Research Regarding Membrane Filtration Capacity of Water Collected from Siret River

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Abstract. In the past decade, the high demand and strict legislations regarding pure and potable water production and quality require finding new treatment technologies with higher effectiveness. When compared with conventional treatment technologies, membrane technology is a viable option in water and wastewater treatment due to high performance, ease in implementation, cost-efficiency among other advantages, also, leading to a rapid expansion in use in almost all areas of industry. Polymeric ultrafiltration membranes have been successfully used in various industries since 1969, and in later years they were studied in the water purification sector, mainly as a pre-treatment step to reduce severe fouling that could occur in reverse osmosis filtration stage. Polysulfone (PSf) was the polymer of choice in this study with two concentrations, 25 wt.% and 30 wt.%. Surface SEM morphology, roughness and water affinity were analyzed for the studied membranes. Water from Siret river was used in the permeation tests in order to analyze the retention capacity and anti-fouling ability. The present study revealed higher retention for the 30 wt.% PSf membranes, from the physico-chemical and microbiological point-of-view and lower fouling, also.

1. Introduction
Membrane technology arisen from the need for cleaner water to provide areas with freshwater scarcity or shortage, areas that do not have a well-established treatment plant or areas with low access to clean water. A viable option is to use river water in order to withstand high water demand, is the use of membrane filtration technology of watercourse sources [1]. Conventional treatment plants for potable water production consists in multiple stages with complex processes (coagulation, flocculation, sedimentation, sand filtration, pH correction, chlorination, etc.) for producing the desired water quality, which in almost all stages various chemicals are used (aluminium sulphate, sulphuric acid, lime, chlorine gas, etc.) [2], each requiring strict monitorization and safety precautions. Also, due to increase of pollution in natural waters and rigorous regulation for drinking water quality demand continuous modifications and improvements in conventional treatment plants [3]. Membrane technology offers superior advantages when compared with conventional treatments, such as high water quality, modular construction, majority of chemicals needed are for membrane cleaning meaning very low by-product and residue production [4]. Polymeric membranes fabricated though the phase inversion method are the most promising in water and wastewater treatment. Due to ease in controlling the fabrication parameters, membranes are used in different sectors of industry [5]. Depending on the area of use of membranes, the water permeate quality (boiler feed water, cooling water, ultra-pure water, potable water, water for chemical production, etc.) can be easily controlled to meet customer requirements through various types of membranes, most notably, in the order of...
Retention performance, are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) [5]. Usually, when treating surface water though membrane technology, three stages are needed: prefiltration, ultrafiltration and reverse osmosis [6] in order to prevent severe fouling in the latter stage. The major drawbacks in membrane filtration are caused by the fouling phenomenon and concentration polarization. Fouling occurs when colloidal materials are adsorbed or deposited on the surface and/or in the membrane structure, whereas concentration polarization appear as an accumulation of retained particles on the membrane surface [7]. These issues cause a decrease in water permeation and change in retention capacity, resulting in a lower water production with undesired quality [8] and higher costs due to pressure increase stabilize the flux of permeate. According to Benavente et al. (2016), fouling is related with hydrophilicity and roughness parameters [9]. A membrane with low contact angle and low roughness possess superior anti-fouling properties.

This study will observe membrane performance, depending on two polymer concentrations of 25 wt.% and 30 wt.%, in the retention of natural water collected from Siret river near Galați city. Increasing the polymer concentration will lead to higher retention properties such as permeate quality and fouling resistance, but lower flux.

2. Methods and analysis
2.1. Materials and membrane preparation
Polysulfone (PSf, average Mw. 35 000) and N-methyl-2-pyrrolidone (NMP, C5H9NO, 99%) were purchased from Sigma Aldrich and used without further modifications. Support layer of non-woven polyester fabric (Novatexx 2471) was kindly supplied from Freudenberg (Winheim, Germany). The polymer solutions were obtained through mixing PSf with NMP solvent, Table 1, at constant stirring at room temperature for at least 24 hours.

| Membrane | Polymer type | Polymer concentration [wt.%] |
|----------|--------------|-----------------------------|
| 25_PSf   | PSf          | 25                          |
| 30_PSf   |              | 30                          |

After complete mixing, the homogeneous polymeric solution was casted on the support layer, that was fixed on a glass plate, with a casting knife with an air gap of 250 µm. Subsequently, the casted solution was immersed in a coagulation bath (distilled water) until phase inversion was complete. The formed thin film membranes were stored in distilled water until testing.

2.2. Contact angle measurements
Surface hydrophilicity is inversely proportional with contact angle. The prepared PSf membranes were analyzed using contact angle goniometer (OCA 15EC, DataPhysics). The dropping was repeated minimum 5 times and the average was reported. The software error was below 0.9 µm and the standard deviation was maximum +/- 5.

2.3. Morphological analysis
Membrane surface morphology was analyzed with a scanning electron microscope SEM Quanta 200 (Fei, Philips) after the samples were dried.

Roughness data and 3D images were determined using SEM images of the membrane top-view and ImageJ software (Imagej software, https://imagej.nih.gov/ij/) with two plug-ins. The SurfCharJ plug-in used for roughness values transforms the variation of grey tones in peaks or valleys, lower roughness values corresponding to lower grey tones and vice-versa, resulting in average roughness (Ra). Interactive 3D surface plot plug-in uses a similar concept of data acquisition that transforms the greyness values into three-dimensional peak and valleys [10]. Pore density was studied using SEM
images and Imagej software by pore counting on a defined surface. A total membrane surface of approx. 450 µm² per membrane was carried for total pore counts.

2.4. Permeation test
All permeation tests were carried using a dead-end stirred cell, Sterlitech HP4750 and an operation pressure of 10 bar. The water transport through the studied membranes was calculated with the flux [L m⁻² h⁻¹] equation:

\[ J_{0,1} = \frac{V}{A \times t} \]  

where \( J_0 \) is the pure water flux [L m⁻² h⁻¹], \( J_1 \) is the river water flux [L m⁻² h⁻¹], \( V \) is the permeate volume [L], \( A \) is the membrane active surface [m²] and \( t \) represents the filtration time [h].

The fouling tendency is calculated with the relative flux equation, expressed as the ratio between river water flux and pure water flux, as follows:

\[ R_f = \frac{J_1}{J_0} \]

2.5. Physical and chemical analysis of studied water
The values of chemical oxygen demand (COD-Cr), suspended matter, extractable substances and chlorides indicators were analyzed in a specialized laboratory. 

pH was analyzed with HQ40d portable multiparameter (Hach Lange GmbH, Germany), turbidity was analyzed with 2100P ISOTurbidimeter (Hach Lange GmbH, Germany) and total nitrogen, total ionic iron, lead, zinc, chromium and indicators were analyzed with UV-Vis Spectrophotometer HACH DR5000 (Hach Lange GmbH, Germany).

2.6. Total bacteria count
Total bacteria count was made with a Most Probable Number Method (MPN) with Hach test kit. The procedure consists in transferring a predefined amount of water sample into a tube (A) containing a reaction liquid, followed by hand agitation. Afterwards, 1 mL of the resulted liquid is transferred into another tube (B) of the same reaction liquid.

Table 2. Total bacteria count test chart [www.hach.com].

| Tube | Tube | Tube | Tube | Water quality          |
|------|------|------|------|------------------------|
| A    | B    | C    | D    | ~1 bacterium/mL        |
| +    | -    | -    | -    | ~1-10 bacteria/mL      |
| +    | +    | -    | -    | ~10-100 bacteria/mL    |
| +    | +    | +    | -    | ~100-1000 bacteria/mL  |
| +    | +    | +    | +    | >1000 bacteria/mL      |

The procedure is repeated a total of 4 times (A, B, C and D) for repeated dilution and the tubes are incubated at 35°C for 24 - 48 h. After incubation, the cloudy tubes indicate bacterial growth whilst the clear tubes indicate no bacterial growth, as shown in Table 2. The “+” symbol represents cloudy tubes that showed bacteria growth, while the “-” symbol represents clear tubes which showed no bacteria growth.

3. Results and discussion
3.1. Contact angle measurements
Water contact angle is an important parameter in order to determine the membranes water affinity. It is seen in table 3 that higher concentration of polysulfone results in higher contact angle. Polysulfone is
hydrophobic by nature and thus, increasing its concentration will result in a higher hydrophobic membrane.

Table 3. Membrane properties.

| Membrane | Contact angle [°] | Pure water flux [L m⁻² h⁻¹] | Pore density [pores/µm²] |
|----------|------------------|-----------------------------|------------------------|
| 25_PSf   | 61.33            | 147.418                     | 1.0788                 |
| 30_PSf   | 68.27            | 76.146                      | 0.6413                 |

3.2. Morphological analysis
From top-view SEM images, as show in Figure 1, it can be seen that the membrane with lower PSf concentration (25_PSf) contain a higher pore number, compared with 30 wt.% PSf membrane, as depicted from table 3, also. However, higher polymer concentration lead to smaller pores, meaning that, although flux could have a lower value, retention will be superior. According to Holda et al. (2013), pore size and surface porosity is directly proportional with polymer concentration due to slower solvent (NMP)/non-solvent (water) diffusion during phase inversion which lead to delayed demixing resulting a more closed membrane surface [11]. According to Zinadini et al. (2017), membrane roughness and surface water affinity determines the fouling tendency of membranes [12].

Figure 1. Top-view SEM images for (a) 25_PSf and (b) 30_PSf membranes.

Figure 2. 3D surface (left) and 2D surface (right) images for “Ra” roughness calculation for (a) 25_PSf and (b) 30_PSf membranes using SEM imagery and ImageJ software.

From Figure 2, it is observed that higher polymer concentration lead to lower surface roughness, from 30.7453 for 25 wt.% PSf to 21.1646 for 30 wt.%. One explanation could be the decrease in pore density of the higher polymer concentration membrane, as show in Table 3, meaning lesser valleys.

3.3. Permeation tests
Figure 3 shows the behavior of membranes during the filtration of the Siret River water, from the flux point of view. At the beginning of the retention test, the initial retention flux should ideally start at the last value of pure water flux (Table 3) or even higher due to membrane loosening after compaction with a certain pressure. The pure water flux of 30 wt.% PSf membrane is 76.146 L m⁻² h⁻¹ and an
initial retention flux of 74.3 L m$^{-2}$ h$^{-1}$, while for the 25 wt.% PSf membrane the initial retention flux starts at approx. 122.7 L m$^{-2}$ h$^{-1}$, a difference of approx. 24.7 L m$^{-2}$ h$^{-1}$ when compared with pure water flux. The reason of immediate decrease in flux is due to instantaneous deposition of particles on the membrane surface, blocking approx. 16.7 % of the total pores (ratio between $J_0$ and initial $J_1$ value).

As presented in Figure 3, the retention fluxes of the two membrane types show a highly different initial flux (124 L m$^{-2}$ h$^{-1}$ for 25_PSf and 75 L m$^{-2}$ h$^{-1}$ for 30_PSf) and low difference at final flux (approx. 40 L m$^{-2}$ h$^{-1}$ for both membranes). The 25 wt.% PSf membrane show a 66 % decrease in Siret River water flux, whilst 30 wt.% PSf membrane shows a decrease of 46 %.

Correlating Figure 3 and 4 with the roughness values, it is observable that the lower roughness of 30 wt.% PSf membrane presents a higher anti-fouling ability. The fouling of 25 wt.% membrane is more obvious, reaching to a final value of approx. 0.25.

The low fouling tendency is also observed after a simple rinse with distilled water, as show in Figure 5. After rinsing the samples with distilled water, the higher observable fouling for 25 wt.% membrane could signify that particles from Siret water have adhered on membrane surface and structure more prominent.

Physical and chemical indicators for Siret River water and permeate water quality

The permeates were analyzed though physico-chemical methods. The most notable differences were for COD-Cr, turbidity, suspended matter, iron and zinc indicators.

The pH value has not changed sufficient, due to the fact that both raw and permeate water pH values are in acceptable range of water quality [13].

Turbidity is an optical property of water, in which suspended or dissolved materials (organic and inorganic material, plankton, microorganisms, etc.) absorb or scatter light. Turbidity decreases from 245 NTU to 1.39 and 1.19 NTU for 25 wt.% PSf and 30 wt.% PSf membrane, respectively. The
The turbidity of the membrane with higher concentration of PSf show a lower turbidity, an explanation being that it has smaller pores, thus retaining more matter that increases turbidity value.

Table 4. Physico-chemical analysis of raw water and filtrated raw water with 25_PSf and 30_PSf membranes.

| No. | Indicator                                | Unit     | Siret raw water | 25_PSf permeate | 30_PSf permeate |
|-----|------------------------------------------|----------|-----------------|-----------------|-----------------|
| 1   | pH                                       | pH units | 6.9             | 7.3             | 7.3             |
| 2   | Chemical Oxygen Demand (COD-Cr)          | mgO₂/L   | 259.6           | 0               | 0               |
| 3   | Turbidity                                | NTU      | 245             | 1.39            | 1.19            |
| 4   | Suspended matter                         | mg/L     | 283             | 0               | 0               |
| 5   | Extractable substances                   | mg/L     | 4               | 0               | 0               |
| 6   | Chlorides                                | mg/L     | 143.230         | 141.812         | 141.103         |
| 7   | Total nitrogen                           | mg/L     | 4               | 4               | 4               |
| 8   | Total ionic iron (Fe²⁺ and Fe³⁺)         | mg/L     | 5.23            | 3.20            | 2.28            |
| 9   | Lead                                     | µg/L     | 0.11            | 0.1             | 0.1             |
| 10  | Zinc                                     | µg/L     | 0.32            | 0.19            | 0.1             |
| 11  | Chromium                                 | µg/L     | 0.06            | 0.05            | 0.05            |

The COD-Cr parameter is understood as the indirect measurement of organic and inorganic compounds oxidability in reaction of a strong acid, such as potassium dichromate (KCr₂O₇) [13]. The membranes from this study have reduced to zero the amount of organic matter that can be chemically oxidised. Although COD test is widely used in water and wastewater analysis, its main limitation is the inability in differentiating biodegradable from biologically inert organic matter [14], approved by the results from total bacteria count shown in Table 5.

Suspended matter is composed of fine particles originating from natural sources (plankton, fine plant debris, minerals, etc.) and from human activity (organic and inorganic matter), which could have a negative influence on the ecosystem [15]. Both types of membranes have eliminated the suspended matter. The extractable substances value after membrane filtration were 0, also, for both membrane types, meaning that their sizes were large enough to be rejected by the membranes.

Notable differences were reported for iron and zinc indicators, but were not eliminated from permeate, the membrane with 30 wt.% PSf concentration showing higher permeate quality.

No difference in filtration were reported for chloride, lead, chromium and total nitrogen tests.

3.4. Total bacteria count
Bacteria growth in membrane treatment plants are of high concern, due to the appearance of biofouling on membrane surface and inside its pores, especially for reverse osmosis membranes, which requires additional treatment upstream [16]. The raw water and permeate waters from 25 wt.% and 30 wt.% PSf membranes were subjected to a simple bacteria test. Each sample were prepared in 4 tubes, and noted as follows: for the Siret river water tubes 1, 2, 3 and 4 corresponding with the A, B, C and D tubes explained at the methods section, see 2.6. Total bacteria count test. The permeate samples were prepared in the same manner, tubes 5, 6, 7 and 8 for 25 wt.% PSf membrane and tubes 9, 10, 11 and 12 for 30 wt.% membrane, respectively, as shown in Figure 6.
After 24-48 hours of incubation time of the test tube, it was observed (Figure 6) that the raw water has developed in all tubes bacterial growth, due to the fact that all tubes are cloudy, corresponding to high bacterial presence of >1000 bacteria/mL of sample, as shown in Table 5.

Figure 6. Water sample preparation for total bacteria count test for (1, 2, 3, 4) Siret water, (5, 6, 7, 8) 25_PSf membrane permeate and (9, 10, 11, 12) 30_PSf membrane permeate.

For the 25_PSf membrane permeate samples, it is observed that tubes 5, 6 are cloudy and tubes 7, 8 are clear, which means that the permeate show a total of ~10-100 bacteria/mL of water. The membrane with the lower polymer concentration have managed to reduce bacteria approximately 50%. In the case of the membrane with the highest polymer concentration and the lowest pore sizes, 30 wt.% PSf, the permeate bacteria count was noticeably reduced to ~1-10, approximately 99%.

Table 5. Water quality for studied water samples.

| Water sample          | Water quality [bacteria/mL] |
|-----------------------|-----------------------------|
| Siret water           | >1000                       |
| 25_PSf permeate       | ~10-100                     |
| 30_PSf permeate       | ~1-10                       |

Despite the fact that the permeate quality is 99% free of bacteria, it still poses the risk of illness due to the presence of bacteria, regardless of quantity. According to Romanian law no. 458/2002 regarding the quality of drinking water [17], the maximum value for bacteria presence in potable water is 0.

Although the above stated, the 30 wt.% PSf membrane could be a viable option for the pretreatment of river water upstream in order to reduce high fouling in the reverse osmosis filtration modules, regardless of the destination of water use.

Correlating all the methods of membrane characterization, it is observed that roughness, pore size and density (Figure 2, Figure 1 and Table 3, respectively) determines the membrane fouling behavior (Figure 3, Figure 4 and Figure 5) and retention capacity (Table 4 and 5).

For 25 wt.% PSf membrane, the higher roughness causes higher deposition of particles on the surface and possibly inside the membrane structure, resulting in higher fouling during filtration. Also, the total bacteria from the permeate suggests that possibly a considerable amount of bacteria have
attached on the surface and inner pores, which also approve higher fouling. In the case of 30 wt.% PSf membrane, due to lower roughness and smaller surface pores, all retention performance and anti-fouling property are superior to lower polymer concentration membranes.

4. Conclusions
Retention and fouling capacity of 25 wt.% and 30 wt.% PSf membranes were tested successfully. In terms of pure water flux and water affinity, the 25 wt.% PSf membrane exhibited the highest values. Nevertheless, the membrane hydrophilicity does not influence the fouling tendency during retention of Siret River water, and pure water flux is merely a parameter of standardization, which is an orientative value in membrane science. On the other hand, 30 wt.% PSf membrane show superior stability in flux during retention, higher retention values for removal of suspended matter, extractable substances, total ionic iron and zinc. The chemical oxygen demand values show that the permeate eliminated all oxidizable pollutants from the river water. Turbidity was reduced 99.4% for 25_PSf membrane and 99.5% for 30_PSf membrane. The key result on the bacteria removal capacity demonstrated that the use of 30 wt.% PSf membrane in the filtration of river water is a viable option in the prefiltration stage of reverse osmosis water treatment.

5. References
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