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Academician A. V. Bilyukevich¹, T. V. Plisko¹, A. S. Liubimova¹,
A. V. Penkova², M. E. Dmitrenko²

¹*Institute of Physical Organic Chemistry of the National Academy of Sciences of Belarus, Minsk, Republic of Belarus,*

²*Saint-Petersburg State University, Saint Petersburg, Russian Federation*

FULLERENOL-POLYAMIDE THIN FILM COMPOSITE HOLLOW FIBER MEMBRANES FOR LOW MOLECULAR WEIGHT CUT-OFF ULTRAFILTRATION

Abstract. Fullereneol C₆₀(OH)₂₄ was incorporated into a polyamide (PA) selective layer to develop novel thin film nanocomposite (TFN) hollow fiber membranes for low molecular weight cut-off ultrafiltration. TFN membranes were fabricated using the interfacial polycondensation technique by alternately pumping a fullereneol dispersion into the triethylenetetramine (TETA) aqueous solution and the isophthaloyl chloride solution into hexane through polysulfone hollow fiber membranes. The contact angle of the skin layer was found to decrease sharply from 34 to 21° when the concentration of fullereneol increases up to 0.5 wt. % in the TETA aqueous solution. Antifouling properties of the PA/fullereneol membranes were found to be superior to the initial membrane. The maximum fouling recovery ratio was observed for the TFN membrane with 0.3–0.75 wt. % of fullereneol in the TETA aqueous solution.

Keywords: hollow fiber membrane, thin film nanocomposite membrane, fullereneol, interfacial polymerization, fouling

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Академик А. В. Бильдюкевич¹, Т. В. Плиско¹, Е. С. Любимова¹, А. В. Пенькова², М. Е. Дмитренко²

¹*Институт физико-органической химии Национальной академии наук Беларуси, Минск, Республика Беларусь*

²*Санкт-Петербургский государственный университет, Санкт-Петербург, Российская Федерация*

ПОЛУЧЕНИЕ И СВОЙСТВА ТОНКОПЛОЧНЫХ КОМПОЗИЦИОННЫХ ПОЛОВОЛОКОННЫХ МЕМБРАН ДЛЯ УЛЬТРАФИЛЬТРАЦИИ С НИЗКИМ НОМИНАЛЬНЫМ МОЛЕКУЛЯРНО-МАССОВЫМ ПРЕДЕЛОМ ОТСЕЧЕНИЯ

Аннотация. Тонкопленочные композиционные мембраны (ТКМ) для ультрафильтрации с низким номинальным молекулярно-массовым пределом отсека были получены при введении добавок фуллеренола C₆₀(OH)₂₄ в селективный полиамидный (ПА) слой, сформированный методом межфазной поликонденсации при использовании в качестве подложки полволоконной ультрафильтрационной мембраны на основе полисульфона. Межфазную поликонденсацию с образованием тонкого полиамидного слоя проводили при последовательной фильтрации раствора триэтилентетрамина (ТЭТА) в воде и раствора изофталойлхлорида в гексане через полволоконную мембрану. При увеличении концентрации фуллеренола в водном растворе ТЭТА угол смачивания селективного слоя уменьшается с 34 до 21°. Показано, что устойчивость к засорению ТКМ ПА/фуллеренол выше, чем исходной немодифицированной мембраны. Мембраны, полученные с использованием 0,3–0,75 % дисперсий фуллеренола в растворе ТЭТА, характеризовались максимальным значением восстановления потока после фильтрации раствора лизоцима.

Ключевые слова: полволоконная мембрана, тонкопленочная композиционная мембрана, фуллеренол, межфазная поликонденсация, засорение мембран

Для цитирования: Получение и свойства тонкопленочных композиционных полволоконных мембран для ультрафильтрации с низким номинальным молекулярно-массовым пределом отсека / А. В. Бильдюкевич [и др.] // Докл. Нац. акад. наук Беларуси. – 2018. – Т. 62, № 2. – С. 185–192. DOI: 10.29235/1561-8323-2018-62-2-185-192

Introduction. Thin film composite membranes (TFC) are the most frequently used membranes for reverse osmosis (RO), forward osmosis (FO) and nanofiltration (NF). TFC membrane typically consists of a dense, amorphous and very thin (<0.2 μm) active polymer layer formed on the porous support [1]. Most TFC are composite membranes with skin barrier layer prepared from polyamide (PA) which is created by the interfacial polymerization (IP) between two reactive monomers on the top of a porous sup-

port membrane [2]. Besides the trade-off between permeation and rejection the main shortcoming of operating TFC is membrane fouling which may involve pore blocking, plugging and clogging, chemical degradation, cake and film formation on the membrane surface caused by microorganisms, organic matter and inorganic material. The result is always a reduction of the membrane performances in terms of permeability, selectivity and longevity [3].

Nowadays, the main challenge in designing TFC membranes is increasing the membrane fouling resistance without sacrificing membrane performance. In order to avoid the fouling of TFC membranes, chlorine is commonly used as a disinfectant, however this may lead to several harmful side products due to the degradation of the polyamide skin layer [4]. The most effective approaches to increase the fouling resistance of TFC membranes is to improve the hydrophilicity and charge properties of membrane skin layer, to change surface roughness, and to utilize steric repulsion effects [5].

Modification of TFC by using nanoparticles is a novel approach in design of low-fouling membranes yielding in fabrication of thin film nanocomposite membranes (TFN). The advantages of this modification technique include the possibility to incorporate nanoparticles directly into the thin skin layer without altering the existing procedure of TFC membrane production by IP technique and the opportunity of varying type of nanofiller in terms of nature, dimensions, porosity, charge and tailored functionalities [5; 6]. The significant effect of nanoparticle incorporation on the degree of cross-linking, thickness and structure of a skin PA layer as well as on its hydrophilicity, surface roughness and charge has been reported [7; 8]. To enhance antifouling resistance of TFC membranes in terms of scaling resistance and biofouling resistance in RO, FO and NF silver [4], silica, titania and zinc oxide [9] nanoparticles, halloysite nanotubes [10], graphene oxide, clay nanosheets and oxidized multiwalled carbon nanotubes [11] were incorporated into the PA layer.

In this study a novel highly hydrophilic nanofiller -fullerenol $C_{60}(OH)_{22-24}$ - to enhance antifouling resistance of TFC PA membranes is proposed. The main objective of this study was the enhancement of antifouling performance of hollow fiber thin film composite membranes by introduction of fullerenol into the PA skin layer. The novelty of this work is that for the first time fullerenol was used for the modification of PA TFC membranes and the effect of fullerenol concentration in the triethylenetetramine aqueous solution on the structure, performance and antifouling resistance as well as, hydrophilic/hydrophobic balance of the skin layer was studied. However, to the best of our knowledge, no study on the incorporation of fullerenol into the thin PA layer of TFC membranes has been reported yet.

Experimental. Polysulfone (PSF) hollow fiber membrane was prepared in the Institute of Physical Organic Chemistry of the NAS of Belarus using a lab-scale spinning line which described in detail in [12]. The characteristics of PSF hollow fiber membranes (PS-100) are presented in Table 1. Polyvinylpyrrolidone PVP K-15 ($M_n = 1 \cdot 10^4 \text{ g} \cdot \text{mole}^{-1}$) (Fluka) and PVP K-30 ($M_n = 4 \cdot 10^4 \text{ g} \cdot \text{mole}^{-1}$) were used as organic reference solutes for UF experiments. Lysozyme from chicken egg white ($M_w = 14.3 \cdot 10^3 \text{ g} \cdot \text{mole}^{-1}$, isoelectric point of pH 11.35) (Sigma-Aldrich) was used as a foulant in the experiments on assessment of antifouling performance.

Table 1. Characteristics and performance of the PSF hollow fiber membrane

Membrane characteristics	PS-100	PSF-PA
Inner diameter, mm	1.0	1.0
Outer diameter, mm	1.5	1.5
Water flux at $P = 0.1 \text{ MPa}$, $\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$	330	46
Rejection (PVP K-15), %	15	82
Rejection (PVP K-30), %	52	>99
Contact angle, °	45 ± 2	34 ± 2

To modify the hollow fiber membranes by interfacial polycondensation (IP) technique the following reagents were used: triethylenetetramine (TETA, $\geq 99\%$, Sigma-Aldrich), isophthaloyl chloride (IPC, $\geq 99\%$, Sigma-Aldrich). For the preparation of TETA solutions deionized water (Milli-Que, Millipore) was used; as an organic solvent for IPC, hexane ($\geq 99\%$, Kriohrom) was used.

Thin film composite membranes (TFC) were prepared via formation of the ultrathin polyamide (PA) layer by interfacial polymerization (IP) technique on the surface of the skin layer (inside the lumen of hollow fiber membranes). A technique and laboratory equipment for the modification of hollow fiber «inside-out» filtration mode membranes by the IP method have been developed previously [13].

Formation of the thin PA layer was shown not to change membrane dimensions compared to the initial PS-100 membrane (Table 1). It was shown that pure water flux (PWF) and rejection coefficient (R) are significantly affected by the formation of the additional PA skin layer. Pure water flux was found to decrease from $330 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ to $46 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ as well as PVP K-15 and PVP K-30 rejection coefficients were found to increase from 15 to 82 % and from 52 to >99 % respectively (Table 1). The membrane modification by IP technique was revealed to yield in the decreasing the contact angle of the skin layer by 11° due to the formation of hydrophilic PA skin layer on the inner surface of UF membrane (Table 1).

TFN membranes were prepared by incorporation of fullerene into the PA skin layer of TFC membranes. To produce TFN membranes fullerene was dispersed in 0.3 wt. % TETA aqueous solution by sonication in ultrasonication bath for 180 min (Figure 1). Composition, fullerene loading and abbreviations of the prepared TFN membranes are presented in the Table 2.

Average particle size and particle size distribution in 0.5 wt. % fullerene dispersion in 0.3 wt. % TETA aqueous solution were determined by dynamic light scattering (DLS) (Zetasizer Nano, Malvern, UK).

Membrane performance was estimated at an average transmembrane pressure of 1.0 bar. For individual hollow fiber membranes, the flux [J , $\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$] was measured using a custom made filtration system operating in the cross-flow mode described in [12]. Pure water flux (J_0) and solute rejection coefficient (R) were calculated according to [12].

Membrane rejection was assessed using $0.3 \text{ g}\cdot\text{L}^{-1}$ aqueous solution of PVP K-15 and PVP K-30 as a model solution. PVP concentration was measured using an LIR-2 interferometer (Zagorsk Optical and Mechanical Plant, Russia).

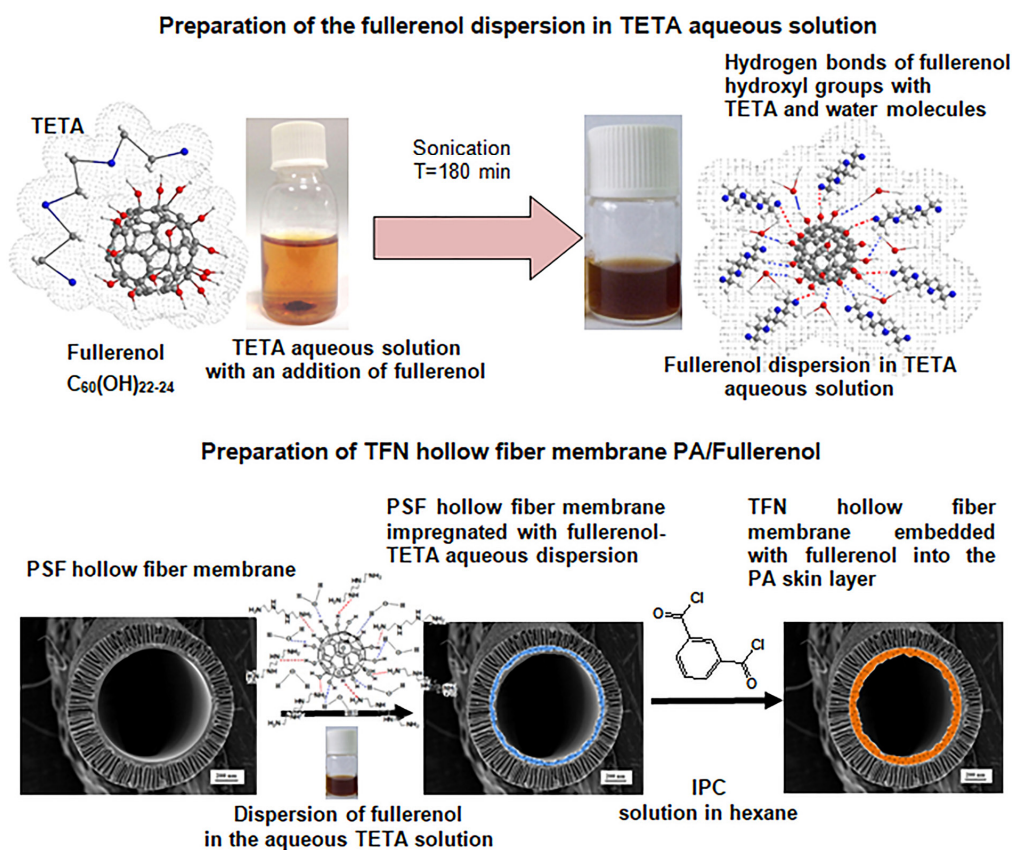


Fig. 1. Schematical representation of the preparation of TFN hollow fiber membranes embedded with fullerene in the PA skin layer

Table 2. Composition, performance and contact angle of the TFC and TFN membranes

Sample abbreviation	Concentration of fullereneol in aqueous phase, mass. %	PWF, L·m ⁻² ·h ⁻¹	R (PVP K-15), %	R (lysozyme), %	Contact angle, °
PSF-PA	0	46	82	69	34 ± 2
F-0.05	0.05	42	83	69	32 ± 2
F-0.1	0.10	42	82	68	30 ± 2
F-0.3	0.30	33	88	71	24 ± 2
F-0.5	0.50	36	88	71	22 ± 2
F-0.75	0.75	35	88	72	21 ± 2
F-1.0	1.00	33	88	76	21 ± 2
F-1.5	1.50	36	88	74	21 ± 2

Membrane rejection was also determined using the 0.4 g·L⁻¹ solution of lysozyme in phosphate buffer (0.05 M, pH 7.0). The protein contents were analyzed with UV–Vis spectrophotometer (Metertech UV–VIS SP 8001) at a wavelength of 280 nm.

Structure of the inner surface of the samples was studied on an HT-206 atomic force microscope (MicroMash, Estonia).

In the experiments on the assessment of antifouling performance, lysozyme (0.4 g·L⁻¹ aqueous solution) was used as a protein foulant. The experiments were performed according to the following procedure. The membranes were compacted at 1.0 bar for 30 min and the pure water flux (J_0) was measured at the transmembrane pressure of 1.0 bar for 30 min. Then, the foulant-containing aqueous solution was filtered through the membranes at the same transmembrane pressure for 2 h and the foulant solution flux (J_p) was measured. The fouled membranes were washed by deionized water for 0.5 h in the ultrafiltration process and the pure water flux of the washed membranes (JWF) was measured. This procedure was repeated 2 times. Antifouling performance of the prepared membranes was estimated by the flux recovery ratio (FRR) (Eq. 1), reversible flux decline ratio (DR_r) (Eq. 2), irreversible flux decline ratio (DR_{ir}) (Eq. 3) and total flux decline ratio (DT) (Eq. 4) [12].

$$\text{FRR} = \left(\frac{\text{JWF}}{J_0} \right) 100 \% \quad (1)$$

$$\text{DR}_r = \left(\frac{\text{JWF} - J_p}{\text{PWF}} \right) 100 \% \quad (2)$$

$$\text{DR}_{ir} = \left(\frac{\text{PWF} - \text{JWF}}{\text{PWF}} \right) 100 \% \quad (3)$$

$$\text{DT} = \left(\frac{J_0 - J_p}{J_0} \right) 100 \% \quad (4)$$

Results and Discussion. *Characterization of fullereneol aqueous dispersions.* Fullereneol dispersions were prepared by addition of 0.05–1.5 wt. % of fullereneol in 0.3 wt. % TETA aqueous solution. The dispersions were shown to be stable over 1 month excluding the dispersion with the fullereneol concentration of 1.5 wt. %.

It was reported [14] that even highly diluted fullereneol aqueous solutions are strongly associated. In our case the bimodal particle size distribution of the 0.5 wt. % fullereneol dispersion in TETA aqueous solution was found. The size of 94 vol. % of particles in the dispersion are distributed between 14 and 59 nm with the maximum at 21 nm. The remaining 6 vol. % of fullereneol associates were revealed to be much larger with the diameter distributed from 90 to 340 nm with a maximum at 190 nm.

Thus, one can conclude that fullereneol forms stable polydisperse systems in TETA aqueous solutions with high dispersion degree which can be applied for TFN membrane fabrication by IP technique.

Analysis of the effect of fullereneol loading on membrane permeability allows concluding that membrane modification by fullereneol leads to the formation of the membranes with lower pure water flux and higher rejection which indicates the changes in the structure of PA skin layer (Table 2).

Modification of thin film composite membrane by fullereneol was revealed to enhance the hydrophilicity of the PA skin layer which is proved by the contact angle decrease (Table 2). The concentration

of 0.3 wt. % of fullerene in the aqueous phase is considered to be the threshold after which a significant effect of fullerene on the performance and membrane hydrophilicity is observed. When the fullerene concentration reaches 0.3 wt. % PWF, rejection coefficients and contact angle change essentially compared to the unmodified PSF-PA membrane. The lowest contact angle of 22–21° is observed for the fullerene concentration of 0.5–1.5 wt. % for F-0.5, F-0.75, F-1.0 and F-1.5 membranes.

AFM studies of the skin layer surface reveal that typical ridge-and-valley structure is observed for all studied membranes. Table 3 reveals the statistical roughness information in terms of root-mean-squared surface roughness (R_q) and average roughness (R_a) at a scan size of $5 \times 5 \mu\text{m}$. These roughness characteristics can strongly affect the adsorption/desorption of foulants on the membrane surface and control the membrane fouling. Incorporation of the fullerene to the PA layer was shown to change the surface significantly yielding in the formation of agglomerates in the ridges which border the pore orifices. Average surface roughness increases tenfold and root-mean-squared roughness – approximately 8-fold upon introduction of 0.05 wt. % of fullerene to the TETA aqueous solution. The R_q and R_a parameters are decreased when the concentration of fullerene is increased up to 0.5 wt. % and after that, by further increasing of fullerene content, the roughness parameters are slightly increased (Table 3).

Table 3. Surface parameters of the PS-100, TFC and TFN hollow fiber membranes prepared using different concentration of fullerene in the aqueous phase

Sample abbreviation	R_a (nm)	R_q (nm)
PS-100	1.7	2.7
PSF-PA	2.4	4.4
F-0.05	24.9	35.9
F-0.1	20.0	24.9
F-0.3	16.2	20.7
F-0.5	9.9	12.3
F-0.75	13.6	17.5
F-1.0	11.4	16.3
F-1.5	14.7	18.4

Figure 2 shows the normalized flux decline of the membranes during the lysozyme solution filtration experiments. When contacted with the fouling feed solution of lysozyme, the membrane permeate flux was prone to decrease due to the deposition of foulants onto the surface. However, as seen from the Fig. 2,

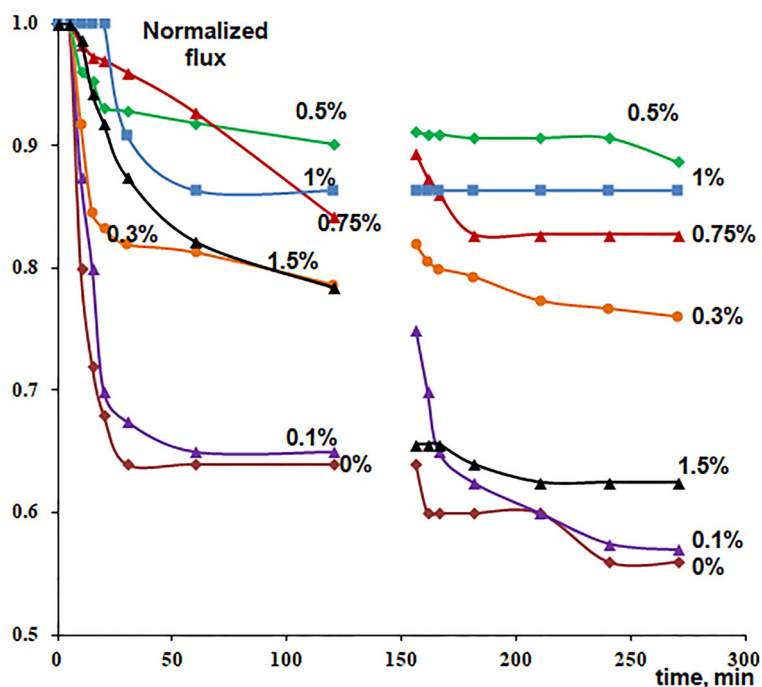


Fig. 2. Flux decline trends for the TFC and TFN membranes during the filtration of lysozyme solution

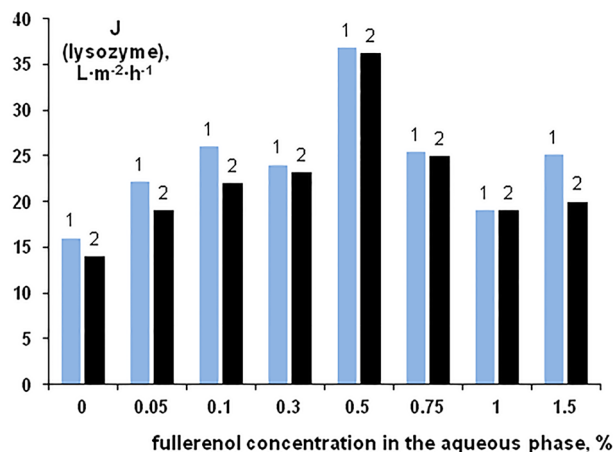


Fig. 3. Fouling (lysozyme) solution flux after the 1 cycle (1) of filtration (120 min) and after the 2 cycle (2) of filtration (120 min) for TFC and TFN membrane with different fullerene concentration in the aqueous phase

the normalized flux decline for membranes embedded with fullerene was much lower compared to the pristine PSF-PA membrane. The highest normalized flux after two filtration cycles is observed for F-0.5 (0.89) membrane, which is much higher than for the pristine TFC membrane (0.56). This means the changes of the fouling behavior of membranes upon the incorporation of fullerene to the PA layer. Figure 3 illustrates the effect of different concentration of fullerene in the aqueous phase on the lysozyme flux of the membranes after 120 min filtration of lysozyme solution during the first and second filtration cycles. As shown in Fig. 3, the lysozyme flux after 120 min filtration was 16 L·m⁻²·h⁻¹ for the PSF-PA membrane, whereas this value was much higher for the membranes containing fullerene and depends on its concentration in aqueous phase. Lysozyme solution flux was found to have the maximum value at the fullerene concentration of 0.5 wt. % in the aqueous phase.

To investigate the antifouling property of the membranes in detail, the fouling parameters of the membranes during the first and second filtration cycles were calculated and presented in Table 4. The FRR value of the PSF-PA membrane was 54 % after the first cycle of filtration and decreases up to 49 % after the second (Table 4). For membranes F-0.05 FRR value increased to 79 and 72 %, respectively for the first and second filtration cycle. Upon the further increase of fullerene concentration FRR significantly increases and reaches maximum (93 and 91 % for the 1st and 2^d filtration cycle respectively) for F-0.5 membrane (Fig. 4, Table 4). The best antifouling performance showed membranes F-0.3, F-0.5 and F-0.75 in the first and the second filtration cycles. It can be found from Fig. 2, 3 that F-0.5 membrane has the highest lysozyme solution flux after 2 cycles of the filtration.

Table 4. Fouling parameters of the TFC and TFN membranes

Sample abbreviation	FRR, %		DR _p , %		DR _{ir} , %		DT, %	
	1 cycle	2 cycle	1 cycle	2 cycle	1 cycle	2 cycle	1 cycle	2 cycle
PSF-PA	54	49	14	32	38	38	52	70
F-0.05	79	72	36	29	17	26	50	55
F-0.1	86	83	33	31	13	17	48	48
F-0.3	89	88	18	18	9	12	30	30
F-0.5	93	91	6	13	6	13	13	12
F-0.75	89	86	17	14	9	14	29	29
F-1.0	85	76	27	18	11	24	42	42
F-1.5	70	67	29	11	12	33	44	44

It was found that fullerene incorporation yields in the decrease of total flux decline ratio of the membranes with the minimum at F-0.5 (13 % in the first filtration cycle) and F-0.3 (12 % in the second filtration cycle) (Table 4). The irreversible flux decline ratio was found to increase more than twice when 0.05 and 0.1 % of fullerene is added to the aqueous phase. However with the further increase of fullerene concentration DR_{ir} decreases gradually and reaches its minimum (6 %) at the concentration of fullerene 0.5 % in the 1st filtration cycle and 12–14 % for 0.1–0.5 % of fullerene for the 2nd filtration cycle. Reversible fouling was revealed to decrease significantly upon the fullerene incorporation to the PA layer and have the minimum of 6 % for F-0.5 membrane in the 1st filtration cycle and 11–14 % for F-0.3, F-0.5 and F-1.0 membranes in the 2^d filtration cycle.

The significant differences in antifouling capability of membranes are due to the differences in the membrane surface characteristics: surface roughness and hydrophilicity (contact angle). Figure 4 demonstrates the correlation between FRR, average roughness and contact angle of TFC and TFN membranes with different fullerene loading. Upon the addition of the low concentration of fullerene (0.05–0.1 wt. %) to the aqueous phase R_a increases significantly from 2.4 to 24.9 and 20 respectively and contact angle slightly decreases by 2–4° (Table 2, 3, Fig. 4). However, the improved hydrophilicity results in the significant increase of lysozyme solution flux (J_p) and FRR and decrease of DT and DR_{ir} for F-0.05 and F-0.1 membranes (Fig. 2–4, Table 4). The increased surface roughness yields in the sharp increase of reversible fouling ratio because of the accumulation of protein in the «valleys». Upon the further increase of fullerene up to 0.3–0.5 wt. % the correlation between surface parameters changes: surface roughness and contact angle decrease to a great extent and reach their minimum compared to the other TFN membranes loaded with fullerene (Fig. 4). The improved antifouling performance of the F-0.5 membranes can be attributed to the higher degree of hydrophilicity (contact angle $21 \pm 2^\circ$) and the lower average roughness of the membrane surface (9.9 nm). The improvement of membrane hydrophilicity (Table 2) reduces membrane fouling by influencing the surface adsorption characteristics of the membrane. However, as shown in Table 3, the surface of PSF-PA membrane represented the smoothest structure (the lowest roughness parameters), but its contact angle is 12° higher compared with F-0.5 membrane (Table 2). Thus, the fouling resistance of PSF-PA membrane is low compared to TFN membranes. Also, the observed the highest J_p and FRR, and the lowest DR_{ir} and DT trends are in an agreement with the lowest roughness parameters and highest hydrophilicity of the F-0.3–F-0.5 membranes (Fig. 2–4, Table 2–4).

Conclusions. For the first time fullerene $C_{60}(OH)_{22-24}$ was incorporated into the thin PA layer and hollow fiber TFN membranes for ultrafiltration with low-molecular weight cut-off were fabricated by IP technique. Contact angle of the skin layer was found to decrease sharply from 34 to 21° when the concentration of fullerene increases, due to the high density of hydrophilic hydroxyl groups of fullerene. TFN membranes with fullerene addition were found to have the superior antifouling performance compared to the initial membrane. Lysozyme solution flux and FRR increased upon fullerene introduction and passed through the maximum at the concentration of fullerene of 0.5 wt. %. DR_{ir} and DT were revealed to decrease when fullerene was added and passed through the minimum value at fullerene concentration 0.3–0.75 wt. %. These fouling parameters trends are in good agreement with the combination of hydrophilicity and roughness trends of the PA skin layer.

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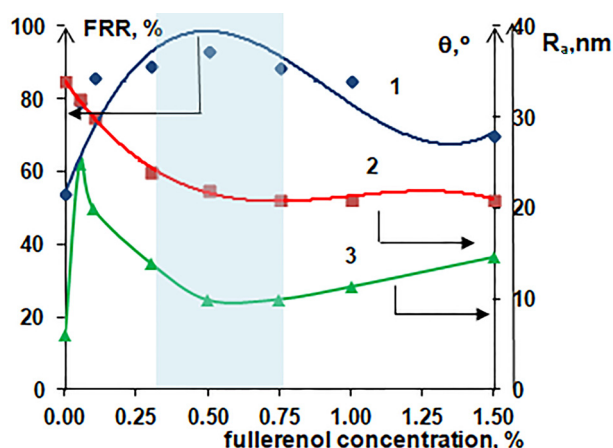


Fig. 4. Correlation between FRR (1), contact angle (θ) (2) and average roughness (R_a) (3) of the skin layer of TFC and TFN membranes versus fullerene concentration. Blue region is the fullerene concentration region with the highest antifouling resistance of the TFN membranes due to the combination of the lowest contact angle and lowest average roughness compared to other TFN membranes

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Information about the authors

Bilydukevich Alexandr Victorovich – Academician, D. Sc. (Chemistry), Professor, Director. Institute of Physical Organic Chemistry of the National Academy of Sciences of Belarus (13, Surganov Str., 220072, Minsk, Republic of Belarus). E-mail: uf@ifoch.bas-net.by.

Plisko Tatiana Victorovna – Ph. D (Chemistry), Senior researcher. Institute of Physical Organic Chemistry of the National Academy of Sciences of Belarus (13, Surganov Str., 220072, Minsk, Republic of Belarus). E-mail: plisko.v.tatiana@gmail.com.

Liubimova Alena Sergeevna – Researcher. Institute of Physical Organic Chemistry of the National Academy of Sciences of Belarus (13, Surganov Str., 220072, Minsk, Republic of Belarus). E-mail: liubimova_elena@mail.ru.

Penkova Anastasia Vladimirovna – Ph. D. (Chemistry), Associate Professor. Saint-Petersburg State University (7–9, Universitetskaya Emb., 199034, Saint Petersburg, Russian Federation). E-mail: a.penkova@spbu.ru.

Dmitrenko Mariia Evgen'evna – Assistant. Saint-Petersburg State University (7–9, Universitetskaya Emb., 199034, Saint Petersburg, Russian Federation). E-mail: dmitrenko.me@mail.ru.

Информация об авторах

Бильдюкевич Александр Викторович – академик, д-р хим. наук, профессор, директор. Институт физико-органической химии НАН Беларуси (ул. Сурганова, 13, 220072, Минск, Республика Беларусь). E-mail: uf@ifoch.bas-net.by.

Плиско Татьяна Викторовна – канд. хим. наук, ст. науч. сотрудник. Институт физико-органической химии НАН Беларуси (ул. Сурганова, 13, 220072, Минск, Республика Беларусь). E-mail: plisko.v.tatiana@gmail.com.

Любимова Елена Сергеевна – науч. сотрудник. Институт физико-органической химии НАН Беларуси (ул. Сурганова, 13, 220072, Минск, Республика Беларусь). E-mail: liubimova_elena@mail.ru.

Пенькова Анастасия Владимировна – канд. хим. наук, доцент. Санкт-Петербургский государственный университет (Университетская наб., 7–9, 199034, Санкт-Петербург, Российская Федерация). E-mail: a.penkova@spbu.ru

Дмитренко Мария Евгеньевна – ассистент. Санкт-Петербургский государственный университет (Университетская наб., 7–9, 199034, Санкт-Петербург, Российская Федерация). E-mail: dmitrenko.me@mail.ru.