The use of polymeric and ceramic ultrafiltration in biologically treated coke oven wastewater polishing

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ABSTRACT

The main scope of the presented research was to treat coke oven wastewater stream after the biological loop using low pressure-driven membrane filtration. The process was focused on reducing the content of substances that could intensify the phenomenon of reverse osmosis membrane fouling. For this purpose, four types of polyethersulphone (PES) ultrafiltration (UF) membranes of molecular weight cut-off (MWCO) equal to 10, 5, 3 and 1 kDa, respectively, and two ceramic disk membranes (5 and 8 kDa) with zirconia active layer were applied in a cross-flow mode filtration performed at the constant pressure. During experiments, the influence of membranes MWCO, type of material, as well as the transmembrane pressure (TMP) on the process capacity and the permeate quality, evaluated based on chemical oxygen demand (COD) value, was examined. Experimental results indicated that in the tested range of TMP (0.1–0.3 MPa), the application of polymeric membranes was more beneficial, since they allowed for the operation at the higher rate of the initial capacity and they were less susceptible to fouling in comparison with ceramic ones. The separation with tested UF polymeric membranes also enabled the better reduction of COD, with the highest rejection of 67% noted for 5 kDa PES membrane at TMP of 0.2 MPa. The 5 kDa membrane was found to be preferable due to its capacity, lowest fouling affinity and contaminants removal efficiency.

Keywords: Coke oven wastewater; Pretreatment; Low-pressure membrane filtration; Ultrafiltration

1. Introduction

Cokemaking industry possesses highly negative impact on natural environment because of harmful byproducts emissions, which include dust, BTEX, phenol, ammonia and tars [1,2]. Cooling and cleaning of coke oven gas and processing of coal derivatives results in the formation of the liquor, which account for up to 5% of product obtained during one cycle of coking [3]. Raw coke oven liquor, after tars separation and ammonia stripping, is known as a raw coke oven wastewater or phenolic wastewater [4]. One of the intensively developed concept to utilize this highly loaded stream is the application of membrane technologies, which are more frequently used and can successfully compete with traditional treatment schemes [5]. Membrane technologies may be applied as ‘polishing’ systems, whereby wastewater already treated by a conventional wastewater treatment plant is further treated to desired quality. Smol et al. [6] introduced the ultrafiltration (UF) process for removal of refractory polycyclic aromatic hydrocarbons retained in the wastewater after biological loop, while Jin et al. [7] studied the performance of membrane bioreactor (MBR) with submerged modules integrated with nanofiltration (NF)/reverse osmosis (RO) units intended for water reuse. In other case, membrane techniques may be introduced to existing system to treat the raw wastewater directly. Minhalma and Pihno [8,9] integrated the NF process with conventional steam stripping method for ammonia, phenol and cyanide removal from model solution simulating raw ammoniacal coke oven liquor, which allowed to obtain cyanide-rich permeate and a cyanide-depleted concentrate enriched in ammonium and phenols in batch concentration mode with the permeate recovery of about 40%.

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Korzenowski et al. [10] applied NF process to fractionate cyanides/ammonium solutions – NF-270 membrane performance was found to be highly dependent on pH of the solution, as well as on its composition. In the ternary solutions, for pH values lower than 9, the rejection of ammonium chloride was 75% and sodium cyanide was 45%. Ammonium chloride was then concentrated mainly in the retentate stream, while sodium cyanide in the permeate stream. Yin et al. [11] applied NF combined with diafiltration to separate high concentration of ammonium thioulate from ammonium thiocyanate presented in raw coke oven wastewater. Tested system was able to selectively retain \((\text{NH}_4)_2\text{S}_2\text{O}_3\) with an average rejection of 93.4% at high salt concentrations. Kumar et al. [12] investigated applicability of cross-flow microfiltration (MF)–NF system in separating cyanide from coke oven wastewater. Rejection of cyanide increased substantially (from 86% to 93%) with the increase of pH (from 7.0 to 10.0) for all tested membranes. The NF1, with negative charge, enabled to remove 94% of cyanide, while yielding a high flux of 79 L/h at a pH of 10.0 and at a relatively low pressure of only 13 kg/cm². Kwiecińska et al. [13,14] conducted series of experiments on the application of low-pressure membrane filtration processes as a pretreatment method in purification of wastewater formed during coal gasification process. Additionally, membrane separation technologies can be applied as an independent system as it was shown by Kumar et al. [15], who designed the novel system by integration of forward osmosis (FO) with NF. Their FO–NF system succeeded in separation of more than 98% of the major contaminants present in the coke oven wastewater, thereby allowing for water reuse. Removal of contaminants from real coke oven wastewater could be achieved along with pure water flux of 46 L/(m²h) in FO system under optimized conditions. NF module ensured continuous recovery and recycle of 99% of the draw solute with the recovery of reusable water at the rate of 45 L/(m²h).

In the water reclamation by NF or RO technology, which are used to remove dissolved molecules from effluent to be reused [16], the membrane unit feed is often the effluent from biological treatment process, which beside of undecomposed refractory compounds, also contains biologically active sludge flocks, which can cause membrane fouling [17,18]. Thus, a pretreatment process prior to the NF or RO system is required to alleviate this phenomenon. Low-pressure driven membrane techniques, that is, MF or UF operate by a surface removal mechanism, and resemble a fine screen or a sieve. It has been found that the use of MF or UF pretreatment prior to NF or RO system can significantly reduce the fouling of latter systems over the conventional pretreatment processes [16,19,20].

Furthermore, in comparison with other pretreatment methods, such as, for example, chemical coagulation [20], UF is recognized as a compact and easily automated process and, usually, it requires less power and chemicals.

Presented researches aimed to recognize the efficiency of low-pressure membrane filtration pretreatment of real effluents from biological loop of coke oven wastewater treatment plants. In the current research, the efficiency was evaluated in terms of removal of chemical oxygen demand (COD). Volumetric flux stability and the resistance to fouling phenomenon of polymeric and ceramic membranes differed in molecular weight cut-off (MWCO) was also investigated.

### 2. Experimental

#### 2.1. Membrane filtration

Laboratory scale set-up KMS Cell CF1 by Koch Membrane Systems (Fig. 1), operated in a cross-flow mode was employed during low-pressure filtration experiments. The installation was equipped with the feed tank of a capacity of 0.5 dm³ and a membrane module for flat-sheet membranes with an effective separation area of 28 cm². To prevent damage, the membrane was kept on a highly porous stainless steel support. The permeate was continuously collected outside the membrane module, while the retentate was recirculated to the feed tank.

During experiments four types of polyethersulphone (PES) UF membranes (Synder Filtration, USA), that is, ST, MT, VT and XT with corresponding MWCO equal to 10, 5, 3 and 1 kDa, respectively, and two DisRAM ceramic disk membranes (TAMI Industries), that is, Fine UF-5 kDa and Fine UF-8 kDa with zirconia active layer were used. The filtration of real biologically treated coke oven wastewater was preceded with the characterization of membranes’ transport properties. For this purpose, a dependence of deionized water volumetric flux on a transmembrane pressure (TMP) in the range of 0.1–0.3 MPa was determined.

To evaluate the performance of UF process as a pretreatment method, wastewaters after biological loop were filtered at a TMP of 0.1–0.3 MPa until 80% of initial feed volume was recovered in the form of permeate. After wastewater filtration, the deionized water flux was established for membranes neither chemically nor hydraulically cleaned in order to evaluate the impact of membrane fouling on the process capacity.

The volumetric flux \(J\) (L/m² h) across the membrane was calculated based on the measured volume of collected permeate according to Eq. (1) as follows:

\[
J = \frac{\Delta V}{A \times \Delta t}
\]

where \(\Delta V\) – permeate volume collected over \(\Delta t\) period (L); \(A\) – membrane effective separation area (m²) and \(\Delta t\) – time of permeation and sample collection (h).

Relative fluxes of coke oven wastewater through new conditioned membrane and of deionized water after real

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![Fig. 1. KMS Cell CF1 laboratory-scale membrane filtration unit.](image)
sample filtration were calculated according to Eqs. (2) and (3) as follows:

\[
\alpha_P = \frac{J_P}{J_0} \\
\alpha_D = \frac{J_D}{J_0}
\]

(2)

(3)

where \( J_P \) – volumetric flux of coke wastewater (L/m\(^2\) h); \( J_D \) – volumetric flux of deionized water after real sample filtration (L/m\(^2\) h); \( J_0 \) – initial volumetric flux of deionized water, (L/m\(^2\) h); \( \alpha_P \) – relative permeate flux (–) and \( \alpha_D \) – relative deionized water flux (–).

2.2. Analytical methods

Feed directed to UF separation, as well as permeate and concentrate samples were analysed for COD determined by a spectrophotometric method using HACH Lange procedures at DR-6000 spectrophotometer. The removal rate of examined contaminants (indicated as COD) was calculated on the basis of Eq. (4) as follows:

\[
R = \left(1 - \frac{C_P}{C_f}\right) \times 100\%
\]

(4)

where \( R \) – removal rate of contaminant (%); \( C_P \) – concentration of COD in the permeate (mg O\(_2\)/L) and \( C_f \) – concentration of COD in the feed (mg O\(_2\)/L).

3. Results

3.1. Membrane characteristics

Transport properties of polymeric PES and ceramic membranes were evaluated on the basis of the TMP dependency of deionized water volumetric flux in the range of 0.1–0.3 MPa (Fig. 2).

Experimental results indicated that fluxes measured for all tested polymeric membranes were similar despite differences in MWCO values (Fig. 2). Such results can be explained by typical membrane structure features, that is, membrane porosity (number of pores in a unit area of a membrane) and pores size distribution. Hence, the obtained results for ST, MT, VT and XT membranes could result from one of the discussed parameters. Membrane with greater number of smaller pores may exhibit similar performance to a membrane, which possess less transportation channels, but of a bigger average diameter.

Comparing the data presented in Fig. 2, one can see, that deionized water fluxes obtained for ceramic disk membranes were higher when compared with polymeric ones. This can be attributed to the fact that ceramic membranes are thought to be more porous in comparison with PES-based ones, and the polymeric material, despite its outstanding oxidative, thermal and hydrolytic stability and good mechanical property, possesses relatively hydrophobic character [21,22]. Thus, the higher fluxes at lower TMPs obtained for ceramic disks [23,24]. Furthermore, factors like, for example, surface roughness, may play an important role.

3.2. Wastewater filtration

The influences of TMP on permeate fluxes and membranes capacity obtained for polymeric PES membranes are illustrated in Figs. 3–6.

Despite differences in MWCO, during experiments conducted under TMP of 0.10 MPa, permeate fluxes took
similar values and were stable in case of all membranes. Main difference arises from the filtration time required to recover 80% of initial feed volume which was in following order XT-1 kDa > VT-3 kDa > MT-5 kDa > ST-10 kDa, that is, it shortened with increasing MWCO. Secondly, in case of two membranes, that is, ST-10 kDa and VT-3 kDa (Figs. 3 and 5, respectively), increasing of TMP to 0.15 MPa had no influence on membrane capacity, while for MT-5 kDa and XT-1 kDa membranes (Figs. 4 and 6, respectively), permeate flux increased with increasing the driving force.

Comparing data presented in Figs. 3–6, it was seen that filtration using MT-5 kDa exhibited the highest stability of performance despite the TMP applied. Furthermore, regular increase in membrane capacity was observed with TMP increase. In case of other membranes, the impact of pressure on the performance was less explicit.

For comparative investigation, TMP of 0.30 MPa (Figs. 7(a) and (b)) was selected. It could be seen that filtration using MT-5 kDa exhibited the highest stability of performance despite the TMP applied. Furthermore, regular increase in membrane capacity was observed with TMP increase. In case of other membranes, the impact of pressure on the performance was less explicit.

Calculated values of relative permeate fluxes \( \alpha \) (Fig. 8) indicated, that filtration using VT and MT membranes allowed for the operation at the highest rate of initial capacity average permeate flux was observed. On the other hand, the filtration using XT-type membrane of the lowest MWCO 1 kDa characterized with the most significant loss in permeate capacity.

The comparison of experimental results regarding application of polymeric and ceramic membranes with MWCO of 5 kDa presented in Figs. 7(a) and (b) enabled to notice that filtration using polymeric PES membrane required shorter time in order to collect the required volume of permeate in comparison with ceramic ZrO\(_2\) membrane characterized with the same MWCO (the drastic fouling of ceramic membranes led to the limited performance of the experiments, as shown in Fig. 7(b)). The decline of C-5 kDa membrane capacity after 5 h of filtration has carried out only at 0.3 MPa reached 69% (Fig. 7(b)), while in case of MT-5 kDa polymeric membrane the permeate flux was practically stable (Fig. 7(a)). Moreover, the filtration with ceramic 8 kDa membrane at 0.1 MPa capacity was so poor that after ca. 3 h of the process, it was decided to increase the pressure to 0.3 MPa (Fig. 7(b)). It resulted in the improvement of the process capacity, which, however, was followed by the drastic flux decrease in time. Thus, it was concluded, that ceramic membranes were more susceptible to fouling phenomenon and were stated to be unsuitable for cokewere wastewater treatment.
and VT membrane was the least susceptible to the fouling phenomenon.

Relative permeate fluxes for C-5 kDa and MT-5 kDa membrane confirmed previous conclusion regarding poor fouling resistance revealed by ceramic material. Value of $\alpha_P$ for C-5 kDa membrane was more than twice lower when compared with MT-5 kDa membrane with corresponding cut-off and did not exceed the 25% of initial deionized water flux.

As shown in Fig. 9, membranes characterized by lowest MWCO value, that is, VT and XT, were those, which showed the highest recovery of transport properties. It was most likely due to the fact that fouling phenomenon resulted mainly from the formation of the dense filtration cake on the membrane surface, and not from the pore blocking. On the other hand, C-5 kDa and C-8 kDa ceramic membranes showed a high water flux decrease due to intensive membrane fouling.

Nevertheless, considering process capacity and affinity of tested membranes to fouling, it was concluded, that MT membrane of cut-off 5 kDa would be the preferable one, as it revealed the highest and the most stable flux during the wastewater treatment, while the severeness of its fouling was acceptable ($\alpha_P = 0.63$ and $\alpha_D = 0.76$).

In order to determine the overall efficiency of biological effluents, UF as a pretreatment for further purification in NF/RO system, the removal rate of contaminants indicated as COD was evaluated. In Fig. 10 removal rates of COD using different membranes are presented.

The removal rate of COD was around 60% for the polymeric PES membranes and ca. 10% for the tested ceramic membranes. The lowest removal of 10% was found for the C-5 kDa, while the more open one, C-8 kDa retained 12% of COD present in biologically treated coke wastewater. It could also be noticed that MWCO of tested polymeric membranes had slight influence on COD reduction, which ranged from 57% to 67%. Thus, the main selection criteria for process evaluation was based on relative and average permeate volumetric fluxes and fouling resistance.

COD removal rates, obtained during conducted experiments, were found to be higher in comparison with those presented in the literature by other researchers. Jin et al. [7] showed that by combining a MBR equipped with submerged membrane module for flat-sheet membranes with pore size of 0.1 μm into the anaerobic, anoxic and oxic processes system, around 19.2% of COD could further be reduced, and the turbidity in MBR effluent was completely removed. SDI results also showed a great advantage in combining the MF module into the biological reactor as a pretreatment method for further wastewater purification in NF-RO system.

Sun et al. [25] investigated the integrated UF–NF/RO membrane system to the treatment of phenolic wastewater. As in the case of presented results, also in case of Sun and coworkers experiments, the Synder XT UF membrane exhibited very good performance with almost complete removal of suspended solids and partial removal of organic compounds (56.4% as COD).

A laboratory-scale, anaerobic–anoxic–oxic submerged membrane bioreactor (A1/A2/O-MBR) system [26] used to treat real coke oven wastewater was compared with conventional anaerobic–anoxic–oxic activated sludge (A1/A2/O-CAS) system tested in parallel as control. The overall obtained average removal efficiencies of COD and phenol in MBR-based system were 89.8% and 99%, respectively. The MBR equipped with hollow fibre MF membranes with nominal pore size of 0.4 μm, was more efficient and reliable in pollutant removal than the control A1/A2/O-CAS system, especially
at high and varying loading rates. The same system operated with complete sludge retention was capable of removing 87.9% of COD and 99.4% of turbidity from highly toxic coke oven wastewater. According to authors calculation, the MF membrane rejected 7.1% of COD [27].

Mielczarek et al. [28,29] investigated the applicability of UF as a pretreatment method for RO unit in the membrane filtration system applied to raw coke wastewater treatment. The involved commercial HZ15 (PS, 20 kDa), PW (PES, 10–12 kDa), DS-GM (TF, 8 kDa) and PVDF (30 kDa) flat-sheet polymeric membranes allowed for the COD reduction of 10.8%, 16.2%, 40.1% and 16.9%, respectively. UF using self-prepared polysulphone membranes [30,31] allowed to reduce COD by 40%. Another research on application of UF in treatment of biologically treated coke oven wastewater [6] showed that UF with capillary ZW-10 membranes with pores size of 0.04 μm was able to reduce the COD value from 369.3 to 298.6 mg/L, which corresponded to ca. 20% reduction.

In this research, among all polymeric and ceramic membranes tested for polishing of biologically treated coke oven wastewater intended for further purification in NF/RO system for technological grade water reclamation, the MT-5 kDa membrane was found to be preferable due to its capacity, lowest fouling affinity and contaminants removal efficiency.

4. Conclusions
- Five types of polyethersulphone membranes with MWCO of 20, 10, 5, 3 and 1 kDa, as well as two ZrO2 ceramic membranes with MWCO equal to 5 and 8 kDa were applied in UF of biologically treated effluents.
- Comparing membrane capacities observed during wastewater filtration, it was found that ceramic membranes were more susceptible to fouling phenomenon.
- Narrow polymeric membranes (5, 3 and 1 kDa) exhibited the best permeate capacity and were the least vulnerable to fouling resulting of pore blocking.
- In case of more open membrane (10 kDa), fouling was mainly a result of the deposition of contaminants inside membrane pores making the capacity recovery process less effective.
- Application of UF as method for biological effluent polishing, intending its further purification in NF and RO units showed that separation with tested UF membrane allowed for reduction of COD by more than 57%, 66% and 67% in case of XT/ST, VT and MT polymeric PES membranes, respectively, which was stated to be suitable level, while considering NF/RO membrane fouling prevention.
- Ceramic membranes exhibited worse performance in the case of COD removal, and the rejection rate was not higher than 12% obtained for C-8 kDa membrane.

Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>(\Delta V)</td>
<td>Permeate volume collected over (\Delta t) period, L</td>
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<tr>
<td>(A)</td>
<td>Membrane effective separation area, m²</td>
</tr>
<tr>
<td>(\Delta t)</td>
<td>Time of permeation and sample collection, h</td>
</tr>
<tr>
<td>(I_p)</td>
<td>Volumetric flux of coke wastewater, L/m² h</td>
</tr>
<tr>
<td>(I_d)</td>
<td>Volumetric flux of deionized water after real sample filtration, L/m² h</td>
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<tr>
<td>(I_o)</td>
<td>Initial volumetric flux of deionized water, L/m² h</td>
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<tr>
<td>COD</td>
<td>Chemical oxygen demand, mg O₂/L</td>
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<tr>
<td>MWCO</td>
<td>Molecular weight cut off, kDa</td>
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<tr>
<td>TMP</td>
<td>Transmembrane pressure, MPa</td>
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<tr>
<td>(\alpha_{p})</td>
<td>Relative permeate flux, –</td>
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<tr>
<td>(\alpha_{d})</td>
<td>Relative deionized water flux, –</td>
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<td>(R)</td>
<td>Removal rate, %</td>
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<tr>
<td>(C_p)</td>
<td>Concentration of COD in permeate, mg O₂/L</td>
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<tr>
<td>(C_f)</td>
<td>Concentration of COD in feed, mg O₂/L</td>
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