Nicolaus Copernicus University in Toruń
Wrocław University of Technology, Wrocław
University of Technology and Life Sciences, Bydgoszcz

PROCEEDINGS
OF THE XXVth INTERNATIONAL SYMPOSIUM ON PHYSICO-CHEMICAL METHODS OF SEPARATION

"ARS SEPARATORIA 2010"

JULY 4-7, 2010, TORUŃ, POLAND

Wydawnictwo Naukowe Uniwersytetu Mikołaja Kopernika
Toruń 2010

COMPOSITE MEMBRANES FOR BSA SEPARATION

Adriana CUCIUREANU[1)], Gheorghe BATRINESCU[2)], Stefan Ioan VOICU[1)] and Gheorghe NECHIFOR[1)]

[1)] Politehnica University of Bucharest, Faculty of Applied Chemistry and Materials Sciences, Str. Gheorghe Polizu 1-7, sector 1, Bucharest, Romania 011061

[2)] National Institute for Research and Development for Industrial Ecology – ECOIND, Sos. Panduri 90-92, sector 5, Bucharest, Romania 050663

Abstract

The results on BSA (bovine serum) separation by membrane techniques are reported. Polysulfone-polyaniline (PSf-PANI) porous composite membranes are obtained by phase inversion with chemical reaction. PANI is obtained in-situ by oxidative aniline polymerization. The obtained composite membranes are characterized by water permeation at different pH and pressure. Polysulfone-polyaniline porous composite membranes UF processes performance to BSA separation are reported.

1. INTRODUCTION

The membrane techniques that use composite membranes are applied in various areas, replacing in many instances the technologies that use simple membranes. Polysulfone-polyaniline porous composite membranes (PSf-PANI) seem to be an interesting perspective because of PSf base properties and special ability to be applied in bioanalysis and bioseparation.

In this paper the results on the separation of albumin from bovine serum (BSA) using polysulfone-polyaniline (PSf-PANI) porous composite membranes are reported. The PSf-PANI membranes were obtained by phase inversion, immersion-precipitation new technique, with chemical reaction.

2. RESULTS AND DISCUSSIONS

Polysulfone-polyaniline porous composite membranes were prepared by phase inversion, immersion-precipitation technique with the procedure consisting of the following steps: polysulfone solubilization in mixed solvents, filtration of polymer solution for gels removal, air removal into a desiccator, polymer film formation from polymer solution, coagulation of polymer film and chemical reaction [1, 2].

Polysulfone-polyaniline porous composite membranes are obtained by polysulfone coagulation followed by oxidative polymerization of aniline.

The base polymeric materials are PSf and PANI obtained in-situ. The solvent N-methylpyrrolidone (NMP) and aniline (in appropriate proportion), viscosity correction agents poly(vinylpyrrolidone) (PVP) and poly(ethylene glycol) (PEG) were used.

The membranes were prepared in two versions: V1 – using water as nonsolvent, V2 – using water with added aniline as nonsolvent. In each version three composite membranes were obtained, using three different solutions 10, 12, and 14 wt% PSf. The proportion between the base polymer PSf and aniline was the same in all three solutions [3].

The water permeation at different pH (1, 3, 5, 7, 9, 11) and pressures (2, 4, 5, 6 bar) through the obtained membranes was determined. The installation was the KMS Laboratory Cell CF-1 (Koch-Membrane-Germany) assuring a tangential flow mode in separated process. The water flux was calculated from Eq. (1):

$$J = \frac{V}{S \cdot t} \quad [l/(m^2h)] \qquad (1)$$

where: J – flux, V – permeate volume, S – membrane effective area, t – time necessary for the permeate volume to be collected. The water flux at different pH and pressure for the ultrafiltration membranes are presented in Tables 1 and 2.

Table 1. Water flux at different pH and pressure, obtained for the V1 composite membranes.

Type of membrane	Pressure (bar)	Water flux ($l/(m^2h)$)					
		pH=1	pH=3	pH=5	pH=7	pH=9	pH=11
10% PSf+PANI	2	25	20.8	23.9	48	38	36
	4	47.3	47.3	49.3	91	78	85.8
	5	57.7	65.2	73.2	108.4	115.6	115.7
	6	79.2	80.5	87.9	142	139	124.3
12% PSf+PANI	2	74.2	87.9	111.2	139.2	150.9	111
	4	169.1	181.1	274.5	299	318.4	270.5
	5	226.1	248.6	398.1	450.6	400	362.8
	6	267.5	290.9	467.9	561.6	502.4	447.4
14% PSf+PANI	2	15	11.8	12.3	16.1	13.3	13.2
	4	30.3	27.9	30.6	34.4	31.8	29.3
	5	39.6	35.7	39.9	45.3	42.4	40.1
	6	45.4	47.9	56.3	56.5	54.4	53.4

The graphic representation of the hydrodynamic water permeability, L_p (calculated as $J/\Delta p$), for the V1 and V2 membranes are shown in Figs. 1 and 2. The following observations can be made:

- the maximum values of L_p are observed for pH = 7.4 for all the investigated membranes and pressures; at this pH the conformation of polyaniline macromolecules is responsible for the loose structure of membranes;

- the membrane 12%PSf+PANI (both versions V1 and V2) shows the highest water permeability;
- L_p slightly increases with the applied pressure;
- the aniline addition to coagulating bath improves hydrodynamic properties of the composite membranes; this phenomenon may be explained by a looser structure of the PANI-PSf composite membrane due to the modification of the conformation and orientation of macromolecules.

Table 2. Water flux at different pH and pressure, obtained for the V2 composite membranes.

Type of membrane	Pressure (bar)	Water flux ($l/(m^2h)$)					
		pH=1	pH=3	pH=5	pH=7	pH=9	pH=11
10% PSf+PANI	2	31.9	34.2	59.5	72.7	63.5	54.4
	4	81.4	75.4	138.4	160.4	135.3	113.5
	5	118.3	109.4	207.9	199.3	180.7	152.4
	6	141.9	132.7	254.8	240.1	217.9	188.1
12% PSf+PANI	2	85.1	83.2	127.4	186.2	121.8	122.9
	4	188.1	195.1	317.3	370.2	273.3	259.4
	5	255.7	274.7	440.4	498.7	359.7	340.9
	6	312	324.3	575.6	594.4	440.4	416
14% PSf+PANI	2	28.7	31.4	37.2	49.4	31.8	32.8
	4	73.2	76.9	91.1	108.8	77	82.6
	5	102.9	104	128.5	151.7	110.7	118.3
	6	130.4	139.6	174.9	194.5	150.5	151.2

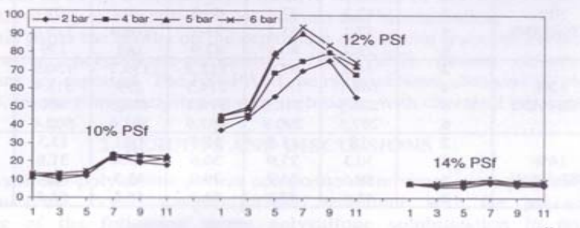

Fig. 1. Hydrodynamic water permeability, L_p, at different pH and pressures for the V1 composite membranes.

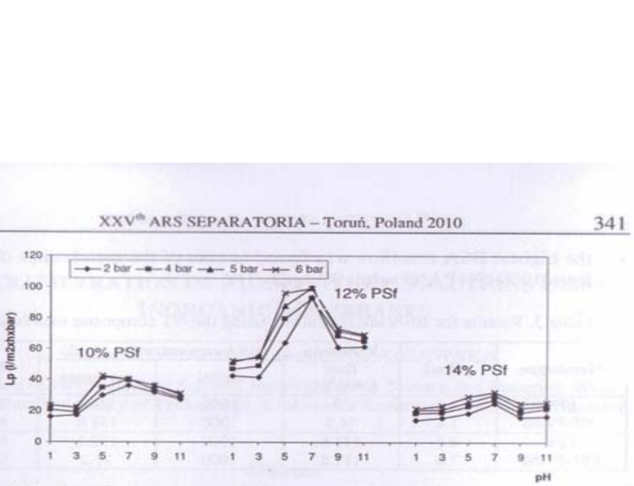

Fig. 2. Hydrodynamic water permeability, L_p, at different pH and pressures for the V2 composite membranes.

Composite membrane performance in terms of protein separation was established by determining the percent rejection coefficient of BSA, *R*. It was calculated from Eq. (2):

$$R = (1 - C_p / C_{in}) \cdot 100 \quad [\%] \qquad (2)$$

where C_{in}, C_p are solute concentrations in the feed, permeate, respectively.

Only the composite membranes obtained from solutions 10%PSf+PANI and 12%PSf+PANI were tested. The applied pressure was 4 bar. The experiments at two different pH of BSA solution were performed. In the first experiment 1 g/l BSA solution dissolved in citric acid-sodium citrate buffer at pH = 4.9 was used. In the second experiment 1 g/l BSA solution dissolved in tris-HCl buffer at pH = 7.4 was used [4]. For each experiment the initial feed volume was 500 ml and during the experiment 250 ml of permeate and 250 ml of concentrate were collected. The protein concentrations of permeate, concentrate and feed solution were determined by Lowry method [5,6].

The permeate flux, BSA concentrations in permeate and the retentions are presented in Table 3 (V1 membranes) and in Table 4 (V2 membranes). The results show that:

- for both types of membranes (version V1 and V2) the retention of BSA and permeate flux are the highest for the solution of pH = 7.4;
- independently of pH, the BSA retention by the V2 membranes is higher than that by the V1 membranes;
- the permeate flux determined in BSA separation is lower than the water flux at the corresponding value of pH;
- the values of the BSA retention determined for the membranes obtained from 12%PSf+PANI solution are higher than those for the membranes obtained from 10%PSf+PANI solution;

- the highest BSA retention was found in case of the membranes obtained from 12%PSf+PANI solution at pH=7.4.

Table 3. Results for BSA ultrafiltration, using the V1 composite membranes.

Membrane	pH sol	Permeate flux [l/9m²h)]	BSA concentration (mg/l)		R [%]
			initial	permeate	
10% PSf+PANI	4.9	39	1000	244.4	75.56
	7.4	74.5	1000	188.8	81,12
12% PSf+PANI	4.9	133.6	1000	152.2	84,78
	7.4	187.8	1000	77.2	92,28

Table 4. Results for BSA ultrafiltration using the V2 composite membranes.

Membrane	pH sol	Permeate flux [l/(m²h)]	BSA concentration (mg/l)		R [%]
			initial	permeate	
10% PSf+PANI	4.9	121.1	1000	184.3	81.57
	7.4	150.5	1000	79.3	92.07
12% PSf+PANI	4.9	217.4	1000	82.8	91.72
	7.4	284.08	1000	3.9	99.61

3. CONCLUSIONS

The increased polyaniline/polysulfone ratio in the composite membrane leads to:
- improvement of the hydrodynamic performance of the composite membranes (the permeate flux for the V2 composite membrane is higher than that for the V1 membrane);
- increase of the BSA rejection by the composite membrane with a higher PANI content.

Regarding the BSA separation the best composite membrane obtained in this study is the 12% PSf+PANI solution type, corresponding to pH of 7.4.

REFERENCES

[1] G.Nechifor, G. Popescu, N. Luca, A.M. Nechifor, *Rev. Roum.*,1994, *39*, 885.
[2] A.M. Urmeni, M. Avramescu, G. Nechifor, M.H.W.Mulder, *Euromembrane*, 1999, 28.
[3] Gabriela Paun, Gheorghe Batrinescu, Dana Garganciuc, Georgeta Popescu, *Procese membranare la separarea si concentrarea unor compusi bioactivi din medii lichide naturale*, Ed. Cartea Universitara, Bucuresti, 2006, p.65-80.
[4] T. Bialopiotrowicz, P. Blanpain, F. Rene, M. Lalande, *Ars Separatoria Acta*, 2002, *1*, 111.
[5] I.F. Dumitru, D. Iordachescu, *Biochimie practica*, Bucuresti, 1988, p.113-114.
[6] V.L. Singleton, R. Orthofer, R.M. Lamuela-Raventos, *Methods Enzymol.*, 1999, *299* , 152.

ULTRAFILTRATION OF MODEL WHEY SOLUTIONS USING INORGANIC MEMBRANES

Anna OZYGAŁA and Daniela SZANIAWSKA

Division of Environmental Science, Faculty of Food Science and Fisheries, West Pomeranian University of Technology, Krolewicza Kazimierza 4B, 71-550 Szczecin

Abstract

The results of ultrafiltration (UF) studies using inorganic α-Al_2O_3/ZrO_2/TiO_2 1.0 kDa membrane and model whey solutions are presented. Experiments to test lactose and turbidity retention and membrane permeability were conducted at three levels of transmembrane pressure (0.1, 0.2 and 0.3 MPa), three levels of pH (6.5, 4.5 and 3.0) and two levels of initial lactose concentration (5 and 10%). The best lactose rejection was obtained for TMP 0.3 MPa and pH 4.5 for initial lactose concentration 5%.

1. INTRODUCTION

Recently, in order to reduce the costs of raw materials and concurrently convert wastes to useful substances, the possibility of producing of lactic acid from whey are being investigated. Whey, by-product from the cheese manufacturing, is composed of mainly water (93%), lactose (ca. 5%), soluble proteins (0.9-1%), fat (0.1-0.3%) and varying concentration of mineral salts and vitamins.

The fermentation processes focused on the bioconversion of the whole whey is one of many ways of waste lactose utilization. In whole whey fermentation soluble proteins bring a part of the nitrogen source needed for microorganisms. The bioconversion includes two key stages: fermentation and product recovery. A membrane permeation system that removes lactic acid from fermentor can be a solution to overcome main disadvantage of conventional fermentation system: low lactic acid concentration caused by product inhibition. Moreover, membrane system is the solution providing reuse of microorganisms and no converted lactose. Hydride technology, like combinations of fermentors and membranes, works the best when developed as one concept [1,2].

The main goal of the study is experimental analysis of the possibility of applying of inorganic membranes in continuous system for lactic acid production from whole whey. The first step of the research obeys an ultrafiltration of a model whey solution with the aim to analyze effect of the classic operating filtration parameters: transmembrane pressure (TMP), pH