MODELING OF ULTRAFILTRATION PROCESS EFFICIENCY IN COKE PLANT WASTEWATER TREATMENT WITH THE USE OF INDUSTRIAL MEMBRANES

Abstract: In the research conducted there was determined the coke plant waste treatment efficiency in the integrated process that combines ultrafiltration with the reverse osmosis system. In both pressure filtration methods commercial Osmonics membranes were applied. The degree of removal efficiency was evaluated according to changes in the values of selected pollution indicators that characterized “raw” and cleaned wastewater. On the basis of the relaxation method assumptions there was made an attempt to predict the efficiency of the membranes used at the initial stage of ultrafiltration process carried out in non-stationary arrangement. The values of the initial permeate flux and saturation flux, experimentally determined, as well as time constants, determined graphically, allowed to calculate theoretical temporary permeate flux for selected low pressure membranes.

Keywords: ultrafiltration, coke plant wastewater, high pressure membrane techniques, commercial membranes, mathematical model

Introduction

Great diversification of toxic substances found in coke-plant waste, such as polycyclic aromatic hydrocarbons, heterocyclic compounds, oils, tars, cyanides, sulphides, sulfates, thiosulphates, ammonia, and heavy metals extort the application of integrated purification systems that combine single processes used in sewage treatment technology [1–2].

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New efficient methods are being searched in order to guarantee the required removal efficiency of wastewaters treatment that will allow to pour them into natural receivers or reuse them for technical purposes, such as coke quenching. One of them are pressure-driven membrane processes.

The application of those processes requires the reduction of fouling process, which is caused by the substances presented in cleaning waste (pore blocking effect). It restricts permeate volume flux and its declination velocity in the process of pressure filtration, and it decides of membrane usability.

In this work there has been made an attempt to define the possibility of predicting the polysulfone ultrafiltration membranes efficiency in the coke plant wastes treatment using ultrafiltration-reverse osmosis system. The experiment was carried out on the basis of relaxation model, which describes the permeate flux changes in the membrane filtration in the non-stationary arrangement [3–5].

Testing equipment

In the process of coke plant wastes membrane treatment there was used the apparatus unit equipped with a plate-frame membrane module of the type: SEPA CF-NP produced by an American company: Osmonics. It is equipped with: a container of 8 dm$^3$ capacity, rotameter, the high-pressure pump, manometers and valves. The module membrane worked in cross-flow system with return retentate. The installation applied in the research is presented in Fig. 1.

![Testing equipment for coke plant wastewater treatment](image)

Fig. 1. Testing equipment for coke plant wastewater treatment: 1 – tank, 2 – rotameter, 3 – plate and frame module membrane, 4 – manometer, 5 – high pressure pump

Materials and methods

Raw wastewater

The treated coke plant wastes came from ISD Steelworks Częstochowa Coke Plant “Koksownia Częstochowa Nowa” Ltd. The sewage was initially treated mechanically
where tars, oils and stable impurities were removed and then they were subject to the gas desorption in order to remove ammonia. Table 1 shows the values of the chosen pollution indexes which are characteristic for coke plant sewage after initial treatment stage.

Table 1

<table>
<thead>
<tr>
<th>Indicator</th>
<th>Unit</th>
<th>Value</th>
<th>The indexes of sewage pollution which is carried away to the receiver(^1)</th>
<th>Technical water – to quenching of coke(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>—</td>
<td>8.70–10.9</td>
<td>6.50–9.00</td>
<td>—</td>
</tr>
<tr>
<td>COD</td>
<td>mgO(_2)/dm(^3)</td>
<td>6500–3100</td>
<td>125</td>
<td>—</td>
</tr>
<tr>
<td>BOD(_5)</td>
<td>mgO(_2)/dm(^3)</td>
<td>20–80</td>
<td>25.0</td>
<td>—</td>
</tr>
<tr>
<td>Volatile ammonia as NH(_4^+)</td>
<td>mgNH(_4^+)/dm(^3)</td>
<td>25.0–134</td>
<td>10.0</td>
<td>82.0</td>
</tr>
<tr>
<td>TC</td>
<td>mgC/dm(^3)</td>
<td>1184.6</td>
<td>n.s.</td>
<td>—</td>
</tr>
<tr>
<td>TOC</td>
<td>mgC/dm(^3)</td>
<td>963.1</td>
<td>30.0</td>
<td>—</td>
</tr>
<tr>
<td>Phenols</td>
<td>mg/dm(^3)</td>
<td>20.0–30.0</td>
<td>0.10</td>
<td>15.0</td>
</tr>
<tr>
<td>Cyanides</td>
<td>mg/dm(^3)</td>
<td>10.0–50.0</td>
<td>0.10</td>
<td>9.00</td>
</tr>
<tr>
<td>Conductivity</td>
<td>mS/cm</td>
<td>7.25–10.9</td>
<td>n.s.</td>
<td>—</td>
</tr>
</tbody>
</table>

TC – total carbon, TOC – total organic carbon, n.s. – not standardized.
\(^1\) Regulation of the Minister of Environment dated 28 January 2009 amending the Regulation on of the conditions to be met for the introduction of sewage into the water or soil, and on substances particularly harmful to the aquatic environment (Journal of Laws No. 27 item 169).

Membranes

In the research were applied 4 types of ultrafiltration polymer flat membranes (HZ15, PVDV, PW, DS-GM) and one reverse osmosis polymer membrane ADF. All the flat membranes were produced by the American Osmonics company from different polymers. Their characterization provided by the producer are shown in Tables 2 and 3.

Table 2

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Polymer</th>
<th>Indicator</th>
<th>Cut-off</th>
<th>pH</th>
<th>(J)/psi</th>
<th>Pressure [bar]</th>
<th>Cl [ppm]</th>
<th>Temperature [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>UF</td>
<td>PS</td>
<td>HZ15</td>
<td>20K</td>
<td>0.5–13</td>
<td>85/30</td>
<td>1.7</td>
<td>5000</td>
<td>80</td>
</tr>
<tr>
<td>UF</td>
<td>PES</td>
<td>PW</td>
<td>10–12K</td>
<td>2–11</td>
<td>85/30</td>
<td>2</td>
<td>5000</td>
<td>90</td>
</tr>
<tr>
<td>UF</td>
<td>PF</td>
<td>DS-GM</td>
<td>8K</td>
<td>2–11</td>
<td>275/30</td>
<td>14</td>
<td>5000</td>
<td>90</td>
</tr>
<tr>
<td>UF</td>
<td>PVDV</td>
<td>PVDV</td>
<td>30K</td>
<td>1–11</td>
<td>275/30</td>
<td>2</td>
<td>5000</td>
<td>90</td>
</tr>
</tbody>
</table>
Table 3

The characteristics of commercial reverse osmosis membrane applied in coke-making wastewater treatment [4]

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Polymer</th>
<th>Indicator</th>
<th>Retention coefficient [%]</th>
<th>pH</th>
<th>$J_0$/psi</th>
<th>Pressure [bar]</th>
<th>Cl [ppm]</th>
<th>Temperature [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>RO</td>
<td>polyamide (AD)</td>
<td>ADF</td>
<td>99.5</td>
<td>4–11</td>
<td>15/800</td>
<td>54</td>
<td>1000</td>
<td>50</td>
</tr>
</tbody>
</table>

Analytical methods

At the first stage of the experiment the membranes were subjected to conditioning process which allowed to form their structures in a stable way. This process consisted in the filtrating of deionized water through the membranes at the changeable trans-membrane pressure within the range of $0.2 \cdot 10^6$ Pa to $0.8 \cdot 10^6$ Pa and with the flow speed above the surface equal: 2.0 m/s. The membranes were conditioned up to the moment of stabilization of the size of deionized water flux within the time.

At the further stage of the experiment their transport properties were determined: the relation between volumetric flux of deionized water and the time of the low-pressure filtration process at the $0.4 \cdot 10^6$ Pa and with the flow speed above the surface equal: 2.0 m/s.

In the next stage of the research there was stated the usefulness of the membrane in coke plant wastewater preliminary treatment. The evaluation criteria were: changes of the values of the membrane hydraulic permeability and relative penetrability of the lead under low-pressure filtration and the degree of the load of impurities removal. The effectiveness of the process was evaluated on the basis of the impurities indexes changes which characterized crude and treated sewage. There was determined COD, TC, TOC and concentration of ammonium nitrogen, cyanides and phenols. The COD indicators were obtained by means of the test method on the HACH DR 4000 spectrophotometer, while the determination of: TOC, and TC was achieved by means of high temperature catalytic oxidation method with the usage of a chromatograph. Concentration of ammonium nitrogen was determined by distillation directly method, phenols were determined by $p$-nitroaniline titration method and concentration of cyanides was determined by titration of barbituric acid.

The research results demonstrated, that the pollution indicators for the cleaned sewages for all types of membranes were too high in comparison with the standards. Therefore, they were treated additionally with the reverse osmosis method where the ADF Osmonics membrane was applied.

The degree of the removal efficiency was evaluated according to pollution indicators changes, as it was in the case of the low pressure filtration process.

At the last stage of the research there was made an attempt to define the possibility to predict commercial membranes efficiency in the coke plant wastewater treatment based on relaxation model assumptions, which shows the permeate stream changes in the membrane filtration carried out in nonstationary arrangement.
Results and discussion

The transport properties of the ultrafiltration polysulfone membranes

Transport properties of membranes were determined by précising the dependence of the flux of volumetric deionized water on the transmembrane pressure. The carried out measurements proved the significantly diversified dependence of the hydraulic membranes productivity on different structure density and polymers used (Fig. 2).

From all ultrafiltration membranes tested, the DS-GM membrane had the lowest volumetric flux ($J_{\text{H}_2\text{O}} = 0.037 \cdot 10^{-5} \text{ m}^3/\text{m}^2 \cdot \text{s}$; $\Delta P = 0.4 \text{ MPa}$), whereas the highest efficiency had the HZ-15 membrane ($J_{\text{H}_2\text{O}} = 2.865 \cdot 10^{-5} \text{ m}^3/\text{m}^2 \cdot \text{s}$; $\Delta P = 0.4 \text{ MPa}$). Indicated dependences $J_{\text{H}_2\text{O}} = f(\Delta P)$ were described by the means of exponential equations, and high values of correlation coefficient showed the right selection of regression line according to measurement results.

![Graph showing dependence of volumetric flux of deionized water on ultrafiltration membranes pressure](image)

Fig. 2. Dependence of volumetric flux of deionized water on ultrafiltration membranes pressure

The selection of the most beneficial ultrafiltration membrane to the coke plant wastes pretreatment

Membrane efficiency, its relative penetrability, and degree of removal efficiency were the factors to determine which of the membranes were the most useful for the initial coke plant wastewater treatment. Figure 3 shows the dependence of the flow of purified wastewater flux on the low pressure filtration time.

It was stated that during the coke plant wastewater low pressure filtration DS-GM membrane had the lowest volumetric permeate flux. After 90 minutes of ultrafiltration process, 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 ($0.636 \cdot 10^{-5} \text{ m}^3/\text{m}^2 \cdot \text{s}$). Figure 4 shows the comparison of relative permeability changes in the discussed process.
The relative penetrability of the membrane was defined as the quotient of the temporary experimental flux of permeate \( J_v \) to the stabilized flux of deionized water (for the same transmembrane pressure and of flow speed above the surface).

The highest relative permeability had DS-GM membrane, and the lowest PVDV membrane. Its permeability value was significantly lower.

The degree of wastewater purification was determined by the change of pollution indicators in “raw” and cleaned wastewater. Coke-plant wastewater were characterized by the following pollution indicators: COD – 4519.6 mgO\(_2\)/dm\(^3\), TC – 1186.4 mgC/dm\(^3\), TOC – 963.1 mgC/dm\(^3\), and the concentration of phenols and cyanides consequently: 27.3 mg/dm\(^3\) and 38.1 mg/dm\(^3\) (Table 4).

The most advantageous was considered DS-GM industrial membrane. The pollution indicators rate in its case was the lowest.
The stages of pollutions removal in coke-making wastewater ultrafiltration process with use of commercial membranes

<table>
<thead>
<tr>
<th>Indicator</th>
<th>Unit</th>
<th>Raw wastewater</th>
<th>Cleaned wastewater</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>PVDV</td>
<td>PW</td>
</tr>
<tr>
<td>COD</td>
<td>mgO₂/dm³</td>
<td>4519.6</td>
<td>3755.9</td>
</tr>
<tr>
<td>TC</td>
<td>mgC/dm³</td>
<td>1186.4</td>
<td>590.8</td>
</tr>
<tr>
<td>TOC</td>
<td>mgC/dm³</td>
<td>963.1</td>
<td>523.8</td>
</tr>
<tr>
<td>Volatile ammonia as NH₄⁺</td>
<td>mgNH₄⁺/dm³</td>
<td>131.6</td>
<td>119</td>
</tr>
<tr>
<td>Cyanides</td>
<td>mg/dm³</td>
<td>38.1</td>
<td>36.3</td>
</tr>
<tr>
<td>Phenols</td>
<td>mg/dm³</td>
<td>27.3</td>
<td>24.9</td>
</tr>
</tbody>
</table>

TC – total carbon, TOC – total organic carbon.
<table>
<thead>
<tr>
<th>Indicator</th>
<th>Unit</th>
<th>Raw wastewater</th>
<th>Treated wastewater</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>UF/DS-GM</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Unit</td>
</tr>
<tr>
<td>COD</td>
<td>mgO₂/dm³</td>
<td>4519.6</td>
<td>2711.7</td>
</tr>
<tr>
<td>TC</td>
<td>mgC/dm³</td>
<td>1186.4</td>
<td>451.7</td>
</tr>
<tr>
<td>TOC</td>
<td>mgC/dm³</td>
<td>963.1</td>
<td>378.1</td>
</tr>
<tr>
<td>Volatile ammonia as NH₄⁺</td>
<td>mg/dm³</td>
<td>131.6</td>
<td>98.0</td>
</tr>
<tr>
<td>Cyanides</td>
<td>mg/dm³</td>
<td>38.1</td>
<td>35.5</td>
</tr>
<tr>
<td>Phenols</td>
<td>mg/dm³</td>
<td>27.3</td>
<td>24.2</td>
</tr>
<tr>
<td>Conductivity</td>
<td>mS/cm</td>
<td>8.41</td>
<td>7.9</td>
</tr>
</tbody>
</table>

TC – total carbon, TOC – total organic carbon, n.s. – not standardized.
Cleaned wastewater was characterized by the following pollution indicators: COD – 2711.7 mgO₂/dm³, total carbon TC – 451.7 mgC/dm³, total organic carbon TOC – 378.1 mgC/dm³, and the concentration of phenols and cyanides consequently: 24.2 mg/dm³ and 35.5 mg/dm³.

However, all the values exceeded significantly the standards of quality that allow to pour cleaned wastewater into water container or drainage. It was also inadequate to reuse it as a medium for coke quenching. Taking this into consideration a decision of applying a reverse osmosis process was taken (Table 5).

The additional treatment of coke plant wastes after their initial treating were characterized by the following pollution indicators: COD – 109 mgO₂/dm³, concentration of total organic carbon and total carbon consequently: 22 mgC/dm³ and 15 mgC/dm³, concentration of ammonium nitrogen in calculated as volatile ammonia as NH₄⁺ was 21 mgNH₄⁺/dm³. In the permeate participation of cyanides and phenols was not stated.

The obtained results of research can lead to the conclusion that the sewage additionally treated in the process of reverse osmosis still did not meet the standards of quality given by the decree of Environment Minister from 28th 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 for water environment, the concentration of ammonium nitrogen was high. In the research the concentration of ammonium nitrogen calculated as volatile ammonia NH₄⁺ was two times higher, before having been carried out by steam stripping process. Treated wastewater can be used as technical water for quenching of coke.

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

In this work there was made an attempt to define the possibility of predicting the polysulfone ultrafiltration membranes efficiency in the process of treating the coke plant wastes, based on relaxation model assumptions, which describes the permeate stream changes in the membrane filtration carried out in the non-stationary arrangement [3, 5–8]. There was mathematically determined the dependence of theoretical, temporary permeate flux on the time of the pressure filtration and then it was compared with the experimental flux. In the relaxation model the balance of mass transportation in the process of membrane filtration is presented by equation [5].

\[
\frac{d}{dt} (J - J_w) + \frac{t}{t_0} (J - J_w) = 0
\]

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

That allows to determine the permeate flux changes in the process of filtration. The knowledge about the initial fluxes: initial \( (J_0) \), equilibrium – saturation \( (J_w) \) and time constant \( (t_0) \) enables the solution of the following equation:
where: \( J_{t=0} = J_0 \), 
\( J_{t \to \infty} = J_\infty \), 
\( t_0 \) – time constant.

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

\[
t_0 = \left| \frac{1}{a} \right|
\]

where: \( a \) – the straight line coefficient \((y = a \cdot t)\) characterizes the filtration process for the examined membrane.

The formula conversion (2) allows to determine the relation between the theoretical, temporary, volumetric flux of permeate \((J_t)\) and the time of the filtration process:

\[
J_t(t) = (J_0 - J_\infty) e^{\frac{t}{t_0}} + J_\infty
\]

The theoretical average value of the permeate stream is determined by solving the equation (5):

\[
J_a = \frac{1}{t_0} \int_0^{t_0} J_t(t) dt = J_0 - \frac{(J_0 - J_\infty)}{e} = J_0 - 0.37 \left( J_0 - J_\infty \right)
\]

within the integration limits: \( t = 0 \) and \( t = t_0 \).

Whereas experimental average value of flux was described by equation:

\[
J_{ae} = \frac{1}{t_r} \int_0^{t_r} J_e(t) dt
\]

where: \( t_r \) – time longer than: \( t_0 \) in which the volumetric permeate stream achieves the equilibrium value determined as \( J_\infty \).

In Table 6 there were compared experimentally the quantities which are characteristic for the ultrafiltration process of treating coke plants wastes on the selected ultrafiltration membranes, and graphic way of determining the time constant. Below on Figure 5 shows, however, the example of graphic way of determining the time constant: \( t_0 \) for the best DS-GM membrane.
Table 6

Properties of coke making wastewater ultrafiltration process characteristics

<table>
<thead>
<tr>
<th>Membranes</th>
<th>( J_0 \cdot 10^{-5} ) [m(^3)/m(^2)/s]</th>
<th>( J_0' \cdot 10^{-5} ) [m(^3)/m(^2)/s]</th>
<th>( t_0 ) [min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PW</td>
<td>0.578</td>
<td>0.231</td>
<td>250</td>
</tr>
<tr>
<td>PVDV</td>
<td>0.482</td>
<td>0.162</td>
<td>167</td>
</tr>
<tr>
<td>DS-GM</td>
<td>0.046</td>
<td>0.029</td>
<td>143</td>
</tr>
<tr>
<td>HZ-15</td>
<td>1.485</td>
<td>0.636</td>
<td>200</td>
</tr>
</tbody>
</table>

The obtained results enabled us to conclude, that the highest time constant value was obtained for PW ultrafiltration membrane. It proves, that in its case the permeate flux size decreases the slowest. Consequently, its lifetime should be longer.

In the next stage we compared the changes of temporary permeate fluxes obtained in the experiments with temporary permeate fluxes determined mathematically on the basis on relaxation model that occur in the process of low-pressure filtration (Fig. 6).

It is clear that the values of temporary experimental volumetric permeates fluxes in comparison with the theoretical fluxes are lower, especially at the first stage of ultrafiltration process (PVD, PW, HZ-15), and the difference depends on the membranes structure and their resistance to a fouling process.

There was also made a comparison between volumetric permeates fluxes of the experimental average and the theoretical average (Fig. 7).

For all the membranes tested the temporary theoretical fluxes values were higher than those obtained in the low pressure filtration process. The highest medium theoretical flux was noticed for HZ-15 membrane and it was equal to 2.04 \( \cdot 10^{-5} \) m\(^3\)/m\(^2\)/s and it was 40.5 % higher than experimental flux. DS-GM membrane was characterized by the lowest medium theoretical permeate flux: 0.034 \( \cdot 10^{-5} \) m\(^3\)/m\(^2\)/s. It was the same as medium temporary permeate flux.
Fig. 6. Dependence of experimental and theoretical volumetric permeate flux on the coke plant wastewater ultrafiltration pre-treatment with the usage of testing membranes

Fig. 7. Comparison between experimental and theoretical average volumetric flux of permeate in coke plant wastewater ultrafiltration treatment with the usage of commercial membranes
Higher theoretical flux values, both temporary and medium, can be explained with the fact, that the mathematical method, applied in the calculations, do not consider the complex of physical and chemical processes that occur in the membrane surface and pores. It is observed that the fouling process is more intensive for the membrane with more open structure and at the first stage of filtration.

That 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 nonstationary arrangement, should be used for prediction of ultrafiltration efficiency for dense structure membranes.

Conclusion

1. The applied integrated system of ultrafiltration – reverses osmosis did not cause appropriately high degree of treatment. It did not enable to carry them to the natural receiver. The concentration of nitrogen ammonium was on the level 21 mg\(\text{NH}_4^+\)/dm\(^3\). It was 2 times higher than normal. Treated wastewater can be used as technical water – for coke quenching.

2. The research showed, that temporary theoretical and average permeate of flux that were determined on the basis of relaxation model assumptions are higher than fluxes calculated in experimental way. This model, which describes changes of ultrafiltration permeate of flux in coke-making wastewater treatment, should be used to forecast ultrafiltration membranes efficiency, which have lower cut-off.

Acknowledgement

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References

MODELOWANIE WYDAJNOŚCI PROCESU ULTRAFILTRACYJNEGO Oczyszczania Ścieków Koksowniczych Z Zastosowaniem Membran Komercyjnych

Instytut Inżynierii Środowiska, Wydział Inżynierii i Ochrony Środowiska Politechnika Częstochowska

Abstrakt: W przeprowadzonych badaniach określono efektywność oczyszczania ścieków koksowniczych w układzie zintegrowanym łączącym ultrafiltrację z procesem odwróconej osmozy. W obu procesach filtracji ciśnieniowej stosowano membrany komercyjne amerykańskiej firmy Osmonics. Stopień oczyszczania ścieków oceniano na podstawie zmiany wartości wskaźników zanieczyszczeń, takich jak: stężenie węgla ogólnego oraz organicznego, cyjaneków, fenoli, ChZT oraz azotu amonowego charakteryzujących ścieki surowe i oczyszczone. Korzystając z modelu relaksacyjnego, podjęto próbę prognozowania wydajności membran stosowanych w procesie ultrafiltracji ścieków, prowadzonym w układzie niestacjonarnym. Doswiadczalnie wyznaczone wartości strumieni początkowych permeatów, strumieni nasycenia oraz wyznaczone w sposób graficzny stałe czasowe umożliwiły obliczenie teoretycznych chwilowych strumieni permeatów dla wybranych membran niskociśnieniowych.

Słowa kluczowe: ultrafiltracja, ścieki koksownicze, ciśnieniowe techniki membranowe, membrany komercyjne, model matematyczny