

APPLICATION OF PRESSURE-DRIVEN MEMBRANE PROCESSES IN TREATMENT OF SWIMMING POOL WATER SYSTEM

Edyta ŁASKAWIEC ^a, Mariusz DUDZIAK ^b, Joanna WYCZARSKA-KOKOT ^c

^a MSc Eng. (PhD Study); Institute of Water and Wastewater Engineering, Faculty of Energy and Environmental Engineering, Silesian University of Technology; Konarskiego 18, 44-100 Gliwice
E-mail address: edyta.laskawiec@polsl.pl

^b Associate Prof. DSc PhD Eng.; Institute of Water and Wastewater Engineering, Faculty of Energy and Environmental Engineering, Silesian University of Technology; Konarskiego 18, 44-100 Gliwice
E-mail address: mariusz.dudziak@polsl.pl

^c PhD Eng.; Institute of Water and Wastewater Engineering, Faculty of Energy and Environmental Engineering, Silesian University of Technology; Konarskiego 18, 44-100 Gliwice
E-mail address: joanna.wyczarska-kokot@polsl.pl

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Abstract

The paper presents usefulness of membrane processes (ultrafiltration (UF) and nanofiltration (NF)) for treatment of backwashing water of pool water system. The backwashings were taken from circulations located in two indoor facilities from pools of various functionalities. Moreover, the used samples had different quality in terms of physical and chemical parameters. The test used various membranes, both in respect of the polymer that they were made of and their separation capacity. Transport and separation properties of ultrafiltration (MW and V5) and nanofiltration (DK and HL) membranes were specified. Furthermore, backwashing water samples before and after membrane process treatment were subjected to Microtox[®] toxicity test. The conducted processes helped to reduce turbidity and specific absorbance at UV_{254nm}^{1m} , both during ultrafiltration as well as nanofiltration. Much higher hydraulic performance was observed in ultrafiltration membranes. After each filtration cycle a Microtox[®] toxicity test was carried out which revealed reduced washings toxicity in relation to bacteria in all tested samples.

Streszczenie

W pracy określono przydatność procesów membranowych (ultrafiltracji UF i nanofiltracji NF) do oczyszczania popłuczyn filtracyjnych z instalacji wody basenowej. Popłuczyny zostały pobrane z obiegów zlokalizowanych w dwóch obiektach krytych, o różnym przeznaczeniu niecek. Próbkę charakteryzowały się zróżnicowaną jakością, opisaną parametrami fizykochemicznymi. Badania prowadzono z wykorzystaniem różnych membran, zarówno pod względem tworzącego ich polimeru, jak i zdolności separacyjnych. Wyznaczono właściwości transportowo-separacyjne membran UF (MW i V5) i NF (DK i HL). Dodatkowo próbki popłuczyn, przed i po procesie membranowym poddano przesiewowemu testowi toksyczności Microtox[®]. Odnotowano obniżenie ilości substancji wpływających na mętność wody oraz związków organicznych wyrażonych wskaźnikiem absorbancji w UV_{254nm}^{1m} , zarówno w procesach ultrafiltracji, jak i nanofiltracji. Znacznie wyższą wydajnością hydrauliczną odznaczały się membrany ultrafiltracyjne. We wszystkich przeprowadzonych cyklach filtracyjnych stwierdzono obniżenie toksycznych właściwości popłuczyn w stosunku do bakterii *Aliivibrio fischeri* w teście Mirotox[®].

Keywords: Swimming pools waters; Washings; Ultrafiltration; Nanofiltration.

1. INTRODUCTION

According to the German standard DIN 19643, 4 to 6 m³ of water per 1 m² of filter bed is required for proper performance of the swimming pool filter bed rinsing process. In the case of large swimming pools with several systems, the demand just for water for rinsing filter beds is very large. A typical swimming pool treatment system, consisting of 4 filters with the diameter of 1.800 mm that are washed on average once every two days, requires 600 to 900 m³ per month. Due to the huge demand for water and the high cost of water consumption and wastewater drainage, there is a growing interest in recovery of water from swimming pool washings [1]. Washings contain a large quantity of suspended solids and dissolved substances. Particularly problematic, from the standpoint of use of washings, is their high content of byproducts of disinfection, admixtures, and pollutants present in chemicals used in the surface coagulation process [2, 3].

Pressure-driven membrane processes with different distribution of substances make it possible to separate pollutants on the molecular level and, consequently, broadly use both in processes of preparation of ultrapure water and for removal of micro pollution from water streams. Ultrafiltration is based on a sieve transport mechanism and stops particles with dimensions larger than the diameter of the membrane pores. Ultrafiltration membranes make it possible to stop small suspended solids, colloids, bacteria, and viruses. Nanofiltration is based on a sieve transport mechanism and the Donnan exclusion principle, and nanofiltration membranes make it possible to completely stop particles with the diameter of 1 nm or larger and to divide ions with different valence [4, 5]. Given the above, both techniques were evaluated with regard to treatment of washings from swimming pool systems. The main trends are based on using membrane processes in the treatment of drinking

water circuits [6, 7], there is not much research on membrane processes in pool water treatment [8]. Therefore, it is necessary to broaden the relevant knowledge in this area.

The present paper presents the results of studies on treatment of samples of washings taken from swimming pool systems in the process of ultra- and nanofiltration based on selected physico-chemical parameters (turbidity, ultraviolet absorbance). Additionally, a toxicological assessment was performed using the Microtox® bacteria test in order to document the changes in the toxicological quality of the washings before and after the membrane filtration process.

2. MATERIALS AND METHODS

2.1. Membrane filtration methods

Flat ultrafiltration and nanofiltration membranes made by Osmonics Inc. (USA), with different physico-chemical parameters, were used in the tests. The characteristics of the membranes and the operating parameters of the processes are given in Table 1.

The membranes were placed in a steel filtration cell with the volume of 380 cm³ where the active surface of the membrane was equal to 38.5 cm². Before the filtration started, the new membranes were conditioned by filtering deionized water in order to stabilize the volume of the permeate stream. The process was performed in a one-direction filtration layout for collection of 50% of the feed. The treatment process was performed in three consecutive cycles without changing the membrane. After each cycle, the membrane was rinsed with deionized water. This was done in order to document the occurrence of disadvantageous phenomena accompanying membrane filtration, i.e. fouling and scaling, caused by organic and inorganic pollution.

Table 1.
Characteristics of membranes and operating parameters of the process

Process	Membrane symbol	Membrane material	Limit molar mass, Da	Process pressure, MPa	Volume flow rate of deionized water J_w^* , 10 ⁵ m ³ /m ² ·s	Recovered permeate %
UF	MW	Polyacrylonitrile (PAN)	200,000 -500,000	0.5	5.46	50
	V5	Polyvinylidene difluoride (PVDF)	200,000	0.2	2.06	
				0.5	1.24 ÷ 1.46	
NF	DK	Composite (epidermal layer - polyamide)	150-300	3.0	3.03	
	HL				3.03	

*Tested independently for each filtration cycle.

In order to evaluate the transport properties of the membranes, the volumetric flow rate of deionized water, J_w (in the course of conditioning of the membranes with water), and of permeate, J_v (in the course of the proper filtration process), were determined using the following formula:

$$J_w(J_v) = \frac{v}{F \cdot t} \quad (1)$$

Where:

J_w – volumetric flow rate of deionized water [$\text{m}^3/\text{m}^2 \cdot \text{s}$],

v – volume of water or permeate [m^3],

F – active surface area of the membrane [m^2],

t – filtration time [s].

In order to determine the separation properties of membranes, the retention (R) was determined based on the reduction of the values of pollution indicators:

$$R = \left(1 - \frac{C_p}{C_n}\right) \cdot 100\% \quad (2)$$

Where:

R – retention of the pollutants [%],

C_p – concentration (indicator value) of pollutants in the permeate stream [NTU or m^{-1}],

C_n – concentration (indicator value) of pollutants in the feed [NTU or m^{-1}].

The intensity of the reduction of the hydraulic performance of the membrane was determined by way of determination of an 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 of deionized water (membrane conditioning process). This parameter is a measure of the disadvantageous phenomena accompanying membrane filtration.

$$\alpha = \frac{J_w}{J_v} \quad (3)$$

Where:

α - relative volumetric permeate stream, -

J_w – volumetric flow rate of deionized water [$\text{m}^3/\text{m}^2 \cdot \text{s}$],

J_v – volumetric flow rate of washings [$\text{m}^3/\text{m}^2 \cdot \text{s}$].

2.2. Analytical procedures

In order to evaluate the quality of the washings and of the filtrates, selected physicochemical parameters were measured. The conductivity (C) and the reaction (pH) of the samples were measured with the

inoLab® 740 (WTW, (Measurement and Analytical Equipment) multi-parameter meter. Ultraviolet absorbance, at the wavelength of 254 nm, was measured using the UV VIS Cecil 1000 made by Analytik Jena AG, with the optical path length of the cuvette d equal to 1 cm. The UV_{254} value was determined using the measurement method presented by US EPA [9], and the final result of the analysis is presented in m^{-1} . Ultraviolet absorbance $UV_{254\text{nm}}^{\text{Im}}$ is a substitute parameter for analyzing the total organic carbon (TOC) and provides information on the potential of formation of byproducts of disinfection. However, one must keep in mind that this measurement is not completely selective [10,11]. The Hach® portable Pocket Colorimeter™ II device was used to determine the total chlorine concentration and the free chlorine concentration using the colorimetric method. Moreover, the concentration of ammoniacal nitrogen and nitrate nitrogen was measured using the photolyser 400 (Dinotec) tester. The turbidity of the samples was determined using the EUTECH Instruments TN-100 turbidimeter. The color was measured using the UV VIS Spectroquant® Pharo 300 (Merck) spectrophotometer.

2.3. Toxicological assessment

The tested washings samples taken before and after the membrane filtration process underwent an additional toxicological assessment performed by way of the Microtox® bacteria test. This was done in order to evaluate the effectiveness of the membrane processes performed in elimination of toxic substances present in the washings. The test was performed in accordance with the *Screening Test* procedure of the MicrotoxOmni system in the Microtox Model 500 analyzer made by Tigret Sp. z o.o., which performed the function of an incubator and a photometer. The percentage of inhibition of bioluminescence compared to the control sample (bacteria not exposed to a potential toxicant) was measured after 5 and 15 minutes of exposure. The results were evaluated based on the toxicity classification [12, 13]. Before the test commenced, the concentration of free chlorine in the samples was measured again. Presence of free fluoride may have a significantly influence on the increased toxicity of the samples, which is due to the destructive action of chlorine on the *Aliivibrio fischeri* bacteria. The measurement did not indicate presence of free chlorine in the samples before the toxicological analysis.

2.4. Characteristics of washings

The tests were performed on samples of washings taken from systems of pools used for different purposes (sports pool (SP), recreational pool (RP), jacuzzi bathtub (JB)) located in indoor swimming pool complexes. The washings taken from SP and RP systems were a mix of streams from two separate systems drained to a common settling tank. The washings were taken during the night in the course of washing of the sand and gravel pressure filter beds that are the main elements of the swimming pool water treatment systems in those facilities. The physicochemical analyses described in the Analytical procedures chapter were performed in the morning on the following day. The quality characteristics of the washings are shown in Table 2.

The results presented herein are the average values determined in the tests and the standard deviation did not exceed 5% in any of the cases presented.

3. RESULTS AND DISCUSSTION

3.1. Transport properties of UF and NF membranes during filtration of washings

In the course of the process of ultrafiltration of washings from the systems of the sports pool (SP) and the recreational pool (RP) performed using a polyacrylonitrile membrane (MW) at transmembrane pressure equal to 0.5 MPa, a reduction of the permeate stream compared to the initial value determined for deionized water ($5.46 \cdot 10^{-5} \text{ m}^3/\text{m}^2 \cdot \text{s}$) was observed; on average, the reduction was equal to approx. 26%, regardless of the filtration cycle (Fig. 1). The membrane rinsing performed between successive cycles did not restore the initial value of the volumetric flow rate of permeate

(JV). In the same process conditions, filtration of washings was performed using a Polyvinylidene difluoride membrane (V5). This membrane was characterized by a lower initial volumetric flow rate of deionized water ($1.46 \cdot 10^{-5} \text{ m}^3/\text{m}^2 \cdot \text{s}$), compared to the MW membrane. The polyacrylonitrile UF membrane was characterized by a larger reduction of the permeate stream in the course of the process (Fig. 1). Compared to the initial value determined for deionized water, the permeate stream was reduced by approx. 28-31%, depending on the filtration cycle.

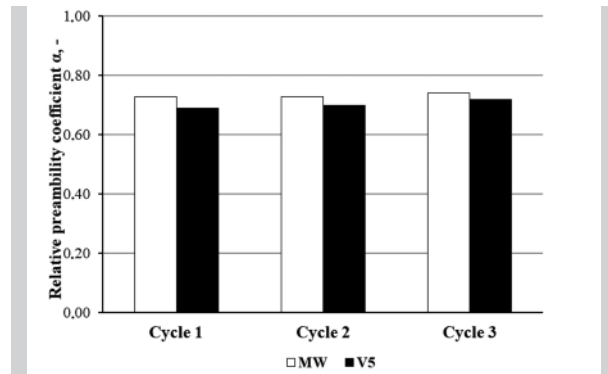


Figure 1. Hydraulic performance of the MW and V5 ultrafiltration membranes ($\Delta P=0.5 \text{ MPa}$) during filtration of washings from SP and RP swimming pool systems

Later, washings taken from the jacuzzi bathtub (JB) system were filtered in a UF process using the V5 membrane at two different transmembrane pressures: 0.2 MPa and 0.5 MPa (Fig. 2). The observed values of the average relative permeability coefficients were lower at the pressure of 0.2 MPa than at the pressure of 0.5 MPa. Moreover, a significant impact of turbidity and absorbance $UV_{254\text{nm}}^{1\text{m}}$ on the

Table 2. Characteristics of post-process washings from swimming pool systems

Parameter	Unit	System	
		SP + RP (sports pool and recreational pool)	JB (jacuzzi bathtub)
Color	m^{-1}	9.00	2.00
Turbidity	NTU	27.60	9.22
pH	-	7.37	7.65
Conductivity (PVC)	$\mu\text{S}/\text{cm}$	1,350	3,300
$UV_{254\text{nm}}^{1\text{m}}$	m^{-1}	20.90	6.80
Total chlorine	$\text{mgCl}_2/\text{dm}^3$	1.28	0.73
Free chlorine	$\text{mgCl}_2/\text{dm}^3$	0.37	0.33
Chlorine, combined	$\text{mgCl}_2/\text{dm}^3$	0.91	0.40
Ammoniacal nitrogen	$\text{mgN-NH}_4/\text{dm}^3$	1.90	0.10
Nitrate nitrogen	$\text{mgN-NO}_3/\text{dm}^3$	19.00	4.00

hydraulic performance of the membrane was found (the comparison was performed at the transmembrane pressure of 0.5 MPa). Washings with a much smaller load of suspended solids (jacuzzi bathtub system, Table 1) caused a smaller reduction of the hydraulic performance of the ultrafiltration membrane. The value of the average relative permeability coefficient was on average 28% higher than the value of this parameter determined for the washings from the systems of the SP and RP swimming pools.

Fig. 3 shows the average values of average volumetric flow rate of permeate (α) for the nanofiltration membranes in the course of treatment of washings from the SP and RP systems. The average relative permeability coefficient for the cycles that were conducted was below 0.40. Moreover, with successive filtration cycles, the value of this parameter decreased and eventually, after three cycles of the membrane marked as HL, it was equal to only 0.27. In the case of the DK membrane, the values of this parameter were a little higher. The rinsing of the membrane with deionized water performed between successive cycles did not restore the initial performance.

3.2. Pollution separation effectiveness

Fig. 4 shows the separation properties of the tested UF membranes with reference to the value of ultraviolet absorbance (R_{UV254}) and turbidity ($R_{turbidity}$). In the course of filtration of washings from the SP and RP systems, the MW membrane demonstrated high values of the average pollution retention coefficients measured using those indicators. In the case of ultraviolet absorbance, the value of the retention coefficient was on the level of 85% and the reduction of turbidity in all the tested cycles was larger than 96%. The high values of removal of suspended solids and

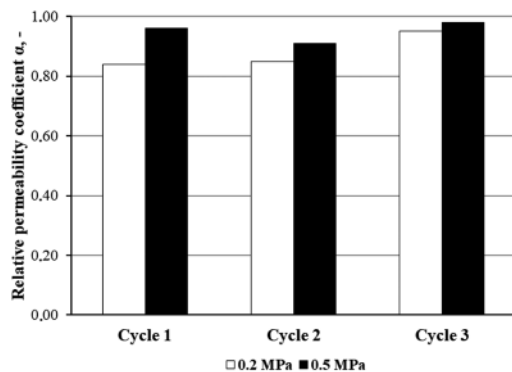


Figure 2. Hydraulic performance of the V5 ultrafiltration membrane at $\Delta P = 0.2$ and 0.5 MPa during filtration of washings from the JB system

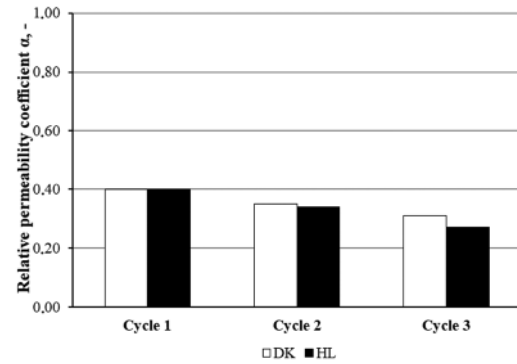


Figure 3. Hydraulic performance of nanofiltration membranes (DK and HL) at $\Delta P=3$ MPa for washings from the SP and RP systems

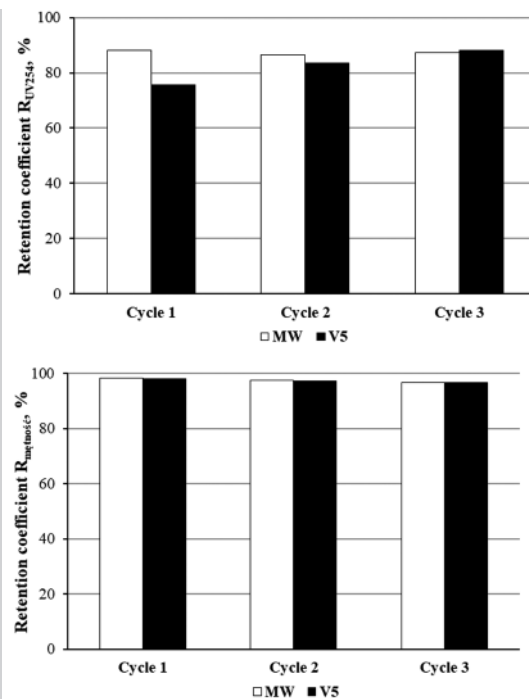


Figure 4. Separation properties of ultrafiltration membranes MW and V5 ($\Delta P=0.5$ MPa) in relation to reduction of a) absorbance R_{UV254} b) turbidity $R_{turbidity}$ of washings from the SP and RP systems

fine particles in the course of filtration of the same washings were also observed in the case of the V5 membrane. Initially, the retention coefficient R_{UV254} was smaller in the case of the V5 membrane than the MW membrane. However, in successive filtration cycles, the separation ability of the membrane increased. This was due to the formation on the surface of the membrane of the so-called secondary membrane characterized by lower porosity compared to the original membrane [14-15].

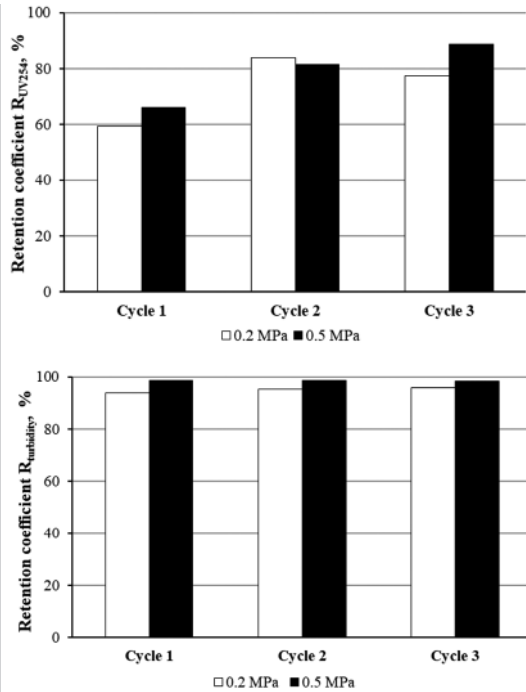


Figure 5. Separation properties of the V5 membrane at different transmembrane pressure values (0.2 MPa and 0.5 MPa) defined by the values of the average retention coefficients a) absorbance R_{UV254} and b) turbidity $R_{turbidity}$ of washings from the JB system

Fig. 5 shows a comparison of the separation abilities of the V5 membrane at different transmembrane pressure values, i.e. 0.2 MPa and 0.5 MPa. In most of the filtration cycles performed, the values of average pollution retention coefficients were higher at the pressure of 0.5 MPa compared to filtration cycles performed at the pressure of 0.2 MPa.

Fig. 6 shows a comparison of the separation properties of the DK and HL nanofiltration composite membranes during treatment of washings. The DK membrane was a little more effective in eliminating the pollution present washings characterized by the value of ultraviolet absorbance. The values of the retention coefficients were equal to 100%. With regard to reduction of turbidity, the HL membrane was more effective than the DK membrane, and its retention coefficient was more than 99%.

3.3. Toxicological assessment

The toxicological assessment was performed using the Microtox® test on the samples from the SP and RP systems before and after the filtration process. Fig. 7 shows the changes in the values of inhibition of

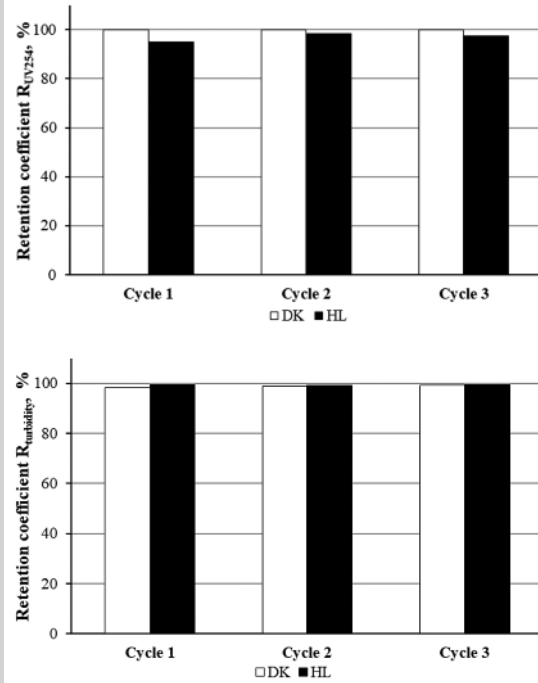


Figure 6. Separation properties of nanofiltration membranes (DK and HL) defined by the retention average ratio for a) absorbance R_{UV254} b) turbidity $R_{turbidity}$ of the washings from the SP and RP systems

bioluminescence of samples of washings: raw and after the UF and NF process. In accordance with the toxicity classification, the washings taken before treatment in the UF process were considered as toxic for the *Aliivibrio fischeri* bacteria. The inhibition of bioluminescence was equal to 56–65% after 15 minutes of exposure. After 5 minutes of exposure, the value of that parameter was slightly lower. The samples taken before the NF process were characterized as samples of low toxicity and the pollution they contained caused inhibition of bioluminescence in the range of 41 to 50%. Such differences could be related to the sample storage time and the instability of the compounds contained in the washings (the NF process was performed one week after the samples were taken and some of the toxic compounds may have decomposed). Consequently, even though all filtrations were performed using the same washings, the samples to be analyzed were each time taken before the start of the process. The most important in this case was the full reduction of toxicity in all the samples that underwent membrane filtration and the achievement of stimulation of metabolic processes in bacteria in the Microtox® test.

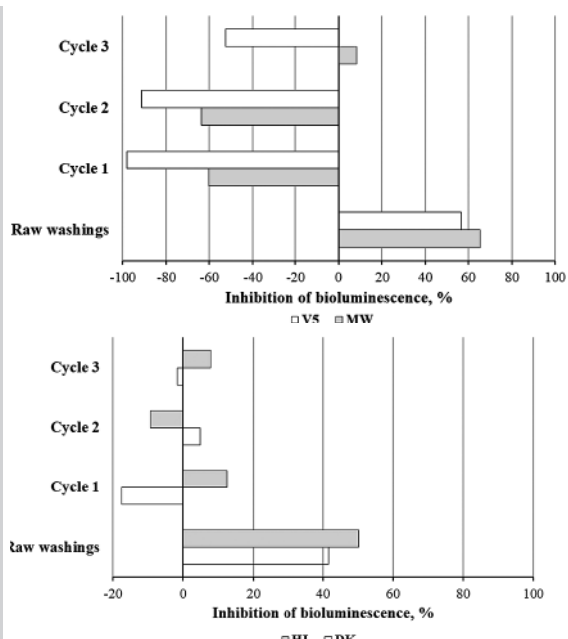


Figure 7. Changes in the value of inhibition of bioluminescence of samples of washings before and after a) ultrafiltration for the V5 and MW membranes ($\Delta P=0.5$ MPa) and b) nanofiltration for the HL and DK membranes ($\Delta P=3$ MPa)

4. CONCLUSION

The membrane processes (UF and NF) performed in the tests significantly improved the quality of the washings from swimming pool systems. Nanofiltration separated pollutants more effectively but its hydraulic performance was much lower than that of ultrafiltration. Thus, it can be concluded that preliminary preparation of washings is necessary before membrane filtration (e.g. by way of a coagulation and/or sedimentation process). The quality of the washings had a significant impact on the effectiveness of the UF process. Both lower turbidity and lower ultraviolet absorbance UV_{254nm}^{1m} contributed to the higher quality of permeate. The UF process significantly reduced the turbidity and the ultraviolet absorbance UV_{254nm}^{1m} of post-process washings. Pressure-driven membrane process performed on a technical scale may enable recovery of water from post-process washings from swimming pool systems. Of particular importance is the fact that the permeates obtained were not toxic for the *Aliivibrio fischeri* bacteria's.

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