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**Enhanced Performance of Submerged Hollow Fibre Microfiltration by Fluidized
Granular Activated Carbon**

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ABSTRACT

The effect of fluidized granular activated carbon (GAC) on membrane filtration performance was investigated using a bench-scale upflow hollow fibre membrane filtration setup under constant flux operation. The membrane fouling tendencies were compared among five different experimental parameters, namely, GAC size, GAC packing amount, hollow fibre spacing, filtration/idle duration, and fluidization/idle duration. The results indicate that larger-sized GAC particles, higher packing amounts and a ratio of hollow fibre spacing to fluidized particle size of approximately 3-5 are most beneficial for fouling control. Unexpectedly, the intermittent filtration (under continuous fluidization) could not further alleviate membrane fouling compared to continuous filtration, possibly due to inefficient interaction of fluidized GAC particles with membrane surface in absence of permeate driving force. To lower energy consumption, the optimization of intermittent fluidization (under continuous filtration) was performed. Results indicate that the nature of the cake layer formed during non-fluidization period determined the membrane fouling development rather than the fluidization time span. Finally, by comparing the membrane permeability, sodium alginate rejection rate, and membrane properties before and after GAC abrasion, the GAC scouring on membrane integrity was negligible.

Key words: Hollow fibre spacing; GAC particle size; Intermittent fluidization; Membrane fouling; Membrane integrity

1. Introduction

Water and wastewater recycling processes using membrane separation technology have been developed for a few decades [1]. However, the occurrence of membrane fouling due to the unfavourable interactions of the filtered substances with membranes reduces the membrane performance and increases the operating cost. Plenty of studies on fouling control strategies in membrane filtration processes on the basis of physical, chemical, and mechanical cleaning have been carried out and reported [2,3] .

Periodically physical cleaning (hydraulic approaches, pneumatic approaches, sonication, and vibration, etc.) is generally performed as effective strategies to recover the membrane performance [4]. Among these approaches, the addition of suitable fouling reducers in membrane filtration processes has been attempted. Some filter-aid agents facilitate to reduce the interaction or modify the adherence mode between the potential foulants and membrane surfaces by adsorption [5], flocculation [6], or formation of a second membrane on the primary membrane surface [7]. On the other hand, some particles enhance shear-induced diffusion [8] or provide mechanical abrasion force along the membranes due to their physical natures [9]. According to the inertial lift model in a cross-flow filtration process, the presence of the added particles enhances the shear stress on the membrane surface and increases lateral inertial lift velocity (i.e., an increase of shear-induced diffusion). Thus, the added particles tend to remove the existing cake layers from membranes or prevent the foulants further deposition on membranes, both of which facilitate membrane filtration [9].

The potential of preventing membrane fouling by using liquid fluidized particles (such as glass beads, steel beads) has been illustrated in a few early-published research literatures [10-12]. These studies emphasized that the fluidized particles as turbulence promoters could increase mass transfer, therefore improving the permeate flux and rejection rate. Recently,

researchers have proven that the mechanical scouring induced by the added granular activated carbon (GAC, suspended via aeration) facilitated to mitigate cake layer fouling in aerobic membrane bioreactors (MBRs) [9,13-17]. Meanwhile, the integration of liquid fluidized GAC particles with membrane filtration has been proposed to polishing the anaerobic bioreactor effluent, and the presence of GAC particles could prevent deposition of potential foulants on the membrane surface [18-21]. However, it should be realized that GAC particles at a relatively high dosage may affect membrane integrity, fouling behaviours and operation cost [22,23].

Two-phase GAC fluidization requires the minimum fluidization velocity (U_{mf}), above which the frictional pressure drop across the bed of GAC particles becomes constant [24]. Theoretically, the minimum velocity to fluidize GAC particles is dependent on particle size and amount [24]. On the other hand, the fluidization velocity and GAC configurations determine the scouring shear force along the membranes. Thus, besides membrane performance, the total energy consumed for GAC fluidization and membrane filtration needs to be carefully evaluated. To minimize energy usage in membrane filtration while ensuring filtration performance, the optimizations of GAC particle fluidization and membrane filtration conditions are necessary. However, so far, there is lack of studies on this issue.

In this study, a bench-scale upflow hollow fibre membranes filtration cell was used to simulate liquid GAC fluidization-microfiltration process. A model foulant solution consists of sodium alginate, bovine serum albumin, humic acid and bentonite was used to simulate the bioreactor effluent. The membrane performance, fouling control mechanism, and calculated energy consumption were systematically evaluated with regard to various GAC properties (GAC size, GAC packing ratio), membrane module configuration (hollow fibre spacing) and filtration/fluidization conditions (intermittent/continuous filtration, intermittent/continuous

fluidization). Whether GAC scouring could influence hollow fibre membrane integrity was further assessed.

2. Materials and Methods

2.1. Model foulant solution

The model foulant suspension was formulated to simulate the effluent of an anaerobic bioreactor. Accordingly, bovine serum albumin (BSA, 100 mg/L, Sinopharm Chemical Reagent Co. Ltd., China), sodium alginate (SA, 100 mg/L, Hanawa Chemical, Japan), humic acid (HA, 100 mg/L, Aldrich-Sigma, USA), and bentonite (100 mg/L, Aldrich-Sigma, USA) were used to represent protein, polysaccharides, humic substances, and suspended particles, respectively.

2.2. Filtration cell setup

A bench-scale hollow fibre membrane filtration assay was setup to investigate the membrane performance in the presence of GAC fluidization (Figure 1a). The feed solution was pumped to the filtration cell and retention solution was recycled back to the feed beaker. The feed pump provided a certain upflow velocity which ensured GAC fully fluidized. A pulse damper (Core-Palmer, USA) was used to eliminate pulsation in the feed flow. The permeate flux was regulated by controlling the flowrate of the permeate pump (Core-Palmer, USA). An electronic balance (Mettler Toledo, Switzerland) measured the weight of permeate collected over time and two pressure transducers (Cole-Palmer, USA) measured the feed pressure and permeate pressure respectively. Transmembrane pressure (TMP) was calculated as the difference of feed pressure and permeate pressure. The permeate weight and TMP were recorded via Labview (National Instruments, USA) installed on a computer.

The filtration cell had a fluidization channel with dimension of 0.15 m (H) x 0.022 m (W) x 0.01 m (T) (Figure 1b). Each membrane module contained three PVDF hollow fibres with a nominal pore size of 0.1 μm and an effective membrane area of 14.13 cm^2 . The spacing among the hollow fibres in each membrane module was controlled 0, 2 and 5 mm respectively, whereas the looseness of each hollow fibre was kept at 0%, i.e. no movement of hollow fibres.

The GAC particles purchased from Calgon Carbon Corporation (USA) were separated into different sizes (0.5-1, 1-1.4, and 1.4-2 mm) by sieving (W.S. Tyler Industrial Group, USA). Before experiment, the fresh GAC particles were washed with distilled water to remove the trapped air within the GAC particles and fine carbon powder loosely attached on GAC particles. Then the GAC particles were soaked into the model solution for a few hours to reach adsorption saturation (Figure S1 in the supplementary data). In this study, the saturated GAC particles were fluidized to the similar height (90% of the filtration channel height) for all the experimental conditions.

2.3. Threshold flux determination

The threshold flux (i.e., the critical flux which demarcates between low-fouling and high-fouling) of the model mixture was determined using the following protocol [25]: (i) Incrementally increasing the flux at 15 min intervals, (ii) Calculating the slope of the TMP profile ($d(\text{TMP})/dt$) at each flux step, and (iii) Determining the threshold flux, which is the flux whereby the regression lines of the low fouling region and the high fouling region intersects.

2.4. Membrane fouling resistance, fouling rate, and cake layer fouling reduction ratio

Membrane resistance (R) is calculated by the equation $R = \text{TMP}/(\mu J)$, where μ is the permeate viscosity and J is the permeate flux. The filtration experiments with and without the addition of GAC were conducted, where the latter served as a control experiment. Three steps were performed to determine the resistance values: (1) R_m (clean membrane resistance) – The experiment was run for 10 min with distilled water and without GAC addition; (2) $R_{m+\text{cake layer+irreversible}}$ (total resistance) – The experiment was run with the model foulant and with or without GAC addition; (3) $R_{m+ \text{ irreversible}}$ – After the fouled membranes had been flushed with distilled water for 5 min, the experiment was run for 15 min with distilled water and without GAC. Cake layer fouling resistance was achieved by subtracting $R_{m+ \text{ irreversible}}$ from $R_{m+\text{cake layer+irreversible}}$. Cake layer fouling reduction ratio was calculated as the equation: $[\text{R}_{\text{cake layer (without GAC)}} - \text{R}_{\text{cake layer (with GAC)}}] / \text{R}_{\text{cake layer (without GAC)}}$. Membrane fouling rate ($d\text{TMP}/dt$) was achieved by calculating the slope of the TMP profile at a certain period of time. Under each condition, more than triplicate experiments were performed. The averaged results and standard deviations (as error bars) are presented in the tables and figures.

2.5. Intermittent filtration and intermittent fluidization experiments

GAC particles with size of 1.0-1.4 mm and mass of 7.5 g, and hollow fibre spacing of 5 mm were employed for all the intermittent filtration and intermittent fluidization experiments. For the intermittent filtration experiments, the upflow velocity of 0.021 m/s was maintained to fluidize GAC particles to the tested height, i.e. 90% of filtration cell channel height during the whole experiment. According to the threshold flux (data not shown), the permeate flux was fixed at 90 LMH during the filtration period with different idle intervals. In fact, at the flux of 90 LMH (i.e., maximum threshold flux), linear slow TMP rise could ensure a long-term operation, beyond which the rapid exponential TMP jump was noticed.

For the intermittent fluidization experiments, the permeate flux was fixed at 90 LMH during the whole experiment. The feed pump was regulated to achieve the upflow velocity of 0.021 m/s during fluidization period and 0.001 m/s during fluidization idle period (in order to continuously feed the model solution).

2.6. Membrane integrity test

Membrane permeability (P , $L/m^2\text{hr/kPa}$) was calculated as $P = \text{Flux}/\text{TMP}$. Before each test, the clean water permeability of virgin hollow fibre membrane module (P_0) was measured at a constant flux of 90 LMH. GAC particles (1-1.4 mm, 7.5g) were added into the hollow fibre filtration cell (hollow fibre spacing at 5 mm) and GAC fluidization was performed at an upflow velocity at 0.021 m/s for 15 h. Such fluidization time period is employed to simulate the initial interaction of GAC with membrane surface. After that, the GAC particles were carefully removed and the clean water permeability of the hollow fibre membrane (P_{GAC}) was measured at a constant flux of 90 LMH. The membrane permeability change rate (ΔP_{GAC}) was calculated as $(P_{\text{GAC}} - P_{0\text{ GAC}})/P_{0\text{ GAC}}$. In the absence of GAC fluidization, the upflow velocity at 0.021 m/s was employed in the hollow fibre filtration cell for 15 h and then the clean water permeability of the hollow fibre membrane (P_{control}) was measured at a constant flux of 90 LMH. The membrane permeability change rate ($\Delta P_{\text{control}}$) was calculated as $(P_{\text{control}} - P_{0\text{ control}})/P_{0\text{ control}}$. Multi hollow fibre samples were examined ($n=6$).

The sodium alginate (Hanawa Chemical, Japan) solution reprehensive of polysaccharides was used as a model solution (The size distribution was shown in Figure S2). After the clean water membrane permeability test, sodium alginate solution (100 mg/L) was used as feed solution and the filtration was carried out at a flux of 90 LMH for 30 min. The permeate at the last 10 min was collected for total organic carbon (TOC) measurement by a TOC analyzer

(Shimadzu, Japan). The sodium alginate rejection rate (R) was calculated as $(\text{TOC}_f - \text{TOC}_p)/\text{TOC}_f$. Multi hollow fibre samples were examined ($n=4$).

2.7. Membrane morphology observation

After membrane clean water permeability test, the membranes were pre-treated using a Heraeus vacuum oven (Thermo Scientific, USA) at 60°C for 15 hr to remove the moisture content. After the membranes were sputter-coated with platinum, a field emission SEM (JEOL, Japan) was used to characterize the membrane surface morphology. An atomic force microscope (AFM, Park systems, Korea) was employed to observe the membrane morphology and to measure the membrane roughness properties.

2.8. Membrane pore size distribution and FT-IR analysis

The pore size distributions of the membranes were determined by a capillary flow porometer (Porous Materials, Inc., USA). The major functional groups of the membrane surfaces were monitored by a FT-IR spectroscopy (Shimadzu, Japan).

3. Results and discussion

3.1. Effect of hollow fibre spacing

Three hollow fibre spacings (0, 2, and 5 mm) and three size ranges of GAC particles (0.5-1, 1-1.4, and 1.4-2 mm) were tested in this study. For each experiment, 7.5 g of GAC particles was consistently used. To reach the same fluidization height (90% of the total height of the membrane filtration channel in order to avoid the GAC particles blocking the outlet of the recirculation line), fluidization velocities of 0.012, 0.021, and 0.031 m/s were employed for the GAC particles in the size ranges of 0.5-1, 1-1.4, and 1.4-2 mm, respectively. To

accelerate the fouling process at such a low concentration of model foulant, the permeate flux was fixed at 90 LMH (i.e., close to the threshold flux).

Three preliminary observations should be noted. (1) As presented in Figure S1, the adsorption capacity of the GAC particles was saturated within 1 h. For continuous filtration lasting more than 1 h, the GAC particles play the role of scouring rather than physical adsorption to reduce membrane fouling. Accordingly, to study the scouring behaviour of fluidized GAC, the GAC particles were saturated by the model foulants prior to the experiments. (2) In this work, cake layer fouling rather than irreversible fouling plays the dominant role in deteriorating membrane performance. As shown in Table S1 of the supplementary data, in the absence of fluidized GAC, the resistance due to irreversible fouling was within the range of $0.03 - 0.19 \times 10^{12} \text{ m}^{-1}$, which was less than 5% of the total fouling. (3) The presence of the fluidized GAC significantly reduced cake layer fouling, regardless of GAC particle size and hollow fibre spacing. Figure 2 contrasts the cake layer fouling resistance of hollow fibre membrane module with and without fluidized GAC particles.

The spacing between each hollow fibre is an important design parameter for a hollow fibre module. Generally, a high fibre packing density achieves a larger surface area per unit volume, but the trade-off lies in poor fluid distribution and high pressure drop across the module [26]. In the GAC fluidization-hollow fibre filtration system, the hollow fibre spacing additionally dictates the numbers of GAC particles between the fibres and hydrodynamics of GAC particles, both of which influence the scouring efficiency of the GAC particles along the membrane surface.

Expectedly, as shown in Figure 2, regardless of the absence or presence of GAC, membrane fouling was dramatically alleviated when a spacing distance between the fibres was applied

relative to that without spacing. The spacing between the fibres allows the liquid and solid to be fully contacting the membrane surface, facilitating shear along the membrane surface. In the absence of fluidized GAC particles, when the hollow fibre spacing increased from 2 mm to 5 mm, almost no further fouling reduction (as shown in a p -value > 0.1 in a T-test) was observed. This may be attributed to the same magnitude of shear on the membrane at the same liquid velocity [27].

On the other hand, in the presence of GAC fluidization, the interplay between particle size and hollow fibre spacing influences the extent of fouling mitigation. For the GAC particles of the smallest size range of 0.5-1.0 mm and largest size range of 1.4-2.0 mm, negligible decrease of cake layer resistance was noticed (as shown by p -values of 0.572 and 0.209, respectively, in a T-test) as the spacing increased from 2 mm to 5 mm. However, for the intermediate particle size (i.e., 1.0-1.4 mm), the cake layer resistance was at a spacing of 5 mm slightly lower than that observed at 2 mm (as shown by the p -value of 0.002 in a T-test). This phenomenon could be explained by the number of GAC particles in contact with the hollow fibres as depicted in Table 1, and subsequently different extents of wall effects [28]. For the smallest size range of GAC particles (i.e., 0.5-1.0 mm), 2-4 and 5-10 GAC particles can be fluidized between two fibres at a spacing of 2 mm and 5 mm, respectively. Although the increased number of GAC particles for the 5mm spacing is expected to enhance scouring, it should be noted that only the GAC particles in close proximity to the hollow fibre surface could perform effective scouring, hence increasing the number of GAC particles beyond 2-4 (as in the case of 2 mm spacing) did not benefit the alleviation of membrane fouling. For the GAC particles in the intermediate size range (i.e., 1.0-1.4 mm), 1-2 and 3-5 GAC particles could be fluidized between two fibres at a spacing of 2 mm and 5 mm, respectively. The significant improvement of membrane performance as the spacing increased from 2 to 5 mm

for particles in this size range was the increased contact between the particles and the membrane surface due to the increased number of particles. For the GAC particles in the largest size range (i.e., 1.4-2.0 mm), 1 and 2-3 GAC particles could be fluidized between two fibres at a spacing of 2 mm and 5 mm, respectively. In both spacing ranges, the numbers of GAC particles are relatively smaller, hence insignificant differences in membrane performances were observed. These results suggested that the optimal ratio of hollow fibre spacing to fluidized particle size should be around 3-5. In fact, the applied hollow fibre spacing should be determined by the size range of the fluidized GAC particles. It should be noted that possible wall effect cannot be ruled out from the observed phenomenon, and the extent of pressure drop in such a liquid GAC fluidization system should be monitored in future study in order to quantitatively describe possible wall effect which may affect GAC scouring efficiency.

3.2. Effect of GAC particle size

To compare the effect of GAC particle size on membrane performance, the averaged cake layer fouling reduction (Table 2) was calculated as a ratio of the cake layer fouling resistances in the presence of fluidized GAC to that of control experiment (without fluidized GAC) based on the data shown in Figure 2. The higher the cake fouling layer reduction ratio is, the more effective the scouring effect of the GAC particles is. It was found that, at a hollow fibre spacing of 0 mm, cake layer fouling reduction ratios were similar among all three ranges of GAC particle sizes investigated. However, with the widening of the hollow fibre spacing, the influence of GAC particle size on cake layer fouling reduction ratio became more significant. When the hollow fibre spacing was 2 mm, the cake layer fouling reduction ratio was similar for the GAC particles ranged at 0.5-1.0 and 1.0-1.4 mm, but dramatically higher for the GAC particles ranged at 1.4-2.0 mm. When the hollow fibre spacing was 5 mm,

the cake layer fouling reduction ratio increased monotonically with GAC particle size. Evidently, the larger GAC particles are more effective in the alleviation of membrane fouling.

In a fluidized system, the shear caused by the particles can be approximated by [29]:

$$\gamma = \left(\frac{U_l(1 - \varepsilon)(\rho_p - \rho)g}{\mu} \right)^{\frac{1}{2}} \quad (1)$$

where U_l is the superficial liquid velocity, ε is the bed voidage (i.e., ratio of volume occupied by interstitial voids to the volume of the particle bed) at U_l , $(\rho_p - \rho)$ is the difference between apparent particle and water densities, g is the gravitational acceleration, and μ is the liquid viscosity. It is noted that the same amount of GAC particles (7.5 g) with different particles sizes was used to scour the same area of membrane surface. The bed voidages of fluidized GAC particles tested were almost the same. Because the larger GAC particles (1.4-2 mm) required higher U_l (0.031 m/s) to be fluidized, the larger particles in turn impose higher shear on the membrane surface, thereby enhancing fouling mitigation.

Unfortunately, the trade-off with using the larger GAC particles for more effective fouling mitigation is the higher minimum fluidization velocity U_{mf} required, which therefore incurs higher energy costs. Generally, the energy consumed by the liquid recirculation pump for GAC fluidization is a major contribution to the energy consumption of the process [18]. The theoretical energy requirement by the pump is obtained by [30]:

$$P = \frac{Q_R \rho g H}{1000 \xi} \quad (2)$$

where P is the pump energy demand (kW), Q_R is the volumetric liquid flow rate (m^3/s), ρ is the pumped fluid density (kg/m^3), g is gravitational field strength (9.8 N/kg), H is system head (m, which is equivalent to 10 times of the pressure difference between the top and

bottom of the liquid column in the reactor (bar)), and ξ is pump efficiency. Because higher Q_R is needed to fluidize the larger GAC particles, P has to increase proportionally.

It is expedient to compare the effect of varying GAC particle size at the same upflow velocity, as depicted in Table 3. It is noted that at the same upflow velocity, as GAC particle diameter increases, the mass of GAC particles required to achieve a similar fluidized bed height increases. However, the difference in head loss was negligible (less than 6%), therefore, a similar pump energy consumption was assumed. Table 3 shows the cake resistance decreased as GAC particle size increased at the same upflow velocity, which indicating greater GAC particles facilitated fouling alleviation. At the same upflow velocity, the initial packing ratios were higher for the greater GAC particles (Table 3), accordingly, less bed voidages of fluidized greater GAC particles. Therefore, the greater GAC particles had higher scouring force compared to the smaller GAC particles (Equation 1). While, in the cost optimization of the process, the following trade-off needs to be balanced: although greater-sized GAC could significantly alleviate membrane fouling, the increased capital cost of GAC need to be considered.

Surprisingly, at the same hollow fibre spacing and upflow velocity, the cake layer resistances for the GAC particles with the smallest diameters of 0.5-1.0 mm (Table 3) were more than twice higher than that in the absence of GAC fluidization (Figure 2). This implies that the GAC particles of smaller diameters could act as potential foulants, especially after the organic foulants are deposited on the membranes, since the strong affinity between the GAC particles and the organic foulants is known to aggravate such fouling tendency [31].

3.3. Effect of filtration intermittent frequency

Many previous studies have illustrated that intermittent filtration can achieve better membrane performance compared to continuous filtration. Such improvements are attributed to the fact that the shear force induced by liquid or/and gas flow is greater than the affinity force between the foulants and membrane in the absence of the permeate drag force. Thus, the formed cake layers can be efficiently removed from the membrane surface by shear when permeate filtration is idle.

In this study, the periodically intermittent filtration was performed during GAC fluidization. Figure 3a indicates the membrane fouling rates at different filtration intermittent frequencies during 3 h-fluidization/filtration period of time. Unexpectedly, compared to continuous filtration, the filtration at 9.5 min on/0.5 min off, 9 min on/1 min off or 8 min on/2 min off insignificantly affected the membrane fouling rate (p -value >0.1 , T-test). This hints that the fluidized GAC particles could not further benefit fouling reduction during the idle period of permeate filtration.

This phenomenon could be explained by the different net force directions of the fluidized GAC particles in the presence and absence of permeate filtration (Figure 3b). During the filtration period, the permeate drag force increases the affinity of the foulants and membrane surface. In the presence of GAC fluidization, the combined drag force and shear force drive the fluidized GAC particles towards membrane surface, which create more opportunities for the GAC particles to scour the formed foulants layers from membrane surface.

3.4. *Effect of fluidization intermittent frequency*

As indicated as Equation 2, the energy consumed by the recirculation pump for fluidizing the particles is a major component of the total energy requirement of the process. To reduce energy consumption, periodically intermittent fluidization with continuous permeation is proposed in this study. Figure 4 describes the membrane fouling patterns at the different fluidization intermittent frequencies. When the non-fluidization period was fixed at 1 min, extending the GAC fluidization period from 1 min to 3 min appeared to decrease the fouling tendency. However, further increasing the GAC fluidization time to 5 min showed no significant improvement of membrane performance (Figure 4a). At the optimal intermittent fluidization condition (1 min off/3 min on and 1 min off/5 min on), the fouling development was almost comparable to that in the continuous fluidization condition. This indicates that the GAC scouring effect is associated with not only GAC properties, but also the nature of the formed cake layer.

To further illustrate the effect of formed cake layer nature on GAC scouring efficiency, different non-GAC fluidization time periods (1, 3, and 5 min) were employed at the same permeate flux (90 LMH) in order to form various cake layers (Figure 4b), while the ratio of non-fluidization time to fluidization time was fixed at the same value (i.e., 1:3). Compared to the TMP level during GAC fluidization at 5 min off/15 min on, the TMP levels during GAC fluidization at 3 min off/9 min on and 1 min off/3 min on were much lower. For a longer non-fluidization period, the formed cake layers tended to be much thicker and denser, hence the shear force provided by the fluidized GAC particles could not overcome the binding force between foulant layers. As a result, part of the fouling layers could not be removed by the fluidized GAC particles for the longest non-fluidization period tested (i.e., 5 min off/15 min on).

3.4. Effect of fluidized GAC on hollow fibre membrane integrity

In GAC fluidization-membrane filtration processes, GAC particles perform as scouring agents to remove cake layers formed on the membrane [18]. Inevitably, the direct interactions of GAC with the membrane cause damage the membrane surface, especially during the early stage of filtration whereby cake layers are lacking. In a recent study, Meier explained the four phenomena involved in mechanical effects of PAC particles on nanofiltration membrane processes by evaluating the development of flux (i.e., permeability) and rejection (MgSO_4 solution) with time [32]. Namely, (1) particles induced increases of permeate flux and rejection because of particles moving in the boundary layer to create the secondary flows, (2) particles caused an increase of permeate flux with a decrease of rejection due to the damaged membrane functional layer, (3) particles resulted in decreases of permeate flux and rejection, since the particles tend to form the porous cake layers and hinder the back transport of solute to the bulk flow, and (4) particles led to a decrease of permeate flux and an increase of rejection because the particles perform as “secondary membrane” above the membrane [32]. In this study, we compared the clean water permeability and sodium alginate rejection rate of the hollow fibre membranes in the absence and presence of GAC fluidization to illustrate whether fluidized GAC particles influence membrane integrity. The size distribution of sodium alginate solution (100 mg/L) can be found in the supplementary data (Figure S2).

Considering the effect of upflow velocity on membrane integrity, the clean water permeability and sodium alginate rejection of the hollow fibre membrane at the same upflow velocity and operation time in the absence of GAC fluidization was tested as control experiments. Figure 5 shows that the clean water permeability increase rate and sodium alginate rejection in the absence and presence of GAC scouring was statistically similar

respectively (p -value=0.4 and 0.95, respectively, in a T-test). This reveals that the fluidized GAC particles had no significant influence on membrane integrity.

The membrane surface morphology was further observed by SEM and AFM. The SEM images (Figures 6a and b) show that, after GAC abrasion, the number of open pores is relatively less. This may be attributed to the fact that GAC tended to release fine carbon particles during fluidization. Such released fine carbon particles may perform as potential foulant deposits on the membrane surfaces, hence blocking and narrowing membrane pores. Membrane roughness properties were examined by analyzing AFM images (Figures 6c and d), which show insignificant change of membrane roughness (p -value=0.89 in a T-test), thereby re-affirming the lack of membrane damage by the GAC particles.

In addition, FT-IR spectroscopy was performed to analyse the main chemical groups of the membrane functional layer in the absence and presence of GAC abrasion (Figure 7a). In the literature, the major peaks at the wavenumbers of 764 and 796/839 cm^{-1} were used to characterise PVDF skeletal bending and CH_2 groups, respectively, on the membrane surface [33]. In this study, the functional peaks identified by FT-IR are shown in Figure 7a. Compared to the control membrane (upflow only), the change in peak intensity was negligible after GAC abrasion, thus further affirming that the GAC particles do not compromise the membrane integrity.

The pore size of the control membrane (upflow only) mainly ranges from 0.075 μm to 0.085 μm (Figure 7b). After GAC abrasion, a slight leftward shift of the membrane pore size distribution was observed, the finding of which corresponds well to the SEM images and further proves that the finer carbon particles released during fluidization tended to block some pores in the membrane.

4. Conclusions

The fluidized GAC particles significantly reduced cake layer fouling in a combined GAC fluidization-hollow fibre membrane filtration process, but could not mitigate irreversible fouling. Such cake fouling reduction was related not only with GAC size and packing amounts, importantly, with the ratio of hollow fibre spacing to fluidized particle size. Further comparison of GAC particle size and packing amounts were performed based on the energy consumption. It was found that the greater-sized GAC particles with more packing amounts most benefited to fouling control. However, the increased capital cost of GAC particles need to be considered. Compared to continuous filtration in the presence of GAC fluidization, the intermittent filtration could not further improve membrane fouling reduction. During the filtration idle period, inefficient interaction of fluidized GAC particles with membrane surface was proposed due to lack of permeate driving force. Intermittent fluidization was proposed as an approach to reduce energy consumption. Whether the formed cake layers could be efficiently removed by GAC particles was majorly determined by the cake layer nature. Such observations emphasize that both the choice of suitable GAC particles and the optimization of filtration modes are important to effectively control membrane fouling in a combined GAC fluidization-hollow fibre membrane filtration process.

Although GAC scouring performs well to remove cake layers, almost no GAC-induced membrane integrity loss was noticed during the initial filtration period (i.e., the direct interaction between GAC particles with clean membrane surface). However, inevitably, the fine carbon particles could be released from GAC. This phenomenon could be more obvious at pilot-plant or full-plant due to much higher upflow velocity is required. Whether these fine carbon particles benefit to or harm to membrane performance needs to pay more attention.

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Graphical abstract

Highlights

- > Larger-sized GAC benefited for fouling control than smaller-sized GAC
- > Increasing GAC packing amounts facilitated fouling mitigation
- > A ratio of hollow fibre spacing to fluidized particle size of 3-5 is beneficial for fouling control
- > Intermittent fluidization facilitated better membrane performance per energy consumption
- > The GAC scouring on membrane integrity was negligible

FIGURE 1. A schematic diagram of GAC fluidization-filtration setup (a) and details of filtration cell (b).

FIGURE 2. Effect of hollow fibre spacing and GAC size on cake layer resistances in the absence and presence of fluidized GAC particles (v represents the liquid upflow velocity).

FIGURE 3. Effect of intermittent filtration on membrane fouling rate in the presence of fluidized GAC particles ($n > 3$) (a) and a diagram illustrating the force towards the GAC particles in the presence and absence of permeate filtration.

FIGURE 4. Effect of intermittent fluidization on membrane fouling tendency in the presence of fluidized GAC particles ($n=2$): (a) different off/on ratio with fixed non-fluidization period; (b) different fluidization period with fixed off/on ratio.

FIGURE 5. Comparison of membrane permeability and sodium alginate rejection rate in the absence and presence of fluidized GAC particles (n=6).

FIGURE 6. SEM and AFM images of membrane surfaces (n=4). (a) and (c) upflow only; (b) and (d) GAC fluidization.

FIGURE 7. FTIR analysis of membrane surface and membrane pore size distribution (n=2).

Table 1. The calculated number of GAC particles between two hollow fibres

Size Range of GAC particles	Spacing = 0 mm	Spacing = 2 mm	Spacing = 5 mm
0.5-1.0 mm	0	2-4	5-10
1.0-1.4 mm	0	1-2	3-5
1.4-2.0 mm	0	1	2-3

TABLE 2. Effect of GAC size on the averaged cake layer fouling reduction ratio.

Hollow fibre space (mm)	GAC size (mm)		
	0.5-1.0	1.0-1.4	1.4-2.0
0	0.36	0.41	0.40
2	0.31	0.35	0.70
5	0.26	0.53	0.73

TABLE 3. Choice of GAC size on a basis of similar pump energy consumption¹

Upflow velocity (m/s)	0.021			0.031		
GAC size (mm)	0.5-1.0	1.0-1.4	1.4-2.0	0.5-1.0	1.0-1.4	1.4-2.0
GAC mass (g)	6	7.5	NA ²	3	6	7.5
Initial packing ratio (%)³	39±3	57±5		20±1	45±4	53
System head (m)⁴	0.160	0.164		0.154	0.160	0.164
Cake layer resistance ($\times 10^{12} \text{m}^{-1}$)	2.25±0.50	0.49±0.06	NA ²	2.91±1.58	0.50±0.13	0.27±0.01

¹ All experiments were performed at a hollow fibre spacing of 5 mm and the GAC particles were fluidized to 90% of the filtration channel height.

² The upflow velocity of 0.021 m/s is less than the minimum fluidization velocity of GAC particles with a size range of 1.4-2.0.

³ Initial packing ratio (%) was calculated by dividing the GAC packing height to the filtration channel height.

⁴ GAC density is approximately $2 \times 10^3 \text{ kg/m}^3$.