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## Effects of Pre-ozonation on Membrane Filtration of Oil-in-water Emulsions Using Different Polymeric (PES, PAN, PTFE) Ultrafilter Membranes

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### ABSTRACT

Emulsified oily contaminants of wastewaters cannot be eliminated effectively by conventional treatments, but they pose significant risks both to the environment and to human health, therefore their efficient elimination is imperative. Membrane filtration is a promising technique for the effective purification of oil-in-water emulsions; however, the accumulation of hydrophobic contaminants on the membrane surface quickly leads to significant water flux reduction, which is a limiting factor of the economic utilization. In the present comparative study short-term ozonation was investigated as a suitable pre-treatment to achieve lower flux reduction during the separation of micro- or even nanoscale crude oil droplets by ultrafiltration with different membranes. Results confirmed that pre-ozonation modifies the surface charge (zeta-potential) of the oil droplets which resulted in the reduced accumulation of contaminants on the membrane surface and higher fluxes in the case of every investigated ultrafilter membranes: polyethersulfone (PES), polyacrylonitrile (PAN), polytetrafluoroethylene (PTFE). Filtration experiments were carried out using ultrapure and model groundwater matrices for a more thorough discussion of achievable advantages, and it was concluded that in the case of low ionic strength the PES membrane provided the highest flux; however, in the case of realistic water matrix (model groundwater) the application of acetone-conditioned PTFE ultrafilter membrane – combined with pre-ozonation – was much more beneficial. Overall, pre-ozonation decreased the total resistance in all cases; however, the reversibility of the measured filtration resistance and flux reduction was strongly dependent on both the matrix and the membrane surface material.

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## Introduction

Water source protection and clean water supply are major challenges of the 21st century (Cosgrove and Loucks 2015), and since oily contaminants of wastewaters pose significant risk to the environment and human health, their efficient elimination is imperative (Cai et al. 2018; Trinh et al. 2018; Wu et al. 2018). Conventional technologies, such as hydro cyclones, centrifugation or dissolved air floatation are inefficient in separating finely dispersed oil droplets, especially when the droplets are smaller than 20  $\mu\text{m}$  (Chakrabarty, Ghoshal, and Purkait 2008; Cheryan and Rajagopalan 1998; Lin and Rutledge 2018; Wu et al. 2018). Membrane separation techniques can be useful for the purification of both oily wastewaters – produced in large quantity by many industrial processes such as oil/gas, food and metal processing industries – and hydrocarbon contaminated groundwaters (Kota et al. 2012). Overall, microfiltration (Abadi et al. 2011; Abbasi et al. 2010; Hu and Scott 2008; Masoudnia et al. 2014; Scharnagl and Buschatz 2001;

Shokrkar et al. 2012; Wei et al. 2017) can ensure higher flux, whereas ultrafiltration (Chakrabarty, Ghoshal, and Purkait 2010; Masoudnia et al. 2014; Melbiah, Nithya, and Mohan 2017; Shokrkar et al. 2012) provides higher purification efficiency, but membrane fouling poses a major problem in both cases, which limits their utilization due to economic reasons (Cai et al. 2018; Lin and Rutledge 2018; Liu et al. 2017; Padaki et al. 2015; Tanudjaja and Chew 2018; Trinh et al. 2018; Wu et al. 2018).

Ceramic (Abadi et al. 2011; Abbasi et al. 2010; Hu et al. 2015; Hua et al. 2007; Matos et al. 2016) and different polymeric membranes, such as polysulfone – PS (Chakrabarty, Ghoshal, and Purkait 2008, Mi-Jung Um et al. 2001), polyethersulfone – PES (Chen et al. 2009a; Kiss et al. 2014; Masoudnia et al. 2014; Yin and Zhou 2015), polyacrylonitrile – PAN (Chen et al. 2009b; Melbiah, Nithya, and Mohan 2017; Salahi et al. 2010; Scharnagl and Buschatz 2001), polytetrafluoroethylene – PTFE (Hong, Fane, and Burford 2003; Hu and Scott 2007, 2008;

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Lin et al. 2011; Wang et al. 2018; Wei et al. 2017) and polyvinylidene fluoride – PVDF (Hu and Scott 2007; Masoudnia et al. 2014) are widely investigated for the elimination of oily contaminations. Among the polymeric membranes the following three are thoroughly investigated: (i) PES has excellent mechanical and chemical resistance and it is widely used because of its high stability, easy processing and environmental endurance (Van der Bruggen 2009; Yin and Zhou 2015); (ii) PAN has relatively good chemical stability and can be welded easily by heat to produce membrane envelopes used in several membrane filtration modules (Scharnagl and Buschatz 2001); (iii) PTFE membranes have outstanding durability and chemical resistance and high porosity (Wei et al. 2017); however, the originally hydrophobic membranes have to be modified or conditioned before their application in water purification. Until now, there is no general agreement about the most beneficial polymer material in relation with the membrane filtration of oil-in-water emulsions. Although membrane separation is able to satisfy the environmental standards and can ensure the reuse of wastewater, but there is a general agreement, that the adhered hydrophobic contaminants result in the deterioration of performance, with a consequent increase of energy and membrane replacement costs. Thus, the development of possible solutions for this problem is of great interest.

Investigations regarding fouling mitigation solutions can be divided into two main groups: (i) the development of antifouling membranes with novel membrane materials or modified commercial membrane surfaces (Yin and Zhou 2015; Van der Bruggen 2009; Kertész, Cakl, and Jiráňková. 2014; Wang et al. 2018, Fard et al. 2018; Hou et al. 2018; Cai et al. 2018; Chen et al. 2009b; Melbiah, Nithya, and Mohan 2017); and (ii) investigation of suitable pre-treatments, such as destabilization, ion exchange, gas injection, oxidation which can reduce the adherence and the accumulation of contaminants on the surface and in pores (Matos et al. 2016; Metcalfe et al. 2016; Park 2002; Um et al. 2001; Xue et al. 2016; Zouboulis, Zamboulis, and Szymanska 2014). The fouling mechanism is determined mostly by the electrostatic and van der Waals interactions between the colloidal particles and the membrane surface (Lin, Lu, and Chen 2014; Liu et al. 2017; Tanudjaja and Chew 2018; Wu et al. 2018) and is also influenced by the same interactions between the particles, since the type of membrane fouling which is caused by oil droplets has the following characteristic stages: droplet attachment, clustering, deformation and coalescence as it was described by (Tummons et al. 2016) (Tummons et al. 2016). Pre-ozonation can cause beneficial changes in these interactions via partial oxidation, which results in lower filtration resistance and/or higher purification

efficiency in the case of various water contaminants, e.g. antibiotics (Alpatova, Davies, and Masten 2013), humic acid (Byun, Taurozzi, and Tarabara 2015; Jermann et al. 2008), natural organic matters (NOMs) (Cheng et al. 2016) and other pollutants (Guo et al. 2014; Hyung et al. 2000; Kiss et al. 2014; Park 2002; Yu, Graham, and Fowler 2016; Zouboulis, Zamboulis, and Szymanska 2014). Moreover, in our previous studies (Veréb et al. 2018, 2017) it has been proven that applying appropriate filtration conditions, short-term pre-ozonation of oil-in-water emulsions can result in higher flux and lower resistance during microfiltration.

To extend our previous investigations, in the present comparative study the combination of pre-ozonation with ultrafiltration was examined in detail. Achievable fluxes and different filtration resistances (membrane, reversible and irreversible resistances) were measured at different filtration conditions in the presence and absence of a short-term pre-ozonation. Moreover, using the optimal filtration parameters three different, widely used polymeric ultrafilter membranes (i.e. PES, PAN and PTFE) were compared concerning the achievable fluxes, reversible and irreversible filtration resistances, fouling mechanisms and purification efficiencies to get information about the surface material-dependance in these aspects. Benefits provided by the pre-ozonation regarding the above-mentioned membranes were also compared. According to the DeJaguin-Landau-Verwey-Overbeek (DLVO) theory (Brant and Childress 2002), the typical inorganic water components, such as carbonate, sulfate, chloride anions and sodium, calcium, magnesium, potassium, iron cations can modify the interactions between the contaminants and the membrane surface. Therefore, the quality of the water matrix can also affect the adherence of the contaminants and the resulting fouling mechanisms, thus the experiments were carried out in ultrapure water and model groundwater for an in-depth discussion of attainable advantages of pre-ozonation.

## Materials and methods

### Production of oil-in-water emulsions

Oil-in-water emulsions ( $c_{\text{crude oil}} = 100 \text{ mg L}^{-1}$ ) were prepared by intensive stirring (35000 rpm; Skil F0151415AC, China) for 1 minute followed by ultrasonic homogenization (Hielscher UP200S, Germany) at 24 kHz frequency (100% amplitude and pulse) for 10 minutes at 25°C, using crude oil as contaminant (provided by MOL Zrt. from Algyó, Hungary), and ultrapure water (PureLab Pulse, ELGA LabWater, UK) or model groundwater as investigated matrices. The composition of model groundwater was very similar to the real groundwater located in South Hungary

containing the following salts: 2.26 g L<sup>-1</sup> NaHCO<sub>3</sub>, 53.4 mg L<sup>-1</sup> NH<sub>4</sub>Cl, 19.1 mg L<sup>-1</sup> CaCl<sub>2</sub>, 20.9 mg L<sup>-1</sup> KCl, 93.5 mg L<sup>-1</sup> NaCl, 4.5 mg L<sup>-1</sup> FeCl<sub>3</sub> and 35.1 mg L<sup>-1</sup> MgSO<sub>4</sub> (Sigma Aldrich; analytical grade). In the case of model groundwater the pH value was 8.2 ± 0.1, while in the case of ultrapure water it was 5.2 ± 0.1. The size distribution of oil droplets and zeta potentials were measured by dynamic light scattering (Malvern ZetaSizer4, UK; λ = 633 nm, T = 25 ± 0.1°C) directly after their production and their pre-ozonation.

### Pre-ozonation

The ozone was generated from clean oxygen (Messer; 3.5) by a flow-type ozone generator (BMT 802N, Germany) and it was bubbled through a diffuser into a batch reactor containing 400 mL of the given oil-in-water emulsion, equipped with a magnetic stirrer. The applied flow rate was 1 L min<sup>-1</sup> and the ozone concentration of the inlet and outlet was measured using a WPA Biowave II type UV spectrophotometer (λ = 254 nm) to determine the absorbed volume of ozone. If pre-ozonation was applied, its duration was only 5 minutes in all cases, as our previous studies (Veréb et al. 2018, 2017) proved that longer pre-ozonation can result in pore blocking, due to the fragmentation of oil droplets, and lower purification efficiency because of the generated water-soluble organic oxidation by-products. The applied 5 min long pre-ozonation resulted in 30 ± 5 mg L<sup>-1</sup> absorbed ozone dose. After the treatment the remaining dissolved ozone was purged by oxygen to avoid the damage of the used membrane.

### Membrane filtration experiments

Membrane filtration experiments were carried out in a batch-stirred membrane reactor (Millipore XFUF07601, USA), which was equipped with circular (76 mm diameter; active filtration area: 37.4 cm<sup>2</sup>) PES, PAN and PTFE ultrafilter (UF) membranes (New Logic Research INC, USA), with a pore size of 50 nm. The PTFE, due to its hydrophobicity, was conditioned with 100 mL acetone (Spektrum 3D, 99.5% purity) for 1 h and then rinsed with ultrapure water to eliminate the unadhered acetone from the surface. This conditioning method (Hong, Fane, and Burford 2003) ensured high water flux through the originally hydrophobic membrane via the formation of a thin polar layer on the surface and inside the pores. In the case of hydrophilic PES and PAN membranes, simple water soaking was applied before the experiments. Using PES UF membrane, various filtration parameters were applied, such as 0.1 and 0.3 MPa transmembrane pressure and 50 and 350 rpm stirring speed in the case of both utilization and omission of short-term

pre-ozonation. During the comparison of the three different membranes, the estimated optimal filtration parameters (0.1 MPa transmembrane pressure and 350 rpm stirring speed) were applied in the case of both the presence and absence of short-term pre-ozonation. In all cases, 250 mL of initial volume was filtered until the production of 200 mL permeate (and 50 mL of retentate), which resulted in a volume reduction ratio (VRR) of 5.

The total filtration resistance ( $R_T$ ) was calculated from the steady-state flux by using the resistance-in-series model described as follows:

$$R_T = R_M + R_{Irrev} + R_{Rev} [m^{-1}] \quad (1)$$

where  $R_M$  is the own resistance of the membrane,  $R_{Irrev}$  is the irreversible filtration resistance and  $R_{Rev}$  is the reversible resistance. The membrane resistance ( $R_M$ ) was calculated as:

$$R_M = \frac{\Delta p}{J_W \eta_W} [m^{-1}] \quad (2)$$

where  $\Delta p$  is the transmembrane pressure [Pa],  $J_W$  is the water flux of the clean (unused) membrane [m<sup>3</sup> m<sup>-2</sup> s<sup>-1</sup>] and  $\eta_W$  is the viscosity of the water [Pa s]. The irreversible resistance ( $R_{Irrev}$ ) was determined by re-measuring the water flux of the used membrane after the filtration, followed by a purification step (intensive rinsing with distilled water):

$$R_{Irrev} = \frac{\Delta p}{J_{WA} \eta_W} - R_M [m^{-1}] \quad (3)$$

where  $J_{WA}$  is the water flux after the cleaning procedure. The reversible resistance ( $R_{Rev}$ ; caused by the unadhered oil layer and concentration polarization layer) can be calculated as:

$$R_{Rev} = \frac{\Delta p}{J_c \eta_{WW}} - R_{Irrev} - R_M [m^{-1}] \quad (4)$$

where  $J_c$  is the flux at the end of the filtration of the given oil-in-water emulsion and  $\eta_{ww}$  is the viscosity of the emulsion.

To evaluate the fouling resistance of the membranes in different conditions, the flux decay ratio (DR) and flux recovery ratio (FRR) were also calculated:

$$DR = \frac{J_w - J_c}{J_w} 100\% \quad (5)$$

$$FRR = \frac{J_{WA}}{J_w} 100\% \quad (6)$$

where  $J_W$  is the water flux of the clean membrane,  $J_c$  is the flux at the end of the filtration of the given oil-in-water emulsion and  $J_{WA}$  is the water flux after the cleaning

procedure. To characterize the membrane fouling mechanisms, the widely used (Bowen, Calvo, and Hernández 1995; Hermia 1982; Hu and Scott 2008; Zhao et al. 2016) *Hermia* filtration law – consisting of complete, internal, and intermediate pore blocking and cake layer formation – can also be applied as a mathematical model. Under constant pressure, which was applied during the filtration experiments, the equation is:

$$\frac{d^2t}{dV^2} = k \left( \frac{dt}{dV} \right)^n \quad (7)$$

where  $t$  is filtration time,  $V$  is the volume of the permeate,  $k$  is a constant and  $n$  is a value illustrating the different fouling mechanism (complete pore blocking:  $n = 2$ , intermediate pore blocking:  $n = 1$ , internal pore blocking:  $n = 1.5$ , cake layer formation:  $n = 0$ ). More detailed description of the investigated filtration laws and their utilization can be found in our recent paper (Veréb et al. 2018) and in other publications (Aryanti, Wardhani, and Supandi 2016; Brião and Tavares 2012; Hermia 1982; Iritani and Katagiri 2016).

### Membrane surface characterization

The hydrophilicity of the investigated membranes was characterized by measuring the contact angle formed between the membrane surface and distilled water. Ten microliters of distilled water were carefully dropped onto the surface and immediately measured. The measurements were carried out using the sessile drop method (Dataphysics Contact Angle System OCA15Pro, Germany) and were repeated five times to calculate the average values. In the case of PES membrane, the contact angle was determined to be  $55.9 \pm 0.8^\circ$ , which was  $34.1 \pm 0.5^\circ$  for the PAN membrane. The pure PTFE membrane was hydrophobic as the contact angle was  $105.5 \pm 2.5^\circ$ , but after the acetone conditioning, the surface became so hydrophilic, that the contact angle could not be measured (it can be regarded as zero).

### Purification efficiencies

The purification efficiencies were determined by measuring the chemical oxygen demand (COD) and the extractable oil content (TOG/TPH) of the feed and the permeate. COD was measured by a standard potassium-dichromate oxidation-based method, using standard test tubes (Lovibond). The digestions were carried out in a COD digester (Lovibond, ET 108) for 2 h at  $150^\circ\text{C}$  and the COD values were measured with a COD photometer (Lovibond PC-CheckIt). Extractable oil content was measured by a Wilks InfraCal TOG/TPH

type analyzer, using hexane as extracting solvent. The purification efficiency ( $R$ ) was calculated as:

$$R = \left( 1 - \frac{c}{c_0} \right) \cdot 100\% \quad (8)$$

where  $c_0$  is the COD or the TOG/TPH value of the feed and  $c$  indicates the values of the permeate.

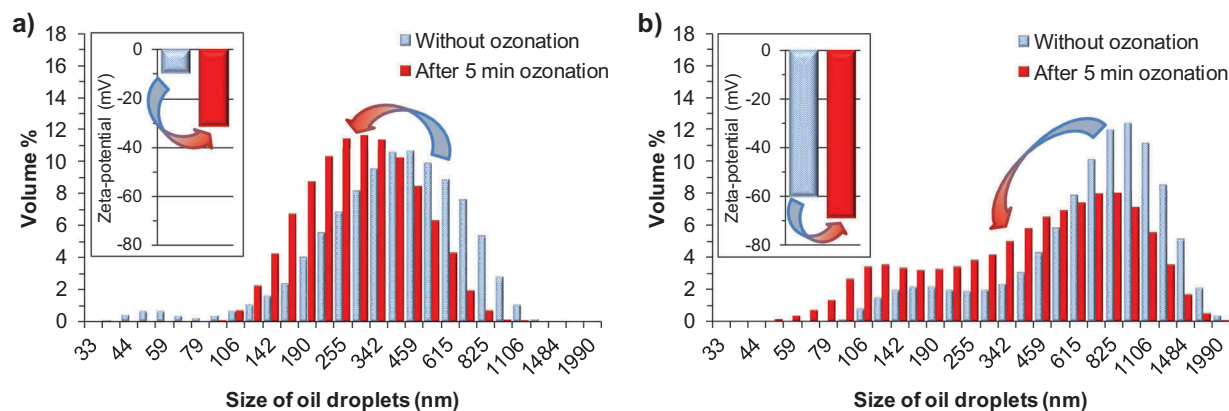
## Results and discussion

### Characterization of the prepared and the pre-ozonized emulsions

Firstly, the size distribution and zeta-potential value of the two different oil-in-water emulsions (prepared in ultrapure and model groundwater matrices) were determined by dynamic light scattering in the case of both the presence and absence of the 5 min pre-ozonation (Figure 1). Similar changes were observed in both emulsions: the size distributions shifted to the smaller droplet sizes, whereas the zeta-potential values indicated more negative charged surfaces after pre-ozonation. However, there are some notable differences between the two matrices: in the case of groundwater matrix, the emulsion contained significant amount of slightly bigger droplets (in the 1106–1990 nm region) compared to ultrapure water matrix both in the case of pre-ozonized or untreated emulsions, which could be caused by the possible coagulation effect of the higher ionic strength and the presence of iron(III) ions and formed iron(III)-oxide-hydroxides. Moreover, in case of ultrapure water matrix the pre-ozonation eliminated all the detectable amount droplets smaller than 106 nm, whereas in the case of groundwater matrix, ozonation resulted in the slight production of nanoscale oil droplets (Figure 1,  $d = 51 - 106$  nm region). This can be related to different oxidation pathways, since in groundwater matrix the pH value was 8.2, due to the relatively high amount of hydrogen carbonate ions, which results in the production of high amount of  $\text{OH}\cdot$  radical. In the case of pure water matrix, characterized by lower pH value (5.2), the direct oxidation of ozone is dominant (Hoigné and Bader 1983).

### Effect of filtration parameters on the ultrafiltration of the emulsions

As the next step, the beneficial filtration properties, such as the transmembrane pressure and stirring intensity were investigated in the case of PES UF membrane using two different transmembrane pressure values (0.1 and 0.3 MPa) and two different stirring speeds (50 and 350 rpm) during

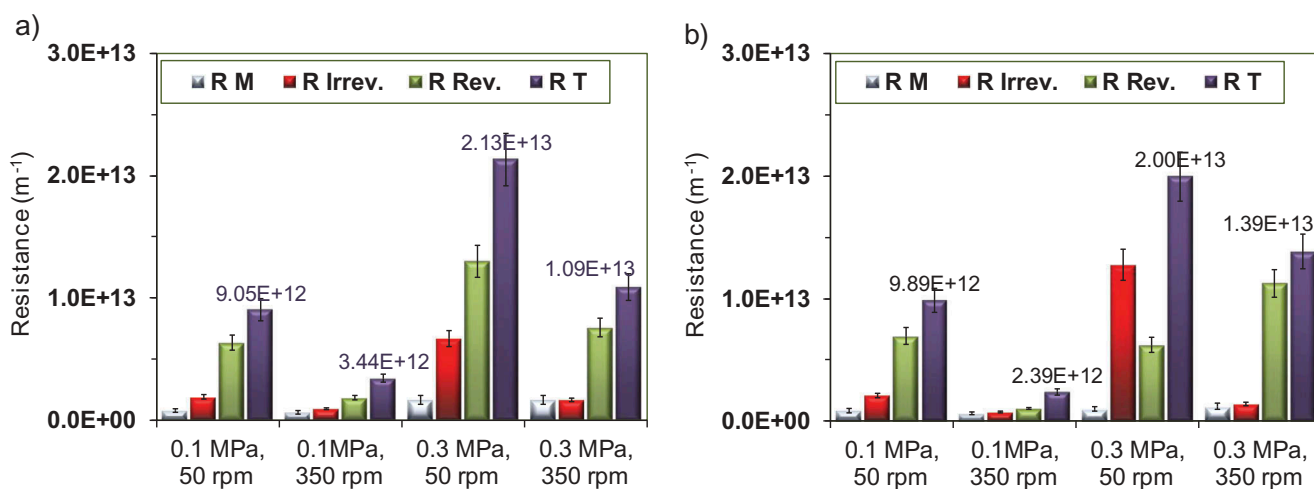


**Figure 1.** Effects of pre-ozonation on size distribution and zeta-potential values of the oil droplets in the case of (a) ultrapure water matrix and (b) model groundwater matrix.

the ultrafiltration of both pre-ozonized and not pre-treated emulsions. Different filtration resistances ( $R$ ), such as the own resistance of the used membrane ( $R_M$ ), the reversible resistance ( $R_{Rev}$ ) and the irreversible resistance ( $R_{Irrev}$ ) were measured by applying the previously detailed calculations (for more details see section 2.3.) and as the sum of these values the total resistance ( $R_T$ ) was also determined (Figure 2). Both Figure 2a (not pre-treated emulsion) and Figure 2b (pre-ozonized emulsion) represent that more intense stirring significantly reduced the total resistance, and the same is true for lower transmembrane pressure.

Higher stirring speed resulted in decreased adherence ability of the oil droplets, while higher transmembrane pressure could promote the second and the third stages of membrane fouling mechanism, which are the clustering of the droplets followed by deformation and coalescence. These steps finally can produce a hydrophobic layer acting as a water barrier on the membrane surface and its thickness correlates with the lower stirring intensity.

Moreover, high transmembrane pressure can support the entering of the adhered oily contaminants into the pores. These mechanisms explain why the highest irreversible resistances were measured at the lowest stirring speed coupled with the highest transmembrane pressure. Furthermore, in the case of the ultrafiltration of the investigated oil-in-water emulsions, the absolute value of the flux could not be increased even with three times higher transmembrane pressure. At 350 rpm stirring speed, the 0.1 MPa transmembrane pressure resulted in 105 and 151  $L m^{-2} h^{-1}$  final fluxes, in the case of the absence and the presence of the pre-ozonation, respectively, whereas these values were 100 and 78  $L m^{-2} h^{-1}$  by applying 0.3 MPa pressure, respectively. (Abadi et al. 2011) (Abadi et al. 2011) observed similar results as the flux was nearly constant at the 0.075 – 0.175 MPa transmembrane pressure region during the microfiltration of oily wastewater with ceramic membrane. The results are also in line with our previous publication (Veréb et al.



**Figure 2.** Effects of transmembrane pressure and stirring speed on the filtration resistances of PES membranes during the ultrafiltration of (a) not pre-ozonized and (b) pre-ozonized emulsions.

2017), in which similar investigations were carried out using a microfilter membrane. Although the pre-ozonation was able to modify the surface charge of the droplets (see Figure 1) and to reduce their adherence onto the surface, but once the unfavorable filtration properties – slow stirring, and high pressure – overcompensated the increased electrostatic forces, the fragmented droplets were able to create a more significant barrier on the membrane surface. This is indicated by the much higher irreversible resistance in the case of the pre-ozonized emulsion, when 0.3 MPa transmembrane pressure and 50 rpm stirring speed were applied. Considering the above-mentioned results, low transmembrane pressure and intensive stirring are crucial parameters for the ultrafiltration of oil-in-water emulsions to prevent the adherence of oil droplets on the surface and/or their entrance into the pores. Moreover, based on the results from Figure 2, the significant beneficial effect of pre-ozonation on filtration resistance can be realized only by using these conditions.

#### Effects of pre-ozonation on membrane filtration in the case of different UF membranes

After the determination of beneficial transmembrane pressure and stirring speed, the effects of pre-ozonation on achievable fluxes and filtration resistances were investigated in the case of different UF membranes. Oil-in-water emulsions prepared in both ultrapure and model groundwater matrices, were filtered with PES, PAN and PTFE ultrafilter membranes, by applying 0.1 MPa transmembrane pressure and 350 rpm stirring speed, with and without the utilization of 5 min pre-ozonation until the volume reduction ratio was 5. Figure 3 represents the measured flux curves in the case of ultrapure water matrix, while Figure 4 in the case of groundwater matrix.

In the case of ultrapure water matrix (Figure 3) during the filtration of the non-ozonized emulsions (Figure 3a) the fluxes were quickly reduced in the case of all the investigated ultrafilter membranes. The highest flux was measured with the use of PES membrane, as detailed below. In the case of pre-ozonized emulsions (Figure 3b) a more rapid flux reduction was observed, but at higher volume reduction rates (VRR = 3 – 5) considerably higher fluxes were measured in all cases (compared to the filtration of the not pre-ozonized emulsion with the same membrane; see Figure 3a, b): at the end of the experiments (VRR = 5) the measured fluxes were 2.94, 2.41 and 1.25 times higher in the case of PAN, PTFE and PES membranes, respectively. As a result of the modified flux curves, the total filtration time significantly decreased from 2689 and 3568 s to 1456 and 2158 s in the case of PAN and PTFE membranes, respectively, while just a slight decrease was observed in the case of the PES membrane (from 1287 to 1259 s).

In the case of model groundwater matrix (Figure 4), during the filtration of the non-ozonized emulsions (Figure 4a), at the beginning of the experiments significantly higher fluxes were measured compared to the ultrapure water matrix-based emulsions for all three membranes (see the y axes of Figures 3 and 4), which were attributed to the significantly larger and more negative oil droplets in this water matrix. However, at higher volume reduction rates (VRR = 3 – 5), considerably lower fluxes were stabilized, which suggest the continuous accumulation of the contaminants on the membrane surface. Despite the drastic flux reductions observed for all three membranes, it seems that in this case (Figure 4a) the PTFE ultrafilter membrane provided by far the highest flux and the slowest flux reduction ( $106 \text{ L m}^{-2} \text{ h}^{-1}$ ; at VRR = 5), whereas there was no significant difference

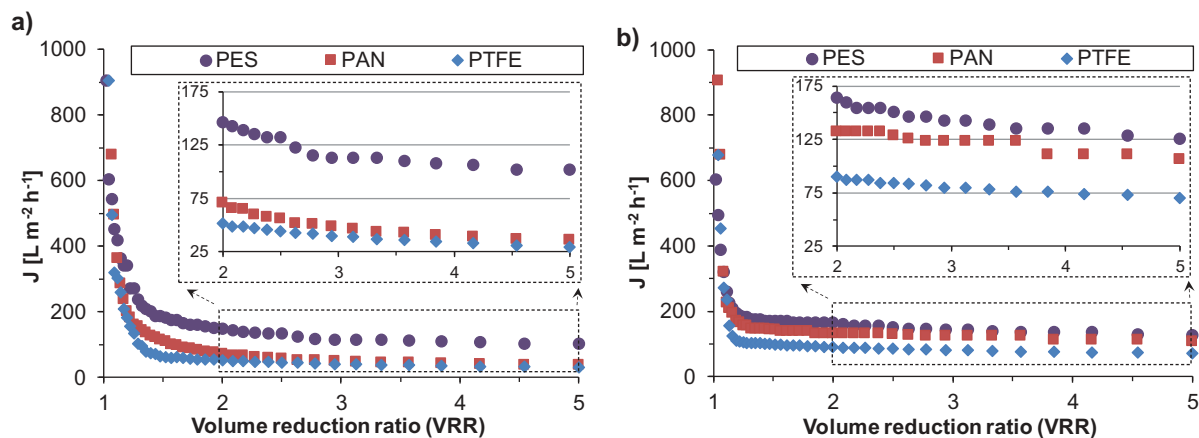
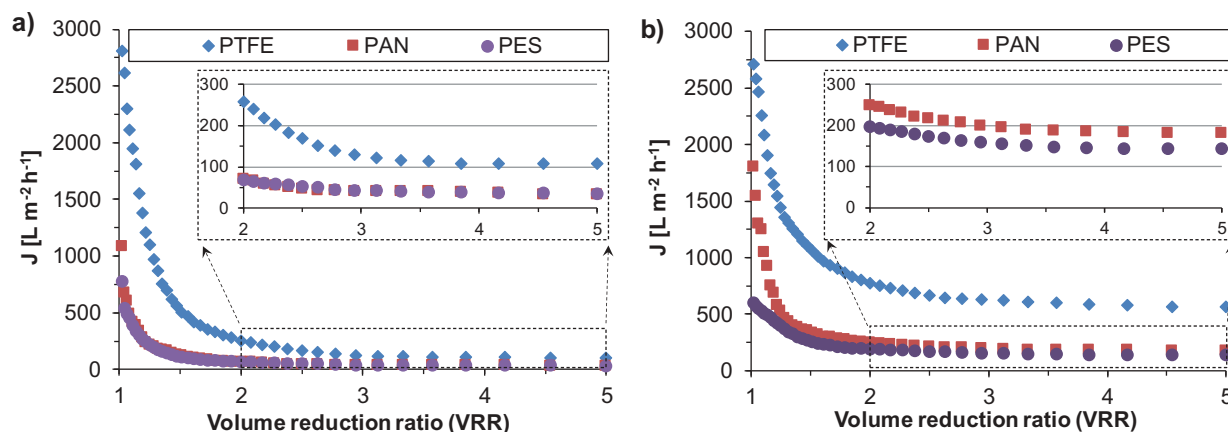


Figure 3. Flux curves measured during the ultrafiltration of oil-in-water emulsions prepared in ultrapure water matrix in the case of (a) not pre-ozonized and (b) pre-ozonized emulsions.



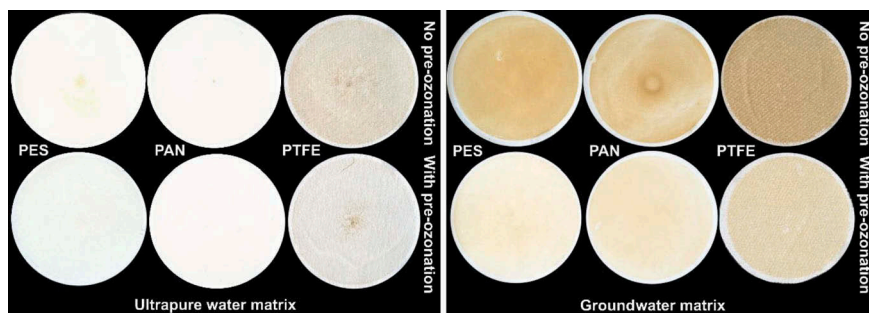
**Figure 4.** Flux curves measured during the ultrafiltration of oil-in-water emulsions prepared in model groundwater matrix in the case of (a) not pre-ozonized and (b) pre-ozonized emulsions.

between the PES and PAN membranes, both yielding negligible fluxes ( $36$  and  $39 \text{ L m}^{-2} \text{ h}^{-1}$ , respectively). After the short-term pre-ozonation of the emulsions, much higher stabilized fluxes were measured (Figure 4b) in the case of all three investigated membranes ( $574$ ,  $142$  and  $180 \text{ L m}^{-2} \text{ h}^{-1}$  using PTFE, PES or PAN membranes, respectively), and the utilization of PTFE membrane resulted again the highest flux. Moreover, the beneficial effect of pre-ozonation on the flux was most significant when the PTFE membrane was applied, shown by the  $5.41$  times higher flux. In the case of groundwater matrix the necessary total filtration times were also significantly decreased by the pre-ozonation in all cases, from  $667$ ,  $2797$  and  $2841 \text{ s}$  to  $202$ ,  $881$  and  $687$ , respectively, in the case of PTFE, PES and PAN membranes, respectively.

The determined higher fluxes caused by the short-term pre-ozonation of both emulsions are in parallel with the visually observed thinner contaminant layer seen on the photographs of the used membranes (Figure 5). However, in terms of flux reduction, the amount of contaminants influence it to a lesser extent compared to other, more important aspects. This can be confirmed by the following observations: in the

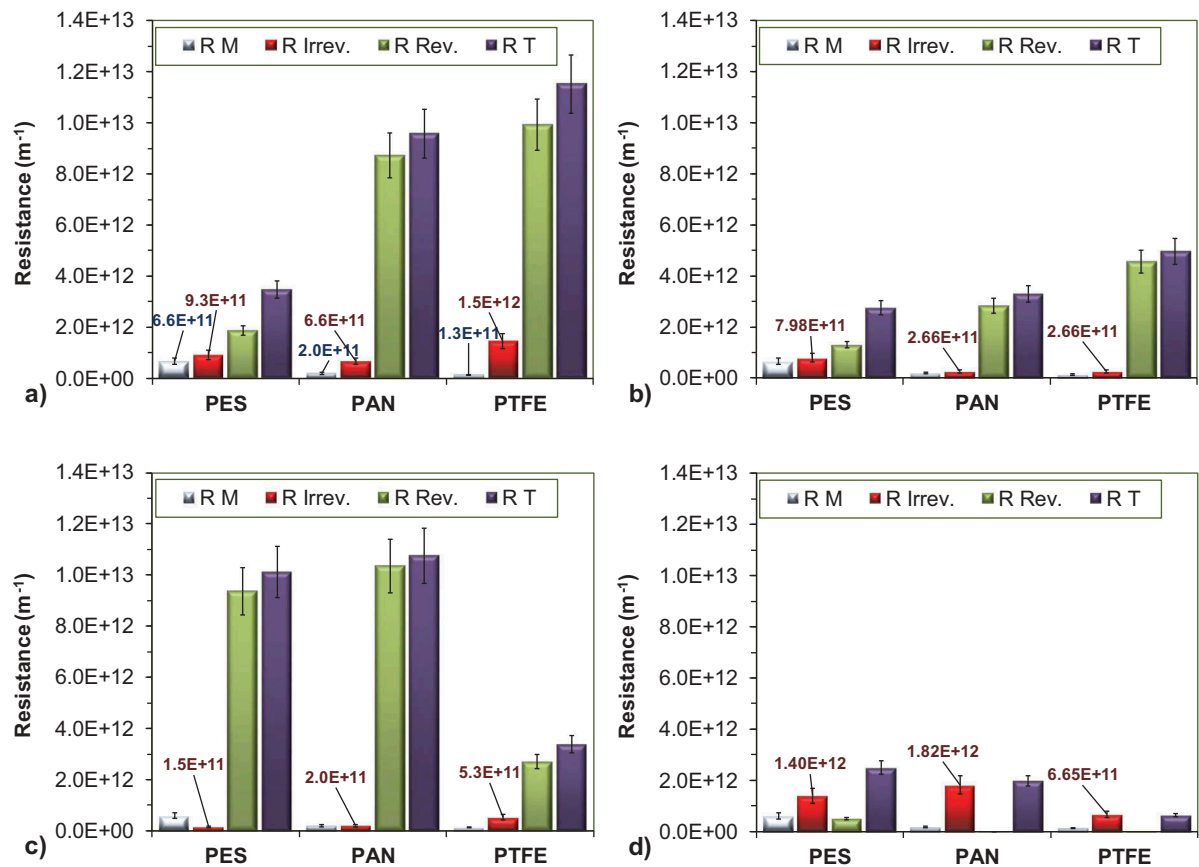
absence of pre-ozonation the PES membrane provided the highest flux in the case of ultrapure water matrix and the PTFE membrane when model groundwater matrix was used, but these membranes were not less contaminated than the other membranes in the same series (see in Figure 5a the PES and PAN membranes and in Figure 5b the PTFE and PAN membranes). Therefore, as it was expected, the structural and surface properties of the cake layer and also the interactions between the membrane surface and the contaminants play a greater role in flux reduction.

For the further discussion of these results the previously detailed filtration resistances, such as membrane ( $R_M$ ), reversible ( $R_{Rev.}$ ) and irreversible ( $R_{Irrev.}$ ) resistances were calculated in each case (Figure 6). In the case of the ultrapure water matrix, when pre-ozonation was not applied (Figure 6a) the PES membrane provided by far the lowest total resistance, whereas on PAN and PTFE membranes much higher total resistances were determined, caused mainly by the remarkable reversible resistances. In the case of PAN membrane the estimated high resistance can be related to the processes, which were thoroughly described by



**Figure 5.** Photographs of the used membranes in the case of (a) ultrapure water matrix and (b) model groundwater matrix.





**Figure 6.** The calculated membrane ( $R_M$ ), reversible ( $R_{Rev.}$ ), irreversible ( $R_{Irrev.}$ ) and total ( $R_T$ ) resistances, in the case of (a,b) ultrapure water matrix and (b, c) model groundwater matrix, (a, c) without and (b, d) with the utilization of pre-ozonation.

(Chen et al. 2009b) (Chen et al. 2009b) during the microfiltration of oil-in-water emulsion with PAN membrane. They reported that the relatively higher initial water flux caused a rapid buildup of a significant concentration polarization layer, and hydrophobic interactions between the oil droplets and the membrane surface resulted intense coalescence. In the case of PTFE membrane, the presence of acetone (which was used for surface conditioning) provided not only outstanding water flux at the beginning of the filtration, but also the possibility of better adherence of the highly hydrophobic oil droplets, resulting in similar processes like in the case of PAN membrane. The determined highest irreversible resistance of these series for the PTFE membrane is also in good agreement with these mechanisms.

Pre-ozonation resulted in the formation of significantly more negatively charged surfaces of the oil droplets as the zeta-potential value decreased from  $-9.6$  mV to  $-31.7$  mV (Figure 1a). In relation with the DLVO theory, which determine the interactions between the surfaces as the resultant of electrostatic and Van der Waals forces, the following can be considered: more negative oil droplets resulted in significantly increased

repulsive electrostatic forces between the droplets and the membrane surface, therefore the previously major van der Waals interactions were suppressed, since the value of these polar/nonpolar character-based interactions decreases with the distance between the droplets and the membrane surface. As a result of these changes, the total resistances were significantly decreased via the pre-ozonation, mostly in the case of the PAN and PTFE membranes (Figure 6b). The suppressed van der Waals interactions can also be confirmed by the significantly lower irreversible resistances of the PAN and PTFE membranes compared to the filtration of the not pre-ozonized emulsions (Figure 6a,b). Moreover, the increased repulsive electrostatic forces between the droplets contributed to the formation of a less compact oil layer and can be interpreted as a barrier against the clustering of the droplets which is the second stage in the fouling mechanism (Tummons et al. 2016).

In the case of model groundwater matrix very different results were observed. On one hand, during the filtration of not pre-ozonized emulsions much thicker and more colorful cake layers formed on all membranes (Figure 5b), compared to the ultrapure water matrix (Figure 5a). This can be related to the presence of

iron(III)-oxide-hydroxides, promoting the accumulation of the complex contaminants. On the other hand, in the case of PES and PAN membranes significantly higher, whereas in the case of PTFE membrane much lower reversible resistances were measured, in comparison with the ultrapure water matrix (Figure 6a,c). Therefore, the increased reversible resistances in the case of PES and PAN membranes are more likely originating from the contaminant/membrane interactions than the contaminant/contaminant interactions. Furthermore, this also indicates that the acetone-conditioned PTFE surface resulted in significantly inhibited interactions between the membrane and contaminants. After pre-ozonation, significantly less amount of the contaminants was accumulated on the membranes (Figure 5b) and negligible reversible resistances were measured (Figure 6d) on all three investigated membranes. This can be explained by the more negatively charged oil droplets (see the zeta-potential values in Figure 2b) which resulted in increased electrostatic repulsive force between the droplets themselves, and between the droplets and membrane surfaces. On the other hand, in the case of this water matrix, pre-ozonation resulted in the significant fragmentation of the droplets and the appearance of nano-scale droplets ( $d < 100$  nm; Figure 2b), which can also be attributed to the increased irreversible resistances in the case of PAN and PES membranes. In the case of the PTFE membrane, only a slight increase of the irreversible resistance was measured; therefore, with the nearly zero reversible resistance, PTFE membrane provided the lowest total filtration resistance by far.

The fouling resistance of the membranes was also investigated, which can be characterized by the flux decay ratio (DR) and flux recovery ratio (FRR). For a deeper discussion of the effect of pre-ozonation on the ultrafiltration, and the effect of the water matrix on the combined treatment, the DR and FRR values were

also calculated (Figure 7a and b). As the lower DR and higher FRR values mean better antifouling properties, the following observations have to be discussed.

In relation with the DR values, which can be interpreted as the percentage decline of the original flux at the end of the filtration – but has no correlation with the exact flux values –, pre-ozonation resulted in higher antifouling properties in all cases (Figure 7a). The antifouling effect of pre-ozonation was more significant in the case of the realistic groundwater matrix, as pre-ozonation resulted in the decrease of DR values from 94.1, 98.1 and 96.1 to 76.1, 91.6 and 78.8, respectively, in the case of PES, PAN and PTFE membranes, respectively. Although, the decrease of DR values are similar in the case of PES and PTFE membranes, the PTFE membrane showed by far the highest flux at the end of the filtration of the emulsion (Figure 4b), while the low DR value in the case of PES membrane can be related more likely to the low original flux than to the good applicability of this membrane for the filtration of this emulsion.

FRR values can be interpreted as a percentage recovery of the original water flux after the purification procedure, but has no correlation with the exact original flux, nor with the flux during the filtration of the emulsion. Regarding the FRR values, pre-ozonation resulted in increased antifouling properties only in the case of the ultrapure water-based emulsion, mostly in the case of PTFE (FRR increased from 8.3 to 33.3). In the case of groundwater matrix, pre-ozonation had nearly no effect on FRR (a slight decline from 20.0 to 16.7 was calculated) in the case of PTFE membrane, despite the fact, that the exact value of the flux significantly increased via the pre-ozonation (Figure 4a,b), due to the drastic reduction of the reversible resistance (Figure 6c,d). In the case of PES and PAN membranes, pre-ozonation significantly decreased the FRR values from 79.6 and 50.0 to 30.0 and 8.4, respectively, despite the significantly reduced total resistance, but this is in line with the

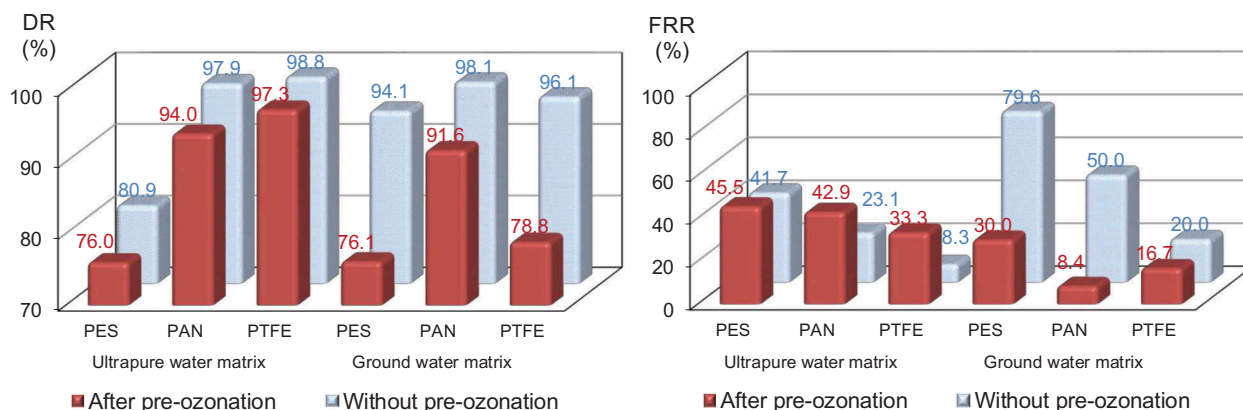


Figure 7. (a) Flux decay ratios (DR) and (b) flux recovery ratios (FRR) at different conditions.

determined increased irreversible resistances (Figure 6c,d). Considering that zeta potential values become more negative after pre-ozonation, at this point the reduced FRR values in the case of groundwater matrix can be related to two different causes: (1) the intensive droplet fragmentation (Figure 1b) or (2) the oxidation-caused changes of the surface polarity of the iron(III)-oxide-hydroxide-containing complex contaminants. Both of these interpretations can be connected to the highly oxidative  $\text{OH}\cdot$  production in this matrix.

### Membrane fouling models

For further characterization of the fouling mechanisms in different conditions, the widely used Hermia filtration law was also applied to determine which fouling model (complete pore blocking, intermediate pore blocking, internal pore blocking or cake layer formation) describes the measured flux curves the best. The rates of different  $R^2$  values can also indicate the possible contribution of the other three fouling mechanisms. The linearized forms of the models (Aryanti, Wardhani, and Supandi 2016; Hermia 1982; Veréb et al. 2018) were fitted onto the measured flux curves, and the correlation coefficients were determined (Figure 8a,b).

Figure 8a,b show that cake layer formation gave the best fitting in all cases, but some interesting differences were observed. In the case of the absence of pre-ozonation – particularly in the case of model ground water matrix – apart from the cake layer formation model, the intermediate pore blocking model also gave good fitting, but after pre-ozonation the fitting of this model was worse in both matrices. This can be interpreted as less amount of blocked pores on the surface, which is in good agreement with the observed higher fluxes and lower total filtration resistances after the pre-ozonation, in the cases of both matrices and all the used membranes. It is also shown that the higher irreversible resistances in the case of the ground water

matrix caused by pre-ozonation (Figure 6c,d) were more likely related to the changes of the cake layer, the interactions between the contaminants and the membrane surface, than to the droplet fragmentation. The fouling constants of the best fitting cake layer formation model were also calculated (Figure 9). These fouling constant values are in line with the total resistance values (Figure 4) and represents well, that the pre-ozonation resulted in the reduction of the total fouling effect of the formed cake layer in the cases of both matrices and all the used membranes. In ultrapure water matrix, the slowest fouling was observed during the application of the PES membrane, whereas in model groundwater matrix, the PTFE membrane showed the slowest fouling.

### Purification efficiencies

The purification efficiencies were also determined in all cases by measuring the chemical oxygen demand and the extractable oil content of the permeates, but no significant differences were observed. The purification efficiencies were higher than 99% in all cases, as it was expected from the oil droplet size distributions and pore sizes of the used ultrafilter membranes. In addition, it can be noted, that ozonation can produce water-soluble organic compounds from the oily pollutants, which are able to easily flow through the ultrafilter membranes, but the applied short-term pre-ozonation did not result a measurable increase in the organic contaminant content of the permeates.

### Conclusions

Low transmembrane pressure and intense stirring proved to be crucial parameters during the ultrafiltration of oily emulsions for the mitigation of the accumulation of the droplets on the membrane surface. Moreover, significant beneficial effect of pre-ozonation on filtration resistance could be realized only by using these conditions.

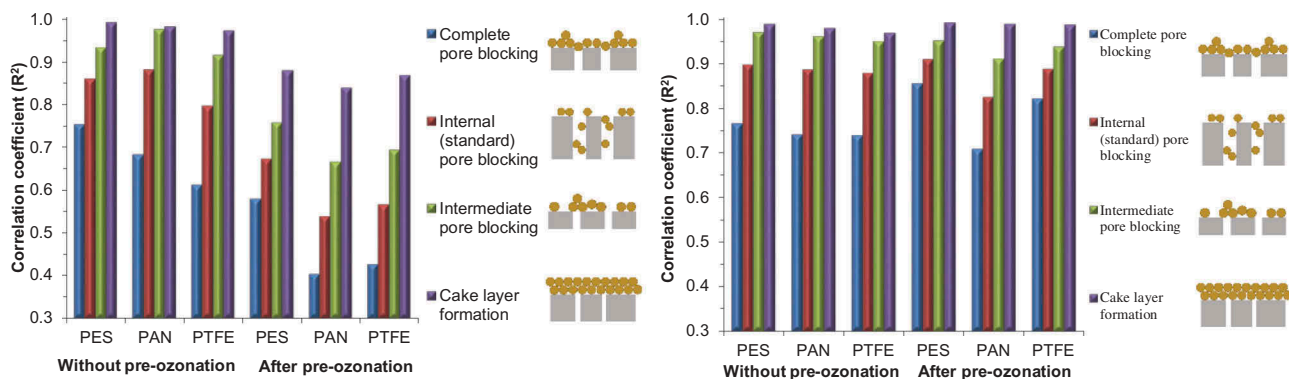
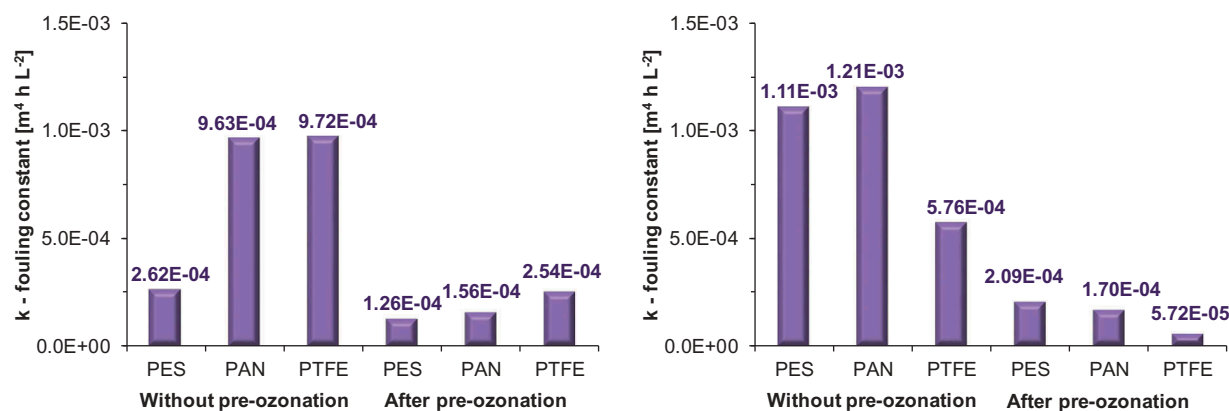


Figure 8. Correlation coefficient ( $R^2$ ) values of the fitted fouling models in the case of (a) ultrapure water matrix and (b) model groundwater matrix.



**Figure 9.** Fouling constants ( $k$  values) of the fitted cake layer formation model in the case of (a) ultrapure water matrix and (b) model groundwater matrix.

Pre-ozonation caused similar changes in the emulsions independently from the matrix, as the size distribution shifted to the smaller droplet sizes, and zeta-potential values decreased significantly. The increased negative surface charge resulted in reduced accumulation of the contaminants on the membrane surface and higher fluxes in the case of all investigated ultrafilter membranes. After pre-ozonation, in ultrapure water matrix PES membrane provided the highest flux; however, in the case of realistic water matrix (model groundwater) the beneficial effect of pre-ozonation on the flux was the most significant when conditioned PTFE membrane was applied.

In the case of model groundwater matrix much more contaminants were adhered on all the investigated membrane surfaces in comparison with ultrapure water matrix, which resulted in much higher reversible resistances in the case of PES and PAN membranes; however, PTFE membrane yielded much lower reversible and total resistance. Therefore, the high reversible resistances of PAN and PES membranes were deduced to be related to the contaminant/membrane interactions. After pre-ozonation, negligible reversible resistances were measured, but irreversible resistances significantly increased when PAN and PES membranes were applied, whereas in the case of PTFE membrane, only a slight increase of irreversible resistance was determined, which – with nearly zero reversible resistance – resulted in the lowest total filtration resistance by far.

On the basis of DR values, pre-ozonation improved the antifouling property in all cases. In the case of ultrapure water matrix this improvement was the most significant when PES membrane was applied, meanwhile in groundwater matrix PES and PTFE membranes also presented better antifouling properties, in comparison with the absence of pre-ozonation. Regarding the FRR values, pre-ozonation improved antifouling properties only in the case

of ultrapure water. In the case of groundwater matrix, pre-ozonation slightly decreased the percentage recovery of the original water flux in the case of PTFE membrane, and significantly decreased when PES and PAN membranes were used. By fitting the well-known filtration models, the cake layer formation gave the best fitting in all cases, but in the case of the absence of pre-ozonation, particularly in the case of model ground water matrix, beside the cake layer formation, the intermediate pore blocking model gave good fitting too, but after the pre-ozonation the fitting of this model was worse in both matrices. This can be interpreted as less amount of blocked pores on the surface due to the pre-ozonation.

The purification efficiencies were higher than 99% in all cases and no significant differences were observed when different conditions were applied. Overall, pre-ozonation was able to increase the achievable fluxes in each case; however, the reversibility of the filtration resistance, flux reduction and fouling mechanism were also strongly dependent on both the matrix and membrane material.

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