REMOVAL OF AMETRYN USING MEMBRANE BIOREACTOR PROCESS & ITS INFLUENCE ON CRITICAL FLUX

Dimuth Navaratna[1*] and Veeriah Jegatheesan[2]

School of Engineering and Physical Sciences, James Cook University, Townsville, QLD 4811, Australia
*Corresponding Author; [1]Email: dimuth.navaratna@jcu.edu.au ; [1]Telephone: +61-7-47815535
[2]Email: jega.jegatheesan@jcu.edu.au ; [2]Telephone: +61-7-47814871

Abstract: Compared to the Conventional Activated Sludge Process (*ASP*), Membrane Bioreactors (*MBRs*) have proven their superior performance in wastewater treatment and reuse during the past two decades. Further, MBRs have wide array of applications such as the removal of nutrients, toxic and persistent organic pollutants (*POPs*), which are impossible or difficult to remove using ASP. However, fouling of membrane is one of the main drawbacks to the widespread application of MBR technology and Extra-cellular Polymeric Substances (*EPS*) secreted by microbes are considered as one of the major foulants, which will reduce the flux ($L/m^2/h$) through the membrane. Critical flux is defined as the flux above which membrane cake or gel layer formation due to deposition of EPS and other colloids on the membrane surface occurs. Thus, one of the operating strategies to control the fouling of MBRs is to operate those systems below the critical flux (at *Sub-Critical flux*). This paper discusses the critical flux results, which were obtained from short-term common flux step method, for a lab-scale MBR system treating Ametryn. This study compares the critical flux values that were obtained by operating the MBR system (*consisting of a submerged Hollow-Fibre membrane with pore size of 0.4µm and effective area of 0.2m*^{2}) at different operating conditions and mixed liquor properties. This study revealed that the critical flux values found after the introduction of Ametryn were significantly lower than those of obtained before adding Ametryn to the synthetic wastewater. It was also revealed that the production of carbohydrates (*in SMP*) is greater than proteins, subsequent to the introduction of Ametryn and this may have influenced the membrane to foul more. It was also observed that a significant removal (*40-60%*) of Ametryn from this MBR during the critical flux determination experiments with 40 minutes flux-step duration.

Key Works: Membrane Bioreactors (MBRs), Critical Flux, Mixed Liquor Suspended solids (MLSS), Extra-cellular Polymeric Substances (EPS), Ametryn

1 Introduction

Membrane Bioreactor (MBR) process, which is a combination of biological treatment and membrane filtration for separation of biomass, is one of the most novel wastewater treatment processes available at present. Bioreactor and membrane filtration cannot be considered as individual unit operations in MBRs, as these processes interact in many different ways. For the past two decades, many MBR plants have been installed in the treatment of domestic and industrial wastewater in the world. MBR technology is now becoming very popular at an approximate market value of US$217 million and a growth rate of 10.9% in 2005 (Simon Judd, 2007) due to its wide array of advantages over conventional treatment technologies, such as the production of superior quality of treated effluent, confining to smaller footprints, higher efficiency in removal of micro-pollutants and persistent organic pollutants and its ability to produce higher quality effluent even when the sludge is bulked. The demand for MBR systems increases steadily because they are now becoming more cost-effective, due to continuous fall in the costs of membrane module and related accessories that could be associated with high competition and advances in technology as well as the imposition of more stringent environmental laws and regulations in every state and region in the world. Due to fast-growing industry applications of MBR technology in wastewater treatment, the number of related research studies continued to increase for finding solutions to the presently identified drawbacks of MBR systems (mainly fouling of membrane) and for optimization of their performance (especially in nutrient removal, the treatment of micropollutants such as pesticides, herbicides, pharmaceuticals, etc.), to use them as a reliable treatment process.

MBRs mainly comprises of either microfiltration or ultrafiltration and as shown in Figure 1; in the submerged MBR systems the membranes are placed inside (Flat-Sheet or Hollow Fibre membranes) bioreactors and in the side-stream MBR systems the membranes (multi-tube/ tubular) are placed

outside the bioreactor (Simon Judd, 2007 and Le-Clech et al., 2006). Presently, most of the MBRs are operated aerobically (98%) and the rest are anaerobically (Mulligan and Gibbs, 2003). In submerged MBRs, air is supplied for biodegradation and membrane cleaning (coarse bubbling).

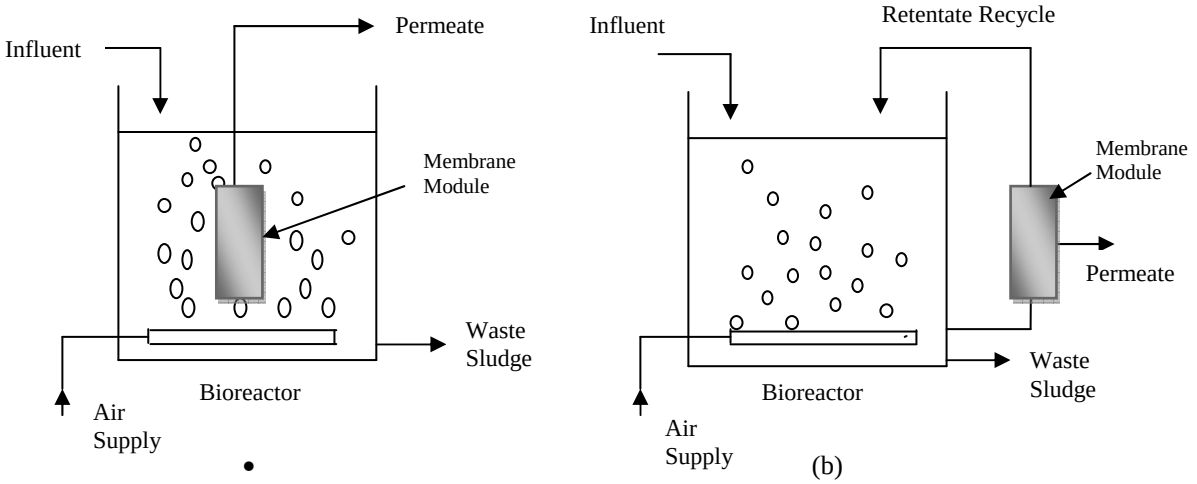


Figure 1 – *Configurations of MBR Systems: (a) Submerged MBR; (b) Side-Stream MBR*

Membrane fouling, which is caused due to the restriction, occlusion or blocking of membrane pores (Simon Judd, 2007) at the surface of the membrane, reduces the permeate flux (volumetric flow rate per unit membrane area) through the membrane. Thus, fouling is considered as the main obstacle to the widespread application of MBR. Fouling of membrane is mainly caused due to physical (nominal particle size of microbial flocs), chemical (hydrophobicity) and biological (extra-cellular polymeric substances (EPS) and viscosity) factors related to biomass. According to Meng et al. (2009), fouling mechanisms in a MBR are: (a) adsorption of solutes and colloids within or on membrane surface; (b) deposition of sludge flocs onto the membrane surface; (c) formation of cake layer on the membrane surface; (d) detachment of foulants attributed mainly to shear forces; (e) the spatial and temporal changes of the foulant composition such as the change of microbial community and biopolymer components in the cake layer during the long term operation. Most of the previous research work (Laspidou and Rittmann, 2002; Jang et al., 2006; Le-Clech et al., 2006; and Rosenberger et al., 2006) confirmed that Soluble Microbial Products (SMP which is referred to as free EPS) and bound EPS (eEPS), which are secreted by microorganisms, are the main organic compounds that cause fouling of membrane. Free and bound EPS mainly consist of polysaccharides (carbohydrates) and protein, and they play a major role in the formation of cake and gel layers on the membrane.

Operating MBRs at subcritical flux (below the "critical flux", where the flux starts to form the cake or gel layer on the membrane surface) is considered as one of the most practical strategies to control the fouling of membranes in MBR. In addition to this, subcritical flux operation reduces the consumption of energy and hence minimizes the operational cost of MBR. Field, et al. (1995) originally introduced the concept of the critical flux in microfiltration using an empirical approach and they defined the "critical flux" as "a flux below which a decline of flux with time does not occur (that is at subcritical flux, where $\frac{dTMP}{dt} = TMP' = 0$) and above which (supercritical flux) fouling is observed". However subsequent to that, Le-Clech et al. (2003) showed that a zero rate of TMP increase may never be obtained ($TMP' \neq 0$) during their short-term (common flux step method) critical flux determination tests carried out for synthetic and real sewage. Since then, different types of short-term critical flux determination and long-term sub-critical flux operational studies have been carried out under different feed-wastewater characteristics, biomass/sludge conditions and operating operations (Bouchot et al., 2006; Defrance and Jaffrin, 1999; Fan et al., 2006; Fane et al., 2002; Ndinisa et al., 2006; Torre et al., 2009; Van der Marel et al., 2009;

Le-Clech et al., 2003; Ognier et al., 2004; Saroj et al., 2008; Guglielmi et at., 2007a and b; Jinsong et al., 2006).

Feed-wastewater characteristics influence the mixed liquor/ sludge conditions (mixed liquor suspended solids (MLSS), SMP and eEPS) of MBRs. Therefore, mixing micropollutants such as herbicides to the feed wastewater would have an impact on the production of SMP and eEPS, and hence to the membrane filterability and fouling of membrane. The value of critical flux is a measure of fouling of membrane and the critical flux values for the laboratory-scale MBR system is evaluated and compared in this study to identify the influence of herbicides in fouling of membrane. This paper discusses the results obtained during the critical flux tests, which were carried before and after introduction of Ametryn to the MBR system.

Ametryn, which is a herbicide, is commonly used for controlling weeds (Table 1) in farmlands located in the Great Barrier Reef (GBR) Catchments in North Queensland (Australia). Ametryn falls to the category of second generation herbicides (Photosystem II) and it is fairly persistent and bio-accumulated in the environment. Therefore, Ametryn that is found in very low concentrations (a micropollutant having a concentration of µg/L or ng/L) is also considered as a Persistent Organic Pollutant (POP). A comprehensive review on impacts, existence, transport and treatment of these herbicides found in GBR catchments has been carried out elsewhere (Navaratna et al., 2010). As a broad objective of this overall research study, the laboratory-scale MBR is researched to optimise the removal of Ametryn from wastewater, while studying critical flux determination and subcritical operations of this MBR system. This paper also describes the early performance of Ametryn removal from this MBR system during the critical flux determination studies.

2 Material and Methods

2.1 Experimental setup

Figure 2 shows the laboratory-scale MBR system installed at the hydraulics laboratory at School of Engineering, James Cook University, Townsville, Australia. The reactors are made out of Perspex and the maximum hydraulic capacities of the feed tank and the MBR are 50 and 15L respectively. A hollow fibre polyethylene (PE) membrane module (pore size 0.4µm, effective area 0.2m^2) is submerged in the MBR reactor. Air to the MBR is supplied from the central compressed air system via air regulators and valves, an air flow meter and perforated PVC manifold approximately with 20 holes (diameter around 1.5mm for providing coarse bubbling aeration) and installed at the base of the MBR. As a backup air supply, a portable compressor is also used. Peristaltic pumps are used to feed the MBR tank at a uniform feed rate and to pump out permeate (treated effluent) from the MBR through the membrane. A vacuum pressure gauge is fitted to measure TMP. Peristaltic pumps are connected to an electronically controlled timer to operate them intermittently (12 minutes “on” and 3 minutes “off”). One of these pumps is used when required for backwashing the membrane with treated water, which has very low turbidity.

The recipe of synthetic wastewater fed to the MBR system during this study consists of Glucose ($C_6H_{12}O_6$ – 710mg/L), Ammonium Acetate (CH_3COONH_4 – 200mg/L), Sodium Hydrogen Carbonate ($NaHCO_3$ – 750mg/L), Ammonium Chloride (NH_4Cl – 30mg/L), Potassium Di-Hydrogen Phosphate (KH_2PO_4 – 30mg/L), Potassium Hydrogen Phosphate (K_2HPO_4 – 60mg/L), Magnesium Sulphate ($MgSO_4.7H_2O$ – 50mg/L), Calcium Chloride ($CaCl_2.2H_2O$ – 30mg/L) and Sodium Chloride (NaCl – 30mg/L). In addition to these chemical compounds, Ametryn was added 1 mg/L approximately. In order to prepare the stock solution, a precisely measured quantity of Ametryn was dissolved in methanol, mixed with distilled water and then methanol was evaporated. The COD concentration of synthetic feed wastewater was maintained around 700±50mg/L.

Activated sludge (approximately 8,000 mg/L) was brought from the Cleveland Bay Wastewater Purification Plant in Townsville (QLD, Australia) and acclimatized in the bioreactor. The laboratory-scale MBR system has been operated for over 400 days continuously adjusting influent, sludge and operating parameters.

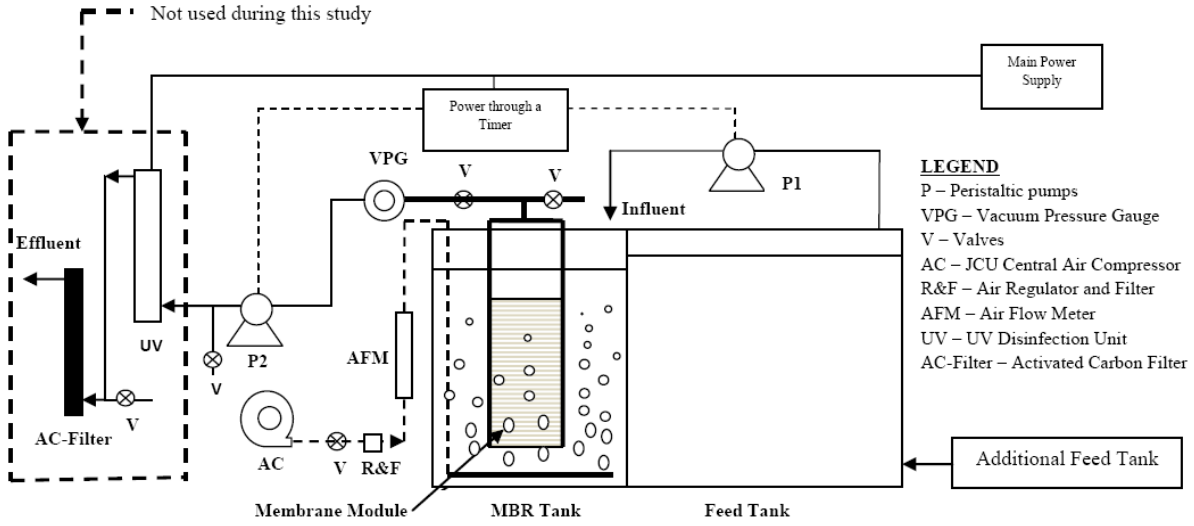
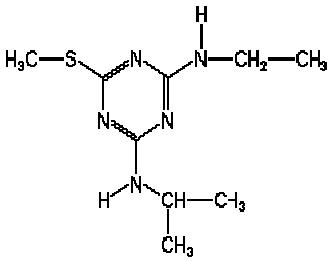


Figure 2: *Schematic of the Experimental Setup*

Table 1: *Characteristics of Ametryn*

Molecular Weight (g/mol)	227.33	
Molecular Formula	$C_9H_{17}N_5S$	
Melting Point (^oC)	84-85	
Appearance	White Powder	
Solubility	185 mg/L (water 20^oC) and readily dissolves in solvents (acetone)	
Purpose	methyl-thio-triazine herbicide to control grass	
IUPAC Name	N2-ethyl-N4-isopropyl-6-methylthio-1,3,5-triazine-2,4-diamine	

2.2 Laboratory analysis

During these studies, dissolved oxygen (DO), pH and turbidity were measured using YSI DO 200 dissolve oxygen meter, WP-80 TPS pH and temperature meter and HACH 2100P turbidimeter respectively. Mixed liquor suspended solids (MLSS) concentration was analysed using the standard methods (1985). COD measurements were carried out adopting Photometric method using Spectroquant COD cell test kits and Thermo-reactor TR-320. EPS extraction was carried out using the method stated by Bin et al. (2008) with a slight modification. Initially, a 100ml of mixed liquor sample was allowed to settle for 45 minutes to 1 hour and the supernatant was removed. The settled sediment/sludge was then diluted with 40ml of distilled water and mixed in a mechanical shaker for 5 minutes at 150 rpm. Then the diluted sludge mixture was centrifuged at 8000 rpm for 10 minutes and the supernatant was collected, which is considered as soluble microbial products (SMP) or free EPS. Subsequent to that the remaining sludge was re-suspended with 40 mL of 0.1N NaOH solution allowing it to mix thoroughly in the same mechanical shaker at 150 rpm for 120 minutes before it was centrifuged again at 13,000 rpm for 15 minutes at 4^oC. Finally, the supernatant (eEPS or bound EPS) was extracted. Both SMP and eEPS samples were neutralised separately with diluted HCl. SMP and eEPS Protein and Carbohydrate concentrations were determined by using Lowry method (Lowry et al., 1951) with bovine serum albumin as reference and Dubois et al. (1956) method with glucose as standards respectively. Diluted Sludge Volume Index (DSVI) was estimated by diluting the mixed

liquor by four folds, allowing solids to settle for 30 minutes in a 1L measuring cylinder. High performance liquid chromatography (HPLC) method was used to analyse the feed and permeate Ametryn concentrations.

2.3 Critical flux determination methods

The critical flux was determined in different occasions in MBR operation by changing the controlling parameters of MBR. Several short term critical flux determination experiments were carried out using the common flux step method, which was described by Le Clech et al. (2003). The flux step durations were chosen as 20 and 40 minutes for the experiments discussed in this paper. Flux step height was kept as a constant throughout these studies at 3 L/m^2/h. The tests were carried out with and without intermittent permeate suction for above flux step durations. Experiments were conducted before and after introduction of Ametryn to the MBR system. The membrane module was cleaned chemically using 3g/L NaOCl solution as per the procedure described by the manufacturer before every experiment.

3 Theory/ Calculations

The flux through the membrane J (m^{3}m^{-2}s^{-1}) can be related to the applied trans-membrane pressure ΔTMP (Pa), viscosity of the fluid μ (Pa s) and the membrane resistance R (m^{-1}) according to Darcy's Law:

$$J = \frac{\Delta TMP}{\mu R} \tag{1}$$

$$R = R_m + R_n + R_c + R_p \tag{2}$$

$$R = R_m + R_f \tag{3}$$

Where, R_m is the hydraulic resistance of the clean membrane, R_n is the irreversible resistance due to fouling, R_c is the membrane resistance due to cake or gel layer formed by concentration polarization (mainly in ultrafiltration), deposition of suspended solids, colloids and solutes, and R_p is the membrane resistance due to pore blocking occurred by deposition of soluble and colloidal substances. R_f is the sum of R_m, R_n and R_p and depends on applied trans-membrane pressure and the system mass transfer properties. For microfiltration, the fouling by concentration polarization could be ignored due to the large size of particles retained in the reactor (Lim and Bai, 2003).

During these short-term critical flux determination experiments, pressure of the mixed liquor in the reactor has to be kept constant and the TMP assumed to vary only with changes in permeate pressure due to fouling. For each flux step, three TMP values were recorded (initial TMP=TMP_i, intermediate TMP=TMP_{im} and final TMP=TMP_f). Then the following parameters were estimated;

Initial TMP increase, $\Delta TMP_0 = TMP_i^n - TMP_f^{n-1}$ (4)

Rate of increase of TMP, $\frac{dTMP}{dt} = \frac{TMP_f^n - TMP_i^n}{t_f^n - t_i^n}$ (5)

Average TMP, $TMP_{ave} = \frac{TMP_f^n + TMP_i^n}{2}$ (6)

In the above expressions, "n", "i" and "f" are denoted the flux step number, initial and final observations made for each run, respectively.

4 Results and Discussion

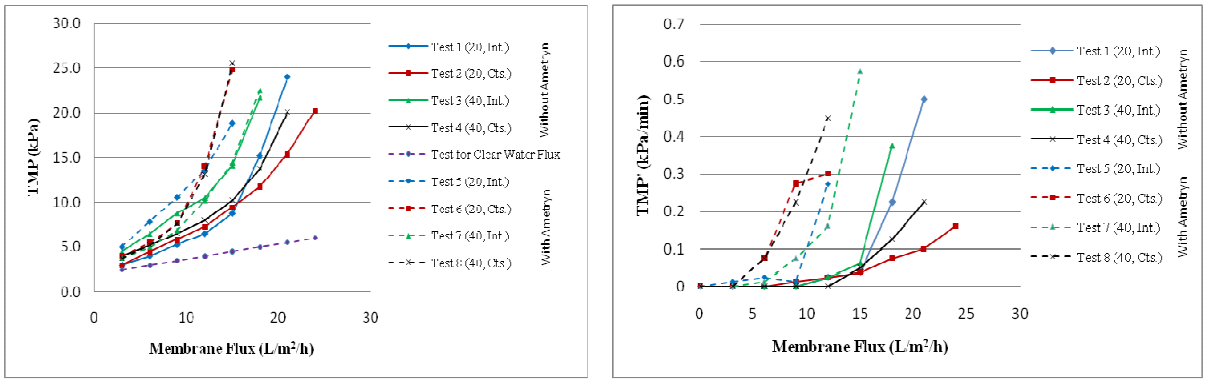
Table 2 shows the results obtained for the eight short-term (common flux step method) critical flux determination tests (Test 1 through 8) for before and after the introduction of Ametryn. When comparing the critical flux values obtained from tests carried out before and after the introduction of Ametryn, it can be seen that there is a significant reduction of Ametryn in MBR permeate (40-60%) in the tests carried out after introducing Ametryn. On the other hand, by observing the critical flux values obtained for Tests 5 through 8, the tests carried out with intermittent permeate suction (12 minutes "on" and 3 minutes "off") show higher values of critical flux, compared to that of the tests carried out with continuous permeate suction mode. However, this pattern was not observed for Tests 1 through 4, probably due to the differences in the way the cake layer formed during the two different wastewater and MBR mixed liquor conditions before and after the addition of Ametryn.

Table 2: *Operating conditions and results during critical flux determination tests*

Parameter		← Before Ametryn →				← After Ametryn →			
		Test 1	**Test 2**	**Test 3**	**Test 4**	**Test 5**	**Test 6**	**Test 7**	**Test 8**
Suction Mode		INT	CTS	INT	CTS	INT	CTS	INT	CTS
Flux step duration (minutes)		20	20	40	40	20	20	40	40
Average MLSS (mg/L)		7478	7478	10383	10383	7962	7962	9195	9195
DSVI (mL/g-MLSS)		123	123	150	150	156	156	126	126
Average SMP (Soluble EPS)/ (mg/L)	Protein	138.53	138.53	146.70	146.70	76.87	76.87	112.24	112.24
	Carbohydrates	39.43	39.43	50.99	50.99	64.59	64.59	77.66	77.66
Average eEPS (Bound EPS)/ (mg/L)	Protein	913.09	913.09	959.64	959.64	815.76	815.76	712.99	712.99
	Carbohydrates	228.65	228.65	270.31	270.31	210.87	210.87	253.69	253.69
Estimated Critical Flux ($L/m^2/h$) – when dP/dt (TMP')>0.075kPa/min		15-18	18-21	15-18	15-18	9-12	6-9	9-12	6-9

INT – Intermittent Permeate flux (12 minutes "ON" and 03 minutes "OFF)
CTS – Continuous Permeate Flux

The components of EPS (protein and carbohydrates of soluble EPS-SMP and bound EPS-eEPS) in mixed liquor of a MBR system is considered as the most influential organic substances that cause fouling of membrane. According to EPS results shown in Table 2, it can be seen that the concentrations of protein in SMP and bound EPS are less in Tests 5 through 8 compared to that of Tests 1 through 4. This describes that this reduction of protein in SMP and bound EPS have not been contributed significantly to increase the critical flux values in this study. However, it can be seen that more concentration of carbohydrates in SMP (52-64%) for the tests, which were carried out after introducing Ametryn. It was found that the critical flux values are significantly smaller when Ametryn was introduced, compared to that of tests carried out before introducing Ametryn. Thus, concentration of carbohydrates in SMP of mixed liquor is the main organic foulant that could be causing the fouling of membrane.

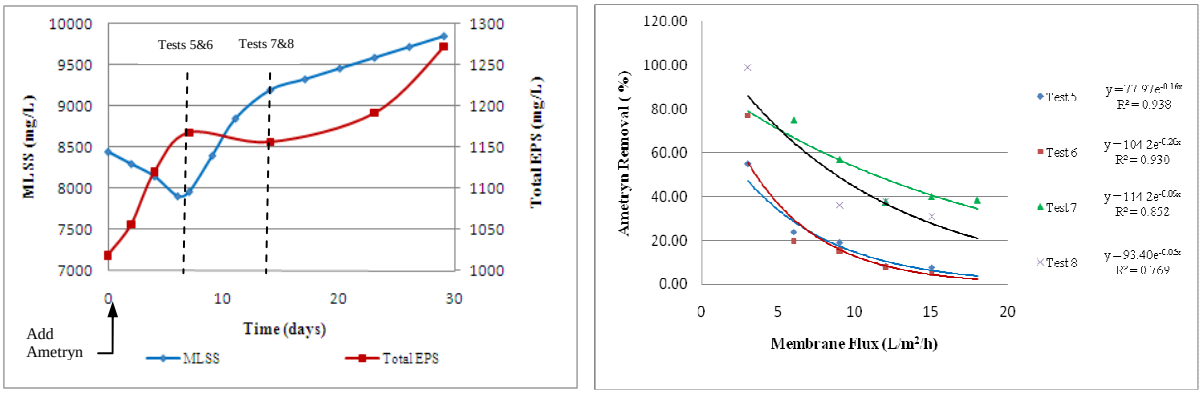


(a) (b)

Figure 3: *Short-term flux-step test results: (a) Average TMP and (b) TMP' versus membrane flux*

Figure 3(a) shows the average TMP variations with membrane flux during the short-term flux step tests that were carried out before and after introduction of Ametryn to the MBR system. Field et al. (1995) defined two distinct forms of critical flux values namely strong and weak. The strong form is the flux at which the TMP starts to deviate (exponentially) from the clear water flux curve, which is linear as shown in Figure 3(a). On the other hand, the weak form is the flux that shows a significant fouling of membrane from the start-up of the filtration and therefore, the trend curves for TMP against flux of Tests 1 through 8 are above that of the clear water flux curve.

Figure 3(b) shows the variation in the rate of fouling of membrane TMP' with membrane flux for Tests 1 through 8. These trend curves are used to estimate the critical flux values (Table 2) of each test. In this study, the critical flux values were determined for the flux value corresponding to $TMP' > 0.075$ kPa/min and from Table 2 it can be seen that the critical flux decreased significantly after the introduction of Ametryn irrespective of the type of test conducted.



(a) (b)

Figure 4: *(a) MLSS and Total EPS variation during the first 29 days after the introduction of Ametryn (b) Ametryn removal by the MBR during short-term critical flux tests*

Figure 4(a) shows the variation of the concentrations of MLSS and total EPS (soluble and bound EPS) of mixed liquor of the MBR during the first 29 days of operation after the introduction of Ametryn. During this period, MBR was operated at a flux of 5.1L/m^2/h with intermittent permeate suction (12 minutes "on" and 3 minutes "off") and an infinite sludge retention time (SRT) as there was no sludge disposal carried out intentionally. From Figure 4(a), it can be seen that the concentrations of MLSS and total EPS show opposite and different trends (total EPS increases, when MLSS decreases). This confirms that the concentration of EPS does not fluctuate always with MLSS positively or negatively in MBR operation.

Table 3: *Variation of Protein and Carbohydrates in SMP and eEPS from the day that Ametryn was introduced to the laboratory-scale MBR system*

Days elapsed from the introduction of Ametryn	MLSS/ (mg/L)	SMP		eEPS	
		Protein/ (%)	Carbohydrates/ (%)	Protein/ (%)	Carbohydrates/ (%)
7	7962	-7.80	-11.46	26.66	-3.35
14	9195	34.63	6.46	10.70	16.27
29	9847	-18.29	-3.70	40.72	4.69

Negative values indicate "reduced % of concentration" compared to that of the day Ametryn was introduced to the MBR system

By analysing the results illustrated in Table 3, it can be seen that protein in eEPS is the only EPS component that has been increased after adding Ametryn to the system. However, this production of protein in eEPS is reduced after the day 7, but showed an increase of protein in SMP and carbohydrates of eEPS. However, this change in the production of EPS components during the day 7 and 14 has resulted to maintain the total EPS at a stable level. Subsequent to this period, it again shows a higher production of protein in eEPS and that contributes the total EPS in MBR to depict greater rate of increase as shown in Figure 4(a). Although, reason/s for these fluctuations of EPS components are not confirmed in this paper, the studies are being continued to analyse the impact of herbicides and pesticides such as Ametryn on the production of EPS in MBR systems.

Figure 4(b) shows the variation of Ametryn removal % with membrane flux during the critical flux determination experiments carried out after the introduction of Ametryn to the synthetic feed of the laboratory-scale MBR system. The percentage of Ametryn removal declines exponentially with the increase in membrane flux. Tests 5 and 6, which were carried out with shorter flux-step duration (20 minutes) and lower MLSS (7962mg/L), show a greater decrease in Ametryn removal with membrane flux compared to that of Tests 7 and 8, which had longer flux step duration of 40 minutes and higher MLSS (9195mg/L). Further, both Tests 7 and 8 show higher removal of Ametryn (about 50-60% for the critical flux of those tests) compared to the removal observed in Tests 5 and 6. When comparing Tests 7 and 8, it can be observed that Test 7, which was operated under intermittent permeate suction mode, gives a better removal of Ametryn compared to Test 8, which was studied under continuous permeate suction mode at similar MLSS. This study is being continued to observe the improvement in the removal of Ametryn the MBR system used in this study.

5 Conclusions

In this study, critical flux values for a laboratory-scale MBR (PE membrane - 0.4µm and 0.2 m^2) were obtained using short-term (common flux-step method) tests under different hydrodynamic and sludge environments. Synthetic solutions with and without Ametryn were used as the feed for MBR. It could be seen that carbohydrate in SMP was higher (52-64%) in tests that were carried out after Ametryn was added, and this could have probably caused higher fouling propensity. However, on the other hand, it was found that production of protein in eEPS had been increased significantly after adding Ametryn to the MBR feed. Further, at early stages of operation (within the first month), it was seen that a removal of 50-60% of Ametryn by the MBR for a feed solution that contained 1mg/L of Ametryn.

References

Bin, Z., Baosheng, S., Min, J., Taishi, G., Zhenghong, G., 2008. Extraction and analysis of extracellular polymeric substance in membrane fouling in submerged MBR. Desalination. 227, 286 – 294

Bouchot, M. E., Espinasse, B., Cabassud, C., 2006. Fouling effects and critical flux in relation with module design and aeration conditions for a side stream outside/in filtration system. Desalination. 199, 487-489.

Defrance, L., Jaffrin, M.Y., 1999. Comparison between filtration at fixed transmembrane pressure and fixed: application to a membrane bioreactor used for wastewater treatment. Journal of Membrane Science. 152. 203-210.

Dubois, M., Gilles, K. A., Hamilton, J. K., Rebers, P. A., Smith, F., 1956. Colorimetric method for determination of sugars and related substances. Analytical Chemistry. 28, 350-356

Fan, F., Zhou, H., Hussain, H., 2006. Identification of wastewater sludge characteristics to predict critical flux for membrane bioreactor processes. Water Research. 40, 205-212.

Fane, A. G., Chang, S., Chardon, E., 2002. Submerged hollow fibre membrane module – design options and optional considerations. Desalination. 146, 231-236.

Field, R.W., Wu, D., Howell, J.A., Gupta, B.B., 1995. Critical flux concept for microfiltration fouling. Journal of Membrane Science. 100, 259-272.

Guglielmi, G., Chiarani, D., Judd, S. J., Andreottola, G., 2007a. Flux criticality and sustainability in a hollow fibre submerged membrane bioreactor for municipal wastewater treatment. Journal of Membrane Science. 289, 241-248.

Guglielmi, G., Saroj, D. P., Chiarani, D., Andreottola, G., 2007b. Sub-critical fouling in a membrane bioreactor for municipal wastewater treatment: Experimental investigation and mathematical modelling. Water Research. 41, 3903-3914.

Jang, N., Shon, H., Ren, X., Vigneswaran, S., Kim, I.S., 2006. Characteristics of bio-foulants in the membrane bioreactor, Desalination 200 (2006) 201-202

Jinsong, Z., Chuan, C. H., Jiti, Z., Fane, A. G., 2006. Effect of Sludge Retention Time on Membrane Bio-Fouling Intensity in a Submerged Membrane Bioreactor. Separation Sci. and Tech. 41: 7, 1313-1329.

Judd, S. (2007). The status of membrane bioreactor technology. Trends Biotechnology. 26(2) 109-116.

Laspidou, C.S., Rittmann, B.E., 2002. A unified theory for extracellular polymeric substances, soluble microbial products, and active and inert biomass, Water Research 36 (2002) 2711-2720

Le-Clech, P., Chen, V., Fane, T.A.G., 2006. Fouling in membrane bioreactors used in wastewater treatment, journal of Membrane Science 284 (2006) 17-53

Le-Clech, P., Jefferson, B., Chang, I.S., Judd, S.J., 2003. Critical flux determination by the flux-step method in a submerged membrane bioreactor. Journal of Membrane Science. 227, 81-93.

Lim, A.L., Bai, R., 2003. Membrane fouling and cleaning in microfiltration of activated sludge wastewater, Journal of Membrane Science 216 (2003) 279-290

Lowry, O. H., Rosebrough, J., Farr, A. L., Randall, R. J., 1951. Protein measurement with Folin Phenol reagent. Journal of biological Chemistry. 193, 265-275

Meng., F., Chae, S., Drews, A., Kraume, M., Shin, H., Yang., F., 2009. Recent advances in membrane bioreactors (MBR): Membrane fouling and membrane material, Water Research 43 (2009) 1489-1512

Mulligan, C.N., Gibbs, B.F., 2003. Innovative Biological Treatment Process for water in Canada, Water Qual. Res. J. Canada, 200 Volume 38, No. 2, 243-265

Navaratna, D., Shu, L., Jegatheesan, V., 2010. Existence, impacts, transport and treatments of herbicides in Great Barrier Reef catchments in Australia, in: Virkutyte, J., Varma, R. S., Jegatheesan, V. (Eds.), Treatment of Micropollutants in Water and Wastewater. IWA Publishing, London, UK, Chapter 11, pp. 425-463.

Ndinisa, N. V., Fane, A. G., Wiley, D. E., 2006. Fouling control in a submerged flat sheet membrane system: Part I – Bubbling and hydrodynamic effects. Separation Science and Technology. 41: 7, 1383-1409.

Ognier, S., Wisniewski, C., Grasmick, A., 2004. Membrane bioreactor fouling in sub-critical filtration conditions: a local critical flux concept. Journal of Membrane Science. 229, 171-177.

Rosenberger, S., Laabs, C., Lesjean, B., Gnirss, R., Amy, Jekel, M., Schrotter, J.C., 2006. Impact of colloidal and soluble organic material on membrane performance in membrane bioreactors for municipal wastewater treatment, Water research 40 (2006) 710

Saroj, D.P., Guglielmi, G., Chiarani, D., Andreottola, G., 2008. Subcritical fouling behaviour modelling of membrane bioreactors for municipal wastewater treatment: The prediction of the time to reach critical operating condition. Desalination. 231, 175-181.

Standard Methods for the examination of water and wastewater(1985), 16th edition. APHA. AWWA. WPCF (ISBN 0-87553-131-8)

Torre, T. D., Iversen, V., Moreau, A., Stüber, J., 2009. Filtration characterization methods in MBR systems: A practical comparison. Desalination and Water Treatment. 9, 15-21.

Van der Marel, P., Zwijnenburg, A., Kemperman, A., Wessling, M., Temmink, H., Van der Meer, W., 2009. An improved flux-step method to determine the critical flux and the critical flux for irreversibility in a membrane bioreactor. Journal of Membrane Science. 332, 24-29.

Acknowledgements

We thank Dr. Shane Askew of Advanced Analytical Center of James Cook University for analysing the concentration of Ametryn in permeate and feed samples using HPLC, Dr. Joy Morgan for releasing the Chemistry Laboratory for analysing COD and preparation of Ametryn stock solution and Dr. Jennifer Elliman for releasing the Bacteriology Laboratory of Veterinary and Biomedical Sciences for extracting and analysing of EPS.