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Carwash Oily Wastewater Separated by Ultrafiltration

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Abstract: In the present study, oily wastewater generated during car washing was separated using ultrafiltration (UF). Wastewater was collected from the settling tank of two manual car washes. In addition to pollutants removed from cars, such wastewater contains surfactants, the impact of which on the process of ultrafiltration has been analyzed. For this purpose, the application of commercial UF polyethersulfone (PES) membranes (10 and 100 kDa) and polyvinylidene fluoride (PVDF) tubular membranes (100 kDa) was comprehensively examined. Almost 100% removal of oil contaminants was achieved; however, intensive fouling was noticed. The membrane morphology and deposit composition were studied using a scanning electron microscope coupled with energy dispersion spectrometry. The fouling phenomenon was reduced by washing the membranes with an alkaline cleaning agent (pH = 11.5), which is used in car washes to remove insects. The filtration/membrane washing cycle was repeated many times to achieve stable operation of the membrane modules. The UF process was carried out for 120–140 h, and the separation efficiency was analyzed based on the rejection of dextrans, COD, BOD, total N and P, turbidity, and anionic surfactants. It has been found that cyclic repeated washing did not deteriorate the membrane's performance, and a permeate with a turbidity of 0.12–0.35 NTU was obtained. Thus, cleaning agents used for washing cars can also be used for membrane cleaning.

Keywords: ultrafiltration; oily wastewater; carwash wastewater; fouling

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1. Introduction

Oils and greases are used to reduce friction in various car mechanisms. They are generally isolated from the environment; however, small leaks often occur due to seal damage. As a result, when washing cars, the wastewater generated during the car wash also contains oil contaminants [1–3]. Their content is most often in the range of 10–50 mg/L; nevertheless, concentrations above 500 mg/L also occur [4]. This is a very important challenge for researchers since effluents containing such amounts of oil contaminants may destroy the ecological environment and seriously endanger human health [5]. Therefore, the treatment of oily wastewater is necessary.

Industrial methods used for oily wastewater treatment include conventional methods, such as precipitation, centrifugal, flotation, coagulation, and biological treatment. However, it has been widely documented that they are usually not efficient for the separation of wastewater with low oil concentration and finely dispersed oil droplets [6–9].

Undoubtedly, the membrane processes can be used most effectively for the treatment of this wastewater [10]. Pressure-driven membrane processes, such as microfiltration (MF), ultrafiltration (UF), and nanofiltration (NF), are most often used to remove oil contaminants from water [10–13]. The main issue that hinders their use is the formation of deposits on the membrane surface (fouling) [14–16].

One of the methods to reduce the intensity of the above-mentioned phenomenon is pre-treatment using conventional cleaning methods. Such extensive multi-stage installations

have been successfully used to treat wastewater from car washes [17,18]. These solutions are used in large automatic stations. However, in many countries, small manual car washes dominate. Unfortunately, their owners will not invest in the construction of expensive multi-stage purification systems. However, simple and small membrane installations are accepted. Hence, the possibility of using such types of installations is investigated in this work.

During the long-term operation of modules, apart from fouling, the degradation of membranes is also an operational challenge. Organic substances may interact with the polymeric membrane matrix. Therefore, one of the major constraints is the durability of membranes, particularly during the separation of wastewater containing various surface-active contaminants (e.g., oils and surfactants) [19]. Such changes in the properties of membranes often occur very slowly; hence, they can only be observed after several weeks of wastewater filtration [20]. Meanwhile, in many publications, the wastewater treatment process is often presented on the basis of short tests, which does not allow for a proper assessment of the possibilities of industrial application [5]. For this reason, in the present work, multi-week tests on the separation of wastewater from a car wash were carried out. For this purpose, selected membranes with high chemical resistance, such as polyethersulfone (PES) and polyvinylidene fluoride (PVDF), were used.

Wastewater from the car wash is collected in a settling tank from which it flows through an oil separator. This allows for the oil suspension to be separated; however, the finely dispersed oil droplets are not retained [3]. It should be noted that the remaining oil content is small, and standards are usually met, allowing for such pre-treated wastewater to be discharged to the municipal sewage treatment plant. According to the requirements of some countries, a significant portion of the water should be treated and returned to car washing [21,22]. In this case, the application of the UF process is recommended.

Ultrafiltration is a known and effective method for the treatment of oily wastewater [23,24]. However, as has been indicated above, the main challenge in the application of the UF process is the occurrence of the fouling phenomenon. To wash cars, detergents and alkaline agents are used, which, in addition to oil, are also present in the wastewater. Such washing agents may affect the separation of oils as well as the fouling of membranes [25], which was investigated in this study by conducting long-term UF tests.

It is widely accepted that the fouling of membranes makes it necessary to clean them periodically [10]. In the case of separation of oily wastewater, alkaline detergent solutions are used to wash the membranes, for instance, P3 Ultrasil 11 from Hankel (Germany) [26]. Such agents are aggressive; therefore, repeated cleaning may cause membrane degradation. The effects presented in several publications, e.g., three–five work cycles, provide limited information [27]. Therefore, in the present work, long-term research was carried out. The membranes were washed with alkaline agents in a much larger number of cycles. To wash the membranes, a solution of Insect agents was used, which is used in car washes to remove insects. These agents, similar to P3 Ultrasil 11, contain NaOH, EDTA tetrasodium salt, and surfactants [26–28]. Its advantage is that, unlike commercial agents used for membrane washing, it is approved for use in car washes. Long-term tests check whether it can also be used to wash tested membranes and whether its use does not affect the separation of oil contaminants.

2. Materials and Methods

The UF process was tested using real wastewater collected from a car wash settling tank. Wastewater was collected in autumn from two manual car washes. The installations were supplied with tap water, which was softened using ion exchangers. Cars were washed with a detergent solution, which was prepared by adding 0.5% Active Green agent concentrate to softened water. A 0.5% wax solution (Hydrowax) was used to polish car bodies. An alkaline agent (Insect) containing NaOH was used to remove insects from the car surface. The composition of these cleaning agents was presented in work [29]. The ingredients of these agents may cause fouling; hence, synthetic wastewater prepared by

mixing commercial agents (0.5% Active Green and 0.2% Hydrowax) was also used in the UF tests.

The diagram of the UF installation used is shown in Figure 1. Feed was taken from the tank (2 L) using a model 3CP1221 piston pump (CAT PUMPS, Hampshire, England) and returned to the tank after passing through the UF modules.

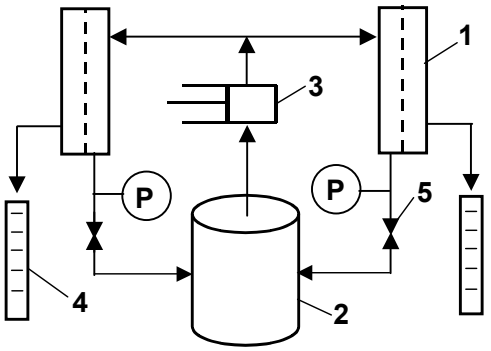

Figure 1. UF installation set-up. 1—UF module; 2—feed tank; 3—pump; 4—measurement cylinder; 5—valve; P—manometer.

Two types (UE10 and UE50) of commercial ultrafiltration PES membranes from TriSep Corporation (Goleta, CA, USA) were used in this study. The nominal molecular weight cut-offs (MWCO) declared by the manufacturer were 10 kDa and 100 kDa for the UE10 and UE50 membranes, respectively. The PES membranes were mounted on the plate cross-flow modules, and the active membrane area was 24 cm^2. The modules were made of ASI 316 acid-resistant steel, and their construction and selection of operating conditions were presented in work [29]. Additionally, a PVDF tubular FP100 membrane (100 kDa) from PCI (Kostrzyń, Poland) was also applied for UF studies. In this case, the feed flowed inside the tube with 12.5 mm diameter and 25 cm long.

The UF studies were carried out at a transmembrane pressure (TMP) of 0.1 MPa. Changes in the membrane permeability were measured for deionized (DI) water at TMP in the range of 0.1–0.3 MPa. The procedure of membrane cleaning was performed with the alkaline 0.5% Insect solution (pH = 11.5). The prepared Insect solution (1 L) was recycled for 30 min through the UF module. Before and after this operation, the UF installation was rinsed with DI water (2L). Permeate flux was reported in units of L/(h m^2), abbreviated as LHM. The estimated measurement error was 2–4%.

In addition to carwash wastewater, synthetic oily wastewater was also used in the UF research. An emulsion concentrate containing 526 mg oil/L was used to prepare them. The oil emulsion concentrate was prepared by adding 5 mL of engine oil to 1 L of DI water. Subsequently, the content was intensively shaken for 15 min, and then the mixture was subjected to the action of ultrasounds (Sonic-6D, 620 W, POLSONIC, Warszawa, Poland) for 60 min. These operations were repeated at least 5 times during 3 consecutive days. The emulsion was then stabilized for over a month. During this time, some of the oil separated due to coalescence, but the remainder formed a stable emulsion, both in terms of concentration and droplet size distribution.

The determination of oil droplet size distribution was carried out using a laser light scattering system, Mastersizer 3000E (Malvern Instruments, Grovewood Rd, UK).

The oil content in the solutions was examined by an infrared method using an oil content analyzer OCMA 500 manufactured by Horiba (Osaka, Japan). This apparatus performs an automatic extraction of oil from aqueous solutions with S316 solvent (Horiba, Osaka, Japan). The volume ratio of solvent to water sample amounted to 10:20 mL. OCMA 500 analyzer allows you to detect oil in water at a level of 0.1 mg/L.

The changes in membrane performance were analyzed based on the changes in rejection of dextrans (molecular weight of 20–500 kDa, Polfa, Warszawa, Poland), biological oxygen demand (BOD), chemical oxygen demand (COD), and surfactants. The Hach cu-

vette tests were used to determine the concentration of surfactants (LCK 334—nonionic; LCK 344—anionic), COD (LCK 1014), and BOD (LCK 555). The concentration of dextrans was analyzed using a high-performance liquid chromatograph (UlitiMate 3000, Dionex, Sunnyvale, USA) with a PolySep-GFC-P 4000 column (Phenomenex, Torrance, LA, USA).

The membrane morphology and deposit composition were studied using an SU8020 (Hitachi High Technologies Co., Tokyo, Japan) scanning electron microscope (SEM) coupled with energy dispersion spectrometry (EDS). All samples were sputter-coated with chromium.

The pH of solutions was measured using a 6P Ultrameter (Myron L Company, Carlsbad, CA, USA). Elemental analysis in the liquid samples was performed by inductively coupled plasma—optical emission spectrometry (ICP-OES) (Optima 5300 DV, Perkin Elmer, Waltham, MA, USA). The concentration of elements such as Fe, Cu, Zn, P, Al, K, Ca, Mg, Ba, Mn, etc. was measured.

3. Results and Discussion

3.1. Carwash Wastewater

Wastewater was collected from two manual car washes (Manual 1 and Manual 2). At these stations, the effluents from car washing, after flowing through the settling tank and oil separator, were discharged into the municipal sewage system. Active Green solution was used to create foam in car washes, which gave the wastewater a slightly green color. The composition of the collected samples is presented in Table 1. Wastewater from the Manual 1 car wash contained more suspension and oil, which resulted in higher COD and BOD values.

Table 1. Composition of wastewater collected from manual car washes.

Parameter	Manual 1	Manual 2
COD [mg/L]	240	181
BOD [mg/L]	30	16
Turbidity [NTU]	28.2	19.1
pH	7.9	7.6
N total [mg/L]	3.92	3.52
P total [mg/L]	3.95	4.61
Anionic surfactants [mg/L]	3.12	1.96
Oil [mg/L]	9.3	7.6

In addition to organic pollutants, car wash wastewater contains various metals. Elements detected in wastewater by ICP analysis, in amounts above 0.1 mg/L, are presented in Table 2. The content of the marked ingredients for manual car washes was similar. For comparison, wastewater from an automatic car wash was also tested, which contained significantly less Na. This was due to the water-softening process. The car washes were supplied with water from the municipal water supply network, which was softened with ion exchangers in manual car washes. They were regenerated with NaCl solution, which resulted in an increase in Na concentration in the wastewater.

3.2. Membrane Performance

In the UF tests, two membranes made of PES (UE10 and UE50) and a tubular membrane FP100 with a skin layer made of PVDF were used. These membranes (Figure 2), like most commercial UF membranes, have an asymmetric structure with a thin skin layer 0.1–1 μm thick, exposed to the feed side [10,30]. This skin is supported on a highly porous layer 50–250 μm thick, giving the requirement of high permeability and mechanical strength of membranes. The structure of the UE10 membrane was similar to the UE50 images shown in Figure 2 [29]. The MWCO value declared by the UE50 and FP100 manufacturers was similar (100 kDa). However, the surface of the FP100 membranes was much more uneven, and in some places, there were pores with sizes of 0.1–0.2 μm (Figure 2a).

Table 2. Elemental ICP analysis [mg/L]—wastewater collected from manual and automatic car washes.

Element	Manual 1	Manual 2	Automatic
Na	455.02	431.52	147.36
K	11.86	10.95	17.63
Ca	67.85	90.24	77.58
Mg	10.68	19.66	19.89
Fe	9.83	9.46	1.49
P	0.62	0.22	1.22
Ba	7.32	5.26	0.46
Cs	11.56	8.36	0.74
Mn	0.42	0.85	0.23
Sr	0.37	1.13	0.55
Pt	0.21	0.34	0.33
Al	0.19	0.35	0.39

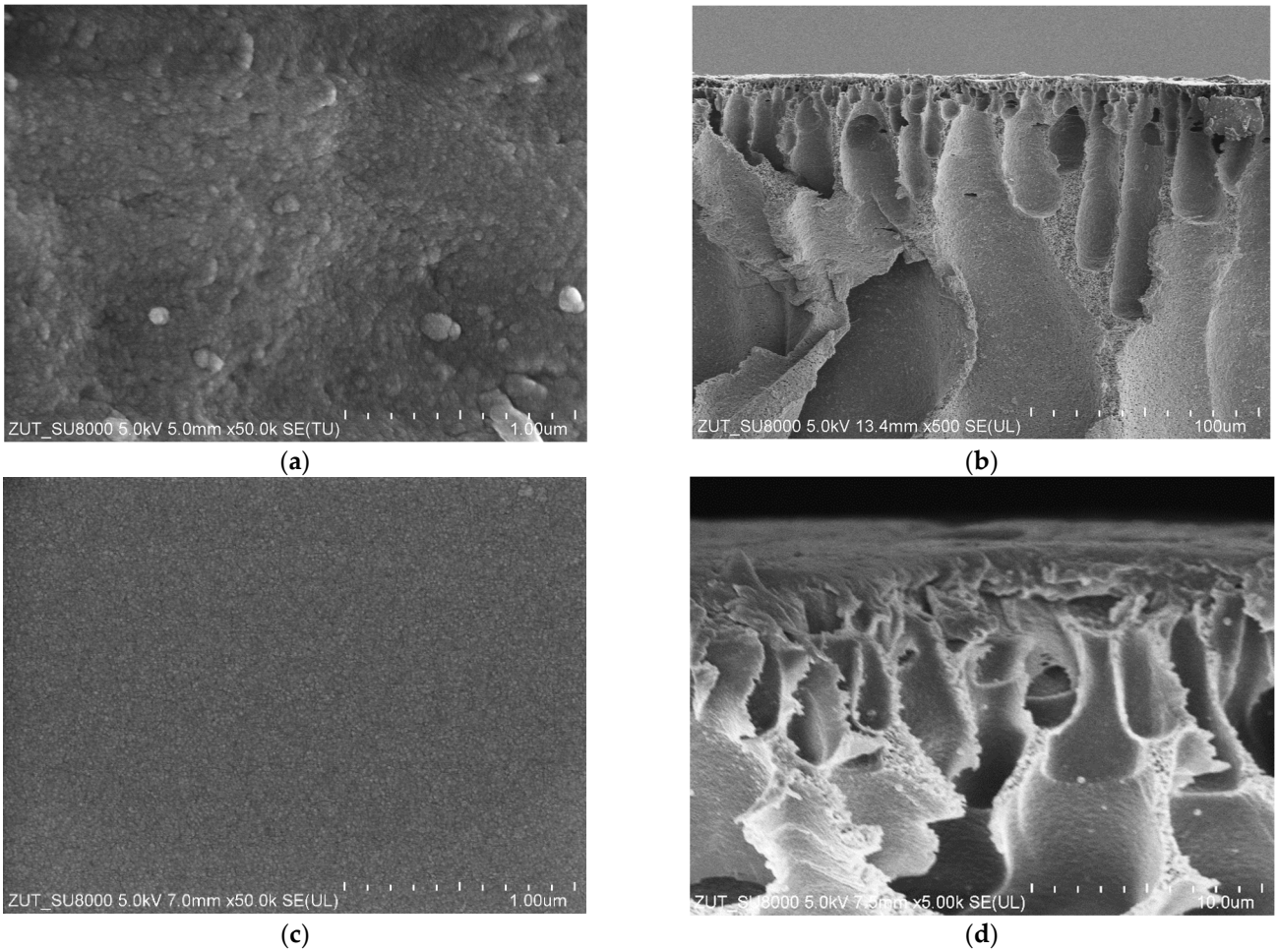

Figure 2. SEM images membrane surface and cross-section. Membrane FP100: (**a**) surface; (**b**) cross-section; and membrane UE50: (**c**) surface; (**d**) cross-section.

In the case of the UE10 membrane (10 kDa), the MWCO value was 10 times lower than that declared by the manufacturer for UE50 and FP100 membranes. Dextran separation tests, however, did not show such a significant difference and UE50 membranes retained dextrans at only 10–20% less (Figure 3). The lowest retention rate was demonstrated by FP100 membranes, which retained 500 kDa dextran by 80%. SEM examinations showed

pores up to 0.2 µm on the surface of these membranes (Figure 2a), which probably resulted in a deterioration of the separation of the tested dextrans solutions.

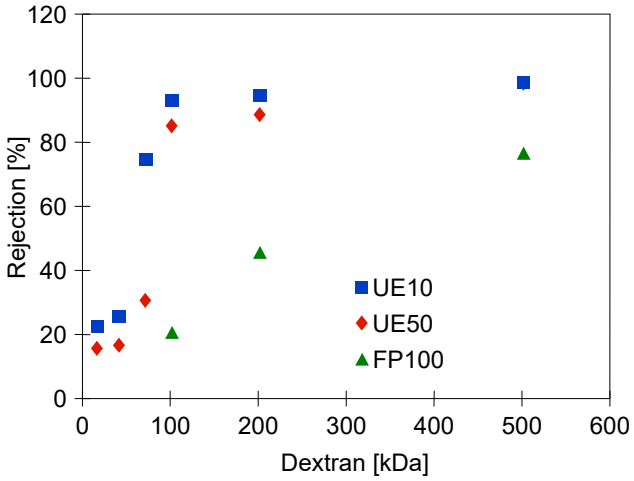

Figure 3. Dextran (0.5 g/L) rejection by studied membranes. TMP = 0.1 MPa. Measurement errors below 2%.

The deposit layer on the membrane surface usually improves the separation properties of the UF process [25]. It has been shown that not only the pollutants removed from cars but also the components of the liquids used to wash them cause the fouling phenomenon [28]. It is worth noting that waxes used to polish the car body can also be deposited on the membranes. The results of the separation of the mixture containing 0.5% Active Green and 0.2% Hydrowax are shown in Figure 4. Samples of the feed and permeate were collected after 5 h of filtration tests. Although the lowest degree of retention was obtained as before for FP100 membranes, the differences were not as significant as in the case of dextrans separation (Figure 3). Compared to UE10 membranes, the more porous UE50 membranes retained the ingredients to a greater extent which resulted from their greater fouling [29].

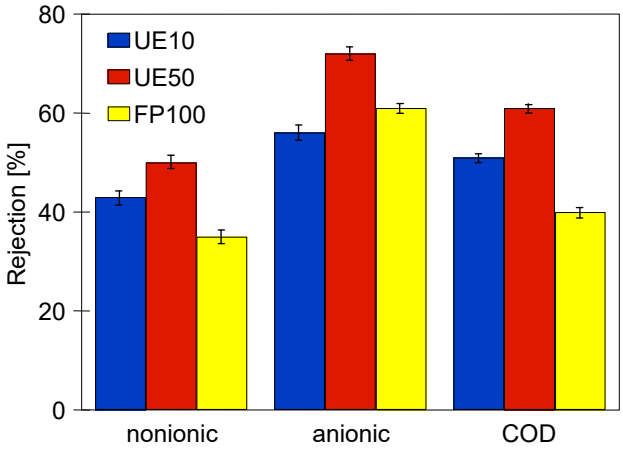

Figure 4. Rejection of COD and surfactants (anionic, nonionic) during UF of synthetic wastewater (mixture 0.5% Active Green + 0.2% Hydrowax). Results were obtained for pristine membranes after 5 h of UF process duration.

3.3. Ultrafiltration Oil Emulsion with Surfactants

In addition to concentration, the size of oil droplets also has a significant impact on the emulsion filtration process and membrane fouling [23,31]. Surfactants stabilize the dispersion of oil in water; thus, their presence affects the intensity of fouling. Membrane permeability may also be reduced by the adsorption of surfactants on their surface [29,32].

Therefore, in order to determine the influence of oil on the fouling, in the first stage of the process, the membranes were stabilized using the foaming agent solution (Figure 5). The permeate flux obtained for DI water after adding 0.5% Active Green decreased from 1300 to 600 LHM (UE50) and from 290 to 190 LHM for UE10 membranes. A further decrease was recorded, and after 7 h, the permeate flux stabilized at 350 and 170 LHM for UE50 and UE10, respectively.

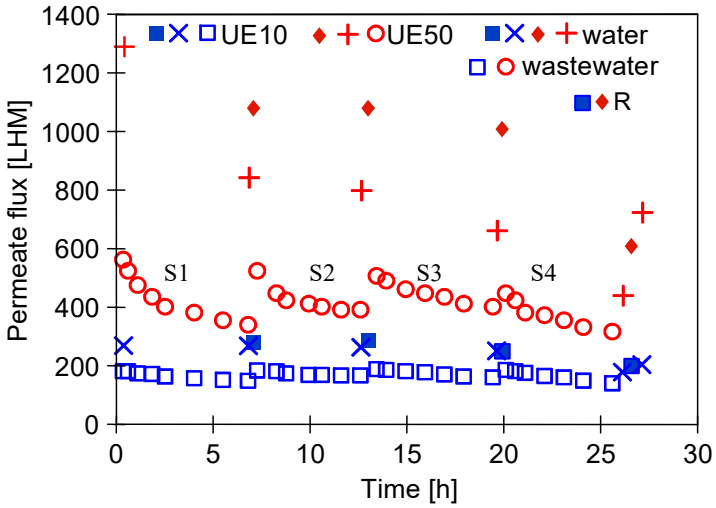

Figure 5. Changes in the permeate flux (wastewater) and maximum permeate flux (water) during filtration of 0.5% Active Green solution through UE10 and UE50 membranes. R—after terminate series, S1–S4 membranes were washed (30 min) with 0.5% Insect solution (pH = 11.5).

Membrane rinsing with DI water significantly increased the flux; however, it did not restore the initial value. Values similar to the initial flux were obtained only after 30 min of washing the membranes with an alkaline 0.5% Insect solution (Figure 5, R). Significantly greater performance decreases were observed for the UE50 membranes. This finding indicates their greater susceptibility to fouling. In paper [33], it was indicated that an increase in MWCO leads to a greater fouling caused by surfactants. In the present study, after 27 h of the UF process, the maximum permeate flux for UE50 decreased to 600 LHM, while for UE10, it was 180 LHM. Rejection tests carried out after 22 h of the process showed that slightly better efficiency was achieved for the UE50 membrane (Figure 6), which also indicated greater fouling of this membrane.

During the filtration of 0.5% Active Green, the rejection degree of nonionic surfactants was 20% higher than that obtained for the feed containing 0.5% Active Green and 0.2% Hydrowax (Figure 4). However, the retention of anionic surfactants and COD was over 10% lower. These results indicate that the composition of the treated wastewater and the resulting fouling have a significant impact on separation efficiency. The degree of surfactant rejection is also significantly influenced by their concentration. Surfactants exist as monomers in water when their concentrations are below the critical micelle concentration (CMC). When the CMC value is exceeded, the emerging micelles are better retained, and for the PES membrane (10 kDa), a surfactant rejection of 60–80% was achieved [33].

After filtering the Active Green solution (Figure 5), the installation was rinsed with DI water and fed with an oil-in-water emulsion. After adding the emulsion concentrate to DI water, the oil content in the feed was 12.6 ppm. For such a feed, the permeate flux was 410 and 210 LHM for UE50 and UE10, respectively (Figure 7). It is important to note that no oil was detected in the obtained permeates, which indicated that the tested membranes retained it 100%. This was probably due to the fact that most of the oil drops in the feed had sizes above 1 μm (Figure 8).

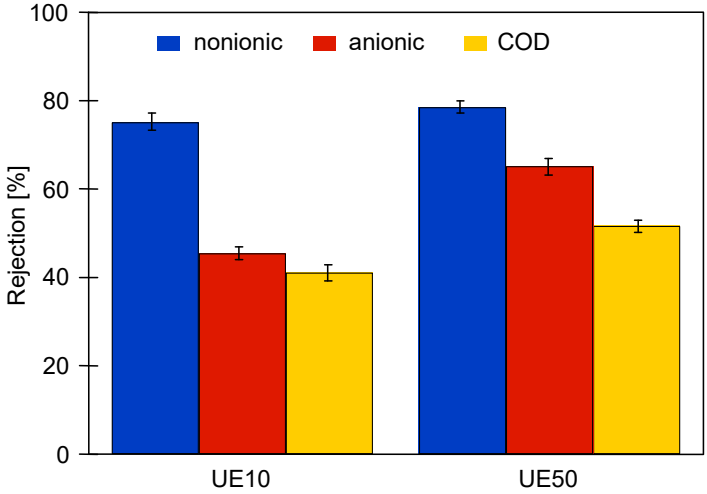

Figure 6. Rejection of COD and surfactants (anionic, nonionic) after 22 h UF of 0.5% Active Green solution (Figure 5).

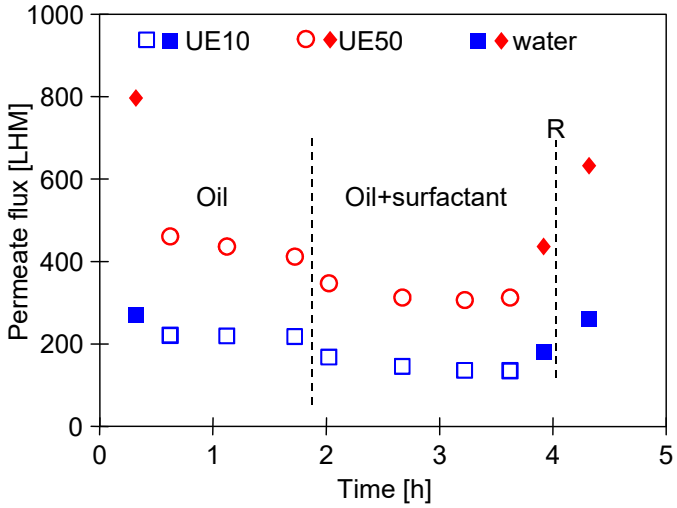

Figure 7. Changes in the permeate flux during filtration oil emulsion (Oil) and synthetic oily wastewater (Oil + surfactant) through UE10 and UE50 membranes. R denotes cleaning of membranes with 0.5% Insect solution (30 min).

Studies on the size distribution of oil droplets in the feed showed changes occurring over the process time. Initially, the feed contained oil drops mainly with sizes of 10–100 µm (Figure 8, t = 5 min). After 20 min of circulation of the feed in the UF installation, the disappearance of larger drops and an increase in the share of drops with sizes below 20 µm were observed. After 40 min of the UF process, the droplet size distribution profile in this range almost did not change, but larger droplets disappeared. The fact that the oil content in the feed decreased from 12.6 to 8.4 mg/L indicates that larger drops settled on the surface of the UF installation. As a result of coalescence and creaming, some of the drops were released on the surface of the feed in its tank.

After 2 h of filtration of the oil emulsion, 0.1% of Active Green foaming agent was added to the feed. As a result, the flux decreased by 30% (Figure 7, Oil + surfactant). At the same time, there were changes in the size distribution of oil drops (Figure 9). Apart from small changes in the range of 0.2–20 µm, much larger drops in the range of 20–200 µm appeared in the feed. Moreover, during the 120-minute measurement, the number of drops in the range of 300–1000 µm increased significantly. It can be assumed that the addition of the surfactant caused large oil drops to be washed off the surface of the UF installation. The addition of surfactants stabilized the emulsion and prevented further coalescence, and

no oil separation was observed on the surface of the feed in its tank. The adsorption of the surfactant on the oil droplets makes them more plastic, which facilitates the droplet's deformation and penetration into the pores [23]. However, an analysis of the permeate composition carried out after adding Active Green did not show the presence of oil. The application of the Hermia model showed that during the UF of carwash wastewater, the dominant fouling mechanism was the cake formation [29,34]. A similar result for emulsions stabilized with surfactants was presented in [32]. The formation of cake on the membranes surface of membranes improves the efficiency of this process [25].

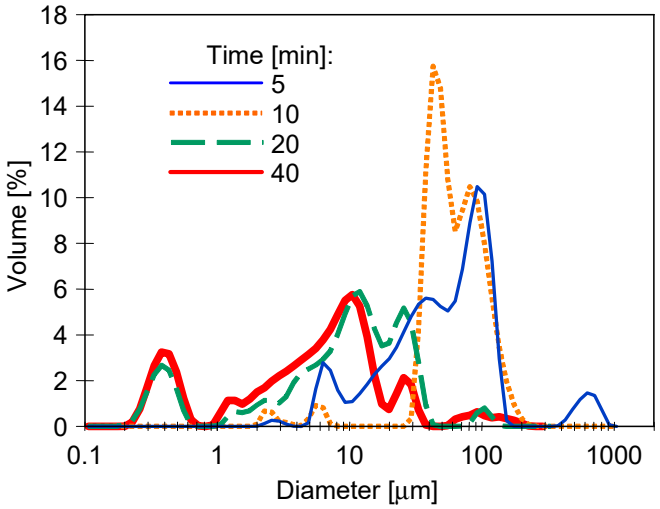

Figure 8. Changes in oil droplet size distribution in the feed during UF process. Feed–engine oil emulsion (18.5 mg/L).

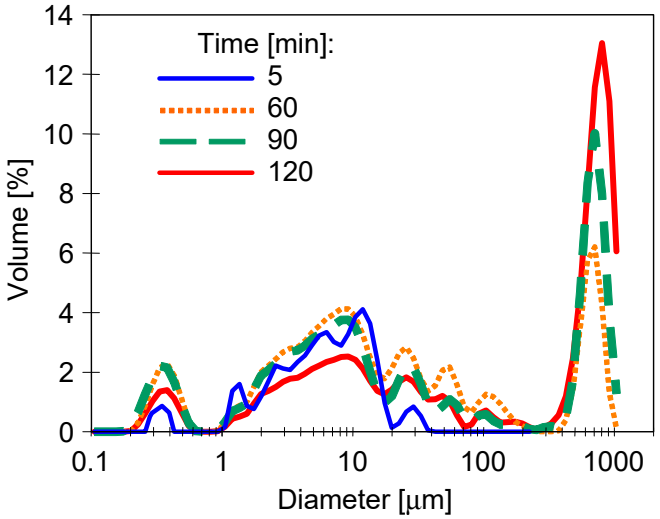

Figure 9. Changes in oil droplet size distribution in the feed during UF process. Feed–synthetic oily wastewater (Oil + surfactant).

Studies on droplet size changes with/without surfactants in a dynamically mixed emulsion were additionally performed using the MS3000E apparatus with the Hydro EV attachment, which has a unique dip-in centrifugal pump and stirrer design that achieves full and rapid dispersion in standard laboratory beakers. The stirrer speed in the tests was set at 1000 rpm. Laboratory beakers were filled with an emulsion containing 15.8 mg/L of oil, and after the first measurement, a 5 mL 0.1% solution of Active Green was added to it. After adding surfactants, the initial droplet size distribution (t = 1 min) changed quickly (t = 7 min) and then changed only slightly (Figure 10, t = 60 min). The resulting oil

droplet size distribution profile was similar to that obtained in the UF installation (Figure 9). This result confirms that the presence of surfactants in the emulsion stabilizes as well as influences the oil droplet size distribution.

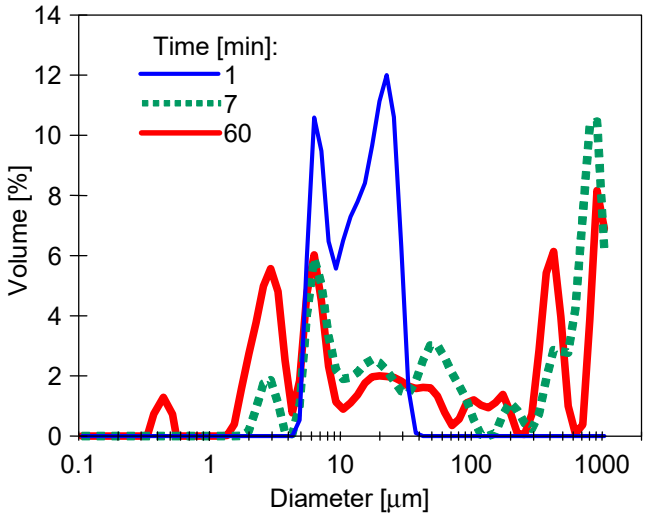

Figure 10. Changes in oil droplet size distribution in the synthetic oily wastewater (Oil + surfactant) during recirculation inside MS3000E apparatus. Time t = 1 min—only engine oil dispersed in the DI water.

The results presented in Figures 9 and 10 showed that in the presence of surfactants, there are also larger oil drops in the emulsion. Such drops adsorb more easily on the membrane surface, which may explain the observed drop in efficiency after adding Active Green agent to 310 LHM (UE50) and to 140 LHM (UE10) (Figure 7). A reduction in permeate fluxes after adding a surfactant was also found in other studies [32,35]. After washing the membranes with 0.5% Insect solution, the maximum permeate flux increased to 630 LHM (UE50) and 260 LHM (UE10) (Figure 7). This washing operation was repeated cyclically during 57 h UF of the oil emulsion with the addition of 0.1% Active Green (Figure 11, rinsing). As a result, the obtained maximum permeate flux (feed–water) was relatively stable for the first 20 h of the test, after which it decreased, and after 35 h, UF stabilized at the level of 400 LHM (UE50) and 220 LHM (UE10).

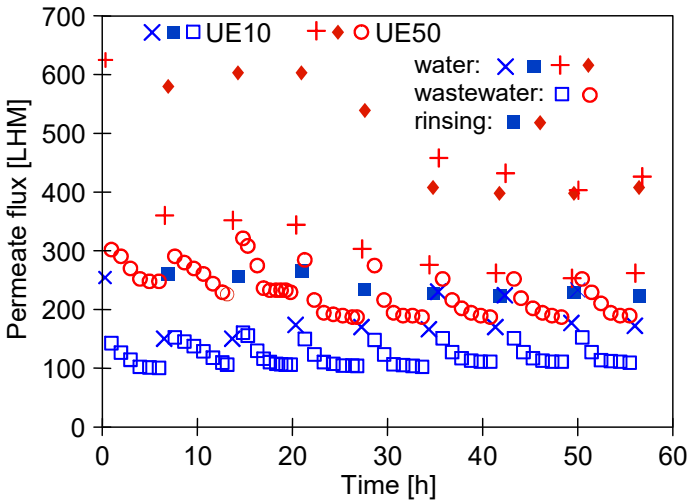

Figure 11. Changes the permeate flux during filtration of synthetic oily wastewater through UE10 and UE50 membranes (wastewater). Water–permeate flux obtained for feed DI water before and after membrane cleaning (rinsing).

Fouling systematically reduces the module's performance; hence, the effectiveness of membrane cleaning is important. The obtained results indicate that after completing the separation of the Active Green solution (Figure 5) and the synthetic oily wastewater (Figure 11), washing the membranes with a 0.5% Insect solution allowed for obtaining a permeate flux similar to the initial one (Figure 12a). A worse effect was obtained for UE50 membranes, the efficiency of which, despite washing, decreased by 30% (Figure 12b).

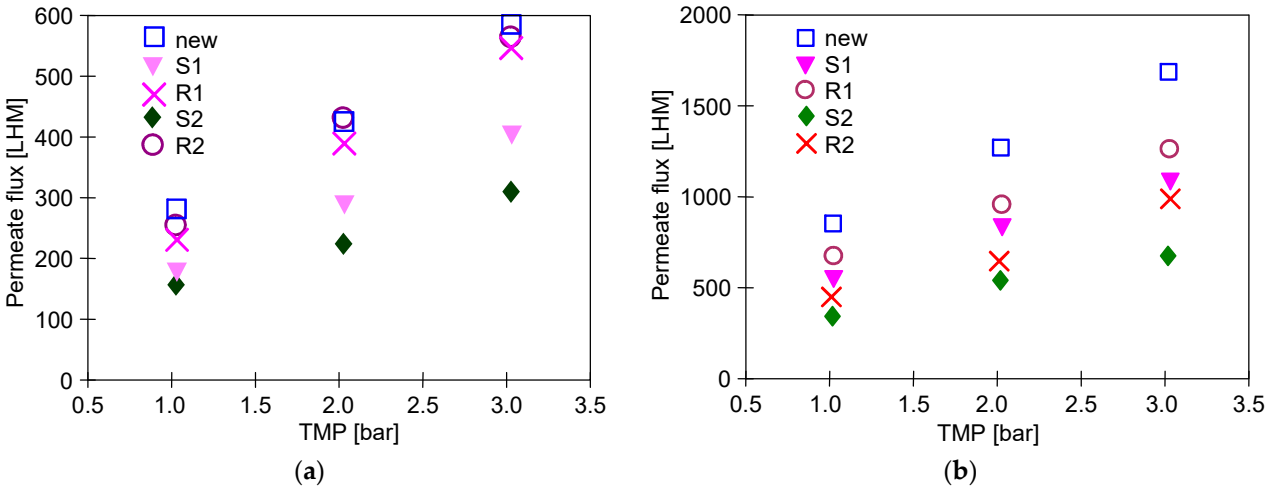

Figure 12. The influence of TMP on the permeate flux for UE10 (**a**) and for UE50 (**b**) membranes after UF process (S1, R1—Figure 5) and (S2, R2—Figure 11). S1, S2—membranes rinsed with water; R1, R2—membranes washed with 0.5% Insect solution.

The obtained results (Figure 12) indicate that irreversible fouling was much greater in the case of UE50 membranes. This is also confirmed by the image of membranes removed from the modules after these tests. More contaminants accumulated on the UE50 membrane, making its surface darker (Figure 13).

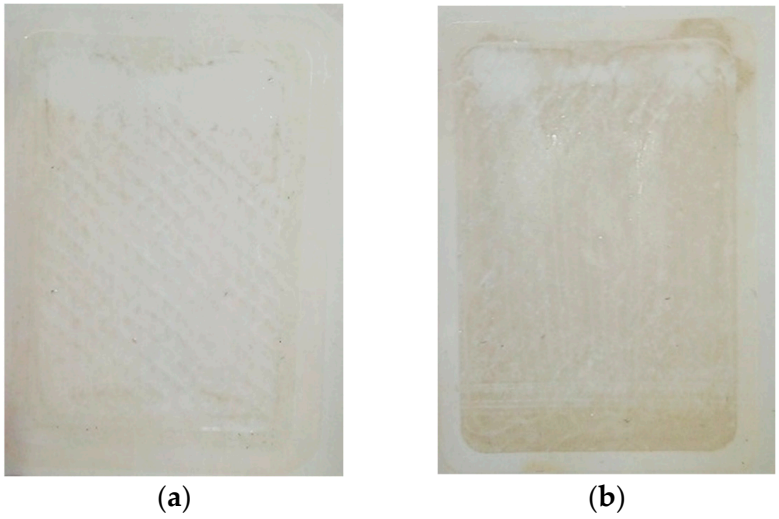

Figure 13. Images of surface of PES membranes collected from UF modules after treatment of synthetic oily wastewater: (**a**)—UE10; (**b**)—UE50.

3.4. Carwash Wastewater

Tests on the separation of real wastewater from the car wash confirmed the effectiveness of cyclically repeated membrane washing with the Insect solution, which allowed for maintaining a stable permeate flux during 140 h of the UF process. To increase the cleaning effect, the Insect solution filled the modules every few days for 40 h. As a result, a signifi-

cant increase in the maximum flow was achieved (Figures 14 and 15, S points). The tested PES membranes are blended with polyvinylpyrrolidone (PVP) to increase hydrophilicity. It has been shown that long-term contact with Insect solutions containing NaOH resulted in the removal of PVP from the membrane matrix and an increase in pore size [29]. This increased membrane permeability and a slight increase in permeate flux after 100 h UF was observed.

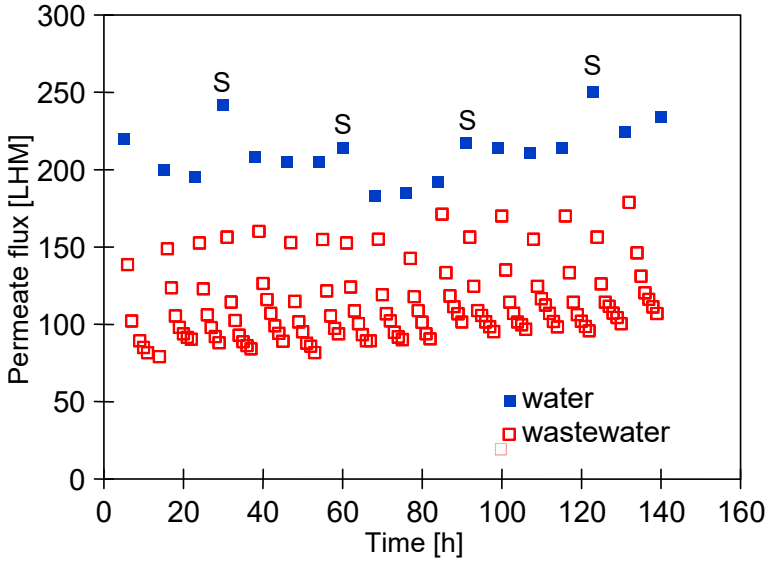

Figure 14. Changed permeate flux during filtration of carwash wastewater. Membrane UE10. Water–permeate flux after membrane washing with 0.5% Insect solution (30 min). S points —membranes soaked for 40 h in 0.5% Insect solution.

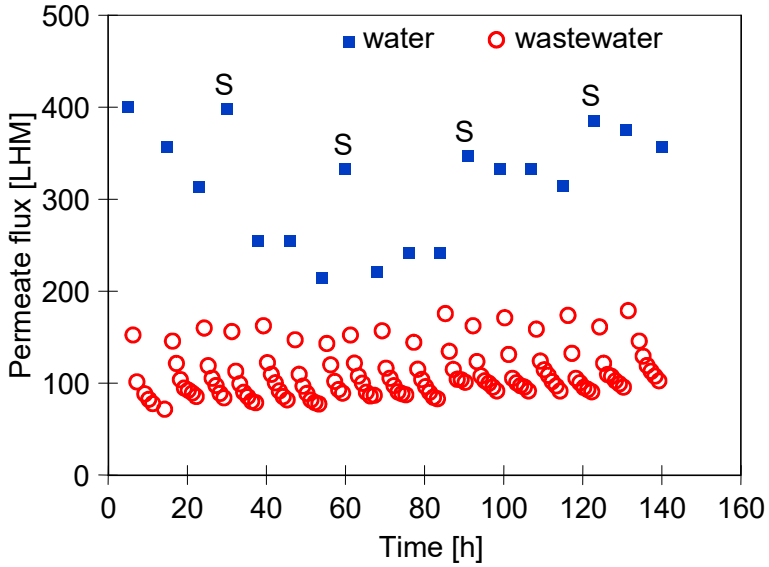

Figure 15. Changed permeate flux during filtration of carwash wastewater. Membrane UE50. Water–permeate flux after membrane washing with 0.5% Insect solution (30 min). S points—membrane soaked 40 h into 0.5% Insect solution.

The increase in porosity of PES membranes caused by the leaching of PVP from the matrix membrane did not significantly affect the degree of separation (Figure 16). Throughout the entire UF study period, the turbidity of the obtained permeate was in the range of 0.15–0.32 NTU, which resulted in almost 100% suspension rejection. A slight increase in the NTU value was observed after soaking the membranes for 40 h, i.e., after

a greater reduction in the thickness of the fouling layer. For the first 60 h, the modules were fed with wastewater from the Manual 1 car wash, which was more turbid than the wastewater collected from the Manual 2 car wash (Table 1), which, however, did not deteriorate the purity of the obtained permeate.

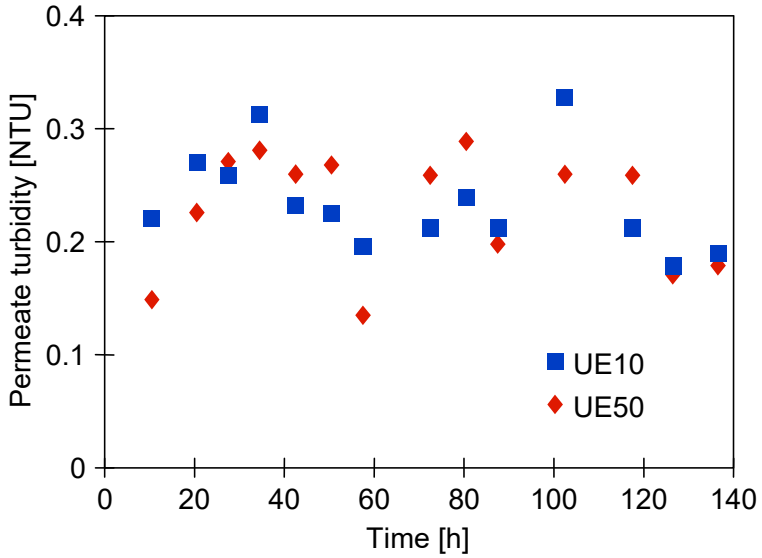

Figure 16. Changes permeate turbidity during UF carwash wastewater (Figures 14 and 15).

Stable UF performance was also obtained for the FP100 tubular membranes fed with Manual 2 wastewater (Figure 17). Also, in this case, the turbidity removal was close to 100%. During the tests, the membranes were rinsed only for 30 min with Insect solutions without a two-day soaking. After 40 h of this process, the efficiency stabilized at the level of 70 LHM, which was almost twice lower than for UE50 membranes with a similar MWCO value (100 kDa). This was probably due to the intensification of fouling caused by the greater surface porosity of the FP100 membranes (Figure 2a). However, a more intense fouling phenomenon led to an improvement in the degree of separation, and consequently, the permeate turbidity was at the level of 0.12 NTU (Figure 18).

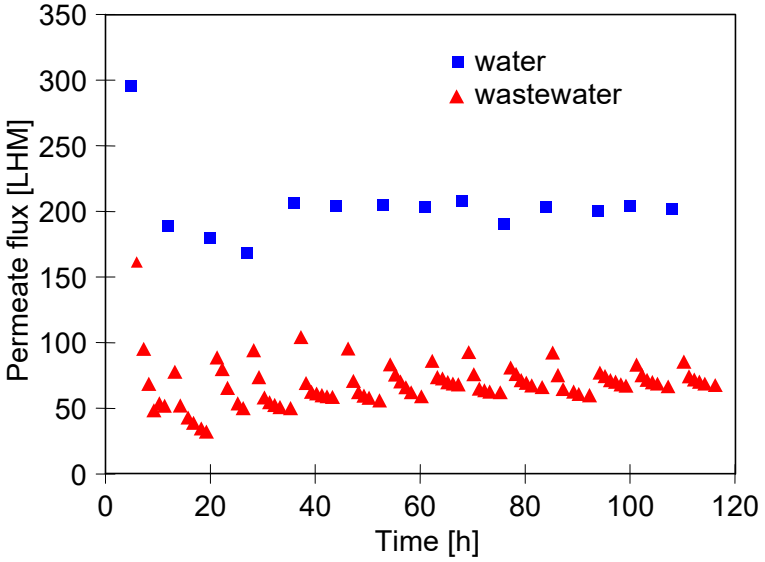

Figure 17. Changed permeate flux during filtration of carwash wastewater. Membrane FP100. Water–permeate flux after membrane washing with 0.5% Insect solution (30 min).

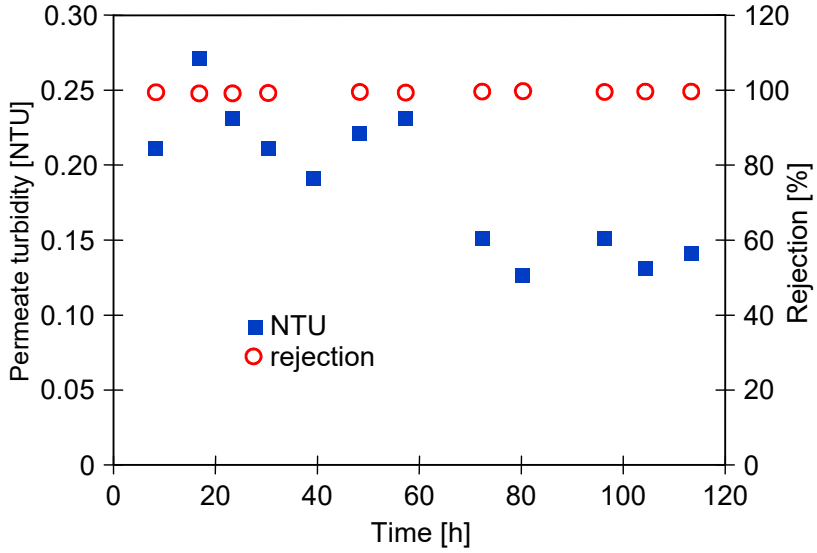

Figure 18. Changes permeate turbidity during UF carwash wastewater (Figure 17). Membrane FP100.

SEM observations of the membranes after completing the carwash wastewater filtration tests confirmed that intense fouling occurred during wastewater separation (Figure 19). The resulting precipitate caused the surface of the membranes to be much darker than that shown in Figure 13b. After intensive rinsing in a 0.5% Insect solution, most of the precipitate was removed, and the colour of the membrane was close to white. However, SEM examinations showed that a thin layer of impurities still remained on the membranes (Figure 19b,d,e). As a result, the initial permeate flux was not completely recovered after washing the membranes (Figures 14, 15, and 17, feed–water). As demonstrated, the presence of this precipitate layer led to an improvement in the degree of separation.

Roughly speaking, UF membranes retain suspensions and oil drops well but dissolved substances less well. As a result, the rejection values of COD and surfactants were lower (Figure 20). It can also be noticed that compared to the separation of synthetic wastewater (Active Green + Hydrowax mixture), the values of some parameters have changed significantly. It has been demonstrated that the degree of COD retention decreased almost twofold, similar to the retention of anionic surfactants by FP100 membranes. It is interesting to note that for UE10 and UE50 membranes, surfactant rejection also decreased, but only by about 10%.

UF membranes do not desalinate water; therefore, as expected, the retention of detected elements usually does not exceed a few percent (Table 3). This is due to the fact that UF membranes have pores that are too large to separate ions. Some of the detected elements, such as Fe, P, and Al, were retained by over 50%, which was due to the fact that these elements, in addition to creating ions, also occur in suspensions [36].

In [33], a significant increase in element retention of over 60% with the addition of the anionic surfactant SDBS was observed. Noteworthy, a similarly high degree of metal retention was demonstrated as an effect of the gel layer formation UF [36]. The applied TMP = 0.3 MPa increased the compression of the gel layer, which, however, resulted in low-permeate flux (10–20 LHM). In another study, it was shown that the retention of metals depends mainly on the form of their occurrence. For instance, most of the P is attached to particulate matter or participating in gel formation, while the P present in the permeate fractions could most likely be related to orthophosphate molecules (PO_4^{3-}), which are able to pass through the membrane pores [36]. In the examined case, the obtained permeate contained approximately 100 mg/L of all detected elements (mainly Na—Table 3); thus, it can be used for foam washing of cars.

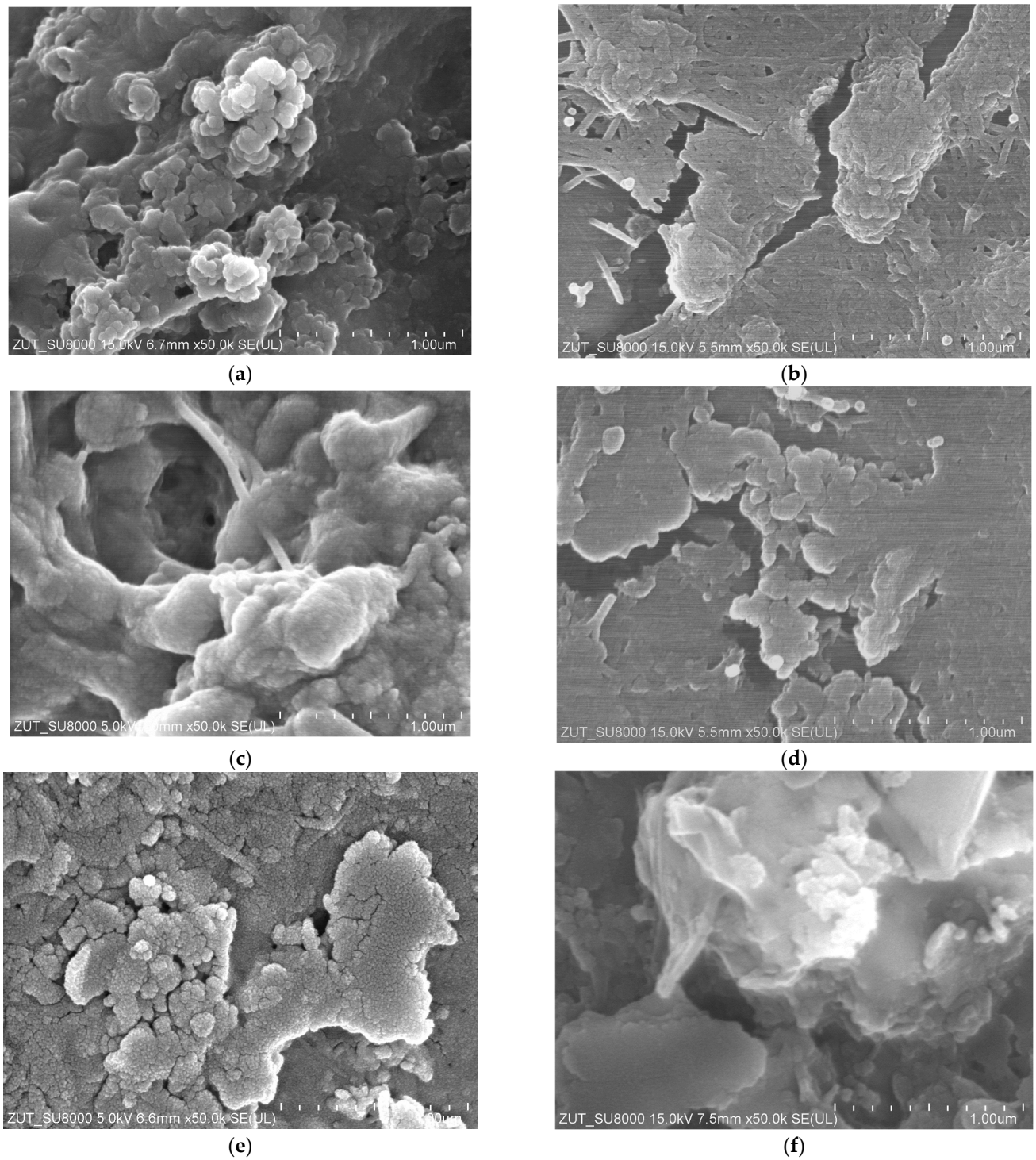

Figure 19. SEM images of membrane surface after wastewater separation. Membrane UE10: (**a**) fouled; (**b**) washed. Membrane UE50: (**c**) fouled; (**d**) washed; and membrane FP100: (**e**) fouled; (**f**) washed.

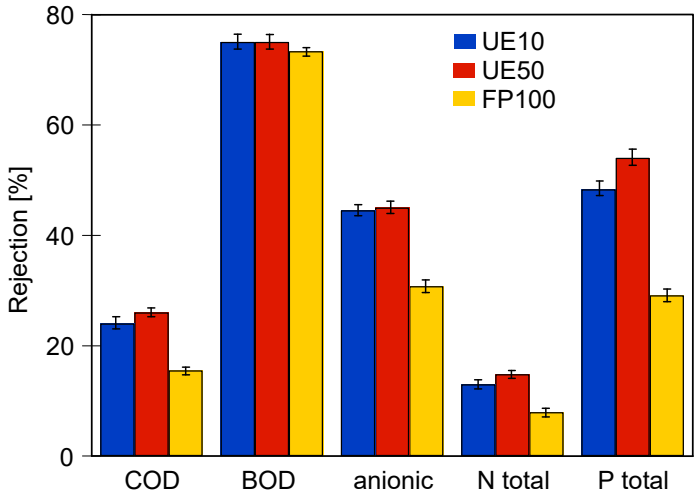

Figure 20. Removal of COD, BOD, anionic surfactants, N total, and P total during UF of carwash wastewater (Manual 2).

Table 3. Retention (R [%]) detected elements by studied membranes.

Elements	UE10	UE50	FP100
Na	2.5	3.3	1.6
K	6.3	7.1	6.4
Ca	3.3	3.3	0.8
Mg	1.5	1.5	0.1
Fe	59.2	61.2	27.1
P	50.0	54.7	23.3
Ba	23.5	23.5	8.2
Cs	23.8	23.8	9.1
Mn	30.4	30.4	12.1
Sr	6.8	6.8	6.3
Pt	0.5	0.5	0.1
Al	56.1	55.1	40.1

4. Conclusions

In the present study, it has been clearly documented that the PES and PVDF membranes (10–100 kDa) effectively removed oil contaminants from both synthetic emulsion (DI water) and carwash wastewater containing surfactants. The close to 100% removal of turbidity (NTU < 0.3) and a significant part of the remaining wastewater components allow for the obtained UF permeate, which may be used as process water in the car wash, especially at the stage of pre-washing and foam generation.

Both washing agents used in the car wash and oil contaminants cause significant fouling during carwash wastewater filtration; hence, cyclical chemical cleaning of the membranes is required. For this purpose, a 0.5% Insect solution (pH = 11.5) was applied, which is used in car washes to remove insects. Finally, it should be pointed out that membrane cleaning, carried out for 30 min and repeated 17–23 times during several weeks of UF testing, did not damage the membranes and did not affect the degree of wastewater separation achieved.

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References

1. Gönder, Z.B.; Balcıoğlu, G.; Vergili, I.; Yasemin Kaya, Y. Electrochemical treatment of carwash wastewater using Fe and Al electrode: Techno-economic analysis and sludge characterization. *J. Environ. Manag.* **2017**, *200*, 380–390. [CrossRef]
2. Jönsson, C.; Jönsson, A.-S. The influence of degreasing agents used at car washes on the performance of ultrafiltration membranes. *Desalination* **1995**, *100*, 115–123. [CrossRef]
3. Fayed, M.; Shewitah, M.A.; Dupont, R.R.; Fayed, M.; Badr, M.M. Treatability study of car wash wastewater using upgraded physical technique with sustainable flocculant. *Sustainability* **2023**, *15*, 8581. [CrossRef]
4. Kuan, W.-H.; Hu, C.-Y.; Ke, L.-W.; Wu, J.-M. A review of on-site carwash wastewater treatment. *Sustainability* **2022**, *14*, 5764. [CrossRef]
5. Wang, B.; Feng, S.; Wang, C.; Liu, X.; Chen, L.; Yan, D. Nanostructure-based oil–water separation: Mechanism and status. *Separations* **2023**, *10*, 569. [CrossRef]
6. Tang, L.; Tan, X.-j.; Cui, F.-y.; Zhou, Q.; Yin, J. Reuse of carwash wastewater with hollow fiber membrane aided by enhanced coagulation and activated carbon treatments. *Water Sci. Technol.* **2007**, *56*, 111–118. [CrossRef] [PubMed]
7. Padaki, M.; Surya Murali, R.; Abdullah, M.S.; Misdan, N.; Moslehyani, A.; Kassim, M.A.; Hilal, N.; Ismail, A.F. Membrane technology enhancement in oil–water separation. A review. *Desalination* **2015**, *357*, 197–207. [CrossRef]
8. Chakrabarty, B.; Ghoshal, A.K.; Purkait, M.K. Ultrafiltration of stable oil-in-water emulsion by polysulfone membrane. *J. Membr. Sci.* **2008**, *325*, 427–437. [CrossRef]
9. Chakrabarty, B.; Ghoshal, A.K.; Purkait, M.K. Cross-flow ultrafiltration of stable oil-in-water emulsion using polysulfone membranes. *Chem. Eng. J.* **2010**, *165*, 447–456. [CrossRef]
10. Ahmad, T.; Guria, C.; Mandal, A. A review of oily wastewater treatment using ultrafiltration membrane: A parametric study to enhance the membrane performance. *J. Water Process Eng.* **2020**, *36*, 101289. [CrossRef]
11. Behroozi, A.H.; Ataabadi, M.R. Improvement in microfiltration process of oily wastewater: A comprehensive review over two decades. *J. Environ. Chem. Eng.* **2021**, *9*, 104981. [CrossRef]
12. Mueller, J. Crossflow microfiltration of oily water. *J. Membr. Sci.* **1997**, *129*, 221–235. [CrossRef]
13. Obotey Ezugbe, E.; Rathilal, S. Membrane technologies in wastewater treatment: A review. *Membranes* **2020**, *10*, 89. [CrossRef]
14. Tummons, E.; Han, Q.; Tanudjaja, H.J.; Hejase, C.A.; Chew, J.W.; Tarabara, V.V. Membrane fouling by emulsified oil: A review. *Sep. Purif. Technol.* **2020**, *248*, 116919. [CrossRef]
15. Huang, S.; Ras, R.H.A.; Tian, X. Antifouling membranes for oily wastewater treatment: Interplay between wetting and membrane fouling. *Curr. Opin. Colloid Interface Sci.* **2018**, *36*, 90–109. [CrossRef]
16. Brinck, J.; Jönsson, A.-S.; Jönsson, B.; Lindau, J. Influence of pH on the adsorptive fouling of ultrafiltration membranes by fatty acid. *J. Membr. Sci.* **2000**, *164*, 187–194. [CrossRef]
17. El-Ashtoukhy, E.-S.Z.; Amin, N.K.; Fouad, Y.O. Treatment of real wastewater produced from Mobil car wash station using electrocoagulation technique. *Environ. Monit. Assess.* **2015**, *187*, 628. [CrossRef]
18. Ahmad, J.; Umar, M.; Karim, S.S.; Amaduddin, M.; Akhtar, K.; Shah, F.; Hussain, A. Design of a car wash waste water treatment process for local car wash stations. *J. Pak. Inst. Chem. Eng.* **2017**, *45*, 83–95.
19. Tanudjaja, H.J.; Chew, J.W. Assessment of oil fouling by oil-membrane interaction energy analysis. *J. Membr. Sci.* **2018**, *560*, 21–29. [CrossRef]
20. Antón, E.; Álvarez, R.J.; Palacio, L.; Prádanos, P.; Hernández, A.; Pihlajamäki, A.; Luque, S. Ageing of polyethersulfone ultrafiltration membranes under long-term exposures to alkaline and acidic cleaning solutions. *Chem. Eng. Sci.* **2015**, *134*, 178–195. [CrossRef]
21. Hu, C.-Y.; Kuan, W.-H.; Ke, L.-W.; Wu, J.-M. A study of car wash wastewater treatment by cyclo-flow filtration. *Water* **2022**, *14*, 1476. [CrossRef]
22. Zaneti, R.N.; Etchepare, R.; Rubio, J. Car wash wastewater treatment and water reuse—A case study. *Water Sci. Technol.* **2013**, *67*, 82–88. [CrossRef] [PubMed]

23. Aryanti, N.; Widiasa, I.N.; Susanto, H. Ultrafiltration of oil-in-water emulsion stabilized with surfactants. *IOP Conf. Ser. Mater. Sci. Eng.* **2019**, *620*, 012014. [CrossRef]
24. Moazzem, S.; Wills, J.; Fan, L.; Roddick, F.; Jegatheesan, V. Performance of ceramic ultrafiltration and reverse osmosis membranes in treating car wash wastewater for reuse. *Environ. Sci. Pollut. Res.* **2018**, *25*, 8654–8668. [CrossRef]
25. Traczek, C. Reclaim your losses. *Natl. Pet. News* **2000**, *92*, 36–38.
26. Weis, A.; Bird, M.R.; Nyström, M. The chemical cleaning of polymeric UF membranes fouled with spent sulphite liquor over multiple operational cycles. *J. Membr. Sci.* **2003**, *216*, 67–79. [CrossRef]
27. Weis, A.; Bird, M.R. The influence of multiple fouling and cleaning cycles upon the membrane processing of lignosulphonates. *Food Bioprod. Process.* **2001**, *79*, 184–187. [CrossRef]
28. Tomczak, W.; Gryta, M. Long-term performance of ultrafiltration membranes: Corrosion fouling aspect. *Materials* **2023**, *16*, 1673. [CrossRef]
29. Gryta, M.; Woźniak, P. Polyethersulfone membrane fouling mitigation during ultrafiltration of wastewaters from car washes. *Desalination* **2024**, *574*, 117254. [CrossRef]
30. Omidvar, A.; Masoumi, S.; Monsefi, M.; Jafarzadeh, Y.; ·Nasiri, M.; Hazrati, H. PVC/PMMA blend ultrafiltration membranes for oil-in-water emulsion separation. *Polym. Bull.* **2023**, *80*, 9275–9295. [CrossRef]
31. Fazullin, D.D.; Mavrin, G.V. Effect of the pH of emulsion on ultrafiltration of oil products and nonionic surfactants. *Pet. Chem.* **2017**, *57*, 969–973. [CrossRef]
32. Shi, L.; Lei, Y.; Huang, J.; Shi, Y.; Yi, K.; Zhou, H. Ultrafiltration of oil-in-water emulsions using ceramic membrane: Roles played by stabilized surfactants. *Colloids Surf. A* **2019**, *583*, 123948. [CrossRef]
33. Zhang, X.; Li, F.; Zhao, X. Treatment of surfactants with concentrations below critical micelle concentration by ultrafiltration: A mini-review. *Water Cycle* **2022**, *3*, 50–55. [CrossRef]
34. Tomczak, W.; Gryta, M. The application of polyethersulfone ultrafiltration membranes for separation of car wash wastewaters: Experiments and modelling. *Membranes* **2023**, *13*, 321. [CrossRef] [PubMed]
35. Tummons, E.N.; Chew, J.W.; Fane, A.G.; Tarabara, V.V. Ultrafiltration of saline oil-inwater emulsions stabilized by an anionic surfactant: Effect of surfactant concentration and divalent counterions. *J. Membr. Sci.* **2017**, *537*, 384–395. [CrossRef]
36. Camilleri-Rumbau, M.S.; Popovic, O.; Briceno, K.; Errico, M.; Fjerbæk Søtoft, L.; Christensen, K.V.; Norddahl, B. Ultrafiltration of separated digestate by tubular membranes: Influence of feed pretreatment on hydraulic performance and heavy metals removal. *J. Environ. Manag.* **2019**, *250*, 109404. [CrossRef]