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Process intensification during treatment of NOM-laden raw upland waters: Control and impact of the pre-coagulation regime during ultra-filtration

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ABSTRACT

The use of upstream pre-coagulation coupled with downstream ultra-filtration (UF) has been applied to the clarification of natural organic matter (NOM) laden raw upland water. Such a combination yields a significant increase in possible loading rate and a decrease in the propensity for internal membrane fouling, allowing for an intensification of the process. In particular, the effect of controlling the pre-coagulation regime on the downstream UF has been investigated. It has been shown that zeta potential (ZP) can be used to detect changes in the coagulation process, and hence to determine appropriate dosage levels. This is important, as incomplete coagulation has a detrimental effect on UF membrane performance, particularly in terms of fouling caused by excess iron. Submerged hollow-fibre membrane units yield superior performance with pre-coagulation, and sufficient slow mixing of coagulant guarantees high permeate flow recovery after backwashing. Fouling by NOM can be remedied by conventional cleaning techniques. However, fouling due to excess iron can only be removed by heating the cleaning solution. The associated costs are thus twofold; that of excess coagulant and that of cleaning.

1. Introduction

Turbidity (cloudiness) in natural water is generally caused by fine or colloidal clay particles, while natural colour is mainly due to large, macromolecular organic acids. This natural organic matter (NOM) derives from decaying vegetation, particularly common in upland water sources, and often gives the water an orangey tint [1]. A coagulant causes the very small suspended matter to agglomerate into larger particles, the latter process being assisted by gentle shear during flocculation. The particles then settle rapidly enough to be easily removed.

A conventional clarification process consists of three parts: rapid mixing, flocculation and sedimentation. Rapid mixing ensures added coagulants are thoroughly mixed and dispersed to promote the colloidal destabilisation. This requires plenty of turbulence and back-mixing, which is achieved through stationary devices (baffles, orifices, etc.) or mechanical devices (paddles, turbines or propellers). A separate mixing chamber is often used. The shear-inducing velocity gradients required for flocculation are created in several ways: hydraulically (jets and baffled channels), by air injection (rising bubbles), mechanically (by

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Fig. 1. Solids-contact unit for clarification (Courtesy: Severn Trent Water).

paddles, reel turbines or propellors) or by solids-contact. For mechanical devices, the mean velocity shear gradient is maintained uniformly to avoid both dead zones and floc break-up. Sufficient volume and hence residence time in settlement tanks are required for adequate settling of the flocs. A stage of rapid sand filtration is often also applied as a final measure.

Within the water industry, there is a constant drive towards more compact treatment units – retrofitted to existing sites – and therefore occupying less land space. In addition, water quality standards are constantly tightening. A previous asset management plan (AMP3) of the English and Welsh water companies emphasized compact, high-rate processes [2]. The solids-contact unit (sometimes known as an upflow or sludge blanket clarifier) allows such a process intensification by combining mixing, flocculation and sedimentation in a single unit (as seen in Fig. 1). Since a large volume of flocculated solids is retained in the system, flocculation of incoming solids is enhanced because the frequency of inter-particulate collision is increased. In sludge blanket clarifiers (Fig. 1) the mixing and flocculation are achieved in the centre compartment with agitation and gentle stirring provided by pitched blade impellers. While hydraulic loading rates (throughput/area) for basic sedimentation are 1–1.5 m/h, values of 4 m/h can be achieved with sludge blanket clarifiers.

In recent years, the UK has seen a significant shift towards the dissolved air flotation (DAF) process, particularly with low turbidity upland waters where the flocs settle poorly. Loading rates up to 12 m/h can be achieved. Lamella sedimentation uses inclined plates or tubes (60° to the horizontal), with a greater surface for settling, allowing loading rates up to 40 m/h.

NOM concentrations in UK upland waters have been creeping upwards in recent years, possibly as a result of climate change. Removal of this NOM is critical to meeting water quality standards on trihalomethanes (THMs). THMs are toxic by-products formed from residual NOM during the chlorination and disinfection stages. Health concerns over disease-causing protozoans such as *Cryptosporidium* and *Giardella* have also led to stricter standards. Many water companies acknowledge that conventional clarification, possibly combined with other processes like activated-carbon adsorption, is not necessarily the most cost effective way of removing NOM from upland waters. Cheaper and more intensified solutions are needed, and membranes are one favoured option.

The role of membrane units in water treatment is currently widening. Unfortunately, low-pressure membrane filters often exhibit a gradual reduction in the rate of permeate (filtered water) production, due to the accumulation of fouling material on and within the membrane surface. Schaffer et al. [3] demonstrated that fouling of ultra-filtration (UF) membranes occurs by the adsorption of NOM on and within the pores, while Maartens et al. [4] showed that concentration polarisation of humic acid near the membrane surface and followed by precipitation caused fouling of the same type of membranes.

Membrane filtration performance, in terms of flux and frequency of backwash and chemical cleaning, highly depends on raw water quality. For membranes with hollow-fibre configurations, fouling is partially reversible by applying a counter flow, commonly called backwashing, which removes the majority of accumulated matter. Irreversible fouling, however, requires chemical cleaning.

Regardless of the membrane system used, chemical cleaning is cumbersome and requires shutdown of the unit being washed for several hours. This results in a reduction of the overall plant capacity, and produces a waste stream that may be difficult to dispose of. There are also concerns that repeated chemical cleaning might affect the membrane life. Chemical cleaning should thus be reduced to a minimum, or avoided altogether. For these reasons, irreversible membrane fouling represents a real limitation to the wider application of membrane filtration to most surface waters.

It is possible, however, to first coagulate the NOM and then remove the larger flocs with membrane filters (see Fig. 2). Studies have indicated that the combination of microfiltration (MF) or UF with upstream coagulant dosing is beneficial and synergistic [5], particularly for NOM-laden waters. The macromolecules of NOM, which are small enough themselves to enter membrane pores, are coagulated to produce

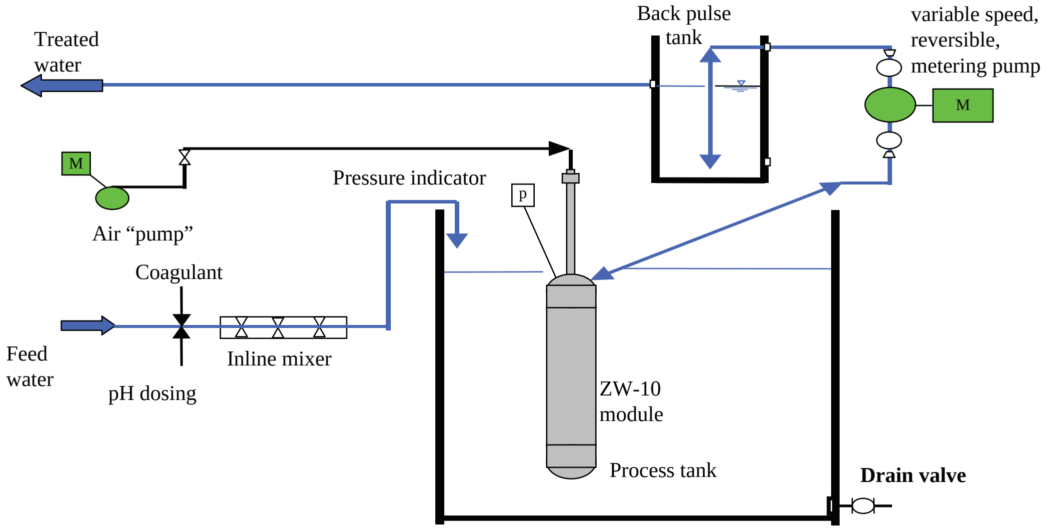


Fig. 2. Schematic of submerged ZW-10 membrane UF unit with coagulant dosing and mixing.

much larger particles, which are rejected. This benefits the membrane flux in three ways:

- Penetration of foulant into the membrane pores is reduced.
- A filter-cake is formed on the membrane surface which removes the small particles.
- Foulant accumulation near the surface is also reduced – larger particles are more easily carried off by the cross-flow.

However, careful control of the coagulation regime is important, as variations in coagulant levels can have a dramatic effect on membrane performance. Prior work on pre-coagulation during membrane filtration has revealed that when coagulation conditions are not optimal small colloidal and iron species are often present which are free to affect and clog the membrane, increasing the cleaning and running costs [6].

Note that an alternative solution would be to use a granular activated-carbon pre-treatment; this has been applied to treat water where the NOM content is very high [7], although again it is an expensive option.

Nearly all colloidal materials in natural raw water carry a negative charge, and they are stabilized by the repulsive forces associated with the interaction between the electrical double layers of neighbouring particles. Chemicals often used in the coagulation of potable water therefore include aluminium and ferric salts, which hydrolyze to produce insoluble hydrates. Addition of such positively charged hydrolysis products acts to reduce or even neutralize the surface charge and hence the zeta potential (ZP) of the colloidal matter (which is closely related) to a value close to zero, hence reducing the repulsive forces between the colloidal particles to a point where the very short-range Van der Waals forces dominate and lead to particle coagulation [8]. It is apparent that an optimum coagulant dose corresponds to a condition where the ZP is close to zero [9]. In the case of NOM, the macromolecules tend to become adsorbed and enmeshed within the growing hydrate particles – a process known as 'sweep' flocculation.

At low coagulant doses, the colloidal particles remain negatively charged and hence their dispersions remain stable. This incomplete coagulation leaves behind residual organic and inorganic material that can subsequently lead to membrane fouling. Judd and Hillis [5] have shown that a low coagulant dose will have a detrimental effect on the membrane performance due to incomplete flocculation of the colloidal material. Soffer and Adin [6] have demonstrated the fouling of UF membranes by colloidal iron hydroxide or oxide. On the other hand, at a high coagulant dose the particles become positively charged and hence acquire dispersive stability again. This counter-acts to reduce the coagulation efficiency [8,9].

The seasonal variation in temperature exacerbates this general problem, since the water temperature has a direct effect on the process of orthokinetic flocculation which is initiated by thermally induced Brownian motion. As the temperature decreases, so too does the flocculation performance. The lower temperature causes the formation of smaller denser flocs. Kang and Cleasby [10] have reported that a low temperature had a detrimental kinetic effect on the flocculation process, slowing the disappearance of the primary particles and the growth of the aggregates. This, in turn, has a significant impact on the removal of excess iron, whether in the form of excess coagulant or as organically bound iron. The reduced size of the flocs diminishes the performance of enmeshment, as there is a reduced surface area to trap smaller particles. Further, the so-called 'pin-flocs' are able to cause subsequent fouling of the membrane. The present work expands on the role of excess iron in the pre-coagulation membrane filtration process.

Traditional practice in the water industry has been to use coagulant overdosing as a means of compensating for variations in raw water quality; there is a lack of accurate and reliable dosing control methods available on the market. In the case of NOM-laden waters, the water is periodically sampled and tested manually by UV_{254} absorption. Unfortunately, impurities in the water such as colloidal or dissolved iron species can give yield false UV_{254} readings, so-called false colour, which leads to inaccurate dosing. Since the optimum coagulant dose generally corresponds to the situation where the ZP is close to zero, the use of ZP as a sensor for closed loop coagulant control is one potential solution. Thus another objective of the present work has been to investigate the use of ZP in controlling coagulant dose.

In addition to a reduction in membrane fouling, the use of membrane filtration permits advantages over conventional clarification. Flocculation and settling times can be reduced from hours to minutes; because the pore size is sub-micron, the flocs only need to grow to micron-size to be filtered. Note that larger sizes are required in practice to ensure coagulant chemical is fully removed. The micron-sized disease-causing protozoans are also filtered out [11], including *cryptosporidium* [12]. In addition, settling tanks as such are not required, although sludge must still be disposed of. All this implies a significant process intensification, with potential loading rates up to 100 m/h.

Studies by Pikkarainen et al. [13] have demonstrated that the use of $FeCl_3$ coagulant behind a membrane pilot plant improves produced water quality by a factor of four, and Guigui et al. [14] have shown the same coagulant improves permeate quality when used with a cellulosic hollow-fibre UF bench-scale system.

Despite the strong technical and economic potential of this process, data on real systems are relatively scarce; systematic studies of coagulant dosing, mixing time and back flushing are almost non-existent. A third objective of this study has thus been to furnish such data.

2. Methodology

To perform experimental runs, water was collected from an inlet pipe at a potable water treatment works fed by an upland reservoir in the UK and operated by Severn Trent Water Ltd.

2.1. Analysis of water quality

An analysis was conducted on the quality of both raw and clarified water samples. The key parameters of interest were total organic carbon (TOC), levels of metallic species including iron, manganese, and aluminium, turbidity and pH.

A Shimadzu TOC-5000A analyser was used to calculate TOC. The determinations of iron, manganese, and aluminium were carried out using a Jenway 6405 UV/Vis spectrophotometer, following the procedures described in Eaton et al. [15]. Turbidity measurements were performed using a Jenway 6035 Turbidimeter. The pH of the samples was measured by a WTW 235 pH meter. ZP measurements were performed using a Malvern Zeta Sizer 3000HS.

The results of the raw water analysis are given in Table 1. Levels of natural iron in the water varied between 0.1 and 0.3 mg/L total iron; the presence of significant quantities of iron species should be noted. A significant portion of this iron (around one-third) is solid and filterable, and hence colloidal or suspended in nature.

2.2. Coagulant testing

Coagulation and flocculation tests were carried out using a six-paddle Stuart Flocculator SW6. The mixing schedules including rates and times can be set, allowing for good reproducibility of the tests. The coagulant used was ferric sulphate, and provided by Severn Trent Water Ltd. The dosage ranged from 0 to 4 mg/L ferric

Table 1
Analysis of raw water quality

	Minimum value	Maximum value
pH	5.93	6.37
TOC (mg/L C)*	5.6	9.94
Total iron (μg/L)	333	420
Total manganese (μg/L)*	37	108
Total aluminium (μg/L)*	141	184
Iron-filtered (μg/L)	222	283
Manganese-filtered (μg/L)*	3.9	22
Aluminium-filtered (μg/L)*	91	155
TOC-filtered (DOC) (mg/L C)*	4.56	8.89
UV_{254} ($cm^{-1\ abs}$)	0.161	0.532
Turbidity (NTU)	0.19	8.9
Colour (mg/L Pt/Co)	34.8	94.2

*Analysis conducted by Severn Trent Water Laboratories.

ion. The coagulant was added to 1 L samples of the raw water. The standardized jar-test procedure consisted of a period of rapid mixing at 250 rpm for 1 min (to allow for coagulation of the NOM), followed by a period of slow mixing at 30 rpm for 10 min (to allow for subsequent flocculation). Water samples were collected periodically throughout the experiment and then filtered through a Whatman 2 filter paper (with a pore size of 8 μm) to remove the flocs. The filtered sample was then tested for UV_{254}, TOC and total iron concentration.

In general, determination of the optimum coagulant dose required an adjustment for both pH and temperature. Jar tests were conducted using a constant coagulant dosage (e.g. 3 mg/L Fe^{3+}) with the pH being adjusted by the drop-wise addition of either dilute sulphuric acid or dilute calcium hydroxide solution. The optimum pH was identified as that corresponding to a maximum removal of TOC.

2.3. Photometric dispersion analyser (PDA)

Optimisation of the mixing regimes was investigated using the PDA. This instrument can monitor flowing suspensions; in particular, it provides an analysis of the state of aggregation of a suspension. The PDA illuminates the growing flocs in the suspension with a narrow beam of light. The fluctuations in the intensity of transmitted light are monitored by a sensitive photodiode, and the readings subsequently converted to voltage. From the fluctuating (AC) signal, a root mean square (RMS) signal is derived. The mean transmitted light intensity (DC) is also measured. The ratio of RMS signal to DC signal [16] allows a quantification of the state of aggregation in the suspension.

$$\text{Ratio} = \frac{\text{RMS}}{\text{DC}} \qquad (1)$$

The RMS signal has been demonstrated to be a fairly sensitive indicator of the state of aggregation [17]. The tests involved using the jar tester, with the same mixing conditions as described above. The sample to be tested was gravity fed to the PDA at a constant flow-rate of 40 mL/min and allowed to run for 20 s before mixing of the coagulant started, in order to establish a base rate. A data logger was used to record the ratio value once per second. Picolog software was used to analyse the raw data.

2.4. Norit membrane (T/RX-300)

A bench-scale Norit X-flow UF membrane was initially used with tube-side feed in dead-end mode. Trans-membrane pressure (TMP) was 1.0 bar. The polyethersulfone/polyvinylpyrrolidone blend hollow-fibre membrane (PES/PVP membrane) had a nominal pore size of 0.04 μm. A microphotograph of the membrane cross-section is shown in Fig. 3.

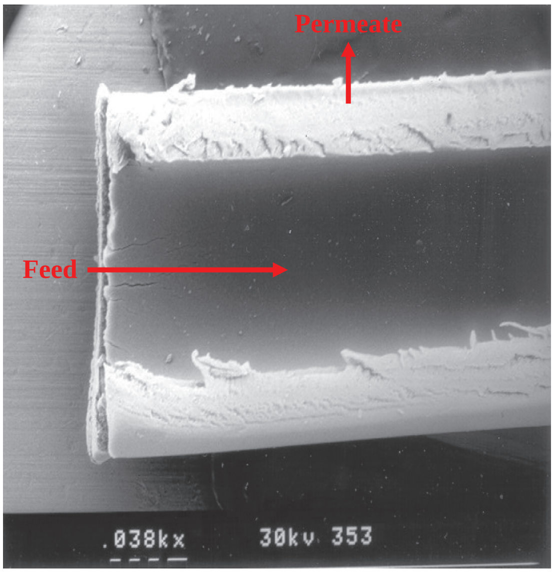


Fig. 3. Photomicrograph of cross-section of hollow-fibre Norit membrane; internal diameter = 0.8 mm.

Following the mixing process, the coagulated and flocculated water was pumped through the membrane. Measurement of the difference in inlet and outlet pressure allowed calculation of the TMP. Analysis of permeate was carried out to determine flow-rate, UV_{254} absorbance and total iron concentration.

The membrane unit was backwashed after each run using distilled water. Periodic chemical cleaning was conducted by alternately soaking the membrane with 1% sodium hydroxide and 1% citric acid solution.

2.5. Zenon ZW10 membrane unit

A pilot rig was also constructed to incorporate a submerged Zenon ZW-10 UF membrane. Coagulant dosing and mixing of the raw water was carried out prior to introduction to the feed tank, from which water then entered the outside of the suspended membrane fibres under suction (see Figs. 2 and 19). Air sparging allowed for removal of the filter cake from the fibres.

Rapid mixing was set at 250 rpm for 1 min; slow mixing times were varied in order to determine the levels of fouling caused by incomplete perikinetic flocculation. Membrane runs were conducted at the optimum coagulant dose as determined by jar testing at pH 4.8 and 18 °C (dependent on the water quality). Backmixing was performed using the clarified water;

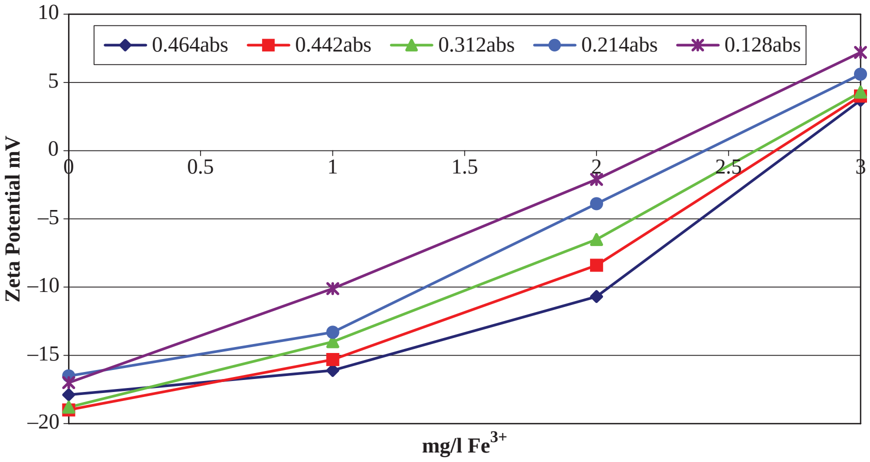


Fig. 4. The effect of ferric sulphate on ZP.

chemical cleaning was performed using a variety of agents. For full details of chemical cleaning, see [18].

3. Results

3.1. ZP measurements to control coagulation

Tests were conducted to determine the changes in ZP with the addition of ferric sulphate. Fig. 4 shows that the raw water initially manifests a negative ZP; the NOM contains humic and fulvic acids whose dissociated acidic groups have a negative charge. Adding the coagulant, with its positively charged hydrolyzed ferric species, neutralizes this charge and the ZP increases. The point at which the ZP attains a zero value is referred to as the iso-electric point; at this point, the flocs have no net charge. A positive ZP is indicative of charge reversal and coagulant overdosing, and a negative ZP would indicate underdosing. Neutral flocs at the iso-electric point are also less likely to adhere to a charged-membrane surface through electrostatic forces.

Since an objective of the present work is to apply the measurement of ZP in the control of coagulant dosing, it was important to investigate the optimum location for the ZP sensor during the mixing process. Fig. 5 shows the changes in ZP which occurred during the mixing process. In this experiment, 1 min of rapid mixing was followed by a period of slow mixing. Excess coagulant was added to highlight the changes to ZP.

The addition of coagulant changes the ZP from −16 to +5 mV (indicative of a slight overdosing). The dispersion of hydrolyzed ferric ions and the formation of pin flocs increases the ZP during rapid mixing. Thereafter, the ZP shows a gradual reduction to a stable value, due to the enmeshment of the excess iron.

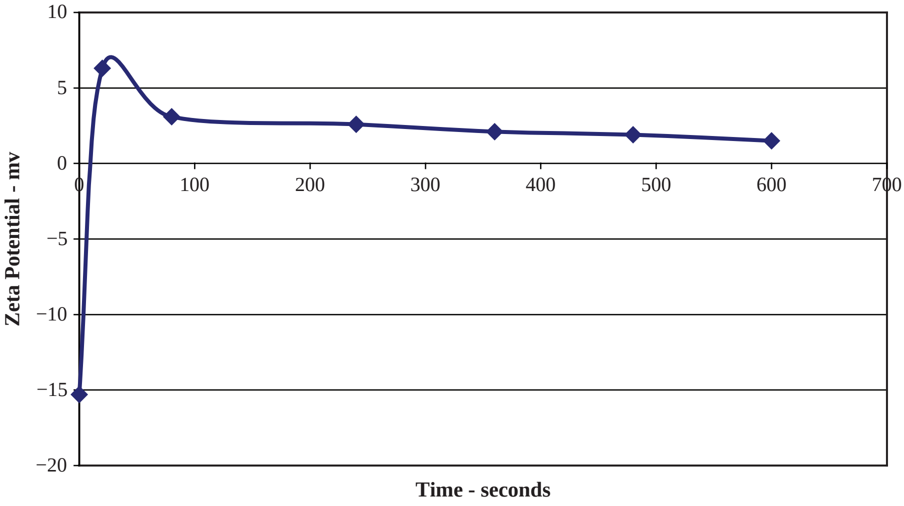


Fig. 5. Changes to ZP during the mixing process.

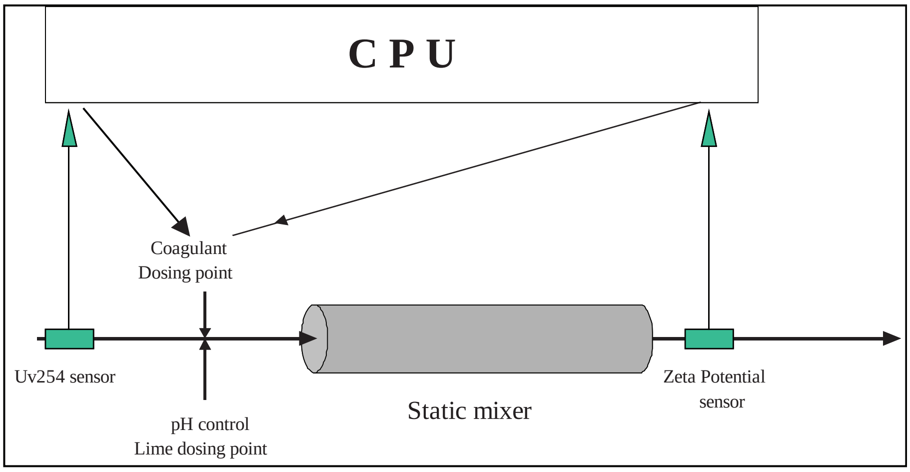


Fig. 6. Schematic of coagulation dosage control loop utilising ZP.

This result indicates that positioning the sensor immediately after rapid mixing would be suitable.

Although some in-line ZP sensors are available on the market, they are designed for fluids with a high solids concentration for use in the mining industry.

In conjunction with Malvern Instruments, a zetasizer 3000HS instrument has been adapted to make the in-line measurements appropriate to the solids concentrations typical of water clarification.

An UV_{254} sensor acts in feed forward control to set the dose, while the ZP sensor acts as a feed backward control to adjust the dose (Fig. 6; see photographs of the in-line UV sensor and ZP in Fig. 7). One particular reason for why it is unsatisfactory to use a UV_{254}

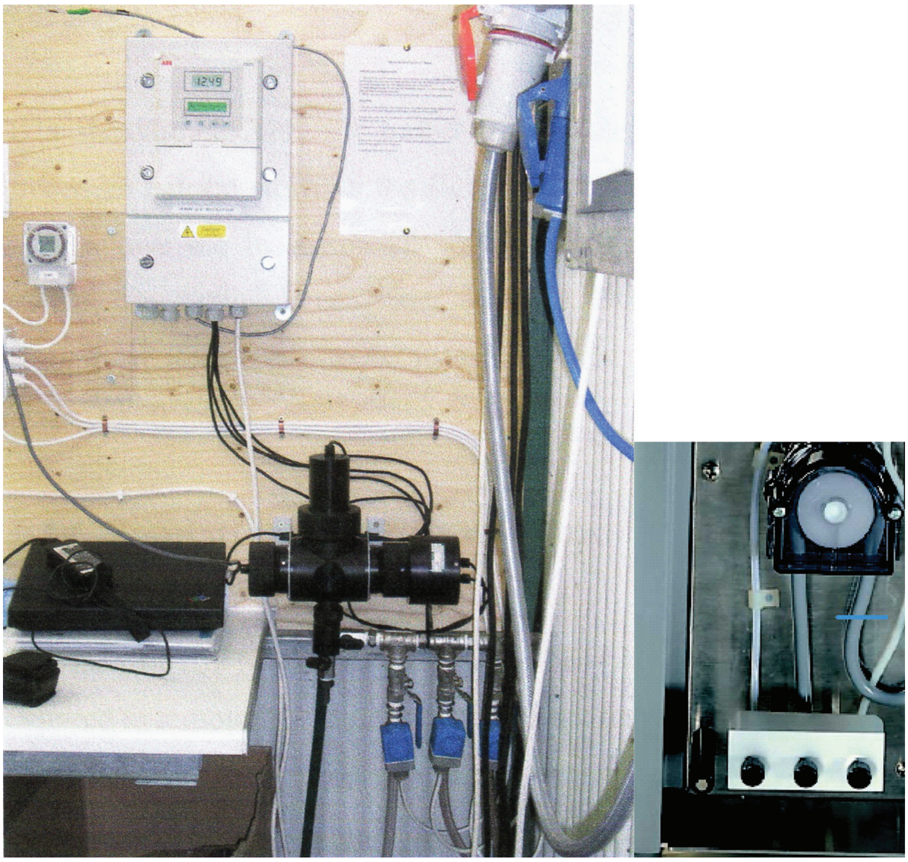
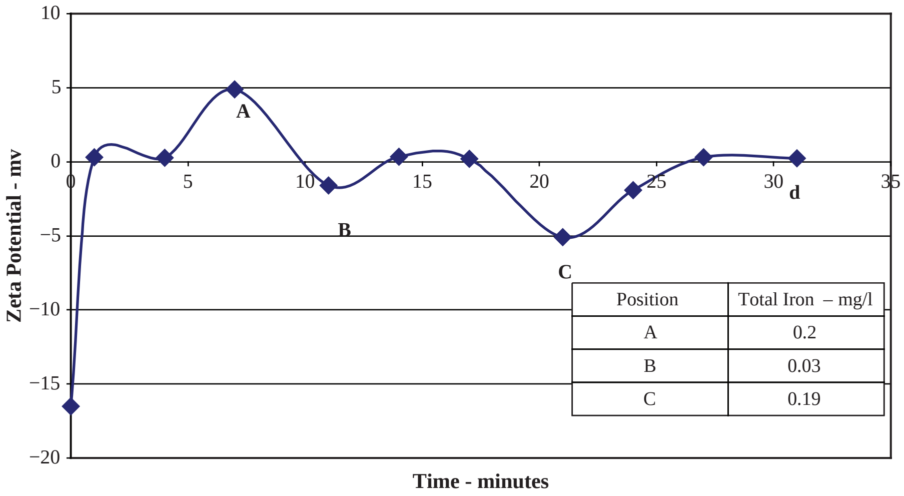


Fig. 7. Photograph of in-line UV_{254} dosage control system and ZP sensor. Inset of mixing system.



Position	Total Iron – mg/l
A	0.2
B	0.03
C	0.19

Fig. 8. Effect on ZP of varying raw water quality and total iron levels.

sensor alone is that components in the water, such as natural iron, give rise to incorrect and thus non-useful readings of UV absorption as a measure of NOM content.

Laboratory-based experiments were conducted with varying levels of NOM in the raw water, at fixed coagulant dose, to see if the changes in ZP could be detected. Fig. 8 shows the changes to ZP which occurred when changes were made to the inlet water conditions. Samples taken were passed through 0.8 μm filters to remove flocs and then tested for total iron levels. The initial addition of coagulant changed the ZP to a value near to zero. A decrease in the NOM content of inlet water now causes an increase in ZP at position A, since the present dosage of coagulant is now in excess. Following a subsequent decrease in the coagulant dosage to a more optimum level, the ZP drops back to a value closed to zero (B). An increase in the NOM content of inlet water now leads to a sub-optimal coagulant dosage and a drop in ZP (C), requiring additional coagulant dosage in order to reach optimum coagulation conditions again (D).

The table inset in Fig. 8 shows the level of total iron present at various points. The iron present at A is due to the presence of excess ferric sulphate coagulant. The presence of iron at B and C is due to the presence of uncoagulated natural iron in the feed water. Only in the case of a near zero ZP (B and D) is this iron mostly removed; in the case of point D, the iron concentration was below the detection limit. Taken together, the plot and the table show that both under- and overdosing can lead to excess iron in solution. This may subsequently prove to be a problem for the downstream membrane, as seen later.

3.2. Extent of aggregation of flocs

Fig. 9 presents the extent of aggregation, as indicated by the ratio measurement in Eq. (1), of flocs as a function of both the mixing time and the coagulant dosage. It is clear that a minimum dosage of 2 mg/L of ferric ions is required to ensure floc formation, which is essentially complete within 4 min. Increasing the dosage further to 3 mg/L has little further effect on the floc formation.

3.3. Removal of NOM

Fig. 10 presents the removal of NOM during the standard mixing procedure. It is evident that the process of both floc formation and iron removal are complete after 2 min. In the case of the raw water used, most of the NOM is in the form of large molecular weight, hydrophobic and acidic material which is easily neutralized and enmeshed within the flocs. However, we must also examine the removal of the iron species.

3.4. Removal of excess iron

NOM can reduce the performance of UF membranes due to external and internal fouling; however, as the results in Fig. 8 have shown, there are other components present in the water, such as natural iron. Since iron is also used as the coagulant, it is valuable to study the removal of iron into the flocs during the mixing process. Experiments were thus conducted on the removal of iron; for these tests, 1 min of rapid mixing was followed by a period of slow mixing, as shown in Fig. 11.

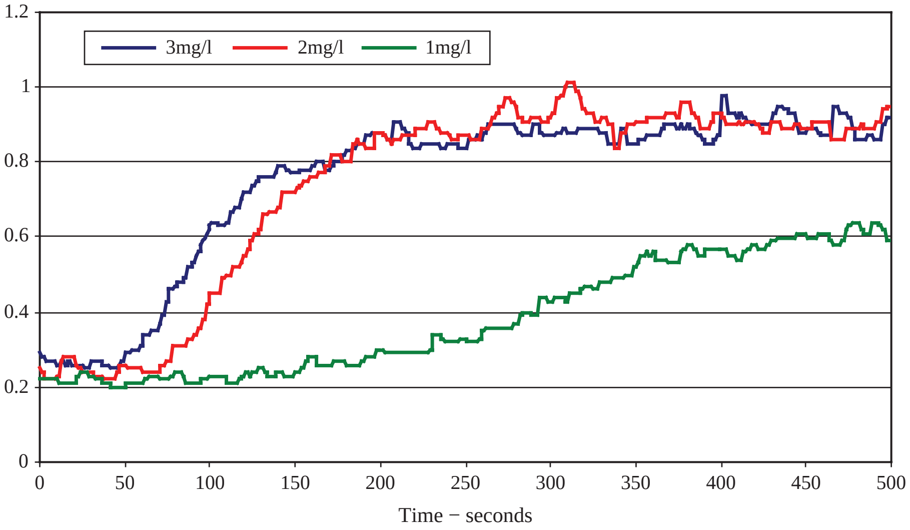


Fig. 9. Extent of floc formation as a function of mixing time and coagulant dosage during standard mixing procedure.

From an initial coagulant dosage of 3 mg/L, the results demonstrate that the rapid mixing is unable to remove all the excess iron from solution; a level of 0.07 mg/L remains (much of this corresponding to the colloidal iron naturally present in the water; see Table 1). Some subsequent slow mixing is required. The initial reduction in iron concentration during rapid mixing is due to the formation of flocs. A number of pin flocs are initially formed by precipitation of iron hydroxide at any given shear rate, leaving residual iron species in the solution. Slow mixing is required to increase the size of the flocs, and remove the remaining iron by enmeshment. However, this process remains incomplete; after 3 min of slow mixing, the level of iron remains constant at 0.02 mg/L, and no further removal occurs. As seen in Fig. 9, this time corresponds to the completion of floc aggregation. In Fig. 12, the effect of a slight increase in coagulant dosage from 3.0 to 3.2 mg/L shows that the time at which the iron has been effectively removed is now significantly delayed, and requires a further 7 min of mixing (i.e. 10 min in total) to reach the same final level or iron. Thus the effect of even a slight coagulant overdosage is seen to be significant.

As a result of the foregoing studies, the optimum coagulation regime prior to performing membrane tests was established as follows:

- Coagulant dose between 2.5 and 3.5 mg/L Fe and a pH of 4.8.
- Mixing regime of 60 s rapid mixing (shear rate $G = 447\ s^{-1}$) followed by 3 min slow mixing (shear rate $G = 20\ s^{-1}$).
- Ambient temperature ∼ 18 °C.

3.5. Application of Norit membrane (T/RX-300)

To study the effect of an upstream pre-coagulation regime on downstream UF of the raw waters, tests

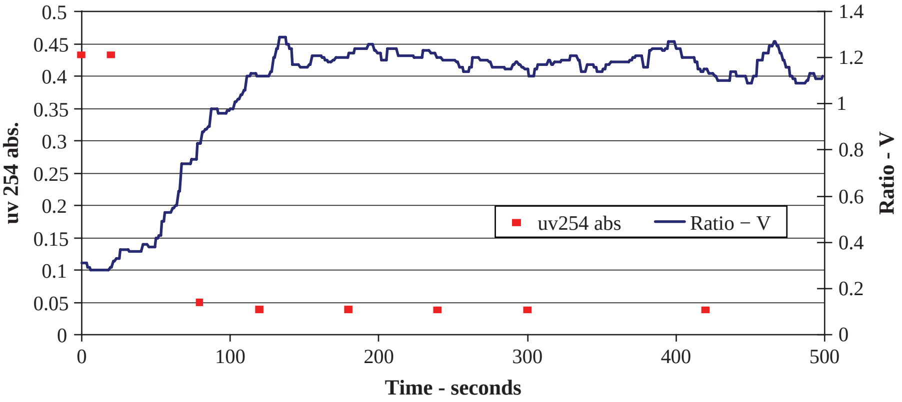


Fig. 10. Removal of NOM during standard mixing procedure.

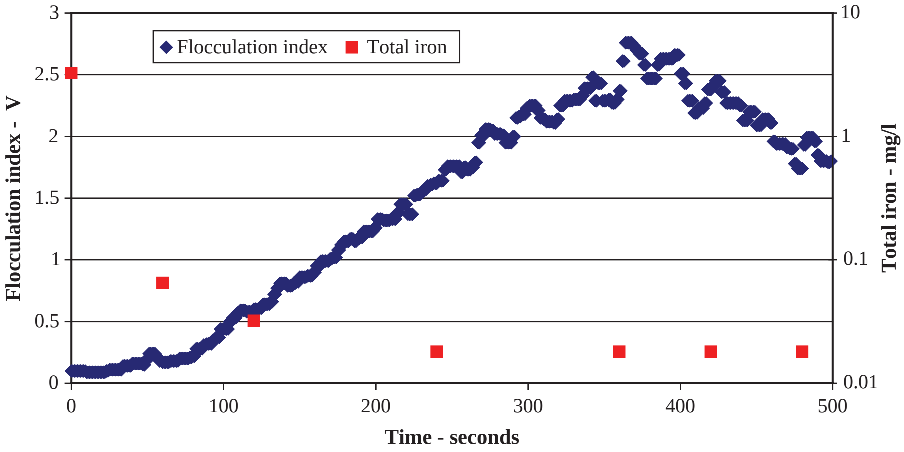


Fig. 11. Removal of iron species during mixing (1 min at 250 rpm then 30 rpm).

were conducted on the Norit bench-scale UF membrane unit, to assess the effects of coagulation on membrane performance. Applying the optimisation results of the PDA experiments, the water was coagulated with 3 mg/L Fe^{3+} at pH 4.8, rapidly mixed for 1 min at 250 rpm and then slowly mixed at 30 rpm for 4 min. The mixing regime would remove a good part of the excess iron from solution, as shown previously in Fig. 11.

The results for membrane performance, as well as visual observation, confirmed that the large flocs (on the order of millimetres in size) formed by the optimum coagulant regime are blocking the hollow-fibre tube (with an internal diameter 0.8 mm), resulting in a reduction of permeate flow at constant TMP. A series of sausage-shaped slugs of floc material start to migrate along the fibre. This is indicated by the apparent step reduction in flow-rate (Fig. 13).

To reduce the problem of tube blocking and flow restriction, the mixing regime was altered. The slow mixing was reduced to 2 min. Although this has the effect of reducing the floc size, residual iron levels are expected to increase in consequence. Fig. 14 shows the membrane performance of this revised mixing regime at two different TMPs. A back flushing regime was implemented to investigate the levels of irreversible membrane fouling; this is indicated by the extent of recovery of the permeate flow-rate after back flushing.

The results show that, at the higher TMP, the flow-rate is reduced at a slightly greater rate (as indicated by the slope of flow-rate versus time). This is possibly due to the higher pressure compressing the flocs to form a tighter and less permeable cake layer. At the lower TMP, a looser cake is formed, allowing water to flow more readily through the cake and into the membrane.

However, recovery of the permeate flow-rate after back flushing clearly shows better performance at the higher TMP. Since the TMP is also the pressure applied in back flushing, it is sufficient to force the cake more

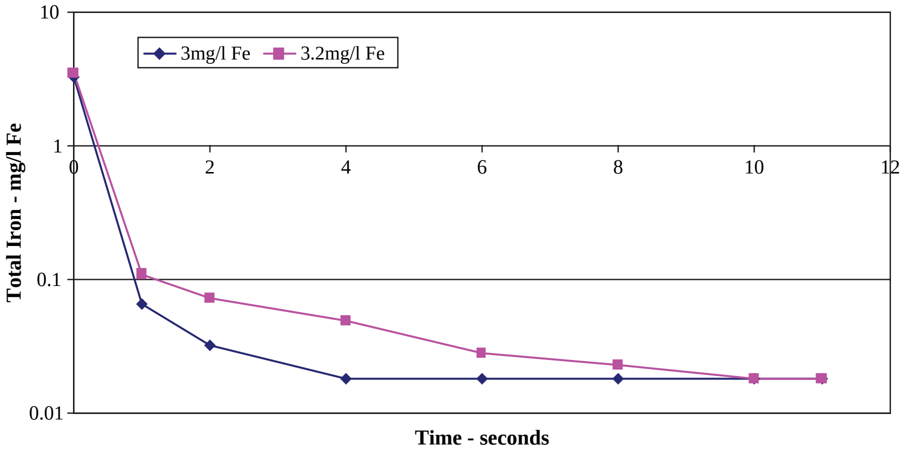


Fig. 12. Effect of slight overdosing of coagulant on removal of total iron.

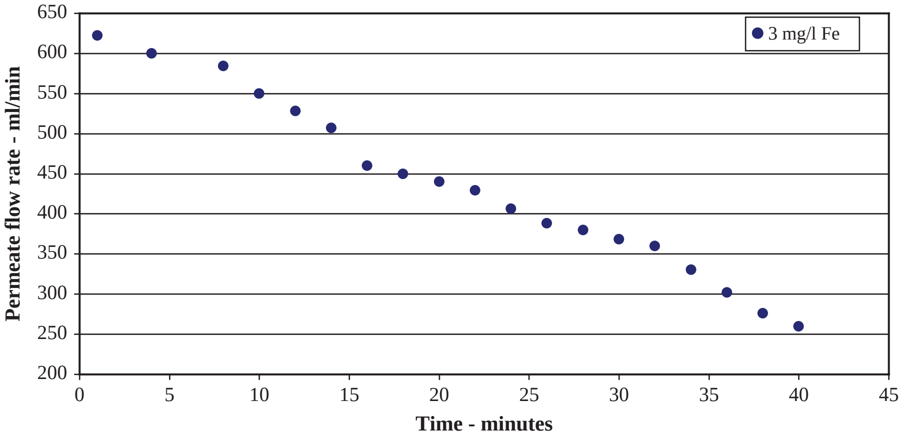


Fig. 13. The effect of optimum coagulant regime on membrane performance.

completely off the membrane surface, leading to a much better flow-rate recovery. At the higher TMP, each backwash cycle recovers 98.9% of the membrane performance.

It should be noted that the recovery after backwashing at the lower TMP is extremely poor, and flow-rates gradually decline, indicating high levels of both external and internal fouling. As stated before, a consequence of the inadequate mixing regime in this experiment is the presence of residual iron in solution (Table 1 indicating that much of this material is solid and filterable). In particular, the organically bound iron fraction is extremely important; with an optimum mixing regime, this iron fraction would be enmeshed onto the larger flocs. Further, at the higher TMP, the more compressed cake acts as a better filter to trap this excess iron, which is subsequently removed by back flushing. However, at the lower TMP, the looser cake does not filter the excess iron, which then moves on to foul the membrane. This iron-based fouling is not removed by back flushing, and consequently chemical cleaning of the membrane is required. Fig. 15 presents SEM images of the membrane surface before and after use; the fouled membrane is covered in a solid deposit of iron which includes some microscopic, colloidal iron.

Although the higher TMP regime shows better recovery, some membrane fouling still occurs. One solution would be to use UF membranes with a greater internal diameter of hollow-fibre, allowing for the use of the optimal mixing regime with its larger flocs. However, a much simpler and preferable solution would be to use a submerged membrane with a shell-side feed such that flocs remain on the outside of the fibres and cause no flow restriction regardless of their size.

3.6. Application of Zenon ZW-10 membrane

Experiments were conducted to investigate the effects of slow mixing retention time, and levels of iron, on the performance of the ZW-10 Zenon submerged UF membrane, as shown in Fig. 2.

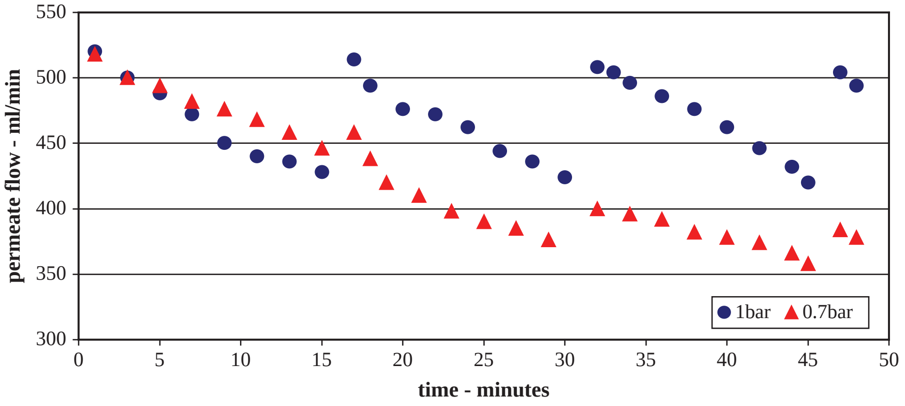


Fig. 14. Membrane performance at two operating pressures and effect of back flushing.

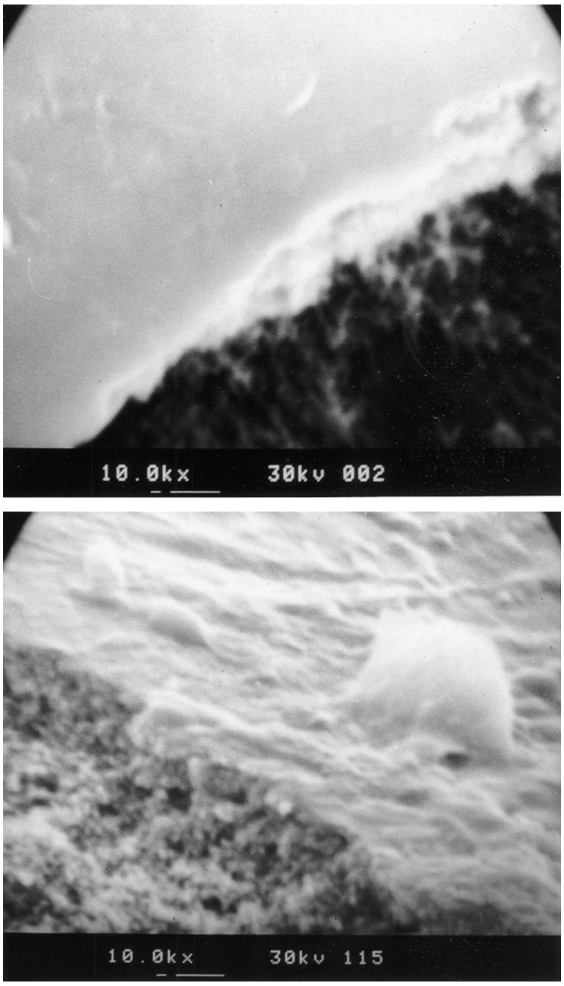


Fig. 15. Fouling of Norit hollow-fibre membrane during tube-side feed: clean membrane (top) and fouled membrane (bottom).

The graph in Fig. 16 shows the changes in permeate pressure at constant flow-rate, during successive cycles of feed and back flush for 2, 4 and 8 min of slow mixing. An increase in suction pressure is indicative of increasing levels of external of internal fouling. An increase in slow mixing time allows the flocs to grow larger and, as a consequence, inorganic components such as iron in the water are enmeshed and removed. This reduces the fouling levels in the membrane, and the recovery after backwashing (following external filter cake removal) improves. At 8 min, recovery is close to 100%. As the maximum operating (suction) pressure of the membrane is 9 psi, it is possible to estimate when each membrane would need to be chemically cleaned. With 2 min slow mixing, the membrane would need cleaning after 1.4 days. This would increase to 1.8 days with 4 min slow mixing, and to 4.8 days with 8 min slow mixing.

The rapid increase in permeate suction pressure after each backwash may be due to the backwash only temporarily and not completely disturbing the external fouling material. Upon resumption of normal flow, this material adheres back onto the membrane. This process is more pronounced at the lower mixing times, where a greater numbers of smaller flocs are formed which are not large enough to settle out and fully separate from the membrane. As mixing time increases, the number of flocs decreases and their size increases, allowing them to settle out. The quick increase in permeate suction pressure may be lessened with a longer period of backwash, allowing not only a removal of the fouling material but also a greater opportunity for it to settle out and separate from the membrane.

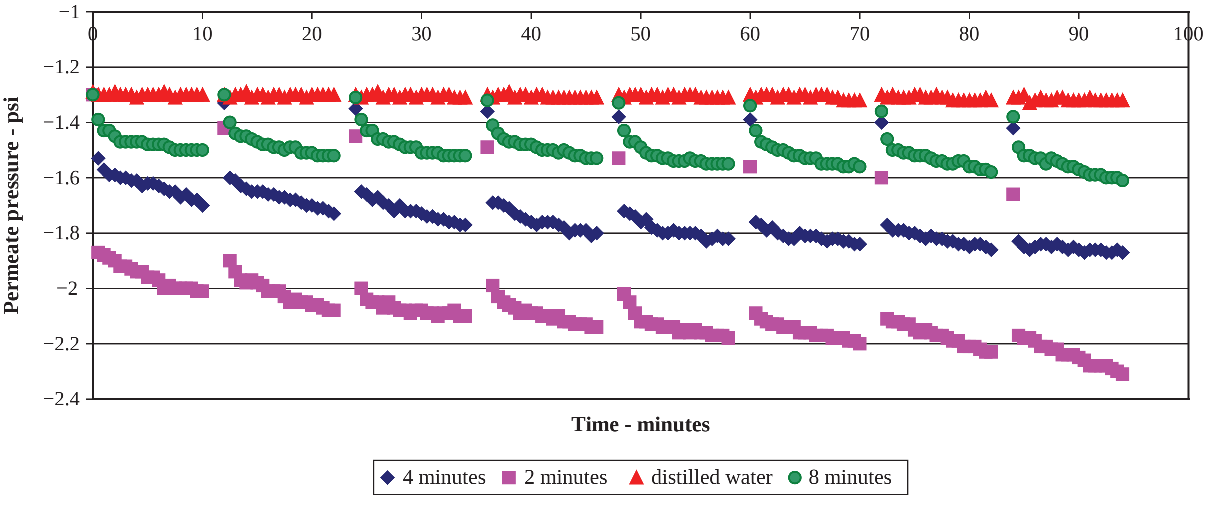


Fig. 16. Effect of slow mixing on permeate suction pressure.

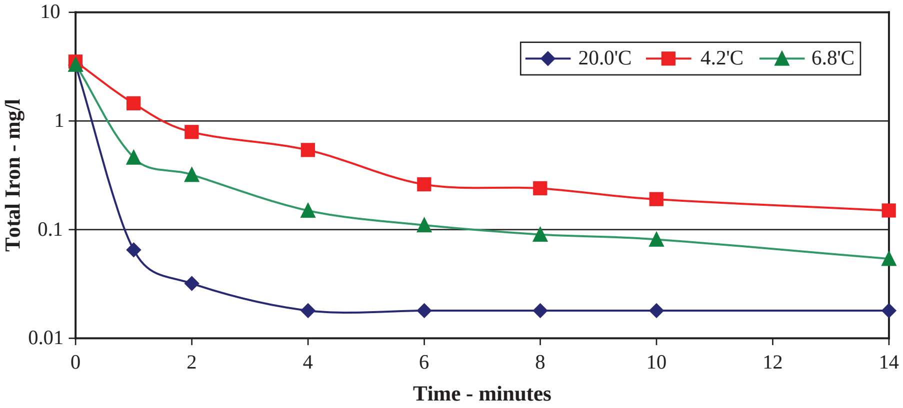


Fig. 17. The effect of temperature on iron removal.

Thus, it can be seen that changing the slow mixing retention time affects the levels of fouling on the membrane following back flushing. As the retention time increases, so the level of fouling decreases. However, these experiments were conducted at 18 °C. During the autumn and winter months, the temperature of the water to be treated will fall, as does the performance of the coagulation and flocculation process. Fig. 17 shows the effect of temperature variation on the removal of residual iron.

3.7. Effect of temperature on iron removal

There is a significant decrease in iron removal as the temperature decreases. At 20.0 °C, the excess iron is removed by enmeshment after 4 min. As temperature falls, so the time required to remove the iron increases. At 4 °C, even after 14 min of mixing there are still significant amounts of iron left in solution. These results are indicative of the performance of the Zenon pilot plant. A water sample was taken from the membrane tank, flocs were filtered out using Whatman 8 μm filters, and the water was tested for iron. The results showed that 0.3 mg/L iron was present in the water entering the membrane. This led to the conclusion that the fouling problems known to arise at the pilot plant during low temperature operation are caused by the incomplete removal of iron during the mixing process. Experiments were conducted to verify this. Using the same mixing regime as Fig. 16, a coagulant dose of 0.3 mg/L Fe^{3+} was added to distilled water in order to simulate the effect that overdosing has on the membrane (Fig. 18).

The results clearly show that residual iron in solution reduces the performance of the membrane.

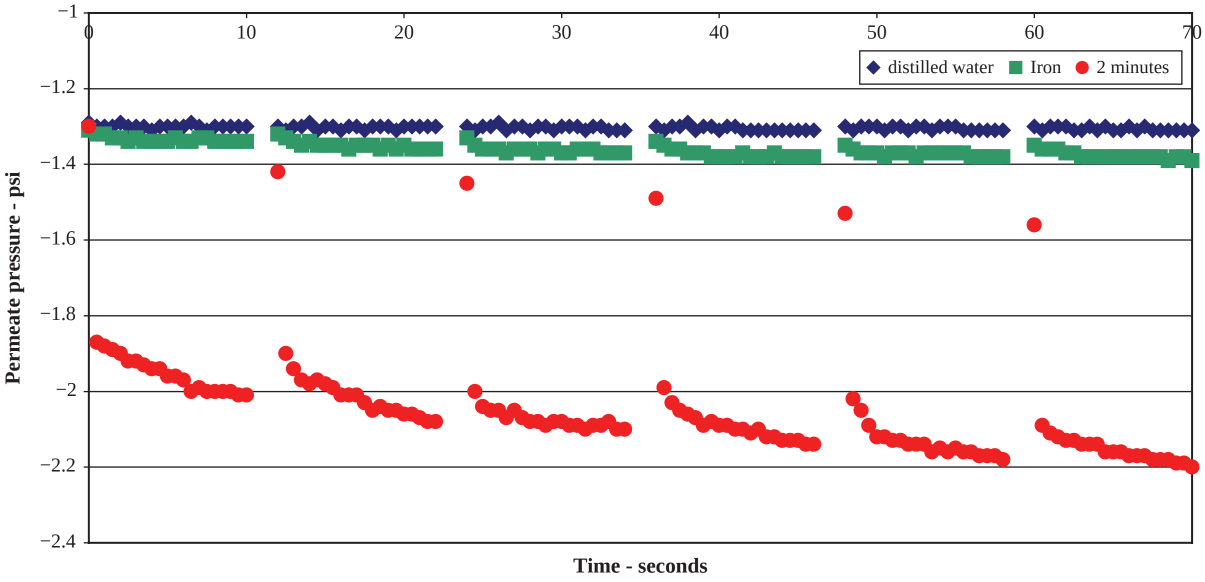


Fig. 18. The effect of residual iron on membrane performance compared with the effect of poor mixing.

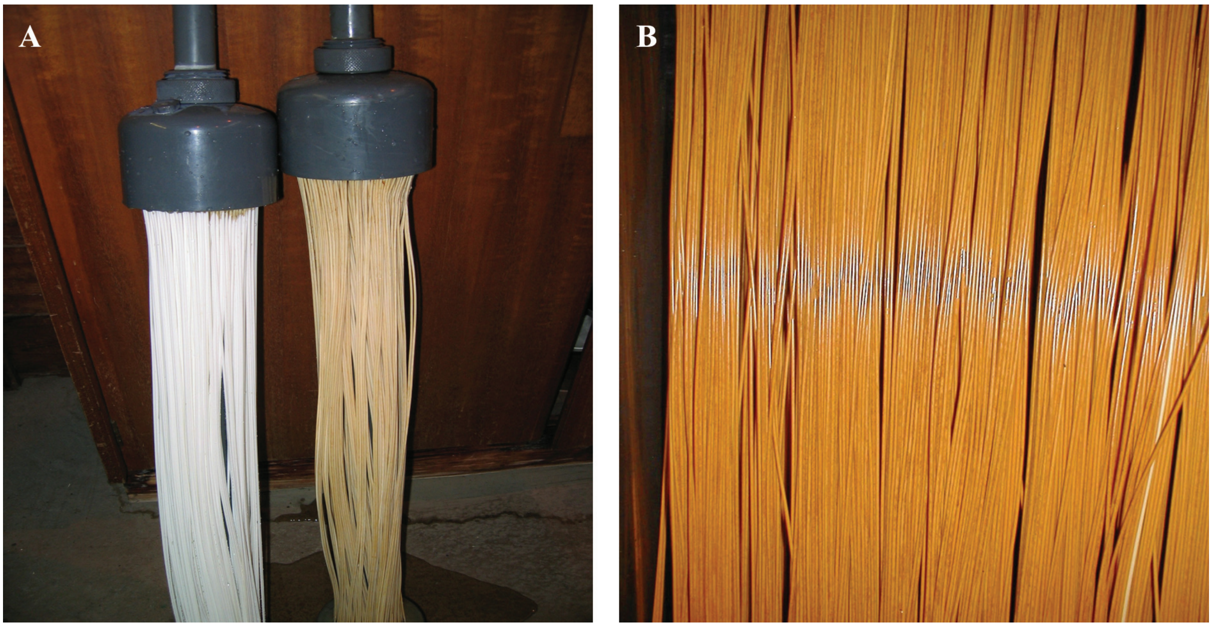


Fig. 19. (a) Appearance of clean membrane fibres (left) and after 2 weeks (right). (b) Appearance of membrane fibres after 6 months.

Although the reduction is slight, it represents a long-term problem in terms of membrane fouling. A cleaning study showed that normal cleaning at 18 °C could reverse the fouling caused by NOM. However, this was unable to remove the iron (Figs. 19 and 20).

In Fig. 19, A shows clean membrane fibres, while B shows membrane fibres after 2 weeks of running with a 0.3 mg/L coagulant overdose. There is a significant change in colour due to the iron. This is highlighted in C, which are the same membrane fibres after 6 months. SEM analysis (Fig. 20) shows that the surface of the membrane is covered with an iron-rich, solid deposit.

With an optimum coagulant dose and no residual iron, irreversible fouling of the membrane is due to NOM and can generally be remedied by normal chemical cleaning using citric acid and sodium hypochloride. Unfortunately, this does not remove the iron left on the membrane by overdosing. Experiments conducted by us (as well as by the membrane manufacturer) confirmed irreversible iron fouling. Table 2 presents results of the membrane recovery as a percent of initial performance, for four different chemical cleaning agents and three temperatures. It is clear that the cleaning solution had to be heated to 35 °C to enable a good recovery of the membrane performance. This, however, comes at the price of higher energy consumption and the increased possibility of permanent damage to the membrane caused by corrosive action of the cleaning agent.

4. Conclusions

Optimum coagulant dosage, slow mixing and temperature are all important in ensuring adequate removal of both the NOM and the added ferric coagulant – and hence to avoid downstream fouling of the membrane. Tests have shown that ZP can be used to detect changes in the coagulation process, and hence to determine appropriate dosage levels. This is important, as incomplete coagulation of naturally present colloidal iron has a detrimental effect on UF membrane performance, particularly as a result of fouling caused by residual iron. Similarly, overdosing of coagulant iron will also lead to problems. Submerged

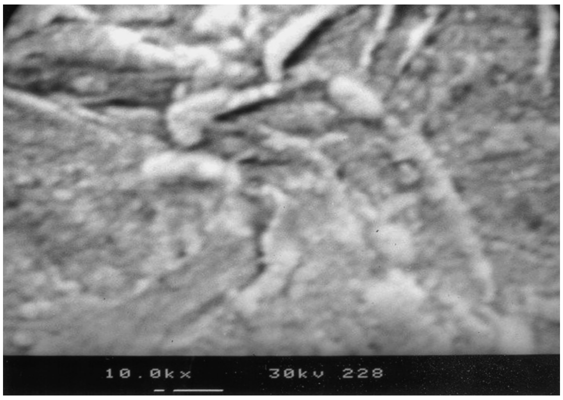


Fig. 20. SEM image of surface of membrane fibres after 6 months.

Table 2
Percent membrane recovery with chemical cleaning at three different temperatures

Cleaning agent	$T = 4$ °C	$T = 18$ °C	$T = 35$ °C
Sodium hypochlorite (%)	2	72	95
Hydrochloric acid (%)	1	51	80
EDTA (%)	1	19	21
Sodium bisulphate (%)	1	22	23

hollow-fibre membrane units yield superior performance to tube-side fed units when used in conjunction with pre-coagulation, and sufficient slow mixing of coagulant guarantees high permeate flow recovery after backwashing. Irreversible fouling caused by NOM can be remedied by conventional cleaning. However, fouling due to residual iron can only be removed by heating the cleaning solution. The associated costs of this cleaning are twofold; that of excess coagulant, and that of enhanced membrane degradation. Further work is thus required to address the problem of fouling caused by the residual iron.

On-going work in our laboratory is testing the use of ZP to control coagulation dosage with different water types and coagulants, including automation of the dosing regime.

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