

Stochastic modeling of adsorption in a batch system

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Abstract

The adsorption of molecules of organic or inorganic compounds in an aqueous solution onto granular activated carbon involves a sequence of steps including: transfer of the molecules from the bulk phase of solution through the relatively stagnant layer of solution adjacent to the external surface and solution in macropores and micropores of the pellet of activated carbon and occupation of the active sites on the inside of the pellet by the molecules. The present work analyzes and models this sequence of steps by resorting to the stochastic population balance of the numbers of molecules of adsorbate in the three states. The first comprises the bulk phase of the solution; the second, the layer of solution adjacent to the external surface and the solution in the macropores; and the third, the active sites on the inside surfaces of the micropores. The master equation has been derived for the case of a single adsorbate compound. The equations for the means, variances, and covariances of the random variables have been obtained through the system size expansion of the master equation. At equilibrium, the equations for the means reduce to the equation of the Langmuir isotherm. The unknown parameters in the equations for the means have been estimated by comparing the calculated results with the experimental data. These parameters have been adopted to predict the evolution of variances and covariances of the numbers of adsorbate molecules in the three states.

1. Introduction

Numerous techniques have been developed in recent years to remove contaminants such as toxic organic or inorganic chemicals from drinking or waste water. Among these techniques, active carbon adsorption, a partitioning process in which the molecules of the contaminants are transferred from a dissolved state in the aqueous phase to the surface of active carbon, has become one of the most effective means for this purpose.

Extensive theoretical and experimental studies were conducted toward elucidation of the adsorption kinetics and isotherm (see e.g. [1–3]). Smith et al. [4] experimentally

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investigated the effects of adsorbent structure, particle size, initial adsorbate concentration, temperature, and adsorbent-solution ratio on the rates of adsorption of 2,4-dichlorophenol. A similar effort was undertaken by Weber and Morris [5] to determine the effectiveness of adsorption of compounds with high molecular weights, e.g., alkylbenzenesulfonates. Weber and Rumer [6] have developed a mathematical model for intraparticle transport of diffusing molecules. In studying the ultimate capacity of adsorption, i.e. the adsorption isotherm, the assumption of monolayer adsorption, which is valid for numerous cases of adsorption by activated carbon from aqueous solutions, has led to the Langmuir isotherm at equilibrium [7–9]. Numerous variants of models for adsorption equilibrium giving rise to different isotherm equations, have also been proposed (see e.g. [3, 10, 11]).

2. Objectives

The adsorption of contaminant molecules from aqueous solution by activated porous carbon includes the transfer of molecules from the bulk through the relatively stagnant aqueous layer adjacent to or in the macropores and micropores of the adsorbent pellet, where they are finally adsorbed onto the active sites. To study the kinetics such as the adsorption rate in the batch, the present work analyzes and models this sequence of steps by resorting to the stochastic population balance [12], an approach based on the probability balance of the transferring of the contaminant molecules among their various states in the batch system; this gives rise to the nonlinear master equation of adsorption. A rational approximation by means of the system size expansion of this equation yields the macroscopic quantities, such as liquid- and solid-phase concentrations, as well as their fluctuations, which are the instantaneous deviations of these concentrations from their mean values.

3. Mechanism and system description

Let us consider a batch system consisting of a dilute aqueous solution of a contaminant and porous pellets of granular activated carbon (GAC) to adsorb the contaminant. The adsorption of molecules of the contaminant onto a pellet of GAC, depicted in Fig. 1, includes the following two steps.

(1) Reversible transport of molecules of the contaminant from state S_1 , which is the bulk phase of aqueous solution to state S_2 , comprising the relatively stagnant aqueous layer adjacent to the pellets of GAC and the aqueous phase in the macropores and micropores inside the pellets of GAC, and vice versa. In other words, transport of molecules from state S_1 to state S_2 is accompanied simultaneously by the inverse transport of molecules from state S_2 to state S_1 .

(2) Adsorption of molecules of the contaminant from the aqueous phase, i.e. state S_2 , to the active sites in the pellets (state S_3), accompanied by the desorption of molecules from state S_3 to state S_2 .

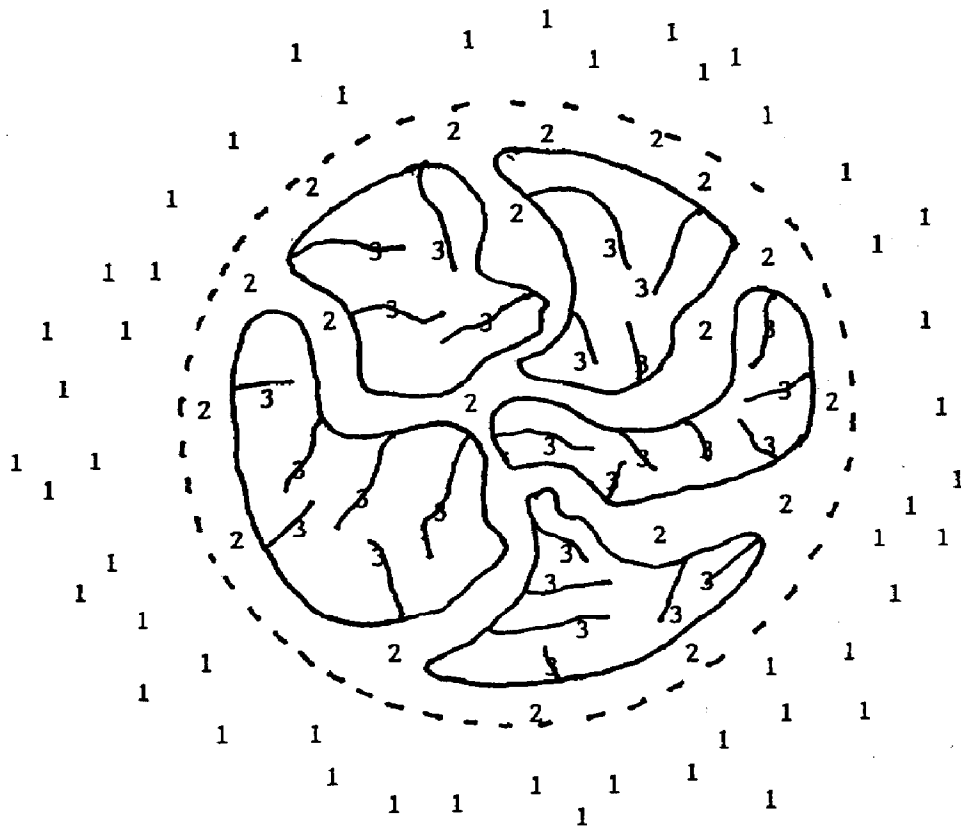


Fig. 1. Conceptual illustration of the adsorption process: S_1 , bulk; S_2 , aqueous phase in stagnant layer, macropores, and micropores; S_3 , active sites in the pellets.

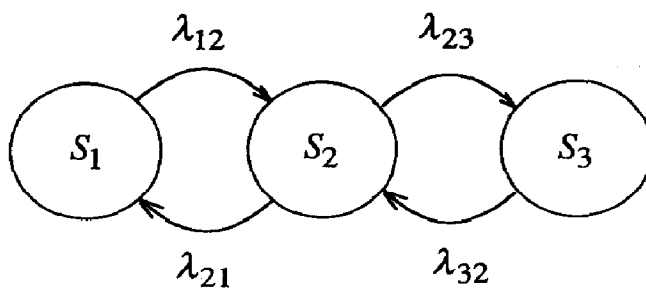


Fig. 2. Transition diagram of adsorption: S_1 , bulk; S_2 , aqueous phase in stagnant layer, macropores, and micropores; S_3 , active sites on the micropores.

4. Modeling

The adsorption system described in the preceding section comprises three states including (Fig. 2): the bulk aqueous phase, i.e. state S_1 ; the relatively stagnant aqueous layer adjacent to the pellet of GAC and in the macropores inside the pellet of GAC, i.e. state S_2 ; and the active sites on the inside surface of the micropores, i.e. state S_3 . Let

$N_1(t)$, $N_2(t)$, and $N_3(t)$ be the random variables representing the numbers of contaminant molecules in states S_1 , S_2 , and S_3 , at time t , respectively. The realization of $N_1(t)$ is n_1 ; that of $N_2(t)$, n_2 ; and that of $N_3(t)$, n_3 . Let $(t, t + \Delta t)$ be a time interval sufficiently small so that at most one molecule will transfer from one state to another during this time interval. Then, one molecule may undergo a transition according to the following probabilistic laws.

(1) Pr[a molecule in state S_1 at time t will be in state S_2 at time $(t + \Delta t)$]

$$= p(n_1 - 1, n_2 + 1, n_3; t + \Delta t | n; t) = \lambda_{12} \Delta t + o(\Delta t). \quad (1a)$$

In this expression, λ_{12} is the transition intensity of a molecule from state S_1 to state S_2 , which is assumed to be proportional to the number of molecules in state S_1 , or

$$\lambda_{12} = k_{12} n_1, \quad (1b)$$

where k_{12} is the number-transfer coefficient from state S_1 to state S_2 that is to be estimated.

(2) Pr[a molecule in state S_2 at time t will be in state S_1 at time $(t + \Delta t)$]

$$= p(n_1 + 1, n_2 - 1, n_3; t + \Delta t | n; t) = \lambda_{21} \Delta t + o(\Delta t). \quad (2a)$$

In this expression, λ_{21} is the transition intensity of a molecule from state S_2 to state S_1 , which is assumed to be proportional to the number of molecules in state S_2 , or

$$\lambda_{21} = k_{21} n_2, \quad (2b)$$

where k_{21} is the number-transfer coefficient from state S_2 to state S_1 that is to be estimated.

(3) Pr[a molecule in state S_2 at time t will be in state S_3 at time $(t + \Delta t)$]

$$= p(n_1, n_2 - 1, n_3 + 1; t + \Delta t | n; t) = \lambda_{23} \Delta t + o(\Delta t). \quad (3a)$$

In this expression, λ_{23} is the transition intensity of a molecule from state S_2 to state S_3 . Since the total number of adsorption sites of the pellets of GAC in the batch, Q , is a finite constant, the transition intensity also depends on the number of available sites $(Q - n_3)$ [7, 8], i.e.,

$$\lambda_{23} = k_{23} n_2 \frac{Q - n_3}{A}. \quad (3b)$$

Note that the right-hand side of this equation is divided by the Avogadro number, A , to render the order of magnitude of k_{23} to be approximately the same as that of k_{12} or k_{21} .

(4) Pr[a molecule in state S_3 at time t will be in state S_2 at time $(t + \Delta t)$]

$$= p(n_1, n_2 + 1, n_3 - 1; t + \Delta t | n; t) = \lambda_{32} \Delta t + o(\Delta t). \quad (4a)$$

In this expression, λ_{32} is the transition intensity of a molecule from state S_3 to state S_2 , which is assumed to be proportional to the number of molecules in state S_3 , or

$$\lambda_{32} = k_{32} n_3, \quad (4b)$$

where k_{32} is the number-transfer coefficient from state S_3 to state S_2 that is to be estimated.

In the statements of all the probabilistic laws given in the preceding paragraph, the vector representing a specific population distribution which serves as the reference state in the population balance calculation, \mathbf{n} , is defined as:

$$\mathbf{n} = (n_1, n_2, n_3).$$

Consequently, n_1 , n_2 , and n_3 are invariant with respect to time, t . Furthermore, $o(\Delta t)$ is a function approaching zero faster than Δt , i.e.,

$$\lim_{\Delta t \rightarrow 0} \frac{o(\Delta t)}{\Delta t} = 0.$$

4.1. Derivation of the master equation

Let $p(n_1, n_2, n_3; t + \Delta t)$ or $p(\mathbf{n}; t + \Delta t)$ be the joint probability of the system under consideration to be in the state having the number distribution of molecules, \mathbf{n} , at time $(t + \Delta t)$. Then, $p(n_1, n_2, n_3; t + \Delta t)$ is determined by the probabilities of occurrences of the following five mutually exclusive events.

(1) At time t , $(n_1 + 1)$ molecules exist in state S_1 , $(n_2 - 1)$ molecules in state S_2 , and n_3 molecules in state S_3 , with a probability of $p(n_1 + 1, n_2 - 1, n_3; t)$. During time interval $(t, t + \Delta t)$, one molecule transfers from state S_1 to state S_2 with a transition probability of $[k_{12}(n_1 + 1)\Delta t + o(\Delta t)]$; see Eqs. (1a) and (1b). The number of molecules in state S_1 will decrease from $(n_1 + 1)$ to n_1 , while the number of molecules in state S_2 will increase from $(n_2 - 1)$ to n_2 . Moreover, it is assumed that the process is Markovian, i.e., the transition of the molecule during time interval $(t, t + \Delta t)$ is independent of its transition during the preceding time interval $(0, t)$. Consequently, the probability for this event to occur is

$$p(n_1 + 1, n_2 - 1, n_3; t)[k_{12}(n_1 + 1)\Delta t + o(\Delta t)].$$

(2) At time t , $(n_1 - 1)$ molecules exist in state S_1 , $(n_2 + 1)$ molecules in state S_2 , and n_3 molecules in state S_3 , with a probability of $p(n_1 - 1, n_2 + 1, n_3; t)$. During time interval $(t, t + \Delta t)$, one molecule transfers from state S_2 to state S_1 with a transition probability of $[k_{21}(n_2 + 1)\Delta t + o(\Delta t)]$; see Eqs. (2a) and (2b). Hence, the probability for this event to occur is

$$p(n_1 - 1, n_2 + 1, n_3; t)[k_{21}(n_2 + 1)\Delta t + o(\Delta t)].$$

(3) At time t , n_1 molecules exist in state S_1 , $(n_2 + 1)$ molecules in state S_2 , and $(n_3 - 1)$ molecules in state S_3 , with a probability of $p(n_1, n_2 + 1, n_3 - 1; t)$. During time interval $(t, t + \Delta t)$, one molecule transfers from state S_2 to state S_3 with a transition probability of $k_{23}(n_2 + 1)\{[Q - (n_3 - 1)]/A\}\Delta t + o(\Delta t)$; see Eqs. (3a) and (3b). As a result, the probability for this event to occur is

$$p(n_1, n_2 + 1, n_3 - 1; t)\left(k_{23}(n_2 + 1)\frac{Q - (n_3 - 1)}{A}\Delta t + o(\Delta t)\right).$$

(4) At time t , n_1 molecules exist in state S_1 , $(n_2 - 1)$ molecules in state S_2 , and $(n_3 + 1)$ molecules in state S_3 , with a probability of $p(n_1, n_2 - 1, n_3 + 1; t)$. During

time interval $(t, t + \Delta t)$, one molecule transfers from state S_3 to state S_2 with a transition probability of $[k_{32}(n_3 + 1)\Delta t + o(\Delta t)]$; see Eqs. (4a) and (4b). Consequently, the probability for this event to occur is

$$p(n_1, n_2 - 1, n_3 + 1; t)[k_{32}(n_3 + 1)\Delta t + o(\Delta t)].$$

(5) At time t , n_1 molecules exist in state S_1 , n_2 in state S_2 , and n_3 in state S_3 , with a probability of $p(n_1, n_2, n_3; t)$ or $p(n; t)$. Thus, the probability of the system to remain as such during time interval $(t, t + \Delta t)$ is

$$p(n_1, n_2, n_3; t) \left[1 - \left(k_{12}n_1 + k_{21}n_2 + k_{23}n_2 \frac{Q - n_3}{A} + k_{32}n_3 \right) \Delta t + o(\Delta t) \right].$$

The conditional probability of more than one molecule transferring from one state to another in time interval $(t, t + \Delta t)$ is $o(\Delta t)$. Thus, by taking into account all the probabilities listed above, we have

$$\begin{aligned} p(n; t + \Delta t) = & p(n_1 + 1, n_2 - 1, n_3; t)[k_{12}(n_1 + 1)\Delta t + o(\Delta t)] \\ & + p(n_1 - 1, n_2 + 1, n_3; t)[k_{21}(n_2 + 1)\Delta t + o(\Delta t)] \\ & + p(n_1, n_2 + 1, n_3 - 1; t) \\ & \times \left[k_{23}(n_2 + 1) \frac{Q - (n_3 - 1)}{A} \Delta t + o(\Delta t) \right] \\ & + p(n_1, n_2 - 1, n_3 + 1; t)[k_{32}(n_3 + 1)\Delta t + o(\Delta t)] \\ & + p(n; t) \left\{ 1 - \left[k_{12}n_1 + k_{21}n_2 \right. \right. \\ & \left. \left. + k_{23}n_2 \frac{Q - n_3}{A} + k_{32}n_3 \right] \Delta t + o(\Delta t) \right\} \\ & + o(\Delta t). \end{aligned} \quad (5)$$

Note that the total number of contaminant molecules in the batch, n_0 , remains invariant during the process of the adsorption, i.e.,

$$n_0 = N_1(t) + N_2(t) + N_3(t). \quad (6)$$

Hence, only two random variables, e.g., $N_1(t)$ and $N_3(t)$, are independent in $[N_1(t), N_2(t), N_3(t)]$.

Transposing $p(n; t)$ to the left-hand side of Eq. (5), expressing n_2 in terms of n_0, n_1 , and n_3 , dividing the resultant equation by Δt , and taking the limit as $\Delta t \rightarrow 0$ yield

$$\begin{aligned} \frac{dp(n; t)}{dt} = & k_{12}(n_1 + 1)p(n_1 + 1, n_3; t) \\ & + k_{21}(n_0 - n_1 - n_3 + 1)p(n_1 - 1, n_3; t) \\ & + k_{23}(n_0 - n_1 - n_3 + 1) \frac{Q - (n_3 - 1)}{A} p(n_1, n_3 - 1; t) \end{aligned}$$

$$\begin{aligned}
& + k_{32}(n_3 + 1)p(n_1, n_3 + 1; t) \\
& - \left[k_{12}n_1 + k_{21}(n_0 - n_1 - n_3) \right. \\
& \left. + k_{23}(n_0 - n_1 - n_3) \frac{Q - n_3}{A} + k_{32}n_3 \right] p(n_1, n_3; t). \quad (7)
\end{aligned}$$

By applying the one-step operator E_{n_i} defined by its effect on the arbitrary function, $f(n_i)$, as (see e.g. [12])

$$E_{n_i}f(n_i) = f(n_i + 1) \quad \text{and} \quad E_{n_i}^{-1}f(n_i) = f(n_i - 1) \quad (8)$$

to Eq. (7), we obtain the following reduced master equation;

$$\begin{aligned}
\frac{dp(\mathbf{n}; t)}{dt} = & (E_{n_1} - 1)[k_{12}n_1 p(\mathbf{n}; t)] \\
& + (E_{n_1}^{-1} - 1)[k_{21}(n_0 - n_1 - n_3) p(\mathbf{n}; t)] \\
& + (E_{n_3}^{-1} - 1) \left\{ k_{23}(n_0 - n_1 - n_3) \frac{Q - n_3}{A} p(\mathbf{n}; t) \right\} \\
& + (E_{n_3} - 1)[k_{32}n_3 p(\mathbf{n}; t)]. \quad (9)
\end{aligned}$$

Solution of the above equation leads to the joint probability distribution of the population of contaminant molecules among the three states, thus providing the complete statistical description of the adsorption process in the batch system. Solution of this class of equations, either analytical or numerical, however, involves solving a large set of differential equations; moreover, it is time consuming. Nevertheless, knowledge concerning the first and second moments of $p(\mathbf{n}; t)$, i.e., means and fluctuations, suffices for a wide variety of practical applications.

4.2. Derivation of the governing equations for means and fluctuations

Direct solution of the master equation, i.e. Eq. (9), leading to the joint probability distribution of $N_1(t)$ and $N_3(t)$, is extremely difficult, if not impossible. Instead, therefore, we evaluate the mean and the quantities defined by higher moments, e.g., variance, of each random variable from the master equation. The third term on the right-hand side of Eq. (9), however, is nonlinear with respect to the random variables, thereby preventing the moments to be evaluated exactly. This difficulty is circumvented here by resorting to the system size expansion, a rational approximation technique based on a power series expansion. It gives rise to the deterministic macroscopic equations and the equations of fluctuations from the master equation [12].

In adopting the system size expansion, a suitable expansion parameter need be selected. It must be a parameter contained in the master equation. Furthermore, it must govern the magnitude of fluctuations, and therefore, the magnitude of jumps. In the system under consideration, the total number of contaminant molecules in the

batch, n_0 , is chosen as the expansion parameter. Then, the random variables, $N_1(t)$ and $N_3(t)$, can be expressed, respectively, as

$$N_1(t) = n_0 \phi(t) + n_0^{1/2} Y_1(t), \quad (10)$$

$$N_3(t) = n_0 \theta(t) + n_0^{1/2} Y_2(t), \quad (11)$$

where ϕ and θ correspond to the deterministic variables in the macroscopic equations, while $Y_1(t)$ and $Y_2(t)$ are the new random variables characterizing the fluctuations of the system. The realization of $Y_1(t)$ or $Y_2(t)$ is y_1 or y_2 , respectively. Equations (10) and (11) indicate that the joint probability, $p(\mathbf{n}; t)$, in Eq. (9) is presumed to have a sharp maximum around the macroscopic values, $n_0 \phi(t)$ and $n_0 \theta(t)$, with the fluctuations of orders $n_0^{1/2} Y_1$ and $n_0^{1/2} Y_2$, respectively [12]. Accordingly, the joint probability of N_1 and N_3 , $p(\mathbf{n}; t)$, is now transformed into the joint probability of y_1 and y_2 , $\Psi(y_1, y_2; t)$, i.e.,

$$p(\mathbf{n}; t) = \Psi(y_1, y_2; t). \quad (12)$$

Substituting $\Psi(y_1, y_2; t)$ into the master equation, Eq. (9), expanding the right-hand side of the resultant expression into Taylor series, and collecting the terms corresponding to the same power of the system size parameter, $n_0^{1/2}$, lead to the equations governing the evolution of the macroscopic terms of the system given below (Appendix A):

$$\frac{d\phi}{dt} = -k_{12}\phi + k_{21}(1 - \phi - \theta), \quad (13)$$

$$\frac{d\theta}{dt} = k_{23} \frac{1}{\beta} (1 - \phi - \theta)(\alpha - \theta) - k_{32}\theta. \quad (14)$$

Collecting the terms of order n_0^0 gives rise to the equations governing the magnitude of fluctuations around the macroscopic values as follows (Appendix B):

$$\frac{d}{dt} E[Y_k] = \sum_{j=1}^2 A_{kj} E[Y_j], \quad k = 1, 2, \quad (15)$$

$$\frac{d}{dt} E[Y_i Y_j] = \sum_{k=1}^2 A_{ik} E[Y_k Y_j] + \sum_{k=1}^2 A_{jk} E[Y_i Y_k] + B_{ij}, \quad i, j = 1, 2, \quad (16)$$

where

$$A = \begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix} = \begin{pmatrix} -(k_{12} + k_{21}) & -k_{21} \\ -k_{23} \frac{1}{\beta} (\theta - \alpha) & -k_{23} \frac{1}{\beta} (1 + \alpha - \phi - 2\theta) - k_{32} \end{pmatrix}, \quad (17)$$

$$\begin{aligned}
 B &= \begin{pmatrix} B_{11} & B_{12} \\ B_{21} & B_{22} \end{pmatrix} \\
 &= \begin{pmatrix} k_{12}\phi + k_{21}(1 - \phi - \theta) & 0 \\ 0 & k_{23} \frac{1}{\beta} (1 - \phi - \theta)(\alpha - \theta) + k_{32}\theta \end{pmatrix}. \tag{18}
 \end{aligned}$$

Equations (15) and (16) are expressions of the first and second moments of the system's fluctuations, respectively.

Taking the averages over Eqs. (10) and (11) yields, respectively,

$$E[N_1(t)] = n_0\phi(t) + n_0^{1/2} E[Y_1(t)], \tag{19}$$

$$E[N_3(t)] = n_0\theta(t) + n_0^{1/2} E[Y_3(t)]. \tag{20}$$

The deterministic terms, $\phi(t)$ and $\theta(t)$, in these expressions are obtained by solving simultaneously the macroscopic equations, Eqs. (13) and (14), while the terms for the means of fluctuations, $E[Y_1]$ and $E[Y_2]$, are the solutions of Eq. (15). Consequently, $E[N_1(t)]$ and $E[N_3(t)]$ can be determined from Eqs. (19) and (20), respectively.

In modeling the active carbon adsorption in a batch, it is reasonable to assume that no fluctuations occur in the system initially, i.e.,

$$E[Y_1(0)] = 0, \tag{21}$$

$$E[Y_2(0)] = 0. \tag{22}$$

Solving Eq. (15), subject to these initial conditions, yields

$$E[Y_1(t)] = 0, \tag{23}$$

$$E[Y_2(t)] = 0. \tag{24}$$

Thus, according to Eqs. (19) and (20), $E[N_1(t)]$ and $E[N_3(t)]$ are, respectively, the solutions of the macroscopic equations, i.e.,

$$E[N_1(t)] = n_0\phi(t), \tag{25}$$

$$E[N_3(t)] = n_0\theta(t). \tag{26}$$

Substituting these two expressions into both Eqs. (13) and (14) leads to

$$\frac{dE[N_1(t)]}{dt} = -k_{12}E[N_1(t)] + k_{21}\{n_0 - E[N_1(t)] - E[N_3(t)]\} \tag{27}$$

$$\begin{aligned}
 \frac{dE[N_3(t)]}{dt} &= k_{23}\{n_0 - E[N_1(t)] - E[N_3(t)]\} \frac{Q - E[N_3(t)]}{A} \\
 &\quad - k_{23}E[N_3(t)]. \tag{28}
 \end{aligned}$$

Solving simultaneously Eqs. (27) and (28) subject to the initial conditions

$$E[N_1(0)] = n_0 \tag{29}$$

and

$$E[N_3(0)] = 0, \quad (30)$$

gives rise to $E[N_1(t)]$ and $E[N_3(t)]$. Taking expectations over Eq. (6) yields

$$n_0 = E[N_1(t)] + E[N_2(t)] + E[N_3(t)], \quad (31)$$

from which $E[N_2(t)]$ is evaluated.

4.3. Expressions in terms of concentrations

By definitions, the liquid-phase concentration C and the solid-phase concentration q can be expressed, respectively, as

$$C = \frac{E[N_1(t)] + E[N_2(t)]}{VA}, \quad (32)$$

$$q = \frac{E[N_3(t)]}{WA}, \quad (33)$$

where V is the volume of solution and W is the weight of adsorbent.

4.4. Equilibrium state - Langmuir isotherm

As $t \rightarrow \infty$, the system reaches equilibrium, and thus the time derivatives on the left-hand side of Eqs. (27) and (28) vanish. In other words, Eqs. (27) and (28) reduce, respectively, to

$$0 = -k_{12}E[N_1(\infty)] + k_{21}\{n_0 - E[N_1(\infty)] - E[N_3(\infty)]\}, \quad (34)$$

$$0 = k_{23}\{n_0 - E[N_1(\infty)] - E[N_3(\infty)]\} \frac{Q - E[N_3(\infty)]}{A} - k_{32}E[N_3(\infty)]. \quad (35)$$

Substituting Eq. (31) into the above expressions yields

$$0 = -k_{12}E[N_1(\infty)] + k_{21}E[N_2(\infty)], \quad (36)$$

$$0 = k_{23}E[N_2(\infty)]\{Q - E[N_3(\infty)]\} - k_{32}E[N_3(\infty)]A. \quad (37)$$

Equation (36) can be rewritten as

$$E[N_1(\infty)] + E[N_2(\infty)] = \left(1 + \frac{k_{21}}{k_{12}}\right)E[N_2(\infty)]. \quad (38)$$

Substituting this expression into Eq. (37) leads to

$$E[N_3(\infty)] = \frac{k_{23}Q[k_{12}/(k_{12} + k_{21})]\{E[N_1(\infty) + E[N_2(\infty)]]\}}{k_{32}A + k_{23}[k_{12}/(k_{12} + k_{21})]\{E[N_1(\infty) + E[N_2(\infty)]]\}}. \quad (39)$$

In the light of Eqs. (32) and (33), this equation reduces to

$$q_{\infty} = \frac{E[N_3(\infty)]}{WA} = \frac{[k_{12}k_{23}/(k_{12} + k_{21})k_{32}](QV/AW)C_{\infty}}{1 + [k_{12}k_{23}/(k_{12} + k_{21})k_{32}]VC_{\infty}} \quad (40)$$

By letting

$$q_m = \frac{Q}{AW} \quad (41)$$

and

$$b = \frac{k_{12}k_{23}V}{(k_{12} + k_{21})k_{32}}, \quad (42)$$

we obtain, from Eq. (40),

$$q_{\infty} = \frac{q_m b C_{\infty}}{1 + b C_{\infty}}, \quad (43)$$

which is the expression for the celebrated Langmuir isotherm [7, 8].

5. Parameter estimation

The governing equations of the present system, Eqs. (27) and (28), contain five parameters, Q , k_{12} , k_{21} , k_{23} , and k_{32} , which can be estimated through the following procedure.

(1) Determine k_{12} from the experimentally measured initial rate of concentration variation. As $t \rightarrow 0$, $E[N_2(t)] \rightarrow 0$ and $E[N_3(t)] \rightarrow 0$; hence, Eq. (27) becomes

$$\lim_{t \rightarrow 0} \frac{dE[N_1(t)]}{dt} = -k_{12}E[N_1(t)]. \quad (44)$$

By substituting Eq. (32) into this expression and noting that $E[N_2(t)] \rightarrow 0$ as $t \rightarrow 0$, we obtain

$$\lim_{t \rightarrow 0} \frac{d}{dt} \ln C(t) = -k_{12}. \quad (45)$$

Thus, k_{12} , reflecting the initial rate of molecular transfer from the bulk to the stagnant layer and macropores, can be obtained from the experimentally measured initial rate of concentration variation.

(2) Calculate Q from Eq. (41).

(3) Express k_{23} in terms of k_{21} and k_{32} in the light of Eq. (42) as

$$k_{23} = \frac{k_{12} + k_{21}}{k_{12}V} k_{32} b. \quad (46)$$

(4) Minimize the objective function, the sum of the squares of the differences between the model-based rates computed numerically from Eqs. (27)–(33) and the corresponding experimentally measured rates, through the random search technique with k_{21} and k_{32} as the decision variables.

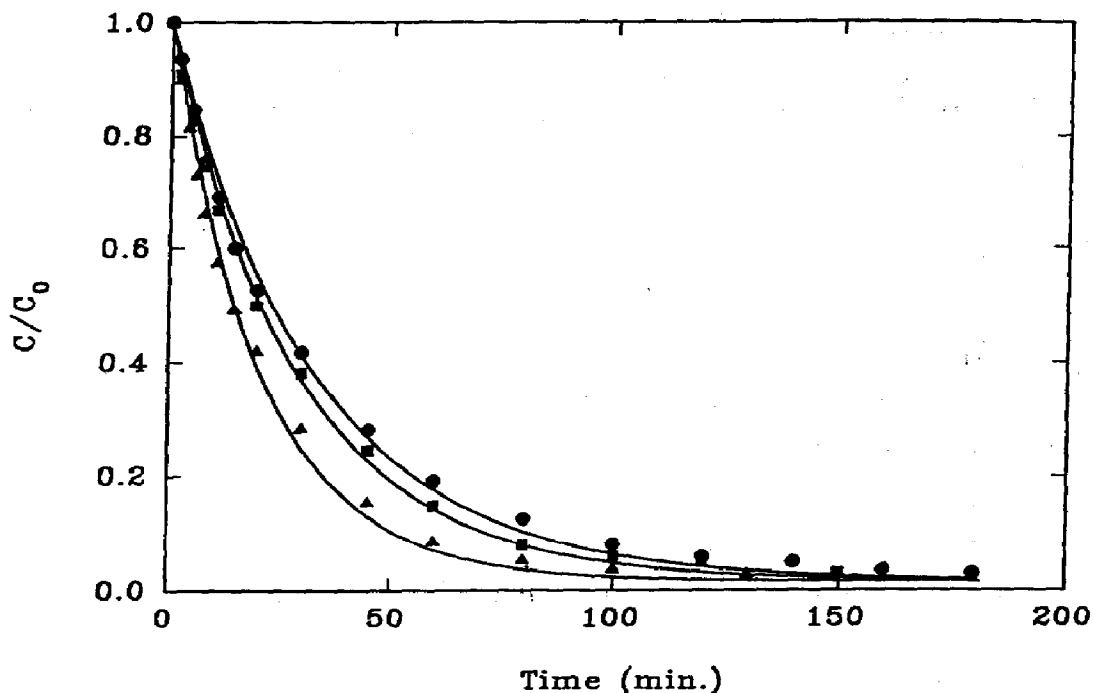


Fig. 3. Comparison between the model and the experimentally measured concentration variations of trichloroethylene in the aqueous solution containing activated carbon particles with various diameters [13]: (—●—) 917 μm ; (—■—) 772 μm ; (—▲—) 647 μm .

6. Results and discussion

The available experimental data by Lee [13] are reproduced in Fig. 3. The data represent the removal of trichloroethylene from its aqueous solution using carborundum activated carbons having essentially the same surface area but various geometric mean diameters of 917, 772, and 647 μm as the adsorbent. The experimental temperature, T , volume of solution, V , the initial concentration of trichloroethylene, C_0 , and the adsorbent loading, W , are 25 $^{\circ}\text{C}$, 1.04 l, 0.007 mmol/l, and 1 g, respectively. The values of parameters of the Langmuir isotherm, q_m and b , determined from the isotherm data of Lee, are 0.41 mmol/g and 172 l/mmol, respectively. The concentration variations of trichloroethylene in the aqueous solution during the adsorption calculated by the present stochastic model, i.e. Eqs. (27), (28), (31), and (32), have been fitted to the experimental data according to the procedure outlined in the preceding section; the results are plotted in Fig. 3. Obviously, the adsorption rate increases slightly with the decrease in the diameter of the activated carbon particles, and the present model agrees well with the experimental data. The uptake of trichloroethylene onto GAC as a function of time, calculated from Eq. (33) with the parameters listed in Table 1, is depicted in Fig. 4.

The values of the number coefficients, k_{ij} 's, evaluated by the procedure outlined in the preceding section, are summarized in Table 1. Obviously, the propensity of

Table 1
Parameters of the present model for activated carbon particles of various sizes

Particle diameter (μm)	Q/A (mmol)	k_{12} (min^{-1})	k_{21} (min^{-1})	k_{23} (mmol min^{-1}) $^{-1}$	k_{32} (min^{-1})
917	0.410	0.030	0.532	145.6	0.047
772	0.410	0.034	0.427	87.5	0.039
647	0.410	0.049	0.206	14.6	0.017

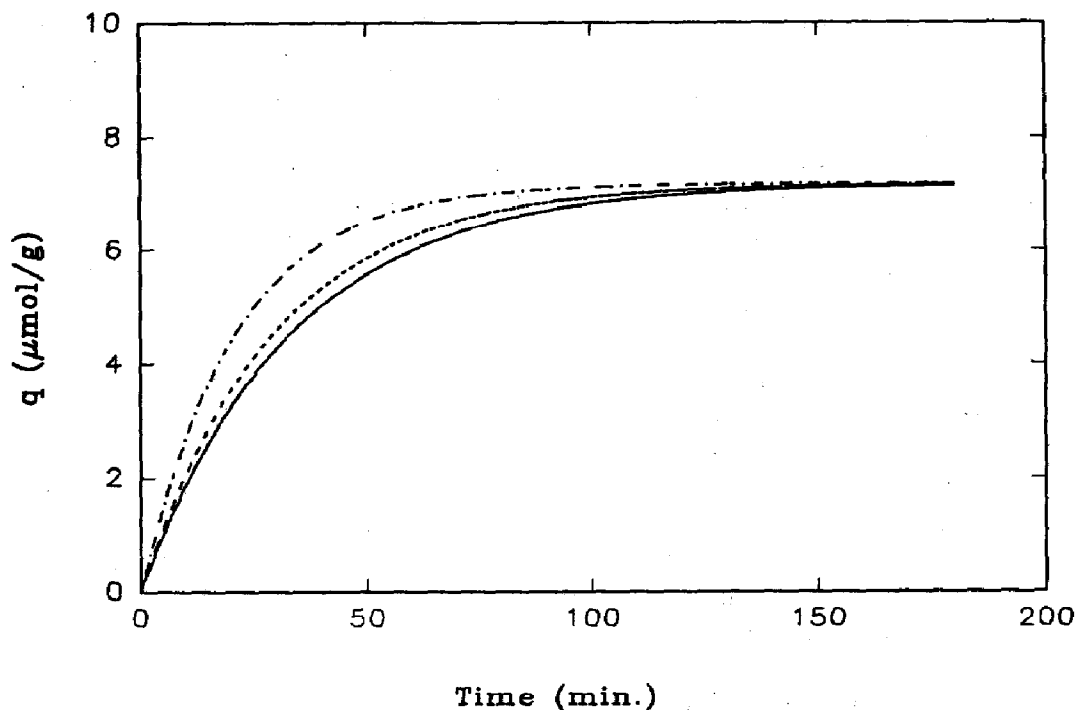


Fig. 4. Model predictions of uptake of trichloroethylene onto activated carbon particles with various diameters: (—) 917 μm ; (----) 772 μm ; (-·-·-) 647 μm .

a molecule of trichloroethylene to transfer from state S_2 to state S_1 , characterized by k_{21} , is larger than that from state S_1 to state S_2 , characterized by k_{12} , for all three different sizes of carbon particles. The net flux of molecules, however, is from state S_1 to state S_2 for unsteady-state adsorption since the number of molecules in state S_1 is much larger than that in state S_2 . Moreover, the propensity of a molecule of trichloroethylene to transfer from state S_2 to state S_3 , characterized by $k_{23}(Q - n_3)/A$, is much larger than that from state S_3 to state S_2 , characterized by k_{32} , indicating that the adsorption of the molecules of trichloroethylene from the macropores to the active sites on the micropores of the particles is almost irreversible.

Because of Eqs. (10) and (11), the variances and covariances of $N_1(t)$ and $N_2(t)$ are expressed as

$$\text{var}[N_1(t)] = n_0 E[Y_1(t)^2], \quad (47)$$

$$\text{var}[N_3(t)] = n_0 E[Y_2(t)^2], \quad (48)$$

$$\text{cov}[N_1(t), N_3(t)] = n_0 E[Y_1(t)Y_2(t)], \quad (49)$$

where $E[Y_1(t)^2]$, $E[Y_2(t)^2]$, and $E[Y_1(t)Y_2(t)]$ are obtained by solving the equations for the second moments in Eq. (16). The magnitude of fluctuations of the concentration in the aqueous solution around its macroscopic value due to the molecular number variations, characterized by the variances and covariances in Eqs. (47)–(49) is of order $n_0^{-1/2}$ (see e.g. [12]), where n_0 is the size of the system whose magnitude is of the order of the Avogadro number under the experimental condition of Lee [13]. Consequently, these fluctuations are negligible compared to the mean concentration. The slight scattering of the experimental data might be attributable to inherent experimental errors and nonideal experimental conditions, such as imperfect operating procedure, instrumental noises, nonuniform bulk concentration, and irregular structure of the particles of GAC. It is worth noting, however, that for an ultra-dilute system, the fluctuations due to the molecular number variations could become significant.

The present work parallels that of Argyelan et al. [14]; nevertheless, the mechanism conceived in deriving the model of the former is substantially different from that of the latter. Moreover, the former resorts rationally to the system-size expansion to circumvent the difficulty in solution arising from the nonlinearity of the model while the latter resorts, apparently arbitrarily, to the decoupling of the nonlinear term in their model so that the conditional-expectation approach can be adopted. The latter also seem to have introduced a physically indefensible conversion factor to transform the molecular number to the molar concentration in the solid state.

In principle, the current stochastic model can be extended to the more general cases such as the continuous flow adsorption system, the system with multiple adsorbates and competitive adsorption. Nevertheless, for the latter extension, the transition intensities need to be modified to address the complications attributable to the interference and competition among the adsorbates.

7. Concluding remarks

A stochastic model has been proposed to describe the adsorption dynamics of molecules of a contaminant in aqueous solution on the activated carbon in a batch. The master equation has been derived for the case of a single contaminant compound. The variations of the macroscopic values with time, such as concentrations in the aqueous solution and in the carbon particles, have been obtained through the system size expansion of the master equation; the equilibrium of these concentrations

naturally gives rise to the Langmuir isotherm. The predicted concentration variations are in accord with the available experimental data. The present model is capable of predicting the temporal variations of the adsorption rates of a single adsorbate in a batch system and may be extended to the case of multiple adsorbates and competitive adsorption.

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Nomenclature

A	Avogadro number
b	coefficient of the Langmuir isotherm equation
C	liquid-phase concentration, mmol/l
C_0	initial liquid-phase concentration, mmol/l
$\text{cov}[N_i(t)N_j(t)]$	covariance of random variables $N_i(t)$ and $N_j(t)$
$E[N_i(t)]$	mean of random variable $N_i(t)$
$E[Y_i(t)]$	mean of random variable $Y_i(t)$
$E[Y_i(t)Y_j(t)]$	cross-moment of random variables $Y_i(t)$ and $Y_j(t)$
k_{ij}	number-transfer coefficient from state S_i to state S_j
n_i	realization of random variable $N_i(t)$, $i = 1, 2, 3$
$N_i(t)$	random variable representing the number of contaminant molecules in state S_i , $i = 1, 2, 3$
n_0	total number of contaminant molecules in the system
q	solid-phase concentration, $\mu\text{mol/g}$
q_∞	coefficient of the Langmuir isotherm equation
Q	total number of adsorption sites in the system
V	volume of solution
W	weight of adsorbent
$Y_1(t)$	random number characterizing the fluctuations of $N_1(t)$
$Y_2(t)$	random number characterizing the fluctuations of $N_3(t)$

Greek letters

α	Q/n_0
β	A/n_0
$\theta(t)$	deterministic variable corresponding to the macroscopic property of random variable $N_3(t)$
λ_{ij}	transition intensity of a molecule from state S_i to state S_j
$\phi(t)$	deterministic variable corresponding to the macroscopic property of random variable $N_1(t)$

Appendix A: Derivation of the macroscopic equations, Eqs. (13) and (14), by system size expansion

The realization of Eq. (10) and that of Eq. (11) can be written, respectively, as

$$n_1 = n_0 \phi(t) + n_0^{1/2} y_1, \quad (\text{A1})$$

$$n_3 = n_0 \theta(t) + n_0^{1/2} y_2. \quad (\text{A2})$$

Recall that in the context of deriving the master equation, the state or dependent variable of interest is the joint probability of the population distribution, $p(n_1, n_2, n_3; t)$, and the realization of random variables at time t , i.e., n_1, n_2 , and n_3 , at the reference state, is regarded to be invariant with respect to time. Consequently, the time derivatives of Eqs. (A1) and (A2) are, respectively,

$$\frac{dy_1}{dt} = -n_0^{1/2} \frac{d\phi}{dt}, \quad (\text{A3})$$

$$\frac{dy_2}{dt} = -n_0^{1/2} \frac{d\theta}{dt}. \quad (\text{A4})$$

Hence, the left-hand side of Eq. (9) can be rewritten as

$$\begin{aligned} \frac{dp(n; t)}{dt} &= \frac{d\Psi(y_1, y_2; t)}{dt} = \frac{\partial \Psi}{\partial t} + \frac{\partial \Psi}{\partial y_1} \frac{dy_1}{dt} + \frac{\partial \Psi}{\partial y_2} \frac{dy_2}{dt} \\ &= \frac{\partial \Psi}{\partial t} - n_0^{1/2} \frac{d\phi}{dt} \frac{\partial \Psi}{\partial y_1} - n_0^{1/2} \frac{d\theta}{dt} \frac{\partial \Psi}{\partial y_2}. \end{aligned} \quad (\text{A5})$$

The step operator, E_{n_1} , changes n_1 into $(n_1 + 1)$ and, therefore, y_1 into $(y_1 + n_0^{-1/2})$. Thus, it can be expanded into Taylor series as

$$E_{n_1} = 1 + n_0^{-1/2} \frac{\partial}{\partial y_1} + \frac{1}{2} n_0^{-1} \frac{\partial^2}{\partial y_1^2} + \dots \quad (\text{A6})$$

Similarly,

$$E_{n_1}^{-1} = 1 - n_0^{-1/2} \frac{\partial}{\partial y_1} + \frac{1}{2} n_0^{-1} \frac{\partial^2}{\partial y_1^2} + \dots, \quad (\text{A7})$$

$$E_{n_3} = 1 + n_0^{-1/2} \frac{\partial}{\partial y_2} + \frac{1}{2} n_0^{-1} \frac{\partial^2}{\partial y_2^2} + \dots, \quad (\text{A8})$$

$$E_{n_3}^{-1} = 1 - n_0^{-1/2} \frac{\partial}{\partial y_2} + \frac{1}{2} n_0^{-1} \frac{\partial^2}{\partial y_2^2} + \dots \quad (\text{A9})$$

Substituting Eq. (A5) into the left-hand side and Eqs. (A6)–(A9) into the right-hand side of Eq. (9) yield

$$\frac{\partial \Psi}{\partial t} - n_0^{1/2} \frac{d\phi}{dt} \frac{\partial \Psi}{\partial y_1} - n_0^{1/2} \frac{d\theta}{dt} \frac{\partial \Psi}{\partial y_2}$$

$$\begin{aligned}
 &= k_{12} \left\{ \left(1 + n_0^{-1/2} \frac{\partial}{\partial y_1} + \frac{1}{2} n_0^{-1} \frac{\partial^2}{\partial y_1^2} + \dots \right) - 1 \right\} [(n_0 \phi + n_0^{1/2} y_1) \Psi] \\
 &\quad + k_{21} \left\{ \left(1 - n_0^{-1/2} \frac{\partial}{\partial y_1} + \frac{1}{2} n_0^{-1} \frac{\partial^2}{\partial y_1^2} + \dots \right) - 1 \right\} \\
 &\quad \times \{ [n_0 - (n_0 \phi + n_0^{1/2} y_1) - (n_0 \theta + n_0^{1/2} y_2)] \Psi \} \\
 &\quad + k_{23} \beta^{-1} n_0^{-1} \left\{ \left(1 - n_0^{-1/2} \frac{\partial}{\partial y_2} + \frac{1}{2} n_0^{-1} \frac{\partial^2}{\partial y_2^2} + \dots \right) - 1 \right\} \\
 &\quad \times \{ [n_0 - (n_0 \phi + n_0^{1/2} y_1) - (n_0 \theta + n_0^{1/2} y_2)] (\alpha n_0 - n_0 \theta - n_0^{1/2} y_2) \Psi \} \\
 &\quad + k_{32} \left\{ \left(1 - n_0^{-1/2} \frac{\partial}{\partial y_2} + \frac{1}{2} n_0^{-1} \frac{\partial^2}{\partial y_2^2} + \dots \right) - 1 \right\} [(n_0 \theta + n_0^{1/2} y_2) \Psi] \\
 &= k_{12} \left(n_0^{1/2} \phi \frac{\partial \Psi}{\partial y_1} + \frac{\partial (y_1 \Psi)}{\partial y_1} + \frac{1}{2} \phi \frac{\partial^2 \Psi}{\partial y_1^2} + \dots \right) \\
 &\quad + k_{21} \left(-n_0^{1/2} (1 - \phi - \theta) \frac{\partial \Psi}{\partial y_1} + \frac{\partial (y_1 \Psi)}{\partial y_1} + \frac{\partial (y_2 \Psi)}{\partial y_1} + \frac{1}{2} (1 - \phi - \theta) \frac{\partial^2 \Psi}{\partial y_1^2} + \dots \right) \\
 &\quad + k_{23} \beta^{-1} \left(-n_0^{1/2} (1 - \phi - \theta) (\alpha - \theta) \frac{\partial \Psi}{\partial y_2} + (1 - \phi - \theta) \frac{\partial (y_2 \Psi)}{\partial y_2} \right. \\
 &\quad \left. + (\alpha - \theta) \frac{\partial (y_1 \Psi)}{\partial y_2} + (\alpha - \theta) \frac{\partial (y_2 \Psi)}{\partial y_2} + \frac{1}{2} (1 - \phi - \theta) (\alpha - \theta) \frac{\partial^2 \Psi}{\partial y_2^2} + \dots \right) \\
 &\quad + k_{32} \left(n_0^{1/2} \theta \frac{\partial \Psi}{\partial y_2} + \frac{\partial (y_2 \Psi)}{\partial y_2} + \frac{1}{2} \theta \frac{\partial^2 \Psi}{\partial y_2^2} + \dots \right). \tag{A10}
 \end{aligned}$$

Now that we have set

$$Q = \alpha n_0, \tag{A11}$$

$$A = \beta n_0, \tag{A12}$$

because the total number of the contaminant molecules in the batch, n_0 , the total capacity of the micropores of the system, Q , and the Avogadro number A are all fixed. Collecting the resultant terms of order $n_0^{1/2}$ in Eq. (A10) leads to

$$\begin{aligned}
 &-\frac{d\phi}{dt} \frac{\partial \Psi}{\partial y_1} - \frac{d\theta}{dt} \frac{\partial \Psi}{\partial y_2} = k_{12} \phi \frac{\partial \Psi}{\partial y_1} - k_{21} (1 - \phi - \theta) \frac{\partial \Psi}{\partial y_1} \\
 &- k_{23} \frac{1}{\beta} (1 - \phi - \theta) (\alpha - \theta) \frac{\partial \Psi}{\partial y_2} + k_{32} \theta \frac{\partial \Psi}{\partial y_2}. \tag{A13}
 \end{aligned}$$

The terms in the above expression are all proportional either to $\partial\Psi/\partial y_1$ or to $\partial\Psi/\partial y_2$. The conditions for Eq. (A13) to be valid are

$$\frac{d\phi}{dt} = -k_{12}\phi + k_{21}(1 - \phi - \theta), \quad (\text{A14})$$

$$\frac{d\theta}{dt} = k_{23} \frac{1}{\beta} (1 - \phi - \theta)(\alpha - \theta) - k_{32}\theta, \quad (\text{A15})$$

which are the macroscopic equations of the system, i.e., Eqs. (13) and (14), respectively, in the text.

Appendix B: Derivation of the equations of fluctuations by the system size expansion

Collecting the terms proportional to n_0^0 in Eq. (A10) leads to

$$\begin{aligned} \frac{\partial\Psi}{\partial t} = & k_{12} \left(\frac{\partial(y_1\Psi)}{\partial y_1} + \frac{1}{2}\phi \frac{\partial^2\Psi}{\partial y_1^2} \right) + k_{21} \left(\frac{\partial(y_1\Psi)}{\partial y_1} + \frac{\partial(y_2\Psi)}{\partial y_1} + \frac{1}{2}(1 - \phi - \theta) \frac{\partial^2\Psi}{\partial y_1^2} \right) \\ & + k_{23} \frac{1}{\beta} \left((1 - \phi - \theta) \frac{\partial(y_2\Psi)}{\partial y_2} + (\alpha - \theta) \frac{\partial(y_1\Psi)}{\partial y_2} \right) \\ & + (\alpha - \theta) \frac{\partial(y_2\Psi)}{\partial y_2} + \frac{1}{2}(1 - \phi - \theta)(\alpha - \theta) \frac{\partial^2\Psi}{\partial y_2^2}, \\ & + k_{32} \left(\frac{\partial(y_2\Psi)}{\partial y_2} + \frac{1}{2}\theta \frac{\partial^2\Psi}{\partial y_2^2} \right). \end{aligned} \quad (\text{B1})$$

This general form of the linear Fokker–Planck equation can be rewritten compactly as

$$\frac{\partial\Psi}{\partial t} = - \sum_{i,j} A_{ij} \frac{\partial}{\partial y_i} (y_j\Psi) + \frac{1}{2} \sum_{i,j} \left(B_{ij} \frac{\partial^2\Psi}{\partial y_i \partial y_j} \right), \quad (\text{B2})$$

where

$$\begin{aligned} A &= \begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix} \\ &= \begin{pmatrix} -(k_{12} + k_{21}) & -k_{21} \\ -k_{23} \frac{1}{\beta} (\theta - \alpha) & -k_{23} \frac{1}{\beta} (1 + \alpha - \phi - 2\theta) - k_{32} \end{pmatrix}, \end{aligned} \quad (\text{B3})$$

$$B = \begin{pmatrix} B_{11} & B_{12} \\ B_{21} & B_{22} \end{pmatrix} = \begin{pmatrix} k_{12}\phi + k_{21}(1 - \phi - \theta) & 0 \\ 0 & k_{23} \frac{1}{\beta} (1 - \phi - \theta)(\alpha - \theta) + k_{32}\theta \end{pmatrix}. \quad (\text{B4})$$

Multiplying Eq. (B2) with y_k , $k = 1, 2$, and integrating the resultant expressions yield the equations for the means as (see e.g. [12])

$$\frac{d}{dt} E[Y_k] = \sum_{j=1}^2 A_{kj} E[Y_j], \quad k = 1, 2, \quad (\text{B5})$$

which is Eq. (15) in the text. Similarly, multiplying Eq. (B2) with $y_i y_j$, $i, j = 1, 2$, and integrating the resultant expressions give the equations for the second moments as (see e.g. [12])

$$\frac{d}{dt} E[Y_i Y_j] = \sum_{k=1}^2 A_{ik} E[Y_k Y_j] + \sum_{k=1}^2 A_{jk} E[Y_i Y_k] + B_{ij}, \quad i, j = 1, 2, \quad (\text{B6})$$

which is Eq. (16) in the text.

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