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Identification and quantification of foulant in submerged membrane reactor

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ABSTRACT

In submerged membrane system, membrane fouling is linked to the reversible accumulation of macromolecules and solids on the membrane surface and the irreversible sorption of soluble molecules inside the pores. In the first part of the paper, the fouling was analysed at two different aeration rates through the determination of membrane resistance due to (a) sludging ($R_{sludging}$), (b) irreversible biofilm ($R_{biofilm}$) and (c) adsorption of organic ($R_{adsorption}$). These results confirm the importance of aeration for sludge control in the bundle. In the second part of the paper, irreversible foulant obtained at different aeration rates were characterised. Membrane air flow rate limits adsorption of biopolymers onto or into the membrane surface.

Keywords: Submerged membrane bioreactors; Aeration; Membrane fouling

1. Introduction

Membrane bioreactor (MBR) is becoming increasingly popular in wastewater treatment and water reuse applications. It improves the biological reaction and solid liquid separation. This reduces sludge production and achieves the removal of refractory organics [1,2]. However, there is no prediction tool available to simulate the evolution of membrane fouling during the MBR operation in order to choose the optimum operating parameters of MBR. Fouling dynamics are linked to the accumulation of large organic compounds on the membrane surface (reversible fouling), and biofilm development on the membrane surface and organic and molecule adsorption in the membrane pores (irreversible fouling). While the former phenomenon can be controlled by hydraulic means, the latter requires chemical cleaning. The frequency and intensity of chemical cleaning can reduce membrane lifetime. Reversible accumulation on the membrane surface is mainly caused by the suspended solids concentration in the mixed liquor, while the presence of extrapolymeric substances in the mixed liquor (such as soluble microbial products, SMP) is the main cause of the irreversible fouling [3–7].

2. Materials and methods

In this study, experiments were conducted with hollow fibre and flat sheet membrane (Table 1) immersed in reactor to show the role of membrane airflow rate on fouling intensity and reversibility. The reactor seeded with the municipal sludge was continuously fed with a synthetic substrate composed by an organic source (ethanol) and mineral salts (NH_4Cl, KH_2PO_4) in order to keep a ratio COD/N/P equal to 150/5/1. The operating parameters are given in Table 2. The MBR experiments were carried out at a constant permeate flux 20 LMH (L m^{-2} h^{-1}) with a

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Table 1
Membrane module

Parameters	Units	Hollow fiber	Flat sheet
Module		Puron	A3
Membrane material		Polysulfone	PVDF
Pore size	μm	0.05	0.14
Membrane permeability	m^{-1}	$3\ 10^{11}$	$6.12\ 10^{10}$
Fibre external diameter	mm	2.6	
Filtration area	m^2	0.22	0.2
Fibre/Sheet Length	M	0.34	0.21
Fibre/Sheet Number		80	8
Module packing density	$m^2\ m^{-3}$	320	84

mixed liquor suspended solids (X_{SS}) concentration of 4–6 g L^{-1} as shown in Fig. 1. The foulant on membrane were also characterised at different aeration rates.

3. Results and Discussion

3.1. Fouling phenomena analysis and hydraulic resistance determination

The filtration was stopped in both bundles as soon as the transmembrane pressure (TMP) reached 30 kPa (especially bundle M2). A specific cleaning process was developed in this study in order to access to different scale of fouling. Then, it is possible to differentiate the roles in hydraulic resistance due to (i) Macro-scale: sludge accumulation ($R_{Sludging}$) on the membrane surface or inside the bundle (between fibres), (ii) Micro-scale: presence of an irreversible thin biofilm on the membrane surface ($R_{Biofilm}$) and (iii) Nano-scale: adsorbed compounds inside the pores ($R_{Adsorption}$). To differentiate these three phenomena, the total hydraulic resistance was calculated according to Darcy law ($R = TMP/(\mu J_w)$) and compared when (1) the module was rinsed under tap water (until no sludge accumulation could be visually observed inside the bundle), (2) when each fibre was wiped to remove biofilm after the first step of rinsing, and (3) the membranes were chemically cleaned by soaking it in sodium hydroxide solution (20 h–4 g L^{-1}), citric acid solution (5 h–22 g L^{-1}) and sodium hypochlorite (5 h–0.2 g L^{-1}) to obtain the initial clean membrane resistance.

Table 2
Experimental conditions

Parameters	Units	Hollowfibre membrane modules	
		M1	M2
Organic load (OL)	gCOD/L/day	1.5	
Hydraulic retention time, HRT	h	5.7	
Sludge retention time, SRT	d	No extraction	
Permeate flux	LMH	20	
TSS concentration	g/L	4–6	
Substrate concentration	gCOD/L	0.70	
Membrane aeration	$M^3_{air}/m^2_{membrane}/h$	1.36	0.45
	$W.m^{-2}$	1.5	0. 5
	$NL.h^{-1}$	300	100

Fig. 2 compares the hydraulic resistance in both bundles due to each phenomenon. The discontinuous line (value of 10^{12} m^{-1}) is the reference line. For the experimental conditions studied, the effect of sludging on the hydraulic resistance can be observed when operating with low membrane airflow rates. Sludging can be avoided by increasing aeration (in this case, an increase to 1.36 $m^3\ m^{-2}\ h^{-1}$). Membrane aeration appears to have an effect also on biofilm resistance (Fig. 2(b)). This may be due to higher shear stresses (reducing biofilm thickness) in bundle M1. Figs. 2(b) and 2(c) show that the resistance due to biofilm and soluble adsorbed molecules are of the same order of magnitude.

These results confirm the importance of good sludge control in the bundle. This is also largely dependant on the suspended solid concentration in the mixed liquor (hence the importance of optimizing sludge retention time (SRT) and organic loading (OL)). If sludging can be avoided, hydraulic resistance is mainly due to the presence of biofilm and adsorbed soluble compounds (which can be minimized by the choosing suitable values of SRT and OL or by appropriate suspension conditioning). Moreover, the biofilm layer seems to be also minimized by shear stresses.

3.2. Characterisation of irreversible foulants (biofilm deposit and adsorbed compounds)

Size exclusion chromatography (SEC) coupled with column (protein-pak 25A) was used to separate the molecular weight distribution in order to characterised soluble compounds in terms of the molecular weight distribution (MWD). Two detectors UV (254 nm) and fluorescence (Ex:Em 250:340 nm) were used for the organic fractions. MilliQ water with phosphate (pH 6.8) and NaCl (0.1 M) was used as eluent. The separation ranges could cover from 1,000 to about 50,000 Da. Standards of MW of various polystyrene sulfonates (PSS: 210, 1,800, 4,600, 8,000, and 18,000 Da) were used to calibrate the equipment. The molecular weight distribution is given in Table 3.

When the sludge were supposed to be in a steady state conditions, five runs of 2-day operation were

1. Feed tank
2. Feed pump
3. Bioreactor
4. Bioreactor air distributor
5. Horizontal rotating
6. Filtration cell
7. Membrane air distributor
8. Air compressor
9. Membrane module
10. Peristaltic pump
11. Permeate
12. Pressure sensor
13. Computer
14. Higher liquid level due to gaz hold-up inducing a natural circulation of the mixed liquor between the filtration and biological tanks

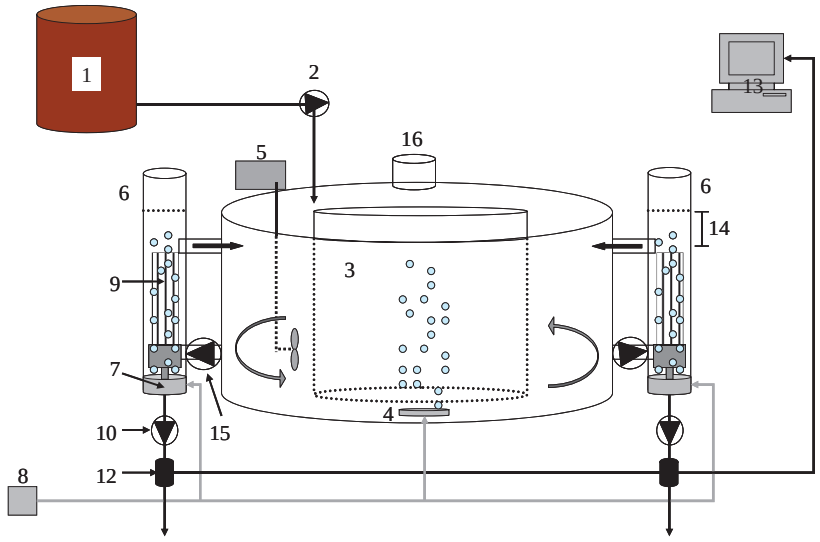

Fig. 1. Experimental set-up of hollow fibre membrane bioreactor.

carried out to compare the influence of membrane airflow rates (0.5–1.5 $m^3/h/m^2$) on the retention and adsorption of soluble compounds on the membrane surface and their influence on fouling dynamics. The laboratory scale MBR system was operated at a predetermined sludge concentration, organic load and permeate flux (4–5 gTSS/L, OL = 1.5 gCOD/L/d and 10 LMH aeration rate, respectively). The substrate used was made from an easily biodegradable source: ethanol and mineral salts (the same substrate used in Section 2). Experiments were carried out with flat sheet systems to identify soluble molecules encountered both in biofilm and adsorbed organic fraction in the pores. The description of MWD analysis by HPSEC can be found elsewhere [8].

Fig. 3(a) and 3(b) represents a typical chromatogram of influent, soluble mixed liquor and permeate obtained with both UV and fluorescence detector, during the experiment.

The five main peak families detected were biopolymers (BP, 35 kDa), humic acids (HA, 1 kDa), building blocks (BB, 750 Da), low MW acids (AC, 250 Da) and amphiphilic compounds (AM, < 200 Da). BPs include polysaccharides and proteins; BB are considered as hydrolysates of humic substances; acids are all free mono- and diprotic low-molar-mass organic acids; low MW and amphiphilics (slightly hydrophobic) compounds include sugars, alcohols, aldehydes, ketones and amino acids [9–12].

The BP and AM peaks were detected in influent but intensities were very small compared to those of the fluorescence mixed liquor chromatogram. This observation confirms that the BPs were mainly produced by sludge biomass activity in our experiment, and the same conclusion applies for amphiphilic compounds. Conversely HA, BB and AC peaks identified in mixed liquor were assumed to come from the influent.

A specific process to remove irreversible adsorbed organic matter biofilm (both biofilm and irreversible layer) from the membrane surface was used and described as below. Membrane was soaked in a cleaning solution (2.5 g NaOH in 500 mL; 0.125 M, pH = 12.6) for 3 h under constant shaking, the extract was then filtered through glass fibre filter of 0.45 μm. The filtrate was then neutralized to pH 7 by adding dilute sulphuric acid and underwent for COD, SMP and MWD analyses. More details of the extraction method can be found elsewhere [9]. Waste cleaning solution was analysed to identify MWD profile according to membrane airflow rates. Fig. 3(c) and 3(d) shows that the same families of compounds found in mixed liquor were found as well in waste obtained from cleaning. The cleaning solution chromatograms show the presence of BP, BB and amphiphilic compounds (AM called AM1, AM2, AM3) which were adsorbed onto or into membrane surface. It can be seen that AM molecules were newly detected on/in the membrane surface.

Based on UV responses, intensities of the BPs significantly increased for air flows ranging from 0.5 to 1.5 $m^3\ m^{-2}\ h^{-1}$. According to fluorescence responses, the intensities of the BP and AM increased as well.

Membrane air flow rate was not found to have any impact on the adsorption of other compounds other than BP and AM. However, as BP is considered as a major foulants, this result seems to be interesting by showing clearly that membrane air flow rate limits adsorption of BPs onto or into the membrane surface.

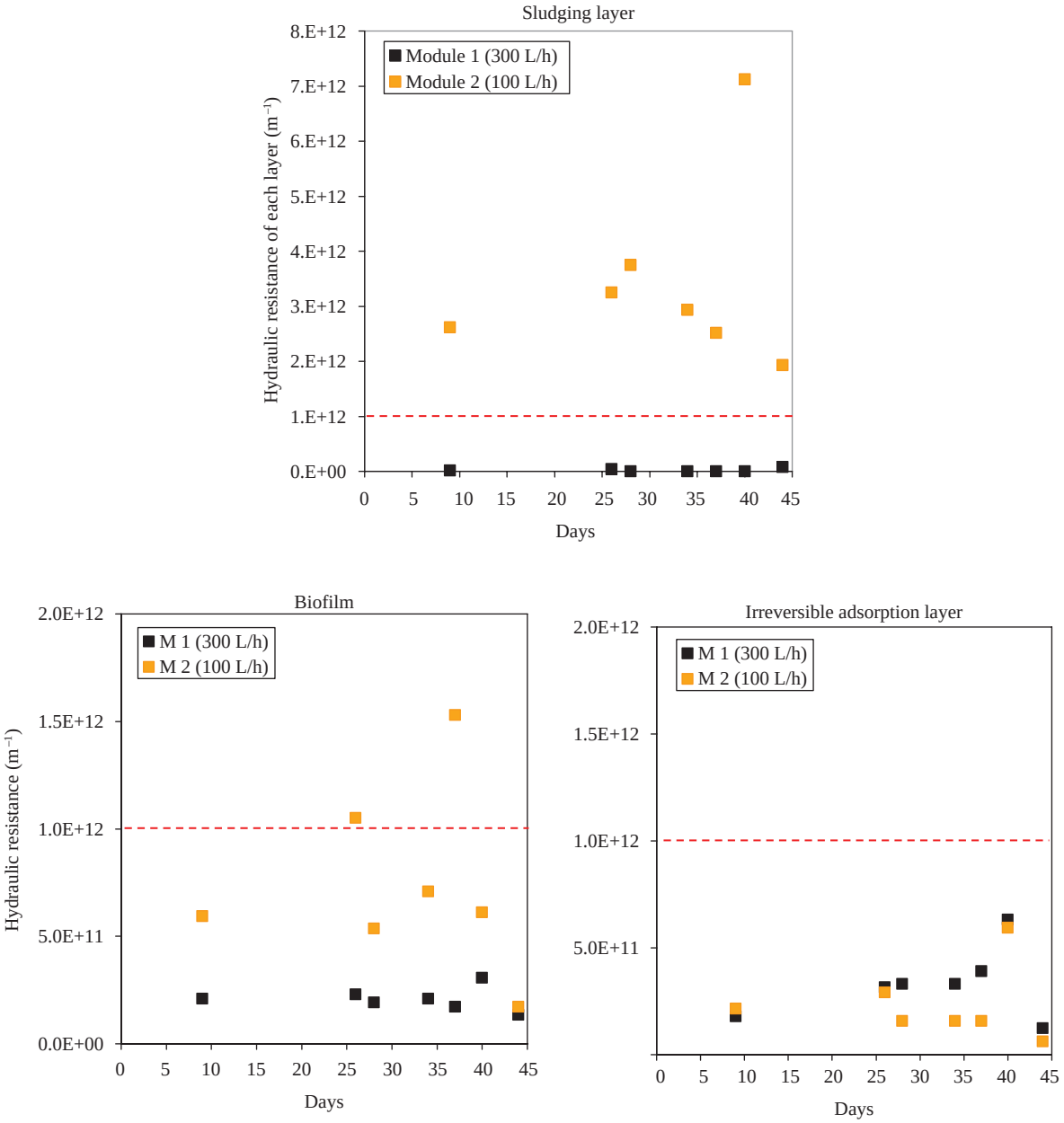

Fig. 2. Hydraulic resistance due to sludge accumulation, biofilm and adsorbed compounds.

Thus the use of higher membrane aeration rate can reduce the foulant attachment. This in turn helps to extend membrane functioning without any significant TMP drop and cleaning procedure. It can be noted that the influence of airflow rate appeared less important when its value reached 1 $m^3\ m^{-2}\ h^{-1}$ (Fig. 4).

4. Conclusion

The results clearly showed the influence of membrane aeration on the different hydraulic resistance scale: Macro-scale (sludging), micro-scale (biofilm) and nano-scale (adsorbed molecules). It is also important to know what kind of predominant fouling appears in order to compare the same phenomenon and not different scale of fouling. The influence of SPM in irreversible membrane fouling is pointed out. In fact, analysis of chromatograms allowed the identification of these main fouling components. According to the synthetic substrate composition, these biological by-product components consisted of large macromolecules (BPs MW was 35 kDa) and lower compounds (MW lower than 200 Da).

Table 3
Substance MW and their average retention due to membrane separation

	Substance	MW (Da)	Retention % (peak area)
BP	Biopolymers	35,000	95
HA	Humic acids	1,000	3
BB	Building block	750	5
AC	Low MW acids	250	10
AM	Amphiphilics	<200	6
AM-1	Amphiphilics	<200	28
AM-2	Amphiphilics	<200	33
AM-3	Amphiphilics	<200	Not eluted in mixed liquor

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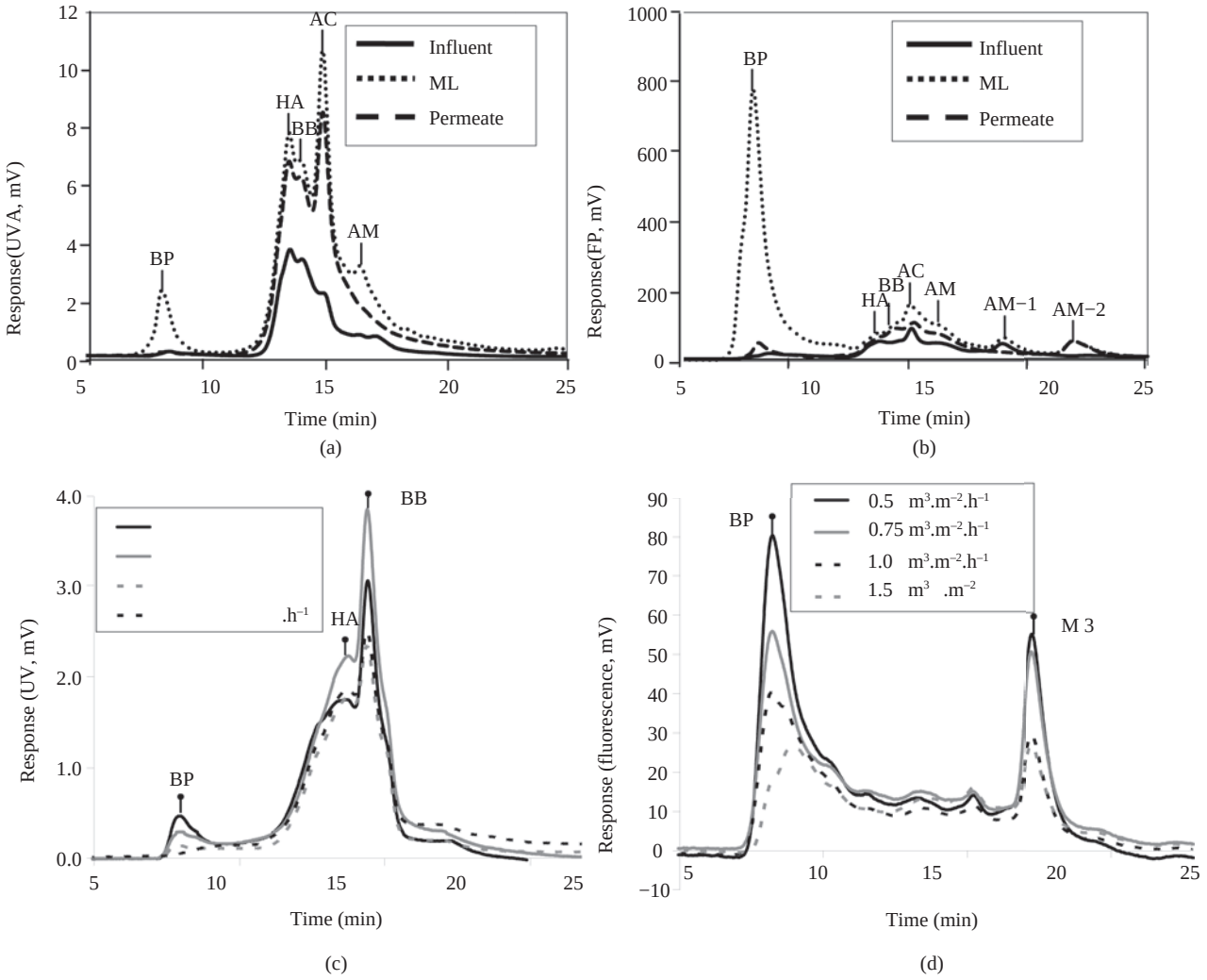

Fig. 3. MWD basic profile for bioreactor (a,b) and membrane cleaning solution (c,d).

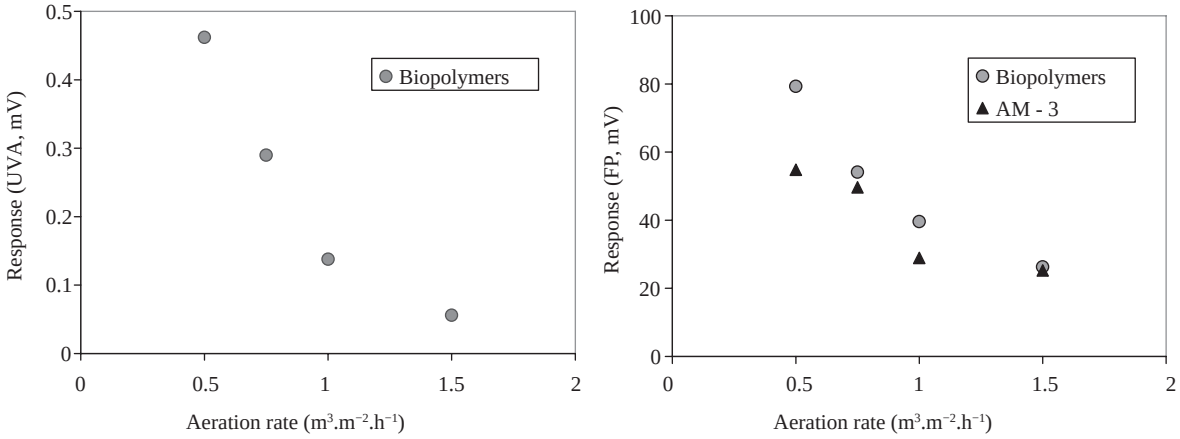

Fig. 4. Response intensity in cleaning solution vs. membrane aeration rate (UV spectra and fluorescence spectra).

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