PRETREATMENT OF SEAWATER FOR ORGANIC REMOVAL USING POWDER ACTIVATED CARBON

Authors: *Sanghyun Jeong, Tien Vinh Nguyen, Saravanamuthu Vigneswaran**

Presenter: *Sanghyun Jeong*
Student – University of Technology Sydney – Australia

Abstract

This study investigated the effect of powder activated carbon (PAC) dosed in a submerged membrane reactor in removing organic matter from seawater. The maximum adsorption capacity of PAC for organic compounds in seawater was up to 23.1 mg DOC/g of PAC. The PAC adsorption equilibrium results with seawater fitted well with Freundlich and Sips isotherms. More than 86% of organic matter was removed after a contact period of 8 hours with the 1.5g/L PAC. Ho model described well the adsorption kinetics of organic matter on PAC. The addition of PAC into submerged microfiltration reactor not only improved critical flux from 20 $L/m^2.h$ to 40 $L/m^2.h$ but also helped reduce the transmembrane pressure (TMP) of the system. The analyses of fractionation of organic matter showed that PAC was able to remove most of hydrophobic compounds (more than 96%) and a significant amount of hydrophilic compounds (78%).

I. INTRODUCTION

Desalination of seawater for a drinking water supply is increasingly considered in many parts of the world. The reverse osmosis (RO) is extensively used in desalination process but one of the major problems of RO is membrane fouling. This fouling can be reduced by pre-treatment of seawater prior to the application of RO. Membrane processes such as microfiltration (MF) and ultrafiltration (UF) can be used as RO pre-treatment system as they can remove effectively suspended solids and colloids. Pearce [1] showed that UF/MF pre-treatment with waste and brackish water led to higher RO flux, less fouling, chemical dose reduction and better on-stream time. However, the use of MF alone with sea water also leads to MF fouling quickly and thus resulting in unsustainable operation. In addition, the MF alone can not be able remove dissolved organic matter effectively. Integrated hybrid system incorporating MF with other physico - chemical processes such as adsorption or coagulation can be a solution for this problem.

Incorporation of physico - chemical processes with MF for wastewater treatment has been proved as an effective way for reducing membrane fouling as well as improving water quality [2]. Guo et al. [2] reported that immersed membrane - adsorption hybrid system could remove a majority of organics while reducing the membrane fouling. The addition of adsorbents into the MF reactor removes organic compounds prior to their entry to the membranes surface that cause membrane fouling. Various additives such as alum, natural zeolite and powdered activated carbon (PAC) were used in the submerged membrane reactor for treating wastewater [3-6]. However, there is no much study on the application of PAC into submerged microfiltration with seawater. Another way of reducing MF fouling as well as its operation cost is operating the MF below the critical flux. The adding of PAC can reduce the loading of dissolved organic matter (DOM) on membrane, improve the permeate flux, thereby reducing the membrane fouling.

The objective of the study was to evaluate the performance of PAC on organic removal from seawater through isotherm and kinetic experiments. The effect of PAC on the operation of submerged microfiltration hybrid adsorption system (SMHAS) in terms of the critical flux improvement and removal of specific organic fractions was also experimentally evaluated.

II. MATERIALS AND METHODS

1.1 Materials

1.1.1 Seawater

Seawater collected from Chowder Bay, Sydney, Australia was used in this study. Seawater was pumped from 1 m below the sea surface level and filtered using a centrifuge filtration system to remove the large particles. The average turbidity, pH and dissolved organic carbon (DOC) values of seawater were 0.42 NTU, 8.0 and below 2.5 mg/L respectively.

1.1.2 Powder activated carbon

Powdered activated carbon (PAC, wood based) was used as adsorbent in a submerged membrane adsorption hybrid system. The characteristic of PAC is shown in Table 1.

IDA World Congress – Perth Convention and Exhibition Centre (PCEC), Perth, Western Australia September 4-9, 2011
*REF: **IDAWC/PER11-330***

- 2 -

Table 1   Characteristics of powdered activated carbon (PAC) used in this study

Specification	PAC-WB
Iodine number (mg/g min)	900
Ash content (%)	6 max.
Moisture content (%)	5 max.
Bulk density (kg/m^3)	290–390
Surface area (m^2/g)	882
Nominal size 80% min finer than	75 micron
Type	Wood based
Mean pore diameter (Å)	30.61
Micropore volume (cc/g)	0.34
Mean diameter (μm)	19.71
Product code	MD3545WB powder

2.2   Experimental

2.2.1   Isotherm experiment

Isotherm study was conducted at the room temperature of 25°C. In these experiments, different amounts of PAC (0.01 g to 0.5 g) were placed into 250 mL Erlenmeyer flasks containing 100 mL of the seawater. The flasks were shaken at 110 rpm for 48 hours by a portable bench top platform shaker (Ratex Instrument Company). After 48 hours of contact time, samples from flasks were taken for analysing residual organic compounds.

The Freundlich isotherm is an empirical equation developed based on the assumption that the adsorbent has a heterogeneous surface composed of different classes of adsorption sites, and each site can be modelled by the following equation:

$$q_e = K_F . C_e^{\frac{1}{n}}$$

(1)

Where K_F: a Freundlich constant indicative of the adsorption capacity of the adsorbent
      n: an experimental constant indicative of the adsorption intensity of the adsorbent

The Sips model is another different empirical model representing equilibrium adsorption data. This isotherm model has the features of both the Langmuir and Freundlich isotherm models. The Sips adsorption isotherm model can be written as follows:

$$q_e = \frac{q_m (bC_e)^{\frac{1}{n}}}{1 + (bC_e)^{\frac{1}{n}}}$$

(2)

IDA World Congress – Perth Convention and Exhibition Centre (PCEC), Perth, Western Australia September 4-9, 2011
*REF: **IDAWC/PER11-330***

- 3 -

Where, q_e is the amount of solute adsorbed per gram of adsorbent (mg/g), C_e is the equilibrium concentration of solute in the bulk of the solution (mg/L), q_m is saturation amount of organic adsorbed (mg/g) and b is a constant (L/mg).

2.2.2   Kinetic experiment

In the kinetic studies, 100 mL seawater was transferred to 250 mL Erlenmeyer flasks containing 0.15 g of PAC. The samples were placed on a mechanical shaker and shaken at 110 rpm. Samples were collected at regular time intervals and analysed for residual organic compounds.

Ho pseudo second order kinetic model was used to simulate a number of sorption systems [7]. Ho's pseudo second order model presents the experimental kinetic data for the entire sorption period for most of the systems better than other models. This model has been used extensively by a number of researchers as it could simulate and fit experimental kinetic data for the entire sorption period [8]. The model equation is as follows:

$$q_t = \frac{2k_H q^2 t}{1 + 2k_H q\ t}$$

(3)

Where: k_H : Ho rate constant for adsorption, function of temperature (g/mg.min);
     q: the amount of adsorbate at equilibrium (mg/g); and
     q_t: the amount of adsorbate at any time t, (mg/g).

2.2.3   Submerged membrane experiment

In this study, a submerged microfiltration reactor with and without adding PAC was used for seawater experiments. The schematic diagram of the submerged membrane adsorption hybrid system is shown in Figure 1.
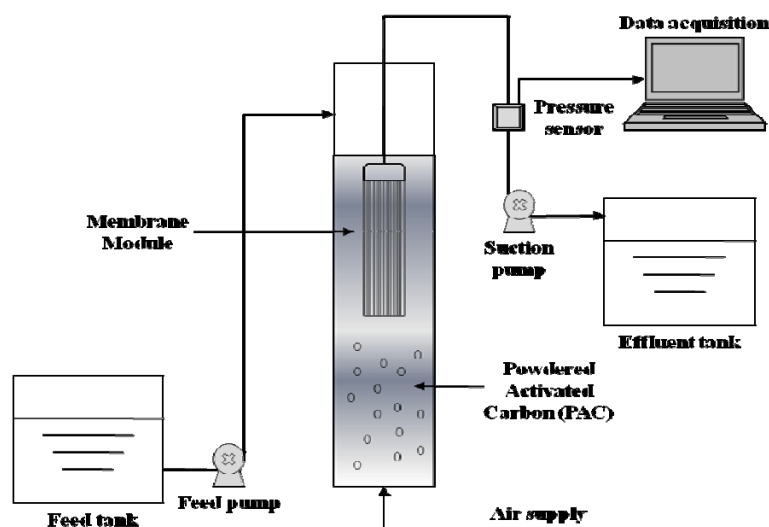

Figure 1 Schematic diagram of the submerged membrane adsorption hybrid system

IDA World Congress – Perth Convention and Exhibition Centre (PCEC), Perth, Western Australia September 4-9, 2011
*REF: **IDAWC/PER11-330***

- 4 -

The experiment was carried out using hollow fibre MF in column type reactor with and without adding PAC. The effective volume of square-column type reactor was 6 L and aeration rate was 10 L/min/m^2 membrane area. The membrane used in this study was hollow fibre microfiltration (MF). Hollow fibre MF (Cleanfil, Polysulfone, Polyethersulfone, PVDF of 0.1µm, Kolon membrane) was vertically submerged directly into a reactor. The U-type membrane length was 48.5 cm with an outer diameter of 2 mm. The combined surface area of the hollow fibre membrane was 0.1m^2. Permeate was pumped out using a peristaltic pump at constant flux. The data of permeate flow rate was acquired to panel automatically to monitor trans-membrane pressure (TMP) in every 5 mins. A careful cleaning of the unit was conducted at the beginning and the end of every experiment. Before each critical experiment, the MF reactor and MF membrane were disinfected and thoroughly cleaned to remove trace organic impurities by applying the following steps: (i) membrane was placed into 0.2% NaOH and 0.2% NaOCl solution using a horizontal shaker at 60 rpm for 3h. (ii) rinsing the unit several times with DI water (heterotrophic count of the DI water was less than 10 bacterial cells per mL) to eliminate chemical residues, and (iii) sterilizing MF membrane modules with DI by increasing flux.

2.2.4   Modified fouling index (MFI)

The modified fouling index (MFI) was established by Schipper and Verdouw [9] to evaluate membrane fouling mechanism. The schematic diagram of MFI experimental set-up is shown in Figure 2. In each experiment, new ultrafilter (UF) with molecular weight cut off 17,500 Dalton and diameter of 47mm were used to avoid the residual fouling. The seawater with and without PAC adsorption were pressurised at 2 bars by N$_2$ gas.
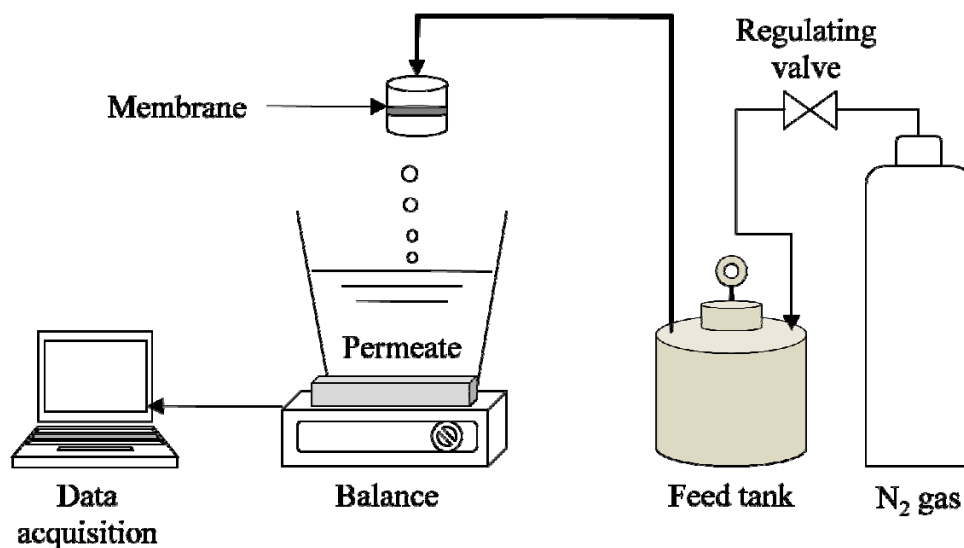

Figure 2 UF-MFI experimental set-up

2.3   Analyses

Organic fractions were measured by DOC-LABOR Liquid Chromatography - Organic Carbon/Nitrogen Detector (LC-OCND). This system uses size-exclusion chromatography to separate classes of dissolved organic materials (organic acids, bases and neutral species) before measuring by a catalysed UV oxidation. LC-OCD was measured to identify the different classes of organic compounds present in

IDA World Congress – Perth Convention and Exhibition Centre (PCEC), Perth, Western Australia September 4-9, 2011
*REF: **IDAWC/PER11-330***

- 5 -

seawater to cause organic fouling. It gives the both qualitative and quantitative information of the organic matter present in seawater after treatment.

III.   RESULTS AND DISCUSSION

3.1   Isotherm experiment

Adsorption isotherm experiment was conducted to evaluate the adsorption capacity of PAC. The equilibrium results were then fitted with Freundlich and Sips isotherm equations. The adsorption curves simulated by both models fitted well with the observed values. The simulated and the experimental concentrations of the remaining organic are shown in Figure 3. The model equations and the isotherm parameters are shown in Table 2.
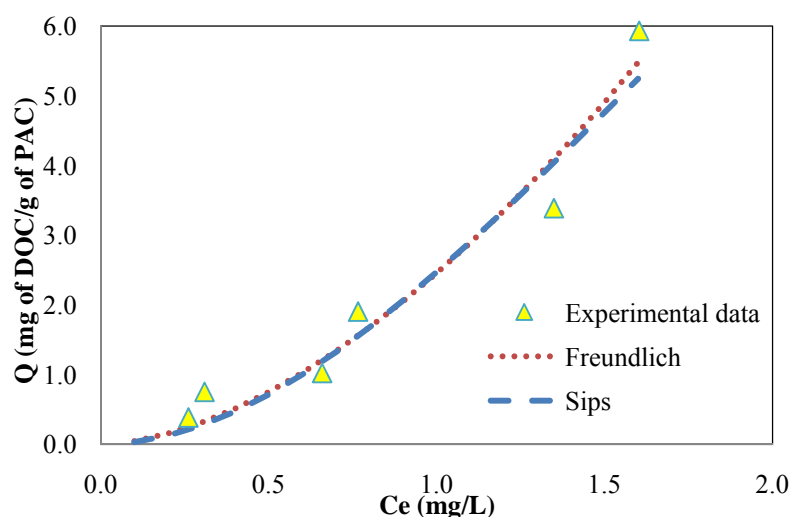

Figure 3 Prediction of equilibrium adsorption of organic by different adsorption models (Initial organic concentration = 2.2 mg/L, contact time = 48 hours, mixing rate = 110 rpm, temperature = 25°C)

Table 2 Isotherm equations for organic removal using PAC

Isotherm equations	Parameters	Values
Freundlich	k_F (mg/g)(mg/L)$^{-1/n}$	2.46
	n	0.59
	r^2	0.95
Sips	k_s	0.12
	q_m (mg/g)	23.12
	n	0.52
	r^2	0.94

IDA World Congress – Perth Convention and Exhibition Centre (PCEC), Perth, Western Australia September 4-9, 2011
*REF: **IDAWC/PER11-330***

- 6 -

It can be seen that organic adsorption capacity (q_m) estimated by the Sips model was up to 23.1mg/g. This prediction shows that there is not much difference between these two models in describing the adsorption of organic by PAC. The correlation coefficient (r^2) for both isotherms ranged from 0.94 to 0.95, representing a good fit of the observed data.

3.1.1 Fractionation of organic matter

In this study, about half of DOC in raw seawater was hydrophilic in which a majority of organic matter had a molecular weight less than 1000 Da. The percentage of humic substances (MW $\approx$ 1,000 Da), low molecular weight of neutrals (MW < 350 Da) and building block (MW $\approx$ 300-500 Da) in hydrophilic part were 33%, 27%, and 23% respectively.

The results indicated that with concentration of 5 g/L, the PAC was able to remove almost hydrophobic compounds (more than 96%) and a significant amount of hydrophilic compounds (78%). The PAC could remove a majority of high molecular weight fractions with 93% removal of biopolymer (MW $\approx$ 20,000 Da) (Table 3).

As expected, the DOC removal efficiency was proportional to the PAC doses. However, the effect of PAC dose on removal of different organic fractions was different. Hydrophobic compound removal efficiency strongly depended on PAC doses whereas the removal of hydrophilic compound was not notably affected by the change of PAC doses. PAC even at very low concentration of 0.1 g/L could remove 60% and 74% of humic substances and low molecular weight of neutrals respectively. However only a slight increase in the removal efficiency of humic substances and low molecular weight of neutrals was observed when the PAC was increased by 50 times to 5 g/L.

Table 3 Removal efficiencies of organic matter fraction by PAC adsorption

PAC concentration (g/L)	DOC (%)	Hydro-phobic (%)	Hydro-philic (%)	Bio-polymer (%)	Humics (%)	Building blocks (%)	Neutrals (%)
0.10 g/L	27	5	56	54	60	51	74
0.25 g/L	39	15	69	64	66	64	82
0.75 g/L	65	59	71	79	66	72	80
1.50 g/L	70	68	72	81	68	76	85
2.50 g/L	86	92	78	93	76	79	85
5.00 g/L	88	96	78	93	78	84	86

3.1.2 Fouling reduction

The reduction of the fouling potential of raw seawater before and after adsorption with 1.5 g/L of PAC was also studied using UF-MFI. Following were the values of UF-MFI of seawater before and after the adsortion by PAC (Table 4).

IDA World Congress – Perth Convention and Exhibition Centre (PCEC), Perth, Western Australia September 4-9, 2011
*REF: **IDAWC/PER11-330***

- 7 -

Table 4 UF-MFI of before and after adsorb by PAC

Sample	UF- MFI (s/L^2)
Seawater	15848
After adsorb by 1.5 g/L of PAC	3852

The addition of 1.5 g/L of PAC led to 70% removal of organic matter such as humics, bio-polymer thereby reducing the membrane fouling. As a result, UF-MFI reduced from 15848 s/L^2 with raw seawater to 3852 s/L^2 with seawater after adsorption by PAC (Table 4).

3.2 Kinetic experiment

The PAC adsorption amount with time was studied during adsorption kinetics experiments. The results of PAC adsorption kinetic of organic compounds are presented in Figure 4. Organic compounds in the seawater were quickly adsorbed within the first eight hours and then the organic adsorption rate only increased marginally. The results show that PAC could remove 67% of organic within first 30 minutes of contact with PAC. After eight hours, 86% of organic was adsorbed (with less than 0.15 mg/L of organic remaining in the seawater).
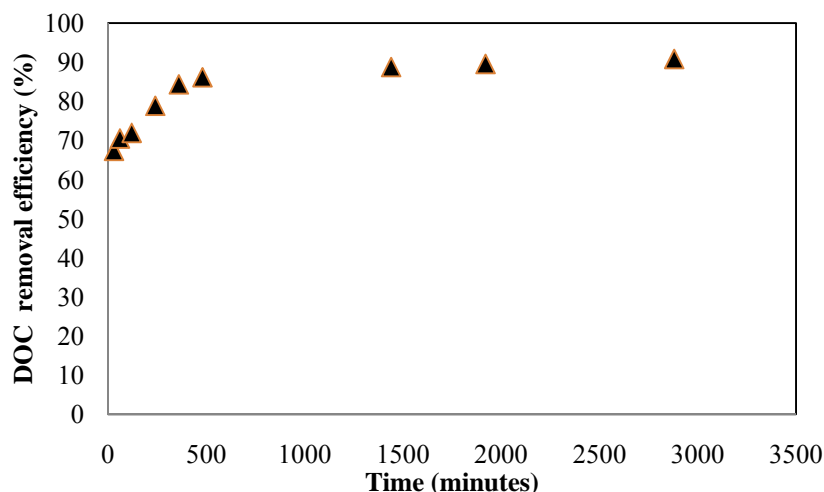

Figure 4 DOC removal efficiency as a function of adsorption time (Initial organic concentration = 1.11 mg/L, PAC = 1.5 g/L, mixing rate = 110 rpm, temperature = 25^0C)

The analyses of organic matter fractions from kinetic experiment also showed that hydrophilic compounds were quickly adsorbed by PAC within the first 30 minutes. There were no much differences between removal efficiencies of biopolymer, humic substances, building block and low molecular weight of neutrals after 0.5h and 48h.

The kinetics of PAC adsorption of sea organic matter can be described by the Ho model. With the q and K_H given in Table 5, the kinetic adsorption data of PAC with synthetic water was also fitted well with the Ho model (Figure 5).

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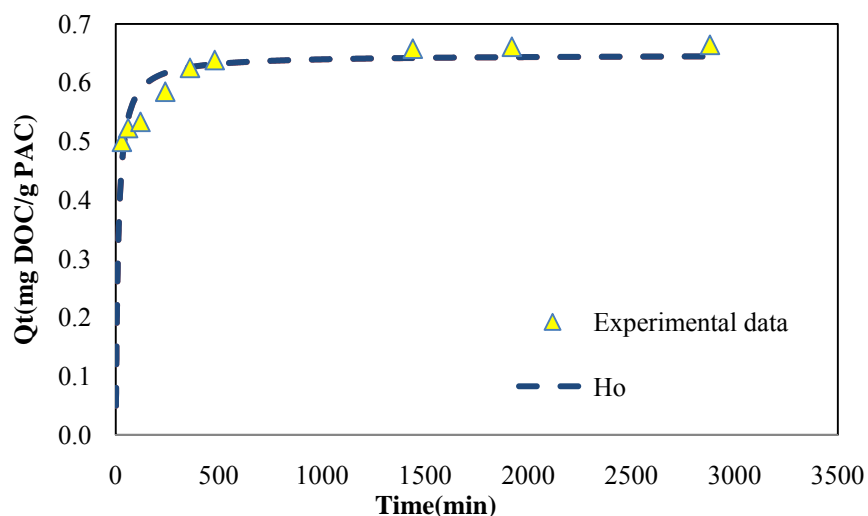*REF: **IDAWC/PER11-330***

- 8 -

Figure 5 Prediction of adsorption kinetics of organic matter by PAC by the Ho model (Initial organic concentration = 1.11 mg/L; PAC = 1.5 g/L, mixing rate = 110 rpm, temperature = 25°C)

Table 5 Adsorption kinetics parameters of Ho model for PAC adsorption

Parameters	Values
K_h	0.064
$q_{e,exp}$ (mg/g)	0.60
$q_{e,cal}$ (mg/g)	0.65
r^2	0.95

The correlation coefficient (r^2) for the modelled plot was more than 0.95 representing a good correlation of the observed data. Thus, Ho model can describe well the adsorption kinetics of organic matter present in seawater.

3.3   Effect of PAC on operation of SMAHS

Critical flux is the flux above which the membrane gets fouled severely and the trans-membrane pressure (TMP) rises dramatically. In this experiment, critical flux was measured quantitatively by a "flux stepping" method. The membrane reactor was operated at a fixed flux for around 60 minutes and the TMP was monitored simultaneously. The flux was then increased and operated at a constant flux for another 60 minutes and so on. As the flux was increased gradually, the critical condition was detected where TMP no longer remained steady but increased with time. And the maximum flux which showed no increase in TMP was taken as the critical flux.

The addition of PAC in submerged membrane reactor led to increase of critical flux. The critical flux increased from 20 to 40 L/m².h when 1.5 g/L of PAC was added into the submerged membrane reactor (Figure 6).

IDA World Congress – Perth Convention and Exhibition Centre (PCEC), Perth, Western Australia September 4-9, 2011
*REF: **IDAWC/PER11-330***

- 9 -

In addition, the adding of PAC also helped in the reduction of TMP of submerged membrane system. At filtration flux 20 L/m^2.h, the TMP of conventional submerged membrane reactor after 1 day of operation was 10 kPa whereas this value was only 1.5 kPa when 1.5 g/L of PAC was added in the submerged membrane reactor. The increase of TMP of submerged membrane reactor with PAC addition at filtration rate of 30 L/m^2.h was also much lower than that of conventional submerged membrane reactor (Figure 7).

(a) Development of TMP without PAC (decreased by 5LMH)

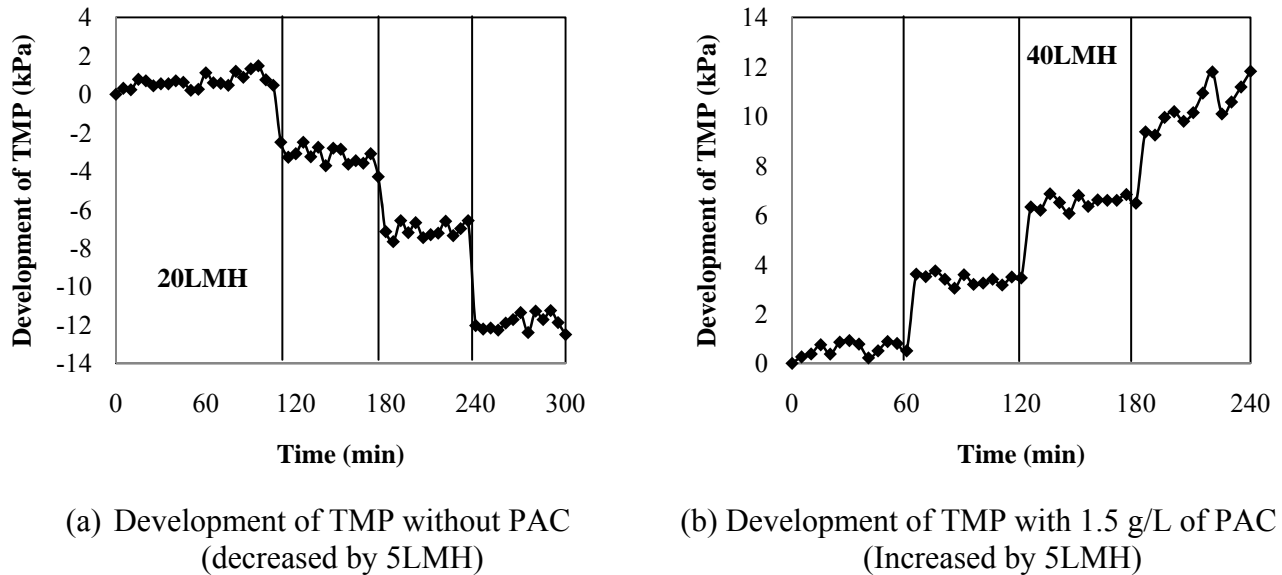(b) Development of TMP with 1.5 g/L of PAC (Increased by 5LMH)

Figure 6 Increase of critical flux by adding of 1.5g/L of PAC (a: seawater only, b: adding of 1.5g/L of PAC)
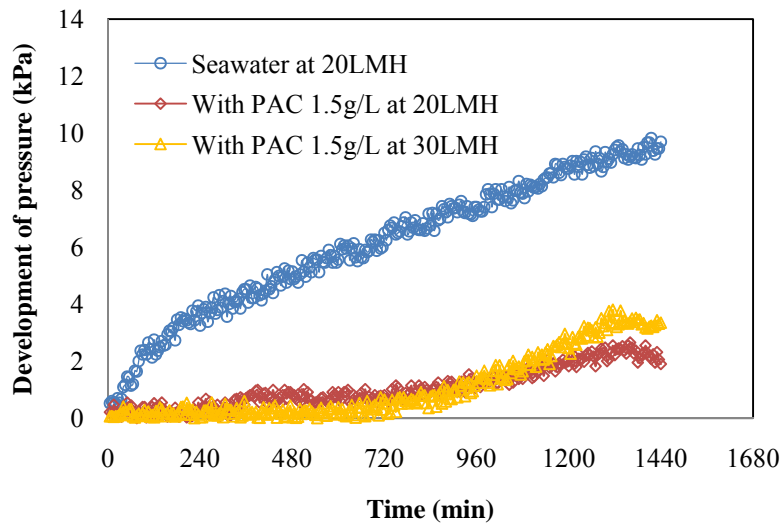
Figure 7 Development of TMPs of a submerged membrane reactor with and without adding PAC (PAC dose 1.5 g/L, aeration rate 1 L/min)

IDA World Congress – Perth Convention and Exhibition Centre (PCEC), Perth, Western Australia September 4-9, 2011
REF: **IDAWC/PER11-330**

- 10 -

3.3.1   Fractionation of organic matter

Table 6 presents that the DOC removal efficiency of seawater by MF alone and by MF with 1.5 g/L of PAC. It can be seen from that only 15.9% of dissolved organic carbon (DOC) was removed by MF alone. In particular, MF alone could remove a minority of hydrophilic fraction in seawater (5.8%). Whereas, when MF with 1.5 g/L of PAC was used, the DOC removal efficiency increased considerably by 76.6% and about 70% of hydrophilic fraction was eliminated due to the adsorption by PAC. Detailed analysis of hydrophilic portion showed that the removal efficiency of biopolymer, humics, building blocks and neutrals were 92.3%, 70.0%, 89.5% and 99.0% respectively.

Table 6 Removal efficiency of organic matter fraction by SMAHS with 1.5g/L of PAC

Sample	DOC	Hydro-phobic	Hydro-philic	Bio-polymer	Humics	Building blocks	Neutrals
Seawater (mg/L)[a]	1.45	0.59	0.86	0.13	0.45	0.19	0.09
Seawater by MF (%)[b]	15.9	32.2	5.8	53.8	-	15.8	44.4
Seawater + PAC 1.5g/L by MF (%)[b]	76.6	81.4	69.8	92.3	70.0	89.5	99.0

[a] Concentrations of the different organic fractions in seawater
[b] Removal efficiencies of different organic fractions in seawater after treatments

IV.   CONCLUTION

In this study, the performance of PAC in removing organic compounds from seawater was experimentally evaluated. The experimental results showed that the PAC adsorption equilibrium with seawater was well fitted with Freundlich and Sips isotherm models. The adsorption capacity of PAC was up to 23.1 mg of organic matter per gram of PAC. Ho model was also found to describe well the adsorption kinetics of organic matter on PAC.

Detailed organic fractions of seawater after adsorption by PAC showed that more than 96% of hydrophobic compounds and 78% of hydrophilic compounds was removed by PAC of 5 g/L. The removal of hydrophobic compound strongly depended on PAC doses and contact time whereas the removal of hydrophilic compound was not affected by the PAC dose.

The addition of PAC in submerged membrane system can improve the critical flux by removing organic before they can contact with membrane surface. The results also showed that the addition of PAC could reduce the increasing rate of TMP and remove a majority of both hydrophobic and hydrophilic compounds.

IDA World Congress – Perth Convention and Exhibition Centre (PCEC), Perth, Western Australia September 4-9, 2011
*REF: **IDAWC/PER11-330***

- 11 -

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IDA World Congress – Perth Convention and Exhibition Centre (PCEC), Perth, Western Australia September 4-9, 2011
*REF: **IDAWC/PER11-330***

- 12 -