Enhanced coagulation, flocculation and immersed ultrafiltration for treatment of low alkalinity and highly coloured upland water

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ABSTRACT

The use of pre-coagulation micro- and ultrafiltration (PC-MF/UF) technology to treat highly coloured upland waters is a relatively new application of a rapidly developing technology. The results presented indicate that there is scope for enhancement of the process by further developing and understanding the pre-treatment conditions. The major challenge faced in this work was that there are no specific references or criteria for treatment of highly coloured upland waters in terms of defining optimum pre-treatment and membrane operating conditions for process engineering purposes. It was found that the cyclical operation of the aeration system and control of pH had a significant impact in reducing the rate of TMP (trans membrane pressure development). Also, significant levels of organics were removed but limited by the relatively high organic content of the raw water. Finally, there appeared to be a limit to the flux at which the membrane could sustain long intervals between chemical cleaning.

Key words | coagulation, immersed, membrane, microfiltration, operation, ultrafiltration

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INTRODUCTION

The application of micro- and ultrafiltration (MF/UF) to surface water treatment is to some extent limited by the fouling due to natural organic matter (NOM). A significant amount of research and a large number of pilot trials have been carried out demonstrating the efficacy of the pre-coagulation micro- and ultrafiltration (PC-MF/UF) process. There is some evidence to suggest that a PC-UF/MF process can successfully operate with reduced flocculation times and hence much smaller floc sizes compared with conventional water treatment processes (Judd & Hillis 2001) The required coagulant dose might also be expected to be lower than the conventional treatment processes (Lerch *et al.* 2005), since coagulant selection and process operation can be optimised for NOM removal at low pH values and lower coagulant doses rather than turbidity (colloidal material) removal and production of a floc amenable to removal by flotation or sedimentation under 'sweep-floc' conditions of higher pH and higher doses (O'Melia 1969; O'Melia & Dempsey 1982; Randtke 1988; Fearing *et al.* 2004).

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Coagulation readily removes large molecular weight (MW) hydrophobic fractions, such as humic and fulvic acid, by charge-neutralisation. The carboxylic groups of the organic matter are negative and are neutralised by the cationic charge provided by the coagulant metal ions. It has been shown that dissolved organic matter (DOM) removal is greater in the charge-neutralisation coagulation pH zone than in the sweep-flocculation zone (O'Melia 1969; O'Melia & Dempsey 1982; Randtke 1988; Fearing *et al.* 2004).

Experience with conventional clarification processes shows that ferric coagulants generally achieve slightly greater NOM removals than aluminium-based coagulants (Fearing *et al.* 2004), and that this is probably due to an enhanced ability to remove intermediate molecular weight (IMW) polyhydroxyaromatics, which have been identified as a key component of recalcitrant NOM. This ability may relate to the vacant *d*-orbital of FeIII, which provides a Lewis base reactive site (a Lewis base being any species with a reactive electron pair), such that iron can form specific chemical bonds with acidic species. Trivalent aluminium does not have this ability, and so cannot form specific chemical bonds in the way that iron can.

Fouling of membranes is generally categorised as being either reversible or irreversible; the latter is only substantially removed by chemical cleaning. Fouling mechanisms generally comprise:

- Coverage of the membrane surface (cake formation). This is the dominant mechanism for UF membranes and leads to measurable retention of the foulant which is largely reversible (i.e. removed by backflushing)
- Foulant adsorption within membranes pores (pore blockage). This is dominant for MF and is less reversible than cake formation (Carroll *et al.* 2000; Fan *et al.* 2000; Lee *et al.* 2002).

It is difficult to determine optimum conditions without bespoke pilot investigations. This is because of a lack of maturity of the technology leading to an empirical approach to design of projects and the diversity of products available.

These investigations aimed to determine the optimum pre-treatment conditions for the Zenon ZW500 series of membranes for the treatment of highly coloured upland water.

PILOT OBJECTIVES

The following were the specific objectives of the pilot study:

- Determine the optimal flux and aeration scheme that will generate stable membrane performance
- Demonstrate that the PC-UF/MF process will produce treated water that will meet all of the applicable standards for treating highly coloured reservoir raw water and clarified water
- Demonstrate the effectiveness of the membrane operating parameters such that chemical cleaning intervals are greater than 2 weeks.

PILOT DESCRIPTION

ZENON supplied a pilot-scale ZeeWeed® 500 out-to-in ultrafiltration system for the evaluation study consisting of three ZeeWeed® 500 membrane elements. A schematic of the ZeeWeed® 500 PC-UF process flow diagram is shown in Figure 1. The pre-treatment consisted of adding low manganese ferric sulphate coagulant to the feed stream. The pH was adjusted with sodium hydroxide to a target of 4.5 to enhance organics removal. After coagulant addition, the feed entered a flocculation tank to generate pin-sized floc that was of sufficient size to be removed by the membrane and also to generate a permeable filtration cake. The system was periodically backpulsed with permeate and every 4 hours the tank in which the immersed membranes are located was emptied (known as tank dump). Table 1 shows the initial operating conditions for the pilot plant.

RAW WATER QUALITY

The raw water to be treated is from the Peak District in the north west of England and is unique in the elevated levels of colour and the low levels of alkalinity. The alkalinity is on average 10 $\mathrm{mg\,l^{-1}}$ as $CaCO_3$ and the pH varies from 5.20 to

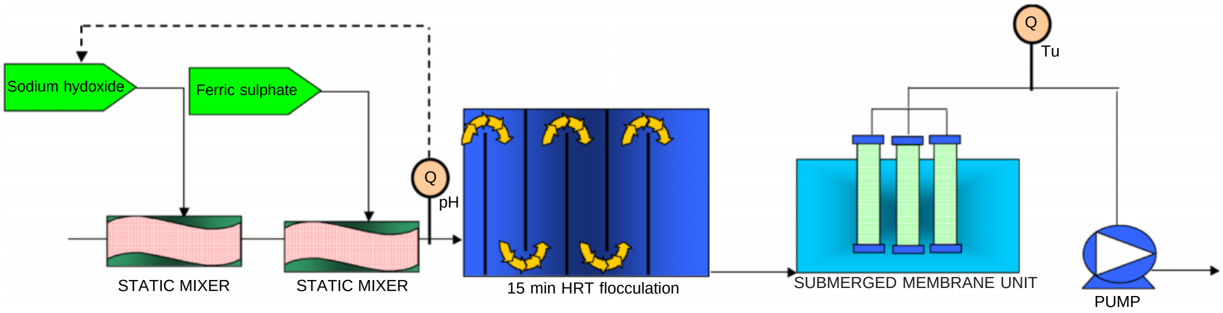


Figure 1 | Process flow diagram.

Table 1 | Initial pilot plant operating conditions

Flux	30 lmh
Aeration	During backwash
Backpulse interval	15 min
Backpulse duration	15 s
Tank drain interval	4 h

6.90. Figure 2 shows the results for raw water colour, both true (filtered) and apparent (unfiltered), for the duration of the pilot trials.

The true colour results show that from October to November true colour levels were between 180 and 200 PtCo units. From December to March levels steadily declined from 180 to 80 PtCo units and during April levels fluctuated between 60 and 80 PtCo units. These results are typical of seasonal variation in coloured upland reservoirs in the north of England. Colour exerts the majority of the coagulant demand and the data shows that coagulant dose would decline over the period shown. What is interesting is the fluctuations in colour levels on a daily basis, emphasising the need for careful control of coagulant dose for optimum operating costs. Figure 3 shows the correlation between total organic carbon (TOC) and both UV absorbance (254 nm) and colour.

Figure 3 shows a very strong correlation between both colour and UV absorbance and TOC. The TOC ranged from 4 mg l^{-1} to 11 mg l^{-1}, which is both a significant variation in concentration as well as a high level of carbon compared with other studies (Jang *et al.* 2005). Figure 4 shows the variation of specific ultraviolet absorbance (SUVA) over the duration of the trial.

Figure 4 shows that, in spite of the variation in organic content of the water, the SUVA remained consistently above 5 l mg-m^{-1} indicating the majority of organic material to be hydrophobic in nature and therefore readily removed by coagulation (Edzwald & Van Benschoten 1990).

Figures 5 and 6 show raw water iron and turbidity levels for the duration of the pilot plant investigations. Iron and turbidity levels appeared to be fairly consistent from October to December 2004; however levels of both iron and turbidity increased significantly in January and did not return to 'normal' levels until April 2005.

MEMBRANE OPERATIONAL PERFORMANCE

The ZeeWeed® 500 pilot trial commenced in November 2004 at an instantaneous flux of 30 lmh (litres $m^{-2} h^{-1}$). Full tank drains occurred every 4 hours giving a recovery of 92%. The

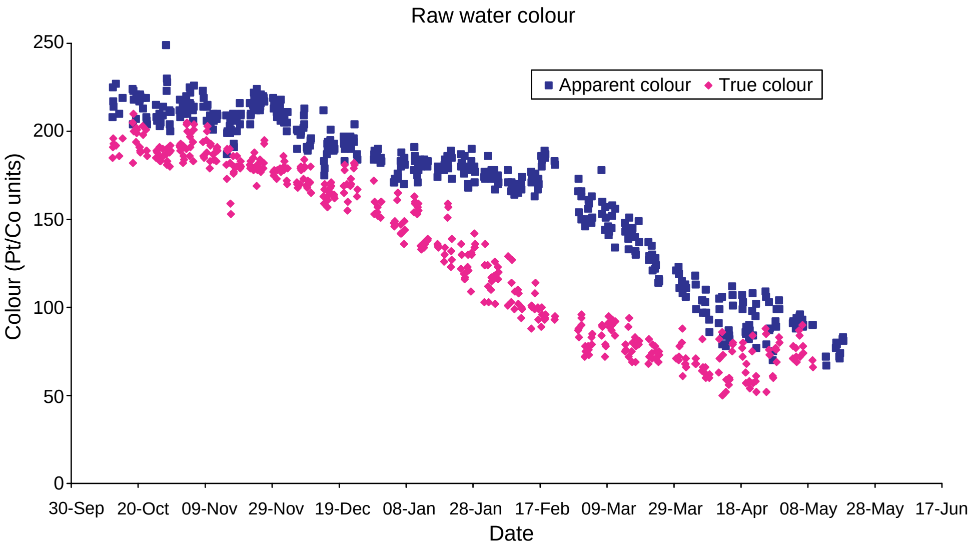


Figure 2 | Raw water colour October 2004 to April 2005.

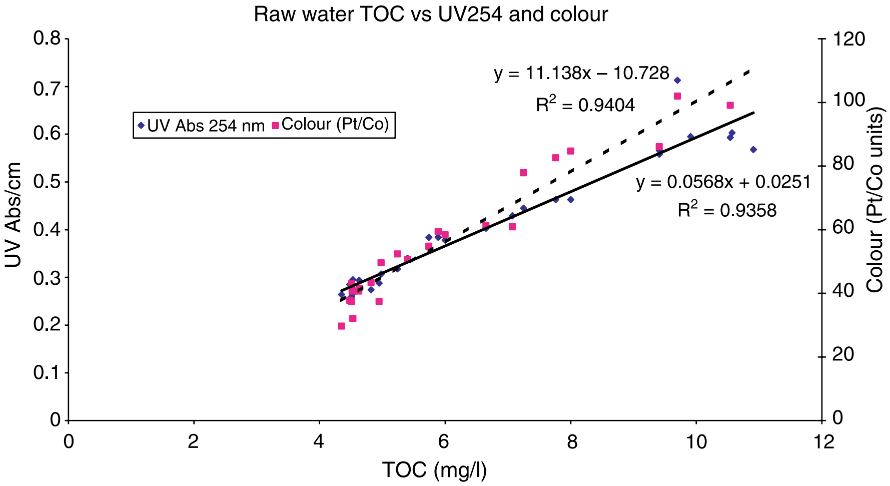


Figure 3 | Relationship of TOC with colour and UV absorbance.

backpulse frequency was 15 min and the duration 15 seconds. Aeration occurred only during backpulse and was set at 28.9 $Nm^3 h^{-1}$ (15.5 scfm). The enhanced coagulation pretreatment was configured initially using 8.5 $mg\,l^{-1}$ (as Fe^{3+}) (see Figure 7) of ferric sulphate and a target pH of 4.5 with a flocculation hydraulic retention time (HRT) of 15 minutes. The coagulation doses used reflect the elevated level of organic material and are similar to those reported by others treating highly coloured upland water (Pikkarainen *et al.* 2004).

Figure 7 shows that it is possible to achieve almost total colour removal under optimum pH and coagulant dose conditions, this is in line with the nature of the coloured organic material as hydrophobic due to its high SUVA (Edzwald & Van Benschoten 1990). The optimum coagulant dose determined form this jar-test was 8.5 to 9.0 $mg\,l^{-1}$, which is the point of maximum measurable organic removal. Jar-tests were performed throughout the trials to establish optimum coagulant dosing as the colour levels reduced (Figure 2). Coagulant doses gradually decreased as raw water colour levels declined. Figure 8 shows the flux and TMP development from November to December 2004.

Initially, the TMP increased from 22 kPa on 29 November to 52 kPa on 5 December, giving an average rate of 4.3 kPa per day, translating into an expected cleaning interval of approximately two weeks. Review of the coagulant dosing and pH control system showed that the pH control system was unable to keep the pH within

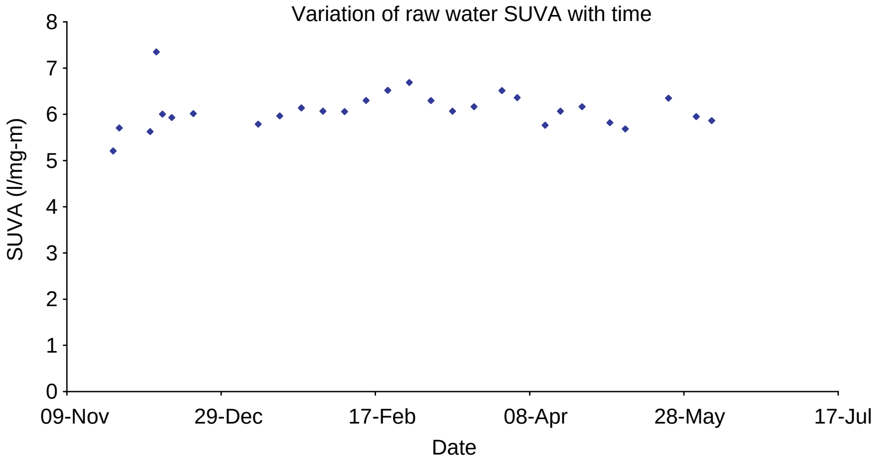


Figure 4 | Variation of raw water SUVA November 2004 to April 2005.

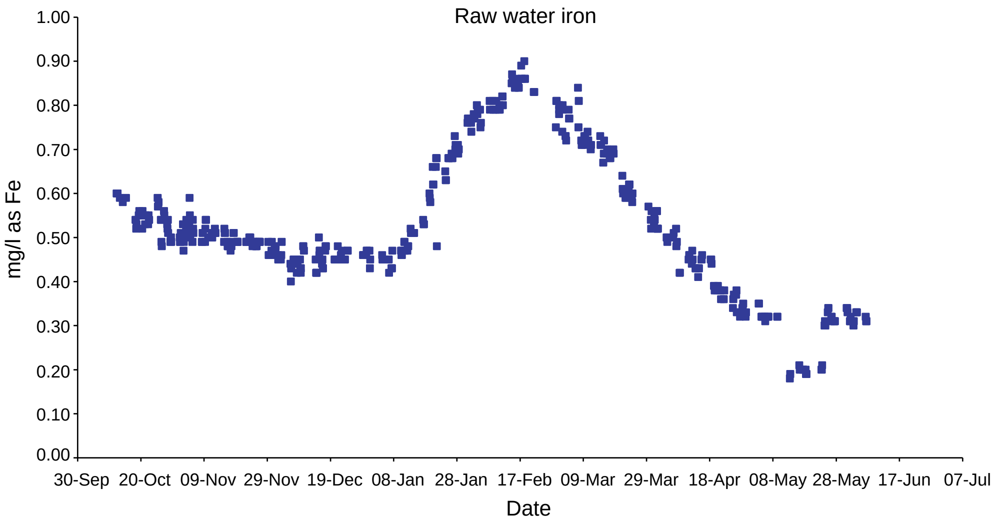


Figure 5 | Raw water iron October 2004 to April 2005.

the operating range set for the study. The pH ranged from 4.4 up to 6.1 with several spikes over 6.5 and average pH of 5.2 against a required target pH of 4.5 for optimum organics removal.

The pH control was improved by adjusting the sodium hydroxide dosing upstream of the floc tank. The impact of improved pH control can be seen in Figure 8. There was an initial recovery of TMP from 52 kPa to 32 kPa followed by a reduced rate of TMP development to 47 kPa over a 10 day period, an average of 1.5 kPa per day, which extrapolates to an interval between chemical cleans of 6 weeks (from clean membrane TMP of 22 kPa to a maximum TMP of 85 kPa). This translates into a threefold reduction in the rate of TMP development. This may be due to changes in the formation and nature of the flocculated material, in terms of its specific cake resistance, resulting in a reduction as optimum pH conditions for coagulation are achieved (Judd & Hillis 2001; Soffer

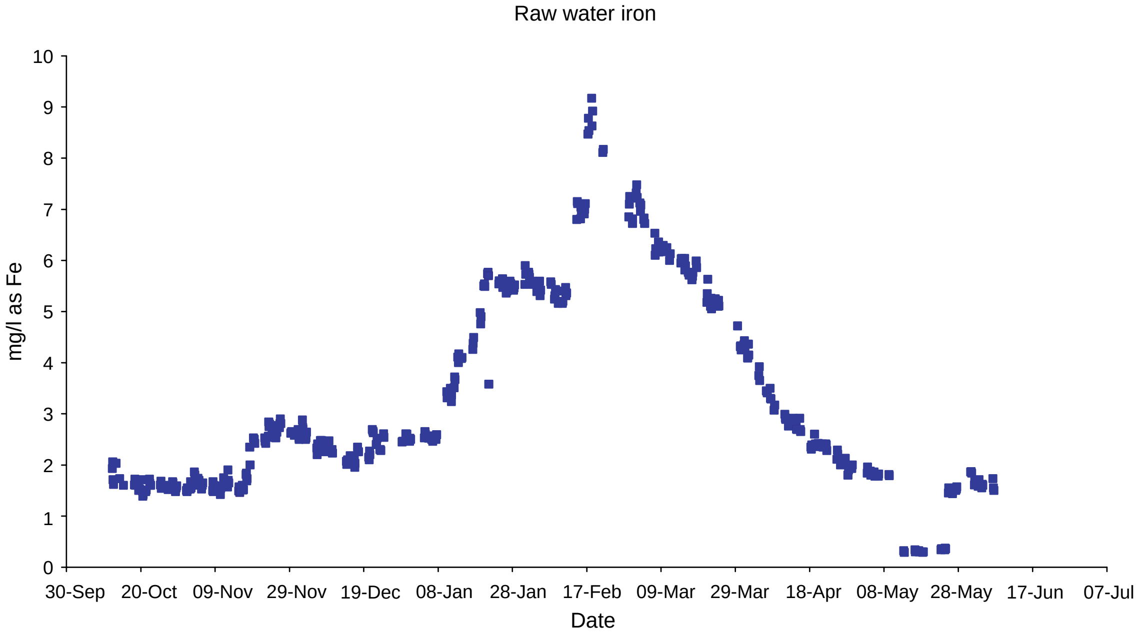


Figure 6 | Raw water turbidity October 2004 to April 2005.

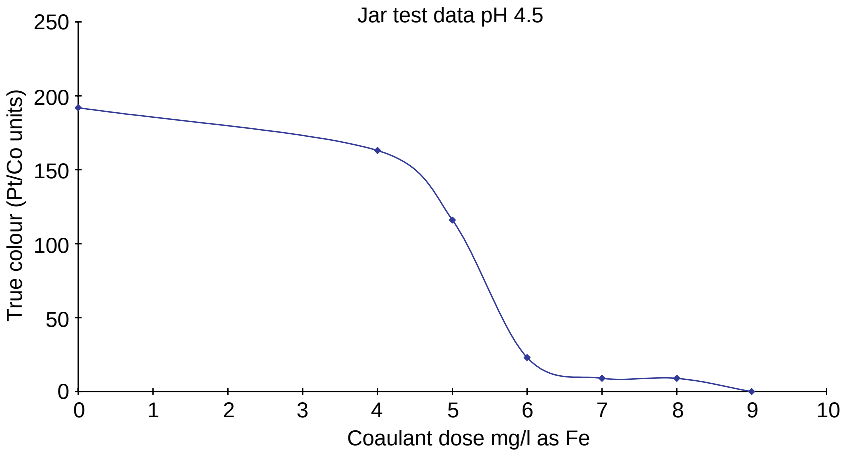


Figure 7 | Jar-test results for determination of optimum ferric dose at pH 4.5.

et al. 2005). There was also a reduction in the raw water colour and subsequent reduction in solids load; however the magnitude of this reduction cannot explain the step change in improvement in TMP development.

Figure 9 shows the rate of TMP development with time following a two-week shutdown during December 2004; initial operating conditions remained unchanged. The membranes were left soaking in a 50 mg l^{-1} chlorine solution for the duration of the holiday period.

Figure 9 shows that upon restart the TMP had recovered from the December shutdown level of 30 kPa to 15 kPa, this is attributed to the cleaning effect of soaking the membranes in the chlorine solution. However, what is apparent is that TMP levels quickly returned to 30 kPa demonstrating that the effect of low-level chlorine soaking was only transient. TMP developed rapidly at or around 10 January; this coincided with an increase in raw water iron and turbidity levels. The operating conditions were changed on 20 January to counter this effect: aeration was put on continuously. This had the effect of recovering the TMP and subsequently controlling it. Since continuous aeration is a relatively expensive mode of operation the operation was changed to a cyclical aeration regime of 10 seconds on 10 seconds off. The switch to cyclical aeration had no

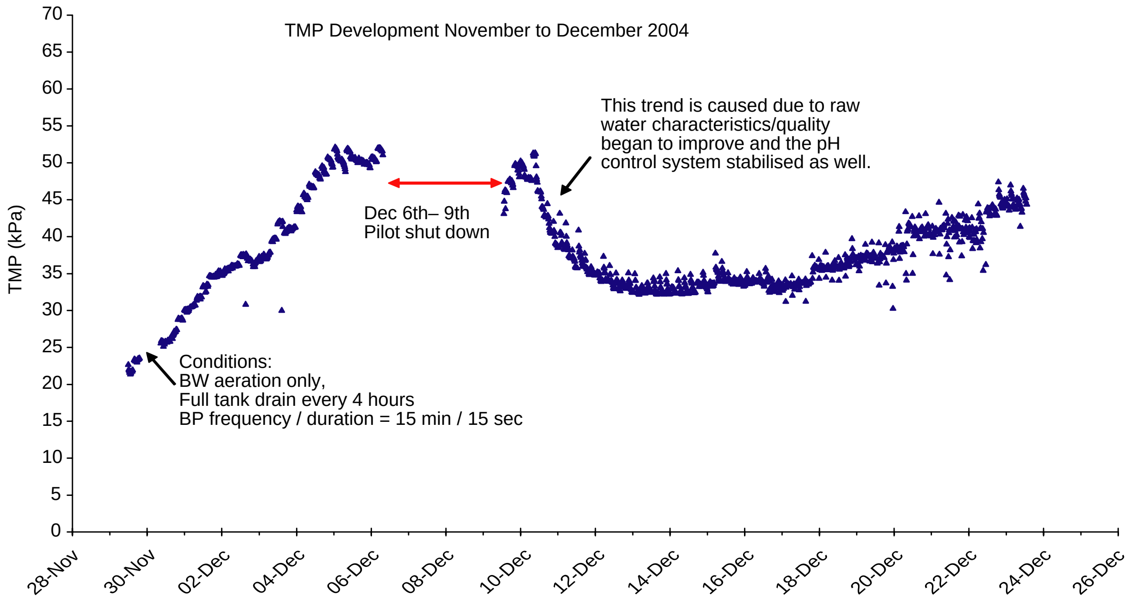
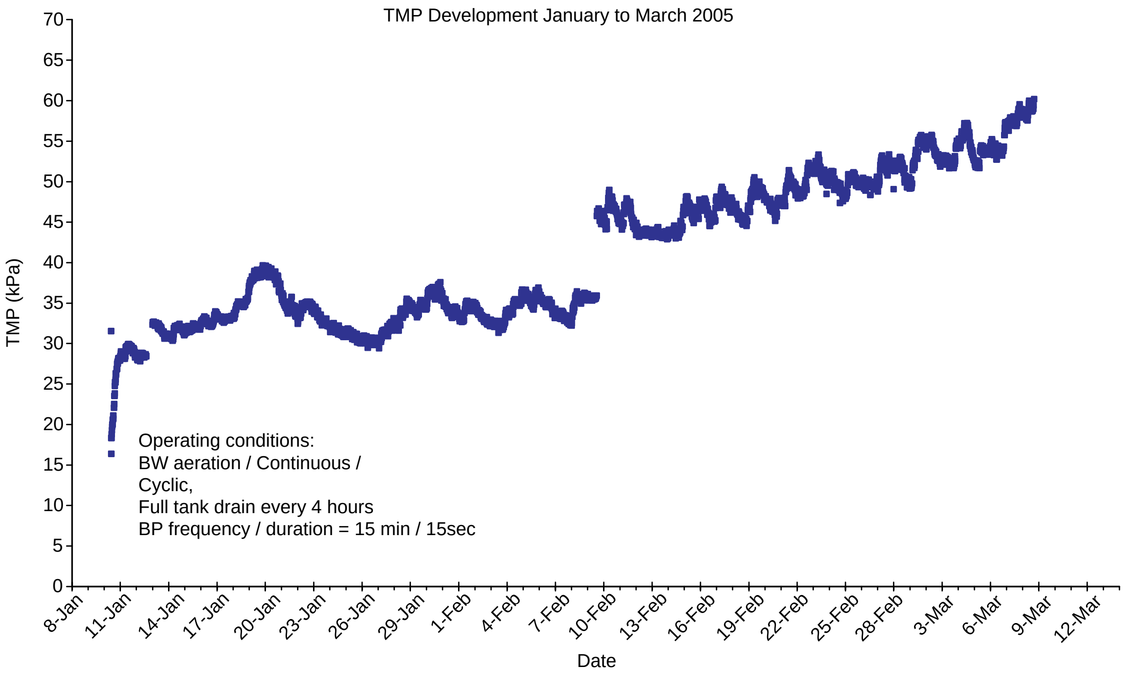


Figure 8 | Flux and TMP from November to December 2004.

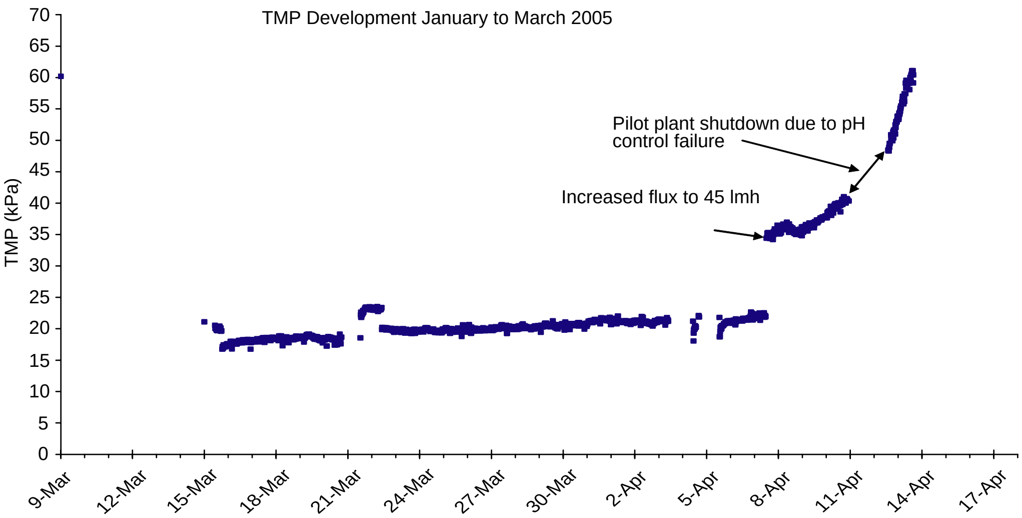

TMP Development January to March 2005

Operating conditions:
BW aeration / Continuous /
Cyclic,
Full tank drain every 4 hours
BP frequency / duration = 15 min / 15sec

Figure 9 | TMP development January to March 2005.

detrimental effect on TMP development. The plant continued to operate with steady TMP development until the middle of March 2005 when a chemical clean was carried out. Figure 10 shows the final operation of the plant from 15 March until 17 April.

Figure 10 shows continued steady TMP development with time at a flux of 30 lmh from 17 kPa to 21 kPa over a 23-day period, indicating low fouling of the membrane. On 8 April the flux was increased without cleaning the membrane, because of the low TMP, to 45 lmh and the immediate effect was a stepped increase in the TMP development owing to the greater flow through the membrane. The rate of TMP development increased to 2.1 kPa per day compared with a development rate of approximately 0.1 kPa per day at a flux of 30 lmh. This deterioration in performance cannot be wholly explained by


TMP Development January to March 2005

Pilot plant shutdown due to pH control failure

Increased flux to 45 lmh

Figure 10 | TMP development March to April 2005.

the 50% increase in flux and seems to indicate a non-linear relationship with TMP development and flux possibly in line with the concept of critical flux in crossflow filtration (Field *et al.* 1995). Also, the HRT of the flocculation tank would have reduced at the increased flow affecting the floc-size distribution of the feed water and thus reducing the permeability of the cake layer (Cho *et al.* 2005).

WATER QUALITY

In addition to on-line feed and permeate turbidity monitoring, a wide spectrum of analytical testing was conducted. Water samples were collected three times per day for on-site analysis and daily for external testing. Since turbidity, colour and iron are of key interest, these results are discussed individually in the following subsections.

Turbidity

The permeate turbidity was below 0.05 NTU for 99% of the time demonstrating the effective removal of the flocculated particles. The average permeate turbidity was 0.036 NTU.

Organics

Current UK regulations (Water Supply Regulations 2000) allow for 20 mg l^{-1} PtCo units of true colour in distributed water. Figure 11 shows that colour levels in the permeate could not consistently meet the regulatory requirement of 20 PtCo units. As discussed previously, the early part of the trial suffered pH control problems where pH was higher than the optimum for colour and NOM removal. However, even with improved pH control colour removal was erratic with occasional excursions about the regulatory limit. As colour levels dropped below 200 Pt/Co units, permeate colour stabilised indicating a limitation to the amount of colour removed by the coagulation process. Of the 160 colour measurement taken only eight exceeded the regulatory limit and all of these occurred when colour levels were in excess of 200 Pt/Co units. Since raw water colour levels were at times in excess of 200 PtCo units the PC-UF process showed colour removal in excess of 90% indicating a significant proportion of the colour to be hydrophobic and readily removed by coagulation. Figure 12 shows that the levels of SUVA in the raw water and permeate remained fairly constant for the duration of the trial indicating that the organic character of the water did not undergo a significant shift in its hydrophobicity.

Dissolved iron

The UK regulations (DWI Guidance on the Water Supply Regulations 2000) stipulate a maximum iron concentration

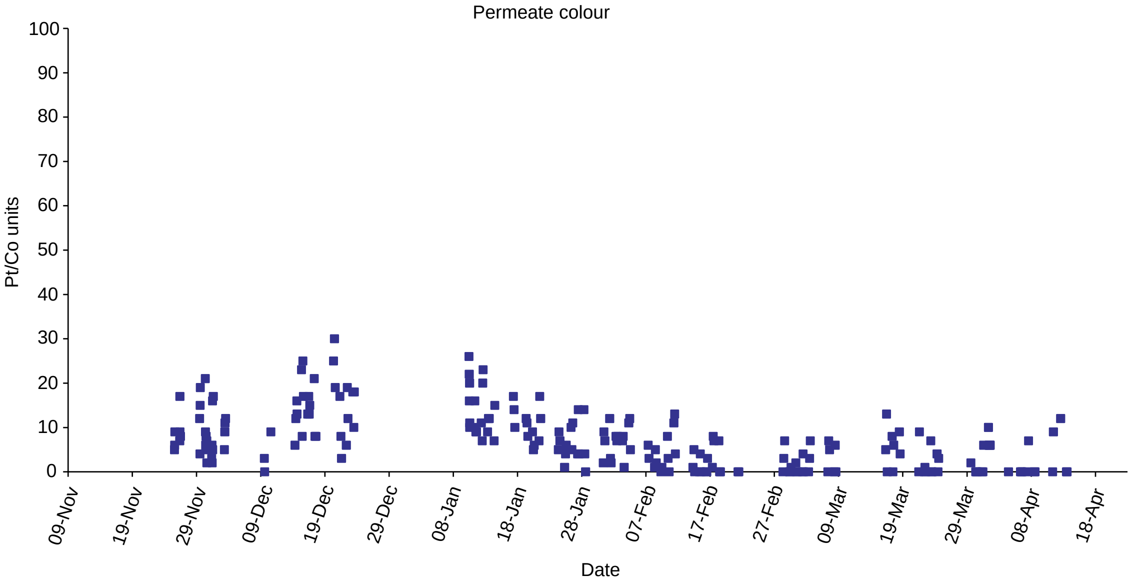


Figure 11 | Permeate colour levels.

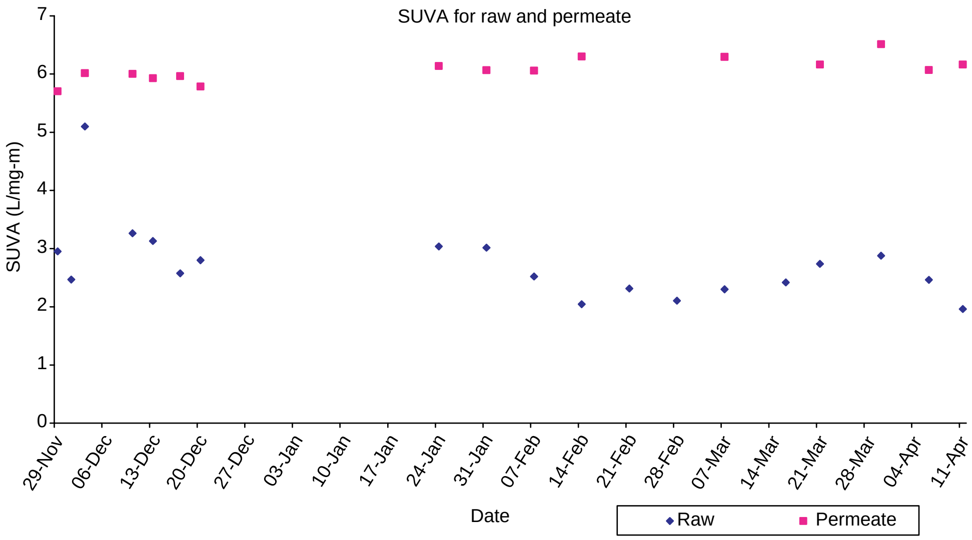


Figure 12 | Comparison of SUVA between raw water and permeate.

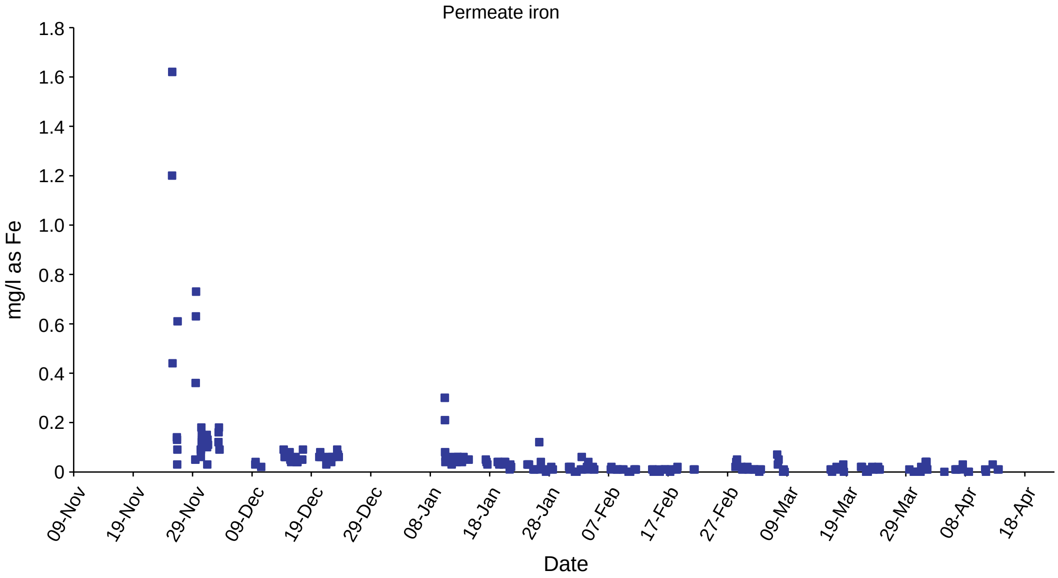


Figure 13 | Permeate iron levels.

of 0.2 mg l^{-1} in drinking water. Figure 13 shows permeate iron levels.

Feed iron content remained above 0.3 mg l^{-1}, with a prolonged spike through the winter months peaking at 0.9 mg l^{-1}. Also, coagulant doses at up to 8.5 mg l^{-1} as Fe were used during the trial. Permeate iron was mostly less than 0.1 mg l^{-1}, and less than 0.05 mg l^{-1} for 62.5% of the measurements. This again demonstrates the effective removal of pre-formed ferric flocculated material by the membrane.

CONCLUSIONS

The pilot plant was able to demonstrate successful treatment of difficult raw water, i.e. a low alkalinity, coloured, upland source. Optimum pH conditions were found to be beneficial to control of TMP development. During periods of poor pH control the system fouled more rapidly; however once control was re-established performance improved. Interestingly, the loss of pH control did not appear to result in irreversible fouling as evidenced by the recovery of TMP using backpulse only.

Stable membrane performance with a predicted cleaning interval of approximately 6 weeks, at peak colour levels, was demonstrated at an instantaneous flux of 30 lmh with ferric sulphate as coagulant, at 92% recovery, a backpulse frequency/duration of 15 min/15 s, 28.9 $\mathrm{Nm}^3\,\mathrm{h}^{-1}$ aeration in intervals of 10 seconds on and 10 seconds off, and a full tank dump every 4 hours.

Increasing flux rates from 30 lmh to 45 lmh produced a rapid increase in TMP development indicating that the flux rate could not be sustained under the operating regime employed. This increase was experienced at a stage in the trial when the membrane fouling was being controlled, as shown by the low level of TMP development, by the backwash operating conditions. In addition, the organic quality of the raw water had reduced and thus the coagulant dose was also reduced indicating that this observation may be independent of feed solids concentration. Also, a reduction in the HRT of the flocculation tank may have altered the permeability of the filter cake due to a reduction in the floc-size.

Iron removal was more affected by loss of pH control as shown by the increases in permeate iron during periods of unstable pH. This may explain why the fouling of the membranes was reversible since if the major component of the fouling was organic then it would be expected that this would only be removed by chemical cleaning.

Jar-tests showed that it is possible to achieve very high levels of colour removal under optimum pH and coagulant dose conditions; this is due to the hydrophobic nature of the organic material as shown by the high SUVA values. At times the PC-MF/UF process was capable of reproducing similar performance to the jar-test; however, at colour levels in excess of 200 Pt/Co units, colour removal was erratic although removal was still 90%.

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