



**LINEE GUIDA**  
**per la preparazione**  
**delle comunicazioni orali/poster**  
**da pubblicare nei**  
**PROCEEDINGS**  
**of the XVIII Workshop on the**  
*Developments in the Italian PhD Research*  
*on Food Science, Technology & Biotechnology*

Conegliano, September, 25-27, 2013

**Università degli Studi di Padova**

**Università degli Studi di Udine**



## **LINEE GUIDA PER LA PREPARAZIONE DEI CONTRIBUTI**

Con riferimento a quanto approvato dal Comitato di Coordinamento nella riunione del 11 febbraio 2011 presso il CRA di Roma, si riportano le **linee guida** per la preparazione dei contributi che i dottorandi dovranno elaborare per la pubblicazione degli Atti del Workshop.

Il Comitato si è proposto di riformulare le modalità di preparazione di detti contributi in modo da differenziarli nettamente da quelle tipiche dei Convegni nazionali o internazionali del settore ed evidenziare la specificità del Workshop quale momento *clou* nella formazione dei dottorandi sia attraverso calibrate lezioni magistrali di specialisti del settore *Food Science and Technology* (FST), sia attraverso la divulgazione delle diverse fasi del lavoro di ricerca svolto dai dottorandi stessi.

Più specificatamente, per il 16<sup>th</sup> Workshop si richiederà quanto segue:

- a) Una **comunicazione orale (max 5 pagine)**, ove i **dottorandi del III anno** esporranno il progetto di ricerca svolto, evidenziandone l'innovazione rispetto allo stato dell'arte, i principali risultati conseguiti e la loro congruenza o differenza rispetto a quanto noto in letteratura, le conclusioni e le prospettive future. Questo documento, se redatto nei tempi stabiliti secondo le istruzioni e l'esempio illustrativo riportati di seguito, verrà pubblicato negli atti del Workshop e, se ritenuto idoneo da una Commissione costituita da 2 docenti dei SSD di riferimento, AGR/15 e AGR/16, comporterà per l'autore l'acquisizione di **4 CFU**. Verificata la presenza del dottorando alle sessioni del Workshop, il Presidente del Comitato provvederà nella Cerimonia di chiusura del Workshop al rilascio del relativo attestato di partecipazione e di certificazione dei crediti acquisiti. È possibile che per tesi di ampio respiro, che abbiano prodotto grandi quantità di dati, sia oggettivamente difficile riassumere tutta l'attività sperimentale in un manoscritto di 5 pagine. Il Comitato dei Coordinatori suggerisce quindi di riportare comunque nel manoscritto una o più sezioni che presentino il lavoro svolto nel triennio in modo organico, evidenziandone gli aspetti innovativi e originali rispetto allo stato dell'arte, di focalizzare la parte sperimentale su uno degli aspetti (magari il più rappresentativo) affrontati e di riservare alle conclusioni le considerazioni relative alle ulteriori prospettive di sviluppo e all'impatto (in termini di scienza pura ed applicata) del lavoro di tesi. Analogamente, nella presentazione orale (15 min, circa 15 diapositive) è necessario che il dottorando fornisca sia un quadro dello stato dell'arte, che del lavoro complessivo svolto nel triennio (inclusi gli elementi di innovazione e di impatto scientifico e applicativo), ma presenti con maggior dettaglio una parte (più o meno ampia) del lavoro sperimentale in modo da consentire ai referee di valutare adeguatamente l'approccio scientifico e metodologico adottato.
- b) Una **comunicazione poster (max 2 pagine)** e un **Poster** (formato **A1**: 594 x 841 mm<sup>2</sup>), ove i **dottorandi del II anno** presenteranno le attività svolte secondo il progetto di ricerca iniziale, i principali risultati conseguiti, evidenziando la eventuale differenza fra i risultati ottenuti e quelli attesi, la riconferma o la riformulazione del programma di ricerca per l'anno successivo. Questo documento, se redatto nei tempi stabiliti secondo le istruzioni e l'esempio illustrativo riportati di seguito, verrà pubblicato negli atti del Workshop e, se ritenuto idoneo da una Commissione costituita da 2 docenti dei SSD di riferimento, AGR/15 e AGR/16, comporterà per l'autore l'acquisizione di **3 CFU**. Verificata la presenza del dottorando alle sessioni del Workshop, il Presidente del Comitato provvederà nella Cerimonia di chiusura del Workshop al rilascio del relativo

attestato di partecipazione e di certificazione dei crediti acquisiti. È fortemente consigliata la partecipazione dei dottorandi.

- c) Un **PhD Dissertation Project (max 2 pagine)**, e un **Miniposter** (formato **A2**: 420 x 594 mm<sup>2</sup>) ove i **dottorandi del I anno** presenteranno un sintetico stato dell'arte sul tema di ricerca che affronteranno nel biennio successivo, il programma delle attività di ricerca con gli obiettivi realizzativi (*milestones*) ed i risultati attesi. Questo documento, se redatto nei tempi stabiliti secondo le istruzioni e l'esempio illustrativo riportati di seguito, verrà pubblicato negli atti del Workshop e, se ritenuto idoneo da una Commissione costituita da 2 docenti dei SSD di riferimento, AGR/15 e AGR/16, comporterà per l'autore l'acquisizione di **2 CFU**. Verificata la presenza del dottorando alle sessioni del Workshop, il Presidente del Comitato provvederà nella *Cerimonia di chiusura* del Workshop al rilascio del relativo attestato di partecipazione e di certificazione dei crediti acquisiti.

**Per i 3 tipi di contributo, ciascun dottorando (e di riflesso il tutore) dovrà autovalutare il proprio manoscritto con il software disponibile sul sito del Workshop, onde evitare un'inutile copia-incolla di lavori già pubblicati su riviste od atti di convegno senza una minima, eppure doverosa riconsiderazione dei dati raccolti durante i 3 anni del corso di DR.**

Workshop Formatting Instructions: Contribution Title

PhD Student Name (e-mail)

Affiliation b(Dept., University, City, Country)

Tutor: Prof. X Y

This document contains the content and formatting instructions for preparing a camera-ready paper for the Workshop. Your paper should be submitted by e-mail a [foodsci.phd2012@unibo.it](mailto:foodsci.phd2012@unibo.it) before June, 15, 2012. The manuscript should start with an abstract of the PhD work (non more than 100 words) which should summarize the scope, aims, results and conclusions. **Do not head** the abstract section with any heading (ex: do not indicate the word Abstract)

## **Titolo in Italiano**

Riassunto in Italiano (max 100 parole)

### **1. Format and Type Fonts**

This chapter contains lay-out and formatting instructions for preparing a camera-ready paper for the Workshop using Microsoft Word. These instructions are to be followed strictly, and it is strongly advised to use the styles indicated in this document in between square brackets. It is strongly advised NOT to use more formatting or styles in your paper than the ones mentioned here. All data should be reported in the: SI Unit System.

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The book size will be 29,7 x 21 cm with a type area of 26,7 x 16 cm.

On A4-size paper, you will have to set the margins to:

Left Margin: 3,0 cm; Right Margin: 2,0 cm; Top and Bottom Margin: 2,0 cm

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Maximum number of pages, including references and figures, for an Oral Communication is **5 pages**, for a Poster or a Mini-Poster is **2 pages**.

Do NOT add page numbers.

Do NOT add Headers or Footers.

#### **1.2 Type font and type size**

[Style: Normal]

Prescribed font is Times New Roman, 10 points, with single spacing, 1 column. However, if your text contains complicated mathematical expressions or chemical formulae, you may need to increase the line spacing. Running text should be justified.

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[Style: Title]

The authors and affiliation should be typed in 10 pt. Times New Roman, Centred

#### **1.3 Section headings**

The way chapter titles and other headings are displayed in these instructions are meant to be followed in your manuscript. It is strongly recommended that you use the preformatted styles for the headings.

Level 1: Times New Roman, 12 pt, Bold, 12 pt before and 6 pt spacing after heading, Title Case

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[Style: Footnote Text]

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#### 1.5 Equations

Make sure that placing and numbering of equations is consistent throughout your manuscript.

$$E=mc^2(1)$$

Leave one extra line space above and below the equation, left align the equation and put the number of the equation flush-right, using a Right Tab on the right margin.

## 2. Illustrations and Tables

### 2.1 General

Illustrations and tables should be originals or sharp prints. As the manuscript will be reproduced in black-white, any illustration must not use colours. Avoid to reference your text to coloured items in the illustrations. All these means will be lost after the printing and will create misunderstanding to the reader. All illustrations should be placed in position on or near the page where they are first mentioned or treated in detail. They should preferably be placed either at the top or at the bottom of the page.

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Set table number (Bold) and title flush (Italic) left above table, with 15 pt before and 6 pts after between text and table. To distinguish tables from the main text, use a smaller type font (Times New Roman, Italic, 9 pt). Horizontal lines should be placed above and below table headings, above the subheadings and at the bottom of the table above any notes. Vertical lines should be avoided.

Position tables at the top or bottom of a page.

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Citations in your text should be collected at the end of your manuscript in a list of References. They should be prepared according to the Harvard style (name/year system) Make sure that your accumulated list corresponds to the citations made in the text body and that all material mentioned is generally available to the reader.

Reference in the text to literature cited is given by the surname of the author(s) followed by the year of publication, e.g. "Smith (1984) has reported ..., which was recently confirmed (Jackson and Sharp, 1986)." For references with more than two authors, text citations should be shortened to the first author followed by "*et al.*". However, in the list of References the names and initials of all authors should be mentioned. Two or more references by the same author published in the same year are differentiated by the letters a, b, c, etc. immediately after the year. The references should be listed in alphabetical order in the list of References.

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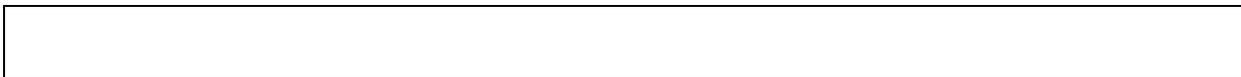
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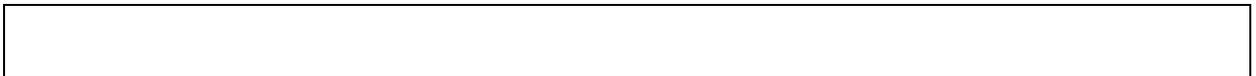
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# **ORAL COMMUNICATIONS**



## Optimal Strategy to Model the Electrodialytic Recovery of Some Fermentation Products

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Tutor: Prof. X Y

This PhD thesis dealt with the assessment of a comprehensive mathematical model of the electrodialytic (ED) recovery of some sodium salts of mono-carboxylic acids from aqueous solutions and establishment of an experimental procedure to determine the effective parameters for designing and optimising ED stacks.

### Strategia ottimale per la modellizzazione del recupero elettrodialitico di alcuni prodotti di fermentazione

Questa tesi di dottorato ha riguardato lo sviluppo di un modello matematico per il recupero elettrodialitico (ED) di alcuni sali sodici di acidi monocarbossilici da soluzioni acquose e di una procedura sperimentale diretta alla determinazione dei parametri essenziali per la progettazione e l'ottimizzazione di unità di ED.

**Key words:** Electrodialysis; organic acids; modelling; transport numbers in solution and electro-membranes.

### 1. Introduction

In accordance with the PhD thesis project previously described (Spitz, 2004), this oral communication reports the main results of the following four activities directed to:

- A1) determine and model the density ( $\rho$ ), kinematic viscosity ( $\nu$ ), and electric conductivity ( $\chi$ ) of sodium chloride, acetate (A), and lactate (L) in aqueous solutions as functions of solute concentration ( $C_B$ );
- A2) assess and model the ED processes in a pilot-plant scale equipped with monopolar membranes as functions of current density (I), feed flow rate ( $Q_F$ ) and  $C_B$ ;
- A3) establish an experimental procedure to determine the effective design parameters for ED stacks;
- A4) assess the really important parameters in ED stack design and optimisation.

### 2. Electrodialysis Applications

Electrodialysis (ED) is a unit operation for the separation or concentration of ions in solutions based upon their selective electro-migration through semipermeable membranes under the influence of a potential gradient (Ho and Sirkar, 1992). ED was commercially introduced to desalinate water about 10 years before reverse osmosis (RO). The production of potable water from brackish water is currently the most important industrial ED application. Also the production of table salt from seawater has achieved a certain commercial importance, especially in Japan and Kuwait, even if it seems to be highly subsidized (Ho and Sirkar, 1992). Despite the first industrial ED application in the food sector dated back to 1960 and concerned the demineralisation of cheese whey for use in baby-foods, other applications concerning tartaric wine stabilization of wine, fruit juice de-acidification, and molasses desalting are gaining increasing importance with large-scale industrial plants.

**Table 1** *Main applications of the ED in the food sector.*

Application	Example
Fractionation	Brackish water desalination
	Nitrate removal from drinking water
	NaCl removal from amino acid solutions
	Cheese whey demineralisation
	Desalting of protein hydrolysates (i.e., soy sauce), sugar solutions, molasses, and polysaccharide dispersions
	De-acidification of fruit juices
	Tartaric wine stabilisation
Concentration	Flavour recover from pickle brines
	Edible table salt production from seawater
	Salts of organic acids from exhausted fermentation media
Splitting	Amino acids from protein hydrolysates
	Conversion of salts into the corresponding free acid and base

The fermentation industry is also interested, especially when the main product of the microbial metabolism is an electrolyte which can inhibit the cell growth and/or metabolite production in either its free or dissociated form, or is dissolved in media rich of impurities removable via numerous and expensive purification steps. In these cases, ED was for instance suggested as an environmentally-friendly alternative to the conventional citric acid recovery process, that gives rise to enormous amounts of calcium sulphate (circa 2 kg of CaSO<sub>4</sub>·2H<sub>2</sub>O per kg of monohydrated citric acid) that are to be disposed (Moresi and Sappino, 1998).

Table 1 summarises the main industrial ED applications in the food sector.

### 3. Mathematical Modelling

To design or optimise an ED process several parameters are to be taken into account, namely stack construction and spacer configuration, operation mode, membrane perm-selectivity, feed and product concentration, flow velocities, current density and voltage applied to the electrodes, recovery rates, etc. Most of the parameters of which are to be determined by independent experiments or existing correlations.

The Maxwell-Stefan (MS) equation represents the simplest mathematical tool for linking the flux of a generic species through the membrane with its interfacial concentrations at the membrane left- and right-sides, as well as with the external electrical voltage applied to the ED electrodes (Krishna and Wesselingh, 1997). To overcome the main problem in the application of the MS mass transfer model to ED processes, i.e. the large number of species diffusivities in the free solution and membrane phase (van der Stegen *et al.*, 1999), the Nerst-Planck (NP) relationship is largely used to describe diffusion and electro-migration contributions to ion transport in ion-exchange membranes. The basic mathematical model consists of water and solute mass balances coupled with the solute and water transfer equations and voltage equation for the ED loop concerned, as given below:

$$\frac{d(n_{BC})}{d\theta} = -\frac{d(n_{BD})}{d\theta} = J_B a_{me} N; \quad \frac{d(n_{WC})}{d\theta} = -\frac{d(n_{WD})}{d\theta} = J_W a_{me} N \quad (1)$$

$$J_B = \frac{t_s}{F} j - L_B \Delta c_B; \quad J_W = \frac{t_w}{F} j - L_W \Delta c_B \quad (2)$$

$$E - E_{el} + E_j + E_D \bar{N}_c = RI \quad (3)$$

$$R = R_c + R_{fc,D} + R_D + R_{fa,D} + R_a + R_{fa,C} + R_C + R_{fc,C} \bar{N}_c + 2R_{ERS} \quad (4)$$

where all symbols are given in section 7.

The contribution of solute polarisation, namely the electric resistance ( $R_f$ ) and junction potential difference ( $E_j$ ) across any boundary layer, was found to be negligible, this being also true for the contribution of solute and water diffusion:  $L_B \approx L_W \approx 0$  (Fidaleo and Moresi, 2004). On the contrary, the Donnan potential difference ( $E_D$ ) in any cell pair, which behaves as a direct current generator with inverted polarities with respect to those of the external DC generator, has to be accounted for  $\Delta c_B$  increases:

$$E_D = 2 t_s \frac{R_G T_K}{F} \ln\left(\frac{c_{BD}}{c_{BC}}\right) \quad (5)$$

The ohmic resistances of the bulk solutions in the concentrating (C), diluting (D), or electrode rinsing solution (ERS) compartment can be estimated via the 2<sup>nd</sup> Ohm's law:

$$R_C \approx \frac{h}{a_{me} c_{B,C} \Lambda(c_{B,C})}; \quad R_D \approx \frac{h}{a_{me} c_{B,D} \Lambda(c_{B,D})}; \quad R_{ERS} = \frac{h_{ERS}}{a_{ERS} c_{B,ERS} \Lambda(c_{B,ERS})} \quad (6)$$

The so called limiting current density ( $j_{lim}$ ) is the first value at which the electrolyte concentration at an anionic (a) or cationic (c) membrane surface falls to zero. Its controlling values generally refer to the diluting compartments and can be estimated as:

$$j_{lim,c} = \frac{F c_{BD} k_m}{(t_c^+ - t^+)} \quad j_{lim,a} = \frac{F c_{BD} k_m}{(t_a^- - t^-)} \quad (7)$$

The solute mass transfer coefficient can be calculated by resorting to the empirical correlation previously developed (data not published):

$$Sh = 0.53 \pm 0.01 \overline{Re}^{1/2} \cdot Sc^{1/3} \quad (8)$$

## 4. Experimental Procedure

In this PhD thesis a five-step experimental procedure was set up by performing in sequence the following independent tests, that is i) zero-current leaching, osmosis, and dialysis; ii) electro-osmosis; iii) desalination; and iv) current-voltage tests. A fifth step was added to perform a few further trials (validation tests) to check for all the parameters estimated. In this way, it is possible to determine sequentially the main physical properties ( $\rho$ ;  $\eta$ ;  $\pi$ ;  $\chi$ ;  $\Lambda$ ;  $\gamma^\pm$ ;  $D_B$ ) of the free salt solutions by resorting to either the open literature or direct measurements; the membrane constants for solute ( $L_B$ ) or water ( $L_W$ ) transport by diffusion via tests i); the effective solute ( $t_s$ ) and water ( $t_w$ ) transport numbers in membranes by tests iii) and ii), respectively; the limiting current intensity ( $I_{lim}$ ), ion transport numbers ( $t_a^-$ ,  $t_c^+$ ), and surface resistances ( $r_a$ ,  $r_c$ ) in anionic and cationic membranes, and solute mass transfer coefficient ( $k_m$ ) by step iv).

## 5. Materials and Methods

A laboratory-scale electrolysers (Aqualyzer P1, Corning EIVS, Le Vesinet, F), previously described (Moresi and Sappino, 1998), was used. Several batch recycle runs were carried out by varying electric current intensity ( $I=0.5-1.5$  A) under constant feed solute concentration ( $C_B \approx 0.5$  M), superficial velocity ( $v_s=3$  cm s<sup>-1</sup>), and temperature ( $T=293$  K). The instantaneous salt concentrations in diluting (D) and concentrating (C) streams were indirectly estimated by measuring the electric conductivity ( $\chi$ ) at 293 K with a WTW conductivity meter mod. Inolab Cond Level 1. Limiting current tests at 293 K were performed to plot voltage ( $\Phi$ )-current ( $I$ ) curves using stacks composed of 19 cation- (CMV) or 19 anion- (AMV) exchange membranes by varying  $C_B$ ,  $I$  and  $v_s$ .

## 5. Results and Discussion

### 5.1 Conductivity measurements

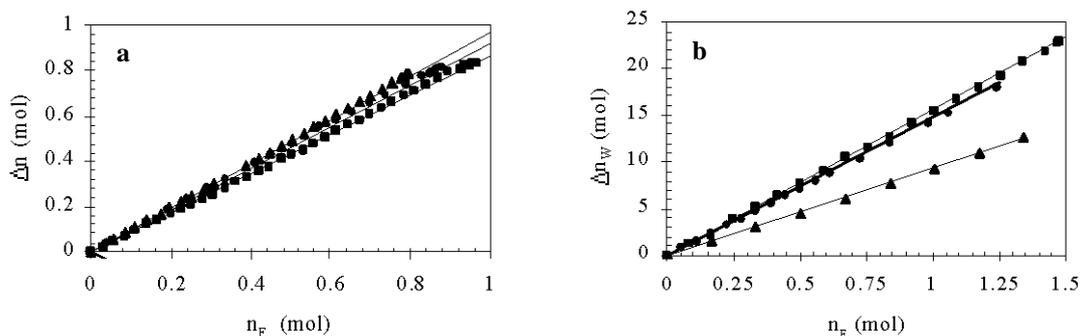
For strong binary electrolytes, the transport numbers for cation ( $t^+$ ) and anion ( $t^-$ ) in dilute solutions can be easily estimated from the equivalent conductance at infinite dilution ( $\Lambda_o = \lambda_o^+ + \lambda_o^-$ ), as extrapolated from the plot of the experimental equivalent conductance ( $\Lambda = \chi/C_B$ ) vs. the square root of solute molar concentration ( $\sqrt{C_B}$ ) at 293 K, the Na<sup>+</sup> equivalent conductance at infinite dilution ( $\lambda_o^+$ ) being equal to 44.95 S cm<sup>2</sup> mol<sup>-1</sup> (Prentice, 1991). In this way, the transport numbers for Na<sup>+</sup> were calculated as shown in Table 2, while those for the anion were their corresponding complement to one.

**Table 2** ED recovery of some sodium salts from model solutions: effect of the salt molecular mass ( $M_s$ ) on the main design parameters (i.e.,  $t^+$ ,  $t_s$ ,  $t_w$ ,  $a_{me}$ ,  $r_a$ ,  $r_c$ ,  $t_c^+$ ,  $t_a^-$ ,  $\epsilon$ ).

Salt	$M_s$ (Da)	$t^+$	$t_s$	$t_w$	$a_{me}$ cm <sup>2</sup>	$r$		$t_c^+$	$t_a^-$	$\epsilon$ Wh g <sup>-1</sup>
						$r_a$	$r_c$			
NaCl	58.4	0.40	0.969±0.002	9.31 ± 0.07	49 ± 2	5.9	6.3	0.99	0.97	0.19
Na-A	82.0	0.56	0.931±0.003	14.8 ± 0.1	52 ± 1	12.0	6.0	0.93	1.00	0.21
Na-P	96.1	0.59	0.982± 0.002	15.23 ± 0.04	50 ± 1	19.1	6.3	0.95	1.03	0.20
Na-L	112.1	0.60	0.876± 0.002	15.60 ± 0.05	41 ± 3	16.4	5.5	0.92	0.96	0.22

### 5.2 Desalination tests

By plotting the net increment (or decrement) in C or D solute ( $\Delta n$ ) or water ( $\Delta n_w$ ) masses vs. the Faraday equivalents of solute transferred ( $n_F = NI \theta / F$ ), as shown in Fig. 1, it was possible to estimate  $t_s$  and  $t_w$ , for each salt studied (Table 2).



**Figure 1** Net increment in C solute (a) and water (b) masses for NaCl (▲), NaA (●) and, NaL (■) vs. the Faraday

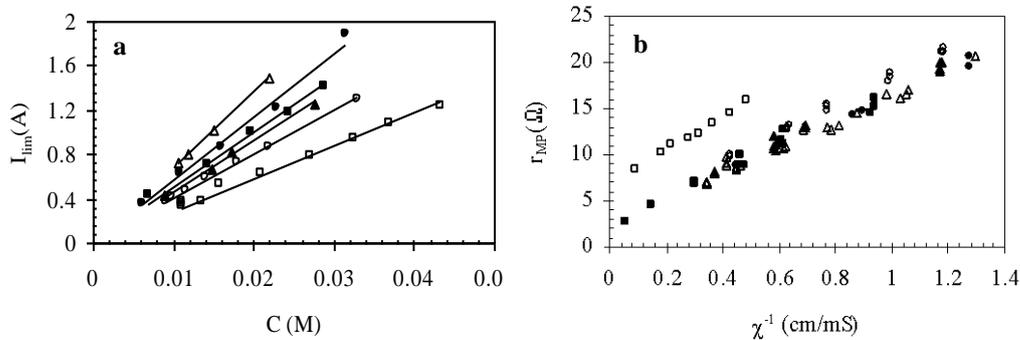
equivalents of solute transferred ( $n_F$ ) using 10 AMV and 9 CMV membranes at 20°C,  $v_s=3 \text{ cm s}^{-1}$  and  $I=1 \text{ A}$ .

### 5.3 Voltage-current tests

A series of E-I experiments using cationic or anionic membranes allowed the limiting current intensity ( $I_{lim,c}$  or  $I_{lim,a}$ ) and overall stack resistance to be determined. By plotting  $I_{lim,c}$  or  $I_{lim,a}$  vs. the solute concentration ( $C_B$ ), two linear graphs can be obtained (Fig. 2a). The ratios between their corresponding slopes  $I_{lim,c}/I_{lim,a}=(t_a^+ t_c^+)/(t_c^- t_a^-)$  were calculated as suggested by Krol *et al.* (1999) and used to estimate the anion transport numbers in the anionic membranes (Table 2). The current within the electro-membranes was almost exclusively carried by the counter ions.

For  $v_s$  ranging from 3.0 to 6.1  $\text{cm s}^{-1}$ , E-I curves were coincident and linear with constant intercepts (i.e.  $E_{el}\approx 2.2\text{-}2.6 \text{ V}$ ) and slopes for  $I<0.75 I_{lim}$ , this being an indirect confirmation of negligible contribution of solute polarisation.

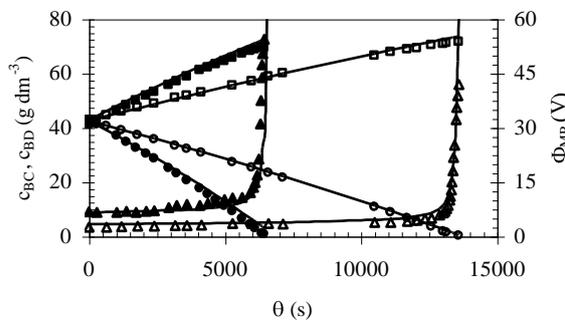
By neglecting the contribution of  $E_j$ ,  $E_D$  and  $R_f$ , it was possible to establish two linear relationships between the apparent resistance ( $R_{MP}$ ) of the anionic or cationic membrane pack and the reciprocal of the solution electrical conductivity ( $\chi$ ) (Fig. 2b) with intercept and slope respectively proportional to the resistance ( $r_m$ ) of the electro-membrane concerned and membrane gap per unit effective membrane surface area ( $h/a_{me}$ ). Fitting each set of data via the least squares method yielded the specific membrane resistances shown in Table 2. The estimated values of  $a_{me}$  were practically coincident with the exposed surface area of electrodes ( $44.6 \text{ cm}^2$ ) and significantly different from the geometrical membrane surface area ( $72 \text{ cm}^2$ ).



**Figure 2** Main results of limiting current tests for NaCl ( $\blacktriangle$ ,  $\triangle$ ), NaA ( $\bullet$ ,  $\circ$ ), NaL ( $\blacksquare$ ,  $\square$ ) as referred to cationic (closed symbols) or anionic (open symbols) membranes: **a)** limiting current intensity ( $I_{lim}$ ) vs. solute molar concentration ( $C$ ); **b)** electrical resistance of membrane pack ( $r_{MP}$ ) vs. the reciprocal of conductivity ( $\chi$ ).

### 5.4 Validation tests

By integrating Eq.s (1) and (2) together with the above independent parameters and Eq.s (3)-(4), it was possible to calculate the instantaneous values of  $c_B(\theta)$  in C and D tanks, as well as the voltage applied to the membrane pack ( $\Phi_{MP}=E-E_{el}-2 R_{ERS} I$ ). As an example, Fig. 4 shows quite a satisfactory agreement between the experimental (closed and open symbols) and calculated (continuous lines) values of  $c_{BC}(\theta)$ ,  $c_{BD}(\theta)$ , and  $\Phi_{MP}(\theta)$  against time ( $\theta$ ) in the case of sodium acetate removal.



**Figure 4** Batch recovery of NaA using 10 AMV and 9 CMV membranes at 293 K,  $v_s=3 \text{ cm/s}$  and  $I=0.75 \text{ A}$  (open symbols) or 1.5 A (closed symbols): solute concentrations in C ( $c_{BC}$ :  $\blacksquare$ ,  $\square$ ) and D ( $c_{BD}$ :  $\bullet$ ,  $\circ$ ) streams, and voltage applied to the ED stack ( $\Phi_{MP}$ :  $\blacktriangle$ ,  $\triangle$ ) vs. time ( $\theta$ ).

### 5.5 ED Recovery of some fermentation products

As the molecular mass ( $M_s$ ) of solute increased from 58 to 112 Da, the transport number for  $\text{Na}^+$  in the corresponding solution tended to increase from 0.4 to 0.6 for the progressively smaller equivalent conductance at infinite dilution of acetate, and lactate ions with respect to that of  $\text{Cl}^-$ . Nevertheless, the current within the electro-membranes was almost exclusively carried by the counter ions. The effective solute ( $t_s$ ) transport number,

that is the Faraday efficiency, ranged from 93 to 98%, even if reduced to 88% for sodium lactate. Despite the water transport number ( $t_w$ ) increased from 9.3 to 15.6, the maximum salt weight concentration in the concentrate ranged from 287 to 349 kg m<sup>-3</sup>. Whereas the surface resistance ( $r_c$ ) of the cationic membranes was about constant ( $6.0 \pm 0.4 \Omega \text{ cm}^2$ ),  $r_a$  tended to increase almost linearly with  $M_S$  ( $r^2=0.8$ ), even if this yielded up to just a 15% increase in the specific electric energy consumption per kg of salt recovered ( $\epsilon$ ) in the case of 90% salt recovery at 1 A and 293 K (Table 2). Finally, the membrane surface area ( $a_{me}$ ) effectively utilised was found to be about two thirds of the geometrical one and just 10% greater than the exposed surface area of electrodes. This confirmed the general rule that recommends to provide the electrodes with bases with the highest degree of open area in the direction perpendicular to the membrane faces so as to maximise utilisation of membrane area and minimise the electrical resistance of stack.

## 6. Conclusions and Future Perspectives

The present ED industry has experienced a steady growth rate of about 15% since 15 years. There are, however, a number of problems, that undoubtedly limit growth in membrane sales, like membrane fouling problems, design considerations, cleanability, investment and membrane replacement costs and competing technologies, such as nanofiltration (NF) and ion-exchange resins (IER). To overcome such uncertainties, long-term laboratory- and pilot-scale experiments are needed to assess membrane process performance and reliability. For instance, in the food biotechnology sector ED applications are still in their infancy, since practically none of the processes studied in laboratory- and pilot-scales have been converted into industrial realities, except for the recovery of Na-L from clarified fermentation broths. This means that ED processing potentialities have not been completely exploited so far probably because of the high specific electro-membrane costs or their short lifetime. The sequence of independent experimental trials outlined here is therefore recommended to estimate the really effective parameters for designing or optimising ED stacks. More specifically, the assessment of the effective membrane resistance, as well as surface area, appears to be of paramount importance if the data collected in a laboratory- or pilot-scale plant are to be safely transferred into an industrial-scale one. In this way, such an optimal strategy is expected to foster novel ED applications in the food sector, as well as in the chemical, pharmaceutical, and municipal effluent treatment areas.

## 7. Nomenclature

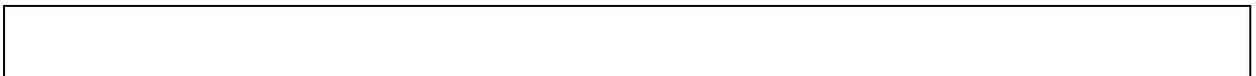
$a_{me}$ , effective membrane surface area per each cell pair (m<sup>2</sup>);  $c_B$ ,  $C_B$ , solute weight and molar concentrations in C, D, or ERS compartment (mol m<sup>-3</sup>);  $D_B$ , diffusivity (m<sup>2</sup> s<sup>-1</sup>);  $E$ , overall potential drop across an ED stack (V);  $E_D$  and  $E_j$ , Donnan and junction potential differences across membranes (V);  $E_{el}$ , thermodynamic electrode potential (V);  $F$ , Faraday's constant (96,486 C mol<sup>-1</sup>);  $h$ , membrane gap (m);  $h_{ERS}$ , electrode channel width (m);  $I$ , electric current intensity (A);  $I_{lim}$ , limiting current intensity (A);  $J_B$  and  $J_W$ , solute and water permeation fluxes (mol m<sup>-2</sup> s<sup>-1</sup>);  $j$ , electric current density (A m<sup>-2</sup>);  $j_{lim}$ , limiting electric current density (A m<sup>-2</sup>);  $k_m$ , solute mass transfer coefficient (m s<sup>-1</sup>);  $L_B$  and  $L_W$ , membrane constant for solute or water transport by diffusion (m s<sup>-1</sup>);  $M_S$ , molecular mass (Da);  $N_c$ , overall number of cell pairs;  $n_B$  and  $n_W$ , solute and water masses (mol);  $R$ , electric resistance ( $\Omega$ );  $R_{ERS}$ , electric resistance of electrode rinsing solution ( $\Omega$ );  $R_f$ , boundary layer electric resistance ( $\Omega$ );  $R_G$ , gas-law constant ( $=8.31 \text{ J mol}^{-1} \text{ K}^{-1}$ );  $R_{MP}$ , apparent resistance of the generic membrane pack ( $\Omega$ );  $Re$ , Reynolds number ( $=\rho v_S h/\eta$ );  $r_m$ , membrane surface resistance ( $\Omega \text{ cm}^2$ );  $Sc$ , Schmidt number [ $=\eta/(\rho D_B)$ ];  $Sh$ , Sherwood number ( $=k_m h/D_B$ );  $T_K$ , absolute temperature (K);  $t^-$  and  $t^+$ , transport numbers for anion and cation in solution;  $t_m^-$  and  $t_m^+$ , anion and cation transport numbers in a generic membrane;  $t_s$ , effective transport number;  $t_w$ , water transport number;  $\chi$ , electric conductivity (S m<sup>-1</sup>);  $\gamma^+$ , molal activity coefficient (dimensionless);  $\Phi_{MP}$ , voltage applied to the membrane pack (V);  $\Lambda$ , equivalent conductance of the corresponding bulk solutions ( $=\chi/c_B$ , m<sup>2</sup> mol<sup>-1</sup>);  $\eta$ , viscosity (Pa s);  $\theta$ , time (s);  $\rho$ , density (kg m<sup>-3</sup>);  $\pi$ , osmotic pressure (Pa).

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# POSTER COMMUNICATIONS



## Recovery of Selected Microbial Metabolites from Model Solutions by Reverse Osmosis

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The first two activities of the PhD thesis project are described. Firstly, the density, viscosity, and osmotic pressure of aqueous solutions of sodium citrate, gluconate, and lactate were determined and correlated to the solute molar concentration ( $C_B$ ). Secondly, recovery of such solutes from aqueous solutions was studied batchwise in a pilot plant equipped with a spiral-wound thin-composite reverse osmosis membrane, thus assessing that the osmotic pressure is the major resistance to overcome.

### Recupero di alcuni metabolici microbici da soluzioni modello per osmosi inversa

Le prime 2 attività del progetto di tesi di dottorato sono descritte. Sono state determinate la densità, la viscosità e la pressione osmotica ( $\pi$ ) di soluzioni acquose di citrato, gluconato e lattato di sodio, correlandole alla concentrazione molare di soluto ( $C_B$ ). Si è studiato il recupero in batch di questi soluti in un impianto pilota, impiegando un modulo di osmosi inversa a spirale e si è ricavato che la permeazione del solvente è limitata da  $\pi$ .

**Key words:** Reverse osmosis, sodium citrate, gluconate, and lactate, membrane resistance, process modelling.

### 1. Introduction

In accordance with the PhD thesis project previously described (Fddff, 2005), this poster reports the main results of the first two activities concerning:

- (A1) the determination and modelling of the density ( $\rho$ ), kinematic viscosity ( $\nu$ ), and osmotic pressure ( $\pi$ ) of di-sodium hydrogen citrate, sodium gluconate, and sodium lactate in aqueous solutions as functions of feed weight ( $c_B$ ) or molar ( $C_B$ ) solute concentration;
- (A2) the assessment and modelling of the RO processes in a pilot-plant scale equipped with a spiral-wound membrane module as functions of transmembrane pressure difference applied ( $\Delta P$ ), and  $C_B$ .

### 2. Materials and Methods

A typical temperature- and pressure-controlled pilot-scale RO plant (VERIND, Rodano, I), previously described (Lo Presti and Moresi, 2000), was used. It was equipped with a thin-film composite spiral-wound membrane module, type SW30-2514 (FilmTec Corp., Div. of Dow Chemicals, Minneapolis, MN, USA) with 0.762-mm and 250-mm channel width and length, and 0.42-m<sup>2</sup> effective surface area. Several batch recycle runs were carried out under constant recirculation flow rate (1 m<sup>3</sup> h<sup>-1</sup>) and temperature ( $T=313$  K) by varying  $\Delta P$  from 40 to 60 Pa. The feed solutions were prepared by dissolving technical grade di-sodium hydrogen citrate, sodium gluconate in or diluting 90% w/w lactic acid solution with deionised water to vary  $c_B$  in the range 50-75 kg m<sup>-3</sup> to simulate the corresponding clarified fermentation medium. The pH of all acidic solutions was set to 5 by adding NaOH. The osmotic pressure ( $\pi$ ) at 310K, kinematic viscosity ( $\nu$ ) at 313K, and density ( $\rho$ ) at 293K of several aqueous solutions containing 0-1.6 kmol m<sup>-3</sup> of the above salts were determined by using a Wescor Vapor Pressure osmometer (mod. 5500), capillary #25-50 Cannon-Fenske viscometers (ASTM, 1964), and calibrated volumetric flasks, respectively. The membrane module was cleaned and stored according to Lo Presti and Moresi (2000).

### 3. Results and Discussion

#### 3.1 Determination of the main physical properties

The physical properties of the solutions tested were correlated to  $c_B$  or  $C_B$  as follows:

$$\rho = \rho_w + c_B \left( \frac{\rho_w}{\rho_B} \right) \quad (1)$$

$$\mu_r = \mu / \mu_w = \exp \left( a C_B + b C_B^2 \right) \quad \pi = \alpha C_B \quad (2)$$

where  $\rho_w$  and  $\rho_B$  are the densities of pure water and pure solute;  $\mu$  and  $\mu_w$  are the solution and water dynamic viscosities;  $\mu_r$  is the relative viscosity;  $C_B$  the solute molar concentration;  $a$  and  $b$  are empirical coefficients;  $\pi$  is the solution osmotic pressure, and  $\alpha$  is known as the first "virial coefficient". All unknown parameters were determined using the least squares method, as reported in Table 1.

**Table 1** Empirical correlations of the density, relative viscosity, and osmotic pressure of several aqueous solutions of the Na salts of citric, gluconic, and lactic acids for  $C_B$  ranging from 0 to 1.8  $\text{kmol m}^{-3}$ .

Solute	Density	$r^2$	Relative viscosity		$r^2$	Osmotic Pressure	$r^2$
	$\rho_B$ ( $\text{kg m}^{-3}$ )		a ( $\text{m}^3 \text{kmol}^{-1}$ )	b ( $\text{m}^6 \text{kmol}^{-2}$ )		$\alpha$ ( $\text{Pa m}^3 \text{kmol}^{-1}$ )	
Citrate	2106	0.999	$0.64 \pm 0.09$	$0.16 \pm 0.01$	0.999	$56.7 \pm 1.2$	0.990
Gluconate	1919	0.997	$0.56 \pm 0.02$	$0.16 \pm 0.02$	0.998	$47.9 \pm 0.5$	0.996
Lactate	1321	0.977	$0.68 \pm 0.07$	$0.23 \pm 0.09$	0.972	$60.7 \pm 1.1$	0.993
All solutes tested	-		$0.52 \pm 0.04$	$0.15 \pm 0.03$	0.983	$4.3 \pm 1.0$	0.967

### 3.2 Modelling of the RO process

According to conventional filtration theory (Cheryan, 1998), the actual mass flux of permeation ( $J_p$ ) through the membrane is given by:

$$J_p = \frac{\Delta P - \Delta \pi}{\left( \frac{1}{\rho_B} + R_m + R_f + R_g \right) \mu} \quad (3)$$

with

$$\Delta P = P_m - P_p = 1/2 (P_i + P_o) - P_p \quad (4)$$

where  $\Delta P$  is defined as the difference between the average pressures in the retentate ( $P_m$ ) and permeate ( $P_p$ ) sides, the former being the half sum of the inlet ( $P_i$ ) and outlet ( $P_o$ ) pressures in the retentate side;  $R_m$  is the intrinsic membrane resistance, and  $R_f$  or  $R_g$  is the membrane resistance due to fouling or polarisation layer. In particular, Eq. (4) was modified by replacing the solvent kinematic viscosity with the retentate one to account for its increase with  $C_B$  (Lo Presti and Moresi, 2000). Moreover, in accordance with Eq. (3) and Table 1, the instantaneous osmotic pressure difference between the retentate and permeate ( $\Delta \pi$ ) was estimated as proportional to the difference between the retentate and permeate solute concentrations at the membrane surfaces.

The intrinsic membrane resistance ( $R_m$ ) was determined by performing several deionised water permeation tests at different  $\Delta P$  (10-60 Pa) and  $T$  (303-313K) values, thus obtaining the following empirical regression:

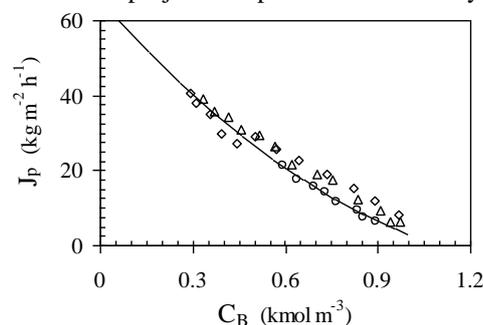
$$R_m = (8.90 \pm 0.13) \cdot 10^{12} T + (3.31 \pm 0.04) \cdot 10^{14} \quad r^2 = 0.99 \quad (5)$$

Whatever the solute under study, the evolution of the RO concentration process was characterised by a similar decline in  $J_p$  as  $C_B$  increased (Fig. 1). This was the direct result of the strict similarity of the  $\pi$ - $C_B$  relationships for all the solutes examined (Table 2).

In all cases, the apparent solute rejection (Cheryan, 1998) was found to be greater than 99%, thus allowing the solute concentration in the permeate to be regarded as virtually zero ( $C_{Bp}=0$ ). Moreover, feed flow rate exhibited little or no effect on  $J_p$ , thus enabling the contribution of polarisation layer to be neglected ( $R_g=0$ ). On the contrary, the contribution of fouling deposited onto the membrane ( $R_f$ ) tended to increase with time. As it got to about one third of the intrinsic membrane resistance, a conventional chemically-based cleaning procedure was capable of restoring the intrinsic membrane resistance of the new membrane.

Fig. 1 shows the experimental permeation fluxes vs.  $C_B$  measured during subsequent batch RO concentration trials of all salts tested as compared to those calculated using the model reported here. Such a modelling exercise might be helpful to optimise the recovery of microbial metabolites from clarified fermentation broths. Thus, the experimental results agree with the expected ones and the original PhD thesis project can proceed without any substantial amendment.

**Figure 1** Effect of  $C_B$  on  $J_p$  during the RO concentration of sodium-citrate ( $\Delta$ ), -gluconate ( $\diamond$ ), and -lactate ( $\circ$ ) under the following operating conditions: feed flow rate (1000  $\text{dm}^3/\text{h}$ ),  $T=313\text{K}$ , and  $P_i=6.1 \text{MPa}$ . The continuous line was calculated as reported in the text.



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# **PhD DISSERTATION PROJECTS**

18<sup>th</sup> Workshop on the *Developments in the Italian PhD Research on Food Science Technology and Biotechnology*, Universities of Padova and Udine, Conegliano 25-27 September, 2013



## Experimental Strategy for the Optimal Design of Ultrafiltration Units Used to Recover Some Food Biopolymers

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This PhD thesis research project is aimed at setting up a batch or total recycle experimental procedure at both bench-top and pilot scales to identify the most appropriate mathematical model to simulate accurately the recovery of selected food biopolymers via tubular or hollow-fibre ultrafiltration modules and provide a basis for their optimal design in an industrial scale.

### Strategia sperimentale per la progettazione ottimale di unità di ultrafiltrazione per il recupero di biopolimeri di interesse alimentare

Questo progetto di tesi di dottorato mira a mettere a punto un procedimento sperimentale, in batch o a riciclo totale, prima in impianto da banco e poi in impianto pilota, atto ad individuare il modello matematico in grado di simulare il processo di recupero di selezionati biopolimeri di interesse alimentare mediante moduli a membrana di ultrafiltrazione tubolari o a fibre cave, consentendone il dimensionamento ottimale in scala industriale.

#### 1. State-of-the-Art

Since the early 60s membrane separation processes have presented quite a limited diffusion and have just more recently begun to be recognised as efficient, economical and reliable separation processes. Depending on membrane pore size, feed cross flow velocity, transmembrane pressure difference applied ( $\Delta P$ ) and permeation flux, membrane filtration processes can be classified as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO), the configuration of their modules being *tubular* (T), *hollow-fibre* (HF), *spiral-wound* (SW) or *plate-and-frame* (PF) (Cheryan, 1998; Daufin *et al.*, 1998; Ho and Sirkar, 1992).

Table 1 lists the main applications of UF membrane processing in the food and beverage sector together with specific membrane type and configuration, range of solvent permeation flux ( $J_{wv}$ ) and solute true rejection ( $r_t$ ). A great number of problems limit UF membrane sale growth like membrane resistance to solvent, fouling problems, design considerations for the incomplete comprehension of mass transfer mechanisms in membrane systems, cleanability, investment and membrane replacement costs, and competing technologies. Formation of a gel-polarised layer onto membrane surface, as well blocking of membrane surface pores or fouling of support materials, results in a more or less pronounced permeation flux decay. Such a decay is still difficult to quantify at the design stage by resorting to any of the numerous transport models available in the literature, that is *non porous or homogeneous membrane models* (i.e. solution-diffusion, extended solution-diffusion, and solution-diffusion-imperfection models), *pore-based models* (preferential sorption-capillary flow, finely porous, and surface force-pore flow models), and *irreversible thermodynamics phenomenological models* (such as Kedem-Katchalsky and Spiegler-Kedem models).

**Table 1** Main applications of UF membrane processes in the food sector.

Application	Example	Type	Membrane module characteristics			
			Material	Cut-off (kDa)	$J_{wv}$ ( $\text{dm}^3 \text{m}^{-2} \text{h}^{-1}$ )	$r_t$ (%)
Fractionation	Milk or whey (protein from lactose and minerals)	PF, SW, T	C, PS, PES	10-100	5-100	70-97
	Oil fractions from oil-in-water emulsions	SW	TFC	8	10-13	70-90
Clarification	Alcoholic juices and beverages	HF, SW, T	PAN, PS, PES	10-100	5-100	70-97
	Removal of colloids, pigments, low MW compounds	HF, T	PAN, PES	10-50	5-50	70-83
Concentration	Albumin and proteins	PF, SW, T	C, PS, PES	10-100	5-30	70-83
	Polysaccharides (karragineen, xanthan)	HF	PS	500	5-10	-

C: Ceramic; PS: Polysulfone; PES: Polyethersulfone; PAN: Polyacrylonitrile; TFC: Thin Film Composite.

For instance, it is difficult to express the real relationship between  $J_{wv}$  and  $\Delta P$  and, in particular, the fact that in

the UF range  $J_{wv}$  is controlled by pressure for  $\Delta P < 6$  Pa and by mass transfer for  $\Delta P > 6-10$  Pa, this effect being counteracted by increasing feed flow rate ( $Q_F$ ) or process temperature ( $T$ ), as well as decreasing feed solute concentration ( $C_B$ ). Moreover, while in the RO range  $J_{wv} - \log C_B$  plot linearly decreases with  $C_B$  increasing and vanishes for  $C_B$  as such that the feed osmotic pressure equals feed input pressure, in the UF range such a plot does not tend to zero, but it may reach a minimum value (definitively different from zero), which remains practically constant or increases up to a maximum value before finally decreasing as solute concentration increases (Pritchard *et al.*, 1995).

Almost all the biopolymers recovered via UF processes exhibit a non-Newtonian behaviour of the pseudoplastic type. This is generally described via the Ostwäld-de Waele model, that allows a quite accurate reconstruction of the liquid apparent viscosity ( $\eta_a$ ) in the intermediate shear rate region only, but at very low shear rates overestimates  $\eta_a$ , thus leading to mass transfer coefficients extremely underestimated. Thus, this PhD thesis project will be directed to select which mathematical model with the minimum number of statistically independent parameters allows the best reconstruction of UF membrane process performances by resorting to well known experimental design techniques to minimise the experimental trials needed.

## 2. PhD Thesis Objectives and Milestones

Within the overall objective mentioned above this PhD thesis project can be subdivided into the following activities according to the Gantt diagram given in Table 2:

- A1) **Determination of the physical properties of a few selected biopolymers** (sodium alginates and pectinate, and whey proteins) in aqueous solutions to model their density, osmotic pressure (A1.1) and rheological behaviour (A1.3) as functions of  $C_B$ .
- A2) **Assessment and modelling of the UF processes in a bench-top plant scale** to identify the mathematical model capable of reconstructing their performances as functions of the main operating variables ( $\Delta P$ ;  $T$ ;  $Q_F$ ,  $C_B$ ) and membrane constitution, porosity and configuration, that is a C-T (A2.1) and a PES HF (A2.2) membrane module. An experimental strategy to limit polarisation layer growth will also be established to optimise both UF module performance.
- A3) **Scaling-up of the UF processes** in the pilot plant scale to validate the prediction capability of mathematical models identified during activity A2 when using commercial C-T (A3.1) and PES-HF (A3.2) UF membrane modules.
- A4) **Optimisation of the UF processes examined** so as to assess their optimal operating conditions (A4.1) and set up a generalised experimental procedure (A4.2) to determine the main engineering parameters necessary to design the UF unit in an industrial scale.
- A5) **Writing and Editing** of the PhD thesis, scientific papers and oral and/or poster communications.

**Table 2** Gantt diagram for this PhD thesis project.

Activity	Months	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
A1) <b>Biopolymer Physical Properties</b>		■	■	■	■																				
1) Density, Osmotic Pressure		■	■																						
2) Rheological Behaviour		■	■																						
A2) <b>UF Process Modelling</b>		■	■	■	■	■	■	■	■	■	■	■	■	■	■										
1) Ceramic Tubular Module		■	■	■	■	■	■																		
2) Hollow-fibre Module								■	■	■	■	■	■	■	■										
A3) <b>Scaling-up of UF processes</b>																■	■	■	■	■	■	■	■	■	■
1) Ceramic Tubular Module																■	■	■	■	■	■	■	■	■	■
2) Hollow-fibre Module																					■	■	■	■	■
A4) <b>UF Process Optimisation</b>																					■	■	■	■	■
1) Optimal UF Processes																					■	■	■	■	■
2) Generalised Exp.l Procedure																							■	■	■
A5) <b>Thesis and Paper Preparation</b>		■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■

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