THE TREATMENT OF SURFACE WATER IN THE HYBRID MEMBRANE REACTOR COMBINING ION EXCHANGE, ADSORPTION AND ULTRAFILTRATION

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Abstract
The paper presents effectiveness of removal of organic contaminants from surface water using hybrid membrane reactor in which ion exchange, adsorption and ultrafiltration processes were performed. MIEX® resin by Orica Watercare, powder activated carbon Norit SX2 and immersed ultrafiltration capillary module ZeeWeed 1 (ZW 1) operating at negative pressure were used. The application of multifunctional reactor had a positive effect on the removal of contaminants and enabled the production of high quality water. Additionally, referring to unit ultrafiltration process it minimalized the occurrence of membrane fouling.

Streszczenie
W pracy przedstawiono efektywność usuwania zanieczyszczeń organicznych z wody powierzchniowej w hybrydowym reaktorze membranowym, w którym realizowano proces wymiany jonowej, adsorpcji i ultrafiltracji. W badaniach wykorzystano żywicę MIEX® firmy Orica Watercare, pylisty węgiel aktywny Norit SX2 oraz ultrafiltracyjny moduł kapilarny zanurzeniowy ZeeWeed 1 (ZW 1) pracujący w podciśnieniu. Zastosowanie wielofunkcyjnego reaktora korzystnie wpływało na efektywność usuwania zanieczyszczeń, uzyskując wodę oczyszczoną wysokiej jakości, a w odniesieniu do procesu ultrafiltracji zminimalizowano problem foulingu membrany.

Keywords: **Natural organic matter (NOM); Ion exchange; Adsorption; Ultrafiltration; Hybrid membrane reactor.**

1. INTRODUCTION

The alternative to conventional water treatment method is the use of membrane technologies, especially in their combination with other processes i.e. hybrid membrane reactors. Such a solution combines membrane filtration, usually microfiltration or ultrafiltration with classical water treatment processes [1]. Main advantages of such a technology are: the possibility of removal of wide spectrum of impurities of various fractions (suspended solids, colloids, dissolved compounds) [2-4], the limitation of exploitation problems of membrane installation related to their blockage (fouling) which results in the decrease of volumetric permeate flux and the decrease of the space required for the system in comparison with classical solutions applied at water treatment plant [5]. The promising technology is the combination of an ion exchange with the adsorption on activated carbon and micro or ultrafiltration placed in one reactor i.e. hybrid membrane reactor. The application of MIEX® resin, which can be both, easily kept as a suspension in the treated water and simultaneously introduced to the reactor with powdered activated carbon (PAC) should be especially considered. It enables the performance of ion exchange, adsorption and membrane filtration at the same time. The main point of the combination of those unit processes is the easy separation of the resin from the activated carbon

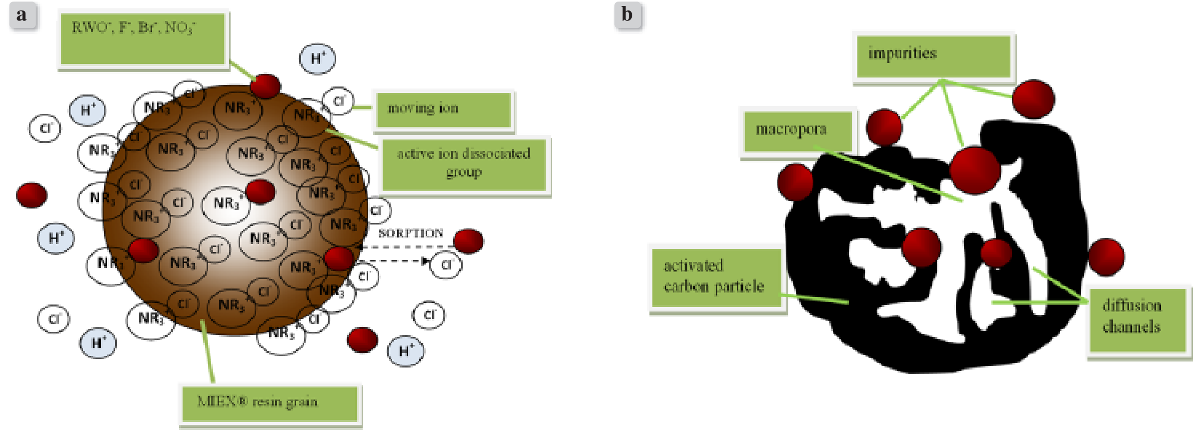

Figure 1.
The scheme of processes mechanisms: a) – ion exchange on the MIEX® resin, b) – the adsorption on the activated carbon

particles. When the mixing in the reactor is off the resin particles immediately sediment according to the magnetic components placed in their structure what enhances the particles agglomeration [3]. On the other hand, the activated carbon characterizes with weak sedimentation properties, thus it is hold in the reactor in the form of suspension and adsorbs the rest of impurities which did not undergo the ion exchange on the resin. In such a system the ion exchange is faster than the adsorption of dissolved substances on the PAC particles [6, 7]. The mechanisms of the ion exchange on MIEX® resin particles and the adsorption on the activated carbon are shown in Figure 1. The main role of the membrane in such a system is to hold particles of both, the resin and PAC in the reactor chamber and to separate them from the purified water and, eventually, to polish the water [8].

The aim of the study was to determine the effectiveness of surface water treatment (to drinking water) in the hybrid membrane reactor in which the MIEX®DOC ion exchange, the activated carbon adsorption on the ultrafiltration with the use of an immersed capillary membrane module were performed.

2. MATERIALS AND METHODS

The subject of the treatment was the surface water collected at the intake of water treatment plant (WTP) Kozlowa Gora in August. The quality of the water in the reservoir is affected by Brynica river water, which is its main tributary. The reservoir has been defined as an eutrophic one according to the seasonal growth of plankton, which causes the increase of water turbidity and difficulties during the treatment [9]. The characteristic of the investigated water is presented in Table 1.

Table 1.
The characteristic of the raw water

Parameter	Unit	WTP Kozlowa Gora
DOC	mg/L	13.55*
TOC	mg/L	15.4
UV_{254}	1/m	26.2*
SUVA**	$m^3/gC{\cdot}m$	1.93
Color	mg Pt/L	20*
Temperature	°C	22.0
pH	-	7.11
Conductivity	μS/cm	322
Turbidity	NTU	20.4
Hardness tot.	$mgCaCO_3/L$	158
Alcalinity	mmol/L	2.40
Calcium	mg/L	41.6
Chlorides	mg/L	42.6

DOC – dissolved organic carbon
TOC – Total organic carbon
* samples filtered via 0.45 µm filter
** specific ultrafiolet absorbance UV_{254}/DOC

The study on the water treatment were performed in the flow tank of volume 20 L. In the reactor the MIEX®DOC ion exchange, the adsorption on powdered activated carbon and ultrafiltration processes were carried out (Figure 2). MIEX® resin (10 mL/L) and activated carbon by Norit SX2 were added to the water treated in the reactor. The immersed capillary module ZeeWeed®1 (ZW1) made of polyvinylidene fluoride was used for the ultrafiltration. The nominal

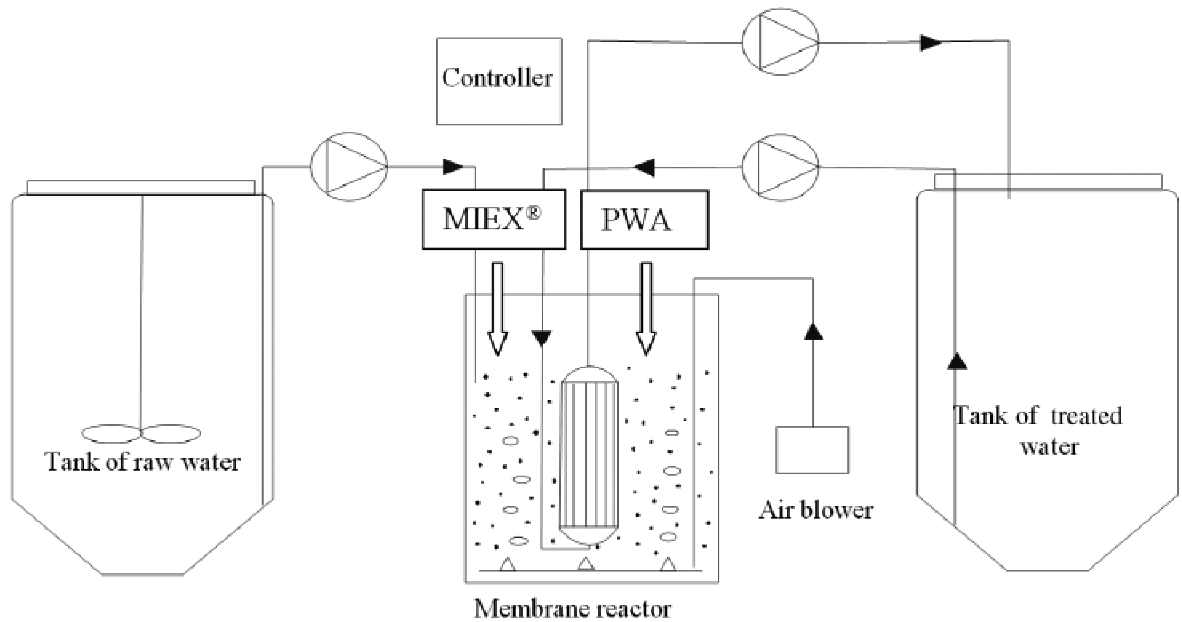

Figure 2.
The scheme of the hybrid membrane reactor

pore size of capillary membranes was equal to 25 kDa and the total effective separation area was 0.046 m^2. The membrane module was operated at the vacuum at the maximum transmembrane pressure of 62 kPa. In order to prevent the formation of a filtration cake and to keep the constant capacity of the filtration the membrane backflushing was periodically performed. The anion exchange macroporous MIEX® resin by Orica Watercare of a mean particle size 150 µm was used for the ion exchange. The resin was added to water in the form of suspension and it was regenerated with the use of 10% NaCl solution. In order to keep particles of the resin and the activated carbon in the suspended state as well as to perform the effective mixing of the reactor chamber content aerating diffusors were placed on the bottom of the reactor.

The treatment of water was made in two systems, sequential and in-line ones, both in the flow mode i.e. at the simultaneous purified water outflow and raw water inflow (the constant volume of the water in the reactor). The sequential system relied on the alternant MIEX®DOC process performance (30 min) and ultrafiltration (120 min), while the adsorption on the activated carbon accompanied those two processes. The in-line system (continuous) relied on the simultaneous performance of processes i.e. the ultrafiltration of the water which was mixed with the resin and the activated carbon.

The effectiveness of the water treatment in the hybrid reactor was determined on the basis of values of water parameters i.e. dissolved organic carbon content (DOC) measured with the use of HiperTOC analyzer by Thermo Electron, absorbance at UV 254 nm measured with UV-VIS CE 1021 by Cecil and color measured with NOVA 400 photometer by Merck.

3. RESULTS AND DISCUSSION

In Figure 3 the comparison of water treatment processes via single-step ultrafiltration, hybrid ion exchange/ultrafiltration and ion exchange/adsorption/ultrafiltration systems performed at the in-line mode are shown.

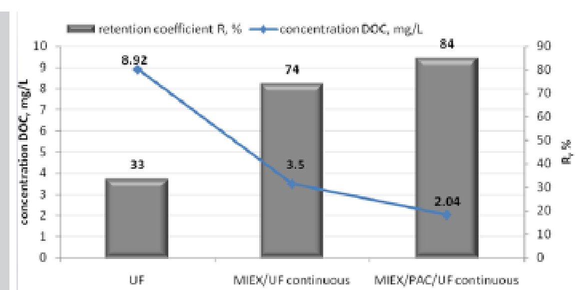

Figure 3.
The comparison of water treatment processes via single-step ultrafiltration, hybrid ion exchange/ultrafiltration and ion exchange/adsorption/ultrafiltration systems

The obtained results revealed that single step ultrafiltration process was ineffective and economically unattractive. It enabled the decrease of DOC by 33%. The concentration of DOC in the purified water was equal to ca. 8.9 mg/L, thus it did not fulfilled the standards on drinking water (i.e. 5 mg/L). During the single-step ultrafiltration the decrease of the membrane capacity caused by the deposition of impurities on the membrane surface and in its pores in the form of colored gel layer was observed. It justified the integration of ultrafiltration with the ion exchange in the hybrid membrane reactor and in case of poor quality of the raw water its enhancement with activated carbon adsorption in order to produce water of high quality. The results presented in Figure 3 show that the combination of MIEX®DOC with ultrafiltration caused the decrease of DOC by 74% and the additionally applied adsorption increased the value up to 84%. The water produced in the hybrid membrane reactor fulfilled standards on the drinking water quality as the DOC concentrations were low and equal to 3.5 mg/L and 2.04 mg/L for MIEX®DOC/UF and MIEX®DOC/PAC/UF, respectively.

In case of the hybrid MIEX®DOC/PAC/UF process both, sequential and in-line operation modes were applied (Figure 4). The similar treatment effects were obtained for both systems. The high efficiency of those systems was obtained and the produced water characterized with the high quality (DOC 3.85-2.02 mg/L, UV254 absorbance 0.004 1/cm, color 1 mgPt/L and turbidity 0.24 NTU). The results of the study are shown in Table 2. According to the obtained results it is preferred to apply those processes in the water treatment technology, especially when the raw water is highly contaminated. The additional advantage of the hybrid system application (regardless of the operation mode) is the limitation of UF membrane blockage phenomenon (Figure 5). The high values of the relative membrane permeability (J_v/J_0) observed after 6 hours of the process performance i.e. 0.95 for in-line mode and 0.98 for sequential mode indicated on the efficient hybrid process performance considering also the membrane module capacity.

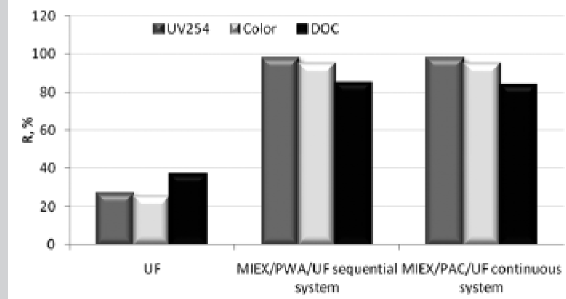

Figure 4.
The comparison of water treatment processes via single-step ultrafiltration, hybrid ion exchange/ultrafiltration and ion exchange/adsorption/ultrafiltration systems

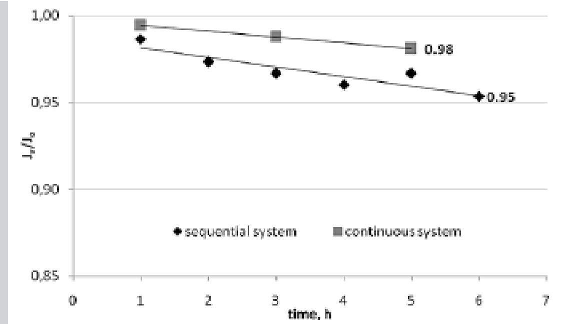

Figure 5.
The comparison of values of the relative membrane permeability in the hybrid ion exchange/adsorption/ultrafiltration process, sequential and continuous systems

The results of the study confirmed the results obtained by other researchers i.e. the combination of classical unit processes with membrane filtration improved the effectiveness of membrane operation as well as the quality of purified water or wastewater.

The hybrid membrane reactor is the practical solution, what was also confirmed during the study. Many researches show the advantages of hybrid membrane reactors by obtaining satisfactory results of water and wastewater treatment [11, 12]. In this study the satisfactory results of water treatment were also obtained despite the poor quality of raw water (high TOC concentration, high turbidity). The application of the hybrid membrane reactor in which the innovative process of MIEX®DOC ion exchange, adsorption and ultrafiltration enabled the production of potable water. The applied immersed capillary membrane module separated all particles of the resin and the activated carbon from the water and additionally polished it. The final product i.e. purified water was transparent and colorless. The membrane assured the constant quality of the treated water at sufficiently short reactor operation (6 hours), however, the stability of the treated water quality despite the ion

Table 2.
The comparison of the results of water treatment in the investigated processes

Parameter	Raw water	Treatment water					
		UF	MIEX®	PAC	Sequential system	Continous system	Per. Con. acc. to Reg. [10]
Absorbance, 1/cm	0.262	0.171	0.06	0.179	0.004	0.005	-
Color, mgPt/L	20	14	2	8	0	1	15
DOC, mg/L	13.55	8.92	6.89	11.23	3.83	2.04	5
Alcalinity, mmol/L	2.4	-	2.1	2.1	2.1	2.1	-
Hardness, mg$CaCO_3$/L	158	-	144	144	146	145	60-500
Chlorides, mg/L	42.6	-	71	42.6	71	71	250
Calcium, mg/L	41.6	-	40	38.4	41.6	42.8	-
pH	7.11	-	7.18	7.58	7.6	7.69	6.5-9.5
Conductivity, mS/cm	0.332	-	0.358	0.318	0.355	0.355	2.5
Turbitity, NTU	20.4	-	0.33	0.36	0.24	0.24	1

exchange effectiveness decrease could have been obtained even after 40 hours of the process run, what was shown during another study [13]. At torrential raw water quality decrease (e.g. during the flood) the doses of the MIEX® resin as well as the activated carbon can be easily modified in order to keep the produced water quality on the constant level as well as to protect the membrane. The crucial advantage of the hybrid membrane reactors is the space requirement, which is much lower in comparison with classical processes used at water treatment plants, what is especially important for small plants.

4. CONCLUSIONS

The results of the study allow to conclude:

1. The application of the single-step ultrafiltration, MIEX®DOC ion exchange or activated carbon adsorption to treat surface water of poor quality were ineffective (concentration of DOC was exceeded, Tab. 2)
2. MIEX® resin added to the membrane reactor improved the quality of the treated water in comparison with single-step ultrafiltration (Fig. 4) and in case of very low raw water quality MIEX® resin could be accompanied by the powdered activated carbon, which additionally purified the water.
3. The ultrafiltration capillary module separated all resin and activated carbon particles from purified water. The preceding of ultrafiltration with the ion exchange and the adsorption significantly limited membrane blockage (fouling)
4. The special property of MIEX® resin is its fast agglomeration which is according to magnetic component placed in its structure, what favors its fast removal from the reactor. On the other hand, poor sedimentation of powdered activated carbon cause it holds in the reactor in the form of suspension and adsorbs low-molecular weight organic compounds (NOM < 10 kDa)
5. The hybrid membrane reactors, according to their compactness, can be especially useful at small water treatment plants. The removal of wide spectrum of impurities of various fractions in one device enables many possibilities of application of the system in water treatment technology.

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