Chemical Engineering Journal 155 (2009) 155–160

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Hybrid PAC-submerged membrane system for trace organics removal
I. Adsorption kinetics study of PAC in a bubbled solution

Yue Jia[a], Rong Wang[a,b,*], Anthony G. Fane[a,b]

[a] School of Civil and Environmental Engineering, Nanyang Technological University, Singapore 639798, Singapore
[b] Singapore Membrane Technology Center, Nanyang Technological University, Singapore 639798, Singapore

ARTICLE INFO

Article history:
Received 20 May 2008
Received in revised form 7 July 2009
Accepted 14 July 2009

Keywords:
Powdered activated carbon (PAC)
Adsorption kinetics
Homogeneous surface diffusion model (HSDM)
Air bubbling
Trace organic removal

ABSTRACT

Part I of this study presents a theoretical method combined with experiments to determine the adsorption kinetics of powdered activated carbon (PAC) in the hybrid PAC-submerged membrane (SM) system with air bubbling for trace organics removal. The homogeneous surface diffusion model (HSDM) was applied to describe the kinetics of the adsorbate uptake. The differences between the model solutions and the corresponding experimental results were minimized by means of Levenberg–Marquardt algorithm so that two kinetic parameters D_S and k_f involved in HSDM were obtained simultaneously. The D_S was found to be 1.14×10^{-16} m^2/s and the k_f value was correlated with the bubbling rate (Q_b) and carbon dosage (C_c), which are required in the modeling of the hybrid PAC-SM system presented in Part II of this study. The k_f was enhanced from 1.18×10^{-4} to 4.18×10^{-4} m/s when the bubbling intensity increased in the intermittent bubbling tests, suggesting that from energy consumption point of view, the high intensity intermittent bubbling is more efficient in improving the liquid film mass transfer than continuous bubbling with the same net bubbling rate.

1. Introduction

Powdered activated carbon (PAC) adsorption has been widely applied as a pretreatment method to assist low-pressure driven membrane filtration processes such as microfiltration (MF) to remove dissolved organic solutes from polluted water. The membranes may be located at the external of an adsorption tank or submerged in the tank directly. In the latter, air bubbles are injected to the tank to provide mixing and introduce shear at the membrane surface to prevent particle deposition. Despite different configurations, in the PAC-MF hybrid system, the solute removal is mainly accomplished by carbon adsorption while the function of low-pressure driven membranes is to separate the PAC particles from the treated water. Thus, to evaluate the efficiency of the target solutes removal, the PAC adsorption performance has to be studied carefully.

PAC adsorption can be quantitatively analyzed by a mathematical approach. The adsorption isotherms, such as the Freundlich isotherm, are used to describe the maximal adsorption capacity of a certain mass of adsorbent. The homogeneous surface diffusion model (HSDM) has been extensively used to describe the kinetics of adsorption for organics from the liquid onto the activated carbon [1–10]. The HSDM contains two kinetic coefficients, i.e. the surface diffusion coefficient D_S and the liquid film mass transfer coefficient k_f, which are the crucial parameters to determine the accuracy of the model solutions and need to be known if a prediction of the system performance based on the modeling is required.

For the systems without air bubbling, Hand et al. [11] have shown that the solving procedure of the HSDM can be simplified by eliminating the liquid film mass transfer coefficients k_f. However, certain experimental procedures are required to ensure a better D_S estimation. Traegner and Suidan [12] searched the two kinetic coefficients simultaneously by fitting the HSDM solutions to the experimental data, through a non-linear least squares fit. Roy et al. [13] introduced a simplified solution technique to solve the HSDM by using orthogonal collocation. The coefficients were determined by minimizing the difference between the model calculations and batch test data using the quasi-Newton method. In their study, three collocation points were chosen for simplicity.

For the PAC suspended submerged membrane system, the required operating procedure, which was presented by Hand et al. [11], may not be ensured as the mixing mechanism is different. Therefore it has not yet been confirmed that the simple approach for non-bubbling systems can be applied to adsorption in the bubbled system.

---

* Corresponding author at: School of Civil and Environmental Engineering, Nanyang Technological University, N1-01a-22, 50 Nanyang Avenue, Singapore 639798, Singapore. 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).

1385-8947/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2009.07.032

Nomenclature

A	total carbon surface area (L^2)
B_i	Biot number based on surface diffusion (non-dimensional)
C_0	initial liquid phase adsorbate concentration (M/L^3)
C	liquid phase adsorbate concentration in bulk solution at any time (M/L^3)
C^*	non-dimensional liquid phase adsorbate concentration in bulk solution at any time
C_c	carbon mass per unit volume of the treated water (M/L^3)
C_S	liquid phase adsorbate concentration at solid–liquid interface (M/L^3)
C_S^*	non-dimensional liquid phase adsorbate concentration at solid–liquid interface
D_S	surface diffusion coefficient (L^2/T)
E_{mb}	parameter in the mass balance (dimensionless)
d_p	adsorbent particle diameter (L)
K	Freundlich isotherm capacity constant ($((M/M)(L^3/M)^{1/n})$)
k_f	liquid film mass transfer coefficient (L/T)
M_C	total mass of carbon in the test (M)
m	the number of data point in the non-linear least squares problem
$1/n$	Freundlich isotherm intensity constant (dimensionless)
$q(r, t)$	adsorbed adsorbate concentration (M/M)
$q^*(R, T)$	non-dimensional adsorbed adsorbate concentration
q_0	initial adsorbed phase adsorbate concentration (M/M)
q_s	adsorbed phase adsorbate concentration at solid–liquid interface (M/M)
q_s^*	non-dimensional adsorbed phase adsorbate concentration at solid–liquid interface (M/M)
q_{avg}	average adsorbed phase adsorbate concentration (M/M)
q_{avg}^*	non-dimensional average adsorbed phase adsorbate concentration
Q_b	air bubbling rate in the batch kinetic test ($L^3_{(air)}/TL^3_{(liquid)}$)
r	radial coordinate (L)
R	non-dimensional radial coordinate
S	least square of the differences between the model calculations and batch tests data
t	time (T)
T	non-dimensional time base on surface diffusion
V	liquid volume (L^3)
Greek letters	
ρ_p	apparent particle density (M/L^3)

The objective of Part I of this study is to determine the adsorption kinetic parameters for the carbon adsorption in an air bubbled system for trace organics removal simultaneously. These can be later applied in the modeling of a hybrid submerged membrane system with similar air bubbling operations (Part II of this study). The approach used is to solve the HSDM using the orthogonal collocation method [14] with 12 collocation points coupled with the Levenberg–Marquardt algorithm [12] to minimize the difference between the experimental results and the model solutions. As such, the D_S and k_f can be determined simultaneously. The experimental data used were collected from specifically designed kinetic tests using air bubbles to provide mixing instead of traditional mechanical stirring.

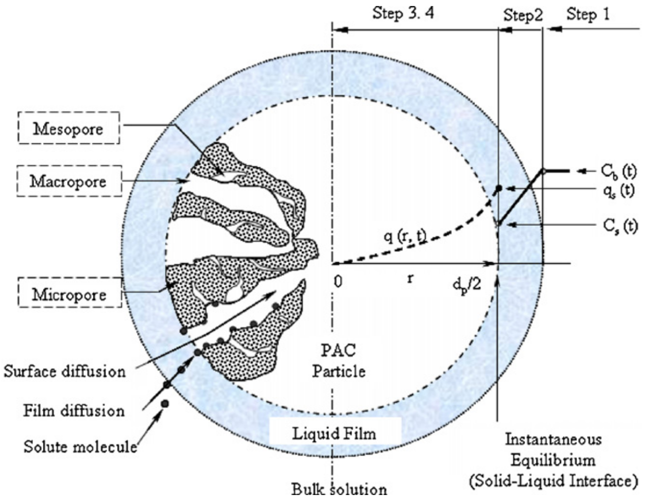

Fig. 1. Schematic diagram of activated carbon particle structure and mechanisms in the HSDM.

2. Theoretical model

2.1. Formulation of adsorption

The adsorption of adsorbates onto activated carbon normally follows four steps (Fig. 1): (1) external diffusion from bulk solution to liquid film, (2) film diffusion through the surface film to particle surface, (3) surface diffusion along the carbon inner surface, (4) adsorption on the active sites in the pores. Since the last step is fairly quick, either the film diffusion or the surface diffusion can be the slowest step, and thus controls the overall rate of carbon adsorption process [15]. The HSDM describes the kinetics of the adsorbate uptake by activated carbon from the liquid solution on the basis of surface diffusion assumption. For adsorption in a closed batch test, the overall mass balance is described as:

$$V\frac{dC}{dt} = -M_c\frac{dq_{avg}}{dt} \tag{1}$$

where C is the adsorbate concentration in the bulk solution, q_{avg} is the average mass of the adsorbate adsorbed within per mass of carbon particles, V is the liquid volume and M_c is the mass of carbon in the test. q_{avg} can be estimated from:

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

where $q(r, t)$ denotes the adsorbate radial concentration within the particle, and d_p is the carbon particle diameter. The mass balance within an activated carbon particle is:

$$\frac{\partial q(r,t)}{\partial t} = D_s\left[\frac{\partial^2 q(r,t)}{\partial r^2} + \frac{2\partial q(r,t)}{r\ \partial r}\right] \tag{3}$$

where D_S represents the surface diffusion (step 3) coefficient within the carbon particles. Eq. (3) describes the changing rate of surface concentration $q(r, t)$ with time t at any distance from the center of the carbon particle r during adsorption. The initial condition for Eq. (3) is:

$$q(r,0) = 0, \qquad t = 0, \qquad r = \frac{d_p}{2} \tag{4}$$

The boundary conditions are:

$$\frac{\partial q(0,t)}{\partial r} = 0, \quad t \geq 0, \ \ r = 0 \tag{5}$$

$$\rho_p D_s \frac{\partial q(r,t)}{\partial r} = k_f(C - C_s), \quad t \geq 0, \ \ r = \frac{d_p}{2} \tag{6}$$

$$q_s = K{C_s}^{1/n}, \quad t \geq 0, \ \ r = \frac{d_p}{2} \tag{7}$$

where k_f denotes the mass transfer coefficient of film diffusion (step 2) and ρ_p represents the apparent particle density. C_s and q_s are the liquid phase and adsorbed phase adsorbate concentrations at the solid–liquid interface, respectively, which are correlated based on the Freundlich isotherm expression of Eq. (7). K and $1/n$ are the Freundlich adsorption constants.

2.2. Dimensionless and parameters determination

It is convenient to convert Eqs. (1)–(7) into a non-dimensional form by substituting the following defined dimensionless parameters for the corresponding ones:

$$C^* = \frac{C}{C_0}, \qquad q^* = \frac{q}{q_0}, \qquad T = \frac{4D_s}{d_p^2}t, \qquad R = \frac{2r}{d_p} \tag{8}$$

where C_0 and q_0 represent the initial liquid and absorbed phase adsorbate concentrations, and q_0 is in equilibrium with C_0. Thus, the integrated form of Eq. (1) at time t with appropriate initial conditions, and Eqs. (2)–(7) can be rewritten non-dimensionally as follows:

$$C^* + E_{mb}q^*_{avg} = 1 \tag{9}$$

with E_{mb} representing the non-dimensional solute distribution parameter:

$$E_{mb} = \frac{M_c q_0}{VC_0} \tag{10}$$

$$q^*_{avg} = 3\int_0^1 q^*(R,T)R^2\,dR \tag{11}$$

$$\frac{\partial q^*(R,T)}{\partial T} = \frac{\partial^2 q^*(R,T)}{\partial R^2} + \frac{2\partial q^*(R,T)}{R\ \partial R} \tag{12}$$

The initial and boundary conditions are:

$$q^*(R,0) = 0, \qquad T = 0, \qquad 0 \leq R \leq 1 \tag{13}$$

$$\frac{\partial q^*(0,T)}{\partial R} = 0, \qquad T \geq 0, \qquad R = 0 \tag{14}$$

$$\frac{\partial q^*(1,T)}{\partial R} = B_i(C^* - C^*_s), \quad T \geq 0, \ \ R = 1 \tag{15}$$

$$q^*_s = C_s^{*1/n} \tag{16}$$

Eq. (15) contains the non-dimensional Biot number defined as:

$$B_i = \frac{k_f d_p C_0}{2D_s \rho_p q_0} \tag{17}$$

The Biot number represents the ratio of the transport rate across the liquid film layer (numerator) to the diffusion rate within the particle (denominator).

The parameters required to solve the equations include geometrical and volumetrical quantities (ρ_p, M_c, V, d_p) which are directly measurable, Freundlich equilibrium adsorption constants (K, $1/n$) which are determined by fitting the isotherm tests' data to the Freundlich isotherm equation [16], and kinetic coefficients (D_S, k_f). Whereas, the kinetic diffusion coefficients cannot be measured directly and a numerical optimization technique is required to search the D_S and k_f. By inputting initial estimates of the parameters, the HSDM is calculated and then compared with corresponding experimental data of closed batch tests. The optimum D_S and k_f are finally identified by minimizing the differences between the model calculations and batch test data. This search procedure is known as a non-linear least squares fit as introduced by Dennis and Schnabel [17] and Traegner and Suidan [12]:

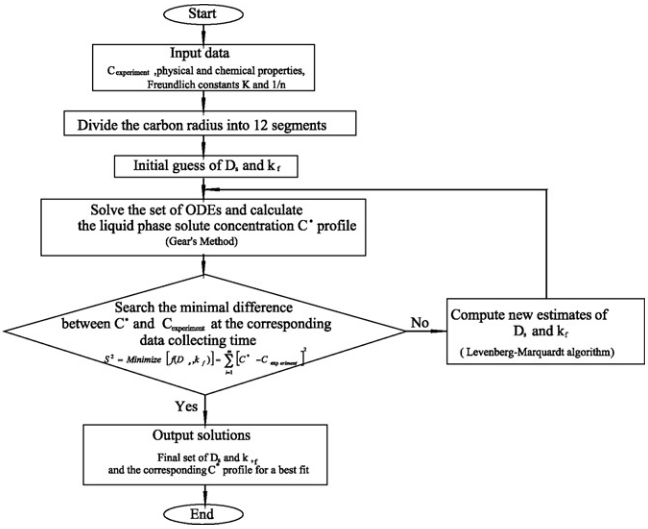

Fig. 2. Flow chart of the adsorption kinetic coefficients searching program.

$$S^2 = Minimize[f(D_s, k_f)] = \sum_{i=1}^{m}[C^* - C_{experiment}]^{2} \tag{18}$$

where m represents the number of data points.

The numerical scheme included converting Eq. (12) into a form suitable for its solution by the orthogonal collocation method (12 collocation points), thus reducing the partial differential equation (PDE) to a set of ordinary different equations (ODEs). The ODEs were integrated in the time domain using the Gear's method [18]. From this scheme, the concentration profile of the adsorbate in the carbon particle q_i^* at any time was obtained, which could lead to the adsorbate concentration in the bulk solution C^* via the mass balance equation. The technique applied to solve the minimization problem (Eq. (18)) is a modified Levenberg–Marquardt algorithm and a finite-difference Jacobian, which was provided by the International Mathematics and Statistical Library [19]. A FORTRAN program was written to couple the HSDM and the Levenberg–Marquardt algorithm to determine the optimum parameters (D_S and k_f). Fig. 2 depicts the calculating procedure of the adsorption kinetics.

3. Materials and methods

3.1. Materials

PAC (Norit SA-2) with median diameter (d_{50}) of 6.3 μm (milled from original PAC) and total surface area (BET) of 1019 m^2/g was used as the adsorbent in this study. Atrazine with initial concentration of 200 μg/L was used as the target compound to represent trace organics normally existed in natural water.

3.2. Adsorption equilibrium tests and bubbling batch kinetic tests

The adsorption equilibrium parameters K and $1/n$ were determined by treating fixed quantities of target solution in nine flasks with a series of increasing amount of carbon and stirred for 48 h at room temperature (25 °C). Samples were then collected from each flask for concentration analysis. In addition, 6-h batch kinetic tests were conducted using air bubbling to provide mixing in a specifically designed apparatus for determination of the kinetic coefficients (D_S, k_f). Air was transported from a cylinder by stainless steel tubing to a ceramic bubble diffuser to generate bubbles (3 mm in median diameter, photographically measured). Sixteen samples were collected at predetermined time intervals in each test. The details of experimental apparatus and sampling method can be found in our previous publications [20,21].

3.3. Concentration analysis

The samples collected from each test were immediately filtered through 45 μm filters (Orange Scientific Pte. Ltd.) to separate PAC from the solution, and then the concentration analysis of each sample was done by a High Performance Liquid Chromatography (WATERS 2695, Separations module, XTerra C_{18} column) with Photodiode Array Detector (WATERS 2996). The mobile phase was acetonitrile (50%) and 10 mM ammonium bicarbonate buffer (50%) at pH 10. The samples were analyzed at a mobile phase flowrate of 1 mL/min at 30 °C and UV absorbance at 223 nm.

4. Results and discussion

The correctness of the developed numerical solution was checked carefully by comparing it to a simple analytical solution (Eq. (19)) which is obtained in the limit of low Biot number (Eq. (17)), assuming that the surface diffusion is fast enough so that only the film diffusion (step 2) controls the adsorption.

$$C = \frac{C_0}{(1+(V/K\cdot M_c))}\left[e^{-((A\cdot k_f/V)+(A\cdot k_f/K\cdot M_c))\cdot t}+\frac{V}{K\cdot M_c}\right] \qquad (19)$$

For the model, a low Biot number (0.004) was applied to the FORTRAN program to obtain a numerical solution. The good agreement ($R^2 = 0.9521$) between the numerical solution and the analytical solution confirms the numerical solution is correct (Fig. 3).

Based on Freundlich isotherm and the adsorption equilibrium test data, the Freundlich constants $K = 70.06 (\text{mg/g})(\text{L/μg})^{1/n}$ and $1/n = 0.151$ were found. Fig. 4 depicts the HSDM fit to the experimental results of the magnetically stirred batch kinetic test with a carbon dosage of 5 mg/L. In this case the optimum kinetic coefficients were determined to be $1.14 \times 10^{-16}\ \text{m}^2/\text{s}$ (D_S) and 5.17×10^{-5} m/s (k_f), respectively. Qi et al. [22] reported that the D_S value was unique for a certain carbon and was not the function of carbon dosage and initial adsorbate concentration over a wide range. Based on this, the determined D_S was used to predict the concentration profile of the residual target compound at different carbon dosages (3 and 8 mg/L) while the k_f was determined for the individual cases (also shown in Fig. 4). The excellent agreement between the modeling results and the experimental data demonstrates that the above introduced method for kinetic parameters searching works well. Therefore, it can be applied to determine the kinetic coefficients of the bubbling mixed adsorption system.

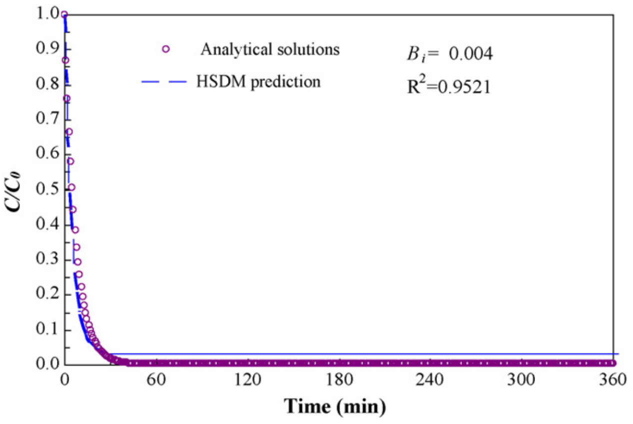

Fig. 3. Check on the accuracy of the numerical solution, batch test, batch dosing of PAC; $C_0 = 200$ μg/L, $M_c = 8$ mg, $V = 50$ L, $K = 70.06 (\text{mg/g})(\text{L/μg})^{1/n}$, $1/n = 1.0$, $k_f = 1.37 \times 10^{-4}$ m/s (magnetic stirred).

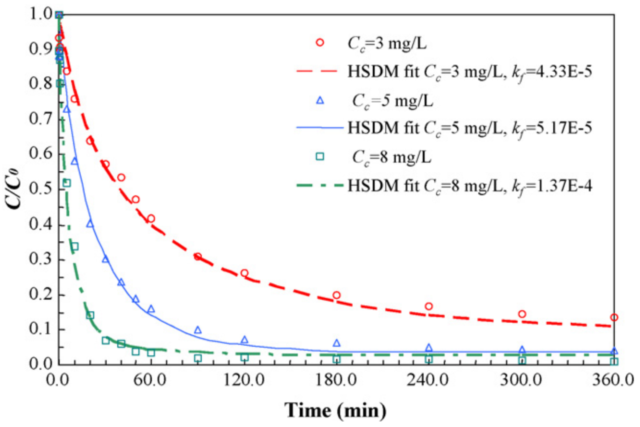

Fig. 4. Verification of the adsorption kinetic coefficients searching methods, magnetic stirring = 62 rpm, $C_0 = 200$ μg/L.

The bubbling batch kinetic test differed from the magnetic stirring test in the method of mixing. Bubbling has an unsteady state characteristic which may induce a local shear with a temporary time effect on the mass transfer. So it is possible for the mass transfer coefficient k_f to be changed at different mixing methods or mixing intensities. However, the surface diffusion coefficient which describes the diffusion along the inner surface within the carbon particles should not be affected by the external mixing mechanism. Instead, it is determined by the carbon characteristics such as carbon size and pore structure as well as the size and configuration of the adsorbate molecule [23]. Therefore in the following section, the value of D_S, which was $1.14 \times 10^{-16}\ \text{m}^2/\text{s}$ obtained previously, was fixed while the k_f for different bubbling rate tests was variable in the best fit of the HSDM solutions with the bubbling batch tests data.

The HSDM fits to the bubbling tests data with 5, 10, 15 mg/L PAC at different bubbling rates are shown in Fig. 5(A, B, C), respectively. The fits are reasonably good, especially at higher bubbling rates. At the lowest bubbling rate, the deviation of the model solution from the experimental data may be due to the insufficient mixing caused by the low rate of bubbling, especially at a relatively low carbon concentration (Fig. 5(A)). It can be seen that the main difference among the experimental data of different bubbling rates lies in the initial stages of the first 180, 120 or 90 min, depending on carbon dosage. There are no significant differences between the residual concentrations at the end of the 6 h kinetic tests. This indicates that the bubbling rate can affect the adsorption kinetics by influencing the time for adsorption to reach the equilibrium (plateau of the curves) without changing the adsorption capacity. At the latter stages, the adsorption tended to be controlled by the surface diffusion inside the particle and seemed not to be sensitive to the mixing conditions in the reactor. The similar residual concentrations at the end of the experiments at different bubbling rates at each carbon dosage further confirm that the surface diffusion parameter D_S is not altered by the bubbling rates. The k_f values were obtained using the method introduced above. It is clear that the mass transfer through the liquid film was enhanced by the increase in the bubbling rates for the three groups of tests, but further increase of the bubbling rate to 5.0 L/min L (data not shown) did not improve the adsorption rate significantly. This result indicates that the bubbling mixing can facilitate the adsorption to a

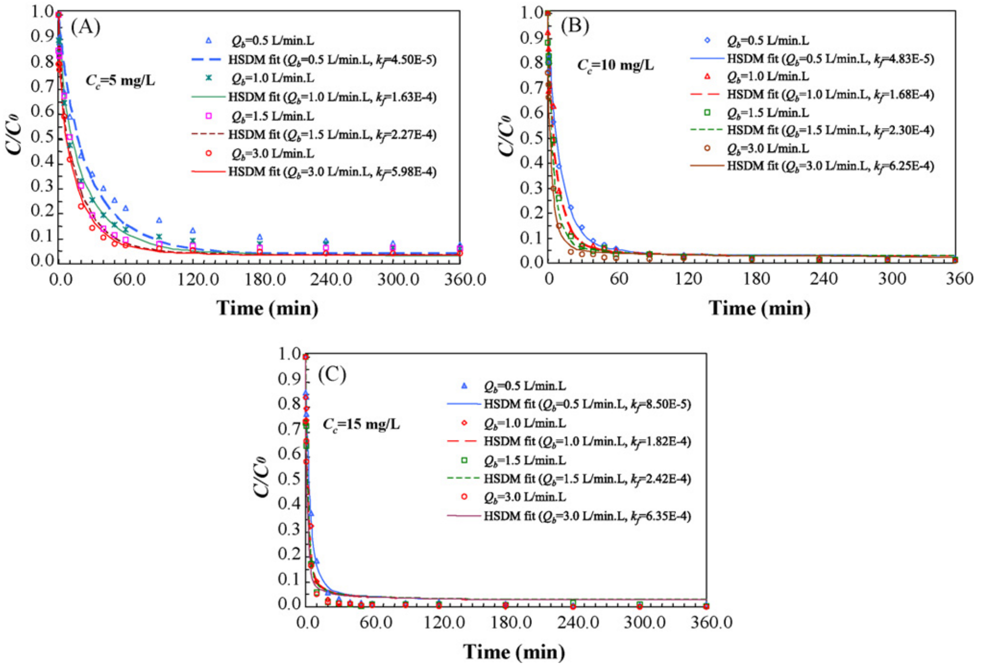

Fig. 5. HSDM fit to the bubbling batch kinetic tests data, $C_0 = 200\,\mu g/L$: (A) $C_c = 5$ mg/L; (B) $C_c = 10$ mg/L; (C) $C_c = 15$ mg/L.

certain level, which represents the limit of the film mass transfer resistance above which the k_f cannot be further reduced by increasing the bubbling rate. In other words, at higher bubbling rates the adsorption process is prone to be controlled by the internal surface diffusion and thus, not influenced by further enhancement of external mixing. The 'plateau' effect, where bubbling reaches a limiting effect has also been observed in fouling control by bubbling for submerged fibers [24,25].

A summary of the k_f values at different bubbling rates (Q_b) and carbon dosages (C_c) is shown in Fig. 6. The correlation of k_f (m/s) with Q_b (L/min L) and C_c (mg/L) can be regressed as the following equation with $R^2 = 0.9935$:

$$k_f = 1.30 \times 10^{-4} \cdot C_c^{0.06} Q_b^{1.29} \tag{20}$$

This empirical equation is suitable for the bubbling mixed adsorption process with the averaged bubble size of 3.3 mm (measured by photography in this study) at any bubbling rates below 3.0 L/min L. From this equation, it can be found that the k_f s not very sensitive to the variation in carbon dosage compared to the air bubbling rate. The reason for this is that k_f is determined by the local velocity gradients which are generated by the bubble passage; solids content (in the 5–15 mg/L range) would have minor impact on local momentum transfer. Eq. (20) provides a quantitative relationship for further evaluating PAC adsorption in the hybrid PAC-SM system and system modeling.

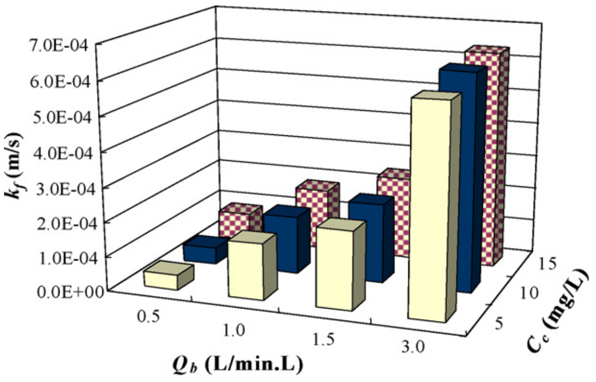

Fig. 6. k_f vs. Q_b at different carbon concentrations.

Comparing the k_f values determined through fitting the HSDM to those determined in our previous study [21] through the first order equation (Table 1), it is evident that at lower bubbling rates as well as for the 62 rpm magnetic stirring conditions, the HSDM produced lower k_f values than the first order method. This difference may be because the first order estimation was obtained by analysis of the data from the initial stage (1 min) of the kinetic tests which places too much reliance on the precision of the concentration analysis. However, the film mass transfer is very fast at the beginning and decreases over time. When the liquid concentration drops, the mass transfer slows down accordingly. So the values determined previously [21] represent the initial trend of mass transfer coefficients among the different bubbling rates. In contrast, the HSDM determined k_f values are base on overall 6 h test data and searched simultaneously with the surface diffusion coefficient D_S through a complicated searching procedure. A k_f value represents the averaged liquid mass transfer of the whole process including the faster transfer at the beginning and slower transfer thereafter. That the difference decreases with the increase of the bubbling rate is possibly due to the thinner film layer at higher bubbling and accordingly the adsorption approaches the equilibrium faster. When the HSDM model was applied to the initial stage data (up to 60 min) it produced a similar k_f value to that obtained from the full batch data. Therefore the k_f and D_S simultaneously determined in this study are considered more accurate for describing the adsorption kinetics and are further used in our following studies.

Table 1
k_f determined in different methods.

Bubbling rates (L/min L)	First order [21] ($\times 10^{-4}$ m/s)	HSDM ($\times 10^{-4}$ m/s)
0.5	3.27	0.45
1.5	4.02	2.27
3.0	5.83	5.98
Magnetic stirred (62 rpm)	3.43	0.52

Table 2
Comparison of the kinetic coefficients between continuous and intermittent bubbling at the same net bubbling rate.

Mixing conditions	D_S ($\times 10^{-16}$ m/s)	k_f ($\times 10^{-4}$ m/s)
Continuous bubbling (0.5 L/min L)	1.14	0.45
Intermittent bubbling (1.5 L/min L, 0.5 s/1.0 s)	1.14	1.18
Intermittent bubbling (3.0 L/min L, 0.5 s/2.0 s)	1.14	4.18

Table 2 summarizes the comparison of k_f values for 0.5 L/min L continuous bubbling with those of intermittent bubbling at two different bubbling intensities but the same net bubbling rate. For the 1.5 L/min L bubbling with 0.5 s-on-1.0 s-off and 3.0 L/min L bubbling with 0.5 s-on-2.0 s-off, the net bubbling rates are both 0.5 L/min L. It is evident that at the same net bubbling rate, high intensity bubbling with a longer rest interval is better than low intensity bubbling with a shorter rest interval. The k_f was improved from 4.50×10^{-5}, 1.18×10^{-4} to 4.18×10^{-4} m/s as bubbling intensity increased from continuous 0.5 L/min L to intermittent 1.5 L/min L (0.5 s-on-1.0 s-off), and to 3.0 L/min L (0.5 s-on-2.0 s-off). Thus, the carbon adsorption process can benefit from a higher intensity bubbling with longer rest periods rather than a continuous lower intensity bubbling. This may be due to the more energetic turbulence introduced by the higher intensity bubbling. These observations provide another strategy for optimization of the submerged hybrid membrane system which combines with PAC adsorption.

5. Conclusions

The kinetic coefficients for carbon adsorption in a bubbling mixed system for trace organics removal were evaluated through both mathematical and experimental methods. The homogeneous surface diffusion model (HSDM) was applied to describe the kinetics of adsorbate uptake. The differences between the model solutions and corresponding experimental results were minimized by means of the Levenberg–Marquardt algorithm so that two kinetic parameters D_S and k_f, which are involved in the HSDM, were obtained simultaneously. From the HSDM fit to batch kinetic tests data, the D_S was found to be 1.14×10^{-16} m^2/s while the k_f altered with different mixing mechanisms as well as mixing intensities, which is in correspondence with the different adsorption rates in the initial stages of batch tests.

1. The k_f value was found to be improved by increase in the bubbling rates over a certain range at three tested carbon dosages. A correlation between k_f and the air bubbling rate Q_b as well as the carbon dosage C_c was obtained by non-linear regression, which is useful for the modeling of adsorption process in the PAC-SM system at the similar bubbling conditions presented in Part II of his study.
2. The k_f value was also observed to be enhanced from 1.18×10^{-4} to 4.18×10^{-4} m/s when the instantaneous bubbling intensity increased in intermittent bubbling tests. This indicates that high intensity intermittent bubbling is more efficient in improving the liquid film mass transfer. This observation should be valuable in further optimization of PAC suspended submerged membrane systems.

Acknowledgement

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] 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.
[3] I.N. Najm, V.L. Snoeyink, Y. Richard, Removal of 2,4,6-trichlorophenol and natural organic matter form water supplies using PAC in floc-blanket reactors, Water Res. 27 (4) (1993) 551–560.
[4] I.N. Najm, Mathematical modeling of PAC adsorption processes, J. Am. Water Works Assoc. 88 (10) (1996) 79–89.
[5] J.S. Kim, S.J. Lee, S.H. Yoon, C.H. Lee, Competitive adsorption of trace organics on membranes and powdered activated carbon in powdered activated carbon-ultrafiltration system, Water Sci. Technol. 34 (9) (1996) 223–229.
[6] U.K. Traegner, M.T. Suidan, B.R. Kim, Considering age and size distributions of activated carbon particles in a completely mixed adsorber at steady state, Water Res. 30 (6) (1996) 1495–1501.
[7] A.J. Slaney, R. Bhamidimarri, Adsorption of pentachlorophenol (PCP) by activated carbon in fixed beds: application of homogeneous surface diffusion model, Water Sci. Technol. 38 (7) (1998) 227–235.
[8] 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.
[9] 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.
[10] S. Chang, T.D. Waite, E.A. Ong, A.I. Schafer, A.G. Fane, Assessment of trace estrogenic contaminants removal by coagulant addition, powdered activated carbon adsorption and powdered activated carbon/microfiltration processes, J. Environ. Eng. 130 (7) (2004) 736–742.
[11] D.W. Hand, J.C. Crittenden, M. ASCE, W.E. Thacker, User-oriented batch reactor solutions to the homogeneous surface diffusion model, J. Environ. Eng. 109 (1) (1983) 82–101.
[12] U.K. Traegner, M.T. Suidan, Evaluation of surface and film diffusion coefficients for carbon adsorption, Water Res. 23 (3) (1989) 267–273.
[13] D. Roy, G.T. Wang, D.D. Adrian, A simplified solution technique for carbon adsorption model, Water Res. 27 (6) (1993) 1033–1040.
[14] B.A. Finlayson, The Method of Weighted Residuals and Variational Principles (with Application in Fluid Mechanics, Heat and Mass Transfer), Academic Press, New York/San Francisco/London, 1972.
[15] V.L. Snoeyink, R.S. Summers, Adsorption of organic compounds, in: R.D. Letterman (Ed.), Water Quality and Treatment, 5th edition, McGraw-Hill, New York, 1999, (Chapter 13).
[16] S.J. Randtke, V.L. Snoeyink, Evaluating, GAC adsorptive capacity, J. Am. Water Works Assoc. 75 (8) (1983) 406–413.
[17] J.E. Dennis Jr., R.B. Schnabel, Numerical Methods for Unconstrained Optimization and Nonlinear Equations, Prentice-Hall, Englewood Cliffs, New Jersey, 1983.
[18] D. Kahaner, C. Moler, S. Nash, Numerical Methods and Software, Prentice Hall, Englewood Cliffs, New Jersey, 1988.
[19] International Mathematics and Statistical Library. Fortran 90 MP Library, IMSL, Visual Numerics, Houston, Texas, 1991.
[20] Y. Jia, R. Wang, A.G. Fane, W.B. Krantz, Effect of air bubbling on atrazine adsorption in water by powdered activated carbons—competitive adsorption of impurities, Sep. Purif. Technol. 46 (2005) 79–87.
[21] Y. Jia, R. Wang, A.G. Fane, Atrazine adsorption from aqueous solution using powdered activated carbon-improved mass transfer by air bubbling agitation, Chem. Eng. J. 116 (2006) 53–59.
[22] S. Qi, S.S. Adham, V.L. Snoeyink Jr., B.W. Lykins, Prediction and verification of atrazine adsorption by PAC, J. Environ. Eng. 120 (1994) 202–218.
[23] S.D. Faust, O.M. Aly, Adsorption Processes for Water Treatment, Butterworth, Boston, 1987.
[24] S. Chang, A.G. Fane, The effect of fiber diameter on filtration and flux distribution-relevance to submerged hollow fiber modules, J. Membr. Sci. 184 (2001) 221–231.
[25] F. Wicaksana, A.G. Fane, V. Chen, Fibre movement induced by bubbling using submerged hollow fibre membranes, J. Membr. Sci. 271 (2006) 186–195.