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Impact of speciation on removal of manganese and organic matter by nanofiltration

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Abstract

The removal of manganese and humic acid (HA) by two nanofiltration membranes, TFC-SR2 and TFC-SR3, was investigated in order to highlight the influence of speciation on manganese and HA retention. Manganese speciation and complexation with HA were modelled to understand how speciation could affect NF removal mechanisms. The behaviour of the two membranes was drastically different for manganese retention. Manganese retention for TFC-SR3 was higher and dominated by size exclusion. Manganese retention for TFC-SR2 varied with pH. At pH 7, i.e. the pH of most natural waters, manganese retention for TFC-SR2 was about 45% versus 90% of TFC-SR3, with fluxes of about 75 and 25 $L.m^{-2}h^{-1}$, respectively. Both membranes showed very high retention of HA (about 80%), being therefore suitable for surface waters where no salt removal is required. Manganese deposit on both membranes was generally low (< 10%), but increased at pH 10 and 12 as manganese deposited as precipitated $MnCO_3$, and the membranes showed a yellow-brownish layer.

Keywords
humic acids, manganese, nanofiltration, speciation

Introduction

Manganese is one of the most abundant elements on Earth and it occurs in surface water and groundwater naturally and as a result of human activities. Manganese is considered harmful to public health at concentrations higher than 0.4 mg/L. Concentration of manganese exceeding 0.1 mg/L creates aesthetic problems of undesirable metallic taste and coloured water at the consumer tap and several countries have set their regulatory limits to 0.05 mg/L (WHO 2004).

In Scotland, surface waters constitute the majority of the water supply and often contain high concentration of natural organic matter (NOM), as well as iron and manganese (Grose *et al.* 1998). Water quality data collected by Scottish Water during 2004, 2005 and 2006 at 524 raw water sample points Scottish-wide showed that iron and manganese exceeded the Scottish maximum permissible values (0.05 mg/L) more frequently than aluminium, arsenic, fluoride, lead and nitrite. In particular, manganese was detected at concentrations up to 20 mg/L (Allen 2008).

Manganese is known to form complexes with humic acids (HA) and tannic acids (TA) (Chiswell & Mokhtar 1987; Guy & Chakrabarti 1976; Lee 1983; Nifant'eva *et al.* 1999). HA represent the largest portion of NOM. NOM is precursor of disinfection by-products, such as trihalomethanes, which are considered carcinogenic (Jacangelo *et al.* 1995). HA are complex and heterogeneous

mixtures of high to low molecular species containing both aromatic and aliphatic components with primarily carboxylic and phenolic functional groups. Most HA groups dissociate at pH >4 and have a negative charge and are insoluble at pH< 2 (Hayes *et al.* 1989).

Removal of manganese together with organic matter is therefore of primary importance in order to comply with regulations and insure that problems of coloured water do not occur. Manganese is conventionally removed by filtration preceded by vigorous oxidation or as a part of the clarification process. Oxidation of manganese to precipitated MnO_2 is an autocatalytic process and requires strong oxidants (ozone, chlorine or potassium permanganate) and a catalyser (manganese ore or filter sand that has to be pre-treated with manganese). The process is difficult to start-up, the filterability of MnO_2 is low and when manganese concentration is higher than 5 mg/L too much solid is produced that shortens filtration cycles and makes the process unprofitable. Furthermore, process control is difficult for waters of variable quality, such as surface waters (Ellis *et al.* 2000). The traditional clarification process has proven to be insufficient for manganese removal; moreover, the presence of dissolved organic matter increases the coagulant demand and further decreases the removal (Mijatovic *et al.* 2004; Potgieter *et al.* 2005a). In Scotland, manganese exceeded its regulatory limit more frequently than the other inorganic elements (included iron) in sample points at the outlet of conventional water treatment plants, indicating insufficient removal to achieve the desired standard (Allen 2008).

Removal of manganese alone or with organic matter by microfiltration (MF) and ultrafiltration (UF) processes has been investigated in several studies, as summarized in Table 1. Soluble manganese passes through MF and UF membranes and pre-treatments that precipitate manganese are necessary to achieve effective removal. Strong oxidation has been shown to be the most effective pre-treatment but this increases the cost of the process, both in economical and environmental terms.

[Table 1]

Nanofiltration (NF) membranes have been applied in the last decades for the removal of specific inorganic compounds (such as arsenic, uranium, and iron) and organic matter (Van der Bruggen & Vandecasteele 2003). However, only a limited number of studies have examined removal of manganese by NF membranes (Lastra *et al.* 2004; Molinari *et al.* 2001; Potgieter *et al.* 2005b). Lastra *et al.* (2004) studied manganese and organic removal in the effluent of a pulp mill, characterized by organic content and temperature much higher than the ones found in natural waters. As a consequence, available results can not be applied to water treatment. Molinari *et al.* (2001) performed manganese removal tests with "tap water", but information on water and membrane characteristics was not provided. Potgieter *et al.* (2005b) used NF membranes for removal of iron and manganese in presence of dissolved organic matter in a South African river. Manganese concentrations in the river water were very low (0.15 - 0.29 mg/L), probably similar to the instrument detection limit, increasing the detection error in the membrane permeate. Different samples with different solute concentrations were used, making results not comparable in a consistent way. The Fyne process using NF PCI membranes has been reported to work satisfactorily for the removal of organic matter, manganese and iron in North America and Scotland (Grose *et al.* 1998; Pearson 2001; Wittmann & Thorsen 2004). However, the obtained removal rates were site and condition dependent and they can not be generalized. This invites to a systematic approach to elucidate underlying mechanisms applicable to water treatment.

The results obtained in the reviewed studies are dependent on the feed water characteristics and on the particular conditions in which the experiments were carried on and they can not be easily compared. In these studies NF was shown to be a suitable process for manganese removal, however its removal mechanisms were not consistently investigated and membrane characteristics (morphology and charge) affecting retention were not taken into account. Furthermore, the impact

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of manganese speciation and complexation with organic matter was not taken into consideration. Although NF is known to remove divalent co-ions, removal is solute specific due to solute speciation and different interaction with the membranes. Relating solute removal and flux to solution pH has been shown to be mandatory for understanding removal mechanisms by NF membranes, as the variation of solution pH affects not only membrane characteristics but also the different forms (species) at which solutes exist (Childress & Elimelech 2000). Despite this, the number of NF studies in which a detailed knowledge of solute speciation is related to the membrane removal mechanisms is limited.

In consequence, the objectives of this study were to:

(1) Model manganese speciation in presence of HA
(2) Investigate and quantify the influence of pH and speciation on removal of manganese and HA by NF
(3) Explain the mechanism of manganese and HA removal by two NF membranes

In order to study manganese and HA removal, TFC-SR2 and TFC-SR3S NF membranes were selected and experiments were carried out at pH ranging from 4 to 12. TFC-SR2 and TFC-SR3 present attractive characteristics for manganese and HA removal, since they have high organics retention and partial retention of inorganics. Speciation of manganese and complexation of manganese and HA were modelled to interpret retention results.

Materials and Methods

Chemicals

Experiments were conducted in ultra-pure water obtained by PuraLab Ultra (Elga LabWater, UK). All chemicals were of analytical grade. Manganese as $MnCl_2$ was purchased from Fisher Scientific UK and HA from Sigma Aldrich UK. Characteristics of Aldrich HA can be found in the literature (Kim *et al.* 1990; Malcom & MacCarthy 1986). Manganese was used at a concentration of 5 mg/L and HA of 5 mgC/L, as these are representative concentrations for Scottish waters (Allen 2008). Electrolyte background solution consisted of 1 mM $NaHCO_3$ and 20 mM NaCl, both supplied by Fisher Scientific. pH was adjusted with1M HCl and NaOH (Fisher Scientific, UK). Nitric acid for sample conservation was purchased by Aristar VWR International, UK.

Stirred cell filtration system

Experiments were performed with an apparatus consisting of three stainless steel stirred cells in parallel described elsewhere (Neale 2009) and depicted in Figure 1. Cells had volume of 990 mL and a diameter of 70 mm, resulting in a membrane area of 38.5 cm^2. The cells were pressurised with filtered lab air; the pressure was kept constant and automatically measured every minute with a pressure transducer (Omega Engineering, UK). Temperature inside the cells and permeate collected on an electronic balance (Advancer Pro, Ohaus, UK) were measured every minute. A digital magnetic stirrer (Fisher Scientific, UK) was used at speed of 300 rpm.

[Figure 1]

Membranes

Two proprietary thin-film composite (TFC) membranes made by a thin layer of polyamide cast on a layer of microporous polysulfone, TFC-SR2 and TFC-SR3, supplied by Koch Membrane, UK, were selected for this study (Koch Membrane System Fluid System Datasheets). All experiments were performed with one batch flat sheet membrane sample provided by the manufacturer and a new membrane was used for each experiment. Membrane characteristics are summarized in Table 2. Permeability was calculated as the average of all measurements performed in this study. Pore radius

and molecular weight cut-off (MWCO) were determined using the methodology described by Nghiem et al. (2004).

The membrane contact angle has been measured using the sessile drop method with a contact angle measuring instrument (Easy Drop, Kruss, Germany). Point of zero charge was measured with an electrokinetic analyser (EKA, Anton Paar KG, Graz, Austria) with the same background electrolyte used in the experiments (1 mM $NaHCO_3$ and 20 mM NaCl). TFC-SR2 and TFC-SR3 membranes are amphoteric, i.e. they have ionizable carboxylic and amine groups and their surface zeta potential is positive at pH lower than the point of zero charge due to the protonation of amine groups ($\equiv NH_2 \rightarrow \equiv NH_3^+$) and negative at higher pH, due to the deprotonation of carboxylic groups ($\equiv COOH \rightarrow \equiv COO^-$) (Childress & Elimelech 1996). The two membranes showed similar surface charge characteristics, with similar point of zero charge (at pH 4.25 for TFC-SR2 and pH 3.84 for TFC-SR3) and similar zeta potential at pH 12 (-26.7 ± 9.2 for TFC-SR2 and -26.8 ± 5.5 for TFC-SR3), while TFC-SR2 was slightly more positively charged at pH 3.5 (2.2 ± 4.7 for TFC-SR2 and 1.2 ± 5.7 for TFC-SR3).

[Table 2]

Experimental Protocol

The experiment protocol was as follows: the membrane was thoroughly rinsed with ultra-pure water, stored in ultra-pure water overnight and compacted for an hour at 8 bar. Pure water flux was measured at 5 bar for 30 minutes before each experiment. 500 mL feed solution, prepared the day before and stirred overnight at 100 rpm, was placed in the cell and pressurized at 5 bar. Permeate was collected in three aliquots of 40 mL each (24% recovery). Pure water flux was measured at 5 bar for 30 minutes after the experiment.

Three types of experiment were conducted:

1. Mn^{2+} only: feed solution contained 5 mg/L of Mn^{2+} and background electrolyte. A stock solution of 100 mg/L of Mn^{2+} was acidified and stored at < 4 ºC.
2. HA only: feed solution contained 5 mgC/L of HA and background electrolyte. A stock solution of 100 mgC/L of HA was wrapped in aluminium foil and stored at < 4 ºC for not more than 2 weeks.
3. Mn^{2+} and HA: feed solutions contained 5 mg/L of Mn^{2+}, 5 mgC/L of HA and background electrolyte.

Error bars were determined by considering pure water flux variation due to the use of different membrane samples, variation in temperature and pressure during different experiments and within the same experiment and error in determining solute concentration due to error in pipette, in balance, volumetric flask and instrumental error. Pure water flux variations were found to be 4.3% for TFC-SR2 and 8.5% for TFC-SR3, the instrumental error for ICP-OES (inductively coupled plasma atomic emission spectroscopy) was 3.6% and for total organic carbon (TOC) was 5.8%, variation in pure water flux was used to determine variation in retention and deposit for the membranes, with the exception of experiments with HA using TFC-SR2 where error due to TOC was considered instead.

Analytical Methods

Samples and blanks were analysed for manganese with ICP-OES (Perking Elmer Optima 5300 DV, UK) after being acidified with nitric acid to pH<2 for conservation (Clesceri *et al.* 1998). Calibration standards were made using ICP multi-element standard and manganese standard (Merck, Germany) and verified using a certified reference material, ICP multi-element standard solutions VI (CertiPUR, Germany). Total Organic Carbon (TOC) was measured with a TOC $V_{CPH/CPN}$ Shimadzu analyser in a non-purgeable organic carbon mode. Calibration standards were

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made using potassium hydrogen phthalate (Acros Organics, UK). Samples were analysed for TOC the same day of the experiments. Ultraviolet absorbance at 254 nm was measured with an UV Visible Spectrophometer Cary 100 (Varian, UK). Samples were analyzed within a few hours from collection. Conductivity and pH measurements were conducted using a pH/Cond 340i meter (WTW, Germany).

Speciation Modelling

Visual MINTEQ 2.5 (U.S. Environmental Protection Agency 1991) was used in this study to model both manganese speciation and manganese and HA complexation as a function of pH. Modelling was carried out for the experimental conditions Mn^{2+} fixed at 5 mg/L, 20 mM of background electrolyte, pH from 4 to 12 and pressure fixed at 5 bar. It was assumed that no redox reaction for Mn(II) occurred during the experiments, despite the presence in the stirred cells of dissolved oxygen at concentrations higher than in a solution in equilibrium with the atmosphere. The oxidation reaction of Mn(II) into Mn(IV) is very slow (days) in absence of catalytic effects and aeration alone has been shown to be insufficient to precipitate manganese as MnO_2, the dominant form of Mn(IV) (Chiswell & Mokhtar 1986; Handa 1970). As a consequence, Mn (II) was considered the only oxidation state for manganese during the experiments.

The NICA-Donnan Model present in Visual MINTEQ 2.5 (U.S. Environmental Protection Agency 1991) was chosen as it has been extensively validated over experimental data for several elements, such as H^+, Ca^{2+}, Cd^{2+}, Cu^{2+}, Pb^{2+}, Al^{2+} (Benedetti *et al.* 1995; Christl *et al.* 1995; Kinniburgh *et al.* 1999; Pinheiro *et al.* 2000) and Fe^{3+} (Weber *et al.* 2006a; Weber *et al.* 2006b). Detailed description of the NICA-Donnan model can be found in the literature (Kinniburgh *et al.* 1999; Merdy *et al.* 2006). NICA sub-model simulates specific metal-NOM binding and uses two binding functions corresponding to the carboxylic and phenolic groups of HA. A continuous distribution of binding sites types is assumed. Donnan sub-model simulates non-specific binding due to the electrostatic forces caused by the net negative charge of dissociated carboxylic and phenolic groups. The organic matter is considered as a gel phase with homogenous charge and potential distribution and counter-ions are assumed to accumulate in the gel volume. The two sub-models are interrelates, as the concentration of ions accumulated electrostatically competes with the ions bind specifically, and they were used simultaneously. As specific experimental data with manganese ions were not available in the literature, NICA-Donnan model parameters derived by Milne *et al.* (2003) were used. Manganese parameters were estimated using the variation of the hydrolysis behaviour as an indication of the likely binding capacity of humic substance (Milne *et al.* 2003).

Results and Discussions

Manganese and HA speciation

The distribution of manganese species alone or in presence of HA was modelled as a function of pH. Modelling the complexation of metals with HA presents several difficulties, due to the heterogeneous and complex nature of humic binding sites, the presence of electrostatic interactions and the competing binding of protons as they interact with the same sites as metals ions (Merdy *et al.* 2006).

Figure 2 (A) and (B) show the percentage of manganese in solution and manganese precipitate in absence and presence of HA. Figure 2 (C) details the concentration of dissolved manganese, expressed as logarithmic of the activity, versus pH in absence of HA. Dissolved manganese species in presence of HA showed the same trends, albeit with slightly different concentrations (results not reported).

[Figure 2]

At pH<7, dissolved manganese is mainly present as Mn^{2+}, $MnHCO_3^+$, $MnOH^+$ and $MnCO_3$ (aq). $MnCO_3$ precipitation starts at pH 7.1 (dashed line in Figure 2(C)) and it is complete at pH 9.6. Figure 2(A) and (C) are in agreement with published investigations on the chemistry of manganese in natural waters (Chiswell & Mokhtar 1986; Chiswell & Mokhtar 1987).

In presence of HA, the distribution of dissolved manganese species does not vary greatly and Mn^{2+}, $MnHCO_3^+$, $MnOH^+$ and $MnCO_3$ (aq) remain the dominant dissolved manganese species (results not presented). As shown in Figure 2(B), $MnCO_3$ starts precipitating at pH 7.2 and the precipitation is completed at pH 8.5. The presence of HA does not influence the pH at which manganese starts precipitating, but lowers the pH at which the maximum quantity of precipitate is present from pH 9.6 to 8.5. Furthermore, in presence of HA, there is 35% less precipitation of $MnCO_3$ as the manganese forms complexes with HA.

The obtained speciation graph in presence of HA must be used with caution, given the number of assumptions done and the use of parameters that have not been experimentally validated. However, the results are in general agreement with the literature. Organic matter was shown to influence the solubility of inorganic compounds (Lee 1983) and in particular to increase metal ion solubility through binding with dissolved organic matter (Kinniburgh *et al.* 1999; Schäfer 2001; Weber *et al.* 2006b). The increase of metal-HA complexes with pH was observed for Fe^{3+} (Weber *et al.* 2006b) and Ca^{2+} (Hong & Elimelech 1997) and this is due to the availability of carboxyl functional groups of HA at higher pH (Hong & Elimelech 1997).

Membrane flux

Figure 3 shows the ratio of pure water flux after (J) and before (Jo) the experiments versus pH. Water flux decline after the experiments was not observed, showing that membrane fouling did not occur. Lack of fouling was attributed to the short duration of the experiments, the low concentrations of the solutes and the relatively low flux obtained in the stirred cells. The absence of fouling allowed relating the obtained retention results directly to the membrane characteristics and solute speciation, without considering membrane and solute modification due to the formation of the fouling layer.

[Figure 3]

In some cases, especially for TFC-SR3 water flux after experiments was enhanced, resulting in a flux ratio greater than one. This phenomenon was observed in a study by Hong and Elimelech (1997) and was attributed to the hydrophilization of membrane surface by adsorbed solutes. Adsorption of negative solutes, such as HA, can increase the membrane negative charge, thus its hydrophilicity. However in this study, flux enhancement occurred for TFC-SR3 also when Mn^{2+} alone was present indicating that ions can enhance permeability also. As shown in Figure 3, TFC-SR2 experienced a slight flux ratio increase at higher pH due to pore opening with increased charge repulsion, while no trend could be observed for TFC-SR3.

During the experiments the permeability was relatively constant for both membranes (Figure 4), if error fluxes are taken into account (4.3% for TFC-SR2 and 8.5% for TFC-SR3, error bars not shown for clarity). This was also observed by Schäfer (2001) for other TFC membranes. When electrolyte only was used, TFC-SR2 showed a slightly flux increase at pH 8, while maximum flux for TFC-SR3 was obtained at pH 6. This is in contrast with the Donnan exclusion theory that predicts maximum flux and minimum electrolyte retention at the membrane zero point of charge (at around pH 4 for both membranes, see Table 2).

[Figure 4]

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Solute retention and precipitation

Manganese and HA retention was calculated for HA only, manganese only and when both were present (Figure 5).

[Figure 5]

Manganese retention was higher for TFC-SR3 membrane in agreement with salt retention reported by the manufacturer and NaCl retention determined in this study (Table 1). Furthermore, manganese retention by TFC-SR3 (Figure 5(B)) did not show high variation with pH (error in calculating manganese retention 7.8%) and it was high (94.7%) at lower pH when manganese is mainly present as dissolved Mn^{2+} (Figure 2). Hydrated radius for Mn^{2+} has been calculated as 0.44 nm (Nightingale 1959), while the calculated pore radius of TFC-SR3 was 0.38 nm (Table 2). Hydrated radius has been shown to predict better than crystal and Stokes radius ion passages through membranes (Tansel *et al.* 2006). When the hydrated radius is larger than the membrane pore radius, as for TFC-SR3, steric hindrance effects are believed to be predominant (Schaep *et al.* 1998). As a consequence, ions are hindered to enter the pores and size exclusion is the main removal mechanism.

Manganese retention by TFC-SR2 (see Figure 5(A)) was high at pH 4 (92.2%) and at pH 10-12 (99.1%) with a minimum (37.3%) at pH 8. At pH 10 and 12 manganese is predominantly present as visible $MnCO_3$ (s) that precipitated on the membrane and manganese removal was mainly due to size exclusion. Between pH 7 and 4 almost all manganese is present as soluble Mn^{2+}. High manganese retention at pH 4 can not be explained by steric hindrance, as the hydrated radius of Mn^{2+} (0.44 nm) is smaller than the average pore size of TFC-SR2 (0.52 nm), nor by charge repulsion forces between the membrane surface and the solute, as TFC-SR2 has point of zero charge at pH 4.25 (Table 2). Minimum retention of ions is expected in correspondence of the point of zero charge of the membrane surface, when the repulsion forces are minimum (Mänttäri *et al.* 2006). In this study, instead, minimum retention for TFC-SR2 occurred at pH 8, higher that the point of zero charge of the membrane surface.

Childress and Elimelech (2000) observed minimum retention of NaCl at the point of zero charge of the membrane pores, which they showed to be higher than the point of zero charge of the membrane surface. When pores are charged, the electrostatic repulsion between the membrane functional groups causes the pore to expand; at their point of zero charge the pore size would not be reduced, flux would be maximum and salt retention minimum. They inferred that for "loose" porous membranes pore charge could be more important than surface charge in controlling flux and salt retention. Pore charge becomes important when solutes are not hindered to enter the pores. When the hydrated radius is smaller than the pore radius, ion can enter the pores and electrostatic and friction forces within the pores acquire importance (Pontalier *et al.* 1997). This mechanism might be confirmed by the experimental results for TFC-SR2, as the flux is maximum at pH 8 (Figure 4) where manganese retention is minimum (Figure 5(A)). This mechanism might also explain the increase of retention at pH 6 and 4, where the pores will be positively charged.

Considering the error of TOC analysis and of retention calculation (6.9% and 11.4% respectively), retention of HA was high for both membranes (about 80%) and did not present a specific trend with pH. These results were confirmed by retention calculated by analysing samples with ultraviolet absorbance at 254 nm (results not presented). The ratio UV_{254nm}/TOC (SUVA) was calculated as an indication of the aromaticity of the samples and SUVA retention was determined as a function of pH. Both membranes showed high aromaticity retention (83-93% for TFC-SR2 and 80-100% for TFC-SR3) and no trend with pH could be observed. The presence of manganese did not affect HA retention. Also manganese retention was not affected by the presence of HA, as it is evident by the same trend of the curves for Mn^{2+} only and for Mn^{2+} and HA in Figure 5. Even though several

studies documented the formation of complexes between manganese and HA (Chiswell & Mokhtar 1987; Guy & Chakrabarti 1976; Lee 1983; Nifant'eva *et al.* 1999) and the NICA-Donnan model predicted that 37% of manganese in solution would complex to HA at pH above 7.2 (Figure 2), a significant enhancement of manganese and HA retention when both elements were present was not observed. In the case of TFC-SR3 membrane, high retention was already achieved due to size exclusion mechanisms, while for TFC-SR2, precipitation might overlap with complexation effects.

It can be concluded that at pH 7, i.e. the pH of most natural waters, the behaviour of the two membranes was drastically different for manganese retention. TFC-SR3 presented retention above 95%, due mainly to size exclusion, while TFC-SR2 presented retention of about 45%. At pH 7 both membranes had high retention of HA (about 80%) showing to be particularly suitable for surface waters. To achieve a drinking water quality of 0.05 mg/L with the feedwater concentration of 5 mg/L a retention of 99% is required. This can only be achieved at pH 10 and 12 for both membranes.

Mass deposit on the membrane

Mass deposit on the membranes was determined to substantiate the results obtained in the previous section. The deposit of manganese and HA on the membranes was calculated with the following mass balance equation:

$$M_D = V_F C_F - V_P C_P - V_C C_C \quad (1)$$

where M_D is amount of solute the deposit, V_F, V_P, and V_C are the volume of feed, permeate, and concentrate, respectively, and C_F ,C_P, and C_c are the concentration of feed, permeate and concentrate, respectively.

[Figure 6]

As shown in Figure 6, the deposit of solutes was low, generally less than 10%. However, when Mn^{2+} only was present in solution, manganese deposit was higher for pH 10 and 12, as manganese deposited as precipitated $MnCO_3$, and the membranes showed a yellow-brownish layer (Figure 6 (A) and (B)). For both membranes, manganese deposit at high pH was generally less when HA were present. Considering the high error associated with HA mass deposit calculation (10.0%), HA deposit with and without manganese can be considered negligible for both membranes This result agreed with mass deposit calculations obtained using UV absorbance data (results not presented) and visual observations, confirming that fouling did not occur during the experiments.

The short duration of the experiments and the low concentration of the solutes did not allow to obtain fouling conditions. However, in longer filtration operation the presence of HA and manganese precipitation at high pH is likely to decrease membrane flux and reduce membrane performance including decrease of solute retention. Further studies are required to investigate this phenomenon.

Conclusions

This study investigated the removal of manganese and HA by two NF membranes, TFC-SR2 and TFC-SR3, as a function of pH.

- The two membranes showed different behaviour respect to manganese retention
- Both membranes had high retention of HA (about 80%)
- Solute deposit on both membranes was speciation dependent.

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TFC-SR3 had higher manganese retention (about 96%) for all the investigated pH and this was attributed to size exclusion. Manganese retention for TFC-SR2 varied with pH: higher retention was obtained at pH 10 and 12, due to manganese precipitation as insoluble $MnCO_3$, and at pH 4, while lower retention was observed at pH 6 and 8. At pH 7, i.e. the pH of most natural waters, manganese retention for TFC-SR2 was about 45%, versus 90% for TFC-SR3. For both membranes, the manganese regulatory limit in the permeate (0.05 mg/L) was only reached at pH 10 and 12 (99% retention). Both membranes showed to be particularly suitable for surface waters where NOM is present. On both membrane, HA deposit was negligible and manganese deposit was generally low (< 10%), but increased at pH 10 and 12 as manganese deposited as precipitated $MnCO_3$, and the membranes showed a yellow-brownish layer.

The complexation model showed formation of manganese-HA complexes at pH values above 7. However, significant enhancement of manganese and HA retention when both elements were present was not observed during the experiments, as manganese retention was not affected by the presence of HA and vice versa HA retention was not affected by the presence of manganese. In the case of TFC-SR3 membrane, high retention was already achieved due to size exclusion mechanisms, while for TFC-SR2, precipitation might overlap with complexation effects.

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Table 1

Feed Water	Source	Process	Pretreatment	Mn Removal	Reference
Mn	artificial	MF	aeration	not effective	(Abdur Rahman *et al.* 2000)
			pH level of 9.7	97%	
			H_2O_2 + UV irradiation	not effective	
Mn	artificial	MF	H_2O_2 + UV irradiation ay pH 9.3	95% after 50 h	(Teng *et al.* 2001)
			Mn sand	over 95%	
Mn	natural GW	MF	fluidised-bed with Cl_2 oxidation	90%	(Takizawa *et al.* 2001)
			fluidised-bed with biological oxidation	87%	
			fixed-bed with biological oxidation	100%	
Mn and Fe	- artificial - natural GW	MF	oxidation + $KMnO_4$	96%	(Ellis *et al.* 2000)
Mn and Fe	artificial	MF/ UF	aeration	not effective	(Jimbo & Goto 2001)
			$KMnO_4$	not effective	
			ClO_2	not effective	
			NaClO	90%	
Mn	artificial	UF	Polyacrilic acid dosed to form Mn complexes	Almost 100% at pH 9, 5% at pH 4	(Han *et al.* 2007)
Mn	artificial	UF	None	14.7-17.4%	(Kabsch-Korbutowicz & Winnicki 1996)
Mn and HA	river water	MF	Biological oxidation	90% but bacteria not effective al water temperaute < 5 ºC	(Suzuki et al. 1998)
			PAC + biological oxidation		
Mn and HA	artificial	UF	None	17- 38%	(Kabsch-Korbutowicz & Winnicki 1996)
Mn, Fe and NOM	Dam water spiked with $MnCl_2$ and $FeCl_2$	UF	Chlorination (3 mg/L of Cl_2)	31%	(Choo *et al.* 2005)

Table 2

	MWCO (1)	Estimated pore radius	Retention $MgSO_4$ (1)	Retention NaCl (2)	Average Permeability (3)	Point of zero charge (4)	Contact Angle
	g/mol	nm	%	%	L. $h^{-1}.m^{-2}.bar^{-1}$	pH	º
TFC-SR2	486	0.52	95	21	16.1	4.25 ± 0.01	61.5 ± 2.5
TFC-SR3	167	0.38	99.4	30	5.7	3.84 ± 0.01	48.5 ± 1.4

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Figure 1

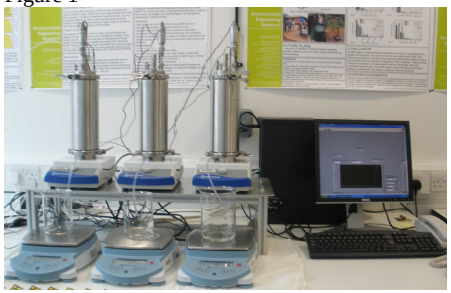

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Figure 2

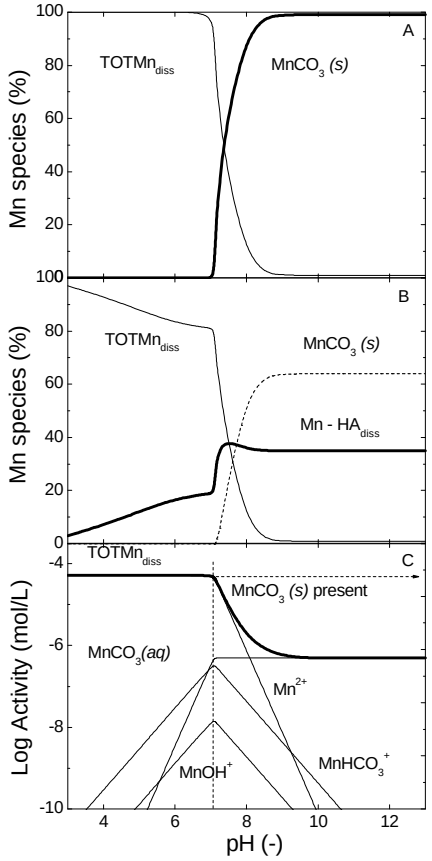

Figure 3

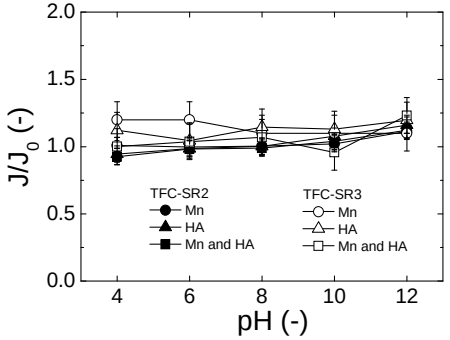

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Figure 4

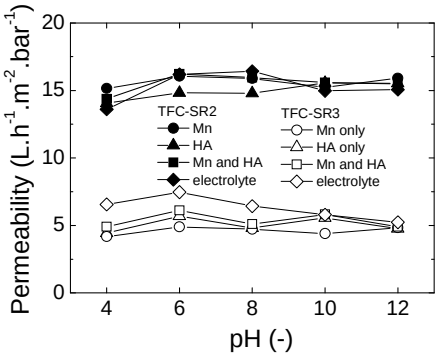
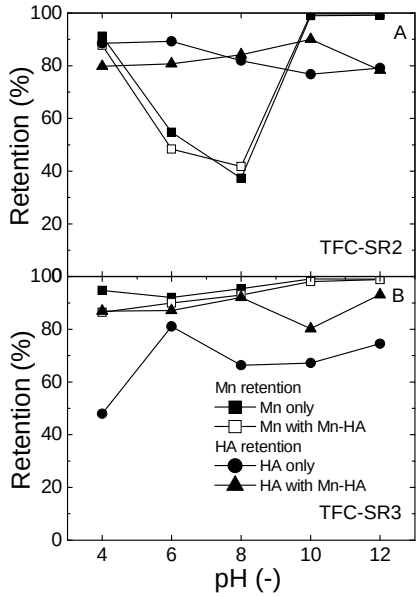


Figure 5



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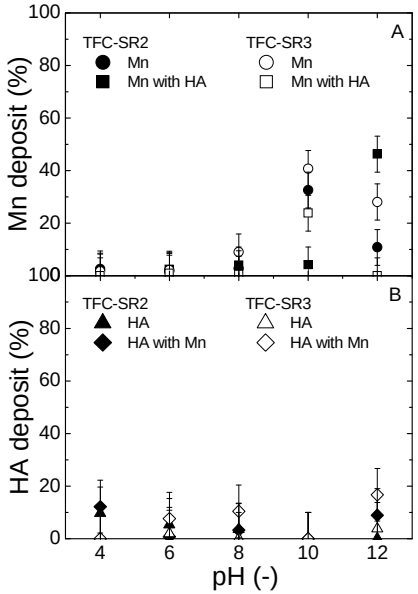
Figure 6