



Modeling performance of commercial membranes in the low-pressure filtration coking wastewater treatment based on mathematical filtration models

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ABSTRACT

Based on the results achieved in the coking industry wastewater ultrafiltration treatment and the presumptions of relaxation mathematical model carried out in non-stationary system, and based on the assumptions of the model of hydraulic resistance to filtration, the changes in the volumetric permeate flux in the process of membrane filtration has been described. The research was conducted on the effectiveness of the treatment of wastewater from coke plant industry. Coking industry wastewater treatment was carried out with the use of American GE-Water ultrafiltration membranes. The process of ultrafiltration was performed at 23°C, using transmembrane pressure of around 0.4 MPa and linear wastewater flow rate of 2 m/s. For all the examined membranes, the transport characteristics corresponded to the relation between the volume flux of de-ionized water and transmembrane pressure of 0.2–0.8 MPa. The level of wastewater purification was defined for raw and cleaned wastewater indicators. None of the ultrafiltration membranes allowed the high level of pollutants to be removed. Thus, they were treated by reverse osmosis method (RO). The calculations based on the assumptions of the mathematical filtration models made it possible to predict the efficiency of commercial ultrafiltration membranes used in the process.

Keywords: Coke plant wastewater; Industrial membranes; Low- and high-pressure membrane techniques; Mathematical filtration models

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1. Introduction

It is commonly known that coking plants adversely affect the environment, particularly given the difficult generation of biodegradable ($BOD_5/COD < 0.02$) post-trial coke wastewater, loaded with a large load of toxic substances [1]. The content of the liquid wastes can be, among others, polycyclic aromatic hydrocarbons, heterocyclic compounds, oils, tars, and substances of inorganic character: cyanide, sulfides, sulfates, hyposulfite, ammonia, and ions of heavy metals [2]. Therefore, coking wastewater before being discharged to the receiver is supposed to be subjected to purification process. Depending on the type of pollution, treatment methods should be chosen at the lowest cost possible, provided that the highest degree of removal from impurities is maintained. The usage of integrated ultrafiltration–reverse osmosis system seems to be a promising solution in the treatment of coke plant wastes. However, during the realization of the pressure membrane processes, one can observe a decrease in the membranes' permeability and the independence of the size of permeate stream from the transmembrane pressure. The decrease of permeate flux with time causes the lowering of effectiveness of the membrane process, and it has a negative impact on its efficiency. There are a lot of models describing the reasons for volumetric lowering of permeate flux during the process of filtration carried out for the determined and non-determined conditions of exploitation [3]. The obtained results of the carried out research made it possible to verify the pressure model of membrane filtration on the basis of the change of permeate flux size within the time at the determination of time constant, which characterizes the lowering of the effectiveness process to the value below that of economical profitability [4].

The authors attempted to assess the effectiveness of coke wastewater treatment in the ultrafiltration–reverse osmosis system with the use of commercial ultrafiltration membranes.

In addition, they attempted to predict the efficiency of commercial ultrafiltration membranes based on the relaxation model assumptions and hydraulic filtration resistance model.

2. Materials and methods

In the process of membrane treatment of coke plant wastes, the apparatus unit used was equipped with a plate-frame membrane module of the type: SEPA CF-NP produced by an American company, GE-Water. The installation applied in the research is presented in Fig. 1 [3].

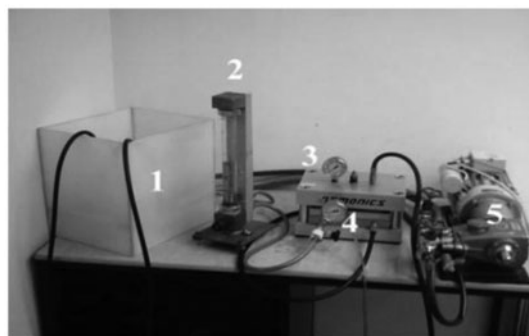


Fig. 1. Photo equipment to conduct the coke wastewater by pressure membrane filtration: 1—tank, 2—rotameter, 3—membrane module, 4—manometer, 5—high pressure pump.

2.1. Raw wastewater

The treated coke plant wastes came from a coke plant near Czestochowa. Table 1 shows the values of the chosen indexes of pollution which are characteristic of coke plant wastes after initial treatment. Initially, it was subject to mechanical treatment; so tar substances, oils, and solids were removed, and then it was submitted to phenol removal processes and gas desorption in order to remove ammonia.

2.2. Membranes

In the research we applied four types of ultrafiltration commercial polymer flat membranes (HZ15, PVDV, PW, DS-GM) and one reverse osmosis polymer membrane ADF. All the flat membranes were produced by the American company, GE-Water, from different polymers. Their characterization provided by the producer is shown in Tables 2 and 3.

2.3. Analytical methods and analytical identification

In the first stage of the study after the application of flat polysulfone membranes, for permanent formation of their structure, they were subjected to preconditioning. This conditioning consisted of filtering de-ionized water through them at the changeable transmembrane pressure within the range of 0.2–0.8 MPa and with the flow speed above the surface equal to 2.0 m/s. The membranes were conditioned up to the moment of stabilization of the size of de-ionized water flux within the time. In the following stages of the experiment, the usefulness of the searching membrane for the treatment of coke plant wastewater was determined. The evaluation criteria were changes in the values of the membrane flux and the degree of removing the load of impurities. The effectiveness of

Table 1

The characteristics of coke plant wastes coming from Czestochowa Coke Plant, after initial treatment

Indicator	Value	The indexes of sewage pollution which is carried away to the receiver ^a	Technical water—to quenching of coke ^b
pH	9.41	6.5–9.0	–
COD, mg O ₂ /dm ³	4,519.6	125	–
BOD ₅ , mg O ₂ /dm ³	50	25	–
Volatile ammonia as NH ₄ ⁺ , mg NH ₄ ⁺ /dm ³	131.6	10	82
TN, mg N/dm ³	1820	30	–
TC, mg C/dm ³	1,184.6	–	–
TOC, mg C/dm ³	963.1	30	–
Phenols, mg/dm ³	381	0.1	15
Cyanides, mg/dm ³	27.3	0.1	9
Sulfides, mg S ²⁻ /dm ³	0.92	0.2	–
Conductivity, mS/cm	8.41	ns.	–
The overall alkalinity, mval/dm ³	29.92	10	–
General iron, mg/dm ³	2.71	10	–
The concentration of calcium ions, mg Ca ²⁺ /dm ³	64.79	20	–
The concentration of magnesium ions, mg Mg ²⁺ /dm ³	7.96	20	–

TC—total carbon, TOC—total organic carbon.

^aDirective of the Environment Minister from day 28 of January 2009 r. in the matter of conditions one should fulfill which at inserting sewages to waters or the Earth, and in the matter of substances particularly harmful to the environment aqueous (Log. Act. 2006 No. 137 item. 984), RLM = 100,000 and under.^bBAT—Best Available Techniques for coking plant, December 2005; ns.—not standardized.

Table 2

The characteristics of commercial ultrafiltration membranes applied in the treatment coke-making wastewater [2,3]

Membrane	Polymer	Indicator	Cut-off (kDa)	pH	Pressure (MPa)	Cl (ppm)	Temperature (°C)
UF	Polyethylene glycol	DS-GM	8	2–11	1.4	5,000	90
UF	Polyethersulfone	PW	10–12	2–11	0.2	5,000	90
UF	Polystyrene	HZ15	20	0.5–13	0.17	5,000	80
UF	Polyvinylidene fluoride	PVDV	30	1–11	0.2	5,000	90

Table 3

The characteristics of commercial reverse osmosis membrane applied in treatment coke-making wastewater [1,2]

Membrane	Polymer	Indicator	Retention coefficient (%)	pH	Pressure (MPa)	Cl (ppm)	Temperature (°C)
RO	polyamide (AD)	ADF	99.5	4–11	5.4	1,000	50

the process was evaluated on the basis of the change of indexes of impurities which characterize raw and treated wastes. The following were also determined: chemical oxygen demand (COD), total organic carbon (TOC) and total carbon (TC), concentration of phenol index, free cyanide, and ammonium nitrogen. The amount of COD was determined by means of HACH DR 4000 spectrophotometer, and TOC and TC were determined by means of high-temperature catalytic oxidation method with the usage of a chromatograph.

The concentration of free cyanide, phenol, and sulfides was determined by a test using cell tests from HACH LANGE DR spectrophotometer 2800. The study also determined the contact angle of the membranes.

The coke plant wastes treated in the low-pressure filtration process were still characterized by the indexes which were impossible to be removed, and thus they were cleaned thoroughly by means of reverse osmosis method ($\Delta P = 2$ MPa, $u = 2$ m/s).

3. Results and discussion

3.1. The transport properties of the ultrafiltration polysulfide membranes

Transport properties of membranes were determined while clarifying the dependence of the flux of volumetric de-ionized water on the transmembrane pressure. The carried out measurements proved the significantly diversified dependence of the hydraulic membranes' productivity.

Depending on the volume of water fluxes from the pressure applied in all cases the functions of the power series were described. High values of correlation coefficients clearly showed a proper choice of the regression line to the measurement results (Fig. 2).

Of all the ultrafiltration membranes tested, the DS-GM membrane had the lowest volumetric flux ($J_{H_2O} = 0.037 \cdot 10^{-5} \text{ m}^3/\text{m}^2\cdot\text{s}$; $\Delta P = 0.4 \text{ MPa}$), whereas the highest efficiency had the HZ-15 membrane ($J_{H_2O} = 2.865 \cdot 10^{-5} \text{ m}^3/\text{m}^2\cdot\text{s}$; $\Delta P = 0.4 \text{ MPa}$).

3.2. Measurement of contact angles of membranes

Measurement of contact angle goniometer was performed using a drop method (sessile drop method), which is based on measuring the wetting angle between a drop of de-ionized water, air, and surface membrane (Table 4).

It is assumed that the membrane has high hydrophilic properties if the angle of wetting with de-ionized water is less than 45° [4], intermediate if the angle ranges from 45° to 90° , and highly hydrophobic if the angle is greater than 90° [5]. The study showed that the membranes used in the ultrafiltration studies could be characterized as somewhere in between

Table 4

The contact angle of ultrafiltration membranes

Membrane	Contact angle ($^\circ$)
DS-GM	45
PW	60
HZ-15	58.5
PVDV	51

hydrophobic and hydrophilic. The value of contact angles ranged from 45° (DS-GM) to 60° (PW).

3.3. The selection of the ultrafiltration membrane to the pre-treatment of coke plant wastes

Membrane efficiency and degree of removal efficiency were the factors determining which of the membranes was the most useful for the initial coke plant wastewater treatment.

Fig. 3 shows the dependence of the flow of purified wastewater flux on the low-pressure filtration time.

It was found that during the low-pressure filtration of coke plant wastewater, DS-GM membrane had the lowest volumetric permeate flux. After 90-min process of ultrafiltration, the steady permeate flux had the value of $0.0289 \cdot 10^5 \text{ m}^3/\text{m}^2\cdot\text{s}$. However, the highest permeate stream had the HZ-15 membrane with the stream 22 times higher ($0.636 \cdot 10^5 \text{ m}^3/\text{m}^2\cdot\text{s}$).

Degree of removal of pollution load was assumed to be a criterion for assessing the effectiveness of the ultrafiltration wastewater treatment. The degree of wastewater purification was determined by the change of pollution indicators in raw and cleaned wastewater

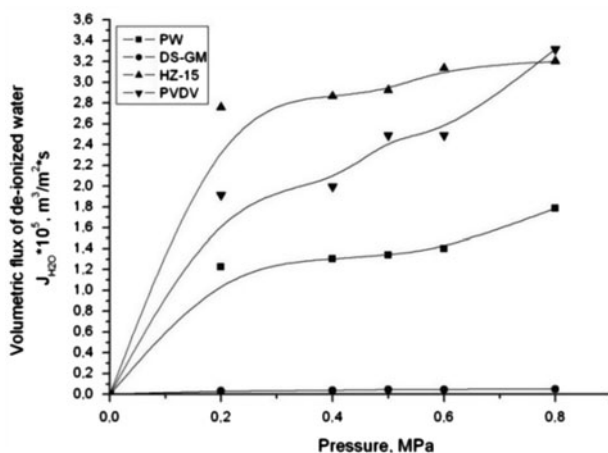


Fig. 2. Dependence of volumetric flux de-ionized water on use i.e. pressure for ultrafiltration commercial membranes.

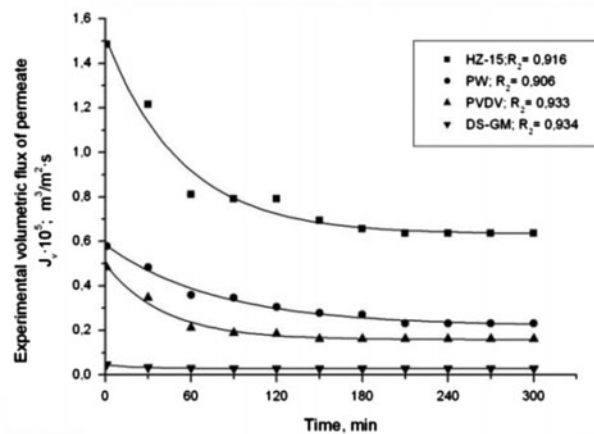


Fig. 3. Dependence of temporary experimental volumetric fluxes on time treatment coke-making ultrafiltration process ($\Delta P = 0.4 \text{ MPa}$).

Table 5

The characteristics of commercial ultrafiltration membranes applied in initial treatment coke-making wastewater [1,2]

Membranes	Treated wastewater					
	COD	R^* (%)	TC	R^* (%)	TOC	R^* (%)
PW	3,789	16.9	590.8	50.2	523.8	45.3
DS-GM	2707.6	40.1	451.7	62	378.1	60.7
HZ-15	4029.1	10.8	855.4	27.9	727.1	24.5
PVDV	3755.9	16.2	698.6	41.1	64.6	32.8

R^* — the degree of removal of pollutants.

(Table 5). Coke plant wastewaters were characterized by the following pollution indicators: COD—4,519.6 mg O₂/dm³, TC—1,186.4 mg C/dm³, TOC—963.1 mg C/dm³, and the concentration of phenols and cyanides, consequently: 27.3 mg/dm³ and 38.1 mg/dm³. The most advantageous was the DS-GM industrial membrane. The pollution indicators' value in this case was the lowest. Cleaned wastewater was characterized by the following pollution indicators: COD—2,711.7 mg O₂/dm³, total carbon TC—451.7 mg C/dm³, total organic carbon TOC—378.1 mg C/dm³, and the concentration of phenols and cyanides, consequently: 24.2 mg/dm³ and 35.5 mg/dm³.

However, all the values significantly exceeded the standards of quality that make it possible to pour cleaned wastewater into water container or drainage. It was also inadequate for reuse as a medium for quenching of coke. Taking this into consideration a

decision of applying reverse osmosis process was taken (Table 6).

The obtained research results can lead to the conclusion that the wastes additionally treated in the process of reverse osmosis still did not meet the standards of quality given by the decree of the Minister of Environment on 28 January 2009 concerning the conditions which should be fulfilled to pour away the sewage into water and to the soil, and concerning the substances which are particularly harmful to water environment since the concentration of ammonium nitrogen was high. A twofold excess over the permissible levels of volatile ammonium ions in terms of N-NH₄⁺ was found. This is way the sewages should be subjected to stripping process before carrying them to the natural receiver. Treatment of wastewater can be used as technical water—for quenching of coke.

3.4. The modeling of the low-pressure filtration process in the process of treating the coke plant wastes

This paper attempts to examine the possibility of forecasting the size of ultrafiltration permeate fluxes in the process of coking wastewater. The calculations are based on the assumptions of model relaxation, describing the changes in the permeate flux of membrane filtration system carried out in non-stationary [6,7]. The dependence of the theoretical, temporary permeate flux was determined at the initial time of the pressure filtration process, and then it was compared with the experimental flux.

Table 6

The efficiency of treatment the coke plant wastewater in the integrated ultrafiltration–reverse osmosis system

Indicators of pollution	Raw wastewater	Treated wastewater		Permissible standards	Technical water—to quenching of coke
		RO Value	R^* (%)		
pH	9.41	8.05	–	6.5–9.0	–
COD, mg O ₂ /dm ³	4519.6	109	97.6	125	–
Volatile ammonia as NH ₄ ⁺ , mg/dm ³	131.6	21	84	10	82
TN, mg/dm ³	1820	25.2	98.6	30	–
TC, mg C/dm ³	1184.6	22	98.2	–	–
TOC, mg C/dm ³	963.1	15	98.4	30	–
Phenols, mg/dm ³	381	0	100	0.1	15
Cyanides, mg/dm ³	27.3	0	100	0.1	9
Sulfides, mg/dm ³	0.92	0	100	0.2	–
Conductivity, mS/cm	8.41	0.89	–	ns.	–
The overall alkalinity, mg/dm ³	29.92	1.5	94.9	10	–
General iron, mg/dm ³	2.71	0.116	95.7	10	–
The concentration of calcium ions, mg Ca ²⁺ /dm ³	64.79	0	100	20	–
The concentration of magnesium ions, mg Mg ²⁺ /dm ³	7.96	0	100	20	–

In the relaxation model the balance of mass transportation in the process of membrane filtration is presented by the equation [6]:

$$d/dt(J - J_{\infty}) + t/t_0(J - J_{\infty}) = 0 \tag{1}$$

by the assumptions that $J(t)_{t=0} = J_0$.

This allows us to determine the permeate flux changes in the process of filtration. The knowledge about the initial fluxes: initial (J_0), equilibrium—saturation (J_{∞}), and time constant (t_0) enables the solution of the following equation:

$$\ln\left(\frac{J - J_{\infty}}{J_0 - J_{\infty}}\right) = -\frac{t}{t_0} \tag{2}$$

where $J_{t=0} = J_0$, $J_{t \rightarrow \infty} = J_{\infty}$, t_0 —time constant.

The time constant which characterizes the velocity of flux disappearing was determined from Eq. (2) by means of graphic method:

$$t_0 = |1/a| \tag{3}$$

where a —the straight line coefficient ($y = a \cdot t$) characterizing the filtration process for the examined membrane.

The theoretical average value of the permeate flux is determined by solving Eq. (2):

$$J_e = \frac{1}{t_0} \int_0^{t_0} J_e(t) dt = J_0 - \frac{(J_0 - J_{\infty})}{e} = J_0 - 0.37(J_0 - J_{\infty}) \tag{4}$$

within the integration limits: $t = 0$ i $t = t_0$.

The experimental average value of flux can be described by equation:

$$J_{ae} = \frac{1}{t_r} \int_0^{t_r} J_e(t) dt \tag{5}$$

where t_r —time longer than t_0 in which the volumetric permeate flux achieves the equilibrium value determined as J_{∞} .

Fig. 4 presents the example of the graphical determination of the time constants characterizing the rate of decline t_0 permeate fluxes for commercial ultrafiltration membranes.

In Fig. 5, a comparison of the average experimental with the average theoretical permeate fluxes obtained in the purification process of coking wastewater for commercial and polysulfone membranes prepared in the laboratory is shown.

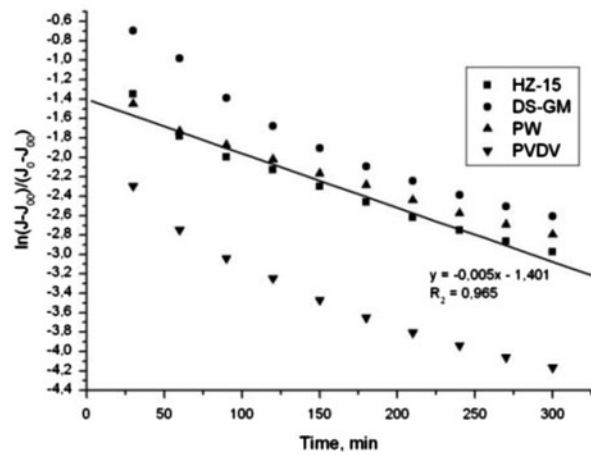


Fig. 4. Determination of characteristic decline time t_0 for ultrafiltration coke making wastewater treatment of commercial membranes.

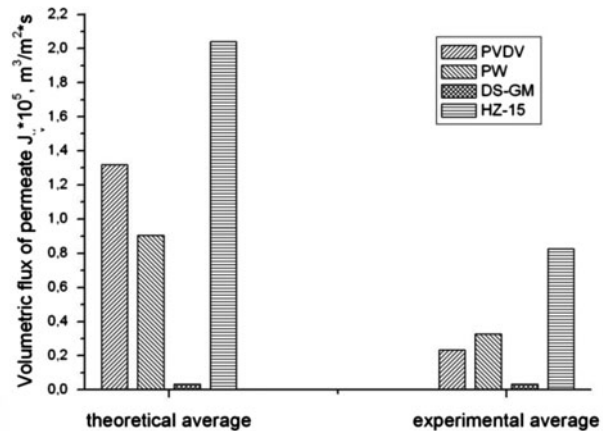


Fig. 5. Comparison of the average experimental with the average theoretical permeate fluxes obtained in coking wastewater treatment process.

For all tested membranes the temporary theoretical fluxes values were higher than those obtained in the coke-making wastewater low-pressure filtration process.

Higher theoretical fluxes values, both temporary and medium, can be explained by taking into account that the calculations used in the applied mathematical method do not consider the complexity of physical and chemical processes that occur in the membrane surface and pores. This could lead to the conclusion that the relaxation method applied in the research, which shows changes in the ultrafiltration permeate flux in coke plant wastewater treatment in a non-stationary arrangement, should be used in order to predict the ultrafiltration efficiency for dense structure membranes.

3.5. Predicting the performance of ultrafiltration membrane in the process of coke wastewater treatment based on the model of hydraulic filtration resistance

During the next step of the research, we made some attempts to predict the ultrafiltration commercial flat membranes' efficiency in the purification process of coke plant post-process wastewater on the basis of the assumptions of hydraulic model of filtration resistance [8,9]. It takes into account both the changes in the resistance values posed by a new membrane to a "filtrating medium" and the interaction between the polymer membranes and the substances presented in the coke wastewater. The dependence of permeate flux size on transmembrane pressure described by Darcy's equation (6) was used to determine the resistance of the individual components of the membrane.

$$J_v = \Delta P / \eta \cdot R_{\text{total}} \quad (6)$$

where J_v —temporary volumetric flux of permeate [$\text{m}^3/\text{m}^2\text{s}$], ΔP —transmembrane pressure [Pa], η —dynamic viscosity of liquid [Pa s], and R_{total} —total hydraulic resistance of working membrane [m^{-1}].

It is assumed that the total hydraulic resistance of "working" R_{total} membrane is the sum of the constituents which include "new membrane" resistance and resistance which is a result of concentration polarization and fouling occurring on the membrane surface. Eq. (6) can therefore be summarized as follows:

$$J_v = \Delta P / \eta \cdot (R_m + R_f + R_{\text{cp}}) \quad (7)$$

where R_m —membrane resistance value of the "new" [m^{-1}], R_{cp} —polarization layer resistance [m^{-1}], and R_f —resistance due to the fouling phenomenon [m^{-1}].

Non-working membrane resistance value (R_m) was determined from Eq. (6) that describes the transport of de-ionized water over time $J_{\text{H}_2\text{O}} = f(t)$. Due to these processes' $R_{\text{total}} = R_m$ conditions after the equation transformation (6), we obtained the following relationship:

$$R_m = \Delta P / \eta \cdot J_{\text{H}_2\text{O}} \quad (8)$$

where $J_{\text{H}_2\text{O}}$ —experimental temporary flux of de-ionized water [$\text{m}^3/\text{m}^2\text{s}^{-1}$].

Resistance caused by fouling phenomenon involves the deposition of the substances existing in the filtered medium on the membrane surface and/or in the pores of the substances presented in the filtered medium. It consists of the resistance caused by adsorption inside the membrane pores, resistance caused by gel layer resistance, and the resistance resulting from the

formation of a filter cake on the membrane surface, the so-called secondary diaphragm. It can therefore be described by the equation:

$$R_f = R_a + R_{\text{gel}} + R_p \quad (9)$$

where R_a —resistance to the phenomenon of adsorption [m^{-1}], R_{gel} —generated resistance to gel layer [m^{-1}], and R_p —resistance to the formation of secondary membrane [m^{-1}].

As it is known, fouling can be reversible or irreversible. In the first case, membrane cleaning provides its initial performance restoration; in the other one it is impossible. It was assumed that the resistance caused by fouling phenomenon is the sum of both reversible and irreversible fouling; therefore [8,9]:

$$R_f = R_{\text{fn}} + R_{\text{fo}} \quad (10)$$

where R_{fo} —resistance to reversible fouling [m^{-1}] and R_{fn} —resistance to irreversible fouling [m^{-1}].

The resistance generated by irreversible fouling is a result of permanent blocking of membrane pores; so, it is difficult to reconstruct its initial performance. To determine its value the size of the de-ionized water volumetric flux for the membrane after ultrafiltration coking wastewater treatment was specified.

$$R_{\text{fn}} = (\Delta P / \eta \cdot J_{\text{pH}_2\text{O}}) - R_m \quad (11)$$

where R_{fn} —resistance to irreversible fouling [m^{-1}], $J_{\text{pH}_2\text{O}}$ —experimental temporary flux of de-ionized water after pressure filtration plant, [$\text{m}^3/\text{m}^2\text{s}$].

To determine the value of the experimental polysulfone membranes' reversible fouling resistance, the following formula was used:

$$R_{\text{fo exp.}} = R_{\text{total}} - R_m - R_{\text{fn}} \quad (12)$$

Theoretical resistance value connected with reversible fouling was determined from the equation [6]:

$$\frac{d}{dt}(R_\infty - R_{\text{fo}}) + \frac{1}{t_{\text{Ro}}}(R_\infty - R_{\text{fo}}) = 0 \quad (13)$$

After integrating, we obtained the equation [6]:

$$R_{\text{fo}} = R_\infty \left[1 - \exp\left(-\frac{t}{t_{\text{Ro}}}\right) \right] \quad (14)$$

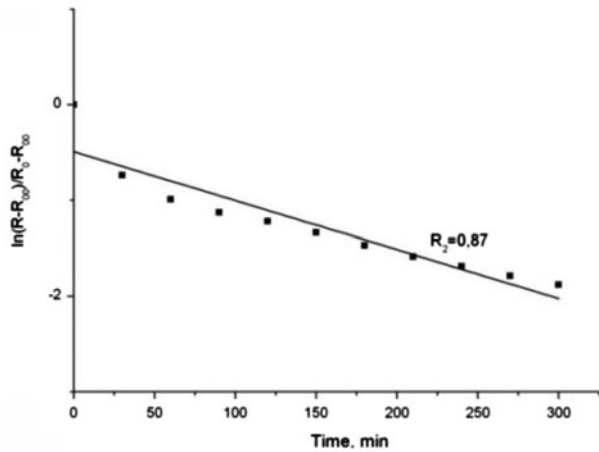


Fig. 6. Time constants t_{R0} designated for commercial ultrafiltration membrane.

where R_{fo} —initial reversible fouling resistance ($R_{fo} = 0$ at $t = 0$) [m^{-1}], R_{∞} —reversible fouling resistance after an infinitely long period of time [m^{-1}], t_{R0} —time constant [min^{-1}].

The establishment of permanent t_{R0} enabled the rearrangement of Eq. (14) to the form [6]:

$$(R_{\infty} - R_{fo})/R_{\infty} = \exp(-t/t_{R0}) \tag{15}$$

After logarithming, we obtained the equation of a straight line that goes through the origin of the coordinate system. From the straight line, the inclination coefficient was determined, which made it possible to calculate the theoretical reversible fouling resistance.

Fig. 6 shows the example of the graphical determination of time constants t_{R0} for the commercial membrane (HZ-15).

Fig. 7 illustrates the comparison between the total membrane resistance, the “new” membrane resistance, and the resistance related to the fouling phenomena.

The last of the designated resistance components is the layer polarization resistance. The phenomenon of concentration polarization is the formation of the boundary layer solution with a concentration above the average concentration of the feed solution in the immediate membrane vicinity. It contributes to the decrease of membrane productivity and changes in the membrane separation properties. The following relationship [9] describes the resistance induced by the generated polarization layer:

$$R_p = \phi \Delta P \tag{16}$$

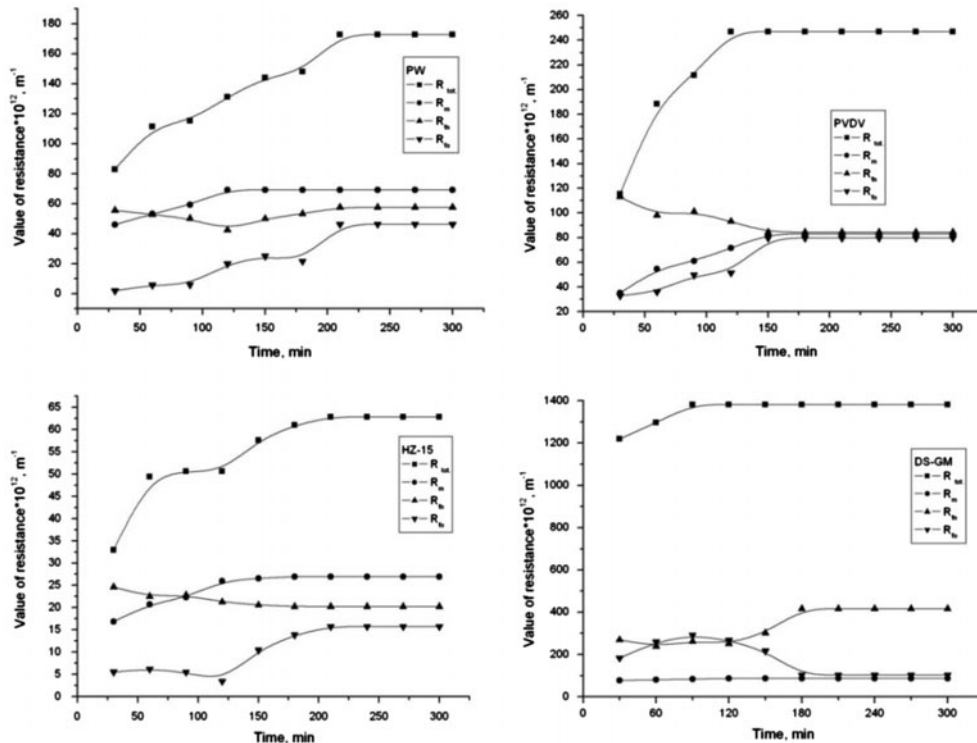


Fig. 7. Comparison of changes in resistance R_{total} , R_{mv} , R_{fv} , $R_{fo,exp}$ commercial membranes during treatment the post-trial ultrafiltration coke wastewater.

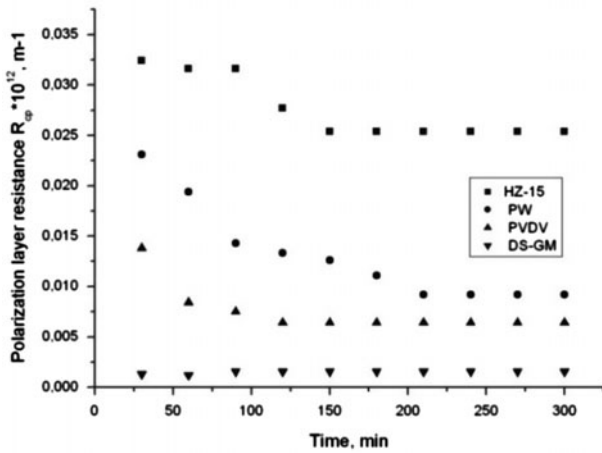


Fig. 8. Dependence of the resistance values changes for polarizing layer of ultrafiltration membrane on time of coke pre-processed water ultrafiltration treatment.

where ϕ —resistance index characterizing the ability of mass transport through the membrane [s/m].

The value of resistive index can be calculated from the following mathematical relation [8]:

$$\phi = 1/J_{lim} \tag{17}$$

for the following limit values $\Delta P=0, J=0; \Delta P \rightarrow \infty, J=J_{lim}$, where J_{lim} —temporary volumetric flux of permeate [m³/m² s].

Fig. 8 shows the dependence of the resistance value changes for polarizing layer of ultrafiltration membrane during coke pre-processed water ultrafiltration treatment.

It is clear that in the case of all tested ultrafiltration membranes, the layer polarization layer resistance values are several orders of magnitude smaller in comparison with other resistance constituents, and they slightly increase in the course of low-pressure membrane filtration. Then, using the experimentally determined resistance constituents values the theoretical values of total polysulfone membrane resistance were calculated (Eq. (7)). This enabled the determination of the theoretical volumetric values of ultrafiltration permeate fluxes obtained in coke wastewater ultrafiltration treatment. Fig. 9 presents the comparison between theoretical permeate fluxes calculated from the hydraulic model of filtration resistance and the size of temporary fluxes determined experimentally.

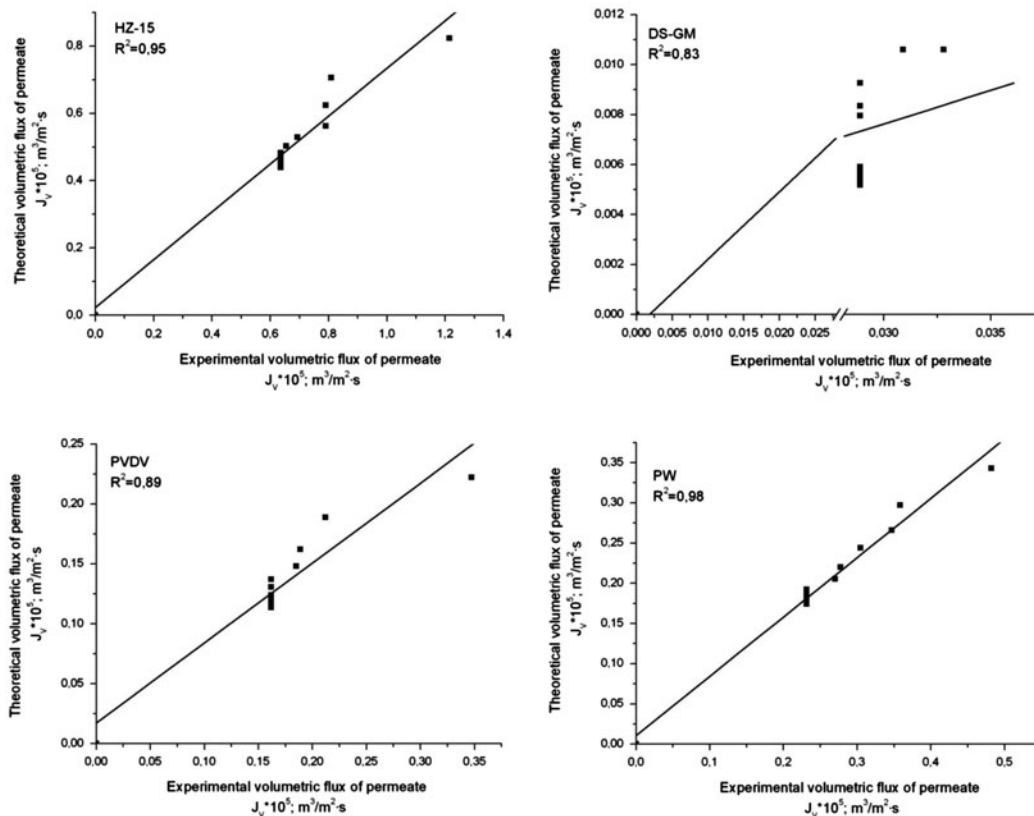


Fig. 9. Comparison between theoretical permeate fluxes calculated from the hydraulic model of filtration resistance and the size of temporary streams determined experimentally.

The high correlation coefficients suggest that the hydraulic model of filtration resistance used in the calculation makes it possible to predict the size of the instantaneous permeate flux in the process discussed.

4. Conclusions

- (1) The applied integrated system of ultrafiltration—reverse osmosis—did not give appropriately high degree of treatment. It did not enable carrying to the natural receiver. The concentration of nitrogen ammonium was on the level $21 \text{ NH}_4^+/\text{dm}^3$. It was two times higher above the normal one. Treatment wastewater can be used as technical water—for quenching of coke.
- (2) The best studied of ultrafiltration membrane distributing properties was commercial membrane DS-GM. Wastewater after the membrane were characterized by the following indicators of pollutants: COD— $2,707.6 \text{ mg O}_2/\text{dm}^3$, the overall concentration of carbon TC— $451.7 \text{ mg C}/\text{dm}^3$, organic carbon TOC— $378.1 \text{ mg C}/\text{dm}^3$, the concentration of phenols and cyanides overall respectively at $24.2 \text{ mg}/\text{dm}^3$ and $35.5 \text{ mg}/\text{dm}^3$.
- (3) Theoretical calculations of the average permeate flux which were carried out on the assumptions of the model are similar to the relaxation data obtained experimentally; however, it was only in the case of more structured membranes. This allows one to draw the conclusion that in such a case it is possible to predict the size of the permeate flux in the post-trial coke wastewater ultrafiltration purification based on the knowledge of the size of permeate fluxes, initial and saturation (equilibrium), and the time constant.
- (4) High values of correlation coefficients obtained by comparing the instantaneous experimental ultrafiltration permeate streams to the instantaneous

theoretical streams suggest that the hydraulic model of filtration resistance used in the calculation allows one to forecast the commercial membranes' performance in the process discussed.

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