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Diagnosing Fouling of Hollow Fibre MF Membranes in Wastewater Reclamation

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Abstract

Fouling in membrane filtration processes is problematic but inevitable as it occurs with the retention of contaminants that accumulate on the membrane surface. The causes of fouling are often specific, depending upon feed water constituents, the membrane, and the operation regime. Therefore, it is desirable that a thorough investigation is performed on fouled membrane elements of the affected plant. This technique is known as "membrane autopsy", which identifies the cause of poor membrane performance, and hence, gives the opportunity to rectify or mitigate the problem and improve future plant design. In this study, the cause of membrane fouling at a small water recycling plant using a hollow fibre microfiltration (MF) system is investigated. A membrane autopsy protocol has been developed for water recycling applications that consists of four major steps: I) tensile testing to investigate the membrane mechanical integrity, (II) direct visual inspection, (III) membrane surface analysis using field-emission environmental scanning electron microscopy (FESEM) (as well as atomic force microscopy (AFM) although it is not used in this case) techniques, and (IV) foulant constituent analysis. Results obtained from this study indicate that the membrane has been fouled by a mixture of colloids and organic matters, enhanced by the presence of multivalent cations. Possible measures to mitigate fouling in this particular case have also been suggested.

Keywords: Microfiltration, water recycling, wastewater treatment, fouling, membrane autopsy.

1. Introduction

One of the major problematic and inevitable issues encountered in almost any membrane filtration plant is fouling, which is caused by a number of foulants including inorganic scales, microorganisms, particulates and organic matter [1]. Fouling often results in a severe productivity loss, premature module replacement and sometimes variation in treated water quality (membrane retention). Therefore, it is desirable that a thorough autopsy investigation is performed on fouled membrane elements of the affected plant. However, membrane autopsy techniques are often sophisticated and expensive and the literature on membrane autopsy is relatively limited [2]. To date, most studies focus mainly on spiral wound modules and nanofiltration (NF) and reverse osmosis (RO) membranes [3-7].

Hollow fibre MF membranes have been successfully used in many water recycling schemes worldwide. Examples of water recycling plants using hollow fibre MF membrane filtration in Australia are Gerringong Gerroa Sewerage Scheme, Water Reclamation and Management Scheme at Sydney Olympic Park, the Illawarra Wastewater Recycling Strategy project, Luggage Point, and Rouse Hill. Summaries of these schemes can be found in a publication by Radcliff [8]. Although widely used and recognised as a well-proven technology for water recycling applications, sporadic premature failure of the membranes does happen in some cases. This is mostly due to inadequate pre-treatment, inappropriate cleaning and operating protocols, and to a much lesser extent it may be attributed to unsuitable membrane materials and module design.

Driven by the need to better understand the performance of hollow fibre MF membranes in a water recycling context, this study aims at

- Investigating the fouling processes specific to a water recycling plant using hollow fibre MF membranes,
- Identifying major foulants and fouling mechanisms relevant to water recycling applications, and
- Providing suggestions to improve the performance of hollow fibre MF membrane filtration process.

2. Description of the Taronga Zoo water recycling plant

Due to contamination of Sydney harbour, Taronga Zoo launched a program to improve the quality of the runoff in partnership with Clean up Australia, Sydney Water Corporation and Department of Health. The existing primary water treatment system, was upgraded to deal with the additional contaminants from the runoff and the first flush runoff and wastewater from animal cage wash downs and moats was directed through this treatment plant. The treatment involves microfiltration as well as ultraviolet treatment for disinfection. Pictures of the treatment plant are shown in Figure 1 and a schematic of the core treatment processes in Figure 2.

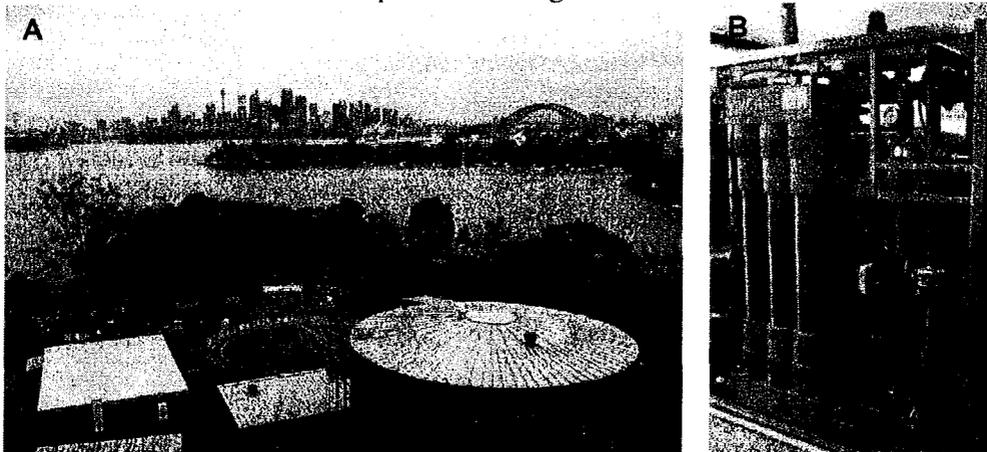


Figure 1 Taronga Zoo water reclamation plant (A) water reclamation plant overlooking Sydney Harbour and (B) microfiltration unit.

Wastewater mainly consists of stormwater, hose down runoffs, and moat fillings. After flowing through a screen and a grit removal chamber, the water is biologically treated with an ANI-Kruger unit. Following intermittent biological treatment, the effluent is filtered using a hollow fibre MF system before being stored in a holding tank.

The treated wastewater is reused by the zoo to wash down animal enclosures, irrigating the Zoo's parks and gardens, refill moats, and flush public toilets (see Figure 3). Feed water quality was not monitored extensively prior to this study, hence no analysis of likely foulants in the feedwater can be provided. However, as stormwater, exhibit and road hose downs make up most of the feed water, suspended solid content and turbidity are expected to vary significantly. Current on-going construction at the site is possibly further contributing to such variation and peak loads. Limited water analysis indicates that suspended solids can be as high as 585 mg/L (see

Table 1).

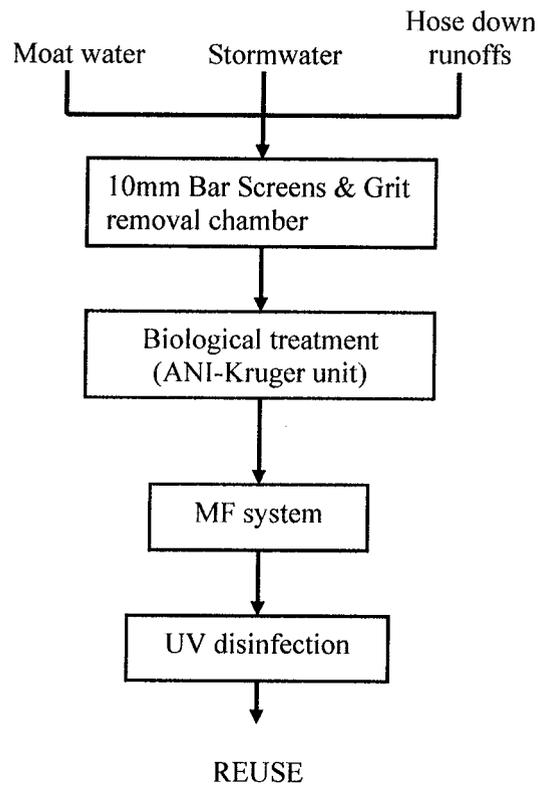


Figure 2 Schematic diagram of the wastewater treatment process in Taronga zoo. Various intermediate storage reservoirs are not included in the schematic.

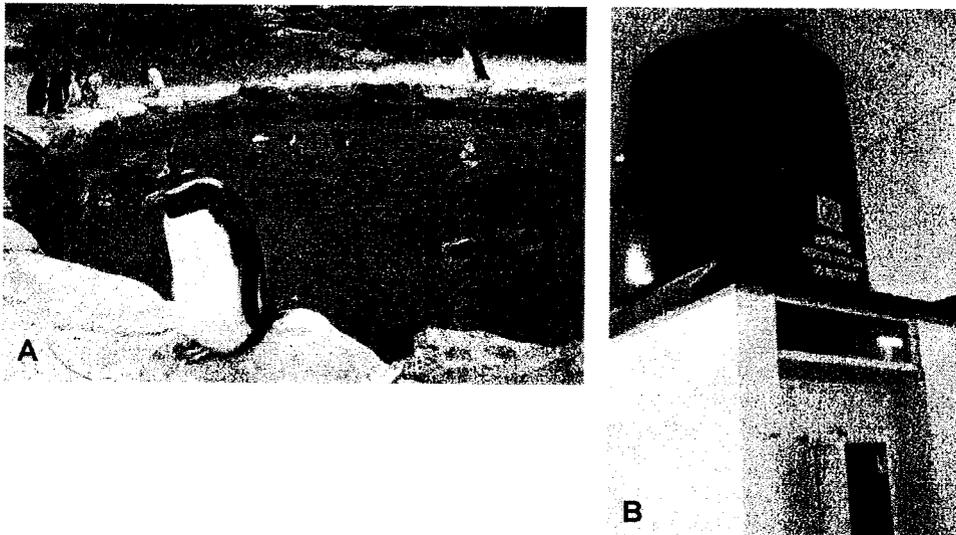


Figure 3 Usage of Water in (A) animal moats and (B) toilet flushing in the Zoo's public toilets.

Table 1: Influent quality to the wastewater reclamation plant (adapted from [9])

	Minimum	Maximum	Average
Dry Weather Flow (m ³ /day)	100	650	250
BOD (mg/L)	2	185	29
Suspended Solids (mg/L)	1	585	80
Total Nitrogen (mg/L)	2.5	27.1	7.2
Total Phosphorus (mg/L)	0.2	4.5	0.9
Faecal Coliforms (cfu/100mL)	103	109	106

3. Materials and methods

3.1. Origin of the membranes

A hollow fibre MF membrane element taken from the water recycling plant is used in this study. The fibres were taken from one replaced module (all six modules are operated in parallel) and it is anticipated that current construction activities in the Zoo adversely affect the module performance due to high suspended solids in the runoff.

3.2. Mechanical strength

Mechanical properties of the membrane fibres were examined using an Instron 4302 tensile testing instrument shown in Figure 4. Load cell and loading rate were 10 N and 50 mm/min respectively. Sample length of 200 mm was selected for study.

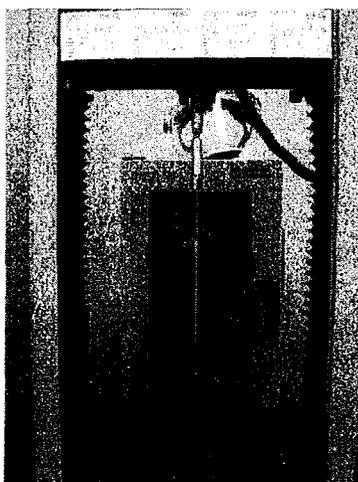


Figure 4: Picture of an Instron 4302 tensile testing instrument.

3.3. Visual analysis

The fouled membrane was carefully inspected using a light microscope (Leica DMR Research Microscope), which is equipped with a digital camera. Direct visual observation of the membrane surface and the membrane element was also conducted. High resolution and high magnification images of the membrane surface were taken using a Hitachi 4500 II Field Environment Electron Microscopy (FESEM).

The FESEM was equipped with an Oxford Isis energy dispersive X-ray analyzer (EDX) that allows semi quantitative analysis of the elemental composition of the foulant layer to be performed. The excitation energy was set at 20 kV. Membrane samples were coated with carbon prior to FESEM analysis. A virgin (clean membrane) sample was also inspected for comparison purposes.

3.4. Foulant extraction

Fifteen fibres with a length of 35 cm were obtained from each membrane element for foulant extraction. They were cut into small pieces, soaked in 50 mL of 0.8 M HNO₃ or 0.1 M NaOH and then ultrasonicated for 180 mins in a typical laboratory sonication bath (Sonicare, SA, Australia). The extracted solution was neutralised using HNO₃, when caustic extracting solution was used. All reagents used in this study are of analytical grade. Standard inorganic elements of the extracted solution were analysed using a Varian ICP-OES with a simultaneous wavelength scanning and total organic content of the solution was analysed using a Shimadzu TOC-V CSH analyser.

4. Results and discussion

4.1. Mechanical strength

Tensile strength is a relatively new parameter investigated in autopsy studies. It presents the mechanical strength of the membrane fibre, and hence is directly related to material properties of the membrane. The impact of fouling on tensile strength is to date very little understood. It can be anticipated that modification of the membrane polymer will impact on the membrane tensile strength, and it will also be a general indicator of the “tiredness” of the material after extensive cleaning and backwashing. The fouled membranes may become more brittle and hence more susceptible to integrity problems or the polymer may become stretched and the actual pore size change. Elongation at break point of five virgin and five fouled membrane samples is presented in Figure 4.

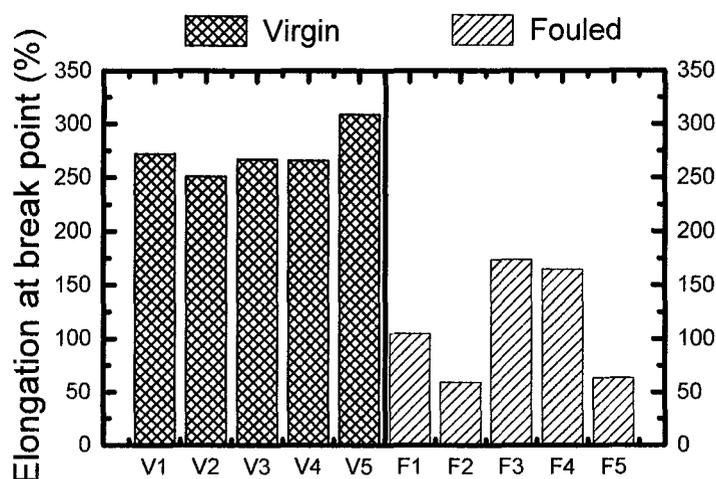


Figure 5: Elongation at break point of the fouled membrane fibres as compared to virgin membrane fibres.

In this case, it appears that the fouled membrane has become more brittle, possibly because the membrane has been allowed to dry prior to testing. This may also be attributed to normal wear and tear during the filtration process and backflush operation. A significant variation in elongation at break point can also be observed for the fouled membrane. However, it is interesting to note that both fouled and virgin membranes have approximately the same young modulus, yield point & elastic profile (data not shown). No clear evidence of material degradation could be observed for the membranes investigated.

4.2. Visual observation

A picture of the virgin, as well as fouled membranes is shown in Figure 6. Visual investigation reveals a strong discolouration of the fouled membranes with a reddish fouling layer. The fouled membrane also demonstrates a severe expansion of the fibres, presumably due to the mechanical stress of filtration and backflushing. Some fragile and brittle characteristics upon touching, in particular near the end of the modules where the fibres were attached to the plotting resin, can also be observed. This is consistent with the results obtained from mechanical testing described above.

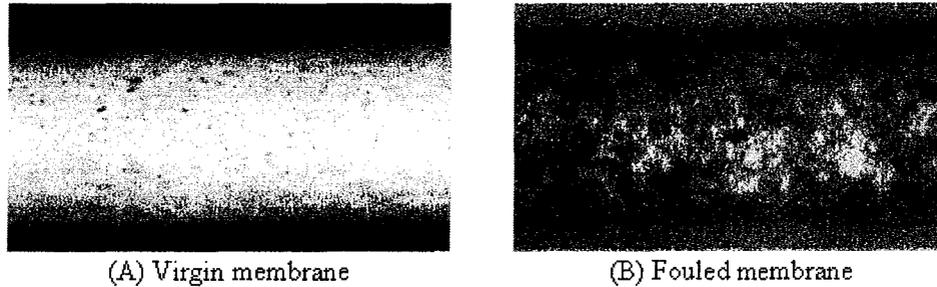


Figure 6: Light microscopic pictures of a virgin membrane (A) and fouled membrane (B). Bar presents 150 μm .

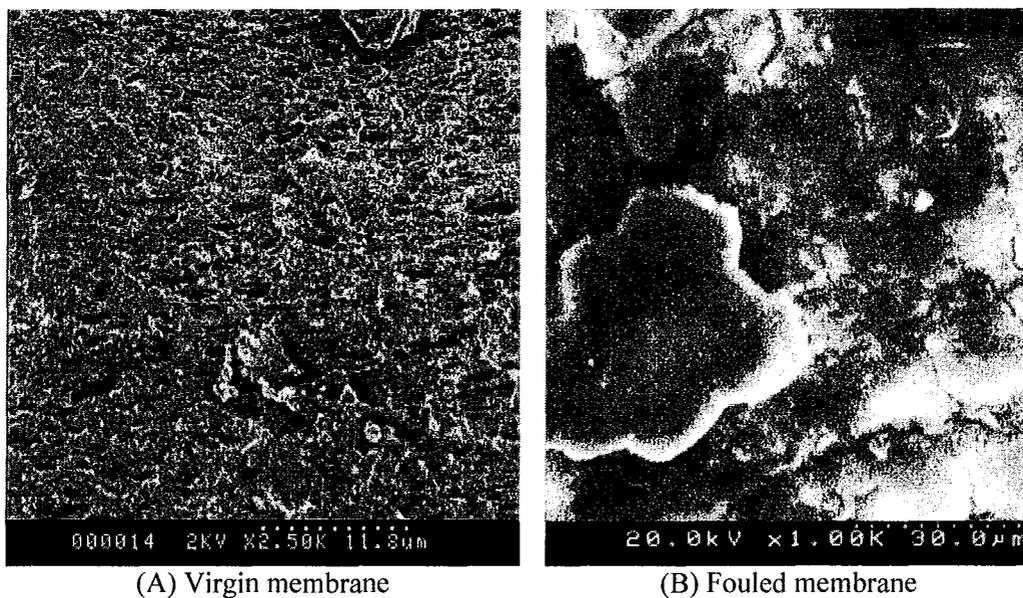


Figure 7: Electron microscopic pictures of a virgin membrane (A) and fouled membrane (B) taken by the FESEM.

The fouling layer morphology is further examined in detail and an electron microscopic picture of the fouling layer is shown in Figure 7. An electron microscopic picture of the clean membrane surface is also presented for comparison purposes. Schäfer *et al.* [1] methodically summarise four distinctive common fouling categories namely scaling/inorganic, organic, colloidal/particulate, and biofouling. There is no evidence of bacteria or fungi on the fouling layer and biofouling is unlikely the main cause in this instance. Figure 7 reveals a firm cake layer on the membrane surface. This cake layer is probably made up of organic matters or colloidal particles or most likely the combination of both. While scaling is uncommon in microfiltration processes and no

evidence of crystallisation can be observed on the fouling layer, it is possible that multivalent cations, for example Ca^{2+} , can act to cement colloidal particles, organic matters, and the membrane surface one another as previously shown in another of our study [10]. This phenomenon has also been exquisitely examined by Li and Elimelech by measuring attractive force between these entities with and without the presence of multivalent cations [11].

It is noteworthy that a reddish colour observed in Figure 6 may reflect the presence of iron oxide. Clays together with silica colloids are typical particulate matters encountered in exhibit and road hose down runoffs, which make up most of the influent in this case, in particular during the construction phase. This hypothesis can be confirmed by examining the elementary composition of the fouling layer and foulant characterisation as showed in the following section.

4.3. Major foulant identification and foulant composition

The presence of metallic elements such as iron, aluminium, calcium, and magnesium is clearly evident in the energy dispersive X-ray (EDX) spectrometry graph of the fouling layer as shown in Figure 8. A significant amount of silica can also be observed. Furthermore, Figure 8 reveals a large peak of oxygen and trace amount of other non-metallic elements such as chlorine, sulphur, and phosphate. Such significant amount of oxygen may be attributed to organic matters present in the fouling layer, although it is prudent to note that it can also be from the membrane polymeric material. While a small peak of oxygen can be observed in the EDX spectrometry graph of the virgin membrane, no chlorine, sulphur, or phosphate can be found (see Figure 8).

Foulants were extracted from the fouling layer in accordance to the extraction protocol described above. Both nitric acid and sodium hydroxide were used as extracting solutions. Acidic solution is typically used to extract inorganic foulants while caustic solution is commonly used to remove organic foulants [7]. Sonication was also applied to ensure that complete extraction could be achieved. Results of the extraction study are presented in Table 2.

Despite the fact that sonication was applied, caustic solution failed to extract foulants from the fouling layer (see Table 2). This is because the fouling layer, in this case, consists predominantly of inorganics and precipitation of metal hydroxyls prevents the extraction process from occurring. The amount of organic matter extracted by the caustic solution is also less than that by the nitric acid solution. As previously discussed, metals with high valency can aggregate or complex with organic matters and hinder them from being extracted. This is consistent with visual observation that a reddish colour of the membrane persists after the extraction process with the caustic solution. In contrast, it appears that acidic solution can completely extract the foulants in this case. The amount of extracted metallic elements is in excellent agreement with EDX analysis. As can be seen in Table 2, iron, calcium, and aluminium are predominant in the fouling layer. A significant amount of organic matter measured by total organic carbon (TOC) can also be observed.

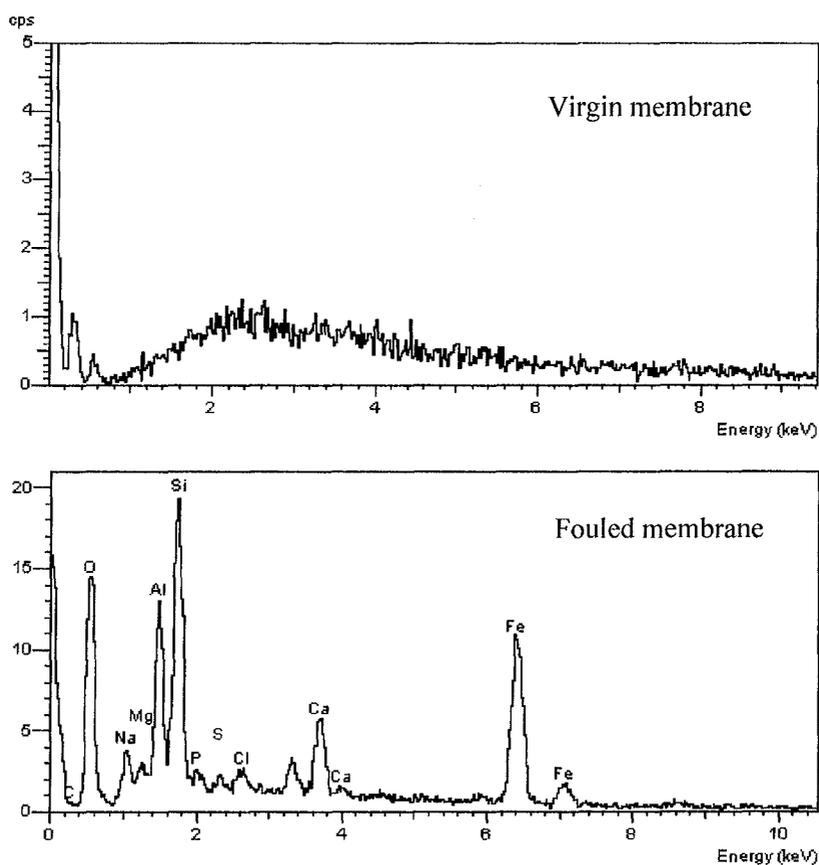


Figure 8: Energy dispersive X-ray spectrometry of the virgin membrane surface (top) and the foulant layer (bottom). Excitation energy was set at 20 000 kV (note difference in y-axis scale).

Table 2: Foulant quantity and composition extracted from the membrane by sonicating the membrane in 0.8 M HNO₃ or 0.1 M NaOH solution for 180 minutes

Foulant	Concentration in the extracted solution (mg/L)	
	Extracting solution	
	0.8 M HNO ₃	0.1 M NaOH
Al	12.9	2.4
Ca	34.3	3.5
Fe	97.2	2.0
K	1.5	1.4
Mg	4.2	0.6
Mn	3.0	0.1
Na	18.7	na*
TOC	32.4	22.6

*na-not available as sodium hydroxyl was used as the extracting solution.

4.4. Implications and possible remediation strategies

Mechanical testing indicates that no material degradation of the membrane due to exposure to oxidants or any other chemical agents has occurred, although the fouled membrane fibres appear to be slightly more brittle. Visual observation by light microscopy and FESEM combined with the results from foulant composition analysis consistently reveals that the membrane has been fouled with a mixture of colloidal

particles and organic matter. Complexation and other interactions between multivalent cations, organic matter, and colloidal particles have most likely worsened the fouling process caused by the suspended solids load itself. It is advisable to enhance pre-treatment prior to the MF unit, possibly by applying coagulants, to maintain a low and stable turbidity level in the feed. Chemical cleaning protocol and air backflushing frequency may also need to be modified for an optimal fouling mitigation approach. Monitoring of the feedwater composition over a period of time will provide further insight into the fouling process.

5. Conclusions

This study demonstrates that the membrane autopsy protocol presented here can be rigorously used to identify the cause of membrane fouling in hollow fibre MF applications. Necessary measures to mitigate fouling can then be suggested for further examination. In this particular instance, it appears that a combination of colloidal particles and organic matter enhanced by multivalent cations is the main cause of membrane fouling. It is expected that membrane fouling will strongly depend on feed water constituent composition and chemistry and also on the operation condition of the water recycling plants. In all cases, this membrane autopsy protocol will serve as a unique and valuable tool to support water recycling applications and trouble shooting. Further work is in progress to investigate the in depth fouling mechanisms and enhanced autopsy approaches.

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