ECOLOGICAL CHEMISTRY AND ENGINEERING A

Vol. 18, No. 12 2011

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APPLICATION OF POLYSULFONE MEMBRANES FOR COKE-MAKING WASTEWATER TREATMENT

MEMBRANY POLISULFONOWE W OCZYSZCZANIU ŚCIEKÓW KOKSOWNICZYCH

Abstract: Considering the complicated and variable type of coke-making sewages their purification strategy is difficult to generalize and it requires an integrated system, which joins biological and physicochemical separated processes. In the paper the researches were presented, which purpose was to define the efficiency of purifying matting pressure membrane techniques – ultrafiltration and reverse osmosis. In the process of low-pressure filtration flat membranes, applied in the laboratory, were different in terms of compactness of structure and porosity.

Keywords: coke-making wastewater treatment, integrated system, membranes pressure techniques, polysulfone ultrafiltration membranes

The aqueous-sewage management environmentally safe is the obligation of each industrial plant. The best solution would be to establish a local sewage treatment plants assuring to neutralize wastewaters.

The negative effect caused by coking plants upon the environment consists in carrying industrial waters cleared in the insufficient rank to plumbing or receivers. The way of cleaning them is of great importance in aspect of nature protection. The coke-making wastewaters industry have changeable compound composition. They contain: polycyclic aromatic hydrocarbons, compounds heterocyclic, oils, tars and substances of inorganic character such as: cyanide, sulfides, sulfates, thiosulfates, ammonia and also heavy metals. One of the ways and the most frequently applied in the wastewater treatment technology and which seems to be environmentally friendly are pressure membrane techniques. It is possible to link them with classical separated processes of purifying wastewaters into so-called hybrid or integrated systems [1–9].

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Apparatus

In the process of membranes cleaning coking industry sewages a system equipped with the plate-frame membrane module of the American Osmonics company of the SEPA CF-NP type, the container of sewers with the radiator was applied as well as cone-and-float meter, the high-pressure pump and manometers and valves. A scheme of the equipment used in investigations is presented below.

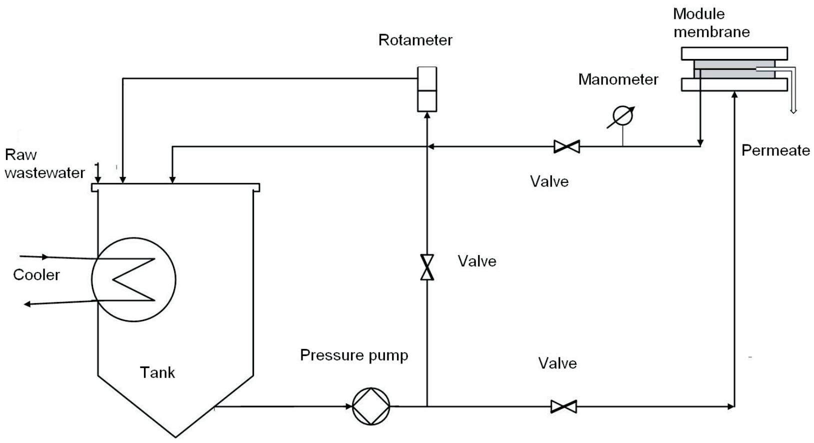

Fig. 1. Scheme of the plate- and frame membrane module applied for cleaning coke-making sewage

Raw wastewater

The process of cleaning was applied in the coke plant effluents coming from Coke Plant ISD Huta Czestochowa "Koksownia" Sp. z o.o., which characteristics are displayed in Table 1.

Table 1

Characteristics of coke-making effluents
from coking plant ISD Huta Czestochowa "Koksownia" Sp. z o.o.

Indicator	Unit	Raw wastewater	Accompanied to receiver set the coefficients of pollutions of sewages*
pH	[-]	8.7–10.9	6.5–9.0
COD	mgO_2/dm^3	4200–3100	125
BOD_5	mgO_2/dm^3	20–80	25
Ammoniacal nitragen	mg NH_4^+/dm^3	25–104	10

* Directive of the Environment Minister from 24th of July 2006 in the matter of conditions one should fulfil which at inserting sewages to waters or soil, and in the matter of substances particularly harmful to the environment aqueous (DzU 2006, nr 137, poz. 984).

As we can observe the values of coefficients describing coke-making wastewater in comparison with standardized values are higher what makes it impossible to pour them directly in to receiver. They are also hard to biodegradation process due to very low value of BOD_5/COD relationship

Analytical methods

During the first stage of researches carried out diversified polysulfone flat membranes were prepared varying from 13 to 17 % mass of the polymer in organic solvent and their appropriate porosity was outlined. In order to form of long-lasting membrane structure they were subjected to the process of conditioning, consisting in pure water filtering with the changeable membrane pressure taking out from 0.5×10^5 Pa to 3.0×10^5 Pa and linear velocity of pure water over membrane surface – 2 m/s. Membranes shaped up to the moment of stabilizing the amount of the flux of pure water.

During the next part of the experiment their transport properties were defined outlining relation between the volumetric flux of pure water from and the trans--membrane pressure changed in the scope of value from 0.5×10^5 Pa to 3.0×10^5 Pa and linear velocity of medium over the membrane surface – 2 m/s.

The last stage of researches consisted in defining the possibilities of applying manufactured ultrafiltrating polysulfone membranes in cleaning coking industry sewages. The usefulness of the membranes depended on: permeability of membranes, relative permeability and the grade of removing the cargo of pollutants from wastewater.

According to interlaboratory studies, purified (with the suitable polysulfone membrane singled out earlier) coke-making industry sewages were characterized by high value of ratio of pollutants which impeded the immediate carrying them to the natural receiver, they were subjected to cleaning with the reverse osmosis method applying of the Osmonics company of the SE type membrane The effectiveness of this process was assessed, as in the case of ultrafiltration taking into consideration the size of the permeate flux and the change in pollutants value of raw and purified sewages characteristics.

Results and discussion

Preparing asymmetric polysulfone membranes and marking their proper porosity

Preparing PSF membranes consisted in pouring the thin film out from membrane solution and gelation into pure water. The membrane solution was prepared by dissolving in period of 24 h polysulfone in *N,N*-dimethylformamide.

The concentration of the polymer changed in the scope from 13 to 17 % weight what resulted in the shift of the porosity and consequently in the density of the membranes structure (Fig. 2).

We can see clearly that the porosity of membranes decrease together with the increase of the concentration of the polymer and their structure became much more

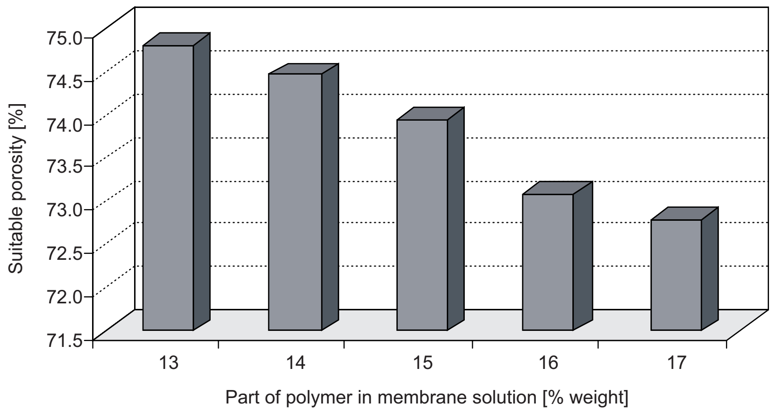

Fig. 2. Dependence of suitable porosity synthesized polysulfone memebranes on content polysulfone in membrane solution

open. So the porosity of the PSF-13 membrane took the 74.8 %, PSF-15 of the 73.94 % and the lowest was the PSF-17 with the 72.8 %.

Transport properties of ultrafiltration polysulfone membranes

Defining the transport property of manufactured membranes consisted in outlining the relation between the temporary volume stream of pure water and the pressure. Measurements made demonstrated that the plumbing membranes productivity dependence on the pressure trans-membrane (Figs. 3, 4).

The biggest volumetric flux of pure water was observed in PSF-13 membrane and the lowest stream was obtained in PSF-17 membrane due to the its clenched structure. For the trans-membrane pressure 3×10^5 Pa it was 97 times smaller in comparison with

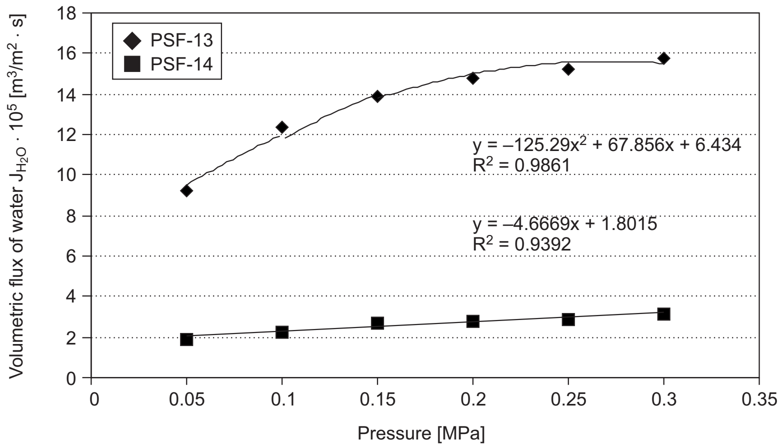

Fig. 3. Dependence of volumetric water flux on use ie pressure for membranes PSF-13 and PSF-14

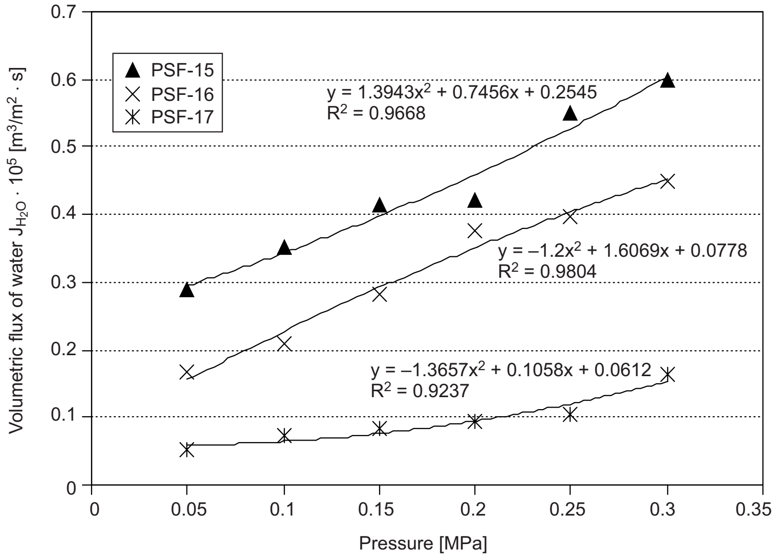

Fig. 4. Dependence of volumetric water flux on use ie pressure for membranes PSF-15, PSF-16 and PSF-17

the flux water for the PSF-13 membrane, in the same conditions of the filtration. In the case of all membranes relations $J_{H_2O} = f\ (\Delta P)$ described quadratic equations and high value of rates proved the correct selection of the regression line (function).

Coke-making wastewater purification in integrated system of ultrafiltartion-reverse osmosis

Investigations carried out in this stage were supposed to allow to outline a polysulfone ultrafiltrating which would be describe itself with the big efficient and would assure the biggest grade of removing charge of pollutants from cleaning wastewater. Coke-making industry sewages was subjected to cleaning with low pressure filtration outlining for each of membranes the relation between experimental temporary flux and the time filtration (Figs. 5, 6).

The biggest flux post-treat was observed in the process of the low-pressure filtration of the PSF-13 membrane. Its value took 2.73×10^{-5} $m^3/m^2 \cdot s$ out after stabilizing.

The fastest decrease of the stream was observed for this membrane at the same time during what was caused by the biggest intensity of the fouling process. In the 125 first minutes the flux permeate diminished 5 times.

Different post-treat properties were observed in PSF-17 membrane which had the lowest stream and in comparison with PSF-13 47.1 % smaller. Also for this membrane the smallest stream decrease was registered.

Changes estimated as the relationship of the experimental volumetric momentary flux, in their relative permeability were also appointed in the ultrafiltration process of cleaning coking industry sewages for examined membranes permeate (Jv) to the initial

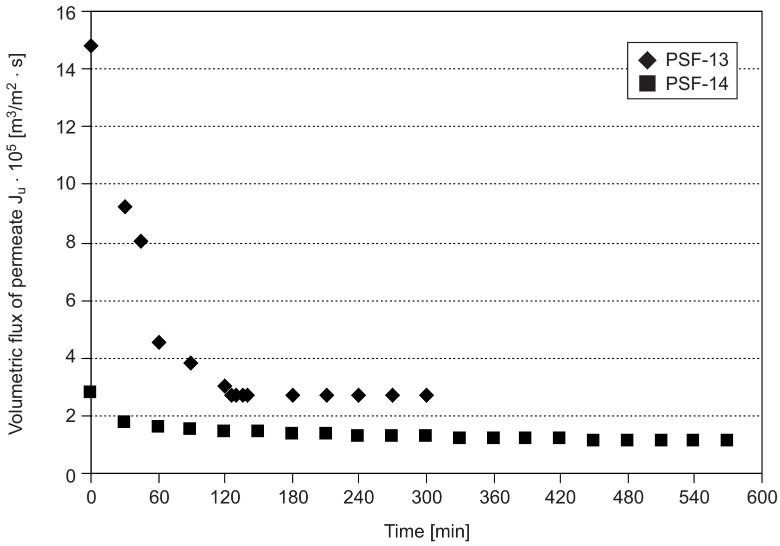

Fig. 5. Dependence of temporary experimental volumetric flux on time treatment coke-making ultrafiltartion process at membranes PSF-13 and PSF-14

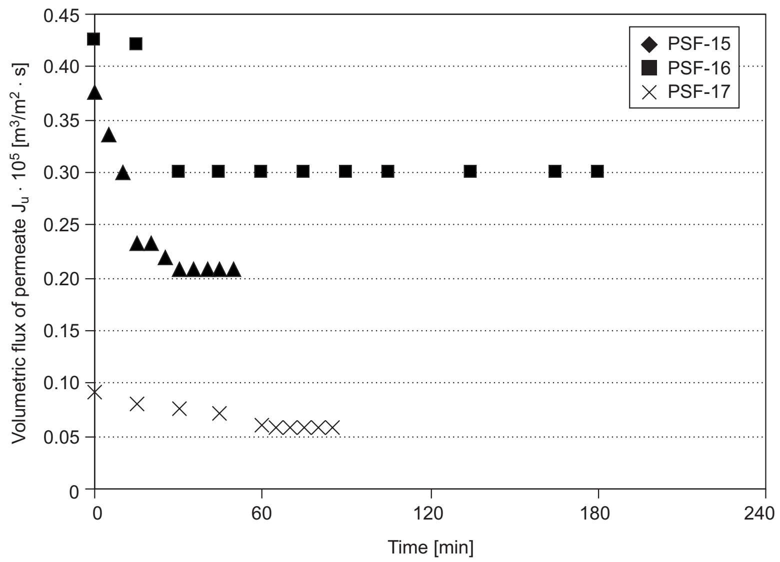

Fig. 6. Dependence of temporary experimental volumetric flux on time treatment coke-making ultrafiltartion process at membranes PSF-15, PSF-16 and PSF-17

flux of pure water (J_0). The change in the permeability of the relative membrane is bound with intensity of the phenomenon setting on its surface and inside pore of the low-pressure process for the membranes fouling separation, into lowering, in the considerable way relative permeability of the membrane. Many factors have effect on to the step of membrane polluting, and the most important are: affinity of chemical substances presented in sewages in comparison with polymer membrane material and the size and the structure of their particles. In Figs. 7 and 8 changes in the relation for the relative permeability of membranes were compared from the time low-pressure filtration carry out for cleaning coking industry sewages.

It has been proved that the lowest relative permeability had PSF-13 membrane and the highest PSF-16. It was demonstrated that the relative permeability of examined

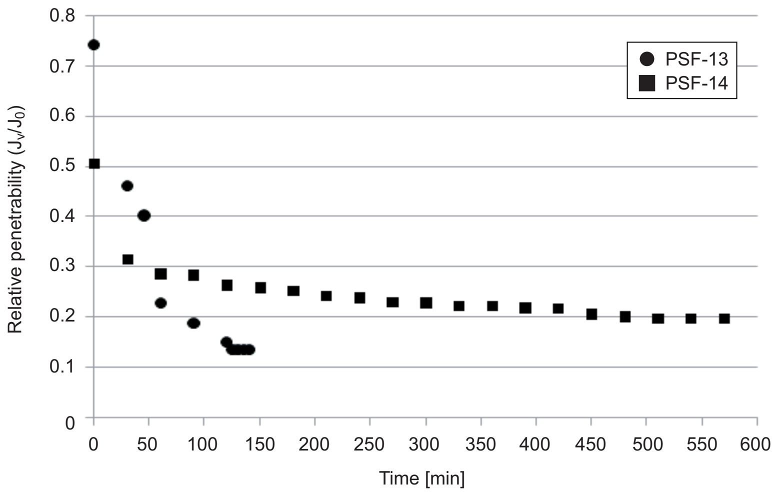

Fig. 7. Compare dependence of changes relative penetrability polysulfone membranes PSF-13 and PSF-14 on time treatment coke-making ultrafiltration process

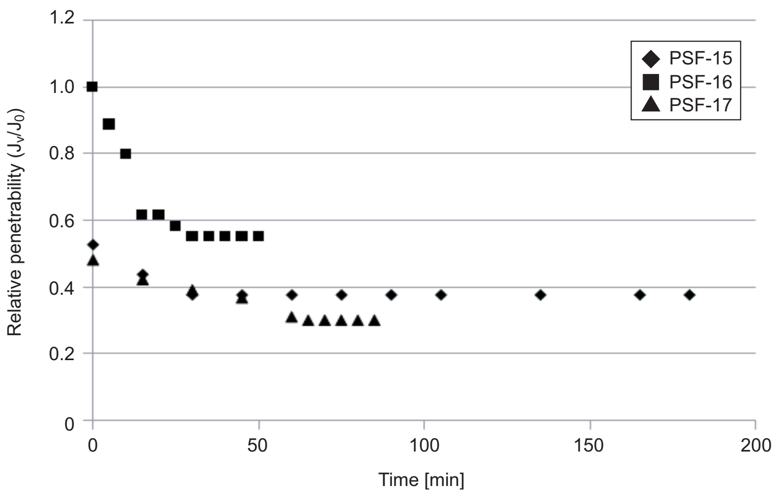

Fig. 8. Compare dependence of changes relative penetrability polysulfone membranes PSF-15, PSF-16 and PSF-17 on time treatment coke-making ultrafiltration process

membranes is a function of the density of their structure. The PSF-13 membrane the most opened structure is relatively easily undergoing the fouling process. The pores are blocked quickly by sewages due to the big diameters. Together with the height membrane polymeric contents their porosity is decreasing and the relative permeability is increasing. Another lowering was observed in the PSF-17 membrane. It is possible to example this fact with the smallest porosity of this membrane that caused layer covering in the form of pollutants as a result in a smaller intensity and blocks the pores of "secondary membrane" which final has the smaller membrane permeability in comparison with membranes with blocked times. The assessment criterion for the effectiveness of low-pressure wastewater filtration was apart from the size of the volumetric flux permeate and relative permeability, step of removing of pollutants. The level of cleaning coke-making wastewater was related with the change of value of the following parameters: COD, TC and TOC, which was typical for "raw" and cleaned sewers. For the PSF-16 membrane additionally a dry substance remains after roasting and conductivity.

From prepared for five polysulfone membranes, as it was expected, none assured the high level of removing charge of pollutants from cleaned sewages appropriately what made it impossible in consequence their immediate carry to the natural environment (Table 2).

Table 2

The stage of removal in process the cargo of pollutions treatment coke-making sewages in ultrafiltration process with use of polysulfone membranes

Membrane	Indicator	Unit	Raw wastewater	Permeate	Degree of removal pollutions [%]
PSF-13	COD	mgO_2/dm^3	3266	2939	10
	TC	mgC/dm^3	720.95	690.7	4.2
	TOC	mgC/dm^3	495.58	481.7	2.8
PSF-14	COD	mgO_2/dm^3	3038.5	2488.5	18.1
	TC	mgC/dm^3	718.2	638.5	11.1
	TOC	mgC/dm^3	483.2	450.8	6.7
PSF-15	COD	mgO_2/dm^3	3808	3027.4	20.5
	TC	mgC/dm^3	707.3	600.5	15.1
	TOC	mgC/dm^3	494.6	448.6	9.3
PSF-16	COD	mgO_2/ dm^3	2754	2087.5	24.2
	TC	mgC/dm^3	616.9	515.1	16.5
	TOC	mgC/dm^3	390.7	340.3	12.9
	DS	g/dm^3	6.28	6.09	3
	Compounds of inorganic substances	g/dm^3	0.605	0.35	42
PSF-17	COD	mgO_2/dm^3	2754	1556	43.5
	TC	mgC/dm^3	616.9	70.7	88.6
	TOC	mgC/dm^3	390.7	63.3	83.8

TC – Total carbon; TOC – Total organic carbon; COD – Chemical Oxygen Demand.

As the most suitable was accepted PSF-16 membrane with 16 % weight of the polymer in membrane solution. Its choice was determaid by the the volumetric flux size of permeate flux, which in comparison with the membrane about the most clenched structure (PSF-17) was over three times higher ($\Delta P = 3.0 \times 10^5$ Pa). Besides that this memebrane had the highest relative permeability.

After using this membrane purified sewages were characterized by the following indexes of pollutants: COD – 2087.5 mgO^2/dm^3, the concentration of total carbon TO of 515.1 mgC/dm^3, total organic carbon of 340.3 mgC/dm^3 and ammoniacal nitrogen 98 $mgNH^+_4/dm^3$. As it can be seen all the values exceeded the acceptable standardized levels. Sewages left after the process of ultrafiltration treatment were subjected to in additional cleaning of the reverse osmosis with the method on polymer for SE membrane. Changes in the volumetric flux of pure water and sewages were measured during the investigations and we can concluded, that outlined fluxes during carry out the process (pure water and permeate) moved close. It proves the fact that the applied osmotic membrane is characterized by a big density (Fig. 9).

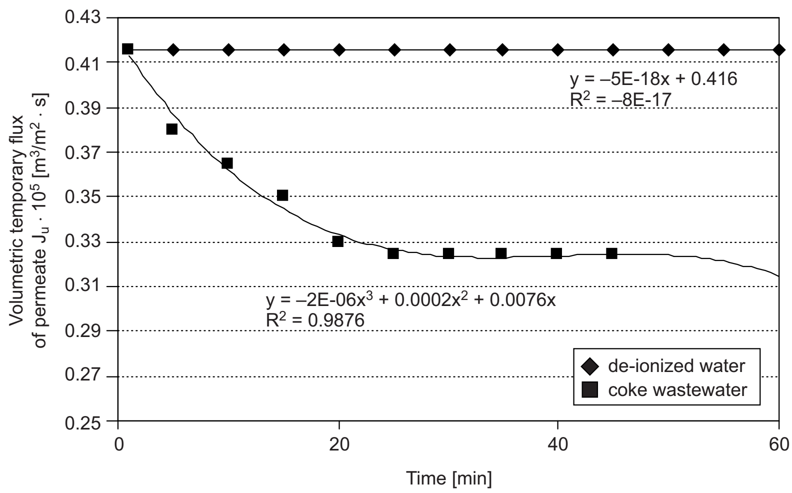

Fig. 9. Dependence of temporary volumetric treatment coke-making wastewater and pure water on time high pressure process

Compared indicators cleaned in the integrated system ultrafiltration-reverse osmosis of pollutants in sewages were described in Table 3.

Unfortunately in this way cleaned effluents did not fulfil qualitative norms presented into the Directive of the Environment Minister from 24th July 2006. Concerning the conditions that should be at inserting sewages into waters or soil, and in the matter of substances particularly harmful to the environment aqueous (Log. Act 2006 number 137 item 984). They stated the exceeding of the acceptable concentration of ammoniacal nitrogen passed 2-ratio (22.4 $mgNH_4^+/dm^3$) that is way the sewages should subjected to the stripping process before carry them to the natural receiver.

Table 3

The efficiency of cleaning in integrated system ultrafiltration-reverse osmosis coke-making sewages

Indicator	Unit	Raw waste-water	Cleaned sewages				Value of coefficients for introduced sewages to land waters
			UF-PSF-16		RO-SE		
			Value	Stage of removal of pollutions [%]	Value	Stage of removal of pollutions [%]	
COD	mgO_2/dm^3	2754	2087.5	24.2	74.3	97.3	125
9TC	mgC/dm^3	616.9	515.1	16.5	29.3	94.3	ns.
TOC	mgC/dm^3	390.7	340.3	12.9	12.1	96.4	ns.
Ammoniacal nitrogen	$mgNH_4^+/dm^3$	131.6	98.0	25.5	22.4	83.0	10

TC – Total carbon; TOC – total organic carbon; ns.– not standardized.

Conclusions

1. Coke-making sewages sequential system of ultrafiltration-reverses osmosis applied in investigations didn't provide properly high degree of treatment.

2. From prepared five polymeric low-pressure filtration membranes the most profitable was a PSF-16 membrane showed itself for 16 % weight contents of the polymer in membrane solution. Since none of membranes assured the high level of coke-making industry wastewater purification the choice was determined by the size of the volumetric flux permeate, which in comparison with the membrane with the most clenched structure (PSF-17) was over three times higher ($\Delta P = 3.0 \times 10^5$ Pa) and had highest relative permeability.

3. Sewages cleaned in the process of the reverse osmosis were characterized by too high concentration on the level, of ammonia 22.4 $mgNH_4^+/dm^3$. They should before carry them to the natural receiver, be subjected to the stripping process.

Acknowledgement

The researches were carried out by BW 401/201/08.

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MEMBRANY POLISULFONOWE W OCZYSZCZANIU ŚCIEKÓW KOKSOWNICZYCH

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Abstrakt: Ze względu na złożony i zmienny skład ścieków koksowniczych strategia ich oczyszczania jest trudna do uogólnienia i wymaga prowadzenia tego procesu w układach zintegrowanych, kojarzących biologiczne i fizykochemiczne procesy jednostkowe. W artykule omówiono badania, których celem było określenie efektywności oczyszczania ścieków koksowniczych w układzie kojarzącym ciśnieniowe techniki membranowe, a mianowicie ultrafiltrację i odwróconą osmozę. W procesie niskociśnieniowej filtracji zastosowano wytwarzane w laboratorium płaskie membrany polisulfonowe różniące się zwartością struktury i porowatością.

Słowa kluczowe: oczyszczanie ścieków koksowniczych, układy zintegrowane, ciśnieniowe techniki membranowe, polisulfonowe membrany ultrafiltracyjne