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Experimental study of NOM characteristics affecting membrane fouling potential

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ABSTRACT

In both, industrialized and developing countries, there is growing concern about the ability of traditional drinking water supply systems and existing technologies to cope with present and future demands and threats. Water supply in Europe faces opportunities as well as challenges promoting the application of advanced treatment technologies such as membrane filtration. This technology can improve drinking water quality and tackle pollutants of concern such as disinfection by-product precursors or trace organics. Although membrane filtration is now applied in an increasing number of installations there is still room for improvement with respect to operational issues. Furthermore, baseline recommendations for a good operational practice have to be developed.

Keywords : Water treatment – Membranes – Fouling – Natural Organic Matter.

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INTRODUCTION

Material separation is a basic need in nature as well as in man-made processes. Membranes are at the center stage these days when it comes to separation of materials and the use of membrane technology has been growing rapidly during the last few decades. Membrane treatment of natural water (surface/sea water) to produce potable/process water and of wastewater for safe disposal are growing at a drastic rate owing to advantages like low energy consumption, ease of use and maintenance. Membrane technology for water treatment is, however, impaired by the problem of fouling. Fouling by organic matter has been identified as the most complicated problem facing MF/UF operations, due to its irreversible nature and difficulties with the cleaning procedure. It also initiates and supports bio-fouling of NF/RO as the organic foulants in the feed water are readily available as nutrients for microbial growth. So a clear understanding of the organic fouling is decisive for improving MF/UF operation performance not only in the production of potable water from direct treatment of surface water, but also in the pre-treatment line prior to sea water reverse osmosis (SWRO). The objective of this work is to investigate the membrane fouling potential of a capillary type PES polymeric membrane filter and fouling mechanism of different organic fractions in the bulk natural surface water.

Background of the investigation:

Natural organic matter (NOM) is described as an intricate mixture of organic compounds that occurs universally in ground and surface waters. After treatment for potable use, there is NOM remaining in the water that reacts with the chlorine used for disinfection to form disinfection by-products (DBPs).

An investigation into how NOM characteristics differ, methods of NOM analysis and its reactivity with themembrane was undertaken. By separating the NOM using filtration steps into fractions, it was possible to gain an insight into the ability of different NOM fractions to foul. It was observed that a particular, difficult to remove fraction was always more problematic. Water analysis methods like TOC and DOC indicate how much total NOM is present in water. However both of the measurements give little information about the nature of the organics in terms of treatability or reactivity with membranes. By measuring bulk water parameters, such as TOC and DOC, the information obtained is not detailed enough to determine how the NOM is changing with its particle/molecular size. To investigate these changes in more detail it was deemed necessary to separate the NOM into its component parts to assess its character.

NOM has been characterised by a wide range of analytical techniques some of which will be discussed in this review. Characterisation is typically undertaken on either bulk NOM material or fractionated NOM material. The advantage of bulk water studies is that 100% of the NOM is present in an unaltered state. Results from such studies are directly applicable for the specific reaction conditions and water. The disadvantage is that the factors that affect the reactions of specific types of NOM cannot be identified or understood.

In some waters, the influence of the inorganic matrix may impede understanding of the behaviour of NOM. The study of isolated NOM fractions can provide operationally defined samples for examination of NOM behaviour although synergistic effects are lost (Hwang et al. 2001). Concentrated samples produced by fractionation can be further analysed by techniques such as elemental analysis, pyrolysis - gas chromatography/mass spectrometry (GC/MS), carbon-13 nuclear magnetic resonance (13C-NMR) and capillary electrophoresis to elucidate structure. It would not be possible to carry out such analyses on bulk water samples due to the high concentrations of DOC required.

A combination of bulk and isolation studies is needed to retain the advantages of both approaches while minimising their disadvantages. It has been identified that a number of relationships exist between water quality parameters and the character and reactivity of NOM. A few simple water quality parameters that can be used as indicators of the organic loading of water and subsequently its fouling potential are discussed here [1-11].

MATERIALS AND METHODS

TOC and DOC measurement
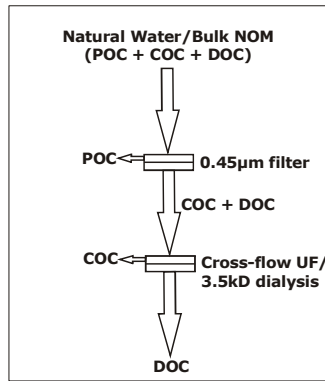
Figure 1: A simple scheme of NOM fractionation steps

In Fig. 1 NOM is separated into particulate organic carbon (POC), colloidal organic carbon (COC) and dissolved organic carbon (DOC). The analytical instrument used in a organic carbon analyser. When bulk water is measured directly the measured value is termed as TOC, which represents the total organic carbon content in the water. A standard method used to measure DOC is to filter the bulk sample first through a 0.45 μm filter to remove particulates. The filtrate then should contain only dissolved carbon content and this when measured gives DOC value.

NOM consists of humic (nonpolar) and non-humic (polar) substances, generally of terrestrial and biological origin respectively (Hwang et al. 2001). Non-polar NOM has been well characterised and is readily removed by coagulation. In contrast, polar NOM has been studied less extensively and is not readily removed by coagulation.
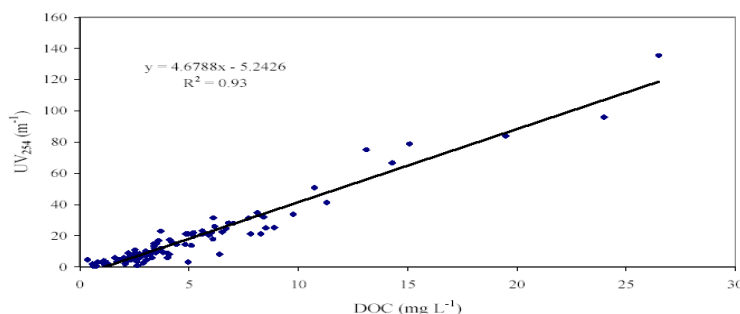
Bulk characterisation of NOM:

Parameters measured include

- DOC (mg L^{-1}),
- ultraviolet absorbance at 254 nm (UV_{254} (m^{-1})) and
- SUVA (= UV_{254}/DOC) (SUVA, is defined as the UV absorbance of a given sample determined at 254 nm and
- divided by the DOC concentration of the solution (expressed in m-1. L mg^{-1} C)).

The key relationships are

- The higher the DOC, the higher the UV_{254}
- The higher the DOC, the higher the organic content of water
- The higher the SUVA, the higher the fouling potential

Figure 2: Relationship between DOC and UV254 for a range of different source waters

Fractionation of NOM

People worked on NOM characterisation have nearly always focussed on dissolved organic matter as in practice, particulate organic matter (POM) is separated from the aqueous phase by filtration through 0.45 µm pore filters. Once the POM has been removed, the choice of which separation method to use for isolation/concentration/fractionation will depend on the objectives of the study, the equipment available and the DOC concentration of the water. Typically the bulk organic matter can be separated on the basis of either molecular charge or size and a range of options for concentration, isolation and fractionation are outlined in Fig. 3. The options for separating the NOM on the basis of adsorption/charge are resin fractionation, chromatography and less often, mineral adsorption. To separate the NOM on the basis of the size of the molecules, the options include membrane fractionation, flow field-flow fractionation (FFFF) and again chromatography. Chromatography is included in both categories as size exclusion chromatography columns can be used to separate organic matter on the basis of molecular size whilst normal chromatographic columns can be used to separate the organic matter on the basis of polarity.
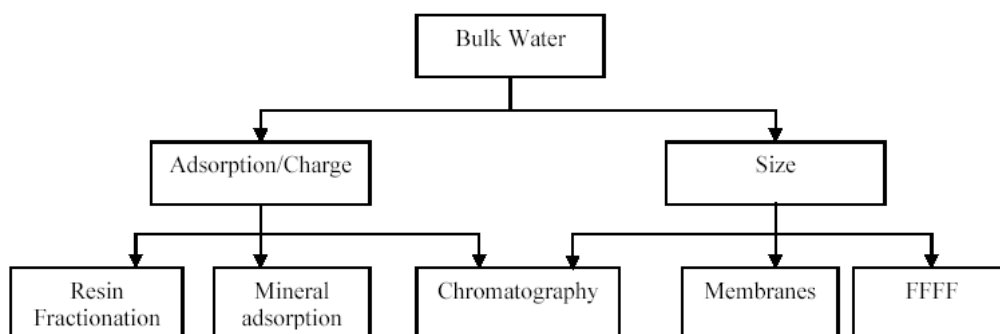

Figure 3. Methods available for isolation, concentration and fractionation of NOM

RESULTS

Organic fractions produced for testing on membrane performance:

1. P   – Pure particulate fraction – size > 0.2µm
2. C   – Pure colloidal fraction – size < 0.2 and > 5kD
3. D   – Pure dissolved fraction – size < 5kD.
4. (C+D)   – fraction containing colloidal and dissolved organics.
5. (P+C)   – fraction containing particulate and colloidal organics.

Normalised permeability (NP)

A survey of the experimental results can be done more conveniently comparing coefficients which represent the impact of coagulation and/or organic size fractions on the fouling behaviour. The results of the fouling experiments were plotted on the basis of Normalised Permeability (NP %) (Permeability divided by pure water permeability) versus time (min). This arrangement was made to compensate for variations in starting point pure water permeabilities.

Permeability decline coefficient (PDC)

Decline of NP with time was quite different for the different fractions filtered, and it is sometimes hard to compare them by just looking into the graphs. A factor called "permeability decline coefficient" (PDC) is introduced to make comparison simpler. It is defined as the overall permeability decline during the filtration time divided by the total filtration time, i.e. the (negative) slope of the NP curve from the beginning to the end of a filtration run.

$$PDC = \frac{\text{Difference of the starting and ending NP during filtration for time T}}{\text{Total filtration time T}}$$

PDC of 1 implies extreme fouling and 0 implies the most ideal condition of best membrane performance with no irreversible fouling (as the reversible foulants are removed by regular pure water backflushing).

Coefficient of influence of coagulation on the membrane performance

Comparing the PDC of a fraction with and without coagulation can also be simplified by the introduction of the coefficient of influence of coagulation on the membrane performance CI-PDC, which is defined as the improvement in the membrane performance (with respect to decrease in the PDC) during the filtration of a fraction with coagulation when compared to that without coagulation.

$$\text{CI - PDC} = 1 - \left[\frac{\text{PDC}_{\text{with coagulation}}}{\text{PDC}_{\text{without coagulation}}} \right]$$

Performance of Mem-1 with the different fractions

Mem-1, which is a PES capillary submerged membrane with a nominal pore size of 0.1 μm from Koch membrane systems, had pure water permeability of 700 – 900 L/m^{2}hbar.

Mem-1 with the different fractions without coagulation

The NP decline curves plotted were extracted from the original experimental results showing the backwash events, by interpolation between the permeability at the beginning of the filtration run and at the end of each filtration cycle. This was done to make comparison between different experimental runs easier (see Fig. 4).
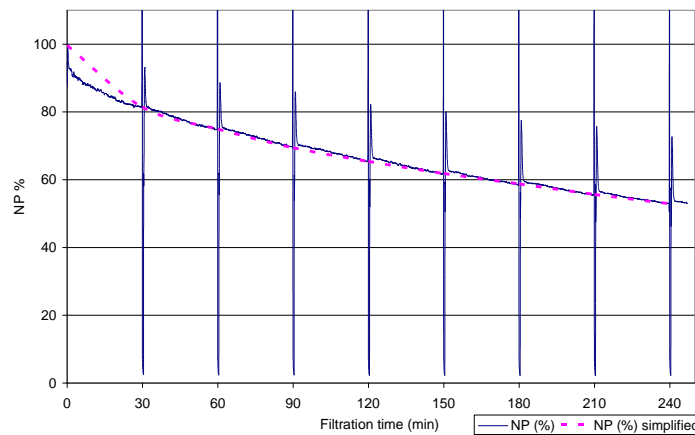
Figure 4: E.g. of originally measured NP (%) decline and its simplified version for fraction (P+C) without coagulation

The fraction (P+C) had the worst fouling effect (see Fig. 5) that resulted in the largest permeability (NP) decline and the highest PDC value (see Fig. 7). The extent of permeability decline of (P+C) was followed by (P), (RW) and (C+D). The colloids (C) and dissolved (D) fractions had nearly the same and least PDC value of all. It can be ordered as - (P+C) > (P) > (RW) > (C+D) = (C) > (D).
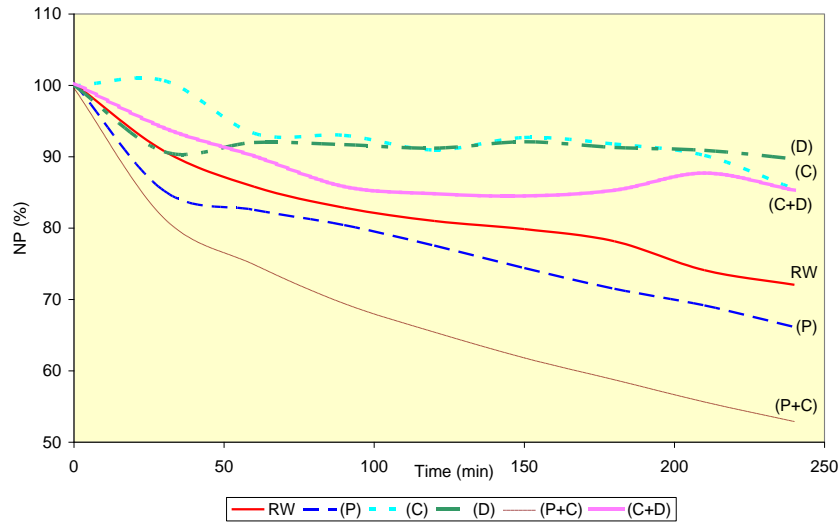
Figure 5: NP decline of different fractions without coagulation filtered on Mem-1

Mem-1 with the different fractions with coagulation:

When coagulated the PDC values of the fractions followed the order – (P) > (P+C) > (D) > (C+D) > (C) > (RW) (see fig. 7). Except the fraction (D), the PDC value of all other fractions improved due to coagulation. The influence of coagulation on PDC, calculated as CI-PDC, was the highest in the case of (P+C), followed by RW, (P), (C+D) and (C). Again, as reported earlier [3], the fraction

(P+C), when coagulated, was not extremely fouling anymore, and coagulation was very effective in negating its fouling potential. CI-PDC values of the fractions follow the order - (P+C) > (RW) > (P) > (C+D) > (C) > (D).
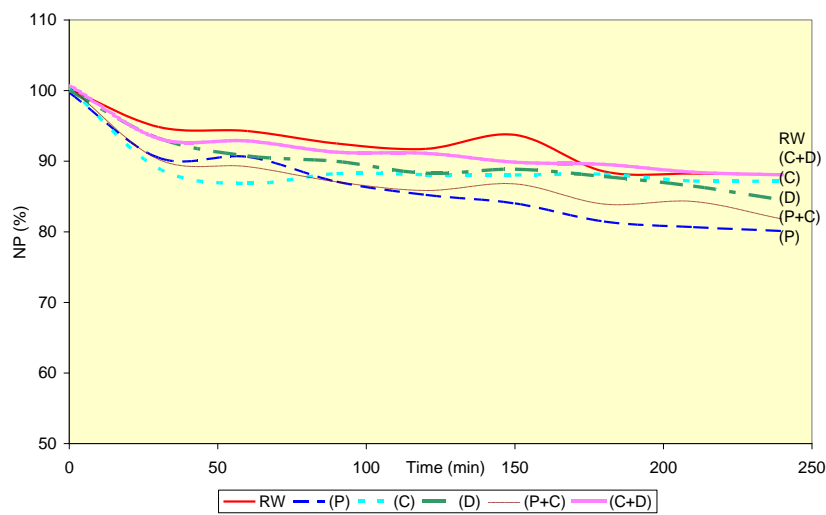

Figure 6: NP decline of different fractions with coagulation filtered on Mem-1

To summarise, on Mem-1, the fraction (P+C) followed by (P) was the most fouling both without and with coagulation. However, the influence of coagulation in minimising fouling was also the highest for this fraction. The fractions (C) and (C+D) seem to have nearly the same fouling potential and coagulation had not much of an effect on minimising fouling. The dissolved fraction was the least fouling of all and coagulation had an adverse effect on its fouling potential. The original raw water was the least fouling when coagulated.
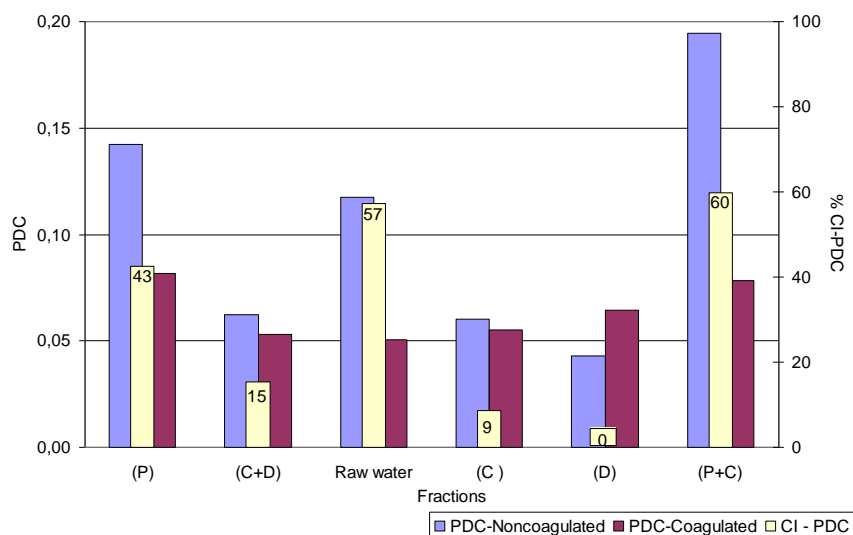
Figure 7: PDC and CI-PDC of different fractions with Mem-1

CONCLUSION

Thus, interactions between organic (size) classes and the membrane material/pore size become indicators to predict organic fouling in MF/UF filtration operation and additionally help evaluate use of pretreatment by coagulation to curtail irreversible organic fouling and provide steady membrane performance.

REFERENCES

[1]   Kaiya Y,Itoh Y,Takizawa S, Fujita K , Tagawa T. J Water Science and Technology 2000; 41: 59-67.
[2]   Shim Y, Lee H J, Lee S , Moon S H, Cho J. Environ. Sci. Technol 2002; 36:3864-3871.
[3]   Howe K J , Clark M M . Environmental science and technology 2002; 36:3571-3576.
[4]   Aiken G R , Leenher J A. Chemistry and Ecology 1993; 8:135-151.
[5]   Sundaramoorthy K , Loi-Bruegger A . Membrantechnik 2005; 14:1-22.
[6]   Laine J M , Campos C , Baudin I, Janex M L. Proceedings IWA 2002.
[7]   Liu C. AWWA Membrane Technology Conf 2013.
[8]   Amy G ,Cho J . J Water Science and Technology 1999; 40: 131-139.
[9]   Cho J , Amy G. Pellegrino J. J Desalination 2000; 127: 283-298.
[10]   Cho J , Amy G. Pellegrino J. J Membrane Science 2000; 164: 89-110.
[11]   Cho J , Amy G. Pellegrino J. J Desalination 1998; 118: 101-108.