Modeling volatile organic compounds sorption on dry building materials using double-exponential model

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Abstract−A double-exponential surface sink model for VOCs sorption on building materials is presented. Here, the diffusion of VOCs in the material is neglected and the material is viewed as a surface sink. The VOCs concentration in the air adjacent to the material surface is introduced and assumed to always maintain equilibrium with the material-phase concentration. It is assumed that the sorption can be described by mass transfer between the room air and the air adjacent to the material surface. The mass transfer coefficient is evaluated from the empirical correlation, and the equilibrium constant can be obtained by linear fitting to the experimental data. The present model is validated through experiments in small and large test chambers. The predicted results accord well with the experimental data in both the adsorption stage and desorption stage. The model avoids the ambiguity of model constants found in other surface sink models and is easy to scale up.

Key words: VOCs Sorption, Gas-phase Mass Transfer Coefficient, Building Materials

INTRODUCTION

Various building materials can emit volatile organic compounds (VOCs), which significantly affects indoor air quality. The emission of VOCs has been investigated in detail [1-6]. However, VOCs can be adsorbed by building materials, which may lower the peak concentrations in the room air. The subsequent desorption of VOC from building materials will prolong their presence in buildings. Recently, there has been an increasing interest in characterizing and modeling the sorption of VOCs on building materials.

Many authors have tried to construct the model for VOC sorption. Zhang et al. [7] classified the existing VOC sorption models into the first-order adsorption/desorption rate model and the equilibrium-interface model. The first-order adsorption/desorption rate model views the sorption sink as a reversible surface phenomenon. Tichenor et al. [8] investigated the adsorption and desorption of five common indoor materials in a test chamber and introduced the linear Langmuir model, where the rates of adsorption and desorption at the material-air interface are linearly proportional to VOC concentrations in the air and in the material, respectively. Two constants, adsorption coefficient (k_a) and desorption coefficient (k_d), were introduced to describe the dynamic effect. An equilibrium coefficient (k_e) was defined to represent the sink strength. Sparks et al. [8] used the linear Langmuir model to predict concentrations of selected VOC. A relatively good agreement between the prediction and measurement was shown. Won et al. [9] conducted a series of experiments in a set of parallel chambers to characterize the sorptive interaction between eight VOCs and several carpets under different environmental conditions. They observed that the linear Langmuir model was appropriate for short-term sorption events. In a later study, Won

et al. [10] performed a large-scale laboratory experiment and a field test to validate the linear Langmuir model. Since only one set of experimental data can be obtained from the experiment, nonlinear fitting technique is usually adopted to get the adsorption coefficient (k_a) and desorption coefficient (k_d) simultaneously. However, it has been found that the fitted parameters may not be unique, depending on different initial estimations of these parameters and the results may differ considerably [7]. Therefore, no comparison can be performed for the same material in different experiments. Moreover, these two parameters are obtained from the fitting to the experimental data. The physical mechanism determining these two parameters is not clear; thus, it is difficult to scale up for other situations.

The equilibrium-interface model assumes that equilibrium always exists at the interface, which can be described by adsorption isotherm. The model parameters include the partition coefficient at the material-air interface and/or the diffusion coefficient of VOC within the material. Little and Hodgson [11] presented a diffusion-controlled sink model with ventilation where VOC concentration in the air was solved by using one-compartment model. An improvement to the sorption model of Little and Hodgson [11] is the introduction of mass transfer resistance through the air boundary layer [12]. Xiong et al. [13,14] extended the model of reference [12] to the case without ventilation and discussed the evaluation of model parameters. Yang et al. [15] developed a numerical model where VOC concentration in the air was solved by using CFD technique. The aforementioned models required the transient diffusion equation in the material to be solved. However, the introduction of the diffusion equation brings about some inconvenience in processing experimental data. The model parameters must be obtained from some specific experiments.

In the present study, a physical-based double-exponential model is derived for VOC sorption on building materials. The sorption rate is described by the mass transfer between the air adjacent to the material and the room air. The presented model is validated through

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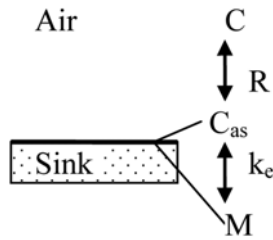E-mail: bqdeng@usst.edu.cn, cnkim@khu.ac.kr

Fig. 1. Schematic that shows the ways of considering the sorption process.

the experimental data.

SORPTION MODEL BASED ON GAS PHASE MASS TRANSFER

The sorption of VOC includes three stages: the mass transfer from the room air to the air adjacent to the material-air interface, the adsorption of VOC on the material surface, and the diffusion of VOC within the material. It is assumed:

1) The thickness of the material is very small compared to the characteristic length of the room. Thus, the material is viewed as a surface sink and the diffusion of VOC in the materials is neglected;

2) Gas phase mass transfer can be used to describe the mass flux from the room air to the material.

3) Equilibrium always exists between the air phase concentration and the solid phase concentration at the interface.

From 1) and 2), the mass transfer between the surface of building materials and the air flow containing VOC, as shown in Fig. 1, can be written as follows:

$$R = h(C_a - C_{as}) \tag{1}$$

where R is the flux of mass transfer to the sink (kg-m^{-2} h^{-1}); h is the gas-phase mass transfer coefficient (m-h^{-1}); C_a is the VOC concentration in the air (kg-m^{-3}); C_{as} the concentration of VOC in the air adjacent to the material surface (kg-m^{-3}).

Assumption 3) can be described by Langmuir adsorption isotherm. In the case of low concentration, it can be simplified to Henry's Law. Taking into account that the concentration of VOCs is relatively low in the room, Henry's Law instead of Langmuir adsorption isotherm is used, which reads

$$M = k_e C_{as} \tag{2}$$

where M is the mass per unit area on the sink (kg m^{-2}); k_e is the equilibrium constant (m).

The concentration change in the building material can be described by a differential equation as follows:

$$\frac{dM}{dt} = R \tag{3}$$

It is assumed that C_a can stand for the concentration in the chamber. Thus, the mass balance can be written as

$$\frac{dC_a}{dt} = NC_{in} - NC_a - LR \tag{4}$$

where N is the air exchange rate (h^{-1}); L is the loading ratio (m^{-1}); C_{in} is the concentration of the VOC in the inlet air (kg m^{-3}).

The solutions of Eqs. (1)-(4) are

$$C_a = A_1 e^{-r_1 t} + A_2 e^{-r_2 t} + C_{in} \tag{5}$$

$$M = \frac{k_e}{Lh}[A_1(N+Lh-r_1)e^{-r_1 t} + A_2(N+Lh-r_2)e^{-r_2 t}] + k_e C_{in} \tag{6}$$

$$R = \frac{1}{L}[A_1(r_1-N)e^{-r_1 t} + A_2(r_2-N)e^{-r_2 t}] \tag{7}$$

where r_1 and r_2 are the roots of the following characteristic equation

$$r^2 - \left(\frac{h}{k_e} + N + hL\right)r + \frac{Nh}{k_e} = 0 \tag{8}$$

r_1 and r_2 are not equal. In general, $r_1 > r_2$ is assumed. When enough time has passed, Eq. (8) reduces to as follows:

$$C_a = A_2 e^{-r_2 t} + C_{in} \tag{9}$$

The coefficients A_1 and A_2 are dependent on the adsorption or desorption. Consider that the polluted air with concentration C_0 starts to flow into the chamber, which means the adsorption stage. Thus, $C_{in} = C_0$ is set. The initial condition is

$$\text{at} \quad t=0 \quad C_a = M = 0 \tag{10}$$

From Eqs. (5) and (6), we can get

$$A_1 = C_0(N-r_2)/(r_2-r_1) \tag{11}$$

and

$$A_2 = C_0(N-r_1)/(r_1-r_2) \tag{12}$$

When the adsorption of VOCs on the building material arrives at equilibrium, consider the situation where the inflow of the polluted air stops and the fresh air starts to flow into the chamber, which means the desorption stage. Thus, during the desorption stage, $C_{in} = 0$. Then at this time the following condition holds:

$$\text{at} \quad t=0 \quad C_a = C_e \quad \text{and} \quad M = k_e C_e \tag{13}$$

where C_e is the concentration of VOC in the air at equilibrium. Correspondingly, we have

$$A_1 = -C_e(N-r_2)/(r_2-r_1) \tag{14}$$

and

$$A_2 = -C_e(N-r_1)/(r_1-r_2) \tag{15}$$

The present model concerns two key parameters: the gas-phase mass transfer coefficient (h) and the equilibrium constant (k_e). As for the gas-phase mass transfer coefficient, some empirical relations can be adopted to evaluate it [16]. For laminar flow (Re$_l$ < 5×10^4),

$$Sh = 0.664 Sc^{1/3} Re_l^{1/2} \tag{16}$$

For turbulent flow (Re$_l$ > 5×10^4),

$$Sh = 0.037 Sc^{1/2} Re_l^{4/5} \tag{17}$$

where Sh = hl/D$_a$ is the Sherwood number, Sc = ν/D$_a$ the Schmidt number, and Re$_l$ = ul/ν the Reynolds number, ν the kinematic viscosity of the air, u the velocity over the material, l the characteristic length of the material and D$_a$ the diffusion coefficient of VOC in the air. This correlation has been used and validated by Huang and Haghighat [17].

The equilibrium constant, which represents the sink strength of the material, is dependent on the assembly of the material and the selected VOC. It should be determined from the experimental data. First, Eq. (9) is fitted to the experimental data in semi-log diagram and the absolute of the slope is the value of r_2. Second, the value of k_e can be evaluated by substituting r_2 into Eq. (8). Lastly, an optimization can be used to minimize the error of model prediction with the experimental data. Here, the step of getting r_2 and k_e is a linear optimization because of only one parameter (k_e) concerned. On the other hand, the present model is easy to scale up for other environmental conditions after getting the value of the equilibrium constant because the equilibrium constant is the property of the material/VOC and independent of the environmental conditions.

The equilibrium constant has an important influence on the VOC concentration in the air, affecting the roots of Eq. (8). From Eq. (8), we can get

$$\text{as} \quad k_e \rightarrow 0, \qquad r_1 \rightarrow +\infty \quad \text{and} \quad r_2 \rightarrow N \tag{18}$$

and

$$\text{as} \quad k_e \rightarrow +\infty, \qquad r_1 \rightarrow N+hL \quad \text{and} \quad r_2 \rightarrow 0 \tag{19}$$

First, the zero value of k_e means that the material has no adsorption capacity. $A_1=0$ and $A_2=-C_0$ can be obtained from Eqs. (11) and (12). Eqs. (5)-(7) can be rewritten as

$$C_a = C_0(1 - e^{-Nt}) \tag{20}$$

$$M \equiv R \equiv 0 \tag{21}$$

Eqs. (20) and (21) are the equations of no-sink model.

Second, the infinite value of k_e means that the material has infinite adsorption capacity. Following Eqs. (11) and (12), $A_1 = -NC_0/(N+hL)$ and $A_2 = -hLC_0/(N+hL)$ exist. Eqs. (5)-(7) can be rewritten as

$$C_a = \frac{NC_0}{N+hL}[1 - e^{-(N+hL)t}] \tag{22}$$

$$R = \frac{NhC_0}{N+hL}[1 - e^{-(N+hL)t}] \tag{23}$$

$$M = \frac{NhC_0}{(N+hL)^2}[(N+hL)t + e^{-(N+hL)t} - 1] \tag{24}$$

Compared with case of $k_e=0$, the existence of the material reduces the concentration of VOC in the air at equilibrium for the case of $k_e \rightarrow \infty$. For an infinite value of k_e, the mass flux between the air and the material tends to be a constant while the VOC concentration in the material tends to be infinite as time goes on.

RESULTS AND DISCUSSION

The present model has been applied to investigate the adsorption and desorption of VOC in test chambers. The model predictions have been compared with the experimental data in a small scale test chamber [18], and in a large scale test chamber [10].

Popa and Haghighat [18] investigated the adsorption and desorption of VOC in a small scale test chamber with a volume of 50 litters. The experiment specifics are listed in Table 1. In Fig. 2 is shown the toluene concentration in the air with time during the adsorption and desorption in an empty test chamber. Here, the adsorp-

Table 1. Experimental parameters (Pope and Haghighat, 2003)

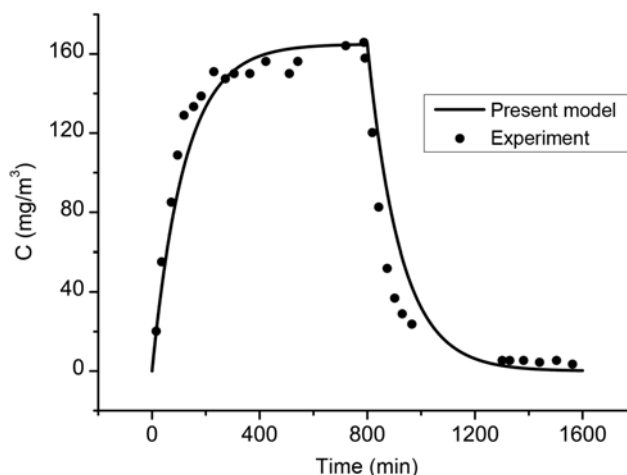| Material	VOC	C_0 (mg m^{-3})	N (h^{-1})	L (m^{-1})	k_e (m)
Acrylic paint	Toluene	82	1.01	3.38	0.096

Fig. 2. Toluene concentration in the air with time during the adsorption and desorption on painted gypsum board.

tion lasts for 800 min. The characteristic length l is taken to be the cube root of the chamber volume in this case. A relatively good agreement with the experimental data has been obtained. Since the equilibrium constant of the walls of empty test chamber is very small, the adsorption of VOC on them can be neglected when other material such as paint is placed in the chamber.

It has been stated that the equilibrium constant should be determined from the experimental data. Here, this procedure is depicted in Fig. 3 for the desorption of toluene from paint. The absolute value of the slope represents the value of r_2. Substituting this value into Eq. (8) yields the value of the equilibrium constant being 0.126 m. R^2 of 0.9932 represents the correlation coefficient, which shows that the experimental data accords very well with Eq. (9). The present
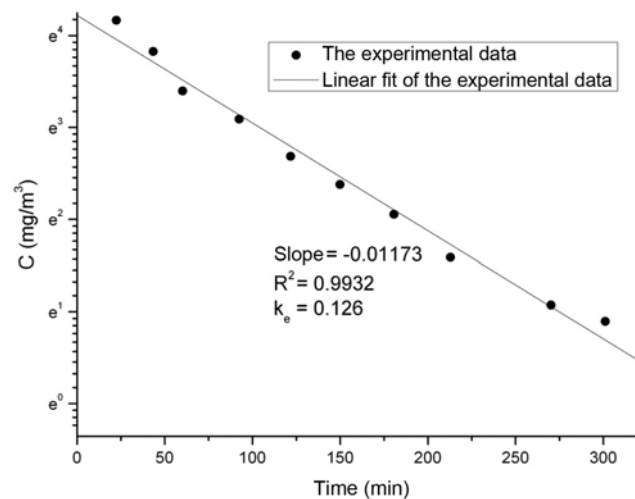

Fig. 3. The determination of equilibrium constant of toluene on paint.
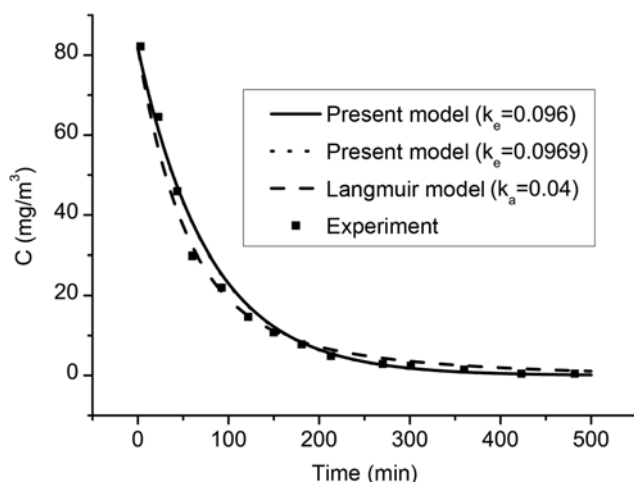
Fig. 4. Toluene concentration in the air with time during the desorption on paint.
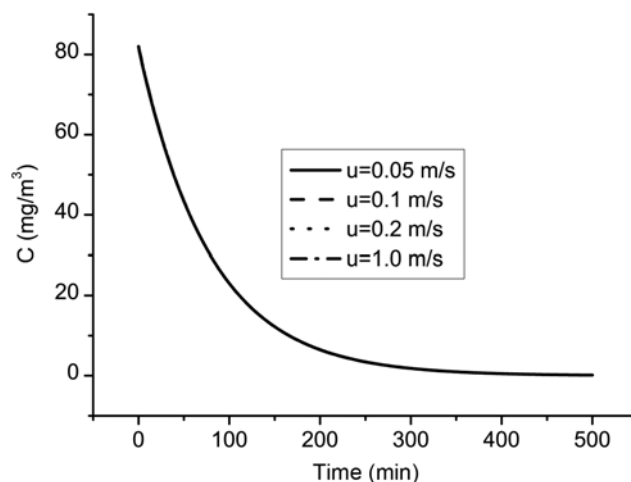

Fig. 5. The influence of air velocity on the desorption of toluene.

equilibrium constant is slightly bigger than 0.096 m, i.e., that of Popa and Haghighat [18]. It may be because the present value is based on the instantaneous equilibrium. The toluene concentration with time during the desorption from paint is depicted in Fig. 4. The predicted concentration of VOC in the air with k_e=0.126 m agrees well with the experimental data from Popa and Haghighat [18]. The predicted result with the Langmuir model is also shown in the same figure, where the adsorption rate constant is 0.04 m-h^{-1} taken from Popa and Haghighat [18]. In the middle stage of the test the Langmuir model seems to be superior to the present model. However, the Langmuir model underestimates the concentration of toluene in the early stage while overestimates it in the long term. Compared to the Langmuir model, the present model shows good performance during the early stage and the long term. In general, both the Langmuir model and the present model describe the experimental data well. However, nonlinear fitting technique is needed in the Langmuir model, while linear fitting is used in the present model.

Since no velocity over the material surface is given by the experiment, it is taken to be 0.1 m-s^{-1} in the current analysis according to the standard guide for small test chambers [19]. The different velocities are compared in Fig. 5. All curves almost coincide with each other. The gas-phase mass transfer coefficients corresponding to four velocities are 1.07e-3, 1.51e-3, 2.14e-3 and 4.79e-3 m-s^{-1}, respectively. This shows that the velocity over the material has little effect on the sorption of VOC.

Won et al. [10] studied the sorptive interactions between VOC and indoor materials in a large scale test chamber. The experimental specifics are listed in Table 2. The cyclohexane concentrations with time during the adsorption on two building materials are shown in
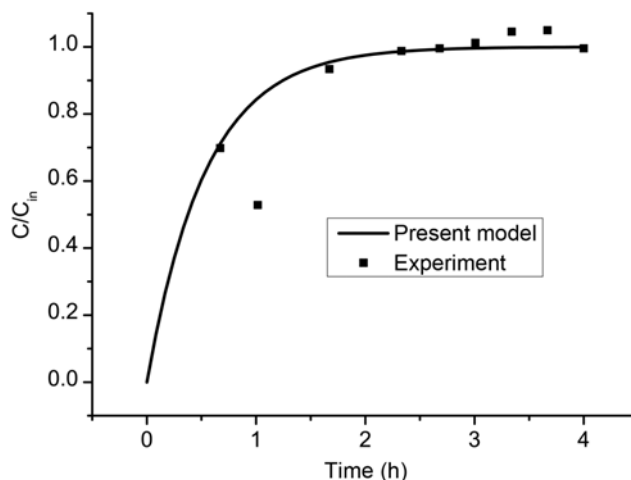

Fig. 6. Cyclohexane concentration in the air with time during adsorption in an empty chamber.

Figs. 6-7. In the case without building materials in the test chamber, the equilibrium constant is assumed to be zero, and a very small nonzero value should be taken to avoid dividing by zero in Eq. (8). The predicted concentrations accord well with the experimental data for cases without building materials (i.e., only with chamber surface) and with a carpet in the test chamber. The toluene concentrations with time during the adsorption in two cases are shown in Figs. 8-9. The predicted results have the same tendency as the experimental data. However, much fluctuation exists in the experimental data, and Won et al. [10] pointed out that chemical analysis problems could be the most likely cause for fluctuations in toluene con-

Table 2. Experimental parameters (Won et al., 2001)

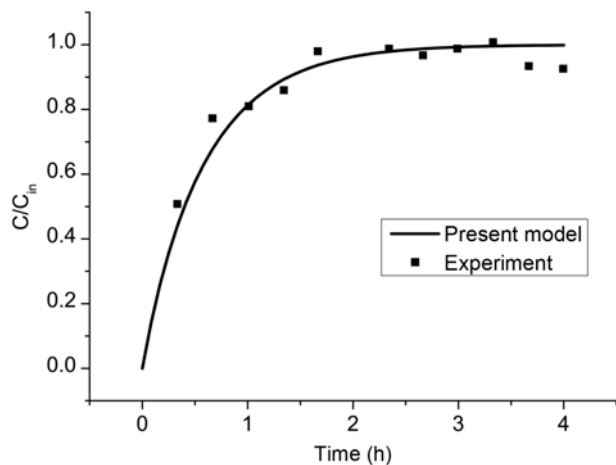| Material	VOC	Inlet VOC rate (mg h^{-1})	N (h^{-1})	L (m^{-1})	k_e (m)
Chamber surface	Cyclohexane	539	1.85	2.8	0
Carpet and underlying pad	Cyclohexane	539	1.85	0.42	0.229
Chamber surface	Toluene	539	1.85	2.8	0
Carpet and underlying pad	Toluene	539	1.85	0.42	1.67

Fig. 7. Cyclohexane concentration in the air with time during adsorption in a chamber with a carpet.
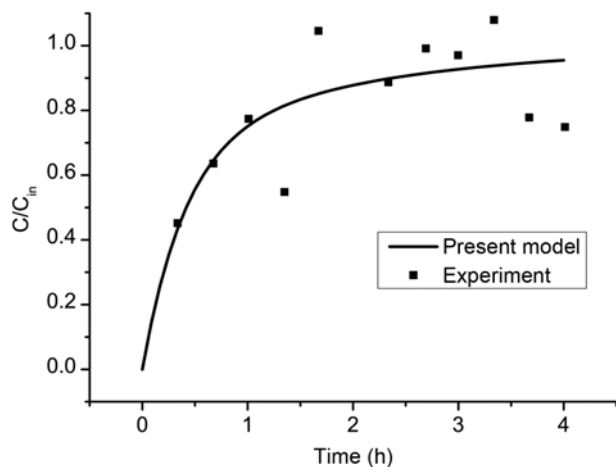

Fig. 8. Toluene concentration in the air with time during adsorption in an empty chamber.
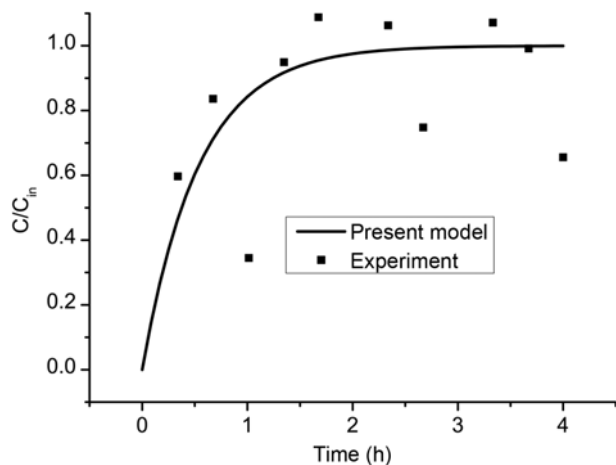

Fig. 9. Toluene concentration in the air with time during adsorption in a chamber with a carpet.

centrations.

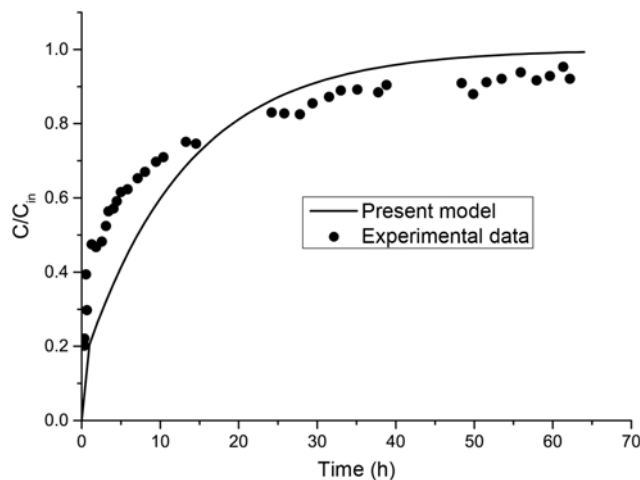The performance of the present model to the sorption in the long

Fig. 10. The concentration of dodecane during long term adsorption.

term is shown in Fig. 10. The experiment was performed in a small chamber with a volume of 50 L [20]. The air exchange rate was $1\,h^{-1}$. The loading ratio was $1.8\,m^{-1}$. Overall, a good agreement between the experimental data and the computational data was obtained.

In general, although the present model cannot interpret the adsorption and the desorption at microscopic level, it offers an alternative to describe them by gas phase mass transfer, which is closely combined with the sorption. However, the Langmuir model is fully empirical, where neither the gas phase mass transfer nor the nature of sorption is concerned.

CONCLUSION

A double-exponential surface sink model for VOC sorption on building materials has been presented. The present model neglects the diffusion of VOC within the material. The mass flux from the room air to the material is described by the gas phase mass transfer between the room air and the air adjacent to the material surface. Also, it is assumed that the air phase concentration adjacent to the material surface always keeps equilibrium with the material-phase concentration. Therefore, there is only one unknown parameter needed in the present model: the equilibrium constant. The equilibrium constant can be obtained by linear fitting to the experimental data. Since the equilibrium constant is dependent on the material and the selected VOC, the present model is easy to scale up for other situations. The present model is validated through experiments in small and large test chambers. The predicted results accord well with the experimental data in both the adsorption phase and desorption phase. The present model avoids the ambiguity of model constants found in other surface sink models.

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