1.0 - Activity progress.

1.1 Introduction.

The increasing demand of water for human requirements and the corresponding water purification processes represent an important topic in the context of the sustainable global development and power generation with low environmental impact. The possibility to obtain water with high purity grade from alternative processes of industrial grade wastewaters purification, also recovering contaminant metal ions, is a relevant matter to be faced and solved.

In the last 50 years, several new technologies for the substance's separation, generally called "membrane processes", have been extensively studied for the above- mentioned aims. These technologies use artificial membranes in order to promote the separation/purification/removal of contaminants according to the pore size of the membranes used and their chemical-physical and morphological characteristics. Such operations occur through separation processes based on the dimensions difference between membrane pores and size of contaminant species to be filtered/separated or through mechanisms of complex's formation and/or of charge repulsion with the aim of avoiding the passage through the membrane pores.

In particular, in this context, membranes based on Polysulfone (PSF) polymer are one of the most widely used materials due to the high hydrolytic, chemical and thermal stability, again high chemical and mechanical resistance, wide pH tolerance (1-13) and to Cl^- ions, in addition to their low cost and application flexibility. The ease of the manufacturing plays an important role as well as the possibility to manage the shape, size and pores distribution. This determines a high possibility of control of separation process. All these aspects make the membranes of PSF ideal candidates for the separation/filtration processes/systems, even for the high efficiency that supply to the process. The hydrophobicity and poor resistance to the so-called "fouling" phenomenon reduce the water permeability, molecular selectivity and own the duration of the process and this aspect represents the main drawback for their application. In order to have more hydrophilic membranes with "antifouling" properties, the choice of the "polymer-solvent-non-solvent system" with the aim of obtaining the correct morphology and usage of suitable additives able to improve the porosity and hydrophilic properties constitute the answer to define the performance of the selected process, in particular selectivity and permeability.

The main objective of the present project consisted into the realization of a joint research on sustainable and non-polluting separation techniques for the purification of industrial grade waste-waters using flat solid asymmetric polymer membrane systems with different morphology and properties.

2.0 - Resume of the 2nd year activity (2018)

The second year of activity covered the period from 01 January 2018 up to 31 December 2018.

During this period, starting from the results obtained in the first year, the activity was devoted to the optimization of the preparation procedure of asymmetric flat solid polymeric PSF membranes. The optimization was pursued maintaining fixed the operative parameters and experimental factors individuated in the previous activity year and revealed helpful to the desired morphology formation (finger-like macro-voids) and evaluating/varying other synthesis parameters. In particular, **six new parameters** were monitored, such

as: the solubilisation temperature (named here $\mathbf{T_s}$) of the starting PSF dispersion, brought from 80 up to 120°C to remove the polymer agglomerations individuated by CS-SEM during the 1st year activity; solubilisation time (named here $\mathbf{t_s}$) of the polymer dispersion (1 or 2 hrs.) for the same reason above-mentioned; the suitable viscosity of PSF dispersion to be stratified, surely correlated to the evaporation time (named here $\mathbf{E_t}$) and to the experimental factors used (e.g.: T_s and t_s, presence and concentration of p-123) with the aim of obtaining membranes with good mechanical characteristics; **Pluronic p-123 surfactant concentration**, whereas present, varied between 50wt.% up to 1wt.%., passing from 30 and 10wt.%, with the aim of improving the mechanical properties and the membrane cross-section morphology; de-mixing time (named here **Dt**), time of stay of the membrane inside the non-solvent coagulation bath and that is determining for the film formation, was varied from 10, 20, 40'' in order evaluate the influence on the transversal morphology and final thickness.

At the end, the initial Doctor-Blade knife thickness (named here **D.B.**), generating the final thickness on the membrane, was varied from the starting 100μm value up to 30 μm individuating the ideal thickness in order to have a sufficient space for the surfactant acting s as a pore-former during the de-mixing process. The synthesis parameters were varied one by one as well as the operating conditions of the synthesis procedure (such as T, V, t) and the new membranes were cast, one for each parameter modified. Cross-section SEM method was used as primary and determining characterisation to individuate the correct morphology and the acquisition or the elimination of the corresponding used parameter.

During the activity progress, hence, a **revised preparation procedure** was defined and a new batch of **14 membrane samples** was developed, always taking into the account the influence of the experimental parameters on final morphology. In the following **table 1**, the membranes developed during the second year are reported, together to their composition and used parameters:

Membrane	PSF, wt.%	p-123/PSF ratio		t_s, min.		T_s, °C		Dt, s			D.B., μm		
	5	Yes	Not	60	120	80	120	10	20	40	30	50	100
PSF2-12 BIS	X		X	X		X			X				X
PSF2-13	X		X		X	X			X				X
PSF2-14	X		X	X		X				X			X
PSF2-15	X		1:2	X		X			X				X
PSF2-16	X		1:2	X		X			X			X	
PSF2-17	X			X			X		X			X	
PSF2-18	X		X	X			X	X				X	
PSF2-20	X		X	X			X		X		X		
PSF2-21	X		X	X			X	X			X		
PSF2-22 BIS	X	1:100		X			X		X		X		
PSF2-23	X	1:10		X			X		X		X		
PSF2-24	X	3:10		X			X		X		X		
PSF2-25	X	1:10		X			X		X			X	
PSF2-26	X		X	X			X			X	X		

Table 1. Membranes prepared during the second-year activity

After the complete joint characterization with partner and evaluation of the results (*see External Report Prot. N.12/2019*), the following membranes (with and without surfactant) have been identified as prototypes to be further investigated/optimized during the third year of activity: PSF2-20 (pure PSF), PSF2-16 (50wt.% surfactant), PSF2 -22BIS (1wt% surfactant), PSF2-24 (30wt% surfactant) and PSF2-23 (10wt surfactant%).

Some characterizations on the membranes during the second year were realised in the third year.

3.0 – Description of the 3rd year activity

The activity of the third year was performed starting from January 01, 2019 up to December 31, 2019.

A preliminary state of the art was performed on the necessary membranes' properties (porosity percentage, pore shape and size, cross-section morphology, hydrophilic characteristics, permeability, selectivity, dynamo-mechanical properties, etc.) using surfactants, polyelectrolytes (here, PEs) and ionic liquids (ILs), as previously decided with partner, to be applied in UF processes. Commercial compounds such as Pluronic p123, Polyethileneimmine-PEI and CYPHOS-104, respectively were further studied (p-123) and newly individuated as possible candidates, since able to trigger defined behaviours in terms of micelles formation, metal ions complexation and charge repulsion mechanisms, respectively with the aim of modifying the pure PSF membranes morphology and to make them suitable for the UF and above-all for the removal/recovering of polluting metals ions.

The pore size of the membranes synthesised up to now was of about 80-120 nm (membranes without surfactant) and 30-40 nm (membranes with surfactant p-123), but not always with a uniform distribution and dimension; the molecular cut-off (MWCO) of the membranes for the application must be of about 2-50 nm. Hence, the pores diameter is equal/wider to the necessary dimension, but, in any case, compatible with the UF range (3 - 100nm).

Operatively, some lacking characterizations on membranes developed during the second-year activity were performed or again verified, whose results were preliminary to the successive activity. In particular:

- lacking cross-section SEM analysis on pure PSF2-26 membrane;
- surface SEM on the most representative membranes developed during the second year (PSF2-12BIS up to PSF2-26);
- AFM membranes on the most representative membranes developed during the second year (PSF2-12BIS, PSF2-16, PSF2-22BIS, PSF2-23, PSF2-24, PSF2-26 - see table 1);
- lacking permeability measurements on the most representative membranes developed during the second year (PSF2-22BIS up to PSF2-26 – see table 1);
- lacking contact angle measurements on the most significant samples developed during the second year (PSF2-26);
- FT-IR measurements on the developed membranes during the second year (PSF2-22BIS up to PSF2-26).

Successively, the new activity was started with the preparation/characterisation of the new samples.

In particular, commercial ionic liquid CYPHOS-104 IL (trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl) phosphinate) introduction into the PSF/solvent/surfactant (whereas present) system was tested and standardised in order to trigger the mechanism of charge repulsion inside the membrane to selectively filter the heavy metal ions. In this context, the following actions were performed:

1. evaluation of the ionic liquid solubilisation efficacy into the system;
2. individuation of the solvent for IL, its concentrations into the polymer dispersion and combinations with surfactant;

3. evaluation of the possible methods of IL solubilisation: mixing with the starting PSF dispersion in DMAc and surfactant (p-123), if present, as well as separated solubilisation phase of IL in organic solvents (decanol). It, in-fact, is not soluble easily (insoluble in water);
4. definition of the parameters for the membrane preparation, such as solubilisation and temperature time (Ts and ts), de-mixing time in the context of the CYPHOS104 presence.

In detail, some critical aspects in the formation of the membrane, were resolved and an important objective was found: the standardization of the preparation procedure of asymmetric pure polysulfone (AM-PSF) membranes containing both surfactant (Pluronic p123) and ionic liquid (CYPHOS104), for the production of films that can be used to separate polluting metal species. Such membranes obtained have demonstrated to have got good properties for the final aims, in particular a suitable morphology with asymmetry and finger-like macro-voids presence, as highlighted by literature in the field.

The fixed parameters after evaluation of the first year were: PSF 5wt.% as concentration, water as solvent; while during the second year were fixed: t_s: 60 ', T_s: 120°C, D_t: 20s, D.B.: 300μm. The samples were developed maintaining fixed these parameters and varying the ionic liquid content. The final preparation procedure was defined, as described in the following paragraph.

3.1 - Membrane preparation procedure

The membrane preparation procedure was finally optimized and it is here briefly described. The final operative parameters are indicated in bold.

PSF polymer concentration **(5 wt.%)** in **DMAc as a solvent** is treated at room temperature (25°C; 10 min.) under magnetic stirring. Surfactant Pluronic p-123 as received, whereas present, is added in the starting PSF/DMAc dispersion at room temperature. Different concentrations of p-123 were investigated (1, 10, 30 & 50 wt.%) and a concentration of **10wt.% of p123** was selected as ideal content for membrane preparation.

Three different Cyphos 104 IL concentrations (1, 1.5, 3wt.%), whereas present, was studied and, hence, added in this phase to the PSF/p123 dispersion, obtaining a complete solubilisation in DMAc at rT. The polymer dispersion solubilisation continues on hot plate at **T_s= 120°C** for **t_s=1hr.** under stirring (300 rpm covered with a watch glass avoiding the evaporation). After, the watch glass is removed and the solvent re-concentration phase of the solution is started. When the solution **viscosity** is adequate, it is immediately stratified by Doctor-Blade on a preheated glass at T=50°C. The calibrated Elcometer® Blade Knife Model 3580 was used setting different thicknesses; a **final thickness of 30 μm** was fixed as ideal. The final membranes have size of about 20 x 30 cm^2 with a good visual manufacture (no bubble or hole). The glass with the stratified solution is quickly immersed into the **non-solvent coagulation bath (H_2O)** at room temperature. The **non-solvent volume is fixed at 4 litres**. After a fixed **de-mixing time Dt=20''**, the membrane is quickly removed from non-solvent bath and placed between two absorbent paper sheets (substituted several times during the next 24 hrs. to assure the drying) under two metal plates to maintain it smooth and dried. Post-casting treatments in IPA and H_2O, (1 and 5 hrs. respectively) are carried to purify the membranes from contaminants and impurities. When the membrane is completely dried (about 72hrs.), the thickness is measured on different points to have a statically valid average value. In this way, new five **membrane samples** (PSF2-

27 to PSF2-31) were synthesized using the described parameters and the different Cyphos 104 IL contents. The ***Table 2*** reports the prepared membranes and the corresponding used parameters and their compositions.

Membrane	PSF, wt.%	Solvent	p-123, wt.%	Cyphos 104, wt.%	ts, min.	Ts, °C	Dt, s	DB, µm
PSF2-27	5	Water	10	1,7	60	120	20	500
PSF2-28	5	Water	10	1,0	60	120	20	300
PSF2-29 (pure PSF)	5	Water	0	0	60	120	20	300
PSF2-30	5	Water	10	0	60	120	20	300
PSF2-31	5	Water	10	3,0	60	120	20	300

Table 2. Membranes prepared during the third-year activity and corresponding parameters used.

Legenda.

PSF, wt.%: PSF concentration
Dt = de-mixing time, s
p-123, wt.%.: p-123 concentration
Cyphos 104, wt.%.: IL content
D.B.: starting light set on doctor-blade device, µm

After preparation, at first, the samples were analysed by SEM to check the morphology and asymmetry generated by the adopted synthesis parameters. The characterisation was performed on the dried samples.

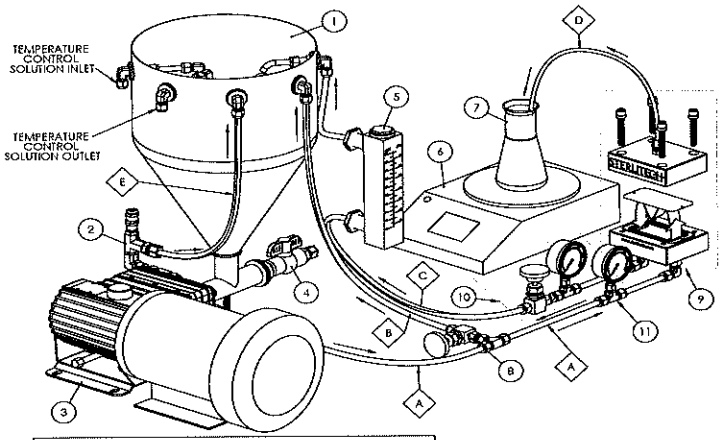
In the research process, the new synthesis parameters were changed one by one, developing asymmetric PSF membranes with superior characteristics (as emerged by the characterisation results), if compared to the previous prototypes. These membranes were cast in three different configurations PSF/solvent, PSF/solvent/surfactant and PSF/solvent/surfactant/IL. Three theoretical different loads of ionic liquid (CYPHOS 104) were used (1, 1.5, 3wt.%), in order to trigger charge repulsion mechanisms inside the polymer matrix and filter contaminated solutions containing Cr^{+3} (e.g.:) using as-received membranes with the actual pore size, but able to repulse the positive charges of the heavy metal solution used as feeding thanks to the ionic liquid presence. The optimal amount of CYPHOS104 has been optimized (1wt.%).

3.2 – Characterisation

At this point, with the aim of individuating the most promising candidates, the new samples were jointly characterised by two research teams in terms of water retention capability (water-uptake) and dimensional analysis @rT into three spatial directions (width, length, thickness variation), wettability (contact angle measurements), porosity (BET), thermal properties (TGA-DSC), structure (X-ray diffraction), morphology (surface/cross-section SEM), permeability tests. In particular, the different characterization techniques have been devoted to the checking of the polymer solubilisation, individuation of the asymmetry, suitable transversal morphology, above-all considering the improvements obtained. Moreover, the optimization of the manufacturing, the size, shape and the pores/channels distribution, hydrophilic properties and, above-all, the correlation between experimental parameters and membranes morphology were taken into account in order to individuate the characteristics for final application (MF, UF, NF).

The final capability of the prepared membranes (pure PSF, with p123 and with CYPHOS104) can be evaluated by filtration *in-situ* measurements. An important system for UF-NF measurements, fit for purpose,

produced by Sterlitech was acquired by CNR-ITAE thanks to the Joint lab findings. In Figure 1, the diagram of the device is reported:

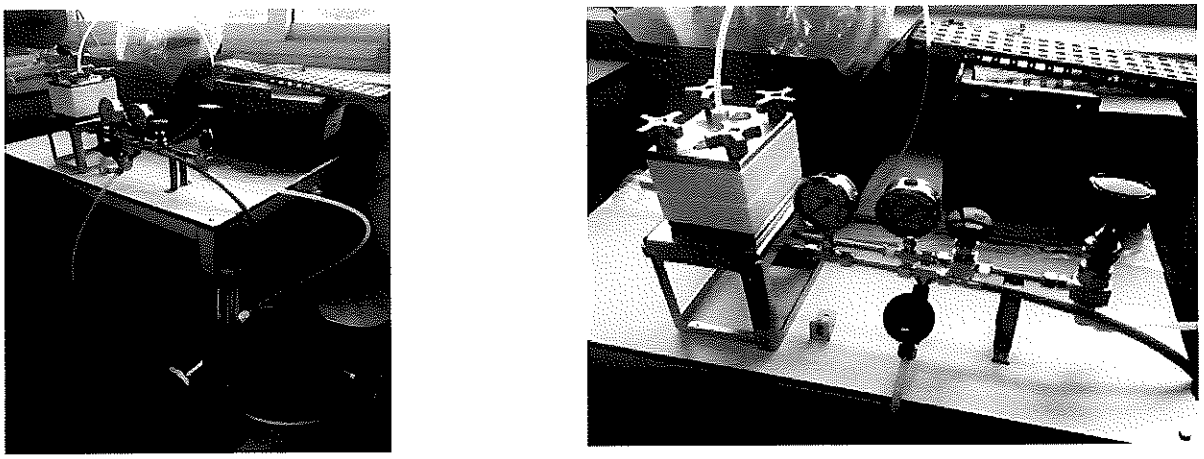


CF042A FLOW DIAGRAM	
ITEM NO.	PART DESCRIPTION
1	CONICAL FEED TANK
2	PRESSURE RELIEF VALVE
3	FEED PUMP
4	DRAIN VALVE
5	FLOW METER
6	SCALE FOR MEASURING PERMEATE FLUX
7	PERMEATE COLLECTOR
8	BY-PASS NEEDLE VALVE WITH 3/8" "T" TUBE FITTING
9	ACRYLIC CF042 CELL ASSEMBLY
10	CONCENTRATE CONTROL VALVE ASSEMBLY (0-400 PSI)
11	FEED PRESSURE GAUGE
A	3/8" HIGH PRESSURE FLEX OR RIGID TUBING, FEED LINE
B	3/8" LOW PRESSURE TUBING, BY-PASS
C	3/8" LOW PRESSURE TUBING, RETURN LINE
D	1/4" LOW PRESSURE TUBING, PERMEATE OUTPUT LINE
E	3/8" LOW PRESSURE TUBING

STERLITECH Corporation
www.sterlitech.com sales@sterlitech.com

Figure 1. Sterlitech filtration system.

The system with the connected cell for filtration UF, NF measurements - important aim of the project - was completely assembled. The following Figure 2 (a-b) reports the photos of the system assembled into the lab:



(a) *(b)*

Figure 2 (a-b). (a) photos of assembled system: (b) UF/NF cell assembled.

Such system can be used as device for: 1) water flux measurements: 2) water permeability tests and 3) filtration tests using feeding solutions containing different contaminant species (heavy metal solutions, such as Cr^{+3}, Pb^{+2}, Cd^{+2} and so on).

Moreover, commercial membranes based on PES, PSF and PVDF by Sterlitech were acquired to be tested and to define the procedures, the commercial references, the operative conditions and the main parameters for

the measurements: time, flux, retained/permeated ratio, permeability, etc.

The measurements into the Filtration Sterlitech System were not realised, due to a soft delay into the funding's disbursement that has caused a delay into the acquisition of the system (deviation from project aims), dealing with a foreign firm, but the system and a protocol for the measurements have been developed. After the end of the project, the most interesting developed membrane samples (pure PSF, containing surfactant and with CYPHOS104) will be tested and compared with the commercial references, in terms of flux, retention capability, permeability tests of the contaminant species. The results will be evaluated, integrated and crossed with the previously obtained results in order to identify the best membrane prototypes, able to efficiently act as filters in UF processes, purifying industrial grade wastewaters polluted from heavy metal ions. The separation/recovery efficiency and performance of this operation will be investigated.

Such operations on the developed prototypes will realised after the closing of the project and the results will be used as opportunities of new financing.

3.2 – Main experimental results

The operating conditions and synthesis parameters, determining the morphology and the goodness of the manufacturing, have been fixed. More in detail:

1. polymer concentration of 5wt.%, water as non-solvent have been defined as optimal parameters;
2. the polymer solubilisation temperature (named T_s) has been fixed in 120°C in order to completely solubilise the polymer agglomerates (individuated by SEM in the previous batch of membranes), the added surfactant and Cyphos 104 IL;
3. the polymer solubilisation time (named t_s) was optimised and fixed in 60 minutes in order to solubilise PSF, surfactant and Cyphos 104 IL;
4. the evaporation time (named E_t) of the solvent in the polymeric solution with the aim of optimising the viscosity factor has been defined to obtain more resistant membranes, capable of withstanding more prohibitive pressure operating conditions for final application;
5. the "de-mixing" (named D_t) in order to enhance the transversal morphology (asymmetry with finger-like macro-voids) has been fixed in 20s as optimal for the best cross-section configuration (SEM);
6. the surfactant concentration was individuated in a 10wt.% since it seems to be the best compromise to complete the channels formation and to have an ordered asymmetric morphology;
7. different initial thickness values to be set on the Doctor-Blade knife (named D.B.) were investigated with the aim of optimising the stratification phase and identify the optimal surfactant distribution, whose acts as a pore-former. The final D.B. thickness was set in 30 μm since it is ideal for surfactant and IL distribution.

Here following, the main experimental results obtained, divided for characterisation, are reported.

XRD on new membranes confirmed the previous results: no significant variation was recorded on samples with and without surfactant and ionic liquid, indicating that the structure is not affected by their introduction.

Regarding **water retention behaviour @rT**, it's possible to affirm that, generally, the water retention increases with surfactant and ionic liquid introduction.

For the **porosity** evaluation, the membranes containing the surfactant and IL are basically more porous, as

expected, except for some negligible experimental exceptions.

Regarding **contact angles** (CA) results, values < 90°C were recorded for all samples also for membranes with surfactant: the membranes have got good hydrophilic properties and those with IL have values into the range of 71-83°.

Regarding **BET measurements**, the new samples synthesised with IL supplied values of higher surface area of about 9-17 m^2/g with a pore size of 28-55 nm that increases with the increase of the Il content.

Regarding **cross-section SEM**, that is surely the determining characterization, it is possible to affirm that the final procedure for membrane preparation permit to obtain a very good transversal morphology with the desired finger-like macro-voids, comparable to the structures reported in literature. The main correlations between the synthesis parameters and final morphology were individuated. The complete treatment of this aspect with the corresponding cross-section images will be reported in the complete external technical report of the project, that will be deposited in 2020 and inserted in "people site" as research product. In any case, it permitted to established:

- synthesis parameters are determining in order to create channels and ordered finger-like morphology inside the transversal section of the solid membranes;
- amount of 10wt.% of surfactant was individuated as the ideal to have the desired configuration, in-fact the membrane PSF2-23, containing a surfactant 10wt.% can be considered the best prototype with surfactant, in terms of morphology. It was prepared by the following parameters: PSF concentration of 5wt.%; 1:10 p-123/PSF ratio; t_s: 60min.; T_s: 120°C; D_t: 20s; D.B.: 30μm, considered the final ideal parameters for membrane preparation.

TG on the membranes with surfactant and IL revealed that these membranes seem to be thermally less resistant, but this soft reduction of stability occurs at T>170°C, not affecting the application range; DSC profiles didn't reveal any important variation if compared to the pure PSF membrane.

IR measurements on surfactant membranes have demonstrated that p-123 only acts as pore-former, not remaining inside the final membrane structure.

Permeability measurements on the membranes with surfactant demonstrated the sample PSF2-12 (pure) and PSF 2-23 (10wt.% of p-123) are the membranes that better follow the Darcy's law: the measurements on the new batch of samples with IL will be completed during the next months and the results will be integrated with previous ones in order to be inserted in the final external report.

4.0 - Dissemination results for 3rd year activity (2019) and collaboration reinforcement

Dealing with a joint lab, it's important to highlight some aspects regarding the linked dissemination, whose details are here following reported.

- The final 36 months project meeting with partner Mexican team was organized at CNR-ITAE (Messina, Italy) from September 30 – October 04, 2019. During the meeting, the evaluation of the experimental data and the main conclusions were carried out;
- two joint conferences on the project topic were realised:
  1. M. Barrera-López Y. Gutiérrez-Piña, L. Hernández-Perales, M. González-Muñoz, A.Saccà, I. Gatto, M.

Ávila-Rodríguez, 9th International Colloids Conference, June 16-19 2019, Sitges-Barcelona (Spain);

2. M. Barrera López, Y. Gutiérrez Piña , L. Hernández Perales, M. Pilar González Muñoz, A.Saccà, I. Gatto, M. Ávila- Rodríguez, XVI Encuentro de la Mujer en la Ciencia. CIO-Leon, Guanajuato (Mexico), May 29-31 2019.

- two technical internal reports with the activity of the 3rd year and the complete project activity will be deposited contemporarily to the economic report;
- 3 months stage (January 2020 – April 2020) is actually in progress at CNR-ITAE on the project topic (student: Sofia Galilea Quiroz Yebra) devoted to the degree thesis. Due to organization matters, the stage was moved from 2019 to January 2020 in order to individuate coherent possibilities to jointly present new project proposals;
- 3 months stage (January 2020 – April 2020) on a different topic (H_2 storage) is actually in progress at CNR-ITAE devoted to the degree thesis;
- two papers are actually in progress on the project activity;
- a complete system for MF, UF, NF (up to 27 bar) and accessories, supplied by Sterlitech Corporation, was acquired by CNR-ITAE with Joint Lab funding with the aim of *in situ* verifying the goodness and the performance of the developed AM-PSF samples. Such system will be jointly used for the future perspectives.

It's possible to affirm the student's exchange between two research teams, started in 2012, was reinforced as well as the mutual collaboration and the joint management of the topic between two research groups. Such activity will be continued in the future.

5.0 – Experimental conclusions

The following final conclusions can be formulated:

- the solubilization time (t_s) has a significant effect on the morphology of the membranes, since if this is very short, the correct channels morphology (finger-like macro-voids) is not generated, but rather a spongy support is formed;
- the most suitable polymer solubilization temperature is 120°C. At this temperature, a complete dissolution of the polymer was achieved, without debris being observed on the surface of the membranes;
- the viscosity of the solution is a determining parameter for the final membrane morphology: the evaporation phase time with the used polymer concentration was fixed in 120 minutes with and without surfactant;
- De-mixing time of 20s, determining for membrane formation, was defined as optimal time, since it generates an adequate morphology and, in particular, more defined finger-like channels into the transversal section; in addition, it was discovered that too low de-mixing times (Dt<20s) prevent the formation of bottom-up finger-like channels along the membrane section, while higher times (Dt> 20s) excessively increase the thickness of the final membrane and deform the channels in section;
- the concentration of Pluronic p-123 was set at 10 wt.% because it generates a transversal morphology with adequate properties;
- starting Doctor-Blade thickness value to be set in order to obtain the most suitable thickness and morphology on the final membrane was fixed equal to 50 μm since it generates a final thickness of about 200 μm; in-fact,

the membranes must have a final thickness of at least 200 microns, since the surfactant has enough space to act as a pore-ex during the mixing process and, moreover, the mechanical properties are satisfactory;

- contact angle measurements showed that membranes have a sufficient hydrophilic character, without that the Pluronic p-123 shows a particular influence on this characteristic;
- the addition of the surfactant softly increases the hydrophilic properties (water-uptake) and generates more defined finger-like channels from side to side of the membrane generating a correct morphology for final application;
- the addition of Cyphos IL generates a higher porosity, both in the surface and transversal direction;
- the asymmetric morphology was reproduced with "finger-like macro-voids" and the correlation with the determining parameters was identified;
- the pore size of the membranes in their current state seems to be suitable for UF processes (80-100 nm for membrane without surfactant and 20-40 nm for membrane with surfactant), even if the distribution of the pores can be further enhanced.

6.0 - General conclusions

A high level of control both of the surface morphology (distribution of pores of the appropriate size) and transversal (finger-like macro-void type) was obtained according to the related parameters. This aspect is particularly decisive for defining the selective capacity of membrane prototypes. The operating conditions and the synthesis parameters determining the morphology, size and distribution of the pores were also defined. In particular:

1. standardization of parameters and the membrane formation procedure, as described in the paragraph 5.0;
2. verification of the reproducibility of the preparation. The membranes taken as reference during the second year (PSF2-20, and PSF2-23), respectively without and with surfactant, were reproduced (PSF 2-29, PSF2-30) to verify the correlation with the operating parameters;
3. preparation of new membranes with ionic liquid (CYPHOS 104). Five new samples were prepared and characterized, the two references (pure PSF and PSF with surfactant) and three samples with three different percentages of CYPHOS IL (1, 1.5, 3wt.%).

At the end, the following membranes that showed the best characteristics (with and without surfactant/ionic liquid) were identified as best prototypes to be used in the application of the project: PSF2-20 and PSF2-29 (pure PSF), PSF2-23 and PSF2-30 (p123 10wt.%), PSF2-28 (p123 10wt.% and IL 1wt.%) and PSF-2-31 (p123 10wt.% and IL 3wt.%). This is thanks to their morphological characteristics, similar to those identified in the literature as ideal, to their hydrophilic, porosity, thermal-mechanical and permeability properties. The final filtration capacity will successively tested thanks to the acquired UF system.

7.0 - Deviations from the planned activity

Here briefly the main deviations from the foreseen activity are listed:

- Evaluation of the temperature influence on the de-mixing process and on the membrane morphology through the use of a thermostatic bath: due to a delay of the company in the realization of the product (November

2019), the acquisition of the device took place only lately. This aspect is being evaluated in this period during the stage of the student and it will be completed after the end of the project;

- evaluation of another type of surfactant (p127): this aspect will be evaluated after the closure of the project;
- investigation of the complexation process using polyelectrolytes (PEI) on the heavy metal solutions feeding in order to increase the size of the contaminant to be filtered using *as-received* membranes with the actual pore size avoiding in this way the passage through the membrane pores;
- *in-situ* filtration tests (UF) through the Crossflow Cell System (by Sterlitech) acquired by the ITAE on the prototypes developed and successive comparison with commercial references: this aspect will be assessed after the closure of the project since, as above-mentioned, there was a delay in the acquisition of the system (July 20019), in the delivery and subsequent complex implementation of the same;
- self-made ionic liquid tests (ILs) provided by the Mexican partner: the partner did not receive the materials from the French colleague who was supposed to synthesize them;
- the other research path foresaw the filtration process modification using the developed *as-received* membranes, complexing the metal of the simulated contaminated solutions (feeding) and increasing the size of the species to be filtered, without changing the pore size or activate charge repulsion mechanisms (as IL). It was hypothesized to pursue this aspect by using polyethyleneimine polyelectrolyte (PEI) to complex the Cr(III) metal solutions and commercial semipermeable membranes acquired with different cut-off (5-30 KDalton). This research path has not been investigated and will be activated after the closing of the project, exploiting it to individuate new funding sources.

8.0 – Further developments and perspectives of the project activity

The membranes synthesis for this application should be continued on basis of the individuated parameters and the obtained results in order to achieve enhanced mechanical-hydrophilic-morphological-thermal properties, correct size and shape of pores and channels compatible with the size of the species to be filtered. Similarly, the effect of other types of additives could be studied, such as PEG or ILs on the membranes or polyelectrolytes (e.g.: PEI) on the feeding solution with the aim of using the membranes *as-received* with the actual pore size, but improving the triggering of charge repulsion mechanisms (using ILs) or increasing the contaminant species size used as feeding through the complexation mechanism (using PEs) of the own feeding. Such aspect could be further investigated/ optimised or newly exploited.

Moreover, the Sterlitech's CrossFlow Cell System - acquired by ITAE thanks to the project funds – will be the core of a deep characterisation and permit to ascertain the ability to separate contaminants and the applicability of prototypes developed. This system, capable of working up to 27 bars (UF-NF), powered by a HydraCell pump regulating the input flow (flow rate up to 6.8 l / min.), once established the measurement protocol, will permit to qualify the membranes prototypes manufactured for the separation of metallic pollutants in UF processes and individuate the more efficient membrane configurations to be proposed as fulcrum of new proposals. In-fact, on the basis of the results obtained, new possibilities to present joint projects on the topic will be evaluated considering the most promising samples based on:

- PSF pure membranes;

- PSF/surfactants membranes;
- PSF/surfactant/ILs membranes.

In conclusion, the research into the membrane filtration processes field presents an infinite number of possibilities to generate materials that adapt to the different process exigencies. This type of research is encouraging because is easily tuneable simply varying the size, shape and the distribution of pores and channels and the membranes composition and morphology as a function of the species to be separated.

Messina, 31/01/2020

The scientific Italian Manager of the project

dr. Ada Saccà

The scientific Mexican Manager of the project

prof. Mario Avila-Rodriguez

CNR - ITAE
Rapp. Int.
02/2020

Project Title: "Joint laboratory on green separation processes for the wastewaters treatment and recovery of contaminating species".

Call: Laboratori Congiunti Bilaterali Internazionali del CNR (II call 2016) - tematico ICT (triennio 2017-2019)". Prot. CNR N. 0082227.

Research area: Industrial Engineering
Key-words: Membrane Process, Wastewaters Treatment, Metal ions

Project Partners: CNR (Italy), University of Guanajuato (MX)

Final Report
Period: January 01, 2017 - December 31, 2019

Autori: A. Saccà
R. Pedicini
A. Carbone
F.V. Matera
I. Gatto
M. Ávila-Rodríguez
M. Pilar González-Muñoz
Sofia Galilea Quiroz Yebra
L. Espitia-Villanueva
S. Gutierrez-Granados
L. Hernandez-Perales
I. Olvera
A. Razo-Lazcano Teresa

Gennaio 2020

Istituto di Tecnologie Avanzate per l'Energia
"Nicola Giordano"

Via S. Lucia sopra Contesse n.5
98126 S. Lucia, Messina, Italy
tel: 090 624246, fax: 090 624247
e-mail: itae@itae.cnr.it
http://www.itae.cnr.it/
C.F. 80054330586
: protocollo.itae@pec.cnr.it

Project Title.

Joint laboratory on green separation processes for the wastewater's treatment and recovery of contaminating species

Research area: Industrial Engineering

Keywords: Membrane Process, Wastewaters Treatment, Metal ions

1.0 Introduction.

The increasing demand of water for human requirements and the corresponding water purification processes represent an important topic in the context of the sustainable global development and power generation with low environmental impact. The possibility to obtain water with high purity grade from alternative processes of industrial grade wastewaters purification, also recovering contaminant metal ions, is a relevant matter to be faced and solved.

In the last 50 years, several new technologies for the substance's separation, generally called "membrane processes", have been extensively studied for the above- mentioned aims. These technologies use artificial membranes in order to promote the separation/purification/removal of contaminants according to the pore size of the membranes used and their chemical-physical and morphological characteristics. Such operations occur through separation processes based on the dimensions difference between membrane pores and size of contaminant species to be filtered/separated or through mechanisms of complex's formation and/or of charge repulsion with the aim of avoiding the passage through the membrane pores.

In particular, in this context, membranes based on Polysulfone (PSF) polymer are one of the most widely used materials due to the high hydrolytic, chemical and thermal stability, again high chemical and mechanical resistance, wide pH tolerance (1-13) and to Cl^- ions, in addition to their low cost and application flexibility. The ease of the manufacturing plays an important role as well as the possibility to manage the shape, size and pores distribution. This determines a high possibility of control of separation process. All these aspects make the membranes of PSF ideal candidates for the separation/filtration processes/systems, even for the high efficiency that supply to the process. The hydrophobicity and poor resistance to the so-called "fouling" phenomenon reduce the water permeability, molecular selectivity and own the duration of the process and this aspect represents the main drawback for their application. In order to have more hydrophilic membranes with "antifouling" properties, the choice of the "polymer-solvent-non-solvent system" with the aim of obtaining the correct morphology and usage of suitable additives able to improve the porosity and hydrophilic properties constitute the answer to define the performance of the selected process, in particular selectivity and permeability.

The main objective of the present project consisted into the realization of a joint research on sustainable and non-polluting separation techniques for the purification of industrial grade waste-

waters using flat solid asymmetric polymer membrane systems with different morphology and properties.

2.0- Description of the 1st year activity.

The first year of activity covers the period from 01 January 2017 up to 31 December 2017.

During this period, the activity was devoted to the development of asymmetric polymeric membranes for filtration/separation processes (MF, UF, NF).

In this first year of the project, starting from the experience of CNR- ITAE (Italy) and the University of Guanajuato partner (Ugto., Mexico) on polymers, their functionalization, solid membranes development (Italy), biphasic liquid systems, separation/filtration methods (Mexico), the starting point was individuated into the development of asymmetric membranes based on polysulfone (PSF), named AM-PSF, particularly suitable for industrial grade wastewaters purification applications. For this aim, the definition of the following intermediate objectives was pursued:

- state of the art on materials and methods;
- preparation procedure of the asymmetric PSF membranes (AM-PSF) with suitable morphology and pore size control (using SEM and BET) to determine the selective capacity of the first prototypes of membranes;
- synthesis parameters for membranes manufacturing determining the AM-PSF morphology;
- experimental operative conditions for membranes manufacturing;
- the role of additives/surfactants to be added to the polymer matrix in order to improve the hydrophilic properties, morphology of the cross section and water permeability behaviour;
- characterization of the developed AM-PSF membranes in terms of XRD, TG-DSC, water retention, dimensional analysis, mechanical properties by dynamo mechanical analysis (DMA) for glass transition (Tg) determination, cross-section and surface SEM, surface area and pore-size distribution by BET device (Itae); contact angle, permeability tests to water flow (Ugto.); zeta-potential and IR measurements (Ugto., in progress). As required by the project, these measurements were carried out jointly performed by both work teams.

In detail, the starting polymer for membranes preparation was identified into PSF, in particular in Polysulphone Bisphenol A (pellets, MF = $C_{27}H_{22}O_4S)n$) supplied by Sigma-Aldrich with average Mw≈35,000 by LS. PSF based membranes seem to be able to supply a correct morphology and pores size for filtration processes, over to have got a series of advantages, as already mentioned.

Also the polymer solvent has been individuated: dimethyl-acetamide (DMAc by Carlo Erba) was chosen for this aim, even due to the high miscibility and the quick exchange with the non-solvents selected for membrane preparation; such aspect guarantees the suitable finger-like macro-voids morphology. More, DMAc is plasticizer and supplies a certain stiffness to the membrane.

The preparation procedure and casting method for solid membranes were selected on basis of a

state of the art; at first, the phase inversion (PI) method through solvent evaporation (SE), used at ITAE for Proton Exchange Membranes (PEM) preparation in Polymer Electrolyte Fuel Cell (PEFC) applications, was investigated and, after the obtained results (SEM), it was discarded because it forms dense membranes with not suitable morphology for final application (PSF1-2 membrane). Successively, the phase inversion (PI) method by means of a non-solvent coagulation bath (NS-CB) technique was evaluated/used pairing with it to the doctor-blade casting technique. The latter was standardised at CNR-ITAE and it has got the advantage to supply wide membranes (up to a size of 20 x 30 cm^2) with high homogeneity of thickness and good mechanical strength. NS-CB technique is able to supply asymmetric membranes with adequate "finger-like macro-voids" morphology, determining flux (J_w) and particularly efficient for filtration operations, control of experimental parameters and operative conditions. It is so possible to obtain membranes with increased hydrophilic properties and reduced fouling phenomenon; in-fact, the membrane composition and coagulation medium control the porosity, pore structure and pore distribution. On basis of literature, also non-solvents for membrane formation were identified (EtOH, H_2O and their mixture) as well as the surfactant in order to increase the hydrophilic properties: it was individuated in Pluronic P-123 (by Sigma-Aldrich). The steps of the process for membranes preparation were defined and a preliminary standardization was performed. In particular, four parameters determining the morphology were evaluated and varied, here following listed: concentration of the starting PSF solution (5-18wt.%), non-solvent (H_2O, EtOH, their 1:1 mixture), "de- mixing time" (Dt) into non-solvent medium generating the membrane formation (20, 600s), two different concentrations of surfactant (1:1 and 1:2 PSF/P123 ratios). P-123 is well known due its ability to supply hydrophilicity to the membranes.

The synthesis parameters were varied one at a time, while the operating conditions of the procedure (T, V, t) were maintained constants for each prepared membrane. Figure 1 schematically reports the membrane preparation procedure, hereafter described through the single steps.

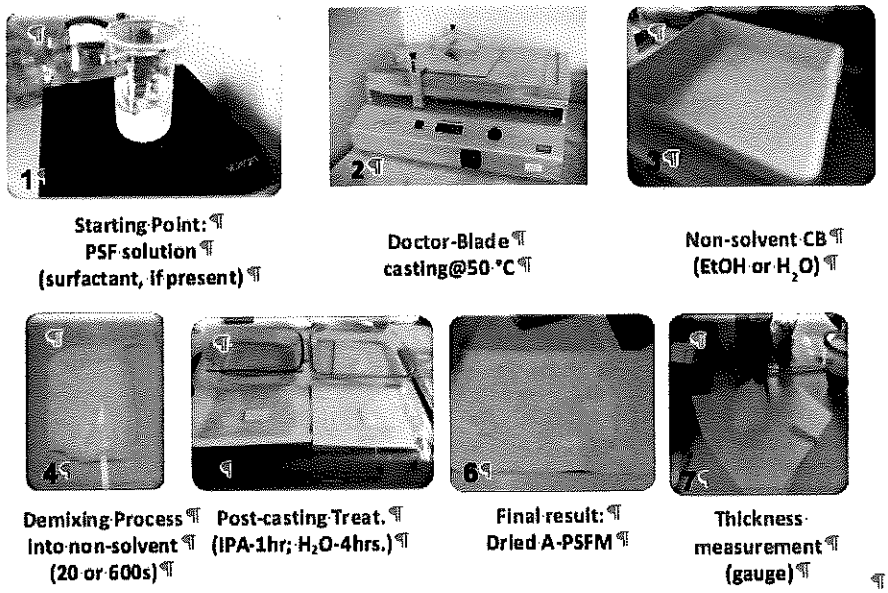


Figure 1. Schematic description of PI process by NS-CB technique. 1) PSF (pellets) dispersion in DMAc; 2) automatic film applicator (doctor-blade) for solution stratification; 3) non-solvent coagulation bath for film immersion; 4) de-mixing process with membrane formation (nascent membrane); 5) post-casting treatment; 6) dried membrane; 7) thickness measurement by gauge.

2.1 - Membrane preparation procedure (1st year)

PSF dispersion (5 or 18 wt.%) in DMAc as a solvent was performed at room temperature (25°C; 10 min.). under magnetic stirring. The solubilisation continues on hot plate at 80°C under stirring covered with a watch glass to avoid the initial evaporation. After about 1 hr., the watch glass is removed and the solvent evaporation phase is started. When the solution viscosity is adequate (about 5 hrs. after PSF dissolution), it is immediately stratified by Doctor-Blade on preheated glass at T=80°C, same temperature of evaporation phase to avoid thermal shocks. The calibrated Elcometer® Blade Knife Model 3580 was imposed to the minimum thickness allowed (100 µm). Previous tests demonstrated a factor of 10 between imposed and obtained thickness. The final membrane has a size of about 20 x 30 cm^2 with good manufacture (no bubble or hole). The glass with the stratified solution is quickly immersed into the non-solvent coagulation bath (EtOH, H_2O, their 1:1 mixture) at T=25°C depending on the prepared membrane. A different prefixed de-mixing time (20" or 600") was used for the membranes preparation (see Table1). The non-solvent volume is fixed at 4 litres. Then, the membrane went freely up away from the glass, removed from the non-solvent bath and placed between two absorbent paper sheets (exchanged several times during the next 72 hrs. to assure the drying) under two metal plates to maintain smooth and dry it. Post-casting treatments deeping in IPA and H_2O, (1 and 5 hrs. respectively) were carried to purify the membranes from contaminants and impurities. When the membrane is completely dried, the thickness is measured on different points to have an average value. The different characterization techniques were applied to the dried samples. In this way, eleven membrane samples (PSF2-1 to PSF2-11) were synthesised using the four investigates parameters (Table 1):

Membrane	Polymer (wt.%)		Non-solvent		Demixing time (s)		Polymer/P123 ratio	
	5	18	HO	EtOH	20	600	yes	not
PSF2-1	x		x			x		x
PSF2-2	x			x		x		x
PSF2-3	x		x		x			x
PSF2-4		x	x		x			x
PSF2-5	x			x	x			x
PSF2-6	x		1/2	1/2	x			x
PSF2-7	x			x		x	1.	

Table1. Prepared membranes

The samples were checked away by SEM (surface and CS), above all in terms of surface porosity and macro-voids morphology to check the consequences caused by the adopted synthesis parameters. The first sample (PSF1-2) prepared by SE is not here reported, since it is resulted dense from SEM.

2.2. - Characterisation (1st year)

The membranes were jointly characterised from two research teams in terms of XRD, TGA-DSC, water retention and dimensional analysis @rT and 60°C into three spatial directions, DMA, BET, cross- section and surface SEM (Itae); contact angle, permeability tests (UGto.); Z-potential and IR measurements (UGto.) are, actually, in progress. In particular, the different characterisation techniques have been devoted to the individuation of membranes morphology, to goodness of the manufacturing, the asymmetry definition into the transversal dimension of membranes, to the size, shape and pores/channels distribution, surface porosity in order to identify the characteristics suitable for the different processes (MF, UF, NF) that the partners will intend to adopt for final aims of the project.

2.2.1 - Experimental results (1st year)

XRD and TG-DSC demonstrated the reliability of the prepared samples and no significant variation was recorded for samples with and without surfactant (XRD), indicating that the structure is not affected by surfactant introduction. A soft stability reduction (TG) at T>200°C for samples with surfactant, but an increased water retention (DSC) were recorded for the same samples.

Regarding **water retention** behaviour, it's possible to affirm that, generally, the water retention @ rT supplies values into range 2- 46% for samples without surfactant (PSF2-1 up to PSF2-6); for samples with surfactant (PSF2-7 up to PSF2-11), the values are extremely higher from 180% up to 355% demonstrating the hydrophilic properties obtained with the surfactant introduction. At T=60°C, generally the values are softly higher for both samples categories, as reported into the Table 2.

Regarding **dimensional analysis**, the results have to be separately evaluated, because the thickness of these membranes is difficult to be measured due to their surface wrinkledness. Some corrective actions will be individuated to reduce the roughness that can be a negative factor for different measurements (the thickness homogeneity guarantees results homogeneity).

In terms of **surface area and pores distribution** (BET), membranes showed not particularly high Surface Area, but susceptible to be improved with pores size into mesopores-range (2nm<pore<50nm) and a little micropores percentage of about 1 nm. PSF2-3 sample supplies the most promising surface area and differential pores volume distribution. The last BET measurements are in progress (samples PSF2-8 up to PSF2-11).

Regarding the **contact angles** (CA) measurements, CA values << 90°C were recorded for all samples without surfactant: hydrophilic properties seem to be sufficient. Instead, for samples with surfactant, hydrophilic properties have to be improved through the introduction of different P-123 concentrations or new surfactants/additives. In-fact, the surfactant introduction supplied the CA values not low as well as those expected, probably due to a not correct P-123 distribution inside the polymer matrix. IR measurements (in progress) will give answer about this aspect. The sample PSF2-11 has supplied a CA value of zero: the drop is completely absorbed into the membrane. It represents a good candidate, but this value has to be modified, probably reducing the used surfactant amount (1,10,20wt.% compared to the polymer) (see corrective actions).

DMA analysis into T range rT-250°, through the □ value determination, supplied evidences about the Glass Transition (T_g): T_g of as received PSF is around 190°C. It didn't record any substantial variation for samples without surfactant compared to pristine PSF. The used parameters, hence, didn't affect T_g of polymer. The measurements on membranes with surfactant must be revaluated because a few variations on some samples were recorded, probably attributable to a softening phenomenon, to be solved through the strengthening of such membranes (see corrective actions).

Permeability tests were performed into an Amicon cell, into 0-30 psi pressure range (permeating deionised water) and the permeated volume was measured (each 30'). From F=V/t formula, whereas F Flux, V water volume permeated, t=30', the flux value was calculated. In this case, only PSF2-1 up to PSF2-4 samples overcame permeability tests. The other samples are little brittle and suffer the pressure operation. In particular, PSF2-3 records a correct linear trend following Darcy's law. PSF2-4 is almost linear with a gap at about 15-20psi. For PSF2-1, the flux initially increases up to 20psi, at P>20psi the permeated volume is reduced. PSF2-2 supplies a low permeated water volume as a pressure function. The membranes with surfactant (the best promising samples) will be tested again after the preparation procedure revision (see corrective actions) that will aim at strengthening the membrane.

Regarding **SEM**, that is surely the determining characterisation, the following figure 2 reports the most representative SEM imagines related to the most promising samples (cross-section and surface), in order to better understand the results in terms of surface porosity and cross section channels size. The employed synthesis parameters for each sample are shown.

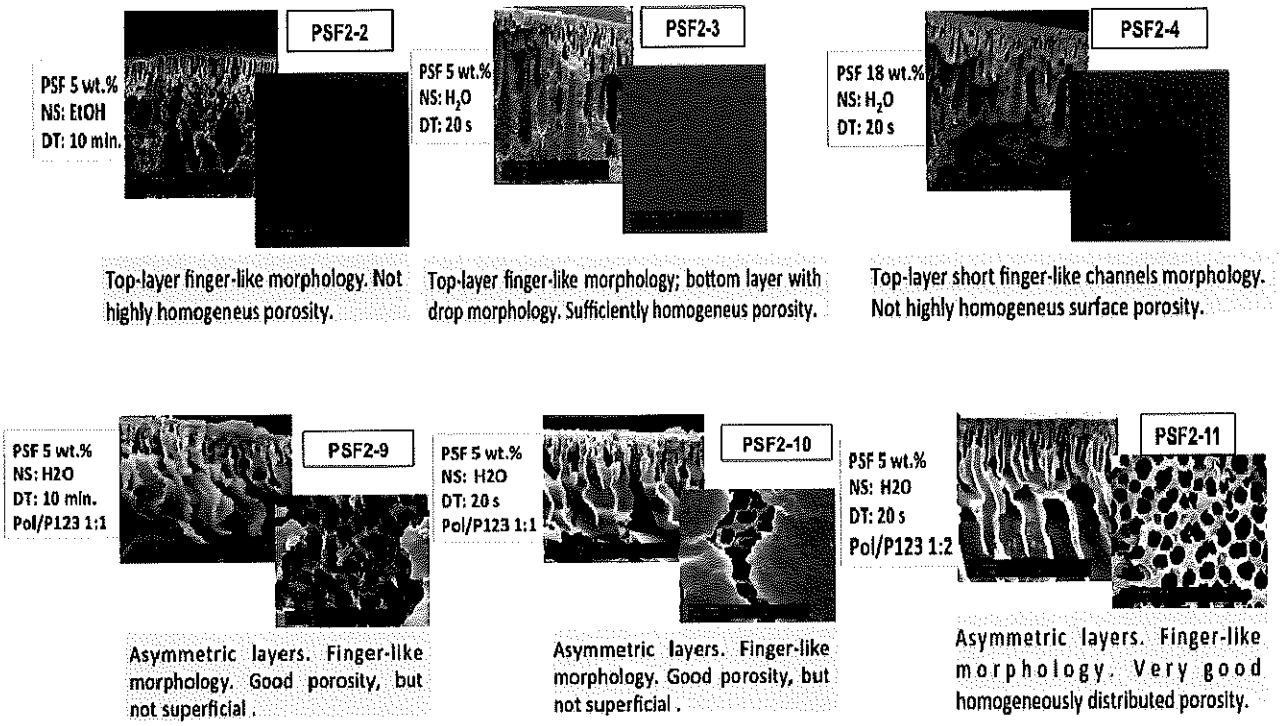


Figure 2. Cross-section and surface SEM images (PSF2-1, PSF2-2, PSF2-3, PSF2-4, PSF2-9, PSF2-10(2), PSF2-11).

PSF2-1 shows a morphology to be separately evaluated (not reported). The samples PSF2-5, PSF2-6, PSF2-7 and PSF2-8 (not reported) have not efficacy morphology. PSF2-2, PSF2-3, PSF2-4 (without surfactant) and PSF2-9, PSF2-10, PSF2-11 (with surfactant) exhibit the most promising cross-section morphologies: finger-like macro-voids (top-layer) are visible into CS-SEM, while surface SEM evidenced porosity, as requested for final aims. In particular, PSF2-9 up to PSF2-11 showed pores size of about 1- 2μm. Although, the pores size remains into MF field, they represent the nearest approximation for asymmetric membranes and are worthy to be further evaluated, particularly PSF2-11, whose surface pores distribution seems to be particularly interesting. The pores/channels dimension will be modified employing, for example, ionic liquids (supplied by partner) and/or additive/polyelectrolytes, such as PEA for final project aims.

3.0 - Conclusions (1st year)

The characterisation results were jointly evaluated, crossed between them reaching the first conclusions, here following briefly summarised:

- miscibility and fast solvent/non-solvent exchange guarantee the correct "finger-like morphology";
- the most performing asymmetric membranes were obtained when lower de-mixing times (Dt) and water as a non-solvent are used (PSF2-3 and PSF2-11);
- mesoporous membranes (2nm<pores<50nm) obtained with CA<90°C (hydrophilic character);
- a good trend (permeability) obtained in terms of Darcy's law for some of the samples;
- asymmetry with "finger-like morphology" obtained and determining parameters identified;

- surface porosity (500nm-2micron) for different samples with channels of about 1-2 micron obtained;
- two membranes identified as the best prototypes to be further optimized.

Crossing permeabilty, CA together to BET and SEM results, PSF2-3 sample (without surfactant) and PSF 2-11 (with surfactant) seem good candidates for final application. It's surely necessary to improve the membranes manufacturing and reduce the pores and channels size as well as to better connect the synthesis parameters to the manufacturing quality of the corresponding membranes in order to select the optimal membrane, but, in any case, important starting points for 2nd year activity were identified.

4. 0 - Dissemination of results and collaboration reinforcement (1st year).

Dealing with a joint lab, it's important highlight some aspects regarding the linked dissemination, whose details are here following reported.

- Two project meetings with partner Mexican team were organised: the first meeting held at CNR-ITAE (Messina, Italy) from 10-12 July 2017; the second meeting at University of Guanajuato (Guanajuato, Mexico) from November 27 -December 5, 2017. During the meetings, the evaluation of the experimental data obtained up to date was performed and an activity progress was jointly drawn up to establish the successive experimental activity, including the necessary corrective actions.
- a joint conference in 2017 on the project topic was realised: Sacca' A., Pedicini R., Carbone A., Matera F., Gatto I., Ávila-Rodríguez M., Gutierrez-Piña Y., Espitia Villanueva L., Falcon Millan G., González-Muñoz M.Pilar, Gutierrez-Granados S., Hernandez-Perales L., Javier Mares F., Olvera I., Razo-Lazcano Teresa A., "Preliminary study on Polysulphone (PSF) membranes employed in separation processes for wastewaters purification application", 5th Int. Conf. Expo on Sep. Tech., Paris (France), Oct. 23-25, 2017. J. Chromatogr. Sep. Tech., Oct. 2017, Vol. 8(7);
- a technical report and the corresponding paper on activity 1st year are actually in progress;
- 3 months stage (May-July 2017) was realised with the corresponding degree thesis (Yair Gutierrez Pina - in Chemistry) on project topic is actually in progress (date foreseen: March 2018);
- an optical device, in particular a modular optical system for contact angle measuring on solid surfaces to check the hydrophilic/hydrophobic properties of developed AM-PSF prototypes was acquired by CNR-ITAE with Joint Lab funding (as reported into the economic report);
- one joint conferences on different topics (PEFC) in 2017 were realised;
- 3 months stage (May-July 2017) was realised (Esperanza Gonzalez Hernandez - Chemical Engineering) on different topic (PEFC) was realised.

In addition, the students exchange between two research teams, started in 2012, was reinforced as well as the mutual collaboration. Moreover, during the 2nd meeting in Guanajuato, on the basis of the jointly conducted evaluation of the obtained results, a prediction of scientific activity for 2nd year with the definition of the next steps was elaborated. It is here following briefly presented.

5.0 - Expected experimental activity (2nd year).

At first, some characterizations have to be completed and/or verified, whose results are preliminary to the successive activity:

- BET analysis on the remaining samples (PSF2-8 up to PSF2-11), in order to verify porosity and pore distribution (ITAE);
- verification of surface SEM analysis on 4 samples (PSF2-8 up to PSF-2-11) with the aim of confirming the surface porosity (ITAE/UGto.): the presence of little artefacts leaves doubts about the pores size and the surfactant distribution on surface;
- verification of contact angle measurements (round-robin analysis) to verify the reliability of hydrophilic characteristics (thanks to contact angle device acquisition from ITAE).

The new activity will be devoted to:

- definition of the membrane preparation procedure;
- selection of the ideal prototype of solid polymer membrane with the best characteristics and morphology;
- selection of the process (UF and/or NF) according to the membrane's characteristics and the polluting ions to be removed for final application;
- acquisition of a separation/filtration cell for water flux measurements.

At this point, having identified a solid membrane prototype, ionic liquids will be evaluated/used in order to:

- reduce the pore size and use the membranes in UF or NF processes;
- trigger mechanisms of attraction/repulsion in the membrane to selectively filter the polluting metal ions (Cr, Pb, Cd, etc.).

6.0 - Corrective actions

The new results will be evaluated and crossed with the previous ones in order to confirm/deny the goodness of the membrane prototypes and identify new membrane configurations for the final selected process. A preliminary state of the art will be performed on the preparation methods of solid polymeric membranes containing polyelectrolytes (PEA) and/or additives for ultra-filtration (UF) processes with a molecular cut-off of about 20-25 kDalton. Subsequently, since the degree of criticality of some parameters/actions was identified, starting from the best prototype without surfactant (PSF2-3), some corrective actions will be carried out:

- SEM highlighted very little polymer agglomerations in some samples: the polymer solubilisation step will be improved increasing the time and/or the solubilisation temperature (non-critical);
- for one of the individuated samples (PSF2-11) as valid prototype, the stiffness of membrane has to be improved increasing the solution viscosity to be stratified (not critical);
- intermediate Dt (30, 40s) will be evaluated to identify the most suitable morphology (critical);

- temperature influence of coagulation bath (10, 20, 30°C) on morphology will be evaluated using a thermostatic bath with suitable size (budgeted with 2018 funding) (not critical);

Starting from PSF2-11 sample with surfactant (PSF/P123 1:2):

- different amounts (1, 10, 20 wt.%) of surfactant (P-123) will be evaluated (critical);
- morphology improvements (porosity, pore size and channels, asymmetry, "finger-like macro-voids") by new samples characterization will be verified (not critical); new characterization techniques will be used, such as AFM spectroscopy (UGto.) to better define the quality of the samples (not critical);
- the preparation procedure for each typology of membrane will be optimized (critical);
- verification of the reliability of the preparation procedure (not critical);
- water permeability tests will be conducted on new samples to select the best prototypes (non-critical).

8.0 - Expected dissemination results (2nd year).

In terms of dissemination, the following results are foreseen:

- two conference joint participations;
- one update conference on the topic;
- one project meeting for results evaluation and activity progress;
- publication of the first paper and report (1st year activity);
- report related to the 2nd year activity.

9.0- Description of the 2nd year activity.

The second year of activity covered the period from 01 January 2018 up to 31 December 2018. During this period, starting from the results obtained in the first year, the activity was devoted to the optimization of the preparation procedure of asymmetric flat solid PSF polymeric membranes. The optimization was pursued maintaining fixed the parameters and experimental factors revealed as helpful in order to have the desired morphology (finger-like macrovoids) and evaluating/varying other synthesis and experimental parameters. In particular, six new parameters were monitored/varied, such as: the solubilisation temperature (named here T_s) of the starting PSF solution, brought from 80 up to 120°C in order to remove the polymer agglomerations individuated by CS-SEM during the 1st year activity; solubilisation time (named here t_s) of the polymer (1 or 2 hrs.) for the same reason above-mentioned; the suitable viscosity of PSF solution to be stratified, surely correlated to the evaporation time (named here E_t) and to the experimental factors used (e.g.: T_s and t_s, presence and concentration of p-123) with the aim of obtaining membranes with good mechanical characteristics; p-123 ratio, whereas present, varied between 50wt.% up to 1wt.%. passing from 30 and 10wt.% in order to improve the mechanical properties, the cross-section morphology for final application; de-mixing time

(named here Dt) was varied from 10, 20, 40'' in order evaluate the influence on the transversal morphology and final thickness. At the end, the Doctor-Blade knife thickness (named here D.B.) was considered varying it from the starting 100□m value up to 30 □m (initial set thickness on the doctor-blade knife) in order to individuate the ideal thickness to be set to have sufficient space to let act the surfactant as a pore-former during the de-mixing process in the non-solvent coagulation bath and moreover to have a suitable final thickness of the membrane samples. The synthesis parameters were varied one at a time as well as the operating conditions of the synthesis procedure (such as T, V, t).

During the activity progress, crossing the obtained results, in particular in term of cross-section morphology by SEM, a revised preparation procedure was defined and a new batch of 14 membrane samples was developed, always taking into the account the influence of the parameters on final cross-section finger-like macro-voids morphology (to be pursued). The following membranes (with and without surfactant) have been identified as the new prototypes to be further investigated/optimized during the third year of activity: PSF2-20 (pure PSF), PSF2-16 (50wt.% surfactant), PSF2 -22BIS (1wt% surfactant), PSF2-24 (30wt% surfactant) and PSF2-23 (10wt surfactant%).

9.1 - Membrane preparation procedure (2nd year)

As above-mentioned, the membrane preparation procedure was partially redefined and optimized with respect the previously one used (see. 12 months Progress External Report N.16/2018). The final modified preparative is here briefly described and the modified parameters are indicated in bold.

PSF dispersion (5 wt.%) in DMAc as a solvent is treated at room temperature (25°C; 10 min.) under magnetic stirring. Surfactant Pluronic p-123 as received, whereas present, is added in the starting PSF/DMAc dispersion at room temperature. Different concentrations of p-123 were investigated and added (1, 10, 30 & 50 wt.%) for membrane preparation. The solubilisation continues on hot plate at T_s= 80 - 120°C (depending on sample) under stirring covered with a watch glass avoiding the initial evaporation for t_s=1hr/2hrs. (depending on sample). After, the watch glass is removed and the solvent evaporation phase is started. When the solution viscosity is adequate (E_t= 90 min. - 180 min. depending on T_s used and p-123 presence/concentration), it is immediately stratified by Doctor-Blade on preheated glass at T=80°C, same or lower T if compared to the evaporation phase to thermal shocks. The calibrated Elcometer® Blade Knife Model 3580 was imposed using different thicknesses set (D.B.=100 - 30 μm). The final membranes have size of about 20 x 30 cm^2 with good visual manufacture (no bubble or hole). The glass with the stratified solution is quickly immersed into the non-solvent coagulation bath (H_2O) at room temperature. The non-solvent volume is fixed at 4 litres. Then, the membrane is quickly removed from non-solvent bath, that is distilled

water, (Dt=10,20,40s depending on prepared sample) and placed between two absorbent paper sheets (exchanged several times during the next 24 hrs. to assure the drying) under two metal plates to maintain smooth and dry it. Post-casting treatments in IPA and H_2O, (1 and 5 hrs. respectively) are carried to purify the membranes from contaminants and impurities. When the membrane is completely dried, the thickness is measured on different points to have a statically valid average value.

The different characterization techniques were applied to the dried samples. In this way, fourteen membrane samples (PSF2-12BIS to PSF2-26) were synthesized using the six investigated parameters. The **Table 2** reports the prepared membranes and the used parameters.

After preparation, at first, the samples were checked away by SEM (only Cross-section SEM, surface SEM will be successively performed from Mexican partner) to check the morphology and the asymmetry generated by the adopted synthesis parameters, necessary for final filtration application.

Membrane	PSF, wt.%	p-123/PSF ratio		t_s, min.		T_s, °C		Dt, s			D.B., μm		
	5	Yes	Not	60	120	80	120	10	20	40	30	50	100
PSF2-12 BIS	X		X	X		X			X				X
PSF2-13	X		X		X	X			X				X
PSF2-14	X		X	X		X				X			X
PSF2-15	X		1:2	X		X			X				X
PSF2-16	X		1:2	X		X			X			X	
PSF2-17	X			X			X		X			X	
PSF2-18	X		X	X			X	X				X	
PSF2-20	X		X	X			X		X		X		
PSF2-21	X		X	X			X	X			X		
PSF2-22 BIS	X	1:10 0		X			X		X		X		
PSF2-23	X	1:10		X			X		X		X		
PSF2-24	X	3:10		X			X		X		X		
PSF2-25	X	1:10		X			X		X			X	
PSF2-26	X		X	X			X			X	X		

Table 2. Prepared membranes and corresponding parameters used.

10.0 - Characterisation

The membranes were jointly characterized by two research teams in terms of XRD, water retention and dimensional analysis @rT into three spatial directions, DMA, cross- section SEM, contact angle in two different configurations (Italian partner). BET and TGA-DSC are actually in progress at CNR-ITAE (Italy), while surface SEM, permeability tests, Z-potential and IR measurements are in progress at University of Guanajuato (Mexican partner). In particular, the different characterization techniques have been devoted to the individuation of the asymmetry and suitable transversal morphology, to the optimization of the manufacturing, to the size,

shape and pores/channels distribution and to the definition of the correlation between experimental parameters used and membranes morphology for final application (MF, UF, NF).

10.1 - Main experimental results (2nd year)

First of all, the corrective actions jointly established with Mexican Partner at the end of the 1st year activity were executed. In-fact, starting from PSF2-3 without surfactant was established to improve the membrane manufacturing increasing time and/or temperature for the polymer solubilisation, since SEM highlighted un-dissolved polymer agglomerations: the action was concluded. Then, membranes thickness and roughness were critical, so the solubilisation temperature, de-mixing time and stratification phase had to be evaluated: these factors were faced and solved. In addition, starting from PSF2-11 with surfactant (p-123/PSF 1:2 ratio), the stiffness of these samples had to be improved, acting on the solution viscosity: such operation was monitored and defined. At the end, different surfactant amounts (1, 10, 20 wt.% against the initial 50wt.%) in order to improve the mechanical properties and enhance the cross-section morphology had to be tested: such step was put in place and defined.

In this context, other operating conditions and synthesis parameters, determining the morphology and the goodness of the manufacturing have been fixed. More in detail:

1. the parameters such as polymer concentration (5wt.%), non-solvent (water), de-mixing time (10-40s) and surfactant concentration (50-1wt.%), evaluated during the 1st year activity, have been further investigate and finally defined;
2. the membranes taken as references without and with surfactant (PSF2-3 and PSF2-11) during the 1st year have been re-synthesised to test the reproducibility;
3. the polymer temperature (here named T_s, increased from 80 up to 120°C) has been modified to completely solubilise the polymer agglomerates, individuated by SEM in the first batch of membranes;
4. the polymer solubilisation time (here named t_s, fixed in 60 min.) was optimised as a function of the operative conditions used;
5. the evaporation time (here named E_t) of the solvent in the polymeric solution with the aim of optimising the viscosity factor as a function of operative conditions has been better defined to obtain more resistant membranes, capable of withstanding more prohibitive pressure operating conditions for final application;
6. the "de-mixing" (here named Dt) in order to enhance the transversal morphology (asymmetry with finger-like macro-voids) has been further studied (10, 20, 40s). In particular, a Dt of 20s has been identified as optimal for the best cross-section configuration (SEM);

7. the surfactant/polymer ratio was further investigated: amount of 1, 10, 30wt.% of surfactant (here named p-123: PSF ratio), in addition to the previously used 50wt.%, were introduced into the polymeric initial dispersion preparing membranes with the correct transversal morphology and good mechanical properties. Amount of 10wt.% seems to be the best compromise to complete the channels formation and to have an ordered morphology;
8. different initial thickness values set on the Doctor-Blade knife were investigated to optimise the stratification phase (here named D.B.), in order to reduce the membranes final thickness and identify the optimal surfactant distribution of the, which acts as a pore-former.

During the research path, the synthesis parameters were changed one at a time, as well as the operating conditions, developing 14 new asymmetric flat PSF membranes (PSF2-12BIS to PSF2-26 - table 2) with superior characteristics, when compared to the prototypes obtained in the first year.

Here following, more details on the experimental results obtained, divided for characterisation, are reported.

XRD on new membranes confirmed the results of the activity 1st year: structure and reliability of the samples are the same; moreover, no significant variation was recorded on samples with and without surfactant, indicating that the structure is not affected by surfactant introduction.

Regarding **water retention** behaviour@rT, it's possible to affirm that, generally, the water retention supplied values into range 20- 76% for samples without surfactant; for samples with surfactant, the values are extremely higher for samples with 50wt.% of surfactant, but proportionally lower for samples with lower surfactant concentrations (30 up to 1wt.%), demonstrating the hydrophilic properties due to the surfactant introduction and the relation between its content and the water retention reduction. For two samples (PSF2-20 and PSF2-21), the measurements have to be repeated.

Regarding **dimensional analysis**, the results are enhanced if compared to those of the previous batch due to the roughness improvement, achieved during this year of the activity. This was a possible thanks to the preparation procedure optimization enhancing the volume measurement, as foreseen during the last year. The elaboration of these data is actually under investigation.

For the percentage **porosity** evaluation, the membranes containing the surfactant are basically more porous, as expected, except of some negligible experimental exception.

Regarding **contact angles** (CA) results, the measurements were performed in two different configurations (with and without the usage of a support tensor). In any case, CA values < 90°C were recorded for all samples, both with and without surfactant: hydrophilic properties were softly improved, above-all for samples with surfactant (see corrective actions). Some measurements without the support tensor - that is more reliable for this kind of samples - have

to be completed.

DMA analysis into T range of rT-220° for T_g value determination supplied an important result if compared to the previous results: the reduction of the surfactant content (up to 1wt.%) reported T_g value to the original value of PSF polymer of about 190°C, demonstrating the recovery of the mechanical properties when the suitable surfactant content is used. The softening phenomenon due to an excessive amount of p-123 (50wt.%) was solved and the relation between factors individuated.

Regarding **cross-section SEM**, that is surely the determining characterization. It was performed on all of new developed samples. Important results and correlations were individuated between synthesis parameters used and final morphology. The complete treatment of this aspect with the corresponding cross-section images will be reported in the external report of the project, deposited in 2019. In any case, it permitted to established:

- synthesis parameters are determining in order to create channels and ordered finger-like morphology inside the transversal section of the solid membranes;
- low de-mixing times (Dt = 10s) not permit to complete the channels formation in the section as well as high de-mixing times (Dt = 40s) creates chaotic structures;
- amount of 10wt.% was individuated as the ideal to have the desired membrane configuration. Surface SEM (Mexican partner) will have to confirm this aspect;
- PSF2-23 sample containing a surfactant 10wt.% can be considered actually the best prototype, in terms of morpphology for final application application, prepared up to now as well as the parameters used for its preparation. It was synthesised by the following parameters: PSF concentration of 5wt.%; 1:10 p-123/PSF ratio; t_s: 60min.; T_s: 120°C; Dt: 20s; D.B.: 30μm.

Mexican partner will perform surface SEM measurements during the next months on new samples, since it has got a more sensitive device suitable for surface porosity measurement.

BET and TG-DSC (Italian Partner) as well as IR, zeta-potential and permeability measurements (Mexican partner) on new batch of samples will be completed during the next months.

11.0 - Conclusions (2nd year)

Some important steps of the preparation process have been standardized and the results have been crossed, reaching the following conclusions:

- a temperature of 120°C is required for the complete solubilisation of the polymer. The polymer agglomerates identified by SEM on the first batch of membranes were not found in the membranes synthesized with new parameters;
- the viscosity of the initial solution is decisive for obtaining membranes with good mechanical characteristics;

- too much low de-mixing times (Dt <20s) prevent the formation of the bottom-up type finger-like channels along the membrane section, while higher times (Dt> 20s) excessively increase the thickness of the final membrane;
- the membranes must have a thickness of at least 150-200 microns, so that the surfactant has sufficient space to act as a pore-former during the de-mixing process in the non-solvent coagulation bath;
- the asymmetric morphology with "finger-like macro-voids" has been reproduced and the correlation with the determining parameters was identified;
- the pore size, at present, seems to be suitable for MF processes. It will be reduced (during 3rd year) by the use of ionic liquids (ILs) and /or polyelectrolytes (PEI) in order to prepare membranes for UF processes;
- the following membranes (with and without surfactant) have been identified as the new prototypes to be further investigated and optimized during the 3rd year of activity: PSF2-20 (pure PSF), PSF2-16 (50wt.% surfactant), PSF2-22BIS (1wt.% surfactant), PSF2-24 (30wt.% surfactant) and PSF2-23 (10wt.% surfactant%).

12.0 - Dissemination of the results and collaboration reinforcement (2nd year)

Dealing with a joint lab, it's important to highlight some aspects regarding the linked dissemination, whose details are here following reported.

- One project meeting with partner Mexican team was organized at CNR-ITAE (Messina, Italy) from 20-24 October 2018. During the meeting, the evaluation of the experimental data obtained up to date was performed and an activity progress was jointly drawn up to establish the successive experimental activity, including the necessary corrective actions;
- a joint conference in 2018 on the project topic was realised: A. Saccà, Y. Gutierrez-Piña, M. Pilar González-Muñoz, R. Pedicini, A. Carbone, F.V. Matera, I. Gatto*, L. Espitia-Villanueva, S. Gutierrez-Granados, L. Hernandez-Perales, I. Olvera, T.A. Razo-Lazcano, M. Avila-Rodriguez, "Preliminary study on asymmetric Polysulphone (PSF) membranes for ultrafiltration processes application into industrial grade wastewaters purification field", Euromembrane 2018, Valencia (Spain), July 9-13 2018;
- an internal report was deposited: Melisa Barrera Lopez, Ada Saccà, Dicembre 2018. Lab. Congiunti Bilaterali Intern. del CNR, tematico ICT (triennio 2017-2019) - Prot. N. 0082227. Rapp. Int. 5/2018;
- the official external report on 2nd year activity is actually in progress;
- 3 months stage (Sept. - Dec. 2018) was realised and the corresponding degree thesis (student: Melisa Barrera Lopez - Chemistry) on project topic is actually in progress;
- a complete cells system for MF, UF, NF (up to 27 bar) and accessories, supplied by Sterlitech Corporation, was acquired by CNR-ITAE with Joint Lab funding with the aim of in situ verifying

the goodness of the developed AM-PSF samples and their performance, even feeding the system by contaminants species;

- a joint book chapter on ultrafiltration topic was edited: "Authors: Pilar González Muñoz, Reyna Guadalupe Turriza Cruz, Lluvia Paola Medina Armenta, Ada Sacca, Teresa Alejandra Razo Lazcano, Mario Ávila Rodríguez, Title: "Retencion de Cr(III) contenido en soluciones acuosas mediante ultrafiltracion asistida por formacion de complejos", CYTED - Chapter 6 in Book: "Sìntesis de Materiales y aplicaciòn de procesos de separaciòn en aguas y soluciones acuosas industriales", Editado por: Andrea Moura Bernardes - Sao Leopoldo: Trajetos Editorial, 2018. ISBN 978-85-696888-22-8;
- 3 months stage (Sept. - Dec. 2018) on a different topic (H_2 storage) was realized and the corresponding degree thesis (student: Claudia Elizabeth Vargas Macìas - Chemical Engineering) is actually in progress;
- two papers are actually in progress on the project activity; another will be drawn-up within the end of 3rd activity.

It's possible to affirm the student's exchange between two research teams, started in 2012, was reinforced as well as the mutual collaboration. Moreover, during the last meeting in Italy, on the basis of the jointly performed evaluation of the obtained results, a prediction of the 3rd year scientific activity with the definition of next steps and aims was elaborated. It is here following briefly presented.

13.0 - Expected experimental activity for 3rd year activity (2019).

At first, based on the results obtained in the 2nd year and their evaluation, jointly realised with the partner on the occasion of the 22nd Annual Progress Meeting (Messina, Italy - October 20-24, 2018), some critical issues were identified, the verification of which is preliminary to the activity of the 3rd year:

- control of the cross-section SEM (Italian partner) on 5 samples to correctly define the thickness of membranes and morphology;
- control of the contact angle measurements (Italian partner) on some of the new samples.

After, some characterizations have to be completed and/or verified, whose results are preliminary to the successive activity:

- TG-DSC analysis on the most representative new samples, in order to verify porosity, pore distribution and verify their thermal properties (Italian partner);
- surface SEM analysis on new samples with the aim of verifying the surface porosity (Mexican partner);

Regarding the real new experimental activity for 3rd year, at first, the procedure preparation will be completely defined and, at the end, the influence of temperature (10, 20, 30°C) on morphology during the de-mixing process in the non-solvent coagulation bath will be evaluated

(a thermostatic bath will be acquired with project's funding). More, semipermeable flat commercial membranes based on PES/PSF for UF will be acquired with the project funding and used as performance references. At the same time, once the preparation procedure will be standardized, a state of the art and standardization procedure for solid membranes (PSF, PES) containing polyelectrolytes and ionic liquids (respectively, PEI and CYPHOS-104) in order to use the membranes *as-received* complexing the contaminant metal solutions used as feeding and/or triggering charge repulsion mechanisms for UF applications will be carried out. New asymmetric membranes, capable of retaining metallic particles, will be synthesised. The ideal amount of PEI and CYPHOS104 will be optimized.

All the membranes developed will be jointly characterized by the usual methods used up to now. In particular, surface and cross-section SEM analysis will be useful to verify the morphology (porosity, distribution of pores and channels, asymmetry, "finger-like macro-voids") as a function of the variations to the procedure; water permeability tests under pressure will be performed for the selection of the best samples. In addition, new techniques will be used, such as AFM (Mexican partner), to better define the quality of samples; while in situ tests by the new system for ultrafiltration measurements (Crossflow PTFE Cell System by Sterlitech Corporation), acquired by the Italian partner with the project funds, will be performed. This system is capable of working up to 27 bars, powered by a HydraCell pump regulating the incoming flow (range up to 6.8 l/min.). Once the measurement protocol will be defined, it will allow qualifying the membranes prototypes, also by means of incoming feeding simulations containing metal contaminants for the final application. The new results will then evaluate and crossed with the previous ones to confirm the goodness of the prototypes, identify new configurations and evaluate other operating parameters useful for the selected filtration process. The following results will be expected:

- definition of membrane preparation procedures according to the type of membrane: pure, with surfactant and/or IL and as a function of the selected process;
- definition of the correlation between the parameters used and obtained morphology;
- selection of solid asymmetric flat membrane prototypes (with/without surfactant and/or ILs);
- selection of the process (MF, UF NF) according to the characteristics of the membranes and the contaminants to be removed.

14.0 - Expected dissemination results for 3rd year activity.

In terms of dissemination, the following results are foreseen:

- one/two conference joint participations;
- one update conference/fair/course (only in Italy or Mexico) on the project topic;
- one project meeting for activity progress (in Italy) and final meeting (in Mexico);
- stage of one/two Italian researchers in Mexico;

- publication of the two papers on the obtained project experimental results;
- technical internal reports on 2nd and 3rd year activity and one external report on the whole project activity.

15.0 - Description of the 3rd year activity

The activity of the third year was performed starting from January 01, 2019 up to December 31, 2019.

A preliminary state of the art was performed on the necessary membranes' properties (porosity percentage, pore shape and size, cross-section morphology, hydrophilic characteristics, permeability, selectivity, dynamo-mechanical properties, etc.) using surfactants, polyelectrolytes (here, PEs) and ionic liquids (ILs), as previously decided with partner, to be applied in UF processes. Commercial compounds such as Pluronic p123, Polyethileneimmine-PEI and CYPHOS-104, respectively were further studied (p-123) and newly individuated as possible candidates, since able to trigger defined behaviours in terms of micelles formation, metal ions complexation and charge repulsion mechanisms, respectively with the aim of modifying the pure PSF membranes morphology and to make them suitable for the UF and above-all for the removal/recovering of polluting metals ions.

The pore size of the membranes synthesised up to now was of about 80-120 nm (membranes without surfactant) and 30-40 nm (membranes with surfactant p-123), but not always with a uniform distribution and dimension; the molecular cut-off (MWCO) of the membranes for the application must be of about 2-50 nm. Hence, the pores diameter is equal/wider to the necessary dimension, but, in any case, compatible with the UF range (3 - 100nm).

Operatively, some lacking characterizations on membranes developed during the second-year activity were performed or again verified, whose results were preliminary to the successive activity. In particular:

- lacking cross-section SEM analysis on pure PSF2-26 membrane;
- surface SEM on the most representative membranes developed during the second year (PSF2-12BIS up to PSF2-26);
- AFM membranes on the most representative membranes developed during the second year (PSF2-12BIS, PSF2-16, PSF2-22BIS, PSF2-23, PSF2-24, PSF2-26 - see table 1);
- lacking permeability measurements on the most representative membranes developed during the second year (PSF2-22BIS up to PSF2-26 - see table 1);
- lacking contact angle measurements on the most significant samples developed during the second year (PSF2-26);
- FT-IR measurements on the developed membranes during the second year (PSF2-22BIS up to PSF2-26).

Successively, the new activity was started with the preparation/characterisation of the new

samples.

In particular, commercial ionic liquid CYPHOS-104 IL (trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl) phosphinate) introduction into the PSF/solvent/surfactant (whereas present) system was tested and standardised in order to trigger the mechanism of charge repulsion inside the membrane to selectively filter the heavy metal ions. In this context, the following actions were performed:

1. evaluation of the ionic liquid solubilisation efficacy into the system;
2. individuation of the solvent for IL, its concentrations into the polymer dispersion and combinations with surfactant;
3. evaluation of the possible methods of IL solubilisation: mixing with the starting PSF dispersion in DMAc and surfactant (p-123), if present, as well as separated solubilisation phase of IL in organic solvents (decanol). It, in-fact, is not soluble easily (insoluble in water);
4. definition of the parameters for the membrane preparation, such as solubilisation and temperature time (Ts and ts), de-mixing time in the context of the CYPHOS104 presence.

In detail, some critical aspects in the formation of the membrane, were resolved and an important objective was found: the standardization of the preparation procedure of asymmetric pure polysulfone (AM-PSF) membranes containing both surfactant (Pluronic p123) and ionic liquid (CYPHOS104), for the production of films that can be used to separate polluting metal species. Such membranes obtained have demonstrated to have got good properties for the final aims, in particular a suitable morphology with asymmetry and finger-like macro-voids presence, as highlighted by literature in the field.

The fixed parameters after evaluation of the first year were: PSF 5wt.% as concentration, water as solvent; while during the second year were fixed: t_s: 60 ', T_s: 120°C, D_t: 20s, D.B.: 300μm. The samples were developed maintaining fixed these parameters and varying the ionic liquid content. The final preparation procedure was defined, as described in the following paragraph.

15.1 - Membrane preparation procedure (3rd year).

The membrane preparation procedure was finally optimized and it is here briefly described. The final operative parameters are indicated in bold.

PSF polymer concentration (5 wt.%) in DMAc as a solvent is treated at room temperature (25°C; 10 min.) under magnetic stirring. Surfactant Pluronic p-123 as received, whereas present, is added in the starting PSF/DMAc dispersion at room temperature. Different concentrations of p-123 were investigated (1, 10, 30 & 50 wt.%) and a concentration of 10wt.% of p123 was selected as ideal content for membrane preparation.

Three different Cyphos 104 IL concentrations (1, 1.5, 3wt.%), whereas present, was studied and, hence, added in this phase to the PSF/p123 dispersion, obtaining a complete solubilisation in DMAc at rT. The polymer dispersion solubilisation continues on hot plate at T_s= 120°C for t_s=1hr. under

stirring (300 rpm covered with a watch glass avoiding the evaporation). After, the watch glass is removed and the solvent re-concentration phase of the solution is started. When the solution viscosity is adequate, it is immediately stratified by Doctor-Blade on a preheated glass at T=50°C.

The calibrated Elcometer® Blade Knife Model 3580 was used setting different thicknesses; a final thickness of 30 μm was fixed as ideal. The final membranes have size of about 20 x 30 cm^2 with a good visual manufacture (no bubble or hole). The glass with the stratified solution is quickly immersed into the non-solvent coagulation bath (H_2O) at room temperature. The non-solvent volume is fixed at 4 litres. After a fixed de-mixing time Dt=20'', the membrane is quickly removed from non-solvent bath and placed between two absorbent paper sheets (substituted several times during the next 24 hrs. to assure the drying) under two metal plates to maintain it smooth and dried. Post-casting treatments in IPA and H_2O, (1 and 5 hrs. respectively) are carried to purify the membranes from contaminants and impurities. When the membrane is completely dried (about 72hrs.), the thickness is measured on different points to have a statically valid average value. In this way, new five membrane samples (PSF2-27 to PSF2-31) were synthesized using the described parameters and the different Cyphos 104 IL contents. The Table 2 reports the prepared membranes and the corresponding used parameters and their compositions.

Membrane	PSF, wt.%	Solvent	p-123, wt.%	Cyphos 104, wt.%	ts, min.	Ts, °C	Dt, s	DB, μm
PSF2-27	5	Water	10	1,7	60	120	20	500
PSF2-28	5	Water	10	1,0	60	120	20	300
PSF2-29 (pure PSF)	5	Water	0	0	60	120	20	300
PSF2-30	5	Water	10	0	60	120	20	300
PSF2-31	5	Water	10	3,0	60	120	20	300

Table 2. Membranes prepared during the third-year activity and corresponding parameters used.

Legenda.

PSF, wt.%: PSF concentration
Dt = de-mixing time, s
p-123, wt.%.: p-123 concentration
Cyphos 104, wt.%.: IL content
D.B.: starting light set on doctor-blade device, □m

After preparation, at first, the samples were analysed by SEM to check the morphology and asymmetry generated by the adopted synthesis parameters. The characterisation was performed on the dried samples.

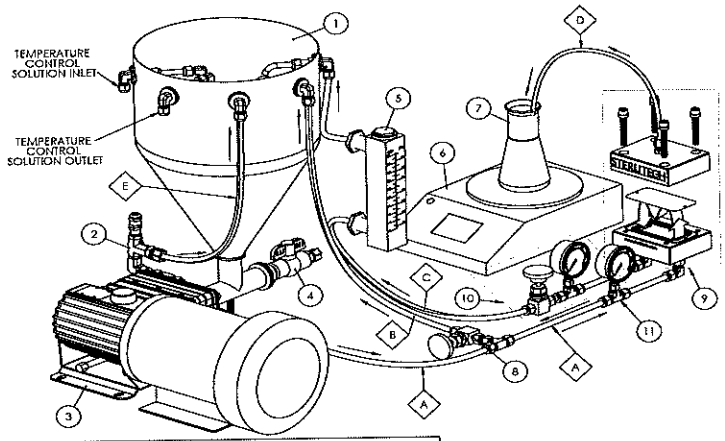
In the research process, the new synthesis parameters were changed one by one, developing asymmetric PSF membranes with superior characteristics (as emerged by the characterisation results), if compared to the previous prototypes. These membranes were cast in three different configurations PSF/solvent, PSF/solvent/surfactant and PSF/solvent/surfactant/IL. Three

theoretical different loads of ionic liquid (CYPHOS 104) were used (1, 1.5, 3wt.%), in order to trigger charge repulsion mechanisms inside the polymer matrix and filter contaminated solutions containing Cr^{+3} (e.g.:) using as-received membranes with the actual pore size, but able to repulse the positive charges of the heavy metal solution used as feeding thanks to the ionic liquid presence. The optimal amount of CYPHOS104 has been optimized (1wt.%).

16.0 - Characterisation

At this point, with the aim of individuating the most promising candidates, the new samples were jointly characterised by two research teams in terms of water retention capability (water-uptake) and dimensional analysis @rT into three spatial directions (width, length, thickness variation), wettability (contact angle measurements), porosity (BET), thermal properties (TGA-DSC), structure (X-ray diffraction), morphology (surface/cross-section SEM), permeability tests. In particular, the different characterization techniques have been devoted to the checking of the polymer solubilisation, individuation of the asymmetry, suitable transversal morphology, above-all considering the improvements obtained. Moreover, the optimization of the manufacturing, the size, shape and the pores/channels distribution, hydrophilic properties and, above-all, the correlation between experimental parameters and membranes morphology were taken into account in order to individuate the characteristics for final application (MF, UF, NF).

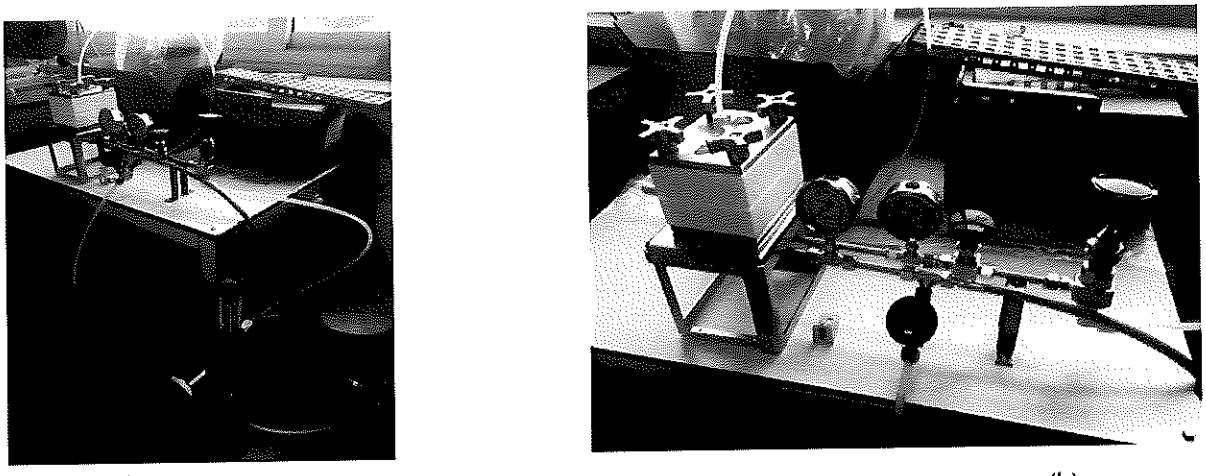
The final capability of the prepared membranes (pure PSF, with p123 and with CYPHOS104) can be evaluated by filtration in-situ measurements. An important system for UF-NF measurements, fit for purpose, produced by Sterlitech was acquired by CNR-ITAE thanks to the Joint lab findings. In Figure 1, the diagram of the device is reported:



CF042A FLOW DIAGRAM	
ITEM NO.	PART DESCRIPTION
1	CONICAL FEED TANK
2	PRESSURE RELIEF VALVE
3	FEED PUMP
4	DRAIN VALVE
5	FLOW METER
6	SCALE FOR MEASURING PERMEATE FLUX
7	PERMEATE COLLECTOR
8	BY-PASS NEEDLE VALVE WITH 3/8" "T" TUBE FITTING
9	ACRYLIC CF042 CELL ASSEMBLY
10	CONCENTRATE CONTROL VALVE ASSEMBLY (0-400 PSI)
11	FEED PRESSURE GAUGE
A	3/8" HIGH PRESSURE FLEX OR RIGID TUBING, FEED LINE
B	3/8" LOW PRESSURE TUBING, BY-PASS
C	3/8" LOW PRESSURE TUBING, RETURN LINE
D	1/4" LOW PRESSURE TUBING, PERMEATE OUTPUT LINE
E	3/8" LOW PRESSURE TUBING

Figure 1. Sterlitech filtration system.

The system with the connected cell for filtration UF, NF measurements - important aim of the project - was completely assembled. The following Figure 2 (a-b) reports the photos of the system assembled into the lab:



(a) (b)

Figure 2 (a-b). (a) photos of assembled system: (b) UF/NF cell assembled.

Such system can be used as device for: 1) water flux measurements: 2) water permeability tests and 3) filtration tests using feeding solutions containing different contaminant species (heavy metal solutions, such as Cr^{+3}, Pb^{+2}, Cd^{+2} and so on).

Moreover, commercial membranes based on PES, PSF and PVDF by Sterlitech were acquired to be tested and to define the procedures, the commercial references, the operative conditions and the

main parameters for the measurements: time, flux, retained/permeated ratio, permeability, etc.

The measurements into the Filtration Sterlitech System were not realised, due to a soft delay into the funding's disbursement that has caused a delay into the acquisition of the system (deviation from project aims), dealing with a foreign firm, but the system and a protocol for the measurements have been developed. After the end of the project, the most interesting developed membrane samples (pure PSF, containing surfactant and with CYPHOS104) will be tested and compared with the commercial references, in terms of flux, retention capability, permeability tests of the contaminant species. The results will be evaluated, integrated and crossed with the previously obtained results in order to identify the best membrane prototypes, able to efficiently act as filters in UF processes, purifying industrial grade wastewaters polluted from heavy metal ions. The separation/recovery efficiency and performance of this operation will be investigated.

Such operations on the developed prototypes will realised after the closing of the project and the results will be used as opportunities of new financing.

17.0 - Main experimental results (3rd year)

The operating conditions and synthesis parameters, determining the morphology and the goodness of the manufacturing, have been fixed. More in detail:

1. polymer concentration of 5wt.%, water as non-solvent have been defined as optimal parameters;
2. the polymer solubilisation temperature (named T_s) has been fixed in 120°C in order to completely solubilise the polymer agglomerates (individuated by SEM in the previous batch of membranes), the added surfactant and Cyphos 104 IL;
3. the polymer solubilisation time (named t_s) was optimised and fixed in 60 minutes in order to solubilise PSF, surfactant and Cyphos 104 IL;
4. the evaporation time (named E_t) of the solvent in the polymeric solution with the aim of optimising the viscosity factor has been defined to obtain more resistant membranes, capable of withstanding more prohibitive pressure operating conditions for final application;
5. the "de-mixing" (named D_t) in order to enhance the transversal morphology (asymmetry with finger-like macro-voids) has been fixed in 20s as optimal for the best cross-section configuration (SEM);
6. the surfactant concentration was individuated in a 10wt.% since it seems to be the best compromise to complete the channels formation and to have an ordered asymmetric morphology;
7. different initial thickness values to be set on the Doctor-Blade knife (named D.B.) were investigated with the aim of optimising the stratification phase and identify the optimal surfactant distribution, whose acts as a pore-former. The final D.B. thickness was set in 30 mm since it is ideal for surfactant and IL distribution.

Here following, the main experimental results obtained, divided for characterisation, are

reported.

XRD on new membranes confirmed the previous results: no significant variation was recorded on samples with and without surfactant and ionic liquid, indicating that the structure is not affected by their introduction.

Regarding **water retention** behaviour @rT, it's possible to affirm that, generally, the water retention increases with surfactant and ionic liquid introduction.

For the **porosity** evaluation, the membranes containing the surfactant and IL are basically more porous, as expected, except for some negligible experimental exceptions.

Regarding **contact angles** (CA) results, values < 90°C were recorded for all samples also for membranes with surfactant: the membranes have got good hydrophilic properties and those with IL have values into the range of 71-83°.

Regarding **BET measurements**, the new samples synthesised with IL supplied values of higher surface area of about 9-17 m^2/g with a pore size of 28-55 nm that increases with the increase of the Il content.

Regarding **cross-section SEM**, that is surely the determining characterization, it is possible to affirm that the final procedure for membrane preparation permit to obtain a very good transversal morphology with the desired finger-like macro-voids, comparable to the structures reported in literature. The main correlations between the synthesis parameters and final morphology were individuated. The complete treatment of this aspect with the corresponding cross-section images will be reported in the complete external technical report of the project, that will be deposited in 2020 and inserted in "people site" as research product. In any case, it permitted to established:

- synthesis parameters are determining in order to create channels and ordered finger-like morphology inside the transversal section of the solid membranes;
- amount of 10wt.% of surfactant was individuated as the ideal to have the desired configuration, in-fact the membrane PSF2-23, containing a surfactant 10wt.% can be considered the best prototype with surfactant, in terms of morphology. It was prepared by the following parameters: PSF concentration of 5wt.%; 1:10 p-123/PSF ratio; t_s: 60min.; T_s: 120°C; D_t: 20s; D.B.: 30□m, considered the final ideal parameters for membrane preparation.

TG on the membranes with surfactant and IL revealed that these membranes seem to be thermally less resistant, but this soft reduction of stability occurs at T>170°C, not affecting the application range; DSC profiles didn't reveal any important variation if compared to the pure PSF membrane.

IR measurements on surfactant membranes have demonstrated that p-123 only acts as pore-former, not remaining inside the final membrane structure.

Permeability measurements on the membranes with surfactant demonstrated the sample PSF2-12 (pure) and PSF 2-23 (10wt.% of p-123) are the membranes that better follow the Darcy's law: the measurements on the new batch of samples with IL will be completed during the next months and

the results will be integrated with previous ones in order to be inserted in the final external report.

17.0 - Dissemination results for 3rd year activity (2019) and collaboration reinforcement

Dealing with a joint lab, it's important to highlight some aspects regarding the linked dissemination, whose details are here following reported.

- The final 36 months project meeting with partner Mexican team was organized at CNR-ITAE (Messina, Italy) from September 30 - October 04, 2019. During the meeting, the evaluation of the experimental data and the main conclusions were carried out;
- two joint conferences on the project topic were realised:
  1. M. Barrera-López Y. Gutiérrez-Piña, L. Hernández-Perales, M. González-Muñoz, A.Saccà, I. Gatto, M. Ávila-Rodríguez, 9th International Colloids Conference, June 16-19 2019, Sitges-Barcelona (Spain);
  2. M. Barrera López, Y. Gutiérrez Piña , L. Hernández Perales, M. Pilar González Muñoz, A.Saccà, I. Gatto, M. Ávila- Rodríguez, XVI Encuentro de la Mujer en la Ciencia. CIO-Leon, Guanajuato (Mexico), May 29-31 2019.
- two technical internal reports with the activity of the 3rd year and the complete project activity will be deposited contemporarily to the economic report;
- 3 months stage (January 2020 - April 2020) is actually in progress at CNR-ITAE on the project topic (student: Sofia Galilea Quiroz Yebra) devoted to the degree thesis. Due to organization matters, the stage was moved from 2019 to January 2020 in order to individuate coherent possibilities to jointly present new project proposals;
- 3 months stage (January 2020 - April 2020) on a different topic (H_2 storage) is actually in progress at CNR-ITAE devoted to the degree thesis;
- two papers are actually in progress on the project activity;
- a complete system for MF, UF, NF (up to 27 bar) and accessories, supplied by Sterlitech Corporation, was acquired by CNR-ITAE with Joint Lab funding with the aim of in situ verifying the goodness and the performance of the developed AM-PSF samples. Such system will be jointly used for the future perspectives.

It's possible to affirm the student's exchange between two research teams, started in 2012, was reinforced as well as the mutual collaboration and the joint management of the topic between two research groups. Such activity will be continued in the future.

18.0 - Experimental conclusions (3rd year)

The following final conclusions can be formulated:

- the solubilization time (t_s) has a significant effect on the morphology of the membranes, since if this is very short, the correct channels morphology (finger-like macro-voids) is not generated, but rather a spongy support is formed;

- the most suitable polymer solubilization temperature is 120°C. At this temperature, a complete dissolution of the polymer was achieved, without debris being observed on the surface of the membranes;
- the viscosity of the solution is a determining parameter for the final membrane morphology: the evaporation phase time with the used polymer concentration was fixed in 120 minutes with and without surfactant;
- De-mixing time of 20s, determining for membrane formation, was defined as optimal time, since it generates an adequate morphology and, in particular, more defined finger-like channels into the transversal section; in addition, it was discovered that too low de-mixing times (Dt<20s) prevent the formation of bottom-up finger-like channels along the membrane section, while higher times (Dt> 20s) excessively increase the thickness of the final membrane and deform the channels in section;
- the concentration of Pluronic p-123 was set at 10 wt.% because it generates a transversal morphology with adequate properties;
- starting Doctor-Blade thickness value to be set in order to obtain the most suitable thickness and morphology on the final membrane was fixed equal to 50 μm since it generates a final thickness of about 200 μm; in-fact, the membranes must have a final thickness of at least 200 microns, since the surfactant has enough space to act as a pore-ex during the mixing process and, moreover, the mechanical properties are satisfactory;
- contact angle measurements showed that membranes have a sufficient hydrophilic character, without that the Pluronic p-123 shows a particular influence on this characteristic;
- the addition of the surfactant softly increases the hydrophilic properties (water-uptake) and generates more defined finger-like channels from side to side of the membrane generating a correct morphology for final application;
- the addition of Cyphos IL generates a higher porosity, both in the surface and transversal direction;
- the asymmetric morphology was reproduced with "finger-like macro-voids" and the correlation with the determining parameters was identified;
- the pore size of the membranes in their current state seems to be suitable for UF processes (80-100 nm for membrane without surfactant and 20-40 nm for membrane with surfactant), even if the distribution of the pores can be further enhanced.

19.0 - General conclusions

A high level of control both of the surface morphology (distribution of pores of the appropriate size) and transversal (finger-like macro-void type) was obtained according to the related parameters. This aspect is particularly decisive for defining the selective capacity of membrane

prototypes. The operating conditions and the synthesis parameters determining the morphology, size and distribution of the pores were also defined. In particular:

1. standardization of parameters and the membrane formation procedure, as described in the paragraph 5.0;
2. verification of the reproducibility of the preparation. The membranes taken as reference during the second year (PSF2-20, and PSF2-23), respectively without and with surfactant, were reproduced (PSF 2-29, PSF2-30) to verify the correlation with the operating parameters;
3. preparation of new membranes with ionic liquid (CYPHOS 104). Five new samples were prepared and characterized, the two references (pure PSF and PSF with surfactant) and three samples with three different percentages of CYPHOS IL (1, 1.5, 3wt.%).

At the end, the following membranes that showed the best characteristics (with and without surfactant/ionic liquid) were identified as best prototypes to be used in the application of the project: PSF2-20 and PSF2-29 (pure PSF), PSF2-23 and PSF2-30 (p123 10wt.%), PSF2-28 (p123 10wt.% and IL 1wt.%) and PSF-2-31 (p123 10wt.% and IL 3wt.%). This is thanks to their morphological characteristics, similar to those identified in the literature as ideal, to their hydrophilic, porosity, thermal-mechanical and permeability properties. The final filtration capacity will successively tested thanks to the acquired UF system.

20.0 - Deviations from the planned activity

Here briefly the main deviations from the foreseen activity are listed:

- Evaluation of the temperature influence on the de-mixing process and on the membrane morphology through the use of a thermostatic bath: due to a delay of the company in the realization of the product (November 2019), the acquisition of the device took place only lately. This aspect is being evaluated in this period during the stage of the student and it will be completed after the end of the project;
- evaluation of another type of surfactant (p127): this aspect will be evaluated after the closure of the project;
- investigation of the complexation process using polyelectrolytes (PEI) on the heavy metal solutions feeding in order to increase the size of the contaminant to be filtered using as-received membranes with the actual pore size avoiding in this way the passage through the membrane pores;
- in-situ filtration tests (UF) through the Crossflow Cell System (by Sterlitech) acquired by the ITAE on the prototypes developed and successive comparison with commercial references: this aspect will be assessed after the closure of the project since, as above-mentioned, there was a delay in the acquisition of the system (July 20019), in the delivery and subsequent complex implementation of the same;
- self-made ionic liquid tests (ILs) provided by the Mexican partner: the partner did not receive the

materials from the French colleague who was supposed to synthesize them;

- the other research path foresaw the filtration process modification using the developed as-received membranes, complexing the metal of the simulated contaminated solutions (feeding) and increasing the size of the species to be filtered, without changing the pore size or activate charge repulsion mechanisms (as IL). It was hypothesized to pursue this aspect by using polyethyleneimine polyelectrolyte (PEI) to complex the Cr(III) metal solutions and commercial semipermeable membranes acquired with different cut-off (5-30 KDalton). This research path has not been investigated and will be activated after the closing of the project, exploiting it to individuate new funding sources.

21.0 - Further developments and perspectives of the project activity

The membranes synthesis for this application should be continued on basis of the individuated parameters and the obtained results in order to achieve enhanced mechanical-hydrophilic-morphological-thermal properties, correct size and shape of pores and channels compatible with the size of the species to be filtered. Similarly, the effect of other types of additives could be studied, such as PEG or ILs on the membranes or polyelectrolytes (e.g.: PEI) on the feeding solution with the aim of using the membranes as-received with the actual pore size, but improving the triggering of charge repulsion mechanisms (using ILs) or increasing the contaminant species size used as feeding through the complexation mechanism (using PEs) of the own feeding. Such aspect could be further investigated/ optimised or newly exploited.

Moreover, the Sterlitech's CrossFlow Cell System - acquired by ITAE thanks to the project funds - will be the core of a deep characterisation and permit to ascertain the ability to separate contaminants and the applicability of prototypes developed. This system, capable of working up to 27 bars (UF-NF), powered by a HydraCell pump regulating the input flow (flow rate up to 6.8 l / min.), once established the measurement protocol, will permit to qualify the membranes prototypes manufactured for the separation of metallic pollutants in UF processes and individuate the more efficient membrane configurations to be proposed as fulcrum of new proposals. In-fact, on the basis of the results obtained, new possibilities to present joint projects on the topic will be evaluated considering the most promising samples based on:

- PSF pure membranes;
- PSF/surfactants membranes;
- PSF/surfactant/ILs membranes.

In conclusion, the research into the membrane filtration processes field presents an infinite number of possibilities to generate materials that adapt to the different process exigencies. This type of research is encouraging because is easily tuneable simply varying the size, shape and the distribution of pores and channels and the membranes composition and morphology as a function of the species to be separated.

Messina, 31/01/2020

The scientific Italian Manager of the project

dr. Ada Saccà

The scientific Mexican Manager of the project

prof. Mario Avila-Rodriguez