Double exponential decay empirical model for indoor building materials TVOC emissions

Yan Zhang$^{1,2,*}$, Yang Liu$^{1,2}$, Yongfa Wu$^{1,2}$, Yuru Niu$^{1,2}$, Jinxia Jiang$^{1,2}$ and Hongyan Guan$^3$

$^1$School of Science, Beijing University of Civil Engineering and Architecture, Beijing 100044, China
$^2$Beijing Key Laboratory of Functional Materials for Building Structure and Environment Remediation, Beijing University of Civil Engineering and Architecture, Beijing 100044, China
$^3$China Building Material Test & Certification Group Co., Ltd., Beijing, 100024, China

$^*$Corresponding author: zhangyan1@bucea.edu.cn (Y. Zhang).

Abstract. The double exponential decay model is proposed to simulate the total volatile organic compound emissions of indoor building materials. The simulation results are in better agreement with the experimental data than the classical model, and the release characteristic of volatile organic compounds is more accurately described.

1. Introduction

Volatile organic compounds (VOCs) released from building materials are considered to be a major contributor to indoor air pollution. These volatile organic compounds can damage our health and even harm our lives. Therefore, the quality of indoor air is increasingly concerned by the public and research [1-3]. The releases of volatile organic compounds in building materials have a long and complex process. Therefore, it is necessary to clarify the process of transporting volatile organic compounds in building materials.

The prediction models used to study formaldehyde and VOCs emissions in indoor building materials mainly include empirical models and mass transfer models [4]. The empirical model requires a large amount of experimental data, the versatility is poor and the various parameters in the model are empirical parameters, and the exact physical meaning cannot be explained. Furthermore, the experimental results obtained from empirical models may produce large errors in predicting emissions of volatile organic compounds in building materials.

The empirical models mainly include adsorption effect models and exponential models. The adsorption effect model was used to predict the release of volatile organic compounds in the room, and the actual measurement data was found to be at least 2.8 times of the prediction data [5]. The exponential decay model can predict the long-term emission of volatile organic compounds well, but it was established under the assumption that building materials could release volatile organic compounds indefinitely. The theoretical prediction results were higher than the actual results [6]. In fact, the empirical models depend largely on empirical parameters, while the determination of empirical parameters requires a large amount of experimental data, so the versatility of the model is poor. Moreover, most empirical models cannot explain the release mechanism of VOCs.
The mass transfer model considers the mass diffusion process of VOCs in the building material and the diffusion process in the environment chamber. Based on mass transfer theory, Huang et al. [7] established a prediction model for the emission of volatile organic compounds in dry building materials. The result showed that the model had a good agreement between the experimental result and the CFD result. In addition, Zhang and Xu [8] established an analytical model of convective mass transfer. Based on Zhang and Xu’s model, Deng and Kim [9] further modified the model and the prediction accuracy was improved greatly. Recently, the researches of mass transfer models have been attracted many scholars [10-15]. The mass transfer model has a good physical basis, but the acquisition of its parameters is usually dependent on other tests.

The purpose of the study is to establish a predictive model with good versatility and physical meaning to discuss the total volatile organic compounds (TVOCs) emission in the indoor environment. The model is established under the coupling of convective mass transfer equation and mass balance equation in environmental chamber. By comparing the experimental data and the simulation results, it can be found that the model is superior to the traditional empirical model.

2. Model development

The classical empirical model [16] to predict the concentration of TVOCs in environmental chamber is as follow:

\[ C_{\text{air}} = at^b \]  

(1)

where \( C_{\text{air}} \) is the concentration of TVOCs in the environmental chamber, \( a, b \) are both constants, \( t \) is time.

The model fits the experimental data accurately in the early stage, but the fitting effect is not ideal in the later stage, mainly because the model lacks theoretical basis and limits its use conditions. Therefore, we need to establish a predictive model with good versatility and physical meaning to discuss the emissions of TVOCs in indoor environments.

The release of TVOCs occurs not only at the interface between the material and the air but also in the air. Both periods should be considered when discussing the emissions of TVOCs. At the air-material interface, the concentration of TVOCs in the material will be greater than in the air because of the adsorption of the material. Then the concentration of TVOCs between in the material and the interface can be expressed as [14]:

\[ C|_{\delta=t} = K_{ma}C_{\text{air}} \]  

(2)

where \( C \) is the concentration in the material, \( K_{ma} \) is the interface partition coefficient of TVOCs between the material and the interface. \( C_{\text{air}} \) is the concentration in the interface, \( \delta \) is the thickness of the material.

Volatile organic compounds are mainly released from the surface pores of building materials. The surface pore structure of the building material can affect the TVOCs emission rate. Therefore, the porosity of the material surface must be considered. Then the convective mass transfer at the material-air interface can be modified as follows [17-18]:

\[ -vD \frac{\partial C}{\partial x} \bigg|_{\delta=t} = h(C_{\text{air}} - C|_{\delta=t}) \]  

(3)

where \( v \) is the areal porosity, which is tested and calculated by mercury intrusion porosimetry, \( D \) is the diffusion coefficient, and \( h \) is the convective mass transfer coefficient.

The process of TVOCs emission in the environmental chamber can be described with the mass balance equation. The variation of the concentration of TVOCs with respect to time in the environmental chamber is equal to the amount released from the surface of the building material minus the amount lost in the vent [19]. The mass balance equation can be obtained under the following assumptions: (1) The air in the environment chamber does not contain VOCs; (2) The VOCs can be completely mixed into the air.

\[ \frac{dC_{\text{air}}}{dt} = - L \epsilon D \frac{\partial C}{\partial x} \bigg|_{\delta=t} - NC_{\text{air}} \]  

(4)

where \( L \) is the loading rate, and \( N \) is the air exchange rate in the environmental chamber.
Considering that the environmental chamber does not have VOCs, the initial condition is as follow:

\[ C_{air}(0) = 0. \]  \hspace{1cm} (5)

Assuming that the concentration of TVOCs at the boundary of building material is exponential decay, which can be written as:

\[ C_B = Ae^{-Bt} + C_c. \]  \hspace{1cm} (6)

where \( A \) and \( B \) are constants, \( C_c \) is the concentration of TVOCs come from chemical reaction.

Substituting Eqs. (2)-(3) into the Eq. (4), we can get:

\[ \frac{dC_{air}}{dt} + (Lh + N)C_{air} = \frac{Lh}{K_{ma}} C \left|_{t=0} \right. . \]  \hspace{1cm} (7)

Then, substituting Eq. (6) into Eq. (7), the equation is established as:

\[ \frac{dC_{air}}{dt} + (Lh + N)C_{air} = \frac{Lh}{K_{ma}} (Ae^{-Bt} + C_c) \]  \hspace{1cm} (8)

We can obtain

\[ C_{air} = e^{-[Lh+N]t} \left[ \frac{Lh}{K_{ma}} (Ae^{-Bt} + C_c) e^{[(Lh+N)B]t} + C_1 \right] \]

\[ = C_1 e^{-[Lh+N]t} + \frac{LhC_c}{K_{ma}(Lh+N)} + \frac{ALh}{K_{ma}} \frac{1}{Lh+N-B} e^{-Bt} \]  \hspace{1cm} (9)

The initial condition is

\[ C_{air}(0) = C_1 + \frac{LhC_c}{K_{ma}(Lh+N)} + \frac{ALh}{K_{ma}(Lh+N-B)} = 0 \]  \hspace{1cm} (10)

\[ C_1 = -\frac{LhC_c}{K_{ma}(Lh+N)} - \frac{ALh}{K_{ma}(Lh+N-B)} \]  \hspace{1cm} (11)

So, the concentration in environmental chamber can be expressed as:

\[ C_{air} = -(\frac{LhC_c}{K_{ma}(Lh+N)} + \frac{ALh}{K_{ma}(Lh+N-B)})e^{-(Lh+N)B} + \frac{ALh}{K_{ma}(Lh+N-B)} e^{-Bt} + \frac{LhC_c}{K_{ma}(Lh+N)} \]  \hspace{1cm} (12)

The final form is as follow:

\[ C_{air} = a_1e^{-b_1t} - (a_1 + c_1)e^{-b_2t} + C_1 \]

Where

\[ a_1 = \frac{LhC_c}{K_{ma}(Lh+N)} , \ b_1 = B , \ b_2 = -(Lh+N) , \ c_1 = \frac{ALh}{K_{ma}(Lh+N-B)} \]  \hspace{1cm} (13)

If we ignore the chemical reaction, Eq. (13) can be written as the following double exponential decay empirical model

\[ C_{air} = a_1e^{-b_1t} - a_1e^{-b_2t} \]  \hspace{1cm} (14)

3. Results and discussion

An experiment was performed on the emission of TVOCs in an approximately 1 m³ environmental chamber. The model of the environmental chamber used in this experiment is VWH-1000, and the brand is Hainate. The experimental conditions are presented in Table 1. The interior wall coating or wood coating was placed in the chamber parallel to the direction of the airflow. Formaldehyde was emitted into the air, and then, the air was collected by 3-methyl-2-benzothiazolinone hydrazone (MBTH). The concentration of formaldehyde was measured by spectrophotometry every 24 hours until it reached equilibrium.
Table 1. Experimental parameters.

| Parameter | Value         |
|-----------|--------------|
| Temperature (℃) | 23±0.5       |
| Relative humidity (%) | 45±1         |
| Air exchange rate (h⁻¹) | 1±0.01       |
| Dimensions of the environmental chamber (m × m × m) | 0.80×1.10×1.14 |
| Dimensions of the building material (m × m × m) | 1.00×0.50×0.008 |

Fig. 1 shows the release of interior wall coating. In the early stage of TVOCs release, there is a process filling the environmental chamber with TVOCs, where the concentration of TVOCs rises rapidly and reaches the peak quickly. At the of TVOCs release, the concentration of TVOCs decreases slowly. It can be concluded that the present model has a better agreement with the experimental data than classical model. At the same time, the parameter and the root mean square error (rmse) are shown in Table 2.

Table 2. Fitting parameters and the root mean square error (rmse).

| Model               | a     | b     | a₁    | b₁    | b₂    | rmse  |
|---------------------|-------|-------|-------|-------|-------|-------|
| Present model       | —     | —     | 0.697 | 0.005 | 0.514 | 0.022 |
| Classical model     | 0.780 | 0.166 | —     | —     | —     | 0.141 |

Fig. 2 shows the release of wood coatings. It can be seen that the TVOCs release law of wood coatings is similar with the interior wall coating. The concentration drops slowly after filling the chamber. In addition, it can be seen from Fig. 2 that the double exponential model is obviously superior to the classical model at each stage. The values of relative parameters and rmse are shown in Table 2.
Fig. 2. Chamber concentration of the TVOCs emitted by wood coating.

Table 3. Fitting parameters and the root mean square error (rmse).

|                | $a$  | $b$  | $a_1$ | $b_1$ | $b_2$ | rmse |
|----------------|------|------|-------|-------|-------|------|
| Present model  | —    | —    | 11.405| 0.025 | 1.814 | 0.584|
| Classical model| 10.338| 0.259| —     | —     | —     | 2.410|

4. Conclusions

The double exponential decay model has been established to fit the total volatile organic compound emissions of building materials in environmental chamber. The fitting result shows that the present model is more consistent with the experimental data, as the rmse is much less than that of classical model.

Acknowledgments

This work was supported by the National Key Research Program of China (No. 2016YFC0700601), the National Natural Science Foundation of China (No. 21878018), the Joint Funding Project of Beijing Municipal Natural Science Foundation and Beijing Municipal Education Commission (No. KZ201810016018).

References

[1] Huang, L., Nicholas, N., Peter, E., Daniel, A., Olivier, J., Jane, B. (2019) Integrating exposure to chemicals in building materials during use stage. The International Journal of Life Cycle Assessment, 24: 1009-1026.

[2] Wolkoff, P., Nielsen, P. (1996) A new approach for indoor climate labeling of building materials emission testing, modeling, and comfort evaluation. Atmospheric Environment, 30: 2679-2689.

[3] Markus, R., Siegfried, M., Birger, H., Helmut, K. (2018) VOC Emissions after Building Renovations: Traditional and Less Common Indoor Air Contaminants, Potential Sources, and Reported Health Complaints. Indoor Air, 8: 91-102.

[4] Yu, L.K., Yu, Y.B., Zhang, G.Q. (2004) emissionmodels of VOCs indoor building materials and their application. HVAC, 8: 102-104.

[5] Won, C., Shaw, T., Corsi, R.L. (2001) Sorption coefficients for interactions between volatile organic compounds and indoor surface materials from small-scale, large-scale, and field tests. In: 4th International Conference on Indoor Air Quality, Ventilation and Energy Conservation in Buildings (IAQVEC 2001). Changsha.
[6] Park, H.S., Ji, C., Hong, T. (2016) Methodology for assessing human health impacts due to pollutants emitted from building materials. Building and Environment, 95: 133-144.

[7] Huang, H., Haghighat, F. (2002) Modelling of volatile organic compounds emission from dry building materials(Article). Building and Environment, 37: 1349-1360.

[8] Zhang, Y.P., Xu, Y. (2003) Characteristics and correlations of VOC emissions from building materials, Int. J. Heat Mass Transfer, 46: 4877-4883.

[9] Deng, B.Q., Kim, C.N. (2004) An analytical model for VOCs emission from dry building materials. Atmos. Environ, 38: 1173-1180.

[10] Fariborz, H., Huang, H.Y. (2003) Integrated IAQ model for prediction of VOC emissions from building material. Building and Environment, 38: 1007-1017.

[11] Shen, X.Z., Chen, Z.Q. (2010) Fractal diffusion of VOCs in dry porous building materials. Building and Simulation, 3: 225-231.

[12] Hu, H.P., Zhang, Y.P., Wang, X.K., et al. (2007) An analytical mass transfer model for predicting VOC emissions from multi-layered building materials with convective surfaces on both sides. International Journal of Heat and Mass Transfer, 50: 2069-2077.

[13] Choi, D.H. (2015) Evaluation of VOC Emission Characteristics of Adhesive-bonded Building Materials for Residential Buildings Using Numerical Modeling. Journal of the architectural institute of Korea planning & design, 31: 105-112.

[14] Cao, L.Y., Shen, J. (2010) An Analytical Model for Voc Emission from Porous Building Materials. Advanced Materials Research, Advanced Materials Research, 113-116: 1861-1861.

[15] Wang, X.K., Zhang, Y.P., Zhao, Y.R. (2006) Study on characteristics of double surface VOC emissions from dry flat-plate building materials. Chinese Science Bulletin, 51: 2287-2293.

[16] Tsinghua University. (2013) Research on Some Key Problems in Labeling of VOC Emissions from Furniture. http://kns.cnki.net/kns/detail/detail.aspx?FileName=1015007157.nh&DbName=CDFD2015.

[17] Mocho, P., Desauziers, P., Plaisance, H., Sauvat, N. (2017) Improvement of the performance of a simple box model using CFD modeling to predict indoor air formaldehyde concentration. Building and Environment, 124: 450-459.

[18] Zhang, Z., Jiang, J.X., Bai, Y., Liu, J.M., Shao, H.Q., Wu, C.D., Guo, Z.B. (2019) A fractional mass transfer model for simulating VOC emissions from porous, dry building material. Building and Environment, 152: 182-191.

[19] Liu, W.W., Zhang, Y.P., Yao, Y. (2013) Labeling of volatile organic compounds emissions from Chinese furniture: consideration and practice. Chinese Science Bulletin, 58: 3499-3506.