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MODELING PERFORMANCE IN REVERSE OSMOSIS WASTEWATER TREATMENT POST-TRIAL COKE IN THE INTEGRATED SYSTEMS BASED ON THE ASSUMPTIONS OF THE RELAXATION MODEL

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The paper presents the results of studies on coking wastewater, coming from the coke plant "Koksownia Czestochowa Nowa" in two integrated systems associating coagulation volume and advanced oxidation with reverse osmosis. The process of coagulation were performed using iron sulfate (III), (PIX 113) of 400 mg/dm^3 and wastewater acidity at pH = 9. The second processes – advanced oxidation was carried out using Fenton's reagent. The concentration of iron (II) was 0.8 g/dm^3 and hydrogen peroxide 2.4 g/dm^3. Coke post-process water after its initial treatment was subjected to high-pressure membrane filtration. In the process of reverse osmosis a flat polyamide membrane ADF of Osmonics was used. Transmembrane pressure was 2 MPa and the linear speed of water on the membrane surface of 2m/s. Comparison of the effectiveness of wastewater treatment in both tested systems has shown that the system combining the advanced oxidation with reverse osmosis is more effective.

In addition, this study attempts to model effectiness of the process of reverse osmosis in both studied systems, based on the assumptions of a relaxation model. An experimentally determined dependence of changes in volume of treated wastewater fluxes from the time of the high-pressure membrane filtration, and the values of time constant efficiency of the process characterized by a decrease to below economic viability allowed us fo verify this model.

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Keywords: Coking wastewater, volume coagulation, advanced oxidation, relaxation model, reverse osmosis.

1. INTRODUCTION

A large variety of contaminants present in the coke–plant wastewater that include polycyclic aromatic hydrocarbons, heterocyclic compounds, oils, tar and inorganic substances such as cyanides, sulfides, sulfates, thiosulphate, ammonia and heavy metals makes its purification more difficult [1,2].

To ensure the required quality of treated coke plant wastewater which can be directly discharged into the natural receiver or used for technical purposes, there is a demand in more effective and highly efficient processes for its purification. Among the physicochemical methods applied in the treatment of coke-plant wastewater, loaded with impurities that appear in the form of colloids and fine suspension , there is a coagulation process. Due to the fact that this wastewater also contains in its composition organic compounds resistant to biodegradation, and being toxic in nature, the treatment of advanced oxidation process with Fenton's reagent is more often used [3].

Since, however, as revealed by the study, none of these methods provided a sufficiently high degree of pollutant removal in coke-plant wastewater cleaning it was post-treated by reverse osmosis method. There has also been made an attempt to predict, in both integrated systems, the efficiency of the filtration processes on the basis of relaxation model that assumed changes in the permeate flux during membrane filtration process carried out in non-stationary arrangement.

2. THE SUBSTRATE OF THE RESEARCH

The treated wastewater came from Coke Plant Coke "Koksownia Czestochowa Nowa" Ltd. First, it was the subject of 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 trough the intermediate tank to the storage tanks. Post-gas water separated from the tar and oils was subjected to phenol removal and sent to the ammonia stripping columns.

Table 1 shows the values of selected pollutants indicators characterizing coke oven effluent after pre-purification [3,4].

Table.1. Characteristics of wastewater from Coke Plant, "Koksownia Czestochowa Nowa Sp. z o. o” after the pre-treating.

Determination	Unit	Value	The indexes of sewage pollution which is carried away to the receiver (Journal of law, 2006 number 137, item. 984)
pH	-	8,5	6,5 - 9
Conductivity	mS/cm	6,83	-
COD	mg O_2/dm^3	4102	125
TC	mg C/dm^3	1208	-
TOC	mg C/dm^3	1182	30
TN	mg N/dm^3	540	30
Phenol index	mg/dm^3	2042	0,1
Ammonium nitrogen	mg NH_4^+/dm^3	408	10
Cyanide	mg/dm^3	24,8	0,1
Sulfides	mg/dm^3	3,37	0,2
General Iron	mg/dm^3	2,15	10

3. APPARATUS

Coke oven wastewater physical-chemical treatment i.e. coagulation volume and the chemical process of oxidation in depth was conducted with the use of vascular reactor with a capacity of 3.0 dm^3, whose contents were stirred with a magnetic stirrer [3].

In the process of high-pressure membrane filtration for coke- plant wastewater treatment an apparatus with a slab-type membrane module SEPA CF-NP from American company Osmonics., a sewage tank with a capacity of 8 dm^3 with a cooler, rotameter, high-pressure pump and pressure gauges and valves were used. Installation arrangement is shown in Figure 1 [4].

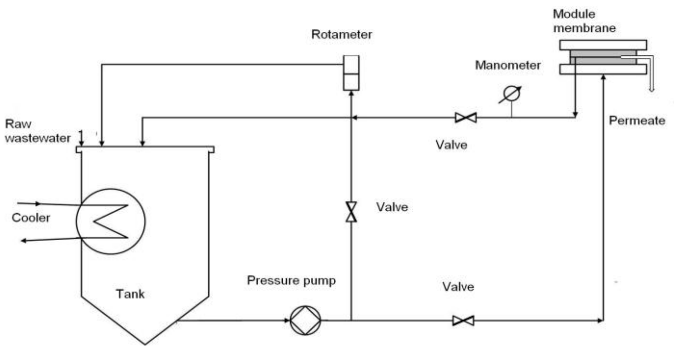


Fig.1. Scheme of apparatus for high pressure membrane filtration plant coke

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 x 140 mm (total surface of the membrane was 155 cm^2, and the filtration area 144 cm^2). The whole was introduced into a steel enclosure in order to provide the sealing arrangement [4].

4. THE METHODOLOGY OF RESEARCH AND ANALYTICAL DETERMINATIONS

Coke-plant waste water was treated in two integrated systems, whose block diagrams are shown in Figure 2

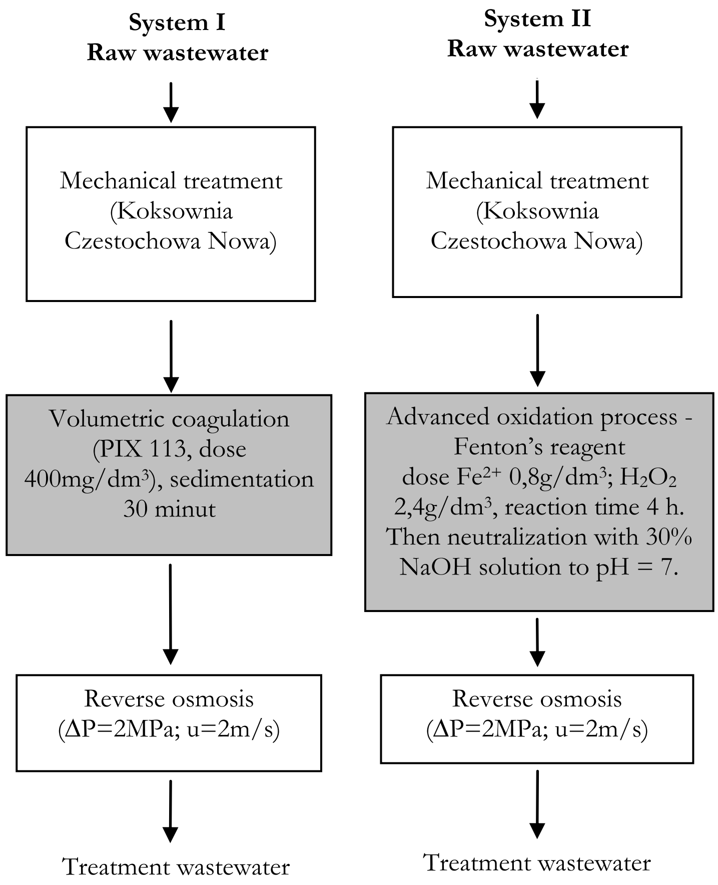


Fig.2. Diagram of coke plant wastewater purification

In the first system in the process of coagulation volume, part of the colloidal substances (causing membrane fouling) was removed from subjected wastewater, and then, using the method of reverse osmosis, it was post-treated. In the second system, in the first stage of treatment advanced oxidation process with Fenton's reagent was applied, providing pollutants mineralization in the coke-plant wastewater, and next it was finally cleaned in the process of high pressure filtration.

The earlier studies had shown that the most useful coagulant applied in coke plant wastewater treatment was the sulphate (VI) iron (III) under the trade name PIX-113, manufactured by Chemical Plant Kemipol [Bielsko-Biala 2011]. Therefore, in the process of coagulation this coagulant was used in order to obtain the initial adjustment pH = 9. The coagulant dose was 400 mg/dm3. The process of mixing the sewage with a coagulant was conducted in two stages. The quick stirring lasting 1 minute was to mix the entire contents of the reactor, while the slow stirring that ran for 30 minutes ensured the flocks formation, forming larger agglomerates subsequently. After 30 minutes of sedimentation the effluent was introduced into the high-pressure membrane module.

In the second test system of oxidation with Fenton's reagent the dosage of iron and hydrogen peroxide was 0.8 g/dm^3 and 2.4 g/dm ^{3}, while the pH of the effluent was adjusted to the value of 5. After 5 minutes of quick stirring of the wastewaters with a mixture of oxidizing treatment they were subjected to four – hour oxidation. After this time the contents of the reactors were neutralized with 30% NaOH solution to pH = 7, then stirred for 30 minutes and after another 30 minutes of sedimentation the sewage was sent to the osmotic module.

The coke-plant wastewater final treatment after the initial screening process was conducted on a commercial polyamide osmotic membrane ADF, manufactured by U.S. Company Osminics. There was determined the characteristics of de-ionized water transport for the membrane with the diaphragm (Δ = 0.5-2 MPa, u = 2 m/s), then under the pressure of 2.0 MPa and linear velocity of 2 m/s the wastewaters were subjected to purification process. The effectiveness of the treatment was evaluated according to the relativity between the experimental, instantaneous permeate stream, membrane relative permeability and the time of filtration process. There was also determined the change in the pollution indicators for the raw and cleaned sewage. Next the chemical oxygen demand (COD), total organic carbon (TOC), total coal (TC) and the concentration of ammonia nitrogen and total, phenol index, free cyanides and sulphides were determined. COD factors were established through a test method on a spectrophotometer HACH DR 4000; TOC, TC and total nitrogen concentrations through a method of high temperature catalytic oxidation using a gas chromatograph Multi N/C 2100 and the concentration of free cyanide, phenol index and sulphide were determined using cuvette tests from HACH LANGE spectrophotometer DR 2800th.

5. RESULTS AND DISCUSSION

5.1 Effectiveness of post-trial coke wastewater treatment in the integrated tested systems

Figure 3 presents changes in permeate fluxes volume in the process of high-pressure membrane filtration of coke-plant water post-treatment for both systems.

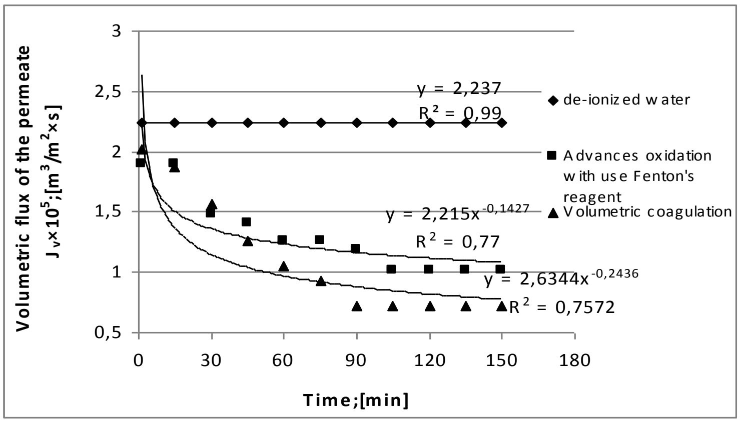


Fig.3. The dependence on the experimental temporary flux of de-ionized water and treated wastewater from the time of the reverse osmosis process

The reverse osmosis membrane employed in the system where the process of cleaning was subjected to advanced oxidation process demonstrated higher efficiency. After 105 minutes of high pressure filtration the stabilized permeate flux was 28.7% higher compared to the permeate flux obtained in the process of reverse osmosis where it was treated by pre-coagulation and its volume stood at $0.726 \cdot 10^{-5}$ [$m^3/m^2 \cdot s$]. The permeate streams each with the same mass obtained in both processes were respectively 2.2 and 3.1 times lower in comparison with a flux of de-ionized water. Figure 4 presents the comparison of the changes depending on the relative permeability of the membrane osmotic membrane process time in both systems.

It was also observed that the osmosis membrane used to purify the wastewater subjected to a process of advanced oxidation indicated higher relative permeability. Its value after the stabilization of the permeate flux was $0.455 \cdot 10^{-5}$[$m^3/m^2 \cdot s$] while, in the first system, was 28.9% lower. Table 2 compares the efficiency of coke–plant wastewater purification in both integrated systems.

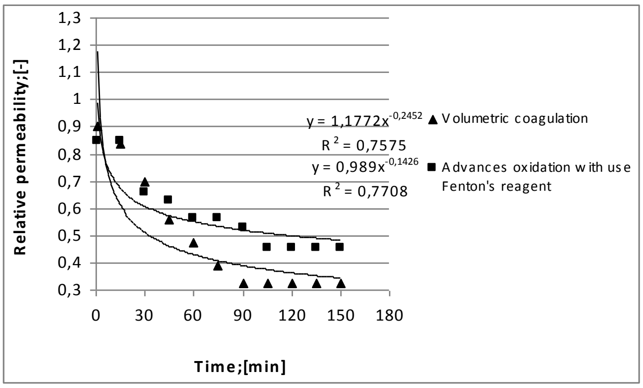


Fig.4. Dependency between the relative osmosis membrane permeability and the time of coke- plant membrane treatment after coagulation and advances oxidation pre-treatment

Table 2. Comparison of coke wastewater treatment effectiveness in the integrated systems

Indicator	Unit	Raw wastewater	Treatment wastewater							
			Volumetric coagulation		Reverse osmosis		Advances oxidation		Reverse osmosis	
			Value	R*, %	Value	R*, %	Value	R*, %	Value	R*, %
COD	mgO_2/dm^3	4102	2097,1	48,9	113,8	97,2	2049,9	50	110	94,6
TC	mgC/dm^3	1207,8	1080	10,6	33,2	97,3	568,6	52,9	30,2	94,6
TOC	mgC/dm^3	1182,5	983,2	16,8	20,9	98,2	568,6	51,9	19,8	98,3
Phenols-phenol index	mg/dm^3	530	408,1	23	0	100	234	55,8	0	100
Ammonium nitrogen	mg/dm^3	408	285,6	30	20,8	94,9	235,6	42,3	20,9	94,9
Free cyanide	mg/dm^3	24,8	19,88	17,6	0	100	18,1	27	0	100
Sulfides	mg/dm^3	1,86	0,175	90,6	0	100	0	100	0	100

* R- the degree of removal of pollutants [%]

The results obtained suggest that sewage post- treated in the reverse osmosis processes in both systems 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 meet 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 two- fold excess over the permissible levels of volatile ammonium ions in terms of $N-NH_4+$. It stood at around 20.8 mg/dm^3. Therefore, coke-plant wastewater before discharging into natural receiver or drains should be additionally after-treated eg. in stream stripping process. However, it could be recycled to the coke production cycle and used for coke cooling.

5.2. Modeling of high-pressure membrane filtration in coke wastewater treatment based on assumptions of the model relaxation.

This paper attempts to examine the possibility of forecasting the size of permeate fluxes in the reverse osmotic process coke wastewater in both systems research.

Calculations are based on assumptions of the model relaxation, describing the changes in the permeate flux of membrane filtration system carried out in non-stationary [1,5]. There was determined the dependence of theoretical, temporary permeate flux since the time of carrying out the high pressure filtration coke wastewater 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 [1,2,5]:

$$\frac{d}{dt}(J-J_{\infty})+\frac{t}{t_0}(J-J_{\infty}) = 0 \tag{5.1}$$

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

That allows to determine the permeate stream changes in the process of filtration. The knowledge about the initial streams: initial (J_0), equilibrium – saturation (J_{00}) and time constant (t_0) enables the solution of the following equation:

$$\ln\left(\frac{J - J_{oo}}{J_0 - J_{oo}}\right) = -\frac{t}{t_0} \tag{5.2}$$

where: $J_{t=0} = J_0$,
$J_{t\to oo} = J_{oo,}$
t_0 – time constant

The time constant which characterizes the velocity of flux disappearing was determined from the equation (5.2) by means of graphic method:

$$t_0 = |1/a| \tag{5.3}$$

where: a- the straight line coefficient (y = and x t) characterizes the filtration process for the examined membrane.

The formula conversion (5.2) allows to determine the relation between the theoretical, temporary, volumetric stream of permeate (J_t)and the time of the filtration process:

$$J_t(t) = (J_0 - J_{oo}) \exp\left(\frac{t}{t_0}\right) + J_{oo} \tag{5.4}$$

The theoretical average value of the permeate stream is determined by solving the equation (5.4):

$$J_{e.} = \frac{1}{t_0}\int_0^{t_0} J_t(t)dt = J_0 - \frac{(J_0 - J_{00})}{e} = J_0 - 0{,}37\,(J_0 - J_{oo}) \tag{5.5}$$

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

Whereas experimental average value of stream was described by equation:

$$J_{a.\,e.} = \frac{1}{t_r}\int_0^{t_r} J_{e.}(t)\,dt \tag{5.6}$$

where: t_r - time longer than : t_0 in which the volumetric permeate stream achieves the equilibrium value determined as: J_{oo}.

In Table 3 and Figure 5 compares obtained by the experimental value of permeate fluxes initial and saturation, and time constants were determined graphically for RO processes in the two systems integrated.

Table.3. Values designated fluxes J_0 and J_{00} and the time constant t_0 in the post-treatment coke plant wastewater by reverses osmosis system.

Type of system	$J_0 \cdot 10^5$, $m^3/m^2 \cdot s$	$J_{00} \cdot 10^5$, $m^3/m^2 \cdot s$	t_0, min.
Volumetric coagulation - RO	2,237	0,726	208,3
Advances oxidation-RO	2,237	1.018	250,0

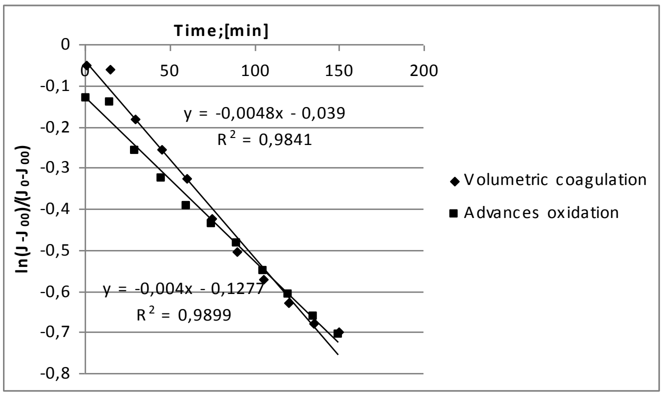
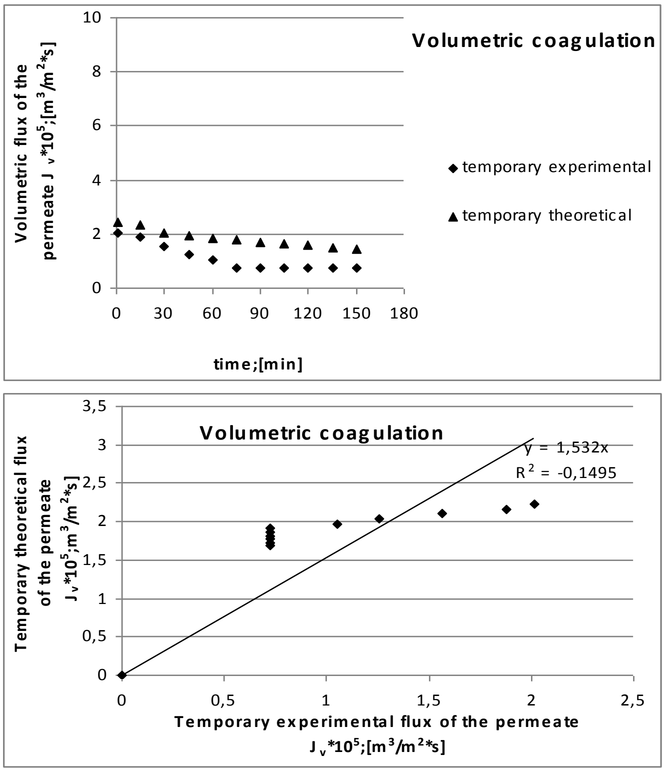


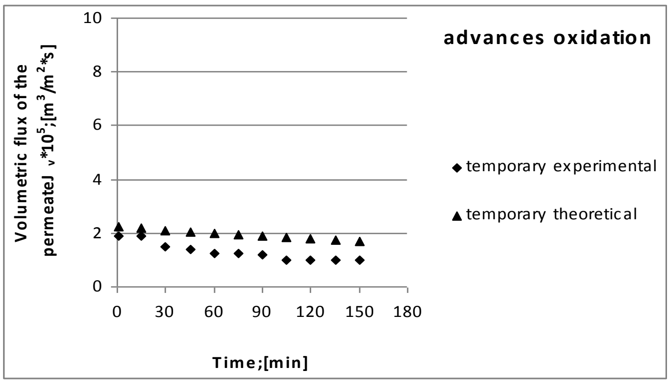
Fig.5. Determination of time constant t_0 for the process of filtering the high coking wastewater using polyamide membrane ADF

Figure 6 compares the size of temporary experimental permeate fluxes obtained in the process of the osmotic coke-plant wastewater post-treatment after the initial cleaning methods such as coagulation and advanced oxidation and the values of theoretical fluxes.

a)



b)



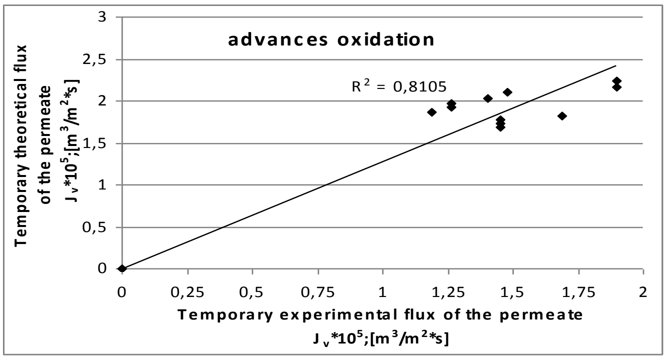


Fig.6. The graphic comparision of temporary average fluxes of permeate with temporary theoretical assigned from relaxation model

In both integrated systems there was observed a decline in the permeate streams during high-pressure membrane filtration. In the membrane cleaning of under-process water, pre-treated initially by coagulation, the difference between the initial volume of the permeate flux and its equilibrium value was 63.9% while in the case of screening in advanced oxidation process it was smaller and stood at the level of 46.4%. It was proved that ,since at the initial stage of the process the temporary experimental and theoretical flow volumes were the same or similar , as time went on these differences have grown especially for the coagulation system. This phenomenon was probably caused by the process of concentration polarization and, primarily, by the presence of sludge post - coagulation fine slurry, which was not succumbed to sedimentation in the process of reverse osmosis and intensified the phenomenon of fouling, contributing to a membrane resistance increase caused by the sediment layer in the membrane surface (secondary membrane) and blocked the pores.

It can be concluded that the employed relaxation model allows to predict the size of temporary permeate flux in the system that combines in-depth oxidation and reverse osmosis (R^2=0.81) but it can not be used for this purpose in the coagulation system-reverse osmosis (R^2=0.42). This can be explained by the fact that the mathematical model applied for theoretical flux measurement does not take into account the complexity of the processes occurred in the interaction of filtered fluid components and the membrane polymer. It seems that the favorable performance in predicting the high-pressure membrane process would be in this case, the hydraulic resistance model of filtration resistance.

Figure 7 shows the comparison of experimental average with the average theoretical permeate fluxes generated in the process of post-trial treatment of coke in the water systems tested.

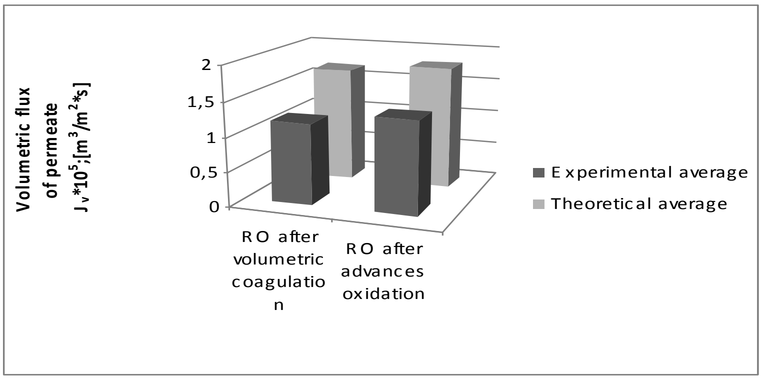


Fig.7. Comparison of average experimental and theoretical permeate obtained in the coke –plant wastewater treatment in both integrated systems

The average osmotic theoretical flow was higher for the system with in-depth pre-oxidation. It developed at the level of $1.785\cdot10^{-5}$ [m^3/m$^2\cdot$s] and it was about 1.33 times higher compared to the experimental stream. A similar relationship was observed for the coagulation volume system. The average value of the theoretical permeate flux in this case was 42.5% higher compared to the average experimental flux ($1.177\cdot10^{-5}$ [m^3/m$^2\cdot$s]).

6. CONCLUSIONS

1. Integrated systems such as coagulation volume- reverse osmosis and oxidation-depth-reverse osmosis employed in coke-plant wastewater treatment did not provide a sufficiently high degree of pollutants removal due to the excessively high concentration of ammonia (20.8 mg/dm^3). Before discharging it into a natural receiver it should be subjected to a stream stripping gas process. However, It can be used as technical water for coke cooling.
2. Among the examined integrated systems better effects were achieved with the initial depth oxidation with Fenton's reagent and the reverse osmosis post-treatment. The pollution indicators for the sewage after this treatment presented the values of : COD-110mg/dm^3, TC-30,2mg/dm^3, TOC-19,8mg/dm^3 and the phenol concentration index, cyanide and sulfide content amounted to 0mg/dm^3.
3. The relaxation model used in the calculations allows to predict the size of temporary permeate flux in the system that combines in-depth oxidation and reverse osmosis but cannot be used for this purpose in the coagulation system-reverse osmosis. This can be explained by the fact that the mathematical model applied for theoretical flux measurement does not take into account the complexity of the processes in the interaction of filtered fluid components and the membrane polymer. It appears that the favorable performance in predicting

the high-pressure membrane process would in this case, the hydraulic model of filtration resistance.

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MODELOWANIE WYDAJNOŚCI PROCESU ODWRÓCONEJ OSMOZY W OCZYSZCZANIU POPROCESOWYCH WÓD KOKSOWNICZYCH W UKŁADZIE ZINTEGROWANYM W OPARCIU O ZAŁOŻENIA MODELU RELAKSACYJNEGO

S t r e s z c z e n i e

W pracy zaprezentowano wyniki badań oczyszczania ścieków koksowniczych, pochodzących z zakładu koksowniczego „Koksownia Częstochowa Nowa”, w dwóch układach zintegrowanych kojarzących koagulację objętościową oraz pogłębione utlenianie z procesem odwróconej osmozy.

Proces koagulacji realizowano z zastosowaniem siarczanu żelaza (III), (PIX 113) o dawce 400 mg/dm^3 i pH ścieków na poziomie pH=9. Drugi z procesów - pogłębione utlenianie przeprowadzono stosując odczynnik Fentona. Stężenie jonów żelaza (II) wynosiło 0,8 g/dm^3 natomiast nadtlenku wodoru 2,4 g/dm^3. Poprocesowe wody koksownicze po ich wstępnym oczyszczeniu poddawano wysokociśnieniowej filtracji membranowej. W procesie odwróconej osmozy stosowano poliamidową membranę płaską ADF amerykańskiej firmy Osmonics. Ciśnienie transmembranowe wynosiło 2 MPa natomiast liniowa prędkość ścieków nad powierzchnia membrany 2m/s. Porównanie efektywności oczyszczania przedmiotowych ścieków w obu układach badawczych wykazało, że skuteczniejszym okazał się system łączący pogłębione utlenianie z odwrócona osmozą.

Ponadto w niniejszej pracy podjęto próbę modelowania wydajności procesu odwróconej osmozy w obu przebadanych układach w oparciu o założenia modelu relaksacyjnego. Wyznaczone na drodze doświadczalnej zależności zmiany wielkości strumieni oczyszczanych ścieków od czasu prowadzenia wysokociśnieniowej filtracji membranowej oraz wartości stałych czasowych charakteryzujących spadek wydajności procesu poniżej opłacalności ekonomicznej pozwoliły na weryfikację tego modelu.