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Modelling lumped-parameter sorption kinetics and diffusion dynamics of odour-causing VOCs to dust particles

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Abstract

An analytical algorithm is presented for fast simulation of the adsorption kinetics and diffusion dynamics of odour-causing volatile organic compounds (VOC-odour) which originate in the stored swine manure to airborne dust particles in a ventilated airspace. The model is an extension to the well-known lumped-parameter model (LPM) that incorporates a Langmuir–Hinshelwood (LH) kinetic concept dependent on VOC-odour concentration with diffusion limitation. The basic idea behind the model implementation is to couple the calculations of the two major processes in the VOC-odour/dust particle system: VOC-odour diffusion based on the homogeneous surface diffusion model (HSDM) and surface reaction based on the LH kinetics in an LPM scheme. The LPM employs Laplace transforms and gamma distributions of the rate coefficient to produce a lumped-parameter gamma model (LPGM) for kinetic equation of VOC-odour adsorption to airborne dust particles, whereas the HSDM incorporates the age and size distributions of airborne dust for evaluating the dust-borne VOC-odour dynamics. The integrate assessment of VOC-odour sorption kinetics and diffusion dynamics allows to relate the adsorption rate coefficient, reaction order, and surface effective diffusivity in a complex VOC-odour/dust particle system. The LPGM fitted well with the data obtained numerically from HSDM and successfully determined the adsorption rate coefficient and reaction order for each sorption process. © 2001 Elsevier Science Inc. All rights reserved.

Keywords: Adsorption; Airborne dust; Diffusion; Odour; VOCs

1. Introduction

Exposure assessment models are needed to predict the sorption behaviour of odour-causing volatile organic compounds (VOC-odour) with airborne dust in animal housing. Evidence has been presented that suggested that a high correlation between VOC-odour and suspended particulate matter concentrations in animal housing [1–4]. Sorption kinetics of VOCs to particulate particles has been investigated for years, however, examples of sorption systems that contain

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Glossary

C_i	VOC-odour concentration in lump i (kg m^{-3})
C_w	amount of VOC-odour adsorbed per unit mass of a dust particle at r (kg kg^{-1})
$C_{\mathrm{w_e}}$	amount adsorbed in equilibrium with the bulk VOC-odour concentration (kg kg^{-1})
$C(t)$	total VOC-odour concentration (kg m^{-3})
$C(\bar{t})$	age-averaged VOC-odour concentration (kg m^{-3})
$\bar{C}_\mathrm{w}(t)$	particle-averaged time-varying mass of VOC-odour absorbed per unit mass of dust particle (kg kg^{-1})
$c(k,0)$	initial concentration in LPGM (mg m^{-3})
$c(k,t)$	concentration of each component at various time intervals (mg m^{-3})
D_g	solute distribution parameter
D_s	surface effective diffusivity of VOC-odour in air (cm^2 s^{-1})
$D(k)$	reactant-type function
d_g	geometric mean diameter (μm)
d_p	diameter of a dust particle (μm)
$E_\mathrm{LP}(k)$	mean adsorption rate coefficient in LPGM (min^{-1})
F	dimensionless time-independent function
f_j	weight fraction of the jth fraction
$f(k)$	probability density function of gamma distribution for k
K	Freundlich capacity constant ((m^3 $\mathrm{kg}^{-1})^n$)
$K(k)$	equilibrium constant in LPGM
k	sorption rate coefficient (min^{-1})
k_0	zero-order reaction rate constant (mg $\mathrm{m}^{-3})^{-1}$
k_1	first-order reaction rate constant (min^{-1})
k_i	sorption rate coefficient in lump i (min^{-1})
$\boldsymbol{L}(\cdot)$	Laplace transform operator
$LN(\cdot)$	log–normal distribution
M	total mass of dust particle (kg)
N	total number of reactant types or lumps
n	Freundlich intensity constant
$P(d_\mathrm{p})$	Log–normal probability density function for particle size d_p
Q	dust particle exchange rate (kg s^{-1})
$\dot{q}$	VOC-odour emission rate (m^3 s^{-1})
r_p	radius of a dust particle (μm)
$sd_{LP}(k)$	standard deviation of rate coefficient in LPGM
t	residence time of the dust particle in a ventilated airspace (min)
$\bar{t}$	mean age of dust particle in a ventilated airspace (min)
$U(t)$	dimensionless concentration
$u(t)$	a time-like variable
$\dot{V}$	ventilation rate (m^3 s^{-1})

Greek letters

α	shape parameter in gamma distribution
$1/\beta$	scale parameter in gamma distribution
$\Gamma(\cdot)$	gamma function
μ	shape parameter in LPGM

$1/v$	scale parameter in LPGM
σ_g	geometric standard deviation (μm)
ρ_p	dust particle density (kg m^3)
η	effectiveness factor
η_j	effectiveness factor of the *j*th fraction
Φ	diffusion length modulus
Φ_j	diffusion length modulus of the *j*th fraction

Abbreviation

DLM	diffusion length modulus
HSDM	homogeneous surface diffusion model
LH	Langmuir–Hinshelwood
LP	lumped-parameter
LPGM	lumped-parameter gamma model
LPM	lumped-parameter model
VOC	volatile organic compound

multiple VOC-odour sorption to dust particles are rare. Because of the number of complex processes involved, it is difficult to elucidate the entire process quantitatively.

Sorption reactions often affect the movement and fate of VOC-odour in a dusty livestock environment (Fig. 1(A)) [5]. A theoretical study presented by Liao et al. [5] suggested that the sorption of VOC-odour on airborne dust could be considered to be dominantly controlled by the behaviour of the interactions among VOC-odour, airborne dust, and dust-borne odour. The mechanistic function of airborne dust in the uptake of VOC-odour may be partitioning and/or adsorption (Fig. 1(B)).

The heterogeneous and variable nature of VOC-odour and airborne dust complicates the evaluation of possible types of sorbate/sorbent interactions for a given dusty environment and, hence, limits the predictive application of adsorption or absorption theories. Quantitative modelling of mass transfer and diffusion-based dynamics has been only partially successful in explaining the removal mechanisms in a ventilated airspace such as turbulent diffusive deposition, gravitational sedimentation, and airflow, yet the irreversibility, slow, reversible, and nonequilibrium behaviour can only be explained via the kinetic point of view. The mass transfer and diffusion-based models, however, have been reviewed elsewhere.

The basic concept of *lumping* is not only to reduce the number of variables by grouping them via a linear or nonlinear function but also to define a coarse parameter that can describe the overall phenomenon of a group of parameters in a complex system. The lumped-parameter (LP) kinetics theory was first introduced by Aris and Gavalas [6] and initiated by Wei and Kuo [7] who gave a lumping analysis of unimolecular reaction systems where the lumped species were certain linear combinations of the original ones. Chou and Ho [8,9] reported the theoretical analysis of LP kinetics theory based on the Langmuir–Hinshelwood (LH) kinetic model. The LP concept has also been used in modelling the airborne dust dynamics in a ventilated airspace [10,11] and in quantifying the thermal stratification in aquaculture ponds [12].

Although some theoretical or empirical LP studies have been reported by many researchers such as Chou and Ho [8,9], Gianni and Ocone [13], Aris [14], Li and Rabitz [15], Toth et al. [16], and among others in the last 20 years, a consistent way of analysing the experimental data or some case studies is not available. Therefore, it is difficult to test the applicability or evaluate an LP kinetic model based on experimental data. To overcome this disadvantage, a homogeneous

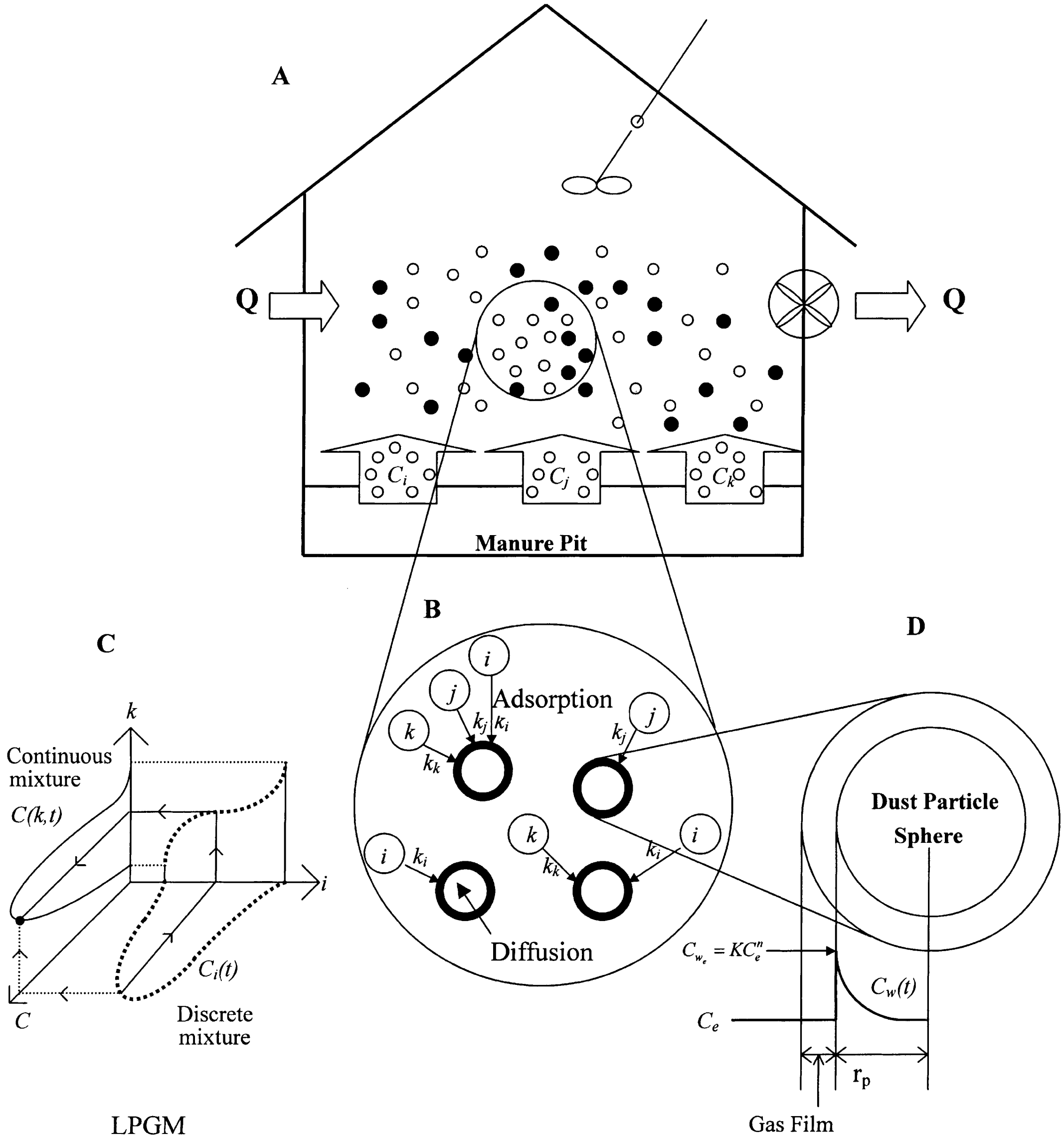

Fig. 1. Schematic illustration of: (A) VOC-odour (○) and airborne dust (●) mixture in a ventilated animal housing; (B) adsorption kinetic and diffusion dynamic behaviours between VOC-odour and airborne dust; (C) an LPGM showing that a discrete and a continuous mixture can be one-to-one mapped in an LP scheme; (D) an HSDM with a nonlinear sorption.

surface diffusion model (HSDM) describing the VOC-odour adsorption on the surface of airborne dust was introduced in this study. Based on the characteristic properties of the lumped-parameter model (LPM), a simple simulation of VOC-odour adsorption on airborne dust in a dusty livestock environment was then constructed and evaluated.

Relatively little research has been carried out on sorption kinetics by undertaking the diffusion dynamics with the objective of proposing a model that integrates both diffusion-based dynamic and nonlinear kinetic reaction models in a ventilated airspace with aerosol-scale heterogeneity. To address this model, an LP nonlinear kinetics model based on the LH kinetic model is introduced and evaluated.

As mass transport, adsorption and reaction all occur in series, the rate of reaction observed is essentially that of the slowest step. The rate of each step is then equal to that of the rate-controlling step. By setting these rates equal to one another, it is possible to combine the corresponding equations in such a way as to eliminate solid phase and interfacial concentrations, parameters that are difficult to evaluate experimentally. This approach referred to as the LH method of rate analysis [17] yields a rate expression given solely in terms of measurable parameters (i.e., solution phase concentrations, equilibrium constants, and rate constants). The observed rate data can be compared with the expressions derived for each potential rate-controlling step to determine which expression is the most appropriate.

It is our intention to assess or predict the LP sorption kinetic property of VOC-odour in a dusty environment. To determine the analytical solution for the LPM of VOC-odour sorption on airborne dust, several unique techniques including gamma distribution, and Laplace transform were employed. Using these unique tools, it was possible to construct an LPM describing the kinetic behaviour of multi-VOC-odour sorption on ambient aerosol in ventilated animal housing. The LPM, hence, provides valuable information about the overall kinetic behaviour of VOC-odour with airborne dust and could serve as a simulation tool to investigate the transport of VOC-odour in ventilated animal housing.

The aim of this research was to quantify adsorption rates of VOC-odour on airborne dust that were subjected to both viewpoints of dynamics and kinetics and to evaluate the effects of reaction behaviour and diffusion mechanism on adsorption rates. This paper describes the theoretical results from an HSDM for the adsorption kinetics of VOC-odour in a dusty environment and the development of a nonlinear kinetic model based on the concept of the LPM.

2. LP sorption kinetics

2.1. LP kinetic model

It is recognized that VOC-odours contain many different sorption components. As a result, it is unlikely that the fitting parameters to any kind of kinetic model can correspond to the actual rates for the mixture of VOC-odours. Given a range of dust particle sizes, it is also unlikely that the assumption of a single mass transfer coefficient can be expected to provide an accurate representation of the distribution of physical constraints on VOC-odour adsorption. This might be resolved by the addition of more compartments or lumps with differing rate limitations. Each lump that was added would introduce more adjustable model parameters to reflect the characteristics of a lumped mixture.

A model thus can be obtained by generalizing the LP concept to consider a continuum of compartments ordered by their sorption rate constants. For such an LPM, if the total mass of VOC-odours emitted from stored manure pit is denoted by $f(k)$, then the likelihood that a randomly selected molecule is in a lump with the sorption rate coefficient k, where

$$\int_0^\infty f(k)\,\mathrm{d}k = 1.$$

Mathematically, $f(k)$ is the probability density function for the sorption rate coefficient k. Conceptually, $f(k)$ could be obtained by taking all of mass and sorting each molecule by the sorption rate coefficient k of its lump and forming the resulting histogram.

A parsimonious representation of the sorption process can be obtained by assuming that $f(k)$ can be described by a simple unimodel and continuous mathematical function. A convenient and flexible one is the gamma density function. The gamma distribution is a distribution of Pearson's Type III in statistics. The unique feature of the gamma distribution is that one end of the distribution is bound to a fixed value, whereas the other end is distributed over a large scale of the variate. The overall shape of the gamma distribution is not balanced as a normal distribution.

As VOC-odours would not behave similarly, their distribution of affinities to airborne dust is not expected to follow a normal distribution. The gamma distribution, therefore, has a greater chance to describe the kinetic behaviour of VOC-odour species than that of the normal distribution. The other reason to utilize the gamma distribution is that this approach may reduce the mathematical terms in the analytical solution.

Therefore, we try to use lumped-parameter gamma model (LPGM) to describe the sorption kinetics of VOC-odours to airborne dust. Several mathematical techniques such as Laplace transform, gamma function, and gamma distribution were employed to solve the complex equations. The presented analytical solution demonstrates that it is possible to construct a systematic way of lumping parameters, and the kinetic properties of an LPM can be analysed.

The gamma density function may be written as

$$f(k;\alpha,\beta) = \frac{1}{\Gamma(\alpha)}\beta^{\alpha}k^{\alpha-1}\mathrm{e}^{-\beta k}, \quad \alpha > 0,\ \beta > 0,\ k > 0. \tag{1}$$

The normalization factor

$$\Gamma(\alpha) = \int_0^{\infty} x^{\alpha-1}\mathrm{e}^{-x}\,\mathrm{d}x, \quad \alpha > 0, \tag{2}$$

is the gamma function, where α and $1/\beta$ are the two parameters of the gamma distribution. Often α is called the shape parameter and $1/\beta$ is called the scale parameter. The mean and variance of the sorption rates are $E(k) = \alpha/\beta$ and $\mathrm{Var}(k) = \alpha/\beta^2$, respectively. If α/β is held constant, then as α approaches infinity the gamma distribution approaches Gaussian distribution, the variance of which decreases as α increases. The gamma distribution also satisfies the physical requirement that sorption rate coefficient must be nonnegative. The mean and variance of each gamma distribution govern the characteristic properties of a lumped mixture.

In a complex system such as a dusty animal housing that involves an airborne dust distribution and multiple VOC-odour species emitted from stored manure pit, a nonlinear kinetic model has a better chance to describe the kinetic behaviour than the conventional zero-, first-, or pseudo-first-order kinetic models. We use an LH sorption model to describe the nonlinear kinetic behaviour in a dusty environment. For an LH sorption system where a VOC-odour species (A) adsorbs onto an airborne dust, we assume that it follows two major mechanisms and a transition. Mathematically, the expression is [16],

$$\frac{\mathrm{d}C_A}{\mathrm{d}t} = -k_1 C_A\left(\frac{1}{1 + k_0 C_A}\right), \tag{3}$$

where k_0 is the zero-order reaction rate constant of the LH model ($(\mathrm{mg\ l^{-1}})^{-1}$); k_1 is the first-order reaction rate constant of the LH model (min^{-1}); and C_A is the concentration of VOC-odour species A ($\mathrm{mg\ l^{-1}}$).

2.2. Analytical solutions for LPGM

A discrete system $\sum C_i(t)$ indicating a discrete mixture of VOC-odours in a dusty environment is characterized by three properties: i (type of reactant or lump i), k_i, and C_i (Figs. 1(B) and (C)).

As was shown in Fig. 1(C), a discrete and a continuous mixture can be one-to-one mapped by using an LP scheme as [9],

$$C(t) = \sum_{i=1}^{n} C_i(t) \approx \int_0^\infty c(k,t)D(k)\,\mathrm{d}k, \tag{4}$$

where $C(t)$ is the total VOC-odour concentration of the lumping system; $C_i(t)$ is the concentration of each individual VOC-odour component; $c(k,t)$ is the concentration of each component at various time intervals; $D(k)$ is a reactant-type function; and k is the rate coefficient for each component.

The reactant-type function $D(k)$, the initial concentration $c(k,0)$, and the equilibrium constant $K(k)$ can be described by a gamma distribution, and they are a function of the rate coefficient k [9],

$$D(k) = qk^{\eta}\mathrm{e}^{-\zeta k}, \quad c(k,0) = pk^{\alpha}\mathrm{e}^{-\beta k}, \quad K(k) = \bar{K}k^{\delta}\mathrm{e}^{-\tau k}. \tag{5}$$

and follows the constraints of

$$\eta + 1 > 0, \quad \alpha + \eta > 0, \quad \alpha + \eta + \delta + 1 > 0, \quad \zeta > 0, \quad \beta + \zeta > 0, \quad \beta + \zeta + \tau > 0,$$

to assure that the integrals converge.

For this adsorption rate distribution, the sorption rate from bulk VOC-odour gas can be computed analytically. For the VOC-odour species in lumps with adsorption rate k, the fraction remaining after t, the residence time of dust particles in a ventilated airspace, is simply $\exp(-kt)$. Thus for total initial concentration $c(k,0)$, the concentration remaining after it is adsorbed to dust particle after time t is

$$C(t) = \int_0^\infty c(k,0)D(k)\mathrm{e}^{-kt}\,\mathrm{d}k. \tag{6}$$

Hence, $C(\cdot)$ represents the Laplace transform of $c(k,0)D(k)$ and can be viewed as a function of t. Let $f(k) \equiv c(k,0)D(k)$ be a given function that is defined from the positive values of k, the Laplace operator $\boldsymbol{L}(\cdot)$ has the following effort:

$$\boldsymbol{L}(f(k)) = \int_0^\infty \mathrm{e}^{-tk} f(k)\,\mathrm{d}k = C(t). \tag{7}$$

The initial concentration $C(0)$ in Eq. (4) can be calculated as,

$$\begin{aligned} C(0) &= \int_0^\infty c(k,0)D(k)\,\mathrm{d}k = \int_0^\infty (pk^{\alpha}\mathrm{e}^{-\beta k})(qk^{\eta}\mathrm{e}^{-\zeta k})\,\mathrm{d}k \\ &= pq\int_0^\infty k^{(\alpha+\eta)}\mathrm{e}^{-(\beta+\zeta)k}\,\mathrm{d}k \\ &= pq\frac{\Gamma(1+\alpha+\eta)}{(\beta+\zeta)^{(1+\alpha+\eta)}}. \end{aligned} \tag{8}$$

After some mathematical manipulation based on the Laplace transform technique, we obtain $C(t)$ in Eq. (6) as,

$$C(t) = pq\frac{\Gamma(1+\alpha+\eta)}{(\beta+\zeta+t)^{(1+\alpha+\eta)}}. \tag{9}$$

Defining a dimensionless concentration $U(t) = C(t)/C(0)$ and substituting Eqs. (5), (8) and (9) into Eq. (6) yields

$$U(t) \equiv \frac{C(t)}{C(0)} = \left(\frac{v}{v+t}\right)^{\mu}, \tag{10}$$

where

$$\mu = 1 + \alpha + \eta, \quad v = \beta + \zeta. \tag{11}$$

Let N be the total number of reactant types or lumps,

$$N = \int_0^{\infty} D(k)\,\mathrm{d}k = \int_0^{\infty} qk^{\eta}\mathrm{e}^{-\zeta k}\,\mathrm{d}k = q\frac{\Gamma(1+\eta)}{\zeta^{(1+\eta)}}. \tag{12}$$

Therefore, we obtain q for $D(k)$ as,

$$q = \frac{N\zeta^{(1+\eta)}}{\Gamma(1+\eta)}. \tag{13}$$

Eqs. (9) and (13) can be used to obtain p for $c(k,0)$ as,

$$p = \frac{C(0)v^{\mu}}{q\Gamma(\mu)} = \frac{C(0)v^{\mu}\Gamma(1+\eta)}{N\zeta^{(1+\eta)}\Gamma(\mu)}. \tag{14}$$

2.3. Overall reaction order and rate coefficient

By taking the derivative of $U(t), \mathrm{d}U(t)/\mathrm{d}(t)$ can be obtained as,

$$\begin{aligned}\frac{\mathrm{d}U(t)}{\mathrm{d}t} &= \mu\left(\frac{v}{v+t}\right)^{\mu-1}\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{v}{v+t}\right)\\ &= \mu\left(\frac{v}{v+t}\right)^{\mu-1}\frac{-v}{[v+t]^2}\\ &= -\mu v v^{(\mu-1)}[v+t]^{1-\mu-2}\\ &= -\frac{\mu}{v}v^{\mu+1}[v+t]^{-(1+\mu)}\\ &= -\frac{\mu}{v}\left(\frac{v}{v+t}\right)^{1+\mu}\\ &= -\frac{\mu}{v}U^{(1+1/\mu)}(t).\end{aligned} \tag{15}$$

We consider a general case in which a time-like variable $u(t)$ is introduced as

$$u(t) \equiv \int F(t')\,\mathrm{d}t', \tag{16}$$

where F is a dimensionless time-dependent function.

We now wish to express $\mathrm{d}u(t)/\mathrm{d}t$ in terms of $U(t)$. Chou and Ho [9] calculated the solution of nonlinear LH kinetics in that $\mathrm{d}u(t)/\mathrm{d}t$ is obtained as,

$$\frac{\mathrm{d}u(t)}{\mathrm{d}t} = \frac{1}{1 + \int_0^{\infty} K(k)c(k,0)D(k)\mathrm{e}^{-ku(t)}\,\mathrm{d}k}. \tag{17}$$

Incorporating $\mathrm{d}u(t)/\mathrm{d}t$ into Eq. (15) yields

$$\frac{\mathrm{d}U(t)}{\mathrm{d}t} = -\frac{\mu}{v}U^{(1+1/\mu)}(t)\frac{\mathrm{d}U(t)}{\mathrm{d}t}, \tag{18}$$

by substituting Eq. (16) into Eq. (17), the LPG–LH kinetic model can then be expressed as,

$$\frac{\mathrm{d}U(t)}{\mathrm{d}t} = -\frac{\mu}{v}U^{(1+1/\mu)}\left(\frac{1}{1+\lambda(U^{-1/\mu}+(\tau/v))^{-(\mu+\delta)}}\right), \tag{19}$$

where

$$\lambda = pqK\frac{\Gamma(\mu+\delta)}{v^{\mu+\delta}}. \tag{20}$$

In comparison with Eq. (3), the adsorption rate coefficient of the LPG–LH kinetic model expressed in Eq. (19) is $-(\mu/v)$ and the reaction order of the LPGM is $(1+1/\mu)$.

Obviously, Eq. (15) is a special case for the system which contained less reactive species (i.e., $c(k,0)$ and $D(k)$ both approach zero as k approaches infinity, and $\alpha+\eta$ approaches zero), then μ is approaching 1; therefore the reaction order $(1+1/\mu)$ becomes 2. In view of Eqs. (17) and (18), when t is approximately equal to zero (i.e., at the beginning of the reaction), we have

$$\frac{\mathrm{d}u}{\mathrm{d}t} \approx \left\{1+\lambda[1+(\tau/v)]^{-(\mu+\delta)}\right\}^{-1} \equiv \Psi < 1, \tag{21}$$

then

$$\frac{\mathrm{d}U}{\mathrm{d}t} \approx -\frac{\mu}{v}\Psi U^{(1+1/\mu)}. \tag{22}$$

For a given gamma distribution, the mean and variance represent the characteristics of the distribution, i.e., they constitute the characteristics of an LP mixture. The rate coefficient, k, of each component in the LPM actually constitutes the mean and variance since k is in the three gamma distributions, $D(k)$, $c(k,0)$, and $K(k)$.

The following explanation reflects this fact. Eqs. (6) and (7) show

$$f(k) = c(k,0)D(k) = pqk^{\alpha+\eta}\mathrm{e}^{-(\beta+\zeta)k},$$

in a specific term and in view of Eqs. (1) and (11), the above expression can be rewritten as

$$f(k;\mu,v) = \frac{1}{\Gamma(\mu)}v^{\mu}k^{\mu-1}\mathrm{e}^{-vk}, \tag{23}$$

with the gamma model, the mean and standard deviations of the adsorption rate coefficients in an LPGM are

$$E_{\mathrm{LP}}(k) = \frac{\mu}{v}, \quad sd_{\mathrm{LP}}(k) = \frac{\mu^{1/2}}{v}, \tag{24}$$

in that μ is the shape parameter and $1/v$ is the scale parameter in the LPGM.

3. HSDM-based diffusion dynamics

3.1. General model descriptions

The most common sorption rate model formulations assume that the sorption process is limited by diffusion. The diffusion process can be modelled by Fick's law for a well-defined geometry or by a first-order mass transfer approximation. Diffusion models based on Fick's law often assume that the sorption process is controlled by an HSDM into a well-defined geometry, usually a sphere (Fig. 1(D)).

HSDM is envisioned to occur along intraparticle pore walls, the surface diffusion coefficient being dependent upon the solid phase solute concentration. The surface diffusion coefficient is often assumed to be constant for the sake of simplicity or because of the lack of information about its concentration dependence.

A general model based on Fick's law should incorporate the major features not only allowing for multiple particle size distributions of airborne dust with different physical properties and sorption parameters for each distribution, but also allowing for an instantaneous equilibrium fraction for each particle size distribution.

3.2. Dust particle phase material balance

If the initial conditions are such that the dust-borne odour can be viewed as functions of time and of the spherical space coordinate, the phenomenon of surface diffusion of the VOC-odour concentration on a single spherical dust particle can be obtained from the mass conservation description as (Fig. 1(D)),

$$\frac{\partial C_{\mathrm{w}}}{\partial t} = D_{\mathrm{s}}\left(\frac{\partial^2 C_{\mathrm{w}}}{\partial r^2} + \frac{2}{r}\frac{\partial C_{\mathrm{w}}}{\partial r}\right) \tag{25}$$

subject to the following initial and boundary conditions:

$$C_{\mathrm{w}} = 0, \quad t = 0, \qquad 0 \leqslant r \leqslant r_{\mathrm{p}},$$

$$\frac{\partial C_{\mathrm{w}}}{\partial r} = 0, \quad t \geqslant 0, \qquad r = 0,$$

$$C_{\mathrm{w}} = C_{\mathrm{w_e}}, \quad t \leqslant 0, \qquad r = r_{\mathrm{p}},$$

where t is the residence time of the dust particles in a ventilated airspace (min), r is a position variable representing the distance from the centre of the particle (μm), C_{w} is the amount of VOC-odour adsorbed per unit mass of a dust particle at r (kg kg^{-1}), D_{s} is the surface effective diffusivity of VOC-odour in air (cm^2 s^{-1}), r_{p} is the radius of a dust particle (μm), and $C_{\mathrm{w_e}}$ is the amount adsorbed in equilibrium with the bulk odour concentration (kg kg^{-1}).

The analytical solution of Eq. (25), i.e., the total amount of VOC-odour adsorbed on the surface of a dust sphere is given by [18],

$$\frac{\bar{C}_{\mathrm{w}}(t)}{C_{\mathrm{w_e}}} = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(\frac{-D_{\mathrm{s}}n^2\pi^2 t}{r_{\mathrm{p}}^2}\right), \tag{26}$$

where $\bar{C}_{\mathrm{w}}(t)$ is the particle-averaged time-varying mass of VOC-odour absorbed per unit mass of dust particle (kg kg^{-1}).

3.3. Age distribution of airborne dust

Consider now a ventilated animal unit, each air entering and VOC-odour emitting from stored manure then into the ventilated airspace will spend some time in the airspace before leaving. It is obvious that the exit time of one dust-borne VOC-odour is different from that of another not only because of the circulation of airflow but also because of the internal mixing in each airspace.

Therefore, there is an exit age distribution in the leaving airflow. The exit age distribution of dust particles in a completely mixed flow reactor is [17],

$$E(t) = \frac{1}{\bar{t}} \exp\left(-\frac{t}{\bar{t}}\right), \tag{27}$$

where $\bar{t} \equiv M/Q$ is the mean holding time or mean age of dust particles in a ventilated airspace, in which M is the total mass of dust particles (kg) and Q is the dust particle exchange rate (kg s^{-1}).

Incorporating the age distribution function into Eq. (26), the age- and particle-averaged amount of dust-borne VOC-odour is given as,

$$\begin{aligned}\frac{\bar{C}_{\mathrm{w}}(\bar{t})}{C_{\mathrm{w_e}}} &= \int_0^\infty \left[1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(\frac{-D_{\mathrm{s}} n^2 \pi^2 t}{r_{\mathrm{p}}^2}\right)\right] E(t)\,\mathrm{d}t \\ &= 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\frac{1}{1 + (n^2\pi^2 D_{\mathrm{s}}\bar{t}/r_{\mathrm{p}}^2)}.\end{aligned} \tag{28}$$

Here we define an effectiveness factor (η) as,

$$\eta \equiv \frac{\bar{C}_{\mathrm{w}}(\bar{t})}{C_{\mathrm{w_e}}}. \tag{29}$$

Effectiveness factor may be expressed as a function of a dimensionless parameter (Φ) as $\eta(\Phi)$, in which Φ is defined as [19],

$$\Phi \equiv \frac{r_{\mathrm{p}}}{\sqrt{D_{\mathrm{s}}\bar{t}}}, \tag{30}$$

and is referred to as a diffusion length modulus (DLM). Therefore, Eq. (28) becomes,

$$\eta(\Phi) = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\frac{\Phi^2}{\Phi^2 + n^2\pi^2}. \tag{31}$$

After some mathematical manipulations by using the following identified mathematical formulas [20]:

$$\coth \Phi = \frac{1}{\Phi} + 2\Phi \sum_{n=1}^{\infty}\frac{1}{n^2\pi^2 + \Phi^2},$$

$$\sum_{n=1}^{\infty}\frac{1}{n^2} = \frac{\pi^2}{6},$$

Eq. (31) can be converted to a closed-form equation as,

$$\eta(\Phi) = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\frac{\Phi^2}{\Phi^2 + n^2\pi^2} = \frac{3}{\Phi^2}(\Phi \coth \Phi - 1). \tag{32}$$

Eq. (32) avoids using a computer for iterative summation of the terms in series shown in Eq. (31) with a criterion for convergence.

3.4. Size distribution of airborne dust

Airborne dust particles in animal housing are not usually homogeneous in size [11,21]. Sieve analysis is often performed to determine a particle size distribution in terms of various size fractions [22]. Incorporating particle size distribution by applying the model to each dust particle size fraction, the overall effectiveness factor becomes,

$$\eta = \frac{C_{\mathrm{w}}(\bar{t})}{C_{\mathrm{w_e}}} = \sum_{j=1}^{N} \eta_j(\Phi_j) f_j, \tag{33}$$

where N is the number of size fraction, η_j is the effectiveness factor of the jth fraction, Φ_j is the DLM of the jth fraction, and f_j is the weight fraction of the jth fraction.

Log–normal distributions have been widely used in characterizing aerosol particle size. The mathematical form of a log–normal probability density function is given by [23],

$$\mathrm{LN}(d_{\mathrm{g}}, \sigma_{\mathrm{g}}) \equiv p(d_{\mathrm{p}}) = \frac{1}{\sqrt{2\pi} d_{\mathrm{p}} \ln \sigma_{\mathrm{g}}} \exp\left(-\frac{(\ln d_{\mathrm{p}} - \ln d_{\mathrm{g}})^2}{2(\ln \sigma_{\mathrm{g}})^2} \right), \tag{34}$$

where $\mathrm{LN}(d_{\mathrm{g}}, \sigma_{\mathrm{g}})$ is a log–normal distribution in that d_{g} is the geometric mean diameter (μm), σ_{g} is the geometric standard deviation (μm); and d_{p} is the diameter of a dust particle (μm). These parameters are varied to correspond to typical aerosol profiles found in animal housing.

Consequently, the size-averaged effectiveness factor has the form,

$$\eta(\Phi) = \frac{\bar{C}_{\mathrm{w}}(\bar{t})}{C_{\mathrm{w_e}}} = \int_0^{\infty} \eta\left[\Phi(d_{\mathrm{p}})\right] p(d_{\mathrm{p}})\, \mathrm{d}d_{\mathrm{p}}. \tag{35}$$

There is no known analytical solution for Eq (35).

3.5. Adsorption equilibrium

The adsorption reaction of the equilibrium VOC-odour concentration at the outer surface of a dust particle is described by means of the Freundlich model,

$$C_{\mathrm{w_e}} = K C_{\mathrm{e}}^{n}(\bar{t}), \quad 0 < n \leqslant 1, \tag{36}$$

where K is the Freundlich capacity constant ($(\mathrm{m}^3\ \mathrm{kg}^{-1})^n$) and n is the Freundlich intensity constant and can be determined by the regression analysis of the isotherm data [24]. The Freundlich model is widely used to describe the sorption equilibrium in environmental systems with heterogeneous surfaces. Although, airborne dust is superficially assumed as homogeneous materials, significant heterogeneity likely exists. Additionally, over time, airborne dust surface slowly reacted by means of physicochemical or biological behaviours, which may further contribute to surface heterogeneity.

In addition, if we assume that all dust particles or sorption lumps exhibit the same nonlinearity and only vary in their sorption maximum, the nonlinear equilibrium relationship can also be developed. Under this circumstance, in estimating the Freundlich model parameters for sorption experiments, one often found that while the capacity constants varied by several orders of magnitude, only a small variation in Freundlich exponents was observed.

3.6. Nondimensionalization of model equations

When applying a steady-state material balance on the bulk VOC-odour phase and incorporating with Eq. (33), the following expression can be obtained:

$$\dot{q}(C(0) - C(\bar{t})) = C_{\mathrm{w_e}} \eta(\Phi) Q, \tag{37}$$

in which $\dot{q}$ is the VOC-odour emission rate ($\mathrm{m}^3\ \mathrm{s}^{-1}$), $C(0)$ is the initial VOC-odour concentration ($\mathrm{kg\ m}^{-3}$), $C(\bar{t})$ is the exhausted VOC-odour concentration ($\mathrm{kg\ m}^{-3}$), $Q = \dot{V}\rho_{\mathrm{p}}$ where $\dot{V}$ is the ventilation rate ($\mathrm{m}^3\ \mathrm{s}^{-1}$), ρ_p is the dust particle density ($\mathrm{kg\ m}^{-3}$). Combining Eqs. (36) and (37) and introducing two dimensionless variables

$$U(\bar{t}) \equiv \frac{C(\bar{t})}{C(0)}, \quad D_\mathrm{g} \equiv \frac{QK}{\dot{q}C(0)^{1-n}}, \tag{38}$$

yields a dimensionless system equation in a mass transfer-controlled regime (i.e., $C(\bar{t}) \approx C_\mathrm{e}(\bar{t})$),

$$U(\bar{t}) = 1 - D_\mathrm{g} U^n(\bar{t})\eta(\Phi), \tag{39}$$

where D_g is referred to as a solute distribution parameter representing the ratio of the distribution of VOC-odour between the gas and solid phases.

Hence, HSDM equation for $U\bar{t}$ becomes,

$$\begin{aligned} U(\bar{t}) &= 1 - \frac{QK}{\dot{q}C(0)^{1-n}} U^n(\bar{t}) \int_0^\infty \eta(\Phi(d_\mathrm{p}))p(d_\mathrm{p})\ \mathrm{d}(d_\mathrm{p}), \\ &= 1 - \frac{QK}{\dot{q}C(0)^{1-n}} U^n(\bar{t}) \int_0^\infty \frac{3}{\Phi^2(d_\mathrm{p})}(\Phi(d_\mathrm{p}) \coth \Phi(d_\mathrm{p}) - 1)p(d_\mathrm{p})\ \mathrm{d}(d_\mathrm{p}), \end{aligned} \tag{40}$$

where $\Phi(d_\mathrm{p}) = d_\mathrm{p}/\sqrt{D_\mathrm{s}\bar{t}}$.

Here we also consider the mean holding time, $\bar{t}$, as the time unit in LPGM, therefore, Eqs. (10) and (40) together constitute an expression representing the LPGM-based sorption kinetics and HSDM-based dynamics of VOC-odour in a dusty livestock environment. In the present study, we treat the numerical results obtained from Eq. (40) as the experimental data. Eq. (10) can then be fitted and tested against experimental data. By writing Eq. (10) as

$$\ln U(t) = -\mu \ln\left(1 + \frac{t}{v}\right), \tag{41}$$

parameter estimation of μ and v can be formulated as a nonlinear regression problem. A conceptual representation of the relationship between LPGM and HSDM is illustrated in Fig. 2. Fig. 2 also gives the algorithm for using this integrated concept to calculate the adsorption rate coefficient and reaction order for each experiment data set.

4. Model applications

4.1. Input parameters

A typical pig unit measuring 6 m × 2.5 m × 2.4 m with a totally slatted floor is chosen for illustrative purpose of model applications. This unit has one negative pressure ventilation system of one high end-wall exhaust fan with a continuous slot inlet. The body weight of each pig is estimated to be 70 kg.

Two different dust particle size ranges were considered accounting for a sample of airborne dust produced by particle sources found in animal housing: 0.5–5 and 0.52–21.3 μm as measured, respectively, in a swine growing housing [22] and a swine nursery [25]. Two different log–normal dust particle size distributions thus were used based on the measurements: $\mathrm{LN}(2, 1.65)$, a 2 μm gmd with a gsd of 1.65; and $\mathrm{LN}(8, 3)$, an 8 μm gmd of 3 gsd. Base value of the surface effective diffusivity (D_s) is taken from the mean order of magnitude of three intensive VOC-odours found in confined animal buildings (at a temperature of 25°C and a moisture content of swine manure 80% (v/v)): *p*-cresol ($3.89 \times 10^{-6}\ \mathrm{cm}^2\ \mathrm{s}^{-1}$), toluene ($1.05 \times 10^{-5}\ \mathrm{cm}^2\ \mathrm{s}^{-1}$), and *p*-xylene ($6.90 \times 10^{-6}\ \mathrm{cm}^2\ \mathrm{s}^{-1}$) [26]; the resulting value is $7.12 \times 10^{-6}\ \mathrm{cm}^2\ \mathrm{s}^{-1}$.

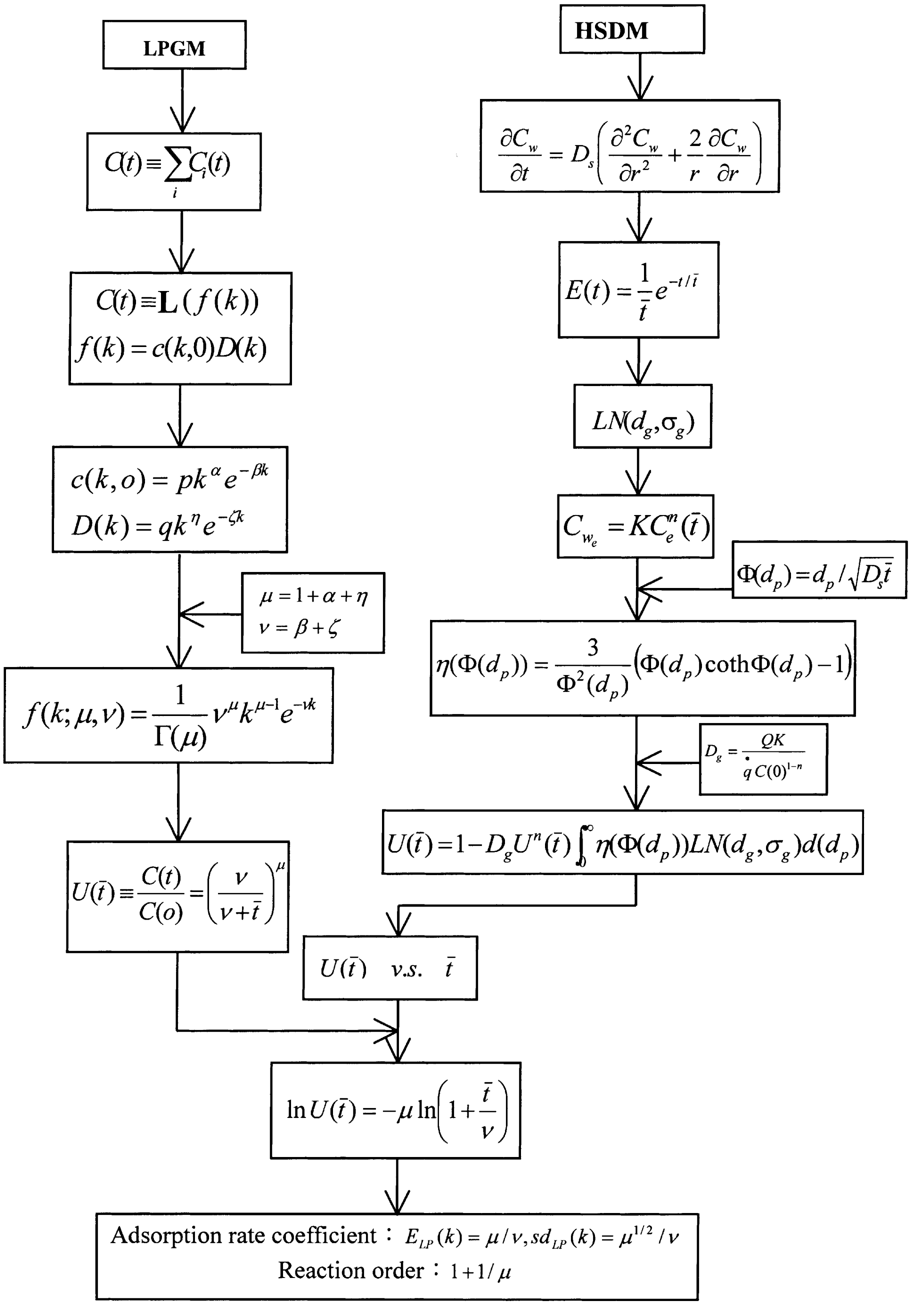

Fig. 2. A conceptual algorithm shows a numerical simulation procedure to predict adsorption rate coefficient and reaction order for VOC-odour adsorption to airborne dust by fitting LPGM to HSDM.

In order to assess the utility of the models, independent simulations were conducted in which the operating variables such as D_g and D_s were varied over a wide range of values by changing the ventilation rate ($\dot{V}$), adsorption capacity (K, n), and VOC-odour emission rate ($\dot{q}$), etc. The numerical integration scheme used to solve HSDM is a subroutine DQDAGI, whereas the iterative, nonlinear, least-squares curve-fitting technique used in LPGM is based on a subroutine DUNLSF using a modified Levenberg–Marquardt algorithm with a finite difference Jacobian, both are provided by IMSL Subroutines Library [27] and done in double precision with FORTRAN 90.

4.2. Sensitivity analysis of HSDM

A sensitivity analysis of HSDM in changes to particle size distribution ($\mathrm{LN}(d_g, \sigma_g)$), solute distribution parameter (D_g), and surface effective diffusivity (D_s) is shown in Figs. 3(a) and (b). Fig. 3(a) shows that the relative VOC-odour concentration as a function of the mean age of airborne dust varied with wide ranges of $\mathrm{LN}(d_g, \sigma_g)$ and D_g at the constant $D_s = 1.0 \times 10^{-6}$ cm^2 s^{-1}. Reducing d_g and σ_g in log–normal distribution produces moderate variation in adsorption profiles (Fig. 3(a)). In view of Eq. (30), reducing the mean particle size by one order of magnitude reduces the required mean age by two orders of magnitude to achieve approximately the same exhaust air quality where square of dust particle radius and mean age are directly proportional.

Fig. 3(a) also reveals that at the same mean age, the narrower the dust particle size distribution the lower the VOC-odour concentration. When the mean age tends to infinity, the exhausted VOC-odour concentration converges to a constant value indicating that dust particles become fully saturated with bulk VOC-odour as the same age of airborne dust reaches infinity (Fig. 3(a)).

The consideration of size distribution is important to the study of exposure dose assessment due to its sensitivity on the size of the inhaled particle carrying VOC-odour. The most important implication of the changes in particle size distributions will have two effects. First, the changes in sizes will affect the deposition of the particles onto the surface of animal housing and thus affect the amount of dust-borne odour products available for inhalation. Second, the changes in sizes will alter the particles' deposit within the respiratory tract. If the number of particles is relatively small, then the adsorption is low and the dominant contribution to the exposure dose for workers and animals is from the fine dust.

Figs. 3(a) and (b) indicate that the removal rate of VOC-odour concentration can only be increased by increasing D_g, i.e., by increasing airborne dust exchange rate (Q). By the definition of D_g in Eq. (38) also reveals that airborne dust with the favourable Freundlich exponential parameter (n) in the range of $0 < n \times 1$ will yield the lowest VOC-odour concentration in the exhaust air. As n decreases, VOC-odour adsorption to the airborne dust surface becomes more important.

Fig. 3(b) shows a sensitivity of HSDM to changes in different ranges of D_g, D_s, and $\mathrm{LN}(d_g, \sigma_g)$. At the constant D_g and $\mathrm{LN}(d_g, \sigma_g)$, a decrease in D_s by several orders of magnitude is equivalent to

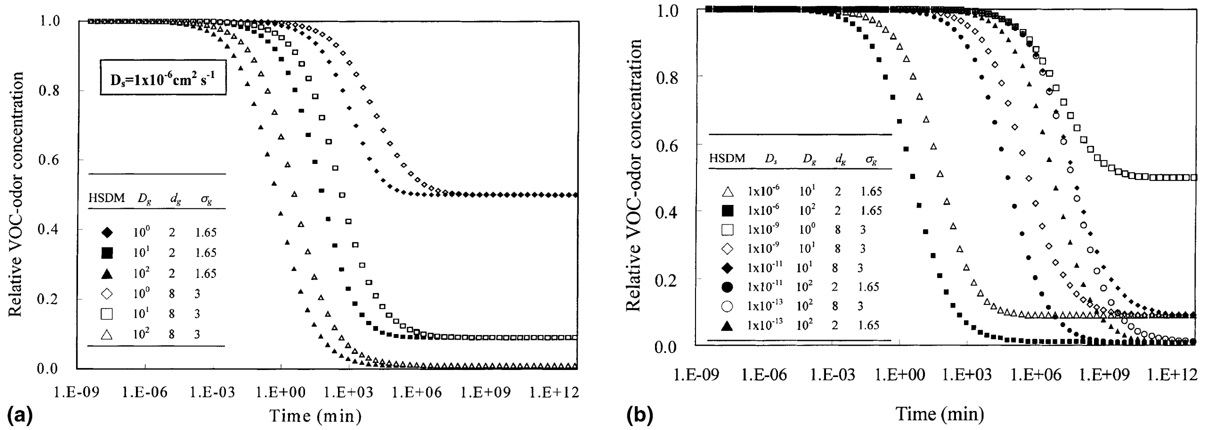

Fig. 3. Sensitivity of HSDM in changes to particle size distribution ($\mathrm{LN}(d_g, \sigma_g)$), solute distribution parameter (D_g), and surface effective diffusivity (D_s): (a) at constant $D_s = 1 \times 10^{-6}$ cm^2 s^{-1}; (b) D_s varied from 1×10^{-6} to 1×10^{-13} cm^2 s^{-1}. Base value: $D_s = 1 \times 10^{-6}$ cm^2 s^{-1}.

an increase of the mean age by approximately the same orders of magnitude. This relationship is again shown in Eq. (30) where D_s and mean age are inversely proportional. Fig. 3(b) also reveals that at the same mean age and $\mathrm{LN}(d_g, \sigma_g)$, increasing D_s lowers the VOC-odour concentration in the exhaust air.

4.3. Fitting LPGM to HSDM

Of eight simulation samples accounting for the experimental data sets obtained from HSDM were chosen to estimate their sorption rate coefficients and reaction orders by a nonlinear regression fitting of LPGM to HSDM. Model parameters used for the eight simulation samples are listed in Table 1. The model parameters were not adjusted to make the prediction of the results obtained from the simulation samples and therefore the model simulations constitute an independent prediction to the data from HSDM. The modelling approach assumes the most homogeneous mixture structure of airborne dust and VOC-odour in this constant equilibrium and rate properties throughout the simulation samples are assumed.

It is believed that, however, the scatter in each of the simulation samples may reflect the heterogeneous nature of the mixture of airborne dust and VOC-odours. This obscured the observation of the effect of varying D_g values (10^1–10^2) and D_s values (1.0×10^{-6}–1.0×10^{-13} cm^2 s^{-1}) on changes in μ, v, and $E_{\mathrm{LP}}(k)$ for each sample. In view of the D_g defined in Eq. (38), the Freundlich heterogeneity parameter (n) provides a convenient measure of equilibrium nonlinearity. Under this condition, the agreement of a model simulation with samples is taken as a demonstration that the model contains sufficient mechanistic details to predict the behaviour of the simulation sample systems.

Two parameters μ and v may refer to as adjustable parameters and their use entails in fitting the data obtained numerically from HSDM. Figs. 4(a)–(d) show that the LPGM with two parameters, μ and v, can fit the trend of the entire adsorption profiles obtained from HSDM ($r^2 = 0.99$) and successfully described the initial rapid adsorption of VOC-odour to dust particles as well as the following slow adsorption. Table 2 gives the μ and v values for eight simulation samples as well as the estimated mean value and standard deviation of adsorption rate coefficient k and reaction order for each profile.

As shown in Figs. 4(a)–(c) a significant fraction of VOC-odour was adsorbed rapidly in the initial adsorption phase. Although it is not clearly shown in Figs. 4(a)–(c) with a time scale of min, it took less than 10 min for the VOC-odour concentration in the gaseous phase to reach approximately 50% of the 10^3 min isotherm value. After the initial adsorption of VOC-odour to the dust particle, the adsorption rate decreased significantly and VOC-odour concentration was still less than 80% of the 10^3 min sorption uptake equilibrium value after an elapsed time of 10^7 min.

Table 1
Model parameters used for eight simulation samples

Simulation sample	D_s (cm^2 s^{-1})	D_g (–)	d_g (μm)	σ_g (–)
1	1×10^{-6}	10^1	2	1.65
2	1×10^{-6}	10^2	8	3
3	1×10^{-9}	10^1	8	3
4	1×10^{-9}	10^2	2	1.65
5	1×10^{-11}	10^1	8	3
6	1×10^{-11}	10^2	2	1.65
7	1×10^{-13}	10^1	8	3
8	1×10^{-13}	10^2	8	3

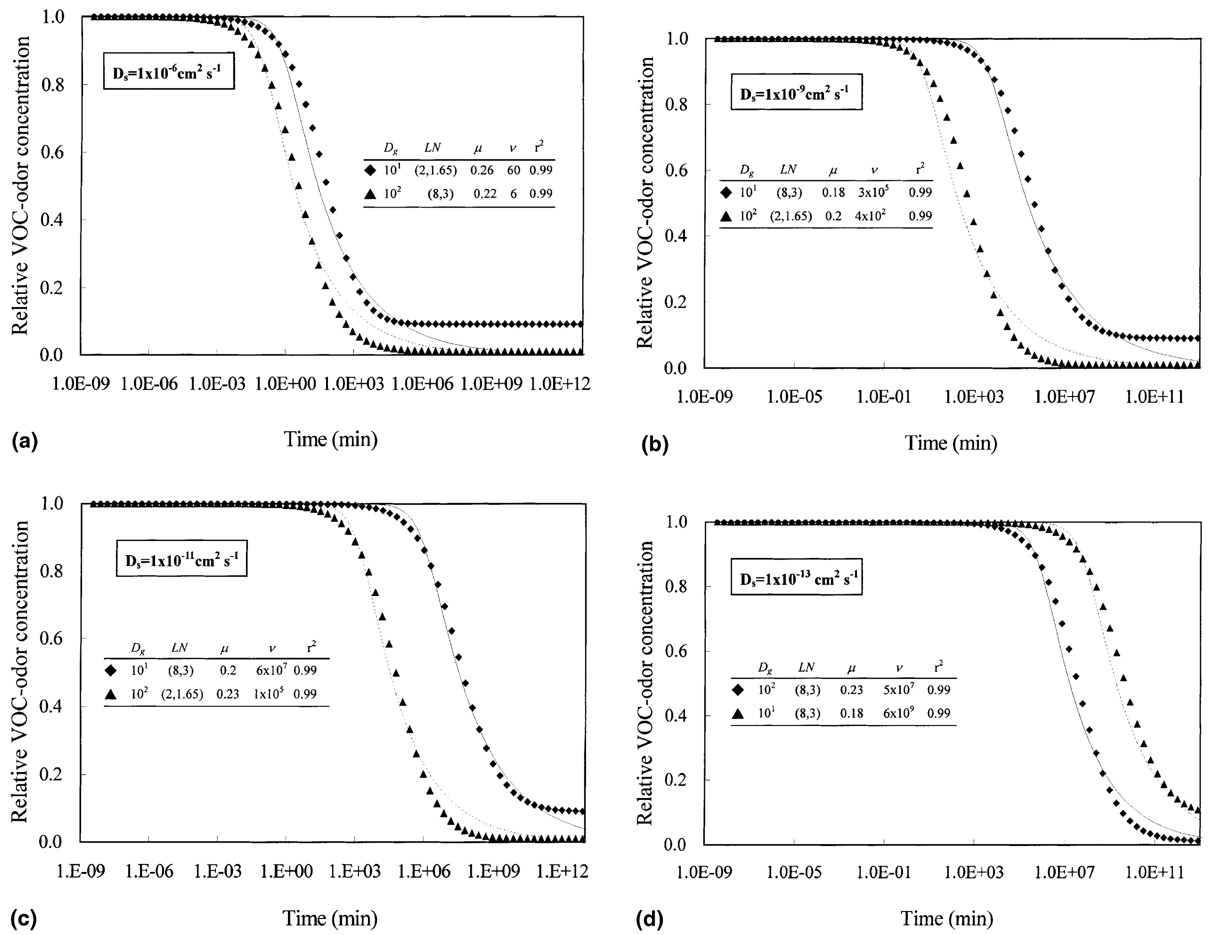

Fig. 4. Simulation results of eight simulation samples data obtained from HSDM fitted with LPGM. The HSDM are denoted by filled symbols, whereas the predictions with the LPGM are depicted by solid and dashed lines.

Table 2
Estimated adsorption rate coefficients and reaction orders for eight simulation samples

Simulation sample	μ^{a} (–)	v^{a} (min)	$E_{\mathrm{LP}}(k) = \mu/v$ (min^{-1})	$sd_{\mathrm{LP}}(k) = \mu^{1/2}/v$ (min^{-1})	Reaction order $(1 + 1/\mu)$
1	0.26	60	4.3×10^{-3}	1.1×10^{-3}	4.8
2	0.22	6.0	3.7×10^{-2}	7.8×10^{-2}	5.5
3	0.18	3×10^{5}	6.0×10^{-7}	1.4×10^{-6}	6.5
4	0.20	4×10^{2}	5.0×10^{-4}	1.1×10^{-3}	6.0
5	0.20	6×10^{7}	3.3×10^{-9}	7.4×10^{-9}	6.0
6	0.23	1×10^{5}	2.3×10^{-6}	4.8×10^{-6}	5.4
7	0.18	6×10^{9}	3.0×10^{-11}	7.1×10^{-11}	6.5
8	0.23	5×10^{7}	4.6×10^{-9}	9.6×10^{-9}	5.4

[a] Estimated by trial and error nonlinear regression of Eq. (41).

These modelling approaches attempt to account for variations in sorption rates that might be caused by particle size variations, under the assumption that particle size is the relevant differential length scale. Comparison of Figs. 4(a)–(d) shows that introduction of particle size effect in model formulation that already includes an instantaneous equilibrium fraction produces a moderate variation in model fits for each simulation sample. These modelling approaches attempt to account for heterogeneities by accounting for variations in particle size and by introduction of an instantaneous equilibrium fraction. The reaction orders that are shown in Table 2 ranged from 4.8 to 6.5 also reflect the heterogeneity and nonlinearity in a complex VOC-odour/dust particle mixture [28].

The most important implication obtained from the fitting of LPGM to HSDM is that the mixture of reactants is considered to be a combination of gamma distributions (i.e., $c(k,0)$, $D(k)$, $K(k)$), and the characteristic properties such as rate coefficient and reactant type of the gamma distribution can be analysed by calculating the mean and variance. The shape and scale parameters can then be determined. If a new mixture with similar VOC-odours but with various initial concentrations needs to be investigated, or the impact of an important component in a mixture needs to be estimated, we can simply calculate the new mean and variance of each distribution and predict the new sorption rate coefficient and reaction order for the mixture. The related initial and long-term impact can also be simulated.

The advantage of using an LPGM approach is that the numerous sorption lumps may still be described by a limited number of adjustable parameters, μ and v in this case. This method may provide a more accurate and physically reasonable description of the kinetic behaviour. The disadvantage of this model is that it has no explicit predictive capability, i.e., free parameters in the analytical formula can only be obtained from a matching procedure to results from measurement. Another disadvantage is that the LPGM and HSDM are not asymptotically agreed well as the mean age of dust approaches infinity. Future research is needed to find the correlations for μ and v with airborne dust, VOC-odour, and residence time data for the LPGM to be useful as a predictive tool.

5. Conclusions

We developed a model called HSDM that accounts for the adsorption of VOC-odour on the surface of airborne dust in animal housing based on age and size distributions of airborne dust. The HSDM based on one Fickian surface effective diffusion rate, however, is often insufficient to describe the diffusion process. Therefore, we developed another model called LPGM based on a continuous distribution of sorption date coefficient in an LP scheme. We chose a gamma distribution because it is characterized by only two parameters (μ and v), it is nonnegative, it allows a parameter estimation of μ and v to be formulated as a nonlinear regression equation fitting to HSDM.

Further research is recommended to compare LPGM with other kinetic models, to determine if the shape and scale parameters vary with properties of the VOC-odours, and to evaluate the ability of LPGM to describe the sorption experimental data. Agreement of the LPGM fit with the data obtained from HSDM would support the mechanistic hypothesis of a continuum in an LP scheme. Adequate description of the sorption process is crucial for predicting the fate and transport of VOC-odour presented in animal housing. From this preliminary evaluation, it appears that LPGM based on a continuum of sorption rates may prove to be of practical value in describing the sorption process of livestock generated VOC-odour to airborne dust surface.

These results may be useful to those who are faced with the problems of selecting proper kinetic models and/or lumps for complex reaction systems. This analysis capability has crucial environmental implications. For instance, the technique of lumping a mixture potentially can be applied to more complex systems such as heavy metal distributions in sediment and ecological risk assessment: metal toxicity in bottom sediments in aquatic systems to evaluate or predict the total toxicity or ecotoxicity of complex systems.

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