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New insights into the fouling mechanism of dissolved organic matter applying nanofiltration membranes with a variety of surface chemistries

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ABSTRACT

Nanofiltration (NF) membrane fouling by DOM remains a major and poorly understood issue. To acquire a better insight we studied the fouling of the DOM fractions humic acids (HAs) and fulvic acids (FAs), with and without Ca^{2+}, on native and grafted ceramic NF membranes. Grafting with two methods and three different grafting groups allowed to create a range of membranes with a variety of surface chemistries, and a wide range of surface polarity, much broader than ever used in previous studies. A typical polymer (polyamide) NF membrane was included for comparison. All obtained results reveal that membrane fouling is not determined by membrane hydrophilicity/hydrophobicity as a general and sole criterion, but rather on the whole of the surface chemistry determining the amount and strength of the possible foulant–membrane interactions. As a consequence the effect of inorganic ions on the fouling is also dependent on the surface chemistry. Important new insight in the DOM fouling mechanism was acquired, shedding new light on the state-of-the-art knowledge.

1. Introduction

With the increasing demand for **clean and fresh water**, many new technologies of water purification are being developed. Since the last two decades, membrane technology has emerged as a worthwhile treatment to comply with existing and pending water quality regulations (Singh, 1998; Wiesner and Chellam, 1999; Meng et al., 2009; Guo et al., 2010; Hwang et al., 2010; Diagne et al., 2012; Freeman and Shorney-Darby, 2011). Currently, particular interest has been raised in the use of **nanofiltration (NF)** as a single-step treatment alternative, offering a resourceful approach to meet multiple water quality objectives such as control of organics, inorganics and micro pollutants via a combination of charge interaction and size exclusion (Eriksson, 1998; Hilala et al., 2004; Lerch and Lee, 2004; Panglisch and Gimbel, 2005; Han et al., 2013). In addition, specific attention increases for ceramic NF membranes combining robustness with high water flux due to its high hydrophilicity.

However, **fouling** is still a major and poorly resolved problem in all membrane-based separation processes especially for water treatment (Chang et al., 2002; Goosen et al., 2004; Drews, 2010; Ni et al., 2011; Ajmani et al., 2012). Prosperous and effective applications of membrane technology has been critically limited and hampered by membrane fouling. Membrane fouling is attributed to the physicochemical interactions between the impurities present in the feed, and the membrane surface. Therefore, fouling of membranes and especially NF membranes, depends on many parameters such as membrane material, surface roughness (Elimelech et al., 1997), surface chemistry, porosity, operational conditions, and of course feed water quality (Nyström et al., 1995). Fouling, associated with accumulation of substances on the membrane surface or within the membrane pores by charge or other strong interactions, is known as **irreversible fouling** (or chemical fouling) and can only be removed by chemical cleaning (Clark et al., 1991; Su et al., 2000; Sun et al., 2013).

A wide spectrum of ingredients or impurities in water contributes to irreversible fouling. These include **dissolved organic matter (DOM)**, soluble inorganic compounds, and microbes. DOM forms a major organic constituent in water especially in surface and ground water, and it has been considered to be a significant foulant (Hong and Elimelech, 1997; Maartens et al., 1998; Yuan and Zydney,

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1999, 2000; Manttari et al., 2000). The role of DOM in fouling of membranes has been pointed out by a number of investigators (Howe and Clark, 2002; Lee et al., 2006; Huang et al., 2007; Katsoufidou et al., 2010; Zularisam et al., 2011; Aryanti et al., 2015). Many researchers came to the conclusion that irreversible fouling is stronger for more hydrophobic membranes, than for more hydrophilic membranes (Kulovaara et al., 1999; Ma et al., 2001; Mohammadi et al., 2002) Furthermore, it has been abundantly shown that membrane fouling by DOM is significantly enhanced in the presence of **divalent cations (e.g. Ca^{2+})** (Jucker and Clark, 1994; Nystrom et al., 1996; Hong and Elimelich, 1997; Yuan and Zydney, 2000; Lin et al., 2015)

Different aspects of DOM are important for its fouling behavior: charge, size and polarity. Primarily, several researchers focused on fouling instigated by humic acids (HAs) and ascribed it to hydrophobic interactions (Krasner et al., 1996; Nabe et al., 1997; Kulovaara et al., 1999; Yuan and Zydney, 1999; Ma et al., 2001; Mohammadi et al., 2002; Giasuddin et al., 2007; Lee and Cho., 2004; Costa et al., 2006; Yamamura et al., 2007; Katsoufidou et al., 2008; Aryanti et al., 2015). HAs are larger size molecules rich in aromatic carbon, but having also polar groups such as carboxylic and phenolic groups. During the last few years, membrane fouling by the hydrophilic part of DOM, known as fulvic acids, was also considered comprehensively (Kimura et al., 2004; Tian et al., 2013a,b). Fulvic acids (FAs) are typically smaller in size, having less aromatic carbon but relatively more polar functional groups. Unfortunately, despite all these investigations, DOM membrane fouling has continued to be a poorly understood phenomenon, as no clear understanding of DOM fouling could be acquired hitherto (Huang et al., 2007; Jermann et al., 2007; Katsoufidou et al., 2010; Zularisam et al., 2011; Tian et al., 2013a,b). Additionally, we want to stress that the majority of these studies have been performed on polymeric membranes. To the best of our knowledge, a detailed DOM fouling study on ceramic NF membranes has not been reported elsewhere.

In this paper, we were able to acquire important new insights into the fouling mechanism of DOM, and in specific the role of ions (Ca^{2+}). This was obtained by determining HAs and FAs fouling with and without Ca^{2+} on ceramic (TiO_2) NF membranes with a wide variety of surface chemistries. This is a unique approach, allowing to study DOM fouling for a broad range of surface polarities, much broader than in any previous studies. To vary the surface chemistries, two types of surface modifications were used: phosphonic acid grafting (Randon et al., 1995; Mutin and Guerrero, 2005) and a recently developed innovative method based on **Grignard chemistry** (Meynen et al., 2009; Rezaei Hosseinabadia et al., 2014; Mustafa et al., 2014). For comparison also a commercially available polymeric (polyamide) NF membrane was included in the study.

We want to stress that this is also the first systematic study with focus on understanding the impact of inorganic ions on DOM fouling of ceramic membranes (particularly TiO_2 NF membranes).

2. Materials and methods

2.1. Membranes and chemicals

Commercially available, small-scale tubular (monochannel tubes having an outer diameter of 1 cm, and an inner diameter of 0.7 cm) TiO_2 NF membranes (denoted Native), with an average pore diameter 0.9 nm were acquired from the company Inopor Gmbh. The molecular weight cut-off (MWCO) communicated by the supplier is 450 Da, characteristic for NF membranes ($200 < MWCO < 1000$ Da). Flat sheet, thin film composite polyamide NF membranes (denoted PolyA) having a backing material of polyester, and a total membrane thickness of 0.0065 inches (0.165 mm) were provided by Synder Filtration. The MWCO as communicated by the supplier is 600 Da, again in the correct range for NF membranes. All necessary chemicals such as methyl phosphonic acid, methyl magnesium bromide, propyl magnesium bromide, phenyl magnesium bromide, calcium chloride, and humic acids (HAs) were purchased from Sigma Aldrich chemical company. Fulvic acids (FAs) was purchased from a company named Wuhan Shengtong Jinde Chemical Co., Ltd, China. The alkaline cleaning agent P3 Ultrasil 110 was delivered by Ecolab manufacturers. Pure water (reverse osmosis quality water) with a conductivity of less than 15 μs/cm and pH 6.5–7 was used for all filtration experiments and as a solvent for phosphonic acids graftings.

2.2. Grafting of TiO_2 NF membranes

Native TiO_2 NF membranes are highly hydrophilic membranes, containing abundant −OH groups on their complete pore surface. To vary the surface chemistry of these membranes, different native membranes were grafted using two different chemical modification agents: phosphonic acids (PA) and Grignard reagents (GR). Three different functional groups, i.e. methyl (M) groups, phenyl (P) groups, and propyl (Pr) groups, were grafted by both techniques. Details of both grafting procedures can be found in the previous paper (Mustafa et al., 2014). Modified membranes are denoted by a three letter code: MGR/PGR/PrGR stand for a membrane grafted with methyl/phenyl/propyl using the Grignard grafting technique; MPA/PPA/PrPA stands for a membrane grafted with methyl/phenyl/propyl using the phosphonic acid grafting technique.

It is important to mention that even for the same functional group, both grafting techniques deliver different surface chemistries (Mustafa et al., 2014). Grignard modification leads to a partial replacement of the surface −OH groups of the native membranes, and to a unique direct bond of the organic groups to the metal atom not involving an oxygen atom (M-R bond) (Meynen et al., 2009; Rezaei Hosseinabadia et al., 2014). In contrast, the reaction of the phosphonic acid groups with the surface of a native membrane occurs via condensation reactions with one or more OH-groups resulting in the formation of one or more oxygen bridging (M-O-P-R) bonds. Fig. 1 visualizes the different types of membrane surface chemistry for the membranes that were used in this fouling study. As will be shown in section 3.1 PPA and PrPA membranes lead to membranes with such a high hydrophobicity that no water flux could be measured. As a consequence, these membranes were not incorporated in this fouling investigation.

For most membrane types, different specimens (2–5) were used to study the reproducibility of the results.

2.3. Model foulants solutions

As explained in the introduction, in surface and ground water DOM is a major and common foulant especially in combination with inorganic salts or ions (e.g. Ca^{2+}). DOM is a mixture of many different natural organic compounds that can be divided into two parts. One part consists of smaller size molecules (molecular weight between a few Da to 5 kDa) known as FAs. Fig. 2A gives an example of the typical structure of a FAs molecule (Buffle et al., 1977). The other part, known as HAs, contains large molecules (molecular weight can be between 5 kDa and 50 kDa). An example of the typical structure of a HAs molecule is shown in Fig. 2B (Stevenson, 1994).

FAs are fairly soluble under all conditions due to its relative high charge/polarity, while the solubility of HAs depends upon different factors such as concentration of inorganic ions and pH (Tipping et al., 1988). Complexation of DOM with inorganic ions increases