DETERMINATION OFMOLECULAR SIZE FRACTION OF NATURAL ORGANIC MATTER IN WATER USING ULTRATION MEMBRANES

El-Azizi, Ibrahim Massaoud

Tajura Research Center, P. O. Box 30878, Tajura, Tripoli – Libya
E-mail: el_azizi2001@yahoo.com

ABSTRACT

This study focuses on applying of Ultrafiltration membranes (UF) as a fractionation technique for size estimation of natural organic matter (NOM) in two types of RO concentrates (Type A, and Type B) that collected from two different water treatment pilot plants using different pretreatment techniques before reverse osmosis systems. Ultrafiltration membranes from Koch with nominal molecular weight cutoff (MWCO) of 1000Da, 10,000Da and 50,000Da respectively were selected for fractionation processes.

Flux over time is measured during fractionation processes in both RO concentrates. Rapid decrease in flux (ca.40%) were observed in type (B) RO concentrate during fractionation process in all UF membranes whereas, the flux is remained stable during fractionation processes in type (A) RO concentrate. Type (B) RO concentrate contains high molecular weigh fraction of NOM, which is responsible for flux decline due to the adsorption or a maximum accumulation of NOM fractions on membrane surface. The adsorption or accumulation of NOM fractions causes pores blockage or formation of a cake layer on the membrane surface, which creates a resistance layer to the permeate flux.

Fractionation results showed that *ca.* 80% of NOM in both RO concentrates consists of molecular size fraction less than 1000Da.

TOC concentration and UV absorbance at 254 nm values were determined in both RO concentrates. Results showed that these values are higher in type (B) RO concentrate compared to type (A). The smaller values of TOC and UV absorbance are due to the applying of ozone as a pretreatment step in type (A) RO concentrate. Effect of ozone on NOM properties in type (B) RO concentrate was studied. TOC concentration, UV absorbance were investigated before and after ozonation process. Obtained results showed a slightly decrease in TOC concentration (16%) and a significant decrease in UV absorbance value (54%). Reason is that ozone leads to breakdown the double bonded of NOM converting the large molecular size fractions of NOM into smaller fractions, which pass easily through the membrane pose.

INTRODUCTION

Natural organic matter (NOM) is a term using to describe the complex mixture of organic compounds present in natural water, with varying concentration and characteristics. NOM is formed as a result of the breakdown of animal and plant materials in the environment. NOM can be divided into humic and nonhumic fractions; the humic fraction is more hydrophobic in character and comprises humic and fulvic acids. The nonhumic fraction is less hydrophobic in character and comprises hydrophilic acids, proteins, amino acids, and carbohydrates [2]. The presence of NOM in raw-water sources has a significant impact on the efficiency of several drinking water treatment steps, and thus on drinking water treatment costs and drinking water quality. The molecular weights fractions of humic substances are vary within a broad interval below 1000 Da. up to more than 100,000 Da. Carlson [1] had reported that 75% of dissolved carbon in a lake water consisted of organic compounds smaller than 3000Da. Until recently, humic substances were characterized by nonspecific parameters based on their carbon content (i.e DOC), by their ability to adsorb UV light (i.e. UV absorbance at 254 nm), or by their potential to form trihalmethanes (THM).

NOM absorb light over a wide range of wavelength (λ), whereas inorganic chemicals typically present in natural water do not absorb light significantly at λ>~ 230 nm [3]. As a result, the absorbance of light by natural waters is a semi-quantitative indicator of the concentration of NOM in the water. In the water treatment industry, light absorbance at 254 nm has been found useful for monitoring the concentration of dissolved organic carbon (DOC) on line, once the correlation between DOC and A254 has established for the particular water.

Ozone has high oxidation performance and has high effectiveness for decolorlation, odor removal and disinfection purpose. Ozone is now more widely used in advance water treatment and wastewater treatment to improve the quality of produced water. Applying of ozone as advanced pretreatment step increases the lower molecular weight fractions, and decreases the higher molecular weight fraction results in a significant change in NOM properties.

My sore [7] studied the effect of ozonation on NOM found that low molecular weight fractions of NOM increased from about 10% to 40% of DOC at ozone dose of 1mg of O_3/mg of DOC. Owen [2] reported that the average humic fraction percentage for ozonated sample was 33%, whereas the average of the raw water humic fraction percentages for this water sample was 52%. This indicated that the removal of NOM by coagulation, after ozonation, maybe more difficult. Significant amounts of humic material remained after coagulation, suggesting that coagulation is not optimizing the NOM removal. If ozone is combined with membrane technology, a better quality of water with low cost expected to be produced [6].

Several methods exist for characterizing the size of macromolecules in solution, including size-exclusion chromatography, field flow fractionation, and ultrafiltration (UF). Ultrafiltration is a relatively inexpensive and simple technique for fractionation of macromolecules in water. A particular advantage of the ultrafiltration technique is its ability to process comparatively large amount of water. Ultrafiltration membranes are typically characterized by molecular weight cutoff values, which are generally established by calibrating a membrane using molecules of known molecular weight. Membrane manufactures generally calibrate membranes and specify cutoff values based on the rejection characteristics of globular molecules [5].

Ultrafiltration and Micro filtration membrane processes can effectively remove turbidity and large molecular weight fraction of organic material, but these membranes can not remove dissolved organic matter (e.g. low molecular weight organic). NOM is limiting the capacity of the membranes due to the accumulation of mainly organic matter on the membrane surface. The accumulation of such organic matter is leaded to the formation of a fouling layer on the membrane surface. This fouling layer reduces the flux through the membrane. Therefore, sufficient removal of dissolved organic matter from water requires additional removal process such as Nanofiltration and reverse osmosis membranes [8].

This study focuses on applying of ultrafiltration as fractionation technique for size estimation of NOM in water and effect of pretreatment (ozone) on the properties of NOM.

MATERIALS AND METHODS

Water Samples

Two types of RO concentrates were collected from two water treatment pilot plants using different raw water sources and different feedwater pretreatment techniques before reverse osmosis systems. Pilot plant (A) uses coagulation, flocculation, sedimentation, rapid sand filtration, ozonation, granular activated carbon (GAC) filtration, and slow sand filtration. Pilot plant (B) uses coagulation, flocculation, sedimentation, rapid sand filtration, and ultrafiltration.

Ultrafiltration Membranes

Ultrafiltration (UF) membranes from Koch with nominal molecular weight cutoff of 1000Da, 10000Da, and 50,000Da, respectively, were used for fractionation of NOM in RO concentrates. The characteristic of UF membrane model is presented in Table 1.

Table 1. Characteristic of UF membranes of Koch model.

Membrane manufacture	Koch
Membrane Material	Sulfonate Polysulfone
Nominal MWCO	1000, 10,000, 50,000 Da
Hollow Fiber Diameter	1.1 mm
Hollow Fiber Length	0.64 m
Total Hollow Fiber Surface Area	0.46 sq.cm
Operation Mode	Dead-end

The UF membranes were operated in dead-end operation mode. In dead-end filtration the feed flow is perpendicular to the membrane surface. The retained particles are accumulated and form a type of cake layer at the membrane surface. The thickness of the cake layer increases with filtration time and consequently the permeation rate decreases with increasing the cake layer thickness.

The membranes were cleaned very well before each filtration cycle. Sodium hypochlorite and citric acid were used as chemical cleaning agents. Before each filtration cycle deionized water was filtered through the UF membranes until the TOC concentration of deionized water in the influent and effluent was to be equal. This is to be sure that there's no OM released from the membrane material.

Analytical Methods

Dissolved organic matter (DOC) in terms of TOC concentration was measured in RO feedwaters and concentrates using Total organic carbon analyzer (TOC). Ultraviolet absorbance of NOM at λ=254 nm was measured using Ultraviolet spectrometer and 5cm quartz vessel.

RESULTS AND DISCUSSION

Fractionation of NOM in RO Concentrates

Type (A) and type (B) RO concentrates were collected and fractionated using UF membranes from Koch with nominal molecular weight cutoff of 1000Da, 10,000Da, and 50,000Da respectively. The TOC concentration of Type (A) and Type (B) RO concentrates before fractionation processes were 4.8 mg/L and 14.5 mg/L respectively. Fractionation results (Table 1) showed that about 80% of dissolved organic matter in both RO concentrates consist of molecular size fractions less than 1000Da. The molecular size fraction bigger than 50,000Da is higher in type (B) RO concentrate than in type (A) due to the effect of ozone which is used as pretreatment step in pilot plant (A).

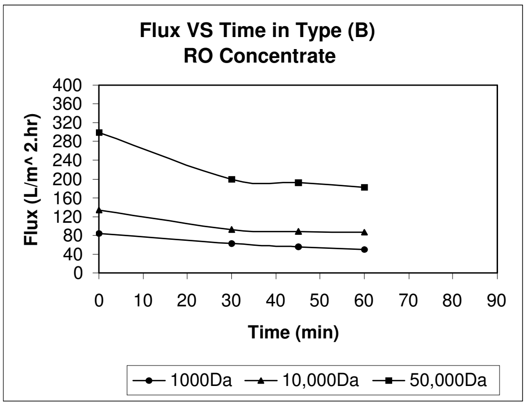
Table 1. Rejection of NOM by UF membranes in type (A) and type (B) RO concentrates

Type of water	1000 Da	10000 Da	50000 Da
Type (A) RO concentrate	14.6%	14.6%	8.3%
Type (B) RO concentrate	17.9%	17.2%	14.5%

The obtained results are in an agreement with the results that obtained by Newcombe [4]. He had investigated the size fraction of NOM in Mypoga reservoir, and had found that 80% of NOM consists of molecular size fraction less than 3000 Da. Carlson *et al.* [1] had investigated the molecular size fraction of NOM in Sliver Lake water found that 75% of DOC in natural water consists of molecular size fraction smaller than 3000 Da. However, using of smaller pore size membranes <1000 Da is needed to investigate the molecular size fraction of NOM in natural waters.

Flux Decline

Flux over time is measured during each fractionation process. Rapid decline in flux (*ca.*40%) was observed in type (B) RO concentrate after one hour of fractionation processes (Figure 1). A general trend that the flux decreases due to the adsorption of NOM on the membrane surface, which caused pore blockage, or accumulation of NOM particles in the membrane surface and forming a cake layer. The formed cake layer is created a resistance to the permeate flux. The Flux was stable in type (A) RO concentrate during one hour of experimental run (Figure 2), due to the less adsorption or accumulation of molecular size fraction of NOM on the membrane surface. In type (A) RO concentrate NOM molecules became smaller after using of ozone and activated carbon filtration as pretreatment steps which decrease the number of blocked pores of the membrane.



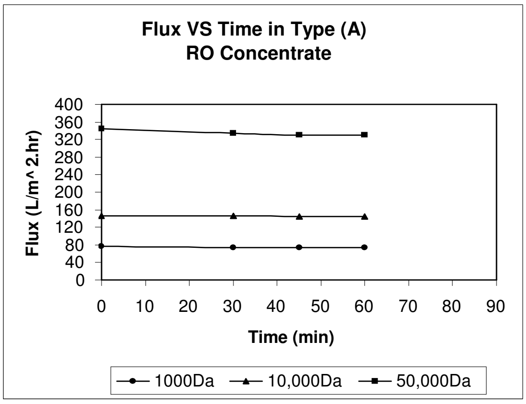


Figure 1. Flux VS time in fractionated Type (B) RO concentrate

Figure 2. Flux VS time in fractionated Type (A) RO concentrate

TOC and UV Absorbance Measurements

Natural organic matters that are aromatic in structure or that have conjugated double bonds absorb ultraviolet light over wide range of wavelength. Ultraviolet absorbance (UV) at 254 nm is often used as a simple measurement for DOC that is especially effective for water containing aquatic. The specific UV absorbance (SUVA) is an instructive measurement for water supplies. SUVA value is calculated using the following formula:

$$SUVA = -\frac{UV}{TOC}\left[\frac{L}{mg.m}\right]$$

TOC concentration, UV absorbance and SUVA values were determined and it was found that the type of NOM in both RO concentrates is hydrophilic, low aromatic and has low molecular weight fraction. The higher UV absorbance and SUVA values show that the molecular size fraction of NOM in type (B) RO concentrate is higher compared to type (A) RO concentrate. The smaller UV absorbance and SUVA values in type (A) RO concentrate is due to applying of ozone as pretreatment step.

Figures 3 and 4 show the TOC, UV absorbance and SUVA values in fractionated type (A) and type (B) RO concentrates using UF membranes with different MWCO. Results showed that no change in these values after applying UF membranes for fractionation processes with different MWCO. Membrane cutoff is less important to TOC, UV, and SUVA values in the range of 1000 – 50,000Da.

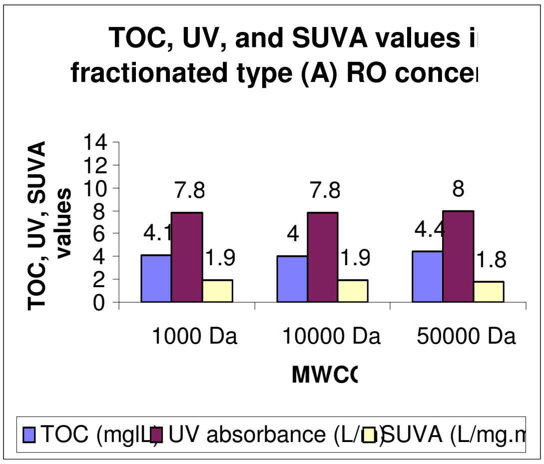


Fig. 3 TOC, UA absorbance and SUVA values in fractionated type (A) RO concentrate.

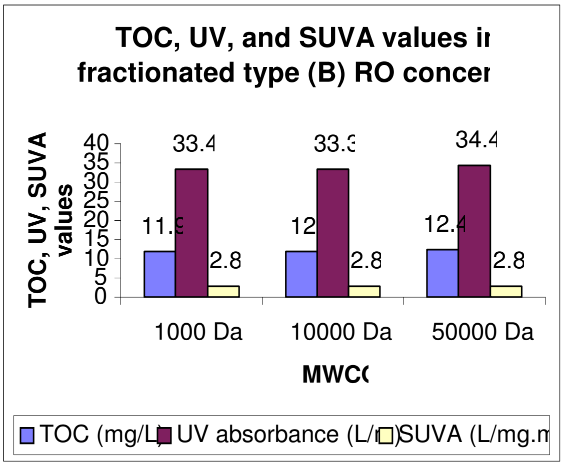


Fig. 4 TOC, UV absorbance, and SUVA values in fractionated type (B) RO concentrate

Effect of Ozone on NOM

Ozone has high oxidation performance is widely used in advance water treatment to improve the quality of produced water. To investigate the effect of ozone on the properties of NOM, type (B) RO concentrate was collected and ozonated at KIWA company with ozone dose of 0.42 mg of O_3 / mg of TOC. TOC concentration, UV absorbance, and SUVA values were measured before and after the ozonation process (Figure 3).

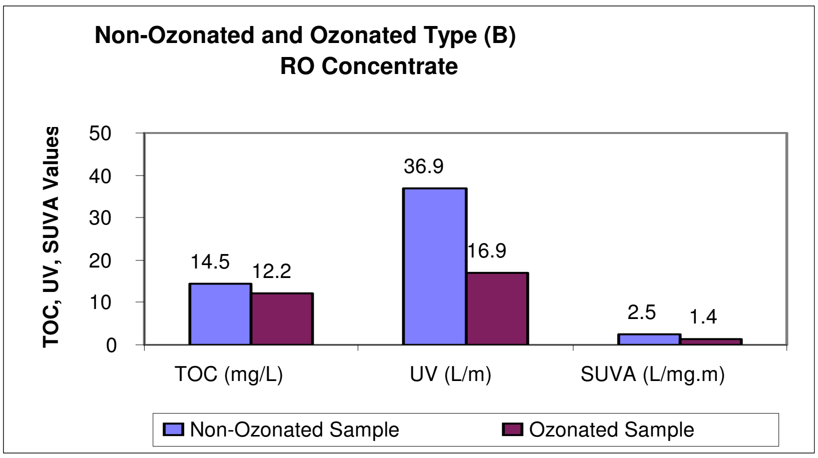


Figure 3. TOC concentration, UV absorbance and SUVA values of non-ozonated and ozonated type (B) RO concentrate

A little reduction of TOC concentration (*ca.*16%) is achieved by ozonation. The significant decrease was observed in UV absorbance value (*ca.* 54%) and SUVA value (*ca.* 44%). These results are in agreement with the results obtained by Owen [2]. He reported that the percentage of humic fraction of raw water sample was 52% whereas; the humic fraction percentage after ozonation became 33% only. After ozonation process NOM molecules become smaller which decreases the number of blocked pores size of the membrane.

CONCLUSIONS

Ultrafiltration as a fractionation technique is a very suitable and time saving technique for fractionation of molecular size fraction of NOM in water.

Molecular size fraction of NOM in type (A) and (B) RO concentrates using UF membranes of (1000Da, 10000Da and 50000Da) showed that 80% of molecular size fraction of NOM in both RO concentrates less than 1000Da.

Flux decline of about 40% was observed during fractionation process in type (B) RO concentrate; whereas the flux was stable in type (A) RO concentrate. Less fouling problems in waters containing lower molecular size fraction of NOM.

The UV spectroscpoic investigation of NOM in type (A) and type (B) RO concentrates showed that NOM in type (B) RO concentrate is contained more double bonded fractions compared to type (A) RO concentrate.

The effect of ozonation on the properties of NOM in type (B) RO concentrate was investigated. About 54% decrease of UV absorbance, 44% decrease in SUVA and slightly decrease (16%) in TOC concentration values was observed.

REFERENCES

1- Carlson G., Silverstein J. (1997) "Effect of ozonation on sorption of natural organic matter by biofilm" Water res. Vol.31, No.10, pp 2467-2478.

2- Douglas M., Owen, Gary L. Amy, Zaid K. Choodhury, Rajendra Paode, George Mc coy, and Kathy Viscosil (1995) "NOM characterization and treatability" Journal AWWA, pp 46-63.

3- Gregory V. Korshin, Chi-Wang Li, and Mark M. Benjamin (1996) "Monitoring the properties of natural organic matter through UV spectroscopy: A consistent theory" Water Res. Vol. 31, No. 7, pp. 1787-1795, Elsevier Science Ltd.

4- Galye Newcombe, Mary Drikas, Shoeleh Assemi, and Ronald deckett, (1996) "Influence of characterised natural organic material on activated carbon adsorption: I. Characterization and concentrated reservoir water" Water Res. Vol.31, No.5, pp.965-972, Elsevier Science Ltd.

5- James Kllduff, and Walter J. Weber Jr. (1992) "Transport and separation of organic macromolecules in ultrafiltration processes" Environ. Sci. Technol. Vol.26, No.3, pp. 569-576.

6- Mori Y., Oata T., Hashino M., Takamura M., and Fujii Y. (1998), *"Ozone-*microfiltration system" Desalination, vol.117, pp. 211-218, Elsevier Ltd.

7- Mysore S. Chanrakanth and Gray L. Amy (1996), "Effect of ozone on the colloidal stability and aggregation of particles coated with natural organic matter", Environ. Sci. Technol. Vol.30, No. 2, pp.431-443.

8- Suzuki T., Watanabe Y., Ozawa G., and Ikeda S. (1998), "Removal of soluble organics and manganese by a hybrid MF hollow fiber membrane system" Desalination, vol.117, pp. 119-129, Elsevier, LTD

9- Thersen T., Harz A. and Fdegraad H. (1997) *"Influence of raw water* characteristics and membrane pore size on the performance of ultrafilters for NOM (humic substances) removal" Blackwell Science Ltd, IWSA world congress.