PROJECT AMEDEUS
“EVALUATION OF A NOVEL MBR FILTRATION TECHNOLOGY FROM A3 WATER SOLUTIONS”

DELIVERABLE D19

SIXTH FRAMEWORK PROGRAMME
Priority 1.1.6.3
“GLOBAL CHANGE AND ECOSYSTEMS”

SPECIFIC TARGETED RESEARCH PROJECT

Project acronym:	AMEDEUS
Project full title:	Accelerate Membrane Development for Urban Sewage Purification
Proposal/Contract no.:	018328 AMEDEUS
Instrument	STREP
Priority	Global Changes and Ecosystems
Duration:	Oct. 2005 – May 2009

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Public report

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PROJECT AMEDEUS
“ACCELERATE MEMBRANE DEVELOPMENT FOR URBAN SEWAGE PURIFICATION”
FINAL ACTIVITY REPORT

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Public report

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Abbrevations

$Lp_{\text{after cleaning}}$= Permeability after cleaning (L/h.m^2.bar, 20°C)
Lp_{new}: Permeability of the new membrane (L/h.m^2.bar, 20°C)
R: Percentage of recovered permeability after cleaning (%)
SADm: Specific Air Demand per membrane surface ($Nm^3/m^2_{\text{membrane}}$)
SADp: Specific Air Demand per permeate volume ($Nm^3/m^3_{\text{permeate}}$)

Introduction

The Work Package 3 of the European project AMEDEUS aims to develop and assess three innovative concepts of submerged low-pressure (suction pressure) MBR provided by three European Companies: A3 Water Solutions, Polymem and INGE.
The Work Package is organized in three, successive and identical phases to ensure the development, test and optimisation of the three technologies in close and exclusive collaboration of Anjou Recherche (AR) with each of the SMEs. Each phase includes a first part related to the development of the innovative module concept and the construction of the filtration reactor by the SMEs, immediately followed by a second part related to the evaluation and optimisation of the technology with Anjou Recherche.

This report deals with the evaluation of the first technology developed by A3 Water Solutions. The technology concept is based on a block of flat sheet microfiltration membranes, made of PVDF. The modules can be easily stacked on top of each other (in double deck configuration) and the aeration system is installed below the modules: the resulting turbulence in the gas-liquid mixture ascending through the spaces between the individual membrane plates enables to detach the filtration cake deposits.

A flexible platform, that will accommodate the membrane technologies was first conceived and built in Anjou Recherche during the first 6 months of the European project. Then, the evaluation of A3 Water Solutions technology started in June 2006 and finished in July 2007. Two industrial modules in double deck configuration were tested in the pilot platform. In parallel, lab-scale trials allowed to find alternative cleaning products to chlorine, for MBR application.

I. Material & Methods

I.1 Pilot trials

I.1.1 A3 technology

The A3 membrane filtration concept is based on a block of flat sheet microfiltration membranes, made of PVDF with a pore size of 0.1 µm, as shown in Figure 1. The module is built with multiple filtration plates arranged in parallel with defined spaces between every single plate. The membrane cushions are fixed by moulded sides, in which the filtrate is collected as shown in Figure 1. To ensure maximum filtration efficiency, an aeration ramp with fine to medium-size bubbles is installed below the filtration module stack. The resulting turbulence in the gas-liquid mixture ascending through the spaces between the individual membrane plates enables to detach the filtration cake deposits. The modules can be easily stacked and aligned. Triple and quadruple-deck could be envisaged. Because of the closed upstream channel the air bubbles stream up through the stacked modules without any leakage, the specific energy consumption concerning the layer control can be lowered. Therefore, the air consumption of a simple module and stacked modules are equal. Filtration occurs from outside to inside of the plates. The modules operate usually in filtration / relaxation mode.

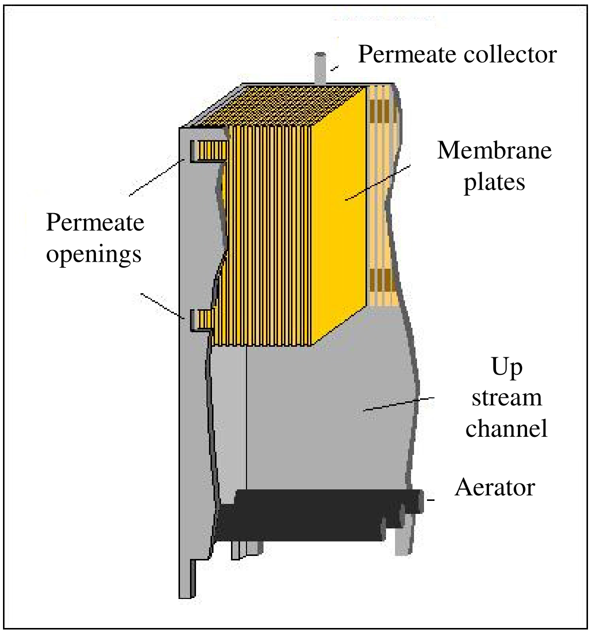


Figure 1 MaxFlow Membrane-Module

I.1.2 Pilot plant design with A3 Water Solutions' technology

Anjou Recherche, the research centre of Veolia Water, has built a flexible pilot platform as shown in Figure 2, which will be operated for about eleven months with each membrane technology. The pilot is fed by municipal wastewater from the town of Maisons Laffitte by a pump after screening through a 1mm drum screen. The mean feed water characteristics are given in Table 1.

Parameter	Average	Minimum	Maximum	Samples number
COD (mg/L)	530	257	1206	179
TN (mg/L)	59	9	143	174
$N-NH_4^+$ (mg/L)	41	19	54	176
TSS (mg/L)	171	58	727	162
pH	7.7	6.9	8.2	170

Table 1 Mean feed water quality

The pilot is composed of a biological tank (1.6 m^3 of sludge volume) and a membrane tank (2.6 m^3 of sludge volume) as shown in Figure 3. The wastewater enters the biological tank in which the nitrification and the denitrification occur. This tank is intermittently aerated and agitated with an impeller to ensure that sufficiently high oxygen concentrations can be reached for biological processes. Mixed liquor is circulated with a pump from the biological tank to the filtration tank. The filtration tank consists of an aerated tank in which two MaxFlow membrane-modules are immersed (2x 70 m^2). A pump is used to extract the permeate water from the membrane. The permeate water is collected in a storage tank and is partly re-circulated to the membrane tank. The concentrated mixed liquor is returned to the biological tank. The biological operating conditions are maintained constant during all the trials in order to consider only the impact of the hydraulic operating conditions. The chosen conditions are typical of a treatment with MBR system. The mean biological operating conditions are given in **Table 2**.

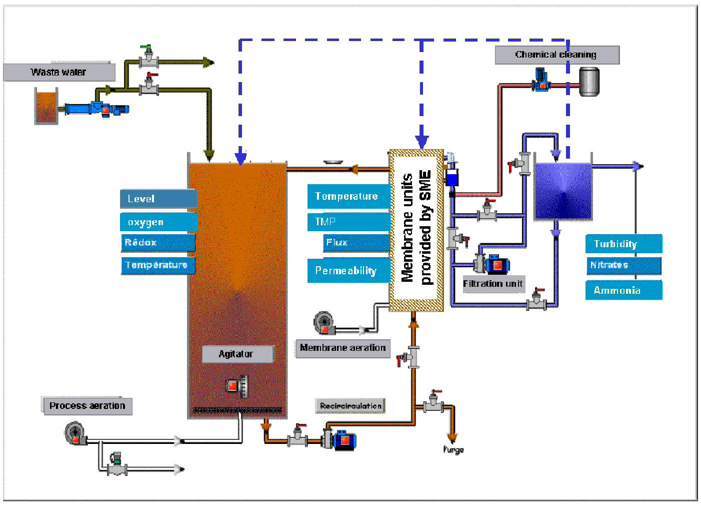


Figure 2 Pilot platform **Figure 3 Pilot plant design**

Table 2 Mean biological operating conditions

Parameter	Design	Average	Minimum	Maximum
SRT (days)	25	28	22	32
Volumetric loading rate (kg COD.m^{-3}.d^{-1})	1.3	1.36	0.58	3.09
F/ M ratio (kg COD.kg MLSS^{-1}.d^{-1})	0.13	0.12	0.06	0.30
Sludge concentration evaluated over the total volume(gMLSS/L)	10	11.3	3	21
Sludge concentration measured in the biological tank (gMLSS/L)	8.7	9.6	3	17
HRT (h)	8.4	8.2	4.2	14.2

The hydraulic performances of the membrane modules are monitored online by the supervision system and the pilot is equipped with a data acquisition system. This allows the membrane performances (transmembrane pressure, filtration flow rate, temperature), the quality of the permeate water (ammonia and nitrate concentrations) and the characteristics of the sludge (suspended solids, redox, oxygen concentration) to be recorded in real time.

In parallel, the raw water and permeate analyses were performed every day on 24h-mean samples to evaluate the treatment performances of the pilot unit. The mixed liquor was also analyzed every week in order to see if the fouling of the membrane and the filtration performance could be due to the evolution of liquid filterability or other parameters.

I.2 Laboratory trials

The laboratory trials have the objective to find alternative cleaning reagents to chlorine for MBR application.

To perform these trials, A3 Water Solutions delivered to Anjou Recherche some membrane samples. The characteristics of the membrane material are reported in the Table 3.

Table 3 Membrane characteristics

Application	Wastewater
Membrane type	Microfiltration
Pore size (µm)	0.1
Material	PVDF
Filtration type	External/Internal
TMP max. (bar)	0.7
Operating TMP (bar)	0 - 0.2
Temperature (°C) max	50
pH (T°C < 30 °C)	2 - 11
Permeability L/h.m^2.bar, 20 °C	> 1500

The presented trials were focused more on the cleaning of long term irreversible membrane fouling (adsorption and pore blocking). The irreversible fouling is defined here as the remaining fouling after removal of the cake layer deposit with de-ionised water. Several protocols were developed to foul irreversibly the membrane samples and to test the selected cleaning reagents: 1) lab scale cleaning tests on flat sheet new membrane fouled over 24h with sludge supernatant; 2) lab scale cleaning tests on flat sheet membranes coming from a MBR pilot plant after 5 months of immersion; and 3) membrane cleaning tests directly in the MBR pilot plant after one year of filtration.

I.2.1 Permeability measures

The Membrane Center of excellence ARAMIS (Veolia) has developed new lab scale protocols to foul membrane samples and perform different cleaning experiments for replacing chlorine in MBR plants.

A laboratory filtration unit, specially adapted for flat sheet membranes, shown in Figure 4, was built in September 2006: a cross-flow filtration cell (Rawflow 100) was selected in order to have similar hydraulic conditions as the one observed in a typical MBR plant equipped with flat sheet membranes. The cross-flow speed velocity used was 0.41 m/s. Two pressure sensors were installed, one at the feed inlet and one at the recycled feed outlet, and a pump was chosen to obtain a continuous and stable flow. The feed water was pumped into the filtration cell in which two flat sheet membranes with an active surface of 110 cm^2 were installed (Figure 6). Retentate and permeate could be recycled in the storage tank. The photo and the diagram of the installation are presented in Figure 4 and Figure 5.

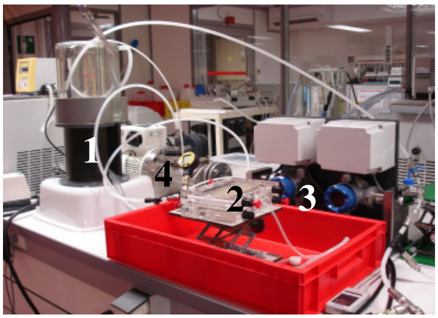


Figure 4 Cross-flow filtration cell to measure flat sheet membrane permeability

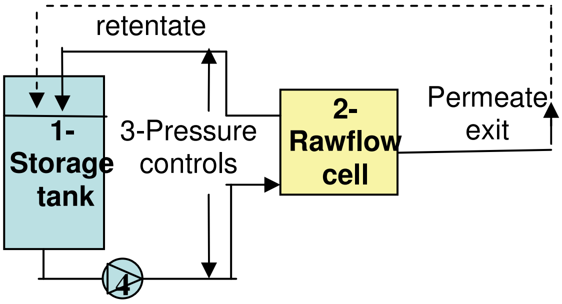


Figure 5 Design of the pilot to measure flat sheet membrane permeability

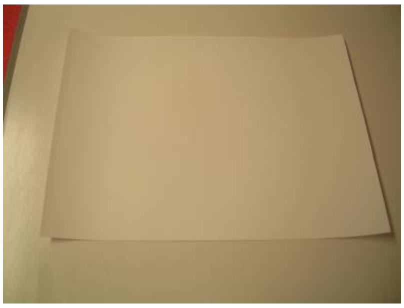


Figure 6 Samples of flat sheet membrane

An adapted protocol was established to prepare the membrane in order to have a stable permeability value at start of trial. The laboratory unit and the membrane were first rinsed and then the membrane sample soaked with a chlorine solution at 100 ppm. Then, the laboratory unit was rinsed with de-ionized water until a chlorine concentration of 0.5 ppm or less was reached in the storage tank and permeate. The initial permeability of the membrane sample with de-ionized water was finally measured at 0.2 bar during 3 hours of filtration.

I.2.2 Fouling and cleaning experiments performed at lab scale

Anjou Recherche developed a lab scale protocol to foul new membrane pieces with sludge supernatant. Mixed liquor taken from the MBR pilot plant was pre-screened at 50 µm and then at 25 µm as shown in Figure 7. The total and soluble COD of the screened supernatant were measured in order to check the quality of the supernatant.

Figure 7 Sludge supernatant preparation

Two membrane samples, whose water permeability was previously measured with ultrapure water following the protocol defined for the membrane characterization, were fouled in a second laboratory unit similar to the first pilot unit shown in Figure 4. The protocol, to obtain a long term fouling on the membrane with a drop of 75% permeability, was established in a reasonable time. Fouling periods of 24 hours and 48 hours have been tested: the “24 hours” fouling experiment was selected because the further permeability drop between 24h and 48h was not significant. During the 24 hours of operation, the return liquor and permeate were totally recycled in the storage tank. The feed water was changed after 12h of filtration. The samples were rinsed with de-ionised water to remove any cake deposits before measuring the permeability. Samples permeability was measured with de-ionised water during 30 min under a pressure of 0.2 bar before cleaning.

Photos were also taken after the fouling and the cleaning in order to see visually the effect of the cleaning product.

After repeating the tests on 3 membrane samples, the more promising products were then tested on the flat sheet membranes fouled in the pilot plant in order to verify their effectiveness on a real fouling.

I.2.3 Fouling performed at full scale and cleaning experiments at lab-scale

Two immersed flat sheet membranes (1.83 m^2) were fouled by filtration directly into the MBR pilot plant during 5 months. The hydraulic operating conditions were adapted to accelerate the fouling mechanism by using a high flux (30-40 $L/h.m^2$). The cake layer was removed three times with a tap water jet in order to accelerate the development of irreversible fouling. After 5 months of operating time, membrane samples were cut and rinsed with de-ionised water: their permeability was measured during 3 hours under a pressure of 0.2 bar in the similar laboratory unit shown in Figure 4 before cleaning. Cleaning was carried out similarly to sludge supernatant fouled membrane samples with the selected chemicals. Each reagent was tested on 3 membrane samples.

Figure 8 Flat sheet membranes immersed in the pilot plant

Photos were also taken after the fouling and the cleaning in order to see visually the effect of the cleaning product.

I.2.4 Tests at full scale

Two intensive cleanings were performed during the pilot trials on the commercial A3 Water Solutions MaxFlow-Membrane-Modules: one by soaking the membrane in a standard chlorine solution and the other in a reagent selected from the previous results.

I.2.5 Cleaning products selection

A dozen of cleaning reagents, listed in Table 4, classified into four classes of reagents were considered: sodium hypochlorine as reference, other detergents, and enzymes products and chemicals acids.

Table 4 Cleaning reagents

	Nature	Reagent	Formula/ Notation	Concentration
1	Detergent	Sodium hypochlorine	NaOCl	200 ppm and 1900 ppm Cl-
2	Detergent	Caustic soda	NaOH	0.013% (w/w)
2	Detergent	Hydrogene Peroxide (50%)	H_2O_2	0.5 %(w/w) H_2O_2
2	Detergent	A3 Activor A 101 (KOH, NaOH, NTA-Na-Salts)	A101	1% (w/w)
3	Enzymes	Ultrasil 67 +Ultrasil 69 new (ECOLAB)	U67 + U69new	0.5 % (w/v) and 1 % (w/v)
3	Enzymes	Filzym p (REALCO)	Filzym p	1% and 2% (w/w)
3	Enzymes	A3 enzymes product	SERL	1% and 2% (w/w)
4	Acid	Hydrochloric acid	HCl	0.056 % (w/w)
4	Acid	Citric acid	$C_6H_8O_2$, $1H_2O$	1 % (w/w)
4	Acid	A3 activor A 103 (HNO_3, H_3PO_4..)	A 103	1% (w/w)

The cleaning reagents to be tested satisfied the membrane tolerance with a pH range between 2 to 11. The cleaning conditions for the lab tests were defined as following: two hours soaking at room temperature 20°C. A soaking was chosen in order to have only the chemical effect and avoid any mechanical effect. The chosen time and temperature of the cleaning were in accordance with the cleaning conditions in full-scale MBR plants.

I.2.6 Results interpretation

The results were interpreted first from the de-ionised water permeability values of the new, fouled and cleaned samples. The following criterion was also used to compare the chemicals effectiveness:

Percentage of recovered permeability after cleaning: $R = \frac{Lp_{aftercleaning}}{Lp_{new}} * 100$

Lp_{new}: Permeability of the new membrane (L/h.m^2.bar, 20°C)
$Lp_{after\ cleaning}$= Permeability after cleaning (L/h.m^2.bar, 20°C)

II. Results & Discussion

II.1 Pilot trials results

II.1.1 Mixed liquor characteristics

The trials started in June 2006 for 12.5 months. The mixed liquor was regularly characterized in order to depict possible changes of its characteristics. The characteristics of the MBR activated sludge remained relatively constant exept during some biological disruptions and in the range of usual MBR mixed liquor. The measured parameters are given on average in Table 5.

Table 5 Mean sludge characteristics in the biological tank

Parameter	Average	Minimum	Maximum	Samples number
Mixed liquor concentration in biological tank (gMLSS/L)	9.6	3	17	208
COD of the sludge supernatant (mg/L)	44.2	10.4	189	206
Mean floc size D50 (µm)	28.6	24	35.3	38
Viscosity (Pa.s)	0.008	0.004	0.018	58
CST (s)	10.6	6.7	26.9	53
Specific resistance (10^{12} $m^{-1}.kg^{-1}$)	10.4	2.6	24	50
Polysaccharides concentration (mg/L)	6.4	<2	27.8	47
Proteins+ Humic acids concentration (mg/L)	18.5	8.6	32.1	43
Proteins+ Humic acids/ Polysaccharides (mg/L)	5.3	0.7	14.2	35

II.1.2 Quality of the treated water

The quality of the treated water throughout the trials is given in Table 6. The biological treatment was according to the expectations in MBR: the COD concentration in the effluent was on average 16.7 mg/l and always less than 70 mg/l, the total suspended solids were totally removed with a very low turbidity in the treated water (<0.1 NTU). The total coliforms concentration in the permeate water was on average 7.4 nb/100ml and varied from 0 to 32 nb/100ml. The presence of coliforms detected in some permeate samples can be related to the difficulty to take a sterile sample. The removal was at least 6.7 log but varied depending on the raw water characteristics.

The average total nitrogen removal was only around 55% since the start of the trials due to the excessive membrane aeration for the quantity of activated sludge volume. This pilot design was chosen in order to fit to all module sizes that will be tested in the framework of the AMEDEUS project. Other European manufacturers plan to deliver modules with smaller membrane area.

Table 6 Quality of the treated water

Parameter	Average	Minimum	Maximum	Samples number	Mean removal rate
COD (mg/L)	16.7	4	69	182	96.6%
TN (mg/L)	26.9	12	79	167	54.5%
Total coliforms (nb/100mL)	18	0	110	10	7.2 log
Thermotolerant coliforms (nb/100mL)	1.5	0	6	10	6.7 log

II.1.3 Optimization of the filtration operating conditions

The initial clean water membrane permeability was around 1600 L/m².bar at 20°C.

The filtration operating conditions were optimized in order to operate with a maximum flux and the lower membrane air consumption. At start, the optimised filtration flux was sought when operating with standard operating conditions of A3 Water Solutions: 8min of filtration followed with 2 min of relaxation; a membrane air flow rate of 0.34 $Nm^3/h.m^2_{membrane}$. The filtration net flux was increased step by step from 10 to 26.4 $L/m^2.h$ at 20°C by 3-5 $L/m^2.h$ increments approximately every 2 weeks as shown in Figure 9. For a net flux of 26.4 $L/h.m^2$ at 20°C, the membrane permeability stabilized after a rapid decrease at around 550 $L/h.m^2.bar$ at 20°C.

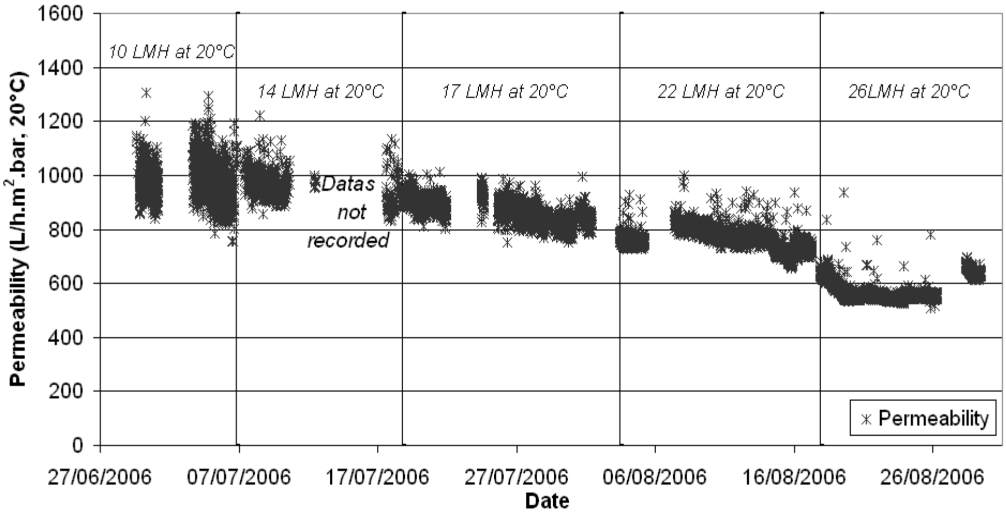


Figure 9 Operating flux

A new cleaning strategy, combining the use of daily backwashes and maintenance cleanings every 1-2 weeks, was developed. To test the effectiveness of this new cleaning strategy, the membrane air flow rate was decreased from 0.34 to 0.21 $Nm^3/h.m^2_{membrane}$ to obtain a fouling. The decrease of the membrane air flow rate led to a permeability drop of around 14% as shown in the first zone of the Figure 10. The cleaning strategy was then implemented: it stopped the permeability drop tendency and the permeability stabilized during 4 weeks as shown in the second zone of the Figure 10 with a net flux of 25.5 $L/h.m^2$ at 20°C by keeping a 0.21 $Nm^3/h.m^2$ membrane air flow rate. To ensure that the permeability stabilisation was due to the cleaning strategy, the cleaning strategy was stopped and the same conditions as for the first zone were used. That led to a new decrease of the permeability of 16 % as shown in the third zone of the Figure 10. So, the developed cleaning strategy was efficient to maintain the membrane performances with a net flux of 25.5 $L/h.m^2$ at 20°C by keeping a 0.21 $Nm^3/h.m^2_{membrane}$ membrane air flow rate.

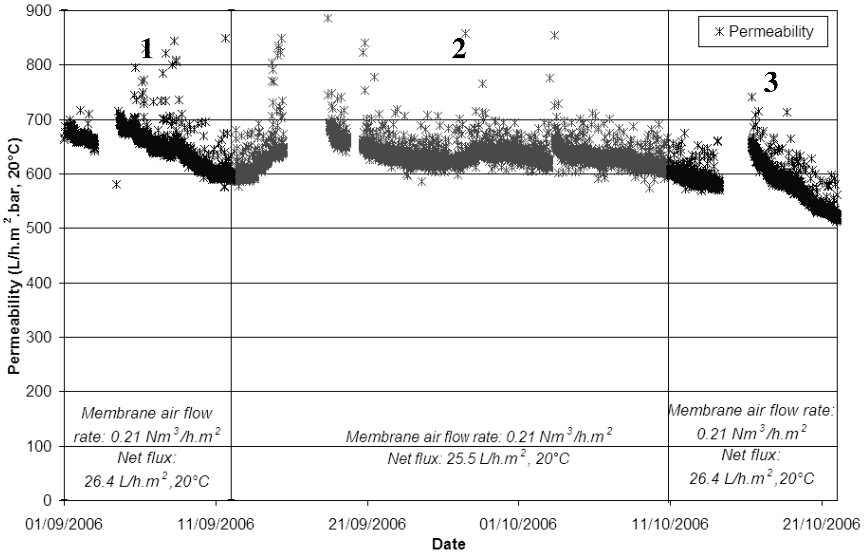


Figure 10 Validation of novel cleaning strategy under optimised filtration flux

Following this period, some biological disruptions occurred that caused biological foaming in the pilot. During one week, the process operated with low membrane air flow rate and low filtration flux. After this week, a permeability drop to 250-300 L/h.m^2.bar at 20°C was observed when operating again with a flux of 25.5 L/h.m^2.bar at 20°C and a membrane air flow rate of 0.21 Nm^3/h.m$^2_{membrane}$. But with the previous cleaning strategy found and without an intensive cleaning, the membrane permeability successfully recovered over 2 weeks as shown in Figure 11. The fouling mechanisms due to the changes in mixed liquor quality were not clearly identified as no correlation with the mixed liquor parameters could be drawn.

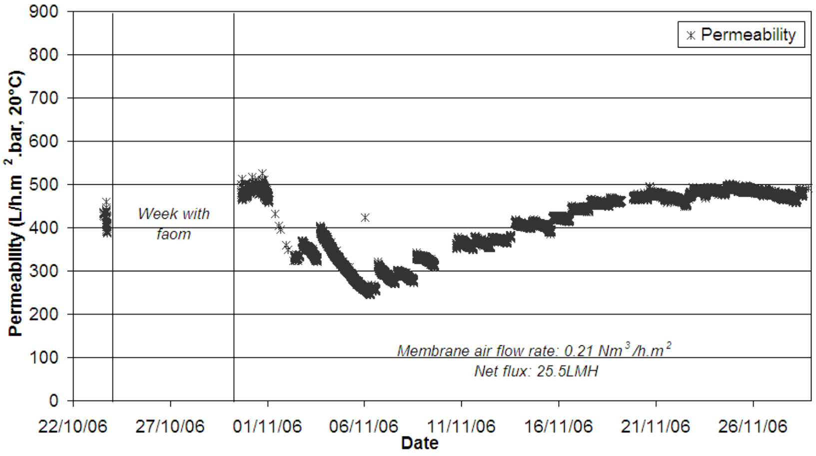


Figure 11 Recovery of the membrane permeability after fouling event

II.1.4 Impact of peak flows on the membrane performances

One more field of interest was to see if the-stabilized system can handle peak flows without any significant drop of the permeability. To investigate this, peak flows were programmed to occur twice a day during two hours (between 9:00 and 11:00 and between 15:00 and 17:00) with a 50% increase of the instantaneous filtration flux and of the feed flow rate. The same membrane air flow rate and operating conditions as previously were maintained during these trials.

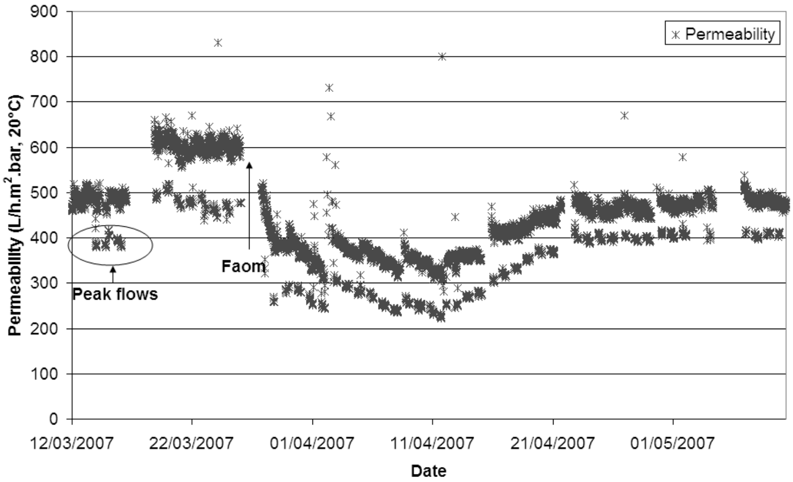


Figure 12 Peak flow trials

During the peak flows as shown in Figure 12, a decrease of the permeability was observed but the same membrane performance was recovered after the peak flows (probably no dynamic fouling but head loss in pipings). No loss of permeability was observed from the beginning of the peak flow tests up to 26 March 2007. At the end of March 2007, biological foaming occurred and some mixed liquor was lost, causing a decrease of the suspended solids in the system from 13 to 5 g/L. Because of the biological stress due to the formation of foam and the loss of biomass, the membrane permeability decreased from 600 to 300-350 L/h.m^2.bar at 20°C. In spite of that, the operating conditions and peak flows were maintained. With these conditions, a recovery of the membrane permeability was observed with the recovery of a better sludge quality. So, it was concluded that the process can support peak flows of 2h at a 1.5 higher filtration flux twice a day even after fouling event due to biological stress.

II.1.5 Increase of the MLSS concentration

After the impact of the peak flows on the membrane performances were tested, the mixed liquor concentration in the membrane tank was voluntary increased up to 20 gMLSS/L by decreasing the recirculation flow rate and increasing the volumetric loading (increase of the feed flow rate and decrease of the sludge volume in the biological tank). The same operating conditions as previously were kept. The results are shown in the Figure 13.

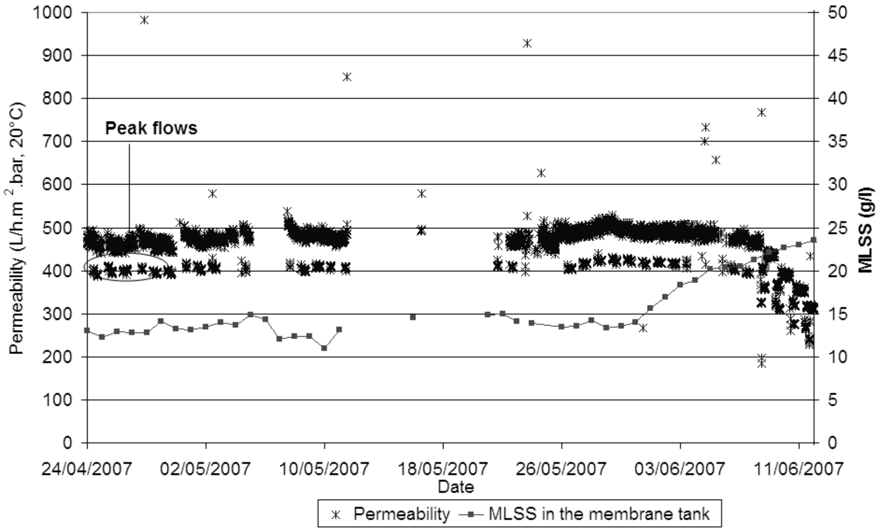


Figure 13 Increase of the MLSS concentration

The Figure 13 shows a drop of the permeability when the mixed liquor concentration was superior to 20 gMLSS/l that seems to be due to the peak flows impact.

II.1.6 Crash test

To test the ability of the modules to recover from clogging, a crash test was performed at the end of the trials on the bottom module. The same operating conditions as previously were kept and the membrane air was stopped, to simulate a failure of the aeration system in a full-scale plant, until a Trans Membrane Pressure (TMP) of 0.45 bar was reached as shown in Figure 14. The pilot was then operated with the normal operating conditions, but with a higher TMP and could support the next peak flow. During the following two days the TMP gradually decreased and reached its value before the crash test. It could be demonstrated that the crash test did not adversely affect the membrane performance.

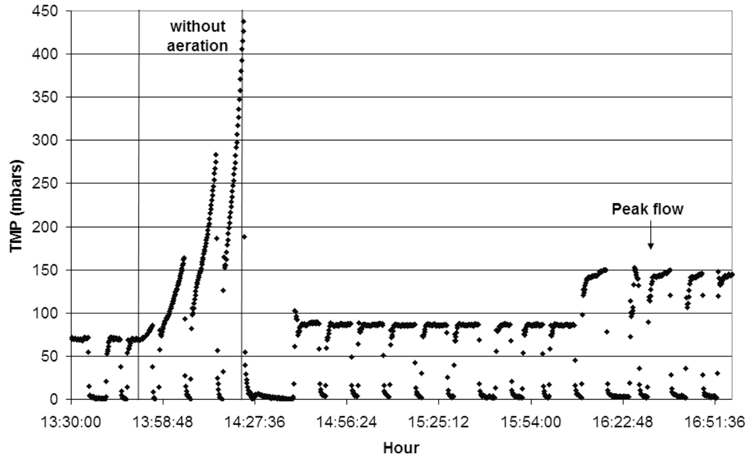


Figure 14 Crash test

II.1.7 Impact of the double-deck configuration

Throughout all the trials, the permeability of each module (top and bottom) was measured once per week as shown in Figure 15. Both modules seem to follow a similar fouling pattern. This observation was noted also for the evolution of the critical flux determined in-situ of each module. The double-deck configuration did not affect the membrane performances.

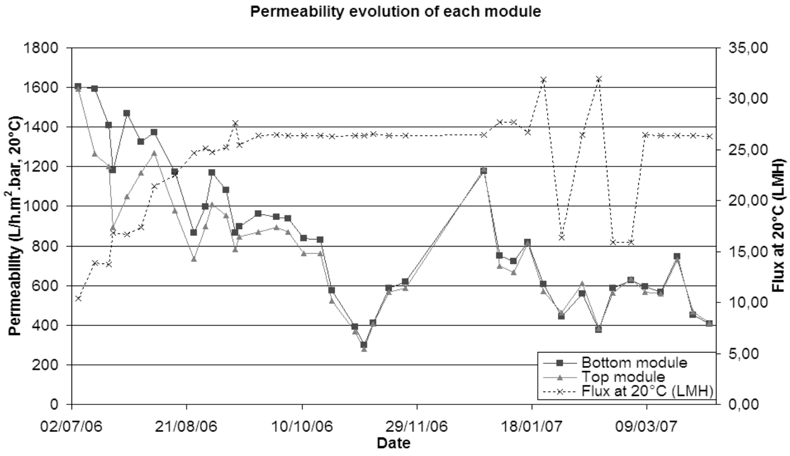


Figure 15 Evolution of the permeability of each module

II.1.8 Pilot trials conclusions

These trials enabled to develop optimal operating conditions with the A3 Water Solutions technology that allow the system to support fouling due to the biological stress, peak flows or membrane blockage due to the air membrane breakdown.

Under typical biological operating conditions (MLSS=10 gSS/L; SRT= 28.6 days; F/M ratio=0.13 kgCOD/kgMLSS/d), the net optimum flux found was of 25.5 L/h.m^2 at 20°C for a relatively low membrane air flow rate of 0.2 Nm^3/h.m$^2_{\text{membrane}}$ and an adapted cleaning strategy for flat sheet membrane using backwashes and maintenance cleanings. These operating conditions corresponded to a permeability around 500-600 L/h.m^2.bar at 20°C. The results of the trials showed that these filtration operating conditions helped to recover and maintain the permeability even after the membrane had suffered some biological fouling. The process can also support peak flows of 2h at a 1.5 higher filtration flux twice a day even after fouling due to some biological stress. The membrane performance can be also recovered after severe membrane clogging due to the air membrane breakdown. The double-deck configuration did not affect the membrane performance thorough the trials.

The trials lasted 12.5 months and finished in June 2007. Further tests will be performed at pilot-scale and full-scale by A3 Water Solutions to validation the results obtained at Anjou Recherche and to further develop the novel MBR filtration system.

II.2 Lab-scale trials results

II.2.1 Cleaning tests on sludge supernatant fouled membrane samples

The chosen dozen cleaning reagents were first tested on sludge supernatant fouled membrane samples. The fouling protocol is described in paragraph I.2.2. The permeability of each new membrane sample, after fouling and after cleaning is reported in the Figure 16. The soluble COD concentration for each test is also indicated.

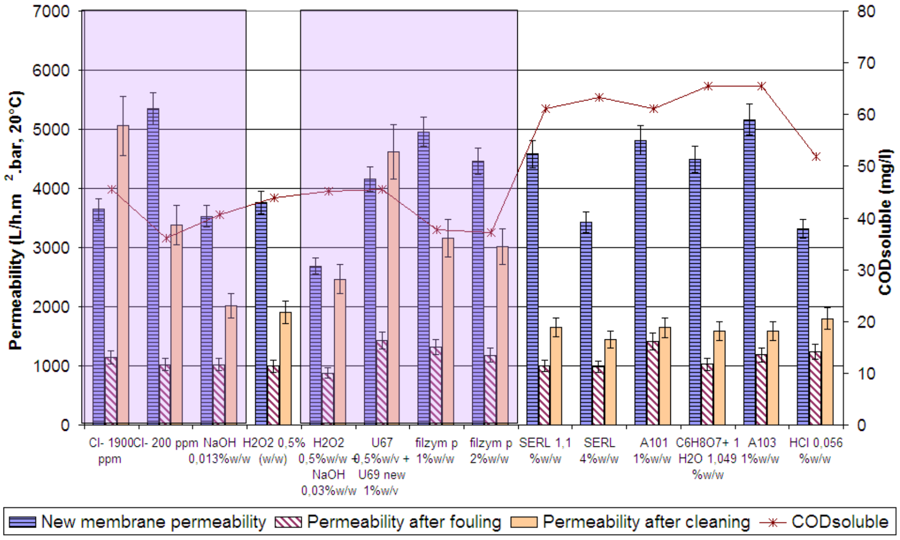


Figure 16 Cleaning results with each reagent on sludge supernatant fouled membrane samples

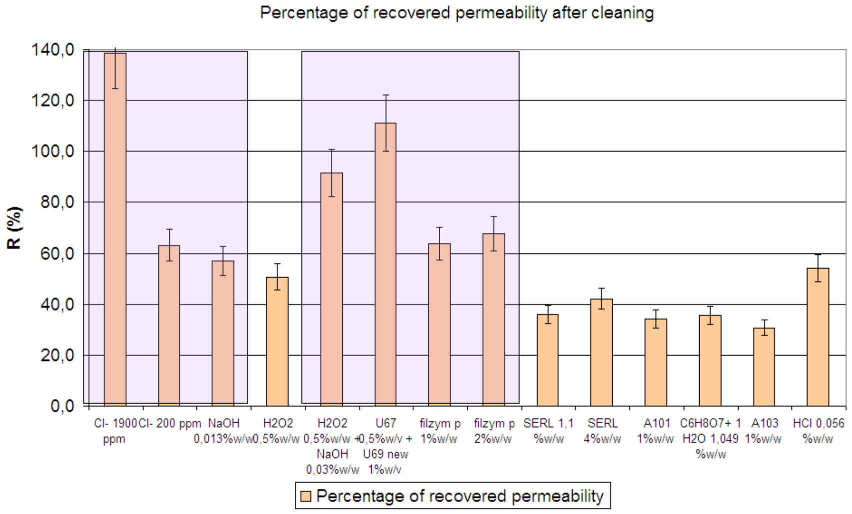


Figure 17 Percentages of recovered permeability after cleaning

The average permeability of the new membrane was around 3700 L/h.m^2.bar at 20°C but a variation of 33.5% can be observed: the initial water permeability values were relatively heterogeneous as shown in Figure 16. After fouling with the supernatant, a mean permeability of 1170 L/h.m^2.bar, 20°C was measured on the different samples with a lower variation of 17%.

With regard to the cleaning reagent effectiveness, Figure 16 shows that acid cleaning was not efficient. Cleaning with detergents (caustic soda and hydrogen peroxide with caustic soda) and enzymes reagents (Ultrasil and Filzym p products) gave better results: the percentages of recovered permeability were higher than 55% as shown in Figure 17. Tests with the best reagents were repeated three times in order to confirm their cleaning effectiveness. The results of the repeated tests are given in Figure 18. Figure 19 presents the results in term of percentage of recovered permeability.

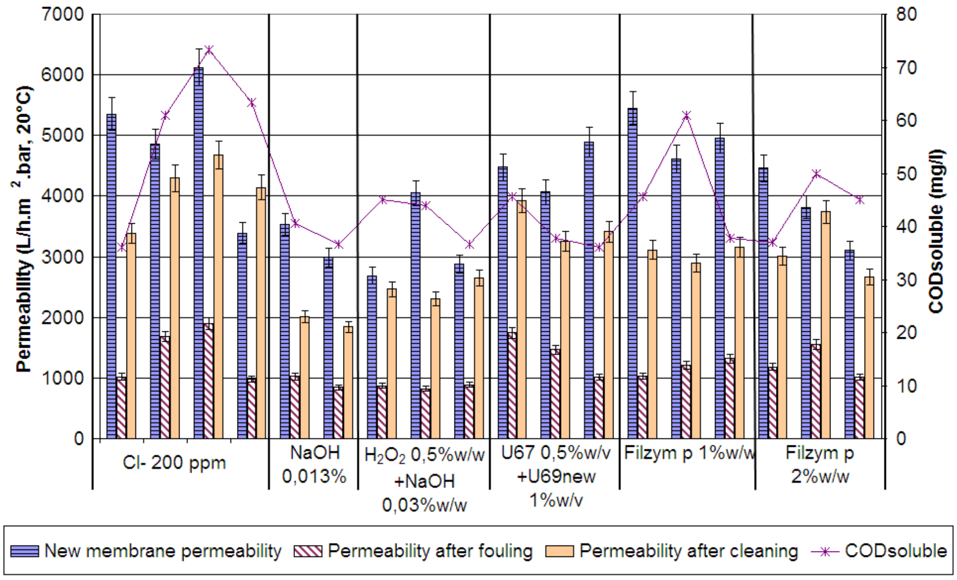


Figure 18 Cleaning results with each reagent on sludge supernatant fouled membrane samples

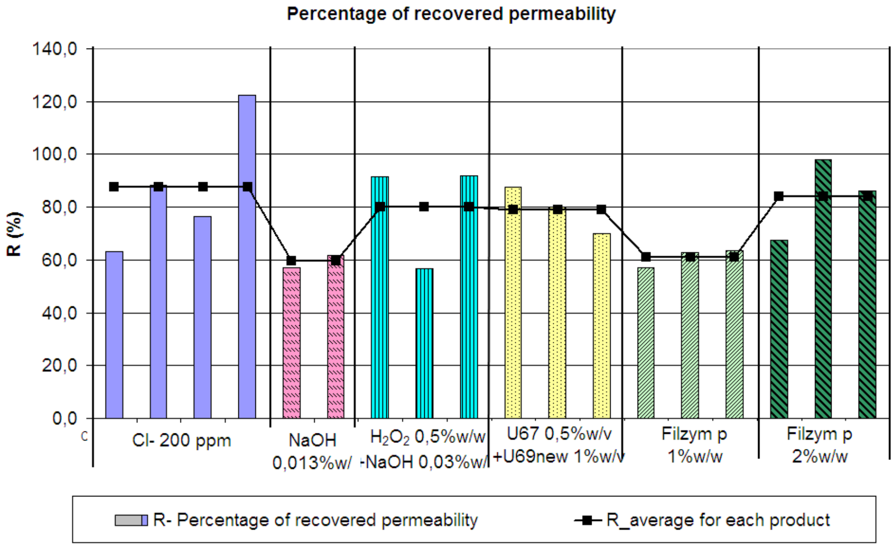
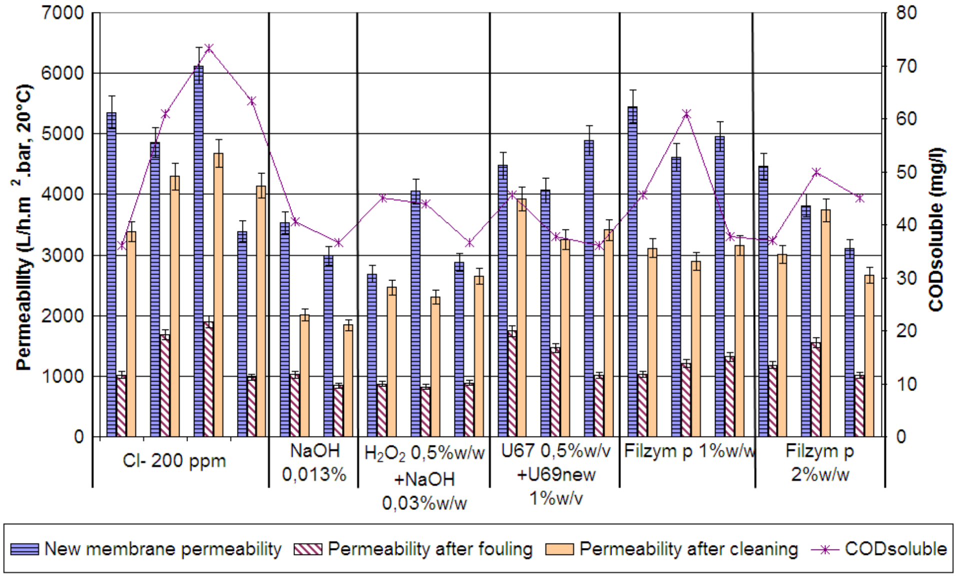


Figure 19 Percentages of recovered permeability after cleaning

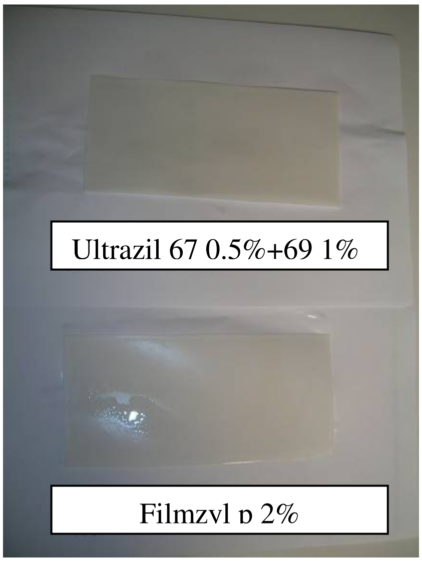


The results of Figure 18 and Figure 19 show that the chlorine solution at 200 ppm, the hydrogen peroxide with caustic soda at pH 11, the Ultrasil and Filzym p reagents at 2%w/w provided similar cleaning performances. Caustic soda seemed to be less efficient than the others according to permeability values and percentage of recovered permeability. The results for Filzym p at a concentration of 2%w/w seemed to be slightly better according to the percentage of recovered permeability than at a concentration of 1%w/w. Following these results, caustic soda and Filzym p 1%w/w were considered as the least efficient and therefore were not tested further.

Photos were also taken after fouling as shown in Figure 20 and after cleaning as shown in Figure 21. The visual aspect allows also to note the cleaning reagent effectiveness as shown in the Figure 21 for the Ultrasil 67 0.5%w/v+ 69new 1% w/v and Filmzyl p 2%w/w products.

Membranes after fouling

Figure 20 Membrane samples after fouling



Membranes after cleaning

Figure 21 Membrane samples after cleaning

In Figure 22, the aspect of membrane samples after cleaning with the different reagents is shown. It seems that the more efficient the cleaning product is, the more the membrane get back to the intital white colour after cleaning. The visual aspect of the samples after cleaning confirmed the previous observations done in regard with the effectiveness of the different cleaning reagents. The chlorine at 200 ppm and 2000 ppm, Hydrogen peroxide with caustic soda at pH 11, Filzym 1%w/w and 2%w/w, Ultrasil U67 0.5%v/w +U69new 1%v/w enabled to recover a white membrane piece after cleaning. The samples cleaned with caustic soda at pH 11 are more yellowish and for acid and A3 products the colour did not change a lot after the cleaning.

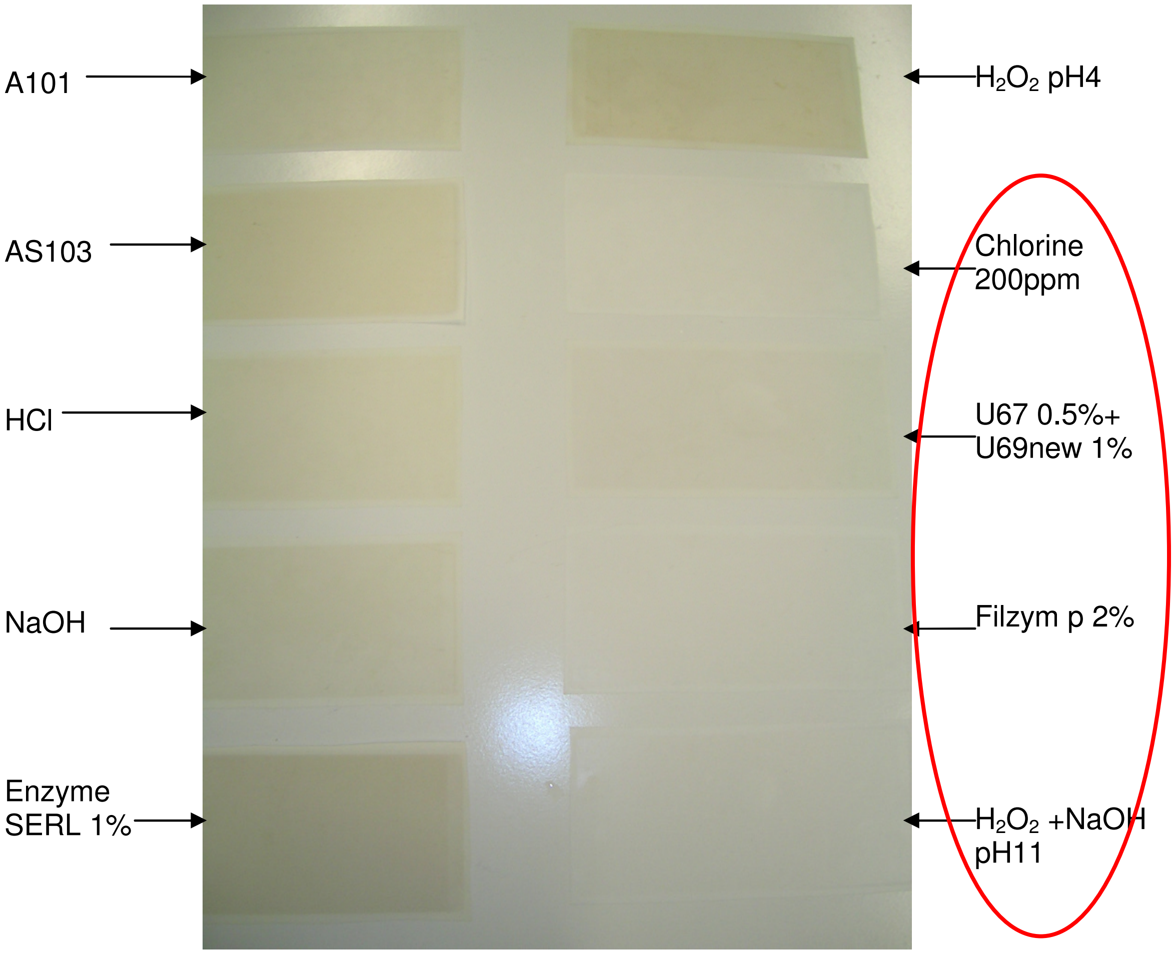


Figure 22 Comparison of the aspect of membrane pieces after cleaning with different agents

II.2.2 Cleaning tests on fouled membrane samples operated at high flux in MBR pilot plant

Two flat sheet membrane plates were operated for 5 months in the MBR pilot plant. After removing the cake deposit with a tap water jet, membrane samples were cut. Samples with similar permeability were selected to perform cleaning tests. The tests with each chemical were repeated 3 times. The results in term of permeability are given in Figure 23.

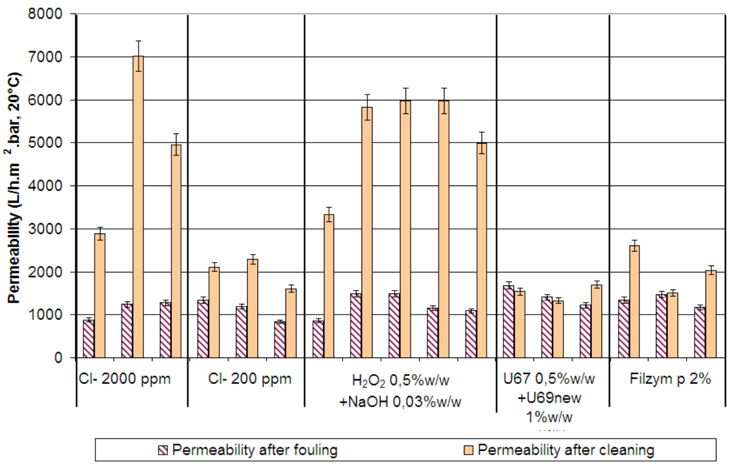


Figure 23 Repeated trials on fouled membrane samples operated at high flux in MBR pilot plant

After fouling, an average permeability of 1240 L/h.m^2.bar at 20°C was measured on the different samples with a variation of 35%. Some differences were observed between fouled membrane with supernatant (Figure 18) and fouled membrane in MBR pilot plant operated at high flux (Figure 23). It was difficult to compare the effectiveness of the reagents with the latter because the new membrane permeability of the cut membrane samples was unknown. Only tendencies could be given: hydrogen peroxide with caustic soda and chlorine solution at 2000 ppm allowed the best cleaning effectiveness, following by chlorine solution at 200 ppm and Filzym p at 2%w/w. Cleaning with Ultrasil reagent was not efficient. Cleaning differences observed between the 2 fouling protocols (membrane fouled with sludge supernatant and in MBR pilot plant) can be explained by a different fouling nature on the membrane and in particular, by the presence of a additional thin cake layer on the membrane surface of the in MBR pilot plant fouled membrane. When filtering at high flux, stronger and different cake deposit could be formed on the membrane. That can explain why the chlorine solution at a 2000 ppm concentration was more efficient than the one at 200 ppm in this case, while no difference of effectiveness was observed for sludge supernatant fouled membrane experiment. The better effectiveness of the hydrogen peroxide in this case can be related also to the fact that the membrane from the plates appeared stripped and, therefore damaged by the peroxide hydrogen.

The visual inspection showed that the more efficient the cleaning reagent was, the whiter the membrane was after cleaning. The aspect of membrane samples after a cleaning with the different products is shown in the Figure 24. The soaking with 2000 ppm chlorine solution gave the whiter membrane. The sample cleaned with hydrogen peroxide and caustic soda was a little more yellowish. Then, the less coloured samples after cleaning are successively the samples cleaned with: the 200 ppm chlorine solution, the Filzym p 2%w/w and the Ultrasil U67 0.5%v/w +U69 1%v/w.

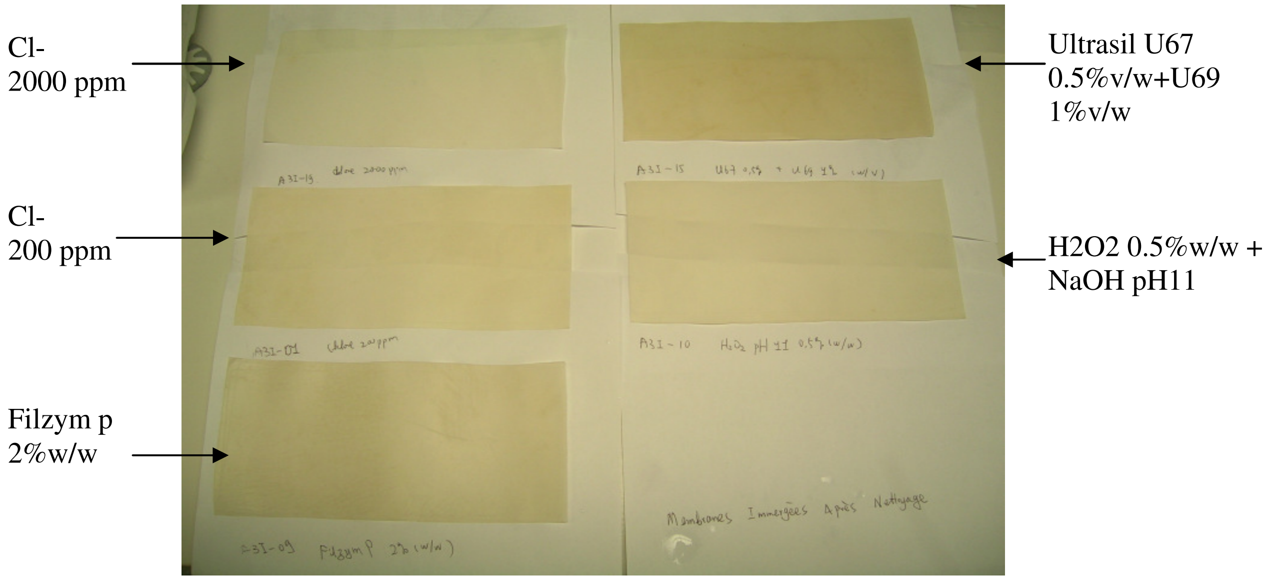


Figure 24 Membrane samples after cleaning

A complementary experiment was performed by soaking fouled membrane samples operated at high flux in MBR pilot plant in the selected chemicals at different concentrations. Colour evolution was observed with time. The test was repeated three times. The results are given in Table 7. The "++++" corresponds to the samples the more coloured and the "–" to whiter samples. The colour evolution was similar for the different concentrations of hydrogen peroxide, Ultrasil and Filzym p reagents but differences were observed for the chlorine solutions at 2000 ppm and 200 ppm: the more concentrated the solution was, the faster the membrane became white. The results did not change a lot by soaking 2h or 4h but after one night of soaking, all the membrane samples became white with the exception of the ones cleaned with Ultrasil which appeared less efficient than others. Hydrogen peroxide with caustic soda seemed to react slower than chlorine solution which is in contradiction with the permeability results presented in Figure 23.

Table 7 Colour evolution (visual) during the soaking of membrane samples

Product	Before cleaning	2h of soaking	4h of soaking	1 night of soaking
Filzym p 2,65% (w/w)	++++++++	+++++	+++	-
Filzym p 2% (w/w)	++++++++	+++++	++++	-
U67 0,5%(w/v)+U69 1% (w/v)	++++++++	+++++	++++	+
U67 1%+U69 2%	++++++++	+++++	++++	+
H_2O_2 0,5%(w/w) + NaOH 0.03%w/w	++++++++	+++	++	-
H_2O_2 0,2% (w/w)	++++++++	+++	++	-
Cl- 200ppm	++++++++	++	+	-
Cl- 2000ppm	++++++++	+	+	-

II.2.3 Full scale cleaning tests

Two intensive cleanings by soaking were performed during the pilot runs with the MaxFlow membrane module, whose initial permeability in sludge was around 950 L/h.m^2.bar at 20°C: one with chlorine at 1000 ppm during 4h at 17°C and one with the hydrogen peroxide at 0.5%w/w and caustic soda at 0.03%

during 2 hours at 23°C. The hydrogen peroxide with caustic soda was chosen because it gave similar results to the chlorine solution at 2000 ppm for the membrane fouled in the pilot plant. The first intensive cleaning was done during 4h instead of 2h because the temperature was relatively low. During the pilot runs, maintenance cleanings were performed with chlorine at 200 ppm too. The membrane permeability, before and after the cleanings, is given in
Table 8.
The intensive cleaning with hydrogen peroxide at 0.5%w/w and caustic soda at 0.03% appeared less efficient than the one with chlorine at 1000 ppm. Its effectiveness was quite similar to maintenance cleaning efficiency with 200 ppm chlorine. Moreover, the concentration in hydrogen peroxide was the maximum that the membrane can accept whereas a 2000 ppm chlorine solution concentration can be used.
This procedure also showed that full scale test remains essential to validate the chemical reagent efficiency and that laboratory trials can only provide indicative results. This demonstrates also the difficulty to simulate real long-term irreversible fouling in an accelerated way.

Table 8 Cleaning tests at full scale

	Permeability before cleaning ($L/h.m^2.bar$, 20°C)	**Permeability after cleaning ($L/h.m^2.bar$, 20°C)**
Chlorine - 1000 ppm (Intensive cleaning)	500	820
Chlorine - 200 ppm (Maintenance cleaning)	550	580
Hydrogen peroxide - 0.5%w/w (Intensive cleaning)	450	500

II.2.4 Other criteria for the choice of the cleaning reagents

The reagents must not be only compared in term of effectiveness. Other criteria as price, impact on membrane material, impact on environment, risks for the operators and cleaning implementation problems as foam formation must be taken into consideration. Table 9 sums up advantages and disadvantages of each cleaning reagent tested.

Table 9 Advantages and disadvantages of the cleaning reagents

Products	**Advantages**	**Disadvantages**
NaOCl	- cheap	- prohibited / restricted in some countries - formation of by-products (TMH) - dangerous for the health of the users (by inhalation) - membrane ageing
H_2O_2	- cheaper than enzymes products - alternative to NaOCl	- more expensive than NaOCl - can damage organic membranes - explosion risks
Ultrasil	- without danger for the users	- more expensive than NaOCl and H_2O_2 but a little less than Filzym p - foam formation
Filzym p	- without danger for the users	- longer time of cleaning required? - expensive

II.2.5 Cleaning tests conclusions

The Membrane Center of excellence ARAMIS (Veolia) has developed new lab scale protocols to foul membrane samples and perform different cleaning experiments for replacing chlorine in MBR plants. The cleaning investigation was focused on the long term irreversible fouling.

Cleaning tests were successively performed on sludge supernatant fouled membrane samples, on fouled membrane samples operated at high flux in MBR pilot plant for 5 months and on full scale commercial modules of the pilot plant. The results are as follows: chlorine, hydrogen peroxide, Ultrasil and Filzym p reagents were efficient on sludge supernatant fouled membrane samples. These cleaning reagents were then tested on fouled samples operated at high flux in MBR pilot: chlorine solutions at 2000 ppm and hydrogen peroxide gave the best results following by chlorine at 200 ppm and Filzym p at 2%w/w. The Ultrasil reagent was less efficient. These results provided only tendencies of the reagents effectiveness because the initial membrane permeability of the new samples was unknown. A full scale test was finally performed with hydrogen peroxide, one of the most promising chemicals: the effectiveness of intensive cleaning with hydrogen peroxide at 0.5%w/w was close to the effectiveness of maintenance cleanings with chlorine at 200 ppm and worse than the intensive cleaning with chlorine at 1000 ppm.

Therefore, chlorine was the most efficient chemical in all cleaning protocols: its concentration has to be adapted to the fouling nature. For the other chemicals, differences were observed between different experimental protocols. In particular, hydrogen peroxide was more efficient on fouled membrane plates in pilot plant operated at high flux than on sludge supernatant fouled membrane samples and on the full scale commercial module. This difference can be explained by a different fouling nature on the membrane and in particular, by the presence of an additional thin cake layer on the fouled membrane surface operated at high fluxes in MBR pilot plant. Complementary tests need to be performed to understand the reagent action on the fouling and on the membrane. This procedure also showed that full scale tests remain essential to validate the chemical reagent efficiency. It is also essential to take into account others criteria, such as the plant operator’s safety, the cost of the reagent, its impact on the membrane material and on the environment to select the right chemical.

In the future, similar experiments will be performed on other type of membrane for a better understanding of the mechanisms involved and to validate an easy-to-use methodology on fouling and chemical cleaning.

III. Economical analysis

The evaluation of the novel module concept should be first on technical, but also on economical basis. The technical interpretation of the results of the research activities was presented within the chapters before, so that the following chapter only contains the economical evaluation of the operation of the A3 Water Solutions´ MaxFlow membrane modules.

III.1 Pilot trials

As seen in section II.1, the optimum membrane net flux was found at 25.5 L/m².h (at 20 C) with an air flow rate of 30 Nm³/h (0.2 $Nm^3/h.m^2$). In addition it was shown, that the wastewater treatment process of the MBR pilot plant could support peak flows of 2 hours and with a flux up to 150 % of the “regular” flux.

Table 10 Technical specifications for the A3 MaxFlow membrane modules

	Original Single deck	**Original Double deck**	**Novel Double deck**	**Expectations Triple deck**
Net flux at 20°C (l/h.m²)	15	15	26	26

Hourly flow rate (m^3/h)	1.05	2.10	3.64	5.46
Peak flows ($l/h.m^2$)	Not evaluated	Not evaluated	2x 1.5 net flux for 2 x 2h /day	Not evaluated
Specific Aeration Demand ($Nm^3/h.m^2$)	0.72	0.36	0.21	0.14
Specific Aeration Demand ($Nm^3/m^3_{permeate}$)	48	24	8	5
Membrane surface requirement ($m^2/(1000m^3/h)$)	66.7	66.7	38.5	38.5
Footprint filtration system ($m^2/(1000m^3/h)_{permeate}$)	457	228	228	152

Table 10 presents the technical specification of the A3 MaxFlow membrane modules implemented in single, double or triple deck, with the original operation strategy, and the novel operation strategy assessed in the present report. The values are all given for a 20°C condition, as extrapolation of the results obtained with the specific conditions of the trials, i.e. with the municipal wastewater of Maisons-Laffitte and under the assessed design and operation conditions. These values should be considered as indicative only and cannot be generalised to all other sites and conditions, however they demonstrate the dramatic performance improvement achieved with the novel operation conditions under multiple deck design. The membrane surface requirement is calculated considering the achieved net flux. Due to the demonstration of peak flow regime, about 30% less membrane surface may be required when designing with the peak flux.

Figure 25 shows the actual and next expecting improvements for the A3 filtration system in regards with the specific aeration demand per produced permeate unit and per membrane surface resulting in energy savings.

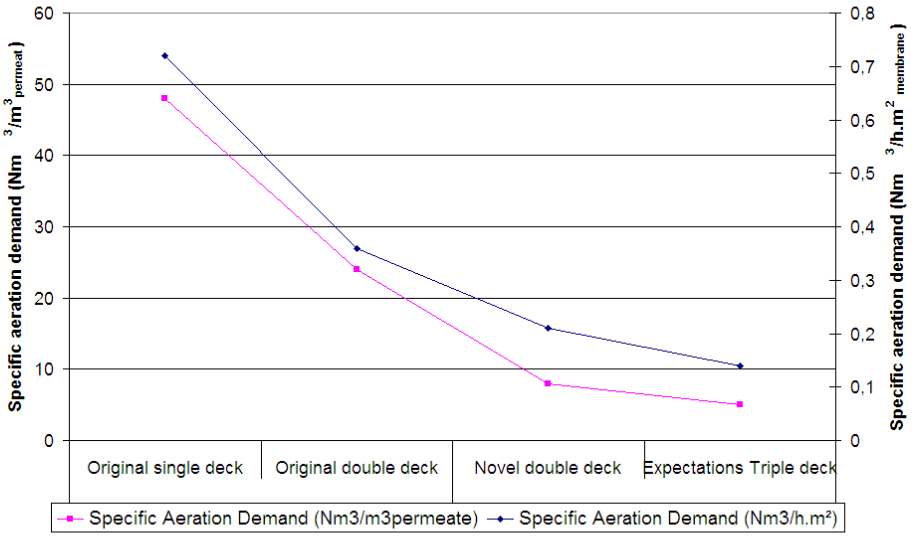


Figure 25 Improvement of the A3 filtration system with the novel cleaning strategy and expectations with the triple deck

Compared with the original single-deck design, the use of the novel double deck concept led to:

- 40% flux increase: less membrane surface is needed that leads to investment costs reduction;
- 70% footprint reduction for the filtration system: the novel filtration system is more compact;

- and more than 80% reduction of the membrane air demand per permeate volume produced: less membrane aeration is needed that leads to significant energy savings. Due to the upstream channel of the double-deck configuration, there is no need to blow additional air into the membrane tank to prevent the formation of a cake layer on the membrane surface and the novel cleaning strategy enables also the decrease of the membrane air flow rate.

The new concept with a specific aeration demand (SADp) of 8 $Nm^3/m^3_{permeate}$ outperforms now the performances of the current market leaders for MBR applications. The full-scale data collected by S. Judd (2007) show that the most optimized plants equipped with Zenon technology requires a specific aeration demand of around 12 $Nm^3/m^3_{permeate}$ and of around 20 $Nm^3/m^3_{permeate}$ for the more optimised plants equipped with Kubota technology as shown in Figure 26. The results obtained with the novel double deck concept at pilot scale are therefore very promising and will have to be verified at full scale.

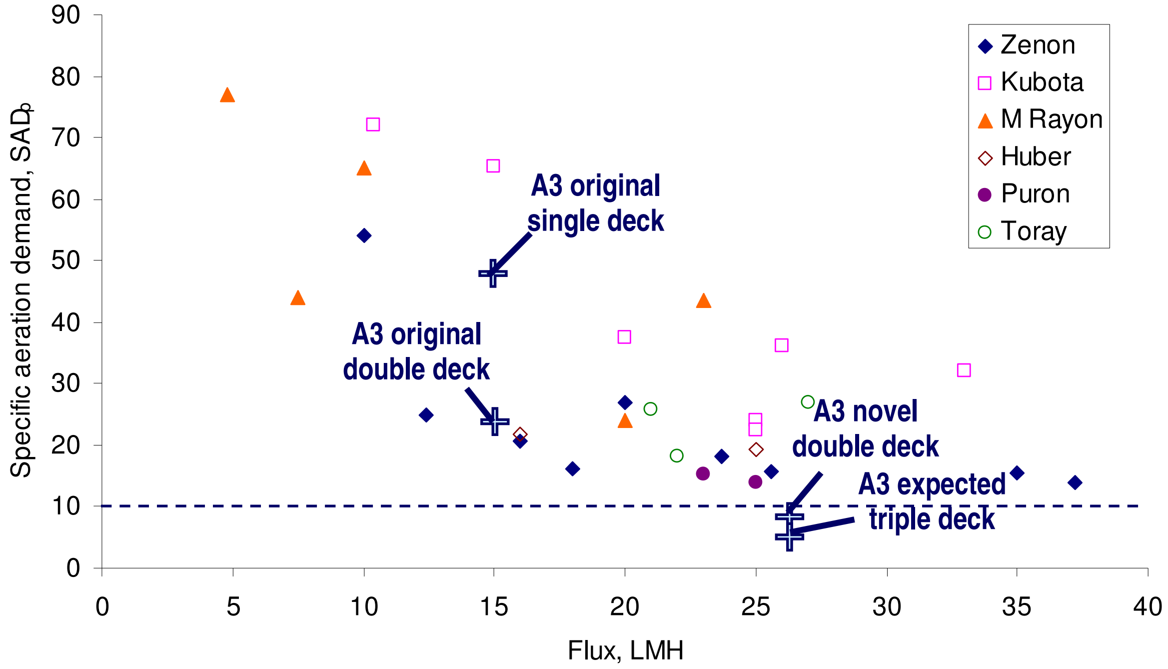


Figure 26 SADp of full scale plants for current market technologies (S. Judd, 2007) and comparision with A3 technology

With the implementation of a triple-deck design, more energy savings is expected by reducing more the membrane aeration demand: a specific air demand of 5 $Nm^3/m^3_{permeate}$ is expected.

It could be also demonstrated that the novel double-deck concept can support fouling events resulting from daily peak flow or biological disturbances. This provides further security to MBR plant designers and operators and lowers their maintenance requirements.

III.2 Cleaning results

In comparison to the described economical development of the membrane operation, only tendencies concerning the economical development of the cleaning strategy can be provided. Due to the indisputable efficiency of chlorine compared to the performances of the other cleaning chemicals an increasing economy can basically be reached by optimising the membrane-cleaning-concept. On this account costs of operation could be declined by using a concept which requires only maintenance cleanings with only little use of chemicals for a long time and only a few intensive cleanings. Hydrogen peroxide at 0.5% w/w at pH 11 was less efficient than chlorine at 2000 ppm and it is more

expensive than chlorine: higher operational costs are attended. It could be only envisaged in countries where chlorine is prohibited.
Most probably, occasional chlorine cleanings to recover the refractory fouling after hydrogen peroxide cleanings may not be avoidable.

Conclusion

The trials performed at Anjou Recherche enabled to optimize the operating conditions and the cleaning strategy for the MBR filtration technology of A3 Water Solutions.

The results showed that the A3 technology can operate at a flux of 25.5 L/h.m^2 at 20°C for a relatively low membrane air flow rate of 0.2 Nm^3/h.m^2 under typical biological operating conditions (MLSS= 11g/L; SRT=28 d; F/M ration= 0.12 kg COD/kg MLSS.d). Compared with the original single-deck design, this led to a 40% flux increase (less membrane surface required), 70% footprint reduction for the filtration system (more compact process), and more than 80% reduction of the membrane air demand per permeate volume produced, leading to significant energy savings. The new concept outperforms now the performances of the current market leaders for MBR applications. It could be also demonstrated that the novel concept can support fouling events resulting from daily peak flow or biological disturbances for MLSS concentrations in the membrane tank inferior to 20 g/L. Few intensive cleanings will be required to maintain or recover the membrane performances that will limit the maintenance operations and costs and will make easier the operators work.

The lab-scale tests showed that chlorine was efficient for all types of fouling. Two other cleaning reagents could be considered to clean the membrane if the use of chlorine is forbidden: hydrogen peroxide at pH 11 and the Filmzym p enzyme reagent. With these reagents, the soaking conditions have to be optimized and the cleaning costs would be more important.

Further demonstration of the novel operation strategy will be performed at pilot- and full scale to validate the results obtained at Anjou Recherche, while considering the decrease of energy consumption. The triple deck module arrangement will be also tested in order to decrease more the membrane aeration per square meter of membrane and therefore further decrease the energy demand of the system.

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ANNEXS

Communications & Publications

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