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ADVANCED TREATMENT OF MUNICIPAL WASTEWATER IN NANOFILTRATION. EFFECT OF MEMBRANES AND OPERATING PARAMETERS ON PERFORMANCE*

POGŁĘBIONE OCZYSZCZANIE ŚCIEKÓW W NANOFILTRACJI. WPŁYW MEMBRANY I WARUNKÓW PROWADZENIA PROCESU NA JEGO EFEKTYWNOŚĆ

Abstract: In recent years, increasing attention is focused on the presence of endocrine disrupting chemicals (EDCs) in the aquatic environment that degrade its quality. These substances and derivatives of their incomplete oxidation, even at low concentrations discharge with effluent streams into natural reservoirs, strongly degrade water quality and pose a serious threat to aquatic ecosystems. Among EDCs, which presence even in trace amount is adverse for biological equilibrium in aquatic environment to which belong inter alia xenoestrogens (*ie* bisphenol A). The aim of this study was to polish wastewater constituting effluent from municipal WWTP in the nanofiltration process. Two types of membranes were used, differ in molecular weight cut-off and material (cellulose acetate, polyethersulphone). The nanofiltration process was carried out in pressure installation enabling conduction of the process in the dead-end mode on membrane area of 0.44 m^2. Polishing effectiveness was evaluated on the base of the reduction degree of typical pollution indicators (COD, TOC, phenolic compounds, total nitrogen) and bisphenol A. Obtained results show that removal efficiency of phenolic compounds in case of applied membranes was comparable. Overall it was found that membranes characterized of diversified hydraulic permeability and resistance to fouling, what constitute important factor during exploitation of membrane processes.

Keywords: EDCs, nanofiltration, wastewater treatment

Pollutions incorporated with effluent streams from *wastewater treatment plant* (WWTP) pose serious threat for purity of surface waters. It was proved many times, that biologically treated municipal wastewater did not fulfil required standards of purity [1, 2]. Particularly noxious are streams coming from municipal WWTP, because they are also often receiver of wastewaters coming from industrial plants, and they do not possess technology suitable for degradation of highly toxic compounds. Therefore many groups of micropollutants get into environment, among which particularly dangerous are heavy metals, polycyclic aromatic hydrocarbons, polycyclic biphenyls and compounds with *estrogenic biologic activity* (EDCs).

The aim of this work was polishing of real wastewater coming from effluent from municipal wastewater treatment plant in nanofiltration process. Studies determined influence of membrane polymer, pH of wastewater and operating parameters (transmembrane pressure) on effectiveness of the process.

Materials and methods

The object of study was wastewater constituting effluent from municipal wastewater treatment plant. The physico-chemical characteristics of wastewater introduced to membrane installation was shown in Table 1.

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Table 1

Characteristics of wastewater

Parameter	Value
COD [mg O_2/dm^3]	160
N-NH_4 [mg N-NH_4/dm^3]	1.1
N-NO_3 [mg N-NO_3/dm^3]	2.49
N_{Tot} [mg N/dm^3]	6.6
P-PO_4 [mg P-PO_4/dm^3]	0.4
Phenolic index [mg/dm^3]	0.29
TC [mg/dm^3]	80.7
TOC [mg/dm^3]	35.57
IC [mg/dm^3]	45.13
pH	7.2

The nanofiltration process was carried out in membrane reactor (volume 0.4 dm^3, membrane filtration area 0.44 m^2), working in dead-end mode at the *transmembrane pressure* (TMP) 2 MPa. The experiments were conducted using two kinds of flat sheet membranes, varied in polymer and *molecular weight cut-off* (MWCO). Prior to the first application, the membranes were conditioned by means of filtration of demineralized water. The characteristic of membranes was presented in Table 2.

Table 2

Characteristic of nanofiltration membranes

	Manufacturer	
	Microdyn Nadir	**GE Osmonics**
Symbol	NP010	CA
Polymer	Polyethersulfone	Acetate cellulose
Molecular weight cut-off	1000	150-300
Retention coefficient NaCl [%][1)]	35	74
Retention coefficient $MgSO_4$ [%][1)]	64	96
Contact angle (θ)	54	54
Zeta potential [mV]	pH 4 = –2; pH 7 = –5; pH 10 = –8[2)]	pH 4 = +1; pH 7 = –7; pH 9 = –9[3)]
Isoelectric point at pH	3.5[2)]	4.4[3)]

[1)] Concentration of NaCl and $MgSO_4$ solution 1 g/dm^3, TMP = 2 MPa
[2)] According to data [3]
[3)] According to data [4]

Temperature of wastewater equalled 15±2°C and pH was adjusted using 1M HCl and NaOH solutions. The effectiveness of polishing was determined on the basis of typical parameters (COD, N_{Tot}, N-NH_4, N-NO_3, TOC, IC, Cl^-) characterizing feed and permeates. Additionally phenolic index to evaluation of impact of other factors on process efficiency was used. It is a number defining the concentration of different phenol compounds in sample. Considering that municipal wastewater biodegrade during treatment on WWTP, it is obvious that compounds consisting in wastewater submit various conversions leading to forming both their less toxic metabolites and more durable derivatives. Determination of phenolic index include the whole amount of phenolic micropollutants such as phenol, alkylophenols (bisphenol A, nonylphenol), nitrophenols, chlorophenols and another derivatives, which resultant through fragmentary degradation or transformation. After each filtration of wastewater, demineralized water was refiltrated, in order to evaluate relative permeate (α_p) and demineralized water (α_w) fluxes. Measurement data have been calculated according to equations in Table 3.

Table 3

Equations to evaluate transport and separation properties of membranes

Property	Parameter	Unit	Equation
Transport	Permeate flux J_v (J_w - demineralized water)	[dm^3/m^2·s]	$J_v(J_w) = \frac{V}{F \cdot t}$
	Relative permeate flux α_p	-	$\alpha_p = \frac{J_v}{J_w}$
	Relative demineralized water α_w	-	$\alpha_w = \frac{J_{wv}}{J_w}$
Separation	Retention coefficient R	[%]	$R = \left(1 - \frac{C_p}{C_n}\right) \cdot 100\%$
V - volume of permeate [dm^3], F - membrane area [m^2], t - time [s], C_p - concentration in permeate [mg/dm^3], C_n - concentration in feed [mg/dm^3], J_{wp} - demineralized water flux after filtration of wastewater [dm^3/m^2·s].			

Results and discussion

Transport characteristic of membranes

In Figure 1 was shown demineralized water flux (J_w) and permeate flux (J_v) depending on time, assigned during filtration of wastewater at TMP 2 MPa.

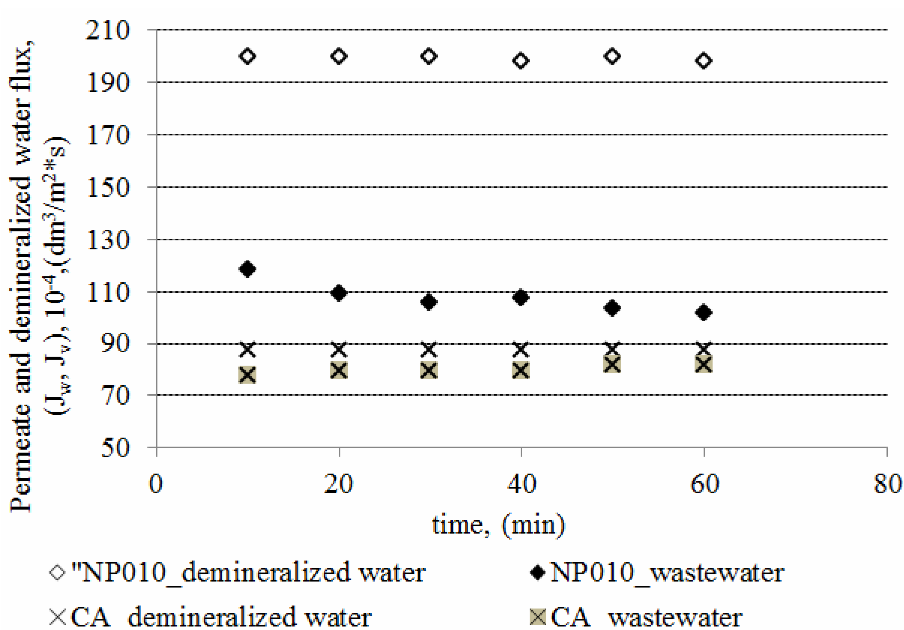

Fig. 1. Fluxes (J_v, J_w) versus time for TMP = 2 MPa

Presented magnitudes are mean value from 10 measurements. Membrane prepared from acetate cellulose (CA) characterized less hydraulic capacity in comparison with membrane NP010, what is proved less permeate and demineralized water flux. This effect could be explained by more extended structure of NP010, which enable more yield in comparison with closed structure of CA. In case of filtration of wastewater permeate flux was only lower by about 10% than demineralized water, what indicated on high fouling resistance of this membrane. For membrane NP010 maximum demineralized water equalled 0.02 $dm^3/m^2 \cdot s$, whereas maximum permeate flux was almost about half lower. Decrease of permeate flux for demineralized water flux of NP010 indicated on fouling. In order to precise description impact of fouling to transport properties of membrane relative permeate flux (α_p) were calculated. Additional intensity of fouling was evaluated on the basis of value of relative demineralized water flux (α_w), which is lower with increasing impact of fouling on membrane hydraulic performance [12].

Coefficient α_p and α_w were presented in Table 4. These values confirmed previous observation, it could be noticed that, membrane CA characterized high fouling resistance and pores of membrane NP010 gave in to substantial locking. Therefore it is obvious, that for membrane CA was recovered 100% of the initial capacity ($\alpha_p = 1$), and for membrane only NP010 65% ($\alpha_p = 0.65$).

Table 4

Relative flux α_p and α_w for membrane after polishing at TMP = 2 MPa

Membrane	**Relative permeate flux (α_p)**	**Relative demineralized water flux (α_w)**
NP010	0.27	0.65
AC	0.91	1

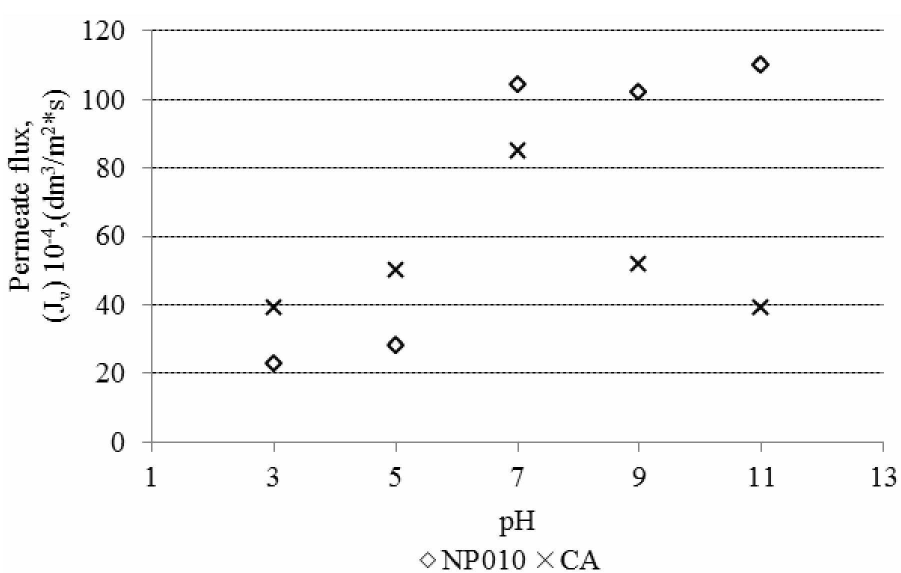

Fig. 2. Permeate fluxes versus pH of wastewater

It was also found that permeate flux was dependant on pH of wastewater (Fig. 2). Hydraulic permeability of both membranes was the lowest during filtration of acid wastewater (pH 3 and 5). This effect could be explained by significant impact of filtrated medium pH on zeta potential of membrane. The literature data [3] indicated that at acid reaction, membrane NP010 had positive charge or weak negative charge (Table 2) which was insufficient to repulse negative charged molecules of micropollutants occurring in wastewater. It caused their adsorption on membrane surface and in pores, leading to partial membrane locking and decrease of permeability. Similar mechanism was also reason of low permeate flux of CA membrane at acid wastewater. This theory was also confirmed in study, in which microscopic images proved that acid reaction of industrial wastewater (pH = 3) caused membrane locking and forming of filter cake on NP010 membrane. Whereas increase of permeate flux at pH = 7 and higher was caused by two phenomena. First was connected with increase of membrane zeta potential in alkaline reaction, leading to increase of electrostatic repulsion between dissociated sulphone groups on membrane surface and dissociated ingredients in wastewater. Molecules of micropollutants did not adsorb on membrane surface but was rejected in retentate. Second, in alkaline pH sulphone groups on membrane surface were dissociated in high rate and repulse mutually, acting membrane structure more open and more permeable.

The effectiveness of polishing wastewater

The effectiveness of polishing of wastewater in nanofiltration process depended on type of membrane (Fig. 3).

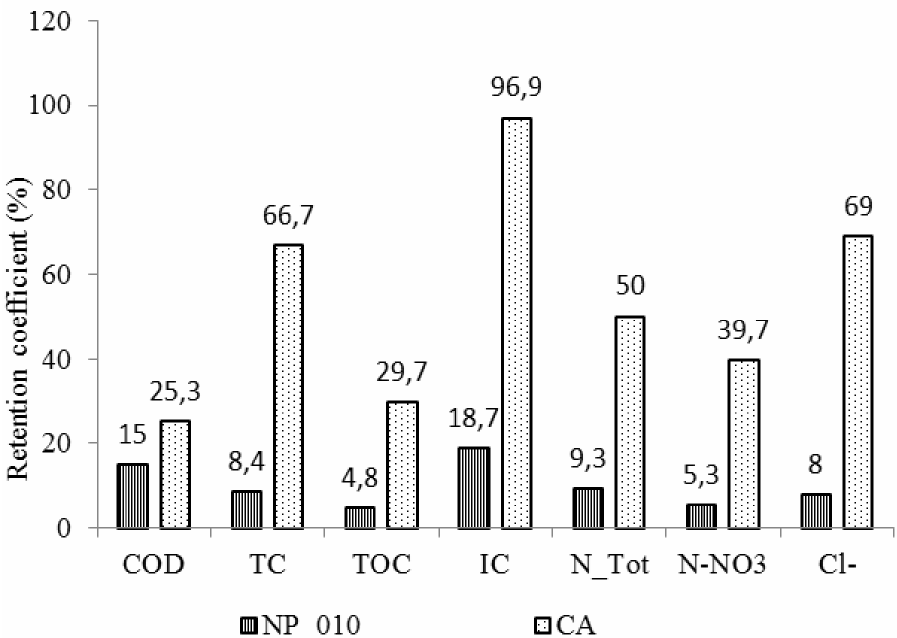

Fig. 3. Impact of membrane on retention coefficient

The removal of organic compounds expressed by COD and TOC were respectively about 40 and 84% higher on CA membrane than NP010. Concentration of total nitrogen, chlorine and inorganic compounds in permeates after filtration on CA membrane was lower in comparison with results for NP010. Low retention of pollutions on NP010 followed mainly from more open structure of this membrane in comparison with CA membrane. Molecular weight cut-off of NP010 was 10 times higher from CA membrane, it means that in case of some non-ionic pollutants, separation mechanism based on sieving effect.

Conclusions

- Considering the efficiency of the process, the susceptibility to fouling and especially quality of obtained permeates, the better membrane was CA.
- Permeate flux obtained at alkaline reaction of wastewater was three times higher in comparison with acid wastewater. It was connected with high rate of dissociation of sulphone groups, that mutually electrostatic repulse and make membrane more open and permeable.
- Highest rate of polishing was obtained for permeate after filtration on CA membrane.

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Abstrakt: Celem niniejszej pracy było pogłębione oczyszczenie ścieków rzeczywistych stanowiących odpływ z komunalnej oczyszczalni ścieków w procesie nanofiltracji. Zastosowane membrany nanofiltracyjne różniły się graniczną masą molową i materiałem, z jakiego je wykonano (octan celulozy i polieterosulfon). Proces filtracji membranowej odbywał się w ciśnieniowym urządzeniu przystosowanym do prowadzenia procesu w układzie filtracji jednokierunkowej (dead-end), na membranie o powierzchni czynnej 0,44 m^2. Efektywność procesu doczyszczania została określona na podstawie stopnia obniżenia bisfenolu A i typowych wskaźników zanieczyszczeń (COD, TOC, IC (węgiel nieorganiczny), $N_{og.}$). Uzyskane wyniki wskazują, że stopień usuwania mikrozanieczyszczeń na badanych membranach był porównywalny. Badane membrany nanofiltracyjne charakteryzowały się zróżnicowaną wydajnością hydrauliczną i odpornością na foulingu, co jest istotne z punktu widzenia eksploatacji procesów.

Słowa kluczowe: EDCs, nanofiltracja, oczyszczanie ścieków