



Performance of submerged membrane bioreactor (SMBR) with and without the addition of the different particle sizes of GAC as suspended medium



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HIGHLIGHTS

- The GAC particle size plays a major role on membrane fouling reduction in membrane bioreactor.
- The superior organic removal with the addition GAC as suspended medium (95%).
- Detailed organic characterisation of MBR effluent for different GAC sizes.
- GAC helped reduce the sludge volume index and transmembrane pressure development.
- The phosphate in SMBR effluent was removed/recovered (90%) using hydrated ferric oxide.

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ABSTRACT

In this study the effect of different particle sizes of granular activated carbon (GAC) on the performance of a submerged membrane bioreactor (SMBR) was investigated. The sizes of GAC used were 150–300, 300–600 and 600–1200 μm . The SMBR was operated at a filtration flux of 20 L/m² h. The removal of dissolved organic carbon (DOC) and chemical oxygen demand (COD) with the addition of GAC was 95%. The concentration of biopolymers, humic, building block and low molecular weight neutral and acids in the SMBR effluent was reduced by 20%, 66–76%, 20–50%, 30–56%, respectively. It helped to reduce the sludge volume index (SVI) and transmembrane pressure (TMP) development by 30–40% and 58%, respectively. However, the removal of NH_4^+ and PO_4^{3-} was relatively low of 35–45% and 34–43%, respectively. The SMBR effluent was rich in PO_4^{3-} and was removed/recovered using hydrated ferric oxide (HFO). The removal of PO_4^{3-} was almost 90%.

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1. Introduction

Membrane bioreactor (MBR) is an efficient, cost effective and reliable treatment process broadly used to treat municipal and industrial wastewater. An MBR process is a combination of both an activated sludge process and a membrane separation process. The growth rate of MBR treatment systems is almost 11% per annum (Drews, 2010). The advantages of the MBR process are (i) small footprint; (ii) complete solid liquid separation; (iii) higher organic removal and (iv) high quality of product. However, the key drawback of a membrane filtration system is membrane fouling. Membrane fouling reduces the membrane permeability. Membrane fouling also leads to frequent chemical cleaning thus increasing the operation and maintenance cost. Fouling of the membrane surface is mainly caused by the deposition of organic and inorganic matters during operation. Membrane fouling occurs

due to the following mechanisms (Meng et al., 2009; Johir et al., 2012): (i) adsorption of solutes or colloids within/on membranes; (ii) deposition of sludge flocs onto the membrane surface; (iii) formation of a cake layer on the membrane surface; (iv) detachment of foulants attributed mainly to shear forces; and (v) the spatial and temporal changes of the foulant composition during long-term operation.

The use of aeration across the membrane surface is the most common approach of minimizing membrane fouling. This helps to scour deposited particles on the membrane surface. However, the use of higher aeration forms a large part of the operating cost of the MBR (Cui et al., 2003; Judd et al., 2007).

As an alternative to a higher aeration rate, membrane fouling could be minimized by the use of medium in suspension in the MBR (Johir et al., 2011). The use of suspended medium (such as activated carbon) could help to adsorb the organic matter and also provide higher shearing stress on the membrane surface (Johir et al., 2011). Many studies have been conducted on the use of adsorbents in a biological treatment tank to see the effect of adsorbents on the

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reduction of membrane fouling (Guo et al., 2005; Lesage et al., 2008; Siembida et al., 2010; Johir et al., 2011; Xing et al., 2012; Jin et al., 2013). A long term (more than 600 days) pilot study by Siembida et al. (2010) with the addition of granular material (Polypropylene) showed that the formation of fouling layers on the membrane were reduced by the abrasion of granular material. They also reported that the MBR process with the addition of granular medium can be operated at a 20% higher flux than the conventional MBR process. In another study, Johir et al. (2011) found that the use of media (granular activated carbon, GAC) helped reduce membrane fouling by around 50% and also helped to remove a higher amount of organic matter. Another study by Pradhan et al. (2012) found that the use of granular support medium in suspension in a submerged membrane reactor reduced the membrane fouling by around 85%. Akram and Stuckey (2008) observed that the addition of powdered activated carbon (PAC) in submerged anaerobic membrane bioreactor helped to remove slowly biodegradable organics (both low and high molecular weight (MW) residual COD). They also reported almost 4.5 times (filtration flux increased from 2 to 9 L/m² h) higher filtration flux with the addition of PAC of 1.6 g/L than without any addition. Fang et al. (2006) had studied the effect of addition of activated carbon on the fouling of an activated sludge filtration system. They found that the filtration resistance was reduced by 22% (from $6.4 \pm 0.5 \times 10^{12} \text{ m}^{-1}$ to $5.0 \pm 0.1 \times 10^{12} \text{ m}^{-1}$) with the addition of activated carbon. Furthermore Li et al. (2005) reported that the addition of PAC in a SMBR helped to reduce membrane resistance by 44%. From the above discussion it is evident that the use of suspended medium in MBR could help to minimize membrane fouling by adsorbing organic matters and by providing extra shearing stress on the membrane surface.

However, no study has been reported on the effect of GAC size which is very important in optimising the aeration and studying the kinetics of organic removal. In this study, the performance of a SMBR with and without the addition of the different particle sizes of GAC (particle sizes: 150–300, 300–600 and 600–1200 μm) were evaluated in terms of the reduction in membrane fouling, sludge volume index (SVI), and removal of organics (DOC and COD), ammonium nitrogen and phosphorus. Characteristics of organic matter present in SMBR effluents were also carried out using Liquid chromatography organic carbon detector (LC-OCD) for better understanding of the effect of different particle sizes of GAC on organic removal. The effect of particle size of GAC on the performance of SMBR is discussed both quantitatively and qualitatively. Also, it is important to remove (or recover) nutrients (nitrogen and phosphorus) which are not often removed by the SMBR alone in significant quantities.

2. Methods

2.1. Membrane bioreactor process

In this study, a SMBR was operated with a flux of 20 L/m² h which corresponded to a hydraulic retention time (HRT) of 2.5 h. A flat sheet membrane with an average pore size of 0.14 μm was used. The membrane module had 8 vertical sheets. The gap between each vertical sheet was 12 mm. An airflow rate of 1.5 m³/m²_{membrane area} h was used to provide shearing stress on the membrane surface. The aeration also provided oxygen to microorganism.

Initially a 10 L membrane bioreactor tank was seeded with 4 L of mixed liquor (sludge) obtained from a domestic sewage treatment plant, Sydney, Australia. After initial seeding the SMBR was continuously feed with a synthetic substrate consisting of ethanol, beef extract, peptone (as organic carbon sources), ammonium chloride (NH₄Cl), and potassium dihydrogen phosphate (KH₂PO₄) as

sources of nitrogen and phosphorus. Synthetic substrate seeding was undertaken to maintain a COD:N:P ratio equal to 150:5:1 with an organic load of 1.5 kg COD m⁻³ d⁻¹. The pH was maintained using sodium bicarbonate. The concentrations of DOC, COD, NH₄⁺, NO₃⁻, and PO₄³⁻ in the feed solution were 129.8, 158.6, 7.1, 0.5 and 3.2 mg/L, respectively. The SMBR was acclimated for 40 days with the synthetic substrate till it become stable in terms of mixed liquor suspended solids (MLSS, $6.0 \pm 1 \text{ g/L}$), mixed liquor volatile suspended solids MLVSS ($4.9 \pm 0.5 \text{ g/L}$), pH (6.9 ± 0.5), dissolved organic carbon (DOC, $\sim 18 \text{ mg/L}$). Following initial acclimation, the SMBR were operated with and without the addition of suspended medium. The sludge retention time (SRT) was maintained at 20 days by withdrawing a predetermined quantity of sludge every day. The suspended medium used in this study was GAC. The GAC used in this study had different particle sizes of 150–300, 300–600 and 600–1200 μm . The concentration of GAC used was 2 g/L. The GAC concentration was chosen based on our previous study (Johir et al., 2011). The GAC was added into the SMBR only at the start of the experiment, and no more was added thereafter. The optimum aeration rate for SMBR with and without the addition of GAC will be different. Moreover, incorporation of GAC will reduce the optimum aeration rate. Our earlier study investigated the effects of air flow (air scouring) and addition of granular medium in suspension (mechanical scouring) on membrane fouling reduction (Pradhan et al., 2012). They have reported that an increase of air flow rate to 1200 L/m² h (from 600 L/m² h) helped to reduce TMP development by 32% (without the addition of suspended media). However, almost the same (31%) reduction of TMP development was observed with a lower aeration rate of 600 L/m² h when GAC was used as suspended medium. This implies that the use of GAC as suspended medium reduced the air supply requirement by 50%. However, in this study the aeration rate was kept constant at 1.5 m³/m² h in order to compare the TMP development and membrane fouling reduction with no GAC and with the addition of different particle sizes of GAC.

After each experiment the total membrane resistance (R_t), cake resistance (R_c), pore blocking resistance (R_p) and membrane resistance (R_m) were measured. The details of the calculation and measurement procedure to obtain these resistances are reported elsewhere (Johir et al., 2011).

After measuring the membrane resistances, the membrane was cleaned using 5% (w/v) of NaOH solution for 3 h. After cleaning the membrane with NaOH, the membrane was then cleaned in sequence with citric acid (0.5%) for 3 h followed by another 3 h cleaning with NaOCl (200 ppm). After cleaning, the clean membrane flux was measured and it was almost the same as that of virgin membrane flux with a small variation of only less than 3%.

2.2. Analytical methods

The MLSS and MLVSS were measured by filtering the mixed liquor through 1.2 μm filter paper followed by drying for 3 h in an oven at 100 °C. The sample was then kept in a desiccator for 24 h to measure the MLSS. It was then kept in an oven at 550 °C for 30 min followed by another 24 h in a desiccator to measure the MLVSS.

The MLSS and MLVSS concentration with GAC was determined as follows: a known volume of mixed liquor with GAC was collected and was put in rotary shaker at 150 rpm for 30 min to detach the biomass attached on the GAC medium. It was then filtered using a sieve with a pore size of 150 μm . As the GAC particles used were 150 μm or more, the GAC particles were retained on the sieve. The sieve was also carefully washed several times using distilled water to make sure that no biomass was attached on the sieve. The mixed liquor after sieving was collected and was subjected to MLSS and MLVSS by filtering and drying as described ear-

lier in this section. In both cases (with and without GAC) the MLSS and MLVSS measurement was triplicated and the average value was reported.

Sludge volume index (SVI) was determined by standard methods (APHA, 1995). The measurement of SVI was done with mixed liquor containing both the biomass and GAC. However, the presence of GAC did not have any significant effect on the SVI measurement as most of the GAC particles settled down within a short time (less than a minute). The validation of this procedure was checked as follows: initially the SVI was measured for mixed liquor after an acclimation period of 40 days before the addition of GAC. This was compared with the SVI of mixed liquor with the addition of GAC for the same mixed liquor. The SVI values in both cases were almost the same with a variation of less than 2%. Measurements of NH_4^+ , NO_3^- and PO_4^{3-} were carried using the cell test method (Spectroquant, Merck) and a photometer (NOVA 60, Merck).

Size exclusion liquid chromatography with carbon detector (LC-OCD, liquid chromatography-organic carbon detection) with a TSK HW 50-(S) column and a 0.028 mol/L phosphate buffer was used to measure dissolved organic carbon (DOC), dissolved organic nitrogen (DON) and the fractionation of DOC (such as hydrophilic and hydrophobic organics). It provides quantitative information on organic matter as well as qualitative information on molecular size distribution (MWD) of organics present in the wastewater.

3. Results and discussion

3.1. Biomass concentration and sludge properties

The concentration of biomass in terms of MLSS and MLVSS are presented in Table 1. After the acclimation period, the concentration of MLSS and MLVSS did not vary (only minor changes of 10%) with the addition of different sizes of GAC particles. The food to microorganism (F:M) ratio was almost constant within the range of 0.21–0.23 d^{-1} . The SVI values (Table 1) were below 150 mL/g which indicate a good settleability of the sludge. The use of GAC as suspended medium in the size ranges of 150–300 and 300–600 μm helped to reduce the SVI by around 30–40% (Table 1). This indicated that the use of GAC prevented the bulking properties of sludge. Previous study also reported lower SVI with the addition of powdered activated carbon (PAC) in MBR (Satyawali and Balakrishnan, 2009) due to the role of PAC in incompressible floc formation. Another study by Li et al. (2005) reported that the sludge viscosity was reduced by 45% with the addition of PAC. In all cases, the concentration of dissolved oxygen was more than 2 mg/L.

3.2. Organic, ammonia and phosphate removal

The removal of organic matter, ammonia and phosphate with and without the addition of GAC of different particle sizes is presented in Table 2. The removal of DOC and COD without the addition of GAC was $89.2 \pm 0.9\%$ and $84 \pm 0.3\%$, respectively. The removals of DOC and COD with the addition of GAC of different particle sizes were 94–95% and 93–95%, respectively. Thus, an

additional 10% DOC and COD removal could be achieved by incorporating GAC in the SMBR. The DOC concentration in the SMBR effluent with the addition of GAC is almost half (5.9–7.5 mg/L) than that without the addition of GAC (DOC was around 14.6 mg/L). The COD concentration in SMBR effluent with the addition of GAC was also almost 35–40% lower than that without GAC addition. This indicated that the addition of GAC helped to further reduce organic matter. The higher removal of organic matter with GAC could be attributed to the adsorption of organics by GAC. Among of the three different sizes of GAC, the highest removal ($95.6 \pm 0.7\%$) of DOC was found with the smallest particle of GAC (150–300 μm) which can be explained in terms of the higher surface area. The removal of DOC with GAC particle sizes of 300–600 and 600–1200 μm was around 94%. In addition, the uptake rates of DOC and COD with and without the addition of GAC of different particle size were around 0.21 g-DOC/g-MLVSS d and 0.25 g-COD/g-MLVSS d, respectively.

The removal of ammonium nitrogen without the addition of GAC was 36.6 ± 1.4 . The removal of ammonium nitrogen with the addition of GAC of different particle sizes was 35–45%. The lower removal of ammonium nitrogen with and without the addition of GAC could only be due to the partial nitrification as GAC could not adsorb ammonium ions. Another possible reason of the lower removal of ammonium nitrogen or partial nitrification could be due to lower hydraulic retention time (2.5 h) employed in the SMBR. This time was not sufficient for the microorganism to assimilate the nutrients. From literature it is found that in a conventional membrane bioreactor the nitrification occurs with higher HRT of 6 h or more (Viero et al., 2007). The removal of nitrogen was also assessed in-terms of Total Kjeldahl Nitrogen (TKN) as well as total nitrogen. The nitrogen source of the synthetic wastewater mainly comes from the NH_4Cl (7.1 mg- NH_4^+ /L) and a very small amount (0.3 mg/L) as dissolved organic nitrogen (DON) from beef extract. The concentration of NO_3^- and NO_2^- in synthetic wastewater was 0.5 and 0.01 mg/L, respectively. The concentration of Total Kjeldahl Nitrogen (TKN) (which is the sum of ammonia-nitrogen and dissolved organic nitrogen) in synthetic wastewater was 5.7 mg/L as N. The removal of TKN without and with the addition of different particle sizes of GAC of 150–300, 300–600 and 600–1200 was between 22% and 36% (Table 2). On the other hand the removal efficiency of total nitrogen (which is the sum of nitrate-nitrogen, nitrite-nitrogen, ammonia-nitrogen and dissolved organic nitrogen) with and without the addition of GAC of different sizes was relatively low and between $9.4 \pm 3.4\%$ and $21.3 \pm 3.4\%$. The lower removal of nitrogen in-terms of total nitrogen was due to the presence of higher concentration of NO_3^- in the effluent due to nitrification. A mass balance calculation of nitrogen was made to estimate the amount of nitrogen that was nitrified which is sum of the differences between the effluent and influent nitrite nitrogen and nitrate nitrogen. However, the concentration of nitrite could be neglected as the value of nitrite was very low (less than 0.03 mg/L). Only significant readings were nitrate nitrogen, dissolved organic nitrogen and ammonia nitrogen. From the calculation it was found that the amount of nitrogen nitrified was 0.8–1.0 mg/L with and without the addition of GAC of different sizes. From the calculation of the assimilated amount of nitrogen, it was found that the amount of nitrogen assimilated without the addition of GAC was 0.75 ± 0.2 mg/L. The amount of nitrogen assimilated with the addition of different sizes of GAC of 150–300, 300–600 and 600–1200 μm were 0.55 ± 0.2 , 1.25 ± 0.2 and 1.05 ± 0.2 mg/L, respectively. The amount of assimilated nitrogen was calculated from the differences between the total influent and effluent nitrogen. Thus the nitrogen balance calculation along with TKN and nitrogen removal efficiency indicated a lower removal efficiency of nitrogen.

The removal of phosphate without the addition of GAC was $43.7 \pm 6.0\%$ whereas with the addition of GAC of different particle

Table 1
Biomass concentration and sludge properties with and without the addition of GAC in SMBR.

GAC particle size (μm)	MLSS (g/L)	MLVSS (g/L)	F:M	SVI (mL/g)	DO (mg/L)
0	6.6 ± 0.6	5.20 ± 0.2	0.23	90 ± 5	4.5–6.5
150–300	7.0 ± 0.5	5.48 ± 0.3	0.21	50 ± 5	
300–600	6.6 ± 0.4	5.41 ± 0.3	0.23	50 ± 5	
600–1200	6.8 ± 0.1	5.85 ± 0.5	0.23	65 ± 5	

Table 2

Removal of organic, ammonia and phosphate with and without the addition of GAC in SMBR (all the concentrations are in mg/L).

GAC particle size (μm)		DOC	COD	NH_4^+	NO_3^-	NO_2^-	DON	TKN as N	Total N	PO_4^{3-}
0	Influent	129.80	158.60	7.10	0.50	0.01	0.20	5.70	5.85	3.20
	Effluent	14.6 \pm 1.2 (89.2 \pm 0.9)	25.3 \pm 0.5 (84.0 \pm 0.3)	4.5 \pm 0.1 (36.6 \pm 1.4)	5.01 \pm .2	0.01	0.6 \pm 0.05	4.0 \pm 0.2 (29.8 \pm 3.8)	5.1 \pm 0.2 (12.8 \pm 3.4)	1.8 \pm 0.2 (43.7 \pm 6.0)
150–300		5.9 \pm 0.9 (95.6 \pm 0.7)	8.0 \pm 0.5 (95.0 \pm 0.3)	4.6 \pm 0.2 (35.2 \pm 2.8)	4.1 \pm 0.1	0.01	0.8 \pm 0.01	4.4 \pm 0.2 (22.8 \pm 3.5)	5.3 \pm 0.2 (9.4 \pm 3.4)	1.9 \pm 0.3 (40.6 \pm 9.0)
300–600		7.3 \pm 0.5 (94.5 \pm 0.4)	10.5 \pm 1.0 (93.3 \pm 0.6)	4.1 \pm 0.2 (42.2 \pm 2.8)	4.3 \pm 0.2	0.03	0.6 \pm 0.01	3.7 \pm 0.2 (35.0 \pm 3.5)	4.6 \pm 0.2 (21.3 \pm 3.4)	2.1 \pm 0.2 (34.3 \pm 6.2)
600–1200		7.5 \pm 1.5 (94.2 \pm 1.2)	10.5 \pm 0.5 (93.3 \pm 0.3)	3.9 \pm 0.5 (45.0 \pm 7.0)	4.5 \pm 0.3	0.01	0.6 \pm 0.02	3.6 \pm 0.4 (36.8 \pm 7.0)	4.8 \pm 0.2 (17.9 \pm 3.4)	2.1 \pm 0.2 (34.3 \pm 6.2)

Note: The values within the bracket () are the % removal efficiency and values without bracket are the concentration in mg/L.

sizes were in the range of 35–45%. Phosphorus present in wastewater can be removed by precipitation and/or adsorption, or by luxury uptake and only a small amount of phosphorus is used for cell metabolism and growth (Radjenović et al., 2008). To calculate the amount of P adsorbed on the membrane surface, a filtration test (with same membrane) with synthetic water spiked with only P was conducted. The amount of P removed by the membrane was less than 5%. This indicated that the adsorption of P on the membrane surface was minimal. Furthermore, the GAC used as suspended medium also showed no adsorption of P. Thus, the P removal could only be due to cell metabolism and growth. From the influent and effluent P concentrations presented in Table 2 a mass balance of P removal was calculated. The total amount of P coming to the SMBR system was about 100.2 mg-P/day. The amount of P retained in the SMBR with and without the addition of GAC of different particle sizes were in the range of 34–43.8 mg-P/d. The amount of mixed liquor sludge discharged everyday was 0.5 L/d. Thus the amount of P retained in the SMBR following sludge removal was between 32 and 41.5 mg-P/d. Therefore the amount of P underutilised for cell metabolism and growth during the SMBR operation with and without the addition of GAC was 0.6–0.7 mg-P/g-MLSS-d and was relatively low and coincides with the removal of P presented in Table 2. In addition, the COD:P ratio could also be used to assess the performances of biological nutrient removal in the SMBR process (Galil et al., 2009). From the COD and P removal (presented in Table 2) it was found that the $\text{COD}_{\text{used}}:\text{P}_{\text{removed}}$ ratio was between 291 and 412 with and without the addition of different sizes of GAC particle. The higher $\text{COD}_{\text{used}}:\text{P}_{\text{removed}}$ ratio indicated that the SMBR process was P limited (Galil et al., 2009). In this study, we used a lower HRT in the MBR to reduce the footprint of the system and to remove/recover the phosphate by hydrated ferric oxide (HFO) which can ultimately be used as fertiliser.

3.3. Organic characteristics of SMBR effluent with and without the addition of GAC in SMBR

A detailed organic characterisation of SMBR effluent was made using LC-OCD to investigate the changes in different types of organic matter with and without the addition of different particle sizes of GAC. From the characteristics of organic matter present in SMBR effluents, it is found that the removal of both hydrophobic and hydrophilic organic matter increased with the addition of GAC (Table 3). Without the addition of GAC, the removal of hydrophobic organic was 86% whereas, with the addition of GAC it was around 96%. On the other hand, the concentration of hydrophilic organic matter in the SMBR effluent with and without the addition of different particle sizes of GAC was 4.4–6.2 and 12.2 mg/L, respectively. This indicated that the use of GAC as suspended media helped to reduce hydrophilic organic matter by 50–60%. Nguyen et al. (2012) also reported that GAC can effectively remove hydro-

phobic as well as hydrophilic organic matter. They have reported that GAC can adsorb higher amounts of hydrophobic compounds, whereas the removal of hydrophilic compounds is due to hydrophobicity-independent mechanisms such as anion exchange, surface complexation and hydrogen bonding which play significant roles in sorption of organic/trace organics onto GAC. Among the three different particle sizes of GAC, the smallest size (150–300 μm) of GAC removed relatively higher amount of hydrophilic organic matters. Furthermore, the addition of GAC of different particle sizes as suspended medium reduced the concentration of biopolymers by 20% (from 1.53 to 1.20 mg/L). The concentration of humic, building block and low molecular weight (LMW) neutral and acids in SMBR effluent with the addition of different particle sizes of GAC was reduced by 66–76%, 20–50%, 30–56%, respectively. From these results it is found that the addition of GAC helped to remove lower molecular weight of organics than that of higher molecular weight organics (such as biopolymers). From the literature it is found that the lower removal of biopolymers by GAC could be due to the high molecular weight of biopolymers which prevented access to the internal pore structure of the GAC particles (Velten et al., 2011).

3.4. Effect of GAC particle size on membrane fouling reduction

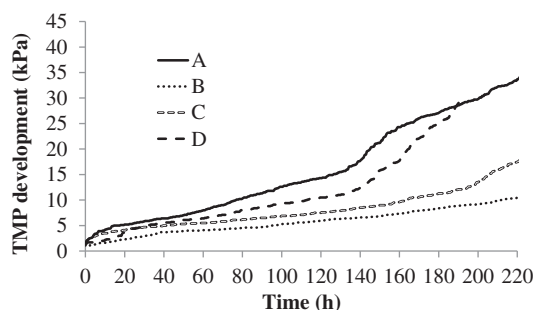
The TMP development profile with time with and without the addition of different particle sizes of GAC is presented in Fig. 1. The development of TMP was high (38.9 kPa) without the addition of GAC. The development of TMP with different sizes of GAC of 150–300, 300–600 and 600–1200 μm were 21.3, 16.0 and 28.5 kPa. The lower development of TMP with the addition of GAC is due to the combined effect of adsorption of organic matter by GAC and extra mechanical scour on the membrane surface created by GAC used as suspended medium. From our previous study (Johir et al., 2011) we also found that the addition of GAC helped to reduce membrane fouling by 50%. Other studies also reported a significant reduction of membrane fouling by the addition of support/suspended media into MBR. For example Fang et al. (2006) reported a 22% reduction of membrane cake resistance by the addition of PAC. Li et al. (2005) reported a 44% reduction of membrane resistance with the addition of PAC.

The lowest TMP development (16 kPa) was achieved with GAC particle sizes of 300–600 μm . The second lowest TMP development was with GAC particle sizes of 150–300 μm of 21.3 kPa. The lower (around 25%) development of TMP with GAC particle size of 300–600 μm could be due to higher mechanical scour onto membrane surface. The higher reduction of TMP development with GAC particle size of 300–600 μm can also be validated from the membrane resistance results reported in Table 4. The values of total membrane resistance (R_t), cake resistance (R_c) and pore blocking resistance (R_p) are presented with and without the addition of GAC of different particle sizes as suspended medium. The values indicated that with the addition of GAC the R_t reduced by 60% (from 35.00 to

Table 3

Organic characteristics of SMBR effluent with and without the addition of GAC in SMBR (all the units are in mg/L).

GAC particle size (μm)		DOC	HOC (hydrophobic)	CDOC (hydrophilic)	Biopolymers	Humic	Building blocks	LMW neutrals and acids
	Influent	129.8	26.80	102.0	5.04	56.2	21.5	19.82
0	Effluent	14.6 \pm 1.2	3.50 \pm 0.1	12.20 \pm 0.5	1.53 \pm 0.1	4.84 \pm 0.1	2.15 \pm 0.2	2.65 \pm 0.5
150–300		5.9 \pm 0.9	1.30 \pm 0.1	4.6 \pm 0.2	1.23 \pm 0.1	1.15 \pm 0.2	1.10 \pm 0.2	1.21 \pm 0.5
300–600		7.3 \pm 0.5	1.40 \pm 0.5	6.40 \pm 0.5	1.20 \pm 0.1	1.21 \pm 0.5	1.30 \pm 0.1	1.56 \pm 0.2
600–1200		7.5 \pm 1.5	1.40 \pm 0.5	6.80 \pm 0.3	1.20 \pm 0.1	1.61 \pm 0.7	1.76 \pm 0.1	1.90 \pm 0.5

**Fig. 1.** Trans-membrane pressure (TMP) development profile with time with and without the addition of different particle sizes of GAC (A = without GAC; B = with GAC particle size of 300–600 μm ; C = with GAC particle size of 150–300 μm ; D = with GAC particle size of 600–1200 μm).

$13.00 \times 10^{12} \text{ m}^{-1}$). It is also found that R_c and R_p with the addition of GAC of particle size of 300–600 μm was lower ($R_c = 8.2 \times 10^{12}$ and $R_p = 4.5 \times 10^{12} \text{ m}^{-1}$) than that with particle sizes of 150–300 and 600–1200 μm ($R_c = 11.2$ and $15.6 \times 10^{12} \text{ m}^{-1}$ and $R_p = 6.9$ and $10.2 \times 10^{12} \text{ m}^{-1}$, respectively). Some of the larger particles of GAC (600–1200 μm) used as supported medium, was found to settle down after 5 days of operation, thus resulting higher TMP development afterwards. Smaller particles of GAC of 150–300 μm led to relatively higher R_t and R_c values than GAC particle sizes of 300–600 μm . This may be because due to the fact that the smaller GAC particle was not able to prevent the deposition of sludge particle on the membrane surface. This helped to building comparatively compact cake layer resulting in a higher R_c value. Although smaller particle size (150–300 μm) of GAC showed slightly higher organic removal (Tables 2 and 3) than larger particle size of GAC of 300–600 μm but showed slightly higher TMP development. Fouling of the membrane was not only due to the deposition of organics onto the membrane surface but also due to the deposition of sludge particles (higher R_c value) onto membrane surface. Thus, it is very important to choose the correct size of the GAC particles to optimise organic removal with lower TMP development. In addition, the settling of larger particle size of GAC of 600–1200 μm could be minimized by using a higher aeration rate. However, the use of higher aeration rate is not cost effective.

The effect of GAC on the membrane surface after the addition of GAC was tested physically by measuring the clean water flux and

Table 4 R_t , R_c and R_p with and without the addition of different particle of GAC (membrane resistance, $R_m = 0.59 \times 10^{12} \text{ m}^{-1}$).

GAC particle size (μm)	R_t ($\times 10^{12} \text{ m}^{-1}$)	R_c ($\times 10^{12} \text{ m}^{-1}$)	R_p	
			(% of R_t)	($\times 10^{12} \text{ m}^{-1}$) (% of R_t)
0	35.00	20.4	58.28	14.1
150–300	19.20	11.2	58.33	6.9
300–600	13.00	8.2	63.08	4.5
600–1200	25.90	15.6	60.23	10.2

the turbidity of the MBR effluent. It was found that the GAC particle did not have any adverse effect on membrane surface as the clean water flux was the same as that of a virgin membrane and as the filtered turbidity was reasonably low (less than 0.2 NTU). This result can also be validated from the findings of others. For example Siembida et al. (2010) used granular polypropylene particle size of 2.2–3.0 mm in a submerged membrane bioreactor for more than 600 days. They examined the membrane surface with SEM and found only brush marks on the membrane surface which did not affect the membrane performance.

From the experimental investigation it is evident that the use of GAC could help to reduce the membrane fouling resulting from the adsorption of organic matter and by providing extra scouring effect on the membrane surface. However, it is important to investigate the long term effect of GAC on the adsorption of organic matter.

3.5. Removal and recovery of PO_4^{3-} from SMBR effluent by HFO column

In this study, an anthracite filter mixed with hydrated ferric oxide (HFO) was used to remove PO_4^{3-} from the SMBR effluent. The PO_4^{3-} was not removed to a sufficient level by the SMBR (Table 2). Thus it had to be removed in a sustainable manner.

Column experiments packed with anthracite and HFO were conducted at a filtration velocity of 2.5 m/h. The filtration column was packed with 36 g of anthracite (particle size of 0.6–1.18 mm) as an inert material with varying percentage of HFO by mass (0%, 1%, 5%, and 10% of anthracite) in-filled in the anthracite medium to investigate the effect of different amounts of HFO on the removal of phosphate.

The adsorption capacity of PO_4^{3-} by HFO (doses of 0.1–7.0 g/L) was first evaluated using a batch equilibrium study. From the batch equilibrium study, it was found that the removal of PO_4^{3-} increased from 11.3% (with 0.1 g/L of HFO) to 90.4% with 7.0 g/L of HFO. Furthermore, the equilibrium (isotherm) data was successfully fitted with Langmuir isotherm model (figure is not shown). From the Langmuir isotherm model, the maximum adsorption capacity of PO_4^{3-} was found to be 41.9 mg- PO_4^{3-} /g-HFO. This result is in agreement with the findings of previous study (Gupta et al., 2012). They reported the maximum adsorption capacity of P by HFO of 14 mg-P/g (or 42.9 mg- PO_4^{3-} /g). Gupta et al. (2012) also have investigated a comparative removal of P by purolite ion exchange resin and HFO. A 50% higher adsorption capacity of P by HFO (14 mg-P/g) than purolite ion exchange resin (7 mg-P/g) was reported.

From the literature, it is found that oxides of polyvalent metals such as Fe^{3+} , Ti^{4+} and Zr^{4+} exhibit very favourable ligand sorption properties for phosphate through the formation of inner sphere complexes (Blaney et al., 2007). Moreover, a new phosphate-selective sorbent, referred to as hybrid anion exchanger (HAIX) has been successfully used to remove phosphorus. HAIX is essentially a polymeric anion exchanger within which hydrated ferric oxide (HFO) nanoparticles have been dispersed irreversibly (Blaney et al., 2007).

The results of the HFO/anthracite column experiment are presented in Fig. 2. The performance of the filtration column was ana-

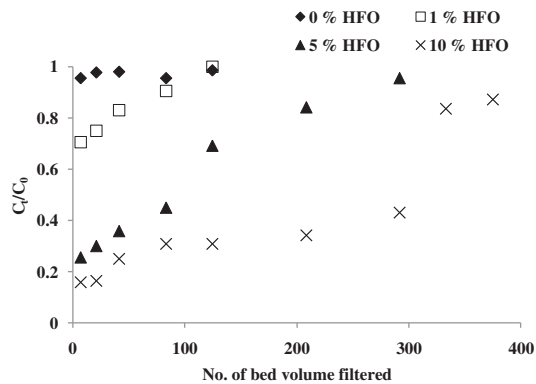


Fig. 2. PO_4^{3-} removal by HFO from SMBR effluent (0%, 1%, 5% and 10% of HFO by mass with anthracite coal as inert material was used as filter medium; influent PO_4^{3-} concentration to the post treatment HFO adsorption column was 2.2 mg/L).

lysed in terms of phosphate removal. From Fig. 2, it is clear, as expected, that the anthracite filter medium itself was not effective in removing of PO_4^{3-} . The incorporation of HFO helped to remove PO_4^{3-} . The removal of PO_4^{3-} increased with high percentages of HFO. With 1% of HFO, the filtration column was saturated ($C_t/C_0 = 1$) within 125 bed volumes, whereas it took place after 350 bed volumes with HFO of 10% (here, C_t is the effluent PO_4^{3-} concentration with time (t) and C_0 is influent PO_4^{3-} concentration). The No. of bed volume is defined as flow rate * time/volume of filter medium). From the Fig. 2 it is also found that at the beginning (within 10 min) of the operation the C_t/C_0 values with 0%, 1%, 5% and 10% of HFO were 0.95, 0.70, 0.25 and 0.16, respectively. The lower values of C_t/C_0 and longer bed volume filtered with 10% of HFO could be due to the greater availability of adsorbing sites of HFO for the adsorption PO_4^{3-} . Thus it can be concluded that HFO can be used as an absorbent/ion exchanger with other inert materials such as anthracite or sand to remove PO_4^{3-} from a high rate membrane bioreactor. The breakthrough adsorption capacity for different % HFO mixed with anthracite in the column was calculated. The adsorption capacity of HFO was found 36–39 mg- PO_4^{3-} /g-HFO which is slightly lower than that obtained from the equilibrium study (41.9 mg- PO_4^{3-} /g-HFO). This could be due to the change in operational condition. In equilibrium study it is assumed that all the HFO particles dispersed properly in water will have 100% availability of adsorption sites. On the other hand in the column some HFO particle may interact with anthracite particle as well as among HFO particles themselves resulting in minor losses of adsorption sites. Further, HFO is not suitable for long-term use in fixed-bed columns due to its lack of mechanical strength although HFO has higher adsorptive capacity for phosphate (Blaney et al., 2007). Thus the application of HFO on the P removal may not be cost effective as the recovery of HFO material is difficult.

4. Conclusion

The removal of organics with the addition GAC as suspended medium was high (95%). The size of GAC particle played a major role on membrane fouling reduction. Total membrane resistance (R_t) reduced by 60% with GAC particle sizes of 300–600 μm . A simple treatment of 10% HFO + 90% anthracite mixed column showed a high removal (or recovery) of PO_4^{3-} from the SMBR effluent. It could be operated for a long time before the HFO became exhausted as the number of filter volume is more than 300 for 10% of HFO.

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References

- Akram, A., Stuckey, D.C., 2008. Flux and performance improvement in a submerged anaerobic membrane bioreactor (SAMBR) using powdered activated carbon (PAC). *Process Biochem.* 43, 93–102.
- APHA, American Public Health Association, 1995. *Standard Methods for the Examination of Water and Wastewater*, 21st Centennial ed. APHA, Washington.
- Blaney, L.M., Cinar, S., SenGupta, A.K., 2007. Hybrid anion exchanger for trace phosphate removal from water and wastewater. *Water Res.* 41, 1603–1613.
- Cui, Z.F., Chang, S., Fane, A.G., 2003. The use of gas bubbling to enhance membrane processes. *J. Membr. Sci.* 221, 1–35.
- Drews, A., 2010. Membrane fouling in membrane bioreactors—characterisation, contradictions, cause and cures. *J. Membr. Sci.* 363, 1–28.
- Fang, H.H.P., Shi, X., Zhang, T., 2006. Effect of activated carbon on fouling of activated sludge filtration. *Desalination* 189, 193–199.
- Galil, N.I., Malachi, K.B.-D., Sheindorf, C., 2009. Biological nutrient removal in membrane biological reactors. *Environ. Eng. Sci.* 26 (4), 817–824.
- Guo, W.S., Shim, W.G., Vigneswaran, S., Ngo, H.H., 2005. Effect of operating parameters in a submerged membrane adsorption hybrid system: experiment and mathematical modelling. *J. Membr. Sci.* 247, 65–74.
- Gupta, M.D., Loganathan, P., Vigneswaran, S., 2012. Adsorptive removal of nitrate and phosphate from water by a purolite ion exchange resin and hydrous ferric oxide columns in series. *Sep. Sci. Technol.* 47 (12), 1785–1792.
- Jin, L., Ong, S.L., Ng, H.Y., 2013. Fouling control mechanism by suspended biofilm carriers addition in submerged ceramic membrane bioreactors. *J. Membr. Sci.* 427, 250–258.
- Johir, M.A.H., Rupak, A., Vigneswara, S., Kandasamy, J., Grasmick, A., 2011. Influence of supporting media in suspension on membrane fouling reduction in submerged membrane bioreactor (SMBR). *J. Membr. Sci.* 374 (1–2), 121–128.
- Johir, M.A.H., George, J., Vigneswaran, S., Kandasamy, J., Sathasivan, A., Grasmick, A., 2012. Effect of imposed flux on fouling behavior in high rate membrane bioreactor. *Bioresour. Technol.* 122, 42–49.
- Judd, S., 2007. Membrane bioreactor technology costs. In: *Proceedings of International Membrane Science and Technology Conference*, November 2007, Sydney, Australia.
- Lesage, N., Sperandio, M., Cabassud, C., 2008. Study of a hybrid process: adsorption on activated carbon/membrane bioreactor for the treatment of an industrial wastewater. *Chem. Eng. Process.* 47 (3), 303–307.
- Li, Y.-Z., He, Y.-L., Liu, Y.-H., Yang, S.-C., Zhang, G.-J., 2005. Comparison of the filtration characteristics between biological powdered activated carbon sludge and activated sludge in submerged membrane bioreactors. *Desalination* 174, 305–314.
- Meng, F., Chae, S.-R., Drews, A., Kraume, M., Shin, H.-S., Yang, F., 2009. Recent advances in membrane bioreactors (MBRs): membrane fouling and membrane material. *Water Res.* 43, 1489–1512.
- Nguyen, L.N., Hai, F.I., Kang, J., Price, W.E., Nghiem, L.D., 2012. Removal of trace organic contaminants by a membrane bioreactor-granular activated carbon (MBR-GAC) system. *Bioresour. Technol.* 113, 169–173.
- Pradhan, M., Vigneswaran, S., Kandasamy, J., Ben Aim, R., 2012. Combined effect of air and mechanical scouring of membranes for fouling reduction in submerged membrane reactor. *Desalination* 288, 58–65.
- Radjenović, J., Matošić, M., Mijatović, I., Petrović, M., Barceló, D., 2008. Membrane bioreactor (MBR) as an advanced wastewater treatment technology. *Handb. Environ. Chem.* 5 (S/2), 37–101.
- Satyawali, Y., Balakrishnan, M., 2009. Effect of PAC addition on sludge properties in an MBR treating high strength wastewater. *Water Res.* 43, 1577–1588.
- Siembida, B., Cornel, P., Krause, S., Zimmermann, B., 2010. Effect of mechanical cleaning with granular material on the permeability of submerged membranes in the MBR process. *Water Res.* 44, 4037–4046.
- Velten, S., Knappe, D.R., Traber, J., Kaiser, H.P., von Gunten, U., Boller, M., Meylan, S., 2011. Characterization of natural organic matter adsorption in granular activated carbon adsorbers. *Water Res.* 45, 3951–3959.
- Viero, A.F., Sant'Anna, G.L., Nobrega Jr., R., 2007. The use of polyetherimide hollow fibres in a submerged membrane bioreactor operating with air backwashing. *J. Membr. Sci.* 302 (1–2), 127–135.
- Xing, W., Ngo, H.H., Guo, W.S., Listowski, A., Cullum, P., 2012. Optimization of an integrated sponge – granular activated carbon fluidized bed bioreactor as pretreatment to microfiltration in wastewater reuse. *Bioresour. Technol.* 113, 214–218.