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# Evaluation of effectiveness of natural organic compounds removal from water in hybrid processes

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## Abstract

Natural organic matter (Natural Organic Matter – NOM) represents a mixture of diverse chemical structure and different properties. The humic substances constitute an important component of NOM, and they are responsible for water color and taste, also they can contribute to the formation of disinfection by-products (DBP). Therefore, removal of NOM is considered to be one of the important technological operations during water treatment.

The present study evaluate the effectiveness of NOM removal from water by one of the hybrid process and the results showed that the use of this process allows to improve the efficiency of water purification and also reduces the intensity of blocking membranes. Batch adsorption tests of heated aluminum oxide particles (HAOPs) showed that the NOM removal efficiency has been between 86 to 77% at a dose 5 and 10 mg·dm<sup>-3</sup>, respectively for both tested natural water.

**Key words:** *clogging of the membrane, fouling, hybrid processes, transport properties*

## INTRODUCTION

Declining resources of potable water are social and political as well as economic problem in many parts of the world. In addition, the requirements for the quality of the water are getting more strict and generally include wide range of needed analyses. Natural organic matter (NOM) is the degradation product of plant and animal organisms and thus it is a common component of water. It is a mixture of various chemical structure and different properties. The humic substances are an important component of NOM and usually they are responsible for water color and taste, and also contribute to the formation of disinfection by-products (DBP). Therefore, NOM removal is considered to be one of the very significant technological operations during purification of surface water. Usually, water purification systems for the removal of suspended solids and NOM use the coagulation process combined with sediment run-offs. In recent years,

growing interest in water treatment for potable water gained the membrane filtration.

The membrane is a permeable or semi-permeable phase, and it can be made from organic or inorganic materials. It restricts the movement of selected components from a stream. Membrane separation process is based on the filtration phenomenon. Generally, in the water treatment technology there are two basic membrane types used e.g. ultrafiltration membranes (UF) and microfiltration (MF). They are characterized by very high efficiency of pollutants removal in a wide range of concentrations. The biggest obstacle with membrane application in water and wastewater technology is the phenomenon of blocking the membranes' pores called fouling.

Membrane fouling is generally categorized into the following areas: inorganic fouling and biological fouling as well as organic fouling. The main reason of the inorganic fouling is a deposition on membrane surface of inorganic scales (clays, silica salt, and met-

al oxides). The organic fouling is caused by natural organic matter (NOM) found in the surface water (humic acids, proteins and carbohydrates), and bio-fouling is caused by microbial attachment to the membrane surface [AL-AMOUDI, LOVITT 2007].

Fouling leads to the decrease in the hydraulic membrane performance and deterioration in the quality of the permeate, increasing the operating costs at the same time. The decrease in hydraulic performance during water filtration containing organic substances through membranes, is due to the increase in the flow resistance value by blocking the membrane [BODZEK *et al.* 2005; KABSCH-KORBUTOWICZ *et al.* 2006; KABSCH-KORBUTOWICZ, URBANOWSKA 2010; KONIECZNY *et al.* 2006; 2007].

The proper operation of membrane demands managing of fouling process. However the nature of fouling and membrane fouling processes is a complex phenomenon that has not been defined precisely [AL-AMOUDI, LOVITT 2007]. Therefore there are various ways to control and minimize this phenomenon and selecting a proper pretreatment method seems to be the cornerstone of water purification. In recent years, attention has been drawn to the possibility of using the hybrid process. These methods connect the coagulation process with membrane filtration. Such systems give the possibility to partially remove organic carbon from water as well as significant removal of suspended solids and microorganisms [URBANOWSKA, KABSCH-KORBUTOWICZ 2016]. The phenomenon of coagulation followed by filtration on membranes also contributes to the removal of part of the impurities responsible for fouling.

Some studies have shown that the PAC (powdered activated carbon) in combination with UF or MF membranes reduces dissolved organic carbon (DOC) and removes compounds of low molecular weight (LMW) in quantities of 50–65% or 70% [JEONG *et al.* 2013]. However MOZIA and TOMASZEWSKA [2004] reported that the addition of PAC increased the fouling of a regenerated cellulose UF membrane.

Numerous studies have shown that the application of the process of MIEX®/DOC allows to effectively remove NOM from water [MOŁCZAN, KARPIŃSKA-PORTELA 2009; RAJCA 2012]. Others suggest that the use of heated aluminum oxide particles (HAOPs) in conjunction with the water treatment on the UF or MF membranes is an effective method of removing NOM [CAI *et al.* 2008; CHANG, KIM *et al.* 2007; 2008; 2010; MALCZEWSKA *et al.* 2015; 2016].

This paper compares the effectiveness of NOM removal by HAOPs when pre-coated onto the membrane surface prior to membrane filtration. The current study is a continuation of research on potential benefits of pre-depositing a layer of adsorbent particles onto a membrane and then passing the feed through the particles, along with fouling phenomena investigation in experiments involving filtration with consideration of NOM removal.

## MATERIALS AND METHODS

Analyzed water comes from two lake in Seattle, Washington. The first one is the Greenlake, which is a glacial lake, of an area of 1.05 km<sup>2</sup>, the average depth of 3.8 m, and a maximum depth of 9.1 m. At present, the Lake is fed by rainfall, storm run-off and municipal water supply. The following values have been recorded (at the depth of 1.0 m): chlorophyll-a – 2.87 µg·dm<sup>-3</sup>, total nitrogen – 35.5 µg N·dm<sup>-3</sup>, NO<sub>2</sub><sup>-3</sup> – 5 µg·dm<sup>-3</sup>, NH<sub>3</sub> – 3.0 µg·dm<sup>-3</sup>, total phosphorus – 10.5 µg·dm<sup>-3</sup> [King County 2016]. The average value for the raw water at UV<sub>254nm</sub> is 0.048.

In addition another surface water was also analyzed. Water from Lake Union, which is also a glacial lake. The Lake has an area of 235 ha, and the average depth is 10 m. The tested surface water was characterized by the following parameters: chlorophyll-a – 6.4 µg·dm<sup>-3</sup>, total nitrogen – 0.289 mg·dm<sup>-3</sup>, NH<sub>3</sub> – 0.021 mg·dm<sup>-3</sup>, total phosphorus – 0.0088 mg·dm<sup>-3</sup> [King County 2016]. The average value for the raw water at UV<sub>254nm</sub> is 0.037.

The water samples were analyzed on a UV-Vis spectrophotometer at a wavelength of 254 nm. UV<sub>254nm</sub> was measured with a dual-beam Lambda-18 spectrophotometer with a 1 cm quartz cell (Lambda-18, Perkin-Elmer, USA). UV Absorbance at a wavelength of 254 nm is considered to be indicator of the presence of humic and fulvic acids which are an integral component of the NOM. Absorbance differences between raw water subjected to filtration and permeate (treated water) indicate the degree of organic compounds removal.

To determine the contents of the DOC the TOC Analyzer (Shimadzu TOC-VCSH) have been used.

HAOPs has been prepared according to the methodology described in detail in the publication of CAI *et al.* [2008]. After the neutralizing aluminum sulphate (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·18 H<sub>2</sub>O) solution was warmed during the night at a temperature of 110°C. The solution after cooling was used for test.

## ADSORPTION TESTS

Adsorption tests have been carried out according to the methodology described in the paper by CAI *et al.* [2008]. In this study to 100 ml of tested water various doses of coagulant have been added. So, prepared suspension was mixed for two hours at a constant rotational speed of 200 rpm and the temperature of 21°C, and then the mixture was subjected to sedimentation for 30 minutes, then the supernatant was filtered by 0.45-mm filters (millipore filters), and the UV<sub>254nm</sub> absorbance have been measured. Figure 1 shows the effectiveness of removing organic compounds by HAOPs for different dose and pH, while Figure 2 shows the differences in the reduction of absorbance by HAOPs and aluminium sulphate (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·18 H<sub>2</sub>O). The pH was adjusted by the addition of 1 N NaOH or 1 N HCl, and monitored before and after mixing.

## FILTRATION

The membrane used for research have had a diameter of 47 mm, and the effective area of 9.62 cm<sup>2</sup>. The nominal pore size was 0.05 μm (Microdyn-Nadir MP005). The experiment was conducted using a dead-end flow filtration, and raw water was pumped using a peristaltic pump with constant flow of 100 (LMH) dm<sup>3</sup>·(m<sup>2</sup>·h)<sup>-1</sup>. Transmembrane pressure (TMP) was measured using a transducer (PX302-100GV, Omega Engineering, IC Stamford, CT), and followed by data acquisition by the Agilent Technologies Analyzer. The results of the UV<sub>254</sub> removal from the feed was monitored during the filtration at preselected time along with DOC.

## RESULTS AND DISCUSSION

The mechanism for removing organic compounds using coagulation is reported to consist of charge neutralization, humic and fulvic acid precipitation and adsorption on metals [BODZEK, PŁATKOWSKA 2009]. The type and dose of coagulant need to be evaluated before pretreatment can be apply.

### ADSORPTION TESTS

The results of the adsorption test for both lakes were similar, therefore only one example of adsorption test is presented on a Figure 1 (for the Green Lake water). The relationship between changes are presented as normalized UV and coagulant dose. The result was normalized by dividing the intensity at specific wavelength (at 254 nm) by that UV<sub>254nm</sub> absorbance of raw lake water.

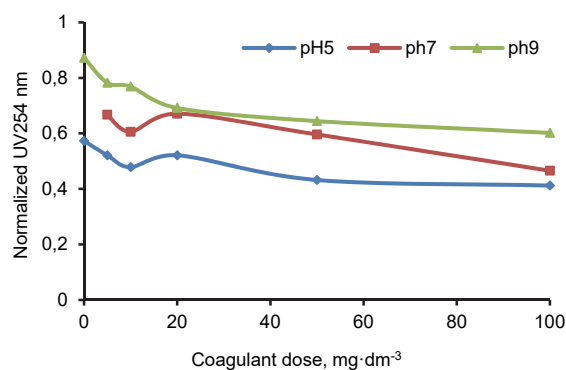


Fig. 1. Relationship between UV absorbance and coagulants dose depending on pH; source: own study

Analysis of the results showed that best effectiveness of coagulation was observed in an acidic environment (pH 5), but due to the practical aspects of technological process (no need of water neutralization after the coagulation) the pH 7.0 have been used.

By comparing the effectiveness of removing organic compounds using HAOPs with aluminium sulfate (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·18 H<sub>2</sub>O) it was observed that below 10 mg·dm<sup>-3</sup> effectiveness of HAOPs is greater than the

aluminum sulfate (for 5 mg·dm<sup>-3</sup> effectiveness of HAOPs was 39.4% and in the case of the alumina it was 22.52%).

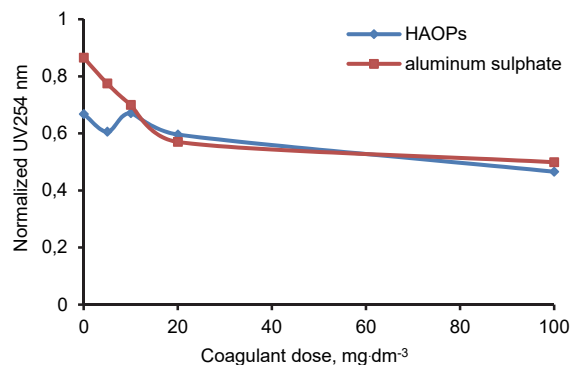


Fig. 2. Determination of the effective dose HAOPs in relation to aluminum sulphate in the batch test; source: own study

## FILTRATION

Figure 3 shows the TMP that is required to maintain the constant flux, as a function of specific volume filtered (V<sub>sp</sub>, defined as the cumulative permeate volume per unit of membrane area).

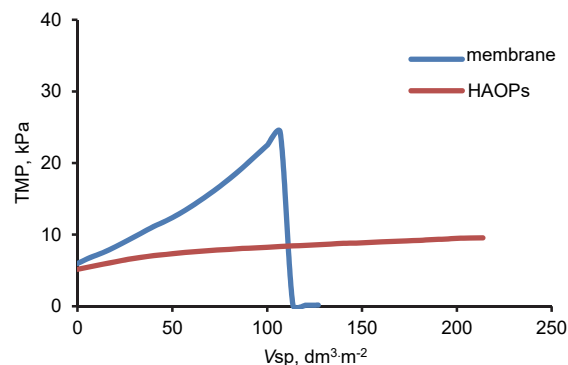


Fig. 3. Transmembrane pressure (TMP) profiles during membrane filtration; source: own study

Filtration tests confirm the effectiveness of HAOPs in removing NOM compounds which are responsible for fouling (blocking membrane pores). Presented filtration test (Fig. 3) was conducted in parallel, at one system the feed (Green Lake water) was directly delivered onto membrane surface, while the second system was equipped with the same type of membrane on which HAOPs have been pre-coated in accordance with the methodology specified in the papers by CAI *et al.* [2008]. Both systems worked in the same conditions. The system provided only in the membrane indicates rapid fouling during filtration corresponding to minimal NOM removal (less than 20%). In contradiction the effectiveness of NOM removal from water achieved by HAOPs was 69%. In addition, the dissolved carbon (DOC) removal in the case of HAOPs in relation to the filtered raw water the decrease of 47% have been observed.

In a subsequent test, the flux through the membrane/HAOPs unit was set at 100 LMH, and the unit was operated for two, 24-h treatment cycles, with manual cleaning (the adsorbent layer was rinsed off) after cycle. The pressure loss profile and the  $UV_{254}$

removal efficiency are shown in Figure 4. Significant amounts of NOM were removed when HAOPs were pre-deposited on the membrane (removing 76% of the  $UV_{254}$  from the raw water (Lake Union) at the beginning of the run and 70% at the end).

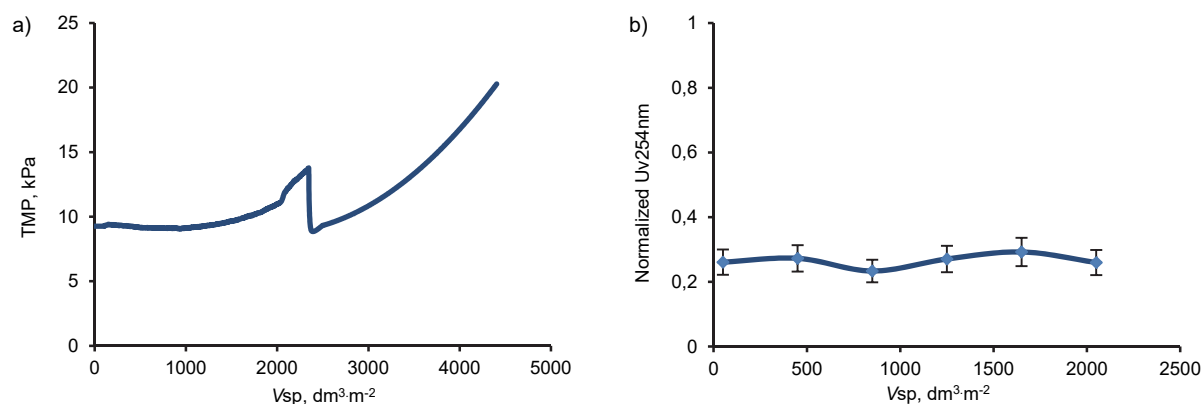


Fig 4. (a) Pressure loss across the system and (b) normalized UV 254 nm (permeate/feed) whereas samples were collected at pre-selected intervals for analysis of UV absorbance and dissolved organic carbon (DOC); TMP = transmembrane pressure,  $V_{sp}$  = cumulative permeate volume per unit of membrane area; source: own study

Water treatment and wastewater using membrane processes is an increasingly popular technique, because it has high purification efficiency. However, the fouling (block/coating membrane) is the bigger obstacle. It is related to water quality as well as the properties of the membrane. The processes followed by filtration on membranes also have importance for the process of blocking the membranes. Coagulation and adsorption before membrane filtration are often recommended as a method that minimizes fouling.

Presented results confirmed that hybrid adsorbent/membrane process consisting of a pre-treatment step in which water is passed through a pre-deposited layer of HAOPs is successful technique to prevent NOM from plugging up membranes. Further work on the effectiveness of the HAOPs in the technical scale or pilot plant with simultaneous amplification of the analytical techniques used in the identification of the NOM are required.

## SUMMARY AND CONCLUSIONS

In the presented studies showed that the use of the HAOPs can be an effective method of removing NOM from surface water (for both tested natural water the NOM removal was between 86 to 77% at a dose 5 to 10  $mg \cdot dm^{-3}$ , respectively).

The effectiveness of the water purification using HAOPs depends on many factors, and presented research have allowed stated the importance of dose and pH. Analysis of the results showed that best effectiveness of coagulation was observed at pH 5, but the NOM removal efficiency had been lower by 28% at pH 7.0.

Presented results confirm existing reports that passage of feed through a thin layer of pre-coated HAOPs removes NOM and membrane foulants and

substantially removes the majority of the  $UV_{254}$  from the raw water. In a filtration test, the effectiveness of  $UV_{254nm}$  achieved by HAOPs was 69% and in case of the dissolved carbon (DOC) the removal was 47%.

Presented study does not allow to clearly determine the effectiveness of organic compound removal from surface water, due to the different water composition as well as the membrane properties, therefore the need to conduct further research is suggested.

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## Beata MALCZEWSKA

### Ocena skuteczności usuwania naturalnych związków organicznych z wody w procesach hybrydowych

#### STRESZCZENIE

Naturalne związki organiczne (ang. natural organic matter – NOM) są produktami rozkładu organizmów roślinnych i zwierzęcych. Stanowią one mieszaninę o bardzo zróżnicowanej budowie chemicznej i zróżnicowanych właściwościach. Substancje humusowe stanowiące istotny składnik NOM są odpowiedzialne za kolor i smak wody, dodatkowo przyczyniają się do powstawania ubocznych produktów dezynfekcji (DBP). Dlatego usuwanie NOM jest uważane za jedną z istotnych operacji technologicznych w trakcie oczyszczania wód.

Zwykle w układach oczyszczania wód powierzchniowych do usuwania zawieszin i NOM wykorzystuje się proces koagulacji połączony z sedymentacją. W ostatnich latach coraz większe zainteresowanie w uzdatnianiu wody do celów pitnych odgrywają procesy membranowe. Przedmiotem badań była analiza skuteczności usuwania naturalnych związków organicznych z wody w procesie hybrydowym, a uzyskane wyniki wskazują, że zastosowanie procesu hybrydowego umożliwia poprawę skuteczności oczyszczania wody, a także ograniczenie intensywności blokowania membran. W obu przypadkach analizowanych wód naturalnych skuteczność usuwania NOM przez HAOPs (heated aluminium oxide particles) mieściła się w zakresie od 86%, gdy stężenie wynosiło  $5 \text{ mg} \cdot \text{dm}^{-3}$  i 77%, gdy stężenie wynosiło  $10 \text{ mg} \cdot \text{dm}^{-3}$ .

**Słowa kluczowe:** *fouling, procesy hybrydowe, własności transportowe, zatykanie membran*