Desalination and Water Treatment
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1 (2009) 139–149

Roles of various mixed liquor constituents in membrane filtration of activated sludge

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Received 15 March 2007; Accepted 18 September 2008

ABSTRACT

The roles of various mixed liquor constituents in the membrane filtration of activated sludge were investigated. Bench-scale filtration tests with four mixed liquor fractions (whole mixed liquor, mixed liquor supernatant, filtrate I (<8.0 μm), and filtrate II (<0.45 μm) or the soluble fraction) were carried out at different permeate fluxes. It was found that due to its high contents of organic carbon compounds, macromolecules and small supra-dissolved particles, which were most likely to adsorb onto and/or clog in the membrane structure, the soluble fraction (<0.45 μm) of mixed liquor ranked first in terms of its contribution to the total mixed liquor fouling, followed by the colloidal fraction (0.45–8.0 μm) and the unsettleable microfloc fraction (>8.0 μm). In particular, the study revealed that large flocs were able to exert dual effects on membrane filtration. Depending on the hydrodynamic conditions, they could either act as membrane foulants causing fouling via particle deposition and cake formation, or serve as "moving filters" entrapping soluble and colloidal substances and thus alleviating the fouling. A "steric hindrance effect" mechanism was postulated to explain the positive effect of large sludge flocs on membrane filtration.

Keywords: Membrane fouling; Activated sludge; Soluble fraction; Mixed liquor constituents; Steric hindrance effect; MBR

1. Introduction

Due to the recent development of cost-effective membrane technology and the formulation of increasingly stringent environmental regulations, the coupling of membrane filtration with activated sludge treatment in a membrane bioreactor (MBR) has produced an appealing process alternative for the wastewater treatment industry [1]. However, even though MBR technology offers many attractive features for wastewater treatment, the membrane fouling caused by accumulation of mixed liquor constituents on the membrane surface and/or within the membrane pore structure, is of concern, since it limits the economy of treatment if the fouling problem is not well addressed [2].

Research work has been carried out on the roles of different mixed liquor fractions in membrane fouling. Wisniewski and Grasmick [3] quantified the contributions of three main classes of foulants (settleable, supra-colloidal, colloidal and soluble) to membrane fouling. It was reported that half of the total resistance was due to the soluble compounds and the settleable sludge flocs exerted only a small influence on membrane filtration. Subsequent studies further revealed that soluble and colloidal substances in activated sludge mixed liquor were responsible for the majority of the observed deterioration of membrane performance [4–6]. Our previous research also confirmed that soluble microbial products (SMP) played an important role in irreversible membrane fouling in a membrane enhanced biological phosphorus removal process, since a mixed liquor with a relatively high SMP concentration exhibited a greater fouling propensity than

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a mixed liquor with a lower SMP concentration [7]. In view of the available research results, it seems that the soluble fraction of mixed liquor is the major contributor to membrane fouling and the particulate fraction of mixed liquor, on the other hand, can be neglected due to its insignificant impact on membrane filtration. If this is true, then the membrane filtration of activated sludge would be, to some extent, analogous to a direct filtration of the liquid fraction of mixed liquor.

In contrast to the above, Lee et al. [8] compared the filtration performance of attached and suspended growth microorganisms in two submerged membrane bioreactors. They reported that despite the similar characteristics of the soluble fractions in the two reactors, the rate of membrane fouling in the attached growth system was about seven times higher than that of the suspended growth system. This implied that the presence of sludge flocs somehow mitigated membrane fouling in the suspended growth system and thus, the influence of the particulate fraction of mixed liquor could not be neglected.

Clearly, the research findings on the roles of various mixed liquor fractions and/or components in membrane fouling are not consistent with one another. To address this inconsistency, a thorough and systematic investigation of the behaviour of different mixed liquor constituents in the membrane fouling process was required. The present study was undertaken to meet this research need. The objectives were to clarify the roles of various mixed liquor constituents in membrane filtration and to gain insight into the interactions among the mixed liquor constituents and their effects on membrane fouling. Size exclusion-based mixed liquor fractionation techniques were used to separate mixed liquor fractions. Short-term bench scale filtration tests were then applied to the resultant mixed liquor fractions at different fluxes to study the fouling behaviour of mixed liquor constituents under different filtration conditions. An examination of the physical and biochemical characteristics of the soluble fraction of mixed liquor was also performed in order to further elucidate the fouling induced by this particular fraction.

2. Materials and methods

2.1. Mixed liquor sampling and fractionation

It has been known that the fouling characteristics of activated sludge are largely determined by the nature of the mixed liquor tested. Different mixed liquors may exhibit different fouling behaviours. To have a relatively complete understanding of the roles of mixed liquor constituents in membrane filtration, therefore, two types of activated sludge mixed liquor, i.e. an MBR mixed liquor and a conventional mixed liquor, were examined in the present study. The samples were collected from the aerobic zones of a membrane enhanced biological phosphorus removal (MEBPR) process and a conventional enhanced biological phosphorus removal (CEBPR) process operated at the University of British Columbia (UBC) wastewater treatment pilot plant. Both processes utilized three reaction zones, i.e. anaerobic, anoxic, and aerobic compartments, in series. A custom-built ZeeWeed membrane module (Zenon Environmental, Oakville, Ontario, Canada), with a nominal membrane pore size of 0.04 μm, was installed in the aerobic zone of the pilot-scale MEBPR process for separation of suspended solids from treated wastewater. A secondary clarifier was used in the pilot-scale CEBPR process for solids–liquid separation. For the purpose of comparison, the two treatment processes shared the same sewage influent and the same design and operating parameters (except for the aeration intensity). Two experimental runs were carried out at the UBC pilot plant during the period of this study: March 2003–December 2003 for Run I and December 2003–June 2004 for Run II. The sludge retention time (SRT) was controlled at 12 days for both experimental runs and only the hydraulic retention time (HRT) was changed from 10 h in Run I to 7 h in Run II. Details of the design, operation and wastewater treatment performances of the two processes are given elsewhere [7].

During Run I, grab samples (4 L) of activated sludge were taken from the aerobic zones of each process and were immediately transported to an environmental lab for fractionation. Fig. 1 illustrates the steps and means for fractionation of the mixed liquor samples. First, approximately 1 L of mixed liquor was retained as the original whole mixed liquor, and the remaining 3 L was centrifuged at 2000 × g for 5 min and the supernatant was collected. Second, about 2 L of the supernatant was then filtered through 8.0 μm membrane filters and the filtrate was collected and designated as Filtrate I. Third, half of this filtrate was immediately subjected to a second filtration using 0.45 μm filter papers and the resulting filtrate was designated as Filtrate II, or the soluble fraction

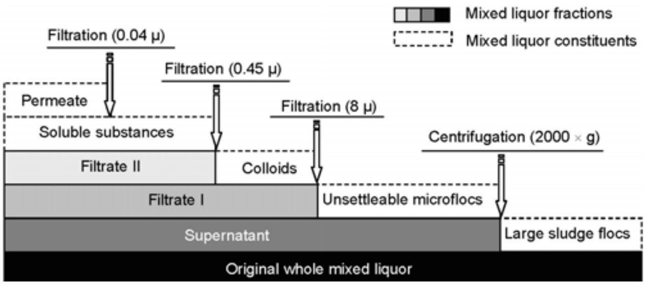

Fig. 1. Scheme for fractionation of activated sludge mixed liquor.

Table 1
Characteristics of the four fractions of both the MEBPR and CEBPR mixed liquor (all units in mg/L)

Mixed liquor fraction	MEBPR		CEBPR	
	TSS[a]	TOC[b]	TSS	TOC
Whole mixed liquor (large flocs + microflocs + colloids + solutes)	2330	—	1230	—
Supernatant (microflocs + colloids + solutes)	88	12.5[c]	37	6.5[c]
Filtrate I (colloids + solutes)	—	9.0	—	4.5
Filtrate II (solutes)	—	7.5	—	3.0

[a]Total suspended solids; [b]Total organic carbon. [c]Floating materials removed.

of the mixed liquor. In the present study, the term "soluble" was defined in accordance with the traditional definition, which refers to substances that are able to pass through 0.45 μm filter paper. It was evident that the mixed liquor fractionation approach used here was mainly based on the principle of size exclusion. The characteristics of the resultant mixed liquor fractions are presented in Table 1.

In addition to the steps for mixed liquor fractionation, Fig. 1 also demonstrates the relationship of the mixed liquor fractions to mixed liquor constituents. Clearly, individual mixed liquor constituents were actually the difference between two neighboring mixed liquor fractions. By comparing the filtration performance of the two mixed liquor fractions (i.e. supernatant and Filtrate I), the effect of particular mixed liquor constituents (i.e. unsettleable microflocs) on membrane filtration could be roughly assessed. An exception was that membrane permeate could be regarded as either a mixed liquor fraction or a collection of mixed liquor constituents with sizes smaller than 0.04 μm.

2.2. Bench-scale filtration tests

The resultant mixed liquor fractions, namely the original whole mixed liquor, supernatant, Filtrate I, and Filtrate II or the soluble fraction of mixed liquor, were filtered separately at constant permeate flux using the bench scale filtration apparatus depicted in Fig. 2. The membrane module used in this work was comprised of four 0.1 m membrane hollow fiber loops, with a polyvinylidene fluoride (PVDF) skin and a nominal membrane pore size of 0.04 μm. In the filtration tests, the membrane loops were submerged in a mixed liquor fraction and the permeate was collected at room temperature via a Masterflex peristaltic pump. No backflushing or relaxation was applied and the system was operated with continuous suction in a constant-flux mode for 30 min. Aeration at a volumetric flow rate of 15 m^3 air/m^3 liquid·h was provided around the membrane loops during the suction and the change of transmembrane pressure (TMP) with time was monitored via a pressure transducer installed on the permeate line (Fig. 2).

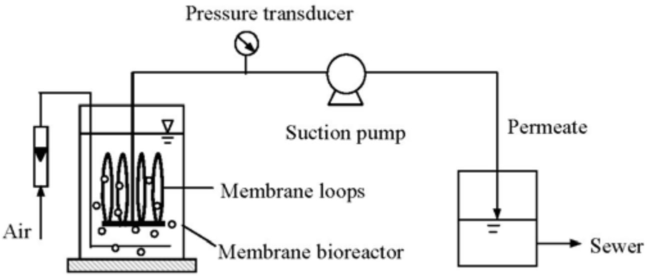

Fig. 2. Experimental set-up of bench-scale filtration tests.

As indicated above, previous literature reports about the effect of various mixed liquor fractions on membrane fouling are very contradictory. Considering that different MBR systems with different hydrodynamic conditions were used in those studies, it was anticipated that the differences in the bioprocess design and in particular, in the membrane operating conditions, might have contributed to the apparent discrepancies. Permeate flux is one of the most influential operating parameters with respect to membrane fouling [9]. In the present study, therefore, three constant fluxes (23 L/m^2·h, 33 L/m^2·h and 68 L/m^2·h) were applied in the bench-scale filtration tests with the different mixed liquor fractions considered, in an attempt to examine whether the mixed liquor constituents exhibited different fouling propensities at different permeate fluxes.

Virgin membrane loops were used in each filtration test. Before filtering a mixed liquor fraction, a clean water filtration test was performed to estimate the hydraulic resistance caused by membrane itself, as modeled by Eq. (1). Subsequently, the mixed liquor fraction was filtered using the same set of membrane loops and the total hydraulic resistance was calculated in the same way as with clean water. Then, the hydraulic resistance due to fouling was derived by subtracting the resistance induced by the membranes from the total hydraulic resistance, as indicated in Eq. (2).

- Darcy's law:

$$J = \Delta P/(\mu R_t) \quad (1)$$

- Resistance-in-series:

$$R_t = R_m + R_f \tag{2}$$

where J is the membrane flux, $m^3/m^2 \cdot s$; ΔP the transmembrane pressure (TMP), Pa; μ the permeate viscosity, Pa·s; R_t the total hydraulic resistance, 1/m; R_m the hydraulic resistance due to the membrane itself, 1/m; and R_f the hydraulic resistance due to fouling, 1/m.

2.3. Analysis of the soluble fraction of mixed liquor

To elucidate further the role of soluble organic substances (<0.45 μm) in the membrane fouling, the chemical and physical characteristics of the soluble fraction of mixed liquor were analyzed in terms of total organic carbon (TOC), molecular weight (MW) distribution and fine particle size distribution. A Phoenix 8000 UV-Persulfate TOC analyzer (Dohrmann) was used to measure the content of TOC in accordance with Standard Method 5310C [10]. The number average and weight average molecular weight (Mn and Mw, respectively) were estimated by gel permeation chromatography (GPC) using a Agilent 1100 HPLC system equipped with an autosampler, an isocratic pump, a thermostatted column compartment, a multiple wavelength detector (MWD), a refractive index detector (RID), and two Waters Styragel columns (HR5E and HR1) in tandem. Tetrahydrofuran (THF) was used as the eluent and was supplied at 1 mL/min. Column temperature was 50°C and the columns were calibrated with polystyrene standards. Both samples and polystyrene standards were analyzed by MWD at 280 nm. Based on the Mn and Mw measurements, polydispersity, which is a measure of the distribution of molecular mass in a batch of polymers and is defined as Mw divided by Mn, was calculated for each sample. The value of polydispersity is always greater than 1. The narrower the molecular weight distribution, the closer to the unity (1) will be the corresponding polydispersity.

For the measurement of fine particle size distribution, a Malvern Hydro 2000S was used. Since the particles contained in the soluble fraction of mixed liquor (Filtrate II) were smaller than 0.45 μm in size and close to the lower limit of the instrument (0.020–1000 μm), the measurement was challenging and very susceptible to noise and errors. For this reason, the measurement cell and all the parts that might have contacted the sample were thoroughly cleaned. Distilled deionized water was used for background measurement and a degassing operation using the Degas function of the instrument was performed prior to the measurement to eliminate fine air bubbles.

3. Results and discussion

3.1. Contribution of mixed liquor constituents to membrane fouling at a low permeate flux

To compare the fouling propensity and assess the contribution of different mixed liquor constituents to the total membrane fouling, a series of short-term bench-scale filtration tests were designed, as described previously. The four fractions of both the MEBPR mixed liquor and the CEBPR mixed liquor, i.e. the original whole mixed liquor, the supernatant, the Filtrate I (<8.0 μm), and the Filtrate II (<0.45 μm), were first subjected to the filtration tests at a constant low flux of 23 L/m²·h, the operating flux in the MEBPR process at the UBC pilot plant. The change of TMP over time during the filtration of each mixed liquor fraction was monitored, and the results are presented in Fig. 3. Fig. 3(a) illustrates the TMP evolution during the filtration of the four MEBPR mixed liquor fractions, while Fig. 3(b) shows the TMP evolution during the filtration of the CEBPR mixed liquor fractions. As can be seen from both Fig. 3(a) and Fig. 3(b), after the initial lag period required for the pump to establish a stable vacuum throughout the system, the TMP increased

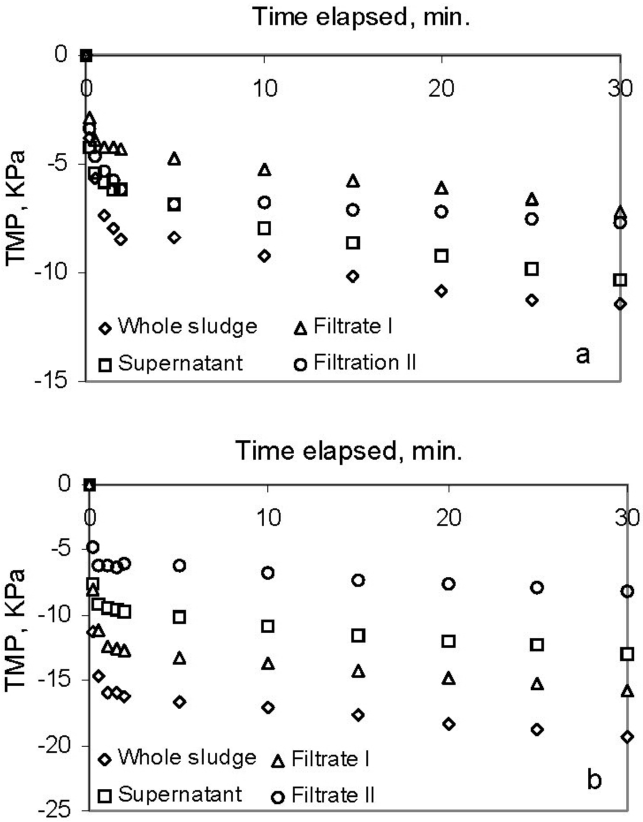

Fig. 3. Transmembrane pressure during the filtration of the four fractions of (a) an aerobic MEBPR mixed liquor and (b) an aerobic CEBPR mixed liquor at a flux of 23 L/m²·h.

linearly with time. It should be noted that because different new membrane loops were used for filtration of different mixed liquor fraction, the hydraulic resistance caused by membranes was different in each filtration test, resulting in apparently higher or lower TMP profiles.

From the measured TMP values, the hydraulic resistances due to fouling after the initial lag period were calculated in accordance with the resistance-in-series model and Darcy's Law [Eqs. (1) and (2)], and the results are shown in Fig. 4. It can be seen that for both the MEBPR mixed liquor and the CEBPR mixed liquor, the resistances due to fouling increased linearly with time at different rates for the different mixed liquor fractions. The rate of increase in hydraulic resistance due to fouling, that is the slope of each line in Fig. 4, was defined as the fouling rate. From Fig. 4(a), for example, the fouling rate of the supernatant of the MEBPR mixed liquor was 0.213×10^{11} 1/m·min. The rate of fouling induced by the original whole mixed liquor was taken as a reference value. The individual fouling rates measured for each fraction were compared to this reference to estimate the percentages of the whole mixed liquor fouling contributed by the individual mixed liquor fractions. The results are illustrated in Fig. 5. It is evident that the supernatant, Filtrate I and Filtrate II of the MEBPR mixed liquor accounted, respectively, for about 93%, 66%, and 34% of the whole mixed liquor fouling under the experimental conditions used. In other words, the relative fouling rates of these fractions to the whole mixed liquor were 93%, 66%, and 34%, respectively. For the CEBPR mixed liquor, the relative fouling rates as percentages of the whole mixed liquor fouling were 96%, 95%, and 65%, respectively.

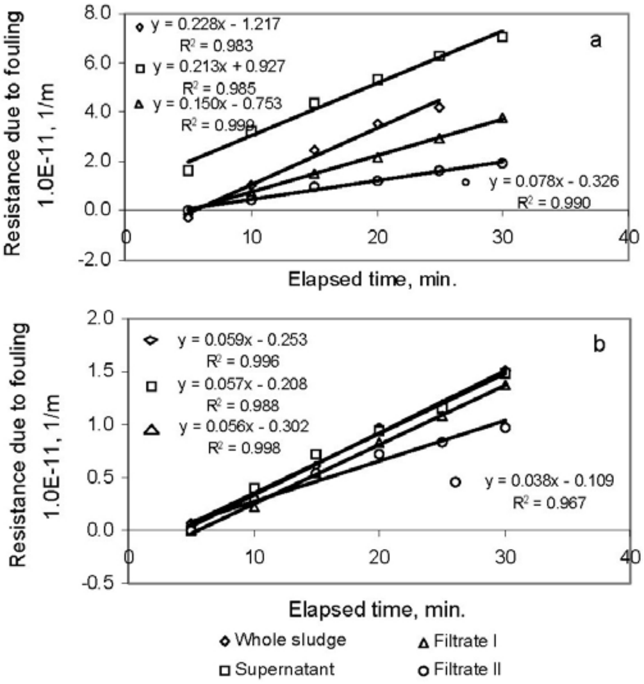

Fig. 4. Hydraulic resistance due to fouling in the filtration of the four fractions of (a) the aerobic MEBPR mixed liquor and (b) the aerobic CEBPR mixed liquor at a flux of 23 L/m^2·h.

It was assumed that the differences between the percentages in Fig. 5 represented the contribution of some particular mixed liquor constituents to membrane fouling. For example, the difference of 7% between the MEBPR whole mixed liquor (100%) and its supernatant (93%) indicated the contribution of the large MEBPR sludge flocs to the total fouling. Similarly, the differences in the percentages between the supernatant and Filtrate I and between the Filtrate I and Filtrate II represented the contribution of unsettleable microflocs and colloids to the whole mixed liquor fouling, respectively. The relative contribution of the different mixed liquor constituents to the whole mixed liquor fouling was thus calculated and the results are summarized in Fig. 6. It should be pointed out that all the calculations were based on the assumption that the fouling caused by the different mixed liquor fractions/constituents is simply additive.

It is readily noticed in Fig. 6 that for both mixed liquors, large sludge flocs accounted only for a very small portion of the short-term fouling (4–7%). Fine particles and colloids between 0.45 and 8.0 µm were responsible for about one-third of the total short-term fouling (30–32%). A large part of the membrane fouling (33–65%) was attributable to the soluble fraction of the mixed liquor. Obviously, these results were congruent with the afore-

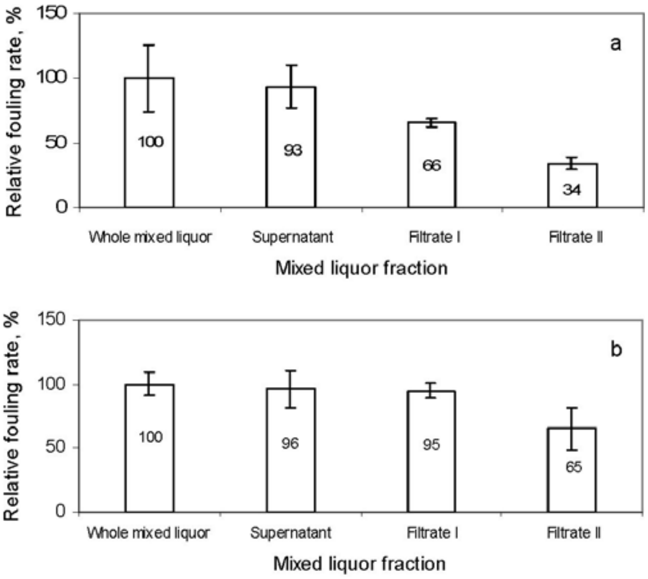

Fig. 5. Relative fouling rates of the individual mixed liquor fractions to the whole mixed liquor fouling at a flux of 23 L/m^2·h: (a) aerobic MEBPR mixed liquor; (b) aerobic CEBPR mixed liquor.

mentioned research work [3–6], indicating that under the experimental conditions applied, the soluble and colloidal substances in the activated sludge mixed liquor were the major constituents causing membrane fouling (65–95%) in the bench scale filtration tests and, by contrast, large sludge flocs appeared to play a small role (4–7%) in the deterioration of membrane performance.

It may also be inferred from Fig. 6 that, due to greater retention by the membrane in the pilot-scale MEBPR process, there was a larger proportion of unsettleable microflocs or supra-colloids (> 8.0 μm) in the MEBPR mixed liquor than in the counterpart CEBPR mixed liquor. This would result in a larger contribution of such constituents to the total fouling than those of the CEBPR mixed liquor (28% vs. 1%). In addition, because the concentrations of the various mixed liquor constituents (especially the soluble and colloidal substances expressed as TOC) in the MEBPR mixed liquor fractions were as much as 100% higher than those in the CEBPR mixed liquor fractions (Table 1), greater absolute fouling rates were measured for the former (the line slopes in Fig. 4). This suggests that not only the type of sludge constituents, such as large sludge flocs, microflocs, fine colloids, and soluble substances, as discussed above, but also the amount of mixed liquor constituents, exerted a significant influence on the membrane fouling process.

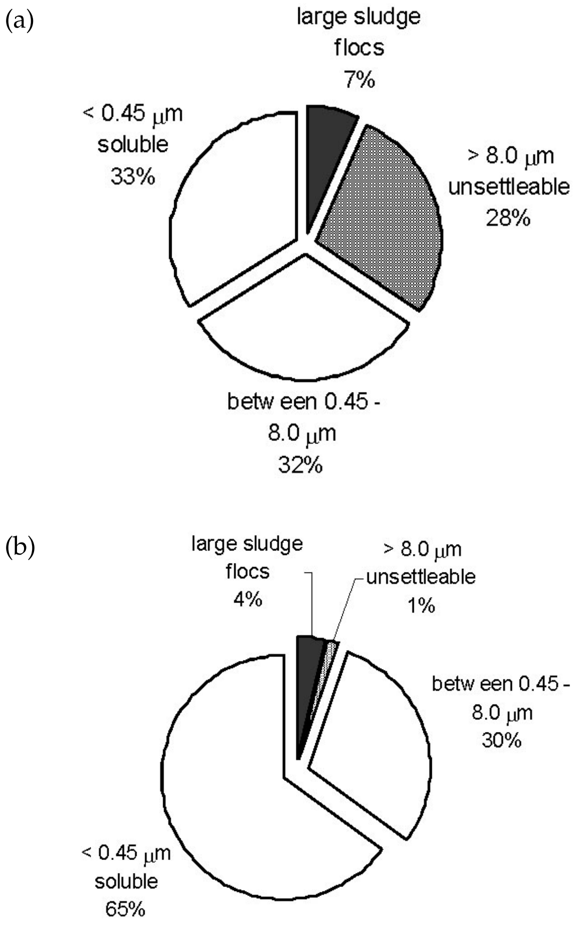

Fig. 6. Relative contribution of the different constituents of (a) aerobic MEBPR mixed liquor and (b) aerobic CEBPR mixed liquor to the short-term membrane fouling at a flux of 23 L/m^2·h.

It was indicated in our previous study that the long-term membrane fouling observed in the pilot-scale MEBPR process was hydraulically irreversible and was likely caused by organic adsorption and deep pore clogging [7]. The reversible fouling induced by particulate deposition and superficial pore blocking was reduced to a minimum due to the vigorous aeration and frequent backflushing applied in the system. It was believed that soluble and fine colloidal substances in the soluble fraction of mixed liquor tended to adsorb onto the membrane surfaces and were thus most likely associated with the irreversible adsorption and deep pore clogging, while colloids and unsettleable microflocs mainly contributed to pore blocking, and large sludge flocs were apparently most responsible for particulate deposition.

3.2. Behavior of large sludge flocs in membrane filtration at high permeate fluxes

After the filtration tests at the lowest flux of 23 L/m^2·h were completed, the permeate flux was increased to 33 L/m^2·h and 68 L/m^2·h successively. To reduce the required experimental work, only the MEBPR mixed liquor fractions were subjected to the high-flux membrane filtration. The TMP was monitored and the fouling rate of each mixed liquor fraction in the high-flux filtration tests was derived in the same manner as for the low-flux tests.

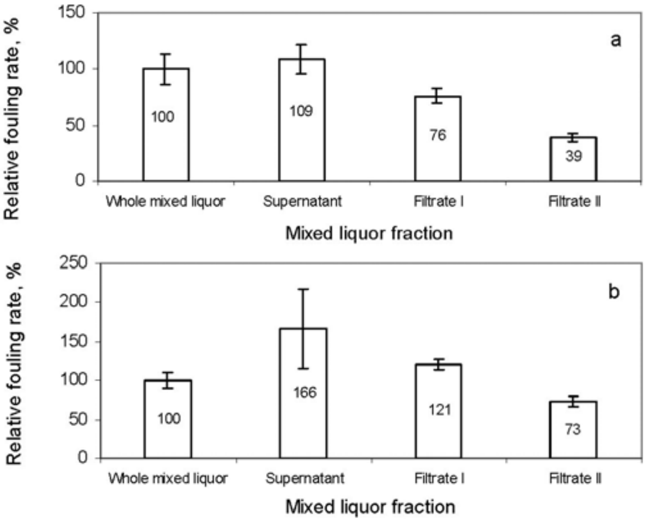

Fig. 7. Relative fouling rates of the individual MEBPR mixed liquor fractions to the whole mixed liquor fouling at the increased fluxes of (a) 33 L/m^2·h and (b) 68 L/m^2·h.

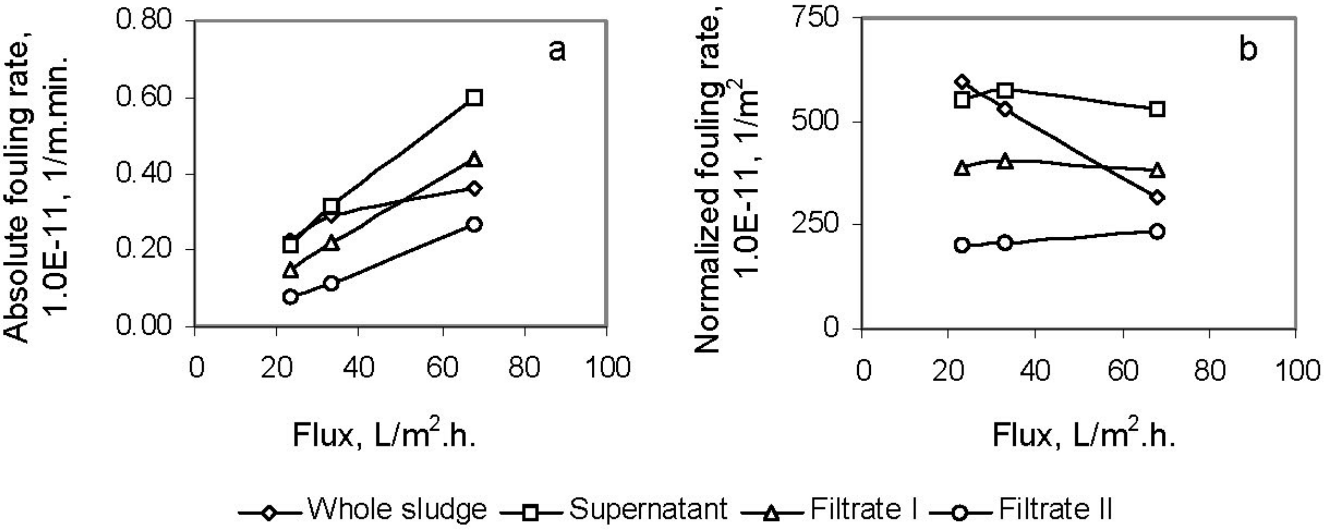

Fig. 8. Fouling rates of the four fractions of the aerobic MEBPR mixed liquor at different operating fluxes: (a) absolute fouling rates; (b) normalized fouling rates.

Fig. 7 shows the relative fouling rates of the four MEBPR mixed liquor fractions at the fluxes of 33 L/m^2·h and 68 L/m^2·h. Recall that at the low flux of 23 L/m^2·h, the whole mixed liquor had the highest relative fouling rate (100%), and the supernatant, Filtrate I and Filtrate II exhibited lower fouling rates in descending order (Fig. 5). When the permeate flux was increased, however, the relationship among the fractions was different. At the flux of 33 L/m^2·h, the fouling rate of the supernatant unexpectedly exceeded that of the whole mixed liquor [Fig. 7(a)]. This phenomenon became more apparent when the flux was further increased to 68 L/m^2·h, since not only the supernatant but also Filtrate I demonstrated higher fouling propensity than the original whole mixed liquor: the relative fouling rate of the supernatant was 166% and Filtrate I 121% of that of the whole mixed liquor [Fig. 7(b)]. This suggests that when suspended solids were removed from the mixed liquor, the fouling process was accelerated. In reverse, it could be inferred that if sludge flocs were added back to the membrane feed, the filtration resistance might be mitigated to some extent. Therefore, the presence of large sludge flocs appeared to be beneficial to the alleviation of membrane fouling.

An analysis of the fouling rates of the four MEBPR mixed liquor fractions at the different membrane fluxes provided further insight into the above phenomenon. Fig. 8(a) shows the absolute fouling rates of the four mixed liquor fractions at fluxes of 23, 33 and 68 L/m^2·h, respectively. It was evident that for any mixed liquor fraction, the absolute fouling rate increased with an increase of the permeate flux. However, when the fouling rates were divided by the actual flux (23, 33 or 68 L/m^2·h), the resultant fouling rates at the unit flux of 1 L/m^2·h, or the normalized fouling rates, did not change with an increase in the permeate flux for the supernatant, Filtrate I and Filtration II [Fig.8 (b)]. In contrast, the normalized fouling rates for the large sludge flocs exhibited a declining trend with increasing flux, as demonstrated in Fig. 8 (b). This implied that the role of large sludge flocs in the membrane filtration of mixed liquor was considerably affected by the membrane operating conditions. As the flux increased, the relative contribution of large sludge flocs to fouling decreased, or, the impact of large particles on the minimization of fouling increased.

These experimental results are in agreement with the observations of Lee et al. [8], which indicated better filtration performance with a suspended growth MBR rather than an attached growth MBR. Similar findings were also reported from a different standpoint by Defrance et al. [11], who investigated the additivity of filtration resistance induced by individual mixed liquor components and found that the sum of resistance due to each constituent at the same respective concentration as in the mixed liquor was 50% higher than the measured total resistance. Therefore, the fouling caused by individual mixed liquor constituents was concluded to be antagonistic, rather than additive.

3.3. Steric hindrance effect of large sludge flocs

The results presented in Fig. 7 are understandable if the large sludge flocs are considered as "moving barriers" that intercept fine particles and dissolved matter before they reach the membranes. A representation of the steric hindrance effect of sludge flocs on membrane filtration is presented in Fig. 9. In a quiescent environment, sludge flocs tend to attach onto or deposit on the membrane surface to form a cake layer. While in a flowing setting,

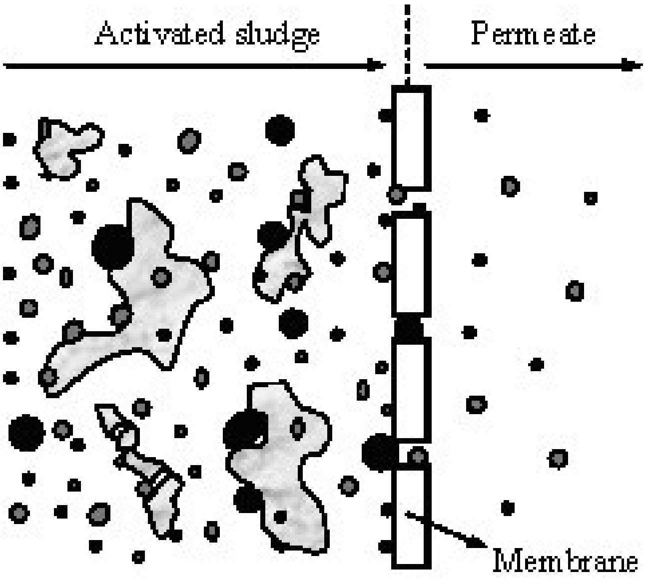

Fig. 9. Postulated mechanism for the steric hindrance effect of large sludge flocs on membrane filtration.

large sludge flocs are also believed to be able to sterically hinder the movement of other mixed liquor constituents and thus aggregate or adsorb fine particles and soluble organics onto their porous structures. This process is analogous to the phenomenon of sweep flocculation that occurs in chemically-assisted clarifiers. A number of mechanisms can cause particle aggregation, including Brownian motion, velocity gradients and turbulent diffusion. As the flocculation rate constant is proportional to velocity gradient and the second or third power of particle size [12], the aggregation process would be favored when the velocity gradient becomes greater at an increased flux and large particles are present. This is probably why the steric hindrance effect of large sludge flocs becomes more prominent at higher fluxes.

It could be imagined that at an increased flux, the frequency of contact between particles, dissolved substances and large sludge flocs increases, such that more small foulants are intercepted and retained within the floc structure. As a result, fewer particles and soluble organics are transported to the vicinity of the membranes to cause fouling. When filtering mixed liquor supernatant, great numbers of fine particles and organic substances are readily transported to the membrane surfaces without any obstruction due to the absence of large sludge flocs. Many of these small particles become adsorbed onto the membranes, causing a severe deterioration of membrane performance. Therefore, not all the mixed liquor constituents result in membrane fouling at all times: large sludge flocs may play a positive role in the filtration of activated sludge, particularly at high flux, due to their steric hindrance effect.

The experimental results obtained at both low and high flux suggested that sludge flocs very likely have dual effects on membrane filtration. They could either act as membrane foulants causing membrane fouling via particulate deposition and cake formation, or serve as "moving barriers" that entrap soluble and colloidal substances, thus mitigating the fouling. The two attributes may coexist and their relative importance may change with the system design and hydrodynamic conditions. In some cases, one effect might outweigh the other. For example, in the suspended growth membrane system reported by Lee et al. [8] and in the present high-flux filtration tests as well, the positive effect of steric hindrance appeared to surpass the negative effect of particulate deposition. In other cases, such as the previous low-flux filtration tests, the two effects offset each other and most of time the positive effect was masked. As a result, the outstanding negative fouling effect was observed, as reported in many previous research papers [3,11]. Considering the possible dual effects of large sludge flocs on membrane filtration, the research findings reported earlier, which seemed to be inconsistent in regard to the roles of various mixed liquor fractions and/or components in membrane fouling, may actually be consistent under the steric hindrance concept.

3.4. Characteristics of the soluble fraction of mixed liquor

Although the roles of mixed liquor constituents in membrane filtration could change with the system design and operating conditions, Filtrate II or the soluble fraction that contained the soluble and fine colloidal substances was, in many cases, one of the most important mixed liquor fractions with respect to membrane fouling. It was observed in our previous study that under turbulent hydrodynamic conditions (i.e. intensive aeration and backflushing), the fouling caused by sludge cake formation and superficial pore blocking could be prevented to a large extent, but the fouling due to adsorption and/or deposition of soluble and colloidal substances onto the membrane structure was hard to mitigate hydraulically and it accumulated day by day and became the major fouling mechanism in the pilot scale MEBPR system [7]. Therefore, the soluble fraction of mixed liquor can by no means be neglected, especially in regard to irreversible fouling.

To better understand the characteristics of the soluble fraction of mixed liquor so as to further elucidate the fouling mechanisms involved, activated sludge grab samples were collected from the three compartments of both the MEBPR and CEBPR processes during the pseudo-steady state operation of Run II. Sludge fractionation was performed immediately, and the resultant soluble fractions of these mixed liquor samples were then

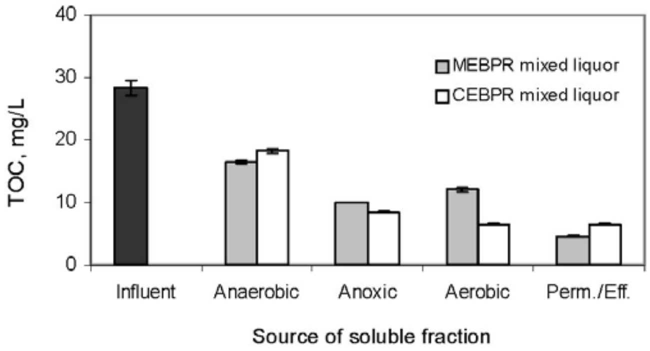

Fig. 10. TOC levels in the MEBPR permeate and in the soluble fractions of the influent, CEBPR effluent, and the mixed liquors collected from both the MEBPR process and the CEBPR process in May 2004. Error bars represent standard deviation (n = 3).

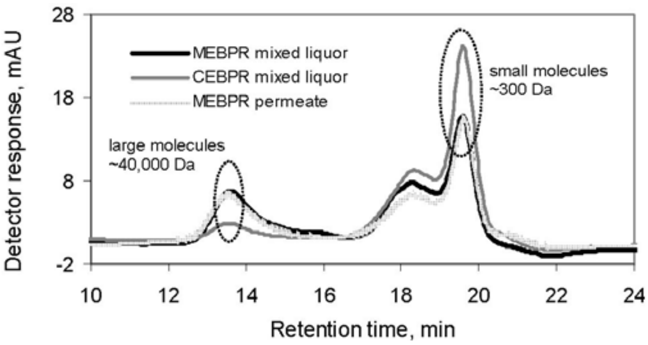

Fig. 11 Molecular weight distribution of the THF-dissolved substances in MEBPR permeate and soluble fractions of mixed liquors collected from aerobic zones of MEBPR and CEBPR processes.

analyzed in terms of fouling-related chemical and physical properties such as total organic carbon (TOC), molecular weight (MW) distribution, and fine particle size distribution.

Fig. 10 shows the TOC levels in the soluble fractions of the collected mixed liquors, the influent and the CEBPR effluent as well as the TOC level in the MEBPR permeate. It should be pointed out that the term "soluble" here has the same meaning for the mixed liquors, influent, and CEBPR effluent, which refers to the substances that are smaller than 0.45 μm in size, while the TOC in the MEBPR permeate represents the finer materials that could pass through 0.04 μm membranes. It can be seen in Fig. 10 that, as in most activated sludge systems, the soluble TOC content in the CEBPR process exhibited a consistent decline from the influent, through the anaerobic, anoxic, and aerobic zones sequentially, to the final effluent. In contrast, there was a measurable increase in the TOC content of the soluble fraction of mixed liquor in the aerobic zone of the MEBPR process. The dissolved TOC level in the aerobic zone was significantly higher than that of the permeate and of the preceding anoxic zone as well. This was likely because of the continuing accumulation of soluble microbial products and macromolecules within the aerobic zone due to the presence of a membrane barrier [13,14].

Table 2 shows the retention efficiencies of the membrane for dissolved TOC in the MEBPR process. Obviously, a significant portion, i.e. about 42–76%, of the soluble organic carbon matter was retained in the system by the membranes. These retained substances likely aggravated fouling and hindered the filtration process. It has been reported that permeate flux was inversely proportional to the log values of the differential TOC between membrane feed and permeate [15]. Therefore, the greater the difference in TOC levels between the two sides of membranes (i.e. the mixed liquor to be filtered and the permeate), the larger the filtration resistance. The enrichment of dissolved organic carbon in the aerobic zone of the MEBPR process may have been an important factor that led to the higher fouling propensity of the MEBPR mixed liquor, relative to that of a reference CEBPR mixed liquor.

The MW distributions of the soluble fraction of mixed liquor and the permeate were measured using gel permeation chromatography (GPC) and the results are presented in Fig. 11 and Table 3. Only the substances that could be dissolved in the eluent tetrahydrofuran (THF) were mapped in this GPC analysis. As large molecules were eluted first, followed by small molecules, it can be concluded from Fig. 11 that both the aerobic MEBPR mixed liquor and the corresponding permeate contained material with molecular weights of approximately 40,000 Da, as well as material of much smaller molecular weight (~300 Da). The ranges of their MW distributions were very broad, as indicated by their high polydispersity (Table 3). In contrast, the soluble fraction of the aerobic CEBPR mixed liquor mainly consisted of small molecules (~300 Da), and few large molecules were measured, leading to a monodispersed MW distribution (Table 3). Since large molecules contributed more TOC than small molecules, these results were basically consistent with the preceding TOC analysis, which showed a higher soluble TOC content in the MEBPR than in the CEBPR, as a result of the influence of the membrane barrier. The research of Shin and Kang [16] indicated that the compounds accumulated in an MBR comprised large, aromatic, hydrophobic and double bond-rich organics that originated from decayed biomass. It is assumed that compounds of similar characteristics and source may have accumulated in the MEBPR system of the present study.

Fig. 12 illustrates the fine particle size distributions of the soluble fractions of the mixed liquor in the aerobic zones of the two processes. It was not surprising that, due to the vigorous aeration normally employed in a

Table 2
Dissolved TOC retained in the MEBPR system

Experimental run	Sampling date	TOC in soluble fraction of MEBPR aerobic zone mixed liquor, mg/L	TOC in permeate, mg/L	TOC retained, %
Run I	18/08/2003	19.0	11.0	42
	12/11/2003	12.5	4.0	68
Run II	29/03/2004	18.3	4.4	76
	31/05/2004	12.0	4.6	62

Table 3
Molecular weight distribution of the soluble fractions of mixed liquor and the MEBPR permeate

Molecular weight distribution	Aerobic MEBPR mixed liquor	MEBPR permeate	Aerobic CEBPR mixed liquor
Number average molecular weight (Mn), g/mol	3,739	8,918	326
Weight average molecular weight (Mw), g/mol	47,411	46,264	327
Polydispersity (Mw/Mn)	12.68	5.19	1.00

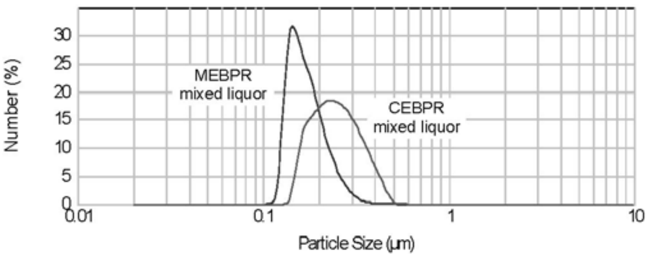

Fig. 12. Fine particle size distributions of the soluble fractions of mixed liquor collected from aerobic zones of MEBPR and CEBPR processes.

submerged MBR, the MEBPR mixed liquor contained more small supra-dissolved particles (0.1–0.45 μm), as defined in Poele et al. [17], than did the CEBPR mixed liquor. Particles with diameters that are close to the pore size of a membrane generally have the greatest impact on the membrane filtration process [18]. Accordingly, the distributions shown in Fig. 12 explain the lower filterability of the MEBPR mixed liquor than the CEBPR mixed liquor in terms of the fouling mechanism of pore clogging.

The results presented in Figs. 10–12 indicate that the soluble fraction of the aerobic MEBPR mixed liquor was mainly characterized by high levels of soluble organic carbon compounds that were rich in both macromolecules and fine dissolved particles, which were concluded to cause irreversible fouling via organic adsorption and deep pore clogging.

4. Conclusions

Due to its high contents of organic carbon compounds, macromolecules and small supra-dissolved particles that were most likely to adsorb onto and/or clog in the membrane structure, the soluble fraction (<0.45 μm) of activated sludge mixed liquor ranked first in terms of its contribution to the total mixed liquor fouling, followed by the colloidal fraction (0.45–8.0 μm) and the unsettleable microfloc fraction (>8.0 μm).

Large sludge flocs might exert dual effects on membrane filtration in MBR systems. At low permeate flux, they induce hydraulic resistance probably via particulate deposition or cake layer formation, though this effect is relatively small and perhaps even negligible under strong aeration conditions. At high flux, however, large sludge flocs seem to be able to mitigate fouling. A “steric hindrance” mechanism was postulated, which suggests that large sludge flocs can intercept soluble and colloidal substances in their porous structures before they reached the membrane surface. This positive effect of large sludge flocs on membrane fouling outweighed the negative effect of particulate deposition under high permeate flux and strong aeration conditions.

Acknowledgements

This work was funded by the Natural Science and Engineering Research Council of Canada (NSERC). Financial and technical support from Zenon Environmental Inc., Stantec Consulting, and Dayton and Knight Ltd. is also acknowledged.

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