Effects of powdered activated carbon dosing on sludge characteristics and estrogen removal in membrane bioreactors

W. Yang, M. Paetkau and N. Cicek

ABSTRACT

Sludge characteristics associated with filterability as well as the removal of a natural estrogen 17β-estradiol (E2) and a synthetic estrogen 17α-ethyinylestradiol (EE2) were investigated in submerged membrane bioreactors (MBR) with and without the addition of powdered activated carbon (PAC) under the same experimental conditions. Positive impacts of PAC dosing on membrane fouling and the removal of E2 and EE2 were demonstrated over a six months stable operational period. Experimental results showed that PAC dosing resulted in lower concentrations of soluble extracellular polymeric substances (EPS) and colloidal total organic carbon (TOC) in the PAC-MBR sludge. The average soluble EPS and colloidal TOC concentrations in the PAC-MBR sludge was 60.1% and 61.8% lower than the control MBR sludge, respectively. Regardless of PAC dosing, concentrations of colloidal TOC were strongly related to concentrations of soluble EPS and soluble carbohydrates in the sludge. In addition, the mean flocs size of the sludge with PAC dosing was shifted from 49.4 μm to 60.3 μm. PAC dosing in the MBR increased the removal rates of E2 and EE2 by 3.4% and 15.8%, respectively.

Key words | endocrine disrupting compounds, estrogen, membrane bioreactor, powdered activated carbon, sludge characteristics

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INTRODUCTION

Membrane bioreactor (MBR) technology has been advancing rapidly around the world both in research and commercial applications in the last decades (Yang *et al.* 2006). Membrane fouling, which has been widely recognized to be one of the major limitations to faster commercialization of MBRs, has been investigated from various perspectives in many studies; these perspectives include the causes, characteristics, mechanisms of fouling, and methods to prevent or reduce membrane fouling. Flux improvement can be achieved with powdered activated carbon (PAC) addition because PAC plays an important role in reducing the biomass cake resistance and changing the filtration characteristics of the sludge in bioreactors. In addition, PAC might have a scouring effect for removing the cake layer from membrane surfaces. The first application of PAC addition for flux enhancement in a membrane anaerobic bioreactor was published in 1999 (Park *et al.* 1999). In this study, a flux improvement with PAC addition was achieved, especially with a higher PAC dosage of up to 5 g/L. From then on, a number of studies were conducted, aiming to use PAC dosing as a membrane fouling control method (Ng *et al.* 2006; Hu & Stuckey 2007).

The occurrence and behaviour of endocrine disrupting compounds (EDCs) including estrogens in wastewater treatment plants has gained considerable attention in recent years. By dosing PAC in the bioreactor, the characteristics of the sludge (PAC-sludge) can be expected to vary. PAC-sludge is hypothesized to possess higher adsorption capacity, which would increase its capacity to adsorb substances including estrogens to its surface. A couple of studies have

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been conducted to test the efficiency of PAC in further eliminating estrogens in MBR. Korner *et al.* (2001) reported that additional activated carbon filtration was very efficient in further eliminating estrogenic activity from WWPTs effluents. On the contrary, other investigators have shown that the estrogenic activity in aqueous phase leaving the MBR system was not further reduced by polishing with either granular activated carbon (GAC) or PAC (Holbrook *et al.* 2002).

With the expansion of MBR installations for wastewater treatment and water reuse, there needs to be an assessment as to whether PAC dosing is able to enhance the MBR performance including the removal of estrogen. Meanwhile, the removal behaviour of estrogens in MBRs and alternative ways to enhance estrogen removal in MBRs need be studied. The objective of this study was to investigate the effects of PAC dosing on sludge characteristics and estrogen removal in bench-scale MBRs.

MATERIALS AND METHODS

Experimental set-up

Two bench-scale MBRs, one without PAC dosing and the other with PAC dosing, were operated in parallel with the same feed at similar experimental conditions (Figure 1). A hollow fiber membrane module with a surface area of 0.08 m^2 from Korea Membrane Separation Ltd. was submerged in each bioreactor. The dimension of membrane modules was 150 mm (L) × 180 mm (H) and the pore size of the membrane fibers was 0.4 μm. The working volume of each bioreactor was 3.0 L. Coarse bubble air-diffusers at the bottom of membrane module were used to provide dissolved oxygen (DO) for biomass growth and to introduce vigorous shear force on the membrane surface to reduce membrane fouling.

Operation of MBRs

The two investigated MBR systems were operated at constant flux mode by withdrawing the permeate through peristaltic pumps from the outside-to-inside hollow membrane fibers. The two MBR systems were fed with identical synthetic wastewater (Yang *et al.* 2009). The water levels of the bioreactor were controlled by floating valves. To control membrane fouling, a cyclic pumping mode with 10 minutes ON and 2 minutes OFF was used. Solids retention time (SRT) of both MBR and PAC-MBR remained 25 days by wasting portion of mix liquor from bioreactors daily. Hydraulic retention time (HRT) of both MBRs was 5.8–6.0 hour, depending on membrane flux. During the experimental period, trans-membrane pressures (TMP) of the two MBR systems were monitored every day. Temperature, DO, and pH in the bioreactors were measured on a regular base.

In the PAC-MBR, PAC with particle size range from 50 to 150 μm was added into the bio-reactor at a dosage of 2.0 g/L. The PAC dosage remained at the same level by re-supplementing the bioreactor with a certain amount of PAC regularly. The selection of the particle size of PAC was based on previous studies. Smaller particles provide quicker rates of adsorption, but might tend to increase the small particle population of the activated sludge and shift

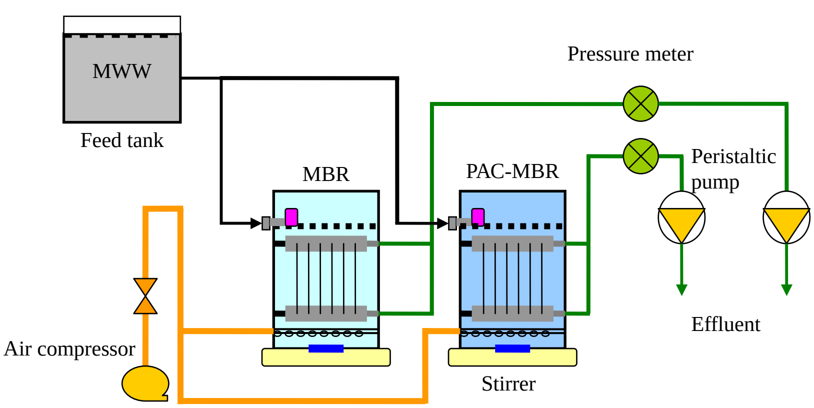

Figure 1 | Schematic of the bench-scale MBR and PAC-MBR.

the flocs size to lower ranges (Ng *et al.* 2006). However, PAC with an average size of 100 μm was reported to shift the particle size distribution of the mixed liquor broth to a relatively higher range (Park *et al.* 1999). Based on these results, the PAC with a relatively higher particle size range would be suitable for dosing into MBR systems.

Analytical methods

For wastewater and sludge samples, mixed liquor suspended solid (MLSS), mixed liquor volatile suspended solid (MLVSS), chemical oxygen demand (COD) and soluble COD were measured according to standard methods. Total organic carbon (TOC) was measured by a TOC analyzer (Phoenix 8000, USA). The difference of TOC between the filtrate passing through a 1.2 μm filtration paper (GF/C, Whatman, USA) and the permeate directly collected from the MBRs was referred to as colloidal TOC. Soluble extracellular polymeric substances (EPS) were measured as supernatant after the centrifugation of the sludge samples at 10,000*g* for 30 min and calculated by summing the contents of the carbohydrate and protein fractions. Carbohydrate was measured according to Dubois *et al.* (1956) and protein was measured according to modified Lowry's method (Lowry *et al.* 1951). The bound EPS was measured as extract after 1 hour heat extraction at 100°C (Chang & Lee 1998). The particle size of sludge was measured by a laser particle counter (Spectrex PC-2000, USA). A yeast estrogen screen (YES) assay was used to quantify estrogenic activity associated with E2 or EE2 in samples. Prior to the YES assay, samples were extracted by using cyclohexane extraction for the enrichment of estrogen concentrations. The methodology of YES assay and cyclohexane extraction has been published in previous literature (Yang & Cicek 2008). The average extraction efficiencies of E2 from MBR and PAC-MBR sludge were 82.3% and 71.0%, respectively. The average extraction efficiencies of EE2 from MBR and PAC-MBR sludge were 76.7% and 64.2%, respectively.

RESULTS AND DISCUSSION

Two identical MBRs were seeded with activated sludge from a full-scale pollution control center in Winnipeg, Manitoba, Canada. After eighty days of start-up and acclimation, stable operation and consistent performance was achieved in both MBR systems. One of the MBRs was then dosed with PAC, and the other MBR was operated as a control. The control MBR and PAC-MBR were then run in parallel for more than 6 months.

Biomass growth

Figure 2 shows MLVSS concentrations of the two investigated MBRs during the whole experimental period. It should be pointed out that, in Figure 2, no PAC was added in PAC-MBR during the start-up and acclimation stage (before 80 days operation). Before PAC was added in one of two bioreactors, the biomass concentrations were nearly identical at all sampling points. The MLVSS concentrations remained stable in the two bioreactors at 5.5 ± 0.2 g/L for one SRT before PAC was added into one of the bioreactors on day 80.

During the first SRT (25 days) period after PAC was added into PAC-MBR reactor, the MLSS and MLVSS concentrations in the PAC-MBR increased gradually whereas the MLSS and MLVSS concentrations in the control MBR remained quite stable. The average MLVSS concentration of MBR and PAC-MBR after 105 days operation was 6.1 ± 0.4 g/L and 10.1 ± 0.3 g/L, respectively. As the dosage of PAC in PAC-MBR remained at 2.0 g/L and the volatile content at 550°C of PAC is 96.7%, the MLVSS concentration in the PAC-MBR was expected to be 1.93 g/L higher than that in MBR provided the biomass growth in the control MBR and PAC-MBR were

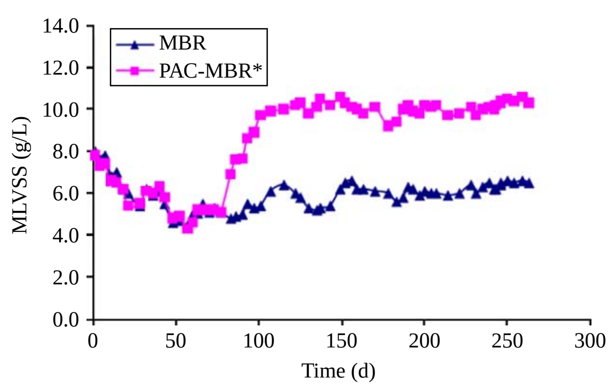

Figure 2 | Comparisons of MLVSS between MBR and PAC-MBR *No PAC dosing before 80 days.

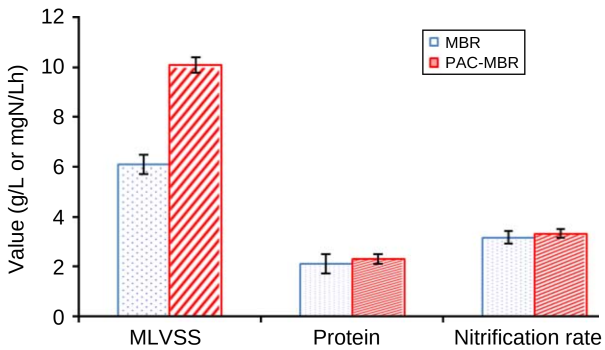

Figure 3 | Comparison of biomass characteristics between MBR and PAC-MBR.

the same. However, the average MLVSS concentration in the PAC-MBR after 105 days operation was 4.0 g/L higher than that in MBR. To examine whether PAC dosing imposed any significant impact on the biomass growth, the protein content and nitrification rate of the sludge from MBR and PAC-MBR bioreactors were compared. As shown in Figure 3, there was no significant difference in both protein content and nitrification rate of the sludge from MBR and PAC-MBR. This indicates the biomass content in MBR and PAC-MBR sludges was not significantly different. The higher MLVSS concentration of PAC-MBR sludge than expected was attributed to the adsorption and accumulation of incoming soluble organic substances on the PAC surface. It is also possible that more PAC was added than extracted from the MBR on a daily basis due to settling of the PAC in the reactor.

EPS in the MBR and PAC-MBR

There are a number of studies which have shown the main foulants with regard to membrane fouling in MBRs are EPS excreted from cells (Chang & Lee 1998). To reveal whether PAC dosing had significant impacts on the concentration of EPS in the sludge, EPS was analyzed in the MBR and PAC-MBR. Table 1 presents the concentrations of soluble EPS and bound EPS in the sludge of MBR and PAC-MBR.

As shown in Table 1, soluble carbohydrate, protein and the total soluble EPS of PAC-MBR sludge were significantly lower than the MBR sludge. The average soluble EPS of PAC-MBR sludge was 60.1% lower than the control MBR sludge. In contrast, there was no significant difference in bound EPS including carbohydrate and protein between PAC-MBR sludge and MBR sludge. Meanwhile, a slower rate of TMP increase was observed in the PAC-MBR. This indicates that soluble EPS would have greater impacts on membrane fouling than would bound EPS. This might be due to the fact that the bound EPS are mainly present within the MLSS flocs while the soluble EPS are the main components of colloidal substances in the sludge. Colloidal particles have been widely recognized as being more responsible for membrane fouling than MLSS flocs.

It should be pointed out that bound EPS mentioned in this study referred to the portion of carbohydrate and protein in sludge that could be extracted by the method described in the previous section. It is possible that more EPS substances were accumulated in the PAC-MBR sludge but could not be extracted by current extraction method due to the high adsorption ability of PAC.

Colloidal particles in the MBR and PAC-MBR

In this study, the difference between filtrate from a 1.2 μm filter and the permeate from MBR systems was used to measure colloidal TOC. This is in line with other studies which used similar methods to represent the concentration of colloidal particles in activated sludge (Fan *et al.* 2006). Although the nominal pore size of membrane fibers used in MBRs is 0.4 μm, the fouled membrane fibers were able to retain smaller particles due to the additional filtration provided by the cake formed on the membrane surface. This was supported by the experimental data that the TOC of the filtrate passing through a 0.22μm filter was higher than the TOC of the permeate from the MBRs.

Table 1 | Summary of soluble and bound EPS in MBR and PAC-MBR

	Soluble EPS (mg/L)			Bound EPS (mg/L)		
	Carbohydrate	Protein	Total	Carbohydrate	Protein	Total
MBR	71.3 ± 23.4	115.5 ± 45.9	186.8 ± 67.6	332.3 ± 239	319.9 ± 47.6	652.2 ± 196.3
PAC-MBR	38 ± 20.7	36.6 ± 14.3	74.5 ± 34.1	328.1 ± 237.9	306.9 ± 95	635 ± 150.4

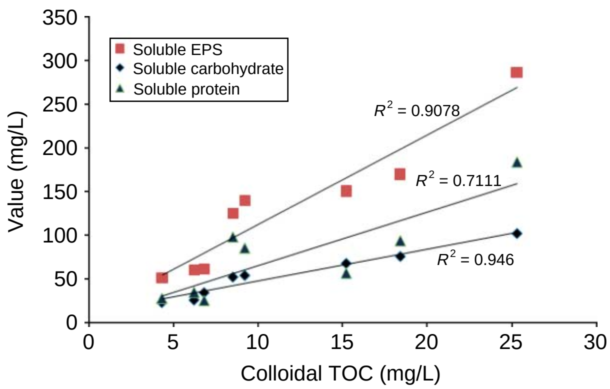

Figure 4 | Correlation between colloidal TOC and soluble EPS.

The results of colloidal TOC measurements showed that the average of colloidal TOC of the PAC-MBR sludge and MBR sludge was 6.5 mg/L and 17.0 mg/L, respectively. At each sample point, the colloidal TOC of the PAC-MBR sludge was consistently lower than the MBR sludge. The lower colloidal TOC in PAC-MBR sludge might be associated with the slower rate of TMP increase in the PAC-MBR. Fan *et al.* (2006) found a good correlation between colloidal TOC and soluble EPS in a pilot-scale MBR system. Figure 4 plots the soluble carbohydrate, soluble protein and soluble EPS as a function of colloidal TOC, whether or not the sample was obtained from the MBR or PAC-MBR. Consistently, a higher soluble EPS in the sludge resulted in a higher colloidal TOC. It is reasonable because the soluble EPS in the sludge liquor, excluding that in the permeate, could constitute the main components contributing to colloidal TOC.

As shown in Figure 4, the linear regression between soluble carbohydrate and colloidal TOC had the highest coefficient of correlation. However, little correlation existed between the soluble protein and colloidal TOC with the coefficient of correlation of 0.7111. This indicates that soluble carbohydrates would have greater impact on membrane fouling than would soluble proteins.

Effect of PAC dosing on particle size distribution

PAC dosing may affect the flocs size of the activated sludge in the bioreactor. Figure 5 shows the floc size distribution in both the PAC-MBR and the control MBR systems. In comparison with the MBR sludge, the particle

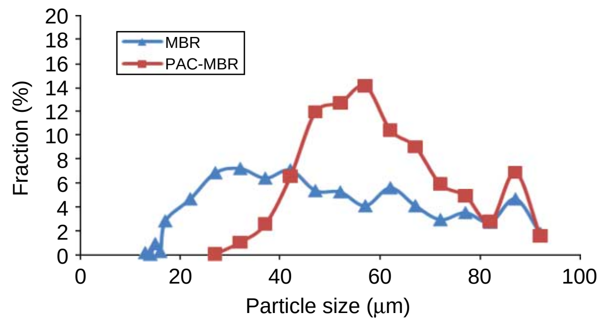

Figure 5 | Comparison of particle size distribution between MBR and PAC-MBR sludge.

size distribution of the PAC-MBR sludge was shifted to a relatively higher range. The mean floc size of the PAC sludge was 60.3 µm, higher than that of the control MBR sludge 49.4 µm. This may be explained by the fact that the dosed PAC could adsorb and coagulate dissolved organics, colloidal particles and free bacteria onto the PAC-MBR sludge surface. Thus the overall particle distribution with PAC dosing was changed to a greater particle size range. The larger particle sizes of sludge would be beneficial to alleviate membrane fouling during MBR operation.

Effects of PAC dosing on estrogens removal

A natural estrogen E2 and a synthetic estrogen EE2 were selected as target contaminants to demonstrate the removal of estrogens in MBR and PAC-MBR. E2 and EE2 were chosen because they have been known to be released from a wide variety of wastewater treatment plants and because they possess relatively high estrogenic activity (Cicek *et al.* 2007). The average removal rate of E2 and EE2 by the control MBR was 89.0% and 70.9%, respectively (Figure 6).

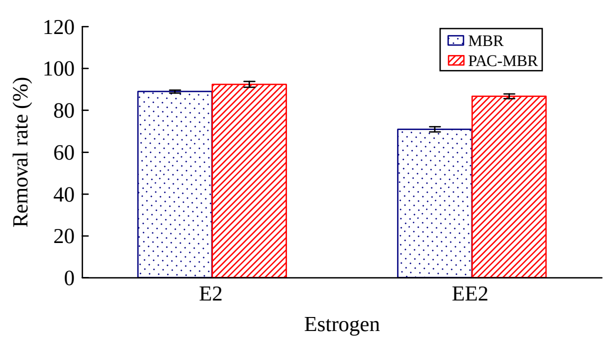

Figure 6 | Comparison of E2 and EE2 removal in MBR and PAC-MBR sludge.

These removal efficiencies are consistent with the results from previous studies in activated sludge process (Cicek *et al.* 2007). The synthetic estrogen EE2 appeared to be removed to a lesser extent than E2, which is reasonable because of its more stable chemical structure. PAC dosing increased the removal efficiencies of both E2 and EE2 in the MBR system. In comparison with the control MBR, the removal rate of E2 and EE2 in the PAC-MBR was increased by 3.4% and 15.8%, respectively. The impact of PAC dosing on EE2 removal was found to be greater than E2 removal. This may be due to the greater hydrophobic properties of EE2, which results in its greater adsorption capacity to the sludge and PAC.

CONCLUSIONS

Two bench-scale MBRs, one without PAC dosing and the other with PAC dosing, were operated in parallel at similar experimental conditions to examine the effects of PAC dosing on sludge characteristics and estrogen removal. The following conclusions can be drawn from the study:

(1) PAC dosing had little impact on the biomass growth and the biological activity of the sludge.
(2) PAC dosing significantly reduced the concentrations of soluble EPS and colloidal TOC in the PAC-MBR sludge. Also, the overall particle size distribution of the sludge with PAC dosing was shifted to a greater particle size range. Those effects resulted in a slower rate of TMP increase in the PAC-MBR during the operation of MBRs.
(3) Regardless of PAC dosing, concentrations of colloidal TOC were strongly correlated to soluble EPS, especially to soluble carbohydrate.
(4) PAC dosing in the MBR increased the removal rate of E2 and EE2 by 3.4% and 15.8%, respectively. The greater impact of PAC dosing on EE2 removal might be due to its greater hydrophobic properties.

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