Manuel Palencia^{1*}, Tulio A. Lerma^{1,2}, María Elizabeth Berrio^{1,2}

¹ Department of Chemistry, Faculty of Natural and Exact Science, University of Valle, Cali, Colombia

² Mindtech Research Group (Mindtech-RG), Mindtech s.a.s., Cali, Colombia

Corresponding author: manuel.palencia@correounivalle.edu.co

Graphical abstract

Thin-film composite by in situ polymerization of 4-chloromethyl styrene functionalized with N-methyl-D-glucamine in pore-type microreactors

Abstract

In situ polymerization of (4-vinylbenzyl)-N-methyl-D-glucamine (VbNMDG) for the formation of thin-film composite membranes with boron retention capacity is reported. VbNMDG was synthesized from vinylbenzyl chloride and N-methyl-D-glucamine, afterward, a mixture constituted by VbNMDG, a radical initiator and a crosslinking reagent was injected and polymerized in the inside of the pores of the membranes. Functionalization of vinyl monomer was verified by nuclear magnetic resonance. Analyses of scanning electron microscopy (SEM), diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy and contact angle measures were performed to unmodified and modified membrane surface. Changes on the surface porosity and permeability were evaluated from Hagen-Poiseuille model. In addition, boron retention capacity was evaluated by diafiltration experiments. Results suggest that active layer was modified as a result of polymerization reaction; in consequence, the pore diameter and hydraulic permeability were significantly decreased.

Keywords

Thin-film composite
Ultrafiltration membrane
N-methyl-D-glucamine
Interpenetrating polymer network

Compositos de películas delgadas mediante polimerización in situ de 4-clorometilestireno funcionalizada con N-metil-D-glucamina en microreactores tipo poro

Resumen

La polimerización in situ de (4-vinilbencil)-N-metil-D-glucamina (VbNMDG) para la formación de membranas compuestas de películas delgadas con capacidad de retención de boro se reporta. VbNMDG se sintetizó a partir de cloruro de vinil bencilo y N-metil-D-glucamina, posteriormente, una mezcla constituida por VbNMDG, un iniciador radical y un reactivo entrecruzador se inyectó y polimerizó dentro de los poros de las membranas. La funcionalización del monómero vinílico se verificó por resonancia magnética nuclear. Análisis de microscopía electrónica de barrido (SEM), espectroscopia de infrarrojo por transformada de Fourier mediante la técnica de reflectancia difusa (DRIFT) y medidas de ángulo de contacto se realizaron a las superficies modificadas y sin modificar. Los cambios en la porosidad superficial y la permeabilidad se evaluaron mediante el modelo de Hagen-Poiseuille. Adicionalmente, experimentos de retención de boro se evaluaron mediante experimentos de diafiltración. Los resultados sugieren que la capa activa se modificó como resultado de la reacción de polimerización, en consecuencia, el diametro y la permeabilidad hidraulica se disminuyen significativamente.

Palabras claves

Compositos de películas
delgadas
Membranas de ultrafiltración
N-metil-D-glucamina
Redes poliméricas
interpenetrantes

Received: 08-09-2017

Accepted: 02-10-2017

Publishing date: 15 - Noviembre - 2017

Revision Code: 20170908-AAAA [Pag. 66 - 76]

Corresponding author:

manuel.palencia@correounivalle.edu.co

Thin-film composite by in situ polymerization of 4-chloromethyl styrene functionalized with N-methyl-D-glucamine in pore-type microreactors

Manuel Palencia^{1*}, Tulio A. Lerma^{1,2}, María Elizabeth Berrio^{1,2}

¹ Department of Chemistry, Faculty of Natural and Exact Science, University of Valle, Cali, Colombia

² Mindtech Research Group (Mindtech-RG), Mindtech s.a.s., Cali, Colombia

Corresponding author: manuel.palencia@correounivalle.edu.co

Abstract

In situ polymerization of (4-vinylbenzyl)-N-methyl-D-glucamine (VbNMDG) for the formation of thin-film composite membranes with boron retention capacity is reported. VbNMDG was synthesized from vinylbenzyl chloride and N-methyl-D-glucamine, afterward, a mixture constituted by VbNMDG, a radical initiator and a crosslinking reagent was injected and polymerized in the inside of the pores of the membranes. Functionalization of vinyl monomer was verified by nuclear magnetic resonance. Analyses of scanning electron microscopy (SEM), diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy and contact angle measures were performed to unmodified and modified membrane surface. Changes on the surface porosity and permeability were evaluated from Hagen-Poiseuille model. In addition, boron retention capacity was evaluated by diafiltration experiments. Results suggest that active layer was modified as a result of polymerization reaction; in consequence, the pore diameter and hydraulic permeability were significantly decreased.

Keywords

Thin-film composite
Ultrafiltration membrane
N-methyl-D-glucamine
Interpenetrating polymer
network

1. Introduction

Thin-film composite membranes (TFCMs) are semipermeable porous membranes manufactured for use in water purification, water desalination, batteries and fuel cells. A TFCM can be considered as a molecular sieve constructed from two or more layered materials with a film of approximately 100 nm in thickness [1-2]. These membranes have a thin and dense active layer that controls membrane performance (permeability and selectivity), and a much thicker porous substrate that provides mechanical support to the active layer. In order to achieve high values of permeability and selectivity,

active layers ultrathin and hydrophilic are preferred [1]. TFCMs are commonly prepared by spin coating, interfacial polymerization and from polymeric-inorganic hybrid materials [1-3]. At the present time, there are commercially available asymmetric ultrafiltration polymeric membranes with an active layer of approximately 100 nm in thickness. These membranes can be chemically modified by surface functionalization of active layer or physically modified by adsorption of polymer on the membrane surface (layer-by-layer method) [4-5]. Many studies have been reported using chemical or physical modification strategies for the incorporation of new functional

characteristics (i.e., selectivity, retention capacity, complexing and antifouling properties). However, chemical modification is seen limited to the chemical reactivity of active layer and physical modification is associated to reversible processes which no guarantee a total stability for a wide range of operating conditions [1, 6].

Another alternative for the modification of polymer materials is via interpenetrating polymer networks (IPNs). This is a fast and versatile route for fabrication of new polymer systems with new properties obtained from individual polymers. IPNs are polymeric structures formed when two distinct multi-functional polymers are entangled at the molecular level. IPNs are classified depending of network configuration as sequential IPN (SIPN), simultaneous IPN (SIPN) and semi-IPNs. Thus, IPNs are formed when one of the monomers is added and polymerized in an existing polymer, SIPN are produced by two non-interfering polymerizations from a mixture of the monomers and semi-IPNs are SIPNs in which only one of the polymers is crosslinked while the other is linear [8-10].

Nanoreactor can be defined as a reactor used to carry out chemical reactions in a space at nanometric scale. Common examples of the use of a very small space as a chemical reactor for the confinement of reagents are emulsion drops, zeolite pores and porous membranes based on metal oxides [11-17]. For polymerization reactions, nanoreactors are usually used to produce particles in the nanoscale and, in consequence, its role is to prevent the fusion and growth of solid polymer particles during the polymerization process [13]. Since ultrafiltration polymer membranes have available space in the inside of the pores to contain chemical substance with capability to react, it is expected that pores can be used as polymerization nanoreactors. However, the shape, the size and the tortuosity of the pores no permit the total confinement of reaction mixture for the production of particulate material. In fact, the connectivity of internal pores is common in membranes based on polymeric fibers [18-20], and therefore the polymerization can be extended along the entire membrane. This internal interconnection of the pores permits that the active layer of asymmetric membranes can be used as support for the polymerization of vinyl monomers in the production of interpenetrating polymer networks (IPNs).

IPNs are polymeric structures formed when two distinct multi-functional polymers become entangled at the molecular level and are formed when at least one of the multi-functional monomers is reacted in the presence of the other polymer [21-26]. Since, in the formation of IPNs, the superposition of polymer chains is produced without the formation of covalent interactions between the polymeric structures it is clear that the primary resin must be chemical inert to the polymerization reactions to produce the secondary resin. From a physical point of view, formation of the network can be understood as the growth of polymer chains around of molecular fibers, and therefore, when reference is made to the active layer of ultrafiltration membranes to be the primary resin, the growth of polymer chains must be around polymer fibers whose diameter can be of the order of nanometer. However, as free radical polymerization reaction implies the activation of many monomers simultaneously, it is expected that with the adequate monomer concentration the IPN can be formed in the active layer of ultrafiltration membranes. Another aspect to consider is the miscibility of polymers (primary and second resins) since polymer phases aggregation can occur between incompatible polymer systems (by instance, polar and apolar chains) [21-23].

The objective of this work was evaluating the use of ultrafiltration membrane pores as polymerization reactors for the formation of IPNs. The main projections of this research are the design of new polymer materials based in IPNs with defined shapes and by combination of nanofibers with molecular chains. In addition, depending of membrane configuration, the development of novel polymer systems can be carry out by the combination of chemical and physical properties of individual polymers.

2. Materials and methods

2.1 Reagents and materials

N-methyl-*D*-glucamine (NMDG, Aldrich, USA) and vinylbenzyl chloride (VBCl, Aldrich, USA) were used in the synthesis of (4-vinylbenzyl)-*N*-methyl-*D*-glucamine (VbNMDG). *N,N*-methylenebis-acrylamide (MBA, 98 %, Aldrich, USA) and ammonium persulphate (Aldrich, USA) were used as crosslinker and polymerization initiator reagents,

respectively. 1,4-dioxane (Aldrich, USA) and bi-distilled water were used as reaction solvents.

Cellulose disk-shaped asymmetric membranes with 100 kDa molecular mass cut-off (Biomax PBGC, manufactured by Millipore Co.) were used. A stirred-cell filtration unit (Millipore, model 8050) was used as flow injection system and in diafiltration experiments; components and operation modes of the filtration system have been described in previous publications [27-28].

Boron aqueous solutions were prepared from boric acid (H_3BO_3 , Aldrich, USA) using bi-distilled water. Nitric acid (HNO_3 , Aldrich, USA) and sodium hydroxide (NaOH , Aldrich, USA) were used to control the pH.

2.2 Synthesis of VbNMDG

Synthesis of VbNMDG was performed using as a reference the batch method previously reported by Urban et al. [29]. This reaction was carried out using three levels of VBCl concentration (21.9, 43.8, and 65.7 mmoles) with a 1:2 molar ratio (VBCl:NMDG).

Functionalization of VBCl with NMDG was verified by RMN. Thus, the ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrophotometer operating at 400 MHz and 100 MHz, respectively, using dimethyl sulfoxide- d_6 , DMSO, as solvent and tetramethylsilane as internal reference ($\delta = 0.00$ ppm). In addition, a polymerization test of aqueous phase was performed (this test is based in the polymerization reaction of the aqueous phase in presence of initiator and crosslinker reagents; the presence in the aqueous phase of double bond $\text{C}=\text{C}$ associated to the VBCl only is possible when the functionalization was satisfactorily performed).

2.3 Formation of IPN in the membrane pores

Modification of ultrafiltration membranes was performed by injection of functionalized monomer in the inside of the membrane pores in presence of radical initiator and crosslinker reagents (2.0 % mol of ammonium persulphate and 8.0 % of MBA with respect to the monomer). For that, reaction mixture was prepared and by ultrafiltration introduced in the membrane using N_2 gas at 100 kPa of pressure. Later, membranes were placed in a parallel plate system designed to avoid the contact with active

layer and prevent the folding of membrane by heating. Later, this plate system was heated by 12 h using an airflow oven at 30 °C in order to carry out the polymerization.

2.3.1 Percent of resin incorporated to the membrane: Modified membranes were washed with bidistilled water using a stirred-cell filtration unit (100 mL of water at 100 kPa) and dried using an airflow oven at 30 °C until constant mass in order to determine the percent of resin and mol number of NMDG chains incorporated. Previous to the modification the membrane masses were measured.

2.3.2 Determination of surface porosity: Surface porosity was determined from mass of dried membrane (w_0) and the mass membrane with the pores are completely filled with water ($w_{\text{H}_2\text{O}}$) using the Eq. (1).

$$\varepsilon = \frac{w_{\text{H}_2\text{O}} - w_0}{A_m \Delta y} \quad (1)$$

where Δy and A_m are the thickness and area of the membrane, respectively.

2.3.3. Surface analysis: Unmodified and modified membrane surfaces were analyzed by diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) and scanning electron microscopy (SEM). Elemental composition of membranes was performed by energy dispersive spectrometry (EDS) from SEM images.

2.3.4. Permeability test: Permeability test consisted in the measurement of the permeated water mass and the permeation time at different applied pressures, ΔP , (100, 200, 300, and 400 kPa). Details have been previously reported [27-28]. Changes in the permeability coefficient (L) were determined by Darcy's law and Hagen- Poiseuille equation

$$J = L \Delta P = \left(\frac{\varepsilon r_p^2}{8 \eta \Delta y} \right) \Delta P \quad (2)$$

where J is the volumetric flow, r_p is the pore radius, η is the viscosity of water, Δy is the thickness of the membrane and ε is the surface porosity ($\varepsilon = n_p \pi r_p^2 A_m^{-1}$, where n_p and A_m are the number of pores on the surface and the membrane area, respectively) [30].

2.3.5 Measurements of contact angle: Changes of membrane hydrophilicity were analyzed by contact

angle (θ) by drop deposition method. ± 3 μL drops of bidistilled water were deposited on the membrane surface and the process was captured on video format to be analyzed [27–28]. Images analysis was performed using the Digital Micrograph software (Gatan inc.).

3. Results and discussion

3.1 Synthesis of VbNMDG

In Figures 1 and 2, ^1H and ^{13}C NMR spectra are shown. The multiplicity of the proton signals is indicated by the following abbreviations: singlet (s), doublet (d), double doublet (dd) and multiplet (m). In these spectra, the signals confirm the structure of VbNMDG monomer.

In ^1H NMR spectra (DMSO- d_6 , 400 MHz) the following signals are observed: δ 2.11 (s, 3H, CH_3), 2.41 (m, 1H, CH_2 , a), 2.54 (m, 1H, CH_2 , a), 3.39 (m, 1H, CH_2 , b), 3.52 (s, 2H, CH_2 , c), 3.46 – 3.67 (m, 3H, CH, d), 3.60 (m, 1H, CH_2 , b), 3.78 (m, 1H, e), 4.30 – 4.57 (m, 5H, OH), 5.23 (d, $J = 11.0$ Hz, 1H, f), 5.79 (d, $J = 17.7$ Hz, 1H, g), 6.74 (dd, $J = 10.9$, 17.7 Hz, 1H, h), 7.29 (d, $J = 8.1$ Hz, 2H, i), 7.40 (d, $J = 8.0$ Hz, 2H, j).

In ^{13}C NMR spectra (DMSO- d_6 , 100 MHz) the following signals are observed: δ 42.29 (CH_3 , a), 60.11 (CH_2 , b), 61.75 (CH_2 , c), 63.49 (CH_2 , d), 70.28 (C, e), 63.37–72.12 (3C, f), 113.71 (C, g), 125.88 (C, h), 129.09 (C, i), 135.37 (C, j), 136.48 (C, k), 138.73 (C, l).

In addition, polymerization test was positive. Note that polymerization was performed from aqueous fraction and the vinyl precursor, VbCl, is insoluble in water therefore the polymerization reaction is an evidence of that vinyl groups are in the aqueous phase; therefore, polymerization test can be considered as indirect test for verification of functionalization of VbCl.

3.2 Formation of IPN in the membrane pores

3.2.1 DRIFT analysis: Reactions for the formation of IPN is shown in the Fig. 3 (free radical polymerization of VbNMDG in the presence of MBA). As this polymerization reaction occurred in the inside of membrane pore, the result was a secondary resin entangled between the active layer fibers (primary resin). The presence of VbNMDG resin was verified by DRIFT.

Figure 1. ^1H NMR spectra for VbNMDG

Figure 2. ^{13}C NMR spectra for VbNMDG

Figure 3. Reactions for the formation of IPN

In the Fig. 4 can be seen the DRIFT spectra of unmodified and modified membranes, in addition, representative DRIFT signs are summarized in the Table 1. The main signs in the spectra correspond to stretching vibration of C–N bonds of tertiary amines (1167 and 1129 cm^{-1}) since these bonds can be directly associated with the VbNMDG monomer and therefore with the formation of secondary resin. Results suggest that synthesis of poly(VbNMDG) can be performed in the porous layer of asymmetric membranes.

Figure 4. DRIFT spectra of unmodified and modified membranes

Table 1. Representative DRIFT signs for modified and unmodified membranes

Sample	Signal (cm ⁻¹)	Assignment
Unmodified membrane	3700 - 3000	stretching vibration of –OH
	2909	asymmetric and symmetric stretching vibration of methylene and methyl groups
	1653 and 1176	C=O and C–O stretching vibrations, respectively
	1554	Deformation of CH ₂
Modified membrane	3700 - 3000	stretching vibration of –OH
	1662	C=O stretching vibration associated to active layer
	1167 and 1129	stretching vibration of N–H bonds of tertiary amines

Table 2. Incorporation of NMDG unit for modified membranes

Parameter	Membranes		
	MM ₁	MM ₂	MM ₃
Unmodified membrane mass (g)	0.2041	0.2019	0.2151
Modified membrane mass (g)	0.2133	0.2110	0.2487
Incorporation percent (%)	4.5	4.5	15.6
NMDG groups (mmol)	0.047	0.048	0.172

3.2.2 Percent of resin incorporated to the membrane: Monomer concentrations used in the functionalization and membrane modification experiments were identified to be MM₁, MM₂ and MM₃ (for 21.9, 43.8, and 65.7 mmols of VBCI, respectively). Besides, MM₀ corresponds to blank experiment.

Results of incorporation grade of NMDG units are summarized in the Table 2. It can be seen that, for high concentration of VBCI (MM₃), the amount of resin incorporated was 3.5 times larger than for MM₁ and MM₂. This result can be explained by considering of monomer and radical chain concentration effects on the kinetic of

polymerization (gel effect) [31-32]. An empirical observation was that, for high monomer concentrations, polymerization was seen to be faster by the formation of a viscous solution at short times; therefore, for MM₃ in a small volume of confinement (pores), the auto-acceleration of the polymerization rate is expected. Gel effect is due to diffusion limitations of reactive radical species that slow down the termination reaction leaving the propagation and the initiation reactions unaffected. In consequence, polymerization rate for MM₃ is faster and the resident time of reactive mixture in the inside of the membrane shown the following order MM₃ > MM₂ = MM₁.

Figure 5. Images of SEM: EDS analysis and active layer (A and B), polypropylene support (C and D) and cross section (E and F) for modified and unmodified membranes

3.3.3. SEM analysis: Images of SEM for modified and unmodified membranes are shown in the Fig. 5 (EDS analysis, active layer, polypropylene support and cross section for MM₀ and MM₁).

Elemental analysis by EDS showed a decrease of carbon percent (from 81.53 % to 76.62 %) and an increase of oxygen percent (from 18.43 % to 23.21 %) at the active layer of modified membrane respect to unmodified membrane. This result is congruent with the incorporation of NMDG chains since its structural unit has a greater number of oxygen

atoms. In addition, a decrease of the membrane surface heterogeneity was evidenced (see Fig. 5A and 5B) and can be explained by the VbNMDG polymerization in the inside of the pores. Thus, formation of secondary resin could be related with two effects on functionality of membrane. The first effect is the possibility of complete pore blocking and in consequence membrane changes from porous to dense membrane.

On the other hand, the second effect is the pore reduction and therefore membrane remains a porous

Table 3. Surface porosity and permeability data for modified membranes and values of pore radius and pore number calculated by Hagen- Poiseuille equation.

Parameter	Membranes		
	MM ₁	MM ₂	MM ₃
Initial surface porosity	0.21	0.21	0.24
End surface porosity	0.27	0.15	0.24
Variation (%)	28.6	-28.6	0.00
Initial permeability (m/skPa) x10 ⁻⁷	8.32	8.99	9.34
End permeability (m/skPa) x10 ⁻⁷	2.23	1.87	4.07
Variation (%)	-73.2	-79.2	-56.4
Initial pore radius (nm)	2.4	3.2	3.1
End pore radius (nm)	1.4	1.7	2.0
Initial pore number	14775656	8658412	10973688
End pore number	56679035	21501672	25777999

material but different permeability features. In order to clarify this point, surface porosity and permeability were studied (see section 3.3.4).

From SEM images of polypropylene support significant changes were not evidenced (see Fig. 5C and 5D). In addition, since polypropylene fibers have a mean diameter around of 2×10^4 nm (value estimated from four measures performed at the Fig. 5C) and C-C bond has a length of 0.154 nm ($\sim 2 \times 10^5$ times smaller than polypropylene fibers), it is clear that, in the propagation stage of polymerization reaction, radical chains must achieve a high molecular weight in order to may anchor the secondary resin to the support. On the other hand, another point to consider is the phase separation during the formation of IPN. Whereas VbNMDG monomer and cellulose active layer have polar groups, polypropylene support is apolar on nature and with a pore size very large in comparison with pore size of active layer. Therefore, the absence of IPN in the support can also be explained by phase separation.

From analysis of cross-section, no evidence of formation of a surface polymer layer on the membrane was evidenced (see Fig. 5E and 5F). However, contact angle measures with water shown an increase of hydrophilicity surface. Contact angle change from 72.1 ± 0.3 to 51.8 ± 0.2 for unmodified and modified membranes, respectively. The increase of hydrophilicity can be easily understood as a result of the addition of hydrophilic NMDG chains to the active layer. Therefore, results suggest that secondary network was mainly formed in the inside of the pores and in consequence the decrease of surface heterogeneity can be explained as a result

of the pore size decrease. In addition, the effect of thickness on permeability can be assumed to be negligible.

3.3.4. Surface porosity and permeability: Values of surface porosity and permeability for modified membranes are shown in the Table 3. Results evidence that for the three VbCl concentration levels the functionality of membrane is conserved. Pore number and diameter were calculated from Hagen-Poiseuille model.

For unmodified membranes, mean surface porosity was 0.22 ± 0.017 whereas for modified membrane this value was 0.22 ± 0.063 . Therefore, by considering mean values, our results suggest that the surface porosity is not affected by the formation of IPN, namely, though in some cases surface porosity changes as a result of polymerization reaction, variation of this parameter is not a determinant factor of end permeability.

On the other hand, mean pore radius was decreased at 40.9 % whereas the mean pore number was increased at 202.1 %. The increase in the pore number and the decrease of pore diameter can be explained by the division of initial pores by the formation of IPN. In addition, the decrease of permeability can be understood as a consequence of the decrease of r_p .

Since permeability depends of product ϵr_p^2 and given that r_p^2 is decreased the end effect is the decrease of the membrane permeability. Therefore, it is concluded that the effect on permeability can be attributed mainly to the reduction of pore diameter by the formation of IPN in the inside of the pores.

4. Conclusions

From our result is concluded that new polymer systems based in IPN can be development by in situ polymerization of vinyl monomers in the inside of active layer of asymmetric ultrafiltration membranes. As result of this reaction, active layer can be modified without changes on support material. The effect of polymerization on permeability can be attributed mainly to the reduction of pore diameter whereas the changes of surface porosity are not a determinant factor on end permeability of the membrane. Also, it is concluded that pore diameter and compatibility of polymers must be considered in the design of this kind of the systems.

Acknowledgments

The authors thank to University of Valle and Mindtech s.a.s. by financial support.

Conflict of interts

The authors declare no conflict of interest.

References

- [1] AM Seman, M. Khayet, N. Hilal. Nanofiltration thin-film composite polyester polyethersulfone-based membranes prepared by interfacial polymerization J. Memb. Sci. 348 (2010) 109-116
- [2] W. Lau, A. Ismail, N. Misdan, M. Kassim. A recent progress in thin film composite membrane: A review, desalination 287 (2012) 190-199
- [3] G. Xu, S. Wang, H. Zhao, S. Wu, J. Xu, L. Li, X. Liu. Layer-by-layer (LBL) assembly technology as promising strategy for tailoring pressure-driven desalination membranes J. Memb. Sci. 493 (2015) 428-443
- [4] S. Yano, K. Iwata, K. Kurita, Physical properties and structure of organic-inorganic hybrid materials produced by sol-gel process, Material Science and Engineering., 6(2-3) (1998) 75-90
- [5] J.C. Wang, P. Chen, L. Chen, K. Wang, H. Deng, F. Chen, Q. Zhang and Q. Fu, Preparation and properties of poly (vinylidene fluoride) nanocomposites blended with grapheme oxide coated silica hybrids, eXPRESS Polymer Letters, 6(4) (2012) 299-307
- [6] E.M.V. Hoek, A.K. Ghosh, X. Huang, M. Liong and J.I. Zink, Physical-chemical properties, separation performance, and fouling resistance of mixed-matrix ultrafiltration membranes, Desalination, 283 (2011) 89-99
- [7] N. Jalanni, M. Seman, C. Faizal. Investigation of new polyester nanofiltration (NF) membrane fouling with humic acid solution J. Technol. 65 (2013) 69-72
- [8] S. Jamal, S. Chang, H. Zhou. Filtration behavior and fouling mechanisms of polysaccharides, Membranes (Basel) 4 (2009) 319-332
- [9] K. Boussu, C. Vandecasteele, B. der Bruggen B. Relation between membrane characteristics and performance in nanofiltration J. Memb. Sci. 310 (2008) 51-65
- [10] G. Murthy, S. Sridhar, M. Shyamsunder, B. Shankaraiah, M. Ramakrishna. Concentration of xylose reaction liquor by nanofiltration for the production of xylitol sugar alcohol Sep. Purif. Technol. 44 (2005) 221-228
- [11] A. L. Machsun, M. Gozan, M. Nasikin, S. Setyahadi, Y. J. Yoo, Membrane microreactor in biocatalytic transesterification of triolein for biodiesel production, Biotechnol. Bioprocess Eng., 15 (2010) 911-916
- [12] H. Yoon, E. J. Dell, J. L. Freyer, L. M. Campos, W.D. Jang, Polymeric supramolecular assemblies based on multivalent ionic interactions for biomedical applications, Polymer 55 (2014) 453-464
- [13] M. S. Silverstein, Emulsion-templated porous polymers: A retrospective perspective, Polymer 55 (2014) 304-320
- [14] N. Li, J. Du, L. Xu, J. Xu, T. Chen, Facile fabrication of hollow hydridosilica nanoparticles with mesoporous shell and their dual effect in Pd nanoparticles immobilization, Chem. Eng. J., 240 (2014) 161-168
- [15] S. De Santis, M. Diociaiuti, C. Cametti, G. Masci, Hyaluronic acid and alginate covalent nanogels by template cross-linking in polyion complex micelle nanoreactors, Carbohydrate Polymers, 101 (2014) 96-103
- [16] K. M. Ho, W. Y. Li, C. H. Wong, P. Li, Amphiphilic polymeric particles with core-shell nanostructures: emulsion-based syntheses and potential applications, Colloid Polym. Sci., 288 (2010) 1503-1523
- [17] E. Tang, S. Dong, Preparation of styrene polymer/ZnO nanocomposite latex via miniemulsion polymerization and its antibacterial property, Colloid Polym. Sci., 287 (2009) 1025-1032
- [18] H. Ma, C. Burger, B. S. Hsiao, B. Chu, Fabrication and characterization of cellulose nanofiber based thin-film nanofibrous composite membranes, J. Membr. Sci. 454 (2014) 272-282
- [19] M. M. Pendergast, R. M. Dorin, W. A. Phillip, U. Wiesner, E. M.V. Hoek, Understanding the structure and performance of self-assembled triblock terpolymer membranes, J. Membr. Sci., 444 (2013) 461-468
- [20] M. Mika, R.F. Childs, J.M. Dickson, B.E. McCarry, D.R. Gagnon, Porous, polyelectrolyte-filled membranes: Effect of cross-linking on flux and separation, J. Membr. Sci., 135 (1997) 81-92

- [21] B. Suthar, H. Xiao, D. Klempner, K Frisch, A review of kinetic studies on the formation of interpenetrating polymer networks. *Pol. Adv. Technol.* 7 (1996) 221-233
- [22] J. Nowers, B. Narasimhan, The effect of interpenetrating polymer network formation on polymerization kinetics in an epoxy-acrylate system. *Polymer* 47 (2006) 1108-1118
- [23] X. Hou, K. Siong, Novel interpenetrating polymer network electrolytes. *Polymer* 42 (2001) 4181-4188
- [24] L. Chikh, V. Delhorbe, O. Fichet, (semi-) interpenetrating polymer networks as fuel cell membranes. *J. Membr. Sci.* 368 (2011) 1-17
- [25] Y. Lipatov, Polymer blends and interpenetrating polymer networks at the interface with solids. *Prog. Polym. Sci.* 27 (2002) 1721-1801
- [26] P. Matricardi, C. Di Meo, T Coviello, W. Hennink, F. Alhanique, Interpenetrating Polymer Networks polysaccharide hydrogels for drug delivery and tissue engineering. *Adv. Drug Deliv. Rev.* 65 (2013) 1172-1187
- [27] M. Palencia, B. Rivas, E. Pereira, A. Hernandez, P. Pradanos, Study of polymer-metal ion-membrane interactions in liquid-phase polymer-based retention (LPR) by continuous diafiltration. *J. Membr. Sci.* 336 (2009) 128-139
- [28] M. Palencia, B. Rivas, E. Pereira, Metal ion recovery by polymer-enhanced ultrafiltration using poly(vinyl sulfonic acid): Fouling description and membrane-metal ion interaction, *J. Membrane Sci.* 345 (2009) 191-200
- [29] B. F. Urbano, B. L. Rivas, F. Martinez, S. D. Alexandratos, Water-insoluble polymer-clay nanocomposite ion exchange resin based on N-methyl-d-glucamine ligand groups for arsenic removal, *Reactive and Functional Polymers*, 72 (2012) 642-649
- [30] B. Rivas, E. Pereira, M. Palencia, J. Sanchez, Water-soluble functional polymers in conjunction with membranes to remove pollutant ions from aqueous solutions. *Progr. Polym. Sci.* 36 (2011) 294-322
- [31] A. Bhattacharya, J. W. Rawlins, P. Ray, Polymer grafting and crosslinking, John Wiley & Sons, New Jersey (USA), 2009, 341p
- [32] M. Cioffi, A.C. Hoffmann, L.P.B.M. Janssen, Reducing the gel effect in free radical polymerization, *Chemical Engineering Science*, 56 (2001) 011-915.