study shows the application of a cross-flow anaerobic membrane bioreactor (AMBR) for the treatment of slaughterhouse wastewater. • The COD and BOD_5 removal efficiency of AMBR were found to be 93.7% and 93.96%. • The methane yield was about 0.2-0.31 L $CH_4.gTCOD^{-1}$ when operated at OLR less than 13.27 $kgTCOD.m^{-3}.d^{-1}$. The increase of the OLR to 16.32 $kgTCOD.m^{-3}.d^{-1}$ affected the removal efficiencies of SCOD and BOD_5, which were drastically decreased to below 53.6% and 73.3%. • A fixed bed reactor for acidogenesis step coupled with the AMBR for methanogenesis step were recommended to improve the performance of the anaerobic digestion at high OLR. It successfully overcame the VFA accumulation problem.	Saddoud and Sayadi (2007)
Landfill leachate COD = 7.2-85 $g.L^{-1}$ BOD_5 = 1.3-48.7$g.L^{-1}$ NH_4^+ = 1.2-4.9 $g.L^{-1}$ Ultrafiltration MWCO=100 kDa HRT=7 days Temp.=37^oC OLR=1-6.27 $gCOD.L^{-1}.d^{-1}$ COD_{feed}=15 to 30 and to 41 $g.L^{-1}$	• This study investigated the long-term performance of anaerobic membrane bioreactor (AnMBR) to treat landfill leachate. • The landfill leachate was treated without any physical or chemical pretreatment. • At the highest OLR, the biogas production was more than 3 volumes of biogas per volume of the bioreactor (50 L). • Removal efficiency of COD was achieved up to 90% and biogas yield of 0.46 Lbiogas.gCODremoved-1. The biomass inside the AnMBR showed a very slow growth.	Zayen et al. (2010)

Table 1.9 The application of AnMBR for wastewater treatment (continued).

Types of wastewater/ Operating condition	Efficiency and Performance	References
Cheese whey COD=68.6 $g.L^{-1}$ BOD_5=37.71 $g.L^{-1}$ TSS=1.35 $g.L^{-1}$ TKN=1.12 $g.L^{-1}$ Proteins=2.71 $g.L^{-1}$ Microfiltration Pore size=0.2 µm Acidogenesis HRT=1 day Methanogenesis HRT=4 days	• Anaerobic membrane bioreactor with phase separation (acidogenesis/methanogenesis) was used to treat cheese whey wastewater. • The acidogenic reactor gave a maximum acidification of 52.25% with up to 5 $g.L^{-1}$ of VFA, acetic acid at 63.7% and 24.7% of propionic acid. • The systems performance during a period of 45 days continuous operation showed that average removals of COD, BOD_5 and TSS reached 98.5%, 99% and 100% respectively. The biogas methane content was greater than 70% of which the methane yield was up to 0.3 L $CH_4.gCOD_{removed}^{-1}$.	Saddoud et al. (2007)
Saline sewage (0-35 $gNaCl.L^{-1}$) COD=465±20 $mg.L^{-1}$ DOC=145±10 $mg.L^{-1}$ Microfiltration Pore size =0.4 µm Temp. =35±1^oC Sparging rate=5 $L.min^{-1}$ Flux=5-8 L. $m^{-2}.hr^{-1}$	• This study examined the effects of powdered activated carbon (PAC) addition and biogas-sparging time by using a submerged anaerobic membrane reactor (SAMBR) treating saline sewage. • The results showed that the value of TMP slightly increased about 0.025 bars when the biogas sparging was changed from continuous to intervals operation (10 min ON and 5 min OFF), • The addition of PAC could decrease in the TMP value by 0.070 bars while increase was about 30% and 5% of DOC removal in the reactor and effluent. The SAMBR can achieve 99% DOC removal with 35$gNaCl.L^{-1}$.	Vyrides and Stuckey (2009)

Table 1.9 The application of AnMBR for wastewater treatment (continued).

Types of wastewater/ Operating condition	Efficiency and Performance	References
Palm oil mill effluent; POME COD=60-87 $g.L^{-1}$ Ultrafiltration MWCO=200 kDa OLR=1-11 $kgCOD.m^{-3}.d^{-1}$	• POME was treated by using a membrane anaerobic system (MAS). The performance of MAS, producing methane and the kinetic parameters (Monod, Contois, Chen and Hashimoto) of the process were determined. • The COD removal was between 96.6% and 98.4% with HRT from 600.4 days to 6.8 days. • The coefficient of growth yield *(Y)* and the specific microorganism decay rate *(b)* were about 0.67 $gVSS.gCOD^{-1}$ and 0.24 d^{-1}. • The methane gas yield production rate was obtained from 0.25 to 0.57 $L.gCOD^{-1}.d^{-1}$. • The three kinetic models gave the minimum solids retention time *(θc)* of between 5 and 16.9 days. The maximum specific growth rate *(μmax)* ranged from 0.259 to 0.384 day^{-1} and the maximum substrate utilization rate *(K)* was in the range of 0.340-0.527 $gCOD.gVSS^{-1}.d^{-1}$.	Abdurahman et al. (2011)
Municipal wastewater COD = 0.4 g.L-1 TSS = 0.3 g.L-1 Ultrafiltration MWCO=140 kDa	• A submerged anaerobic membrane bioreactor (SAnMBR) was applied to treat municipal secondary wastewater. • The treatment efficiency was achieved as 90% of COD reduction, higher than 99.5% of total suspended solid reduction and 0.26 $LCH_4.gCOD_{removal}^{-1}$ of the methane yield rate.	Lin et al. (2011a)

Anaerobic membrane reactors (AnMBR) can achieve COD removals higher than 90% at a low hydraulic retention time (HRT) of about 3 hours to treat a dilute synthetic wastewater (460 mg $COD.L^{-1}$) (Hu and Stuckey, 2006). AnMBR incorporates solids removal and COD reduction in one reactor and membranes can stop biomass being washed out and can retain slow growing bacteria inside the reactor. Typically, flux of AnMBR is around 7-10 $L.m^{-2}$-hr^{-1} with TMP of around 100-200 mbar, and COD removals as high as 94%, and HRT of normally around 12-17 hours but down to 3 hours. Finally, OLR can be as high as 25 $kgCOD.m^{-3}.d^{-1}$ and 16 $kgCOD.m^{-3}.d^{-1}$ with PAC added (Stuckey, 2012). Moreover, the membrane bioreactor quickly regained stable performance after about 4 days when there was overloading of the system (Fuchs et al., 2003).

Nowadays, AnMBR usually is applied for the treatment of high strength wastewaters with high solids (Dereli et al., 2014; Xiao et al., 2015) while low strength wastewaters with low solids (Liu et al., 2012; Martinez-Sosa et al., 2012) are increasing but little research had been done on high strength wastewaters with low solids (Saddoud et al., 2007). So it should be studied and membrane fouling is the key problem to be solved before industrial implementation (Stuckey, 2012; Skouteris et al., 2012).

In this context, latex industry is a very important and strategic industry in Thailand. Nevertheless, it still has a significant negative environmental impact through the rejection of wastewater containing a high level of organic matter. The analysis of the origin of wastewater points out the main influence of serum production in the high degree of pollution of wastewater notably due to the acidification step for skim latex treatment. According to the high content of organic matter in latex serum and the high level of biodegradability of such components, it appears very relevant to develop specific treatment of latex serum by anaerobic processes that allow a significant removal of organic matter and simultaneously an important production of biogas containing a large proportion of methane source of bioenergy. Nevertheless due to the variability of wastewater characteristics and the presence of specific pollutant such as sulfate, the control of anaerobic digesters can present some difficulties notably due to washout of weakly flocculated methanogenic populations. It appears then relevant to associate to the digester a downstream membrane

separation step whose cut-off allows a total retention of bacteria whatever their state of flocculation. Such a system defines the anaerobic membrane bioreactor (AnMBR).

1.3 Objectives

The objectives of this research were to define new concepts to treat skim latex serum and recover rubber content without acidification by microfiltration and to treat latex serum using AnMBR for biogas production.

1.4 Scope of research

The new concepts in this study were based on ideas as follows:

1. Because the rubber particles are very small in skim latex suspension, their retention without coagulation may be envisaged by filtration on porous membranes. The challenges were then to analyse their separation step in terms of rubber particle retention and membrane fouling control.

2. The recovered permeate by microfiltration of skim latex includes mainly soluble organic matter. The challenges are to analyse (i) the potential of methane production when treating latex serum by anaerobic treatment and (ii) the advantage of AnMBR was developed to intensify the treatment of latex serum and recovered a quality of final effluent.

After a first chapter dedicated to an analysis of such a problem statement, this research was built on the following steps synthesized in the different chapters of this report. The diagram of all experiments was shown in Figure1.14.

- Chapter 2: Preparation of latex serum from skim latex suspension by using a lab scale pilot of cross-flow microfiltration equipped with a ceramic membrane module presenting a pore size of 0.22 µm.
- Chapter 3: Study of the biochemical methane potential (BMP) of latex serum (as substrate feeding) to assess its biodegradability for AnMBR. The study was developed in batch and sequencing batch reactors. The effects of different hydraulic retention times (HRT) on biogas production and organic removal efficiency were analysed.
- Chapter 4: Latex serum degradation was studied in a lab scale AnMBR equipped with submerged PVDF (polyvinylidene fluoride) hollow fibre

membranes presenting an average pore size of 0.1 µm. The AnMBR performances were analysed in terms of COD, TSS, VSS, Alkalinity, VFA and biogas evolutions with time in function of the applied organic loading rates. This analysis included the characterisation of membrane fouling by using different methodologies notably scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), fourier transform infrared (FTIR) and atomic force microscopy (AFM).

1.5 The expected benefits

The expected benefits of this research were:

1. To define appropriate filtration/separation conditions including fouling control by using microfiltration for lab scale results implementation to industrial scale applications.

2. To quantify the biogas production and estimate the possible bio-energy recovery on site industry.

3. To analyse the quality of the treated effluent in regards with its residual content and its possibility to reuse.

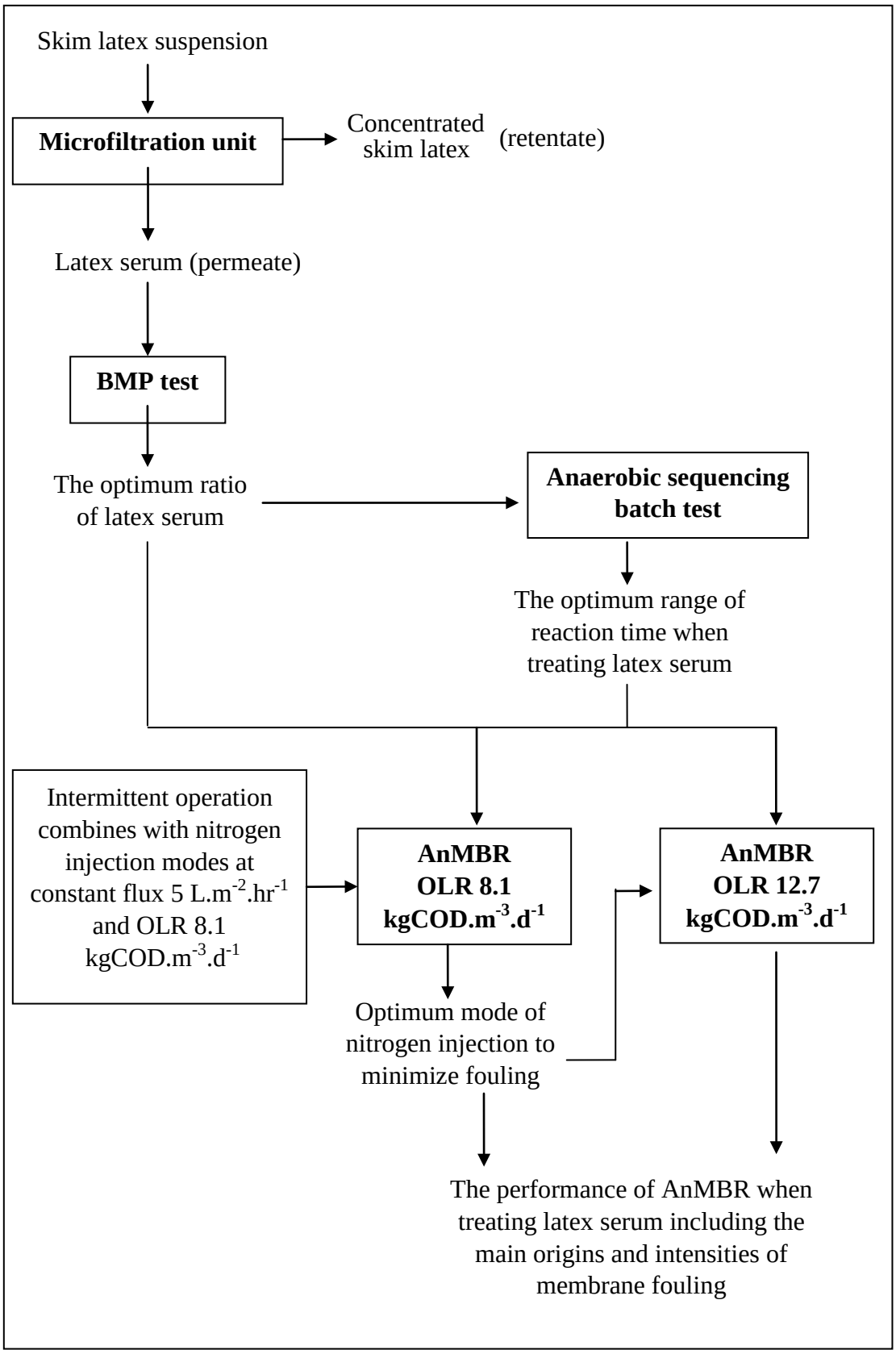


Figure 1.14 Diagram of all experiments.

CHAPTER 2

RECOVERY OF RUBBER CONTENT AND LATEX SERUM FROM SKIM LATEX SUSPENSION BY CROSS-FLOW MICROFILTRATION

To favour the recovery of a concentrated rubber phase from skim latex without coagulation by acidification, it was proposed to introduce a direct separation step by microfiltration on porous membrane with the choice of a membrane cut-off allowing the retention of rubber particles in the retentate phase. Moreover such an operation should allow the recovery of latex serum as the permeate phase without any presence of sulphate ions during anaerobic digestion of latex serum.

The aim of this chapter was then focused on (i) the performance analysis of such an operation including, (i) the evaluation of rubber content in the retentate phase and the volumetric concentration factor VCF that can be reached according to the filtration conditions, and (ii) the identification and quantification of membrane fouling which remains the bottleneck of membrane process development by obliging the development of high membrane surface and/or high energy requirements.

2.1 Materials and methods

A lab scale cross-flow microfiltration unit was used to operate the separation step. The cross-flow system is based on an important circulation of the suspension through membrane channels imposing important parietal shear stresses favorable to minimize the accumulation of compounds on the membrane surface due to their retention by the membrane barrier. Such a circulation is obtained by recycling the suspension by pumping in a loop between the feed tank and the membrane module (Guerra et al., 1997; El Rayess et al., 2011). The choice of cross-flow system was done in relation with the relatively high rubber particle content in the initial skim latex suspension and the supposed rubber content in retentate according to expected VCF.

Indeed, when filtering such concentrated suspensions, an important retention of particles occurs on the membrane surface. This accumulation was determined and minimized to reduce hydraulic resistance. Of course such a cross-flow circulation of concentrated suspensions generally requires high level of energy supply and such a choice must be justified by the economical benefit of recovered products in retentate and/or in permeate.

2.1.1 The lab scale microfiltration unit

Figure 2.1 shows the schematic diagram of lab scale cross-flow microfiltration unit. The system was composed as follows:

- A storage tank (1) containing the skim latex suspension to be treated.
- The filtration module (2) equipped with a tubular ceramic membrane (Figure 2.2).
- A permeate tank (3) used to recover and eventually recycle permeate.
- A recycling pump (4) used to impose (i) transmembrane pressure (TMP) inducing filtration and (ii) longitudinal cross-flow velocity all along the membrane channels.

When the filtration was operated, a part of the skim latex suspension was recovered as permeate (latex serum crossing the membrane barrier), and a part was retained by the membrane cut-off and was present in the retentate phase circulating in the loop between membrane module and storage tank.

The permeate phase was continuously extracted and each hour a new adding of skim latex suspension was done in the feed tank to compensate the volume of filtrate removed of the system during each hour. Because rubber particles were retained by the membrane and maintained in the retentate phase, the filtration was operated with a suspension more and more concentrated with time in the loop.

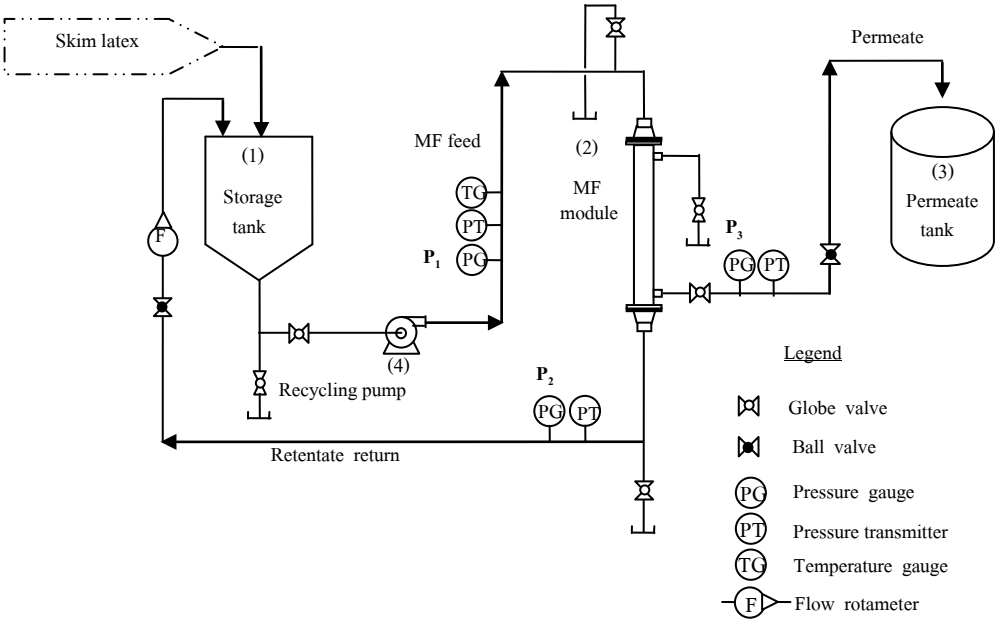


Figure 2.1 The schematic diagram of lab scale cross-flow microfiltration unit.

The membrane was a multichannel (19 channels) tubular membrane as presented in Figure 2.2. This membrane has a 0.24 m^2 effective filtration area and 0.22 µm average pore size (membrane module from China, distributed by Liquid Purification Engineering International Co., Ltd., Thailand). Its characteristics are summarized in Table 2.1.

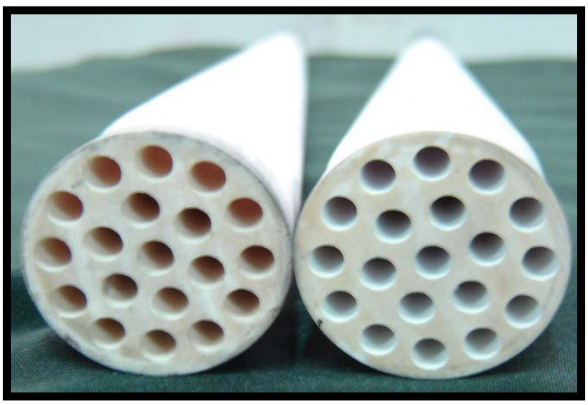


Figure 2.2 Tubular multichannel ceramic membrane.

Table 2.1 Membrane characteristics.

Characteristics	Content/Values
Type	tubular (19 channels)
Membrane material	Ceramic (Support material: α-Al_2O_3, Membrane material: α-Al_2O_3/ZrO_2)
Channel diameter (mm)	3.3
Filtration area (m^2)	0.24
Pore size (μm)	0.22
Hydraulic resistance (m^{-1})	6.75×10^{11}

The cross-flow microfiltration unit was equipped with pressure sensors (P_1, P_2 and P_3) to control on line the longitudinal pressure loss (P_1-P_2) along each membrane channel. Due to the cross-flow circulation, P_1 and P_2 were the static pressures at the entrance and outside of the membrane module, while P_3 was the static pressure upstream the pump in the permeate pipe as indicated in Figure 2.3. The transmembrane pressure TMP can be calculated as follows (Razavi et al., 2003):

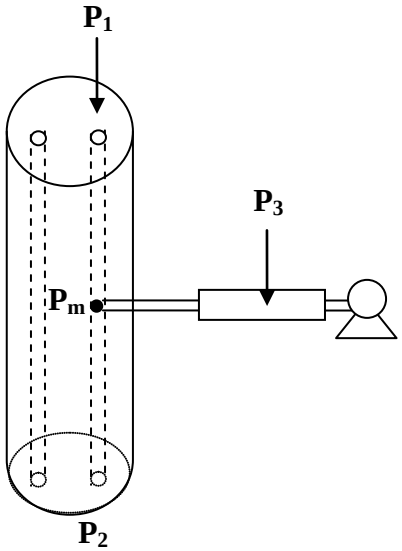


Figure 2.3 The transmembrane pressure.

- The average pressure inside the internal pipe of membrane was equal to:

$$P_m = (P_1 + P_2)/2 \quad (2.1)$$

- The transmembrane pressure (TMP) appeared then as:

$$TMP = P_m - P_3 \quad (2.2)$$

or

$$TMP = (P_1 + P_2)/2 - P_3 \quad (2.3)$$

The specific permeate flux J ($m^3.m^{-2}.s^{-1}$) was measured punctually by quantifying the specific volume $\Delta V/A$ of recovered permeate during a defined time Δt, where A is the membrane surface area:

$$J = (1/A).\ \Delta V/\Delta t \quad (2.4)$$

2.1.2 Operating conditions of cross-flow microfiltration unit

The microfiltration unit was operated at room temperature of 28 ± 2^oC, constant 0.5 bars TMP and constant cross-flow velocity (3 $m.s^{-1}$).

The operations were carried out with continuous removal of permeate for 70 hours. Every hour the volume of permeate was quantified and an equivalent volume of skim latex suspension was added in storage tank to compensate permeate extraction.

Because of permeate removal and membrane selectivity, the rubber content in the circulating suspension was continuously increased with time and a volumetric concentration factor (VCF_t) inside the cross-flow microfiltration unit can be defined as follows:

$$VCF_t = V_{feed} / (V_{feed} - V_{permeate}) \quad (2.5)$$

Where V_{feed} was the cumulated volume of skim latex added in the system between time 0 and t, $V_{permeate}$ was the permeate volume recovered between time 0 and t.

VCF also represents the reduction factor between the cumulative feed volume added between time 0 and t in comparison with the final retentate volume obtained at time t (Karakulski et al., 1998; Cho et al., 2003; Thongmak et al., 2015).

2.1.3 Origin of influent: skim latex suspension

Skim latex suspension was collected from the concentrated latex factory in Songkhla province. Skim latex suspension (containing about 4 %DRC) is a by-product from centrifugation process to produce concentrated latex from fresh latex, it was stabilized by the addition of ammonia with tetramethylthiuram disulphide (TMTD) and zinc oxide (ZnO) (Department of Industry Work (DIW) and DANCED, 2001; Pollution Control Department, 2005; Jawjit et al., 2015).

2.1.4 Analytical methods

The characteristics of skim latex suspension and latex serum were measured as indicated in the ASTM standards and Standard Methods. The different analysed criteria values are given in Table 2.2.

Particle size distribution was realised by laser particle size analyzer (COULTER, LS 230, USA), and related to testing methods which refer to WI-RES-LPSA-001 and laser light scatter particle size analyzer technique. The scattered light detects the particle size distribution from range 0.04 to 2000 μm and the signals were converted to size distribution based on volume.

Table 2.2 Criteria and analytical method for characterisation of latex serum and skim latex suspension.

Parameters	Skim latex suspension	Latex serum	Concentrated latex suspension	Analytical method
Total solids content (TSC)	✓		✓	ASTM D1076: Section 8
Dry rubber content (DRC)	✓		✓	ASTM D1076: Section 9
Volatile fatty acids (VFA)	✓		✓	ASTM D1076: Sections 31–35
Mechanical stability time (MST)			✓	ASTM D1076: Section 16
Total alkalinity as ammonia			✓	ASTM D1076: Section 10
Particle size distribution	✓			Laser particle size analyzer; refer to WI-RES-LPSA-001
pH		✓		pH meter
SCOD		✓		Dichromate closed reflux, titrimetric method
TKN		✓		Macro-Kjeldahl method
BOD_5		✓		5-day BOD test
Protein		✓		Bradford
Turbidity		✓		Nephelometric method

(Source: ASTM standards, 2003; APHA, AWWA and WEF, 2005; Bradford, 1976)

The analyses were realised in triplicate for each parameters.

2.1.5 Determination of membrane fouling

The fouled membrane was cleaned after each experiment to determine the main origins of membrane fouling identified as (i) external fouling by reversible cake layer deposit and accumulation of the largest compounds close or onto the membrane surface due to the membrane selectivity (removable fouling), and (ii) internal fouling due to pore blocking and adsorption of the finest compounds by physic-chemical interactions with the membrane material (irremovable fouling).

Supposing the final membrane resistance as the sum of the different fouling phenomena includes the initial membrane resistance. The Darcy's law (equation (2.6)) was used to compare and quantify each origin of fouling, as follows:

$$R_{total} = TMP/\mu.J = R_m+R_{cake}+R_{fouled} \quad (2.6)$$

Where R_{total} (m^{-1}) is the total hydraulic resistance at the end of experiment (before membrane cleaning), R_m (m^{-1}) is the intrinsic membrane resistance, R_{cake} (m^{-1}) is the external resistance due to the cake layer deposited on the membrane surface, R_{fouled} (m^{-1}) is the resistance due to internal fouling linked to pore blocking and adsorption, TMP is transmembrane pressure (Pa), μ is the dynamic viscosity (Pa.s) of permeate and J is the specific permeate flux ($m^3.m^{-2}.s^{-1}$).

The membrane cleaning was carried out at the end of each experiment as follows:

- Draining latex suspension from the system.
- Rinsing the membrane surface with tap water to remove reversible latex particle deposit and reversible accumulation of compounds close to the membrane (polarisation concentration layer). The rinsing step was carried out after draining off latex suspension, the storage tank was filled with tap water. The recycling of water was operated in the system loop during 2 minutes. Then dirty tap water (tap water contained detached latex particles) was drained off from the system and replaced by new tap water. This cleaned cycle by rinsing was operated till the tap water in the loop was clear (no appearance of latex particles). The system was then filled with distilled water to determine water flux and evaluate the hydraulic resistance remaining after rinsing ($R_{rinsing}$) according to Darcy's law.

- A chemical cleaning was finally used to remove internal fouling. It was carried out for 2 hours by a circulation of a 2 v/v % sodium hypochlorite solution. After rinsing with distilled water, the system was filled with distilled water and a filtration was carried out to determine water flux after chemical cleaning and evaluate the final membrane hydraulic resistance after chemical cleaning by using Darcy's law. If the cleaning was sufficient, the final membrane resistance ($R_{chemical\ cleaning}$) should be equal or closed to the intrinsic membrane resistance R_m.

The hydraulic resistances caused by each fouling origin as cake deposit (R_{cake}) and internal fouling (R_{fouled}) could then be expressed respectively as indicated in equation (2.7 and 2.8):

$$R_{cake} = R_{total} - R_{rinsing} \quad (2.7)$$

$$R_{fouled} = R_{rinsing} - R_m \quad (2.8)$$

2.2 Results and discussion

2.2.1 Characteristics of skim latex suspension

The initial centrifugation to extract latex particles from fresh latex suspension generated 2 fractions, a concentrated fraction containing the largest and heaviest compounds, and a supernatant of centrifugation corresponding to skim latex suspension containing smaller compounds and was a by-product of centrifugation operation.

The fresh latex suspension or natural rubber latex from *Hevea brasiliensis* are colloidal suspensions of latex particles in aqueous medium, it is like milky white opaque colloid containing about 33% and 30% of total solid content (TSC) and dry rubber content (DRC) respectively. After fresh latex harvesting from plantations, ammonia was used to preserve and maintain its quality (Jawjit et al., 2015). The skim latex suspension showed percentages of TSC and DRC around 5.7 and 4.1 respectively that means less than 6 to 7 times of the initial TSC and DRC concentrations in fresh latex suspension. Some characteristics of skim latex suspension are given in Table 2.3. The VFA presents values close to 0.02% which means that the skim latex suspension was of correct quality (no fermentation).

Table 2.3 The characteristic of fresh and skim latex suspension.

Parameters	Fresh latex suspension	Skim latex suspension
Total solid content (%)	33.0±0.7	5.7±0.4
Dry rubber content (%)	29.4±0.7	4.1±0.1
VFA (%)	0.02±0.01	0.02±0.01
Average particle size (µm)	1.21±0.61	0.71±0.57

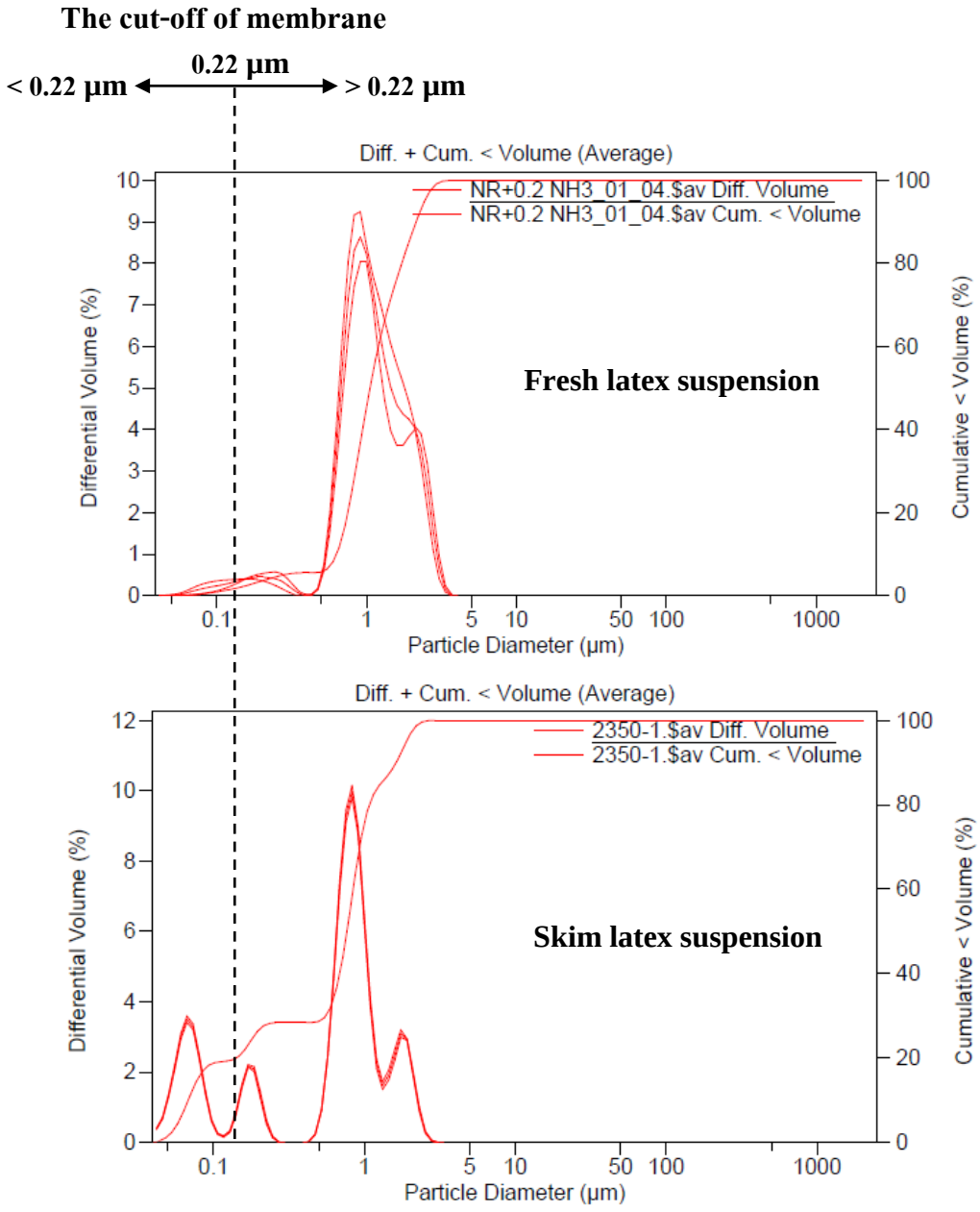


Figure 2.4 Particle size distributions of fresh and skim latex suspension.

A representative particle size distribution of the fresh and skim latex suspension is given in Figure 2.4. It confirms an important presence of small particles lowest than 5 µm with an average size of 0.71 µm for skim latex suspension. The particle size distribution in the fresh latex suspension let appear a large proportion of larger particles.

Such a particle size distribution of skim latex let appear the possible efficiency (70% of particle retention) when filtering on a porous membrane presenting a 0.22 µm cut-off (if the membrane selectivity would be only based on steric effect). In opposite about 30% of the particles should be present in permeate with a high probability of pore blocking or other internal interactions between the lowest compounds and the membrane material.

2.2.2 Semi-batch microfiltration of skim latex suspension

Filtration of skim latex suspension was carried out to (i) recover the maximum of rubber content in retentate and increase the DRC in retentate, and (ii) recover a permeate with the lowest possible DRC, permeate appeared then as a by-product of the filtration, it corresponds to the latex serum phase. The operations were carried out for long running operations, about 70 hours, at a constant 0.5 bars TMP and constant cross-flow velocity of 3 $m.s^{-1}$ that suggested by Thongmak (2009).

2.2.2.1 Membrane selectivity: quality of concentrated skim latex suspension and latex serum

The capacity of retention of rubber content by membrane is illustrated in Figure 2.5. The total solid content (TSC) increase with time corresponds to a simultaneous increase of the volumetric concentration factor (VCF), the membrane barrier appeared then able to progressively concentrate the rubber content in retentate.

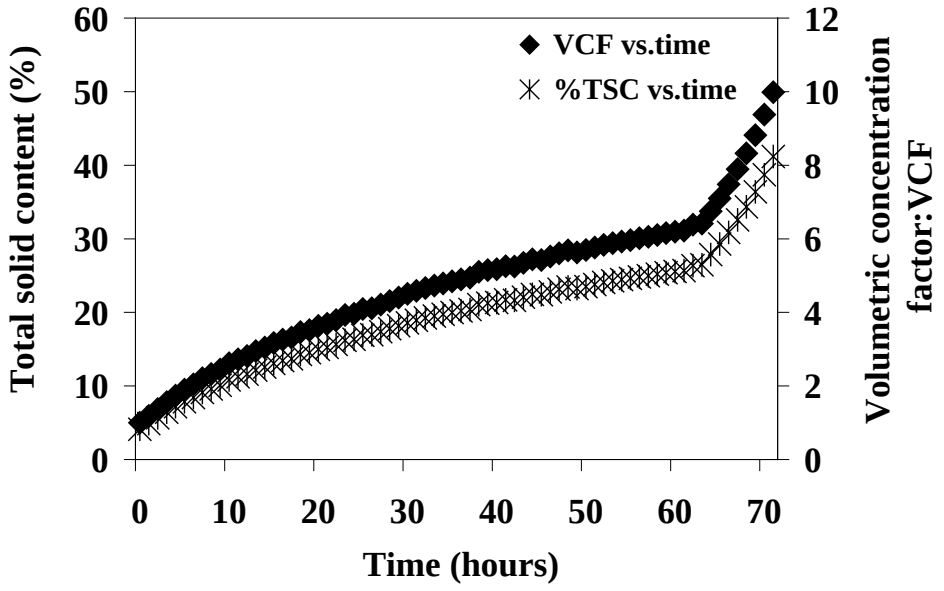


Figure 2.5 TSC membrane selectivity and VCF evolution with time.

Due to the filtration, the permeate volume increased continuously with time as represented in Figure 2.6. After 60 hours of filtration, the VCF reached values more important than 5, corresponding to a DRC close to 30% in retentate. The permeate flux obtained at 60 hours was 8 $L.m^{-2}.hr^{-1}$, such a value corresponded to a decrease of 70% of membrane permeability when comparing this value to the initial permeate flux (26 $L.m^{-2}.hr^{-1}$). In the same time, about 80% of cumulated added feed suspension volume was recovered as permeate.

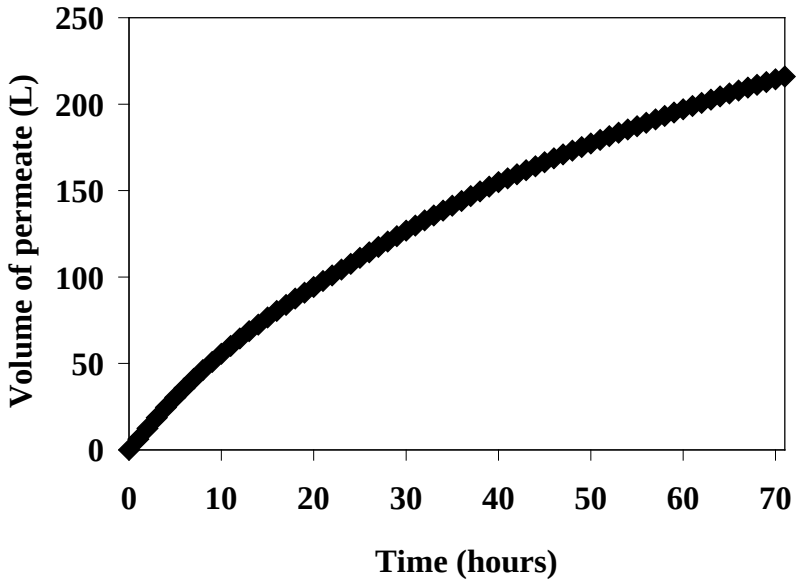


Figure 2.6 Cumulative permeate volumes with time.

After 70 hours, the VCF reached 10 meaning a recovering of 90% of added feed as permeate. The qualities of the corresponding concentrated retentate are given in Table 2.4.

Table 2.4 Characteristics of concentrated skim latex suspension or retentate after filtration.

Parameters	Initial Feed	Retentate	ASTM standard[a]	ISO 2004-1997 standard [a]
Total solids content, %	5.7	39.36	61.3	61.5
Dry rubber content, %	4.1	38.24	59.8	60
Total solids content minus dry rubber content, %	1.4	1.12	2.00max	2.00 max
Total alkalinity as ammonia, %	-	0.26	0.29 max	0.29 max
Mechanical stability time (MST), seconds	-	720	650 min	650 min
VFA, %.	0.02	0.04	-	0.20 max

[a] *Standard specification for centrifuged latex preserved with low ammonia with other necessary preservatives.*

It can be noticed some significant differences between retentate characteristics and standard specifications of concentrated latex suspension for general industrial applications. The dry rubber content DRC appears notably lower than standard recommendations. Nevertheless the possibility of using latex suspension of 30-35% DRC has been reported to produce toy masks, toy balloons and gloves, presenting tensile properties in the range of values expected by market regulations (Kongthong, 2005). So, the possibility of using concentrate retentates (35-40% DRC) as obtained by membrane separation step to produce rubber products of quality has been opened with such results, moreover if the decrease of allergen content in retentates can be proved (because allergen compounds are mainly soluble and could be mainly present in permeate), the industrial value of such concentrated latex suspension could be improved in comparison with skim block or skim crepe obtained by coagulation (low priced products). The other characteristics (total alkalinity, MST,

VFA) are close to the specified values observed in concentrated natural latex, according to standard specifications (Kachornchaikul and Chuayplong, 1988; ASTM, 2003). To produce more concentrated suspensions from skim latex suspension (more close to the standard specification) it appeared important to obtain better membrane fouling reduction. Such an approach also necessitates an analysis of the rheological behaviour of the retentate presenting a viscosity increasing with VCF increasing.

The permeate (latex serum) appeared as a clear (very low turbidity) and yellow solution (Figure 2.7). Table 2.5 shows some serum characteristics after filtration of skim latex suspension.

Figure 2.7 Skim latex suspension (left) and latex serum after filtering (right).

The pH value indicates an alkaline solution due to the addition of ammonia to preserve and protect initial fresh latex suspension from any latex particle coagulation of acidogenic digestion during storage time. This also induces high levels of TKN in latex serum about 2.7±0.2 $g.L^{-1}$. The rubber content in permeate was not significant enough to be quantified. It can be then deduced that the rubber content of skim latex was totally retained in retentate.

Table 2.5 Serum characteristics after filtration (permeate).

Parameters	**Average value ±SD**
SCOD ($g.L^{-1}$)	34±1.8
BOD_5 ($g.L^{-1}$)	14±1.9
TKN ($g.L^{-1}$)	2.7±0.2
Protein ($g.L^{-1}$)	0.5±0.03
Turbidity (NTU)	1.33±0.49
pH	9.57±0.22

Furthermore, latex serum presents high SCOD values (more than $30g.L^{-1}$, with a BOD_5 close to $14g.L^{-1}$). The COD/BOD_5 ratio close to 2 showed a good biodegradability of the organic matter (Gunkel et al., 2007). Moreover latex serum presented a high content in proteins around 0.5±0.03 $g.L^{-1}$. The protein content was investigated by Sridang et al. (2012). The fractions of protein content in latex serum (obtained by microfiltration process) were deduced by using SDS page alkyl amine electrophoresis method. The most of the proteins presented a molecular weight distribution (MW) in a low range between 14 and 36 kDa that corresponded to Glucanase, 29 kDa of Hevamin or Chitin, 20 kDa of small rubber particle protein or Prohevein, 14.2 kDa of rubber elongation factor protein and MW of protein lower than 14.2 kDa of Hevein. Moreover, Yeang et al. (2002) reported ten allergenic proteins of natural rubber latex —Hev b 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10— which are recognized by the International Union of Immunological Societies (IUIS). When comparing the molecular weight of the found proteins in latex serum by microfiltration process and allergenic proteins, it was found that the found proteins in latex serum corresponded to Hev b 2, 6.01, 6.02 and 8 which accords with Mengumpun et al. (2008) who mentioned that proteins such as Hev b 2, 4, 6 and 10 are contained in the water-soluble parts of the latex. Many latex induced allergic reactions are believed to be caused by water-soluble proteins (Yeang et al., 1996).

It can then be a positive point for the quality of the retentate if most of the allergenic proteins are contained in latex serum fraction. Then the concentrated

latex suspension obtained by microfiltration should have low or be free from allergenic proteins.

2.2.2.2 Membrane permeability: Evolution of permeate flux with time, fouling origin and intensity

Figure 2.8 gives an illustration of the permeate flux evolution versus time when working with a more and more TSC content in retentate.

A progressive decrease of permeate flux can be observed meaning that a more and more important membrane fouling was occurred. It was due to the accumulation of matter onto the membrane surface by retention of the largest particles to form a deposit, possible accumulation of large soluble compounds as polarisation layer, pore blocking and progressive modification of deposit properties as it plays also the role of a dynamic barrier able to retain the smallest compounds which progressively modified its structure by closing its porosity and decreasing its permeability. After 70 hours of operation (VCF = 10), the final permeate flux was around 6.50 $L.m^{-2}.hr^{-1}$, such a value corresponded to a 75% drop regarding the initial permeate flux value.

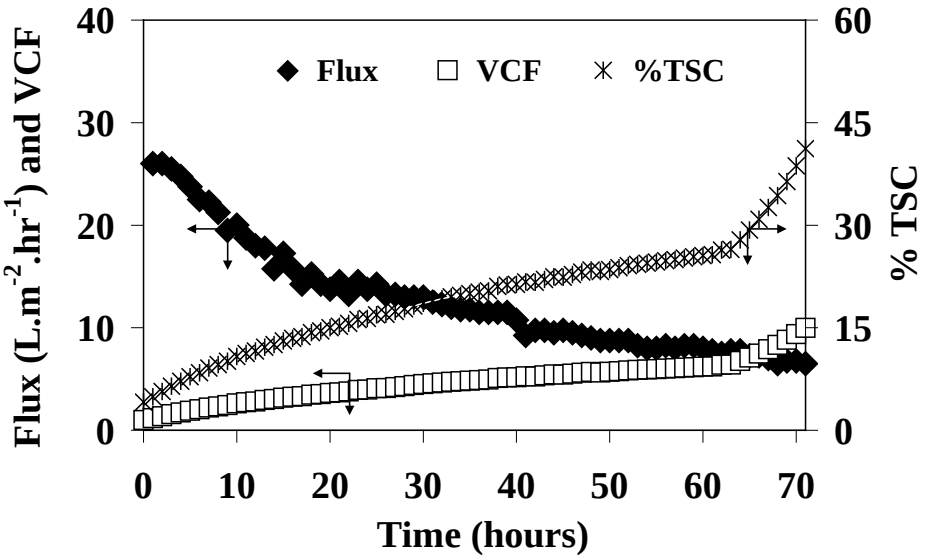


Figure 2.8 The evolutions of specific permeate flux, VCF and the percentage of TSC in retentate with time.

Figure 2.9 shows the total hydraulic resistance and the percentage of TSC in retentate evolution with time. As expected, it increased when permeate flux decrease according to Darcy's law. Such an evolution confirms that more the retentate appeared concentrated, more the membrane fouling appeared important.

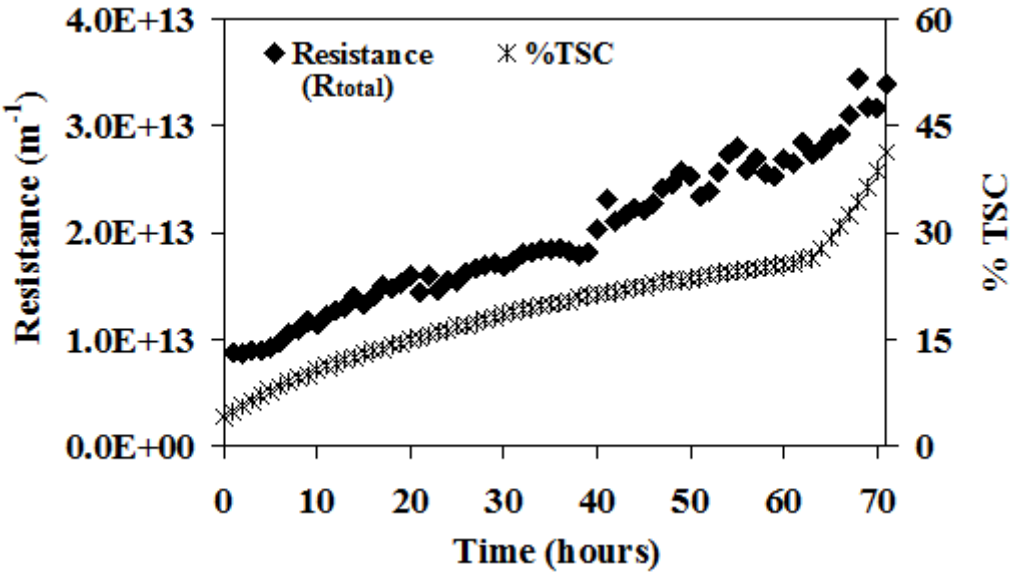


Figure 2.9 The evolutions of total hydraulic resistance and the percentage of TSC in retentate versus time.

At the end of an experiment, when VCF reached important values (close to 10), the fouled membrane was specifically cleaned as indicated in the topic 2.1.5 to identify the main origin of fouling and quantify the specific contribution of external and internal fouling. The results are presented in Figure 2.10.

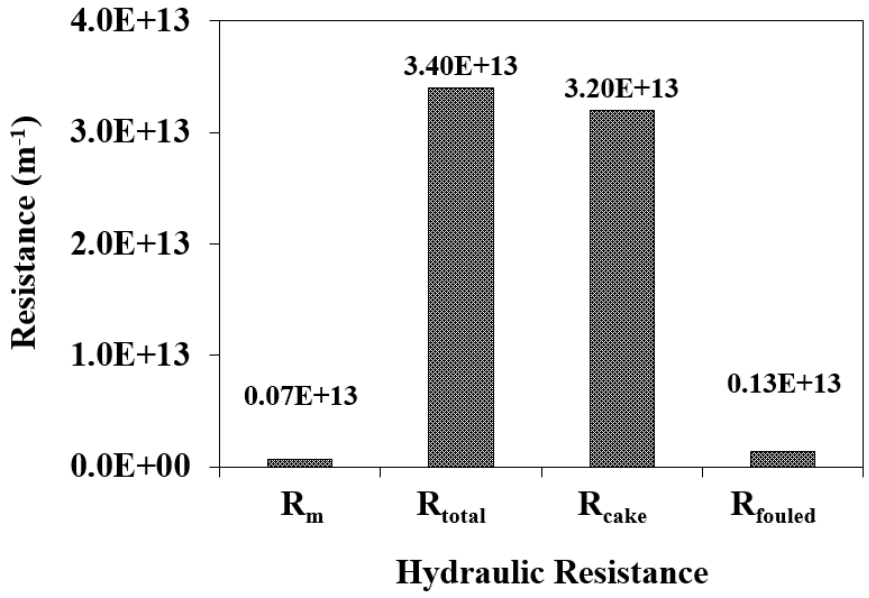


Figure 2.10 Specific contributions of the different membrane fouling origins.

Fouling resistance in this study was found close to 3.2×10^{13} m^{-1} for the external reversible fouling (R_{cake}) and 0.13×10^{13} m^{-1} for the internal irreversible fouling (R_{fouled}). Such values corresponded to other studies obtained when filtering skimmed milk, Grandison et al. (2000) who found $1.07\text{-}7.49\times10^{13}$ m^{-1} and $0.18\text{-}0.28\times10^{13}$ m^{-1} for reversible and irreversible fouling resistance, respectively. It pointed out that the reversible fouling resistance was high when compared to the irreversible fouling resistance meaning that permeate flux was controlled by the evolution of the reversible fouling resistance.

It can be noticed that the external reversible fouling (R_{cake}) represented in this study more than 94% of the total hydraulic resistance. The internal resistance (R_{fouled}) remained in the same range of initial membrane resistance contribution (R_m). This result let also supposed that (i) the reversible accumulation of matter (reversible deposit) close to the membrane surface had limited the internal fouling phenomena as pore blocking or biofilm, and (ii) the smallest compounds entering inside the pores and present in permeate had no significant interactions with the membrane material.

In industrial applications, even if the cake deposit can be minimised by hydraulic means, the internal fouling induces a progressive decrease of the membrane permeability and obliges to a regeneration of the membrane permeability by practising periodical chemical cleaning (Mugnier et al., 2000; Grelot et al., 2010b).

Nevertheless, it remains important to obtain an optimised management of all the cleaning sequences to avoid any reduction of membrane lifetime.

2.3 Conclusions

The concentration of skim latex was envisaged by using filtration on microporous membranes to concentrate rubber content present in skim latex suspension and recover the smallest compounds (proteins, sugars…) in permeate as latex serum solutions. Results have shown that the retentate could reach rubber content DRC in the range of 30 to 40%.

Membrane fouling appeared consequent in this study but it was essentially due to external and easy reversible fouling. The operation improving necessitates an optimisation of fouling control and permeate flux evolution. Such analysis imposes new research including the study of the role of (i) larger membrane cut-off to favour flux permeation without any decrease of rubber content or increase of membrane fouling intensity, (ii) other hydraulic means of external fouling control such as relaxation and backwashing allowing deposit breakage. The rheological behavior of the retentate suspensions also remains a determining criterion to choice the best filtration conditions and the best membrane module configuration, such a behavior must be studied before any industrial development.

Moreover, according to the size of allergen proteins, most of them can be absent from retentate and present in permeate fraction. The industrial benefit of retentate suspensions without allergen compounds can then be improved and let envisage some significant potential of industrial valorization of such retentates.

Permeate (latex serum) appeared as a clear yellow solution containing the smallest soluble organic fractions, the obtained ratio COD/BOD_5 let appear an important level of biodegradability, it then appears possible to develop biological way of treatment of such latex serum solutions to significantly decrease the environmental impact of latex industry wastewater when releasing them in river or spread them on fields.

CHAPTER 3

BIOCHEMICAL METHANE POTENTIAL TEST (BMP) AND ANAEROBIC SEQUENCING BATCH TESTS

The biochemical methane potential (BMP) has been defined as a relevant criterion to envisage substrate digestion using an anaerobic conversion (Raposo et al., 2006; Isci and Demirer, 2007; Elbeshbishy et al., 2012; Kafle et al., 2013). Therefore this chapter presents a preliminary work concerning some investigations on BMP tests to evaluate the methane potential production from latex serum digestion at different substrate to inoculum ratios. Moreover, conventional anaerobic sequencing batch tests were carried out to analyse the influence of the reaction time between liquid phase and biomass (equivalent to the hydraulic retention time, HRT) on the organic matter removal, biogas production and yield coefficients.

3.1 Materials and methods

3.1.1 Source of seed sludge

The sludge used as inoculum in all experiments was taken from an anaerobic wastewater treatment plant of latex factory, Songkhla Province, Southern Thailand. Before being used as inoculum, it was incubated without any substrate addition at room temperature for 1 week to ensure it achieved digestion of fermentable organic matter present in its matrix.

3.1.2 Biochemical methane potential (BMP)

The BMP test was investigated to evaluate the biodegradability of latex serum and methane productivity when an anaerobic digestion was carried out. The BMP test was performed in triplicate in specific vials of 200 mL of working volume and headspace volume of 140 mL as shown in Figure 3.1. The method of the BMP test was carried out as previously reported (Altamira et al., 2008; Elbeshbishy et al., 2012) as follows:

1. The vials were flushed with Nitrogen gas and 50 mL of inoculum was added (39.5 $gVSS.L^{-1}$ in the initial inoculum suspension), the system was then shook during 1 week at 35 ^{o}C for incubation and total removal of biodegradable soluble organic matter. The concentration of soluble COD at the end of this week of incubation could be supposed negligible (less than 0.1 $g.L^{-1}$).

2. 150 mL of latex serum at different initial COD concentrations (8.3, 16.7, 25 and 33 $mg.L^{-1}$) was then added in each vial which led to different ratios of substrate to inoculum (S/X) such as 0.6, 1.3, 1.9 and 2.5$gSCOD.gVSS^{-1}$ (After adding of latex serum, the concentration of inoculum was 10$gVSS.L^{-1}$).

3. Adjusting the pH of the samples at about 7 ± 0.2 by using HCl in aqueous solution.

4. The serum vials were flushed with Nitrogen gas for about 5 minutes and closed with septum before starting the test.

5. The incubation was then carried out at a temperature of 35 ^{o}C with shaking up at 180 rpm (Model of the shaker is IOX400.XX2.C IOI400.XX2.C IOC400.XX2.C, GALLENKAMP, SANYO).

6. Biogas production was measured by inserting a needle into the septum; the syringe displacement due to gas pressure increase allowed the continuous measurement of biogas production. The volume of produced biogas was measured with time until the cumulative gas curve reached a plateau.

Figure 3.1 BMP assay.

The composition of latex serum in these tests was shown in the Table 3.1 presenting the initial composition of the suspension in the bottle according to the different S/X ratios. Ammonia-Nitrogen concentration appeared in ranges of 0.17-1.00 $g.L^{-1}$ and a pH value in each bottle was initially adjusted to about 7.2 within the optimal range of methanogenic activity.

Table 3.1 The composition of suspension in the BMP vials.

S/X	COD ($g.L^{-1}$)	NH_3-N ($g.L^{-1}$)	pH
0.6	6.2	0.17	7.2
1.3	12.5	0.40	7.2
1.9	18.7	0.73	7.2
2.5	24.9	1.00	7.2

3.1.3 Anaerobic sequencing batch tests

The anaerobic sequencing batch tests were used to identify an optimal range of reaction time when treating latex serum before study in anaerobic membrane bioreactor (AnMBR). The reaction time between liquid phase and biomass can be assimilated as the average hydraulic retention time (HRT) of latex solution in each bottle. The experiment was carried out at 30°C in 3 specific bottles continuously shook by magnetic stirrer (Figure 3.2). Each bottle had a 200 mL working volume.

Each bottle was filled with serum latex and seeding sludge (with the same origin and condition during BMP tests). The initial filling conditions corresponded to a 14.2g of soluble $COD.L^{-1}$ and a $10gVSS.L^{-1}$ of final biomass concentration what corresponded to an initial S/X ratio equal to $1.1gSCOD.gVSS^{-1}$. The initial S/X ratio of this test accorded with the optimal ratio from BMP test and was also used as the ratio of reference when working in AnMBR.

Different reaction times or HRTs were chosen in each bottle by imposing different renewal of supernatant with time as follows:

1. In the first bottle, the experiment duration was about 5 days, each day, 150 mL of supernatant was extracted after sludge settling and replaced by 150 mL of latex serum (150 $mL.d^{-1}$). The average time of reaction concerning soluble COD or average HRT can then be considered as equal to 1.3 days.

2. In the second bottle, the experiment duration was about 15 days, each 3 days, 150 mL of supernatant was extracted after sludge settling and replaced by 150 mL of latex serum (50 $mL.d^{-1}$). The average time of reaction or average HRT can then be considered as equal to 4 days.

3. In the third bottle, the experiment duration was about 25 days, each 5 days, 150 mL of supernatant was extracted after sludge settling and replaced by 150 mL of latex serum adding (30 $mL.d^{-1}$). The average time of reaction or average HRT can then be considered as equal to 6.7 days.

The knowledge of initial S/X ratio and HRT allowed the calculation of equivalent average organic and mass loading rates (OLR, $kgCOD.m^{-3}.d^{-1}$, and F/M, $kgCOD.kgMVSS^{-1}.d^{-1}$) as indicated in Table 3.2 for the three experiments.

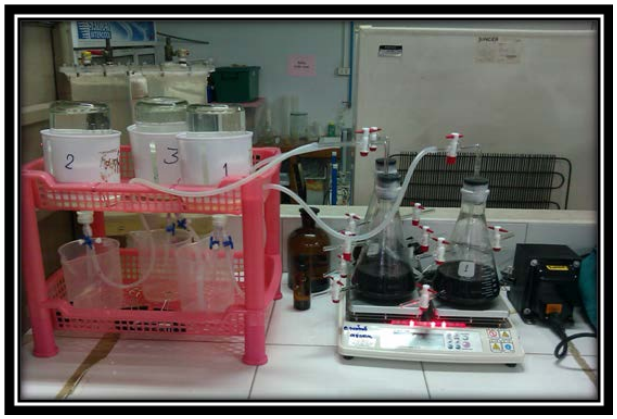


Figure 3.2 Photograph of the anaerobic sequencing batch test.

Table 3.2 Organic and mass loading rates for the anaerobic sequencing batch test.

HRT (d)	OLR ($kgCOD.m^{-3}.d^{-1}$)	F/M ($kgCOD.kgMVSS^{-1}.d^{-1}$)
1.3	8.4	0.84
4.0	2.6	0.26
6.7	1.5	0.15

3.1.4 Analytical methods

For BMP tests and anaerobic sequencing batch tests, the anaerobic digestion efficiency was evaluated by considering the composition of the supernatant

and the biological suspension characteristics in the bottle in comparison with the latex serum composition. Such an evaluation was carried out by measuring the following criteria SCOD, pH, alkalinity, VFA, as showed in Table 3.3.

Moreover the gas production and its composition were evaluated. Biogas production was measured (i) by the syringe displacement for BMP tests as indicated in the topic 3.1.2, and, (ii) for anaerobic sequencing batch tests, by the recovering of water released by the needle at the bottom part of the glass bottle recovering the biogas released from the digester tank (the biogas inducing a pressure increasing that allowed the water extraction) as indicated in Figure 3.3.

Table 3.3 Parameters and analytical method of BMP assay and anaerobic sequencing batch test.

Parameters	**BMP assay**	**Anaerobic sequencing batch test**	**Analytical method**
pH	✓	✓	pH meter
SCOD	✓	✓	Dichromate closed reflux, titrimetric method
Alkalinity (as $CaCO_3$)	✓	✓	Direct titration method
VFA	✓	✓	Direct titration method*
NH_3-N	✓	✓	Macro-Kjeldahl method
TSS and VSS	✓	✓	Dried 103-105 ^oC and Dried 550 ^oC
Biogas composition	✓	✓	Gas chromatography

(Source: APHA, AWWA and WEF, 2005; *DiLallo and Albertson, 1961)

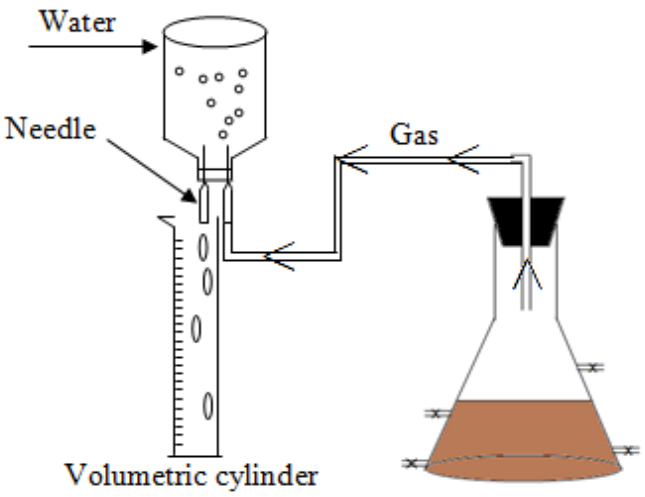


Figure 3.3 Illustration of the biogas production measurement in anaerobic sequencing batch test.

Biogas compositions, notably the CH_4, CO_2 and N_2 contents, were analysed by gas chromatography (Agilent 7890A) equipped with thermal conductivity detector TCD and HP-PLOT Q capillary column, 30m×530µm×40µm. Helium was used as the carrier gas. The oven temperature was programmed to increase from 60 to 250 ^{o}C with a final hold time of 3 minutes and the temperature of inlet and detector TCD was 250 ^{o}C.

3.2 Results and discussion

3.2.1 Potential of latex serum to produce methane: BMP tests

BMP tests were performed to estimate methane production from latex serum (Figure 3.4). Experiments were carried out for four S/X ratios (0.6, 1.3, 1.9 and 2.5gSCOD.gVSS^{-1}).

Figure 3.4 The BMP assays in laboratory.

Table 3.4 presents the soluble COD concentration in supernatant at the final time of test, after 20 days of digestion, for the different S/X ratios. COD removal efficiency of this operation can be deduced by comparing the SCOD at the final time with the initial soluble COD concentration in the bulk due to the initial addition of latex serum (the soluble COD concentration due to the only inoculum can be neglected as indicated in the topic of 3.1.2). The percentage of SCOD efficiency was calculated as follows:

$$\%E_{SCOD} = (1 - SCOD_t/SCOD_o) \times 100 \qquad (3.1)$$

At the end of BMP test, the efficiency of SCOD removal and methane yield coefficient (ratio between the final volume of recovered methane and the final quantity of removed SCOD) were indicated in Table 3.5.

The soluble COD removal efficiency appeared higher than 90% for the three lowest S/X ratios, proving the high degree of biodegradability of organic matter present in latex serum. In opposite, working with the highest S/X ratio appeared a low value of COD removal efficiency (approximately 53%). Neves et al. (2004) indicated that the increase of S/X ratio can induce an overloading in the system due to some accumulation of volatile fatty acid and a significant decrease of pH as noticed in this experiment. A methanogenesis inhibition could then occur notably when pH dropped lower than 6.5.

Table 3.4 The values at the final time of test for the different S/X ratios.

Parameter	S/X			
	0.6	**1.3**	**1.9**	**2.5**
$SCOD_o$ ($g.L^{-1}$)	6.2	12.5	18.7	24.9
$SCOD_t$ ($g.L^{-1}$)	0.18	0.96	1.41	11.61
VFA_t ($g.L^{-1}$)	0.16	0.56	0.96	6.09
$Alkalinity_t$ ($g.L^{-1}$)	1.57	2.79	3.84	1.91
$VFA_t/Alkalinity_t$	0.10	0.20	0.25	3.19
pH_t	6.5	6.8	7.0	5.3

Remark: “o” is the initial values and “t” is the values at the final time in the suspension in assay vials.

At the end of test corresponding to the highest S/X ratio, some accumulation of volatile fatty acids (VFA), about 6.09$g.L^{-1}$ and VFA/alkalinity ratio was too high about 3.19, appeared and can be related to low final pH value, about 5.3 due to insufficient buffering capacity of the media, resulting in a pH decrease. Such low pH value effectively induced some inhibition of methanogenesis as indicated by Neves et al. (2004) and Chen and Hashimoto (1996). Liu et al. (2004) postulated that hydrolysis or acidogenesis step was also negatively affected by too high S/X ratios. Gerardi (2003), mentioned also the importance of VFA/alkalinity ratio that appeared inhibitor when it is higher than 0.8.

The final pH values were higher than 6.5 when working with others ratios (0.6, 1.3 and 1.9 $gSCOD.gVSS^{-1}$), and no significant accumulation of VFA was observed. The VFA/alkalinity ratios were found lower than 0.3-0.4, such VFA/alkalinity range being favourable to anaerobic digestion without acidification risk (Borja et al., 2004).

Table 3.5 The $\%COD_{removed}$ and methane yield coefficient for the different S/X ratios.

S/X	$\%COD_{removed}$	Methane yield coefficient ($NLCH_4.gCOD_{removed}^{-1}$)
0.6	97.1±0.2	0.13
1.3	92.3±0.3	0.29
1.9	92.5±3.6	0.29
2.5	53.4±1.9	0.16

Figure 3.5 (a and b) represents the cumulative biogas and methane productions with time for the different S/X ratios. The biogas and methane productions increased with time and increasing S/X ratio, except at the highest S/X ratio (2.5 $gCOD.gVSS^{-1}$). Some inhibition occurred at the highest S/X ratio not only due to low pH value but also to a possible excessive concentration of NH_3-N (about 1.0 $g.L^{-1}$) in influent which can induce inhibition during anaerobic process as underlined by McCarty (1964) and Mojiri et al. (2012) (the recommended range of NH_3-N concentrations being 0.2-1.0 $g.L^{-1}$).

Considering the three lowest S/X ratios, the increasing biogas and methane productions with increasing S/X ratios showed similar results as reported by Raposo et al. (2006) who found an increase of methane recovered volume with increasing organic loading rate and according to result of Elbeshbishy et al. (2012) who indicated that methane potential of food waste increased with increasing S/X ratios. The production of biogas and methane was proportional to the substrae load applied. The highest methane production of 502 mL was obtained at S/X of 1.9 $gCOD.gVSS^{-1}$ which slightly lower when comparing with digestion of food waste (560-760 mL).

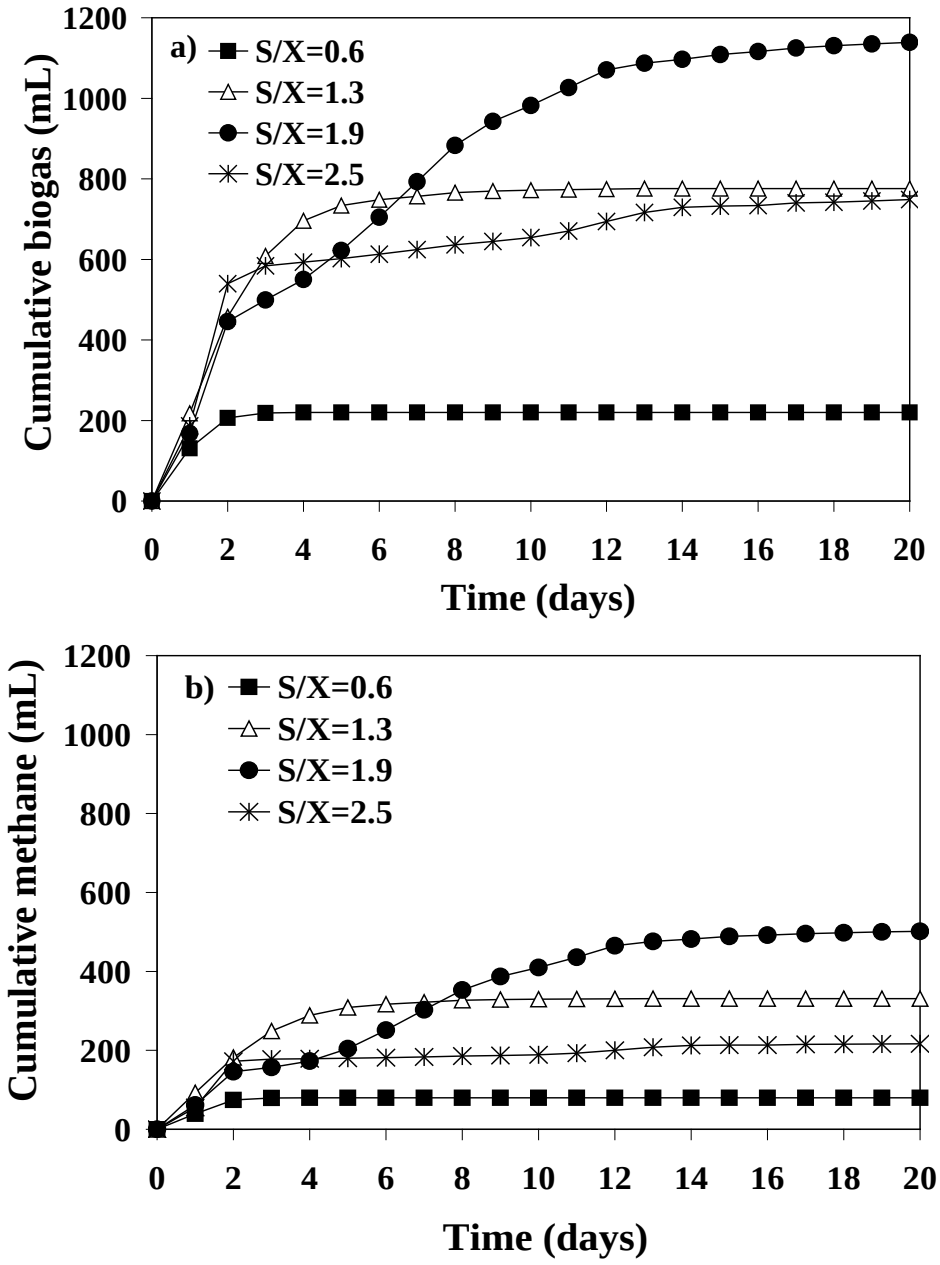


Figure 3.5 BMP tests: a) Cumulative biogas production and b) Cumulative methane production versus time.

Figure 3.6 presents the cumulative methane yield coefficient as a function of digestion time for the different S/X ratios. The highest methane yield coefficient was found at S/X ratios of 1.3 and 1.9, close to 0.3 $NLCH_4.gCOD_{removed}^{-1}$ which slightly lower than the theoretical value of 0.35 $NLCH_4.gCOD_{removed}^{-1}$ (Raposo et al., 2011). The methane yield coefficients obtained in the present work were close

to results of Maya-Altamira et al. (2008) when treated wastewater from fish products for human consumption and pre-treated slaughterhouse effluent, presenting methane yield coefficients about 0.27 and 0.32 $NLCH_4.gCOD_{removed}^{-1}$, respectively.

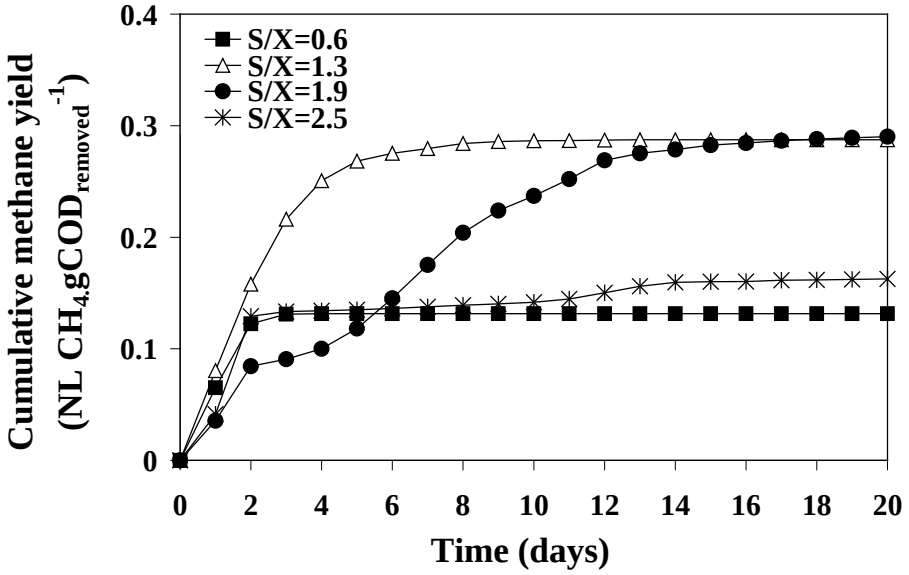


Figure 3.6 Cumulative methane yields at different S/X ratios.

Raposo et al. (2011) indicated that the experimental methane yield measurement can be used to calculate the level of anaerobic biodegradability (BD_{CH4}) under the defined test conditions in comparison with its theoretical value as follows:

$$BD_{CH4}\ (\%) = (Bo_{-Exp}/Bo_{-Th}) \times 100 \qquad (3.2)$$

Where Bo_{-Exp} represents the experimental methane yield coefficient and Bo_{-Th} the theoretical methane yield coefficient calculated from the elemental composition. COD analysis permits the calculation of Bo_{-Th}, 1 g COD removed can produced 0.350 L of methane at 273.15 K (Standard Temperature and Pressure, STP) (Raposo et al., 2011) or 0.395 L at 35 $^{\circ}$C and 1 atm.

Droste (1997) mentioned that in an anaerobic process, the COD removed is converted to methane, the amount of oxygen required to completely oxidize 1 mole of CH_4 at STP is calculated. The balanced reaction is:

$$CH_4 + 2O_2 \rightarrow CO_2 + H_2O \quad (3.3)$$

The total volume of gas produced per kgCOD converted is then 0.35 Nm^3.

The theoretical methane yield Bo_{-Th} was 0.350 L at STP. The experimental methane yields Bo_{-Exp} at the final time of S/X ratios of 0.6, 1.3, 1.9 and 2.5gSCOD.$gVSS^{-1}$ presented the values of 0.131, 0.287, 0.291 and 0.163 L at STP, respectively. When calculated these values with the theoretical methane yield coefficient (equation 3.2), the biodegradability of latex serum at different S/X ratios is shown in Table 3.6. The maximum biodegradability (82-83%) was achieved at S/X ratios of 1.3 and 1.9 which can be postulated that corresponded to high degradation.

Table 3.6 The % BD_{CH4} at different S/X ratios.

S/X	BD_{CH4} (%)
0.6	37.5
1.3	82.1
1.9	83.1
2.5	46.6

It is then significantly beneficial to envisage the development of anaerobic digestion to treat such latex serum wastewater and produce biogas and energy with an important removal of organic fraction from latex wastewater.

3.2.2 The influence of the reaction time: Anaerobic sequencing batch tests

The anaerobic sequencing batch tests were performed to evaluate an optimal range of hydraulic retention time (HRT) when treating latex serum in AnMBR. The experiment was carried out at HRT of about 1.3, 4 and 6.7 days in specific procedure as indicated in the topic of 3.1.3. The results obtained are presented as follows:

Figure 3.7 shows the COD concentration and COD removal efficiency evolutions versus time in supernatant at different HRTs.

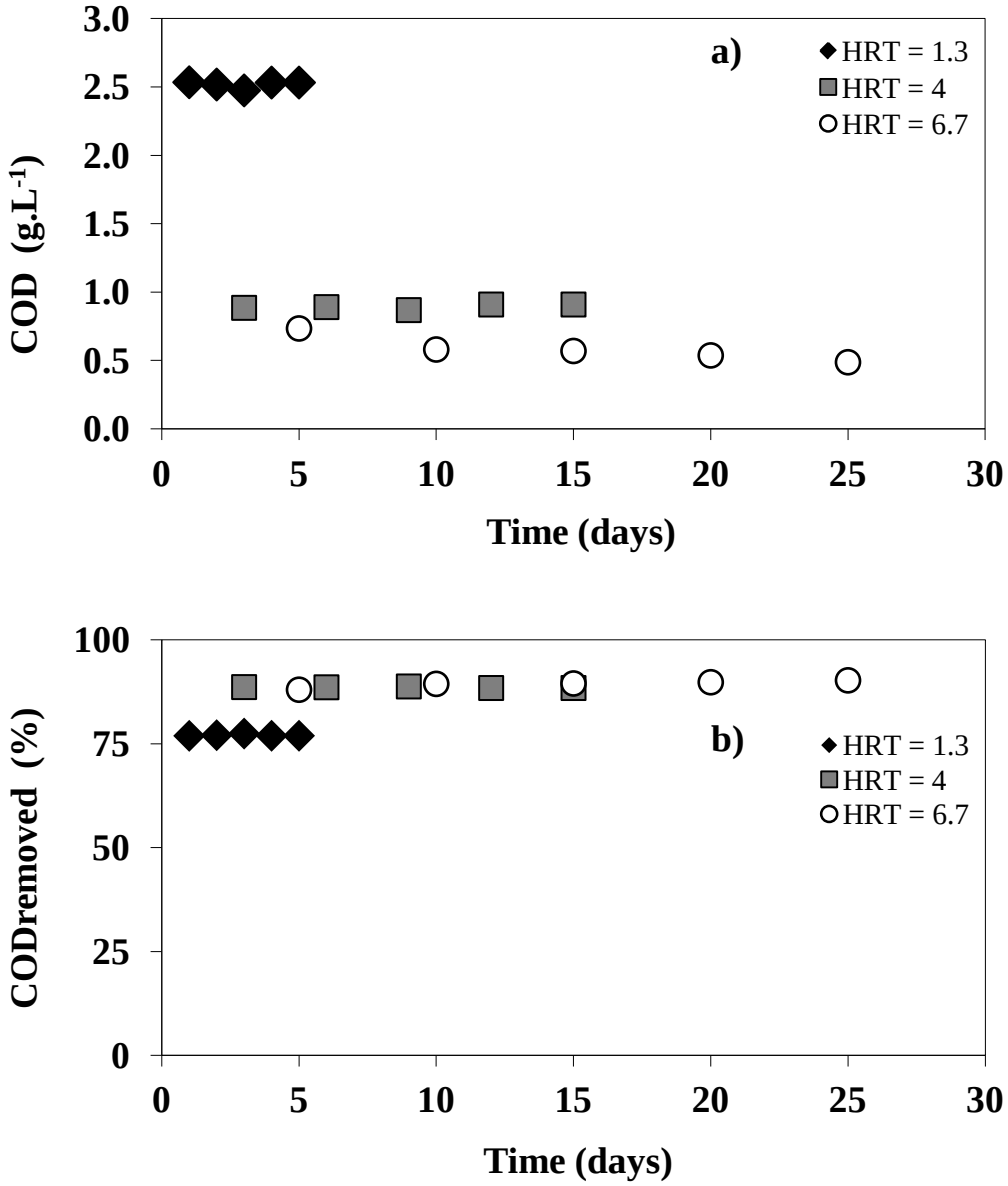


Figure 3.7 The evolution with time of a) COD in supernatant and b) COD removal.

The COD concentrations in supernatant decreased with increasing HRT, they were in the ranges of 2.52±0.03, 0.89±0.02 and 0.58±0.09 $g.L^{-1}$ for HRT 1.3, 4 and 6.7 days respectively. Such values corresponded to COD removal efficiencies close to 77±0.23%, 88.6±0.16% and 89.4±0.84% as confirmed by BMP tests for high biodegradability of latex serum.

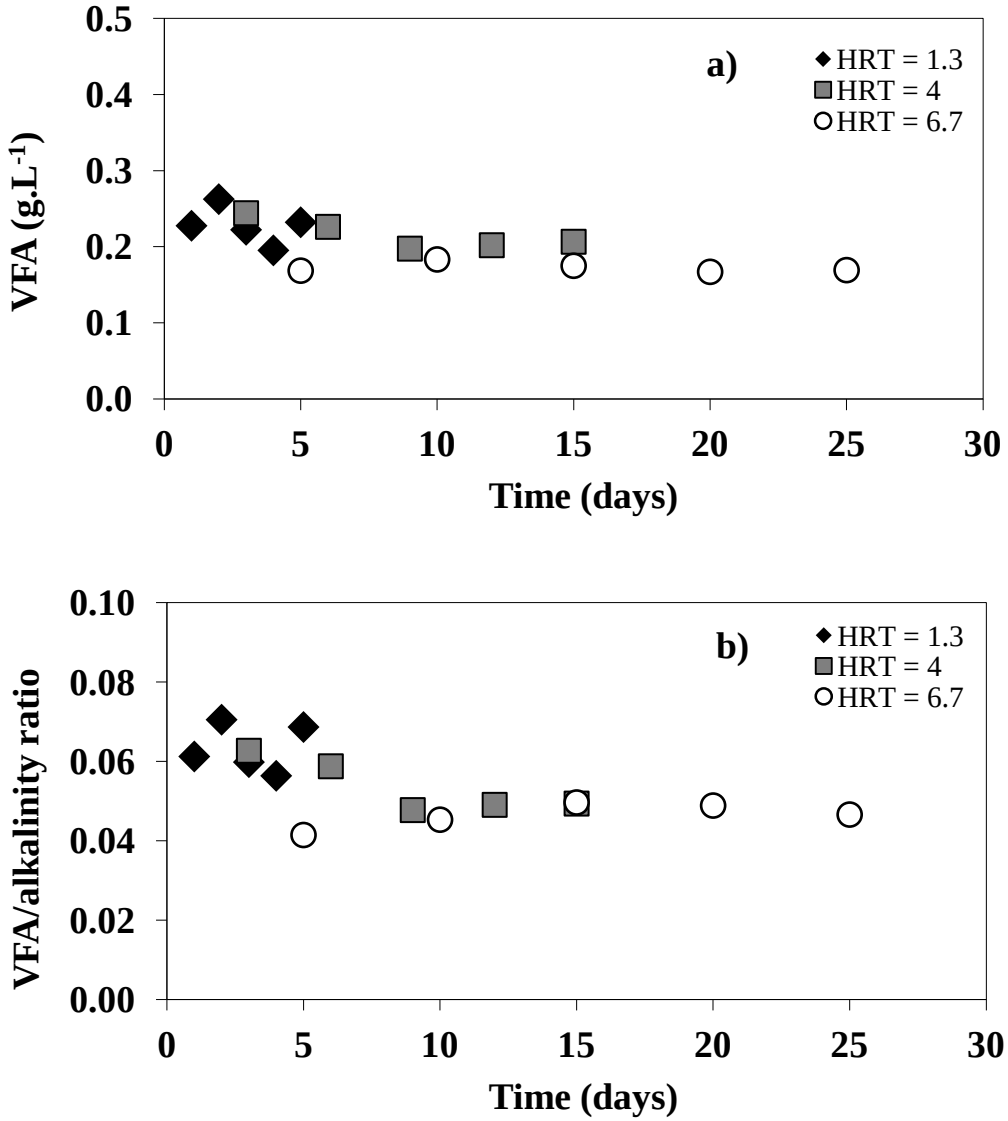


Figure 3.8 Variations of a) VFA and b) VFA/alkalinity ratio at different HRTs.

Figure 3.8 presents the variations of VFA concentration and alkalinity when operated at different HRTs. The VFA concentration slightly decreased when HRT was increased, the VFA values in all cases of experiment were less than 0.4 $g.L^{-1}$ and the remained pH value in the system was not lower than 7 as showed in Figure 3.9.

The VFA/alkalinity ratio was found lower than 0.08 (Figure 3.8) whatever the HRT values. It was then a favourable level for the development of such anaerobic operation without any acidification risk and very far of the critical 0.8 ratio indicating major risk of digester failure (Borja et al., 2004; Khanal, 2008). Figure 3.9

confirms a good pH control in a favourable range for anaerobic digestion of the experiment for all HRT.

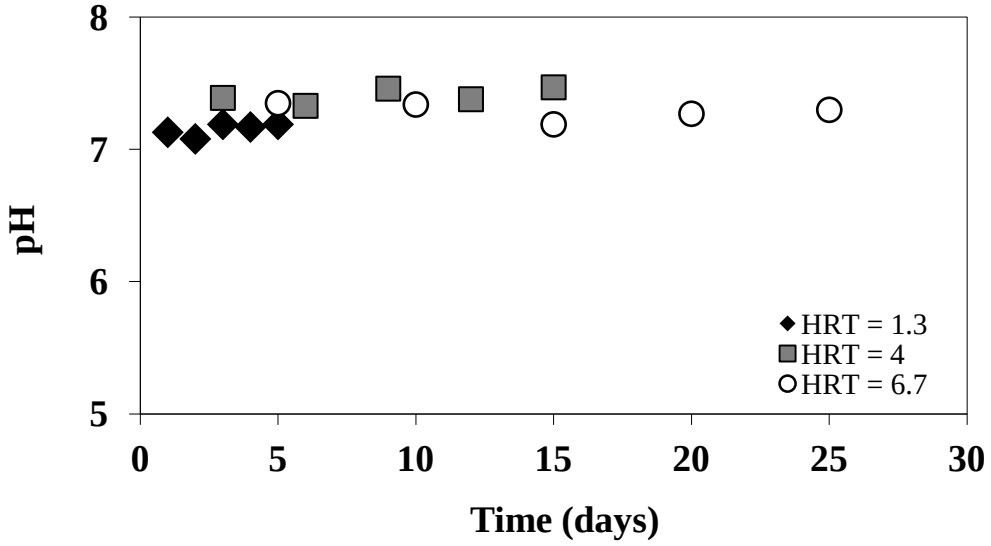


Figure 3.9 The pH evolution with time and HRT in reactor.

Figure 3.10 indicates the biogas and methane production rates at different HRTs. The biogas and methane production rate appeared significantly higher at the lowest HRT or the highest OLR as expected when no inhibition occurs. Similar results were noticed by Gao et al. (2007).

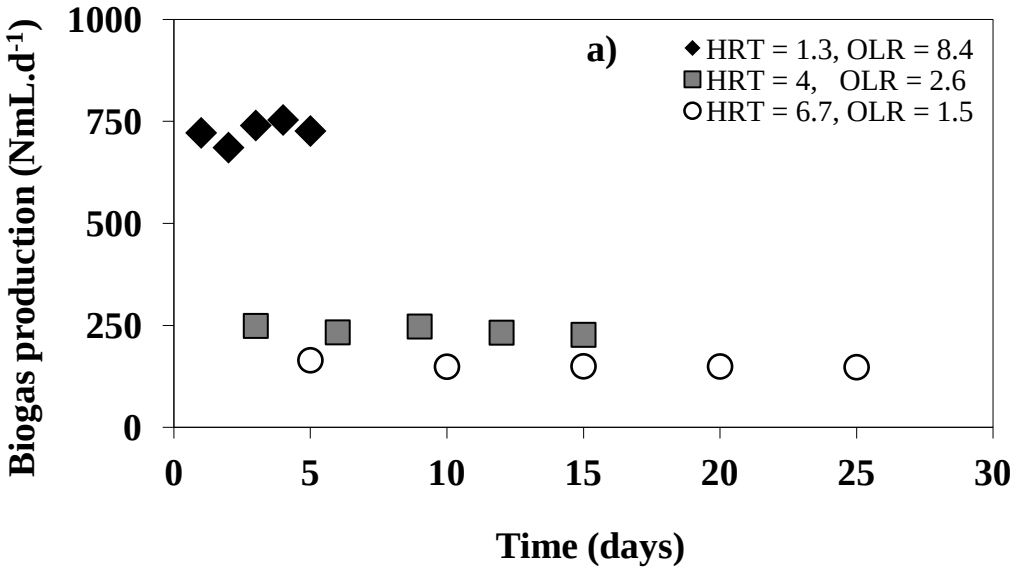


Figure 3.10 a) Biogas and b) methane productions rates versus different HRTs.

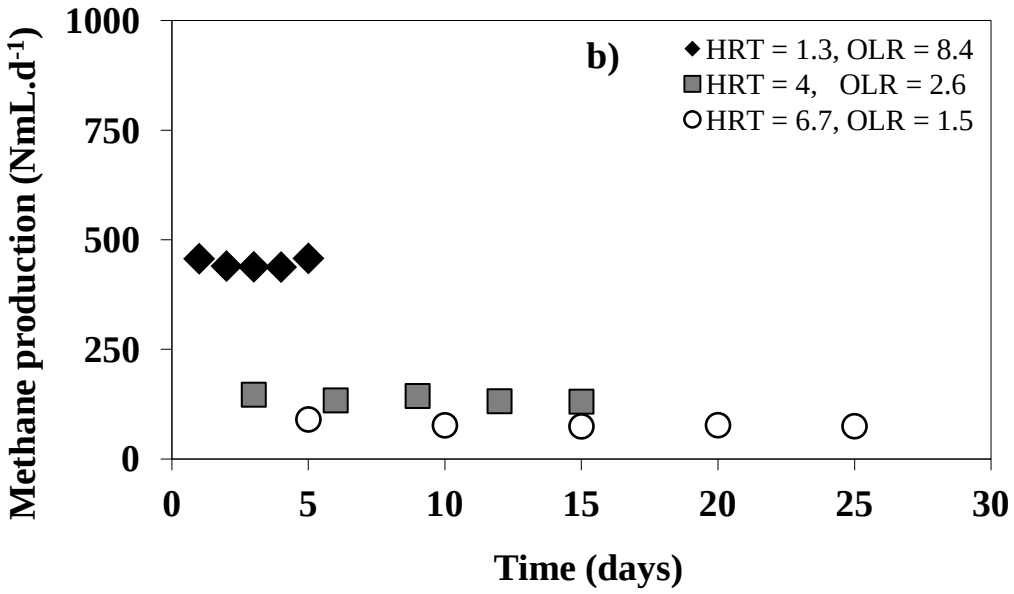


Figure 3.10 a) Biogas and b) methane productions rates versus different HRTs (continued).

The methane (CH_4) content in biogas was found to be between 55 and 64% (Figure 3.11). It slightly increased with increasing OLR as reported by Huang et al. (2011) that a more important methane production with shorter HRT or higher OLR, induced by a more carbon source conversion to methane. The average carbon dioxide (CO_2) content ranged from 27 to 30%. The produced biogas presented CH_4/CO_2 ratio close to 2. Vergara-Fernández et al. (2008) indicated that the biogas produced has a CH_4/CO_2 ratio higher than 1 is adequate for energy recovery. CO_2 is produced from the chemical conversion of HCO_3^- to CO_2. Solubility of CO_2 in the liquid phase is relatively high. The rate of transfer of CO_2 is controlled by equilibrium between the liquid and gas phases (Toprak, 1995). The average content of Nitrogen (N_2) in the biogas was under 12%. The Nitrogen in the biogas originated from the dissolved Nitrogen in the influent solution, it was stripped from the liquid phase by the biogas produced in the fermentation process (Lettinga et al., 1983).

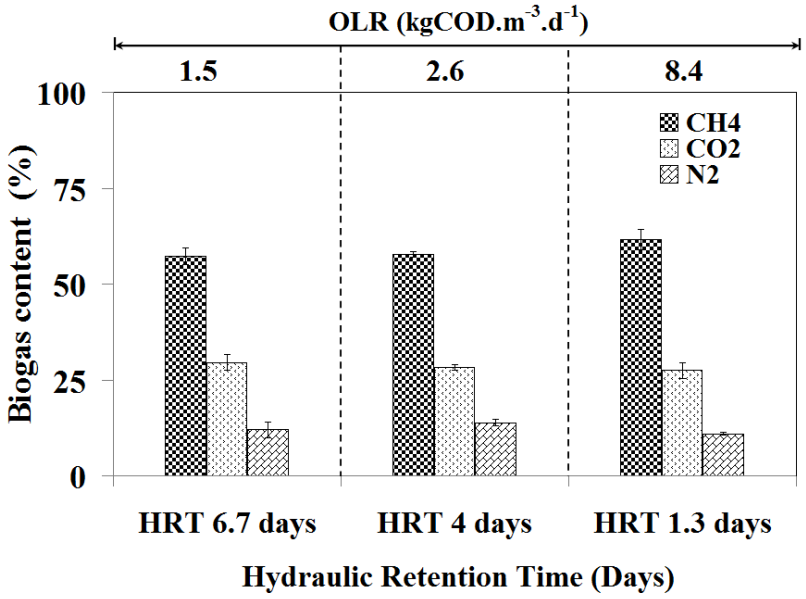


Figure 3.11 The biogas content versus HRTs.

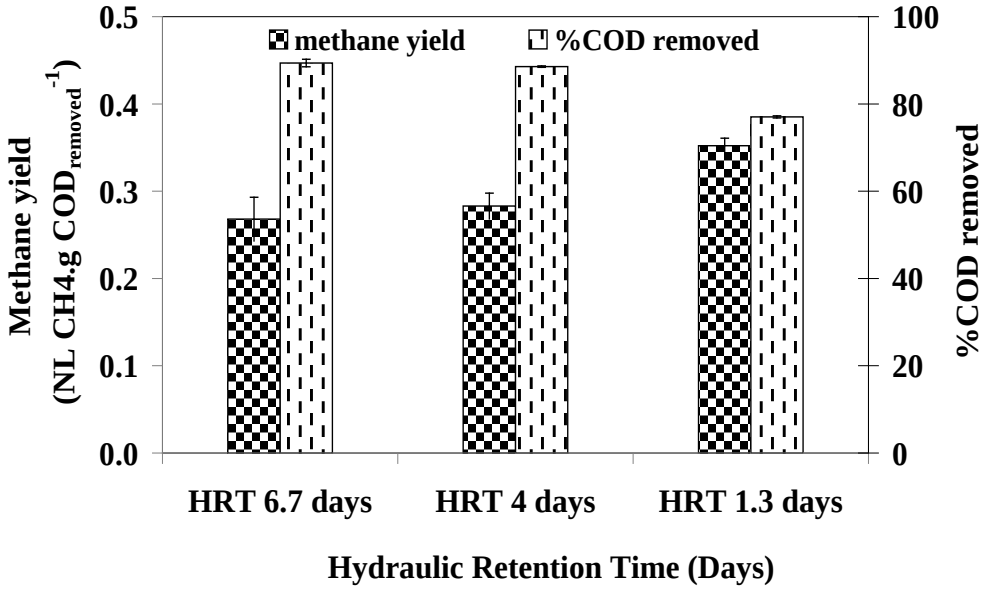


Figure 3.12 Methane yield and COD removal at different HRTs.

Figure 3.12 presents methane yield coefficient values calculated at different HRTs. The highest methane yield was found close to the optimal value of 0.35 $NLCH_4.gCOD_{removed}^{-1}$, it was obtained at the lowest HRT (1.3 days) or the highest OLR (8.4 $kgCOD.m^{-3}.d^{-1}$). Its value was slightly lower, 0.27

$NLCH_4.gCOD_{removed}^{-1}$, at 4 and 6.7 days HRTs. Such values were also close to the better values observed in BMP tests and confirmed the high potential of anaerobic digestion to treat latex serum. The methane yield coefficient slightly increased with increasing OLR as showed in the Figure 3.13. Such an evolution was also observed by Borja et al. (2004), pointing out a linear increase of volumetric methane production with increased OLR. This result pointed out that the HRT should be less than 4 days when tested in anaerobic membrane bioreactor (AnMBR).

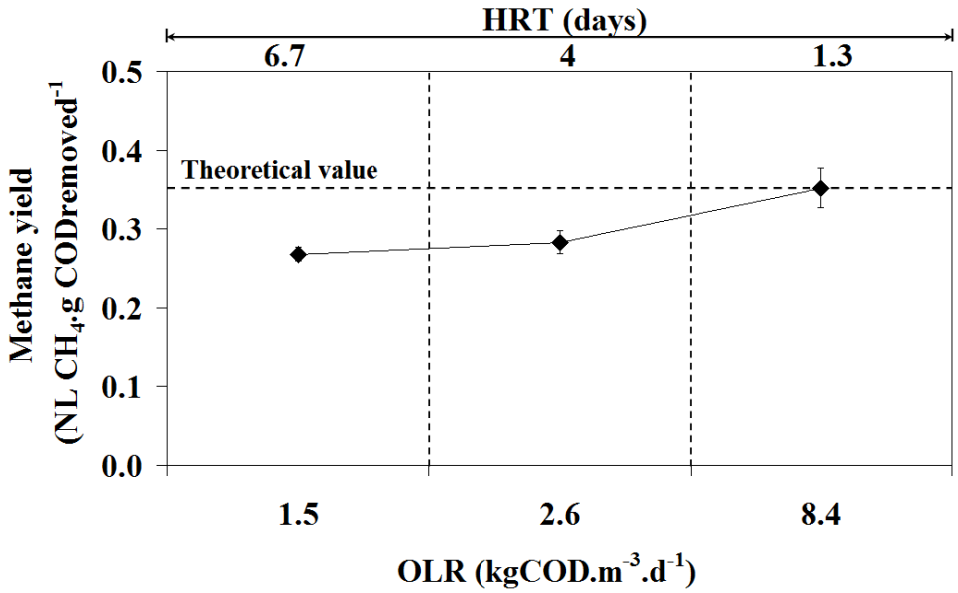


Figure 3.13 The methane yield evolution with OLRs.

3.3 Conclusions

BMP tests and anaerobic sequencing batch fermenter experiments have confirmed the benefits of anaerobic digestion to treat latex serum and resulted in (i) a soluble COD removal efficiency significantly higher than 80% favourable to decrease environmental impact of latex serum releasing, and (ii) a significant production of biogas and methane able to be used as an energy resource for latex industry when such effluents are directly treated on site.

The methane yield coefficient appeared slightly lower in BMP tests (in the range of 0.15 to 0.30 $NLCH_{4produced}.gCOD_{removed}^{-1}$) than when working with an anaerobic sequencing batch test (in the range of 0.27 to 0.35

$NLCH_{4produced}.gCOD_{removed}^{-1}$), probably due to an inferior pH control in BMP tests, notably when working at the highest S/X ratio (2.5 $gCOD.gVSS^{-1}$). Nevertheless, such methane yield coefficient values confirmed the high level of anaerobic fermentation of latex serum when the reactions are controlled.

When working in anaerobic sequencing batch test, the biogas and methane production rate increased with OLR increase and the methane yield coefficient was also slightly higher than when working at the highest OLR (or the lowest HRT). The performance of such tests showed the possibility to work with relatively high OLR values with a simple pH control. It seemed then benefits to test the performances of an Anaerobic Membrane Bioreactor (AnMBR) when working in the highest level of OLR presented here, even more important level. This benefit was investigated and discussed in Chapter 4.

CHAPTER 4

TREATMENT OF LATEX SERUM BY ANAEROBIC MEMBRANE BIOREACTOR (AnMBR)

This chapter presented the performances of an AnMBR when treating latex serum to remove organic matter from such an industrial effluent and recover biogas and methane. Because membrane fouling dynamic appears as a limiting step for MBR development, a specific focus was also developed by (i) studying the influence of different injections of nitrogen gas close to membrane surface to minimize fouling rate and (ii) analysing the main origins and intensities of membrane fouling.

4.1 Materials and methods

4.1.1 AnMBR set-up

The lab scale AnMBR was shown by the schematic diagram in Figure 4.1. This system consisted of two anaerobic chambers connected in series and each chamber had a 6L volume. The first chamber was as an anaerobic digester (chamber 1), the second as a liquid-solid separation step (chamber 2). 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. Moreover, this configuration can offer a cleaning in place, if necessary (Visvanathan and Abeynayaka, 2012).

Biogas was recovered at the upper part of the first chamber. A gas counter was used to measure the biogas production. A computer equipped with Lab-View application was connected to a data acquisition card (National Instruments,

Austin, USA) and used to analyse the collected data of transmembrane pressure (TMP) from membrane in chamber 2.

The performances of the system was quantified and compared for two values of organic loading rates (OLR), 8.1 and 12.7 kgCOD.m^{-3}.d^{-1} (linked to an initial S/X ratio equal 1.2 and 1.8 by comparison with operations in BMP test and sequencing batch reactor as described in chapter 3). The experiments were carried out continuously for both OLRs and each experiment lasted 128 days and can be divided in two mains periods of studying. During the first period, till day 59 for low OLR and after day 75 for high OLR, chamber 2 worked as a settler. This first period was considered as the start-up period.

After start-up period and till day 128, a membrane module was immersed in this second chamber and the solid-liquid separation was carried out by micro-filtration. The system was then considered functioning as an AnMBR.

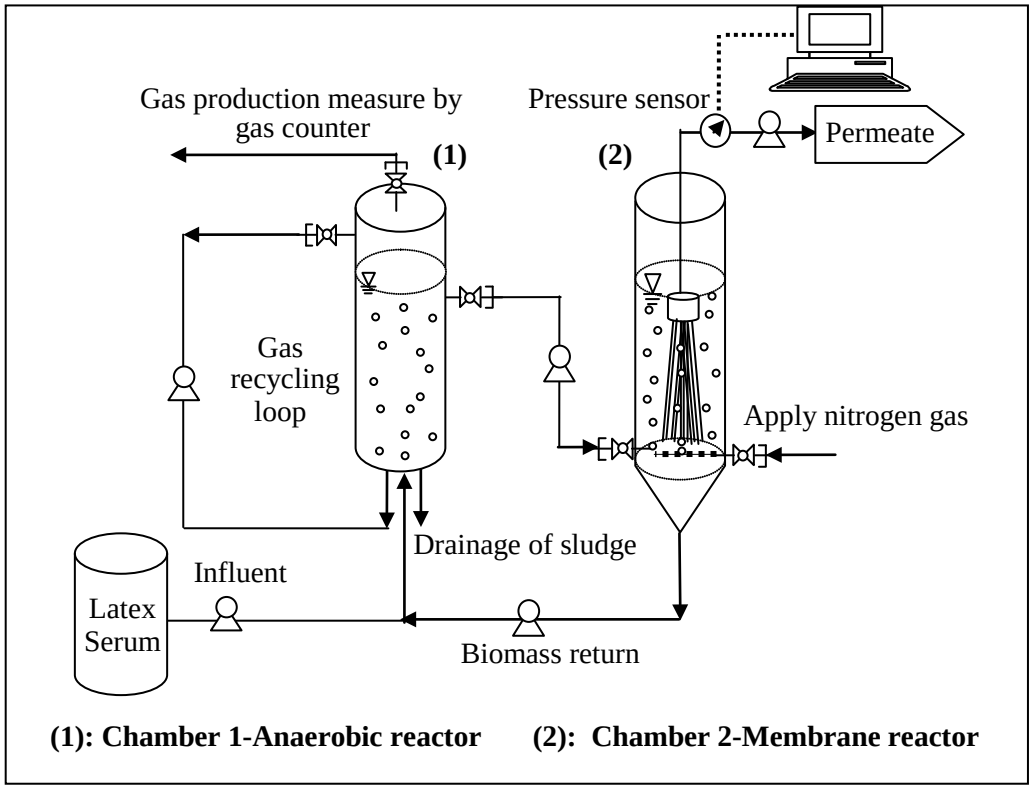


Figure 4.1 The schematic diagram of anaerobic membrane bioreactor.

The membrane module was a bundle of micro-porous hollow fibres (Shanghai Jofur Advanced Materials Co. Ltd, China) as shown in Figure 4.2. The

membranes were made of polyvinylidene fluoride (PVDF). This type of material showed a lower fouling tendency, causing lower irreversible fouling than polyethylene (Yamato et al., 2006; Bienati et al., 2008). The membrane characteristics are shown in Table 4.1, it can be noticed that the membranes present an average pore size of 0.1 µm with a total 0.05 m^2 filtration area.

Figure 4.2 The hollow fibre membrane module (PVDF membrane).

Table 4.1 Hollow fibre membrane characteristics.

Characteristics	Content/Values
Type	hollow fibre (HF)
Membrane material	PVDF
Membrane diameter (mm, inner/outer)	0.7/1.3
Filtration area (m^2)	0.05
Pore size (µm)	0.1
Initial hydraulic resistance (m^{-1}) to water (27°C)	4.2×10^{11}

When the membrane module was immersed in the chamber 2, Nitrogen gas was injected (1 $L.min^{-1}$) into a stainless steel tube placed at the bottom of the membrane module to induce turbulences and limit compound deposition over the membrane surface during filtration periods.

The filtration was operated at constant permeate flux by using a peristaltic pump. A pressure sensor was located in the permeate line (upstream the permeate pump) to

quantify the TMP and its evolution with time. When the TMP reached values close to 25 kPa, the filtration was stopped and the membrane module was removed from chamber 2 and cleaned to identify fouling origins and evaluate the corresponding hydraulic resistances.

4.1.2 Operating conditions in AnMBR

The anaerobic system was functioning at 30±2°C with sequencing conditions of feeding, mixing and solid-liquid separation steps as follows:

- Chamber 1 was functioning according to 3 successive sequences during each hour: (i) 10 minutes for latex serum feeding, (ii) 15 minutes of mixing and reactions, the mixing was realised by biogas injection at an instantaneous flow rate of 0.2 $NL.min^{-1}$, (iii) 35 minutes of settling to decrease the sludge concentration in the supernatant of this chamber.
- During the mixing period, the sludge was extracted from chamber 1 to maintain the chosen solids retention time (SRT) defined as the ratio between the mass of suspended volatile solids inside the bioreactor (assimilated to biomass inside the reactor) and the mass flux of suspended volatile solids removed each day from the system ($X.V / Q_{extracted}.X_{extracted}$). As generally practiced in Membrane Bioreactor, the daily removal of sludge was realised from the reactor when it works in perfectly mixed conditions. The concentration of sludge in extracted flux was then the same in reactor ($X = X_{extracted}$). SRT in MBR is then generally expressed as follows:

$$SRT = V / Q_{extracted} \quad (4.1)$$

Where $Q_{extracted}$ is the volumetric flow rate of the daily sludge removal, V is the reactor volume (and X is concentration of sludge in extracted flux and in chamber 1 during the mixing phase of these experiments).

- After settling the cycle comeback to feeding phase. It can be noticed that the supernatant of chamber 1 was extracted by pumping towards chamber 2 simultaneously with the feeding phase in chamber 1.

- When chamber 2 worked as a settler (start-up period), the settled sludge was recycled towards chamber 1 during 10 minutes each hour, the daily average recycle ratio between recycled sludge and feeding flow rate was 150%. The settled water was flowed from this chamber to effluent storage when the feeding was carried out simultaneously in chambers 1 and 2; the flow of settled water corresponded to the treated water during start-up period.

- After day 75 for each experiment, the system was equipped with a submerged membrane module in chamber 2 and it worked as an AnMBR for continuous operation time, till day 128. The filtration was then carried out during 4 minutes each 5 minutes (operated in a cycle of 4 min-on and 1 min-off) and Nitrogen was injected ($1L.min^{-1}$) during the 4 minutes of filtration.

- The recirculation of sludge between chamber 2 and chamber 1 was operated as indicated for start-up period. Permeate of filtration was considered as the treated water. The specific permeate flux during filtration time was 5.83 $L.m^{-2}.hr^{-1}$, taking into account the period of no filtration (1 minute each 5 minutes), the average specific permeate flow rate was equal to 4.66 $L.m^{-2}.hr^{-1}$.

- The performances of AnMBR were then analysed for the chosen OLR (8.1 and 12.7 $kgCOD.m^{-3}.d^{-1}$) obtained by the dilution of the initial latex serum into two COD concentrations of influent. Hydraulic retention time (HRT) and solids retention time (SRT) were imposed at 2 and 30 days, respectively. 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 (Huang et al., 2011). The initial VSS concentration in each chamber was $10gVSS.L^{-1}$. The seeding sludge was coming from the anaerobic digestion plant of a latex factory, Songkhla Province, Southern Thailand. The pH of feed was kept in the range of 6.8-7.2 by adding sodium hydroxide (1N). The common working conditions are given in Table 4.2.

Table 4.2 Operating conditions of AnMBR for the two different assays at 8.1 and 12.7 kgCOD.m^{-3}.d^{-1}.

Conditions	Values
Total working volume of AnMBR (L)	12
HRT (d)	2
SRT (d)	30
Temperature; ambient temperature (^{o}C)	30±2
COD concentration in influent (g.L^{-1})	16.2 or 25.4
Initial MLVSS concentration (g.L^{-1})	10
Average permeate flux including resting period (L.m^{-2}.hr^{-1})	4.66

- Moreover, during the experiment carried out at low OLR (8.1 kgCOD.m^{-3}.d^{-1}), the membrane module was immersed at day 59 in chamber 2 to investigate the role of Nitrogen gas injection mode on membrane fouling control. Nitrogen gas was injected (1L.min^{-1}) at the bottom of the membrane module to induce turbulences close to the membrane surface and the filtration was carried out during 4 minutes each 5 minutes. Two Nitrogen injections were compared: (i) gas injection during the 1 minute of no filtration during each filtration cycle of 5 minutes, and (ii) gas injection during the 4 minutes simultaneously to the filtration.

Figure 4.3 gives a representation of the functioning conditions for the two successive experiments carried out for both OLR. To favour the comparison, the conditions versus time is proposed (the time of each experiment being the same 128 days). The best mode of gas injection from this test was also chosen to operate at high OLR (12.7 kgCOD.m^{-3}.d^{-1}).

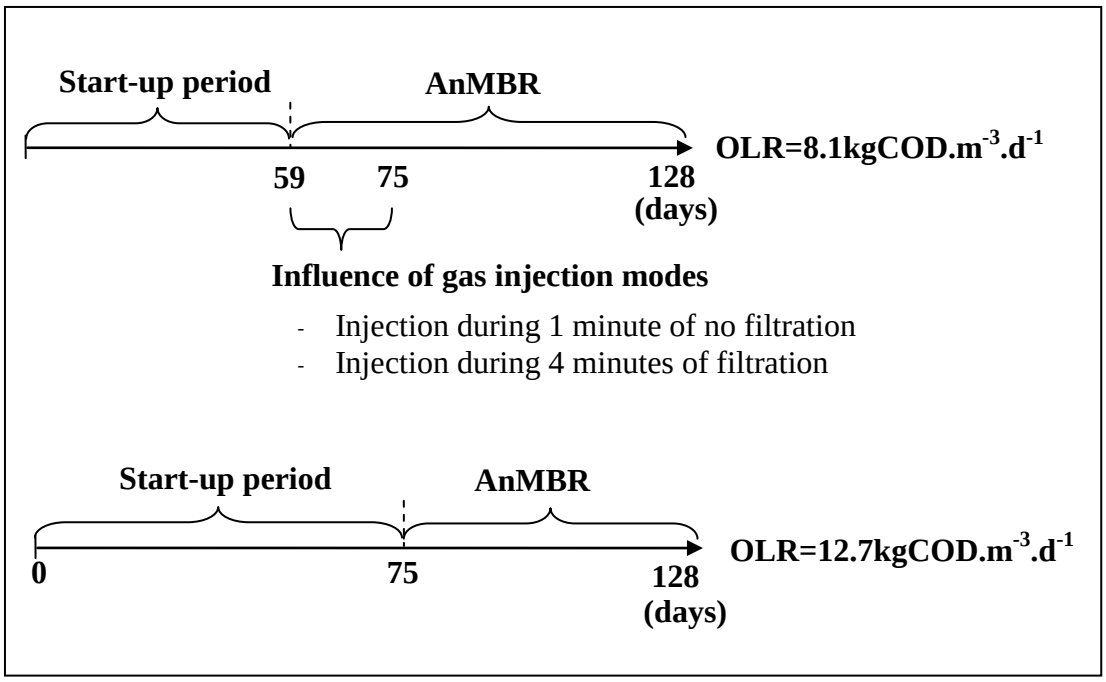


Figure 4.3 Experimental working conditions with time.

4.1.3 Characteristics of latex serum

Influent or substrate was latex serum obtained from a skim latex microfiltration (0.22 µm membrane cut off) as described in the precedent chapter 2 of this study. Latex serum was a light yellow coloured solution with a very low turbidity. The characteristics of latex serum are given in Table 4.3.

Table 4.3 Latex serum characteristics used for the two different assays at 8.1 and 12.7 kgCOD.m^{-3}.d^{-1}.

Parameters	**OLR≈8.1 kgCOD.m^{-3}.d^{-1}**	**OLR≈12.7 kgCOD.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
NH_3-N (g.L^{-1})	0.5±0.03	0.9±0.05
pH	7±0.2	7±0.2

It showed a high concentration of soluble organic matter (COD > 25 g.L^{-1}) and NH_3-N (NH_3-N > 0.9 g.L^{-1}), such a high NH_3-N concentration was due to

ammonia adding to stabilise fresh latex suspension. The ratio COD/BOD_5 (2.13) shows a significant degree of latex serum biodegradability as confirmed in precedent chapter 3. This ratio was closed to indication of Gunkel et al. (2007) who indicated that the COD/BOD_5 ratio of about 2.3 had good biodegradability.

4.1.4 Membrane fouling characterization

4.1.4.1 Hydraulic fouling resistance

A membrane cleaning procedure was carried out as soon as the TMP value reached a level close to 25 kPa, value often considered as critical in MBRs to avoid deposit compression and difficulty of regeneration of membrane permeability (Lin et al., 2009; Cero´n-Vivas et al., 2012). The hydraulic resistance of fouled membrane was then calculated by using Darcy's law:

$$R_{total} = TMP/\mu.J \quad (4.2)$$

Where R_{total} is the total filtration resistance (m^{-1}), TMP is transmembrane pressure (Pa), μ is the dynamic viscosity (Pa.s) of distilled water at the experimental temperature during cleaning step (27.5±1°C), J is the permeate flux ($m^3.m^{-2}.s^{-1}$).

The filtration resistances were analyzed using the resistance in series model (Jeong et al., 2007; Lin et al., 2009; Meng et al., 2009; Xu et al., 2013; Ding et al., 2014; Dereli et al., 2015). The fouled membrane resistance (R_{total}) was then considered as the sum of the initial clean membrane hydraulic resistance (R_m) to water, the resistance due to cake deposit (R_{cake}), the resistance due to pore blocking ($R_{pore\ blocking}$) and the resistance due to adsorption of molecule onto the membrane surface and internal pore wall ($R_{adsorption}$) as follows:

$$R_{total} = R_m + R_{cake} + R_{pore\ blocking} + R_{adsorption} \quad (4.3)$$

The cake deposit R_{cake} was considered as removable fouling when rinsing the membrane with distilled water, $R_{pore\ blocking}$ was considered as irremovable

fouling when a backwashing was carried out, and $R_{adsorption}$ was supposed as irremovable fouling after chemical cleaning of membrane (Meng et al., 2009).

When reaching 25 kPa for TMP, the fouled membrane module was removed from the chamber 2. The cleaning procedure of the fouled membranes was then carried out, it included three successive steps as follows:

(i) The fouled membrane module was put in a specific chamber and rinsed with 1L of distilled water to remove compounds attached on membrane surface. Distilled water was then filtered through the rinsed membrane by pumping (with a peristaltic pump) under a defined permeate flux (30 min) and the hydraulic membrane resistance after rinsing ($R_{rinsing}$) was deduced according to Darcy's law.

(ii) Backwashing was then carried out for 2 hours at 15 $L.m^{-2}.hr^{-1}$ (recommendation by supplier). For backwashing, distilled water was pumped from the inside of the fibre to the outside to remove any compounds blocking mechanically the pores. After that, the backwashed membrane was connected to a peristaltic pump to filter distilled water at a defined permeate flux and the hydraulic membrane resistance after backwashing ($R_{backwashing}$) was deduced by using Darcy's law.

(iii) Chemical cleaning was used in a final step. Membranes were then soaked successively in a 1L of 0.5 v/v % sodium hydroxide solution, 0.5 v/v % sodium hypochlorite solution and 0.5 v/v % hydrochloric acid solution (2 hours for each solution). $R_{chemical}$ was calculated using the permeate flux data of distilled water. If the chemical cleaning was sufficient the final membrane resistance $R_{chemical}$ should be equal to the intrinsic membrane resistance R_m. In this study, the resistance of membrane after cleaning was controlled, not lower than 10% of the intrinsic membrane resistance, for all experiments.

The specific hydraulic resistances due to each fouling origin can be expressed and calculated respectively by the following relations:

$$R_{cake} = R_{total} - R_{rinsing} \quad (4.4)$$

$$R_{pore\ blocking} = R_{rinsing} - R_{backwashing} \quad (4.5)$$

$$R_{adsorption} = R_{backwashing} - R_{chemical} \quad (4.6)$$

4.1.4.2 Bio-fouling Characterization

When TMP reached 25 kPa, the fouled membrane module was taken off from the AnMBR. Characteristics of some membrane samples were then analysed by different methodologies such as (i) extraction of soluble microbial products (SMP) and extracellular polymeric substances (EPS), (ii) Fourier transform infrared (FTIR), (iii) scanning electron microscopy (SEM), (iv) energy dispersive X-ray spectroscopy (EDX), and (v) atomic force microscopy (AFM) techniques. The cleaning solutions were also analysed to identify the main families of compounds present in fouling materials. These methods of analyses were describes as follows:

4.1.4.2.1 Extraction of soluble microbial products (SMP) and extracellular polymeric substances (EPS)

The rinsing water recovered from fouled membrane cleaning was analysed as follows:

- Centrifugation for about 30 minutes at 2,360 ×g. The supernatant from centrifugation was filtrated through a membrane with mean pore size 0.45 µm, permeate then contained the SMP fractions.
- Heating for 10 min at 80 ^{o}C and this step was followed by the same centrifugation and filtration steps, permeate then contained the soluble and bound EPS fractions (Huang et al., 2011; Cero´n-Vivas et al., 2012). Bound EPS was deduced as EPS fractions minus SMP fractions.

The SMP and bound EPS were characterised through protein and carbohydrate concentrations by the colorimetric method of Lowery et al. (1951) and Dubois et al. (1956), which used bovine serum albumin (BSA) and glucose as protein and carbohydrates standards respectively.

4.1.4.2.2 Fourier transform infrared (FTIR) spectroscopy

FTIR spectroscopy (EQUINOX 55, Bruker, Germany) and in house method refer to WI-RES-FTIR-001 were employed to identify the functional groups of organic foulants. The wave number of spectra was calculated from the average of 32 scans and recorded covering 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 hours to obtain dry foulants. Potassium bromide (KBr) pellets containing 0.50% (dry powder) of the sample was prepared and examined in the FTIR spectrophotometer (Meng et al., 2008).

4.1.4.2.3 Scanning electron microscopy (SEM), energy dispersive X-ray (EDX) spectroscopy

Small pieces of clean and fouled membrane were cut to obtain membrane samples. These samples were fixed with 2.5% gluteraldehyde in 0.1M phosphate buffer solution (pH 7.2) for about 2 hrs. After that, each fixed sample was washed with buffer solution three times for about 10 min per 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 SEM (Quanta400, FEI: SEM). Furthermore, SEM coupled with EDX spectroscopy was used to detect the inorganic components of foulants (Wang et al., 2008; Lin et al., 2009).

4.1.4.2.4 Atomic force microscopy (AFM)

The fouled membrane surface was analysed by AFM analysis (Nanosurf®, easyScan 2). The surface roughness of 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 surface.

4.1.5 Analytical methods for biological performances of AnMBR

Samples of influent and effluent were analysed to quantify the performances of AnMBR regarding the following criteria, COD, TKN, Alkalinity, TSS, VSS and VFA quantified as indicated in the Standard Methods and method of DiLallo and Albertson (1961) (methods are indicated in topic 3.14 of chapter 3).

Supernatant of mixed liquor present in chambers 1 or 2 corresponded to suspension obtained after 30 minutes of mixed liquor settling, while permeate corresponded to solution obtained after mixed liquor filtration on porous membrane presenting an average pore size equal to 0.1 µm.

The biogas production was quantified by the gas counter placed on the gas extraction pipe at the top of chamber 1. Biogas composition (in terms of CH_4, CO_2 and N_2) was analysed by a gas chromatography (Agilent, Column-HP-PLOT Q) as described in topic 3.14 of chapter 3.

Volatile fatty acid composition was measured by a gas chromatography (Agilent) equipped with flame ionization detector FID and HP-INNOWax capillary column (30m×250µm×0.25µm). The oven temperature was initially set at 80 ^{o}C for 1min, increasing 20^{o}C.minute^{-1} to 120 ^{o}C and then increasing 10^{o}C.minute^{-1} to 205 ^{o}C for 2 minutes. The temperatures of inlet and detector were 260 and 260 ◦C. The volume injected was 1 µl, before sample injection the sample was filtered with a 0.22 µm of syringe filter.

4.2 Results and discussion

Even the experiments for both OLR conditions were carried out successively, we have chosen to present the results by superimposing the data versus time (as the experiments were carried out simultaneously) to favour the comparison.

4.2.1 Biological performances of the system

The reactor performances are presented for start-up period (day 0 to day 59 for low OLR and day 0 to day 75 for high OLR) when working without membrane in chamber 2 and in presence of a final membrane separation corresponding to AnMBR performances (from day 59 or 75 to day 128) as indicated in Figure 4.3.

4.2.1.1 Organic matter removal

Figure 4.4 presents the evolutions of COD in supernatant (recovered after 30 minutes of sample settling) and permeate (recovered after filtration on porous membrane) for both OLRs.

During start-up period, the COD in supernatant was progressively decreasing till reaching levels close to 4.3 and 11.6gCOD.L^{-1} for OLR of 8.1 and 12.7

kgCOD.m^{-3}.d^{-1}, respectively. According to influent COD concentration, the corresponding COD removal efficiency was about 73.2 and 54.6% respectively.

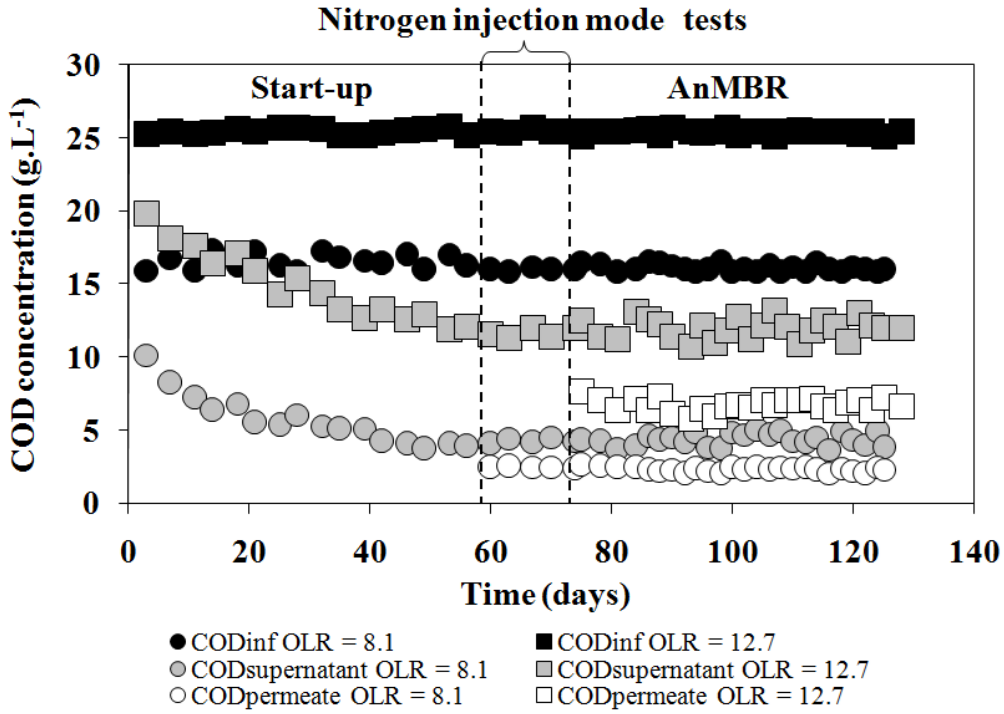


Figure 4.4 Evolutions of COD concentration in supernatant and permeate.

When the membrane module was immersed in the chamber 2, the largest soluble organic compounds and all biomass and suspended solids were then retained inside bioreactors by the membrane selectivity and the system performances were improved for COD removal. COD concentration in permeate was equal to 2.3 and 6.7 g.L^{-1} for OLR of 8.1 and 12.7 kgCOD.m^{-3}.d^{-1}, respectively, corresponded to 86 and 73.5% of COD removal efficiency.

When working with AnMBR, a significant difference of COD concentration can be observed between supernatant and permeate, this difference increased with increasing OLR. Such differences point out (i) the role of the membrane barrier on treated water quality and (ii) because of the membrane selectivity, numerous organic compounds have been accumulated inside the reactor

with an increase of their retention time favourable to their biodegradation and the improvement of COD removal and biogas production (topic 4.2.1.1 and 4.2.1.2).

Nopthavon (2010) reported the performances of anaerobic fluidized bed reactor when treating latex serum from coagulation process by sulfuric acid at HRT 2 days (corresponding to OLR about 16.3 and 12.5 $kgCOD.m^{-3}.d^{-1}$) when controlling the ratio of COD/SO_4^{2-} at 2.5 and 5 in wastewater. The result showed values of COD removal efficiency close to 51±1.4 and 65.3±2.8%, respectively. Promsakul (2014) studied the digestion of latex serum coming from coagulation process by sulfuric acid adding when mixing with process wash water, at ratio of 1:2, she reported that COD removal was achieved at a level of 82.7±1.7% when operating at 7 days HRT (OLR was about 1.8 $kgCOD.m^{-3}.d^{-1}$) with an Anaerobic Baffled Reactor (ABR). A comparison of AnMBR in this study with the mentioned anaerobic treatment systems at the same values/higher values of HRT or the same values/lower values of OLRs pointed out that AnMBR provided more efficient and better quality of effluent. Due to AnMBR offers relevant solutions by ensuring total biomass retention according to the low cut-off of the membrane. All suspended solids and biomass and the largest soluble organic compounds were retained inside bioreactors due to membrane separation, irrespectively granular properties or its settling of biomass.

4.2.1.2 Biogas production and potential of energy recovery

Figure 4.5 presents the evolution of daily biogas production and the percentage of methane in biogas.

The daily 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.

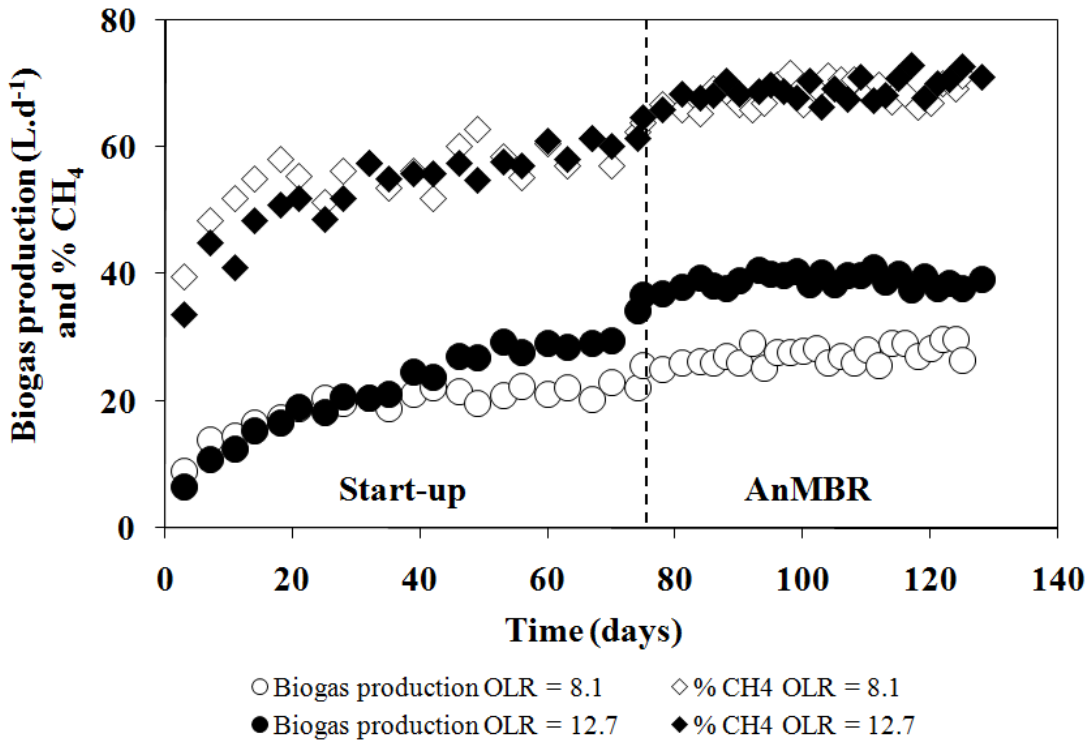


Figure 4.5 Biogas production and percentage of methane.

When working with AnMBR, the daily biogas production was increased of about 33-46% with daily rate of 27.2±1.4 and 38.9±1.2 $NL.d^{-1}$ (0.33±0.02 and 0.35±0.01 NL $biogas_{produced}.gCOD_{removed}^{-1}$), respectively with methane content in biogas higher than 65% corresponding to the methane yield coefficient to 0.22±0.01 and 0.24±0.01 $NL.gCOD_{removed}^{-1}$. Such results clearly point out the potential of the final separation step on membranes not only to increase COD removal but also to increase biogas and methane productions.

4.2.1.3 Biomass accumulation

Figure 4.6 presents the evolutions of MLSS and MLVSS concentrations in bioreactors and MLVSS/MLSS ratio during experiments. Because influent was only composed by soluble organic and mineral fractions (the latex serum was recovery 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).

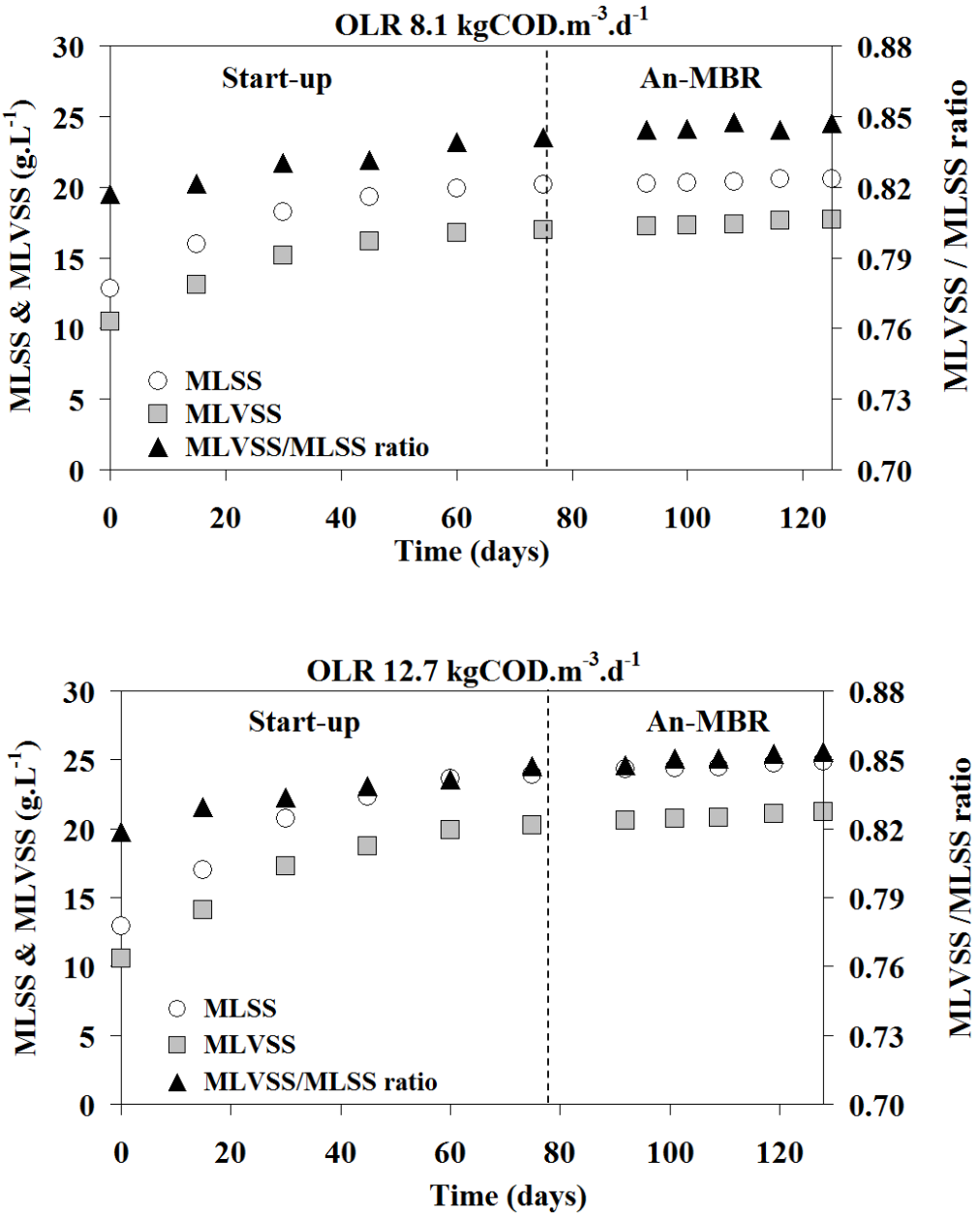


Figure 4.6 Evolutions of MLSS, MLVSS and MLVSS/MLSS ratio with time for both OLRs.

During start-up period, a progressive increase of MLSS and MLVSS concentrations can be observed till reaching levels close to 20 and 17g.$L^{-1}$and 25 and 20 for OLR of 8.1 and 12.7 kgCOD.m^{-3}.d^{-1}, respectively. These increases corresponded to biomass growth linked to COD conversion till reaching steady state

conditions. The set-up of the membranes in chamber 2 induced a slight increase of these criteria, probably linked with the corresponding improvement of COD removal.

4.2.1.4 Kinetic criteria

According to these experimental results, some kinetic criteria were deduced by using common relations as follows:

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

$$R_{COD\ removal} = (COD_{inf} - COD_{eff})/HRT \quad (4.7)$$

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

- Daily biogas production (NL biogas $_{produced}.d^{-1}$) was deduced from the experiment.

- Methane yield coefficient (NL $CH_4.gCOD_{removed}^{-1}$);

$$Y_m = (\text{Biogas production} \times \%CH_4)/ [(COD_{inf} - COD_{eff}) \times Q] \quad (4.8)$$

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.

- Biomass growth rate ($kgMLVSS_{produced}.\ m^{-3}.d^{-1}$);

$$R_x = (\Delta X/\Delta t) + [(Q_{extracted} \times X)/V] \quad (4.9)$$

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

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

$$\mu_{apparent} = R_x/X \quad (4.10)$$

- Bioconversion yield coefficient ($kgMLVSS_{produced}.kgCOD_{removed}^{-1}$);

$$Y_{obs} = R_x/ R_{COD\ removal} \quad (4.11)$$

Table 4.4 Kinetic coefficients calculated from experimental data of the two different OLR for start-up period and AnMBR period.

Criteria	OLR≈8.1 $kgCOD.m^{-3}.d^{-1}$		OLR≈12.7 $kgCOD.m^{-3}.d^{-1}$	
	Start-up	**AnMBR**	**Start-up**	**AnMBR**
COD removal rate ($kgCOD_{removed}.m^{-3}.d^{-1}$)	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 ($kgMLVSS_{produced}.\ m^{-3}.d^{-1}$)	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} ($kgMLVSS_{produced}.kgCOD_{removed}^{-1}$)	0.10±0.01	0.08±0.001	0.11±0.03	0.08±0.002

Some kinetic criteria were then deduced from experimental results, calculated values are given in Table 4.4. As expected, the COD removal rate, MLVSS production and biogas production increased with applied OLR. The results of Rincón et al. (2008) demonstrated that the rate of COD removal increased linearly with an increase of OLR. The methane yield coefficient showed a slight increase when OLR was increased, while Y_{obs} was not affected by OLR modification, and it also shows the advantage of anaerobic process for giving 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 $kgCOD.m^{-3}.d^{-1}$), 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 $kgCOD.m^{-3}.d^{-1}$ at HRT 3 days) obtained with a UASB system (Chaiprapat et al., 2015), when treating a mixture of wash water combined with rubber skim wastewater coming from H_2SO_4 coagulation, and with wash water combined with polymer treated wastewater. From a comparison, the methane yield obtained when treating slaughterhouse wastewater treatment with single stage AnMBR (Saddoud and Sayadi, 2007) 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 days (corresponding to OLR 8.23-4.37 $kgTCOD.m^{-3}.d^{-1}$), with a progressive increase of methane yield with increasing HRT.

4.2.1.5 VFA in the bioreactor

The levels of organic acids are important in anaerobic digestion for two reasons: (i) organic acids (particularly acetic) are the immediate precursors in the metabolic chain leading to methane formation and (ii) if present in too high concentration, such acids are known to cause stress in the microbial population and can ultimately lead to complete process failure (Hill et al., 1987; Hill and Holmberg, 1988). Treating latex serum coming from coagulation process by sulfuric acid addition, Nopthavon (2010) reported that VFA concentration was in the ranges of 4.1-6.5 $g.L^{-1}$ in anaerobic fluidized bed reactor when working at HRT 1 and 2 days, corresponding to OLR in the range of 16.3-24.8 $kgCOD.m^{-3}.d^{-1}$. When treating a mixture of latex serum coming from coagulation process by sulfuric acid with wash water of process at ratio of 1:2, Promsakul (2014) obtained VFA concentration close to 1 $g.L^{-1}$ in anaerobic sequencing batch reactor (ASBR) at HRT 3 days (related to OLR about 4.3 $kgCOD.m^{-3}.d^{-1}$). The research of Siegert and Banks (2005) reported that VFA concentrations above 4 $g.L^{-1}$ was slightly inhibiting when treating glucose, and VFA concentrations greater than or equal to 2 $g.L^{-1}$ caused the inhibition of the cellulolytic activity in batch anaerobic reactor experiments.

Figure 4.7 presents the evolutions of VFA concentration and VFA/Alkalinity ratio at OLR of 8.1 and 12.7 $kgCOD.m^{-3}.d^{-1}$.

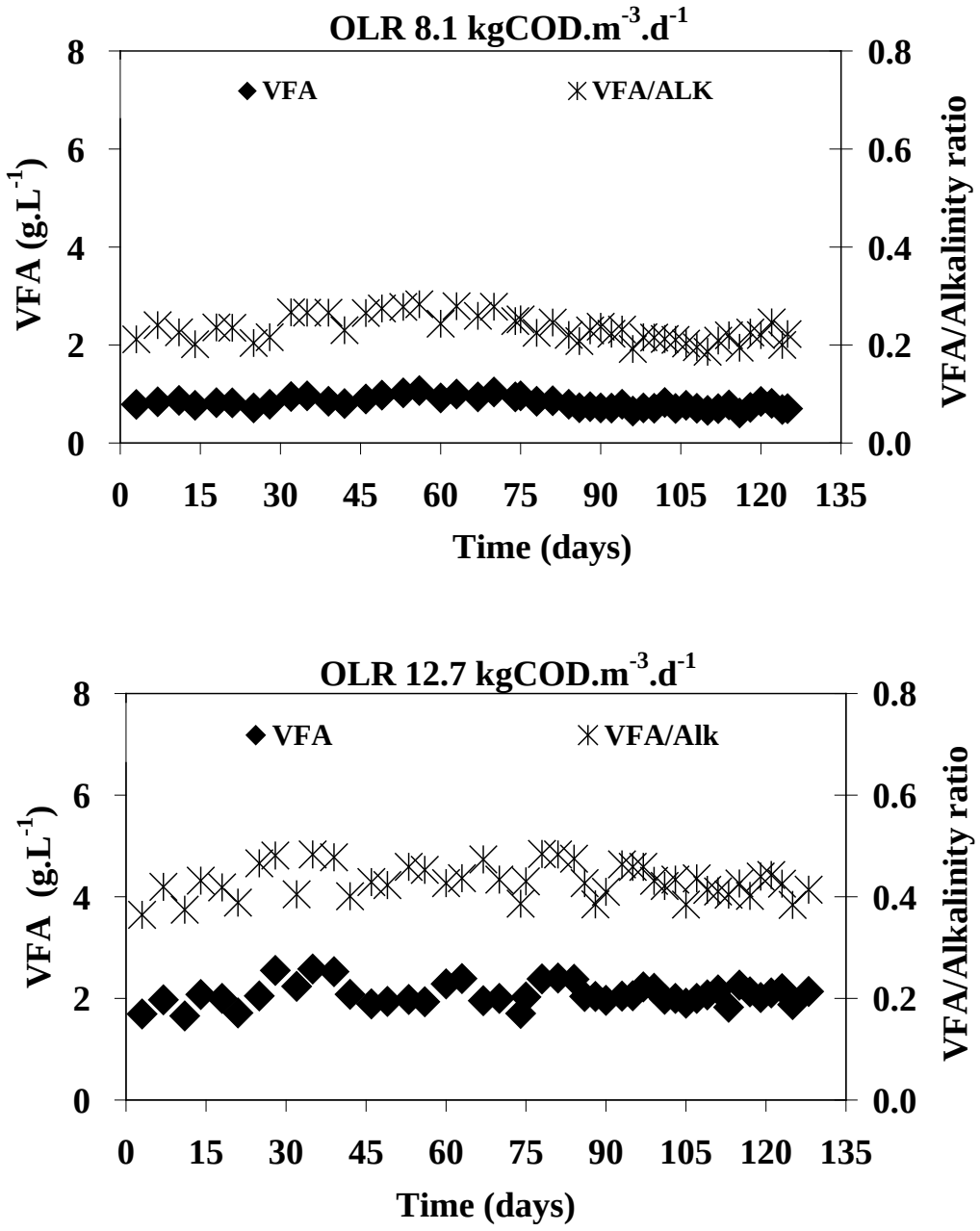


Figure 4.7 Evolutions of VFA concentration and VFA/Alkalinity ratio with time.

The values of VFA concentration were in the range of 0.82±0.11 $g.L^{-1}$ and 2.10±0.22 $g.L^{-1}$ for OLR of 8.1 and 12.7 $kgCOD.m^{-3}.d^{-1}$, respectively. If it was expected that VFA concentration increased when OLR increased (Zinatizadeh et al., 2006), it is nevertheless noticeable to observe that VFA concentration appeared 2.5 times higher when OLR increase was only 50%. High VFA concentrations, notably

for high OLR, pointed out a possible insufficient contact time for the methanogenesis step (Wang et al., 2013b).

When considered the VFA to alkalinity ratio (VFA/ALK), it was found equal to 0.23±0.03 and 0.43±0.03 at OLR of 8.1 and 12.7 kgCOD.m^{-3}.d^{-1}, such values were within the optimum range for anaerobic digestion according to Khanal (2008) where significant pH reduction and then inhibition of methanogenesis occurred at a VFA/ALK ratio of 0.8 or above, resulting in digester failure. During the experiments, pH was controlled to remain in the range of 6.9-7.3 as shown in Figure 4.8

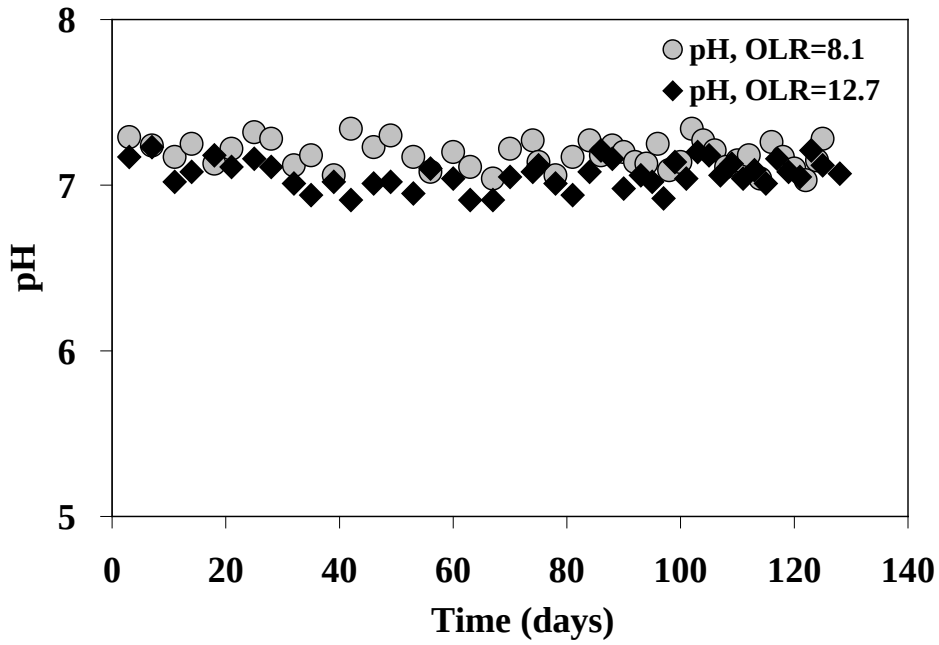


Figure 4.8 The pH evolution with time during experiment.

If the global concentration of VFA is often cited as a determining criterion, the concentration of each VFA is also an important point to analyse anaerobic digestion dynamic. Table 4.5 presents the composition of VFA in reactor at OLR of 8.1 and 12.7 kgCOD.m^{-3}.d^{-1}. The predominance of acetic and propionic acids was evident for both OLRs with concentrations higher than other acid concentrations.

Table 4.5 The compositions of VFA.

VFA composition ($g.L^{-1}$)	OLR ($kgCOD.m^{-3}.d^{-1}$)	
	8.1	**12.7**
Acetic acid	0.55±0.09	1.07±0.24
Propionic acid	0.33±0.07	0.70±0.21
Isobutyric acid	-	0.11±0.03
Butyric acid	-	0.10±0.05
Isovaleric acid	0.02±0.01	0.14±0.05
Valeric acid	-	0.14±0.04

The concentration of acetic and propionic acids remained close to 0.55±0.09 and 0.33±0.07 $g.L^{-1}$ respectively during operation at OLR of 8.1 $kgCOD.m^{-3}.d^{-1}$, these values were about twice higher when operating at high OLR of 12.7 $kgCOD.m^{-3}.d^{-1}$ (1.07±0.24 and 0.70±0.21 $g.L^{-1}$, respectively). Kongjan et al. (2014) found high concentrations of acetate, propionate and butyrate in effluent when investigating the two-stage anaerobic process of skim latex serum from coagulation process by sulfuric acid, they pointed out the linked between the increase of VFA production and the degradation of skim latex serum's protein and fats fractions. Barredo and Evison (1991) suggested that the number of methanogens was affected when the propionate concentration was about 1.5 or 2.2 $g.L^{-1}$ and the methanogen count was affected by at least 2 orders of magnitude when the concentration of propionate was more than 5.9 $g.L^{-1}$. Pullammanppallil et al. (2001) showed that propionic acid concentrations as high as 2.75 $g.L^{-1}$ even at pH below 6.5 did not adversely affect methane production. Hill et al. (1987) suggested that acetic acid levels in excess of 0.8 $g.L^{-1}$ indicated imbalance and proposed that the relationship between propionic to acetic acid ratio could be used as a process indicator which suggested that a propionic to acetic acid ratio (P/A) greater than 1.4 indicate impending digester failure. In this study when considering the P/A ratio, it was found about 0.61±0.10 and 0.65±0.08 for OLR of 8.1 and 12.7 $kgCOD.m^{-3}.d^{-1}$ respectively, significantly lower than the indicated value of digester failure.

4.2.1.6 Ammonium nitrogen concentration in treated water

Figure 4.9 presents the ammonia nitrogen (NH_3-N) concentration in influent and effluent for both OLRs (8.1 and 12.7 $kgCOD.m^{-3}.d^{-1}$). The NH_3-N concentration in effluent was found 0.43±0.03 and 0.86±0.06 $g.L^{-1}$ which was slight lower than concentration in influent. This result was consistent with report by Nopthavon (2010) and Promsakul (2014) who studied anaerobic digestion to treat latex serum coming from coagulation process with sulfuric acid, addition. They reported lower reduction when OLR increase. In anaerobic digestion ammonia is produced as a by-product, principally from the mineralization of organic nitrogen during the deamination of proteins and amino acids. Growth of bacteria can help to degrade and break down the complex protein to amino acids (Ghasimi et al., 2008). Ammonia toxicity can be avoided if the pH in system is controlled within the optimum working range of 6.8 to 7.2 and the concentration of ammonia nitrogen remains in the range of 1.5-3.0 $g.L^{-1}$ (Gerardi, 2003). The concentrations observed in this study should not then induce any inhibition in anaerobic digestion.

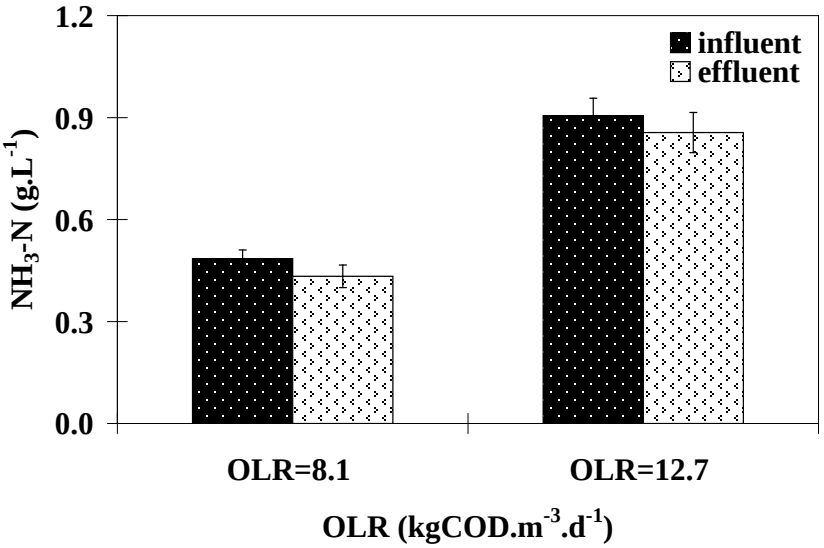


Figure 4.9 NH_3-N Concentrations for both OLRs.

C/N close to 25/1 recommended for optimal biogas production (Gerardi, 2003). In this study, C/N was found about 30/1 and the reduction of NH_3-N concentration was due to microbial uptake and cell synthesis. Fuchs et al. (2003)

indicated that nitrogen demand for anaerobic bacteria growth is almost negligible, if no accumulation of organic matter appears in the bioreactor. Then low removal efficiency of NH_3-N in anaerobic digestion and low quantities of sludge production were occurred (Parawira et al., 2005). In addition, Fuchs et al. (2003) pointed out that nitrogen between influent and effluent only 85–90% of the incoming nitrogen was measured in the permeate.

4.2.1.7 Potential of energy recovery

According to the potential of energy recovery linked to methane production (about $10kWh.Nm^{-3}_{CH4recovered}$, (Gebrezgabher et al., 2010)), it can be easy to estimate the potential of recovered energy when treating $1m^3$ of latex serum, taking into account the COD content in influent, the COD removal efficiency obtained in AnMBR and the methane yield ratio as indicated in Table 4.6.

In this experiment the energy production due to latex serum digestion was close to 30 and 45 $kWh.m^{-3}_{serum}$ for OLR of 8.1 and 12.7 $kgCOD.m^{-3}.d^{-1}$, respectively. Such a potential of energy recovery appears as a significant positive point to encourage the development of anaerobic digestion to treat latex serum and produce energy useful by industrials when treating latex serum directly on industrial sites.

Table 4.6 Potential of energy recovery of $1m^3$ of latex serum.

OLR ($kgCOD.m^{-3}.d^{-1}$)	**COD removed ($kgCOD.m^{-3}_{serum}$)**	**Methane yield ($Nm^3CH_4.kgCOD_{removed}^{-1}$)**	**Energy recovery ($kWh.m^{-3}_{serum}$)**
8.1	14	0.22	30
12.7	19	0.24	45

4.2.2 Analysis of membrane fouling in AnMBR

The application of AnMBR is still restricted and limited due to membrane fouling phenomena. Indeed the biological suspension in submerged anaerobic membrane bioreactors appeared 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 modifies the membrane permeability and obliges frequent chemical regeneration of membranes. The influence of Nitrogen gas injection was carried out to minimize membrane fouling and the main origins and intensities of membrane fouling in AnMBR were analyzed for both OLRs as follows subtopics.

4.2.2.1 Effect of Nitrogen injection mode on membrane fouling dynamic

To carry out sufficient gas injection close to the membrane surface and minimise membrane fouling, two modes of Nitrogen gas injection were compared during a specific period from 59 day to day 75 when working at low OLR (8.1 $kgCOD.m^{-3}.d^{-1}$) under the average specific flow rate 4.66 $L.m^{-2}.hr^{-1}$. Such a choice of Nitrogen gas in place of biogas from the reactor (Van Voorthuizen et al., 2008) was done to ensure an easy control of gas injection in this lab-scale reactor whatever the biological performances at the corresponding biogas production. However, biogas should be applied for industrial scale of AnMBR application.

The membrane module was set-up at day 59 in chamber 2 and the filtration was operating during 4 minutes each 5 minutes (that means no filtration during 1 minute each 5 minutes cycle). Nitrogen injection was investigated at two conditions:

- Injection during 4 minutes of filtration (4 minutes filtration with gas bubbling and 1 minute with no filtration and no gas injection).
- Injection for 1 minute during the no filtration (4 minutes of filtration without gas injection and 1 minute of no filtration with gas bubbling).

Each test was stopped when TMP value reached about 25 kPa to avoid high TMP values affecting the possibility to maintain a constant permeate flux in AnMBR systems (Lin et al., 2010).

Figure 4.10 presents the TMP variations versus time for both injection modes of Nitrogen. TMP changing at constant flux is related to the growing intensity of the membrane fouling due to the accumulation of matter onto the membrane material able to retain a lot of compounds according to the membrane selectivity.

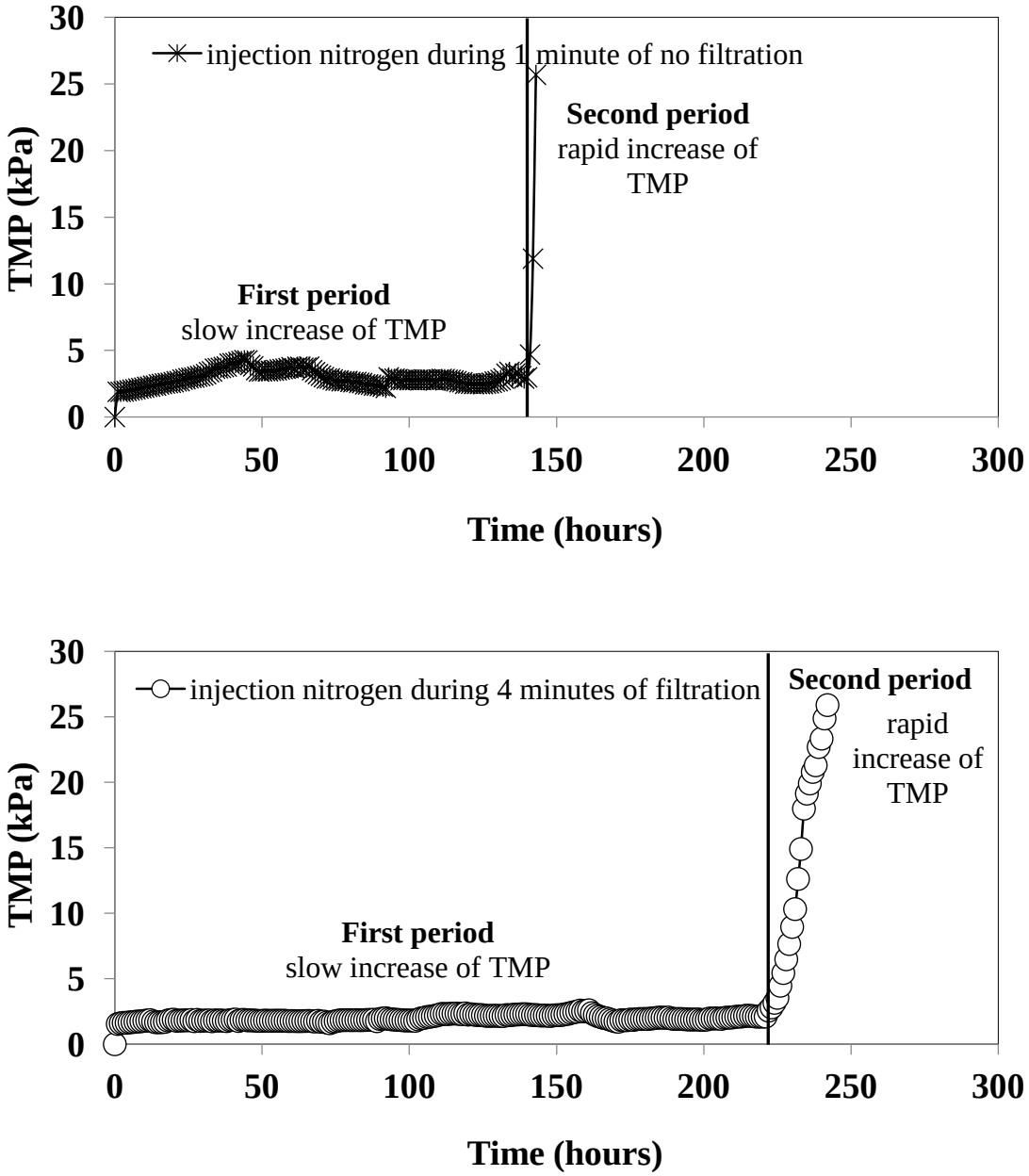


Figure 4.10 TMP change vs. time during different injection modes of Nitrogen.

It can be observed two periods for the TMP evolution as observed by Wang et al. (2008) and Lin et al. (2009), i.e., a slow increase of TMP (first period) followed by a rapid increase of TMP (second period). The first period means that a slow fouling occurred. Ognier et al. (2004) explained such an evolution by adsorption or mechanisms involving some local build-up of deposits adhering strongly to the membrane material, even pore blocking.

The second period corresponding to a drastic TMP increase and a corresponding drastic decrease of membrane permeability due to pore blocking and other intensive fouling phenomena linked to local increase of permeate flux strongly more important than critical flux (Ognier et al., 2004). Le-Clech et al. (2006) reported that the TMP jumped due to pores of the membrane more fouled than others. Zhang et al. (2006) reported that such sudden rises in TMP and fouling was not only due to local flux effect, but also caused by sudden changes of biofilm or cake layer structure.

Results clearly pointed out the benefit of developing gas injection when the filtration was operated. Such a functioning allowed a significant increase of the operation time during the first period. Moreover, the fouling rates represented by the instantaneous variations of TMP versus time, d*TMP*/d*t*, appeared significantly lower when operating a gas injection simultaneously with filtration. The values are given in Table 4.7 for both periods and both gas injection modes.

Table 4.7 The fouling rates (d*TMP*/d*t*) at different gas injection modes.

Gas injection mode	**First period ($kPa.hr^{-1}$)**	**Second period ($kPa.hr^{-1}$)**
Injection during 1 minute of no filtration	0.02	10.50
Injection during 4 minutes of filtration	0.01	1.26

The fouling rate in the first period appeared twice lower when gas injection has been carried out simultaneously to filtration. In the second period the TMP evolution was found significantly higher than during the first period for both gas injection modes. When Nitrogen injection was carried out for 1 minute in absence of filtration, TMP evolution was found about 8 times higher comparing to Nitrogen injection carried out for 4 minutes simultaneously to filtration. When comparing the fouling rates, it appears beneficial to operate with Nitrogen injection for 4 minutes during filtration to minimise membrane fouling.

At the end of each test, the membrane resistance values were measured by developing a specific cleaning procedure of the fouled membranes as defined in the topic of 4.1.4.1. For both conditions, the removable external deposit appeared as the principal cause of fouling as illustrated in Figure 4.11.

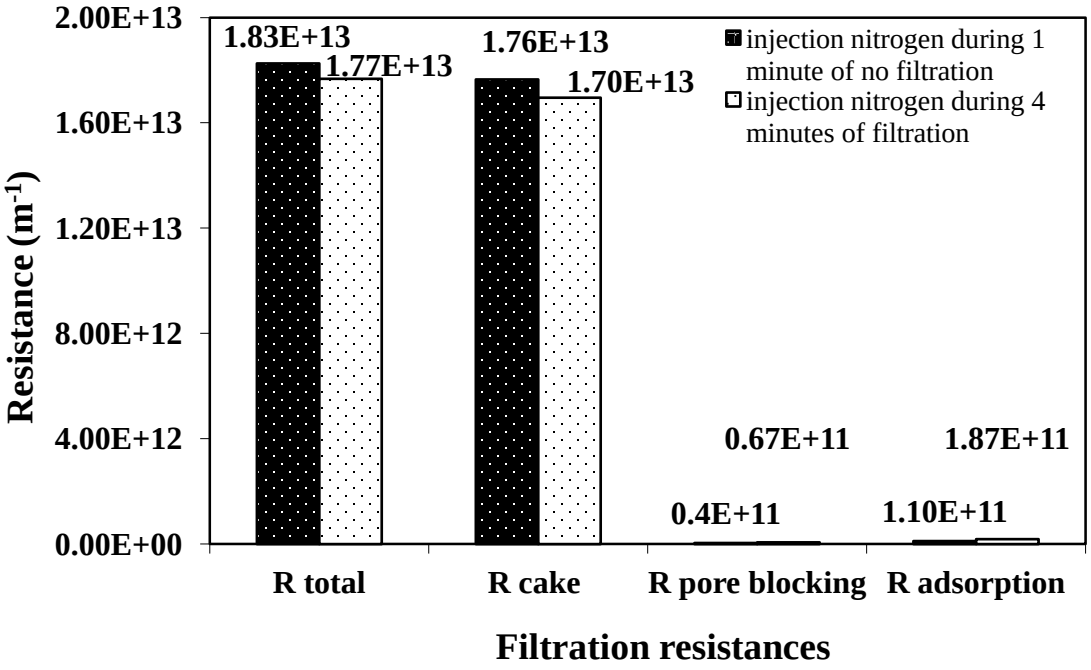


Figure 4.11 Resistance values at the end of filtration after each step of cleaning.

The value of the cake resistance was very close to the total resistance value measured before membrane cleaning, it was in the range of 1.76-1.70×10^{13} (m^{-1}), which was significantly much higher compared to the resistances of pore blocking and adsorption appearing then negligible. Fouling due to pore blocking appeared slightly lower than fouling due to adsorption.

The final resistances of both conditions were not significantly different due to the choice of stopping filtration when TMP reached a level closed to 25 kPa at whatever the functioning conditions. Comparing both experiments, it appeared that the operation time was different and the volume of recovered permeate was also different in accordance with a filtration carried out at constant and identical specific permeate flux for both experiments. So it can be advantageous to compare the hydraulic resistance for the same permeate volume by using specific hydraulic resistance. A specific hydraulic resistance R* (m^{-2}) was then calculated as follows:

$$R^* = R / (V/A) \qquad (4.12)$$

With R* the specific resistance (m^{-2}), V is the cumulated permeate volume (m^3) recovered at the end of each experiment and A the membrane filtration area (m^2). The specific hydraulic resistances R* are presented in Figure 4.12 for both conditions.

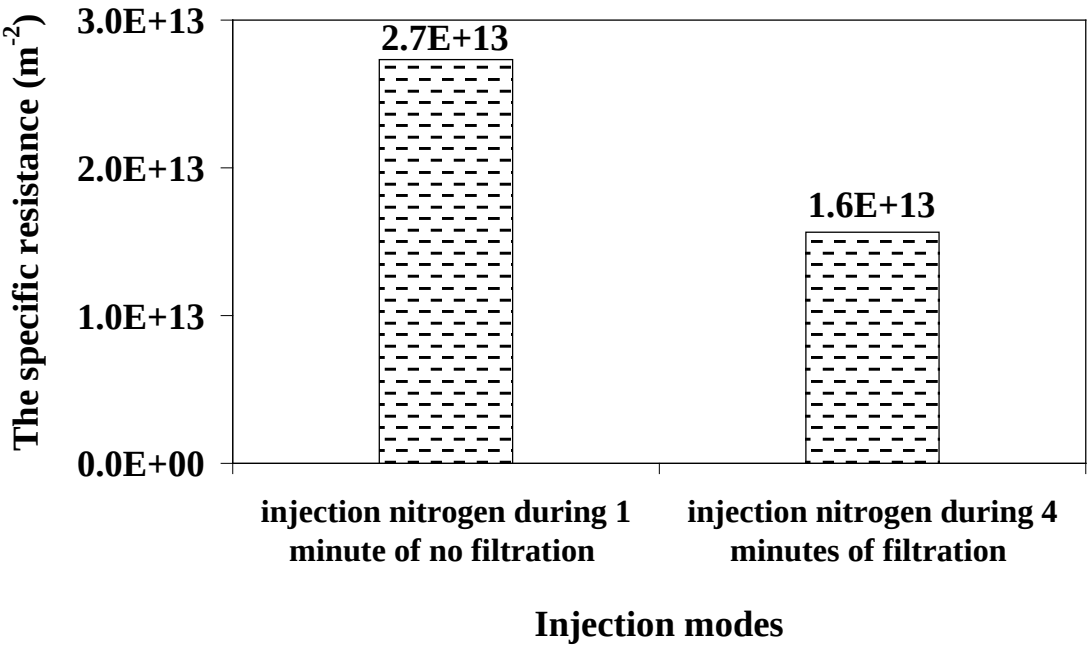


Figure 4.12 The specific hydraulic resistance.

The result confirmed the benefit of working with gas injection during 4 minutes simultaneously with filtration. The specific hydraulic resistance was twice lower than in other case.

The soluble microbial products (SMPs) present in the biological suspension were considered as one of the main factors affecting membrane fouling in MBRs (Huang et al., 2000; Lee et al., 2002; Meng et al., 2006; Liu et al., 2012). They can be adsorbed on the membrane surface, blocking membrane pores and forming a gel structure, even providing possible nutrient resources for biofilm formation (Rosenberger et al., 2005). Meng et al. (2006) revealed that the resistance of membrane fouling increased with increasing concentration of SMPs and SMPs which could fill the void spaces between the cell particles in the cake layer reducing the porosity of cake.

To check the role of SMPs, the membrane cleaning solutions were then analysed as indicated in the topic of 4.1.4.2.1. The results are shown in Figure 4.13.

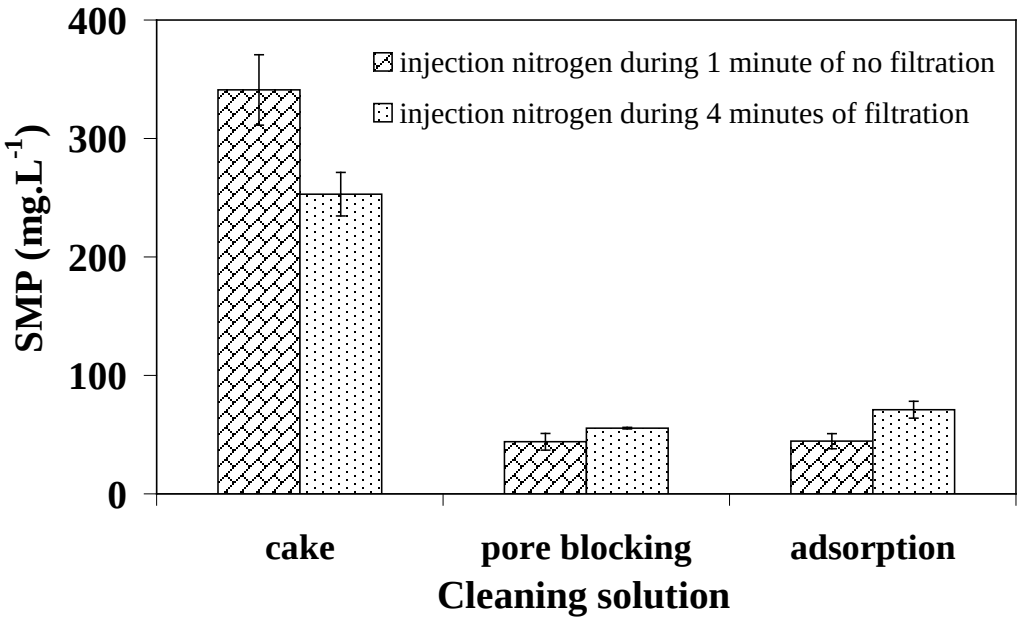


Figure 4.13 Concentration of SMP in cleaning solution.

It appeared a higher concentration of SMPs in cleaning solution used to remove cake deposit. SMP concentrations in specific cleaning solution were similar for pore blocking and adsorption. No significant difference was observed according to the mode of gas injection. Values given in Table 4.8 allowed the identification of the main compounds present in SMPs.

Table 4.8 Proteins and carbohydrates concentration of SMP in different cleaning solution about 1L of volume.

Cleaning solution	**Injection during 4 minutes of filtration**		**Injection during 1 minute of no filtration**	
	Proteins ($mg.L^{-1}$)	Carbohydrates ($mg.L^{-1}$)	Proteins ($mg.L^{-1}$)	Carbohydrates ($mg.L^{-1}$)
cake deposit	25±1.4	228±19.8	18±1.4	323±28.3
pore blocking	11.5±0.7	44±1.4	14±1.4	30±5.7
adsorption	12±1.4	59±8.5	13±1.4	31.5±4.9

For each kind of fouling, it appeared that carbohydrates (C) were more present in cleaning solution than proteins (P). They can then appear as the dominant SMP compounds for membrane fouling. Previous research (Kimura et al., 2004; Rosenberger et al., 2005; Le-Clech et al., 2006; Liang et al., 2007; Salazar-Peláez et al., 2011) also indicated the dominant effect of carbohydrate fractions on fouling. Vivas et al. (2012) reported that carbohydrate fractions appeared to be an important foulant having a higher impact on membrane fouling than proteins and aromatic compounds due to their partially hydrophilic nature comparing to proteins, they can penetrate into the cake layer and membrane pores (Deng et al., 2014; Yao et al., 2010). Ng and Ng (2010) indicated that the propensity of membrane fouling increased when the protein to carbohydrate ratio (P/C) decreased; meaning that fouling rate increased when concentration of carbohydrate increased. The decreasing of P/C ratio could induce a decrease of the hydrophobic and surface charge properties of microbial flocs causing higher resistance in cake formation (Liao et al., 2001).

4.2.2.2 Analyse of fouling in AnMBR

The precedent results points out the role of gas injection on membrane fouling intensity. When working in AnMBR, the gas injection mode was chosen as functioning 4 minutes simultaneously with filtration each 5 minutes cycle, the fifth minute corresponded to a period of no filtration without gas injection. The AnMBR was functioning successively with two OLRs (8.1 and 12.7 $kgCOD.m^{-3}.d^{-1}$), the dynamic of membrane fouling was then analysed as follows subtopics.

4.2.2.2.1 TMP evolutions

The evolutions of TMP with time are shown in Figure 4.14 for both OLRs. As soon as TMP was close to 25 kPa, the membrane module was taken off from the reactor to be cleaned and the fouling was characterised by hydraulic resistance and bio-fouling characteristic as indicated in the topic of 4.1.4.1 and 4.1.4.2.

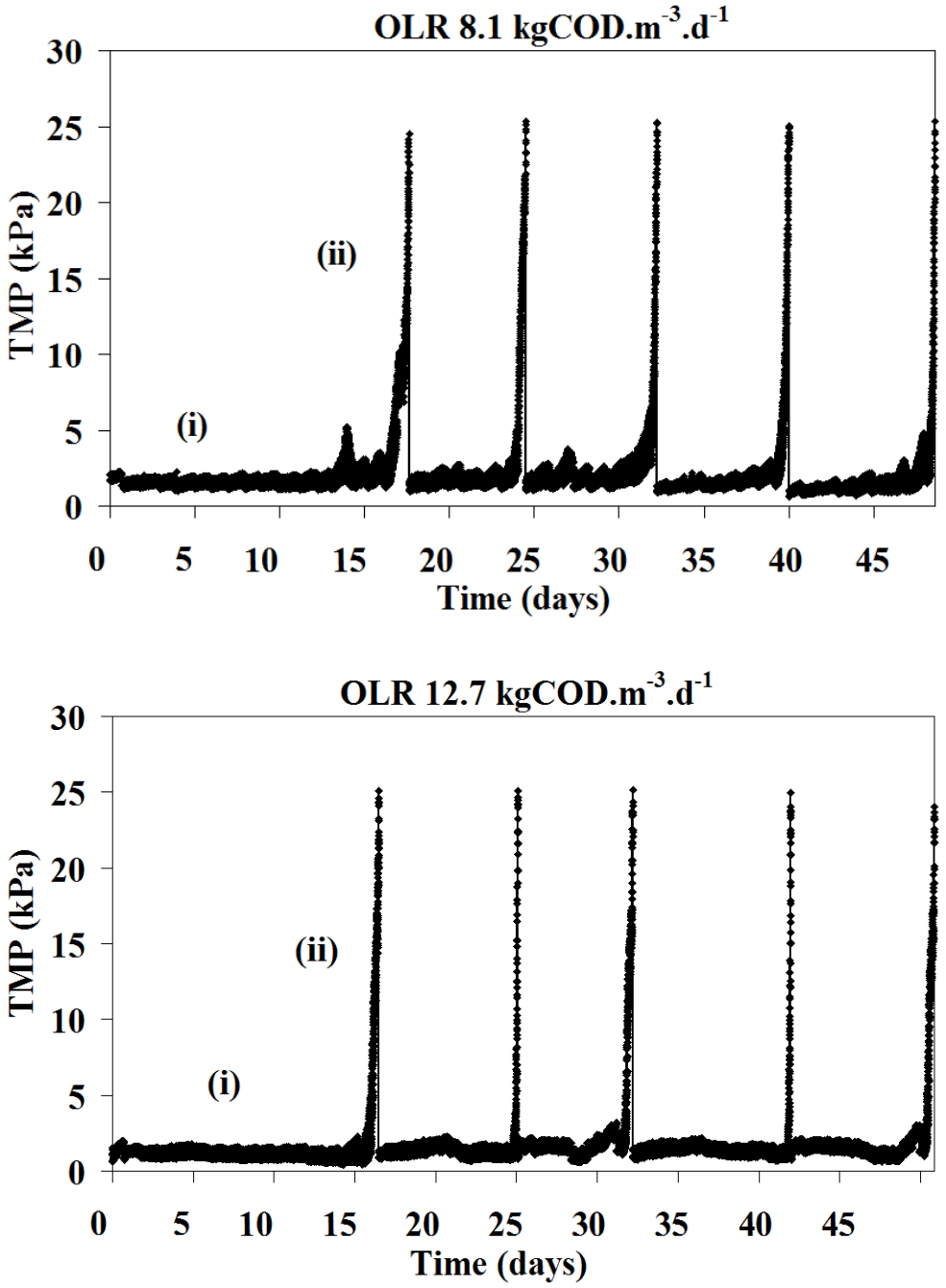


Figure 4.14 The variation of the TMP versus time at different OLRs.

The dynamic of TMP evolutions were similar for both OLRs even the concentration of MLSS (Figure 4.6) and the difference of COD in supernatant and permeate (Figure 4.4) were significantly higher when working at high OLR.

Before reaching 25 kPa, the TMP evolutions could be differentiated in two periods (i) a slow TMP increase following by (ii) a rapid TMP increase. Such TMP evolutions were often observed in SMBR (Lin et al., 2009; Wang et al., 2009). The slow TMP evolution can be explained by the choice of subcritical conditions at the beginning of filtration, the slow TMP means that slow fouling occurred. Ognier et al. (2004) 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 modifies drastically the membrane permeability and deposit porosity (Jeong et al., 2007; Wang et al., 2008). A higher OLR did not result in faster membrane fouling, Birima et al. (2009) 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. Table 4.9 gives the instantaneous TMP variation versus time, dTMP/d*t*, for both phases and both OLRs.

Table 4.9 The fouling rates (dTMP/d*t*) for two OLRs.

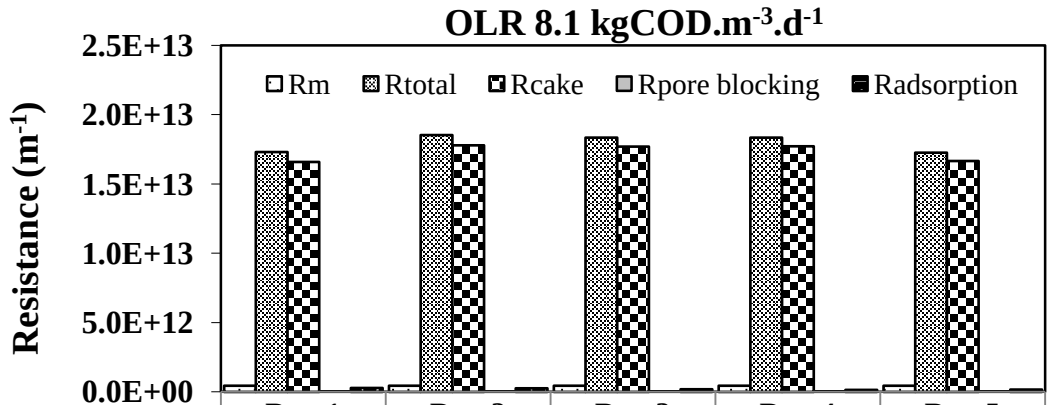
OLR ($kgCOD.m^{-3}.d^{-1}$)	**First period ($kPa.hr^{-1}$)**	**Second period ($kPa.hr^{-1}$)**
8.1	0.018±0.007	1.125±0.430
12.7	0.013±0.003	2.854±1.437

The fouling rate in AnMBR operation showed values similar to values obtained from former experiments in topic 4.2.2.1 (study of the role of gas injection modes on membrane fouling intensity) as showed in Table 4.7. In the second period of high OLR (12.7 $kgCOD.m^{-3}.d^{-1}$) this variation was found twice higher. Annop et al. (2014) showed fouling rate in the range of 0.011 to 0.058 $kPa.hr^{-1}$ for the first and second periods when treating palm oil mill effluent (POME) by two-stage submerged anaerobic membrane bioreactors (corresponding to OLR 27.5-30 $kgCOD.m^{-3}.d^{-1}$ and SRT 30 days). It can be seen that if in the first period the fouling rate was rather similar, it appears lower in the second period probably due to the differences in operating condition and filtration mode.

4.2.2.2.2 Hydraulic resistances

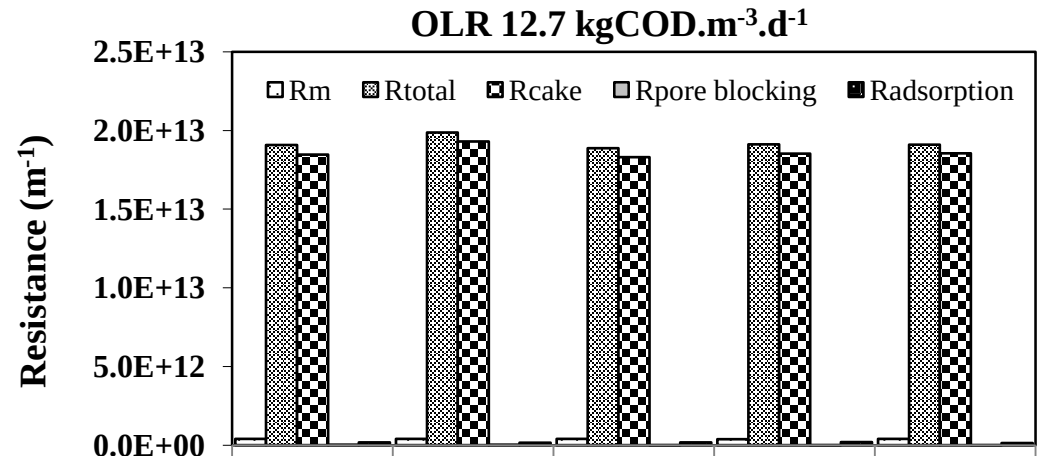
During the 53 days of AnMBR functioning, the membrane module was taken off 5 times from chamber 2 and cleaned according to the specific procedure described in the topic of 4.1.4.1. The different hydraulic resistances were then calculated at each cleaning step, results are given in Figure 4.15.

No significant differences of hydraulic resistance were observed between each cleaning operation, even if slightly higher peaks could be observed for high OLR. Results of Birima et al. (2009) also reported that higher OLR did not result in faster membrane fouling. Results showed for both OLRs that the resistance caused by cake formation ($1.73\pm0.06 \times 10^{13}$ and $1.86\pm0.04 \times 10^{13}$ m^{-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 (In these tests pore blocking appeared slightly lower than to adsorption). Such results appeared similar to results obtained in the former tests (Figure 4.11) and were also previously noticed when working with a submerged AnMBR (Lin et al., 2009), 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 (Wicaksana et al., 2006).



	Run 1	Run 2	Run 3	Run 4	Run 5
Rm	4.42E+11	4.36E+11	4.40E+11	4.42E+11	4.45E+11
Rtotal	1.73E+13	1.85E+13	1.84E+13	1.83E+13	1.73E+13
Rcake	1.66E+13	1.78E+13	1.77E+13	1.77E+13	1.67E+13
Rpore blocking	2.02E+10	2.21E+10	1.16E+10	3.81E+10	2.07E+10
Radsorption	2.87E+11	2.57E+11	1.95E+11	1.57E+11	1.78E+11

Figure 4.15 Membrane fouling resistance.



	Run 1	Run 2	Run 3	Run 4	Run 5
Rm	3.95E+11	3.93E+11	3.93E+11	3.85E+11	3.90E+11
Rtotal	1.91E+13	1.99E+13	1.89E+13	1.91E+13	1.91E+13
Rcake	1.85E+13	1.93E+13	1.83E+13	1.85E+13	1.86E+13
Rpore blocking	2.66E+10	3.01E+10	1.86E+10	1.77E+10	1.98E+10
Radsorption	1.73E+11	1.47E+11	1.69E+11	1.95E+11	1.26E+11

Figure 4.15 Membrane fouling resistance (continued).

4.2.2.2.3 Analyse of cleaning solution of cake deposit

1) SMP and bound EPS in cake deposit

The concentrations of SMP and bound EPS in rinsing water were analysed at the end each test. Results are shown in Figure 4.16. 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 SMP were accumulated inside the MBR (Liang et al., 2007). Meng et al. (2006) pointed out that increasing concentration of SMP led to increasing the membrane fouling and SMP could fill the void spaces of cake deposit which caused to a reduction of cake porosity (a molecular weight of SMP was in a range of 1,000-10,000 Da). But regarding Figure 4.14, these SMP and bound EPS accumulations in cake deposit had not apparent influence on fouling rate. The time of filtration for each run did not show significant difference. Table 4.10 gives the content of SMP and EPS in term of carbohydrates and proteins. Carbohydrates were the major component of both SMP and EPS in both conditions.

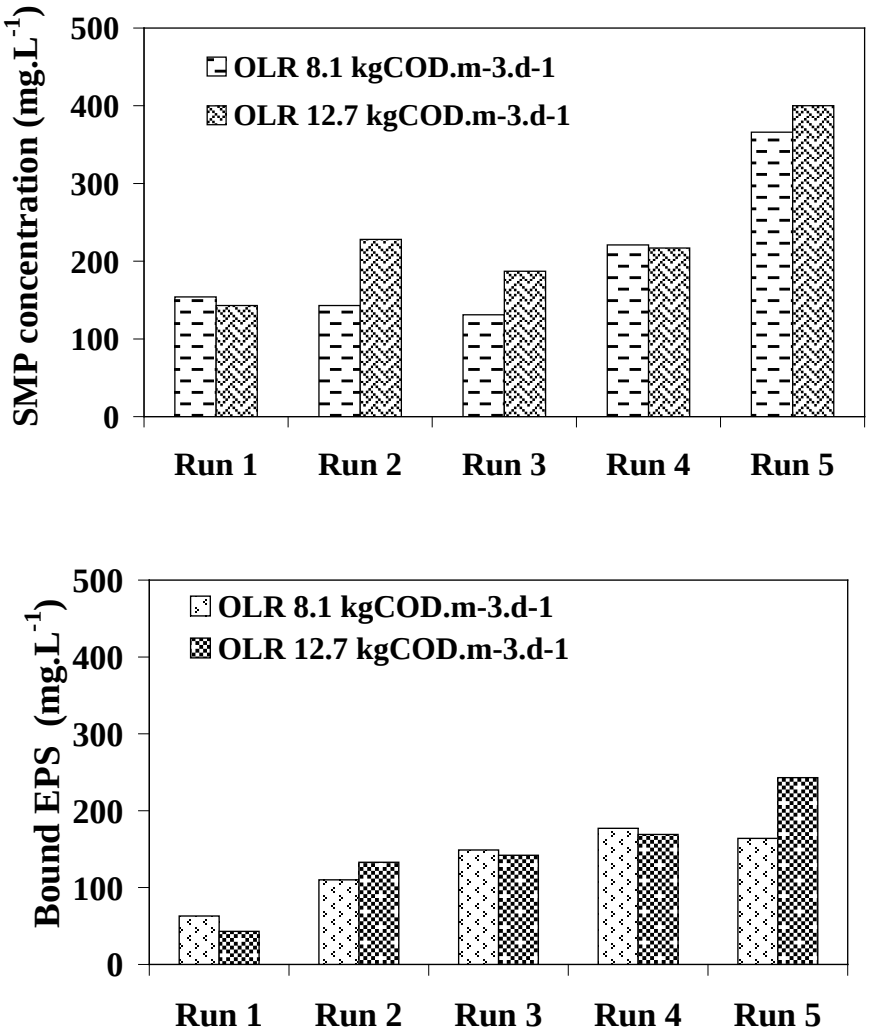


Figure 4.16 SMP and bound EPS concentration in fraction of cake layer.

Table 4.10 Composition and concentration of SMP and bound EPS.

	Parameter	**OLR≈8.1 kgCOD.m^{-3}.d^{-1}**	**OLR≈12.7 kgCOD.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

Carbohydrate impact on membrane fouling seemed then higher than protein impact (more than 10 times). The source of carbohydrates and proteins

accumulated on membrane surface coming from both microbial products (cell lysis, synthesis and substrate metabolism) and also residual component of latex serum which consisted of carbohydrates and proteins in same percentage content (1-1.5% by weight, see Table 1.1). Such observations were also noticed by Cero´n-Vivas et al. (2012), indicating that carbohydrates in SMP and EPS were the major factor affecting membrane fouling and it was in good accordance with investigation of Dvořák et al. (2011) showing that the majority of SMP component retained by the membrane was carbohydrates. Carbohydrates had a higher impact on membrane fouling than proteins due to their partially hydrophilic nature, they can infiltrate into the cake layer and membrane pores (Deng et al., 2014). Besides, carbohydrate to protein (C/P) ratio for OLR of 12.7 kgCOD.m^{-3}.d^{-1} was found slightly lower than for OLR of 8.1 kgCOD.m^{-3}.d^{-1}, a lower ratio of C/P would lead to more severe membrane fouling (Huang et al., 2011).

2) FTIR

Figure 4.17 presents some results of FTIR analyses. FTIR spectra are showed for both OLR. A broad peak near 3421 cm^{-1} indicates the presence of hydroxyl functional group (O-H stretching) (Wang et al., 2008) with the possibility of being polysaccharides due to a significant number of hydroxyl functional groups appearing at broad adsorption peaks above 3000 cm^{-1} wavenumber (Howe et al., 2002). In addition peaks in the range of 1075-1000 cm^{-1} are associated with C-O bonds from alcohol associated with polysaccharides (Chon et al., 2011). A peak in the region of 3000-2850 cm^{-1} is due to the C-H bonds in the alkanes class (Omoike and Chorover, 2004; Kim and Jang, 2006). Two sharp peaks around 1700-1600 cm^{-1} and 1600-1500 cm^{-1} correspond to proteins, namely amides I and II, and a peak in the range of 1310-1200 cm^{-1} corresponds to the presence of amide III (Badireddy et al., 2008). Peaks near 1454 cm^{-1} imply the possible presence of CH_2 group (Omoike and Chorover, 2004). Peaks of 1399 cm^{-1} and 1405 cm^{-1} indicate the presence of COO- group, attributed to amino acids (Badireddy et al., 2008). The region of 960-875 cm^{-1} (O-H) and 850-750 cm^{-1} (N-H) correspond to carboxylic acid and amide (Chon et al., 2011), and at a wavenumber of 760-610 cm^{-1} (O-H) is attributed to carboxylic groups and COOH deformation (Kim et al., 2006). Such results confirm that proteins and

polysaccharides were the main components of cake layer on the membrane surface as reported by Kim and Jang (2006). If the peaks distribution appears similar for both OLR, higher absorbance was found for high OLR, indicating greater production.

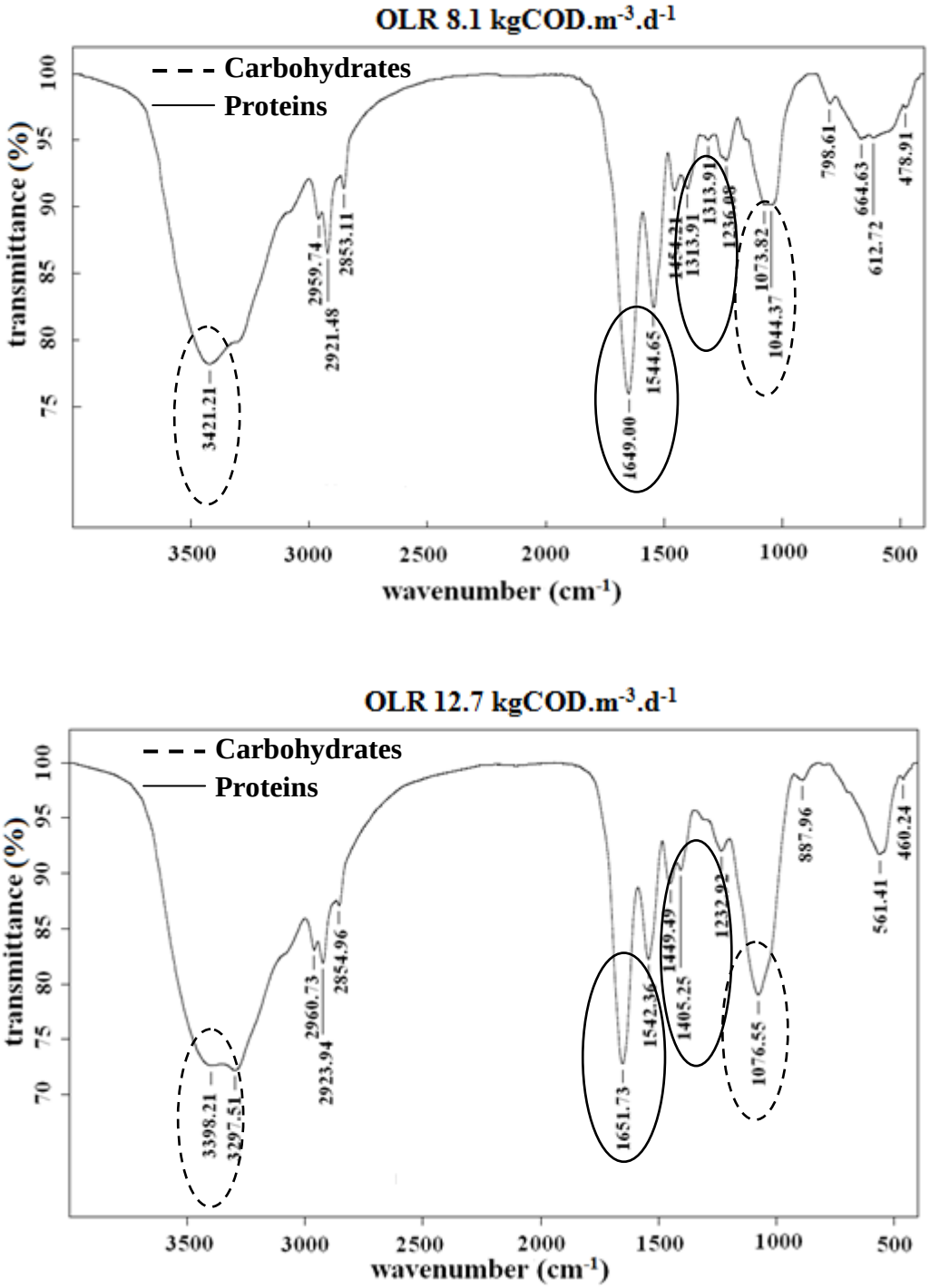


Figure 4.17 FTIR spectra of fouled membrane surface.

4.2.2.2.4 Analyses of fouled membrane surface

1) SEM-EDX

Figure 4.18 shows the SEM images of fouled and cleaned membrane, acquired at the end of one test before and after the chemical cleaning. The fouled membrane was covered with slime layer containing bacteria cells, the appearance of the cleaned membrane confirms the efficiency of chemical cleaning since no apparent fouling or particles can be observed on membrane surface. Figure 4.18 reveals a higher thickness of deposit when working at high OLR. The cross section of fouled membrane presented a thickness of fouling layer in the range of 2.56-5.13 µm and 5.13-10.26 µm for OLR of 8.1 and 12.7 kgCOD.m^{-3}.d^{-1}, respectively.

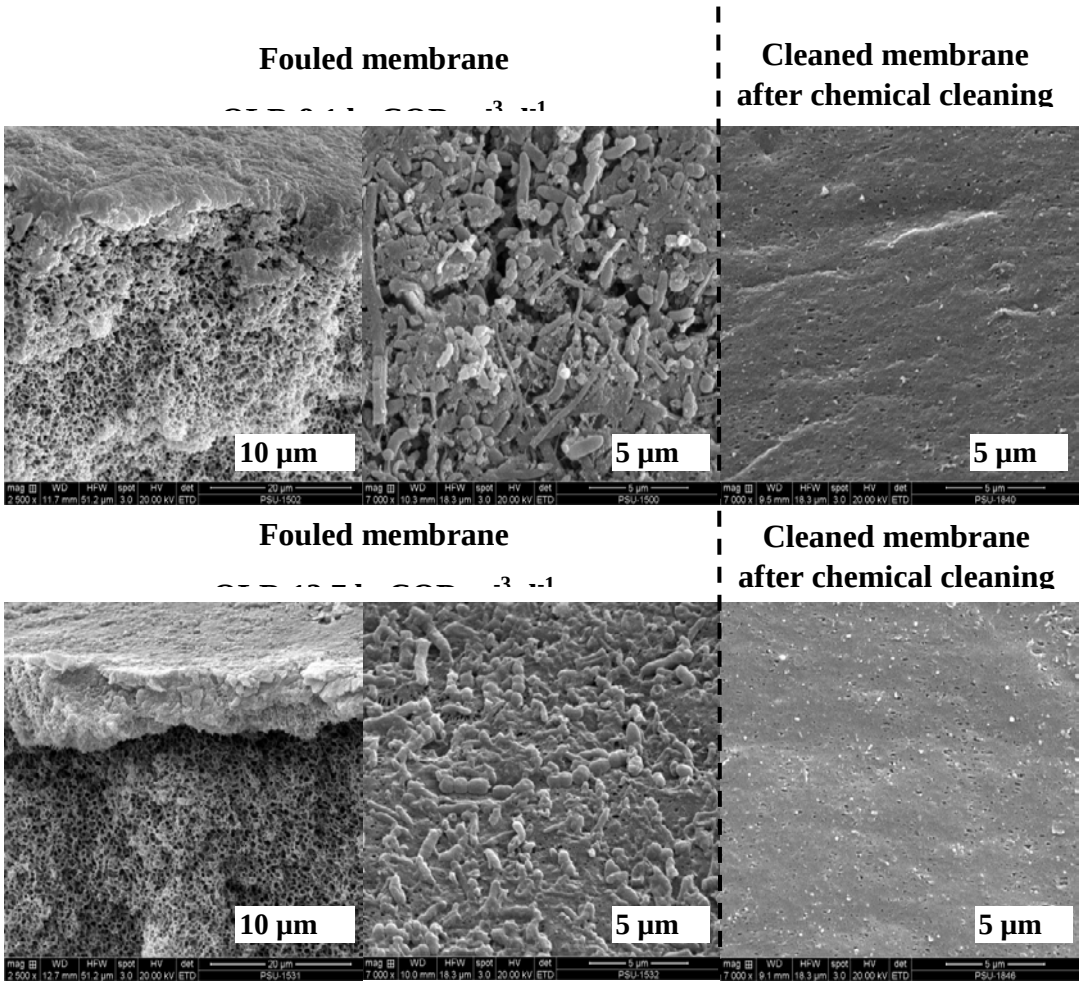


Figure 4.18 SEM photographs of fouled membrane surface and cleaned membrane.

EDX analysis points out the main compounds detected on the membrane surface as indicated in Figure 4.19. 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 case of fouled membrane surface. They are contained in latex serum (Ahmad bin Ibbrahim 1982; Jawjit et al., 2010) and are well known as contributor to fouling layer formation; the inorganic precipitation coupled with the organic foulants further enhanced a cake layer formation (Wang et al., 2008; Lin et al., 2009). However, these compounds and the majority of precipitates disappeared after chemical membrane cleaning.

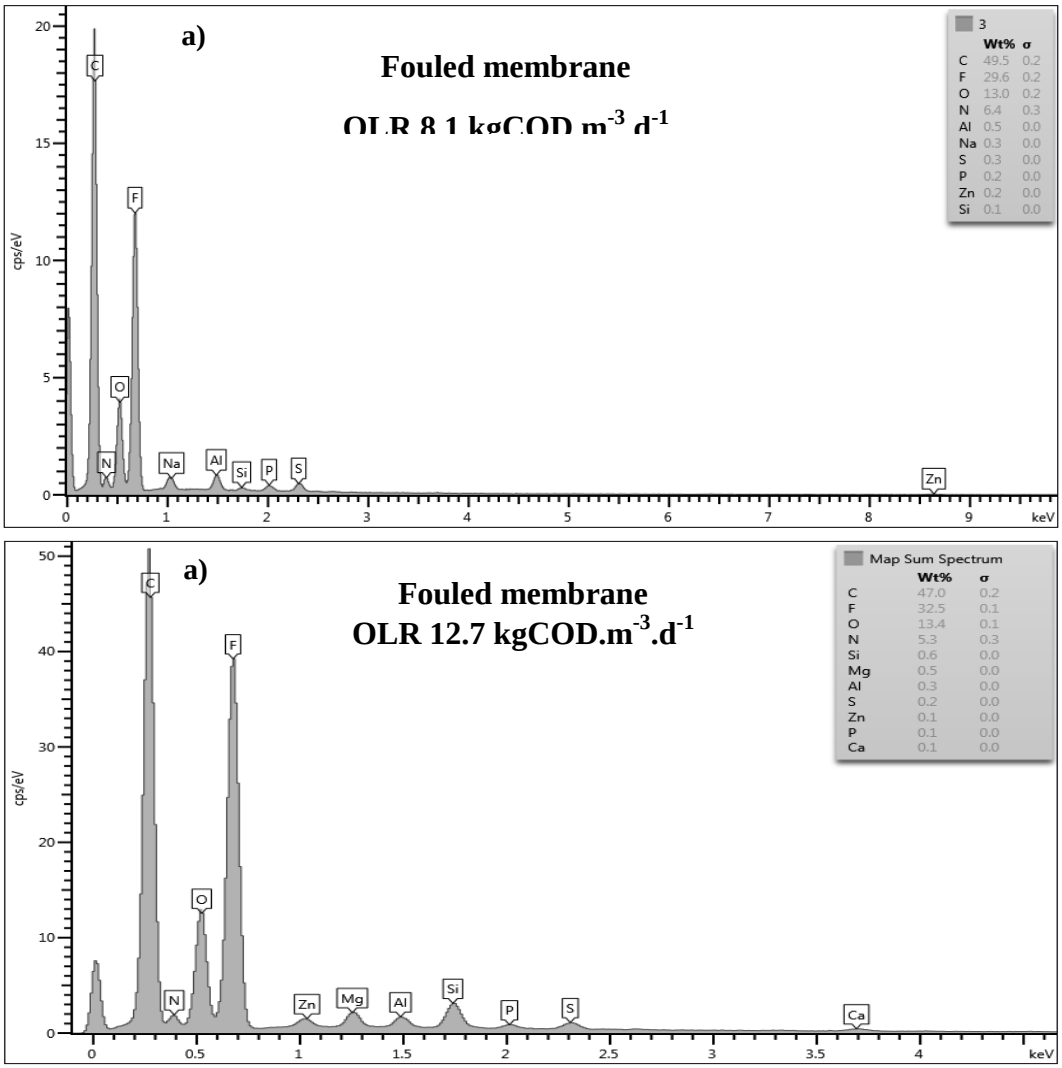


Figure 4.19 EDX analysis of a) fouled membrane surface, b) new membrane surface and c) cleaned membrane surface.

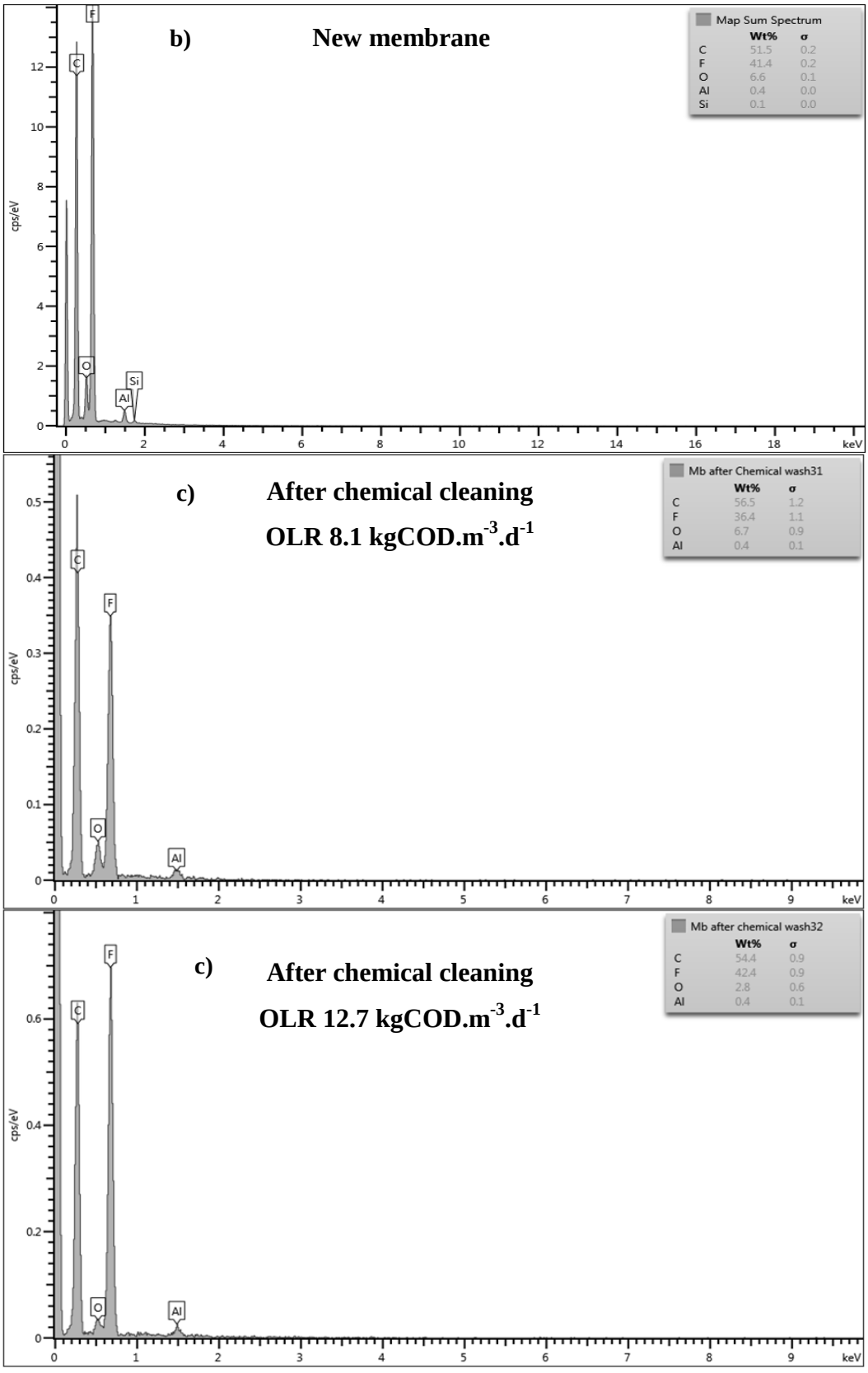
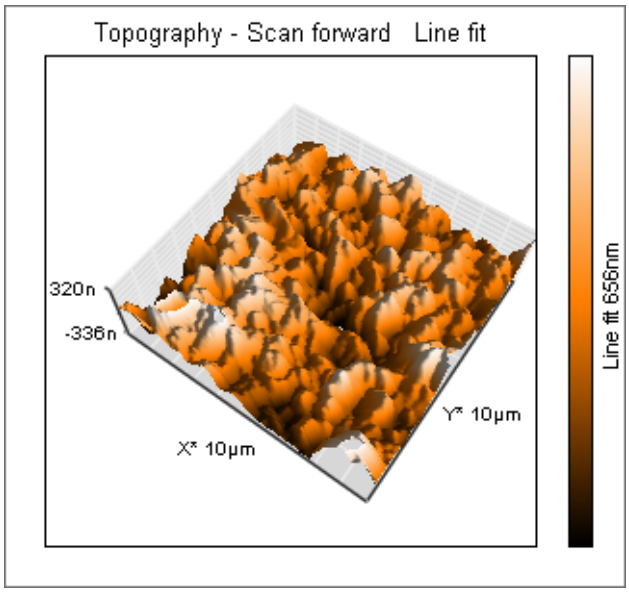


Figure 4.19 EDX analysis of a) fouled membrane surface, b) new membrane surface and c) cleaned membrane surface (continued).

2) AFM

If SEM method allows an evaluation of the cake layer thickness, AFM method gives an average value of the external roughness. Figure 4.20 shows some examples of AFM images of observed cake layer structure.

OLR 8.1 kgCOD.m^{-3}.d^{-1}



OLR 12.7 kgCOD.m^{-3}.d^{-1}

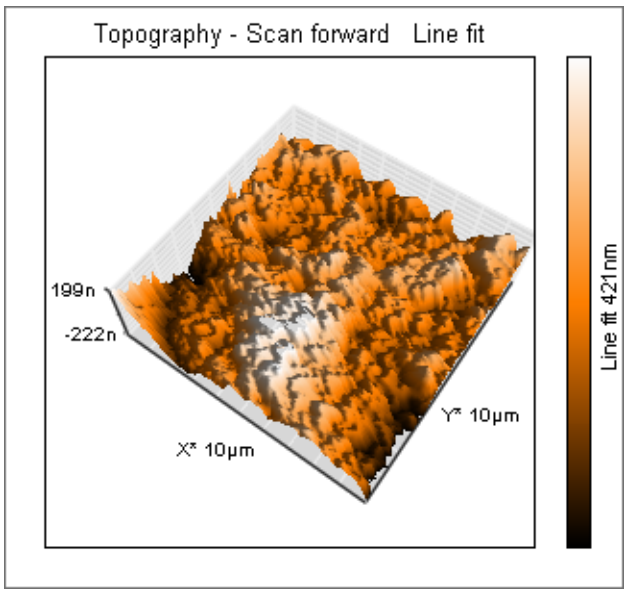


Figure 4.20 AFM images of fouled membrane surface.

The value of root-mean-square roughness (R_{rms}) was identified around 129.8 and 77.82 nm and the mean roughness (R_a) was 100.20 and 58.92 nm at OLR of 8.1 and 12.7 kgCOD.m^{-3}.d^{-1}, respectively. In this study, high OLR showed a higher thickness of cake deposit but a lower roughness related to a more compact structure as soon indicated by Shui-li et al. (2006). 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 (< 25 kPa) and operated at sub-critical flux condition.

4.3 Conclusions

This chapter presents results obtained when treating latex serum with an Anaerobic Bioreactor equipped with a final liquid solid separation operated by settling or by filtration on porous membrane, i.e. Anaerobic MBR AnMBR. The performances of both systems were compared according to (i) the removal of organic matter and the production of biogas and (ii) the dynamic of membrane fouling when operating with the AnMBR. The systems were tested according to two organic loading rates OLR, 8.1 and 12.7 kgCOD.m^{-3}.d^{-1}. The influent, latex serum, was obtained from micro-porous filtration of a skim latex suspension without any acid addition to avoid the presence of sulphide during anaerobic digestion.

Results confirmed the high level of degradability of latex serum with COD removal efficiency equal to 73.2 and 54.6% for OLR of 8.1 and 12.7 kgCOD. m^{-3}.d^{-1} respectively with a final liquid solid separation by settling, these efficiency rose up to 86 and 73.5% respectively when operation with a final filtration on porous membrane proving the capacity of such a porous barrier to increase the retention of small compounds in comparison with a simple settler. The degradation of COD by anaerobic way induced some biogas production, notably methane with a methane yield coefficient close to 0.24 Nm^3.$kgCOD_{removed}^{-1}$. The OLR increase showed a decrease of COD removal efficiency but an increase of the global quantity of COD removed and an increase of biogas production. Such an operation then allowed a potential of energy recovery close to 45 kWh.$m^{-3}_{\text{treated latex serum}}$.

The membrane fouling was mainly due to the structuring of a cake deposit on the membrane surface, this deposit appeared as removable by only water rinsing. The analysis of rinsing solutions showed the dominant role of carbohydrates in the composition of cake layer even if the presence of proteins was also important, in fact it is probably the mixing of these two major families of organic compounds that caused the cake layer structuring. No significant influence of OLR was identified on membrane fouling dynamic but the observation of deposit onto the membrane surface let appear significant differences when comparing both OLR operations, high OLR induced a thicker deposit layer but this layer presented also a lower roughness. The roughness may then appear as a determining criterion to explain the evolution of the deposit hydraulic resistance whatever the role of its thickness.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The objectives of this research were to define new concepts to treat skim latex serum and recover rubber content without acidification and to treat latex serum to recover biogas. The research was built on complementary steps, (i) latex serum recovery by direct microfiltration of skim latex without any coagulation step by acidification, (ii) analysis of biodegradability of obtained latex serum and corresponding biogas production when developing anaerobic biological way, and (iii) benefit of AnMBR as intensive process to transform organic matter present in latex serum into biogas and produce energy for latex industry simultaneously with a significant decrease of environmental impact of the final water effluent..

The results of our original approach can be concluded as follows:

5.1.1 Recovery of rubber content and latex serum from skim latex by cross-flow microfiltration

According to the size of rubber particles in skim latex (average size 0.7 μm), a microfiltration was chosen to separate these particles from the soluble phase. The lab scale unit, equipped with a multichannel ceramic membrane, was operated in cross-flow conditions at constant transmembrane pressure (0.5 bar TMP), constant cross-flow velocity (3 $m.s^{-1}$) and room temperature (28$\pm$2 °C). The 0.22 μm membrane cut-off was chosen to retain and concentrate the rubber particles in a retentate phase, the permeate phase, latex serum, should only contain soluble matter, presenting a high content of biodegradable organic matter.

The results pointed out the efficiency of microfiltration to retain dry rubber content (DRC) in the retentate and the possibility to reach a volumetric concentration factor (VCF) in retentate close to 10, corresponding to a final DRC close to 40% according to the initial DRC in skim latex suspensions close to 4%. Such

a quality of this retentate, obtained without any acid addition, allows the possibility to use such a retentate as a usual matter for rubber material making, even open new possibility to develop new markets for such a by-product when comparing its quality with conventional skim blocks or skim crepes obtained by coagulation steps.

Nevertheless, the filterability of the retentate clearly decreased when VCF increased due to a significant membrane fouling appearance and probably also to a significant increase of retentate viscosity. The dominant membrane fouling origin (94%) appeared as linked to an accumulation of suspended solids onto the membrane surface. This deposit was easily removable by only membrane rinsing what is a positive point to favour fouling control during operation.

The latex serum or permeate appeared as a clear yellow solution presenting a high COD concentration, more than 30 $g.L^{-1}$, with COD/BOD_5 ratio close to 2 confirming a high potential of biodegradability of such a solution.

5.1.2 Biochemical methane potential test (BMP) and anaerobic sequencing batch tests

BMP tests were carried out to analyse the capacity of anaerobic biological way to convert organic matter present in latex serum in biogas. Two types of systems (batch tests and sequencing anaerobic batch reactors) were used.

Batch tests were carried out at different S/X ratios (0.6, 1.3, 1.9 and 2.5$gSCOD.gVSS^{-1}$). The sequencing anaerobic batch reactors were carried out at different HRT (1.3, 4.0 and 6.7 days) or OLR (8.4, 2.6 and 1.5 $kgCOD.m^{-3}.d^{-1}$) to analyse their impact on reaction efficiencies.

The majority of results obtained during BMP tests and sequencing anaerobic batch reactors showed COD removal efficiency higher than 80% confirming the high potential of latex serum to be treated by an anaerobic biological way. The range of methane yield coefficient (0.15 to 0.30 $NLCH_{4produced}.gCOD_{removed}^{-1}$) was large in BMP tests notably due to the appearance of acidic conditions when working at the highest S/X ratio. The values of this coefficient also appeared slightly lower in BMP tests in comparison with values obtained in sequencing anaerobic batch reactor where the pH was under control (in the range of 0.27 to 0.35 $NLCH_{4produced}.gCOD_{removed}^{-1}$). The biogas and methane productions increased in

sequencing batch tests with S/X ratios increasing, except at the highest S/X ratio (2.5gCOD.gMVSS^{-1}). Moreover the biogas and methane production rates increased with OLR increasing (or HRT decreasing) when working in sequencing anaerobic batch test.

5.1.3 Treatment of latex serum by anaerobic membrane bioreactor (AnMBR)

According to precedent results, a lab scale AnMBR was defined to treat latex serum and produce biogas. The experimental conditions were based on the choice of the maximal OLR found in sequencing batch reactor (8.1 kgCOD.m^{-3}.d^{-1}). The performances of AnMBR when treating latex serum obtained by microfiltration were analysed for two organic loading rates (OLR), 8.1 and 12.7 kgCOD.m^{-3}.d^{-1}. The other experimental criteria were fixed at HRT and SRT, 2 and 30 days, respectively. For each OLR, two successive periods were defined, the first one corresponded to the association of the anaerobic reactor with a final separation step by settling, the second period corresponded to the setup of hollow fibre membrane presenting a 0.1 µm cut-off as the final separation step in place of settling. As analysed during this study, the membrane filtration was operated during 4 minutes each 5 minutes simultaneously to a nitrogen gas injection (1L.min^{-1}). The results pointed out the role of the membrane barrier to improve COD removal efficiency and reach to 86 and 73% for OLR of 8.1 and 12.7 kgCOD.m^{-3}.d^{-1} respectively, and consequently biogas and methane productions. If the COD removal was consequent, methane yield coefficient, in the range of 0.22 to 0.24 $Nm^3CH_4.kgCOD_{removed}^{-1}$, appeared significantly less important that results obtained in sequencing batch reactors, even when working at the same OLR. Then, the AnMBR functioning was not perfectly control in terms of methane production. Nevertheless, according to the obtained methane yield coefficients, the potential of energy recovery when treating latex serum by AnMBR was in the range of 30 and 45 $kWh.m^{-3}_{\text{treated latex serum}}$. Such high values (2 to 5 times higher than the energy requirement for microfiltration of skim latex and AnMBR functioning) let to envisage the advantage of such process to cover a significant part of energy requirement of the industrial latex plant. When analysing the membrane fouling resulting of AnMBR functioning, the dominant origin of fouling appeared as the cake

deposit on the membrane surface. This external accumulation of compounds was easily removable by water rinsing, the internal fouling due to pore blocking and adsorption of small compounds in membrane pore could be considered as negligible if a chemical cleaning was practised every 10 days. The analyses of rinsing solutions corresponding to cake detachment pointed out carbohydrates as the major components of fouling material whatever OLR. SEM analyses revealed a more compact and thick deposit when working at high OLR while AFM analyses showed a lower roughness related to a more compact structure in the same conditions of high OLR.

5.2 Recommendations

The expected benefits of this research were:

1. To define appropriate filtration/separation conditions by using microfiltration to implement lab scale results to industrial scale applications including fouling control.

Microfiltration of skim latex showed some great benefit to recover dry rubber content without any acid conditioning. The quality of the retentate containing rubber particles with a DRC close to 40% can open new ways of valorisation of such products. It can then be beneficial to analyse the allergen content of such rubber concentrate assuming that the allergen compounds should more present in soluble phase, i.e. the permeate.

Even the membrane fouling was easy to control by only membrane rinsing, it appeared very important to have a better analysis of the viscosity behaviour of the retentate which increased with VCF. The viscosity behaviour should help the design of the best membrane module configuration, notably the choice between submerged or cross-flow systems and the operational associated conditions when developing such systems at industrial scale up.

2. To analyse the quality of the treated effluent in regards with its residual content and its possibility to reuse.

This study confirmed the great advantage of treating latex serum by anaerobic way to decrease drastically the organic content of such wastewater but also to produce biogas with a significant methane content generating a high potential of

energy recovery. The set-up of an AnMBR pointed out the significant benefit of membrane barrier to improve COD removal and biogas production. Nevertheless, the membrane fouling rate still remained significant, even if the membrane fouling appeared mainly due to some removable fouling mechanisms. It is then important to develop research focused on membrane fouling to define a suitable ways for minimizing the intensity of fouling and favouring its control. New topics of research can then be focused on new configurations of AnMBR and/or on new membrane and membrane module configurations.

If the removal of COD appeared significant, the final characteristics of treated water was still appear some significant level of pollution in terms of residual COD and ammonia. It is then also important to analyse what can be final treatment to (i) minimise the environmental impact of such treated water when released in environment or (ii) recover interested compounds or treated water of sufficient quality to be reused on site.

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List of Publications

1. Thongmak, N., Sridang, P., Puetpaiboon, U., Grasmick, A. (2015) Concentration of field and skim latex by microfiltration– membrane fouling and biochemical methane potential of serum. Environmental Technology 36, 2459-2467.
2. Thongmak, N., Sridang, P., Puetpaiboon, U., Héran, M., Lesage, G., Grasmick, A. (2015) Performances of a submerged anaerobic membrane bioreactor (AnMBR) for latex serum treatment. Desalination and Water Treatment DOI: 10.1080/19443994.2015.1110727.