

An Attempt to Optimise the Process of Nanofiltration of Pool Water Enriched with Compounds Associated with Secretions of the Human Body [†]

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Abstract: This paper discusses the possibilities of purifying pool water by the process of nanofiltration. The analysis was carried out in the presence of substances analogous to the secretions of the human body. The samples of water collected from the school swimming pool was enriched with selected organic and inorganic compounds. The transport-separation properties of nanofiltration membranes were assessed. In the context of the removal of these organic compounds, the measurement of the total organic carbon concentration was of particular importance.

Keywords: swimming pool water; body fluids analogues; pressure driven membrane processes

1. Introduction

It is estimated that during one hour of physical activity one swimmer may excrete 50 mL of urine and 200 ml of sweat, which results in the release into the water of many organic compounds whose structures comprise nitrogen, which quickly reacts with chlorine-based disinfectants [1]. The concentration and composition of disinfection by-product (DBP) precursors classified as body fluid analogues (BFAs) are strongly correlated with the number of swimmers, their hygiene habits, and the intended use of the pool. On the other hand, studies have confirmed the presence of urea, ammonia, uric acid, creatinine, creatine, lactic acid, citric acid, hippuric acid, chlorides, sulphates, cations, and amino acids, e.g., histidine [2–4]. It has been confirmed that micropollutants in the form of DBPs produce various enzymes which cause oxidative stress in the cells of living organisms [5,6]. Numerous studies performed to assess the quality of swimming pool water using toxicological tests have confirmed the genotoxic, cytotoxic, and mutagenic properties of DBPs [5]. It is necessary to look for more and more effective ways to treat swimming pool water, which will make it possible to eliminate both the precursors and the products of their reactions with disinfectants. The work aimed to assess the possibility of using the nanofiltration process (NF) to remove impurities characteristic of pool water. The analysis was based on selected transport-separation properties of the commercial asymmetric membrane.

2. Materials and Methods

2.1. Characteristics of BFA Model Solutions

A solution of substances analogous to the secretions of the human body was prepared based on the selected data presented in the literature [2]. The reference substances (Sigma-Aldrich) were

dissolved in demineralised water at $\text{pH} = 9.2 \pm 0.2$ (Table 1). The applied doses of the initial solution were determined by preliminary tests, based on the personal load of the selected pool facility and the capacity of the basin.

Table 1. Concentration of body fluid analogue (BFA) components in the tested solutions.

| Compounds of BFA Solutions | Concentration in the Stock Solution ¹ (mg/L) | BFA Doses ($\mu\text{L/L}$) | |
|----------------------------|---|---|--------|
| | | 15.60 | 37.20 |
| | | Concentration of the Component in the BFA Solution (mg/L) | |
| Urea | 14,800 | 0.2309 | 0.5506 |
| Ammonium chloride | 2000 | 0.0312 | 0.0744 |
| Creatinine | 1800 | 0.0281 | 0.0670 |
| Hippuric acid | 1710 | 0.0267 | 0.0636 |
| L-histidine | 1210 | 0.0189 | 0.0450 |
| Sodium phosphate dibasic | 4300 | 0.0671 | 0.1600 |
| Citric acid | 640 | 0.0100 | 0.0238 |
| Uric acid | 490 | 0.0076 | 0.0182 |

¹ 25 mL of solution corresponds to the volume introduced by one bather during one h of physical activity.

2.2. Analytical Procedures

In the swimming pool water and feeds containing BFA doses, the concentration of total carbon (TC), organic (TOC) and dissolved (DOC) (after $0.45 \mu\text{m}$ filtration, PVDF syringe filter) were determined using a TOC-L series analyser (Shimadzu). The ultraviolet absorbance was measured at a wavelength of 254 nm measured using the UV VIS Cecil 1000 (Analytik Jena AG: Jena, Germany). Turbidity was determined by a EUTECH Instruments model Turbidimeter TN-100. Measurement of the total and free chlorine concentrations in the pool water samples was made by the photometric method in cuvette tests using a VIS Spectroquant® Pharo 300 UV spectrophotometer (Merck: Darmstadt, Germany). Measurement of the pH and the redox potential of the pool water samples and feeds was carried out with a multi-parameter inoLab® 740 meter (Poland, Wroclaw, WTW, Measuring and Analytical Technical Equipment).

2.3. Characteristics of Pool Water Samples

Samples of pool water used in the research came from a basin with a capacity of 121.06 m^3 , intended for swimming. Two multilayer pressure filters (hydroanthracite - quartz sand) work in the pool water treatment circuit (contact coagulation + rapid filtration). The time of total exchange water in the basin is four h. The personal load of bathers on the day of collection was 15 people per hour. Table 2 presents the values of selected physicochemical parameters in pool water samples (BFA 1) and samples enriched with a solution of human sections (BFA 2 and BFA 3).

2.4. Membrane Filtration Methods

The study used flat nanofiltration membranes (polyamide-TFC) made by DowFilmtec™ (Sterlitech: Kent, WA, USA). The characteristics of the membranes and the operating parameters of the processes are given in Table 3. The membranes were placed in a steel filtration cell with a volume of 380 cm^3 where the active surface of the membrane was equal to 38.5 cm^2 . Before filtration started, new membranes were conditioned by filtering demineralised water to stabilise the volume of the permeate stream (J_0). The transmembrane pressure of all filtrations was 0.8 MPa. Each process was run continuously for 240 min. After each cycle, the membrane was rinsed with demineralised water.

The intensity of the reduction of the hydraulic performance of the membrane was determined by a defined intermediate parameter - the relative volumetric permeate stream α (-), which is the quotient of the streams determined in the course of filtration of the treated solutions and demineralised water (membrane conditioning process), $\alpha = \frac{J_0}{J_v}$. This parameter is a measure of the disadvantageous phenomena accompanying membrane filtration, where J_v is the volumetric flow

rate of permeate ($m^3/m^2 \cdot s$). In order to determine the separation properties of membranes, the rejection R , (%) was determined based on the reduction of the values of pollution indicators: $R = \left(1 - \frac{c_p}{c_n}\right) \cdot 100$, where c_p is the concentration (indicator value) of pollutants in the permeate stream and c_n is the concentration of contaminants in the feed (mgC/L or NTU or m^{-1}).

Table 2. Selected physicochemical parameters of feeds for nanofiltration.

| Parameter | Swimming Pool Water (feed) | | |
|--|----------------------------|--------------------|--------------------|
| | BFA 1 ¹ | BFA 2 ² | BFA 3 ³ |
| pH, (-) | 7.26 | 6.90 | 6.75 |
| Redox potential, (mV) | 380 | 290 | 265 |
| Turbidity, (NTU) | 0.81 | 1.20 | 1.30 |
| UV254, (-) | 5.90 | 7.80 | 9.60 |
| Free chlorine, (mgCl ₂ /L) | 0.23 | 0.20 | 0.21 |
| Total chlorine, (mgCl ₂ /L) | 1.31 | 1.36 | 1.41 |
| TOC, (mgC/L) | 11.60 | 12.92 | 13.18 |
| DOC, (mgC/L) | 9.00 | 10.64 | 11.12 |
| TC, (mgC/L) | 19.41 | 21.63 | 22.19 |

¹ samples of swimming pool; ² water from a swimming pool with a dose of 15.60 $\mu L/L$ BFA solution;

³ water from swimming pool with a dose of 37.20 $\mu L/L$ BFA solution.

Table 3. Characteristics of membranes and operating parameters of the process.

| Feed | Membrane Symbol | MWCO, (Da) | Normalized Flux of Demineralized water $J_0 \cdot 10^{-6}$, ($m^3/m^2 \cdot s$) |
|-------|-----------------|------------|--|
| BFA 1 | | | 6.85 |
| BFA 2 | YMNF903001 | ~200–400 | 6.93 |
| BFA 3 | | | 7.57 |

3. Results and Discussion

The nanofiltration membranes were characterised by high separation capacities (Table 4). The average values of the retention coefficients for the pool water were: 83.55% for the TOC concentration, 76.39% for turbidity, and 80.30% for the absorbance of UV254.

Table 4. Values of parameters related to transport and separation properties of nanofiltration (NF) membranes.

| Filtration Time, (min) | Relative Permeate Flux, α (-) | | | Rejection of TOC, R (%) | | |
|------------------------|--------------------------------------|-------|-------|-------------------------|-------|-------|
| | BFA 1 | BFA 2 | BFA 3 | BFA 1 | BFA 2 | BFA 3 |
| 30 | 86.32 | 79.17 | 78.10 | 63.02 | 99.83 | 96.48 |
| 60 | 84.21 | 79.17 | 76.19 | 88.72 | 92.42 | 82.97 |
| 90 | 86.32 | 79.17 | 74.29 | 96.46 | 82.24 | 90.52 |
| 120 | 84.21 | 79.17 | 72.38 | 92.48 | 77.00 | 83.39 |
| 150 | 80.00 | 79.17 | 72.38 | 85.00 | 87.22 | 82.40 |
| 180 | 84.21 | 79.17 | 70.48 | 87.70 | 81.52 | 80.92 |
| 210 | 80.00 | 77.08 | 70.48 | 74.84 | 87.11 | 91.98 |
| 240 | 75.79 | 72.92 | 66.67 | 80.16 | 78.40 | 92.78 |

Higher values of coefficients were noted for solutions enriched with BFA compounds. For BFA 2, the average removal efficiency was: 85.72% (TOC), 86.67% (turbidity) and 97.28% (UV254). In turn for BFA 3, these were: 87.68% (TOC), 85.96% (turbidity) and 100% (UV254). On the other hand, the interesting relationship between the separation capacities of membranes and the concentration of the tested organic compounds.

With increasing filtration time, the transport capacity of all membranes has decreased. The highest reduction in the α -value was noted for the samples of pool water feed enriched with a BFA 37.20 $\mu L/L$ solution (Table 4). The increase in membrane separation capacities is probably directly related to the observed decrease in the quality of transport. Partial blocking of the pores of the

membrane and reduction of the flowability of some of the compounds contributed to the increase in membrane separation abilities.

4. Conclusions

The nanofiltration process ensures a high degree of removal of low molecular weight contaminants from the pool water. The fundamental obstacle to using the process on a real scale is the process efficiency and phenomena associated with blocking the pores of the membrane and its degradation. This research will be developed to analyse the possibilities of optimising the nanofiltration process, following the optimised pre-treatment, optimal cleaning, and cleaning procedures. Modernisation of swimming pool water treatment circuits is necessary due to the need to improve water quality. It is necessary to implement solutions to reduce the water consumption of facilities and, moreover, also provide waste-free cleaning technologies. For these reasons, the research should be extended to thorough material analysis, including the design of a new type of membrane combining greater efficiency of the filtration process and high efficiency in removing low molecular by-products of disinfection.

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Conflicts of Interest: The authors declare no conflicts of interest.

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