

# Effect Of Membrane Filtration Via Various Membrane Types On Thmfp Reduction

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**Abstract** Natural waters, groundwaters and surface waters, often contain elevated concentrations of natural organic matter (NOM) due to geological composition or biological decomposition of plant and animal material in the water. The most significant component of natural organic matter are humic substances.

Humic substances are undesirable in water because they cause appearance of color, taste and smell. Because of their molecule structure (long carbon chains and/or rings), humic substances often bind a variety of contaminants (heavy metals, pesticides). Significant problem is the heightened concentrations of humic substances since they form toxic and carcinogenic by-products trihalomethanes (THMs) during the water disinfection with chlorine. Humic substances are complex mixtures of organic compounds with different structure, molecular weight, number and position of functional groups depending on the origin and age of the organic material, the type of water, environmental and climatic conditions which results in a different reactivity with chlorine so called trihalomethane formation potential (THMFP). Membrane processes are efficient methods for ions, colloids and solids removal from water based on their molecular weight and chemical structure. This study investigated the effect of membrane filtration via various membrane types (microfiltration, ultrafiltration, nanofiltration and reverse osmosis membranes) on THMFP reduction. Effect of membrane type on pH, electrical conductivity (EC), alkalinity, water hardness and KMnO<sub>4</sub> consumption were also analyzed.

**Keywords:** water, humic substances, trihalomethane, membrane filtration

## 1. Introduction

Natural organic matter is a complex mixture of organic compounds found in natural waters. The presence of NOM is undesirable in drinking water for many reasons (affects organoleptic properties of water, reacts with disinfectants and produces disinfectant by-products (DBPs), affects corrosion processes etc.) (Ødegaard *et al.*, 2010; Matilainen *et al.*, 2011). NOM found in natural waters

consists of hydrophobic and hydrophilic components. These hydrophobic acids can be described as humic substances comprising humic acids (HA), fulvic acids (FA) and humins. NOM often bind with metals contributing to undesirable color, taste and odor problems of water. In addition, NOM tends to interfere with the performance of unit operations, such as biofilm growth, causing membrane fouling (Sillanpää, 2015). Moreover, all disinfection methods reportedly produce their own suite of disinfection by-products (DBPs) and bioreactive compounds in drinking water (Richardson *et al.*, 2007). DBPs have been linked with detrimental health effects such as cancer and birth defects (Gough *et al.*, 2014). Thus, the removal of NOM from water is an emerging issue. The best method for reducing DBP levels is to reduce DPB precursors prior to disinfection (Metcalf *et al.*, 2015). Among various removal technologies, the most common method is coagulation and flocculation, sedimentation and filtration. The coagulation method removes most of the NOM, but the water treatment should be optimized to remove both hydrophobic and hydrophilic organic matter (Matilainen *et al.*, 2010).

Microfiltration (MF) is a low-pressure membrane process usually used for the removal of turbidity and pathogens. Fan *et al.* (2001) reported that the MF process is not very effective at removing NOM and that NOM can cause flux decline in the microfiltration of natural water. The advantage of MF is that its large pore size enables operation at low transmembrane pressures, which makes this operation inexpensive. MF is usually used in combination with other methods, as the first step in drinking water treatment process for removal of microbes or coagulation following phase (Sillanpää, 2015).

Ultrafiltration systems (UF) have been used for successful treatment of turbidity, particulate matter, and microorganisms, but not for the removal of smaller compounds such as NOM. UF membranes have pore size of 0.1 – 0.001 µm, which are much larger than the size of some NOM. Another problem is that the membranes grow fouled when NOM pass through their pores and form a film on the surface of membranes (Droste, 1997).

Membrane surface modification is an attractive approach to reduce membrane fouling by foulants such as NOM (Xi *et al.*, 2006). Only few studies have focused on enhancing

removal of HA such as using the cationic quaternary ammonium compound cetyltrimethylammonium bromide (CTAB) (Nguyen, 2014). Cationic surfactants, e.g. cetylpyridinium chloride (CPC) has been shown to be effective in removing multivalent hazardous anions (Singh *et al.*, 2006).

Micellar-enhanced ultrafiltration (MEUF) is a modified separation of ultrafiltration process. It is a process which involves high selectivity of reverse osmosis and high flux of ultrafiltration (Zaghbani *et al.*, 2009). MEUF is also used to remove multivalent heavy metal ions with ionic surfactants. The principle of MEUF process needs the importance of surfactant's critical micelle concentration (CMC) for the selection of suitable surfactant concentration for MEUF process (Puasa *et al.*, 2011).

The NF process is often selected when the NOM-content/color is high and turbidity low. Problems occurred are linked with capacity loss caused by fouling (Ødegaard *et al.*, 2010). Almost total NOM rejection has been achieved in lab- and bench-scale studies using NF membranes of 200-400 Da. Studies on reverse osmosis (RO) revealed almost complete rejection of humic substances, but the main challenge of NF and RO plants are the concentration of scale-forming minerals and organic materials that decrease recovery rates (Sillanpää, 2015). RO membranes are effectively non-porous, therefore, the mechanism of RO membrane process is selective as it will not allow large molecules or ions pass through the pores, but will allow smaller components such as the solvent to pass freely (Nguyen, 2014).

This paper presents the effect of membrane filtration using various membrane types (microfiltration, ultrafiltration, nanofiltration and reverse osmosis membranes) on THMFP reduction, pH, electrical conductivity, alkalinity, water hardness and  $\text{KMnO}_4$  consumption.

## 2. Materials and methods

### 2.1. Water sample

The raw water was obtained from local waterworks near town of Osijek. The physical and chemical properties of the water sample is summarized in Table 1. The water sample was analyzed before and after filtration on the following parameters: pH, conductivity, alkalinity, water hardness,  $\text{KMnO}_4$  consumption, and UV-absorbance at 203 and 254 nm.

### 2.2. Chemical analysis

The pH and electrical conductivity were measured in situ by a pH meter (Mettler Toledo, Germany) and conductivity meter (Metrel MA5950, Slovenia). Alkalinity, water hardness and  $\text{KMnO}_4$  consumption were titrimetrically determined.

### 2.3. Natural organic matter determination

Natural organic matter is very complex and there is no analytical method which could completely define its structure and functionality. Among analytical methods,

spectroscopic techniques could be used to monitor the structural changes of humic substances caused by oxidation processes (Fukushima *et al.*, 2001; Uyguner and Bekbolet, 2005; Uyguner *et al.*, 2007).

The NOM-containing natural waters were kept at room temperature prior to filtration to assure thermal equilibration. NOM rejection, based on bulk concentration, was calculated as follows:

$$\text{NOM removal, \%} = \frac{C_i - C_f}{C_i} \cdot 100$$

where  $C_i$  is NOM concentration in raw water samples and  $C_f$  is NOM concentration in the permeate.

The trihalomethane formation potential (THMFP) was estimated using indirect parameters. The ratio of absorbance measured at 254 nm and 203 nm indicates the presence of active aromatic rings in organic substances and is correlated with the tendency of NOM for the reaction with chlorine (Kim and Yu, 2005; Golea *et al.*, 2017).

### 2.4. Membranes and filtration protocol

NOM removal from the water sample was investigated by standard filtration method using Sartorius filtration unit using mixed cellulose ester microfiltration membranes with pore size of 0.45  $\mu\text{m}$  and 2  $\mu\text{m}$ . Residual NOM concentration was measured in obtained filtrates.

For modification of UF membranes cetylpyridinium chloride (CPC, 99% pure) was obtained from Sigma-Aldrich (USA). The CPC solutions were prepared to concentrations of 1.0 mM, above the critical micelle concentration (CMC) when the surfactant forms micelles comprising up to 100 surfactant molecules. 1000 mL of the CPC solution was filtered through each membrane prior to filtering the raw waters. The laboratory-scale ultrafiltration (UF) cell used was Pellicon XL which has a peristaltic pump with adjustable speed (60-600 rpm/min) and adjustable capacity (optimal 30-50 mL/min) fitted with modified polyethersulfone membrane which had effective area of 50  $\text{cm}^2$  (Biomax, Millipore, USA). The surface modified polyethersulphone UF-membranes Biomax 10 and Biomax 30 were used.

For nanofiltration experiments a pilot-scale filtration system with the commercial Thin-Film Composite polyamide (PA) membrane (NE 4040-70, Woongjin Chewmical CO., Ltd.) were used. The membrane surface area was 7.9  $\text{m}^2$ . Raw water was pretreated using cartridge filter of 5  $\mu\text{m}$ . The system was managed and controlled through a central programmable logic controller (PLC). Prior to filtration, backwashing of membrane during 2 min is performed. The filtration system is shown in Fig. 2c. For measurements in this report, a constant feed flow rate of 250 L/h was set, where the transmembrane pressure was kept constant at approximately 5.7 bar.

In this research, a domestic water treatment RO system (Universal Aqua Technologies, INC., USA) was used. This

RO system operates using water supply system of 3 to 4.5 bar. First, tap water passes through a 5  $\mu\text{m}$  prefilter to remove suspended compounds. The second step include adsorption on activated carbon for chlorine removal. In the third step, the water passes through a spiral-wound TFC membrane (Dow Filmtec TW30-1812-50 TFC Membrane), after which water flows over a filter made of granulated carbon for the removal of chloramines and trihalomethane. At the end, for odor and dissolved gases removal, the water passes through fine granulated carbon. Quantity of feed water was controlled by a valve in the end of membrane filter by opening and closing of valve.

### 3. Results and discussion

#### 3.1. Microfiltration experiments

From the results shown in Table 1, it is evident that neither pH, conductivity nor  $\text{KMnO}_4$  consumption were reduced using microfiltration. However, the NOM removal efficiency and THMFP (Fig. 1) was slightly higher after filtration on 0.45  $\mu\text{m}$  MF membrane due to smaller pore size. It is well known that MF processes are effective for the removal of particulate contaminants, such as clay, bacteria, algae and protozoa from drinking water, and less effective for the removal of dissolved contaminants. This process is usually applied as coagulation following phase (Carrol *et al.*, 2000).

#### 3.2. Ultrafiltration experiments

Two different surface modified polyethersulfone membranes Biomax 10 and Biomax 30 (Biomax, Millipore, USA) were used with different weight cut-offs (MWCOs) of 10 and 30 kDa.

The removal characteristics of NOM and the reduction of THMFP are shown in Fig. 1. The removal efficiency of NOM increased as the molar ratio of membrane decreased. It is evident that the reduction of THMFP decreased with higher molar ratio of membrane. The highest NOM removal can be seen on Fig.1 where up to 16% NOM was removed from the water with Biomax 10, while the removal efficiency with Biomax 30 was 8%. Xi *et al.* (2006) reported on modification of PES UF membranes by weak acids of methacrylic acid (MA) and 2-acrylamido glycolic acid (AAG), as well as of (2-hydroxyethyl)-methacrylate (HEMA). The MA and AAG grafting reduced the MWCO of the PES membranes, decreased the permeability to less than half of the original flux, but also increased the NOM removal.

From the results shown in Table 2, negligible effect on alkalinity, water hardness and  $\text{KMnO}_4$  consumption can be observed. Moreover, the both modified PES UF membrane (Biomax 10 and Biomax 30) does not influence the pH and conductivity of water.

#### 3.3. Nanofiltration experiments

The results showed that all tested parameters, i.e. conductivity, alkalinity, water hardness and  $\text{KMnO}_4$  consumption were significantly lower after usage of nanofiltration membrane. The conductivity dropped down from 922  $\mu\text{S}/\text{cm}$  to 62  $\mu\text{S}/\text{cm}$ , and the water hardness from 18.42  $^\circ\text{dH}$  to 0.56  $^\circ\text{dH}$ . In addition, the  $\text{KMnO}_4$  consumption was 3.02 mg/L after nanofiltration. This membrane exhibits significantly high rejection of NOM (100%) and therefore, also high percentage of THMFP (100%) (Fig. 1). Similar results reported Cho *et al.* (1999) who tested crosslinked, polyamide TFC membranes. They explained high DOC rejection by the fact that this kind of membrane has a negative charge (like the NOM macromolecules) so that there are charge repulsions between the membrane surface and NOM.

#### 3.4. Reverse osmosis experiments

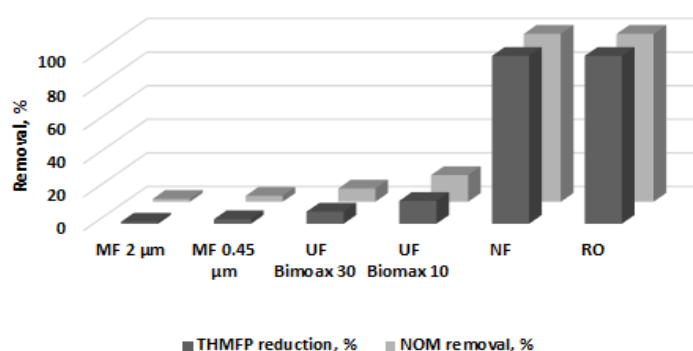
Findings of RO are summarized in Table 1 and Fig 2. Fig. 2 shows the result of THMFP reduction and NOM removal. According to these results, maximum average removal of NOM and THMFP reduction were 100%. Maximum average removal efficiency of  $\text{KMnO}_4$  consumption was 91.36%, water hardness 97.78%, and alkalinity 91.84%, respectively. The pH was 6.6, while the conductivity decreased from initially 922  $\mu\text{S}/\text{cm}$  to 21  $\mu\text{S}/\text{cm}$  (Table 1). Mazloomi *et al.* (2009) investigated efficiency of domestic reverse osmosis in THMs removal using chloroform solutions. They reported a high percentage of chloroform removal and electrical conductivity reduction using RO. The efficiency was 85.67% and 90.46% at 100  $\mu\text{g}/\text{L}$  chloroform and 100  $\mu\text{S}/\text{cm}$ , and 81.98% and 88.22% at 500  $\mu\text{g}/\text{L}$  initial chloroform concentration and 1000  $\mu\text{S}/\text{cm}$ . Results showed that with increase in EC from 100 to 1000  $\mu\text{S}/\text{cm}$ , removal efficiency of chloroform decrease from 100 to 300  $\mu\text{g}/\text{L}$ . More than 98.5% reduction of arsenic by RO reported Pawlak *et al.* (2006).

### 4. Conclusions

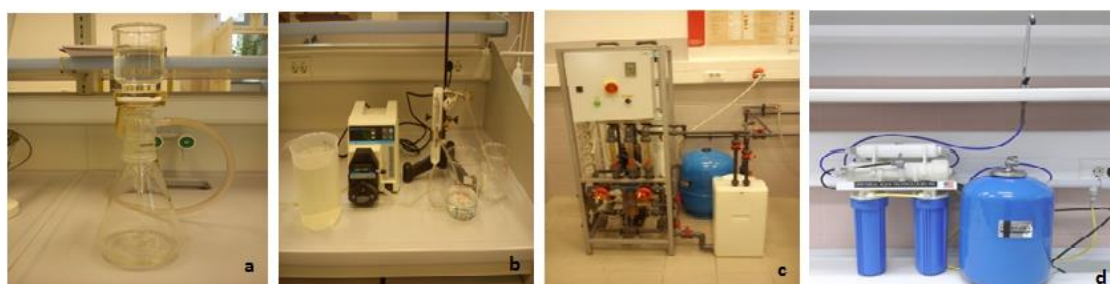
In this study, six types of membranes (MF, UF, NF and RO) were tested for trihalomethane formation potential (THMFP) reduction. Results revealed that MF does not reduce THMFP. Significant changes of pH, electrical conductivity (EC), alkalinity, water hardness and  $\text{KMnO}_4$  consumption were also not observed after the raw water was passed through tested MF membranes. Surface-modified ultrafiltration UF membranes (Biomax 10 and Biomax 30) reduced the THMFP from 10% to 33%. Other analyzed parameters (alkalinity,  $\text{KMnO}_4$  consumption, water hardness, pH and electrical conductivity) of treated waters showed very slight reductions in comparison to its values in raw water. 100% of THMFP reduction was obtained using pilot-system with spiral-wound TFC polyamide nanofiltration membrane. Significant changes of other analyzed water quality parameter were also obtained; EC was decreased

**Table 1.** Physical-chemical parameters of untreated water sample and after membrane filtration

	pH	Electrical conductivity/( $\mu\text{S}/\text{cm}$ )	Alkalinity/(mmol/L)	Water Hardness/( $^{\circ}\text{dH}$ )	$\text{KMnO}_4$ consumption/(mg/L)
raw water	7.0	922	9.8	18.42	14.24
<b>Membrane type</b>					
MF 2 $\mu\text{m}$	7.7	923	9.8	18.45	14.18
MF 0.45 $\mu\text{m}$	7.5	923	9.8	18.37	14.03
UF Bioax 30	7.8	920	9.9	18.48	13.17
UF Biomax 10	7.9	925	10.3	18.37	13.15
NF	6.8	62	0.9	0.56	3.02
RO	6.6	21	0.8	0.41	1.23



**Figure 1.** Effect of THMFP reduction and NOM removal with using different membrane types



**Figure 2.** Filtration units a) microfiltration, b) ultrafiltration, c) nanofiltration, d) reverse osmosis

from 922 to 62  $\mu\text{S}/\text{cm}$ , alkalinity from 9.8 to 0.9 mmol/L, water hardness from 18.42 to 0.56  $^{\circ}\text{dH}$ ,  $\text{KMnO}_4$  consumption from 14.24 to 3.2 mg/L). pH was decreased from 7.0 to 6.8. Similar efficiency was obtained using domestic RO system: 100% of THMFP was reduced, EC was decreased from 922 to 21  $\mu\text{S}/\text{cm}$ , alkalinity from 9.8 to 0.8 mmol/L, water hardness from 18.42 to 0.41  $^{\circ}\text{dH}$ ,  $\text{KMnO}_4$  consumption from 14.24 to 1.23 mg/L. Obtained pH of water after RO membrane was pH was decreased from 7.0 to 6.8. According to obtained results, tested NF and RO membranes are suitable for removal of NOM and effective reduction of trihalomethane formation potential.

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