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Ceramic Membranes Modified by Carbon used for Laundry Wastewater Treatment

Daniel Polak[a*] Maciej Szwast[a], Wojciech Fabianowski[b], Mateusz Rosiński[a]

[a]Chemical and Process Engineering, Warsaw University of Technology, Waryńskiego 1, 00-645 Warszawa
[b]Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warszawa
Daniel.Polak.dokt@pw.edu.pl

Ceramic multichannel membranes made of Al2O3 were modified by carbon structures such as graphite. It has been proved that modifications are stable in time and washing durable.
Carbon coatings changed membrane properties such as surface contact angle and filtration coefficient. Several filtration tests using real laundry wastewater were conducted. Different permeate fluxes and permeate qualities were obtained for different membrane modifications.
The paper describes how different modifications affect the laundry wastewater filtration process conducted using modified membranes.

1. Introduction

One of the industrial branches wherein it is necessary to introduce new technologies and measures aimed at reducing energy consumption, water consumption and negative impact on the environment are industrial laundries. Process-related problems associated with this type of business result from the high demand for water and from the production of wastewater containing many environmentally hazardous biological and chemical substances. Every day, in a laundry, an average of 20 t of dry clothes are processed, which uses about 200 m^3 of water and 120 kg of detergents to wash. In addition to the high consumption of water and detergents, an additional problem is a variable composition of wastewater, depending on the type of material washed and the consumption of detergents. The mixture consists of: solids (fibres, fabric residues), salts (nitrates, nitrites, phosphates, fluorides, bromides, chlorides), dyes, bacteria, bleaches (sodium hypochlorite, hydrogen peroxide), plasticizers as well as anionic and non-ionic surfactants (Søgaard, 2015).
Conventional treatment techniques such as flocculation, coagulation, adsorption or advanced oxidation for laundry wastewater treatment are intended to recover only water. Surfactants are retained on adsorbent beds or become oxidised (Ciabattia et al., 2009). The technique for recovering water and some detergents, in particular surfactants, is microfiltration. In addition, this process allows for a complete removal of suspended matter and bacteria from the water. In the designed and discussed process, laundry wastewater is the feed, concentrated wastewater intended for utilization is the retentate, and finally, permeate, which is the main product of the process, contains recovered water and detergents which can be reused in the laundry process (Szwast, Polak, 2018).
In the case of laundry wastewater which contains a lot of insoluble substances, the fouling phenomenon occurs intensively, specifically fouling the membrane with sediment, which causes the permeate flux to drop. The sediment builds up on the surface of the membrane in the form of a pie or gel and in the pores of the membrane, reducing the diameters of the pores or completely blocking them. In both cases, the hydraulic resistance of the membrane increases, so that the flux of the obtained permeate decreases. Additionally, the sediment layer build-up may be a barrier to some compounds and limit their transport (Szwast et al., 2018). Various strategies are used to reduce the phenomenon of fouling, such as removing the resulting sediment or protecting it from building up during the process. In order to remove the sediment, the membranes are periodically washed using cleaning agents or using a technique of back flush (Rayess et al., 2011). Membrane fouling may be limited by selecting appropriate process parameters, such as feed pressure and the linear

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velocity of the liquid stream flowing along the membrane. The intensity of fouling may also be reduced by modifying the surface properties of the membrane. The improvement of antifouling properties may be achieved by changing wettability, reducing roughness or changing the surface charge of the membrane (Lee et al., 2016). Modification of the structure may involve covering the surface with additional material or attaching specific chemical groups to it. To this end, the membrane may be subjected to a coating process, chemical and electrochemical deposition or chemical vapour deposition (CVD) (Lin, Burggraaf,1993).
The CVD method which was used in the discussed work for membrane modification, is widely applied in the synthesis of nanostructured materials (Dobrzańska-Danikiewicz et al., 2014), surface modification of carbon fibres (Olszówka-Myalska et al., 2009) and porous materials, including membranes (Xomeritakis and Lin, 1994). An advantage of the CVD method, which seems promising for the modification of porous membranes, is the ability to cover both the channels through which the retentate flows as well as the pores of the membrane through which the permeate is transported (Lin and Burggraaf,1993). This is important because blocking of pores is often an irreversible phenomenon.
The purpose of the work was to investigate the impact of modified ceramic membranes by carbon compounds on the recovery process of water and detergents from laundry wastewater. The work focused on the analysis of the filtration process, without conducting a detailed structural analysis of the modified membranes.

2. Research methodology and materials

2.1 Ceramic membranes and their modification

The tests involved 7-channel, commercially available ceramic membranes (Mantec Technical Ceramics Ltd). The membranes have an average pore diameter of 0.35 μm and a porosity in the range of 31%-35%. At the first stage of the tests, the change of the permeate flux and its quality during the filtration process using ceramic membranes was determined. At the second stage, the ceramic membranes were modified by the CVD method and the effects of the modification on the process efficiency was determined. The modification process was carried out using various solvents and various carbon forms. The process can be divided into several stages:

1. Immersing the membrane in the Isopropanol/water mixture in the ratio of 95/5 for 48h and then drying the membrane.
2. Rinsing the membrane with Modification Solution I (the composition of the solution is presented in Table 1).
3. Immersing the membrane in Modification Solution II (the composition of the solution is presented in Table 1).
4. Degassing.
5. Drying (drying time and conditions are presented in Table 1).

Table 1: Membrane modification conditions

Type of membrane	Modification Solution I	Modification Solution II	Drying temperaturę and time
MOD1		Unmodified	
MOD2	*Octadecyltrichlorosilane* (OTS) / Toluene	Flake graphite / Toluene	96h, room temperature
MOD3	(3-*Aminopropyl)triethoxysilane* (3APS) / Isopropanol	Powder graphite / Isopropanol	96h, room temperature

The purpose of the modification was to inoculate $C_{18}H_{37}$ alkyl groups derived from OTS or amino groups derived from 3APS on the membrane surface. The presence of new groups affects the change of the membrane surface charge. Additionally, the groups may be responsible for interaction with compounds found in wastewater. The presence of these groups also increases the hydrophobicity of the surface. Despite such an unfavourable phenomenon, the hydrophobic surface interacts better with graphite, which facilitates its deposition on the membrane.

2.2 Tests of membrane filtration properties

A setup designed by the authors was used to test the recovery process of water and detergents from laundry wastewater using unmodified and modified ceramic membranes. The setup includes a feed tank with a cooling system, a pump, a manometer, valves on a retentate line and on a recirculation loop and a membrane module. The process was carried out as a classic cross flow. The feed flew along the module through internal channels, whereas the permeate was obtained from the outside of the membrane. The tests were carried out at the pressure of 2 bar and with a 500l/h retentate flow, which corresponds to the linear velocity of the retentate at 3 m/s. The filtration area was 100 cm^2. Real wastewater from the laundry Hollywood Textile Service Sp. z o.o. in Sierpc was the feed.

In order to evaluate the efficiency of the filtration process, a change in the flux of the obtained permeate during the process and in physicochemical parameters was determined for assessing its quality. The rate of changes in the permeate flux will help to determine the antifouling properties of the tested membranes. Selected parameters typical of the feed and the obtained permeate included: turbidity, conductivity, interfacial tension (IFT) and chemical oxygen demand (COD). The determination of the IFT parameter allows for an indirect determination of the content of surfactants, because in the case of laundry wastewater, it may be assumed that the concentration of surfactants has a decisive impact on the IFT value. Hanna Instruments devices were used to measure the conductivity and pH. Turbidity was measured by a Lovibond device. To determine the COD value, Nanocolor cuvette tests and the Thermo Genesys10uv spectrophotometer were used. IFT was measured by the pendant drop method using a DataPhysic goniometer.

3. Results and discussion

The first part of the tests determined the change in the quality and quantity of the permeate obtained during the process. This step was carried out using an unmodified ceramic membrane. The physicochemical parameters typical of the feed are presented in Table 2. The filtration process was carried out for 180 minutes. The permeate volumetric flow of and sampling were carried out every 10 minutes up to the 60th minute of the process duration and then every 20 minutes. The results obtained are presented in Figures 1-4.

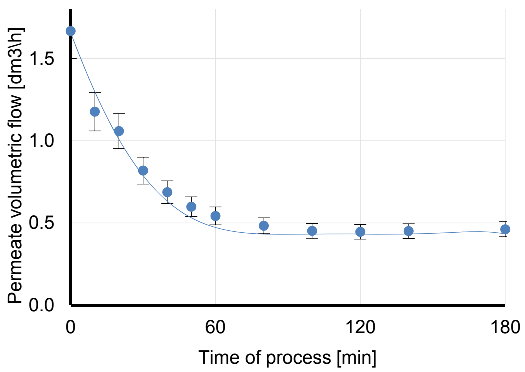

Figure 1: Permeate volumetric flow change in time.

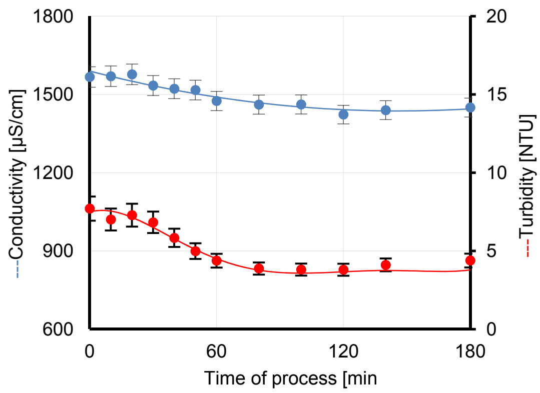

Figure 2: Conductivity and turbidity change in time.

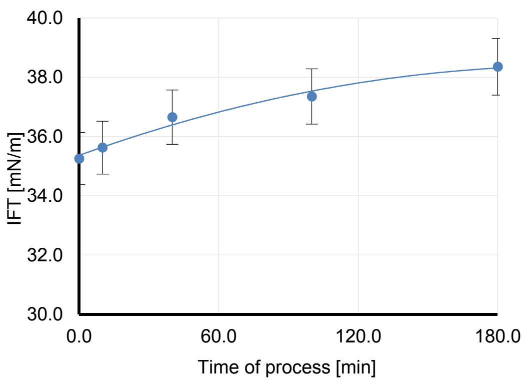

Figure 3: IFT change in time.

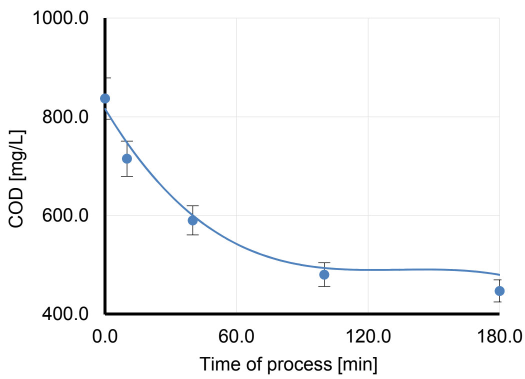

Figure 4: COD change in time.

The obtained data show that the permeate flow decreases in time – first, quite rapidly, when a layer of sediment builds up, and then the operation follows nearly in steady-state conditions resulting from a compromise between the formation and disappearance of the sediment. The changes in conductivity, turbidity and COD values may be equally associated with a growing sediment on the surface of the membrane, which improves the quality of the obtained permeate. In addition, in the case of these parameters, the stage of sediment build-up and operation in steady-state conditions may also be noticed. In the case of INF there is a constant increase during the process, without a clear stabilisation. This is due to the fact that the transport of surfactants through the membrane does not only depend on the changing pore diameter as a result of adsorption of impurities, but also on the quality of the resulting sediment which causes the formation of micelles. However, in the case of IFT, the phenomenon of fouling has an adverse impact, because during the process the IFT value increases, which means that the concentration of surfactants in the permeate stream decreases.

Based on the obtained data it is also possible to conduct a general analysis of the microfiltration process of laundry wastewater with the use of ceramic membranes. To this end, the values of parameters typical of the feed and permeate were compared. For comparison, a sample of permeate was selected after 100 minutes of the process duration, i.e. after the stage of the rapid sediment growth. The determined parameter values are presented in Table 2.

Table 2: Physicochemical properties of feed and permeate

Stream	Turbidity [NTU]	pH [-]	κ [μS/cm]	COD [mg/L]	IFT [mN/m]
Feed	155.9	9.8	1567	1309	32.1
Permeate	3.31	9.5	1462	480	37.4

A clear and transparent solution was obtained after the MF process. The permeate has near-zero turbidity because all solids, such as insoluble salts, fabric residues, fats, and micelles made of surfactants and dirt, were retained on the membrane surface. As regards the feed, the pH of the solution changes slightly. This is due to the fact that the membrane is not a barrier to H^+ or OH^- ions. However, it is possible to notice a decrease in the conductivity after the filtration process, despite the fact that the microfiltration membrane does not retain ions. This is due to the fact that the resulting sediment on the surface of the membrane may be a barrier to some metal ions or surfactants. The permeate is also characterised by a lower COD value. It results from the retention of fats and surfactants forming micelles on the membrane. The sediment build-up may also impede the transport of proteins and other organic substances. The hindered transport of surfactants increases the interfacial tension of the permeate in relation to the feed. The above analysis made it possible to determine the laundry wastewater microfiltration process. It will also help in assessing the effects of the membrane modification on the filtration process.

At the second stage of the tests, the filtration properties of the unmodified membrane and modified membranes were compared. In this case, the permeate stream decrease was also determined during the process and its quality was checked. The tests were carried out in the same way as in the previous part. As the system stabilised faster, the process was carried out for 90 minutes. The measurement of the permeate volumetric flow and sampling were carried out every 10 minutes up to the 50th minute of the process duration and then every 20 minutes. The change of the permeate flux in time is shown in Figure 5, whereas the values of parameters typical of individual streams are included in Tables 3-6. The tables contain only data for the permeate obtained after the process started, and after 5, 10, 40 and 90 minutes of the process duration.

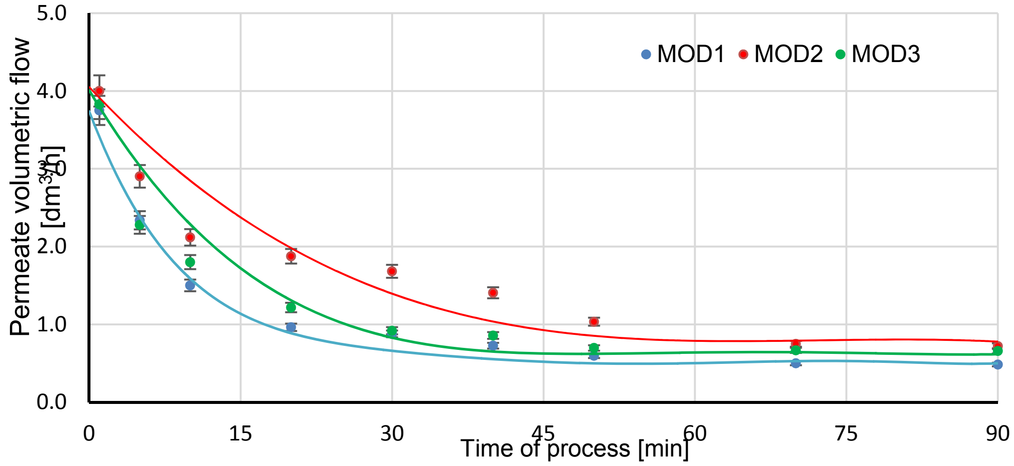

Figure 5: Permeate volumetric flow change in time.

Based on the obtained data, it is possible to conclude that for all the tested modules the filtration process can be divided into two characteristic stages: quick sediment build-up and steady-state system operation. However, larger permeate volumetric flows were obtained for the modified membranes. In addition, it can be noticed that for the membrane covered with natural graphite (MOD2) the stage of sediment build-up is longer than for other membranes. It follows that for modified membranes the phenomenon of fouling is less intensive than for unmodified membranes, in particular for MOD2 membranes.

Also, the permeate quality differs for the individual membranes. Higher values of conductivity and COD were obtained for the modified membranes. This is connected with lower fouling of the membrane with sediment, and thus also with lower blocking of the pores, as well as with higher concentration of surfactants in permeate. This facilitates both the flow of water and some impurities. Permeate turbidity for the individual membranes is at the same low level, so practically all solid impurities were retained on the membrane. The modifications also affect the amount of surfactants recovered. At the initial stage of the process, the IFT values of the permeate and feed are similar. However, along with the sediment build-up for MOD 1 and MOD 3 membranes, the INF increases. This effect is negligible for the MOD2 membrane, i.e. for a membrane characterised by the highest permeate stream.

In addition, it may be concluded that the filtration process in terms of changes in the permeate stream and its quality for modified membranes proceeds in a similar way as presented in the first part of the experiment. The results do not include pH values that do not change significantly during the process.

Table 3: Conductivity [µS/cm] for testing streams.

Stream		Type of module		
		MOD1	MOD2	MOD 3
Feed		1100,0	1100,0	1100,0
Permeate	1 min	624	1088	775,0
	5 min	803	1070	902,0
	10 min	810	1055	880,0
	40 min	792	1047	833,0
	90 min	778	1040	825,0

Table 4: Turbidity[NTU] for testing streams.

Stream		Type of module		
		MOD1	MOD2	MOD 3
Feed		88,3	88,3	88,3
Permeate	1 min	9,2	8,8	10,1
	5 min	11,0	11,5	11,6
	10 min	10,1	10,5	10,1
	40 min	9,3	9,0	4,2
	90 min	6,7	5,2	1,1

Table 5: INF [mN/m] for testing streams.

Stream		Type of module		
		MOD1	MOD2	MOD 3
Feed		29,2	29,2	29,2
Permeate	1 min	30,5	31	30,8
	5 min	30,2	30,9	30,6
	10 min	29,6	29,7	30,1
	40 min	35,6	29,6	33,0
	90 min	42,3	31,6	39,7

Table 6: COD [mg/l] for testing streams.

Stream		Type of module		
		MOD1	MOD2	MOD 3
Feed		1024,1	1024,1	1024,1
Permeate	1 min	462,6	397,8	638,0
	5 min	641,6	578,1	700,2
	10 min	579	651,6	717,6
	40 min	280,6	545,7	498,0
	90 min	199,3	473,6	355,4

The differences between the efficiency of the filtration process with the use of modified membranes result from different properties of the inoculated groups on their surface. It should also be emphasised that the increase in the surface hydrophobicity did not deteriorate the efficiency of the process.

4. Conclusions

The obtained results confirm that the modification of membranes with carbon compounds by the CVD method improves the efficiency of the recovery process of water and detergents from laundry wastewater. It seems that ceramic membrane modified by flake graphite (MOD2) could be successfully used in industrial laundry processes.

In further studies, the interaction between the surface of the membrane and the layer of the new material should be determined using the FTIR and TGA / DSC methods. In addition, the measurement of the contact angle and surface energy of the membrane before and after the modification should allow us to examine the change in surface properties of the membrane. The information received will allow us to determine the mechanism that determines the intensity of the fouling phenomenon.

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References

Ciabattia, I., Cesaro, F., Faralli, L., Fatarella, E., & Tognotti, F. (2009). Demonstration of a treatment system for purification and reuse of laundry wastewater. Desalination, 245(1-3), 451-459.

Dobrzańska-Danikiewicz A., Cichocki D., Wolany W., Łukowiec., 2014, Synteza wielościennych nanorurek węglowych metodą katalityczno-chemicznego osadzania z fazy gazowej. Inżynieria Materiałowa, 35(6), 477-480.

El Rayess, Y., Albasi, C., Bacchin, P., Taillandier, P., Raynal, J., Mietton-Peuchot, M., & Devatine, A. 2011. Cross-flow microfiltration applied to oenology: A review. Journal of Membrane Science, 382(1-2), 1-19.

Lee, J., Ha, J. H., & Song, I. H. 2016. Improving the antifouling properties of ceramic membranes via chemical grafting of organosilanes. Separation Science and Technology, 51(14), 2420-2428.

Lin Y. S., Burggraaf A. J., 1992, CVD of solid oxides in porous substrates for ceramic membrane modification. AIChE journal 38.3, 445-454

Lin Y. S., Burggraaf A. J., 1993, Experimental studies on pore size change of porous ceramic membranes after modification. Journal of membrane science, 79(1), 65-82.): 65-82

Olszówka-Myalska, A., Swadźba, L., Botor-Probierz, A., Janus, T., 2009. Zastosowanie reaktywnego chemicznego osadzania z fazy gazowej (RCVD) do modyfikacji powierzchni włókien węglowych. Kompozyty, 9(1), 19-23.

Søgaard S., 2015, Laundry Operations, Laundry Logics aps, 61-62, 75-81.

Szwast Z., Polak D., Szwast M., 2018, Badanie wpływu parametrów procesowych na jakość i wielkość odzysku wody ze ścieków pralniczych, Inż. Ap. Chem.,57, 5, 156-157.

Szwast, M., and Polak D., 2018, Nowe membrany do filtracji ścieków z pralni przemysłowych. Przemysł Chemiczny 97.

Xomeritakis, G., Lin, Y. S. 1994, CVD of solid oxides in porous media for ceramic membrane preparation or modification. Explicit solutions for deposition characteristics. Chemical engineering science, 49(23), 3909-3922.