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Comparison of post-process coke wastewater treatment effectiveness in integrated and hybrid systems that combine coagulation, ultrafiltration, and reverse osmosis

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The paper presents the results of a study whose target was to determine the effectiveness of coke wastewater, from the coking plant treatment using an integrated system combining volumetric coagulation and ultrafiltration, and a hybrid coagulation "in-line" with ultrafiltration. In both systems, the process of coagulation was carried out using sulfate(VI) iron (III). Coagulant doses varied in the range of 400 mg/dm^{3}–100 mg/dm^{3}. Low-pressure membrane filtration was performed on polysulfone membrane which was obtained from film-forming solution containing 16% weight content of polysulfone and 5 s. time of the solvent evaporation from the membrane surface. The wastewater, after the ultrafiltration process was cleaned thoroughly by means of the reverse osmosis method using the membrane of an American brand GE-Water type ADF. Leaning on the assumptions of the model relaxation, describing the changes in permeate flux during membrane filtration system carried out in non-stationary, an attempt to predict the size of ultrafiltration permeate flux integrated in the system studied, and based on the assumptions of the model the hydraulic resistance to filtration, the calculations allow for predicting the performance of ultrafiltration membrane used in the process. This made it possible to determine experimentally volume changes in the volume of streams permeate time, the total hydraulic resistance associated with the membrane filtration resistance, and the resistance of the membrane components: "new", resistance to the polarizing layer and the resistance due to the setting phenomenon of fouling.

Keywords: Coagulation; Coke plant wastewater; Model of hydraulic resistance filtration; Relaxation model; Ultrafiltration; Reverse osmosis

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1. Introduction

The eco-friendly economy of water-effluent is the responsibility of each industrial plant. The most preferred solution would be to build their own on-site treatment systems in order to neutralize wastewater flows. In the case of coking wastewater, its negative impact on the environment is mainly due to discharging into the natural receivers insufficiently treated post-production water [1]. Therefore, in terms of environment protection, their purification makes great sense. Coke wastewater contains hardly biodegradable substances with carcinogenic and mutagenic nature which include, among others, polycyclic aromatic hydrocarbons, heterocyclic compounds, oils, tars, and inorganic substances, such as cyanides, sulfides, sulfates, thiosulfates, ammonia, and heavy metal ions [2,3]. The use of conventional methods of wastewater treatment in coke industry, such as biological method of activated sludge, volumetric coagulation, sedimentation, or filtration in combination with the pressure membrane techniques, provides more efficient and more cost effective purification of wastewater [4,5]. Integrated/hybrid systems will provide a stable quality of recovered water as a final or semi-final product that could be reused in a technological process. They will also make it possible to supply the losses of cooling water in coke ovens [4,6]. It seems that integration the membrane techniques with others, non-membrane methods in the process of wastewater treatment in the coke industry is becoming a necessity in terms of existing rules.

2. Materials and methods

2.1. The subject of research

The primary wastewater came from coke plant near Czestochowa. It was subjected to mechanical treatment, so tar substances, oils, and solids were removed. This process was conducted in decanters from which tar was transported by pipeline to the underground tank and then through the intermediate tank to the storage tanks. Initially, pretreated wastewater separated from the tar and oils was subjected to phenol removal and sent to the ammonia stripping columns [7]. Analytical studies demonstrate that post-process coke wastewater is characterized by variable pollutants load (COD value of 3348.9 mg/dm^3). Table 1 shows the values of selected pollutants indicators that characterize coke over effluent after pre-purification.

It is clearly seen that all the indicators of pollution far exceed the values indicated in the ministerial regulations, and therefore there is no possibility of discharging untreated coke wastewater into the natural receiver.

2.2. Apparatus

The process of volume coagulation was conducted using the jar test with the reactors of a capacity 2.0 dm^3, whose contents were stirred with a magnetic stirrer [9]. In the process of membrane filtration for coke plant wastewater treatment, an apparatus with a plate-type membrane module SEPA CF-NP from American company GE-Water, a tank with a capacity of 8 dm^3 with a cooler, a rotameter, a high-pressure pump pressure, gauges, and valves were used.

The module consisted of two steel plates between which a flat membrane was placed in a shape of a rectangular sheet with dimensions of 190 × 140 mm (total surface of the membrane was 155 cm^2, and the filtration area 144 cm^2) with the sealing elements and spacers. The system worked in cross-flow system in a closed unit where the retentate recycled to the feed tank. The whole system was introduced into a steel enclosure in order to provide the sealing arrangement. The installation applied in the research is presented in Fig. 1 [10].

2.3. Methodology of research

The coke plant wastewater was treated in two technological systems. The first system included the combination of the physicochemical process, i.e. volumetric coagulation and sedimentation with the pressure membrane processes, ultrafiltration, and reverse osmosis. In the other one, the post-process coke water was purified by "in-line" coagulation (the hybrid system combining coagulation and ultrafiltration), and then it was post-treated in the process of reverse osmosis. The earlier studies had shown that the most advantageous out of the four coagulants (PIX-112, PIX-113, PIX-122, PIX-123) applied in coke plant wastewater treatment was the sulfate(VI) iron(III) under the trade name PIX-113, manufactured by Chemical Plant Kemipol [9]. Therefore, in the coagulation and "in-line" processes, this coagulant was used in order to obtain the initial adjustment pH 9. The coagulant dose in volumetric coagulation was 400 mg/dm^3. The process of mixing the wastewater with a coagulant was conducted in two stages. The quick stirring, lasted for 1 min, was to mix the entire contents of the reactor, while the slow stirring, that ran for 30 min, ensured the flocks formation that produced larger agglomerates subsequently. After 30 min of sedimentation, the effluent was introduced into the ultrafiltration membrane module [7,10].

Table 1
Characteristics of wastewater from coke plant near Czestochowa after the pre-treatment

Indicators	Value	The indexes of wastewater pollution which is carried away to the receiver [8]
pH	9.1	6.5–9.0
COD (mg O_2/dm^3)	3348.9	125
TC (mg C/dm^3)	786.2	–
TOC (mg C/dm^3)	551.6	30
Phenol (index of phenol, mg/dm^3)	534	0.1
TN (mg N/dm^3)	1820	30
Ammonium nitrogen (mg NH_4^+/dm^3)	490.8	10
Total alkalinity (mval/dm^3)	29.92	10
Conductivity (m S/cm)	10.7	–
Free cyanide (mg CN^-/dm^3	11.42	0.1
Sulfides (mg S^{2-}/dm^3)	0.92	0.2
Total iron (mg/dm^3)	2.71	10
Calcium ions (mg Ca^{2+}/dm^3)	64.79	20
Magnesium ions (mg Mg^{2+}/dm^3)	7.96	20

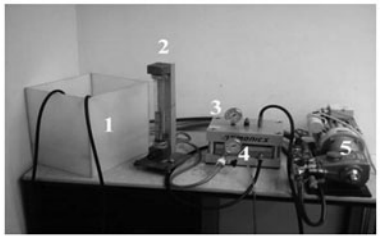

Fig. 1. Photo equipment to conduct the coke wastewater by pressure membrane filtration: 1-tank, 2-rotameter, 3-membrane module, 4-manometer, and 5-high pressure pump.

Low-pressure membrane filtration process was carried out using the laboratory-prepared polysulfone membrane with 16% weight content of polysulfone in the membrane solution and 5 s time of the solvent evaporation from the membrane surface. The treatment of the coke plant wastewater in the ultrafiltration process was performed with the following parameters: transmembrane pressure—0.4 MPa and the linear flow velocity over the membrane surface-2 m/s. Since the post-process coke water after volumetric coagulation and ultrafiltration purification process was still characterized by high values of pollution indicators which prevented against its direct discharging to the natural receiver, it was subjected to reverse osmosis post-treatment process ($\Delta P = 2$ MPa, $u = 2$ m/s). The membrane used in this stage was a polymer membrane type ADF provided from GE-Water.

In the second research system, "in-line" coagulation was combined with low-pressure membrane filtration. The coagulant used was PIX-113, the same as that in the first system, and the dose was varied from 100 to 400 mg/dm^3 for wastewater subjected to pH adjustment equal to 9. The process was carried out using a polysulfone ultrafiltration membrane, with transmembrane pressure equal to 0.4 MPa and a linear velocity of the liquid over the surface of the membrane equal to 2 m/s. As in the first system, wastewater treated in a hybrid system was characterized by very high levels of pollution. Thus, it was post-treated in the process of high-pressure membrane filtration. The process of reverse osmosis was carried out in accordance with the methodology applied in the first system.

The effectiveness of post-process coke water treatment conducted with the use of unit processes, integrated and hybrid systems, was evaluated taking into consideration the changes in the values of indicators characterizing raw and cleaned wastewater. There were determined pH, conductivity, chemical oxygen demand (COD), total organic carbon (TOC), total carbon (TC), phenol index, and the concentration of ammonia nitrogen and total nitrogen, free cyanides and sulfides. The COD test was performed on a HACH DR 4000 spectrophotometer, the concentration of TOC and TC and the concentration of total nitrogen (TN) were determined by high-temperature catalytic oxidation using Multi N/C2100 chromatograph, while the concentration of free cyanide and sulfide, and phenol index were marked applying a cuvette tests with Hach Lange DR 2800 spectrophotometer. pH measurements were performed using electrometrical method with Cole Palmer 59002-00 pH-meter. Additionally, the study determined the overall change in alkalinity, and the concentrations of magnesium and calcium ions.

3. Results and discussion

Fig. 2 compares the changes of permeate flux obtained in the process of ultrafiltration, initially pretreated using coagulation process, with the permeate flux obtained in the process of coagulation "in-line".

The highest volume of permeate flux was observed in the hybrid system in which the coagulant dose was 200 mg/dm^3. Stabilized permeate flux equilibrium after 180 min of filtration shaped at the level of 1.022×10^{-5} m^3/m^{2}s, while the lowest value was obtained for the integrated system in which the post-process coke plant wastewater was purified in the process of coagulation volume at a dose of 400 mg/dm^3 and then, after 30 min of sedimentation, it was post-treated with the use of polysulfone ultrafiltration membrane. Its value after 150 min was about 54.7% lower compared to the hybrid system, in which the dose of coagulant was reduced by 50%. The coke plant wastewater post-treatment after its treatment in the integrated and hybrid systems was performed by means of the reverse osmosis method with the use of polymer membrane of American Company GE-Water ADF.

Fig. 3 presents changes of volumetric permeate flux in time of high-pressure membrane filtration process.

The results show that the best efficiency is represented by a hybrid system in which the coagulant dose used was 200 mg/dm^3. The permeate flux after 105 min of high-pressure membrane filtration was 22.2% lower compared to the experimental temporary flux of deionized water (0.694×10^{-5} m^3/m^{2}s). Instead, the lowest flow equilibrium volume was obtained in the integrated system in which the post-process coke wastewater was purified using volumetric coagulation where the coagulant dose was 400 mg/dm^3, and it was afterwards cleaned using low-pressure membrane filtration (PSF-16 5s). Flux stabilization for this membrane was obtained after 75 and a permeate flux volume was 37.2% lower compared to the most advantageous system. Permeate volumetric fluxes were, respectively, 1.29 and 2.05 times lower in comparison with a deionized water flux.

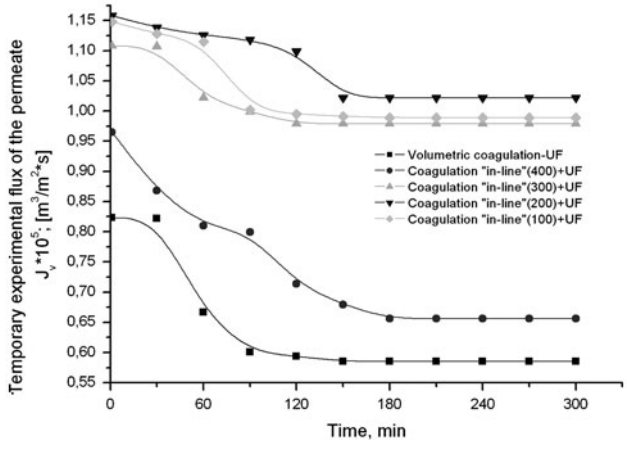

Fig. 2. The dependence of the experimental temporary permeate flux on the time of coke plant wastewater low-pressure membrane filtration.

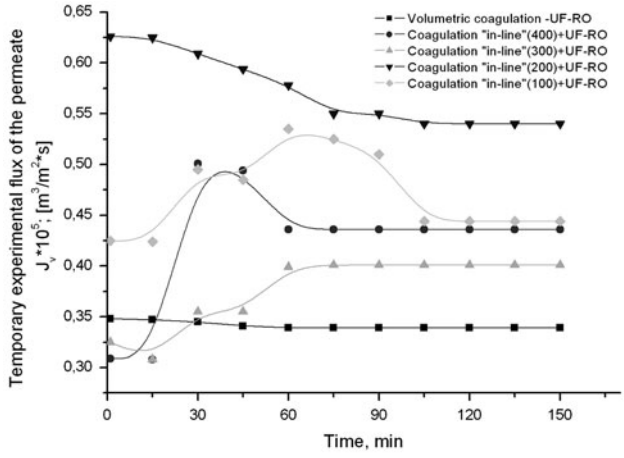

Fig. 3. Dependence of temporary experimental volumetric fluxes on time treatment coke-making reverse osmosis process.

Table 2 shows the characteristics of wastewater treated in the hybrid systems, while Table 3 displays the wastewater treatment in the hybrid system and integrated systems combining volumetric coagulation and sedimentation with the pressure membrane techniques.

The results obtained suggest that wastewater post-treated in the reverse osmosis process still did not meet the quality standards set out in the Regulation of the Minister of Environment of 28 January 2009, on conditions to be met by the introduction of sewage into the water or soil, and on substances particularly harmful to the aquatic environment due to the excessive concentration of ammonia nitrogen. It was found almost a three-fold excess over the permissible levels of volatile ammonium ions in terms of N–NH_4^+. It stood at around 30.0 mg/dm^3. Therefore, coke plant wastewater before discharging into natural receiver or drains should be additionally post-treated e.g. in stream stripping process. However, it could be recycled to the coke production cycle and used for coke cooling.

Table 2
Effectiveness of coke wastewater in the hybrid coagulation "in-line"-ultrafiltration-reverse osmosis systems

Indicators	Raw wastewater	Treatment wastewater															
		In-line 400-UF		RO		In-line 300-UF		RO-ADF		In-line 200-UF		RO		In-line 100-UF		RO	
		Value	*R* [%]	Value	*R* [%]	Value	*R* [%]	Value	*R* [%]	Value	*R* [%]	Value	*R* [%]	Value	*R* [%]	Value	*R* [%]
pH	9.34	8.6	–	8.05	–	8.25	–	7.65	–	8.39	–	7.53	–	8.95	–	7.89	–
COD (mg O_2/dm^3)	3348.9	2291.7	30.6	52.6	98.40	1885	33.30	63.2	97.76	1279.2	59.75	17.7	99.44	1465.2	56.24	60.1	98.20
TC (mg C/dm^3)	786.2	758.7	14.8	29.58	96.11	567.6	17.54	29.59	93.23	513	29.48	29.19	95.96	540.2	31.29	29.85	96.64
TOC (mg C/dm^3)	592.5	551.6	13.3	18.89	96.50	401.4	19.18	17.69	94.42	305.7	36.13	11.34	97.65	385.7	34.90	19.5	96.70
Phenol (index of phenol, mg/dm^3)	534	335.5	37.2	0	100	272	36.0	0	100	77.8	85.43	0	100	154	71.11	0	100
TN (mg/dm^3)	1820	1,280	13.5	47.05	96.82	1,150	24.32	104.3	93.13	899	57.19	56.19	97.32	1,052	42.19	64.5	96.45
Ammonium nitrogen (mg/dm^3)	490.8	224	42.9	21.0	94.64	392		28	93.33	221.2	9.56	17.08	93.01	355.6	27.54	19.85	95.95
Total alkalinity (mval/dm^3)	29.92	15	28.6	1.5	92.58	15	28.6	5.5	73.81	18	56.62	4	90.36	17	43.18	6	79.94
Conductivity (m S/cm)	10.7	7.15	–	0.113	–	7.10	–	0.987	–	5.95	–	0.684	–	6.05	–	0.887	–
Free cyanide (mg/dm^3)	11.42	5.80	49.2	0	100	10.9	5.21	0	100	10.3	3.73	0	100	10.6	7.18	0	100
Sulfides (mg/dm^3)	0.92	0.785	21.9	0	100	0.94	25.98	0	100	0.13	83.54	0	100	0.85	7.60	0	100
Total iron (mg/dm^3)	2.71	1.07	60.5	0.116	92.21	3.25	–	0.193	93.94	3.34	–	0.153	95.29	3.56	–	0.17	93.73
Calcium ions (mg/dm^3)	64.79	49.29	23.9	0	100	32.14	40.00	10.71	80.01	60.7	6.2	7.14	–	45.2	30.23	8.06	87.55
Magnesium ions (mg/dm^3)	7.96	0	100	0	100	0	100	0	100	0	100	0	100	0	100	0	100

Table 3
Effectiveness of coke wastewater in the integrated and hybrid system

Indicators	Raw wastewater	Treatment wastewater							
		Volumetric coagulation–sedimentation-UF		RO		In-line 200-UF		RO	
		Value	*R* [%]	Value	*R* [%]	Value	*R* [%]	Value	R [%]
pH	9.34	9.1	–	7.28	–	8.39	–	7.53	–
COD (mg O_2/dm^3)	3348.9	1652.3	48.1	115	96.4	1279.2	59.75	17.7	99.44
TC (mg C/dm^3)	786.2	673.3	25.0	49.78	94.5	513	29.48	29.19	95.96
TOC (mg C/dm^3)	592.5	551.9	22.1	27.41	96.1	305.7	36.13	11.34	97.65
Phenol (index of phenol, mg/dm^3)	534	349	19.8	0	100	77.8	85.43	0	100
Total nitrogen (mg/dm^3)	1820	1,170	12.0	106.1	92.0	899	57.19	56.19	97.32
Ammonium nitrogen (mg/dm^3)	490.8	322	17.9	42.28	89.2	221.2	9.56	17.08	93.01
Total alkalinity (mval/dm^3)	29.92	0.945	87.4	3	–	18	56.62	4	90.36
Conductivity (m S/cm)	10.7	6.10	–	0.410	–	5.95	–	0.684	–
Free cyanide (mg/dm^3)	11.42	5.6	7.4	0	100	10.3	3.73	0	100
Sulfides (mg/dm^3)	0.92	0.175	85.3	0	100	0.13	83.54	0	100
Total iron (mg/dm^3)	2.71	0	–	0.193	97.4	3.34	–	0.153	95.29
Calcium ions (mg/dm^3)	64.79	15	34.8	0	100	60.7	6.2	7.14	–
Magnesium ions (mg/dm^3)	7.96	50	88.1	0	100	0	100	0	100

3.1. Modeling of ultrafiltration process used in coke wastewater treatment

This paper attempts to examine the possibility of forecasting the size of the permeate flux in coke wastewater treatment in the most advantageous system i.e. a hybrid system. Calculations are based on the assumptions of a relaxation model which shows the changes in the permeate flux during membrane filtration process preformed in non-stationary system [11–14]. There was determined the dependence of theoretical, temporary permeate flux on time of low-pressure filtration and then it was compared with the experimental fluxes.

In the relaxation model, the balance of mass transportation in the process of membrane filtration is presented by equation [11–14]:

$$\frac{\mathrm{d}}{\mathrm{d}t}(J-J_\infty)\frac{t}{t_0}(J-J_\infty)=0 \tag{1}$$

Integration within the limits from t and $t_0=0$ at the assumptions that $J(t)$ $t=0=J_0$.

That allows to determine the permeate stream changes in the process of filtration.

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

Time constant which characterizes the velocity of permeate flux disappearing was determined by the Eq. (2) using graphic method:

$$T_0=|1/a| \tag{3}$$

where a is a straight line coefficient ($y=a\times t$) that characterizes filtration process for the examined membrane.

The formula conversion (2), which is the solution of the Eq. (1) for the following boundary conditions $t=0\rightarrow J=J_0$ and $t=\infty\rightarrow J=J_\infty$, makes it possible to determine the dependence of the theoretical, temporary volumetric permeate stream (J_t) on time of the filtration process.

$$J_t(t)=(J_0-J_\infty)\exp(-t/t_0)+J_\infty \tag{4}$$

where $J_t=0=J_0$, $J_t\rightarrow\infty=J_\infty$, t_0—time constant.

The solution of the above equation allows to specify experimentally the changes in the initial permeate flux (J_0), equilibrium—saturation flux (J_∞) and time constant (t_0) (Fig. 4).

It is clearly seen that the permeate flux decreases in the course of low-pressure filtration of coke plant wastewater. The real volumetric permeate flow value is lower compared with the values of temporary, volumetric theoretical flow, especially in the early stages of

ultrafiltration. This can be explained by the fact that mathematical model used in the calculations of a theoretical flow does not include the complexity of processes occurring on the surface and in membrane pores. In addition, it was proved that while in the initial stage of the process, transitory experimental and theoretical flow volumes were the same or similar, in the course of time the differences increased. This phenomenon was probably caused by the concentration polarization process and, mostly, by the presence of fine post-coagulation sludge, not sedimented, which in-line coagulation–ultrafiltration intensified fouling phenomenon, contributing to an increase in membrane resistance due to deposition of sediment layer on membrane surface (secondary membrane) and blocked the pores.

3.2. Forecasting of ultrafiltration membrane efficiency in coke plant wastewater treatment based on hydraulic resistance model

In the present study, attempts were made to predict polysulfone ultrafiltration membrane efficiency in coke plant post-process wastewater treatment based on the assumptions of hydraulic resistance model in the filtration process [15,16]. 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 a permeate flux volume on transmembrane pressure described by Darcy's Eq. (5) was used to determine the resistance of the membrane.

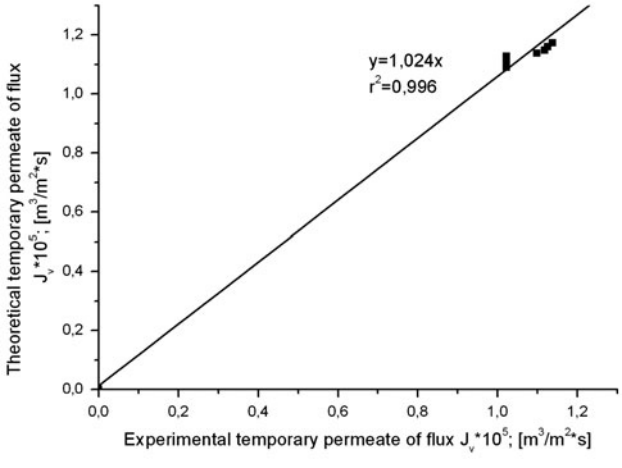

Fig. 4. The graphic comparison of temporary average fluxes of permeate with temporary theoretical obtained in the treatment coke plant wastewater.

$$J_v = \Delta P/\eta\, R_{\text{total}} \tag{5}$$

where J_v— temporary volumetric flux of permeate [$m^3/m^2\,s^{-1}$], 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 membrane is the sum of constituents which include: "new membrane" resistance and the resistance which is the result of concentration polarization and fouling occurring on the membrane surface. Eq. (5) can therefore be summarized as follows [11,15,16]:

$$J_v = \Delta P/\eta\,(R_m + R_f + R_{cp}) \tag{6}$$

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

Non-working membrane resistance value (R_m) was determined from the relation (5) that describes the transport of deionized water in time ($J_{H_2O} = f(t)$). In conditions of the process $R_{\text{total}} = R_m$, so after the transformation of the Eq. (5), we obtain the following relationship:

$$R_m = \Delta P/\eta\, J_{H_2O} \tag{7}$$

where J_{H_2O}—experimental temporary flux of deionized water [$m^3/m^2\ s^{-1}$], η—dynamic viscosity of water at 20°C.

Resistance caused by fouling phenomenon, that is the deposition of the substances existing in the filtered medium on the membrane surface and/or in the pores, consists of the resistance caused by adsorption inside the membrane pores, resistance caused by gel layer, and the resistance that is the result of filter cake formation on the membrane surface, so called secondary diaphragm. It can therefore be described by the equation:

$$R_f = R_a + R_{\text{gel}} + R_p \tag{8}$$

where R_a—resistance related to adsorption phenomenon [m^{-1}], R_{gel}—resistance related to generated gel layer [m^{-1}], and R_p—resistance related to secondary membrane formation [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 [15,16]:

$$R_f = R_{fn} + R_{fo} \tag{9}$$

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

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

$$R_{fn} = (\Delta P/\eta\, J_{pH_2O}) - R_m \tag{10}$$

where R_{fn}—resistance to irreversible fouling [m^{-1}], and J_{pH_2O}—experimental temporary flux of deionized water after pressure filtration plant, [$m^3/m^2\,s^{-1}$].

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

$$R_{fo\,exp.} = R_{total} - R_m - R_{fn} \tag{11}$$

Theoretical resistance value related to reversible fouling was determined from the equation [11]:

$$\frac{d}{dt}(R_\infty - R_{fo}) + \frac{1}{t_{Ro}}(R_\infty - R_{fo}) + 0 \tag{12}$$

After integrating, we obtain the equation [11]:

$$R_{fo} = R_\infty\left[1 - \exp\left(-\frac{t}{t_{Ro}}\right)\right] \tag{13}$$

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

The determination of t_{Ro} permanent enabled to rearrange the Eq. (13) to form [11]:

$$\frac{R_\infty - R_{fo}}{R_\infty} = \exp\left(-\frac{t}{t_{Ro}}\right) \tag{14}$$

After logarithming, we obtain the equation of a straight line that goes through the origin of a coordinate system. From the straight line inclination, there was determined the coefficient t_{Ro}, which allowed for calculating the theoretical reversible fouling resistance.

Fig. 5 presents the comparison between the experimental resistance values related to the reversible

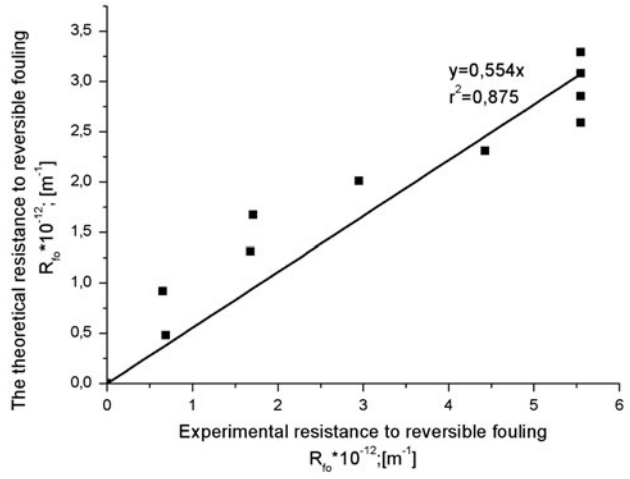

Fig. 5. Comparison of changes in resistance of the $R_{rev\ exp.}$ $R_{rev\ theor.}$ polysulfone membrane during the post-process coke wastewater ultrafiltration treatment.

fouling phenomenon obtained in the coke plant effluent low-pressure filtration and the resistance of the theoretical reversible fouling values determined from Eq. (13) for the hybrid system. Instead, Fig. 6 illustrates the comparison of the resistance values: total, "new" membrane resistance, and the resistance related to fouling phenomena.

The last of the designated resistance components is the polarization layer resistance. The phenomenon of polarization concentration is the formation of the boundary layer solution with a concentration above the average of the feed solution in the immediate membrane vicinity. It contributes to a decrease in membrane productivity and changes membrane separation properties. The following relationship describes the resistance caused by generated polarization layer [15,16]:

$$R_p = \phi\Delta P \tag{15}$$

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

The value of resistive index can be calculated from the following mathematical relation [15,16]:

$$\phi = 1/J_{lim} \tag{16}$$

for the following limit values $\Delta P = 0$, $J = 0$; $\Delta P \to \infty$, $J = J_{lim}$, where J_{lim}—temporary volumetric permeate flux [$m^3/m^2\,s^{-1}$].

Then, using the resistance constituents values, determined experimentally, total polysulfone membrane

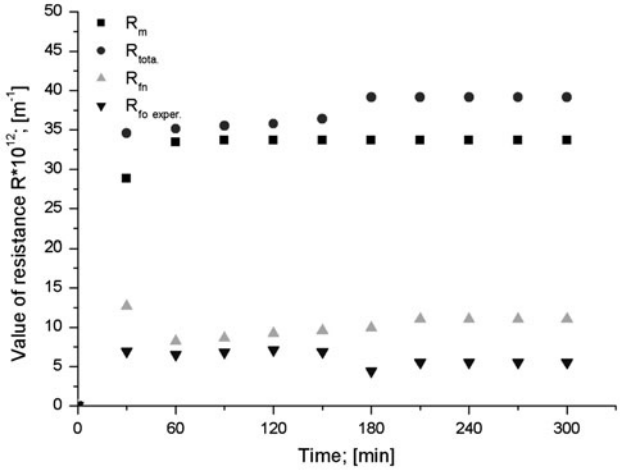

Fig. 6. Comparison of changes in resistance R_{total}, R_m, R_{fn}, $R_{fo\ exp.}$ polysulfone flat membrane during coke wastewater treatment in hybrid system.

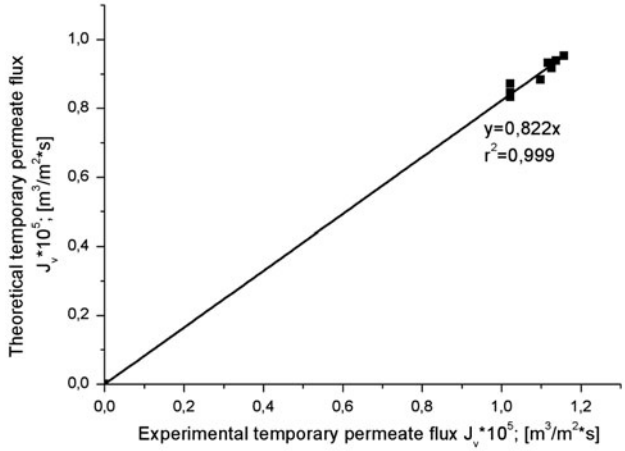

Fig. 7. Comparison between theoretical permeate flux calculated from the hydraulic resistance model of and the size of temporary stream determined experimentally.

resistance was calculated (Eq. (6)). This made it possible to determine the theoretical volumetric permeate flux value obtained in coke wastewater ultrafiltration treatment. Fig. 7 presents the comparison between the theoretical permeate flux calculated from the model of hydraulic filtration resistance and the size of the temporary flux which was determined experimentally.

The high determination coefficient value suggests that the model of hydraulic filtration resistance used in the calculation allows one to predict the size of the instantaneous permeate flux in the process discussed.

4. Conclusions

(1) The hybrid system, in which the dose of coagulant PIX-113 (200 mg/dm^3) was reduced by 50%, proved to be the most advantageous of all the systems tested. Volumetric flux saturation after the time of 180 min was 45.3% higher compared to the integrated system. The post-process coke plant water purified in the hybrid system was characterized by contamination indicators: pH—8.39; COD—1279.2 mg/dm^3; TC—513 mg/dm^3, TOC-305.7 mg/dm^3; the concentration of total nitrogen and ammonium, respectively, at 899 and 221.2 mg/dm^3. The concentration of phenol index stood at 77.8 mg/dm^3, cyanide—10.3 mg/dm^3, sulfide—0.13 mg/dm^3, and total iron—3.34 mg/dm^3.

(2) Since the wastewater post-treated by reverse osmosis is still characterized by high concentrations of ammonia nitrogen (exceeding the allowable concentration four times), it ought to be subjected to a desorption gas process before being discharged into the natural receiver. However, it could be used directly in the coke plant as technical water for coke quenching.

(3) The theoretical instantaneous ultrafiltration permeate flow volume determined on basis of the relaxation model assumptions and the model of hydraulic filtration resistance are similar to those obtained experimentally which is demonstrated by high determination values r^2. So, there is the possibility of predicting the changes in the permeate flux volume in the post-process coke water ultrafiltration treatment based on the knowledge of initial and saturation (equilibrium) permeate fluxes, time constant, and the values of resistance surged in coke plant wastewater flow through the membrane.

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