

## MICROFILTRATION OF COLLOIDS AND NATURAL ORGANIC MATTER

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### ABSTRACT

Surface waters contain colloids and natural organic matter, largely composed of humic substances. In this work the effect of natural organic matter (NOM) and humic substances (IHSS stream humic and fulvic acid reference material) on the deposition and rejection of inorganic colloids (hematite) by GVWP and GVHP microfiltration (MF) membranes was studied. Parameters of interest were solution pH, ionic strength, calcium concentration, primary colloid size (75, 250 and 500 nm), organic type and concentration, as well as membrane type and hydrophobicity, aggregate structure and colloid stability.

The method of preparation of the equilibrated suspensions, and thus their aggregation state, had a large influence on the rejection of the colloids and their aggregates, as well as the association of the particles with the membrane material and flux decline.

The systems studied were grouped into (a) organics in the absence of inorganic colloids, (b) stable primary particles, (c) primary particles at pH extremes with organics, (d) particles pre-aggregated in electrolyte solution prior to adsorption of organics (SPO), and (e) particles stabilised with organics (OPS).

Extreme pH conditions and pre-adsorption of organics onto the particle surface created very stable systems (colloids retained their primary particle size) and the deposition of the colloids at the membrane surface was reduced significantly. This led to a penetration of the particles into the pores and adsorption on the pore walls leading to full rejection in the absence of organics. Flux decline was in this case dependent on colloid size, with the size closest to the membrane pore size causing the greatest flux decline. In the presence of organics, membrane-colloid charge interaction and adsorption were reduced and rejection decreased to near zero for these stable colloid systems.

For aggregates the presence of organics led to a greater flux decline. Rejection of colloids was complete, now determined by the large size of the aggregates formed, which also indicates great mechanical stability of these aggregates.

Calcium played a key role in flux decline of all systems. In the absence of hematite, calcium contributed to organic aggregation and increased flux decline. Calcium led to an increased flux for hematite aggregates (SPO) presumably due to the formation of looser aggregates and a decreased flux for stable colloid-organic systems (OPS) due to destabilisation of these systems.

### KEYWORDS

Colloid Aggregation, Fouling, Microfiltration, Natural Organic Matter (NOM), Water Treatment.

## 1 INTRODUCTION

Microfiltration is a widely accepted process for the removal of particulate matter from surface waters [1], either as a water treatment process alone or as a pretreatment step. In water treatment, the solute content is generally very low, although significant flux decline is frequently observed. During the concentration of a surface water, (Mooney Mooney Dam, NSW) [2], we observed a significant flux decline and variation of rejection behaviour during microfiltration pretreatment prior to concentration with reverse osmosis. An electron microscopic study of the fouling layer showed the presence of very small colloids (nm range), aggregates and organics which embed the colloids in a thick cake (see Figure 1). The colloid-organic matrix is shown in Figure 2. Examination by electron dispersive spectroscopy (EDS) found the colloids to be composed of inorganic materials containing Si, Al and Fe.

In this study a model system has been developed in order to better understand the factors influencing cake formation and its effects on membrane filtration. The iron oxide hematite of different particle sizes (75 nm, 250 nm and 500 nm) was chosen as a representative of an inorganic colloid and a 'standard' humic and fulvic acid, and an Australian natural organic matter (NOM) [2] as representatives of natural organic compounds.

The filtration behaviour of microfiltration membranes was studied at various solution chemistries (pH, ionic strength, type and concentration of organics, calcium concentration) and for different orders of mixing of the hematite with the organics and the background salt solution. The aim of the study is an understanding of colloid-organic interactions and their impact on membrane filtration behaviour.

## 2 BACKGROUND

### 2.1 Colloids and Natural Organic Matter

Typical surface waters contain natural organic matter (NOM), mono- and multivalent ions, low molecular weight organics, micro-organisms, mixed complexes, and inorganic colloids. A large fraction of the natural organic matter is humic material, being negatively charged due to the dissociation of carboxylic acid and hydroxy functional groups. They are of amphipathic nature, i.e. containing both hydrophobic and hydrophilic moieties. Humic substances are more soluble at high pH, occur as long linear chains at high pH and low ionic strength due to charge repulsion of functional groups, and as coiled, spherical molecules at low pH and high ionic strength. Calcium and other multivalent cations are known to form complexes with NOM, and can neutralise part of their surface charge, especially at neutral pH, reducing the size of the molecule and forcing hydrophobic chains towards the aqueous solution [3]. Calcium can also enhance aggregation of NOM [4, 5].

Inorganic colloids in surface waters may be the oxy/hydroxides of Mn, Fe, Al and Si, as well as carbonates and clays, with a size range from a few nanometres up to millimetres [6, 7]. Colloids in natural waters have been extensively characterised and modelled [8-14]. Large particles ( $\gg 1\mu\text{m}$ ) would usually settle prior to treatment, whereas the small particles ( $\ll 1\mu\text{m}$ ) may cause problems with membranes in terms of rejection and fouling. Colloids in the natural environment commonly have a negative surface charge due to an adsorbed layer of natural organic matter, which can lead to stabilisation of the colloids [15].

The interactions of colloids and organics are important for water treatment and the various properties of the organics result in adsorption via several mechanisms including electrostatic interaction, specific chemical affinity and hydrophobic interactions [16]. The humic substances can adsorb at the colloid surface in loops or tails, depending on the solution chemistry, and thus alter the surface morphology of the inorganic colloids [3]. Au *et al.* [17] described organic adsorption on hematite as a complexation between organic and neutral oxide functional groups. It was hypothesised that a layer of NOM forms on the surface regardless of solution chemistry and possibly regardless of the particle surface characteristics.

The adsorption of humic acid (HA) on hematite has been investigated as a function of pH by Fairhurst *et al.* [18]. Adsorption of HA at  $5\text{ mgL}^{-1}$  (as organic carbon) HA on  $50\text{ mgL}^{-1}$  hematite decreased with increasing pH from 65% at pH 2 to 10% at pH 10. The apparent point of zero charge ( $\text{pH}_{\text{pzc}}$ ) of the colloids was shifted from pH 8 (no HA) to a pH  $<2$ . Such charge inversion of colloids has been attributed to the free functional groups on the HA which do not interact with the colloids [19]. These

workers studied the adsorption of organics with various numbers of functional groups on preformed flocs and showed that the zeta potential of colloids with adsorbed organics which had only one functional group was zero. These results mean that humic-covered hematite would be negatively charged in most situations and that the resulting charge depends on the organic type. Au *et al.* [17] measured adsorption densities of HA on hematite of  $1.25$  to  $0.25\text{ mg m}^{-1}$  (pH4 to pH10) and a hydrodynamic layer thickness of the adsorbed layer of 1 to 3 nm.

Tiller and O'Melia [15] studied the colloidal stability of hematite in the presence of natural organic matter (NOM) and various model organic compounds. Adsorption increased with molecular weight of the compound and with its hydrophobicity. The presence of calcium only had a small effect on NOM adsorption at low ionic strength ( $I=0.01\text{M}$ ), but destabilised the NOM coated particles at high ionic strength ( $I=0.1\text{M}$ ). Colloid behaviour at low ionic strength (as in typical surface water) is dominated by double layer interactions. Armirbahman and Olson [3] showed that the presence of  $\text{Ca}^{2+}$  ions reduces the stability of organic coated hematite particles, due to charge screening and complex formation with two humic functional groups. The electrophoretic mobility of hematite particles coated with organics decreased with calcium concentration. A clear distinction between electrostatic, hydrophobic, and steric interactions could not be ascertained, since these effects were considered to be interrelated. Tipping [20] found a decrease in humics adsorption on hematite with increased pH and an increase of adsorption with calcium concentration at any pH.

Chandrakanth *et al.* [21] modelled NOM-Ca-alumina interactions and found that alumina and calcium compete for NOM. By analogy this means that hematite and calcium may compete for NOM sites. Gu *et al.* [22] suggested that ligand exchange (surface complexation) between carboxyl and hydroxyl functional groups was the main mechanism for NOM-iron oxide surface interactions. However, it is possible that a number of mechanisms play a role, including anion exchange (electrostatic interaction), hydrophobic interaction, entropic effect (flocculation is more likely at a lower temperature), hydrogen bonding and cation bridging. The amount adsorbed has been found to be higher at low pH, which corresponds to the results found by Fairhurst *et al.* [18]. Fulvic acid (FA) and NOM were found to adsorb to a similar extent, but hydrophobic fractions adsorbed preferentially. This was confirmed by Korshin *et al.* [23]. Gu *et al.* [24, 25] also found that NOM fractions compete for adsorption onto mineral surfaces when sites are limited, with more aromatic compounds being sorbed preferentially. Edwards *et al.* [26] found that organic acids which contain paired functionalities sorb more strongly onto mineral surfaces. Strong acid groups form more stable complexes.

The interactions between colloids, organics and multivalent ions as described above suggest the importance of these phenomena in the membrane filtration behaviour of natural waters containing colloids and organics. It is the objective of this study to examine the impact of colloid-organic associations on microfiltration in a well defined system that simulates surface water conditions.

### 2.2 Microfiltration

In water treatment, microfiltration (MF) is used in the treatment of waters with high turbidity or as a pretreatment for processes such as nanofiltration or reverse osmosis [1]. In the latter case MF provides removal of particulates which cause severe fouling of the downstream processes. Dissolved organic carbon cannot be easily removed by MF, unless the organics are associated with particulates. This can be achieved by coagulant or adsorbant addition. Chang and Benjamin [27] used iron oxide to increase NOM removal and to control fouling in ultrafiltration, where the particles are deposited on the membrane surface.

In microfiltration, colloids can deposit on the membrane surface or in the pores, depending on size and shape of the colloids. Belfort *et al.* [28] consider flux decline in MF and UF of dissolved macromolecules and suspended particles to proceed in five stages: macromolecular sorption, particle monolayer deposition, built-up of a particle sublayer, sublayer rearrangement and finally non-Newtonian viscous effects, which are not normally expected to occur for dilute suspensions, as in water treatment. They also describe the deposition dependence on particle size. For particles much smaller than the membrane pores, internal deposition can occur, which eventually leads to the loss of pores. Particles of a similar size to the membrane pore will cause pore blockage and particles larger than the pores will deposit as a cake, with the porosity depending on the particle size. Belfort *et al.* indicated that the process of small particles adsorbing in the pores may be a slow process compared to pore plugging,

where a single particle can completely block a pore and therefore flux decline should be more severe for the latter case.

Tarleton and Wakeman [29] showed that small particles in mixtures determine the flux decline in crossflow MF. For overlapping pore and particle size, fouling occurs as a combined effect of pore and surface blockage. For large particles, a dynamic membrane is formed which retains smaller particles and prevents their penetration into pores. This is an effect which may be observed in the MF of surface water, where colloids eventually enhance the rejection of organics. Tarleton and Wakeman [30] also describe the effect of aggregation near the isoelectric point of particles, leading to cake formation at the surface, whereas stable colloids cause irreversible fouling in the membrane pores accompanied by low rejection. It is the deposit formed on the membrane, not the membrane itself, which governs flux and rejection after an initial filtration period [31]. Chang *et al.* [32] studied the effect of particle size (latex, 0.1 to 3 µm) and their mixtures on MF behaviour. Flux increased with particle size for the particle size range studied. The balance between lift force and permeation drag determines layer deposition on a membrane [33]. The lift force depends on shear and increases with particle size. The solvent velocity, particle size and density determine permeation drag. Submicron particles are preferentially transported to the membrane by permeation drag [34, 35].

For aggregates, their density and structure might play an important role. The effect of aggregate structure on flux in ultrafiltration has been reported by Waite *et al.* [36] for a very similar system to that used here, with aggregate structure depending on the aggregation regime. Fast (diffusion limited) aggregation results in a very open structure compared to a denser structure formed in slow (reaction limited) aggregation. The two regimes can be induced by the salt concentration, with increased salt concentration (greater than the critical coagulation concentration) enhancing aggregation due to double layer compression.

Schmitz *et al.* [37] modelled particle aggregation at the membrane surface and found a more complete space filling in the cake for particles which are re-entrained due to crossflow shear. Kim *et al.* [38] studied the ultra- and microfiltration of silver colloids (10 nm) in dilute suspension. At very low and at high salt concentrations cake formation occurred and rejection was high. For salt concentrations from 1 to 10 mM NaCl, particles penetrated into the pores with minimal cake formation. Stirred filtration created a more finely dispersed cake, whereas unstirred conditions allowed aggregation. This was attributed to the changed conditions at the membrane surface. Shear may play an important role in aggregate size especially if no time for equilibration of aggregation is allowed prior to filtration. The results also indicate the importance of aggregation. Chen *et al.* [39] studied the microfiltration of silica colloids. Substantial transmission of particles was observed which delayed cake formation.

Kim *et al.* [40] investigated the importance of pore size on flux decline in the ultrafiltration (UF) of kaolin mixed with various organics, such as humic substances; if the organics are larger than the membrane pore size, they cause a more significant flux decline. In a later study [41], the flux decline of humic substances with a number of UF membranes was found to be independent of the molecular weight to membrane pore size ratio, but attributed to the change in kaolin size distribution in the presence of organics. Nazzari and Wiesner [42] studied flux decline of ceramic membranes in the presence of silica and humic substances. Humic substances created higher reduction in flux than the silica colloids; the humic substances masked effects of pH and ionic strength. Clark and Jucker [43] found in a study of ultrafiltration of humic substances, that FA and HA have a higher hydrophobicity (and therefore higher adsorption capability) at low pH. Adsorption kinetics were found to be faster for FA, possibly due to a higher diffusivity [45, 46].

Fane *et al.* [47] describe different types of cakes that form on MF membranes on filtration of biomass. Abiotic particles can form a low or high voidage cake, which may be determined by the solution chemistry, whereas biomass particles form a cake on the membrane in which the extracellular bacterial polymers (EPS) fill the void space and control the cake resistance. This model is somewhat similar to inorganic colloids coated with humic acid which add adhesive characteristics to the smooth colloid surfaces and fill the space between the inorganic colloids.

In summary, although the MF of colloids is generally well understood, the literature is somewhat limiting in the areas of filtration of colloids much smaller than the membrane pore size and in mixed systems in which aggregation occurs. Systems are in this regard often poorly characterised, especially in the presence of humic substances. In this paper, microfiltration behaviour as a function of aggregate or

stable colloidal system characteristics is reported. Emphasis is placed on developing an understanding of organic, colloid and aggregate characteristics, which are then related to flux, rejection and deposition of colloids and organics in microfiltration.

### 3 EXPERIMENTAL

#### 3.1 Membranes and Chemicals

Two microfiltration membranes (Millipore; hydrophilic (GVWP) and hydrophobic (GVHP)) with nominal pore sizes of 0.22 µm were used in studies reported here. The hydrophilic membrane is a chemically modified hydrophobic membrane. The hydrophilic membrane was chosen for most experiments since it has a reduced adsorption capacity towards hydrophobic organics [43]. The membrane material is a modified polyvinylidene fluoride. A new membrane was used for each experiment. The hydrophobic membrane was soaked in a 50% ethanol solution for 10 minutes to wet the pores and then rinsed with MilliQ water. All membranes were soaked in warm MilliQ water for 30 minutes prior to use to remove any organic contamination.

The chemicals used were of analytical grade and supplied by Ajax Chemicals, Australia. Humic substances were purchased from the International Humic Substances Society (IHSS, USA). Suwannee River Stream Reference Humic and Fulvic Acids were used (both purified and extracted with an ion exchange resin). These organics have been well characterised [44]. NOM was obtained by MF and reverse osmosis (RO) from the Mooney Mooney Dam in the Brisbane Water National Park (NSW, Australia) and also well characterised [2]. Using this method all organics would be concentrated, including hydrophilic fractions and salts. The organic content of the NOM was 6.3%. MilliQ water with a quality of >18MΩ/cm was used for all experiments and preconditioning of membranes.

#### 3.2 Equipment

All experiments were carried out in a magnetically stirred batch cell (volume of 110 mL, membrane area 15.2 10<sup>-4</sup> m<sup>2</sup>) at a pressure of 100 kPa, pressurised with nitrogen gas and stirred at 270 rpm (measured with a Philips PR 9115/00 stroboscope) unless otherwise indicated. A feed reservoir of 1.5 L volume was connected to the stirred cell to provide extended filtration times. A Mettler Toledo PM 6000 balance was used to measure permeate mass. Experiments were conducted at a temperature of 25 °C.

#### 3.3 Colloidal Hematite (α-Fe<sub>2</sub>O<sub>3</sub>)

The monodispersed, spherical hematite particles were prepared after Matijevic and Scheiner [48], also described by Amal *et al.* [16], and had approximate particle diameters of 75 nm (I), 250 nm (II) and 500 nm (III). Monodispersity of the particles was checked and particle size determined using electron microscopy. The particle sol was stored at pH 3 and 4°C to minimise aggregation. Prior to solution preparation, the sol was ultrasonified for 15 minutes to redisperse any coagulated particles.

#### 3.4 Analytical Methods

##### UV/VIS Spectrophotometry

A Varian Cary 1E spectrophotometer was used to scan each sample from 190 to 500 nm, with absorption at 254 nm used to calculate rejection. All samples were measured against a MilliQ reference without pH adjustment, following the suggested standard method for surface water analysis [49]. Results, however, have to be used cautiously, since both colloids (as a function of size) and organics (as a function of chemical characteristics) contribute to UV absorption and effects cannot easily be separated in mixtures. Absorbance by humic acid and hematite (separately) was of a similar order of magnitude at the concentrations used.

##### Total Organic Carbon (TOC)

Total organic carbon was measured with a Skalar 12 TOC Analyser. TOC measurements do not allow measurement of the difference between organics adsorbed on particles and organics in solution. The terms DOC and TOC are being used interchangeably in this work. All glassware used was soaked in 5M KOH for 24h and then rinsed with water to remove any organic contamination.

### **Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES)**

A Perkin Elmer Optima 3000 ICP-AES instrument was normally used to determine the iron content of the particle sol, and experimental solutions. For some samples flame atomic absorption was used. 10 mL of particle sol and filtration samples were mixed with 5 mL HCl (36%) and heated to dissolve the colloidal hematite. All vials were soaked in 1M H<sub>2</sub>SO<sub>4</sub> for 24h and then rinsed with water to remove any inorganic contamination.

### **DELSA Electrophoretic Mobility Analyser**

A Coulter Delsa 440 instrument was used to measure particle mobility. The method is based on the movement of charged particles between two electrodes on imposing a voltage across the measurement cell. Analysis was carried out at 25 °C.

### **Malvern Mastersizer**

Particle size and aggregate fractal dimension were measured with a Malvern Instruments Mastersizer/E. A 100 mm lens was used to measure particle sizes between 200 nm and 110 µm. Measurements were taken immediately after filling the cell to avoid settling effects; no stirring was applied. The method assumes spherical particles and results of polydisperse solutions are to be treated with care.

### **Electron Microscopy**

Surfaces of membrane specimens were thin coated with chromium after freeze drying after the method described by Kim *et al.* [51]. For cross-sections, membranes were freeze dried, broken in the frozen state (under liquid nitrogen) and the sections then coated with a thin layer of chromium. The samples were viewed with a Hitachi S-900 field emission scanning electron microscope (FESEM) at 2 kV.

### **Membrane Zeta Potential**

Streaming potential was measured using a Brookhaven Instruments Corp. BI-EKA commercial instrument. Childress and Elimelech describe the cross flow measuring cell and zeta potential calculation in detail [50]. The tangential streaming potential, from which the surface zeta potential can be calculated using the Helmholtz-Smoluchowski equation, was measured in the presence of 1 mM KCl.

## **3.5 Solution Preparation**

2000 mL glass beakers were used for solution preparation and solutions were equilibrated over night with stirring at 270 rpm. If not indicated otherwise, solutions consisted of 1 mM NaHCO<sub>3</sub>, 0.5 mM CaCl<sub>2</sub> and 20 mM NaCl as a background electrolyte. For experiments in which the calcium concentration was varied, the conductivity was adjusted to 2 mScm<sup>-1</sup>. For all other experiments a background solution as detailed above was used.

The humic substances were kept in 100 mgL<sup>-1</sup> (as organic carbon) stock solutions at 4°C in the dark for short periods of time. Solutions contained 5mgL<sup>-1</sup> organics (as DOC) if not indicated otherwise. 1M NaOH, HCl and NaCl were used for pH and ionic strength adjustment.

Feed solutions containing inorganic colloids and organics were prepared in two different orders (SPO, OPS), both of which could be naturally occurring scenarios when rivers of various origins flow through different environments or when rivers mix. The preparation procedures are described below.

### **Particles without Organics**

To examine the filtration behaviour of stable particles without organics, the particles were dispersed into MilliQ water pre-adjusted to pH 3 or 12 in the absence of salt other than the HCl and NaOH for pH adjustment. At this pH, the particles are far from the point of zero charge (pH 7) and thus mostly stable and dispersed due to electrostatic repulsion (see Figure 3A).

### **Particles mixed with Salt Solution then with Organics (SPO order)**

500 mL of background solution at double concentration was prepared. The particles were added and the mixture stirred at 270 rpm for 10 minutes, allowing for aggregation to take place. Then 500 mL of double concentrated organic solution was added and stirred at 270 rpm for approximately 17 hours.

The pH was adjusted prior to mixing the solutions and pH and conductivity were measured prior to the start of the filtration experiment.

Added salt to a colloid sol will cause aggregation. There are two scenarios, one for low salt and one for high salt concentration. At low salt concentration (or a pH far from the p*H<sub>PZC</sub>*) colloids retain a charge and aggregate slowly due to a relatively strong repulsion. In that case they have time to penetrate into the aggregate structure and form dense aggregates (see Figure 3B). These aggregates are generally mechanically strong. At high salt concentration (or a pH close to the p*H<sub>PZC</sub>*), the charge is shielded and aggregation occurs quickly. The structure of the formed aggregates is loose and aggregates are mechanically weak and prone to shear restructuring (see Figure 3C). With the organics now added to these preformed aggregates, the organics will adsorb on the aggregate surface as shown in Figure 3D.

### **Particles mixed with Organics, then with Salt Solution (OPS order)**

500 mL of organics at double concentration was prepared, and the pH adjusted. The particles were added and the mixture stirred at 270 rpm for one hour to allow for the organics to adsorb on the colloid surface. Then 500 mL of double concentrated background salt solution of adjusted pH was added and stirred at 270 rpm over night. The pH was adjusted prior to mixing the solutions and pH and conductivity were measured prior to the start of the filtration experiment.

Applying this mixing order, the particles adsorb the organics on their surface before they can aggregate by double layer interaction. The systems were generally stable due to steric stabilisation or charge effects. Aggregation of the particles with inverted surface charge may still be possible, especially in the presence of calcium ions. Three scenarios were observed; (i) IHSS FA and HA caused stabilisation of the colloids due to charge repulsion (high negative charge due to organics) and steric effects (see Figure 3E), (ii) NOM caused simultaneous stabilisation and aggregation due to the presence of salt in the NOM (Figure 3F), and (iii) calcium added after stabilisation of the colloids caused destabilisation of the previously stabilised colloids due to charge screening or organic-calcium interactions (Figure 3G).

## **3.6 Membrane Filtration Protocol and Calculations**

Pure water flux was determined for each membrane using 3 L MilliQ water. The last 100 mL of filtrate were analysed for TOC as a control sample. The cell was then filled with the feed solution, the stirring switched to 270 rpm and the pressure adjusted to 100 kPa (if not indicated otherwise). Two types of filtration protocols were used, a *standard* and a *recycle* protocol. Pure water flux was determined after the *recycle* experiments only.

For *standard* experiments samples were taken from the feed solution, three subsequent permeate solutions (270 mL each) and the concentrate (sampled using a pipette in order to avoid disturbance of the deposit on the membrane). About 1 L of feed solution was filtered per experiment. The equipment was further flushed with MilliQ water after the membrane was removed.

For *recycle* experiments, the above procedure was repeated three times; the permeate was collected, sampled and filtered another two times without redispersion of the cake. Samples were taken during each recycle step and the total feed volume was about 1.5 L.

Membrane flux was calculated as

$$J(t) = \frac{V(t)}{A \cdot t} \quad (1)$$

and the flux behaviour in the *standard* experiments is given as the ratio of flux after 800mL permeate collection to initial pure water flux

$$\text{Flux ratio} = \frac{J_{800\text{mL}}}{J_{W0}} \quad (2)$$

whereas for the *recycle* experiments, flux behaviour is described as flux decline which was calculated as

$$\text{Flux decline} = 100 \cdot \left( 1 - \frac{J_{wf}}{J_{w0}} \right) \quad (3)$$

'Flux decline' is therefore the decline in pure water flux of the membranes before and after the experiments. The majority of experiments were recycle experiments. The apparent rejection was calculated as in the following equation

$$R_i = 100 \cdot \left( 1 - \frac{c_{pi}}{c_{bi}} \right) \quad (4)$$

where the concentration in the batch cell was measured and then estimated for the mean permeate sample times via linear interpolation between feed and concentrate concentration. For the recycle experiments the concentration was corrected for sampling.

The deposition of solute (iron and organic carbon) on the membrane was calculated with equation (5) based on mass balance, where  $m$  is the mass of deposit.

$$m = c_F \cdot V_F - c_c \cdot V_{cell} - \sum_{i=1}^9 c_{pi} \cdot V_{Pi} \quad (5)$$

The loss of solute to cell walls is neglected. The error of this method is estimated to be  $\pm 1\%$  absolute mass deposit which shows that relative errors are high when the deposit is low.

## 4 RESULTS AND DISCUSSION

### 4.1 Membrane Characterisation

The zeta potential of both membranes in a clean state and of the pretreated GVHP membrane are shown as a function of pH in Figure 4. Electronmicrographs are shown in Figure 5A and B. It can be seen that the GVWP and GVHP membranes have similar morphology but very different surface charge characteristics. Pretreatment of the GVHP membrane changes the membrane potential significantly such that towards high pH GVWP and GVHP are now identical. The more hydrophilic GVWP membrane has a higher negative charge, which decreases towards low pH, but is negative over the complete pH range. The hydrophobic GVHP membrane has a slight positive charge at low pH, a  $pH_{pzc}$  of 4 and a stable value of about -10 mV is reached at pH 7. The pretreated GVHP membrane has a slight positive charge at low pH and reaches -22 mV at high pH, which is similar to the GVHP membrane at low pH and to the GVWP at high pH. From an applications view point it should be noted that the membranes are negative over most of the relevant pH range.

The pure water fluxes (at a transmembrane pressure of 100 kPa) for both membranes are summarised in Table 1. The flux at these conditions is very high and it can be assumed that permeation drag in experiments with suspensions would overrule forces such as lateral migration [35]. The flux of the GVWP membrane is slightly lower at high pH, when the membrane has a negative charge. For the pretreated GVHP membrane, flux remains relatively stable. Initial fluxes are higher for the GVWP membrane, but for pH 8 when the zeta potential for both membranes is the same, the flux is also the same. It is possible that the GVWP membrane loses its hydrophilicity at high pH.

### 4.2 Properties of Hematite Aggregates

The zeta potential of hematite particles (and in some cases aggregates) as a function of pH in MilliQ water are shown in Figure 6A. The isoelectric point of hematite is observed to be about 7.0, which compares with the previously reported values of about 6.5 [36, 3, 48] and 8.5 [15]. Particle charge depends on the particle size with larger particles having a lower charge. At a pH of 3, colloids will have a high positive charge, resulting in their relative stability. At a pH of 11-12 their charge will be reversed (i.e. very negative) and particles again stabilised. Experiments in which the size effect of primary particles was to be examined, were therefore conducted at pH 3 or 12 to minimise aggregation effects. Particle properties for the three colloid types used are shown in Table 2 and discussed below.

Waite *et al.* [36] and Amal *et al.* [16] have previously shown a hematite charge reversal by organics at pH 3, which is also shown in Figure 6B for colloids in the presence of fulvic acid. In contrast, at pH 8, the charge is not reversed, since at this pH the particles already have a negative charge. However, the negative charge is substantially increased with increase in the organics (humic acid) concentration. The majority of the present experiments were carried out at pH 8 and it was found that  $0.8 \text{ mgL}^{-1}$  (as organic carbon) was sufficient to lower the particle zeta potential by 20 mV, from -13 mV to -33 mV. An increase in organic concentration to  $5 \text{ mgL}^{-1}$  (as organic carbon) decreased the zeta potential only a further 3 mV, showing that particle coating was almost complete. At pH 8 both the organic matter and the hematite were negatively charged. It appears that adsorption of organic matter either by strong specific "surface complexation" or by non-electrostatic means such as hydrophobic interactions or calcium bridging, has superimposed the charge associated with the organic onto the colloid. Humic acid was more efficient in charge reversal than fulvic acid (results not shown). This corresponds to the results of Liang [52], who found that molecules with a longer carbon chain had a larger effect on colloid stability. Amirbahman and Olson [3] reported a smaller residual charge for particles coated with humic acid, compared with fulvic acid. NOM was least efficient in charge reversal (results not shown), possibly due to the fact that NOM was not purified and might be complexed with inorganics and thus have less groups available for binding.

The order of mixing of particles, organics and salt had a large impact on the zeta potential as shown in Figure 6C. The presence of background solution lowered the point of zero charge (compare Figure 6 A and C). Organics adsorbed onto particles after aggregation (SPO) resulted in a more negative zeta potential, whereas if organics were adsorbed on particles first (OPS), the zeta potential was less negative. The importance of the mixing order shows that the pre-aggregated particles (SPO order) act as larger particles which have a lower specific surface area, so that less organics are needed to reverse surface charge. This is supported by the fact that surface potential is stable as a function of organic concentration for SPO, whereas the zeta potential decreases for OPS with organic concentration.

The calcium ions in solution could play an important role in modifying surface charge (Figure 6D). They would tend to shield part of the negative hematite charge as suggested above, or act as a bridge between organics and particles and increase adsorption. Calcium was reported by Liang [52] to increase hematite aggregation and by Tiller and O'Melia [15] to destabilise coated particles. Calcium was found to neutralise colloid charge in the absence of organics (about 4 mM of  $\text{CaCl}_2$  were required, see Figure 6D). The zeta potential of SPO aggregates became less negative (by about 5 mV) in the presence of 4 mM  $\text{CaCl}_2$  (probably due to calcium-organic interactions) or increased adsorption of organics in the presence of calcium as shown by Tipping [20]. For OPS the scatter in results was large, probably due to interactions of colloids and a varied mobility of the colloid-organic associates.

### 4.3 Membrane Filtration of Different Particle Systems

#### *Organics in Absence of Colloids (Hematite)*

All three types of organics were filtered in the absence of colloids to investigate the extent of any flux decline caused by the organics alone. The results are summarised in Table 3. Experiments were conducted at 2.5 mM  $\text{CaCl}_2$ . Humic acid (HA) showed the highest flux decline (78%) compared to fulvic acid (FA, 15%) and NOM (37%). In the absence of calcium this flux decline is reduced significantly (11% compared to 78%). This shows that HA interacts with calcium to form complexes and flocs which adsorb or deposit on or within the membrane. The significant flux decline for NOM can be attributed to a high content of HA in the NOM and the higher concentration of inorganic salt.

The deposition of organics on the membranes is due to either adsorption from solution or deposition due to rejection, which would be the case if the organics were large enough to be retained by the membrane matrix. It is likely that a portion of the NOM is present in colloidal form. In addition, HA is less soluble than FA and may be not fully dissolved. Calcium is expected to cause organic aggregation as reported by Yuan and Zydny and these aggregates can cause severe MF fouling. These workers reported the deposition to occur on the membrane surface. However, considering the small size of such molecules and aggregates this is unlikely for the systems used in this study [5].

The more hydrophobic membrane (GVHP) is observed to induce a slightly higher deposition than the hydrophilic membrane, indicating the influence of hydrophobic interactions. A similar effect has previously been reported by Jucker and Clark for hydrophobic UF membranes [43]. UV analysis confirms the trends observed with DOC analysis, except for NOM. This suggests the deposition of colloids as well as organic adsorption in the case of NOM. For purified organics (FA and HA) adsorption is important, which is enhanced in the presence of calcium, which would screen the organic charge and enhance hydrophobic interactions. It could also enhance bridging effects between negatively charged organics and negatively charged membranes or cause particulate organic aggregation due to charge screening. The deposition mechanism most likely involves a combination of the above. More deposition with the less negatively charged membranes suggests however, that hydrophobic effects play a role.

The results confirm the presence of an 'organic' cake observed in the filtration of surface water. Flux decline is very high considering the small amount of organics deposited, as it would take a considerable amount of time to fill the membrane pores with the small organics. In a surface water system particles are also important contributors to membrane fouling (as shown in Figure 1).

### **Particles in Absence of Organics**

#### *Effect of primary particle size*

Flux decline as a function of primary particle size for particles at pH 3 (without salt solution, thus stable), and at pH 8 with salt solution (thus aggregated particles) is shown in Figure 7 (SPO and OPS results in this figure will be discussed later).

Flux at pH 3 passes through a minimum at a primary particle size of 250 nm. In previous work a minimum flux as a function of particle size for ultrafiltration of colloids was observed [53]. This was ascribed to a transition from polarisation control by Brownian diffusion (decrease with particle size) to inertial lift (increase with particle size). However, this does not seem to explain our results with MF of hematite. Table 4 (No 1, 3, 4, 6, 9) summarises rejection data for a range of experimental conditions, including those in Figure 7. At pH 3 all primary particles have high rejection, even hematite I, which at 75 nm is much smaller than the pore size. Figure 8A and Figure 8B show electron micrographs of the surface and cross section respectively of the membrane after filtration of 800 mL of hematite I solution at pH 3. Colloids can be seen adsorbed at the top surface and the internal surface of the membranes, which suggests that the high rejection (low transmission) may be due to adsorptive removal. This may be due to the fact that at pH 3 the membrane is negatively charged and the hematite is positive.

The high flux ratio for hematite I is presumably because the dilute feed results in slow flux decline by gradual pore closure. The high flux ratio for the largest colloids, hematite III (500 nm) is probably because this particle forms a surface cake of relatively high permeability, resulting in slow flux decline. For the intermediate colloid, hematite II (250 nm), the particle size is similar to the pore size and most readily leads to pore plugging and obstruction which causes more rapid flux decline as seen in the lower flux ratio in Figure 7. The electron micrograph of the membrane cross section for hematite III is shown in Figure 8C. This shows a dense cake layer, blocking pores and particle penetration into the membrane.

#### *Effect of pH*

In order to study the effect of charge, hematite I was filtered with both membranes at pH 12. At this pH both membranes and hematite have a negative charge of similar magnitude (-20mV). Rejection is slightly reduced for both membranes compared to pH 3 (see Table 4 (No 2)), however the membranes do adsorb hematite to a large extent and eventually achieve full rejection. For these conditions, flux declined 75-80% at pH 3 and 95% at pH 12. Fane et al. [54] have previously reported a decrease in flux of an inorganic membrane with increased pH and more negative zeta potential. The same effect can be seen in this case where the hematite colloids form an 'inorganic' membrane with a more negative zeta potential at pH 12. It has to be noted that zeta potential is an average value for the surface potential and does not account for individual surface functional groups. It is possible that there are remaining positive groups even in the presence of organics, which do interact with the membrane surface. Also, the operation of MF at a very high flux will bring the colloids in very close contact with the membrane surface, which means that repulsive forces might be overcome and colloids stick due to low range

forces, such as Van der Waals interactions. Alternatively, the continued adsorption, even in the presence of electrostatic repulsive effects, may indicate strong specific binding between colloid metal centres and membrane functional groups. Once the flux has declined to 2 to 20% of its initial value electrokinetic interactions could increase rejection.

#### *Effect of Aggregation*

Experiments were carried out in the presence of electrolyte solution and pH 8 (in this case to provide a baseline for the aggregation experiments with organics). The rejection of the 75 nm colloids was complete, as shown in Table 4 (No 3). Figure 7 shows that after aggregation the flux ratio is high and independent of primary particle size. Aggregation reduces flux decline. This is similar to observations reported with colloidal silver on addition of electrolyte [38].

The aggregates were mechanically strong and did not break at the membrane surface in the standard (100kPa) experiments. Breakage of some of the aggregates occurred at a relatively high pressure of 300 kPa, with a rejection 20 to 25% lower. Results are shown later in the SPO section (Figure 13). Flux results are not shown, but flux decline was very similar for all transmembrane pressures (50%).

### **Particles at pH 3 with Organics**

To understand the effect of organics on the primary particles, another set of experiments far from surface water conditions (no electrolyte solution and pH 3) was carried out.

In the presence of 5 mgL<sup>-1</sup> (as organic carbon) HA, rejection of colloids was higher and flux decline lower than in the absence of organics. Results are shown in Table 4 (No 4) and Table 5. Organic rejection increased compared to filtration in the absence of colloids (compare Table 3). These effects can be attributed to the adsorption of organics on the colloids which increases negative colloid charge (Figure 6B) and depletes organics in the permeate, as well as the low solubility of HA at this pH and thus the filtration of the precipitate. During electron microscopy (results not shown) aggregation of the colloids in the presence of organics was observed.

### **Particles mixed with Salt Solution then with Organics (SPO order)**

In this mixing order, particles aggregate and then adsorb organics on their surface. A very different deposit occurs on the membrane, when this mixture is filtered. This is shown in Figure 8D, which can be compared to Figure 8A and shows the deposition of large aggregates rather than single particles. The effects of membrane type, organic type and concentration, colloid size, as well as solution chemistry (pH and calcium concentration) will now be examined for this system. The solution chemistry influences the size and structure of the aggregates; other factors likely to influence aggregation, i.e. stirring and transmembrane pressure, are also investigated (see also Waite *et al.* for ultrafiltration of similar systems [36]).

#### *Effect of organic type and concentration*

The organic type does not have an influence on flux and colloid rejection with this particle preparation method. Flux declines 75-85% for all organics and the rejection of colloids is high (greater than 90%). The results are summarised in Table 6 (No 1, 8, 9) and Figure 9A. Rejection drops a little after pressure release (cycles 2 and 3 in Table 6), possibly indicating some aggregate breakage or concentration polarisation effects.

As shown in Table 6 (No 1, 2, 3), HA concentration was varied from 5 to 20 mgL<sup>-1</sup> DOC but the increase in concentration had only a marginal effect on colloid rejection. The aggregates were not redispersed due to the addition of organics which stabilise the particles in the OPS case. The deposition of DOC (results not shown) on the membrane increases with concentration, but colloid deposition is constant at about 90%. Organic rejection decreases with increased concentration, presumably due to the decrease in adsorption on the colloids and flux decline increases with a higher HA concentration.

#### *Effect of primary particle size*

Primary particle size has an effect on the deposition of organics; 12, 9 and 6% of organics are deposited for 75, 250 and 500 nm primary colloids, respectively. Organic rejection increased with decreasing colloid size (see Table 6, No 1, 10, 11), which can be explained by increased adsorption for a higher specific surface area of the smaller colloids. Colloid rejection is almost complete for all sizes as shown in Table 4 and deposition is about 90%. Flux decline increases with smaller primary particle size (see

Figure 7). This can be attributed to the formation of a cake of lower porosity with more interstitial organics.

#### *Effect of calcium concentration*

When the calcium concentration in the background electrolyte was increased, flux decline was lower. Results are shown in Table 6 (No 1, 4, 5) and Figure 10A. The UV<sub>254nm</sub> rejection drops significantly over time at higher calcium concentrations, which could indicate a detachment of some individual colloids from the aggregates. Colloid deposition increases with increasing calcium concentration, and very interestingly, the flux also increases.

These results suggest that aggregate characteristics such as structure have an effect on flux as also shown in our work on ultrafiltration [36]. The addition of larger amounts of electrolyte causes the colloids to aggregate faster due to a reduction in charge repulsion. Faster aggregation results in looser aggregates, which can also induce larger flux [36]. Figure 11 shows the variation of the particle size with calcium concentration. Surprisingly, at a higher calcium concentration the aggregate size is smaller (3-4 µm versus 30-40 µm at low calcium concentration), possibly as a result of a greater extent of breakup of the more tenuous flocs formed at high salt concentrations. However the volume fraction of submicron particles is also lower at high calcium concentration. It is very likely that higher calcium concentration leads to the formation of looser aggregates as has been shown for well defined systems [36].

#### *Effect of pH*

The effect of pH is shown in Figure 12A and results are summarised in Table 6 (No 1, 6, 7). Low pH causes highest flux decline, which corresponds to the observations at pH3 with organics. Organics deposition is 10, 12 and 44%, at pH 4.5, 8 and 10, respectively. At low pH the organics are less soluble and thus have less functional groups available for colloid-organic interactions and precipitates would deposit together with organics adsorbed on hematite. Tipping reported a decrease of adsorption of organics on hematite with increased pH [20]. The increase in organics deposition at higher pH must thus be attributed to the deposition of calcium-organic complexes with the colloids.

#### *Effect of stirring*

In this mixing order, particles are deposited in a cake and stirring may be important in partially removing the deposit or preferentially classifying the particles with smaller ones in the cake as reported by Altmann and Ripperger [33]. Stirring was varied from 0 to 540 rpm. Flux is a little lower at 0 and 540 rpm compared to 270 rpm and rejection decreased more over the filtration volume in the unstirred experiment. This suggests that concentration polarisation effects are operative and smaller particles may deposit preferentially at 540 rpm. However, overall it appears that concentration polarisation effects (and impact of shear on the boundary layer thickness) are minimal with deposition dominated by permeation drag. Deposition is identical (92%) for all three stirring conditions. This behaviour is expected at the high fluxes used in these experiments.

#### *Effect of transmembrane pressure*

Flux increases with transmembrane pressure and thus convection and permeation drag also increase. This is expected to cause increased deposition of particles if they are larger than the size of the pores and if permeation drag is the limiting deposition factor. Increased permeation drag increases the force on the aggregates during deposition and an excessive permeate pressure can lead to aggregate break-up which may result in a reduced rejection.

The flux decline was identical for all pressures (80% decline) and flux increased linearly with pressure. In each case the about same amount of cake was deposited (same volume filtered) and the invariance of flux with pressure implies an incompressible cake. The colloid rejection as a function of filtrate volume for the four transmembrane pressures is shown in Figure 13A in the absence of organics (as discussed earlier) and in Figure 13B with organics. The first three points are the first filtration cycle. The pressure was then released and point four and seven are the first points of filtration cycles two and three, respectively. The results clearly suggest that pressure increase leads to break-up of the aggregates. Low rejection occurs at the start of the filtration cycles, after the pressure was released, the cells refilled and filtration resumed. The now higher flux would facilitate transport of the smaller or broken aggregate fractions through the membrane before larger aggregates deposit again and retain small fractions. A

decline of rejection indicates some concentration polarisation (see first cycle at 300 kPa) with filtration time, but this decrease is much lower than that at the start of the new cycle. If concentration polarisation was dominating, rejection would drop at the end of a cycle rather than at the start.

The presence of organics appears to facilitate aggregate break-up. Flux decline is independent of transmembrane pressure and it is therefore assumed that the cake is not compacted. The aggregate break-up is also reflected in the deposition of hematite as shown in Table 7. Deposition is reduced when aggregates break and rejection decreases. The break-up of the aggregates may be either due to the force on the aggregates during filtration or due to the force of the expanding membrane on the cake when the pressure is released.

Overall, the recycle experiments showed that concentration polarisation effects were negligible; if they were important, flux would increase after permeate recycle. Concentration changes in the cell due to filtration do not seem important either.

#### *Particles mixed with Organics, then with Salt Solution (OPS order)*

In this mixing order, particles are generally stable due to adsorbed organics on their surface. Effects of membrane type, organic type and concentration, colloid size, as well as solution chemistry (pH and calcium concentration) will now be examined for this system. The effects of pressure and stirring were not examined for the OPS system, as no cake was formed in most cases.

#### *Effect of membrane type*

Given the fact that aggregation in the presence of NOM caused major flux decline and not adsorption (see next paragraph), it is evident that the membrane type did not play a major role. Small differences were observed in the deposition of solute, with slightly higher values of deposition for the more hydrophobic GVHP membrane. This again corresponds to the results reported by Jucker and Clark [43].

#### *Effect of organic type and concentration*

Figure 9B shows results of flux ratio (flux divided by initial flux) as a function of organic type. A quite distinctive difference between the fluxes for the three different organic types can be observed, from FA causing very little flux decline to NOM causing almost complete loss of flux.

The difference between NOM and FA or HA is primarily the presence of salts in the NOM powder, which is in this case more important than the characteristics of the different organic species. The salt leads to aggregation of some colloids prior to stabilisation and this generates the most detrimental conditions for flux decline. This can probably be attributed to the formation of very small aggregates which are able to block membrane pores, and this is supported by the initially very low rejection of colloids (Table 8, No 9).

Zeta potential measurements show that particles coated with NOM have the greatest negative charge (results not shown). This supports the hypothesis that salts present in the NOM allow the colloids to aggregate simultaneously with stabilisation by the organics, which reduces surface area and forms very small aggregates (doublets and triplets, <0.2 µm). The relatively small aggregates would be captured in the pores very easily, leading to the detrimental flux declines observed. Rejection and deposition data of hematite confirm these observations (see Table 8, No 1, 8, 9).

The organic concentration was varied (Table 8, No 1, 2, 3) which resulted in a change in particle charge and aggregation. Flux was found to be directly related to deposition of colloids on the membrane and rejection of colloids, both of which are lowest at 10 mgL<sup>-1</sup> (as DOC).

#### *Effect of primary particle size*

Flux decline was most severe for hematite II (250 nm) as also found for organic-free particles stabilised at pH 3 and particles at pH 3 with organics (see Figure 7). Hematite I showed less flux decline compared to Hematite II and III (high flux ratio) and rejection has now, in the presence of organics, dropped to almost zero (see Table 8, 1, 10, 11). For hematite II initial rejection of colloids is not complete (80%) which indicates pore penetration and rejection decreases when pressure is released in recycle experiments. This can be explained by the fact that the membrane has a pore size distribution, allowing some of the 250 nm colloids to pass through. The deposition results are similar for hematite II and III, for which about 89% are deposited. Flux is higher for hematite III than II (Table 8, No 11 vs

10) due to the larger colloid size resulting in a cake with larger "void spaces". Deposition of hematite II is larger than for hematite I with NOM, but the flux is higher (Table 8, No 10 vs 9). This confirms that small colloids, once retained cause a much more severe flux decline. It should be noted here that small colloids will eventually block pores. However, this was not achieved for FA and HA with the rejection remaining low, even after the filtration of 3L (Table 8, No 7 and 8).

#### *Effect of calcium concentration*

Experiments were carried out at 0.5, 2.5 and 4 mM CaCl<sub>2</sub>. Results are shown in Figure 10B and of opposite trend to the SPO data. Calcium can destabilise colloids which were stabilised by organics. This was observed to occur at a concentration between 2.5 and 4 mM CaCl<sub>2</sub> with a resultant increase in colloid rejection from 15 to 95%, which also results in a greater flux decline as shown in Table 8 (No 1, 4, 5). This corresponds to the effect of calcium on stabilised colloids reported by Armirbahman and Olson [3]. Deposition increased with calcium concentration, which indicates that the destabilisation is always present to some extent. The calcium was added after the colloids were stabilised with HA, which is a different scenario to NOM, where salt (which is in the NOM powder) is added simultaneously. In this case, the calcium provides a full destabilisation of the organic-coated colloids at 4 mM, leading to complete rejection and deposition.

#### *Effect of pH*

pH has a strong effect on flux and deposition (see Table 8, No 1, 6, 7). At pH 4.5 flux is lowest and deposition highest. Flux results are shown in Figure 12B. Zeta potential measurements showed lowest colloid charge at low pH. Aggregation is therefore most likely at this pH, which would increase deposition. The results are very similar to aggregation of colloids with NOM. This is supported by an increased rejection of colloids at pH 4.5 (Table 8, No 6 vs 1,7). At pH 10 the organics are most soluble, adsorb strongly on the colloids, thus readily stabilise them and result in low rejection and deposition, and high flux.

In summary, poorly soluble organics, at low pH (4.5) or in the presence of salt (which is often the case with surface waters) and small colloids, which partially aggregate, cause most severe flux decline. Particles prepared with organics in the OPS order show a low flux decline for the small colloids, due to a low rejection and an incomplete adsorption within the pores. The solution chemistry is important, as pH influences the adsorption of organics and thus particle stabilisation. Additionally, calcium can destabilise the previously stable colloids.

## 5 CONCLUSION

The present study contributes to understanding of microfiltration membrane fouling under conditions where permeation drag dominates. Real surface water systems studied were simulated with inorganic colloids and natural organics at various aggregation states. The systems studied were grouped into (a) organics in absence of inorganic colloids, (b) stable primary particles, (c) primary particles at pH extremes with organics, (d) particles pre-aggregated in electrolyte solution prior to adsorption of organics, and (e) particles stabilised with organics.

Filtration of colloids at pH extremes served as a baseline of colloids which are neither aggregated nor stabilised by an adsorbed organic layer. As expected from the literature review, the particle size closest to the membrane pore size (250 nm) caused largest flux decline. Rejection occurred in this case due to a combination hydrophobic, specific and van der Waals forces and could not be explained by charge interaction only.

At pH conditions closer to surface waters and in the presence of an electrolyte solution, the colloids aggregate, are fully rejected and flux decline depends on the deposition on the membrane rather than primary colloid size. This corresponds more or less to a surface water of high turbidity, but no organic content.

Once the organics were added there are two cases to be distinguished. In the first case the colloids are first aggregated in the electrolyte solution before mixing with the organics. The organics adsorb on the aggregate surface and fouling is increased compared to aggregates in the absence of organics. In the second case colloids are first mixed with the organics then with electrolyte solution. Now steric or

charge stabilisation of the colloids occurs due to adsorption of organics on the colloid surface. Rejection now drops to almost zero and fouling depends fully on the primary colloid size. Rejection could be increased in this case by destabilisation of the colloids using calcium.

Comparing OPS and SPO in Figures 9, 10 and 12 showed important differences between the two systems. The organic type has no effect for SPO, whereas for OPS flux decline is low for FA and HA and very high for NOM. Calcium has opposite effects on both systems. For OPS calcium increases flux decline due to destabilisation effects, whereas for SPO the flux decline is lower at higher calcium concentrations. This is presumably due to a different structure of the initial aggregates. PH also shows differences. While for SPO pH would affect aggregate structure, in the OPS case it affects colloid stability and thus highest flux decline occurs when colloids partly aggregate.

Most severe fouling was observed when the smallest (75 nm) colloids were mixed with NOM which contains salt and organics. In this case aggregation and stabilisation effects occur at the same time producing very small aggregates which are detrimental to flux. This is the condition closest to 'real' surface water, where detrimental flux decline is often observed.

Overall the largest difference with the strongest implications on water treatment is the low rejection of the stabilised colloids. Due to their low settleability these systems will be most abundant in most streams and chemically pretreated feedwaters.

These results have application to real systems, for which inorganic colloids and organics will mix very differently, forming a diversity of aggregates and stable colloids. The characterisation of the colloid-organic associates in natural water is clearly critical in predicting likely microfiltration behaviour.

## 6 LIST OF SYMBOLS

A	Membrane area [m <sup>2</sup> ]
c <sub>0</sub>	Initial feed concentration [mgL <sup>-1</sup> ]
c <sub>F</sub>	Final feed concentration [mgL <sup>-1</sup> ]
c <sub>C</sub>	Concentrate concentration [mgL <sup>-1</sup> ]
c <sub>bi</sub>	Bulk concentration (concentration in the batch cell) [mgL <sup>-1</sup> ]
c <sub>pi</sub>	Permeate concentration of i <sup>th</sup> sample [mgL <sup>-1</sup> ]
J	Flux [Lm <sup>-2</sup> h <sup>-1</sup> ]
J <sub>0</sub>	Initial feed flux [Lm <sup>-2</sup> h <sup>-1</sup> ]
J <sub>w0</sub>	Initial pure water flux [Lm <sup>-2</sup> h <sup>-1</sup> ]
J <sub>wf</sub>	Final pure water flux (after experiment) [Lm <sup>-2</sup> h <sup>-1</sup> ]
J <sub>800mL</sub>	Membrane flux after 800 mL feed filtration [Lm <sup>-2</sup> h <sup>-1</sup> ]
m	mass of deposit on membrane [g]
ΔP	Transmembrane pressure [10 <sup>5</sup> Pa]
R	Rejection [%]
t	Time [h]
V	Total filtrate volume [L]
V <sub>cell</sub>	cell volume [L]
V <sub>F</sub>	feed volume [L]
V <sub>P</sub>	permeate sample volume [L]

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## TABLES

**Table 1** Pure water flux of clean MF membranes at a transmembrane pressure of 100 kPa

Membrane	pH [-]	Flux [Lm <sup>-2</sup> h <sup>-1</sup> ]	Average [Lm <sup>-2</sup> h <sup>-1</sup> ]
GVWP	4.5	8110	-
GVWP	8	7874	7968 ± 288
GVWP	10	6378	-
GVHP	8	5116	-
GVHP + EtOH	4.5	8796	-
GVHP + EtOH	8	7924	7803 ± 308
GVHP + EtOH	10	8875	-

**Table 2** Properties of iron particles

Type of Iron Particle	Particle Diameter [nm]	Specific Surface Area [m <sup>2</sup> g <sup>-1</sup> ]	Zeta potential at pH 3 [mV]	Number of particles per 10 mg hematite [-]
Hematite I	75 nm	15.1*	35	8.6 · 10 <sup>12</sup>
Hematite II	250 nm	4.5*	24	2.3 · 10 <sup>11</sup>
Hematite III	500 nm	2.3*	18	2.9 · 10 <sup>10</sup>

\*calculated on the basis of spherical particles of a density of 5.24 g.cm<sup>-3</sup>

**Table 3** Deposition of organics on membrane in the absence of inorganic colloids

Membrane	CaCl <sub>2</sub> [mM]	Organic Type (5 mgL <sup>-1</sup> DOC)	Deposit <sup>x</sup> [% DOC]	Deposit <sup>x</sup> [% UV <sub>254nm</sub> ]	Rejection* [% DOC]	Rejection* [% UV <sub>254nm</sub> ]	Flux decline <sup>o</sup> [%]
GVWP	2.5	HA	13	8	10.1	4.0	78
GVHP	2.5	HA	17	11	16.1	5.9	75
GVWP	0	HA	11	3	13.6	0	11
GVWP	2.5	FA	4	1	7.2	0.3	15
GVWP	2.5	NOM	22	5	17.1	1.8	37

\* rejection is low and values are close to deposition which is not considered in rejection calculations and which leads to considerable error (overestimation, especially in the case of DOC compared to UV) in rejection data. Values are shown to confirm very low rejection of organics by MF.

<sup>x</sup> see equation (5)

<sup>o</sup> see equation (3)

**Table 4** Rejection of Fe (after collection of 400mL permeate volume, GVWP membrane)

No	Experimental Conditions	Fe Rejection [%] and UV <sub>254nm</sub> Rejection [%]					
		Hematite I		Hematite II		Hematite III	
		Fe	UV <sub>254 nm</sub>	Fe	UV <sub>254 nm</sub>	Fe	UV <sub>254 nm</sub>
	All 10 mgL <sup>-1</sup> hematite						
1	pH 3, MilliQ	99	99	93	97	93	99
2	pH 12, MilliQ	85	51	-	-	-	-
3	pH 8, background salt	97	66	-	-	-	-
4	pH 3, 5 mgL <sup>-1</sup> × HA	97	44	96	37	95	26
5	5 mgL <sup>-1</sup> HA, SPO <sup>*</sup> , pH 4.5	90	42	-	-	-	-
6	5 mgL <sup>-1</sup> HA, SPO <sup>*</sup> , pH 8	95	43	93	25	93	21
7	5 mgL <sup>-1</sup> HA, SPO <sup>*</sup> , pH 10	88	45	-	-	-	-
8	5 mgL <sup>-1</sup> HA, OPS <sup>*</sup> , pH 4.5	54	41	-	-	-	-
9	5 mgL <sup>-1</sup> HA, OPS <sup>*</sup> , pH 8	11	6	92	39	94	12
10	5 mgL <sup>-1</sup> HA, OPS <sup>*</sup> , pH 10	6	5	-	-	-	-
11	5 mgL <sup>-1</sup> FA, OPS <sup>*</sup> , pH 8	0	7	-	-	-	-
12	5 mgL <sup>-1</sup> NOM, OPS <sup>*</sup> , pH8	23	15	96	38	97	15

\* OPS = mixing order organics-particles-salt; SPO = mixing order salt-particles-organics  
x all as organic carbon

**Table 5** Flux and rejection of colloids at pH 3 in MilliQ and in the presence of organics (5 mgL<sup>-1</sup> HA)

Colloid	Membrane	DOC		Fe		Flux Decline (%)
		Rejection (%)	Fe Rejection (%)	DOC Deposit (% DOC)	Fe Deposit (% Fe)	
I (MilliQ)	GVHP	-	87	-	94	66
I (MilliQ)	GVWP	-	99	-	100	74
I	GVHP	32	99	17	56	53
I	GVWP	17	97	0	74	70
II	GVWP	23	96	0	95	86
III	GVWP	20	95	13	92	54

**Table 6** Deposition and rejection of hematite colloids, organic rejection, and flux decline as a function of organic type and concentration, calcium concentration and pH (GVWP membrane, SPO)

No	Organic Concentration (mgL <sup>-1</sup> as DOC)	Calcium Concentration (mM)	Hematite	pH (-)	Deposition (% Fe)	Organic Rejection (% DOC)	Flux Decline (%)	Rejection (% Fe)		
								after cycles 1, 2, 3		
1	5 HA	0.5	I	8	91	17	74	96	86	86
2	10 HA	0.5	I	8	93	11	75	94	90	91
3	20 HA	0.5	I	8	88	6	81	88	92	90
4	5 HA	2.5	I	8	95	13	64	97	91	85
5	5 HA	4	I	8	97	12	60	99	98	94
6	5 HA	0.5	I	4.5	92	8	80	90	84	72
7	5 HA	0.5	I	10	87	29	73	88	85	76
8	5 FA	0.5	I	8	93	5	78	95	89	87
9	5 NOM	0.5	I	8	94	8	84	96	88	80
10	5 HA	0.5	II	8	94	12	63	94	94	88
11	5 HA	0.5	III	8	87	6	40	88	77	80

**Table 7** Deposition and rejection of hematite colloids as a function of transmembrane pressure (GVWP membrane, SPO)

Transmembrane Pressure (kPa)	Flux Decline J <sub>w</sub> /J <sub>w0</sub> (%)	Deposition (% Fe)	Rejection (% Fe)		
			after cycles 1, 2, 3		
50	74	93	94	92	87
100	74	91	96	86	86
200	79	85	88	84	90
300	80	78	79	64	68

**Table 8** Deposition and rejection of hematite colloids, organic rejection, and flux decline as a function of organic type and concentration, calcium concentration and pH (GVWP membrane, OPS)

No	Organic concentration (mgL <sup>-1</sup> as DOC)	Calcium concentration (mM)	Hematite	pH (-)	Deposition (% Fe)	Organic Rejection (% DOC)	Flux Decline (%)	Rejection (% Fe) after cycles 1, 2, 3		
1	5 HA	0.5	I	8	18	1	22	11	8	6
2	10 HA	0.5	I	8	4	2	10	0	3	0
3	20 HA	0.5	I	8	10	3	28	5	5	1
4	5 HA	2.5	I	8	27	31	50	12	12	16
5	5 HA	4	I	8	96	28	69	92	90	76
6	5 HA	0.5	I	4.5	71	22	83	54	60	69
7	5 HA	0.5	I	10	7	18	17	6	3	1
8	5 FA	0.5	I	8	18	7/7*	11/16*	15	10	4
9	5 NOM	0.5	I	8	75	7/7*	95/95*	24	84	95
10	5 HA	0.5	II	8	89	7	55	86	83	81
11	5 HA	0.5	III	8	88	9	40	94	93	92

\* repeated

## FIGURE CAPTIONS

- Figure 1** Electronmicrograph of surface water deposit from Mooney Mooney Dam (Gosford, NSW) on a GVWP microfiltration membrane. The crack is due to membrane drying and demonstrates the thickness of the cake.
- Figure 2** Electronmicrograph of surface water colloids and organics. The colloids are embedded in an organic matrix. The colloids were identified as Al, Si and Fe materials.
- Figure 3** Postulated aggregate structures (A) stable hematite colloids in absence of organics, (B) aggregates formed by reaction limited aggregation (RLA), (C) aggregates formed by diffusion limited aggregation (DLA), (D) SPO: aggregates with organics, (E) OPS: colloids stabilised with organics, (F) OPS: colloids stabilised with NOM, (G) OPS: colloids stabilised with organics and destabilised with calcium
- Figure 4** Zeta potential of clean membranes; GVHP, GVWP, and GVHP pretreated with 50% Ethanol solution.
- Figure 5** Electronmicrographs of clean membranes (A) GVWP and (B) GVHP, magnification 10 000.
- Figure 6** Zeta potential of hematite colloids (A) as a function of pH in absence of organics and salt solution, (B) at pH 3 without background solution with fulvic acid and at pH 8 in presence of background solution with humic acid, (C) prepared without organics and with organics in different mixing orders (OPS: organics-particles-salt, SPO: salt-particles-organics), and (D) as a function of calcium concentration, at pH 8 with background solution.
- Figure 7** Flux ratio (flux after collection of 800 mL permeate over pure water flux) as a function of primary colloid size for stable colloids (pH3), at pH3 with organics, aggregates in the absence of organics (pH8), stabilised colloids (OPS), and aggregates (SPO).
- Figure 8** Electronmicrograph of (A) the membrane surface and (B) the cross-section for hematite I (75 nm, pH3, no organics), (C) the cross-section for hematite II (250 nm); (all 10 mgL<sup>-1</sup> hematite, GVWP membrane), and (D) the membrane surface for aggregates (SPO).
- Figure 9** Flux ratio (pure water flux after experiments divided by initial pure water flux), for different organic types (GVWP membrane), (A) for aggregates (SPO) and (B) for stabilised colloids (OPS). OPS experiments for HA and NOM were repeated.
- Figure 10** Flux ratio as a function of calcium concentration (A) for aggregates (SPO, GVWP membrane) and (B) for stabilised colloids (OPS).
- Figure 11** Particle size distribution for as a function of calcium concentration (10 mgL<sup>-1</sup> Hematite I, 5 mgL<sup>-1</sup> HA as DOC).
- Figure 12** Flux ratio as a function of pH (A) for aggregates (SPO, GVWP membrane) and (B) for stabilised colloids (OPS).
- Figure 13** (A) Iron rejection as a function of transmembrane pressure (Hematite I, no organics) and (B) Iron rejection as a function of transmembrane pressure (SPO, GVWP membrane).