

Effect of human body secretions in pool water on the transport and separation properties of polymer membranes

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Received 16 September 2019; Accepted 27 November 2019

ABSTRACT

In this study, we analyzed the effect of human body secretions on the transport and separation properties of membranes with high distribution properties (nanofiltration/reverse osmotic membranes). The problem of low molar mass disinfection by-products is an important issue from the point of view of public health. Therefore, it is necessary to take measures to modernize the pool water treatment circuits in-line with low-waste technologies. The pressure membrane processes presented in this study were characterized by the higher retention of impurities which is characteristic of pool water (e.g., urea, creatinine, and uric acid). In addition, the transport properties of pool water were found to be good with polyamide reverse osmosis (AFC80) membrane, which was slightly altered during the filtration cycles. It should be emphasized that an important factor that allowed to maintain high values of the volumetric permeate flux was the periodic replenishment of the feed with a fresh dose of tap water. Creatinine potentially contributes to the blocking of AFC80 membrane pores. In this study, citric acid (1% solution) was not effective in cleaning the reverse osmosis membranes.

Keywords: Swimming pool water; Nanofiltration; Body fluids analogs; Water treatment; Total organic carbon; Pressure-driven membrane processes; Cross-flow system

1. Introduction

It is assumed that during the disinfection of pool water, some of the molecules of chlorine destroy the bacteria, some get oxidized to organic compounds, some remain unbound, and the rest form chloramines (analyzed in the bound chlorine parameter) by combining with ammonium nitrogen [1]. However, the presence of chloramines is not the only problem with respect to the quality of swimming pool water. Trihalogenomethanes (THMs) (total concentration of trichloromethane, bromodichloromethane, dibromochloromethane, and tribromomethane) are also frequently reported to be high in pool water. THMs are produced when chlorine and natural and/or anthropogenic organic matter react in pool water [2–4].

It is necessary to perform quality control tests such as physicochemical and microbiological analysis of pool

water, but these tests do not give full information about the presence of other pollutants in the pool water, including disinfection by-products (DBPs) and their precursors [3,5]. The following factors favor the formation of DBPs: pH of the treated water; its turbidity (amount of suspension); temperature; concentration of natural and anthropogenic organic matter (determined in the form of organic carbon concentration); bromine ion concentration; and type of disinfectant, its concentration and contact time with water [3,6–10]. Most of these factors are analyzed indirectly by measuring the physicochemical parameters. Pool water quality tests have so far focused on THMs, but compounds such as cyanide halides, haloacetic acids (HAAs), haloacetonitriles are increasingly gaining importance in the quality testing of pool water [4,11]. It is estimated that the quantitative fraction of HAA in the pool water is higher than that of THMs, and their concentration does not correlate with the number of bathers; therefore, it can often be difficult to estimate [12,13].

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Anthropogenic pollution is the primary factor that contributes to the deterioration of water quality in the pool basin, which is introduced directly into the basin. DBPs are formed when bathers introduce organic material into the pool which will react with chlorine; chlorination is a continuous process of pool water treatment (also UV irradiation) [5,14,15]. Depending on the sources, it is estimated that a single bather can secrete approximately 25–77 cm³ of urine and 200–1,000 cm³ of sweat into the pool water along with numerous organic compounds [9,16]. Urea is also released through the skin (it is noteworthy that the surface of the skin contains approximately 8 mg/cm² of urea) [9].

The concentration and composition of the predecessors of DBPs associated with human body secretions strongly depends on the number of people using the basin (this value is usually given as the number of people per hour or per surface area), their hygiene status, and the destination of the pool (swimming, children's recreational hot tub, and others) [48]. Swimming pool water not only contains urea and ammonia but also contains uric acid, creatinine, creatine, lactic acid, citric acid, hippuric acid, uracil, ornithine, chlorides, sulfates, cations (K⁺, Na⁺, Ca²⁺, Mg²⁺, Zn²⁺), and amino acids [5,17–19].

The following additional parameters describe the relationship between water quality and the presence of DBPs: dissolved and total organic carbon (DOC and TOC), total nitrogen, organic nitrogen (taking into account the importance of the moieties present in the urea), total dissolved substances and the absorbance value measured at 254 nm (UV₂₅₄) [20–22]. The amount of carbon compounds present in the pool water depends on the load of bathers in the basin. Contaminants associated with human body secretions introduced into the pool water are the main causes of DBPs. Therefore, the content of TOC shows a strong correlation with human body secretions in the pool water [20,22,23].

Although many of the DBPs can be found at concentrations below 1 mg/dm³ in the pool water samples, their presence may be harmful to people who use such swimming pools [24]. A high rate of genotoxicity has been found to be associated with the low molar mass of DBPs [25–27]. Most UPDs have a molar mass below 1000 g/mol [14,28].

The health benefits that result from regular swimming can only be achieved by reducing adverse effects from DBPs. Although the filtration of residual deposits in the pool water treatment circuits is accompanied by the process of surface coagulation, the efficiency of removing small-molecular contaminants is low (approximately 20%) [26,29]. In addition, many objects will have single-layer residual deposits that do not provide complete removal of pathogenic microorganisms [30].

An alternative to classic swimming pool water treatment systems can be pressure-driven membrane processes that combine high efficiency in removing slurries, microorganisms, DBPs, and micro-pollution [26,31–33]. The knowledge collected about DBPs shows that the removal of aforementioned impurities requires the use of membranes with a low molecular weight limit cut-off (MWCO), a minimum 1,000 Da [31]. The process of nanofiltration (NF) is characterized by a high degree of removal of natural organic matter and THM precursors; therefore, it could be used in the specialized purification system of pool water [34].

The rapid decrease in the transport capacity of the membrane caused by the blockage of the pores by organic compounds is a well-known obstacle in the application of the NF for the purification of pool water [35–37]. Fouling of the membrane increases the operating costs, which reduces the membrane's performance. In addition, frequent cleaning of membranes decreases their separation properties, which leads to the shortening of life of the epidermal layer, which is extremely important in the process of NF using asymmetric membranes [32,38]. Due to the microbiological risk and the need to chlorinate pool water, the factor that should be paid special attention is the sensitivity of membranes to chlorine [39,40]. Sodium hypochlorite has shown great potential as a membrane cleaner [23].

Therefore, in this study, we aimed to analyze the effect of the mixture of chemical compounds from the group of human body secretions (body fluids analogs [BFAs]) on the transport and separation properties of selected membranes with distribution capacities from the border of NF and reverse osmosis. The influence of the theoretical dose of BFA generated by the users of the swimming pool during the course of swimming on the volumetric permeate flux was examined. Furthermore, changes in the concentration of selected physicochemical parameters of pool water quality in the process of periodic dosing of the mixture.

2. Materials and methods

2.1. Physicochemical analysis

Total carbon (TC) and TOC in tap water (matrix) samples, model solutions, feeds, and permeates were measured using a TOC-L series analyzer by catalytic oxidation combustion at 680°C (Shimadzu). The UV₂₅₄ values were measured using the UV VIS Cecil 1000 from Analytik Jena AG, with an optical path length of the cuvette (d) equal to 1 cm. The UV₂₅₄ value was determined based on the measurement method presented by the United States Environmental Protection Agency [41], and the final result of the analysis is presented as per meter. Turbidity was measured using EUTECH Instruments model Turbidimeter TN-100. The pH and redox potential in tap water samples, model solutions, and feeds were measured with a multi-parameter inoLab® 740 meter (WTW, Measuring and Analytical Technical Equipment). Total and free chlorine were estimated with a colorimetric method using a portable Pocket Colorimeter II Device™ (Hach®, Loveland, CO, USA).

2.2. Composition of BFA solution

BFA solution was prepared according to the literature [19,42]. All chemical reagents (BFA components) were of analytical grade (98%–99% purity, Sigma–Aldrich); no additional purification was performed (dissolved in deionized water [DEMw; pH = 9.2]). Table 1 presents the concentration of the analyzed compounds in the model solution. The analyzed doses of the model solution were determined based on the German standard DIN 19643 [43] (according to which one bather should have an area of 4.5 m² of water surface at his disposal). Based on the analysis of the swimming pool case with standard cubic capacity (530 m³). The procedures were followed based on the previous report [44].

Table 1
Concentration of body fluid analogs (BFAs) in the model solutions

Compounds of BFA solution	CAS number ^a	Concentration in the stock solution ^b , mg/L	Concentration of BFA in one dose ^c , mg/L
Urea	57–13–6	14,800	0.0592
Ammonium chloride	12125–02–9	2,000	0.0080
Creatinine	60–27–5	1,800	0.0072
Hippuric acid	495–69–2	1,710	0.0068
L-histidine	71–00–1	1,210	0.0048
Sodium phosphate dibasic	7558–79–4	4,300	0.0172
Citric acid	77–92–9	640	0.0026
Uric acid	69–93–2	490	0.0020

^aCAS number (also CAS Registry Number) is a unique numerical identifier assigned by the Chemical Abstracts Service (CAS) to every chemical substance described in the open scientific literature.

^b25 mL of solution corresponds to the volume introduced by a single bather during an hour of physical activity.

^c4 µg/L is a single dose introduced during the tests.

Since the usual source of supply for the swimming pool water circuit is tap water, it was used as a matrix for the analyzed pollutants. Table 2 summarizes the results of the physicochemical analysis of the fresh tap water (taken in a laboratory).

2.3. Methodology of the membrane filtration processes

Membrane filtration was conducted in a cross-flow system using pipe membranes made of polyamide film (Table 3). We selected AFC30 and AFC80 membranes for the purification process as they are hydrophilic and their resolution is high enough that they can remove small molecules associated with human body secretions. The AFC80 membrane was characterized by slightly higher retention [45,46]. This allowed to compare the potential of processes on the border of NF and reverse osmosis to remove BFA compounds. Different properties of the tested membranes should also be expected in the case of transport properties (their permeability). The filtration circuit was entirely made of steel and equipped with a pipe module adjusted to polymer membranes with an active surface of 240 cm², an intermediate tank with a volume of 15 L, a high-pressure pump with a capacity between 0.5 and 3.0 m³/h (type CRN 3; produced by Grundfos), and a control and measurement apparatus. The temperature of the filtered water was kept at a constant level of 18°C ± 2°C. The flow rate in the cross-flow system was maintained at 500 L/h. Fig. 1 shows the picture of the filtration system.

The membranes were analyzed by performing pressure tests (in the range of 0.2–1.0 MPa) and temperatures tests (from 16°C to 40°C) and by determining their effect on the volume of deionized water stream (Figs. 2 and 3). It is noteworthy that the pool water in the circulation was found to have elevated temperature (26°C to even 38°C). In the case of both membranes, a marked increase in the volume value of the deionized water stream was noted with increasing temperature and transmembrane pressure (TMP; Figs. 2 and 3). The volume of the stream of deionized water during filtration with the AFC80 membrane in the pressure range from 0.2 to 1.0 MPa increased from 0.42 to 4.05 × 10⁻⁶ m³/m²s

Table 2
Physicochemical properties of body fluid analog solution for the nanofiltration process

Parameter	Value in the tap water matrix
pH	7.65
Redox potential, mV	198
Turbidity, NTU	0.10
UV ₂₅₄ , m ⁻¹	0.80
Free chlorine, mgCl ₂ /L	0.10
Total chlorine, mgCl ₂ /L	0.52
Total organic carbon ^a , mgC/L	0.00
Total carbon ^a , mgC/L	57.95
Total nitrogen, mgN/L	>0.20

NTU, nephelometric turbidity unit.

^aAverage value of all conducted determinations (eight times).

Table 3
Characteristics of the membranes (manufacturer data)

Membrane type	AFC30	AFC80
Type of process	Nanofiltration	Reverse osmosis
Manufacturer	PCI Membrane System Inc.	
Membrane material	Polyamide	
Max. membrane, °C	60	70
Max. pressure, bar	60	60
pH range	1.5–9.5	1.5–10.5
Nominal retention character	75% CaCl ₂	80% NaCl
Membrane area, cm ²	240	240

(Fig. 2a). At TMP equal to 1.0 MPa (in the temperature range of 16°C–40°C), the volume of the deionized water stream increased from 3.47 to 6.71 × 10⁻⁶ m³/m²s (Fig. 2b). Analogous relations were observed for the AFC30 membrane, but its transport properties in the tested pressure range were lower. The volume of deionized water during filtration with the AFC30 membrane in the pressure range from 0.2



Fig. 1. Cross-flow filtration system: 1—water coat, 2—manometer, 3—thermometer, 4—flowmeter, 5—regulating valves, 6—high-pressure pump, 7—control box with an inverter, 8—tank, 9—drain from the tank, 10—membrane module, 11—permeate outlet.

to 1.0 MPa increased from 0.18 to $1.34 \times 10^{-6} \text{ m}^3/\text{m}^2\text{s}$ (Fig. 3a). At TMP equal to 1.0 MPa (in the temperature range of 16°C – 40°C), the volume of deionized water stream increased from 0.81 to $3.59 \times 10^{-6} \text{ m}^3/\text{m}^2\text{s}$ (Fig. 3b). For the conditions of interest (TMP = 1 MPa, temperature $18^\circ\text{C} \pm 2^\circ\text{C}$), the volume of permeate flux was about $1.10 \times 10^{-6} \text{ m}^3/\text{m}^2\text{s}$ for AFC30 membrane and about $2.18 \times 10^{-6} \text{ m}^3/\text{m}^2\text{s}$ for AFC80 membrane. However, there were differences in individual values between individual tests, and thus in the stability of filtration conditions.

The membranes (conditioned with deionized water) were subjected to tests at a constant TMP of 1 MPa. The predetermined doses of BFA solution ($4 \mu\text{g}/\text{L}$) were dosed into the feed (tap water). The research was divided into several stages.

The first stage of research (using AFC80 membranes) included three filtration cycles (duration of each was 12 h). During Cycle 1, the feed in the tank was periodically topped up with a dose of fresh tap water (1 L), and in Cycle 2, the dose of freshwater was halved. In Cycle 3, however, only the BFA solution was periodically dispensed. In this way, we intended to check whether there is any effect of dispensing fresh water to the system on the value of the tested separation parameters (TOC, TC, UV_{254} and turbidity) and a change in

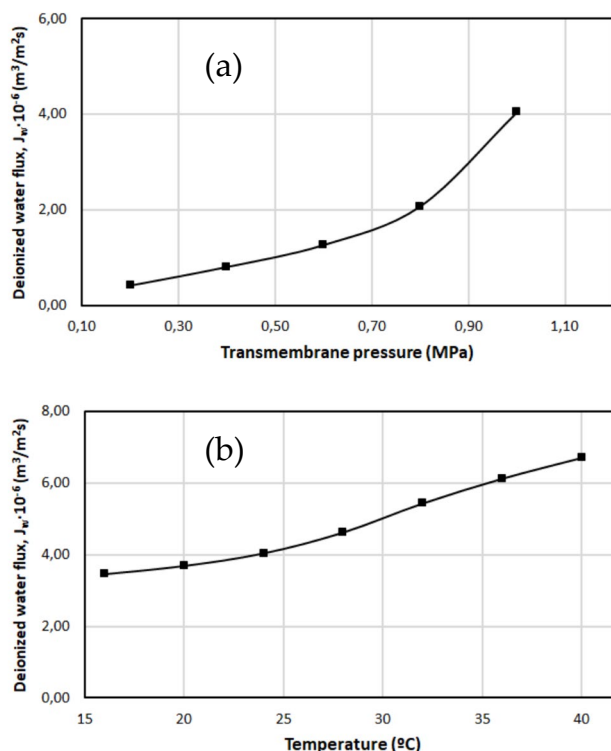


Fig. 2. Characteristics of membrane transport properties based on volumetric deionized water flux, based on (a) transmembrane pressure (at a constant temperature of $18^\circ\text{C} \pm 2^\circ\text{C}$) and (b) temperature change (at a constant TMP of 1 MPa).

the permeate flow performance. Table 4 shows the detailed list of actions taken during the filtration cycles.

During all filtration cycles, samples were withdrawn once every 30 min to assess the transport and separation properties of the membrane. After each cycle, the membranes were rinsed for 1 h with deionized water at the same operational parameters as during filtration.

In the second stage, the transport and separation properties of AFC30 and AFC80 membranes were compared during extended filtration cycles, which lasted for 25 h. The dosage of BFA solution was increased to 1 dose every hour, and the feeds in the circulation were not replenished with fresh tap water. In this stage, the effect of increasing the concentration of compounds on the transport and separation properties of membranes was analyzed. Both filtration cycles were completed by rinsing with deionized water (process duration 1 h).

In the last stage, the effect of human body secretions (compounds with the potential to block the flow properties of pool water) on the transport properties of the AFC80 membrane was analyzed. For this purpose, dosages based on deionized water were prepared, in which the compounds (analytical grade: 98%–99% purity, Sigma-Aldrich) in the doses given in Table 5 were dissolved. After conditioning the membrane, each of the filtration cycles was carried out for 3 h (with TMP equal to 1 MPa and temperature $18^\circ\text{C} \pm 2^\circ\text{C}$). The processes were followed by rinsing with deionized water for 1 h. Then, the membrane was rinsed with 1% citric acid solution for 1 h (Sigma-Aldrich, ACS reagent, $\geq 99\%$).

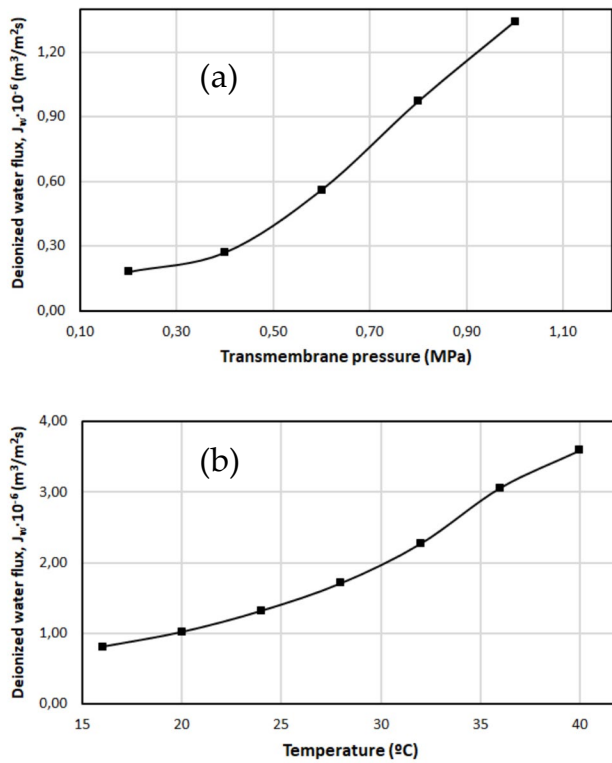


Fig. 3. Characteristics of membrane transport properties based on volumetric deionized water flux, based on: (a) transmembrane pressure (at a constant temperature of $18^\circ\text{C} \pm 2^\circ\text{C}$) and (b) temperature change (at a constant TMP of 1 MPa).

To evaluate the transport properties of the membranes, the volumetric flux rate of deionized (J_w), permeate (J_p) (in the course of the proper filtration process), rising deionized water (J_R) carried out each time after the end of the cycle, and flux after cleaning (J_C) were determined using the following formula: $J_w (J_p, J_R, J_C) = v/F \cdot t \text{ (m}^3/\text{m}^2\text{s)}$, where v is the volume of water or permeate (m^3), F is an active surface area of the membrane (m^2), and t is the filtration time (s).

The intensity of the reduction of the hydraulic performance of the membrane was determined by determining the value of an intermediate parameter—the relative permeate/deionized flux (relative permeability) $\alpha = J_p/J_w$. It is the quotient of the fluxes determined during the course of filtration of the treated solutions and of deionized (J_w). This parameter is a simple measure of the disadvantageous phenomena accompanying the process of membrane filtration. The flux

Table 5
Concentrations of tested compounds from the body fluid analogs in the third stage of research

Chemical compound	Urea	Creatinine
Molecular mass, g/mol	60.06	113.12
Number of the filtration cycle	Concentration in the feed, mg/L	
1	0.5	0.2
2	1.0	0.5
3	2.0	1.0
4	5.0	2.0

Table 4
Tests using AFC80 membranes in first stage of research

Time of the process, h	Action taken during the process		
	Cycle 1	Cycle 2	Cycle 3
0		Insertion feeds to the system	
1	First dose of BFA	First dose of BFA	First dose of BFA
2	1 L fresh tap water	0.5 L fresh tap water	–
3	Second dose of BFA	Second dose of BFA	Second dose of BFA
4	1 L fresh tap water	0.5 L fresh tap water	–
5	Third dose of BFA	Third dose of BFA	Third dose of BFA
6	1 L fresh tap water	0.5 L fresh tap water	–
7	Fourth dose of BFA	Fourth dose of BFA	Fourth dose of BFA
8	1 L fresh tap water	0.5 L fresh tap water	–
9	Fifth dose of BFA	Fifth dose of BFA	Fifth dose of BFA
10	1 L fresh tap water	0.5 L fresh tap water	–
11	Sixth dose of BFA	Sixth dose of BFA	Sixth dose of BFA
12		Continuation of filtration	
13		Emptying the system	
14		Rinsing with deionized water	

BFA, body fluid analogs.

of rinsing water (J_R) and after cleaning by a 1% solution of citric acid (J_C) were determined in an analogous way.

To determine the separation properties of the membranes, the percentage of rejection (R [%]) was determined based on the reduction of the values of pollution indicators: $R = (1 - c_p/c_f) \cdot 100$, where c_p and c_f are concentrations (indicator value) of pollutants in the permeate and feed, respectively, (mgC/L or nephelometric turbidity unit [NTU] or m^{-1}).

3. Results and discussion

In the first stage, effects were seen in the feed supplement treatment with fresh tap water flow on the transport properties of separation membrane AFC80. In Cycle 1, the volumetric permeate flow was in the range of 3.47 – $3.94 \times 10^{-6} m^3/m^2s$ (Fig. 4a). The average value of J_V was $3.66 \times 10^{-6} m^3/m^2s$. In addition, the permeability of the AFC80 membrane in this cycle was in the range of 0.88 – 1.00 , and the average value of α was 0.93 . During Cycle 1, there was no clear relationship between the introduction of a BFA dose and/or a fresh portion of tap water and either a decrease or increase in process efficiency (Fig. 4a).

In the case of Cycle 2, higher values of the permeate flow were noted at the beginning of the process. The value of the relative volume permeate flux was in the range of 1.00 – 1.06 (Fig. 4b), with the average value of α being 0.96 . However, the volume of the permeate flux was in the range of 4.17 to $3.94 \times 10^{-6} m^3/m^2s$ (Fig. 4b), and the average value of J_V was $3.79 \times 10^{-6} m^3/m^2s$.

In the last filtration cycle (first stage of the research), the lowest transport capacity of the AFC80 membrane was recorded. The permeate flow was in the range of 3.47 – $3.82 \times 10^{-6} m^3/m^2s$ (Fig. 4c), and the average value of J_V was $3.61 \times 10^{-6} m^3/m^2s$. The value of the α coefficient was in the range of 0.88 – 0.97 , with the average permeability value of 0.92 .

In the case of the analyzed transport properties of AFC80 membranes, no clear relationship was observed between the time of introduction of the BFA dose and the subsequent decrease in the volume of permeate flux. The accepted dose of $4 \mu g/L$ every 2 h is a theoretical dose and involves the introduction of low concentrations of the analyzed compounds into the system. It is noteworthy that in a real system, the amount of introduced pollutants and their diversity may significantly exceed the assumptions adopted in the laboratory tests. The supplementation of losses in the circulation with fresh tap water is an important aspect because it dilutes the feed and reduces the concentration of dissolved carbon compounds [22,45,47,48]. At the stage of transport analysis, the advantage of this solution was difficult to perceive, the effects were observed in the analysis of separation abilities (pollution retention rates). In addition, laboratory conditions allowed for one-time analyses not exceeding 24 h.

Figs. 5a and b show the effect of BFA dosing in cycles with (and without) water replenishment in the system. In all the analyzed cases, an increase in the concentration of carbon compounds in the permeate was observed along with the increase in the number of doses of the model solution. In Cycle 1, the retention coefficient of TC in the first hours of filtration was about 84%, decreasing during the process and eventually reaching 79.86%. In contrast, the TOC content

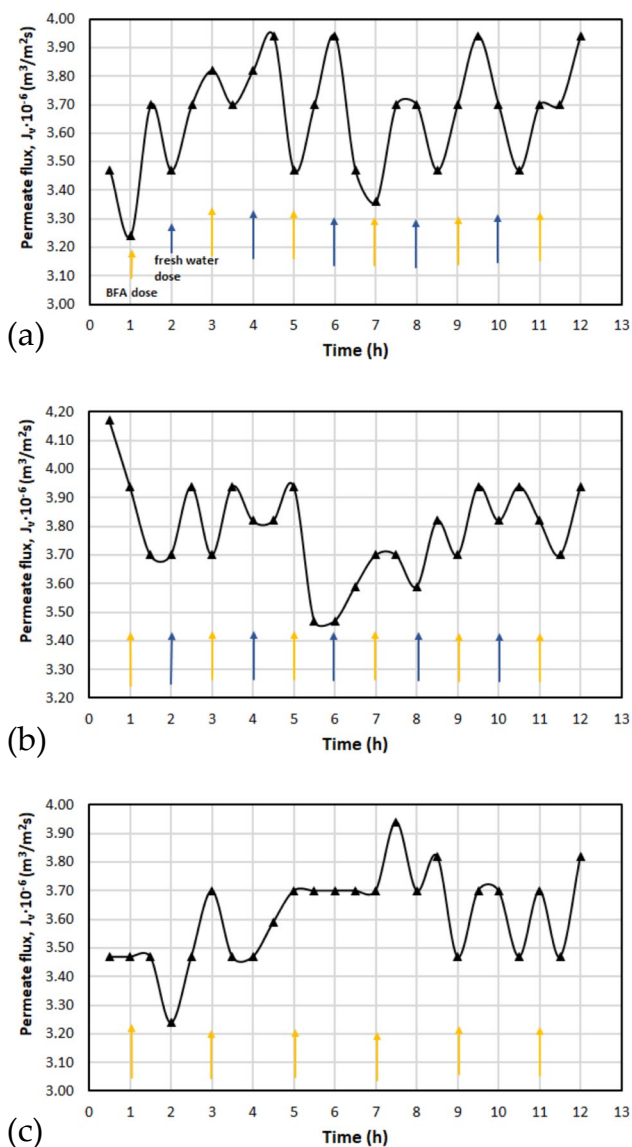


Fig. 4. Value of the volumetric permeate flux in: (a) Cycle 1: BFA + filling with fresh tap water in 1 L volume, (b) Cycle 2: BFA + filling with fresh tap water in 0.5 L volume, and (c) Cycle 3: BFA dosing without topping up with water.

remained zero for a long time; it was only present in the permeates obtained after more than 8 h from the start of filtration, when the TOC concentration was 0.1470 mg C/L , although it increased in subsequent samples and after 12 h of filtration reached a value of 0.3210 mg C/L (Fig. 5b).

Reducing the dosage of fresh tap water during the process contributed to the faster growth of carbon compounds in the permeate and decreased retention capacity of AFC80 membranes. The value of general carbon retention coefficient ranged from 80.75% to 75.01% . The content of TOC in the permeate after 4.5 h of filtration was 0.1420 mg C/L , subsequently decreasing to 0. After filtration, at 6 h, it reached 0.0220 mg C/L and gradually increased to 0.3557 mg C/L at the 12 h filtration (Fig. 5b).

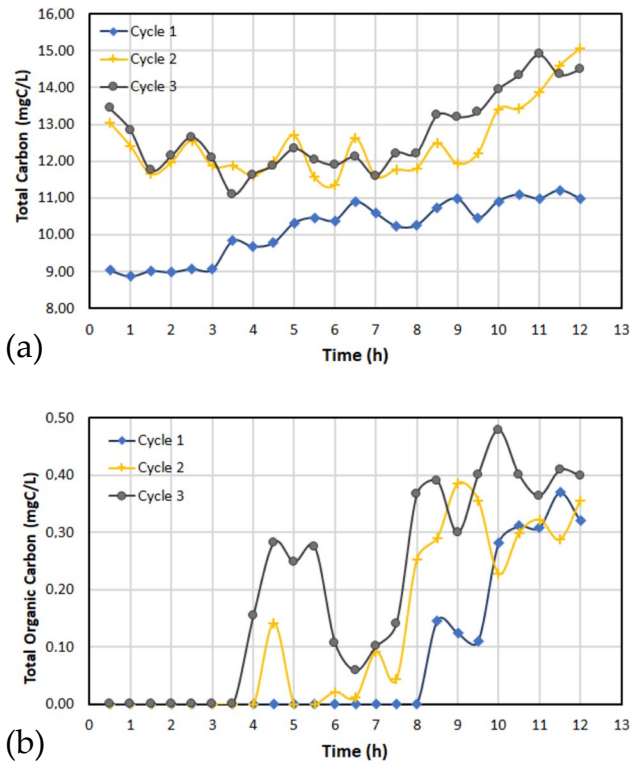


Fig. 5. Values of carbon compounds concentrations in permeates collected during filtration cycles with the AFC80 membrane, by: (a) total carbon concentration and (b) total organic carbon concentration.

The importance of fresh tap water dosing in the system was particularly evident in the last cycle of the experiment. Thus, the fastest appearance of TOC was observed in permeates in Cycle 3. The value of TC retention coefficient ranged from 81.98% to 74.07%. In addition, after 4 h of filtration, the TOC content in the permeate was 0.1549 mg C/L, which increased in subsequent samples. The highest TOC value was obtained after 10.5 h filtration (0.4790 mg C/L), while in the permeate, after 12 h, the concentration of TOC was 0.3994 mg C/L (Fig. 5b).

It should be emphasized that after all filtration cycles were performed, the AFC80 membranes were rinsed with deionized water. This procedure was sufficient because in the analyzed cases, there was no significant reduction in the transport properties of the membranes.

The possibilities of the research system allowed to extend the filtration time to 25 h. At this stage, we compared the results of AFC30 and AFC80 membranes (Figs. 6 and 7). The interval between successive rinses of the membrane was increased and BFA (1 dose per hour) was intensified. AFC30 membrane was characterized by high relative permeability; the α value ranged from 1.07 to 0.80 (the average value was 0.96). The mean volume of permeate flux was $0.997 \times 10^{-6} \text{ m}^3/\text{m}^2\text{s}$ (Fig. 6a).

In the case of AFC30 membrane, the reduction in the volume of the permeate flux noted after 20 h of filtration would require further investigation (Fig. 6a). However, rinsing with deionized water after this cycle increased the permeability of the membrane; the α value was 0.92.

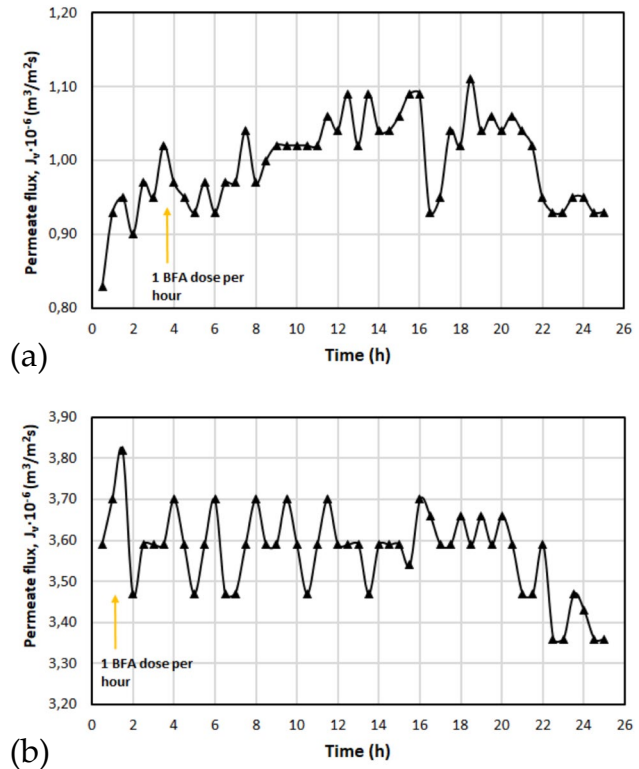


Fig. 6. Permeate flux value in extended membrane filtration processes (1 BFA dose per hour): (a) AFC30 membrane and (b) AFC80 membrane.

A reduction in the transport capacity after 20 h of the start of the filtration was also observed for the AFC80 membrane (Fig. 6b). The relative value of permeability ranged from 0.91 at the beginning of the process to 0.85 at the end of the process). The average value of the α coefficient was 0.91. However, the volume of the permeate flux was in the range of $3.82\text{--}3.36 \times 10^{-6} \text{ m}^3/\text{m}^2\text{s}$ (Fig. 6b), with an average J_v value of $3.57 \times 10^{-6} \text{ m}^3/\text{m}^2\text{s}$.

The separation capacities of AFC80 and AFC30 membranes were also analyzed (Figs. 7a and b). The permeates exhibited a lack of turbidity (mean value of all attempts 0.00 NTU) and low or no impurities. The UV_{254} parameter of the permeates obtained from AFC80 membrane was 0 m^{-1} in the entire range of analysis and was 0.03 m^{-1} for permeates obtained from AFC30 membrane.

The permeate, after filtration with the AFC30 membrane from the beginning of the process, was characterized by twice as low efficiency in decreasing the concentration of TC compared with the AFC80 membrane (Fig. 7a). The similar effectiveness of both membranes in lowering the TOC was, however, a surprise. The concentration of TOC in the permeate after filtration with the AFC80 membrane was in the range of 0.00–2.4200 mg C/L (mean value was 1.1800 mg C/L). In the permeate after filtration, TOC value ranged from 0.0791 to 2.3995 mg C/L (average value was 0.9600 mg C/L) (Fig. 7b).

The low BFA doses applied in our experiments decreased the TOC content in the feed either below the concentrations typical for pool water or were in the lower limits. The range reported in the literature is from 3 to even 125 mg C/L,

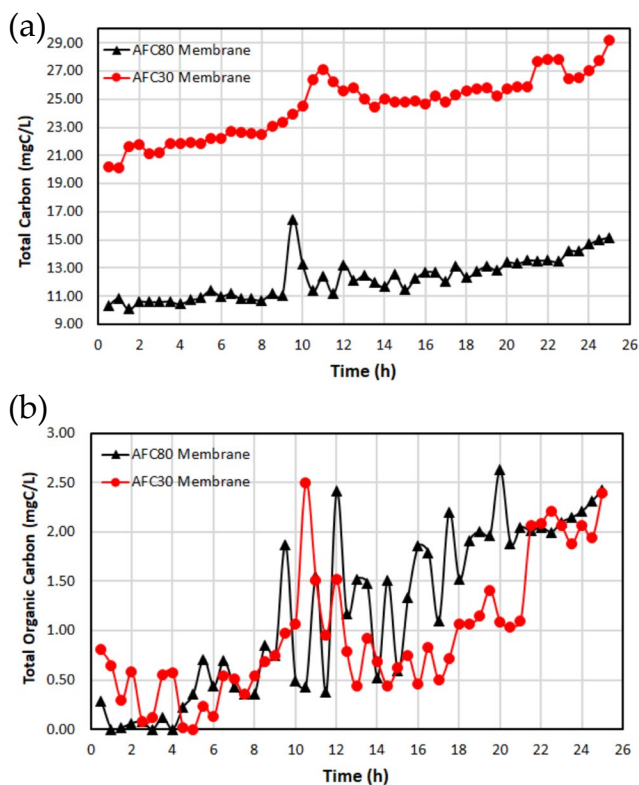


Fig. 7. Concentration of carbon compounds in extended filtration processes, in relation to (a) total carbon concentration and (b) total organic carbon concentration.

depending on the type and purpose of the basin [5,48]. The ultrafiltration tubular membranes working in a cross-flow system prove themselves to reduce the value of absorbance in UV_{254} and turbidity [49]. However, the system of compounds present in the pool water is much more diverse and requires membranes with much higher resolution capabilities, hence the choice of nanofiltration seems reasonable.

The analyses carried out with the use of urea solutions showed that in the tested concentration range, it did not have any significant ability to block the pores of the membrane (Figs. 8a and b). Urea (0.5 and 1.0 mg/L) solutions contributed to an increase in the relative permeability of the membrane from 0.86 to 0.91 and 0.81 to 0.91, respectively. The value of α during the membrane's washing process after the filtration process was 0.91. The flow rate constant was characterized by the membrane during the filtration of urea at 0.5 mg/L concentration; the α value ranged from 0.89 to 0.86 (Fig. 8a). However, 2.0 mg/L urea solution showed a slight deterioration in the transport properties of the membranes (the value of the relative permeability was in the range of 0.86–0.80) (Fig. 8a). The relative permeability of the membrane for rinsed deionized water after the filtration process using a urea solution at a concentration of 5.0 mg/L was 0.97. Rinsing with a 1% citric acid solution improved the transport capacity of AFC80 membranes (the value of the coefficient for rinsing after filtration with the highest concentration of urea was 0.93).

An important precursor of DBPs is creatinine, which forms stable chloramines identified as dichloramines [50].

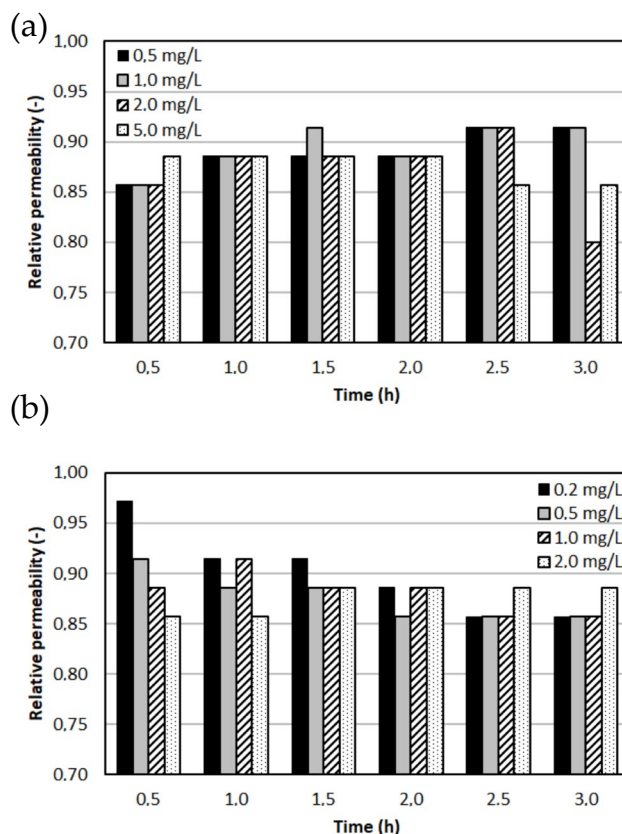


Fig. 8. AFC80 membrane permeability value during filtration of solutions: (a) urea and (b) creatinine (TMP = 1 MPa).

In addition, creatinine was selected as a potential blocking agent for membrane pores [50,51].

In the majority of the cases, the relative permeability of the AFC80 membrane was reduced in the presence of creatinine (Fig. 8b), with the fastest reduction in permeate flux was recorded for the solution containing 0.2 mg/L creatinine (the relative permeability was in the range of 0.97–0.86). However, for a solution with a concentration of 2.0 mg/L, the value of α increased, from 0.86 to 0.89 (Fig. 8b). However, cleaning with a citric acid solution brought about a slight improvement in transport properties. Only the subsequent rinse (with deionized water) allowed to increase the permeability value (range: 0.91–0.94) of the AFC80 membrane.

Given the susceptibility of nitrogen compounds toward the formation of DBPs, citric acid may be used to clean the membranes as a compound not containing such moieties. At the same time, it is known that citric acid may be of great importance in the formation of trihalomethanes and HAAs in contact with disinfectants [41,51]. Due to this reason, it would be required to extend the research on the use of other membrane cleaners, including sodium hypochlorite.

4. Summary and conclusion

- Despite the extensive research conducted on pollution of swimming pool water with human body secretions, the water treatment technologies continue to concentrate on bed filtration (filtration with contact coagulation).

The change of pool water technology seems to be inevitable due to numerous reports on the harmfulness of DBPs.

- The identification of the polluting substances makes it possible to reduce or avoid pollution of membranes. Therefore, not only the pollutants that are analyzed in membrane processes are important but also the matrix in which those pollutants exist also matters (deionized water, tap water, or swimming pool water).
- Among the membranes analyzed, good transport and separation properties were found in the AFC80 membrane. However, it is necessary to conduct new research in this area as more and more complicated cases of impurities being introduced into the pool water system have been reported and because the pool water environment is a very complicated system that includes many pollutants.
- Despite the small fouling effect of the analyzed compounds in this research, it leads to higher operating costs due to a reduction in efficiency of membranes. Moreover, frequent cleaning of membranes reduces their separation properties. For this reason, the maintenance and cleaning of membranes are of particular importance.

Acknowledgments

This study was conducted within the framework of the project funded by the Polish Ministry of Science and Higher Education and the work was conducted as part of the faculty research grant for young scientists: “An attempt to optimize the process of nanofiltration in the presence of selected anthropogenic pollutants characteristic of swimming pool water” (Grant number: BKM-508/RIE-4/2018). This manuscript was prepared as part of the statutory activity of the Faculty of Environmental Engineering and Energy (BK-259/RIE-4/2018).

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