Hybridization of Advanced Oxidation Processes with Membrane Separation for Treatment and Reuse of Industrial Laundry Wastewater

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Abstract: A new attempt to treat and reuse the industrial laundry wastewater using biological treatment followed by advanced oxidation processes (AOPs) and membrane separation is presented. Three various configurations of the hybrid systems were investigated: (1) biological treatment in a Moving Bed Biofilm Reactor (MBBR) – photocatalysis with suspended TiO_2 P25, enhanced with *in situ* generated O_3 – ultrafiltration (UF) – nanofiltration (NF); (2) biological treatment in MBBR– photocatalysis with immobilized TiO_2 P25, enhanced with *in situ* generated O_3 – UF - NF; (3) biological treatment in MBBR – photolysis/ozonation (with *in situ* generated O_3) – UF – NF. For comparison purpose the wastewater was additionally treated in the MBBR – UF – NF mode (4). Application of AOPs contributed to the UF membrane fouling mitigation during treatment of the biologically pretreated laundry wastewater. The highest improvement of the UF permeate flux was found in case of the MBBR effluent treated with application of the immobilized TiO_2 bed which was attributed to the highest efficiency of mineralization observed for that system. Since the applied wastewater contained significant amounts of inorganic ions, mainly Na^+ and Cl^-, the NF as the final polishing step was proposed. The quality of NF permeate was independent on the AOP mode applied and, moreover, significantly higher than the quality of water currently used in the laundry. It was concluded that the NF permeate could be recycled to any stage of the laundry system. Taking into consideration that application of TiO_2 increases the overall treatment costs and that although the O_3/UV pretreatment is less efficient than photocatalysis, it still allows to improve the UF permeate flux for ca. 35% compared to the direct UF of the MBBR effluent, the MBBR – UV/O_3 – UF – NF system was proposed as the most beneficial configuration for the treatment and reuse of the industrial laundry wastewater.

Keywords: Advanced oxidation processes, Photocatalysis, Ozone, Ultrafiltration, Nanofiltration, Laundry wastewater.

1. INTRODUCTION

Laundry wastewater is the wastewater originating from home washing machines, the industrial laundries or from the laundries situated at the factories, such as *e.g*. nuclear power stations [1, 2] or petroleum refineries [3]. Laundry wastewater poses a serious risk to the environment since it contains high amounts of suspended solids and exhibits high chemical oxygen demand (COD) and biological oxygen demand (BOD) values. The main substances present in laundry wastewater are surfactants, contaminants from the washed cloths (fats, dyes, microorganisms, fibres etc.) and salts. The subject literature presents numerous methods of laundry wastewater treatment depending on the type of contaminants. In general, a single process is used very seldom, much often the more complicated systems are necessary to obtain the acceptable levels of the contaminants removal.

The simplest method used for the laundry wastewater treatment is the mechanical treatment. Ahmad and El-Dessouky [3] treated laundry wastewater from a petroleum refinery using sedimentation followed by filtration through a filter bed composed of sand and gravel. However, such a system allowed only to remove turbidity and reduce the values of total suspended solids (TSS), pH and total hardness (TH) to acceptable levels, whereas COD and BOD remained almost unchanged. The treated water was ranked as a low-grade water and was found to be suitable for use in the laundry unit for the first rinse only.

A possibility of application of adsorption using an activated carbon filter (ACF, woven activated carbon fiber) for removal of sodium dodecylbenzenesulfonate (DBS) surfactant from a simulated wastewater (SWW) was investigated by Matsuo and Nishi [2]. They found that it is possible not only to reduce significantly the total organic carbon (TOC) content but also that the adsorption performance of ACF can be easily recovered by vacuum heating treatment. Unfortunately, the SWW did not contain any other contaminants

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typical for the laundry wastewater except from the surfactant, which makes the applicability of the results very limited.

The more advanced processes for laundry wastewater treatment are coagulation and electrocoagulation [4] realized as single processes or in combination with other technologies, *e.g*. electrocoagulation - electroflotation [5], coagulation - microfiltration (MF) [6] or coagulation – ultrafiltration (UF) [7]. During electrocoagulation the formation of metallic hydroxide flocs in the wastewater by electrodissolution of soluble anodes, usually iron or aluminum takes place. The experimental results presented by Janpoor *et al*. [4] revealed that COD, phosphorus, detergent, color and turbidity removal efficiencies under properly selected conditions can exceed 90% and might be enhanced by increasing voltage, hydraulic retention time (HRT) and the addition of extra aluminum plates between the anode and cathode. A combined chemical coagulation–flocculation/UV photolysis system was proposed by Terechova et. al. [8] for treatment of simulated laundry wastewater containing linear alkylbenzene sulfonate (LAS). A mineral ash was used as a coagulant-sorbent, $ZnCl_2$ was a complex former and Praestol-650 (P-650) was applied as a cationic flocculant. Under the optimal conditions ca. 74.5% of LAS was removed from laundry wastewater.

Coagulation with a cationic polymer (Nalcolyte 8105) followed by MF was another technology applied in the treatment of wastewater from an industrial laundry [6]. The authors reported the following benefits of such a system: (1) effective charge neutralization even at the alkaline pH values typical for laundry wastewater; (2) substantially increased particle size over a broad range of coagulant loadings; (3) improved removal of contaminants due to application of microfiltration and (4) a positive influence of coagulation on MF membrane fouling mitigation. However, the removal of COD was not efficient enough (< 65%) and therefore application of an additional purification step, such as reverse osmosis (RO) was proposed by the researchers [6].

Application of UF alone [9] allowed to achieve high removal efficiencies of turbidity (>90%) and COD (>80%). However, the UF permeate still contained contaminants, both organic and inorganic, which precluded its possible recycle and reuse without further purification.

Higher efficiency of the treatment of laundry wastewater can be obtained by application of more complex systems utilizing various physico-chemical processes [10]. Ciabatti *et al*. [10] proposed a prototype plant which consisted of (i) physico-chemical pretreatment (coagulation, flocculation and Dissolved Air Flotation (DAF)); (ii) sand filtration; (iii) ozonation; (iv) Granular Activated Carbon (GAC) filtration and (v) ultrafiltration. The system was installed on-site and was fed with 15 m^3/h of untreated wastewater. The effluent obtained in the pretreatment processes (i) – (iv) met the law limits for discharge to surface water in Italy. Moreover, it was found that the UF permeate could be possibly used in some washing processes of home textiles, although the final rinsing was realized with primary water. However, it was found that despite the complex pretreatment the UF membrane fouling occurred due to the presence of residual surfactants and the chemical cleaning of the membranes was necessary.

A treatment of laundry wastewater in a membrane bioreactor (MBR) technology was also proposed [11-13]. Nicolaidis and Vyrides [13] presented the performance of a full-scale submerged aerobic MBR (9 m^3) applied for the treatment and reuse of industrial laundry wastewater. The system was examined over a period of 288 days. The efficiency of removal of turbidity and total solids exceeded 99%. The COD value in the effluent from the MBR did not exceed 100 mgO_2/dm^3 and the COD removal was above 70%. The treated wastewater (effluent) was recycled to the washing machines and no residual particles were detected during its operation. The authors reported that by application of the submerged MBR for treatment and reuse of laundry wastewater the laundry industry can save 1.13 Euro per 1 m^3 of water. Moreover, the payback period associated with the MBR system implementation is approximately 6 years [13]. However, although the MBR technology is an attractive solution for the treatment and reuse of the laundry wastewater, the produced permeate still contains high concentrations of salts since the UF and MF membranes do not reject these contaminants. Moreover, in case of wastewater from the processes of washing of colored textiles the MBR effluent can contain dye molecules. Therefore, application of additional technologies, such as reverse osmosis (RO) as the final treatment step before a possible reuse of the laundry wastewater is necessary [12].

In the present work we have proposed new hybrid systems coupling biological treatment with advanced

oxidation and membrane separation to treat and reuse the wastewater generated in an industrial laundry. The wastewater was first pretreated in a Moving Bed Biofilm Reactor (MBBR) technology. The MBBR effluent was further treated using one of the advanced oxidation process (AOP): photolysis/ozonation (with *in situ* generated O_3) or photocatalysis using immobilized or suspended TiO_2, enhanced with the *in situ* generated O_3. The AOP-pretreated wastewater was subsequently treated using ultrafiltration followed by nanofiltration (NF). During the investigations the influence of the type of the AOP system on the UF permeate flux and quality was evaluated. Moreover, the effect of the treatment mode on final product (NF permeate) quality was determined.

2. MATERIALS AND METHODS

The wastewater was obtained from the industrial laundry Albatros Sp. z o. o. Sp. K. (branch: Nowe Czarnowo, Poland). The wastewater was collected from the retention tank and then mechanically pretreated. The wastewater used in the research was a mixture of (i) wastewater stemming from washing processes (industrial – laundry wastewater) and (ii) wastewater from the regeneration of ion exchangers that are used for softening of technological water. The latter wastewater stream contained mainly chloride and sodium ions.

The wastewater was pretreated in a pilot scale bioreactor operated in MBBR (Moving Bed Biofilm Reactor) technology. The MBBR was a two - stage aerobic reactor comprising two tanks (130 dm^3 each), where the biofilm grew on small, freely floating polymeric elements with a large contact area. The specific biofilm surface area was 800 m^2/m^3 (Anox™ K5 by Veolia). During the treatment process the enrichment of the raw wastewater with nitrogen compounds and adjustment of pH were necessary. A typical composition of the laundry wastewater before and after the biological treatment is presented in Table **1**. The MBBR effluent was applied in the experiments involving treatment of the wastewater in the hybrid systems coupling advanced oxidation and membrane separation.

Advanced oxidation was conducted in a pilot scale photoreactor presented in Figure **1**. A detailed description of the installation can be found elsewhere [14]. In brief, the main component of the installation was a photoreactor (1) equipped with a UV/vis mercury lamp (Ultralight AG, Germany, 6 kW, UV intensity: ca. 330 W/m^2). Inside the photoreactor a small amount of O_3 was generated in the presence of the UV lamp. The ozone concentration in water was ca. 30 $\mu g/dm^3$. The initial volume of wastewater was ca. 1.3 m^3. The process was realized in a batch mode with a complete recycle. Before the light source was switched on a 30 min. adsorption in the dark was realized. After 60 h of the process the wastewater was taken from the installation for the UF treatment. The commercially available Aeroxide® TiO_2 P25 (Evonik, Germany) was applied in the experiments. The photocatalyst was either suspended in the reaction mixture or immobilized on a fiberglass cloth. The immobilization procedure can be found elsewhere [14].

Membrane separation was conducted in a pilot scale ultrafiltration/nanofiltration unit (Figure **2**). The feed from a feed tank (initial UF feed volume: 80 dm^3,

Table 1: Typical Composition of the Industrial Laundry Wastewater Before and After Treatment in the MBBR

Parameter	Unit	Before	After	Removal [%]
pH	–	7.7 – 8.8	8.3 – 8.6	–
BOD_5	g O_2/m^3	117 – 293	15 – 25	79 – 91
COD-Cr	g O_2/m^3	555 – 862	73 – 75	87 – 91
TOC	gC/m^3	117 – 162	19.0 – 25.5	84
Total P	gP/m^3	4.54 – 7.01	1.84 – 3.10	49 – 66
Total N	gN/m^3	8.79 – 23.09	5.46 – 8.40	53 – 82
Surfactants				
anionic	g/m^3	25.3 – 30.1	1.47 – 5.09	82 – 96
nonionic	g/m^3	34.2 – 44.4	0.93 – 2.67	88 – 98

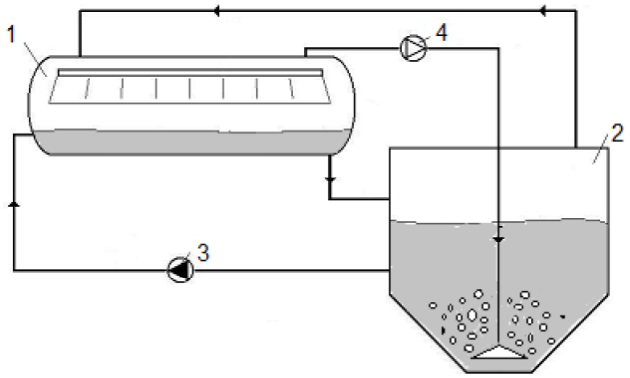

Figure 1: Scheme of the pilot scale AOP installation: 1 – photoreactor (total volume: 0.6 m^3, working volume: 0.06 m^3) with UV/vis lamp; 2 – wastewater tank (1.5 m^3); 3 – pump (wastewater flow: 10 m^3/h); 4 – air compressor (40 m^3/h).

initial NF feed volume: 40 dm^3) was pumped to the UF or NF membrane module by means of a vertical multistage centrifugal pump (CRN5, Grundfos). The switching valves (A) allowed to switch the flow between UF and NF membrane modules, dependent on the currently run process. In the first stage of the investigations the UF retentate and permeate were recycled to the feed tank. During this stage the influence of the AOP treatment on the UF permeate flux and permeate quality was investigated. In the second stage of the research the UF retentate was recycled to the feed tank while the UF permeate (ca. 40 dm^3) was collected for the second stage of the membrane treatment (*i.e*. NF).

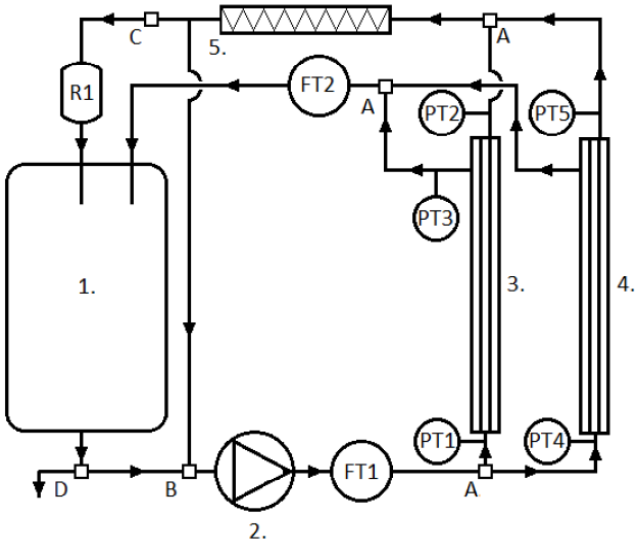

Figure 2: Scheme of a pilot scale UF/NF membrane installation. 1 – feed tank, 2 - vertical multistage centrifugal pump, 3 – UF membrane module, 4 – NF membrane module, 5 – heat exchanger, A – switching valves, B – ball valve, C – needle valve, D – drain valve, FT1 – feed flowmeter, FT2 – permeate flowmeter, R1 – rotameter.

UF was realized with application of a 150 kDa multichannel ceramic INSIDE CéRAM membrane (TAMI Industries). The effective (working) membrane area was 0.35 m^2. The transmembrane pressure (TMP) was in the range of 1 – 3 bar and the feed cross flow velocity was 4.5 m/s. Tap water flux (TWF) measured for this membrane was 97, 207 and 308 dm^3/m^2h for TMP of 1, 2 and 3 bar, respectively. The tap water conductivity was 600 μS/cm.

During NF a polymeric DOW FILMTEC NF90-2540 membrane (filtration area: 2.6 m^2) was used. The feed flow rate was 1.2 m^3/h. The UF permeate collected (i) at TMP of 3 bar in case of the AOP-pretreated wastewater or (ii) at TMP = 1.5 bar in case of the MBBR effluent directly treated using UF was applied as a feed. The TMP during NF was set at 5, 10 or 15 bar. Pure water flux (PWF) through the NF membrane was 52, 93 and 130 dm^3/m^2h for TMP of 5, 10 and 15 bar, respectively. The conductivity of the applied pure water was 28 μS/cm.

Various modes of the hybrid wastewater treatment were investigated: (1) biological treatment – photocatalysis with suspended TiO_2 P25, enhanced with *in situ* generated O_3 - UF –NF; (2) biological treatment – photocatalysis with immobilized TiO_2 P25, enhanced with *in situ* generated O_3 – UF - NF; (3) biological treatment – photolysis/ozonation (with *in situ* generated O_3) – UF – NF; (4) biological treatment – UF – NF.

The efficiency of the wastewater treatment during the AOP and membrane processes was evaluated based on (i) total organic carbon (TOC), total inorganic carbon (TIC) and total carbon (TC) concentration (IL 550 TOC–TN, Hach Lange), (ii) conductivity and total dissolved solids (TDS) content (UltrameterTM 6P, MYRON L COMPANY, USA), (iii) pH (CP-105, Elmetron, Poland), (iv) concentration of inorganic ions using ion chromatography (850 Professional IC, Herisau Metrohm, Switzerland) and (v) turbidity (2100N IS turbidimeter, Hach Lange).

3. RESULTS AND DISCUSSION

3.1. Application of Advanced Oxidation Processes to Biologically Pretreated Wastewater

As shown in Table **1**, the biological treatment allowed to reduce the COD-Cr and BOD_5 values in the laundry wastewater for ca. 87 – 91% and 79 – 91%, respectively. The TOC removal efficiency reached ca. 84% which resulted in the concentrations of organic

carbon in the MBBR effluent in the range of ca. 19 – 25 mgC/dm^3.

The degradation of surfactants in the applied MBBR was also high, however, it was not possible to completely remove these contaminants. Therefore, an additional degradation step based on advanced oxidation was applied to further purify the wastewater before its possible recycle and reuse. Three various AOP configurations were applied in the experiments: (1) photocatalysis with TiO_2 P25 suspended in the treated wastewater, (2) photocatalysis with TiO_2 P25 supported on a fiberglass cloth and (3) photolysis/ozonation (with in situ generated O_3). It should be noted here that since all the above experiments were realized in the installation presented in Figure **1**, the in situ generated O_3 was present in the system in all three cases. Therefore, in the discussion the three types of the experiments will be denoted as: TiO_2(s)/UV/O_3 (mode 1), TiO_2(i)/UV/O_3 (mode 2) and UV/O_3 (mode 3), respectively.

Table **2** summarizes composition of the biologically pretreated wastewater applied in the AOP experiments. The degradation of organic contaminants in time of the processes is shown in Figure **3**. It can be observed that the mineralization of organic contaminants up to 40 h of irradiation followed almost the same course regardless of the treatment mode applied. A small difference can be observed only during the final 20 h of the experiments. In this period a slightly higher efficiency of TOC removal can be seen in case of TiO_2(i)/UV/O_3 system compared to the other two modes. After 60 h the efficiency of mineralization reached ca. 76 – 77% in case of TiO_2(s)/UV/O_3 and UV/O_3, and ca. 92% in case of TiO_2(i)/UV/O_3. One explanation for the higher TOC removal during the final hours of the experiment conducted in the presence of the supported compared to the suspended TiO_2 can be the desorption of organic contaminants from the photocatalyst particles. The data shown in Figure **3** represent the removal efficiency during photocatalysis only. However, before the UV/vis lamp was switched on, a 30 min. adsorption step was realized. In case of TiO_2(i)/UV/O_3 the TOC concentration before and after this step was almost the same, whereas in case of TiO_2(s)/UV/O_3 the organic carbon concentration decreased for ca. 18%. As the photodegradation proceeded the organic contaminants were desorbed from the photocatalyst surface which affected the TOC content in the treated wastewater in case of the TiO_2(s)/UV/O_3 mode. The observed difference can be, moreover, explained in terms of the screening effect of the TiO_2 suspension. That, in addition to the desorption of the contaminants from the photocatalyst surface, might be a reason for the observed lower mineralization rate in case of the TiO_2(s)/UV/O_3 compared to the TiO_2(i)/UV/O_3.

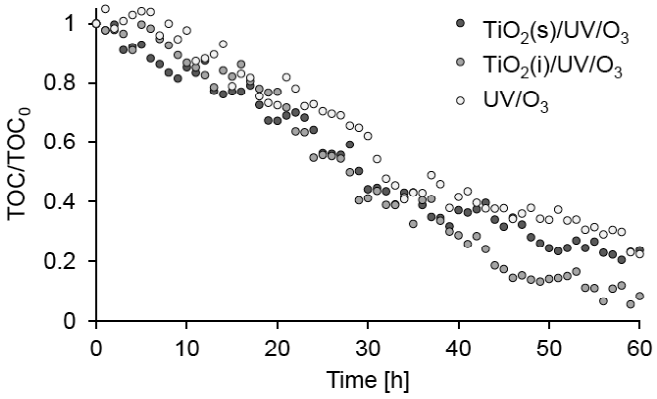

Figure 3: Changes of total organic carbon (TOC) concentration during treatment of the biologically pretreated laundry wastewater by means of (**1**) photocatalysis using suspended TiO_2 P25 (TiO_2(s)/UV/O_3), (**2**) photocatalysis using supported TiO_2 P25 (TiO_2(s)/UV/O_3) and (**3**) photolysis/ozonation (UV/O_3) with in situ generated O_3. Time t = 0 corresponds to the time when the UV/vis lamp was switched on (after 30 min. of adsorption in the dark in case of photocatalytic treatment).

Table 2: Composition of the Biologically Pretreated Wastewater Applied During TiO_2(s)/UV/O_3 (mode 1), TiO_2(i)/UV/O_3 (mode 2), UV/O_3 (mode 3) and UF (mode 4) Experiments

Parameter	Unit	Values
TOC	mgC/dm^3	19.0 – 24.2
TIC	mgC/dm^3	118.3 – 121.8
Conductivity	µS/cm	2366 - 2494
TDS	ppm	1764 - 1870
pH	-	7.9 – 8.2
Turbidity	NTU	11.5 – 21.6

The most important point is, however, a very high efficiency of mineralization observed in the absence of the photocatalyst. These data show that although the O_3 concentration in the wastewater was low (ca. 30 µg/dm^3), a combination of the action of the *in situ* generated ozone and UV light was very efficient method of TOC removal in the investigated system.

Although the concentration of TOC in the AOP-treated effluent was low, the wastewater still contained high concentrations of inorganic ions, as indicated by the conductivity and TDS values (Table **2**). Moreover,

the wastewater after treatment in the TiO_2(s)/UV/O_3 contained suspended photocatalyst particles. In the effluents obtained after TiO_2(i)/UV/O_3 and UV/O_3 the photocatalyst particles were not present, however, the solutions exhibited quite high turbidity (ca. 2 and ca. 10 NTU, respectively). All the above make the obtained effluent impossible to be directly reused in the laundry process. Therefore, membrane separation was applied as the next step of the wastewater treatment.

3.2. Membrane Treatment of the AOPs Pretreated Wastewater (Modes 1 – 3)

The wastewater after the AOP treatment was applied as a feed in the UF process. In case of the TiO_2(s)/UV/O_3 treated wastewater the 2 h or 24 h settling was applied before UF to partially remove the photocatalyst particles. During the sedimentation step the turbidity created by the TiO_2 particles decreased from 4700 NTU to 550 NTU and 30 NTU, respectively. Figure **4** presents a comparison of the permeate fluxes measured during UF of the wastewater after different time of sedimentation. Based on these results it can be concluded that the settling time had no significant influence on the UF permeate flux. These data are in agreement with our earlier investigations on the influence of the TiO_2 concentration on the UF permeate flux through the ceramic TiO_2 membranes [15]. During that research we have found that regardless of the applied cross flow velocity (3–6 m/s), TMP (1–3 bar) and TiO_2 P25 loading (0.5–1.5 g/dm^3) no permeate flux decline took place when TiO_2 suspension in water was used as a feed.

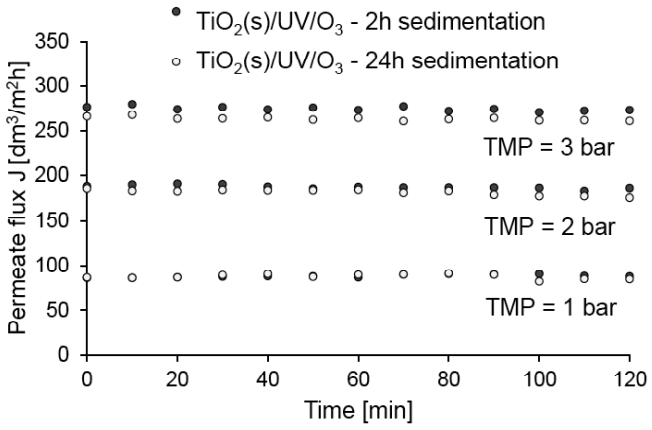

Figure 4: Influence of TiO_2 settling time on permeate flux during ultrafiltration of the laundry wastewater pretreated in TiO_2(s)/UV/O_3 process.

Figure **5** summarizes the permeate fluxes at TMP of 1 – 3 bar measured after 2 h of ultrafiltration of the wastewater pretreated in TiO_2(s)/UV/O_3, TiO_2(i)/UV/O_3 and UV/O_3 modes. It can be seen that the application of TiO_2 had a positive influence on the UF membrane fouling mitigation, what is especially visible at higher transmembrane pressures. The permeate fluxes measured at TMP = 1 bar during UF of the wastewater pretreated in the three different modes were only slightly lower (< 10%) than the tap water flux (TWF). However, as the TMP increased, a difference between the TWF and the fluxes measured during UF of the wastewater can be observed. This difference was the most significant in case of the UV/O_3 pretreated wastewater. The obtained data suggest that the fluxes measured at TMP = 1 bar were below the critical flux value, *i.e*. the value of the flux below which the membrane fouling does not occur [16]. In case of the TiO_2(i)/UV/O_3 pretreated wastewater such a value was also not exceeded at TMP = 2 bar. However, in case of the other types of the UF feed a decrease of the permeate flux at this TMP took place and the most significant deterioration of the permeate flux was observed in case of the UV/O_3 pretreated wastewater.

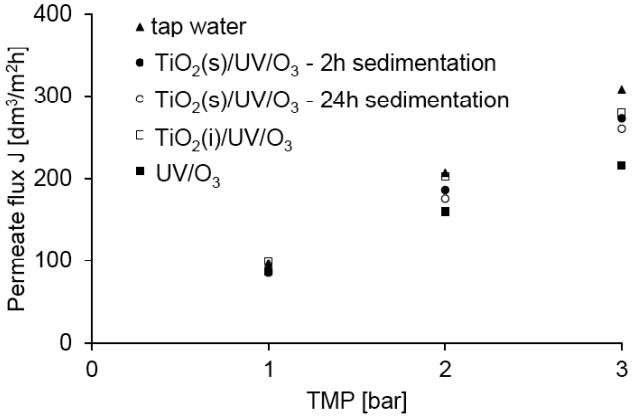

Figure 5: A comparison of permeate fluxes measured after 2 h of ultrafiltration during treatment of the laundry wastewater after TiO_2(s)/UV/O_3, TiO_2(i)/UV/O_3 and UV/O_3 processes.

It is worth noting that the improvement of the flux was not affected by the way in which the photocatalyst was introduced to the system (*i.e*. immobilized or suspended TiO_2). In both cases the flux was higher than when the UV/O_3 system was used. A little higher flux during UF of the TiO_2(i)/UV/O_3 pretreated wastewater compared to that in case of the UV/O_3 treated one can be explained by the slightly higher efficiency of mineralization in the former compared to the latter case (Figure **3**). Furthermore, the less severe flux decline in case of the wastewater pretreated with application of the suspended TiO_2 compared to the UV/O_3 pretreated solution can be attributed to the formation of a more porous filtration cake than in the absence of the photocatalyst particles [17].

In Figure **6** the quality of the UF permeate obtained in the three modes with reference to the composition of the MBBR and AOP pretreated wastewater is shown. Two parameters, namely TOC representing the concentration of organic contaminants, and conductivity representing the content of ionic, mainly inorganic substances are compared. It can be seen that UF did not contribute significantly to the removal of both types of contaminants present in the AOP pretreated wastewater. The concentration of TOC during UF was lowered for ca. 0.5 – 1.5 mg/dm^3 only. These results indicate that the organic contaminants present in the AOP pretreated wastewater exhibited mostly molecular weights below 150 kDa, *i.e*. the value corresponding to the MWCO of the applied membrane. Similarly, the conductivity of UF permeate was similar to the conductivity of the AOP pretreated wastewater. This is reasonable since the UF membranes are not efficient in separation of inorganic salts, such as NaCl present in the applied wastewater. Despite these results, the application of UF was necessary to separate photocatalyst particles from the solution in case of TiO_2(s)/UV/O_3 system. Furthermore, UF allowed also to remove contaminants creating turbidity of the wastewater (Table **2**). The turbidity of UF permeate was below 0.3 NTU, regardless of the process mode examined.

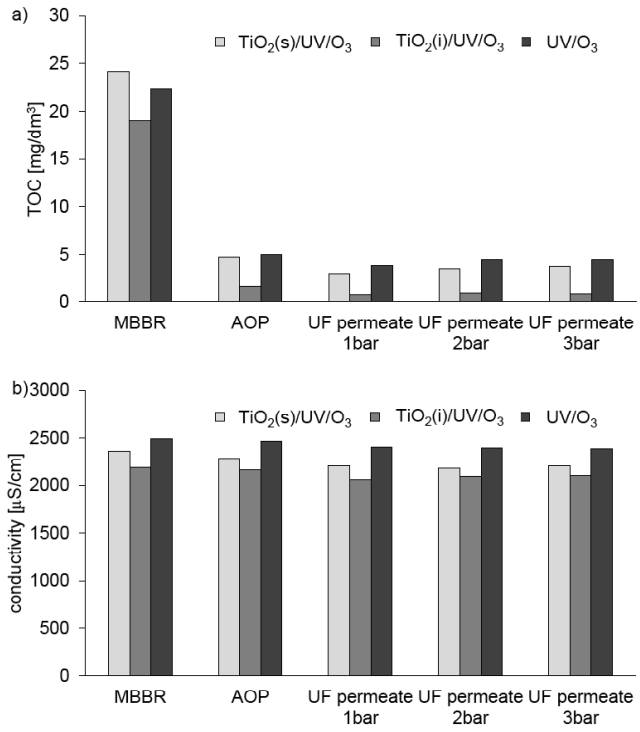

Figure 6: A comparison of the quality of UF permeate obtained at various TMP values and the quality of wastewater pretreated using MBBR and AOPs (TiO_2(s)/UV/O_3, TiO_2(i)/UV/O_3 and UV/O_3): **a**) TOC concentration; **b**) conductivity.

As was explained in the aim of the present research, the investigations were focused on the possibility of not only treatment, but also reuse of the laundry wastewater. Taking into consideration the very high conductivity of the UF permeate, exceeding 2 mS/cm, it can be concluded that such kind of water, despite low turbidity and low TOC content, cannot be directly recycled to the laundry process. Therefore, the UF permeate was further treated during nanofiltration. Figure **7** shows a comparison of the NF permeate fluxes measured at TMP of 5 – 15 bar with reference to the applied pretreatment mode. It can be observed that the fluxes during nanofiltration of the UF permeate were lower than the maximum permeate flux determined with application of pure water. That resulted from the presence of contaminants in the NF feed which contributed to an increase of the osmotic pressure of the solution and thus to a decrease of the driving force of the process. However, it should be also noted that the type of the applied AOP pretreatment had no significant influence on the NF permeate flux (Figure **7**). This can be explained by a similar composition of the UF permeate obtained in the three modes, especially when conductivity is considered (Figure **6b**).

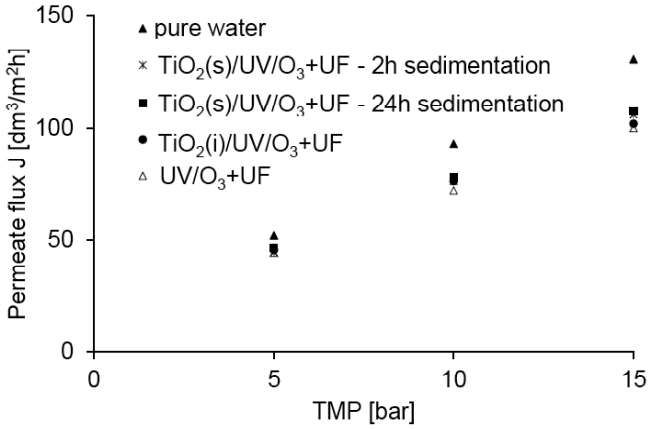

Figure 7: A comparison of permeate fluxes measured during nanofiltration of the laundry wastewater after AOPs (TiO_2(s)/UV/O_3, TiO_2(i)/UV/O_3 and UV/O_3) and UF processes.

Figure **8** presents a comparison of the quality of the NF permeate obtained in the modes 1 – 3, *i.e*. (1) MBBR – TiO_2(s)/UV/O_3 - UF – NF; (2) MBBR – TiO_2(i)/UV/O_3 – UF - NF; (3) MBBR – UV/O_3 – UF – NF. TOC and conductivity were selected as the parameters representative for the content of organic and inorganic contaminants, respectively. It can be observed that the concentration of TOC in NF permeate obtained in modes 1 and 3 was significantly lower than that in UF permeate. On the opposite, in

case of mode 2 the TOC content in UF and NF permeates was similar. The obtained data are consistent with the results discussed in section 3.1. showing that the highest efficiency of mineralization was observed in case of the system with the immobilized photocatalyst bed. At the higher photodegradation rate the decomposition of large molecular organic compounds proceeds more efficiently, thus it can be assumed that the treated wastewater contained mainly low molecular organic contaminants. These substances were not rejected by the NF membrane, as can be found in Figure **8a**). Nonetheless, regardless of the applied mode, the concentration of TOC in permeate did not exceed 1.1 mg/dm^3 (vs. 130 – 162 mg/dm^3 in raw laundry wastewater).

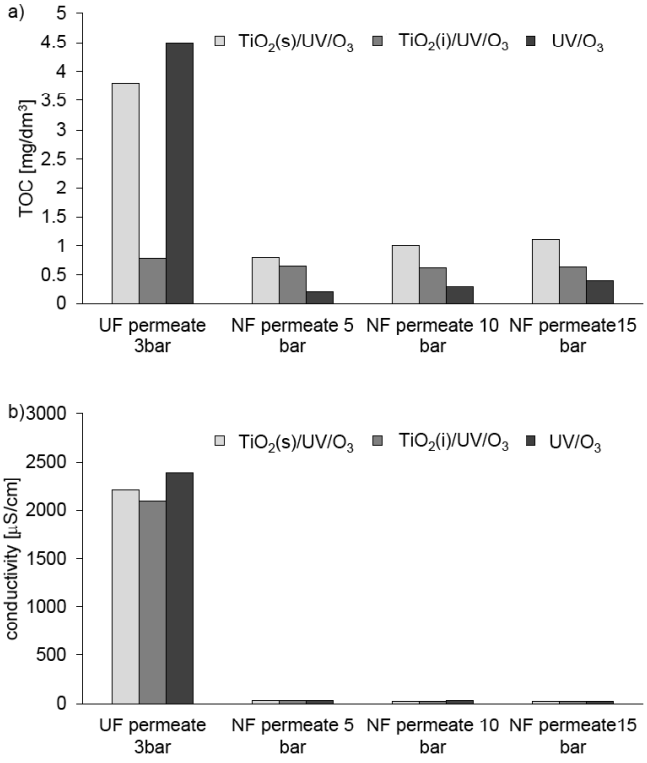

Figure 8: A comparison of the quality of UF permeate applied as a feed in NF and the quality of NF permeate obtained at various TMP values with reference to the treatment mode: **a**) TOC concentration; **b**) conductivity.

Figure **8b**) shows a comparison of the NF permeate conductivity. It can be seen that rejection of ionic contaminants exceeded 98.5%, regardless of the mode applied. The conductivity of permeate did not exceed 34 µS/cm (vs. >2000 µS/cm in UF permeate), in all three modes.

The obtained results revealed that application of photocatalysis as a pretreatment step to UF was more efficient in mitigation of membrane fouling than UV/O_3, regardless of the form in which the photocatalyst was introduced to the system (*i.e*. suspended or supported). The most significant difference was observed at the highest TMP used, *i.e*. 3 bar, at which the permeate flux in case of UV/O_3 pretreated wastewater was lower than that measured for the photocatalytically pretreated one for ca. 17 – 23% (with reference to TiO_2(s)/UV/O_3 and TiO_2(i)/UV/O_3 systems, respectively). In case of NF no significant influence of the AOP mode on the permeate flux was found. The UF and NF permeate quality in terms of organic contaminants content was strongly associated with the efficiency of AOP pretreatment. In general, the UF step did not contribute significantly to the improvement of TOC removal. Similarly, UF was not efficient in ionic contaminants removal. Therefore, for a possible reuse of the laundry wastewater the post-treatment using NF was found to be necessary. Application of NF allowed to obtain a purified water containing less than 1.1 mgTOC/dm^3 and exhibiting conductivity below 34 µS/cm, regardless of the mode applied.

3.3. Treatment of Laundry Wastewater in the MBBR – UF – NF System (Mode 4)

The results discussed in section 3.2. revealed that photocatalytic (TiO_2(s)/UV/O_3 or TiO_2(i)/UV/O_3) pretreatment of biologically treated laundry wastewater can contribute to the membrane fouling mitigation to a higher extent than the UV/O_3 process. In order to evaluate the UF process performance in the absence of any AOP pretreatment the effluent from the MBBR was directly applied as the UF feed. The obtained results are summarized in Figure **9**. It can be seen that the permeate flux during UF of the biologically

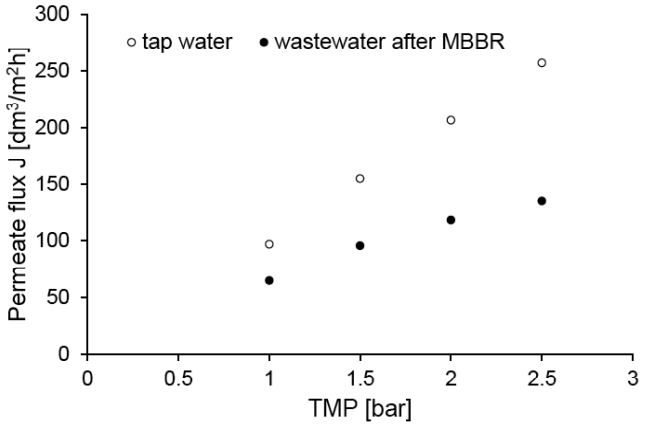

Figure 9: The influence of TMP on permeate flux after 2h of UF of the biologically pretreated laundry wastewater. For comparison purpose the permeate flux measured for tap water is shown.

pretreated wastewater was significantly lower than the TWF. The observed decrease of the flux ranged from 33 to 47% for TMP = 1 – 2.5 bar, respectively. By way of reminder, the permeate flux of the AOP pretreated wastewater measured at TMP = 1 bar was comparable to TWF (Figure **5**). These data clearly show the beneficial influence of the application of AOPs on the UF membrane fouling mitigation.

Removal of TOC during direct ultrafiltration of the MBBR pretreated wastewater was higher than that observed in case of the AOP pretreated one. As was discussed in the previous section, the concentration of TOC during UF of the AOP pretreated wastewater was lowered for ca. 0.5 – 1.5 mg/dm^3 only. In case of ultrafiltration of the wastewater collected directly from the MBBR unit the TOC concentration decreased for ca. 5 – 7 mgC/dm^3, reaching the value of ca. 12 – 14 mgC/dm^3, depending on the TMP applied These data show that the biologically pretreated wastewater contained higher amount of large molecular weight contaminants than the AOP pretreated one. These substances were deposited on the membrane which contributed to the membrane fouling and the observed decrease of the permeate flux.

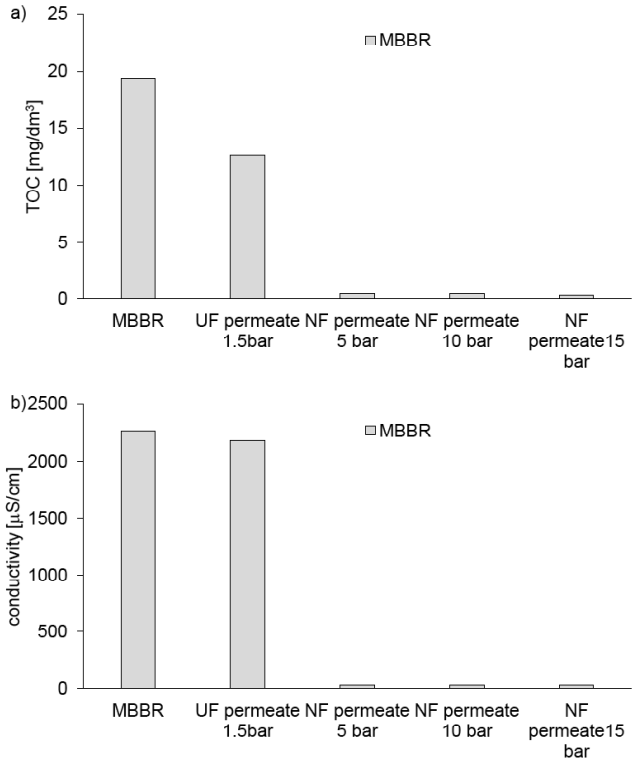

Figure 10: A comparison of the quality of the MBBR effluent, UF permeate collected at TMP = 1.5 bar applied as a feed in NF and the quality of NF permeate obtained at various TMP values: a) TOC concentration; b) conductivity.

Similarly as in case of modes 1 – 3, the UF permeate collected in mode 4 (TMP = 1.5 bar) was post-treated during NF. The NF permeate fluxes measured at TMP of 5 – 15 bar were similar to those observed in the experiments described in section 3.2, which indicates a high efficiency of UF as the NF pretreatment step.

Figure **10** presents the quality of NF permeate with reference to TOC and conductivity. For comparison purpose the values measured for the MBBR effluent and UF permeate collected at 1.5 bar are presented. It can be seen that NF contributed to the removal of both organic and inorganic contaminants to a higher extent than UF. Moreover, comparing the data shown in Figures **8** and **10** it can be found that the pretreatment steps had no significant influence on the NF permeate quality with reference to both monitored quality parameters.

3.4. Comparison of the Efficiency of Treatment of Laundry Wastewater in Modes 1 – 4

Table **3** summarizes the composition of the NF permeate collected at TMP = 15 bar in the 4 examined modes, *i.e*. (1) MBBR – TiO_2(s)/UV/O_3 - UF – NF; (2) MBBR – TiO_2(i)/UV/O_3 – UF - NF; (3) MBBR – UV/O_3 – UF – NF and (4) MBBR – UF – NF. The presented data reveal that the application of AOP pretreatment had no significant influence on the final product (*i.e*. NF permeate) quality. The conductivity of permeate was below 30 µS/cm and was associated mainly with the presence of low amounts (concentrations below 6 mg/dm^3) of Na^+ and Cl^- ions. It is worth noting, however, that the NF permeate quality was significantly higher than the quality of water currently used in the laundry (Table **3**). Conductivity of this water amounts to 550 µS/cm and is affected mainly by the presence of Na^+, Cl^-, SO_4^{2-} and inorganic carbon (TIC). This comparison shows that the obtained product (NF permeate) can be recycled to any stage of the laundry process.

Despite that the NF feed pretreatment (modes 1 – 4) did not influence the NF permeate quality, it affected significantly the UF process performance, especially in terms of membrane fouling and permeate flux. As was already discussed in sections 3.2. – 3.3. the direct application of the MBBR effluent as the UF feed resulted in a significant membrane fouling. This leads not only to a lower productivity of the UF permeate but also creates a need of frequent membrane cleaning. Therefore, a more beneficial solution is application of AOP as the UF pretreatment step. At TMP = 1 bar no significant difference between the permeate fluxes

Table 3: A Comparison of the Composition of Water Currently used in the Laundry and the NF Permeate Obtained at TMP = 15 Bar using the Feed Pretreated in Modes 1- 4: (1) MBBR – TiO_2(s)/UV/O_3 - UF – NF; (2) MBBR – TiO_2(i)/UV/O_3 - UF – NF; (3) MBBR – UV/O_3 - UF – NF; (4) MBBR – UF – NF

Parameter	Unit	Water used in Laundry	NF Permeate at TMP = 15 bar			
			Mode 1	Mode 2	Mode 3	Mode 4
Conductivity	µS/cm	550	22.7	19.4	27.3	29.1
TDS	ppm	370	14.3	12.3	18.2	17.1
TOC	mg/dm^3	1.5	1.1	0.6	0.4	0.3
TIC	mg/dm^3	39	1.5	0.8	0.9	1.3
Cl^-	mg/dm^3	27	4.3	3.8	5.9	4.0
NO_3^-	mg/dm^3	2	0.1	0.1	0.1	0.04
PO_4^{3-}	mg/dm^3	0.05	0.1	b.d.l.	0.04	b.d.l.
SO_4^{2-}	mg/dm^3	63	0.1	0.04	0.06	0.4
Na^+	mg/dm^3	130	4.8	5.4	5.3	4.2
K^+	mg/dm^3	2.5	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Ca^{2+}	mg/dm^3	2.3	1.0	0.6	0.4	1.3
Mg^{2+}	mg/dm^3	0.1	0.2	b.d.l.	b.d.l.	b.d.l.

b.d.l. – below detection limit

measured for the AOP pretreated wastewater and the water flux determined with application of tap water was found which was explained in terms of the critical flux phenomenon. However, at TMP values above 2 bar the photocatalytic pretreatment contributed to the UF permeate flux improvement to a higher extent than the UV/O_3 system. In case of direct UF of the MBBR effluent the permeate flux measured at a TMP of 2 bar decreased for over 40%, whereas in case of the UF of the photocatalytically treated wastewater settled for 2 h the decrease was ca. 10%, and in case of the UV/O_3 pretreated wastewater - ca. 23%.

However, taking into consideration that application of TiO_2 creates an additional cost and that at TMP = 1 bar the permeate flux in case of modes 1 – 3 was only slightly lower than the TWF flux, in our opinion the most beneficial configuration is mode 3, *i.e*. MBBR – UV/O_3 – UF – NF, operated below the critical flux value. Such conditions allow to minimize the UF membrane fouling and simultaneously reduce the cost of AOP by resigning from the photocatalyst addition. Another advantage of this configuration is that there is no need to solve the problem of the spent photocatalyst. Nonetheless, in the proposed configuration there are other waste streams needing utilization, *i.e*. UF and NF concentrates. One solution can be the disposal of the mixed UF and NF retentates in the municipal wastewater treatment plant. However, taking into account that NF concentrate contains high load of NaCl its recovery with application of an NF membrane exhibiting low rejection of monovalent ions can be considered. The recovered NaCl could be further utilized in regeneration of ion exchangers. Nonetheless, to confirm this idea further investigations are necessary.

CONCLUSIONS

It was found that application of AOPs allowed to reduce the UF membrane fouling during treatment of the MBBR pretreated laundry wastewater. The positive influence of utilization of the advanced oxidation was observed in case of both photocatalysis using TiO_2 – UV irradiation – ozonation with *in situ* generated O_3 as well as simple UV photolysis coupled with the ozonation using *in situ* generated O_3 systems. At TMP = 1 bar the difference between the UF permeate fluxes measured for the AOP pretreated wastewater and the tap water was found to be insignificant (< 10%). However, at TMP values above 2 bar the photocatalytic pretreatment contributed to the UF permeate flux improvement to a higher extent than the UV/O_3 system. Nonetheless, taking into consideration that application of TiO_2 creates additional costs compared to the UV/O_3 system it was concluded that a more beneficial solution is the latter one.

Since the laundry wastewater contained significant amounts of inorganic ions, mainly Na^+ and Cl^-

(conductivity > 2300 μS/cm) and taking into consideration that these contaminants are not rejected by UF membranes, before a possible reuse of the treated wastewater the removal of these contaminants was necessary. Therefore, NF was applied as a final treatment step. The quality of NF permeate was independent on the AOP mode applied. Conductivity was below 30 μS/cm, turbidity < 0.1 NTU, and the concentrations of Na^+, Cl^-, Ca^{2+} and Mg^{2+} did not exceed 5.4, 5.9, 1.3 and 0.2 mg/dm^3, respectively. Water of such quality can be recycled to any stage of the laundry system.

Based on the obtained results it was concluded that the most beneficial configuration for the treatment and reuse of the industrial laundry wastewater is the MBBR → UV/O_3 → UF → NF system.

Further investigations on the proposed system should be directed towards the optimization of the UV/O_3 process, evaluation of the maximum water recovery rate and determination of the possibilities of NaCl recovery from NF concentrate.

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REFERENCES

[1] Kichik VA, Maslova MN, Svittsov AA, Kuleshov NF. An ultrafiltration treatment for liquid laundry wastes from nuclear power station. Sov Atom Energy 1987; 63: 689-692. https://dx.doi.org/10.1007/BF01126623

[2] Matsuo T, Nishi T. Activated carbon filter treatment of laundry waste water in nuclear power plants and filter recovery by heating in vacuum. Carbon 2000; 38: 709-714. http://dx.doi.org/10.1016/S0008-6223(99)00158-X

[3] Ahmad J, El-Dessouky H. Design of a modified low cos treatment system for the recycling and reuse of laundry waste water. Resour Conserv Recy 2008; 52: 973-978, https://dx.doi.org/10.1016/j.resconrec.2008.03.001

[4] Janpoor F, Torabian A, Khatibikamal V. Treatment of laundry waste water by electrocoagulation. J Chem Technol Biotechnol 2011; 86: 1113-1120, http://dx.doi.org/10.1002/jctb.2625

[5] Ge J, Qu J, Lei P, Liu H. New biopolar electrocoagulation-electroflotation process for treatment of laundry wastewater. Sep Purif Technol 2004; 36: 33-39, https://dx.doi.org/10.1016/S1383-5866(03)00150-3

[6] Shang X, Kim HCh, Huang JH, Dempsey BA. Coagulation strategies to decrease fouling and increase critical flux and contaminant removal in microfiltration of laundry wastewater. Sep Purif Technol 2015; 147: 44-50. https://dx.doi.org/10.1016/j.seppur.2015.04.005

[7] Šostar-Turk S, Petrinić I, Simonič M. Laundry wastewater treatment using coagulation and membrane filtration. Resour Conserv Recy 2005; 44: 185-196. https://dx.doi.org/10.1016/j.resconrec.2004.11.002

[8] Terechova EL, Zhang G, Chen J, Sosnina NA, Yang F. Combined chemical coagulation-flocculation/ultraviolet photolysis treatment for anionic surfactants in laundry wastewater. J Environ Chem Eng 2014; 2: 2111-2119. http://dx.doi.org/10.1016/j.jece.2014.09.011

[9] Sumisha A, Arthanareeswaran G, Thuyavan YL, Ismail AF, Chakraborty S. Treatment of laundry wastewater using polyethersulfone/polyvinylpyrollidone ultrafiltration membranes. Ecotox Environ Safe 2015; 121: 174-179. https://dx.doi.org/10.1016/j.ecoenv.2015.04.004

[10] Ciabatti I, Cesaro F, Faralli L, Fatarella E, Tognotti F. Demonstration of a treatment system for purification and reuse of laundry wastewater. Desalination 2009; 245: 451-459. http://dx.doi.org/10.1016/j.desal.2009.02.008

[11] Hoinkis J, Panten V. Wastewater recycling in laundries - From pilot to large-scale plant. Chem Eng Process Process Intensif 2008; 47: 1159-1164. https://dx.doi.org/10.1016/j.cep.2007.12.010

[12] Hoinkis J, Deowan SA, Panten V, Figoli A, Huang RR, Drioli E. Membrane bioreactor (MBR) technology – a promising approach for industrial water reuse. Procedia Eng 2012; 33: 234-241. http://dx.doi.org/10.1016/j.proeng.2012.01.1199

[13] Nicolaidis C, Vyrides I. Closing the water cycle for industrial laundries: An operational performance and techno-economic evaluation of a full-scale membrane bioreactor system. Resour Conserv Recy 2014; 92: 128-135. https://dx.doi.org/10.1016/j.resconrec.2014.09.001

[14] Mozia S, Brożek P, Przepiórski J, Tryba B, Morawski AW. Immobilized TiO2 for phenol degradation in a pilot-scale photocatalytic reactor. J Nanomater 2012, Article ID 949764, 10 pages. https://dx.doi.org/10.1155/2012/949764

[15] Mozia S, Szymański K, Michalkiewicz B, Tryba B, Toyoda M, Morawski AW. Effect of process parameters on fouling and stability of MF/UF TiO_2 membranes in a photocatalytic membrane reactor. Sep Purif Technol 2015; 142: 137-148. https://dx.doi.org/10.1016/j.seppur.2014.12.047

[16] Field W, Pearce GK. Critical, sustainable and threshold fluxes for membrane filtration with water industry applications. Adv Colloid Interface Sci 2011; 164: 38-44. http://dx.doi.org/10.1016/j.cis.2010.12.008

[17] Mozia S, Darowna D, Szymański K, Grondzewska S, Borchert K, Wróbel R, Morawski AW. Performance of two photocatalytic membrane reactors for treatment of primary and secondary effluents. Catal Today 2014; 236A: 135-145. http://dx.doi.org/10.1016/j.cattod.2013.12.049

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http://dx.doi.org/10.15379/2410-1869.2016.03.01.01