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In-line Flocculation-Submersed MF/UF Membrane Hybrid System in Tertiary Wastewater Treatment

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Abstract: Coagulation/flocculation pre-treatment of feeds can successfully mitigate the drawbacks of membrane micro- and ultra filtration processes: fouling and limited ability to remove organic pollutants. Laboratory experiments conducted with a synthetic wastewater (representing biologically treated secondary effluent) using 0.1 μm pore size hollow fiber membrane showed that simple in-line flocculation pre-treatment with inorganic coagulants dramatically reduced membrane fouling rates. The hybrid system also ensured over 70% organic matter removal in terms of dissolved organic carbon (DOC). In the experiments in in-line flocculation outperformed clarification pre-treatment at optimum coagulant dosages. Differences in floc characteristics and elevated suspended solids concentrations in the membrane tank may explain this finding, but the exact causes were not investigated in this study. The beneficial effects of in-line flocculation pre-treatment to MF/UF separation were also confirmed in the treatment of septic tank effluent in a membrane bioreactor (MBR). The fouling rate of the 0.4 μm pore size (flat-sheet) membrane was substantially reduced with 10–100 mg L^{-1} ferric chloride coagulant doses, and total dissolved chemical oxygen demand (DCOD) removal also increased from 66% up to 93%. These findings are consistent with the results of other experimental studies and show that pre-treatment controls submersed MF/UF filtration performance.

Keywords: In-line flocculation, membrane, fouling, hybrid system, wastewater reuse

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INTRODUCTION

In recent years low-pressure immersed (or submersed) micro- and ultrafiltration (MF/UF) membrane systems have become popular in water treatment and wastewater reuse applications. Such plants have low energy requirements, modest capital cost due to the open tankage and inexpensive membrane material used, and easy operability. Another very important attribute is their robustness to provide good quality permeate even in rapidly changing feed quality conditions. Nonetheless, their widespread use is hindered by two major shortcomings.

MF/UF has limited ability to remove small colloidal particles and pollutants from water. In drinking water production, the presence of natural organic matter leads to disinfection by-product formation, which is a public health concern. Similarly, the effective removal of organic matter is essential in high-grade wastewater reuse applications. Another shortcoming is membrane fouling, which is the transient or irreversible loss of membrane productivity in terms of transmembrane pressure (TMP) and permeability. Fouling may be abated by various techniques, such as feed pre-treatment, using additional force fields, system operation at low fluxes, manipulating the hydrodynamic conditions, backflushing the membrane with permeate and/or air, membrane relaxation (intermittent operation), and preventive chemical treatment (1). These methods, often in combination, have been used with varying degree of success.

Coagulation and flocculation long have been employed to reduce fouling and improve organic matter removal in cross-flow MF/UF systems (2). The term "in-line flocculation" (or "in-line coagulation") in this paper refers to the use of inorganic coagulants before membrane filtration with no intermediate settling step to separate/remove the solids. Immersed MF/UF systems can also benefit from the use of coagulation/flocculation pre-treatment as first shown by Benedek et al. (3). In such systems, the free tank volume can serve as reactor space. During the last five years, some important research results were published in this particular area, reflecting the growing share of immersed membrane applications in drinking water production and wastewater reclamation. However, several aspects of hybrid membrane systems still received little or no attention to date. This manuscript presents some results obtained with feed pre-treatment using in-line flocculation prior to submersed hollow fibre and flat sheet MF/UF.

EXPERIMENTAL

Materials

In the first phase of the study a synthetic wastewater (4) was used that represented a biologically treated secondary effluent. The total dissolved

Table 1. Raw wastewater characteristics (septic tank effluent)

Parameter	Range
pH	7.2–8.5
Temperature (°C)	19–24
DCOD (mg L^{-1})	97–138
Turbidity (NTU)	140–220
Suspended solids (mg L^{-1})	380–435
Dissolved oxygen (mg L^{-1})	<1

organic carbon (DOC) and pH of this wastewater were in the range of 11.4 to 12.5 mg L^{-1} and 7.4 to 7.8, respectively, following variations in make-up tap water. In some experiments septic tank effluent were used, with major characteristics listed in Table 1.

The chemicals used in the experiments were of analytical grade, purchased from Sigma-Aldrich. For pH adjustment hydrochloric acid, sodium hydroxide and hydrated lime were used.

Apparatus

Figure 1 shows the schematic diagram of the laboratory scale immersed membrane-flocculation hybrid system used in experiments with synthetic wastewater feed. Synthetic wastewater was pumped into the membrane tank (6 L active volume) at constant flow rates. A Tee fitting connected the feed and the coagulant dosing tubes, and a small diameter tube section of variable length ensured adjustable mixing times for coagulation. Compressed

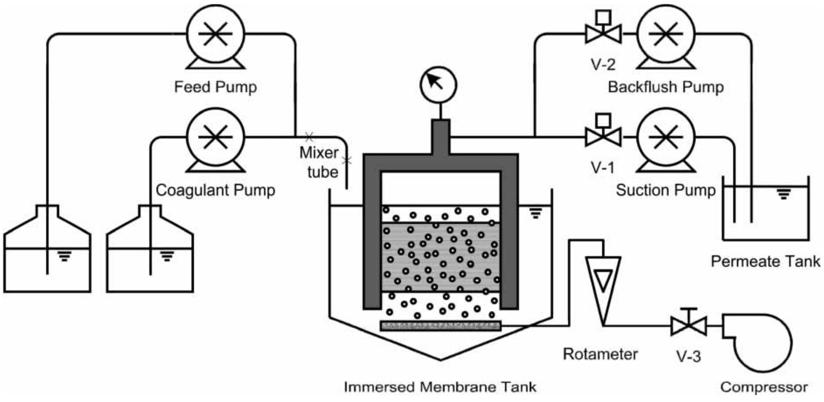

Figure 1. Schematic diagram of hollow fibre MF system.

air was introduced for aeration (10 L min^{-1} rate) via a soaker hose placed at the bottom of the membrane tank. At start-up the initial raw wastewater fill in the tank was slug-dosed with the selected coagulant. Very importantly, the membrane was immersed only after sufficient flocculation time (40 minutes) to commence filtration. In experiments with clarified feeds, wastewater was pre-treated in a separate container and the supernatant was used after two hours quiescent settling. Feed was forced through the membrane by pump suction and permeate was collected in a container for backwash supply. In these experiments a Mitsubishi hollow fiber membrane module was used (hydrophilic PE material, 0.1 μm pore size and 0.05 m^2 total area). Data acquisition and system control was provided by a PLC/SCADA system, described in detail elsewhere (5).

Consecutive experiments used a bench-scale MBR system that treated septic tank effluent (Fig. 2). The MBR tank had 12.4 L active volume and provided 5.3 hours hydraulic retention time. Dissolved oxygen (DO) levels were in the relatively high 5–7 mg L^{-1} range, since dual (fine and coarse) aerators were used to satisfy biological oxygen demand and for membrane bubbling. A relatively low 20 days sludge age was maintained with regard to the influent. The MBR system used a Kubota flat sheet type membrane (chlorinated PE material, 0.4 μm pore size and 0.059 m^2 area). In normal operation the suction pump was stopped for one minute to allow membrane relaxation after each 11 minutes of filtration. In flux decline tests, the filtration phase was maintained for two hours. Operational parameters (DO, temperature, pH, and TMP) were monitored and logged by a computer. Experimental data were corrected to 20°C temperature.

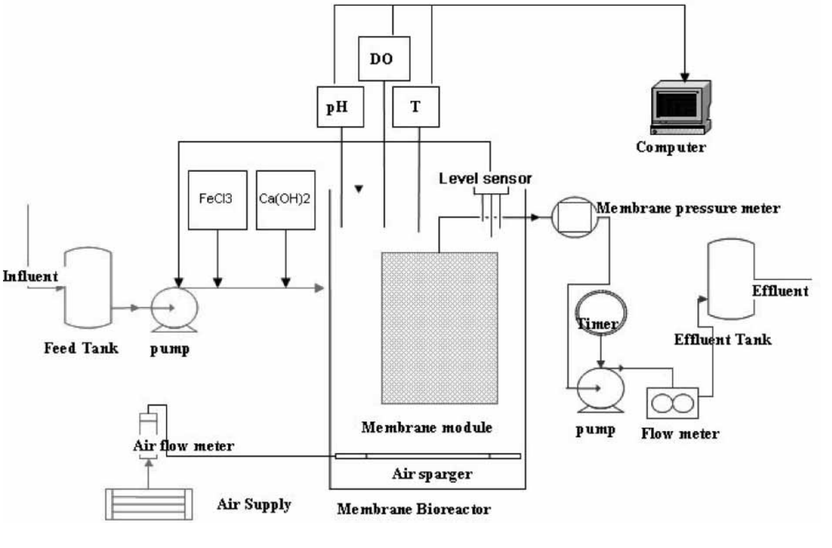

Figure 2. Schematic diagram of MBR system.

Analytical Determinations

Dissolved organic carbon contents of grab wastewater samples were determined using a Phoenix 8000 UV-Persulfonate TOC analyzer. Since all samples were filtered with 0.45 μm Millex syringe membranes, the reported values represent DOC. Turbidity and pH were measured with Hach 2000 and WTW pH-330 meters, respectively. DCOD was determined according to Standard Methods, after 0.45 μm syringe, or direct membrane unit filtration. High pressure size exclusion chromatography (HPSEC) Shimadzu, Corp., Japan with a SEC column (Protein-pak 125, Waters, Milford, USA) was used to determine the MW distributions of organics. Standards of MW of various polystyrene sulfonates were used for calibration.

RESULTS AND DISCUSSION

Filtration of Synthetic Wastewater

The first phase of experiments provided baseline fouling data, with results summarized in Fig. 3, showing the development of TMP with time at 36 L m^{-2} h^{-1} constant flux for several ferric chloride coagulant doses. For convenience, suction (vacuum) data in this paper are shown as absolute values. When no coagulant was added (0 mg L^{-1} coagulant dose) the membrane fouled very rapidly, and the experiment was terminated in about 70 minutes. In-line flocculation captured and concentrated organic matter in flocs to reduce the propensity of feed to foul the membrane. The TMP curves show a typical, rapid initial increase of fouling which lasted for a few minutes in all but one case. For

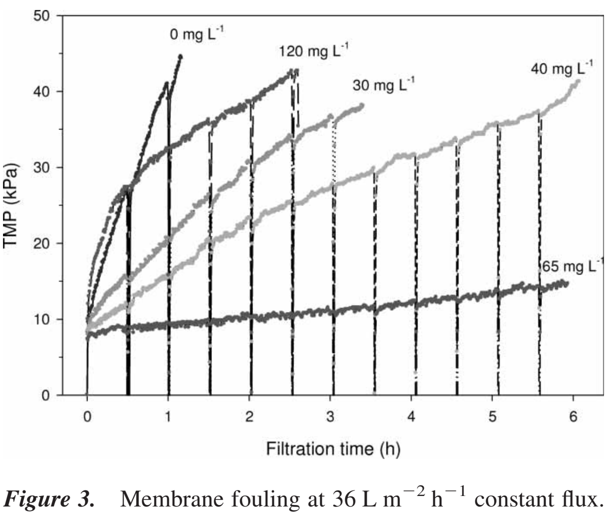

Figure 3. Membrane fouling at 36 L m^{-2} h^{-1} constant flux.

120 mg L^{-1} coagulant dose (large overdosing) this initial TMP increase persisted for approximately 25 minutes to result in a distinctly different, two-segmented curve. Related investigations revealed that this was caused by small floc sizes and poor DOC removal due to slowly progressing flocculation (results are not presented here).

The initial period of MF/UF membrane filtration was controlled by irreversible fouling due to pore plugging and/or restriction (6, 7). This initial phase was followed by the relatively slower and linear increase of TMP in cake filtration conditions, after the noted rapid transition. Since we compared fouling rates in cake filtration conditions, for the 120 mg L^{-1} curve used the second, linear segment to obtain the gradient (fouling rate). The chart reveals that TMP increase rates, which at constant flux by definition are the rates of fouling, strongly depended on applied coagulant doses. The determined irreversible membrane fouling rates are shown in Fig. 4.

The fouling rates decreased with increasing coagulant doses until an optimum dosage was reached. The same optimum coagulant dosage also resulted in minimum settled turbidities in preliminary jar tests, at near zero and slightly negative zeta potentials (charge neutralisation conditions). This finding suggests that settled jar test turbidity can be a simple and practical predictor of fouling to select optimum coagulant dosages. The linkage between residual turbidity and membrane fouling is indirect but apparently strong, and provided by the characteristics of formed flocs. Optimum flocculation provides clean supernatant in jars, and the resulting flocs yield a permeable, effective "pre-filter" cake layer on the membrane to capture foulants.

Minimum fouling occurred at 65 mg L^{-1} coagulant dose (22.38 mg L^{-1} as Fe), and was about 18 times less than for direct membrane filtration with no

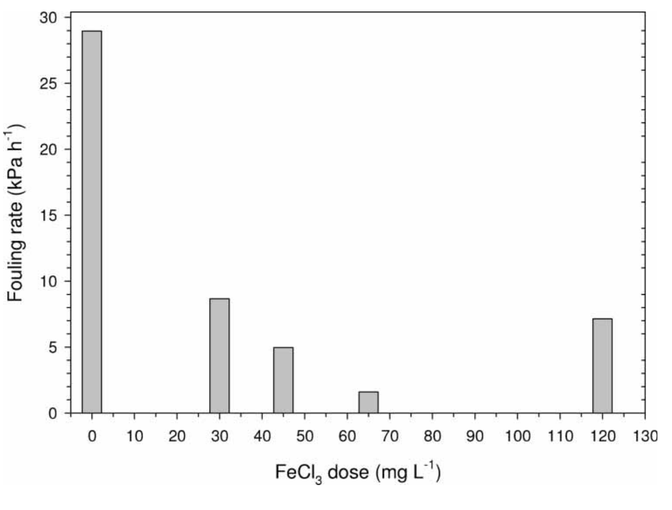

Figure 4. Effect of coagulant dosage on fouling.

coagulant addition. The obtained improvements clearly show that pre-treatment not just influenced but controlled membrane fouling.

Organic Matter Removal from Synthetic Wastewater

High-grade wastewater reuse applications require effective organic pollutant removal. Fig. 5 presents total DOC removal data as function of coagulant dose. In direct filtration mode (zero coagulant dose) the membrane removed average 23% DOC. However, this removal can be attributed more to the cake layer (acting as a dynamic membrane) than to the MF membrane itself. DOC removal was about 10% shortly after backwashes (clean membrane), and improved with time until the next backwash. Using in-line flocculation, DOC removal became up to three times more effective than for direct membrane filtration, thus it can be stated that coagulation controlled the permeate quality. The DOC removal curve shows a monotonous increase that reached a plateau at higher doses. Similar observation was reported in the literature previously (8). The UV_{254} transmittance curve showed a shape similar to that of DOC removal curve (not shown here) to indicate that this parameter could be used as a suitable surrogate measurement.

The effects of coagulation/flocculation pre-treatment on the feed can be better understood by the observation of Fig. 6. The curves were obtained using high-pressure size exclusion chromatography (HPSEC) that provides molecular weight (MW) distribution information. The chromatogram shows that flocculation pre-treatment performed at optimum dosages (at natural pH and with pH adjustment) very effectively removed the large and mid MW

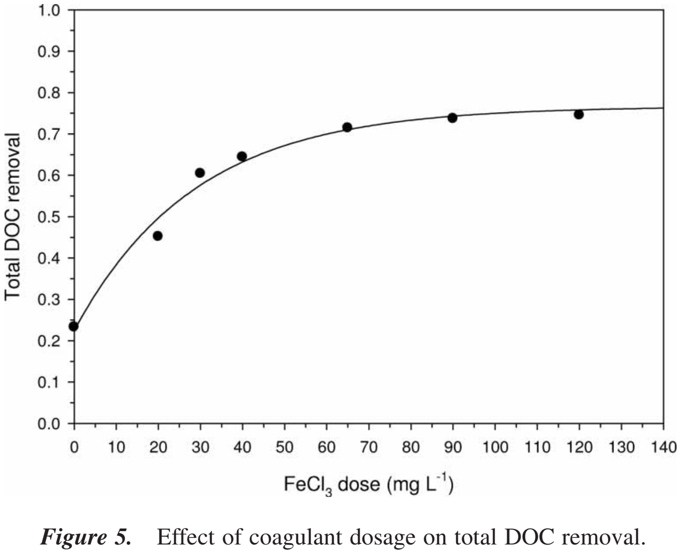

Figure 5. Effect of coagulant dosage on total DOC removal.

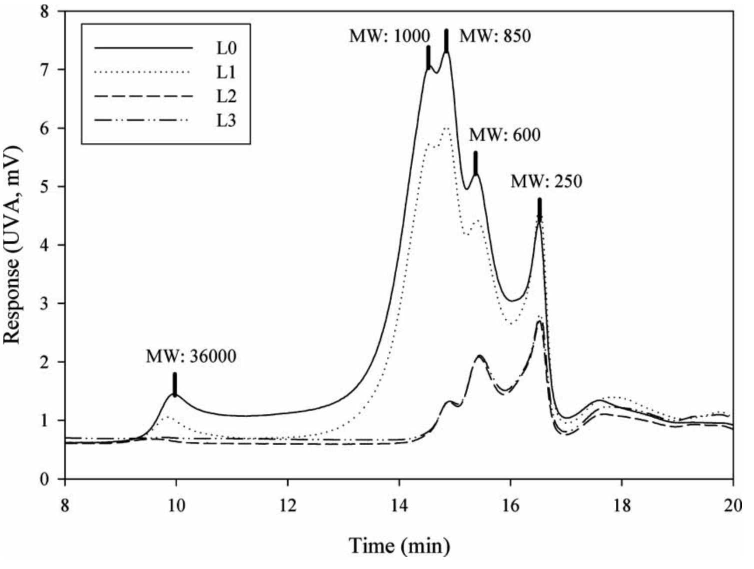

Figure 6. Molecular weight distribution (L0: raw wastewater; L1: 30 mg L^{-1} dose; L2: mg L^{-1} dose at pH 5.7; L3: 65 mg L^{-1} dose at natural pH).

fraction of organic matter and even some dissolved species. Coagulant underdosing (L1 curve) removed only a portion of high and MW fraction and very little dissolved matter. These results show that coagulation/flocculation was very effective in removing both large and small colloidal pollutants, thus able to resolve the noted shortcoming of MF/UF.

Feed Pre-treatment with Clarification and In-line Flocculation

The use of coagulation/flocculation pre-treatment with MF/UF for drinking water production was researched in recent years (8–10), with conclusions that both membrane fouling and permeate quality benefit from these processes. However, there is only scarce information available on the relative performances of in-line flocculation and clarification processes.

Immersed membranes separation is insensitive to feeds that have high suspended solids concentrations, such as occur in MBR applications. In addition, MF/UF fouling is barely affected by particles present in the feed, if they have substantially bigger size than membrane pores. Therefore, in contrast to traditional water treatment, there seem to be no pressing reason to remove flocs from the feed with gravity settling or flotation prior to filtration. Table 2 shows experimental results that confirm this assumption.

Table 2. Fouling rates for synthetic wastewater

Coagulant	Dosage[a] (mg L^{-1})	Membrane flux (L m^{-2} h^{-1})	Fouling rate (kPa h^{-1})	Note
Ferric chloride	60	36	1.66	
Ferric chloride	65	36	1.60	
Ferric chloride	65	48	2.82	
Ferric chloride	65	36	1.89	Clarified feed
Alum	50	36	5.72	
Alum	50	36	6.61	Clarified feed
Alum	50	48	10.87	
Zirconium oxychloride	28	36	1.31	
Zirconium oxychloride	28	36	1.45	Clarified feed

[a]As anhydrous chemical.

These experiments focused on effective fouling reduction, thus only optimal (or near-optimal) coagulant doses were evaluated. Optimum dosages were determined by preliminary jar tests for three inorganic coagulants. Settled jar turbidities were comparable for each coagulant (0.9–1.2 NTU range). The results in Table 2 show that fouling rates strongly depended on the coagulant chemical used. Zirconium oxychloride, a rarely used but very effective coagulant achieved the best results, closely followed by ferric chloride, while alum performed substantially poorer.

However, the most important finding was that in-line flocculation slightly outperformed clarification pre-treatment in the experimental conditions. We did not investigate the exact causes in this study; however, the results do not contradict logical expectations. The specific resistance of cake layer depends on floc sizes and porosity according to the Carman-Kozeny equation. Residual flocs present in clarified feeds consist of the least favourable (small, fractured and light) floc fraction to encounter the membrane and form a cake layer. In a previous study of ultrafiltration, jar supernatant caused bigger fouling than floc suspensions (11). Cake layers formed from flocs present in supernatant may have smaller permeability than the flocs obtained for in-line flocculation. In addition, high suspended solids concentration in the stirred membrane tank induces effective particle collision and agglomeration, thus leads to improved capture of smaller particles. This phenomenon long has been utilized in solid contact and sludge blanket type clarifiers, and can also benefit in-line flocculation.

We notice that our finding is in disagreement with the conclusion of another study (12). The referred work also used ferric chloride coagulant but different feed, membrane, used pH adjustment, and the optimum coagulant doses was almost a dozen times higher (750 mg L^{-1}) than in our experiments.

The importance of proper experimental methodology in the evaluation of in-line flocculation must be emphasized. Early immersion of the membrane, or slug-dosing the reactor with the membrane present leads to precipitation on the membrane, increased pore blocking and fouling rates. Only sufficiently grown flocs should come into contact with the membrane, which we ensured using a dedicated mixer tube. In our conditions a very short, 10 seconds mixing time was sufficient to produce visible (20–30 μm) flocs. Increasing the mixing time to 60 seconds made no significant difference to membrane fouling.

In-line Flocculation for MBR Treatment

In the second phase of this study in-line flocculation pre-treatment was applied to an MBR system that used a flat-sheet (FS) type membrane module. Unlike hollow fiber modules, such membranes cannot be backwashed and employ periodic relaxation to reduce fouling. This system provided polishing treatment to a difficult wastewater influent (septic tank effluent) that posed a challenge to both biological treatment and FS membrane. Thus, it was interesting to evaluate in-line flocculation pre-treatment as a means to improve ostensibly poor plant performance. In the MBR the mixed liquor suspended solids concentration (MLSS) varied in the 1,845–2,050 mg L^{-1} range, which may seem to be modest even for traditional treatment, but in fact was engineered to match the characteristics of raw wastewater. The effective

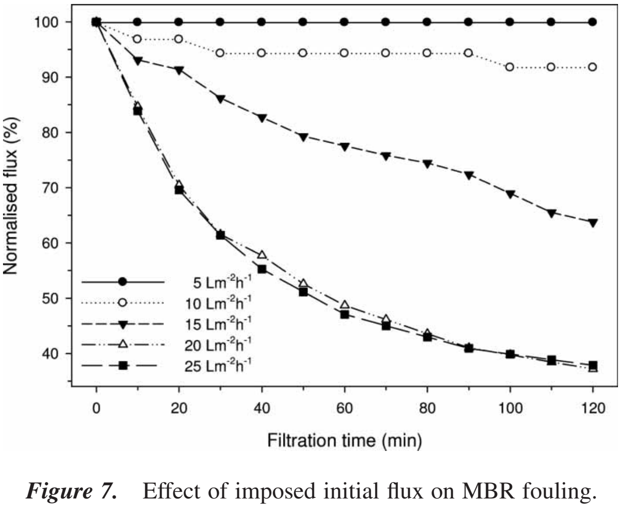

Figure 7. Effect of imposed initial flux on MBR fouling.

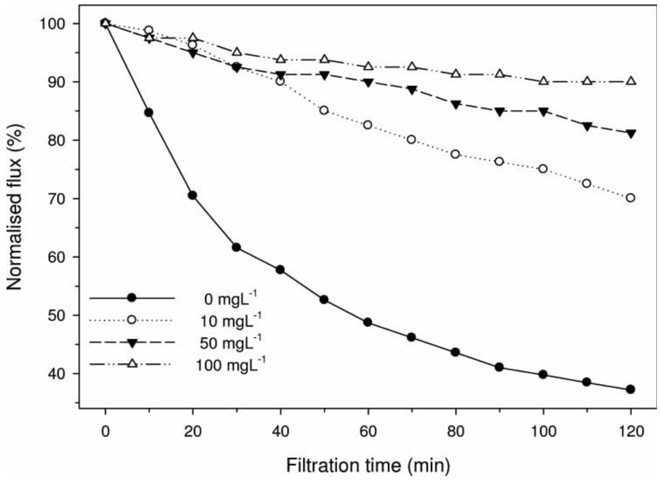

Figure 8. Effect of coagulant dosage on fouling at 20 L m^{-2} h^{-1} initial imposed flux.

coagulant demand range was low, comparable to that used for synthetic wastewater treatment in the first phase of the study. Figure 7 illustrates the fouling propensity of MBR activated sludge feed. The chart shows that 5 L m^{-2} h^{-1} initial flux remained constant during the experiment but at higher initial fluxes membrane permeability was significantly reduced. The extent of fouling increased with initial flux values. A low 10 L m^{-2} h^{-1} initial flux decreased only by 9% but the membrane lost more than 60% of its initial permeability within two hours when the initial flux was doubled to 20 m^{-2} h^{-1} value.

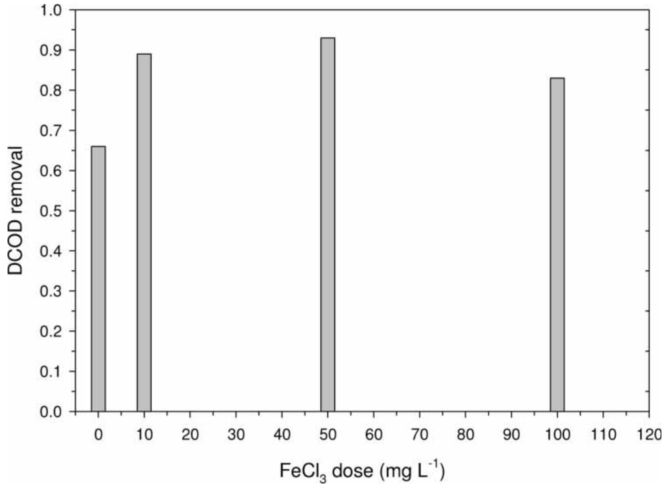

Figure 9. Effect of coagulant dosage on total DCOD removal.

In-line flocculation pre-treatment in conjunction with the MBR system was evaluated at $20\,m^{-2}\,h^{-1}$ initial imposed flux and several coagulant doses. Figure 8 shows that 10 mg L^{-1} dosage nearly halved the permeability decrease. Comparison with Fig. 6 also reveals that a 100 mg L^{-1} coagulant dose increased the flux by 100% with no increase in fouling.

The same pre-treatment simultaneously improved pollutant removal according to Fig. 9. The MBR system removed only 66% of DCOD that indicates the difficult treatability of influent. With the help of in-line flocculation, even a low 10 mg L^{-1} ferric chloride dose resulted in 89% total DCOD removal, which was further improved to 93% at 50 mg L^{-1} dosage (Figure 9). We notice that the coagulant dosing also facilitates better phosphorous removal, but this aspect was not investigated in the present study.

CONCLUSIONS

- In-line flocculation proved to be simple yet effective means to mitigate membrane fouling in two distinctly different low-pressure immersed membrane applications. For direct filtration of synthetic wastewater, optimal coagulant doses reduced fouling rates 18 times. For an MRB system, the imposed flux could be doubled with no increase in fouling.
- Direct membrane filtration of synthetic wastewater removed only 23% of DOC, but over 70% was achieved for the hybrid system. The septic tank effluent feed posed a challenge to the MBR system, as indicated by 66% DCOD removal, and improved up to 93% with in-line flocculation.
- The benefits of reduced fouling and improved permeate quality were simultaneous, and substantial for two dissimilar plants using different original processes and membranes.
- The choice and dosage of coagulant affected both organic matter removal and fouling rates. Jar test residual turbidity measurements reliably predicted optimum dosages to minimise fouling. Ferric chloride showed good performances in both synthetic wastewater filtration and MBR treatment, with 65 and 50 mg L^{-1} optimum doses, respectively.
- In pre-treatment of synthetic wastewater, in-line flocculation outperformed clarification at optimum coagulant dosages, although only slightly. This finding contradicts the conclusion of a previous study, thus deserves a detailed investigation.

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