Universitat Autònoma de Barcelona

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TECHNICAL NOTE 94.42

CI Filtration Unit Optimisation:

Trade-off and selection of best suited membrane

Prepared by/Préparé par	Lasserre, J.C. and Grasmick, A.
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Filtration Unit Optimization
Technical Note 94.42

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Author :
TechnoMembranes Développement
ZAE les Tannes Basses
rue de l'Aramon
34800 Clermont-l'Hérault
✉ www.technomembranes.com
✉ info@technomembranes.com
🕮 04 67 44 91 89
🖷 04 67 44 03 52

Departament de Enginyería Química
Escola Técnica Superior de Enginyería (ETSE)
Universitat Autónoma de Barcelona
Campus de Bellaterra (Barcelona)

Destine :
MELISSA Pilot Plant
Departament d'Enginyeria Quimica
Escola Técnica Superior de Enginyerá (ETSE)
Universitat Autonoma de Barcelona
Campus de Bellaterra
08193 Bellaterra (Barcelona)- Spain

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Customer

Company : **Universitat Autonoma de Barcelona**
Adress : Campus de Bellaterra
08193 Bellaterra - Spain

+34 93 586 81 01
+34 93 581 20 13
Enrique.peiro@uab.es
Contact(s) : **M. Enrique Peiro**

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Redaction : **Jean-Christophe LASSERRE** — Assay Scientist
Alain GRASMICK — External Consultant

Validation : **Julien TROQUET** — General Manager

Index

Applicable documents

Designation	Reference
Proposal – MELiSSA Pilot Plan – Frame Contract 19445/05/NL/CP – "Work Order Compartment I of the MELiSSA Pilot Plant: additional characterization phase"	OFR-ESA-01/06-UAB

Acronyms and definition list

DM	Dry Matter
EC	Electroconductivity
HRT	Hydraulic Retention Time
MBR	Membrane BioReactor
MPP	MELiSSA Pilot Plant
OL	Organic Load
TMP	Trans-Membrane Pressure
VFA	Volatile Fatty Acids
VSS	Volatile Suspended Solid

I. Background

The MELiSSA Pilot Plant (MPP) is located within the premises of Universitat Autònoma de Barcelona (UAB), in Bellaterra (Barcelona), Spain. A new laboratory has been recently set-up at UAB to host the MELiSSA Pilot Plant. This laboratory will enable to host the different compartments, first installed and operated individually, to be completely characterized, and then, step by step, integrated at different levels: liquid, solid and gas.

The present work is presented as part of UAB's response to the ESA Call-off Order related to the "Compartment I of the MELISSA Pilot Plant: additional characterization phase".

The global study will allow the further characterisation of the Pilot Compartment I at the MPP site in UAB. The pilot reactor will be tested for approximately eighteen months. During this period, it will be operated in order to collect data for process, model and control development. The Filtration Unit will be optimised. An up-scaling of the waste preparation system used currently at EPAS will be performed.

The present Technical Note relates to the work which was carried out by TechnoMembranes as part of the global study. This Technical Note mainly involves work related to the filtration unit optimisation.

II. Objectives and program study

According to the previous description, the objectives of this work order are the installation and integration of Compartment I in the MELiSSA Pilot Plant, the performance of a long series of experiments with the proper analyses to fully characterize its operation and to provide data for mathematical model and control algorithms development, the improvement and optimization of the unit to prepare the feed to the reactor, and the optimization of the membrane unit of Compartment I. At the finalisation of the work, Compartment I should be completely operational in the MPP at the corresponding quality standards and ready to be connected to other MPP compartments.

The objectives of this work are to compare different ceramic membranes to identify the best conditions of filtration in terms of:

- optimizing both permeate flux and recycling velocity to minimize energetic cost (i.e greatest permeate flux and lowest recycling velocity), however avoiding the presence of any deposit on the membrane surface;
- avoiding any clogging of membrane pipes (according to pipe diameter of membranes, the sludge concentration and the presence of large pellets in the bulk);
- minimizing the irreversible fouling due to sorption phenomena.

This study includes several phases:

- definition and assembling of hardware;
- test of prototype for one month with inoculum, for prototype validation;
- set-up and validation of VFA analysis method;
- membrane selection;
- continuous tests of selected membranes.

III. Hardware definition and tests

III.1. Membrane Bioreactor design

To carry on the experimentation, a specific experimental pilot was defined. The design of this Membrane Bioreactor is based on CI prototype design. This equipment can work either at controlled TMP or at controlled permeate flux. All of the following trials were performed at controlled permeate flux. This configuration is preferred to study the membrane clogging evolution. The membrane fouling dynamics can be evaluated by the trans-membrane pressure TMP evolution

The next figure gives a schematic representation of the system.

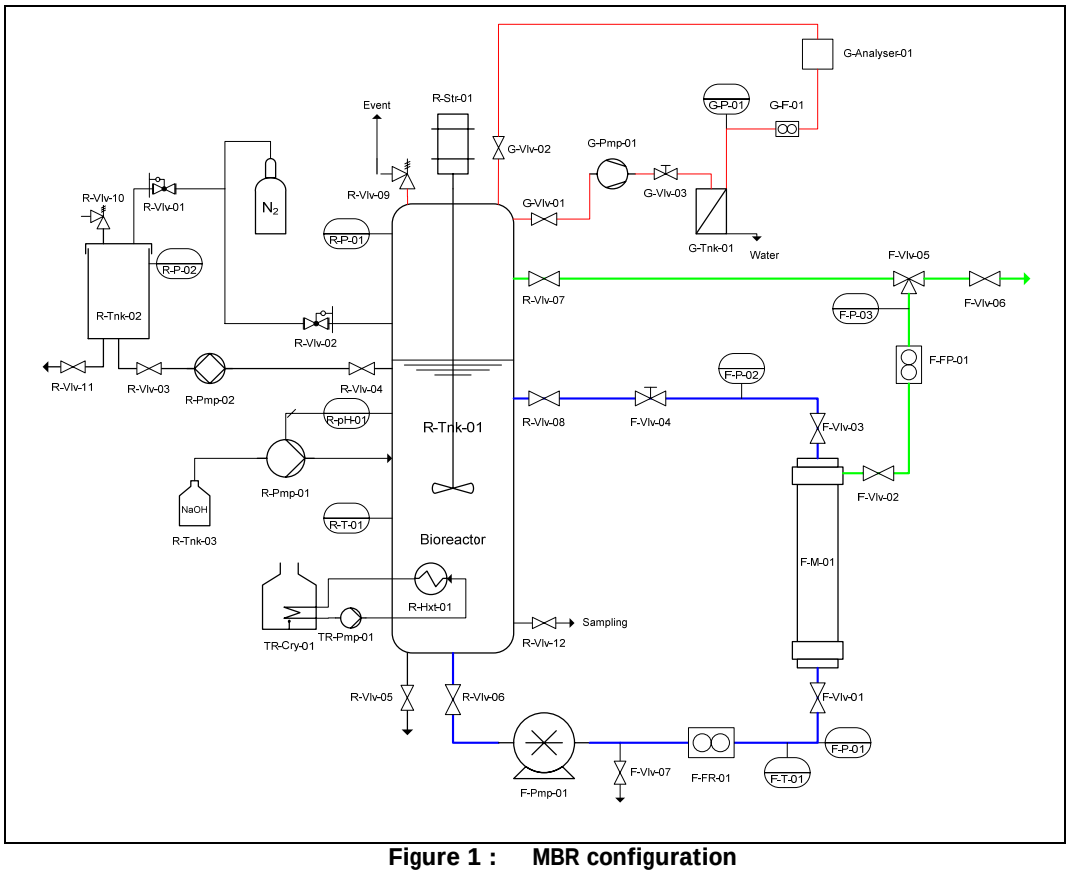

Figure 1 : MBR configuration

The MBR prototype involves:

- a crystal PVC reactor of a working volume of 25 L equipped with a manometer and different sampling devices;
- an helicoidal stirrer;
- an internal heating system by circulation of a coolant;
- a pH regulation system which includes a probe coupled with a reagent injection system (alkali);
- a gas recirculation loop for methane, CO2 and O2 analysis;
- a tangential filtration loop which includes a gear pump, two pressure transmitters, a set of valves and a flowmeter;

- a permeate loop which includes a pressure transmitter, a set of valves, a flowmeter and a membrane module.

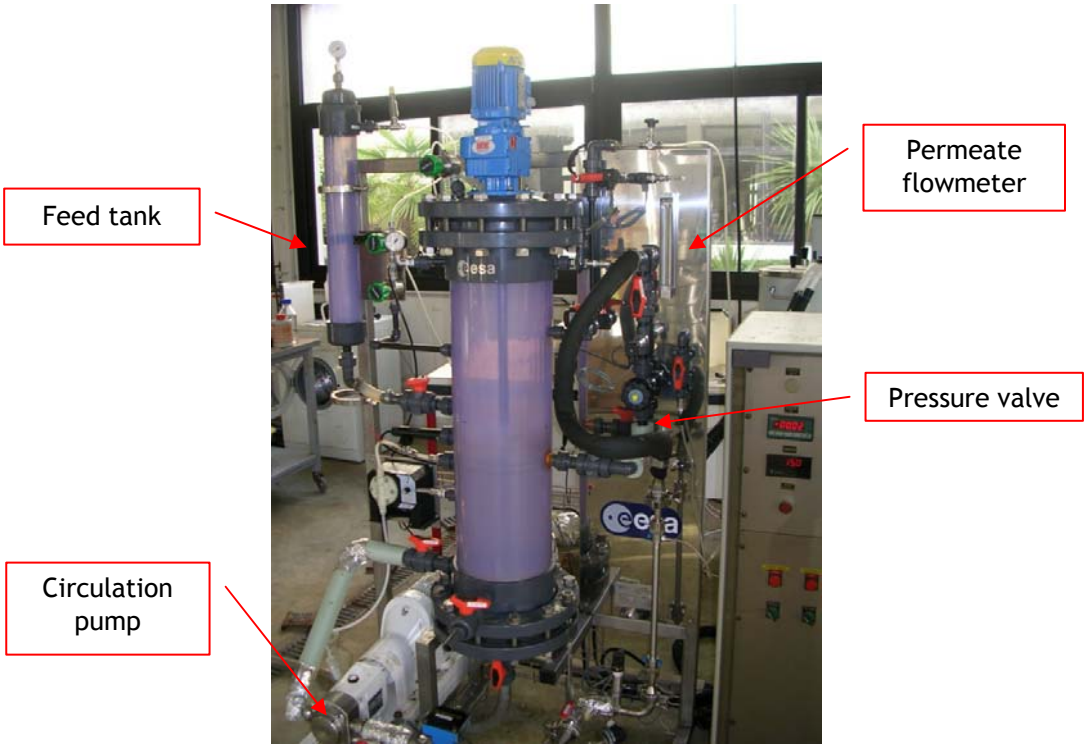

Figure 2 : BRM overview

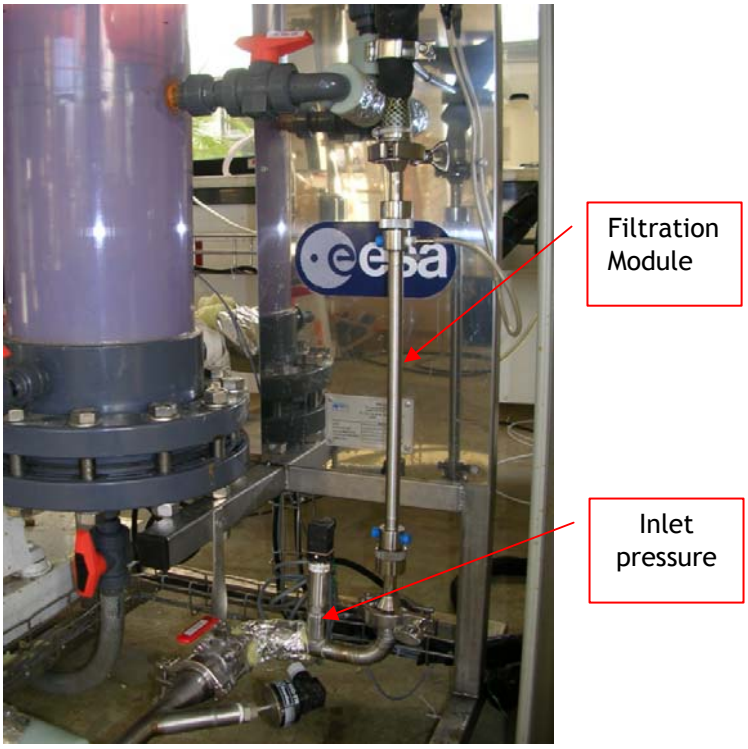

Figure 3 : Filtration Module

The following Tables 1, 2 and 3 provide the detailed characteristics of the selected valves, pumps and monitoring equipments for the Membrane Bioreactor.

Table 1 : Valves specifications

Code	Description	Inlet Pressure	Outlet Pressure	Nominal Flow	Type of valve	Supplier	Model	Fluid	Reference
F-Vlv-01	Inlet Module Valve	0,3 - 3 bar	0,3 - 0,4 bar	100 - 900 l/h	plug valve-2 way			Biomass	Inox DN20 - PN69
F-Vlv-02	Permeate Valve	0 - 3 bar	0,1 - 0,4 bar		plug valve-2 way	George Fischer	Type 546 - DN 10	Permeate	
F-Vlv-03	Outlet Module Valve	0,3 - 3 bar	0,3 - 0,4 bar	100 - 900 l/h	plug valve-2 way	George Fischer	Type 546 - DN20	Biomass	161 546 063
F-Vlv-04	Pressure Valve	0 - 3 bar	0,3 - 0,4 bar	100 - 900 l/h	Diaphragm valve	Burkert	3233	Biomass	
F-Vlv-05	Filtration Permeate	0,3 - 0,4 bar	0,3 - 0,4 bar		plug valve-3 way	George Fischer	Type 343 - DN10	Permeate	
F-Vlv-06	Produced Permeate Valve	0,3 - 0,4 bar	Atmospheric		needdle valve	Swagelok	SS-1RS4	Permeate	
F-Vlv-07	Sampling Valve	0,3 - 3 bar	Atmospheric		plug valve-2 way		1/4" - SUS 316	Biomass	
G-Vlv-01	Gas Loop	0,3 - 0,4 bar	0,3 - 0,4 bar	0,5 l/min	plug valve-2 way	Swagelok	SS-43GM4-F4	Gas (CH4+CO2)	
G-Vlv-02	Gas Loop	0,3 - 0,4 bar	0,3 - 0,4 bar	0,5 l/min	plug valve-2 way	Swagelok	SS-43GM4-F4	Gas (CH4+CO2)	
G-Vlv-03	Flow Valve	0 - 1 bar	0,3 - 0,4 bar	0.5 l/min	needdle valve	Swagelok		gas	
R-Vlv-01	Pressure reducer	6 bar	0,5 - 1 bar		needdle valve	Swagelok	KPR1DFC412A20000	Azote	
R-Vlv-02	Pressure reducer	6 bar	0,3 - 0,4 bar		needdle valve	Swagelok	KPR1DFC412A20000	Azote	
R-Vlv-03	Isolating valve	0,5 - 1 bar	0,5 - 1 bar		plug valve-2 way	George Fischer	Type 546 - DN20	Influent	
R-Vlv-04	Isolating valve	0,5 - 1 bar	0,3 - 0,4 bar		plug valve-2 way	George Fischer	Type 546 - DN20	Influent	
R-Vlv-05	Bioreactor Drain Valve	0,3 - 0,4 bar	Atmospheric		ball-valve	George Fischer	Type 546 - DN20	Biomass	163 546 003
R-Vlv-06	Feed Filtration Loop Valve	0,3 - 0,4 bar	0,3 - 0,4 bar	100 - 900 l/h	ball-valve	George Fischer	Type 546 - DN 15	Biomass	163 546 002
R-Vlv-07	Isolating Permeate Valve	0,3 - 0,4 bar	0,3 - 0,4 bar		plug valve-2 way	George Fischer	Type 546 - DN10	Permeate	
R-Vlv-08	Isolating Retentate Valve	0 - 3 bar	0,3 - 0,4 bar	100 - 900 l/h	plug valve-2 way	George Fischer	Type 546 - DN20	Biomass	
R-Vlv-09	Exhaust Valve Bioreactor	0,3 - 0,4 bar	Atmospheric		exhaust valve	Swagelok		CH4 + CO2 + H20	
R-Vlv-10	Exhaust valve Feed Tank	0,5 - 1 bar	Atmospheric		exhaust valve	Swagelok		N2	
R-Vlv-11	Feed Tank Drain	0,5 - 1 bar	Atmospheric		plug valve-2 way	Swagelok	Tyoe 546 - DN20	Raw Influent	
R-Vlv-12	Sampling Valve	0,3 - 0,4 bar	Atmospheric		plug valve-2 way	George Fischer	Type 546 - DN20	Biomass	

Table 2 : Equipments specifications

Code	Description	Nominal Flow	Inlet pressure	Outlet Pressure	Supplier	Fluid	Type of pump
F-Pmp-01	Circulation Pump	100 - 900 l/h	0,4 bar	0,4 - 3 bar	PCM	Biomass	gear pump
G-Pmp-01	Gas circulation loop	0,5 l/min	0,3 - 0,4 bar	0,5 bar	KNF	Gas (CH4 and CO2)	diaphragm pump
R-Hxt-01	Heat exchanger					Biomass	
R-Pmp-01	NaOH Injection Pump		Atmospheric	0,3 - 0,4 bar	Hanna	NaOH	plunger pump
R-Pmp-02	Bioreactor feed	17 L/h	0,5 - 1 bar	0,3 - 0,4 bar	ATC	Influent	peristaltic pump
R-Str-01	Stirrer				Agitec	Biomass	
R-Tnk-01	Bioreactor						
R-Tnk-02	Feed Tank						
R-Tnk-03	NaOH Tank						
TR-Cry-01	Cryothermostat				Lauda	H20	
TR-Pmp-01	Temperature pump	11 l/s			Lauda	H20	centrifugal pump

Table 3 : Monitoring equipment specifications

Code	Description	Supplier	Model	Range	Nominal Value	Fluid
R-P-01	Bioreactor pressure	Wika		0 - 1 bar	0,3 - 0,4 bar	Gas (CH4 + CO2 + Water)
R-pH-01	Bioreactor pH	Hanna	pH 502	0 - 14	5,2 - 5,6	Biomass
F-FP-01	Permeate Flowmeter	Brooks	R2-15-A Saphir	0 - 1.6 l/h		Permeate
R-T-01	Bioreactor temperature	Cuenot	Pt 100	0 - 100°C	55°C	Biomass
F-P-01	Membrane Inlet Pressure	Hendress	PMP 131	0 - 4 bar		Biomass
F-P-03	Permeate Pressure	Hendress	PMP 131	0 - 4 bar	0,3 - 0,4 bar	Permeate
G-Analyser-01	Gas Analyser	Dräger	X-am 7000			CO2 - O2 - CH4
F-P-02	Membrane Outlet Pressure	Hendress	PMP 131	0 - 4 bar		Biomass
R-P-02	Feed Tank pressure	Wika		0 - 1 bar	0,5 - 1 bar	Gas (N2)
G-P-01	Gas loop pressure	Swagelok		0 - 1 bar		Gas (CH4 + CO2 + Water)
G-F-01	Gas loop flowmeter	Brooks	R-2-15-D Tantale	0 - 78 l/h Air	0,5 l/min	Gas (CH4+CO2)
F-FR-01	Retentate Flow	KROHNE	Deltaflux DN15- PN40	0 - 1000 l/h	100 - 900 l/h	Biomass
F-T-01	Retentate Temperature	Bourdon	PT100 - TR	0 - 100°C	55°C	Biomass

III.2. Hardware tests

To estimate the reactor functioning capacity a first trial was performed from July 1st to July 23rd of 2008.

The results presented are not really representative of the system functioning because:

- the reactor was functioning during a too short period to reach steady state conditions (see the figure representing the gas production);
- the technical team had to improve its knowledge on MBR and analytical methods control

So the comments and figures below have to be considered as first information but not as relevant results. During this period, the HRT was fixed at 20 days.

III.2.1. Start-up

The bioreactor was fed with 20 L of inoculum supplied by UAB and addition of 5 L of demineralised water.

The temperature was gradually increased until reaching 55°C.

The operating procedure included sequencing feeding and permeate extraction, the recycling velocity was maintained constant in the loop. An extraction of 1.25 L of permeate was carried out every day by filtering through the Atech 50 nm membrane (i.e.the membrane initially selected and used for CI).

For a 25 L reactor volume operating at 20 days of HRT, the feeding flow is 1.25 L/day.

Each day feed is prepared using the following procedure, as defined for CI:

- weighing of about 288 g of Fresh Solid Mixture;
- adding demineralised water until a 1.25 L volume is acquired;
- introducing the feed in the MBR.

The composition of the Fresh Solid Mixture supplied by MPP is the following:

- Lettuce 13.8 kg;
- Red Beet 8.6 kg;
- Milled straw 0.5 kg;
- Toilet paper 0.204 kg.

III.2.2. Results

Reactor worked on for 22 days. During the period of extraction, the permeate flux gradually increased from 20 to 50 L/h.m² (the average volume of permeate per day remaining constant and equal to 1.25 L/d corresponding to a HRT equal to 20 days); the tangential velocity was fixed to 4 m/s. The working trans-membrane pressure TMP evolved between 0.2 and 0.7 bar (See Figure 4).

For comparison, the operating conditions applied with the CI compartment were:
- Permeate flux :between 2 and 5 L/h.m²;
- Hydraulic retention time: 10 days;
- Tangential velocity : 2.5 m/s

For these conditions, TMP fluctuated between 0.1 and 0.8 bar.

No direct relation between flux and TMP could be defined for this run (probably due to the evolution of DM concentration inside the reactor, the increase of salinity, and some problems of pH and temperature control) but no critical fouling phenomenon was detected pointing out the interest of the membrane material to the filtration of such suspension.

At the end of this trial, the membrane permeability was measured with water and then the membrane was cleaned. The water permeate flow after trial was equal to 95 L/(h.m².bar) at 25°C what corresponds to 16% of the permeability of the cleaned membrane. Because no deposit was observable on the membrane surface, the permeability variation is due to irreversible fouling (thin biofilm, pore blocking and adsorption).

The water permeate flow after alkali and acid cleanings was equal to 590 L/(h.m².bar) at 25°C (theorical flux: 700 L/(h.m².bar) and Initial flux : 1280 L/(h.m².bar)).

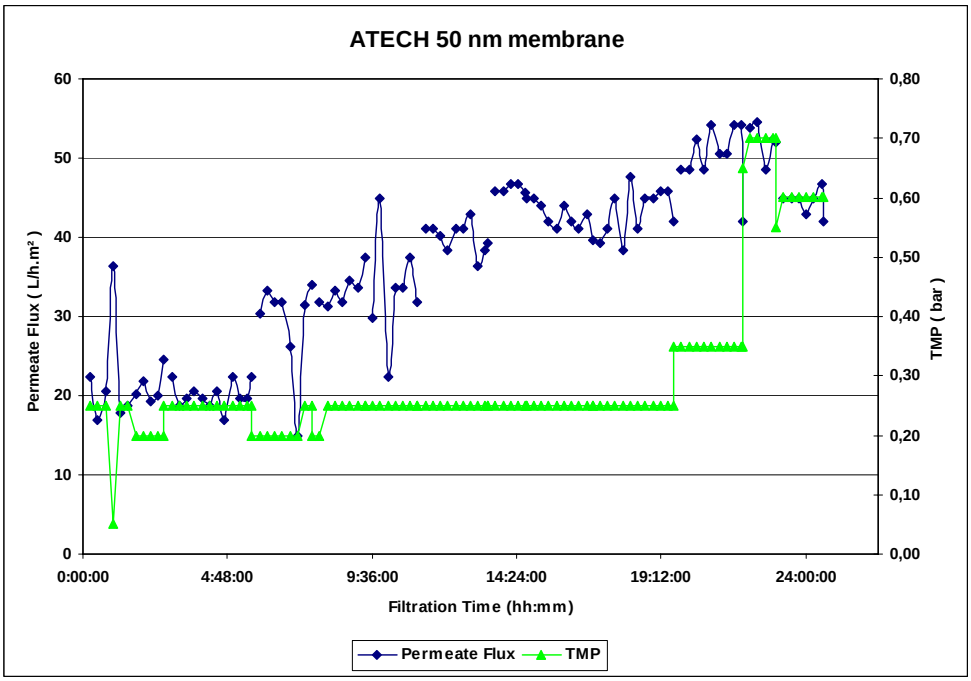

Figure 4 : Evolution of the permeate flux and TMP over time

III.2.3. Reactor follow-up

The evolution of the bulk characteristics is observable on Figures 5, 6, 7 and 8, and the gaseous composition in Figure 9.

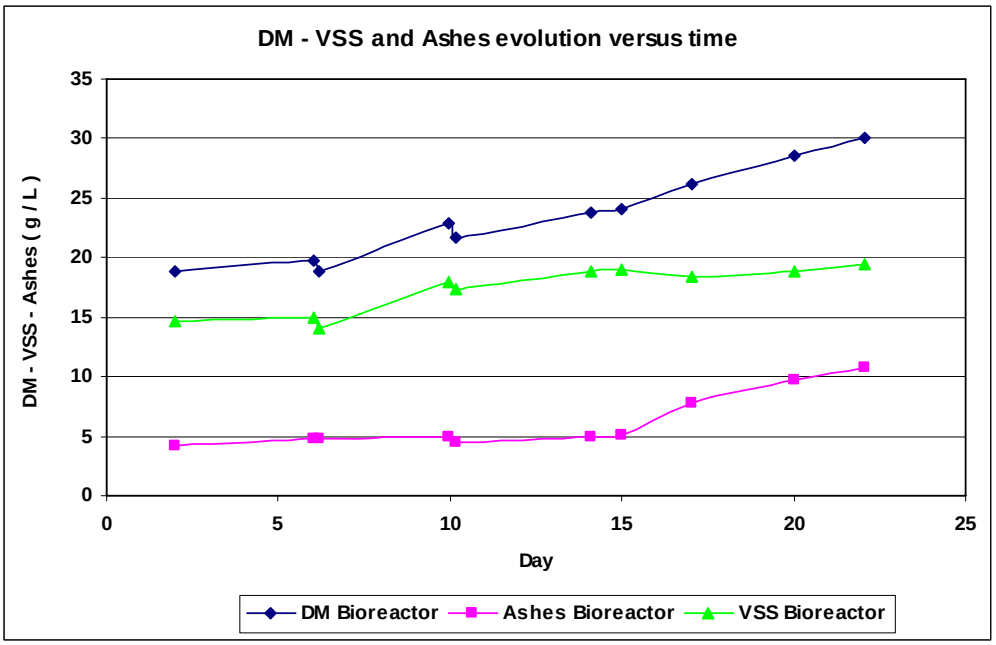

Figure 5 : DM, VSS and ashes evolution versus time

Dry matter concentration increased gradually from 18.8 to 30.1 g/L.
pH was maintained in the range of 5 to 5.5 except for one day.
VFA production appeared effective induced by fermentation.
CO_2 production in the gas phase in the reactor headspace appeared after day 15.

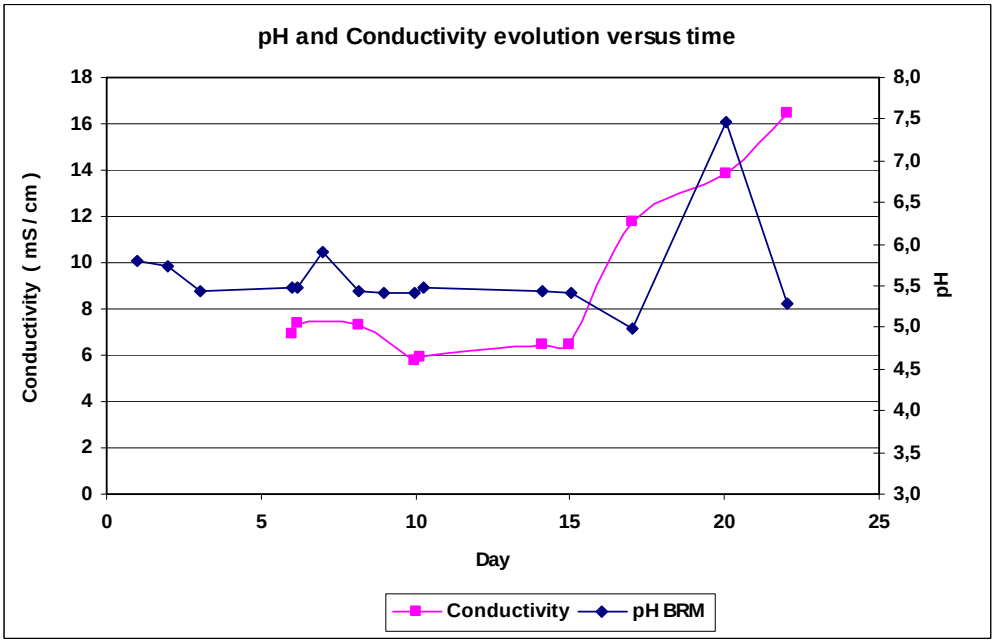

Figure 6 : pH and electroconductivity evolution versus time

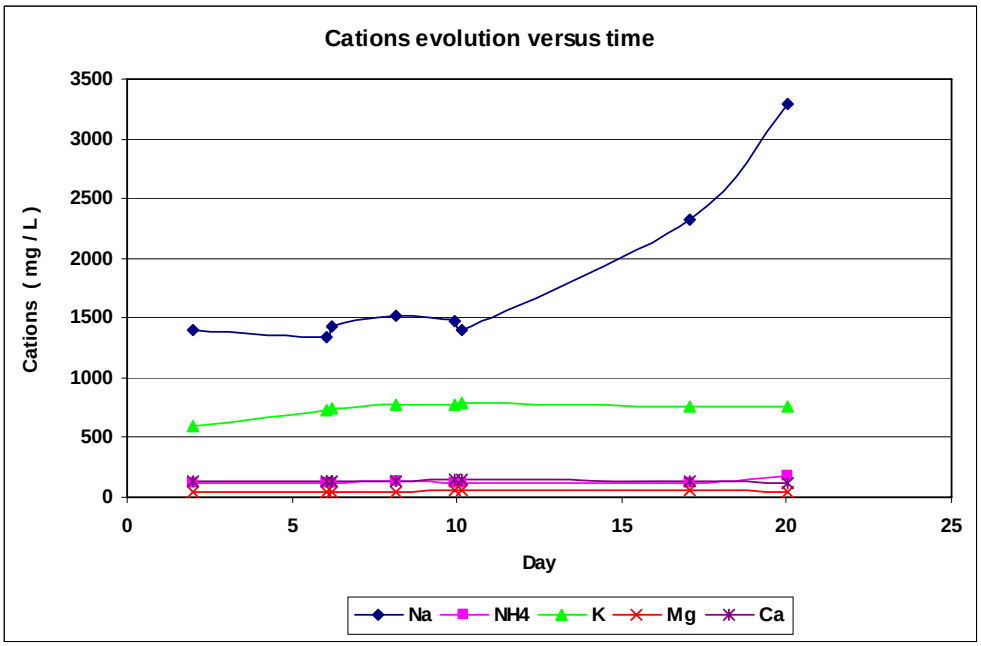

Figure 7 : Cations concentration evolution versus time

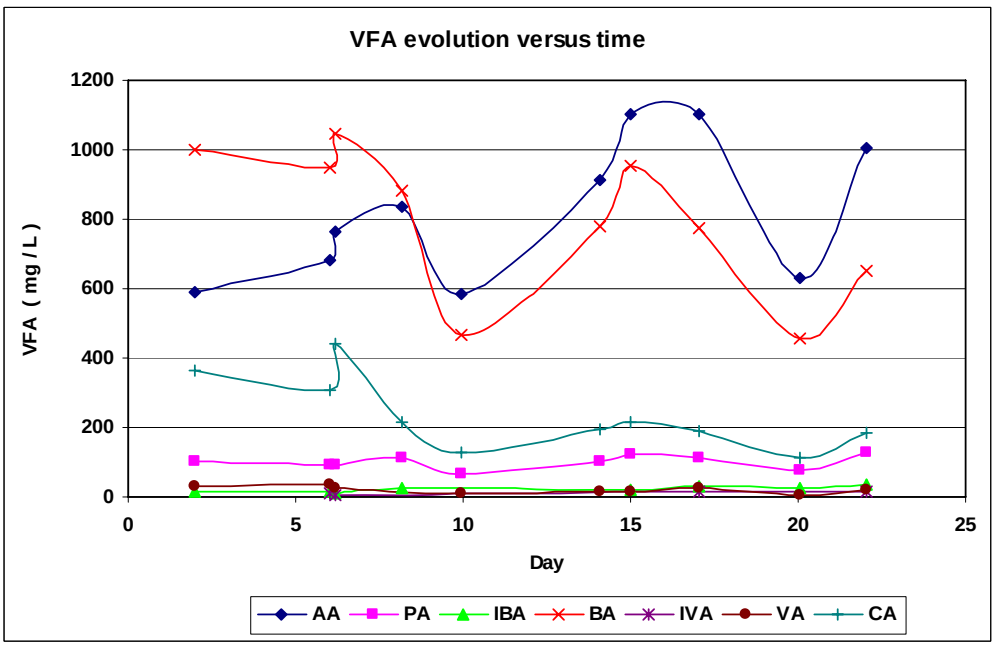

Figure 8 : VFA concentration evolution versus time

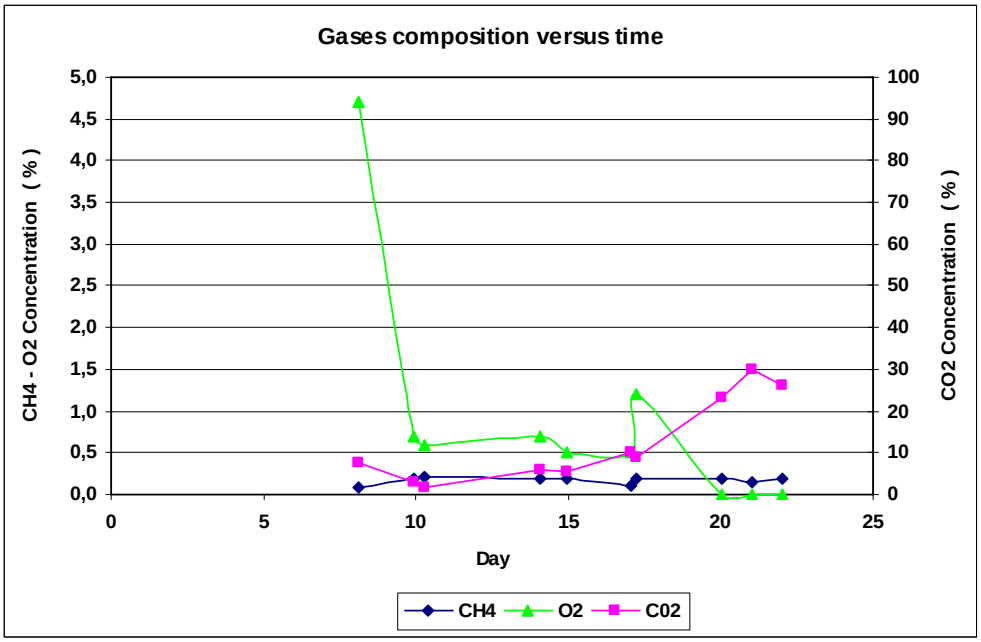

Figure 9 : **Gases composition evolution versus time**

III.2.4. Encountered Problems

Faulty pH regulation:

The reaction being very slow, a high amount of alkali was injected on July 17th.

Since this day, a significant increase of electroconductivity, ashes and sodium concentrations was observed.

III.2.5. Stop of trial

Reactor was drained on July 23rd. (after 22 working days).

Inoculum was recovered in two bottles (20L in a PE bottle and 5 L in a glass bottle). These bottles were hermetically closed and stored in a cold room between 4 and 5°C.

Reactor and the filtration loop were rinsed with demineralised water.

IV. Analytical methodologies

IV.1. Calibration of VFA analysis

IV.1.1. Description of the purchased equipment

The used equipment is a Delsi Instruments . The main characteristics of the equipment are given below:

GC Model: Delsi Instruments DI200
Detector: FID
Injector port: split/splitless
SW: PeakSimple 2.83
Injection mode: split/splitless

IV.1.2. Calibration phase

IV.1.2.1. Materials and reagents

- **Gas chromatography column**

The column used for these experiments is a fused silica STABILWAX-DA semi-capillary column from Restek. Column dimensions are 15m x 0.53mm x 1µm, corresponding to the length, inner diameter and thickness of the stationary phase film, respectively. The stationary phase is bonded with PEG specifically deactivated for acidic compounds.

- **Standards**

The standard solution of a mixture of VFA at concentration of 0.4 g/L was prepared with MilliQ water. Final Mixture solutions of the following concentrations: 0.2, 0.1, 0.05 and 0.025 g/L of each compound were also prepared with MilliQ water from stock solution 0.4 g/L.

Glacial acetic acid was obtained from Riedel-de-Haën. Valeric acid was obtained from Aldrich. Propionic acid, isobutyric acid, butyric acid, caproic acid and isovaleric acid were obtained from Fluka.

In order to keep the syringe clean, methanol from Sigma-Aldrich and MilliQ water were used.

Standards and samples were stored in a fridge (at 4°C). After analysis, samples were frozen (at -18°C).

IV.1.3. Method for analysing VFA and standardisation

IV.1.3.1. Gas chromatography method

This method has been developed by MPP.

A chromatographic method was identified for the analysis of VFA. Helium was used as a carrier gas. H_2 and Air were used in order to get ignition from the Flame Ionisation Detector (FID). The split ratio was 10 taking account of the concentration range of VFA.

Method parameters are described below:

- Injector temperature: 220°C;
- Column temperature program: from 100°C to 160°C at a rate of 10°C/min – 160°C during 4 minutes;
- Pressure: 26.5 kPa;
- Column flow: 8 ml/min;
- Injection size: 1 µL;
- Injection mode: split;
- Liner: Di 200 – L=80;
- Detector temperature: 275°C.

IV.1.3.2. Calibration method

External standard method was chosen for calibration, by using individual calibration curves done for each VFA. Calibration curves of standards and analysis of samples must be performed under identical conditions (Novak, 1988). No adding of internal standard compound to samples is required for this method.

IV.1.3.3. Injection method

The syringe used is a Hamilton 7 500 of 1 µL.

Before and after each sample, the syringe is cleaned 5 times with methanol and 5 times MilliQ water.

IV.1.4. Results

IV.1.4.1. Chromatography

Time of analysis is an important parameter for a control tool: hence retention time of VFA was decreased in order to achieve a shorter time of chromatographic analysis per sample.

The use of a short length column (15m) allowed eluting all VFA in few minutes and still good resolution of peaks was maintained.

As it can be observed on Figure 10, all VFA are eluted separately in 10 minutes.

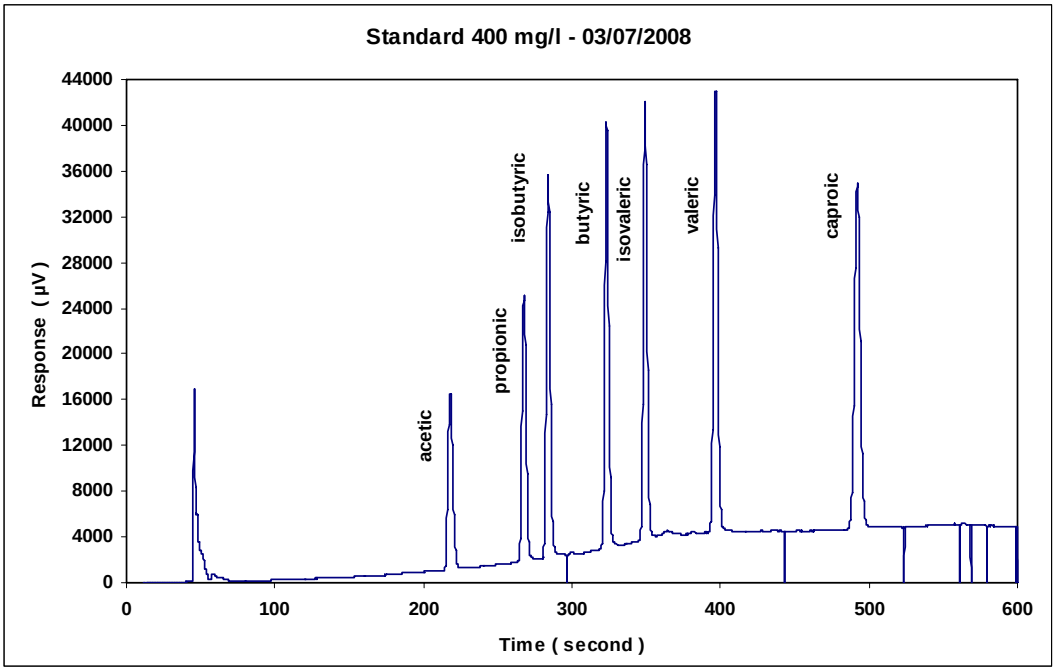

Figure 10 : VFA Chromatogram

IV.1.4.2. Linearity

Calibration curves were obtained by analysing all standard samples, which were analysed in triplicates. Correlation factors (R^2) were calculated for each compound. Good results of linearity ($R^2 \geq 0.998$) for all VFA resulted from these calibration tests (Table 4).

Table 4 : Results of linearity and reproducibility

Compound	Split 10		
	Conc. Range of compound (mg/L)	R^2	RSD* (%) n=3
Acetic acid	25-400	0,9983	3,47
Propionic acid	25-400	0,9981	2,13
Isobutyric acid	25-400	0,9985	2,04
Butyric acid	25-400	0,9989	2,51
Isovaleric acid	25-400	0,9985	2,55
Valeric acid	25-400	0,9984	4,76
Caproic acid	25-400	0,9982	5,26

**Mean value of Relative Standard Deviations (RSD)*

IV.1.4.3. Precision and accuracy

Precision was studied by measuring the reproducibility of peak areas. Reproducibility was measured by calculating the relative standard deviation (RSD) of peak areas for three

repeated analysis of each sample. Results of RSD of individual samples of all different concentrations range from 0.3 to 11%. In addition, average values of RSD of each VFA were calculated from all the RSD values for a given VFA. These averages RSD are represented in Table 4 and range from 2 to 5%.

Accuracy is measured by the relative error existing between the real concentration and the theoretical concentration obtained by the calibration curve of standard samples. Relative errors were calculated for all VFA for all concentrations. Values of relative error of each VFA are represented in Table 5.

Table 5 : Results of accuracy represented by the relative error of analysis of standard samples

Split ratio	Concentration of compound (mg/L)	Relative error (%)						
		Acetic acid	Propionic acid	Isobutyric acid	Butyric acid	Isovaleric acid	Valeric acid	Caproic acid
10	25	20,65	16,51	12,17	13,27	11,45	17,02	15,59
	50	0,75	3,77	4,24	2,81	3,84	3,07	3,66
	100	0,57	0,81	1,22	0,40	1,50	0,32	1,02
	200	5,21	5,70	5,26	4,38	5,15	5,21	5,60
	400	1,08	1,14	1,04	0,91	1,00	1,07	1,12

IV.1.5. Conclusion

Obtained results with standard solutions are similar to those obtained by UAB (TN 62.12).

IV.2. Analysis of liquid samples from compartment I

Retentate sample is collected by using a valve device located at the circulation pump outlet, at the filtration loop level. Sample is collected directly at the tube outlet.

Retentate samples are diluted 5 times by using a Gilson diluter, and filtered through Minisart 0.2µm filters. Permeate samples are diluted 5 times.

If samples are not analyzed in the first 6 hours, they are stored in fridge between 4 and 6°C. Samples are frozen after analysis. Each sample was analysed in triplicate.

Next table shows results obtained on the retentate dating from 24/09/2008.

Table 6 : Results of retentate analyses dating from 24/09/2008 (Dilution x5)

Compound	Concentration (g/L)			Conc.		
	1	2	3	Average	SD	% RSD
Acetic acid	364	433	305	367	64,1	17,4
Butyric acid	388	489	328	402	81,4	20,3
Caproic acid	20	24	19	21	2,7	12,8

RSD are significantly high on samples (between 12 and 20%) comparing to RSD calculated from standards in the same concentration range (<1% for 400ppm and 10% for 25ppm).

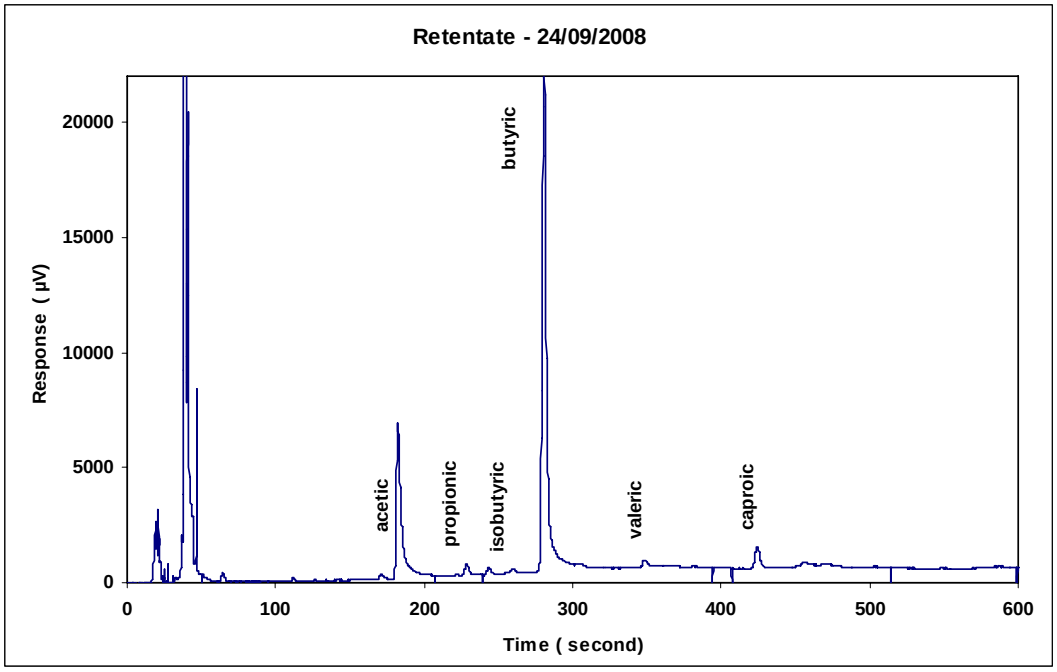

Figure 11 : Retentate Chromatogram

We can also notice a fast pollution of injection liner and septum. So, regular disassembling and cleaning of liner and septum replacement is recommended.

Although, these pollutions cannot explain important gaps measured on samples.

Due to this previous remark, the collected samples, for the long duration test, were sent to the LGCB (Laboratoire de Génie Chimique et Biochimique) of Clermont-Ferrand (F-63000).

The samples were analysed by Liquid Chromatography.

Samples are deproteinized not to clog the HPLC columns. For this, 2 mL of sample are mixed with 0.25 mL of BaOH (0.3 M) and 0.25 mL of ZnSO4 (5%) then centrifuged 5 minutes at 10,000 g and filtered (Filter Millipore of 0.2 µm) before being injected.

The used hardware is a chromatograph Agilent 1100. The HPLC chain used is equipped to two ion exclusion columns (Phenomenex Rezex ROA 300 x 7.8 nm) mounted in series and placed into an oven thermostat at 50°C. The eluent is a solution of sulphuric acid 2mM diluted with MilliQ water /ultrapure water(Millipore, MilliQ plus), degassed continuously with a degasser (Ney, Ultrasonik 300) incorporated into the hardware. The elution flow is set to 0.7 mL.min^{-1} using a pump (HP serie 1100, Agilent Technologies). The chromatograph has a fixed loop automatic injector (Agilent valve Rheodyne) which delivers 10 µL. The different compounds in the sample are detected by means of a refractometer (HP serie 1100). The detector delivered signals are treated by an integrator (HP serie 1100). The acquisition is carried out by the software HPChem (Agilent Technologies). The quantifiable compounds by our method are the cellobiose, the glucose, the fructose, the succinate, the lactate, the formiate, the acetate, the propionate, the isobutyrate, the butyrate, the isovalerate and the valerate for which standard range were established.

V. Membrane selection

V.1. User's requirement

The requirements for this membrane selection have been previously define in TN94.41.

V.2. Tested membranes

The different tested membranes and their characteristics are presented in Table 7

Table 7 : Membranes characteristics

Supplier	Filtration threshold	Length (cm)	Internal diameter (mm)	Surface (cm^2)	Layer	Support material	Theoric Flux ($L/h.m^2.bar$)	Initial Flux ($L/h.m^2.bar$)
Kérasep	0.1 µm	40	6	75	Zirconia	$Al_2O_3 – TiO_2$	>1250	2180
Kérasep	300 kD	40	6	75	Zirconia	$Al_2O_3 – TiO_2$	>300	400
Atech	50 nm	85	8	214	Zirconia	Alpha alumina	700	1280
Exekia	100 nm	25	7	55	Zirconia	Alpha alumina	2030	3670
Tami	300 kD	120	6	226	Titanium	Titanium	800	900

The membrane selection key parameters are as follows:

- the membrane material;
- the filtration threshold;
- the circulation flow (velocity/permeate flow ratio).

The materials tested for the filtration layer are zirconium oxide and titanium oxide. The support material can be alpha alumina, titanium or silica-aluminates.

V.3. Operating conditions

V.3.1. Operating conditions of the bioreactor

To compare the membrane performances, the MBR functioning conditions are imposed as presented in Table 8

Table 8 : MBR functioning conditions

Dry Matter	35 - 45 g/L
Ashes	4 - 6 g/L
pH	5.1 - 5.6
Electroconductivity	4 - 4.5 mS/cm
Temperature	55 ±2.5 °C
Permeate Volume	1.25 - 2.5 L/d
HRT	20 - 10 days

The hydraulic retention time HRT was equal to 20 days from August 25th to September 05th to favour the progressive development of the culture. As soon as the fermentation was observed and stabilized, HRT was decreased to 10 d (with a simultaneous increase of the organic load OL). Since September 08th (day 14), HRT is equal to 10 days.

The functioning of the bioreactor was continuous with a daily feed of substrate (about 2 g DM/L/d) present in a 2.5 L volume of liquid. To compensate the introduction of liquid, a 2.5 L daily volume was extracted from the system on the permeate line when working without sludge extraction (i.e. draining of the bioreactor).

When working with sludge extraction, the global volume of (permeate and sludge extraction) was equal to 2.5 L/d.

V.3.2. Feed preparation and operation procedures

For a 25 L reactor volume operating at 10 days of HRT, the feeding flow is 2.5 L/day.

Each day feed is prepared using the following procedure, as defined for CI:
- weighing of about 577 g of Fresh Solid Mixture;
- adding demineralised water until a 2.5 L volume is acquired;
- introducing the feed in the MBR.

The composition of the Fresh Solid Mixture supplied by MPP is the following:
- Lettuce 13.8 kg;
- Red Beet 8.6 kg;
- Milled straw 0.5 kg;
- Toilet paper 0.204 kg.

The analysis performed on the different lots indicated that the Dry Matter concentration was about 20 g/L and the ashes concentration was about 2.5 g/L.

In these conditions, the organic load introduced in the MBR was equal to 2.1 gDM/L/day.

V.3.3. Operating conditions of the filtration unit

Operating conditions of the filtration are stated in the following Table:

Table 9 : Operating conditions of the filtration unit

Velocity	1 – 4 m/s
Filtrate flow	1.25 – 2.5 L/day
Flux	20 – 70 L/h.m²
TMP	0.1 – 1 bar
Retentate flow	100 – 700 L/h

Two modes of functioning were used:
- sequenced mode;
- continuous mode.

The sequenced mode was used to compare the different membranes.

According to the imposed instantaneous permeate flux and the membrane surface, the daily time of filtration was adapted to check a daily volume of extraction of 2.5 L.

At the end of each production step, the circulation flow was maintained and the permeate flow was stopped.

The continuous mode was used to evaluate the clogging over a period of time on the two membranes which were selected during the previous step.

At the end of each production step, the circulation and permeate flows were maintained. The permeate could be recycled into the MBR if necessary to maintain the defined HRT.

The following Figure shows the DM evolution over the whole period of test as well as the planning of tested membranes.

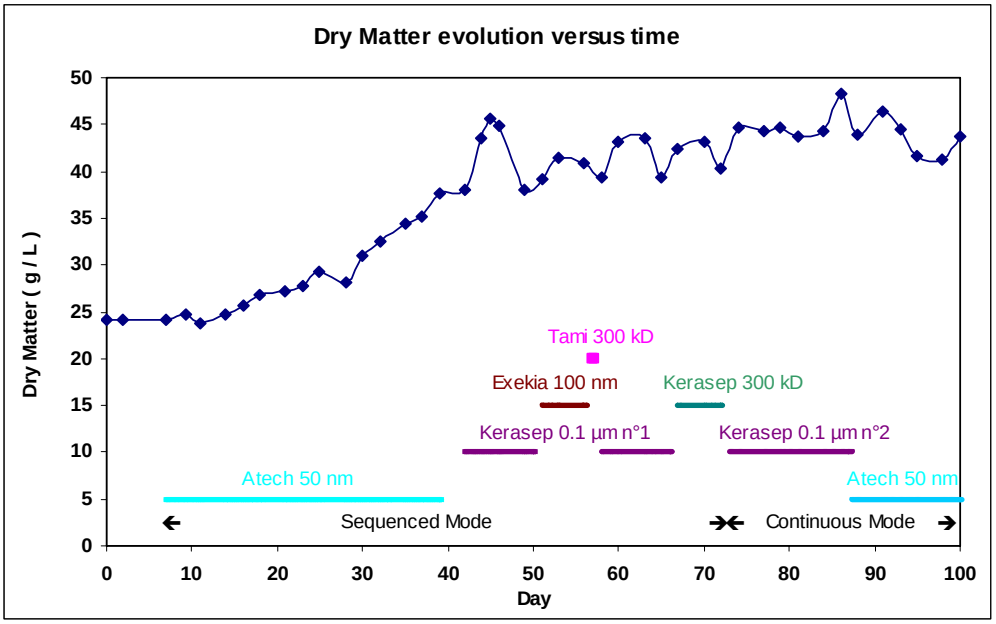

Figure 12 : Dry Matter evolution and membrane tests plan

To minimize compounds accumulation on the membrane surface, an initial high cross-flow velocity (specific tangential flow rates inside the inner channel of the membranes) was chosen in the first runs (3 to 4 m/s). When checking the good behaviour of the system for such velocities, runs were carried on at lower cross-flow velocities (1 to 2 m/s) to decrease the energetic costs linked to retentate circulation.

During the runs, the permeate flux was imposed and the membrane fouling dynamics was evaluated by the trans-membrane pressure TMP evolution (consequence of the membrane fouling).

The longitudinal evolution of the pressure along the membrane length was also evaluated to point out any eventual clogging of the membrane pipe (membrane channel).

The membrane fouling intensity was evaluated:

- before filtration steps, on the new membrane by immersion inside the supernatant of the biological suspension. These tests were performed on each membrane to study the

membrane behaviour with the adsorption of little molecules in the soluble fraction (see paragraph V.5 Preliminary test).

- after all filtration steps by different chemical cleaning solutions.

V.4. Analytical follow-up

V.4.1. Mainly analysis

The conventional criteria to characterise the sludge composition and the pollutant abatement were measured with conventional standard methods.

Table 10 : Analytical parameters for the three phases

Solid phase	Liquid phase	Gaseous phase
Dry matter Ashes pH Conductivity VFA Anions : Cl, PO_4, SO_4 Cations : Na, NH_4, K, Mg, Ca	Dry matter Ashes pH Conductivity VFA Anions : Cl, PO_4, SO_4 Cations : Na, NH_4, K, Mg, Ca	CO_2 CH_4 0_2

In order to provide a good vision of the reactor's operation, the sampling frequency was the following:

- bioreactor : 3 samples a week (50 ml for each sample) filtrate : 3 samples a week (50 ml for each sample)
- influent batch : 1 sample in the first feeding and 1 sample from the last feeding for each batch of influent (50 ml for each sample)
- gas phase : one measurement per day (the gas analyser was installed on the output gas line)

V.4.2. Other analysis

Measurements of the biomass viscosity were carried out using a Haake viscometer.

Its characteristics are as following:

- Supplier: Haake;
- Type: Rotovisco RV20;
- Type of coaxial cylinder sensor system: Mooney-Ewart-system – ME30;
- Viscosity range: 10 – 100 000 mPas;
- Shear rate: 0.5 – 200 s^{-1}.

To determine the type of suspension behaviour, measurements were performed with three shear rates (50, 70 and 100 s^{-1}) and three DM concentrations at 55°C. The following Figure shows the measured viscosity in function of shear rate (the higher concentration corresponds to the suspension inside the reactor, the two others to the same suspension diluted with permeate).

The results point out the role of the concentration on the suspension viscosity. This variation appears as an exponential relation such as:

$$\mu_{C2} = \mu_{C1} \exp^{(k\, C2/C1)}$$

The value of k is depending of the velocity gradient. This kind of relation is commonly presented in literature. Because of the decreasing of viscosity with the velocity gradient the materials let appear a “pseudoplastic” behaviour.

From October 27th to December 04th, viscosity was measured for each retentate sample with a shear rate of 100 s^{-1}.

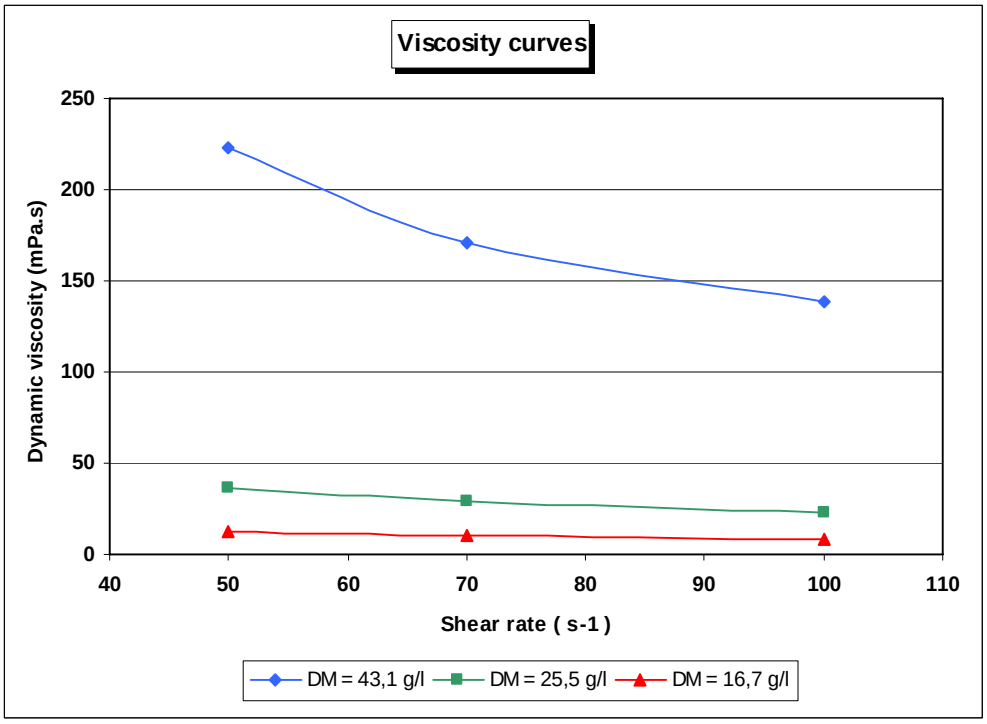

Figure 13 : Viscosity curves

V.5. Preliminary test

Before starting, four membranes were immersed in the biomass to measure the reduction of permeability only due to sorption phenomenon.

These trials were performed by using the MBR filtration loop.

The cross-flow velocity was fixed to 4 m/s and the permeate valve was closed to avoid any permeate production. Each trial lasted 4 hours.

Table 11 : Membranes permeability evolution

	Atech 50 nm	Exékia 100 nm	Tami 300 kD	Kérasep 0,1 µm
Theoric Flux (L/h.m².bar 25°C)	700	2030	800	>1250
Initial Flux (TM results) (L/h.m².bar 25°C)	1280	3670	900	2176
Flux after trial or steeping (L/h.m².bar 25°C)	95	557	555	1970
Flux after cleaning 1 (L/h.m².bar 25°C)	399	3075	515	No cleaning
Flux after cleaning 2 (L/h.m².bar 25°C)	735	2470	525	No cleaning
Final Flux (L/h.m².bar 25°C)	591	1780	669	1970

Initial and final fluxes and flux after trial or streeping have been measured in dead-end filtration.

The results pointed out the very weak sensitivity of the membrane KERASEP (0.1µm) to the irreversible fouling due to only adsorption of organic compounds present in the biological suspension by simple contact with the membrane.

In contrast, the effect of sorption appeared important for the three other membrane materials. The membrane EXEKIA appeared easy to regenerate by the first step of cleaning.

When the permeability of the membrane was not affected by adsorption during immersion tests (Kerasep 0.1µm), no chemical cleaning was practised.

When the regeneration of the membrane was easy, the chemical solutions used were NaOH and HNO_3. If the regeneration was difficult the cleaning procedure must include the presence of an oxidant (Cl_2 or H_2O_2).

Fluxes after cleaning have been measured in cross-flow filtration (on the cleaning pilot).

Atech 50 nm — Cleaning 1 : NaOH 10 g/l; 80°C; 30 minutes;
Cleaning 2 : HNO_3 3 g/l; 70°C; 20 minutes.

Exekia 100 nm — Cleaning 1 : NaOH 10 g/l and H2O2 0.2%; 70°C; 30 minutes;
Cleaning 2 : HNO_3 3 g/l; 70°C; 20 minutes.

Tami 300 kD — Cleaning 1 : NaOH 10 g/l and Cl_2 300 ppm; 70°C; 30 minutes;
Cleaning 2 : NaOH 10 g/l and H_2O_2 0.2%; 70°C; 30 minutes.

V.6. Membrane Bioreactor functioning

V.6.1. New start-up

Due to the faulty pH regulation during the hardware tests, incorrect amount of NaOH was added. As a result a high level of ions was detected in the biomass.

To decrease ashes and sodium concentrations, the reactor was filled with 20 L of inoculum and 5 L of deionised water.

During the first 10 days, the reactor was daily fed with 1.25 L of feeding (HRT = 20 d). After this first period, the introduced quantity was increased to 2.5 L (HRT = 10 d).

The first membrane used was the ATECH 50 nm membrane.

V.6.2. Bioreactor behaviour

Next figures present the evolution of some characteristic criteria of the bulk (solid and liquid phases) and the gas composition during the membrane selection tests (since August 25th) independently of the type of membranes tested.

V.6.2.1. Dry Matter, Volatile Suspended Solid and Ashes

The following Figure shows the DM, VSS and ashes evolution in the Bioreactor.

The initial DM concentration was equal to 24 g/l.

During the first 10 days, the reactor was daily fed with 1.25 L of feeding (HRT = 20 d). The DM concentration remained stable and the VSS concentration increased from 15.5 to 17.4 g/L due to the ashes decrease from 8.6 to 7.3 g/L.

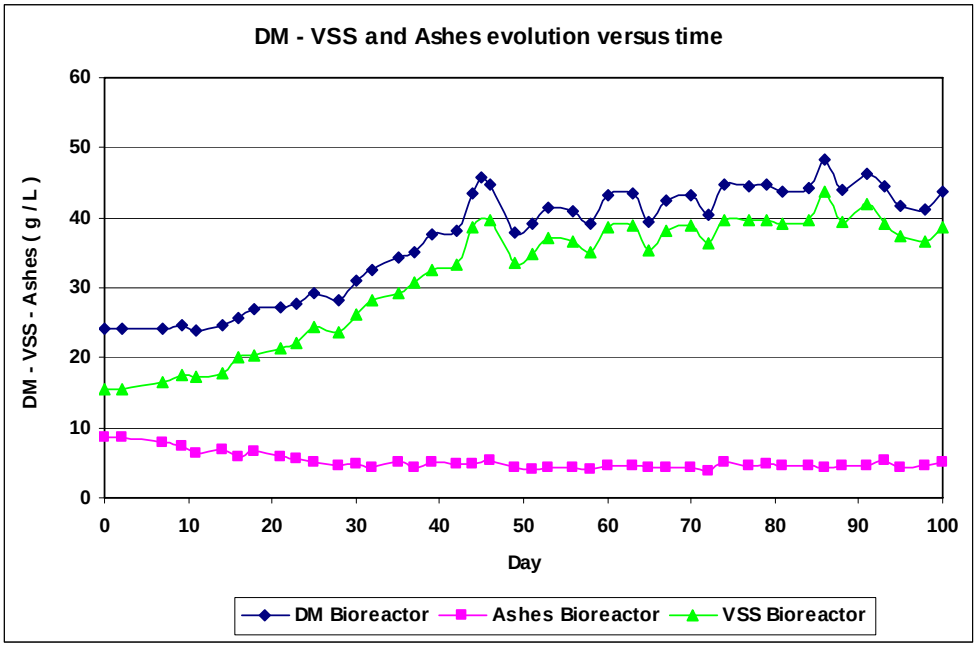

Figure 14 : DM, VSS and ashes evolution versus time in the bioreactor

After, the reactor was daily fed with 2.5 L of feed (HRT=10 d).

The nominal DM concentration (40 g/L) was reached on day 43.

To maintain the DM concentration around this nominal value, regular sludge extractions were performed.

The total sludge drained from the Bioreactor from day 43 to day 100 corresponds to 10.4 L, such a ratio corresponds to a sludge retention time greater than 100d.

Figure 15 allows the comparison of the DM and ashes evolutions inside the MBR and in permeate.

The retention of solids in suspension was total. The presence of DM in permeate corresponds to dissolved salts (the membrane DM retention was 75%) The ashes retention was hardly 10% what proved the membrane did not retain the mineral dissolved matter except if they are present as a solid form (precipitates).

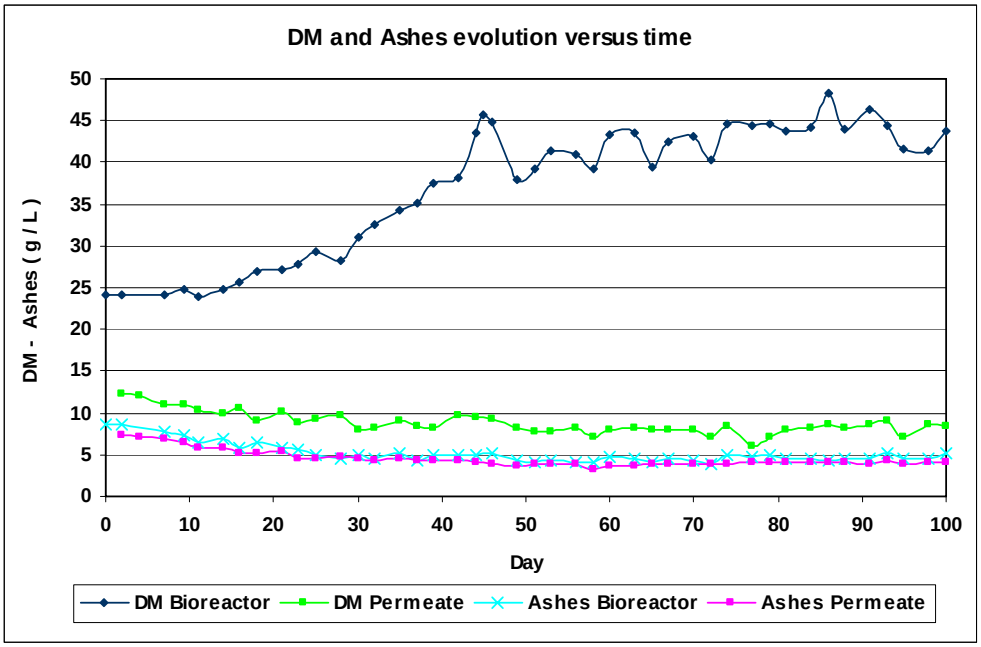

Figure 15 : DM, VSS and ashes evolution versus time in the BRM and permeate

V.6.2.2. Electroconductivity and pH

The following Figure shows the Electroconductivity and pH evolution of the suspension in the Bioreactor.

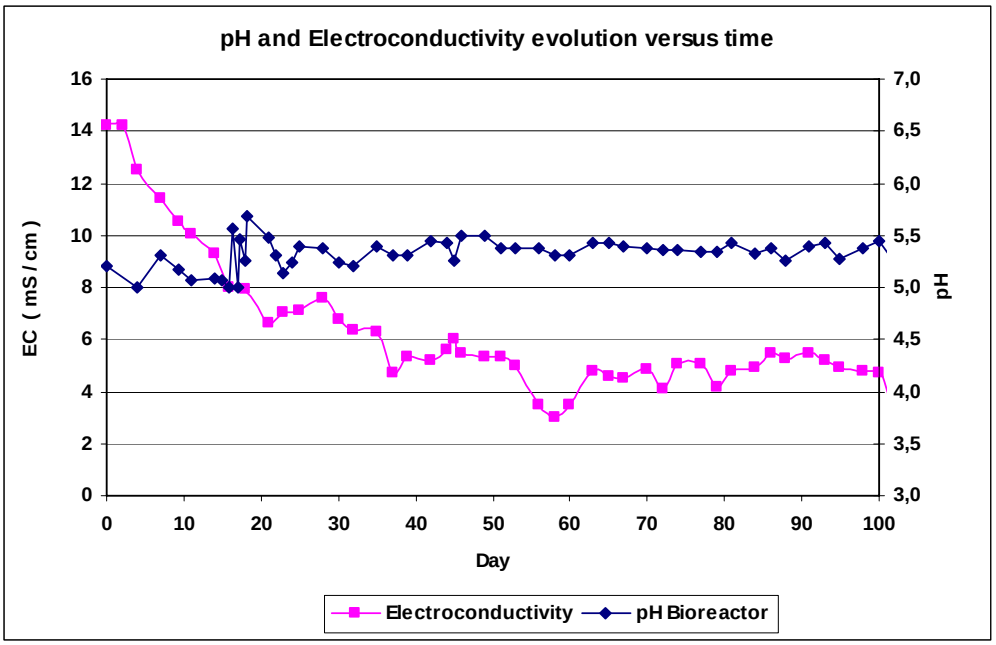

Figure 16 : Electroconductivity and pH evolution versus time in the bioreactor

A slight decrease of EC is observed. It is linked to the choice of practising dilution of feed with demineralised water. The permeate conductivity remains high, the reuse of the treated water must integrate this high conductivity value and a possible need of desalination.

The pH was easily maintained in the imposed range of values to avoid methane production but also salt precipitation.

The pH was controlled in the bioreactor by addition of base (NaOH 2 M). Of course addition of sodium hydroxide also induces the conductivity and the presence of sodium in the treated water.

The following Figure shows the added volume of NaOH versus time.

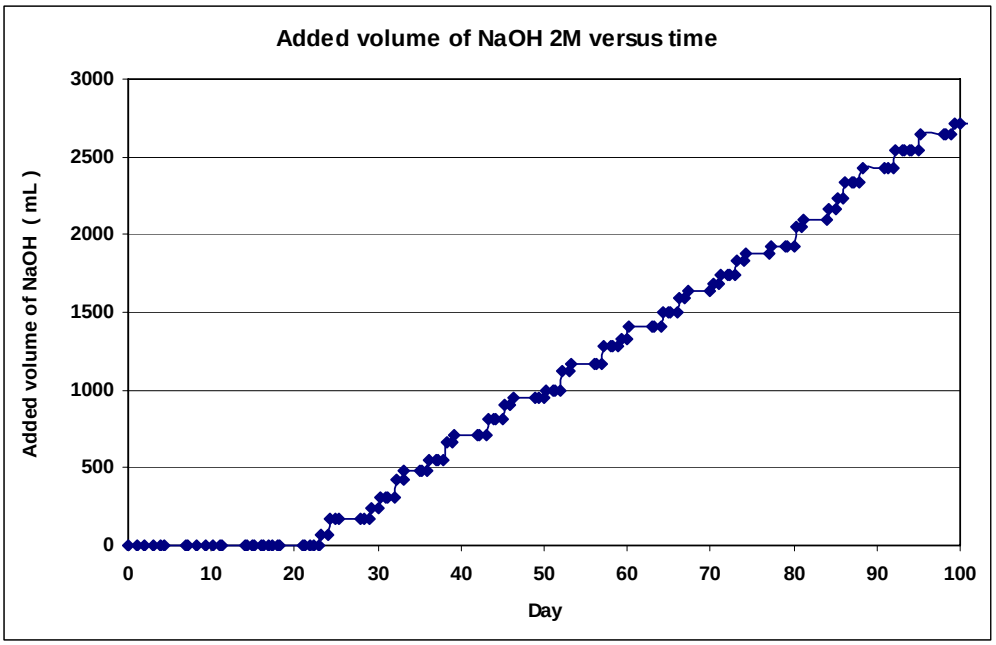

Figure 17 : Added volume of NaOH 2 M

No base was added till October 17th (day 23). Then, the daily added volume was around 35 ml.

The total added volume of base was equal to 2711 ml which corresponds at 217 g of NaOH.

Next Figure allows the comparison of the EC and pH evolutions inside the BRM and in permeate.

The pH was relatively stable in the bioreactor. The pH of the permeate was very similar.

The variation between two measuring of EC can be linked to the EC sensor and the high viscosity of the biomass.

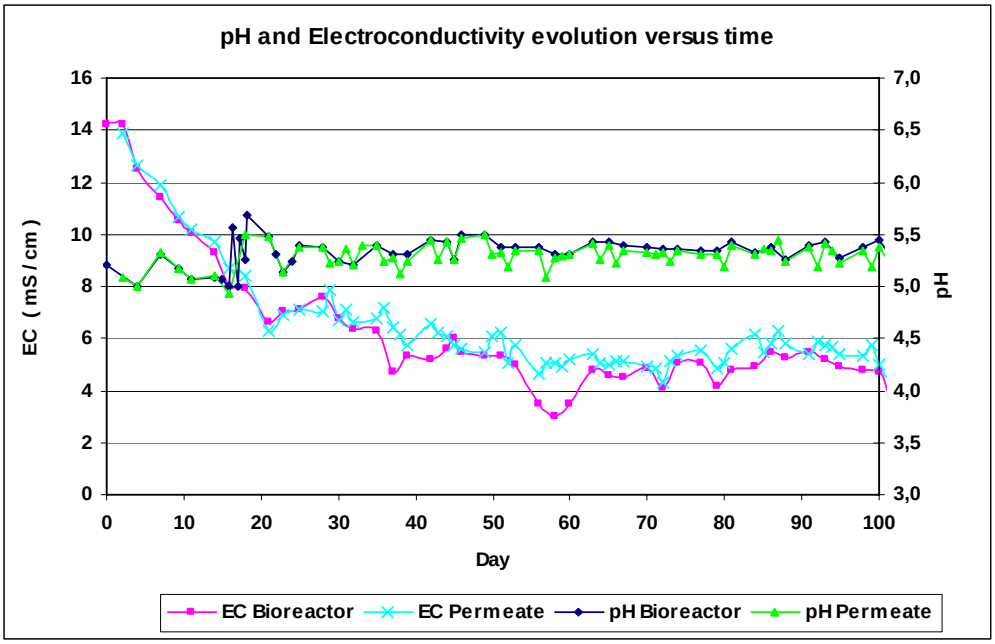

Figure 18 : EC and pH evolution versus time in the BRM and permeate

V.6.2.3. Cations

The following Figure shows the cation concentration evolutions in the Bioreactor.

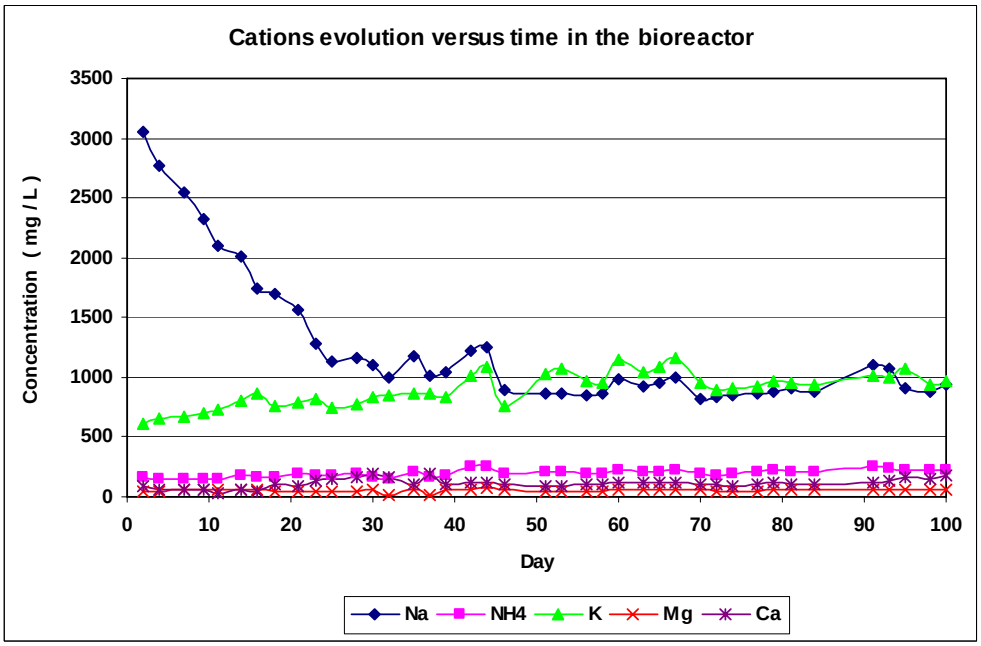

Figure 19 : Cation concentrations evolution versus time in the BRM

The following Figure shows the cation concentration evolutions in the permeate.

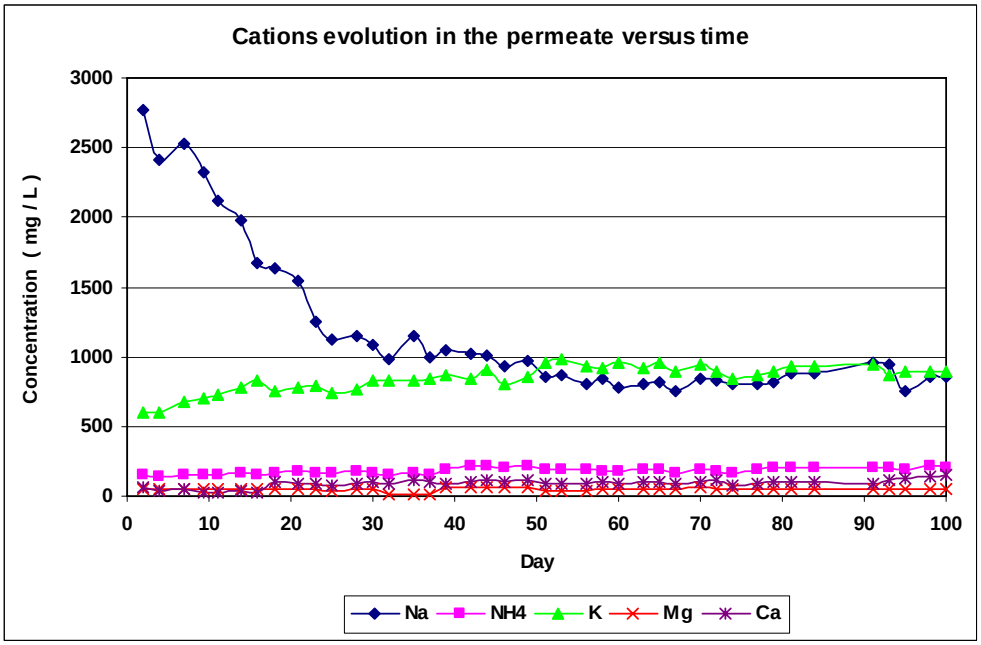

Figure 20 : Cation concentrations evolution versus time in the permeate

These figures show the evolution of the cation concentrations inside the bioreactor and in permeate. No difference can be noticed and then membrane has no effect on the cation retention. Let us notice the importance of the concentrations of cations notably Na, K (linked to the feed composition) and NH4 (linked to the organic matter digestion). Of course if necessary different ways of desalination can be proposed.

V.6.2.4. Anions

The following Figure shows the anion concentration evolutions in the Bioreactor.

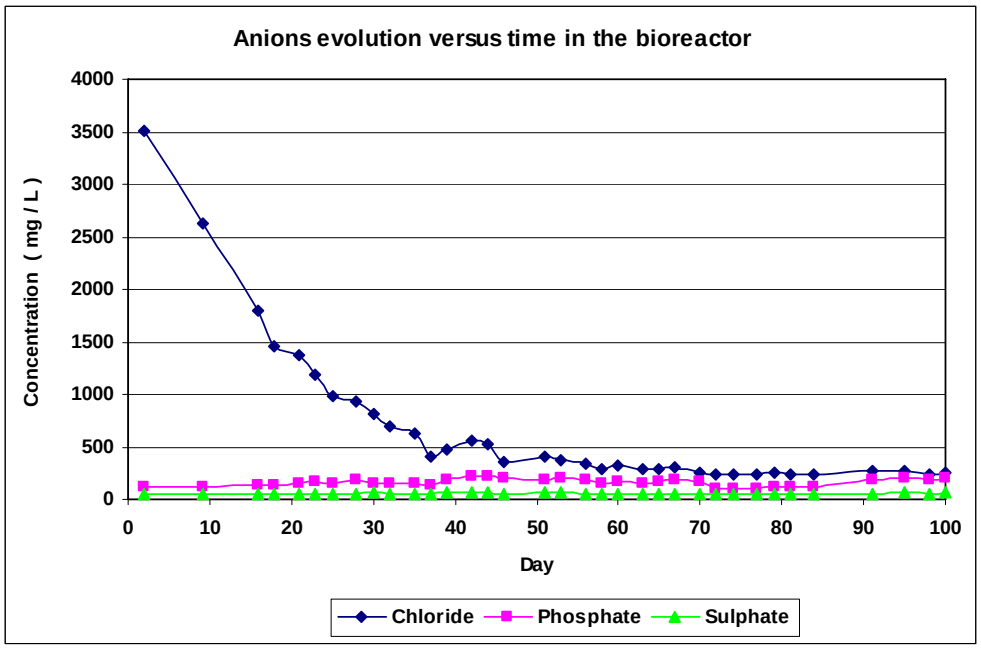

Figure 21 : Anion concentrations evolution versus time in the BRM

The following Figure shows the anion concentration evolutions in the permeate.

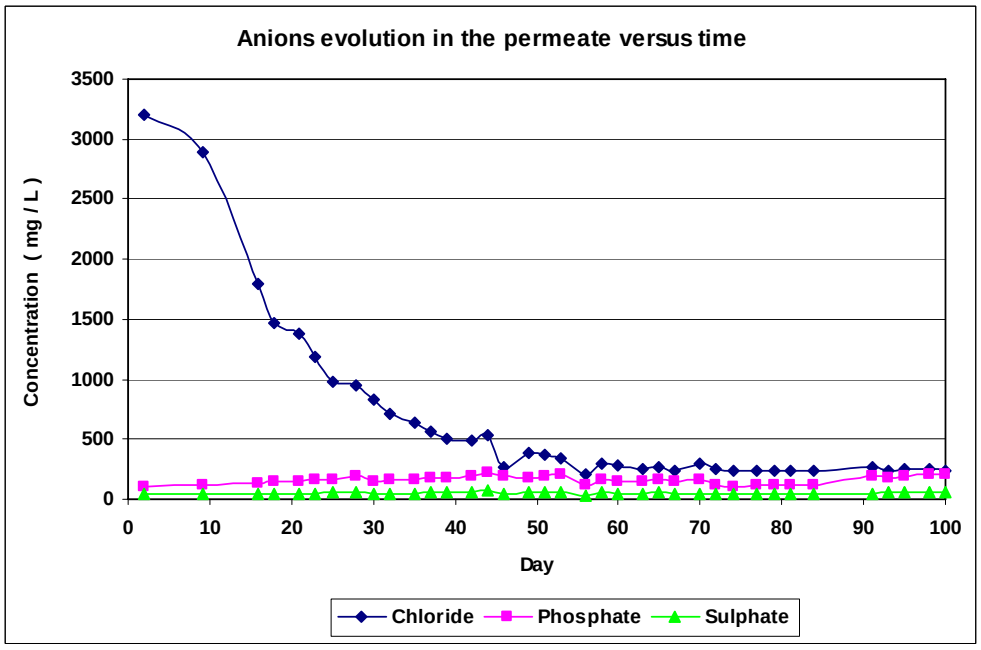

Figure 22 : Anion concentrations evolution versus time in the permeate

The same remarks can be developed for anions with an important presence of Chloride, sulfate and phosphate.

The following Figure shows the VFA concentration evolutions in the bioreactor. These results were obtained by using HPLC method

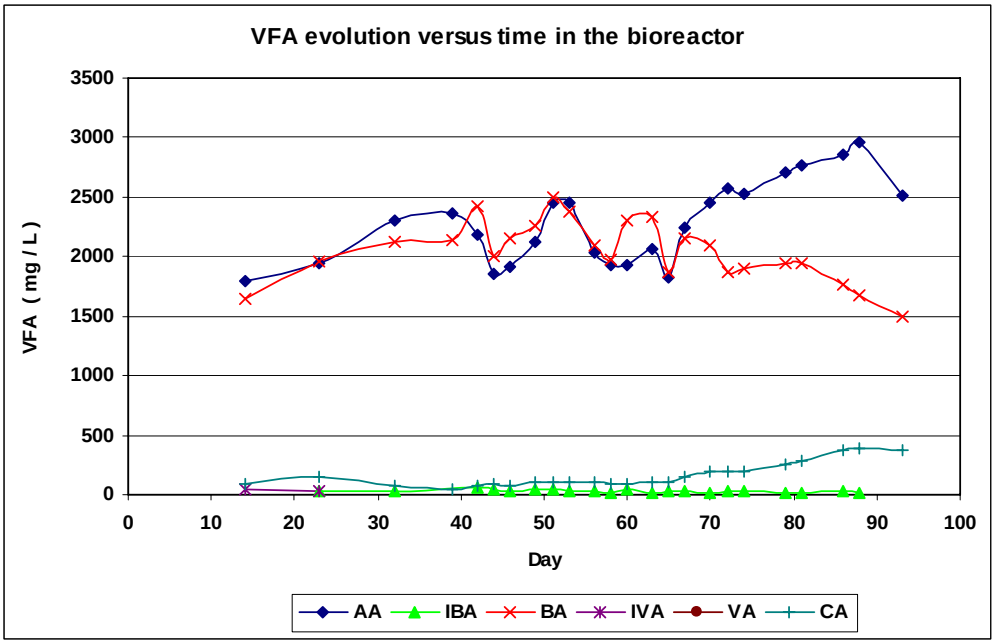

Figure 23 : VFA concentration evolution versus time in the bioreactor

The following Figure shows the VFA concentration evolutions in the permeate.

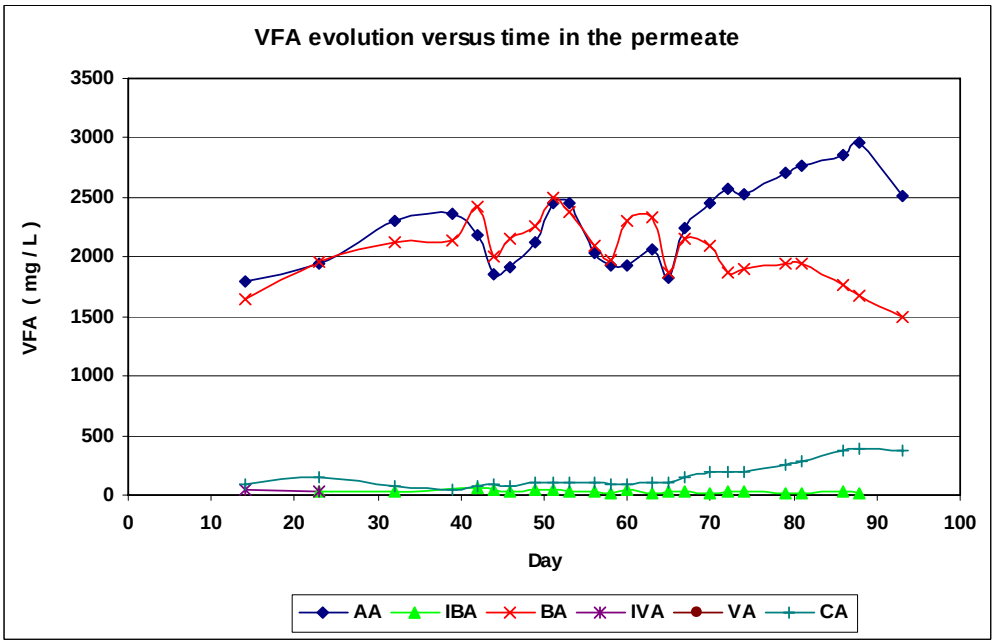

Figure 24 : VFA concentration evolution versus time in the permeate

These figures show:

- the stability of the biological behaviour of the MBR;
- The VFA composition appeared mainly linked to the presence of acetate and butyrate;
- The membrane barrier had no particular effect on the retention of VFA.

The following Figure shows the gas composition evolution in the bioreactor.

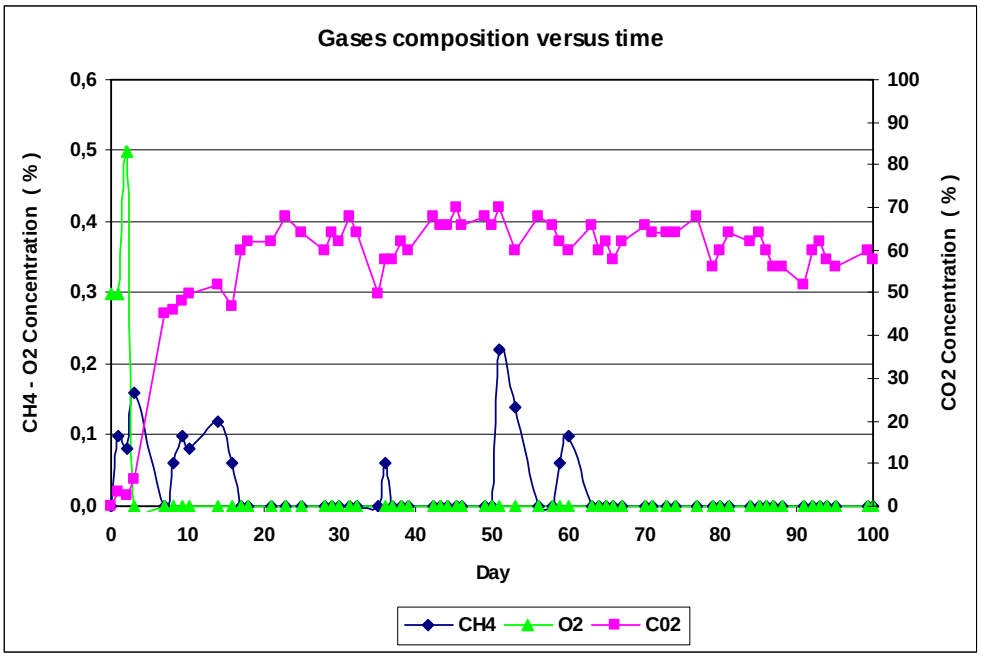

Figure 25 : Gases composition evolution versus time

It can be noticed a constant gas composition since day 25 with a great proportion of CO_2 what confirms the adequate functioning of the bioreactor and the absence of methane proves the absence of any methanogenesis activity.

V.7. Membrane selection in sequenced mode

The following Figure shows the evolution of DM in the MBR as well as the membrane tests plan corresponding to sequencing filtration mode.

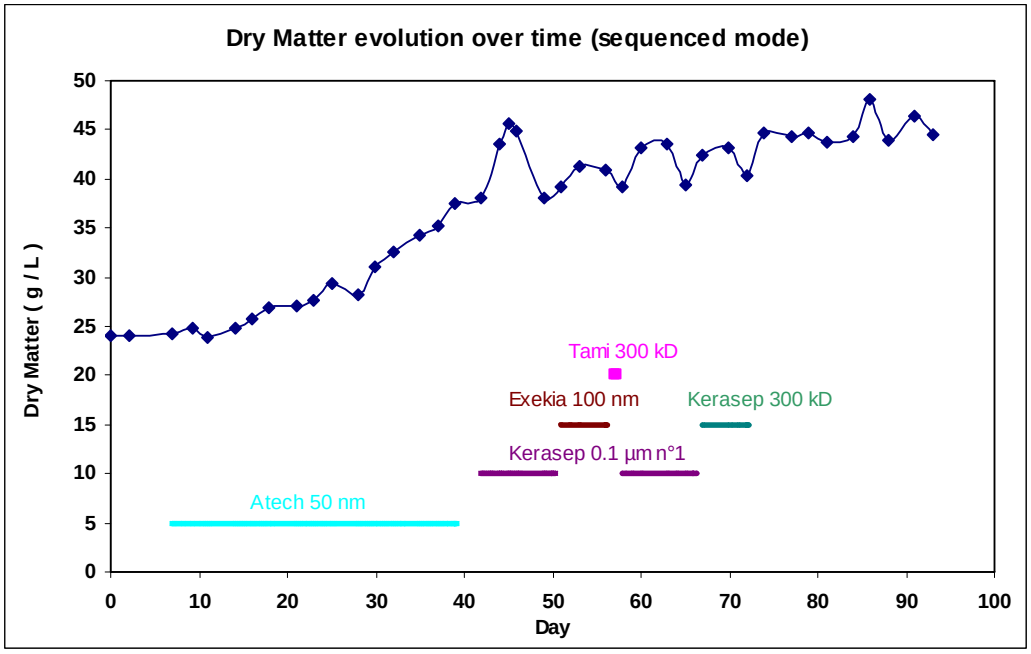

Figure 26 : Dry Matter evolution and membrane tests plan

The MBR was started of semi-continuous culture with the EPAS chosen type of membrane in order to reach 40 g/L of DM.

The other membranes were tested on this reactor operated at 40 g/L of DM. The time of functioning of each membrane was linked to the encountered problems.

V.7.1. Atech Membrane

The ATECH membrane was tested in sequencing conditions from day 5 to day 40. The characteristics of ATECH membrane are the following:

- Supplier: ATECH;
- Filtration threshold : 50 nm;
- Length: 85 cm;
- Internal channel diameter: 8 mm;
- Active Surface: 214 cm^2;
- Layer: Zirconia;
- Support material: alpha alumina;
- Theoric flux: 700 $L/h.m^2.bar$ (25°C);
- Circulation flow for 1 $m.s^{-1}$: 180 L/h.

The filtration performances are showed on Figure 27.

The recycling velocity was fixed to 3 – 3.5 m/s. The filtration mode was sequenced (between 2 and 4.5 hours per days). In absence of filtration, the recycling flow was maintained what is favourable to a hydraulic cleaning of the membrane pipe and surface.

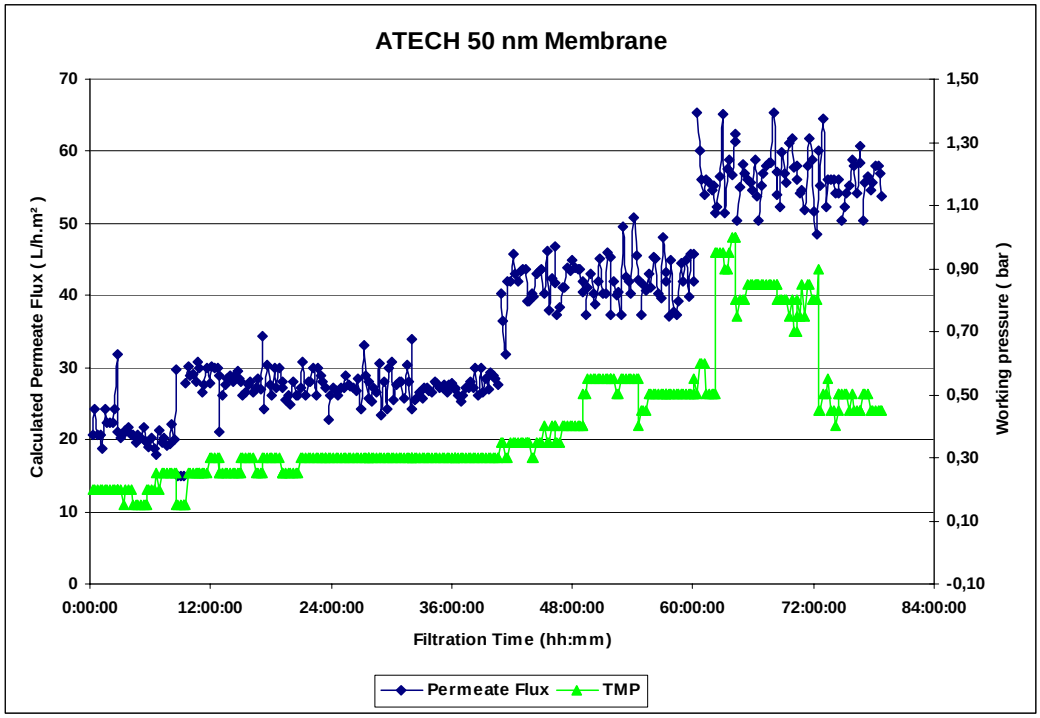

Figure 27 : Evolution of the permeate flux and TMP versus time – ATECH 50 nm

The permeate flow gradually increased from 20 to 57 L/h.m². The working pressure then evolved between 0.15 and 1 bar.

A direct relation can be observed between permeate flux and TMP what proved the absence of deposit on the membrane surface and a membrane permeability evolution mainly due to irreversible fouling.

A higher pressure was measured at the entrance of the module from September 25th to September 30th (from day 31 to 36), it was due to the presence of a vegetable plugging linked to the presence of too large pellets which blocked partially the entrance of the longitudinal membrane channel. This phenomenon points out the role of the channel diameter and the importance to have an efficient crushing of the feed (to avoid such phenomena in aerobic systems a screening (cut off < 3 mm) of the influent is imposed before entering inside the MBR system).

The ATECH membrane was disconnected and cleaned after 40 days of functioning. Without any chemical cleaning, the membrane permeability to water was then equal to 270 L/h.m².bar at 25°C. This value is lower than the permeability of the same membrane after the test performed during the hardware tests (95 L/h.m².bar, July 08) pointing out the importance of a good control of the biological system to minimize the membrane fouling dynamics.

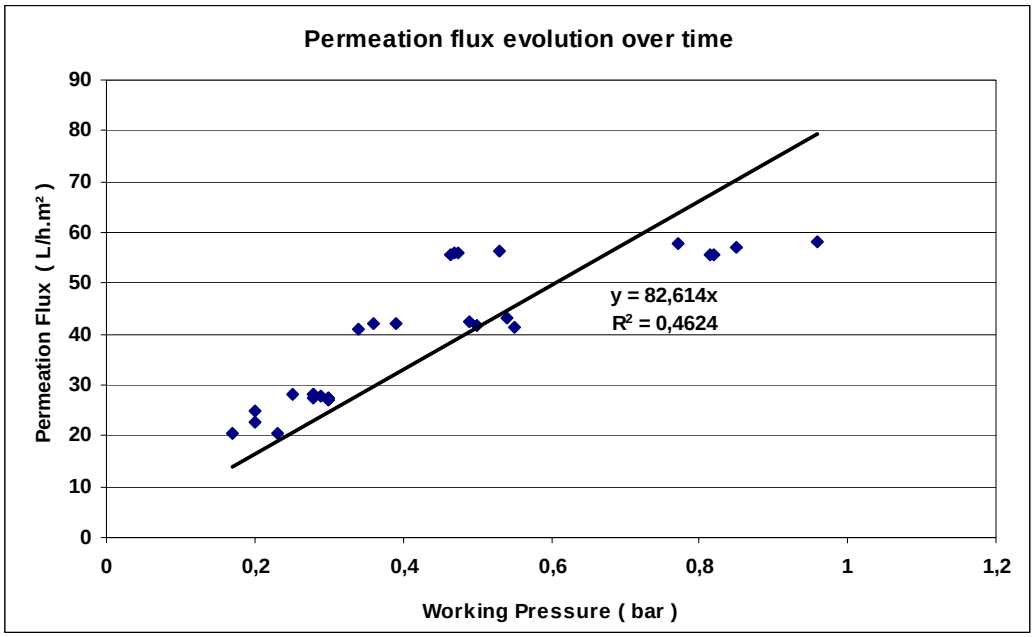

Figure 28 : Permeation flux evolution over time

To have a sufficient membrane regeneration after the tests, the cleaning procedure was performed by using NaOH 10 g/l and Cl2 300 ppm. The cleaned membrane permeability to water was then equal to 1720 L/h.m².bar at 25°C (initial water permeate flow: 1 280 L/h.m².bar).

Gas bubbles were observed in the permeate at the beginning of each filtration step. This bubble presence can be linked either to the specific permeability of membrane to dissolved CO_2 or to the module conception.

This first trial has permitted to show the possibility to work with the ATECH 50 nm membrane using the following conditions:

- **permeate flux: 57 L/h.m²;**
- **TMP: 0,45 to 0,8 bar;**
- **Velocity: 2.8 to 3.4 m.s^{-1}.**

These operating conditions were obtained during the eight extraction steps which lasted 2 hours each. The DM concentration ranged between 32 and 37.5 g/L.

This membrane will be tested in a continuous mode using velocities of 2 and 1 m.s^{-1}.

V.7.2. KERASEP 0.1 µm Membrane

In order to evaluate the cleaning efficiency, this membrane was tested during two periods:

- from 6th to 14th October (day 42 to day 50);

- from 22nd to 30th October (day 58 to day 66).

Between these two test periods the membrane was cleaned and the water permeability checked.

The characteristics of KERASEP membrane are the following:

- Supplier: Orélis;
- Filtration threshold: 0.1 µm;
- Length: 40 cm;
- Internal channel diameter: 6 mm;
- Active surface: 75 cm^2;
- Layer: Zirconia;
- Support material: Al_2O_3 – TiO_2;
- Theoric flux: >1250 $L/h.m^2.bar$ (25°C);
- Circulation flow for 1 $m.s^{-1}$: 100 L/h.

V.7.2.1. First period (from October 6th to October 14th)

The filtration mode was sequenced mode: the daily filtration time evolved between 5 and 7 hours.

The test with KERASEP membrane lasted 9 days. The filtration performances are showed on Figure 29.

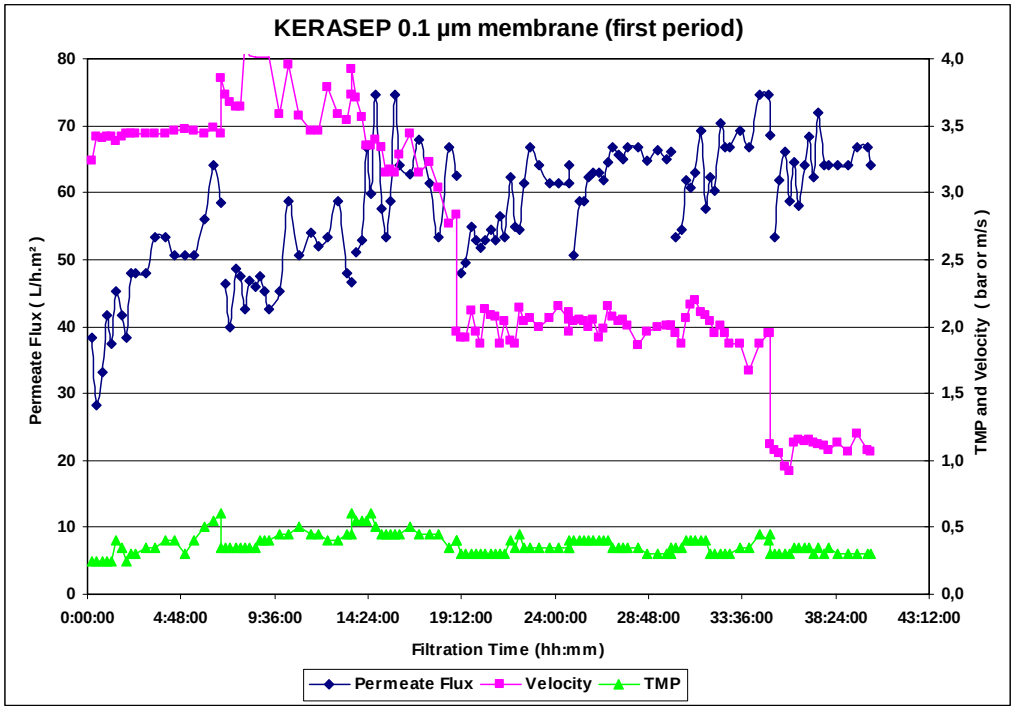

Figure 29 : Evolution of the permeate flux and TMP versus time – KERASEP 0.1 µm

This membrane was tested with a permeate flow between 30 and 67 L/h.m².bar. The working pressure evolved between 0.25 to 0.6 bar.

To minimize the energetic cost due to the sludge recycling in the loop, the recycling velocity was progressively decreased from 4 to 1 m/s. No TMP increase can be noticed when the recycling velocity was decreased, we can even notice a slight TMP decrease, probably due to the simultaneous decrease of pressure inside the loop. So these first results on this KERASEP membrane show the interest to work with lowest recycling velocity according to the defined conditions of filtration (sludge concentration and temperature).

The Membrane was disassembled on the 14th October 2008 and its permeability to water was measured. It was equal to 1150 L/h.m².bar at 25°C (water permeate flow was equal to 1970 L/h.m².bar after preliminary test).

During operation, this value appears 4 times greater than the permeability of the tested ATECH membrane. So this point gives a net advantage to the membrane KERASEP. Nevertheless no comparison was done on the membrane performance in regards with germ removal. In any case no difference of filtered water turbidity could be noticed (about 0.4 NTU for both membranes).

A cleaning procedure was performed with NaOH 10 g/l. The water permeate flow after cleaning was equal to 2038 L/h.m².bar at 25°C. The facility to clean this membrane KERASEP must also be underlined.

V.7.2.2. Second period (from October 22nd to October 30th)

The filtration mode was sequenced mode: the daily filtration time evolved between 5 and 6 hours.

The test with KERASEP membrane lasted 7 days.

The filtration performances are showed on Figure 30.

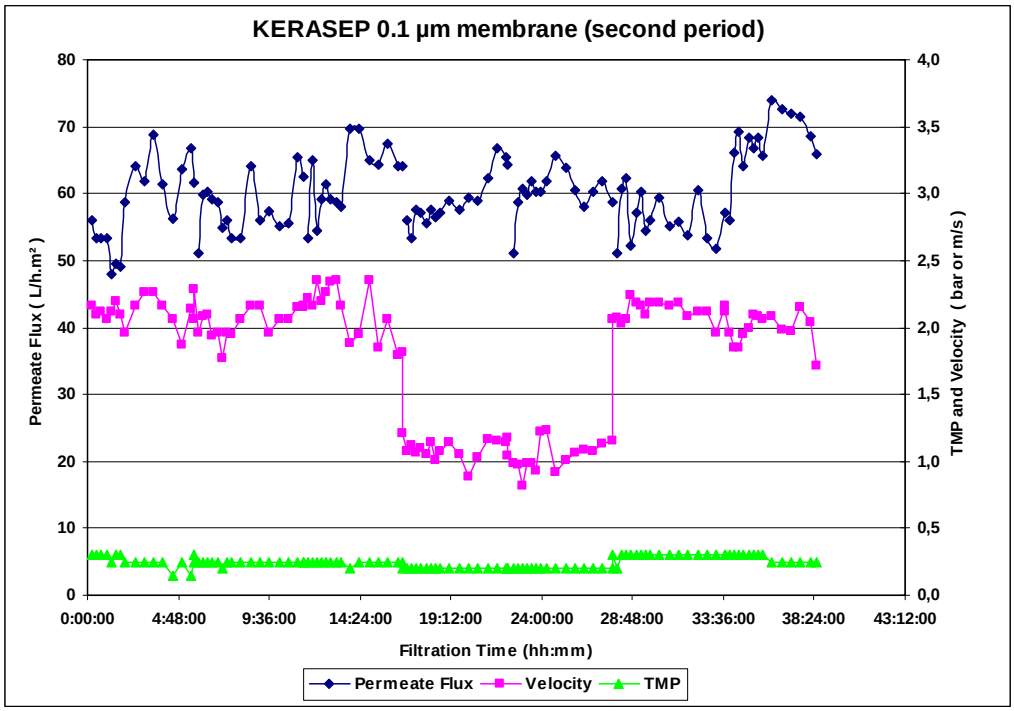

Figure 30 : Evolution of the permeate flux and TMP versus time – KERASEP 0.1 µm

The permeate flux was controlled between 50 and 72 L/h.m² (average flux equal to 59 L/h.m²). Two velocities were tested (2 and 1 m/s). The TMP remained stable at around 0.24 bar independently of permeate flux and velocity variations.

The Membrane was disassembled on October 30th and its permeability to water was measured. It was equal to 615 L/h.m².bar at 25°C (water permeate flow was equal to 2 038 L/h.m².bar after the previous test).

A cleaning procedure was performed with NaOH 10 g/l. The water permeate flow after cleaning was equal to 2137 L/h.m².bar at 25°C. The facility to clean this membrane KERASEP must also be underlined.

This membrane will be tested in a continuous mode using velocities of 2 and 1 m.s^{-1}.

V.7.3. EXEKIA 100 nm Membrane

This membrane was tested from 15th till 20th October. The test with EXEKIA membrane lasted 4 days. The characteristics of EXEKIA membrane are the following:

- Supplier: EXEKIA;
- Filtration threshold : 100 nm;

- Length: 25 cm;
- Internal channel diameter: 7 mm;
- Active surface: 55 cm²;
- Layer: Zirconia;
- Support material: Alpha alumina;
- Theoric flux: 2030 L/h.m².bar (25°C);
- Circulation flow for 1 m/s : 138 L/h.

The filtration mode was sequenced mode: the daily filtration time evolved between 6 and 9 hours.

The filtration performances are showed on Figure 31.

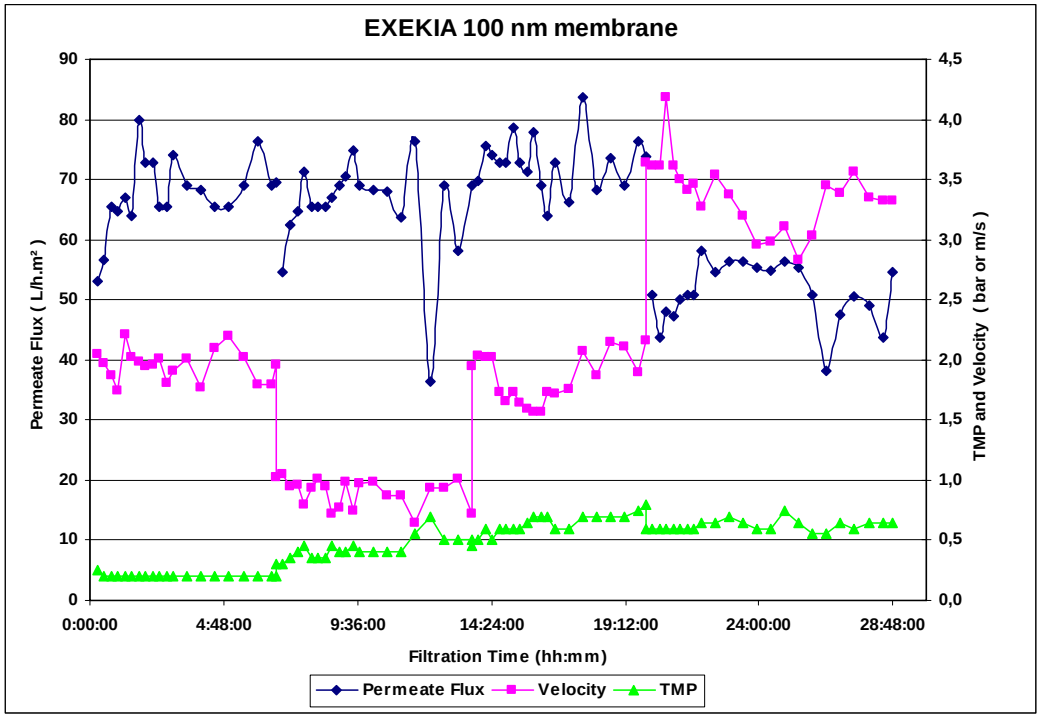

Figure 31 : Evolution of the permeate flux and TMP versus time – EXEKIA 100 nm

During the first extraction, the permeate flow was controlled at 65 L/h.m². The tangential velocity was fixed at 2 m/s. The TMP remained stable at 0.2 bar during the 6 hours and 40 minutes of filtration time.

The second extraction was performed with a tangential velocity of 1 m/s. The permeate flux was controlled at 65 L/h.m². The TMP regularly increased from 0.3 to 0.5 bar. This trial lasted 7 hours.

To avoid a too high TMP evolution, the third extraction was carried out by increasing the tangential velocity from 1 to 2 m/s. The permeate flux was controlled at 65 L/h.m². The TMP steadily increased from 0.45 to 0.8 bar.

In order to decrease the TMP, the last extraction was performed controlling the permeate flux at 50 L/h.m². The velocity was increased from 2 to 3.5 m/s. In these conditions the TMP remained stable at 0.6 bar.

The Membrane was disassembled on the 20th October 2008 and its permeability to water was measured. It was equal to 88 L/h.m².bar at 25°C (water permeate flow was equal to 1780 L/h.m².bar after preliminary test).

A cleaning procedure was performed with NaOH 10 g/l. The water permeate flow after cleaning was equal to 1370 L/h.m².bar at 25°C.

Since the first cleaning was not sufficient to find again the initial characteristics of the membrane a new cleaning was performed with NaOH 10 g/L added by 2 g/l of hydrogen peroxide.

The water permeate flow after this second cleaning was equal to 1830 L/h.m².bar at 25°C.

For an identical permeate flux, the measured TMP with the EXEKIA membrane appears three times greater than the TMP measured with the KERASEP membrane.
A part of this difference can be attributed to the filtration threshold (cut-off). For the EXEKIA membrane the cut-off corresponds to the diameter of pores at the end of the curve of repartition while the KERASEP membrane cut-off corresponds to the diameter of pores at the top of the curve of repartition.

But the regular increase of the TMP observed over time appeared mainly due to a clogging of the membrane pipe because of large variation of the longitudinal pressure variation.

Then this membrane will not be recommended for the long duration test.

V.7.4. TAMI 300 kD Membrane

This membrane was tested the 21st of October 2008. The test with TAMI membrane lasted 1 day. The characteristics of TAMI membrane are the following:

- Supplier: TAMI;
- Filtration threshold : 300 kD;
- Length:120 cm;
- Internal channel diameter: 6 mm;
- Surface: 226 cm²;
- Layer: Titanium;
- Support material: Titanium;
- Theoric flux: 800 L/h.m².bar (25°C);
- Circulation flow for 1 m/s : 100 L/h.

The filtration mode was sequenced mode: the daily filtration time was 1 hour and 30 minutes.

The filtration performances are showed on Figure 32.

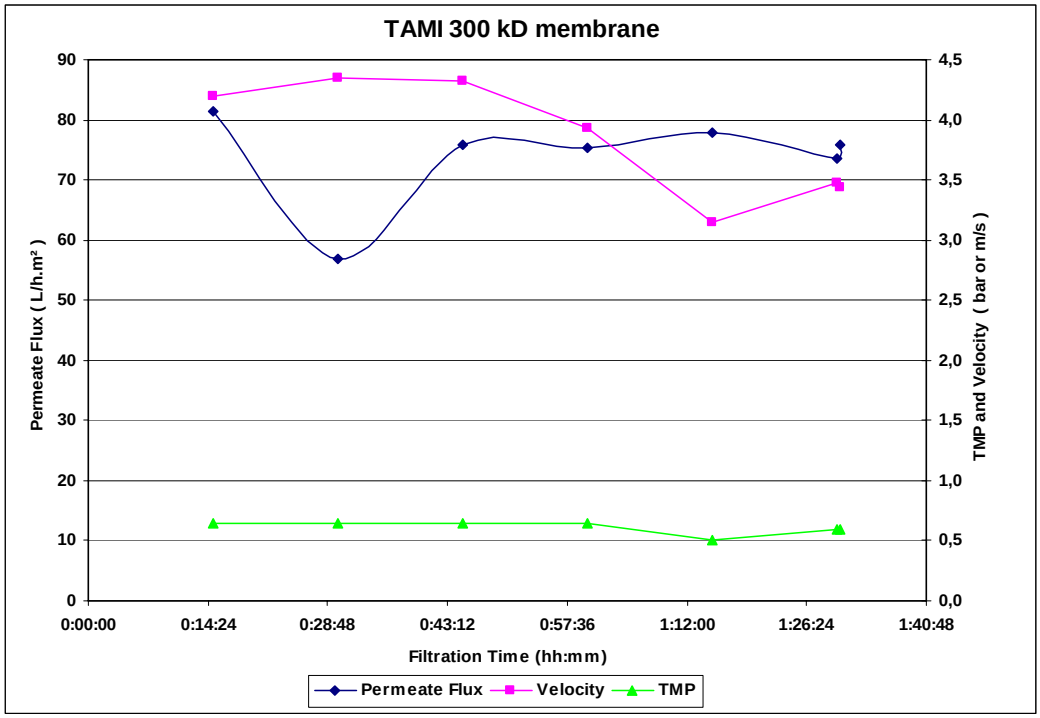

Figure 32 : Evolution of the permeate flux and TMP versus time – TAMI 300 kD

For an average permeate flux equal to 70 L/h.m² and a tangential velocity of 4 m/s the TMP remained stable at 0.6 bar.

According to the length of the membrane (120 cm) the inlet pressure and the drop pressure were significant (1.8 bar for inlet pressure and 1.5 bar for drop pressure).

During and after the permeate extraction step, a lot of clogging of the internal membrane channel was observed. To clean this internal channel the circulation had to be stopped and the membrane disconnected.

A measure of the internal channel of the membrane showed that the diameter was 5 mm instead of 6 mm announced by the supplier.

Regardless of these good performances in term of permeate flow this membrane will not be tested in continuous mode due to its small internal channel diameter.

V.7.5. KERASEP 300 kD Membrane

This membrane was tested from October 31st to November 05th. The test with KERASEP 300 kD membrane lasted 4 days. The characteristics of KERASEP membrane are the following:

- Supplier: Orélis;
- Filtration threshold : 300 kD;
- Length: 40 cm;
- Internal channel diameter: 6 mm;
- Active surface: 75 cm^2;
- Layer: Zirconia;
- Support material: Al_2O_3 - TiO_2;
- Theoric flux: >300 $L/h.m^2.bar$ (25°C);
- Circulation flow for 1 $m.s^{-1}$: 100 $L.h^{-1}$.

The filtration mode was sequenced mode: the daily filtration time evolved between 5,5 and 6 hours.

The filtration performances are showed in Figure 33.

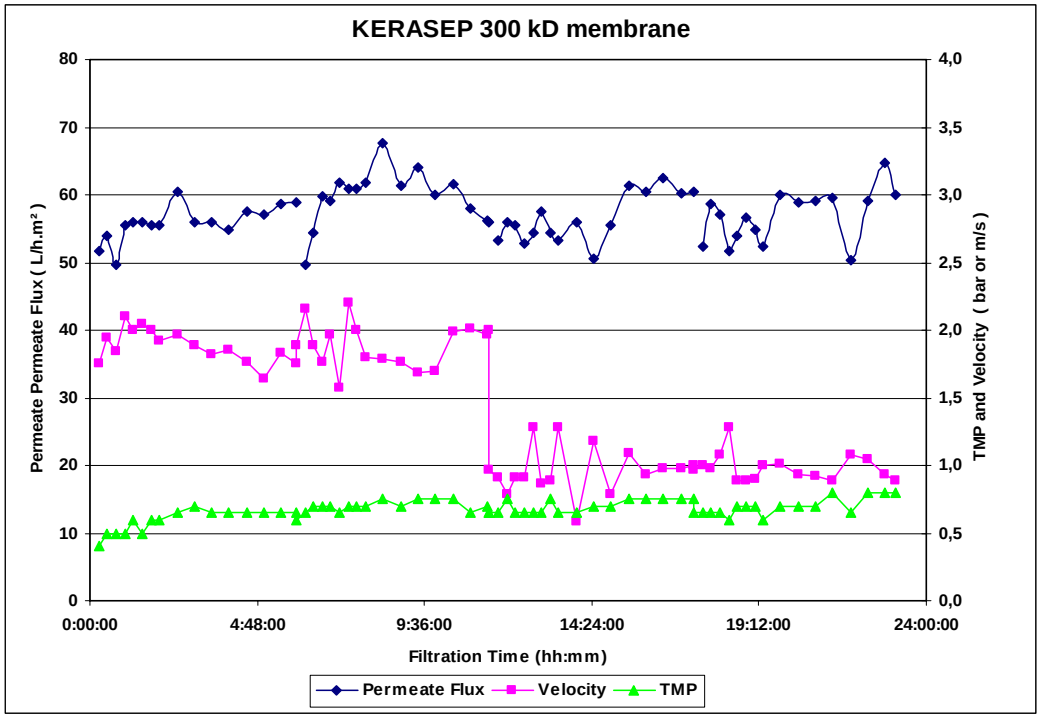

Figure 33 : Evolution of the permeate flux and TMP versus time – KERASEP 300 kD

The two first extraction steps were carried out with a permeate flow controlled at 60 L/h.m² and a tangential velocity of 2 m/s. The TMP regularly increased from 0.3 to 0.65 bar.

The two other extraction steps were performed with a permeate flow controlled at 60 L/h.m² and the tangential velocity was fixed at 1 m/s instead of 2 m/s. The TMP increased from 0.65 to 0.8 bar.

The Membrane was disassembled on the 05th November 2008 and its permeability to water was measured. It was equal to 55 L/h.m².bar at 25°C (water permeate flow was equal to 400 L/h.m².bar before this test).

A cleaning procedure was performed with NaOH 10 g/l. The water permeate flow after cleaning was equal to 250 L/h.m².bar at 25°C.

Since the first cleaning did not find the initial characteristics of the membrane a new cleaning was performed with NaOH 10 g/L added by 2 g/l of hydrogen peroxide.

The water permeate flow after this second cleaning was equal to 330 L/h.m².bar at 25°C.

Because of its difficulty to be regenerated by chemical cleaning, this membrane will not be tested in a continuous mode.

V.8. Membrane selection in continuous mode

The following Figure shows the evolution of DM in the MBR as well as the membrane tests plan. Two membranes were chosen for continuous tests: Kerasep 0.1 µm and Atech 50 nm. Because of the large value of permeate flux in comparison with the imposed feed flux, a permeate recycling was imposed on the system to maintain comparable biological conditions (HRT and SRT).

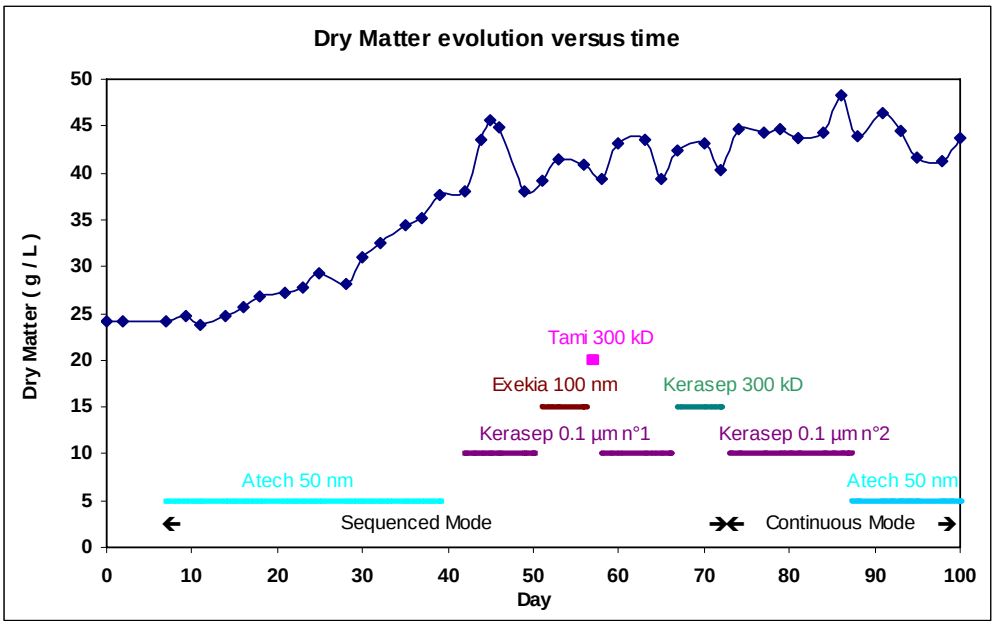

Figure 34 : Dry Matter evolution and membrane tests plan

V.8.1. KERASEP 0.1 µm Membrane

This membrane was tested in continuous mode from November 6th to November 20th, 2008 (from day 73 to day 87).

At the end of each production step, the circulation and permeate flows were maintained.

The permeate was recycled into the MBR to maintain the same HRT as previously.

The total filtration time was equal to 14 days (336 hours).

The permeate flux was controlled at about 60 L/h.m² and the tangential velocity was fixed to 2 $m.s^{-1}$.

Due to the replacement of some parts of the pump head, it was impossible to decrease the velocity under 2 $m.s^{-1}$.

The next Figure shows the permeate flux, TMP and velocity evolution over extraction time.

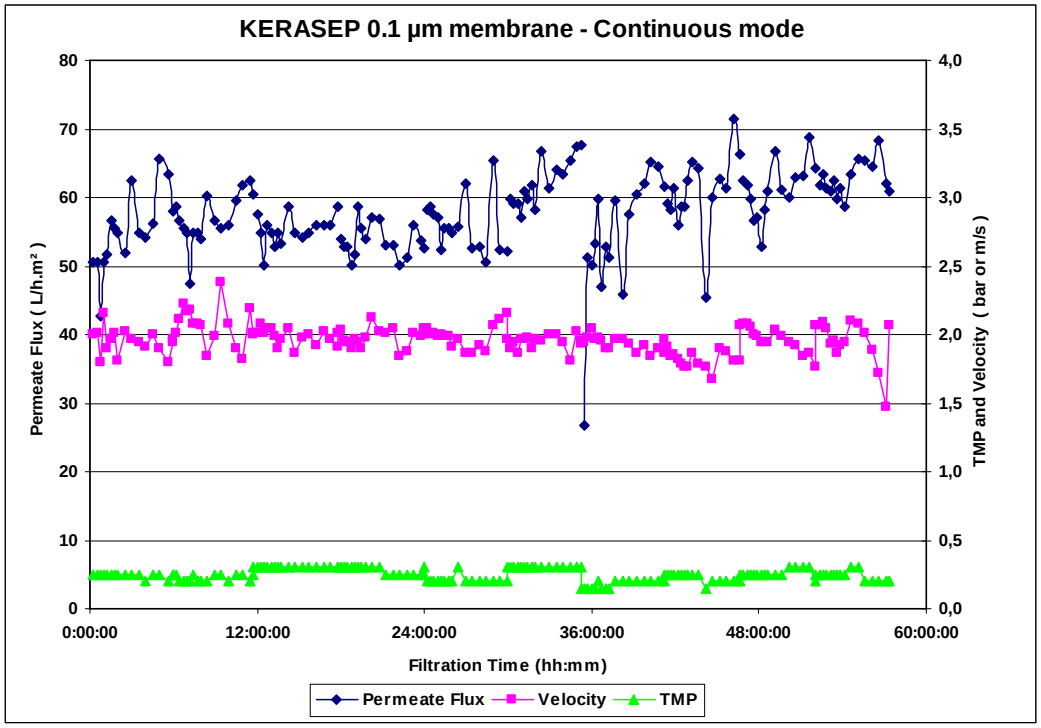

Figure 35 : Evolution of the permeate flux and TMP over time – KERASEP 0.1 µm

No evolution of the TMP was observed during the test. The TMP ranged between 0.15 and 0.3 bar for an average permeate flux controlled at 60 L/h.m².

The Membrane was disassembled on November 20th and its permeability to water was measured. It was equal to 520 L/h.m².bar at 25°C (water permeate flow was initially equal to 2140 L/h.m².bar).

A cleaning procedure was performed with NaOH 10 g/l. The water permeate flow after cleaning was equal to 1960 L/h.m².bar at 25°C.

These results confirm the quality of such a membrane in term of fouling control (no noticeable evolution on the TMP during two weeks of test and the facility to regeneration by conventional cleaning procedure.

V.8.2. ATECH 50 nm Membrane

This membrane was tested in continuous mode from November 21st to December 04th, 2008 (from day 88 to day 101). The total filtration time was equal to 14 days (336 hours).

The permeate flux was controlled at about 60 L/h.m² and the tangential velocity was fixed at 2 then 1 m/s. The next Figure shows the permeate flux, TMP and tangential velocity evolution over extraction time.

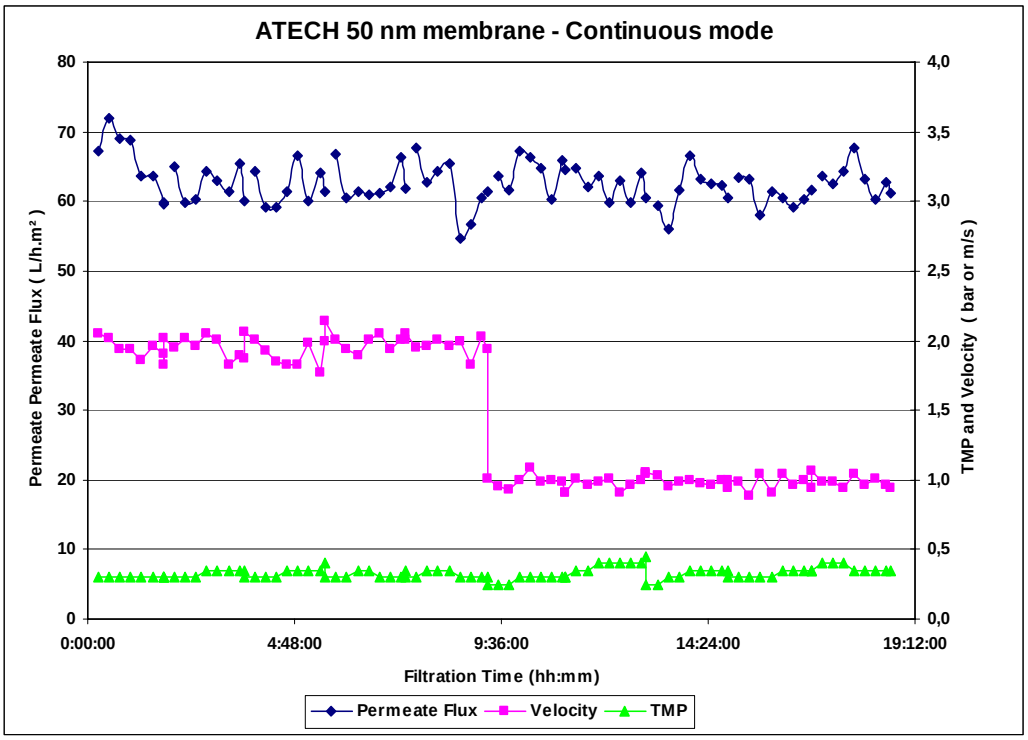

Figure 36 : Evolution of the permeate flux and TMP over time – ATECH 50 nm

No evolution of the TMP was observed during the test. The TMP ranged between 0.25 and 0.45 bar for an average permeate flux controlled at 60 L/h.m².

The Membrane was disassembled on December 04th and its permeability to water was measured. It was equal to 430 L/h.m².bar at 25°C (water permeate flow was equal to 1720 L/h.m².bar before this test).

A cleaning procedure was performed with NaOH 10 g/l. The water permeate flow after cleaning was equal to 890 L/h.m².bar at 25°C.

Because the first cleaning did not allow the find the initial characteristics of the membrane, a new cleaning was performed with NaOH 10 g/L added by 300 mg/l of sodium hypochlorite.

The water permeate flow after this second cleaning was equal to 2000 L/h.m².bar at 25°C.

The membrane behaviour was fine during operation, because of its large channel, the risk of clogging is weaker than with other membranes. Nevertheless, its chemical regeneration appeared more severe than with the Kerasep membrane.

VI. Conclusion

The experiments carried out in July allowed to identify some points to favour analytical methodologies and the control of the experimental MBR pilot.

The experiments carried out from September allowed the comparison of the performances of different mineral membranes according to the fact that the bioreactor was controlled in term of biomass steady state behaviour.

The results point out:

- Whatever the membranes:
  - No difficulty to control the biological activity of the bioreactor; this is also linked to the small massic load imposed on the system which has probably capacity to degrade higher organic load;
  - The total retention of particles by the membranes, the permeate was totally clarified ;
  - No noticeable retention of soluble compounds by the membranes: no differences between salt concentration in permeate and retentate and no retention of VFA;
  - The proportion of CO2 in the gas phase was constant.

- Role of the membrane material and configuration (channel diameter, length and pore size distribution):
  - The high performances of the membrane KERASEP (100nm) in term of permeability control, weak sensitivity to adsorption, weak irreversible fouling intensity (chemical membrane regeneration appeared easy), facility to work with relatively low cross-flow velocity
  - A good performance of the membrane ATEC that nevertheless presents a higher sensitivity to adsorption (the chemical regeneration necessitated more severe cleaning procedure) and a lower permeability (due also to its lower cut off).
  - For both membrane ATEC and KERASEP (100nm) no noticeable differences can be observed in sequencing and continuous mode of functioning. In the tested conditions, a permeate flow of 60 $L.m^{-2}.h^{-1}$ can be obtained under moderated and controlled TMP value varying in the range of 0.2 to 0.3 for Kerasep and 0.3 to 0.5 bar for ATECH. Moreover a chemical regeneration of the membrane once a fortnight appeared sufficient to control the fouling dynamics. Nevertheless the chemical regeneration of the ATECH membrane necessitated more severe conditions.
  - For the other membranes tested in sequencing mode, it appeared some problems linked to channel clogging and difficulty to chemical regeneration. The clogging risk was obvious when the membrane channel (pipe) was too small (it is not recommended to use channel smaller than 6 mm with such concentrated suspension) or when the feed crushing not sufficient (what can oblige to impose a screening of the feed suspension). The interest of large channel to favour the practise a low tangential velocity must be a determining criterion as the sensitivity of the membrane to irreversible fouling.

According to the results obtained and the precedent comments, we propose to carry out the experiment in Barcelone by using the KERASEP (100nm) membrane with two possible lengths (25 and 40 cm).

- Other comments:
  - The possibility to impose a screening (cut off 3mm) of the influent before its introduction in the reactor (to minimise clogging of the membrane channel);
  - The difficulty to analyse the VFA composition in the biological suspension;
  - The importance of the choice of the pump quality on the recycling line;
  - The importance to have a adequate thermal isolation of the system;
  - The necessity to have a mean to measure the gas production simultaneously to its composition.

Figures list

Figures list:

Tables list

Tables list:

VII. Comments

Filtration Unit Optimization
Trade-off and selection of best suited membrane

Comments

Detailed comments

Page/paragraph	Comment
11/Section III.1, first paragraph	Please specify that this design is based on CI prototype design; please clarify that this equipment can work either at controlled TMP or at controlled permeate flux. Clarify when one or the other control strategy is used and why. *(Specified in the text)* The design of this Membrane Bioreactor is based on CI prototype design. This equipment can work either at controlled TMP or at controlled permeate flux. All of the following trials were performed at controlled permeate flux. This configuration is preferred to study the membrane clogging evolution. The membrane fouling dynamics can be evaluated by the trans-membrane pressure TMP evolution.
16/Section III.2.1, first paragraph	Please insert information about the feed composition *(Inserted in the fourth paragraph)* For a 25 L reactor volume operating at 20 days of HRT, the feeding flow is 1.25 L/day. Each day feed is prepared using the following procedure, as defined for CI: - weighing of about 288 g of Fresh Solid Mixture; - adding demineralised water until a 1.25 L volume is acquired; - introducing the feed in the MBR. The composition of the Fresh Solid Mixture supplied by MPP is the following: - Lettuce 13.8 kg; - Red Beet 8.6 kg; - Milled straw 0.5 kg; - Toilet paper 0.204 kg.
16/Section III.2.1, second paragraph	Please compare those data with the ones applied/obtained with the CI compartment *(Inserted in the text)* For comparison, the operating conditions applied with the CI compartment were:

	- Permeate flux :between 2 and 5 L/h.m²; - Hydraulic retention time: 10 days; - Tangential velocity : 2.5 m/s For these conditions, TMP fluctuated between 0.1 and 0.8 bar.
22/Section IV.1.2, fifth paragraph	Please precise temperature *(Inserted in the text) Standards and samples were stored in a fridge* (at 4°C). *After analysis, samples were frozen* (at -18°C)
23/Section IV.1.3.1, first paragraph	Please clarify whether this method is similar to the one used by EPAS and/ or by the MPP. *(Inserted in the text)* This method has been developed by MPP.
28/Section V.1	This paragraph should be updated according to the update of TN 94.41 *(Text modified: the description of requirements has been deleted)* The requirements for this membrane selection have been previously define in TN94.41.
30/Section V.3.3, last paragraph	Can you clarify?, we are not sure to understand *(Clarified in the text)* These tests were performed on each membrane to study the membrane behaviour with the adsorption of little molecules in the soluble fraction
31/Section V.4.1, second paragraph	Can you please specify the average volume of each sample? *(Specified in the text)* - *bioreactor : 3 samples a week* (50 ml for each sample) - *filtrate : 3 samples a week* (50 ml for each sample) - *influent batch : 1 sample in the first feeding and 1 sample from the last feeding for each batch of influent* (50 ml for each sample)
31/Section V.4.1, second paragraph	What about the gas phase? *(Specified in the text)* - gas phase : one measurement per day (the gas analyser was installed on the output gas line)
40/Section V.6.2.4, fourth paragraph	Can you precise which method was used ? GC or HPLC? *(Precised in the text)* These results were obtained by using HPLC method.
57/Section VI, third paragraph	This value (turbidity <0.4 NTU)is not consistent with the requirement which is <0.1 NTU *(Removed from the text, and reason explained)* Due to the presence of coloration into the sample, TM analyser is not adapted to measure a turbidity lower than 0.5 NTU