



Hybrid PAC-submerged membrane system for trace organics removal II: System simulation and application study

Yue Jia^a, Rong Wang^{a,b,*}, Anthony G. Fane^a

^a School of Civil and Environmental Engineering, Nanyang Technological University, Singapore 639798, Singapore

^b Institute of Environmental Science & Engineering, Nanyang Technological University Innovation Center (NTU), Block 2, Unit 237, 18 Nanyang Drive, Singapore 637723, Singapore

ARTICLE INFO

Article history:

Received 20 May 2008

Received in revised form

19 September 2008

Accepted 26 September 2008

Keywords:

PAC

Hybrid submerged membrane system

System simulation

Trace organics removal

Batch and continuous PAC dosing

ABSTRACT

The hybrid powdered activated carbon (PAC)-submerged microfiltration hollow fiber membrane system with air bubbling has been simulated at two operation strategies of batch and continuous PAC dosing for trace organics removal from water. The mathematical models were developed based on corresponding solute mass balance equations and the homogeneous surface diffusion model (HSDM), where the two kinetic parameters D_s and k_f were obtained in Part I of this study. After verification with experiments using atrazine as the model trace organic compound, the developed models were used to predict the product water quality at various operating conditions. It was found that at the batch PAC dosing mode, the trace organic removal can be improved by increasing the bubbling rate or increasing the operation flux. While at the continuous PAC dosing mode, the target compound removal is independent on the bubbling rate, which suggested the possibility of reducing energy consumption by inducing a low bubbling rate. Besides, lower operation flux shows more benefit because of the longer hydraulic retention time. The simulation can provide a better understanding of the system and assist in evaluating various operation strategies properly.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Powdered activated carbon-microfiltration (PAC-MF) system, which combines PAC adsorption with low-pressure driven membrane technique, has shown great potential to achieve dissolved organics removal from contaminated natural water. Basically, the small molecular species that are not usually rejected by the MF membrane alone are adsorbed onto the PAC particles in the hybrid system. This pretreatment converts dissolved organic matter to a particulate phase that can be easily rejected by the membranes. The MF process then separates fine PAC particles, with adsorbed small molecules in the pores, from the treated water. This hybrid system can offset the disadvantage of the large equipment size and space requirement when PAC adsorption is applied in a traditional way, as membranes provide more efficient separation of PAC from treated water than sedimentation or other traditional filtration processes. Moreover, the adsorption pretreatment ensures

high pollutant removal while the low pressure MF process requires relatively low energy [1,2].

Depending on the placement of the membrane module, two configurations of the PAC-MF system can be categorized, i.e. external loop and submerged membrane tank. In the former, the membrane module is arranged in series to the adsorption reactor and operated in cross-flow mode; while in the latter, the membrane module is placed directly in the adsorption tank. Over the past 20 years, experimental and mathematical studies of the external loop PAC-membrane process have been carried out. Modeling the mixing tank and the recycle loop portion of the PAC/UF process as a steady state continuous stirred tank reactor (CSTR) for the removal of TOC [1,3] and trace organics [4] was successful, and the modeling results were verified by both large and small scale pilot plant operations. A series of mathematical models were developed by Campos et al. [5,6] to evaluate different process designs of continuous-flow PAC-membrane reactors which were operated without carbon wastage between backwash events. The organics removal efficiency was studied by modeling various membrane reactor configurations with either a CSTR or a plug flow reactor (PFR) in combination. In these simulations, the liquid film resistance was neglected and the process was assumed to be controlled by surface diffusion only. Matsui et al. [7,8] modeled trace synthetic organic chemical (SOC) removal and found that a pulse PAC addition at the beginning of

* Corresponding author at: School of Civil and Environmental Engineering, Nanyang Technological University, Singapore 639798. Tel.: +65 6790 5327; fax: +65 6791 0676.

E-mail addresses: YJia@pmail.ntu.edu.sg (Y. Jia), rwang@ntu.edu.sg (R. Wang), agfane@ntu.edu.sg (A.G. Fane).

Nomenclature

B_i	Biot number based on surface diffusion
C	liquid phase adsorbate concentration in bulk solution at any time (ML^{-3})
C_c	carbon mass per unit volume of the treated water (ML^{-3})
C_s	liquid phase adsorbate concentration at solid–liquid interface (ML^{-3})
C_0	initial liquid phase adsorbate concentration (ML^{-3})
C^*	non-dimensional liquid phase adsorbate concentration in bulk solution at any time
d_p	adsorbent particle diameter (L)
D_s	surface diffusion coefficient ($L^2 T^{-1}$)
k_f	liquid film mass transfer coefficient (LT^{-1})
p	the number of Δt contained by t
q_{avg}	average adsorbed phase adsorbate concentration (MM^{-1})
$q_{avg,(t-\beta)}$	average adsorbed phase adsorbate concentration on the particles that entered the reactor at time β (MM^{-1})
$q_{avg,(t-\beta)}^*$	non-dimensional average adsorbed phase adsorbate concentration on the particles that entered the reactor at time β^*
$q(r,t)$	adsorbed adsorbate concentration (MM^{-1})
$q^*(R,T)$	non-dimensional adsorbed adsorbate concentration
q_s	adsorbed phase adsorbate concentration at solid–liquid interface (MM^{-1})
q_0	initial adsorbed phase adsorbate concentration (MM^{-1})
Q	liquid flow rate ($L^3 T^{-1}$)
Q_b	air bubbling rate in the batch kinetic test ($L^3_{(air)} T^{-1} L^{-3}_{(liquid)}$)
r	radial coordinate (L)
R	non-dimensional radial coordinate
t	time (T)
Δt	the time step (empirically specified) (T)
T	non-dimensional time base on surface diffusion
V	liquid volume (L^3)
Greek Letters	
β	the time at which the carbon particles are added into the reactor (T)
β^*	non-dimensional time at which the carbon particles are added into the reactor
ρ_p	apparent particle density (ML^{-3})

a filtration cycle resulted in better SOC removal than the continuous addition mode, and that the internal mass transfer was the rate-determining step. All these mathematical models can be used to facilitate the design of PAC-membrane external loop systems in which the membrane filtration rig is installed separately from the adsorption reactor, and to help determine the optimal operating strategies for the proposed organic pollutants treatment from water.

With the development of the membrane filtration technique, the submerged membrane system has attracted worldwide interest. Since the first application in the membrane bioreactor in the late 1980s [9], submerged membrane systems have shown advantages in reducing energy consumption and cost, improving product quality and reducing land requirement. Applying submerged membrane

systems in water treatment for removal of natural organic matter (NOM) and synthetic organic chemicals (SOCs) is a relatively new and promising process. In the hybrid PAC-submerged membrane system, the membrane module is immersed into an adsorption tank which contains suspended PAC particles [10]. Guo et al. [11] recently developed a mathematical model to simulate the total organic carbon (TOC) removal from synthetic wastewater in a submerged membrane-adsorption system. In their simulation, the Talu adsorption equilibrium was used to quantify the adsorption capacity. The author incorporated the TOC adsorptions onto the membrane surface in their modeling and the total amount of PAC was added into the submerged membrane reactor in the batch mode. The effects of a series of operating parameters were evaluated including the pre-adsorption duration, aeration rate, backwash frequency, PAC dose and filtration flux.

In the submerged membrane-adsorption system, air bubbling is applied to the tank to provide mixing and introduce shear at the membrane surface in order to enhance separation efficiency. However, most studies of the PAC-MF hybrid submerged membrane system have mainly focused on the evaluation of the overall contaminant removal efficiency. In fact, the mixing brought about by air bubbling is different from that of conventional mechanical stirring by generating vertical movement of the PAC particles in the solution. Thus, the kinetic parameters of PAC adsorption would be influenced by the manner of air bubble-induced mixing. The objective of this part is to develop mathematical models to describe trace organics removal via adsorption by suspended PAC in a continuous-flow submerged membrane reactor with continuous air bubbling. Atrazine, one of the most widely used herbicides in the world, was chosen as the targeted compound to represent trace organics normally existed in natural water. Operations with batch and continuous PAC dosing modes will be simulated based on corresponding mass balance equations and the single solute homogeneous surface diffusion model (HSDM), where the adsorption kinetic parameters were obtained in Part I of this study [12]. After verification with experiments using atrazine as the model trace organic compound, the developed models will be used to predict the product water quality at various operating conditions. It is expected that the simulation can provide a better understanding of the system and assist in evaluating various operation strategies properly.

2. Mathematical modeling of the hybrid PAC-submerged membrane system

2.1. Formulation of adsorption

The adsorption kinetics was described by the homogeneous surface diffusion model, which has been presented in Part I of this study in details. In summary, the key equations include the following:

$$\frac{\partial q(r,t)}{\partial t} = D_s \left[\frac{\partial^2 q(r,t)}{\partial r^2} + \frac{2\partial q(r,t)}{r\partial r} \right] \quad (1)$$

The initial and boundary conditions are:

$$q(r,0) = 0, \quad t = 0, \quad 0 \leq r \leq \frac{d_p}{2} \quad (2)$$

$$\frac{\partial q(0,t)}{\partial r} = 0, \quad t \geq 0, \quad r = 0 \quad (3)$$

$$\rho_p D_s \frac{\partial q(r,t)}{\partial r} = k_f (C - C_s), \quad t \geq 0, \quad r = \frac{d_p}{2} \quad (4)$$

where,

$$D_s = 1.14 \times 10^{-16} \text{ m}^2/\text{s}, \quad k_f = 1.30 \times 10^{-4} \cdot C_c^{0.06} Q_b^{1.29} \quad (5)$$

q_s and C_s are related by the Freundlich adsorption isotherm,

$$q_s = 70.06 C_s^{0.151} \quad (6)$$

2.2. Formulation of the hybrid PAC-submerged membrane system (HPSMS)

Fig. 1 shows the schematic diagram of a hybrid PAC-submerged membrane system where two PAC dosing strategies were adopted. One is where the total amount of PAC was dosed at the very beginning of each operation, i.e. batch dosing, while the other is where the PAC was dosed into the membrane reactor continuously during the whole process, i.e. continuous dosing. The suspensions are assumed to be fully mixed by the air bubbling and the reactor works as a CSTR. For each dosing strategy, the adsorbate concentration in the influent was kept unchanged during the whole operation. The liquid flow rate was maintained the same from the inlet to the outlet and no PAC was wasted during each operation until backwash of the membrane and the whole system.

2.2.1. Batch dosing of PAC

In this mode of operation, the membrane reactor was assumed to be fully mixed by air bubbling once the total mass of PAC was added into the reactor. The solute mass balance in the reactor can be written as:

$$Q(C_0 - C) = \frac{d(VC + M_c q_{\text{avg}})}{dt} \quad (7)$$

$$q_{\text{avg}} = \frac{3}{(d_p/2)^3} \int_0^{d_p/2} q(r, t) r^2 dr \quad (8)$$

The right hand side of Eq. (7) represents the sum of mass change of the adsorbate that remains in the reactor in the liquid phase and that adsorbed onto the solid phase over time.

By combing Eq. (7) with Eq. (8), the following equation can be obtained:

$$\frac{dC}{dt} = \frac{Q}{V} \left(C_0 - C - \frac{24M_c}{Q \cdot d_p^3} \int_0^{d_p/2} \frac{dq(r, t)}{dt} r^2 dr \right) \quad (9)$$

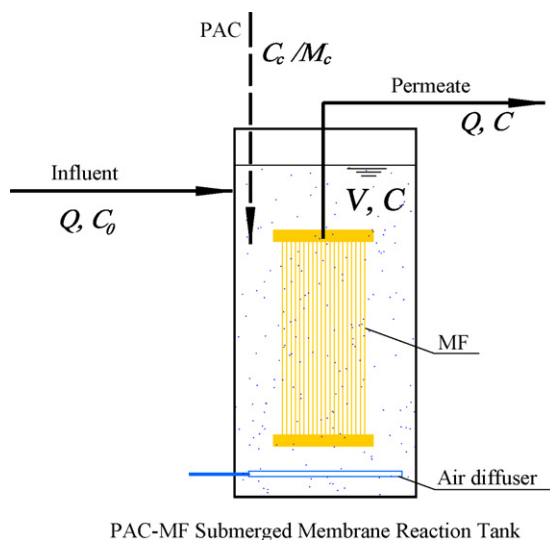


Fig. 1. Schematic diagram of a hybrid PAC adsorption-submerged membrane system.

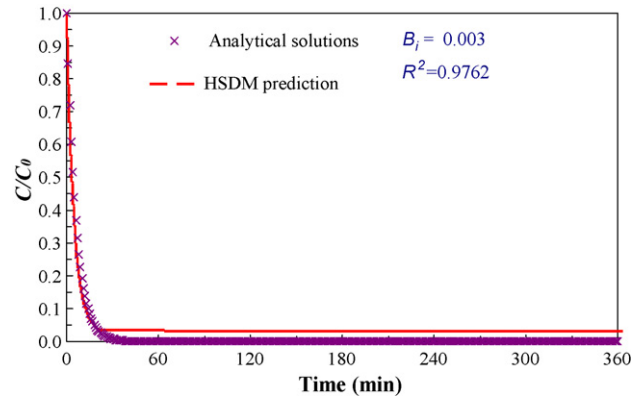


Fig. 2. Check on the accuracy of the numerical solution, continuous flow, batch dosing of PAC; $C_0 = 200 \mu\text{g/L}$, $M_c = 1000 \text{ mg}$, $V = 50 \text{ L}$, $K = 70.06 (\text{L/mg})(\text{L}/\mu\text{g})^{1/n}$, $1/n = 1.0$, $k_f = 1.37 \times 10^{-4} \text{ m/s}$.

Eq. (9), coupled with the HSDM set of Eqs. (1–6), describes the adsorbate concentration profile within the adsorbent particle (q) and the corresponding adsorbate concentration in the bulk solution (C) under the mode of batch dosing of PAC.

It is convenient to convert all the equations into dimensionless forms by using the following defined dimensionless parameters:

$$C^* = \frac{C}{C_0}, \quad q^* = \frac{q}{q_0}, \quad T = \frac{4D_s}{d_p^2} t, \quad R = \frac{2r}{d_p} \quad (10)$$

The details of conversion can be found elsewhere [12]. The numerical scheme included reducing the partial differential equation (Eq. (1)) to a set of ordinary differential equations by applying the orthogonal collocation method with 12 collocation points. Therefore, there were in total 13 ordinary differential equations (ODEs) which contain 13 variables of q_i^* ($i = 1, \dots, 12$) and C^* . The resulting ODEs were then integrated in the time domain using the Gear's method. Thus, the concentration profile of q_i^* and C^* at any time were obtained.

Since when the liquid flow Q approaches zero, the situation is similar to a batch test, the correctness of the developed numerical solutions of this process was also checked carefully by comparing it to the simple analytical solution [12]. Thus, for the model, a very low Biot number ($B_i = k_f d_p C_0 / 2D_s \rho_p q_0 = 0.003$) and liquid flow rate Q ($1.0 \times 10^{-8} \text{ L/min}$) were applied to the FORTRAN program to obtain a numerical solution. The good agreement ($R^2 = 0.9762$) between the numerical solution and the analytical solution confirms that the numerical solution is correct (Fig. 2).

2.2.2. Continuous dosing of PAC

In the mode of continuous dosing of PAC, the PAC was dosed into the submerged membrane reactor throughout the whole operating duration at a constant carbon concentration of C_c . The submerged membrane reactor was assumed to be fully mixed at any time and the solute mass balance in this case can be expressed as:

$$Q(C_0 - C) = V \frac{dC}{dt} + \frac{d}{dt} \left[\int_0^t q_{\text{avg},(t-\beta)} C_c Q d\beta \right] \quad (11)$$

where β is the time at which the particles enter the reactor. As shown in the diagram of Fig. 3, the small batch of PAC particles entering the reactor at time β have a corresponding adsorption time of $t - \beta$, and an average adsorbate concentration of $q_{\text{avg},(t-\beta)}$ in PAC. $q_{\text{avg},(t-\beta)} C_c Q d\beta$ represents the adsorbed organics mass when the adsorbent with a mass of $C_c Q d\beta$ entered the reactor during the time interval of $d\beta$. The integration of $q_{\text{avg},(t-\beta)} C_c Q d\beta$ from 0 to time t gives the total adsorbed mass onto the carbon particles at a

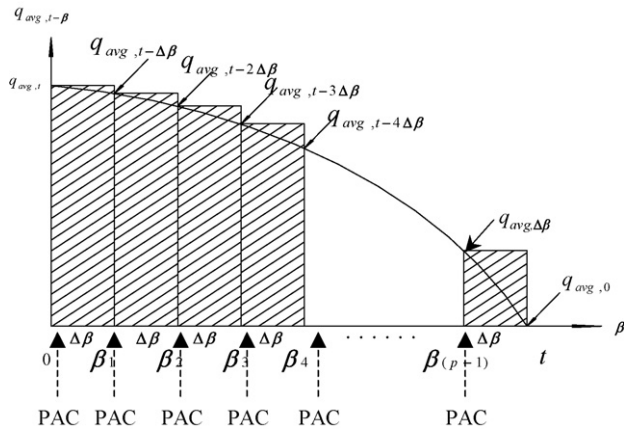


Fig. 3. Schematic diagram of dosing PAC at tiny time intervals (for continuous PAC dosing mode).

given time of t . Thus, the right hand side of Eq. (11) gives the sum of mass change of the adsorbate that remains in the reactor in the liquid phase and that adsorbed onto the solid phase over time.

The item of $\int_0^t ((dq_{avg,(t-\beta)})/dt) d\beta$ on the above equation can be developed as follows:

$$\int_0^t \frac{dq_{avg,(t-\beta)}}{dt} d\beta = \sum_{i=1}^p \left(\frac{dq_{avg}}{dt} \right)_i (\Delta t) \quad (12)$$

where Δt is a time interval when the adsorption time of t is divided evenly into p parts.

Combining Eq. (8) with Eqs. (11) and (12) yields:

$$\frac{dC}{dt} = \frac{Q}{V} \left\{ C_0 - C - \frac{24C_c}{d_p^3} \sum_{i=1}^p \left(\int_0^{d_p/2} \frac{dq(r,t)}{dt} r^2 dr \right)_i (\Delta t) \right\} \quad (13)$$

Eq. (13), coupled with the HSDM set of Eqs. (1–6), describes the adsorbate concentration profile within the adsorbent particle (q) and corresponding adsorbate concentration in the bulk solution (C) under the operation mode of continuous dosing of PAC.

Another two dimensionless parameters were defined as

$$q_{avg,(T-\beta^*)}^* = \frac{q_{avg,(t-\beta)}}{q_0}, \quad \beta^* = \frac{4D_s}{d_p^2} \beta \quad (14)$$

which were used together with the dimensionless parameters given in Eq. (10) to convert the above equations into dimensionless ones. The details of conversion can also be found elsewhere [12]. The numerical scheme to obtain the solution is similar to that used in the batch dosing strategy and the correctness of the developed numerical solutions for this case can be checked similarly as the procedure for batch dosing strategy.

3. Materials and methods

The materials used and the concentration analysis method have been introduced in Part I of this study. The PAC-submerged membrane reactor was set up as shown in Fig. 4. It consisted of a 50 L (effective volume) transparent reaction tank with 5 rows of air diffusing pipes (diffuser #1) located at the bottom. 40 diffusing holes of 0.6 mm diameter were arranged in 5 mm intervals along each pipe. Two other air pipes (diffuser #2) with 40 holes of the same size, were fixed at the bottom of two transparent baffles, and placed in front of each side of a MF hollow fiber module to provide bubbles around 3.5 mm (measured by photography) in diameter for membrane fouling control. The membrane module (Blue star, China) was installed at middle of the tank and the characteristics of the fibers are shown in Table 1.

A dual channel pump head was mounted on a feed/suction peristaltic pump (Masterflux, C/L, Cole-Parmer) so that the feed solution was pumped into the reactor at the same flowrate as the permeate. The permeate was drawn out from the upper of the module

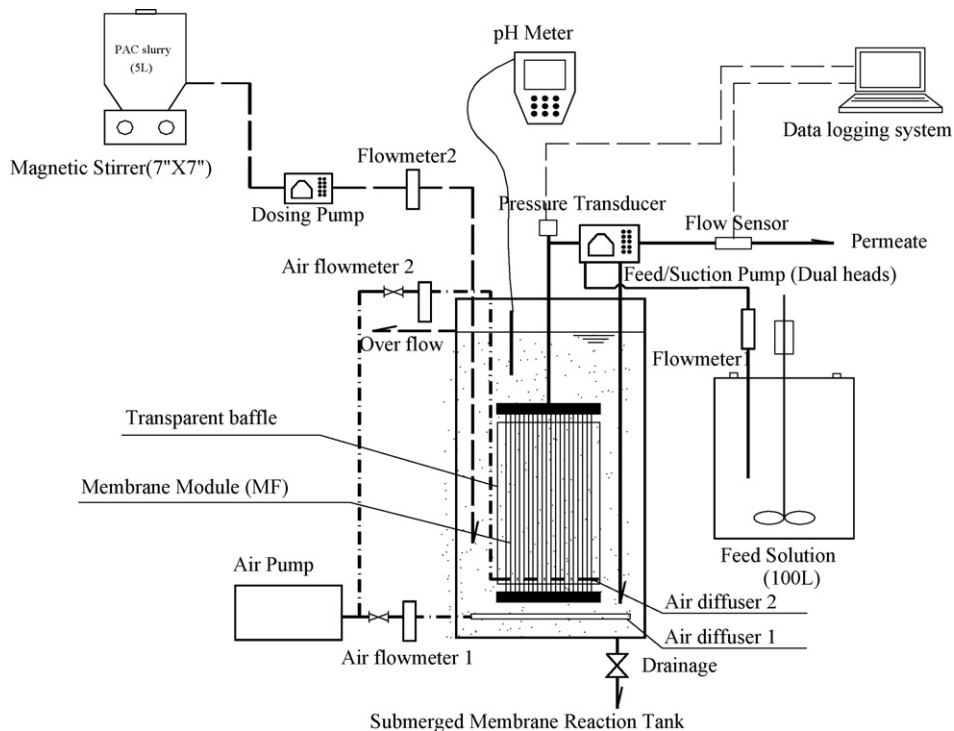


Fig. 4. Experiment set-up of PAC-submerged hollow fiber membrane reactor.

Table 1
Characteristics of the MF hollow fiber membrane module.

Parameter	Value
Material	Poly vinylidene fluoride (PVDF)
Membrane pore size (μm)	0.2
Fiber outer diameter (mm)	1.00
Fiber inner diameter (mm)	0.65
Surface area (m^2)	0.4
Fiber length (m)	0.5
Hydrophilicity	Partially hydrophilic

Table 2
 k_f at different bubbling rates and carbon dosages ($d_p = 6.3 \mu\text{m}$, $C_0 = 200 \mu\text{g/L}$).

Carbon dosage C_c (mg/L)	Air bubbling rate Q_b (L/minL)	Liquid film mass transfer coefficient k_f ($\times 10^{-4}$ m/s)
3	0.4	0.43
4	0.4	0.44
5	0.4	0.44
5	0.8	1.08
5	1.2	1.82
5	1.6	2.63
5	2.0	3.51
5	3.0	5.92
8	0.4	0.46
10	0.4	0.46
10	0.8	1.13
10	1.2	1.90
10	1.6	2.76
10	2.0	3.67
10	3.0	6.19
12	0.4	0.47

at constant flux (60 and $100 \text{ L/m}^2\text{h}$). A similar type of peristaltic pump was used to dose PAC into the reactor. The flowrates of the feed solution and PAC slurry were monitored by two flowmeters (Cole-Parmer). The concentrated PAC slurry was stirred with a magnetic stirrer (Vision Scientific Co., LTD.) to maintain an even PAC concentration during dosing. The flowrates of influent and effluent of the reactor were monitored to minimize the water level change in the reactor during the filtration experiments. The permeate flux was measured by a flow sensor (Cole-Parmer) and the transmembrane pressure was measured by a pressure transducer (Cole-Parmer). The data were collected automatically by a data logging system. All the connectors and pipes used in the system are stainless steel to prevent pipe-leaked contaminants. The solute adsorbed by the membrane was checked by operating the system at a fixed flux of $100 \text{ L/m}^2\text{h}$ for 12 h without PAC addition. The raw water was sucked out through the membrane and then recy-

clered to the reactor. The final atrazine concentration difference was within 3% so that the membrane adsorption can be neglected in this case.

In the continuous-flow tests with batch PAC dosing, the total amount of PAC required in the whole operation cycle was added into the reactor which initially contained $200 \mu\text{g/L}$ atrazine solution and was mixed with air bubbles. Prior to the PAC addition, the feed/suction pump was started for 10 min to precondition the system. The samples were collected from the permeate side at pre-determined time intervals since the addition of PAC.

For the continuous PAC dosing, after the system was preconditioned the PAC was added into the submerged reactor in slurry phase from the concentrated PAC slurry tank (200 mg/L) at a pre-determined constant PAC flow rate. The permeate samples were collected at regular time intervals.

4. Results and discussion

4.1. Model verification

According to Part I of this study, the kinetic coefficient k_f at different bubbling rates and carbon concentration are available by applying the empirical equation (Eq. (5)) and summarized in Table 2.

Fig. 5(A) shows the results of the continuous-flow tests with batch dosing of PAC at 4 and 8 mg/L carbon dosages together with the model simulation. The permeate flux was maintained constant at $60 \text{ L/m}^2\text{h}$ and the bubbling rate per volume of treated water was 0.4 L/min L water for each operation. Excellent agreements between the model predictions and experimental data are observed.

Fig. 5(B) shows the model simulation compared with experimental performance for the continuous dosing of PAC. To check the accuracy of the model simulation at different permeate fluxes which determine the hydraulic residence time (HRT), the tests were conducted at 60 and $100 \text{ L/m}^2\text{h}$ with carbon dosage of 12 and 8 mg/L, respectively. Good agreements were also obtained between theoretical and experimental results. The slight over-prediction in the later part after about 120 min may be attributed to gradual PAC sedimentation in small dead zones such as the corner of the rectangular reactor as well as on some parts of the membrane holder underwater. Therefore, the fully mixed assumption in the model development was not perfectly achieved as the tests continued. Nevertheless, the results shown in these two figures indicate that the models for the two PAC dosing strategies can be used to describe the hybrid PAC-submerged membrane system performance with considerable reliability.

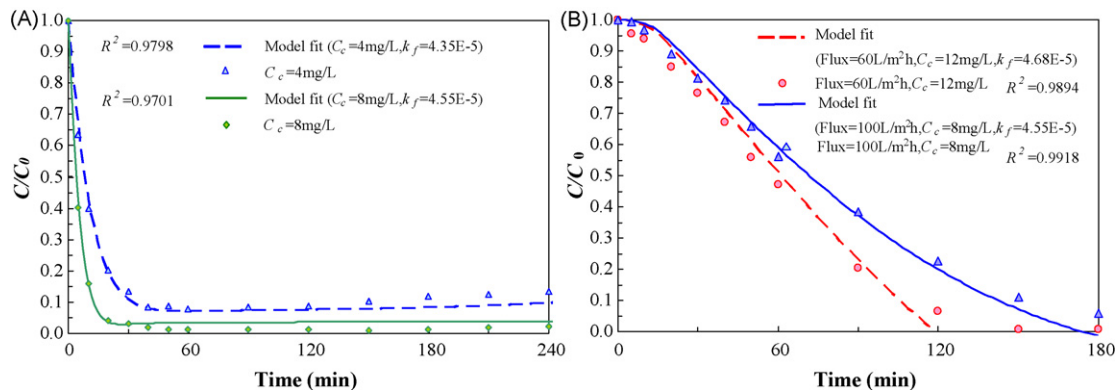


Fig. 5. Model verification for continuous-flow hybrid submerged PAC-MF system ($Q_b = 0.4 \text{ L/min L}$, $C_0 = 200 \mu\text{g/L}$, $D_s = 1.14 \times 10^{-16} \text{ m}^2/\text{s}$); (A) batch PAC dosing, flux = $60 \text{ L/m}^2\text{h}$; (B) continuous PAC dosing.

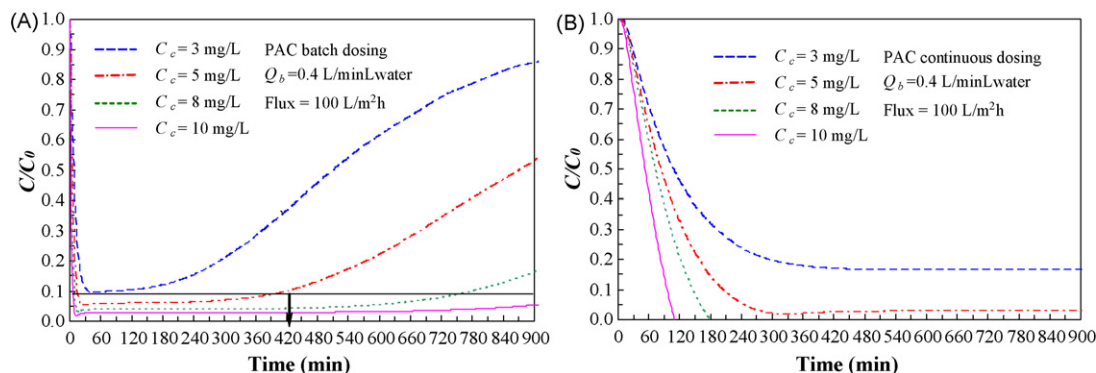


Fig. 6. Model predictions for hybrid submerged PAC-MF at different carbon dosages; (A) batch PAC dosing; (B) continuous PAC dosing.

4.2. Model predictions

The model developed in Section 2 was used to predict the target compound removal by the hybrid PAC-submerged membrane system with changes to three aspects of the operating conditions: different carbon dosages, different air bubbling rates as well as different filtration fluxes for both the batch and continuous PAC dosing methods.

4.2.1. Different carbon dosages

Fig. 6(A) shows the model predictions for the atrazine removal by dosing different amounts of PAC during the batch mode. The contaminated water flowed continuously to the tank which containing a large amount of PAC. The adsorption was fast in the beginning and the atrazine concentration in permeate achieved the lowest value very quickly and then gradually increased with the steady input of more feed water. It can be observed that the time required achieving maximum removal decreased with an increase in the amount of PAC that was dosed. For a better comparison, 90% atrazine removal was assumed to be desired and thus the permeate water quality C/C_0 above 0.1 was considered to be the 'breakthrough'. Obviously, the breakthrough appears later at higher carbon dosages. Comparison between the curves of PAC dosage of 5 and 10 mg/L indicates that doubling the carbon dosage can delay the breakthrough time for more than twice. This implies that for batch PAC dosing operations, adding more PAC at the beginning is beneficial for longer time operations so that the time intervals to supplement fresh PAC can be prolonged.

For the continuous dosing of PAC as shown in Fig. 6(B), the adsorption achieved equilibrium conditions at different times and levels with different dosing rates of small amounts of PAC. Noting that the time required to achieve the maximum removal is dif-

ferent for different carbon dosages, the minimum carbon dosage for achieving a desired target removal can be determined. Under this dosing mode, the atrazine concentration ratio in the permeate decreased gradually from 1.0 at the beginning to a certain level; therefore, the product quality in the beginning of each operation may not meet the requirements so that 'start-up' should involve an initial batch (as in Fig. 6(A)). With the continuous dosing mode it will be necessary to eventually reach a steady state where the PAC inventory in the system is fixed by continuous PAC removal. An approach to this type of modeling is discussed in our later study.

4.2.2. Different air bubbling rates

Fig. 7(A) shows the model predictions of the hybrid PAC-submerged system performance at different air bubbling rates for the batch PAC dosing mode. The target removal is improved by increasing the bubbling rates. As shown in the batch kinetic study (Part I of this study), higher bubbling rates can facilitate the adsorption kinetics, because the air bubbling mixes the suspension and assists the contact of the raw water with the total inventory of PAC particles. The diffusion resistance of the liquid film surrounding the particle surface can be reduced as the film thickness is attenuated by increasing the bubbling rates. Higher bubbling rates provided faster and more uniform mixing which resulted in a better permeate quality, however the effect is relatively marginal unless the bubbling is dropped to 0.4 L/min L water in our system.

In contrast with the batch PAC dosing, operations with continuous PAC dosing shows no sensitivity to increase in the bubbling rates (Fig. 7(B)). There is no obvious difference in the permeate quality profile with different air bubbling rates. This is due to the small amounts of PAC which enter the submerged membrane tank at a constant dosing rate. The beneficial effect of high bubbling rates on the adsorption kinetics acts only on a small increment of PAC

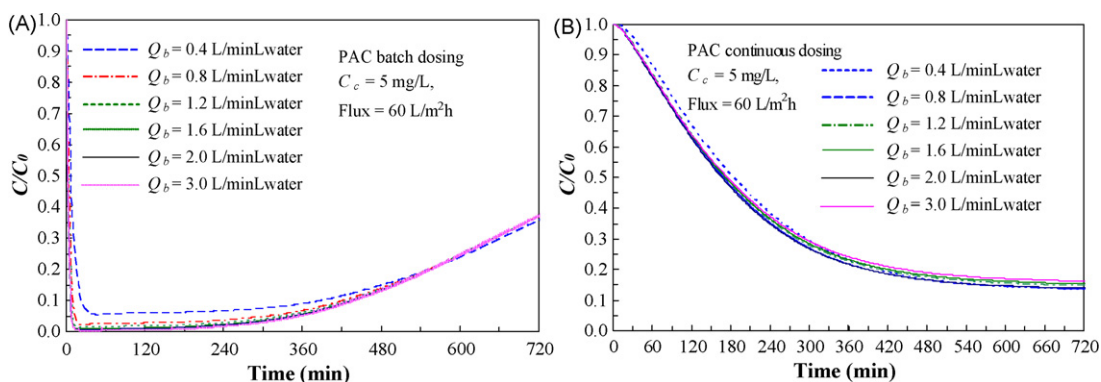


Fig. 7. Model predictions for hybrid submerged PAC-MF at different bubbling rates; (A) batch PAC dosing; (B) continuous PAC dosing.

particles so that there is no a considerable improvement in the overall final permeate quality when a higher bubbling rate is applied. Therefore, from an energy saving point of view, increasing the bubbling rate is not an effective way to enhance the system effluent quality in this case. The bubbling rates for the continuous PAC dosing operation can be decided by aiming to provide proper mixing to keep the PAC in suspension and to maintain sustainable membrane performance. For these purposes, relatively low air bubbling rates or intermittent bubbling (as shown in Part I of this study) can be applied.

4.2.3. Different filtration fluxes

Fig. 8(Ai) and (Aii) shows the change in atrazine concentration in the permeate at batch dosing of PAC (from 40 to 200 L/m²h). Two scenarios are considered:

- (i) fixed PAC amount at different fluxes;
- (ii) different PAC amounts at different fluxes, resulting in constant carbon concentration for different fluxes based on the volume of the treated water.

For scenario (ii), the carbon dosage is based on the volume of the treated water (e.g. carbon concentration is 5 mg/L for each flux in Fig. 8(Aii)), thus a higher filtration flux required more mass of PAC dosed. For instance, operating at a flux of 200 L/m²h actually required around 3.3 times the carbon mass of that used for a flux of 60 L/m²h. It was noticed that after 480 min operation, a higher flux operation resulted in better permeate quality than a lower flux operation although from the lowest tested flux (40 L/m²h) to the highest one (200 L/m²h), the corresponding HRT is decreased from 187.5 to 37.5 min. This is possible because a higher volume of water is treated and the larger amount of PAC dosed can compensate for the time shortage for the adsorption. Therefore, higher flux operation is still reliable in terms of the permeate quality pro-

vided that the supply of PAC is based on the volume of the treated water.

In contrast, for the continuous dose of PAC (Fig. 8(B)), the higher flux operation produced worse permeate quality with time due to the shorter HRT. For a certain carbon dosage, although the total carbon mass for the higher flux operation is also proportionately higher than that for lower flux ones, the carbon is dosed into and accumulates in the reactor steadily with operation time. Therefore, in a small time interval, only a slightly higher carbon mass is added into the higher flux operation than the lower ones. This small amount of carbon cannot compensate for the shortage of retention time. Thus, in Fig. 8(B) it can be observed that at the same carbon dosage based on the treated water volume, the permeate quality at a flux of 40 L/m²h is better than for higher flux operations because its longer HRT ensures more effective contact between the solution and the carbon particles. Obviously, the optimal working conditions for different operating strategies are different.

4.3. Batch and continuous PAC dosing

Although same total amount of carbon is added, the batch and continuous PAC dosing configurations may have different effects on the trace organic concentration in the product water. For the batch PAC dosing mode, the trace organic concentration in the product water reaches the lowest value very soon after the dosing of PAC. While for the continuous dosing mode, the lowest target organic concentration is approached gradually because of the less carbon mass in the beginning of a filtration cycle. Thus, another initial batch dose of PAC is required for a fast removal at the beginning. However, in another aspect, for batch PAC dosing, a 'breakthrough' occurs at a certain time with the proceeding of the operation. A new batch of PAC is required to be added into the system to restore the water treatment capacity of the system. While at continuous PAC dosing mode, no 'breakthrough' happens and once product water quality

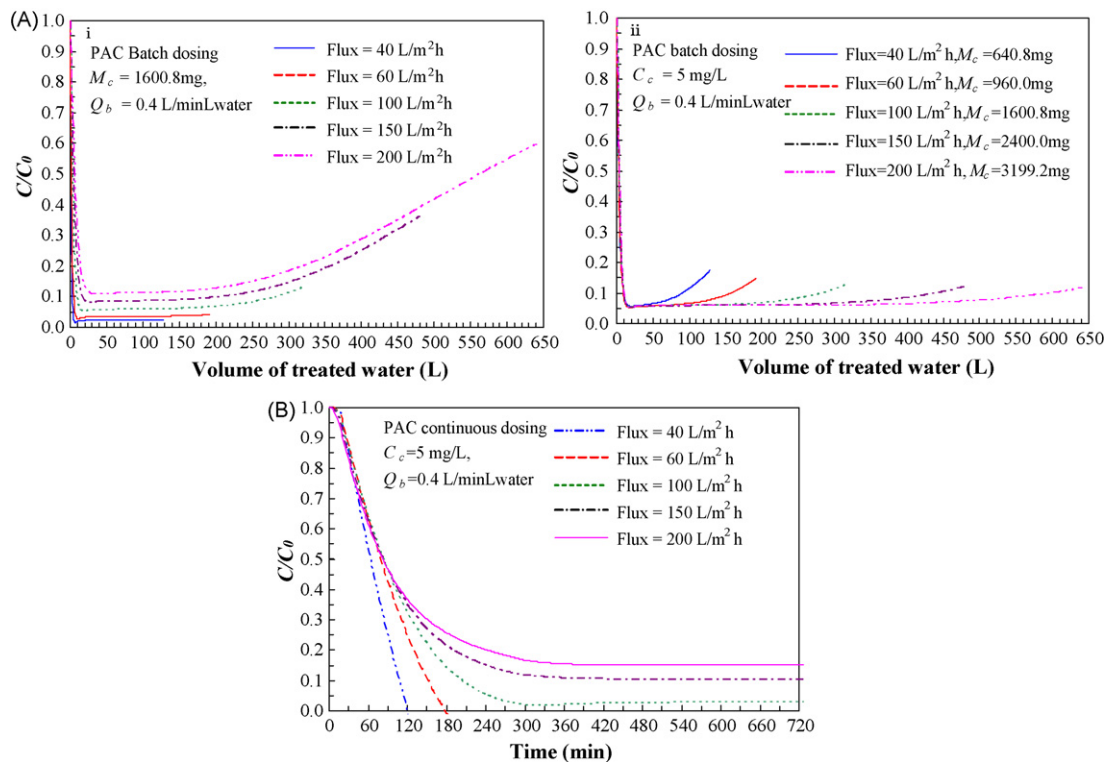


Fig. 8. Model predictions for hybrid submerged PAC-MF at different filtration fluxes; (Ai) batch PAC dosing, fixed PAC amount; (Aii) batch PAC dosing, fixed PAC concentration; (B) continuous PAC dosing.

meets the requirement, the operation can proceed on without changing any system parameter.

Based on the model predictions, the benefit of the batch PAC dosing is the sensitivity of the target organic concentration in the permeate to the different air bubbling rates and fluxes. Higher air bubbling rates and higher fluxes can facilitate the adsorption process and improve the product water quality. In contrast, the target concentration at the continuous PAC dosing operations shows no dependence on the bubbling rates. Therefore, a slight bubbling is sufficient for the mixing in this case and accordingly, reduces the energy consumption. Lower flux is preferable in the continuous PAC dosing operations to take advantage of longer HRT for a sufficient contact of PAC with the pollutants. Whereas for batch PAC dosing at the same carbon dosage (per volume of treated water), higher flux shows benefit.

5. Conclusions

Mathematical models were developed to describe the PAC adsorption-submerged membrane system with air bubbling for trace organics removal from water. The hybrid system performances using two PAC dosing strategies, batch dose and continuous dose, were simulated using the developed model and the results were compared with experimental data with very good agreement.

The model is capable of predicting the trace organics removal by the hybrid PAC-submerged membrane system for different operation strategies. It was found that for the batch PAC dosing mode, the trace organic removal could be improved by increasing the bubbling rate or increasing the operation flux. In contrast, at the continuous PAC dosing mode, the target compound removal was independent of the bubbling rate which suggested the possibility of reducing energy consumption by inducing a low bubbling rate. Lower operation flux showed more benefit to the target compound removal because of the longer hydraulic retention time. Therefore, the model predictions can assist in evaluating the optimal working conditions for real applications in advanced water treatment.

Acknowledgements

The authors gratefully acknowledge the support of the Agency of Science, Technology and Research of Singapore (A*STAR) for funding the Temasek Professor Program in Membrane Technology for Sustainable Water.

References

- [1] S.S. Adham, V.L. Snoeyink, M.M. Clark, J.L. Bersillon, Predicting and verifying organics removal by PAC in an ultrafiltration system, *J. Am. Water Works Assoc.* 83 (12) (1991) 81–91.
- [2] J.M. Laine, D. Vial, M. Pierre, Status after 10 years of operation—overview of UF technology today, *Desalination* 13 (2000) 17–25.
- [3] S.S. Adham, V.L. Snoeyink, M.M. Clark, C. Anselme, Predicting and verifying TOC removal by PAC in pilot-scale UF systems, *J. Am. Water Works Assoc.* 85 (12) (1993) 58–68.
- [4] S. Qi, S.S. Adham, V.L. Snoeyink, B.W. Lykins Jr., Prediction and verification of atrazine adsorption by PAC, *J. Environ. Eng.* 120 (1994) 202–218.
- [5] C. Campos, B.J. Marinas, V.L. Snoeyink, I. Baudin, J.M. Laine, PAC-membrane filtration process. I: model development, *J. Environ. Eng.* 126 (2000) 97–103.
- [6] C. Campos, B.J. Marinas, V.L. Snoeyink, I. Baudin, J.M. Laine, PAC-membrane filtration process. II: model application, *J. Environ. Eng.* 126 (2000) 104–111.
- [7] Y. Matsui, A. Yuasa, K. Ariga, Removal of synthetic organic chemical by PAC-UF systems-II: theory and modeling, *Water Res.* 35 (2) (2001) 455–463.
- [8] Y. Matsui, F. Colas, A. Yuasa, Removal of synthetic organic chemical by PAC-UF systems-II: model application, *Water Res.* 35 (2) (2001) 464–470.
- [9] K. Yamamoto, H. Hiaga, T. Mahmood, T. Matsuo, Direct solid-liquid separation using hollow fiber membrane in an activated sludge aeration tank, *Water Sci. Technol.* 21 (1989) 43–54.
- [10] T. Lebeau, C. Lelievre, H. Buisson, D. Cleret, L.W. Van de Venter, P. Cote, Immersed membrane filtration for the production of drinking water: combination with PAC for NOM and SOCs removal, *Desalination* 117 (1998) 219–231.
- [11] W.S. Guo, W.G. Shim, S. Begneswaran, H.H. Ngo, Effect of operating parameters in a submerged membrane adsorption hybrid system: experiments and mathematical modeling, *J. Membr. Sci.* 247 (2005) 65–74.
- [12] Y. Jia, Hybrid submerged membrane system with sorption media in suspension, PhD thesis, School of Civil and Environmental Engineering, Nanyang Technological University, Singapore, 2007.