Evaluation of the fouling resistance of methyl grafted ceramic membranes for inorganic foulants and co-effects of organic foulants

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ABSTRACT

The application of NF membranes is still a big challenge because of both organic and inorganic fouling. In our previous studies, we have clearly shown that grafting of TiO_2 NF membranes with organic groups, and especially grafting with methyl groups using Grignard reagents, leads to a strong antifouling effect for different organic materials.

In this paper, we study the irreversible fouling of inorganic foulants such as iron and manganese hydroxides/oxides/salts (scaling) of native and grafted ceramic NF membranes. In addition, the influence of the presence of organics on inorganic fouling and co-effects of multiple organic materials (e.g. humic acids and alginate) on the fouling were also measured. As a final test, the potential of the surface grafted ceramic NF membranes is also evaluated in real surface water, where many different foulants are present simultaneously.

In all cases, the strong antifouling effect of methyl Grignard grafting is confirmed. For the investigated membranes with varying amount of polar surface groups, humic acids decrease the fouling tendency of alginate, and calcium or iron ions decrease the fouling tendency of alginate and humic acids. All obtained results can be properly explained by considering the physico-chemical properties of the investigated membranes and model foulants.

1. Introduction

Nanofiltration (NF) has become a promising technology in direct and indirect drinking water production and waste water processing, however, fouling remains a major problem for membrane technology [1,2]. Due to fouling, flux declines sharply and regular chemical cleaning is needed, increasing the operational cost and reducing the membrane lifetime.

The presence of high concentrations of inorganic salts or metal oxides in water is mainly responsible for inorganic fouling or scaling. In NF and reverse osmosis (RO) systems, the dissolved inorganic ingredients are generally concentrated, and the concentration can come close to the solubility limits, increasing the chance of severe membrane fouling by precipitation (scaling) [3–6]. Next to calcium and magnesium, iron and manganese are metal ions commonly found in natural waters. Water percolating through soil and rock dissolves them, and these minerals consequently enter in the ground water supplies [7]. In anaerobic conditions, or at low pH (< 6.5) iron remains in the reduced state (Fe^{2+}), which is often the case in ground water [7] or in deep wells, where oxygen content and pH tend to be low. In these cases, the water contains dissolved iron and/or manganese, both colorless. In aerobic conditions and at a higher pH (i.e. higher than 6.5), iron oxidizes (to Fe^{3+}) and converts to reddish-brown large complexes/colloids (i.e. larger than 700 Da). These colloids or complexes can act as a source of membrane fouling by interacting with the membranes and/or by blocking the pores of membranes. In contrast, manganese usually does not oxidize until a high pH (i.e. pH 9) has been reached and hence predominantly remains in solution in dissolved form (i.e. Mn^{2+}). Manganese oxidizes at or above pH 9 forming a black residue, which also acts as a source of membrane fouling.

In addition, a combination of iron and humic acids (HAs) also acts as a major and strong foulant. HAs contain negatively charged functional groups such as carboxyl and possibly hydroxyl and phenol. These functional groups of the HAs react with the cations present in the water. This happens especially with dissolved metals such as Fe^{2+}, Mn^{2+} and of course Ca^{2+} and Mg^{2+} abundantly present in all natural waters. HAs behave as ligands with high capacity to form metal complexes [8]. Several mechanisms and interactions (such as electrostatic interactions, entropic effects, hydrogen bonds, etc. [9]) are responsible for the formation of the metal-HAs complexes. Erdogan et al. [10] reported that

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iron bonds predominantly to HAs via the carboxyl groups and forms a metal-organic complex. This changes the HAs properties and hence can influence fouling.

Moreover, not only interaction between organics and inorganics can affect fouling but also different organics can interact with each other and increase or decrease fouling. Jermann et al. [11] investigated the co-effect of both humic materials and polysaccharide (i.e. alginate) for the fouling of ultrafiltration (polyethersulphone UF) polymeric membranes. The obtained results showed that the addition of humic materials into polysaccharide solution led to more severe irreversible fouling due to the stronger adsorption of humic acid onto the membranes. For other polymeric membranes (PVDF UF), it is reported that the addition of proteins result in a decreased fouling behavior of alginate as compared to the filtration of the alginate solutions without proteins [12].

Many researchers have used sodium alginate as a model foulant [11–16] as it behaves similar to extracellular polymeric substances (EPS) during the membrane filtration [13,14]. It is noteworthy to mention that EPS is a combination of several different biopolymers. Instead of using all different biopolymers, sodium alginate has been commonly used [15,17–19]. In the presence of multivalent inorganic ions especially calcium ions, alginate forms a gel layer [20], where calcium binds specially to the carboxylic functional groups of the alginate and forms bridges between the alginate molecules. This results in different outcomes in terms of membrane permeate flux decline. On polymeric membranes, most of the studies show that calcium results in more severe permeate flux decline [15–17], while other studies show opposite results [21,22]. The differences in the communications on the co-effects of organic foulants, as well as on the effects of inorganic ions on organic foulants as alginate, most likely point to the distinct influence of the membrane surface chemistry on the results, as also suggested by our previous studies [39].

Up to now, there have been a number of papers published that focus on polymeric membrane surface modification to avoid membrane fouling. In this regard, the membrane modification aims to increase membrane surface hydrophilicity [23–26,28–30] and/or reduce surface roughness [29], surface charge density [22], or carboxyl groups at the membrane surface [23, 25, 26 and 29]. Moreover, researchers also tried to graft specific polymer chains [25,29], incorporate nanoparticles [27,28,31] and form a second NF/UF layer on the support layer [32–35].

Recently, we have developed an innovative method for ceramic membrane surface modification based on Grignard chemistry, allowing the grafting of a wide range of functional groups on the membrane surface [36,37]. This grafting method opens also the possibility of controlled variation of the membrane surface chemistry without affecting the surface roughness and pore size of the membrane [38]. In the previous studies [38–40], we have clearly shown that methyl grafting of TiO$_2$ NF membranes via the Grignard method, leads to a strong antifouling effect for many different organic foulants. Also other grafting methods like methyl phosphonic acids grafting reduce fouling significantly but less efficient due to residual reactive −OH groups when using phosphonic acids. However, the effect on fouling by inorganic materials such as metal oxides was not studied on this type of membranes (native or modified ceramic NF membranes). Moreover, the study of alginate fouling (with and without calcium ions) and co-effects of different organic foulants on ceramic NF membranes also has not been carried out so far. Seen the different results reported before for polymeric membranes (as described above), it is not a priori clear what to expect. Furthermore, the effect of membrane surface chemistry on the mentioned fouling situations has never been investigated systematically.

We therefore measured the fouling tendency of ungrafted and methyl grafted TiO$_2$ NF membranes on their irreversible fouling tendency caused by metal (both iron and manganese) hydroxides/oxides-hydroxides/oxides/salts. In addition, to check the co-effect of different organic foulants on ceramic NF membranes, the fouling by EPS (using sodium alginate as a model foulant mimic EPS) with and without NOM (using HAs as model foulant mimic NOM) was also determined. Rejections of the foulants were investigated to check the effect of the graftings on the membrane permeate water quality. Finally, to validate the results of the model foulant solutions, real surface water (water from Waterproductiecentrum De Blankaart, Belgium) was also used.

2. Materials and methods

2.1. Membranes and chemicals

Small-scale, commercially available monochannel tubular TiO$_2$ NF membranes with an outer diameter of 1 cm, an inner diameter of 0.7 cm, and average pore diameter was 0.9 nm, were used. All membranes were acquired from the company Inopor Gmbh Germany (pore size as communicated by the supplier).

For the grafting of some of these membranes, two different grafting techniques were used (see Section 2.2) [38]. The grafting reagents i.e. methyl magnesium bromide and methyl phosphonic acid are supplied by Sigma Aldrich. A number of model foulants have been used: (1) organic foulants e.g. HAs and sodium alginate (NaA) were purchased from Sigma Aldrich, (2) inorganic foulants e.g. FeCl$_3$·6H$_2$O, MnSO$_4$·H$_2$O and CaCl$_2$ were purchased from Merck. All model foulant solutions were prepared using pure water, with a conductivity of less than 15 mS/cm and pH 6.5–7 (i.e. water processed using reverse osmosis membranes at VITO). Other chemicals such as sulfuric acid and sodium hydroxide were also purchased from the chemical company MERCK. Ecolab manufacturers delivered the cleaning agents such as P3 Ultrasil 110 and P3 Ultrasil 75, for cleaning the filtration system and the fouled membranes. Real surface water (i.e. water from Waterproductiecentrum De Blankaart in Belgium) was provided by the drinking water supplier, De Watergroep, Belgium.

2.2. Grafting of TiO$_2$ NF membranes

TiO$_2$ NF membranes were grafted using two different modification methods: the phosphonic acids (PA) and Grignard reagents (GR) grafting method, as used also in our previous work [38]. In the current paper, only methyl functional groups have been grafted on the membrane surface by both grafting methods, as the methyl group and especially the methyl groups grafted using the GR technique, proved to be the most effective [38–40]. The grafting procedures of both methods are already described in detail in our previous study [38]. In both cases, the membranes were immersed (with stirring and shaking or continuous filtration) for several hours in the appropriate reaction mixture: a mixture of the methyl Grignard reagent in dry diethyl ether for GR grafting, or a mixture of the methyl phosphonic acid in water for PA grafting. After reaction, the membranes were washed in order to remove byproducts or unreacted or loosely bound materials. All membranes were dried at 60 °C under vacuum after washing and before use in performance tests. In case of Grignard grafting, a proper pretreatment (before grafting) of the membranes to remove the adsorbed water from the membrane surface is required because Grignard reaction is moisture sensitive.

Modified membranes are denoted by a three-letter code: MGR are methyl grafted by the Grignard grafting method and MPA are methyl grafted by the phosphonic acid grafting method. We would like to emphasize that even for the same functional group, both grafting techniques deliver different surface chemistries [38,39]. To summarize, three types of TiO$_2$ NF membranes with different surface chemistry are used here to investigate the fouling/antifouling tendency: (1) Unmodified TiO$_2$ membranes (native), (2) MGR membranes, (3) MPA membranes. Visualization of the grafted and the native membranes surface chemistry is shown in Fig. 1.

Remark that our previous work has shown that phosphonic acid grafting leads to high surface coverage [41], while Grignard grafting is