MEMBRANES BASED ON CELLULOSE ACETATE RECOVERED FROM CINEMATOGRAPHIC FILMS FOR PROTEIN RETENTION

Simona COTORCEA (ȚICU)[1], Ioana Alina DIMULESCU[2], Dumitru PAȘCU[3], Cristina BĂRDACĂ[4], Gheorghe NECHIFOR[5], Andreia PÎRȚAC [6]

Cellulose acetate-based membranes have returned to the attention of researchers with environmental protection issues raised by synthetic materials. Unlike synthetic materials, cellulose derivatives are biodegradable, and their use has returned to the forefront. This paper presents the obtaining of membranes for protein separation (BSA) using as raw material cellulose acetate from film films used morally or physically. In addition to the advantage of raw material accessibility, this type of membrane will incorporate silver nanoparticles from motion pictures. The raw material, after washing, cutting, and crushing, is dissolved in a polar aprotic solvent, N-methyl pyrrolidone (NMP) in a concentration of 10% (w / w). By phase inversion membranes are obtained which are compared with some based on standard cellulose acetate. Membranes obtained from cinematographic films have lower fluxes but better protein retention, and the presence of silver nanoparticles ensures their resistance to biofuling and biodegradation.

Keywords: asymmetric membrane, cellulose acetate membranes, protein retention, cellulosic derivative film recovery, silver-cellulose acetate membranes

1. Introduction

The first remarkable results of membranes: artificial kidney [1] and seawater desalination [2] were based on membranes from cellulosic derivatives [3].

[1] PhD student, Dept. of Analytical Chemistry and Enviromental Engineering, University POLITEHNICA of Bucharest, Romania, e-mail: cotorceasimona@yahoo.com
[2] PhD student, Dept. of Analytical Chemistry and Enviromental Engineering, University POLITEHNICA of Bucharest, Romania, e-mail: oanaalinadimulescu@yahoo.com
[3] PhD student, Dept. of Analytical Chemistry and Enviromental Engineering, University POLITEHNICA of Bucharest, Romania, e-mail: dd.pascu@yahoo.com
[4] PhD student, Dept. of Analytical Chemistry and Enviromental Engineering, University POLITEHNICA of Bucharest, Romania, e-mail: cristinabardaca@yahoo.com
[5] Prof., Dept. of Analytical Chemistry and Enviromental Engineering, University POLITEHNICA of Bucharest, Romania, e-mail: doru.nechifor@yahoo.com
[6] PhD student, Dept. of Analytical Chemistry and Enviromental Engineering, University POLITEHNICA of Bucharest, Romania, e-mail: andreia.pascu@yahoo.ro

But, although cellulose acetate membranes were the turning point in the technological development of membranes and membrane processes, this type of membrane was, since the 1980s, almost completely abandoned [4-6].

Thus, the polymers used were extended to synthetic polymers, especially polyaromatic (polysulfones, polyphenylene oxides, polyetherketones, polyamides, polyphenylene oxides), which provided increased physicochemical resistance and superior process performance for prepared membranes [7-11].

The physicochemical resistance in the membrane process proved to be a major disadvantage of membranes based on synthetic polymers that by not being biodegradable raised huge environmental problems, including recycling [12, 13].

It is thus justified, that in the last decade membranes and membrane processes involving membranes based on biopolymers and / or biodegradable polymers have taken on a special scale [14-17].

Reconsideration of biopolymers and biodegradable polymers as a membrane material was supported by the emergence of various nanomaterials that increased both physicochemical characteristics (resistance to various pH, temperature, corrosion, or soiling) and process performance (selectivity and flux) [18-20].

On the other hand, biopolymers and artificial polymers are accessible, biodegradable and can be processed according to established methods and techniques for the preparation of all types of membranes:

- symmetrical, asymmetrical, composite (by structure) [21],
- flat, tubular, lumen fibers (by geometric shape) [22],
- selective, sensitive, hybrid, intelligent (by destination) [23].

This paper addresses the obtaining of asymmetric membranes from recovered cellulose acetate, from used cinematographic films, by the phase inversion method, precipitation immersion technique, intended for the separation of proteins from synthetic solutions.

2. Experimental part

2.1. Materials

Cellulose acetate (Ac-Cell) from cinematographic films and Ac-Cell powder, respectively, Mn = 50000 g / mol, ρ = 1.3g / cm3, (Aldrich, USA).

Bovine serum albumin (BSA) with molecular weight M = 66 kDa, N-methylpyrrolidone, anhydrous sodium carbonate, Folin-Ciocalteu reagent, sodium hydroxide, copper sulphate pentahydrate, sodium citrate was purchased from Sigma-Aldrich.

The solvents were used as delivered: Ethyl alcohol, 96%, (Chimreactiv SRL, Bucuresti); N-methyl-2-pyrrolidone (NMP), liquid, C_5H_9NO, purity GC, 99.5%, ρ = 1,032 g / cm 3, (Darmstadt, Merck, Germany).

Ultrapure deionized water obtained using the Elix Technology Inside system (Milli-Q Integral 15, Merck, Millipore, France).

2.2. Procedures

2.2.1. Membrane preparation [24,25]

The base polymer (Ac-Cell), in the amount determined to prepare a 10% solution, was gradually introduced into the chosen solvent, NMP, with stirring, in a closed vessel, until complete dissolution (a transparent solution is obtained). The obtained 10% AC-Cell solution in NMP was filtered to remove solid impurities (undissolved gels) and then deaerated by standing in a closed vessel for 24 hours.

The filming of the polymer solution was performed at room temperature and humidity, using a certain amount of solution by applying directly to a smooth glass surface (intended for thin layer chromatography) to a thickness of 500 μm.

The immersion in the ethanol-water (EW) coagulation bath in a 1:2 volume ratio was performed after a predetermined time.

Three membranes were obtained from the standard polymer (coded by Ac-Cell 1) respectively, three from the cinematographic films (coded by Ac-Cell 2), using a polymer solution with a concentration of 10% in NMP.

The technical conditions for the realization of all membranes by the phase inversion method, immersion-precipitation technique, are [27]:

- filming tool with a slit of 500 μm,
- glass film support (specific for thin layer chromatography),
- filming speed of approx. 0.5 m / minute,
- immersion immediately after filming in the coagulation bath,
- coagulation time of 30 minutes,
- washing in an ultra-pure water bath (24 hours),
- wet conditioning in a container with 20% aqueous ethyl alcohol solution (by volume).

2.2.2. Determination of fluxes and retention [26, 27]

The ultrapure water fluxes for the two types of membranes in the study were performed at five different pressures, from 0 to 4 atm, at every 0.5 atm.

To determine the fluxes, the membrane samples, three at a time, were introduced simultaneously in the installation with three ultrafiltration stations of the Sartorius micro- or ultra-filtration installation. Then, a volume of 500 mL of ultrapure water was introduced into the supply tank and the pressure was adjusted (from 0 to 4 atm, depending on each experiment). During each experiment the time of collection of a volume of permeate 50 mL was measured to determine the evolution of the flux and permeability throughout the ultrafiltration.

The ultrafiltration experiments using synthetic solutions of 1g / L BSA were carried out under the same conditions (simultaneously on three stations in the installation).

The fluxes from the source phase [26] were determined against the measured permeate mass within a determined time range, applying the following equation:

$$J = \frac{M}{S \cdot t}(g/m^2 h) \tag{1}$$

where: M= permeate mass (g)
S = effective surface of the membrane (m^2)
t = the time necessary to collect the permeate volume (h)

The retention (R%) for the species of interest using the solutions' concentration or absorbance [27] were:

$$R(\%) = \frac{(c_0 - c_f)}{c_0} \cdot 100 \tag{2}$$

where: c_f - is the final concentration of the solute (BSA),
c_o - initial concentration of solute (BSA)

$$R(\%) = \frac{(A_0 - A_s)}{A_0} \cdot 100 \tag{3}$$

where: A_0 - initial sample solution absorbance
A_s - current sample absorbance

2.3. Equipment

The microscopy studies, SEM and HFSEM, were performed on a Hitachi S4500 system (Hitachi High-Technologies Europe GmbH, Germany).

Thermal characterizations were performed using a Netzsch Thermal Analyzer (NETZSCH-Gerätebau GmbH, Germany). The thermal analysis was run in a nitrogen atmosphere at a 10 °C/min heating rate, from the room temperature (25 ^{0}C) up to 900 ^{0}C.

Spectroscopy Bruker Tensor 27 FTIR with Diamond ATR (Bruker) was used to study the interactions between the chemicals used in the developed membranes. FTIR analysis was recorded in the range of 500 to 4000 cm^{-1}.

UV-Vis analysis was performed on a Spectrometer CamSpec M550 (Spectronic CamSpec Ltd., Leeds, UK).

Other devices: Ball Mill Retch (VIOLA – Shimadzu, Bucharest, Romania), vacuum oven (VIOLA – Shimadzu, Bucharest, Romania).

3. Results and discussion

Used movies are an important source of cellulose acetate in many archives. Noting the degradation of archived films, they request the takeover of cellulose acetate films by economic agents with concerns in recycling materials [14,28].

In this case, an extremely useful way of high utilization of cellulose acetate in cinematographic films, without removing the superficial silver, is to obtain membranes [29]. One of the most well-known and viable applications of this type of recovery would be to obtain asymmetric membranes for protein ultrafiltration [30].

The presumed advantages of recovering cellulose acetate from film in this way are:

- preparation method, phase inversion by precipitation immersion, with well-studied parameters and available installations,
- obtaining a desired range of membranes (micro-, ultra- or nanofiltration),
- obtaining membranes that, by incorporating silver nanoparticles, become self-sterilizable,
- the possibility of using membranes in multiple separation-recovery processes (in our case BSA separation),
- low cost of raw material and high value of membranes.

In this study were used for the preparation of asymmetric membranes intended for ultrafiltration: cinematographic films from local archives (Fig. 1a) and standard cellulose acetate powder (Fig. 1b).

a b

Fig. 1. Cinematographic films (a) and cellulose acetate powder (b)

Of course, the film compositions are well known, depending on the archiving period and the supplier, but before starting the membrane preparation tests, a preliminary analysis was performed [31, 32], to allow the choice of the appropriate solvent. Fig. 2 shows the results of the FTIR analysis [Fig. 2a], thermal analysis [Fig. 2b and c], in correlation with the known structure [Fig. 2c].

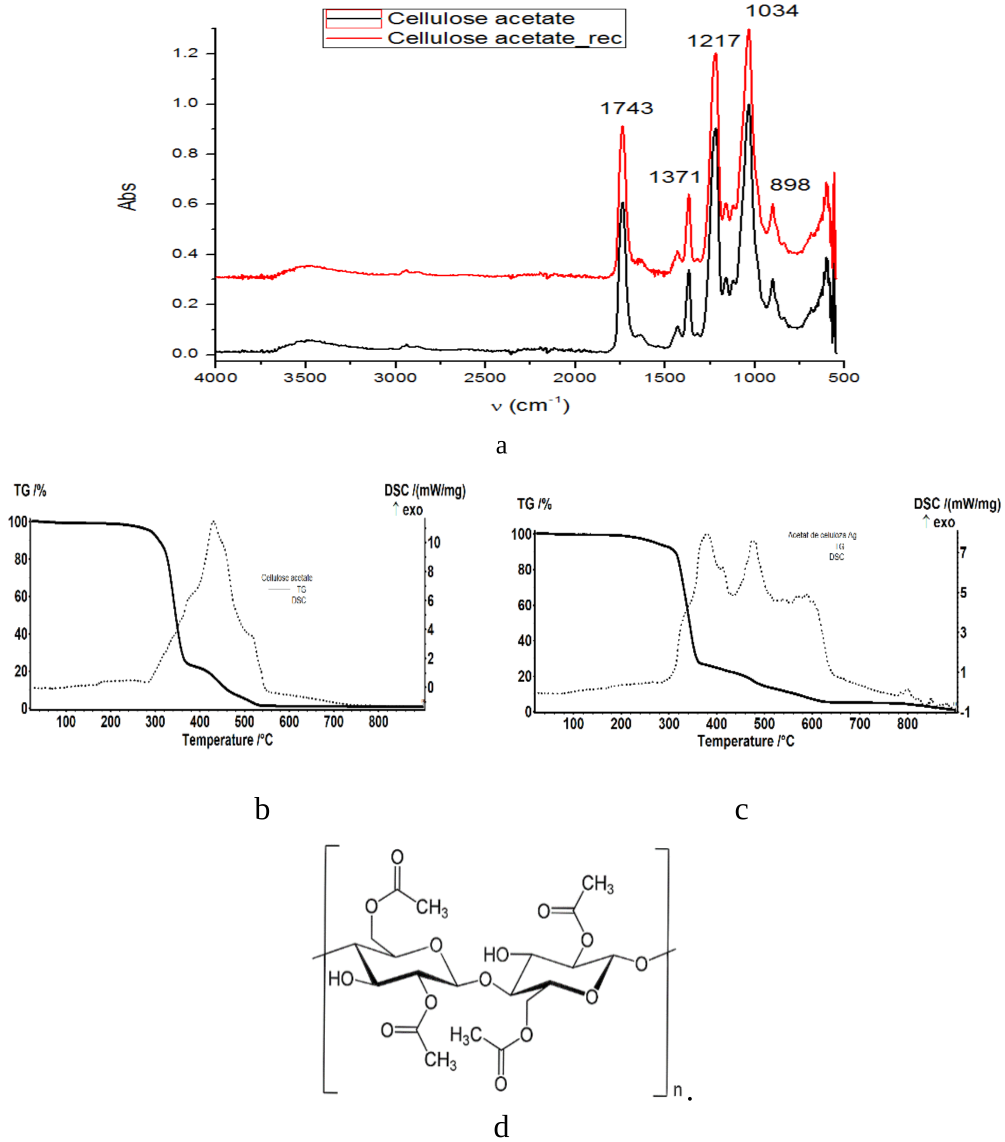
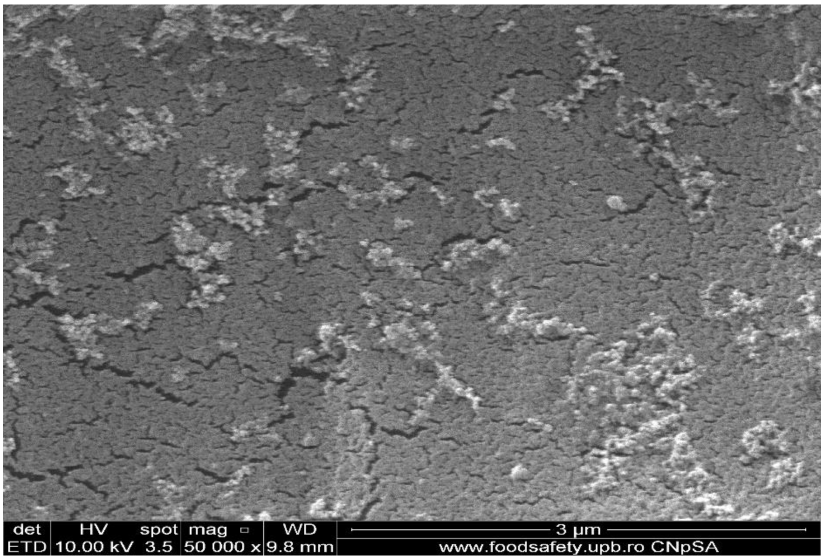
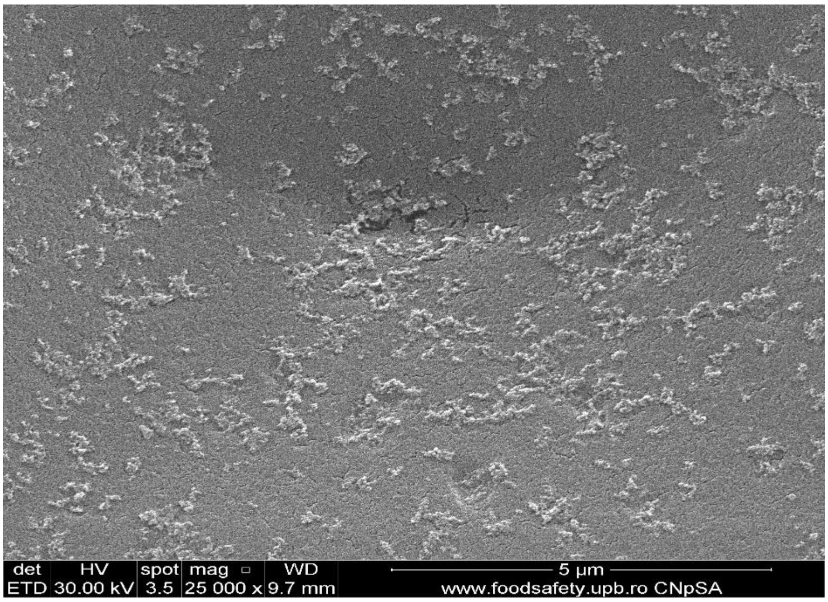


Fig. 2. Acetate powder analysis compared to cinematographic films; a) FTIR, b) thermal analysis of cellulose acetate, c) thermal analysis of films and d) chemical structure

The cinematographic films were examined by scanning electron microscopy (SEM) to observe the morphology of the used film and the distribution of the silver nanoparticles on the surface (Fig. 3).



a

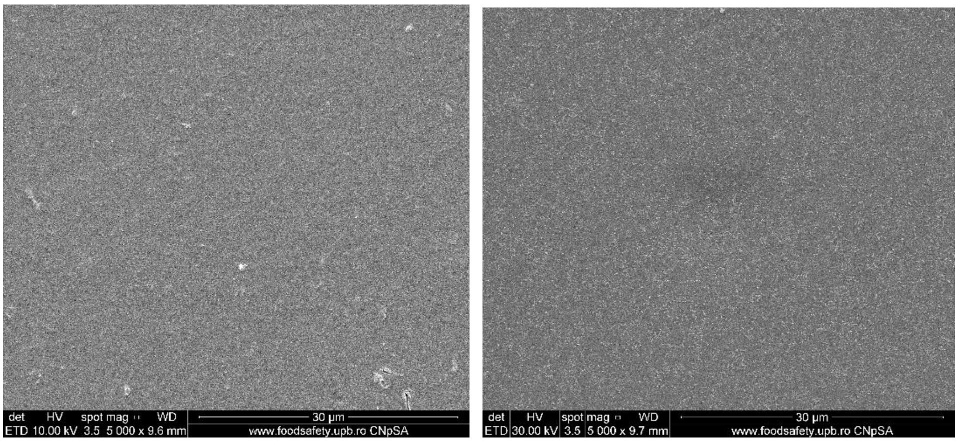


b

Fig. 3. SEM images for cinematographic film: a) morphology of the used film (with microcracks and silver nanoparticles), b) distribution of silver nanoparticles on the surface

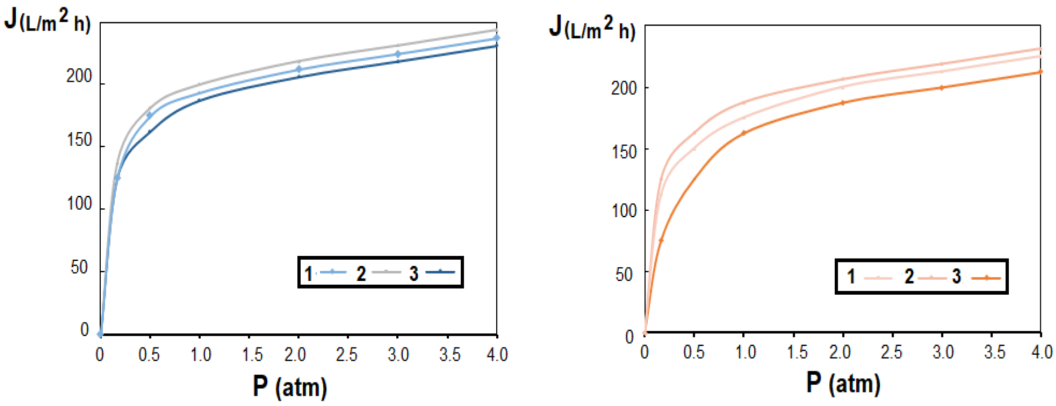
The results of the analysis show that the two types of raw materials are based on cellulose acetate, the influence of silver nanoparticles in cellulose films is noticeable, but very small, at least from a marfo-structural point of view. Once the structure and morphology of the raw materials were confirmed, the two sets of three membranes were made by phase inversion, precipitation immersion technique, from 10% Ac-Cell solution in NMP.

Membranes were characterized by scanning electron microscopy (Fig. 4), pure water permeation (Fig. 5) and bovine serum albumin retention (Fig. 6).



a b

Fig.4. SEM images of the membrane surface: a) AC-Cell 1 membrane, b) recovered Ac-Cell 2 membrane



a b

Fig.5. Comparative permeation of pure water through the two types of membranes: a) three samples of Ac-Cell1 membranes and b) three samples of Ac-Cell2 membranes

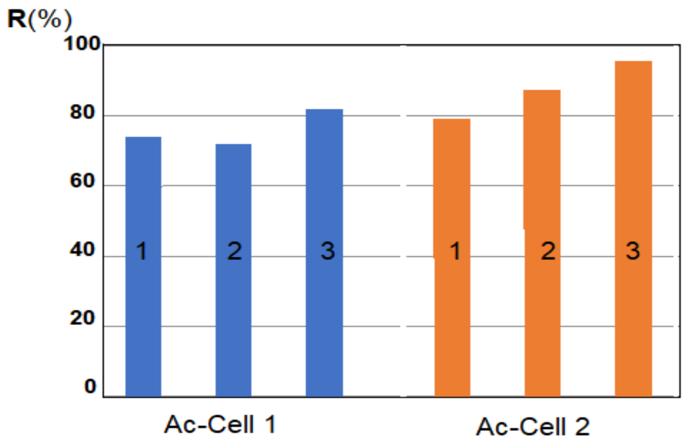


Fig.6. Comparative retention of BSA through the two types of membranes

Standard cellulose acetate membranes have slightly higher pure water fluxes, 200-250 L/ m^2h, at pressures of 1-4 atm, (Fig. 5a), compared to membranes prepared from cinematographic films, 175-225 L / m2h (Fig. 5b), in the same range of working pressures. In the case of BSA retentions, the membranes in standard cellulose acetate have values of 72-82%, and the membranes in cinematographic films 79-93%.

Because morphologically (Fig. 4) the two types of membranes are similar, it can be assumed that the higher retention, in the case of membranes from cellulosic films, is determined by the presence of silver nanoparticles. The use of membranes can be recommended, even if their fluxes are slightly lower, by about 10%.

At a constant working pressure, 2.5 atm, the BSA retention is influenced by its concentration in the initial solution. At lower concentrations, retentions are higher for both membrane samples compared to values at higher concentrations (Table 1).

Table 1

Bovine serum albumin retention (BSA) for the two cellulose acetate membrane samples

Membranes	BSA retention from solution (%)		
	1.5 g/L	2.5 g/L	3.5 g/L
Ac-Cell 1.1.	68.9	66.8	66.4
Ac-Cell 1.2.	71.0	70.2	69.6
Ac-Cell 1.3.	72.1	71.9	71.1
Ac-Cell 2.1.	80.8	78.6	77.9
Ac-Cell 2.2.	87.4	86.7	86.0
Ac-Cell 2.3.	91.2	90.8	89.6

At the same time, it is confirmed that the recovered cellulose acetate membranes (Ac-Cell 2 series - containing silver nanoparticles) have higher retentions than the standard cellulose acetate membranes (AC-Cell 1 series). Thus, if a higher permeate flux is desired, the standard cellulose acetate membranes will be used, and when we pursue higher retentions, the Ac-Cell 2 series of membranes is recommended.

In addition to a higher BSA retention, the presence of silver nanoparticles in the recovered cellulose acetate membranes will also ensure the biocidal effect thus prolonging the life of the membranes [33, 34].

4. Conclusions

Membranes based on biopolymers and artificial polymers have been reconsidered in current studies in the field, due to their superior biodegradability and simple way of preparation in a wide range of morphologies and designs.

The paper presents the results of the use as a raw material of cellulose acetate in used cinematographic films, thus capitalizing on both the polymer and the silver on the surface of the films.

By phase inversion, ultrafiltration membranes were obtained from a 10% cellulose acetate solution. Membranes from recovered cellulose acetate were compared to membranes obtained, under the same conditions, from standard cellulose acetate.

Membranes were characterized morpho-structurally (FTIR, SEM) and in the process of protein ultrafiltration (BSA). Permeate fluxes were higher in standard cellulose acetate membranes (by about 10%), but retentions were higher in acetate membranes from film (by 10%).

The presence of silver nanoparticles in the recovered membrane material can provide resistance to biofouling and biodegradation.

R E F E R E N C E S

[1]. *R. van Reis, A. Zydney,* Bioprocess membrane technology, Journal of Membrane Science, **vol. 297**, no. 1-2, 2007, pp. 16-50.

[2]. *D. B. Burns, A. L. Zydney,* Effect of solution pH on protein transport through ultrafiltration membranes, Biotechnology and Bioengineering, **vol. 64**, no. 1, 1999, pp. 27-37.

[3]. *J. Davey, A. I. Schäfer,* Ultrafiltration to supply drinking water in international development: a review of opportunities, Appropriate Technologies for Environmental Protection in the Developing World, ed. E. K. Yanful, Ghana, Africa, 2007, pp. 151-168.

[4]. *A. Muller, B. Chaufer, U. Merin, G. Daufin,* Prepurification of α-lactalbumin with ultrafiltration ceramic membranes from acid casein whey: study of operating conditions, Journal of Membrane Science, **vol. 83**, 2003, pp. 111-129.

[5]. *A. Rektor, G. Vatai,* Membrane filtration of Mozzarella whey, Desalination, **vol. 162**, 2004, pp. 279-286.

[6]. *R. Atra, G. Vatai, E. Bekassy-Molnar, A. Balint,* Investigation of ultra- and nanofiltration for utilization of whey protein and lactose, Journal of Food Engineering, **vol. 67**, no. 3, 2005, pp. 325-332.

[7]. *S. Butylina, S. Luque, M. Nystroma,* Fractionation of whey-derived peptides using a combination of UF and NF, Journal of Membrane Science, **vol. 280**, no. 1-2, 2006, pp. 418-426.

[8]. *A. Chollangi, M. M. Hossain,* Separation of proteins and lactose from dairy wastewater, Chemical Engineering and Processing: Process Intensification, **vol. 46**, no. 5, 2007, pp. 398-404.

[9]. *E. J. de la Casa, A. Guadix, R. Ibáñez, E. M. Guadix,* Influence of pH and salt concentration on the cross-flow microfiltration of BSA trough a ceramic membrane, Biochemical Engineering Journal, **vol. 33**, no. 2, 2007, pp. 110-115.

[10]. *D.-S. Tang, G.-M. Yin, Y.-Z. He, S.-Q. Hu, B. Li, L. Li, H.-L. Liang, D. Borthakur,* Recovery of protein from brewer's spent grain by ultrafiltration, Biochemical Engineering Journal, **vol. 48**, no. 1, 2009, pp. 1-5.

[11]. *S. K. Karode, B. B. Gupta, T. Courtois,* Ultrafiltration of raw Indian sugar solution using polymeric and mineral membranes, Separation Science and Technology, **vol. 35**, no. 15, 2000, pp. 2473-2483.

[12]. *P. Bacchin, P. Aimar, R. W. Field,* Critical and sustainable fluxes: Theory, experiments and applications, Journal of Membrane Science, **vol. 281**, no. 1-2, 2006, pp. 42-69.

[13]. *G. Gésan-Guiziou, R. J. Wakeman, G. Daufin,* Stability of latex crossflow filtration: cake properties and critical conditions of deposition, Chemical Engineering Journal, **vol. 85**, no. 1, 2002, pp. 27-34.

[14]. *A.C. Nechifor, S. Cotorcea, C. Bungău, P.C. Albu, D. Pașcu, O. Oprea, A.R. Grosu, A. Pîrțac, G. Nechifor,* Removing of the Sulfur Compounds by Impregnated Polypropylene Fibers with Silver Nanoparticles-Cellulose Derivatives for Air Odor Correction. Membranes **vol. 11**, 2021, 256. https://doi.org/10.3390/membranes11040256

[15]. *I.S. Din, A.M. Cimbru, A.A.K.K. Rikabi, S.K. Tanczos, S. Ticu (Cotorcea), G. Nechifor,* Iono-molecular Separation with Composite Membranes VI. Nitro-phenol separation through sulfonated polyether ether ketone on capillary polypropylene membranes. Rev. Chim. (Bucharest) **vol. 69**, no.7, 2018, pp. 1603-1607, https://doi.org/10.37358/rc.18.7.6379

[16]. *I.M. Nafliu, H.N.A. Al-Ani, A.R. Grosu (Miron), P.C. Albu, G. Nechifor,* Iono-molecular separation with composite membranes. viii. recuperative aluminium ions separation on capilary polypropylene S-EPDM composite membranes. Mat. Plast. **vol. 56**, no. 1, 2019, pp. 32-36 https://doi.org/10.37358/mp.18.4.5064

[17]. *M. Ghimpusan, G. Nechifor, A.C. Nechifor, S.O. Dima, P. Passeri,* Case studies on the physical-chemical parameters' variation during three different purification approaches destined to treat wastewaters from food industry. J. Environ. Manag. **vol. 203**, 2017, pp. 811–816, doi:10.1016/j.jenvman.2016.07.030.

[18]. *K. Khider, D. E. Akretche, A. Larbot,* Purification of water effluent from a milk factory by ultrafiltration using Algerian clay support, Desalination, **vol. 167**, 2004, pp. 147-151.

[19]. *T. Mohammadi, A. Esmaeelifar,* Wastewater treatment using ultrafiltration at a vegetable oil factory, Desalination, **vol. 166**, 2004, pp. 329-337.

[20]. *E. Ellouze, R. B. Amar, A. H. B. Salah,* Crossflow microfiltration using ceramic membranes applied to the cuttlefish effluents treatment: effect of operating parameters and the addition of pre or post-treatment, Desalination, **vol. 177**, no. 1-3, 2005, pp. 229-240.

[21]. *D. Abdessemed, G. Nezzal, R. Ben Aïm,* Treatment of wastewater by ultrafiltration, Desalination, **vol. 126**, no. 1-3, 1999, pp. 1-5.

[22]. *C. Fersi, M. Dhahbi,* Treatment of textile plant effluent by ultrafiltration and/or nanofiltration for water reuse, Desalination, **vol. 222**, no. 1-3, pp. 263-271.

[23]. *Y. M. Lo, D. Cao, S. Argin-Soysal, J. Wang, T.-S. Hahm,* Recovery of protein from poultry processing wastewater using membrane ultrafiltration, Bioresource Techology, **vol. 96**, no. 6, 2005, pp. 687-698.

[24]. *C. Bărdacă Urducea, A.C. Nechifor, I.A. Dimulescu, O. Oprea, G. Nechifor, E. Eftimie Totu, I. Isildak, P.C. Albu, S.G. Bungău,* Control of Nanostructured Polysulfone Membrane Preparation by Phase Inversion Method.Nanomaterials vol.10, no.12, 2349, https://doi.org/10.3390/nano101223

[25]. *R.E. Scutariu, G. Batrinescu, G. Nechifor, M. Popescu, A. G. Tenea,* Separation of the collagen protein by ultrafiltration: Effects of concentration on the membrane's characteristics, Polymer Engineering & Science, **vol. 60**, no.10, 2020, pp. 2487-2495. DOI: 10.1002/pen.25486.

[26]. *S. Koter, P. Szczepański, M. Mateescu, G. Nechifor, L. Badalau, I. Koter,* Modeling of the cadmium transport through a bulk liquid membrane. Sep. Purif. Technol. **Vol.107**, 2013, pp.135-143. https://doi.org/10.1016/j.seppur.2013.01.032

[27]. *O. Lowry, N. J. Rosebrough, A. L. Farr, R. J. Randall,* Protein measurement with the Folin phenol reagent, The Journal of Biological Chemistry, **vol. 193**, 1951, pp. 267-275.

[28]. *A.R. Grosu, I.M. Nafliu, I.S. Din, A.M. Cimbru, G. Nechifor,* Neutralization with simultaneous separation of aluminum and copper ions from condensed water through capillary polypropylene and cellulose. UPB Sci. Bull. Ser. B Chem. Mater. Sci. **vol. 82**, 2020, pp. 25–34.

[29] *G. Batrinescu, R.E. Scutariu, G. Nechifor, I.A. Ionescu, V.I. Iancu,* Comparative analysis of the processes of collagen concentration by ultrafiltration using different types of membranes. Journal of Applied Polymer Science **vol. 138**, no. 12, 2021. https://doi.org/10.1002/app.50055

[30]. *D. Y. Kwon, S. Vigneswaran, A. G. Fane, R. Ben Aim,* Experimental determination of critical flux in cross-flow microfiltration, Separation and Purification Technology, **vol. 19**, no. 3, 2000, pp. 169-181.

[31]. *D. Falsanisi, L. Liberti, M. Notarnicola,* Ultrafiltration (UF) Pilot Plant for Municipal Wastewater Reuse in Agriculture: Impact of the Operation Mode on Process Performance, Water, **vol. 1**, 2009, pp. 872-885.

[32]. *A. Fernández, F. A. Riera,* Membrane Fractionation of a β-Lactoglobulin Tryptic Digest: Effect of the Hydrolysate Concentration, Industrial&Engineering Chemistry Research, **vol. 51**, no. 48, 2013, pp. 15738-15744.

[33]. *A. D. Marshall, P. A. Munro, G. Tragardh,* The effect of protein fouling in microfiltration and ultrafiltration on permeate flux, protein retention and selectivity: a literature review, Desalination, **vol. 91**, no. 1, 1993, pp. 65-108.

[34] *S. Yuan, J. Wang, X. Wang, S. Long, G. Zhang, J. Yang,* Poly(arylene sulfide sulfone)hybrid ultrafiltration membrane with TiO_2-g-PAA nanoparticles: preparation and antifouling performance, Polymer Engineering and Science, **vol. 55**, 2015, pp. 2829-2837.