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

Reference:

Ghulam Mustafa, Wyns Kenny, Janssens Siebe, Meynen Vera, Buekenhoudt Anita.- Evaluation of the fouling resistance of methyl grafted ceramic membranes for inorganic foulants and co-effects of organic foulants
Separation and purification technology - ISSN 1383-5866 - 193(2018), p. 29-37
Full text (Publisher's DOI): https://doi.org/10.1016/J.SEPPUR.2017.11.015
To cite this reference: https://hdl.handle.net/10067/1469310151162165141

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

Ghulam Mustafa[+‡], Kenny Wyns[‡], Siebe Janssens[+‡], Anita Buekenhoudt[‡*], and Vera Meynen[+‡]

[‡] VITO NV - Flemish Institute for Technological Research NV, Boeretang 200, B-2400 Mol, Belgium, Tel.: +32 14 335637

[+]Laboratory of Adsorption and Catalysis (LADCA), Department of Chemistry, University of Antwerp, CDE, Universiteitsplein 1, B-2610 Wilrijk, Belgium, Tel.: +32 3 2652368

E-mail: anita.buekenhoudt@vito.be

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 acidsAll obtained results can be properly explained by considering the physico-chemical properties of the investigated membranes and model foulants.

Keywords

Nanofiltration

Membrane fouling

Inorganic fouling

Antifouling grafting

Foulants co-effects

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 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 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. $FeCl_3.6H_2O$, $MnSO_4.H_2O$ 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 figure 1.

Remark that our previous work has shown that phosphonic acid grafting leads to high surface coverage [41], while Grignard grafting is less efficient and leads to only partial surface coverage [42, 37]. Our previous work has also clearly proven the long-term stability of the grafting obtained (e.g. against re-hydroxylation), up to a pH of 10 [38, 39].

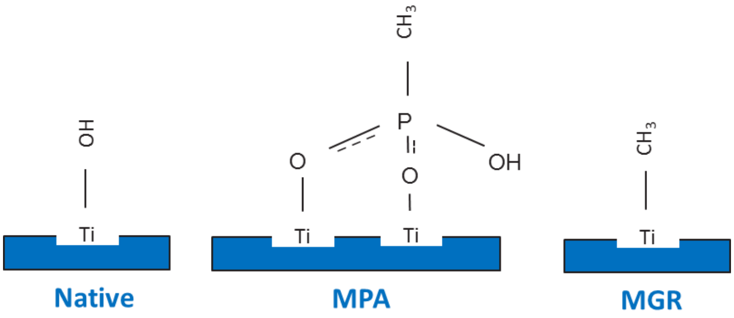

Figure 1. Visualization of the surface chemistry of the grafted and native membranes "Native" denotes a unmodified TiO2 NF membrane; "MPA" a methyl grafted membrane using the phosphonic acid grafting technique; "MGR" a methyl grafted membrane using the Grignard grafting technique. Note: in case of MPA, only a bidentate bonding mode is presented as an example, but different bonding modes are possible.

2.3. Foulant solutions

Both model foulant solutions and a real surface water stream were used in this study. All inorganic model solutions were prepared from the iron and/or manganese salts mentioned in section 2.1. In some cases HAs was added in order to study co-effects. Organic model foulant solutions were also prepared using NaA with and without HAs and Ca^{2+}. Exact compositions and concentrations of the prepared solutions are given in table 1. The concentrations and compositions were chosen to mimic real surface water, ground water or specific waste water (e.g. municipal waste water or water from membrane bioreactors). All model solutions were stirred by a magnetic stirring bar for ~30 minutes to make clear homogenous solutions. In case of model solutions that contain HAs in combination with any other model foulant, first the HAs solution was prepared and then other foulants were added.

Table 1. Compositions and concentrations of the prepared model foulant solutions for the fouling measurements. The pH of all solutions was in the range of neutral pH (i.e. 6.5 -7.5).

Model solutions mimicking surface water containing metal oxides with NOM	**Model solutions Mimicking MBR waste water containing EPS with NOM and Ca^{2+}**
10 mg/L Fe^{3+}	10 mg/L NaA
5 mg/L Mn^{2+}	10 mg/L NaA + 2 mmol/L Ca^{2+}
10 mg/L Fe^{3+} + 5 mg/L Mn^{2+}	5 mg/L NaA + 5 mg/L HAs
1 mg/L Fe^{3+} + 10 mg/L HAs	5 mg/L NaA + 5 mg/L HAs + 2 mmol/L Ca^{2+}

10 mg/L Fe^{3+} + 10 mg/L HAs
real surface water (water from Waterproductiecentrum De Blankaart in Belgium: the composition is given in table 6 (Cf column)

2.4. Fouling measurements

Fouling experiments were performed using all the model foulant solutions and real surface water (i.e. water from Waterproductiecentrum De Blankaart in Belgium), at room temperature. To measure the irreversible fouling tendency of all the membranes under investigation, a specific procedure was adopted (note : with irreversible fouling we mean that part of the fouling that needs chemical cleaning to be removed). The procedure is detailed elsewhere [39]. A brief summary of the procedure is described as follows: before every fouling measurement, an initial pure water flux (stable flux after 1 hour denoted as “J_0”) was measured in cross-flow (CF). Then, fouling was induced by the filtration of the real surface water or model solutions, in dead-end (DE) or in CF mode. In DE, the filtration of the foulant solution was performed until one liter of the two liter feed was permeated at 5 bar transmembrane pressure (TMP), while the CF filtration was performed for ~4 hrs with cross-flow velocity 2 m/s and TMP 5 bar. Finally, again the CF pure water flux (stable flux after 1-2 hours denoted as “J”) was determined. This CF water filtration also acts as forward flushing and removes the reversible part of the fouling [40]. The irreversible fouling tendency of the membranes was eventually evaluated by calculating the normalized flux decline i.e. “J/J_0”.

2.5. Characterization and analysis

All the investigated membranes were characterized by different techniques (pure water flux, water contact angle and molecular weight cut-off) before their use in the fouling tests. The details can be found in our previous paper [38].

Retentions of the salts/ions and the organic solutes were determined by measuring their concentrations in feed and permeate. Different materials (inorganic salts/ions, organic solutes) were measured using different analytical techniques, given as follows:

Iron and manganese concentrations and calcium ion presence were measured by using inductively coupled plasma optical emission spectroscopy (ICP-OES, Optima 3000 DV, Perkin Elmer, Waltham, MA, USA) equipped with a cyclonic spray chamber and a gemcone nebulizer. Organic material concentrations were estimated by measuring the total organic carbon (TOC). The determination of the TOC was performed using a catalytic high temperature combustion instrument with selective detection of CO_2 (Multi N/C 2100, Analytik Jena, Germany). The particle size distribution of oxidized metal particles was measured by laser scattering (Nanosight NS500, Nanosight LTD, U.K.).

Presence of manganese on native and MGR membranes was measured (after fouling measurements) by scanning electron microscopy/energy dispersive x-ray spectroscopy (SEM/EDX) with specifications of the SEM: JEOL JSM-c340f and of the EDX: BRUKER QUANTAX 200 with detector SDD Y FLASH-5030.

2.6. Chemical cleaning

Unless stated otherwise, after filtration of the foulant containing solution, both the membrane and the filtration system were always cleaned before using the system and the membrane for the next measurement.

The membranes and the filtration system were cleaned by using a commercially available cleaning agent P3 ultrasil 110 (an alkaline cleaning agent for organic fouling removal) and P3 ultrasil 75 (an acidic cleaning agent for inorganic fouling removal). In case of alkaline cleaning, a cleaning solution of pH 12 for native and of pH 10 for grafted membranes was used. Similarly, in case of acidic cleaning, a cleaning solution of pH 2 for native and of pH 3 for grafted membranes was used. In each case, the following cross-flow filtration conditions were used: temperature 50 - 60 °C, a TMP of 1-5 bar, a filtration time of 15 - 60 minutes, and cross-flow velocity of ~4 m/s. The pure water flux was re-measured to check the efficiency of the cleaning.

Chemical cleaning experiments demonstrated that fouled grafted membranes (both MGR and MPA membranes) can be efficiently cleaned under milder conditions (pH 10 or 3 at 50 ºC) without affecting the grafting stability. In contrast, more severely fouled native membranes could only be cleaned at pH 12 or 2.

3. Results and discussion

3.1. Membrane characterization

Membrane properties such as surface charge, pore size, hydrophilicity/hydrophobicity of the membrane are critical to determine the fouling. Therefore, we determined the molecular weight cut-off (MWCO), water contact angle (CA) and pure water permeability of all the investigated membranes, before performing the fouling tests. For all types of membranes, different specimens were used, each specimen having a slightly different quality. The obtained experimental results show that both graftings decrease the membrane pure water flux (~25% by PA grafting, while ~50% by GR grafting) due to its increased hydrophobicity. The order of hydrophobicity is confirmed by the water contact angles : 35-45° in case of PA, 50-60° by GR grafting compared to 10-20° for native membranes. These contact angles are also an indirect indication of the remaining OH groups on each membrane surface. The molecular weight cut-off of the membranes remained the same after grafting (~500 Da). More details can be found in our previous work [38,39].

3.2. Reproducibility of results

The results described in each of the tables of the next sections, are the results of one specific membrane specimen per membrane type. This means that the results in each table can be mutually compared. However, as mentioned above, in this study different specimens (2 to 3) of all type of membranes were used, to look at the reproducibility of the results. The slightly different quality of these different specimens lead to different pure water permeabilities (J_0). In this study, the pure water permeabilities of the used native membranes were typically 10 to 20 l/hm^{2}bar. For the MPA membranes the range was 7,5 to 15 l/hm^{2}bar, and for the MGR membranes 4 to 10 l/hm^{2}bar, consistent with the pure water flux decline originating from the grafting (see 3.1).

In our previous work [38,39] it was confirmed that the extent of irreversible fouling increases as the starting pure water flux (J_0) increases, however, the changes are relatively small compared to the pure water flux changes. To give an idea we reproduce here the results already mentioned in [38] : native membranes with J_0 from 7 to 27 l/hm^{2}bar show a normalized flux decline of 0,60 to 0,40 respectively for a fouling mixture of HAs 10 mg/L + 1 mmol/L Ca^{2+}. Moreover, MGR membranes with J_0 from 3,5 to 13 never show any normalized flux decline for this foulant mixture. Similar relatively small changes on irreversible fouling have been obtained when measuring on different membrane specimens in this investigation. However, it was confirmed that these small changes do no compromise the conclusions drawn from this study.

We further remark that it would have been very difficult to perform this study with grafted and ungrafted membranes having the same pure water permeability, as the grafting changes the permeability of the native membrane, and we cannot freely choose the quality of the ceramic NF membranes.

3.3. Inorganic fouling and retentions

A number of fouling tests were performed using model solutions containing only iron and manganese, or a combination of both iron and manganese, or iron with HAs (see table 1 left column). The tests were performed using TiO_2 NF membranes having three different surface chemistries (native, MPA and MGR membranes).

Table 2 compiles all the obtained irreversible fouling results in the form of normalized flux declines. It clearly shows that the irreversible fouling behavior of the MPA membrane is in-between the extremes of the high fouling in case of the native membrane and absence of fouling or mild fouling in case of the MGR membrane, and this for all foulants. Only in case of manganese solution (5 mg/L), the fouling of MPA is similar to the native membrane. The obtained results confirm our previous observations [38, 39].

As explained in our previous work [38, 39], irreversible flux decline of the native membrane can be ascribed to the possible polar interactions between the foulants and the -OH groups that are abundantly available on the full pore surface of the native membrane. Similar types of interactions are also possible in case of the MPA membrane as they still have -OH groups in the grafted groups on the surface (e.g. P-OH). However, it is expected that fewer interactions are possible due to a reduced number of the -OH groups on the membrane surface caused by the grafting [38, 39]. Moreover, the remaining P-OH groups on the membrane surface can be sterically hindered by the grafted $-P-CH_3$ groups. Both effects lead to lower irreversible fouling compared to the native membrane, as reported previously for other organic foulants [38-40]. In case of the MGR membrane, part (partial surface coverage) of the present -OH groups on the membrane surface is replaced by simple methyl groups, preventing interactions with the foulants, and leading to very low irreversible fouling. Remaining Ti-OH groups on the membrane surface are most likely sterically protected by the grafted groups from direct contact with bulky foulants (as iron colloids).

Table 2. Normalized water flux decline of all the investigated membrane types caused by different model foulant solutions of iron, manganese, iron with HAs, and mixture of iron and manganese in DE filtration. The values reported were measured for a native, MPA and MGR membrane specimen with J_0 =10, 15 and 4 l/hm^2bar respectively. Note: 1) iron and manganese represent multiple forms of iron and manganese, 2) chemical cleaning is always performed in-between any two measurements.

Foulant concentrations	J/J_0 native	J/J_0 MPA	J/J_0 MGR
Fe 10 mg/L	0.67	0.93	1
Fe 1 mg/L + HA 10 mg/L	0.46	0.78	0.92
Fe 10 mg/L + HA 10 mg/L	0.72	0.82	0.96

Mn 5 mg/L	0.80	0.82	1
Mn 5mg/L + Fe 10 mg/L	0.57	0.79	1

During the same fouling tests, retentions of the iron and manganese were also measured for all the investigated membranes. The obtained results are given in table 3. Table 3 shows that the retentions of the iron are quite high (more than 95%) throughout the measurements. The retentions of manganese are overall very low compared to the iron retentions (table 3).

Table 3. The obtained retentions of iron and manganese by all the investigated membranes during the fouling measurements using the mentioned model foulants solutions of metal oxides with and without HAs.

Model solutions	Membrane	Iron retention (%)	Manganese retention (%)
10 mg/L Fe	Native	97	
	MPA	98	
	MGR	98	
5 mg/L Mn	Native		7
	MPA		6
	MGR		3
10 mg/L Fe + 5 mg/L Mn	Native	91	10
	MPA	99	7
	MGR	100	7
1 mg/L Fe + 10 mg/L HA	Native	100	
	MPA	100	
	MGR	100	
10 mg/L Fe + 10 mg/L HA	Native	97	
	MPA	97	
	MGR	98	

To discuss in more detail all above-mentioned flux and retention results, and to explain the variation of the fouling with foulants, the specific physico-chemical properties of all the investigated model foulants are considered. This allows us to determine the possible nature and strength of the interactions between the different membranes and the different foulants, and the change of these possible interactions in the presence of calcium ions and other organic materials. The results are divided into four parts and will be discussed separately.

Iron fouling:

Normally, iron present in water oxidizes upon contact with air and readily undergoes hydrolysis to form hydroxides, oxide-hydroxide etc. [43]. Consequently colloidal and stable suspensions are formed from iron hydroxides, oxide-hydroxide and oxides [44]. In the neutral pH (6.5 to 7) of our solutions, generally iron is present in the form of $Fe(OH)_3$ particles or as positively charged complexes [43]. We measured the size of the particles present in our iron solution (10 mg/L), which is 70-164 nm (average 122 nm).

The iron hydroxides/oxide-hydroxides/oxides formed can deposit on, i.e. foul, the membrane surface especially if the surface of the membrane is attractive towards them, as is the case for a membrane with polar functional groups (e.g. the native membrane). A schematic representation of the formed fouling layer is given in figure 2 (left). The iron particles are larger than the membrane pores, preventing them to go through the membrane. Their ability to adsorb strongly with the polar groups enhances the possibility for the formation of a cake layer on the membrane surface during the filtration, initiating fouling. In addition, as this happens, these particles can additionally block the pores (as shown in figure 3 left), further enhancing irreversible fouling. Moreover, because of their large size, high retentions of the iron are obtained, as given in table 3.

As explained in the beginning of this section, the polar interactions, and thus the fouling of the large iron particles is logically higher for the native membranes than for the MPA membranes, and very low for the MGR membranes as their interaction is weakened.

Apparently, the retentions of iron by all the investigated membranes are comparably high and caused by size exclusion, as the MWCO of the native and grafted membranes are similarly low (see section 3.1). However, still, the retentions for the three membranes are slightly different in the following order : R(native) < R(MPA) ~ R(MGR). This order follows the degree of possible interactions (or the degree of fouling): the higher the interactions/fouling the (slightly) lower the retentions (table 3). This correlation has been noticed before [37~~53~~]. The non-ideal (not 100%) retention of the iron, might be caused by some iron remaining in the ion-state and/or some small particles present.

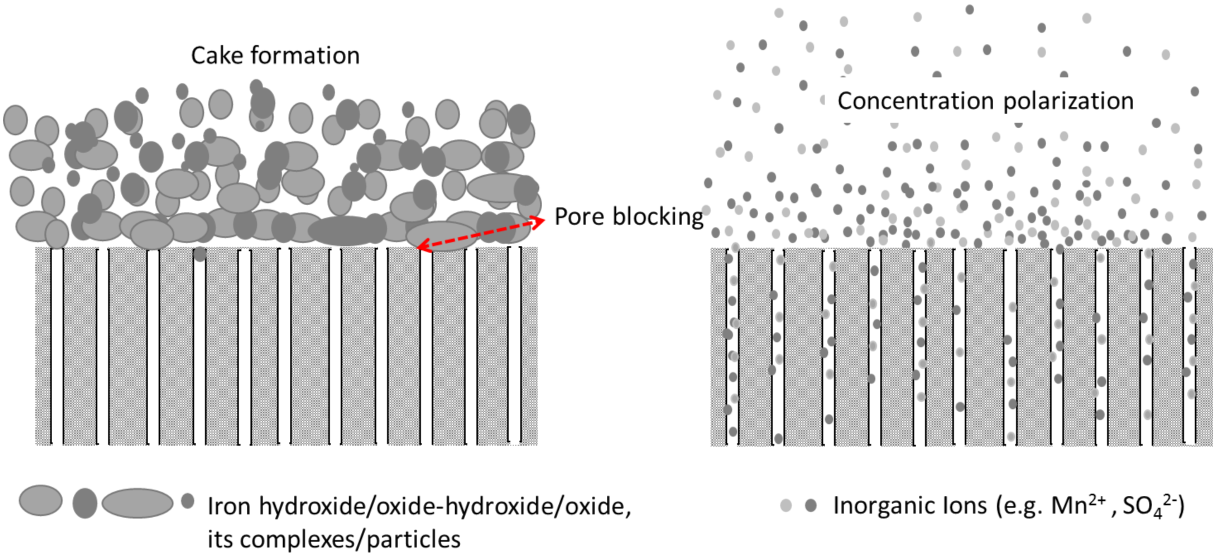

Figure 2. Elucidation of membrane fouling during the filtration of iron (left) and manganese (right) solutions at pH 6.5-7. The red arrow in the left figure points to a place with pore blocking.

Iron with HAs fouling:

The different functional groups of HAs (e.g. carboxylic acids, phenolic, aldehyde etc.) can complex with inorganic ions, especially multivalent ions such as iron or calcium, and form colloidal complexes. Such nanocolloids change conformation according to their ionization state, and can be built from either amphiphilic complexes or assemblies of small molecules [44-46].

In this work, we did filtration of two HAs solutions with two different concentrations of iron (i.e. 1 mg/L and 10 mg/L). The obtained irreversible fouling strength and iron retentions for all the investigated membranes can be explained as follows.

In case of iron 1 mg/L + HAs 10 mg/L solution, all membranes fouled more than in the presence of iron hydroxides/oxide-hydroxides/oxides only, but less than in the presence of only HAs [39]. Here, iron has the same role as calcium, leading to HAs complexation, and hence diminishing the hydrophilic interactions and reducing HAs fouling to some extent. The MPA membrane fouls less than the native, while the MGR is only slightly fouled (table 2), as previously observed when polar interactions are the main fouling driver [39, 40].

The retentions of the iron are about 100% through all three investigated membranes (shown in table 3) because the present iron in the solution is completely or maximum complexed with HAs and these complexes (of iron-HAs) are quite large. Due to size exclusion, they cannot pass through the membranes.

In case of 10 mg/L iron + 10 mg/L HAs solution, the complexation reaction is responsible for further charge neutralization of HAs entities, and thus further reduction of HAs polarity and polar functional groups [47]. Therefore, the fouling degree of all three investigated membranes decreased as compared to the fouling degree by the solution containing iron 1 mg/L + 10mg/L HAs (table 2) However, in this solution there might be some spare iron hydroxides/oxide-hydroxides/oxides (e.g. after the saturation to the HAs surface) present, causing part of the observed irreversible fouling, and resulting in slightly smaller retentions. Remark that the iron retentions for 10 mg/L iron, with and without HAs, are very similar.

Manganese fouling:

Manganese is soluble and less susceptible to oxidation at pH ≤ 7. It is reported that under acidic, neutral or slightly basic conditions, manganese remains in soluble form [7]. In alkaline pH conditions (9 ≤ pH), manganese readily oxidizes to the manganese hydroxides that are less soluble.

In this study, the pH was slightly lower or equal to 7, meaning that most probably manganese remained in soluble state or was only slightly oxidized. In addition, the particle size measurement confirmed that no large oxidized manganese particles were present in the applied conditions. This phenomenon is strongly correlated to the obtained experimental results. It corresponds to the low retentions of the manganese for all the investigated membranes. The small manganese ions (Mn^{2+}) can move through the membrane pores with the water. However, they can be slightly retained by the charge on the membrane surface. As the experimental data of table 3 shows, the manganese retentions are about 2 to 7%, and the highest for the native membrane, intermediate for the MPA membrane, and the lowest for the MGR membrane. The values and order of these retentions for the different membranes are as expected.

Indeed, a native TiO_2 NF membrane with its abundant -OH groups has an isoelectric point (IEP) typically between 6 and 7 [48]. As a consequence, at pH around 7 (as for the Mn solution) we expect about zero charge on the membrane. However, in this case of $MnSO_4$ salt, there will be some specific adsorption of the SO_4^{2-} ions to the TiO_2 pore surface (as observed for Na_2SO_4 in [48]), and this leads to a small, more negative charge on the membrane surface, leading to the observed low manganese retentions. Note that the positive manganese ions are retained together with the negative sulfate ions due to charge neutrality. In case of the MGR membranes, part of the -OH groups on the membrane surface are exchanged by methyl groups, diminishing the overall charge on the membranes, and thus leading to Mn^{2+} retentions lower than the native membrane, as observed. For the MPA membranes, the number of remaining -OH groups are in-between that of native and MGR membranes, most likely giving rise to the intermediate Mn^{2+} retentions

As can be seen from comparing tables 2 and 3, the fouling caused by the manganese model solution, is strongly correlated to the obtained Mn^{2+} retentions: the higher the retentions, the higher the fouling. Indeed, higher retention corresponds to higher concentration polarization, increasing the potential of crystal formation and/or salt precipitation i.e. scaling. This way of fouling is therefore quite different than the one observed for the iron model solution, and this is visualized in figure 2 right.

We remark specifically that this different way of fouling might be also the reason why the MPA fouling is now very similar to the fouling of the native membrane. The steric hindrance of the grafted functional groups that in all other cases leads to an MPA fouling of more or less 50% lower than the native membrane fouling, does not play here in the case of the fouling by small Mn^{2+}. Moreover, as mentioned before, the difference in interaction between manganese ions and -P-OH or -Ti-OH might play a role too.

In order to determine if the filtration type had some influence on the observed retentions of Mn^{2+} in dead-end conditions, we also measured them in cross-flow conditions. In general we found overall somewhat higher retentions (10 to 15%), but the variation for the different membranes is similar: R(native) > R(MPA) > R(MGR).

We performed also similar experiments (dead-end and cross-flow) with a similar model solution formed now with $MnCl_2$ instead of $MnSO_4$, in order to avoid the specific adsorption of the SO_4^{2-}. Nevertheless, the obtained results were very similar to the $MnSO_4$, only all retentions and fouling was somewhat lower, as expected.

The irreversible fouling of the native membranes, and non-fouling of the MGR membranes, was also confirmed by SEM/EDX measurements on the used membranes. The SEM/EDX results showed that manganese is present on the surface of the irreversibly fouled native membrane, while SEM/EDX could not detect any traces of manganese on the surface of the used MGR membrane.

Iron and manganese fouling:

Finally, the obtained fouling and retention results during the combination of iron and manganese are again quite logical. For both native and MPA membranes, the normalized flux decline by the filtration of the Fe–Mn hydroxides/oxide-hydroxides/oxides/salts suspension was higher than the manganese and iron separately, and almost similar (somewhat smaller) as the sum of the flux reductions of the separate solutions (table 2). The MGR membrane remained unfouled. The retentions of the manganese are slightly increased while iron retentions remained high. This higher manganese retentions might be caused by the presence of the large iron particles with which they interact.

3.4. Co-effects of organic foulants

To investigate the co-effect of different organics on the membrane fouling, we measured EPS (using sodium alginate) fouling with and without NOM (using HAs) and with and without inorganic ions (i.e. Ca^{2+}). For this purpose, we only investigate the irreversible fouling tendency of the native and the MGR membrane (most optimal membrane). The obtained experimental results are presented in table 4 in the form of normalized water flux decline.

Table 4. Normalized water flux values of the membranes under investigation due to the DE fouling of sodium alginate (NaA) with and without Ca^{2+} and HAs. The values outside the brackets represent the results obtained for consecutive measurements of NaA (or NaA+HA) with and without calcium without any chemical cleaning in-between the two measurements, while the values inside the brackets represent the results obtained for measurements with chemical cleaning in-between the two measurements. The values reported were measured for a native and MGR membrane specimen with J_0 =20 and 5 l/hm²bar respectively.

Foulant concentrations	J/J_0 native	J/J_0 MGR
NaA 10 mg/L	0.25	1
NaA 10 mg/L + Ca^{2+} 2 mmol/L	0.14	1
NaA 5 mg/L + HA 5 mg/L	0.31 (0,23)	1 (1)
NaA 5 mg/L + HA 5 mg/L+ Ca^{2+} 2 mmol/L	0.22 (0,31)	0,96 (1)

The trend of the obtained results is quite similar as seen before (table 2 in this work, and in previous work [38, 39]), as the MGR remained non fouled and/or mildly fouled, while the native membrane strongly fouled in all cases.

During these experiments, TOC retentions were also measured, which were always higher than 95% and were quite comparable for all the measurements irrespective of membrane surface chemistry, and similar to the HAs retentions described previously [39].

All the results of the alginate (i.e. sodium alginate) fouling with and without HAs and calcium ions can also be explained if we consider the physico-chemical properties of all the investigated membranes and the model foulant solutions, as for the inorganic fouling. The obtained experimental results clearly show that the native membrane fouled maximum by the alginate without inorganic ions, while the MGR membrane was not fouled. This is again ascribed to the interactions between the polar functional groups of the alginate [49, 50] and the -OH groups that are abundantly available on the full surface of the native membrane. In contrast, in case of the MGR membrane, freely available -OH groups are less and sterically hindered for large molecules, therefore, polar interactions between the MGR membrane and the foulants are difficult.

When adding Ca^{2+} to the alginate and without any intermediate chemical cleaning, the native membrane fouling was increased, while the MGR membrane remained unfouled. This can be attributed to the layer-by-layer deposition initiated by the bridging action of the calcium on the adsorbed alginate, similarly illustrated in our previous study but there for HAs [38].

To investigate the co-effect of the organic materials on the irreversible membrane fouling, instead of only alginate with and without calcium, solutions of alginate and HAs with and without calcium were filtrated to induce this fouling. The obtained results were quite similar and can be ascribed to similar reasons. The difference is only that the native membrane fouled slightly less in comparison to the solution where only alginate was present. The reasons for this are: 1) number of the polar functional groups of the alginate are higher as compared to HAs, 2) alginate has the ability to make a gel layer while HAs may decrease this tendency [15], 3) complexation of HAs with alginate decreases the number of free polar functional groups and enlarges their size.

To confirm the effect of the inorganic ions (Ca^{2+}) and the type of interactions influencing the results, again filtrations using mixed solutions of alginate and HAs with Ca^{2+} were performed but this time the membranes were chemically cleaned in-between the measurements to avoid layer by layer fouling assisted by Ca^{2+}. Again the native membrane fouled irreversibly but the MGR did not show any irreversible fouling at all. In the presence of Ca^{2+} fouling of the native membrane decreased as compared to the fouling in the absence of Ca^{2+}. This is exactly similar as explained in [39] for HAs, and is due to the complexation between the Ca^{2+} and the alginate or the HAs diminishing the amount of polar groups of these foulants and enlarging their size [51, 52], similar as mentioned above for iron and HAs.

3.5. Real surface water fouling and retentions

Filtration tests using real surface water were performed to evaluated the membrane fouling tendency and the retentions of the impurities in a realistic situation, were all co-effects of different organic and inorganic foulants play at the same time. This evaluation was done with the best and worst performing membrane being the MGR and the native membrane, respectively. In the case of the real surface water, irreversible fouling was not only evaluated at the DE filtration set-up but also in a CF system. The obtained fouling results are given in table 5.

Table 5. Normalized water flux showing impact of real surface water fouling on the water flux of the MGR and the native membranes. Fouling was induced by the filtration at CF and in DE modes. Chemical cleaning was performed between each measurement. The values reported were measured for a native and MGR membrane specimen with J_0 =10 and 4 l/hm^{2}bar respectively.

Fouling situation	J/J_0 native	J/J_0 MGR
Real surface water at CF filtration	0.84	1
Real surface water at DE filtration	0.80	1

Again, it is very clear from the normalized flux decline that the MGR membrane did not show any irreversible fouling, while the native membrane fouled by the real surface water after the filtrations at both DE and CF modes. Although the difference is small, the native membrane is slightly less fouled after the CF filtration as compared to the DE filtration.

Moreover, retentions of the impurities present in the real surface water by both the MGR and the native membranes are quite comparable, with, in general, somewhat higher retentions for the MGR than for the native membrane as can be observed in table 6. Only the retentions of conductivity and chloride in CF mode are clearly lower for the grafted membrane, while retentions of colored compounds and Ca^{2+} are higher at both DE and CF. The reason for this might be the lower charge at the surface of the MGR membrane and the absence of interactions with the organic components. In DE the retention differences between MGR and native membranes are in general larger than in CF.

Further, the retentions of the impurities present in the real surface water by both the MGR and the native membranes are far higher during the filtration in the CF mode as compared to the filtration at the DE mode, for both membranes. This is most probably due to a denser/thicker fouling layer, or due to more concentration polarization during the DE filtration as compared to the CF filtration. This can also explain the larger differences in retention between MGR and native membranes.

Table 6. The obtained retentions by the MGR and the native membranes during the filtration of the Blankaart water at both CF and DE modes (Cf represents the concentration in feed). The retentions of the native membrane are shown between brackets.

Pollutants and contaminants		**MGR (Native)**	
	Cf (mg/l)	**R% in DE**	**R% in CF**
Total carbon (TC)	55	15 (8)	46 (45)
Total inorganic carbon (TIC)	45	5 (0)	32 (32)
Total organic carbon (TOC)	11	54 (43)	93 (96)
HAs at 254 nm UV/Vis	9	43 (24)	95 (91)
Color at 436 nm UV/Vis	3	72 (55)	97 (77)
Chloride	136	1 (0)	18 (33)
Sulfate	76	0 (0)	58 (51)
Calcium	55	6 (1)	40 (28)
Conductivity (µs/cm)	980	5 (1)	22 (33)

The obtained results for the real surface water nicely validate the results of the model foulant systems discussed in section 3.3 and 3.4. Similarly, the MGR membrane remained unfouled, while the native membrane fouled irreversibly by the filtration of the real surface water in both the DE and CF systems. The fouling mechanism described above and elsewhere for the different model solution of HAs with inorganic ions [38, 39] fits perfectly if we consider the physicochemical properties of the real surface water and the membranes.

In the case of real water filtration in CF, we also followed the flux of the native and the MGR membrane during the fouling. In figure 3, both fluxes and their time variation are shown, relative to their pure water flux before fouling (J_0). This figure clearly shows that for the grafted MGR membrane, the flux during fouling declines much less. In case of the native membrane, both the initial flux decline (from J_0), and the decline in the course of the fouling, is much higher. This shows that not only the irreversible fouling but also the total fouling is lower for the grafted membrane. Figure 3 also confirms our previous observation in different waste waters, where the CF process flux of the MGR membranes is higher and more stable than for the native membranes [40].

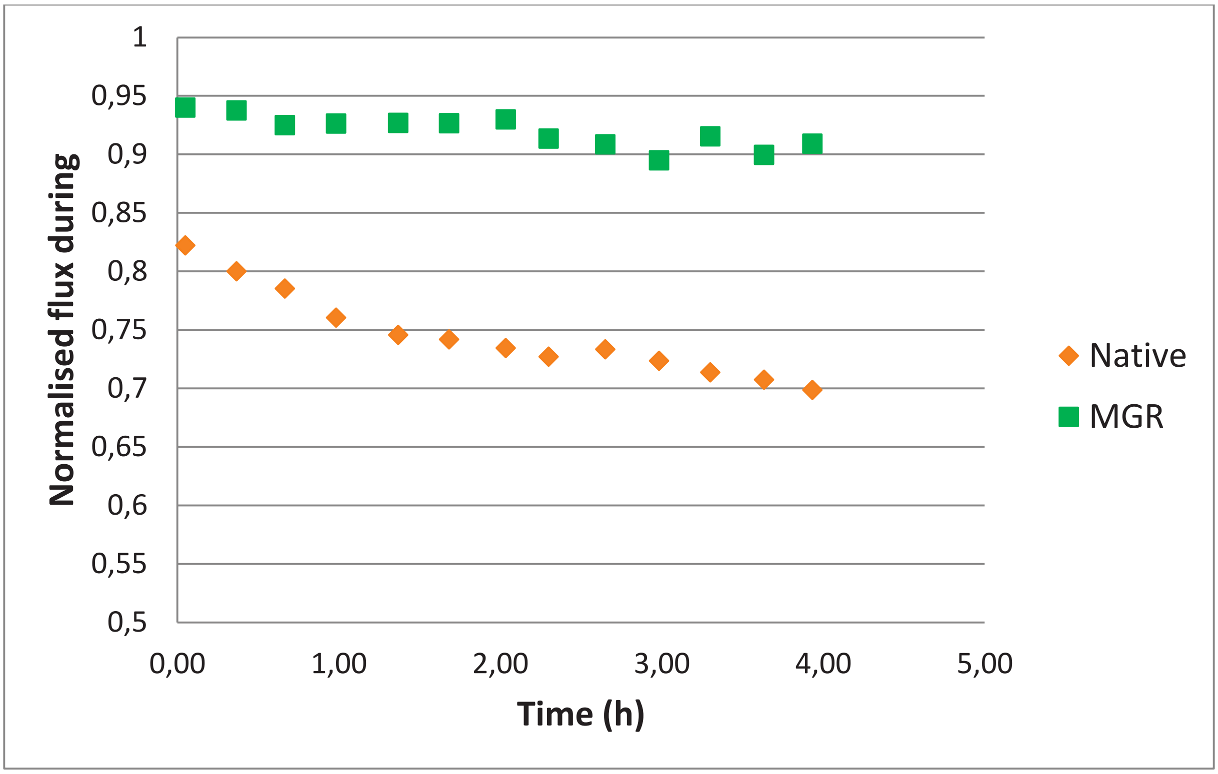

Figure 63. Flux variation as function of time, in case of CF filtration of real surface water over native and MGR membranes. The flux values shown are the absolute flux values divided by the pure water flux before fouling (J_0), for each membrane. The values reported were measured for a native and MGR membrane specimen with J_0 =9 and 4 l/hm^{2}bar respectively.

4. Conclusions

All the experimentally obtained results clearly show that the native membranes showed an irreversible fouling far more than the grafted membranes (especially MGR membranes) by all the used inorganic and/or organic model foulant solutions and real surface water. However, the produced permeate water quality is generally quite comparable or in some cases better for the grafted membranes. In addition, the obtained results showed that organic materials and organic-inorganic interactions have significant co-effects on the membrane fouling, also for ceramic NF membranes. 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. The methyl Grignard grafted membranes remain largely unfouled.

All obtained results can be properly explained by considering the physico-chemical properties and pore size of all the investigated membranes and model foulants. The co-effect of the organic materials can be explained in the same way. Proper explanations include the hydrophilic nature, the amount and accessibility of the OH-groups and steric effects of the membranes. Moreover, the size of the foulant/foulant complexes/agglomerates and co-effects that enhance or reduce their possible interactions with the membranes, have a clear influence on fouling but also on retentions.

Finally, validation with real waste water (water from Waterproductiecentrum De Blankaart in Belgium, provided by De Watergroep) proved that the membranes behave as expected also in real water streams having much more interactions and co-effects that might play a role. The retentions of the grafted membranes were similar or even better than the native membranes with the exception of chloride. The MGR membrane did not only show much less irreversible fouling, but also the flux decline during CF filtration of real surface water was clearly less, as observed before in different waste waters.

In conclusion, the exciting antifouling tendency of the MGR grafted membranes is repeatedly confirmed and proves again its high potential for drinking water production and waste water treatment.

5. Acknowledgement

We are grateful for financial support of the European Commission in the framework of the FP7 CeraWater project (grant number 180909), and the assistance of the partners of this EU project. We are also grateful to the FWO (grant number G012712N) for their support to part of this work. Finally, we express our gratitude to VITO for the PhD grant of Ghulam Mustafa.

6. References

[1] Van der Bruggen, B., Mänttari M., Nyström M., Drawbacks of applying nanofiltration and how to avoid them : A review. Sep. Purif. Techn. 63 (2008) 251-263.

[2] Shon H.K., Phuntsho S., Chaudary D.S., Vigneswaran S., Cho J., Nanofiltration for water and wastewater treatment – a mini review. Drink. Water Eng. Sci. 6 (2013) 47-53.

[3] S. Bhattacharjee G. Johnston, A model of membrane fouling by salt precipitation from multicomponent ionic mixtures in cross-flow nanofiltration, Environmental Engineering Science 19 (2002) 399–412.

[4] S. Lee, C. Lee, J. Kim, Analysis of CaSO4 scale formation mechanism in various nanofiltration modules, J. Memb. Sci. 163 (1999) 63–74.

[5] C.A.C. Van de Lisdonk, J.A.M. Van Paassen, J.C. Schippers, Monitoring scaling in nanofiltration and reverse osmosis membrane systems, Desalination 132 (2000) 101–108.

[6] C.J. Lin, S. Shirazi, P. Rao, Mechanistic model for CaSO4 fouling on nanofiltration membrane, Journal of Environmental Engineering 131 (2005) 1387–1392.

[7] M. Zaw, B. Chris Well, Iron and manganese dynamics in lake water, Water Research 33 (1998)1900-1910.

[8] P. Lubal, D. Siroky, D. Fetsch, J. Havel, The acidobasic and complexation properties of humic acids. Study of complexation of Czech humic acids with metal ions, Talanta, 47 (1998) 401-412.

[9] Y.H. Shen, Sorption of humic acid to soil: The role of soil mineral composition, Chemosphere 38 (1999) 2489-2499.

[10] S. Erdogan, A. Baysal, O. Akba, C. Hamamci, Interaction of Metals with Humic Acid Isolated from Oxidized Coal, Polish J. Environ. Stud. 16 (2007) 671-675.

[11] D. Jermann, W. Pronk, S. Meylan, M. Boller, Interplay of differential NOM fouling mechanisms during ultrafiltration for drinking water production, Water Research 41 (2007) 1713-1722.

[12] E. Negaresh, P. Le-Clech, V. Chen, Fouling mechanisms of model polymeric substances, Asia-Pacific Journal of Chemical Engineering 2 (2007) 394-399.

[13] Y. Ye, P.L. Clech, V. Chen, A.G. Fane, Evolution of fouling during crossflow filtration of model EPS solutions, J. Memb. Sci. 264 (2005) 190–199.

[14] S. Lee, W.S. Ang, M. Elimelech, Fouling of reverse osmosis membranes by hydrophilic organic matter: implications for water reuse, Desalination 187 (2006) 313–321.

[15] K. Katsoufidou, S.G. Yiantsios, A.J. Karabelas, An experimental study of ultrafiltration membrane fouling by sodium alginate and flux recovery by backwashing, J. Memb. Sci. 300 (2007)137–146.

[16] A.J. De Kerchove, M. Elimelech, Formation of polysaccharide gel layers in the presence of Ca^{2+} and K^+ ions: measurements and mechanisms, Biomacromolecules 8 (2007) 113–121.

[17] S. Lee, M. Elimelech, Relating organic fouling of reverse osmosis membranes to intermolecular adhesion forces, Environ. Sci. Technol. 40 (2006) 980–987.

[18] P. Van den Brink, A. Zwijnenburg, G. Smith, H. Temmink, M. van Loosdrecht, Effect of free calcium concentration and ionic strength on alginate fouling in cross-flow membrane filtration, J. Memb. Sci. 345 (2009), 207-216.

[19] O. Smidsrød, Molecular basis for some physical properties of alginates in the gel state, Faraday Discuss Chem. Soc. 57 (1974) 263-274.

[20] G.T. Grant, E.R. Morris, D.A. Rees, P.J.C. Smith, D. Thom, Biological interactions between polysaccharides and divalent cations: the egg-box model, FEBS Letters 32 (1973)195–198.

[21] W.J.C.V.D. Ven, K.V.T. Sant, I.G.M. Punt, A. Zwijnenburg, A.J.B. Kemperman, W.G.J.V. der Meer, M. Wessling, Hollow fiber dead-end ultrafiltration: influence of ionic environment on filtration of alginates, J. Memb. Sci. 308 (2008) 218–229.

[22] K. Listiarini, W. Chen, D.D. Sun, J.O. Leckie, Fouling mechanism and resistance analyses of systems containing sodium alginate, calcium, alum and their combination in dead-end fouling of nanofiltration membranes, J. Memb. Sci. 334 (2009) 244-251

[23] A. Tiraferri, Y. Kang, E.P. Giannelis, M. Elimelech, Superhydrophilic thin-film composite forward osmosis membranes for organic fouling control: Fouling behavior and antifouling mechanisms, Environmental Science and Technology 46 (2012) 11135-11144.

[24] A. Nguyen, S. Azari, L. Zou, Coating zwitterionic amino acid l-DOPA to increase fouling resistance of forward osmosis membrane, Desalination 312 (2013) 82-87.

[25] H.Y. Yu, Y. Kang, Y. Liu, B. Mi, Grafting polyzwitterions onto polyamide by click chemistry and nucleophilic substitution on nitrogen: A novel approach to enhance membrane fouling resistance, J. Memb. Sci. 449 (2014) 50-57.

[26] S. Romero-Vargas Castrillón, X. Lu, D.L. Shaffer, M. Elimelech, Amine enrichment and poly(ethylene glycol) (PEG) surface modification of thin-film composite forward osmosis membranes for organic fouling control, J. Memb. Sci. 450 (2014) 331-339.

[27] A. Nguyen, L. Zou, C. Priest, Evaluating the antifouling effects of silver nanoparticles regenerated by TiO_2 on forward osmosis membrane, J. Memb. Sci. 454 (2014) 264-271.

[28] X. Liu, S. Qi, Y. Li, L. Yang, B. Cao, C.Y. Tang, Synthesis and characterization of novel antibacterial silver nanocomposite nanofiltration and forward osmosis membranes based on layer-by-layer assembly, Water Research 47 (2013) 3081-3092.

[29] X. Lu, S. Romero-Vargas Castrillón, D.L. Shaffer, J. Ma, M. Elimelech, In Situ Surface Chemical Modification of Thin-Film Composite Forward Osmosis Membranes for Enhanced Organic Fouling Resistance, Environmental Science & Technology 47 (2013) 12219-12228.

[30] X. Li, T. Cai, T.S. Chung, Anti-Fouling Behavior of Hyperbranched Polyglycerol-Grafted Poly(ether sulfone) Hollow Fiber Membranes for Osmotic Power Generation, Environmental Science & Technology 48 (2014) 9898-907.

[31] D. Emadzadeh, W.J. Lau, T. Matsuura, N. Hilal, A.F. Ismail, The potential of thin film nanocomposite membrane in reducing organic fouling in forward osmosis process, Desalination 348 (2014) 82-88.

[32] X. Song, L. Wang, C.Y. Tang, Z. Wang, C. Gao, Fabrication of carbon nanotubes incorporated double-skinned thin film nanocomposite membranes for enhanced separation performance and antifouling capability in forward osmosis process. Desalination 369 (2015) 1-9.

[33] W. Fang, R. Wang, S. Chou, L. Setiawan, A.G. Fane, Composite forward osmosis hollow fiber membranes: Integration of RO- and NF-like selective layers to enhance membrane properties of antiscaling and anti-internal concentration polarization, J. Memb. Sci. 394-395 (2012) 140-150.

[34] P.H.H. Duong, T.S. Chung, S. Wei, L. Irish, Highly Permeable Double-Skinned Forward Osmosis Membranes for Anti-Fouling in the Emulsified Oil–Water Separation Process, Environmental Science & Technology 48 (2014) 4537-4545.

[35] S. Qi, C.Q. Qiu, Y. Zhao, C.Y. Tang, Double-skinned forward osmosis membranes based on layer by-layer assembly-FO performance and fouling behavior, J. Memb. Sci. 405-406 (2012) 20-29.

[36] V. Meynen, A. Buekenhoudt, B. Maes, P. Cool, Surface modified inorganic matrix and method for preparation thereof, EP 09155686, WP 2010 IEP 5361620100319, VITO-UA (2009).

[37] S. Rezaei Hosseinabadia, K. Wyns, V. Meynen, R. Carleer, P.A. Adriaensens, A. Buekenhoudt, B. Van der Bruggen, Organic solvent nanofiltration with Grignard functionalised ceramic nanofiltration membranes, J. Membr. Sci. 454 (2014) 496–504.

[38] G. Mustafa, K. Wyns, A. Buekenhoudt, V. Meynen, Novel grafting method efficiently decreases irreversible fouling of ceramic nanofiltration membranes, J. Membr. Sci. 470 (2014) 369–377.

[39] G. Mustafa, K. Wyns, A. Buekenhoudt, V. Meynen, New insights into the fouling mechanism of dissolved organic matter applying nanofiltration membranes with a variety of surface chemistries, Water Research 93 (2016) 195–204.

[40] G. Mustafa, K. Wyns, A. Buekenhoudt, V. Meynen, Antifouling grafting of ceramic membranes validated in a variety of challenging wastewaters, Water Research 104 (2016) 242-253.

[41] A. Roevens, J.G. Van Dijck, M. Tassi, J. D’Haen, R. Carleer, P. Adriaensens, F. Blockhuys, V. Meynen, Revealing the influence of the solvent in combination with temperature, concentration and pH on the modification of TiO_2 with 3PA, Mat. Chem. Phys. 184 (2016) 324-334.

[42] P. Van Heetvelden, E. Beyers, K. Wyns, P. Adriaensens, B.U.W. Maes, S. Mullens, A. Buekenhoudt, V. Meynen, A new method to graft titania using Grignard reagents, Chem. Comm. 49 (2013) 6998-7000.

[43] V.P. Lemos, M. Lima da Costa, R.L. Lemos, M.S. Gomes de Faria, Vivianite and side rite in lateritic iron crust: an example of bioreduction, Quim. Nova, 30 (2007) 36-40.

[44] R.H. Kane, J. Kelly, T.J. Davidson, A Material for Advanced Ethylene Production Processes, CORROSION/84, NACE International, Houston, TX (1984).

[45] K. Ghosh, M. Schnitzer, Macromolecular structure of humic substances, Soil Sci. 129 (1980) 266-276.

[46] A. Piccolo, The supramolecular structure of humic substances, Soil Sci. 166 (2001) 810-832.

[47] A.V. Jung, V. Chanudet, J. Ghanbajo, B.S. Lartiges J.L. Bersillon, Coagulation of humic substances and dissolved organic matter with a ferric salt: an electron energy loss spectroscopy investigation, Water Research 39 (2005) 3849-3862.

[48] T. Van Gestel, C. Vandecasteele, A. Buekenhoudt, C. Dotremont, J. Luyten, R. Leysen, B. Van der Bruggen, G. Maes, Salt retention in nanofiltration with multilayer ceramic TiO_2 memrbanes. J. Memb. Sci. 209 (2002) 379–389.

[49] S.H. Kima, S.Y. Kwak, B.H. Sohnb, T.H. Park, Design of nanoparticle self-assembled aromatic polyamide thin-film-composite (TFC) membrane an approach to solve biofouling problem, J. Memb. Sci. 211 (2003) 157–165.

[50] K. Ebert, D. Fritsch, J. Koll, C. Tjahjawiguna, Influence of inorganic fillers on the compaction behaviour of porous polymer based membranes, J. Membr. Sci. 233 (2004) 71–78.

[51] F.M.M. Morel, J.G. Hering, Principles and applications of aquatic chemistry, Wiley, New York, 1992.

[52] D. Kühbeck, J. Mayr, J. Marleen, M. Hofmann, F. Quignard, D. Díaz, Evaluation of the nitroaldol reaction in the presence of metal ion-crosslinked alginates, New J. Chem. 39 (2015) 2306-2315.