The Effect of a Passive Adsorption Sheet on Reducing Organic Pollutants in Indoor Air

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Abstract

The effect of a thin, passive, adsorbent sheet containing activated carbon on reducing the concentration of volatile organic compounds in indoor air is investigated. A mathematical model is established to describe the conditions in a hypothetical room containing building materials, furniture, an activated carbon sheet, etc. The results of the modelling show that the activated carbon sheet can reduce the concentration of the organic vapour in the room air by a factor of 1.6 – 200, depending on the resistances to mass transfer in the laminar gas film surrounding the activated carbon sheet and in the voids of the sheet. The maximum value 200 is a theoretical limit, if both the film and void resistances could be eliminated. Minimization of the film and void resistances is important to achieve high effect of the activated carbon sheet. This could be done by e.g. dividing a single sheet into several smaller pieces, hanging the sheets at some places where the air flow is relatively high, and making the sheets thin and loose. For some of the model parameters, estimated or assumed values were used in the calculations. Experimental work regarding sorption equilibria and mass transport properties of the species and materials involved is needed for more accurate results.

Introduction

It has been found in recent years that a new building or a newly decorated building often causes the so-called "sick building syndrome". People living in such a building may develop some symptoms due to exposure to toxic volatile organic compounds (VOCs) emitting from modern building materials. This problem will in turn result in a deteriorated health condition of the people living in such a building and economic loss in the companies involved in the construction and management of the building.

Previous studies (Neretnieks et al., 1993 and Christiansson et al., 1992) indicated that the presence of sorbing materials such as furniture, books and curtains in the building will prolong the exposure significantly, even under normal ventilation. People living or working in a new building or in a newly decorated building will thus risk exposure to VOCs for years or even decades.

Many commonly used household cleaning agents also give off VOCs.

It has been found that ventilation is often insufficient to eliminate the problems and often it is impractical to exchange flooring, wallpaper, furniture, etc. We wish to explore the possibility of eliminating or at least decreasing the problem by adsorbing VOCs on an adsorbent in the form of a large sheet. The sheet is to be hung somewhere in the room, e.g. as a curtain, and no forced circulation is to be imposed. The objective of this study is to investigate the effect of such an adsorbent sheet on reducing VOCs. Specifically we investigate activated carbon as the adsorbent. Activated carbon is an effective adsorbent for organic compounds. It contains many small pores, with diameters down to a few Ångstroms (10^{-10} m). Therefore activated carbon has a large interior surface area which provides a much higher adsorption capacity towards VOCs than other ordinary building materials. We have obtained data on the adsorption equilibria, capacities and
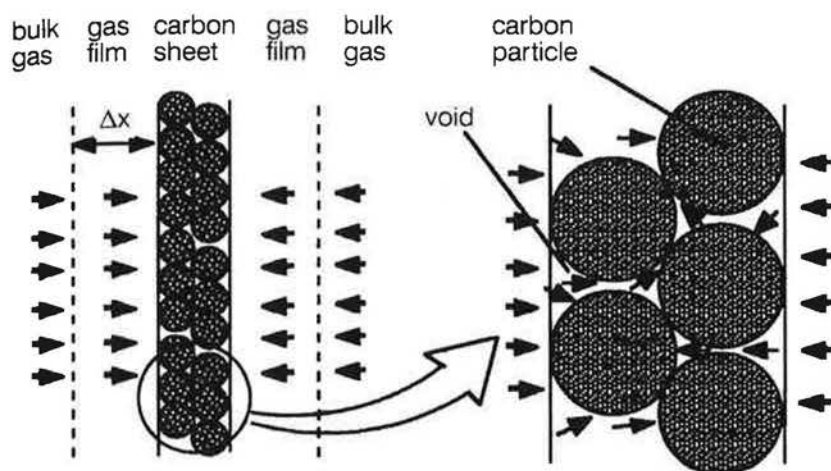
Fig. 1 Mass transfer from bulk gas phase to activated carbon particles

sorption kinetics in earlier investigations (Yu, 1987; Rasmuson, 1984; Jamrozy, 1987).

In the work of Neretnieks et al. (1993) and Christiansson et al. (1992), a compartment model developed by Romero et al. (1991) is used to describe mathematically the conditions in a ventilated room, i.e. the emission, sorption and re-emission of VOCs from/to various building materials and furniture etc. in the room. The compartment model is easy to use, and is especially useful for a quick estimation of the effect to be studied. This study uses the compartment model modified to account for the nonlinear adsorption equilibrium.

The adsorption of VOCs by the activated carbon sheet involves the mass transfer from the ambient air to the activated carbon particles. When the VOCs are transferred from the bulk gas phase into the carbon particles, the organic molecules diffuse first through a laminar gas film, then through the void space between the carbon particles, and further into the particles, as illustrated in Figure 1. This study will investigate the effect of the resistance to mass transfer in the gas film and the effect of the resistance to mass transfer in the interparticle voids.

Modelling

The system to be studied consists of a room, a PVC flooring which is the initial emission source of VOCs, an activated carbon sheet, and a number of other sorbing materials. For simplicity, only one VOC is considered. A ventilation flow rate of 0.5 exchanges per hour is assumed. This flow rate is used by Neretnieks et al. (1993) and Christiansson et al. (1992) as normal ventilation.

The activated carbon sheet is assumed to be composed of carbon particles with a diameter of 1 mm. The sheet is 2 mm thick, 2 m high and 5 m long. The adsorption equilibrium and mass transfer characteristic of the carbon sheet are estimated based on previous studies (Yu, 1987; Yu and Neretnieks, 1990). The carbon sheet with such a dimension and equilibrium characteristic will have an adsorption capacity twice as large as the total amount that is emitted from the PVC flooring.

The Compartment Model

The compartment model has been described in detail elsewhere (Romero et al., 1991). Based on the compartment model, the system is represented by a number of compartments in contact with each other. The air in the room is represented by a compartment. Each piece or each type of building material and each piece of furniture is represented by one or more compartments. The activated carbon sheet is represented by two compartments, one for the interparticle voids and the other for the carbon particles. A model with 23 compartments is illustrated in Figure 2.

Mathematical Equations for the Compartments Representing each Sorbing Material

The equations of mass balance can be generally expressed as

$$V_i \varepsilon_i \frac{dc_i}{dt} + V_i(1-\varepsilon_i) \frac{dc_{si}}{dt} = \sum_{j \neq i} k_{ij}(c_j - c_i) \qquad (1)$$

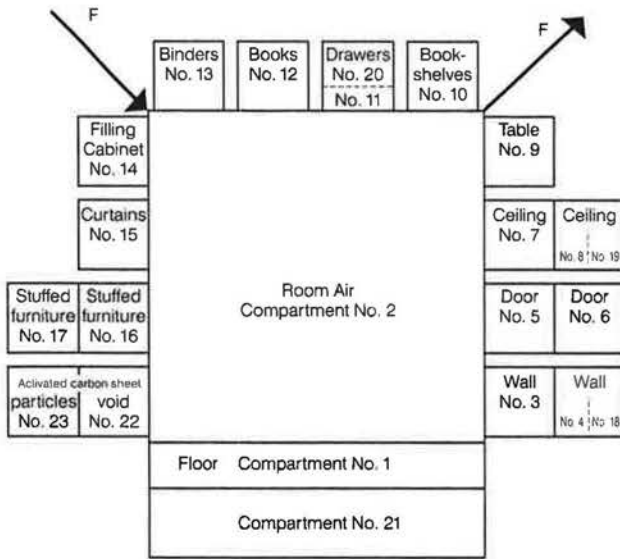where the subscript i denotes the compartment number and the subscript j denotes the number of

Fig. 2 Schematic diagram of a 23-compartment model

the compartment in contact with the compartment i. The first term on the left-hand side of Equation (1) accounts for the mass accumulation in the pores of the compartment i, the second term on the left-hand side accounts for the accumulation in the sorbed phase, and the right-hand side term accounts for the mass transfer from/to various compartments in contact with the compartment i.

The sorbed concentration c_{si} is assumed to be in equilibrium with the gas phase concentration, c_i, based on Henry's Law

$$c_{si} = K_i c_i \qquad (2)$$

which can be replaced into Equation (1) to yield

$$\frac{dc_i}{dt} = \sum_{j \neq i} \frac{k_{ij}}{V_i[\varepsilon_i + (1-\varepsilon_i)K_i]} (c_j - c_i) \qquad (3)$$

The mass transfer coefficient k_{ij} is expressed as

$$k_{ij} = A_{ij}\left(\frac{D}{\Delta x}\right)_{ij} \qquad (4)$$

and

$$\left(\frac{D}{\Delta x}\right)_{ij} = \left(\frac{D}{\Delta x}\right)_i + \left(\frac{D}{\Delta x}\right)_j \qquad (5)$$

where $1/(D/\Delta x)_{ij}$, $1/(D/\Delta x)_i$ and $1/(D/\Delta x)_j$ denote the resistance to mass transfer between the compartments i and j, the resistance to mass transfer from

the interface to the compartment i and the resistance to mass transfer from the compartment j to the interface respectively.

Mathematical Equations for the Compartment Representing the Room Air

A mass balance over the compartment representing the room air leads to the equation:

$$V_i \frac{dc_i}{dt} = \left[\sum_{j \neq i} k_{ij}(c_j - c_i)\right] - Fc_i \qquad (6)$$

where the left-hand side term accounts for the accumulation in the room air, the summation on the right-hand side accounts for the mass transfer from/to the various compartments in contact with the room air, and the second term on the right-hand side accounts for outflow with ventilation. Equation (6) can be rearranged to

$$\frac{dc_i}{dt} = \left[\sum_{j \neq i} \frac{k_{ij}}{V_i} (c_j - c_i)\right] - \frac{F}{V_i} c_i \qquad (7)$$

Mathematical Equations for the Compartments Representing the Activated Carbon Sheet

When an activated carbon sheet is in contact with the room air, the organic molecules will diffuse from the room air into the voids between the carbon particles. Then the molecules will diffuse from the voids onto the particle surface. The molecules will further diffuse into the pores of the particles and be adsorbed on the very large inner surface of the activated carbon.

To describe the mass transfer in the interparticle voids and in the activated carbon particles, the activated carbon sheet is represented by two compartments.

One compartment accounts for the interparticle voids. The volume of the compartment is the volume of the activated carbon sheet times its porosity. The compartment has two contact surfaces. One is in contact with the room air, and its surface area is equal to the total outer surface area (both sides) of the carbon sheet times the porosity. The other surface is in contact with the carbon particles, and its surface area is equal to the total outer surface area of all carbon particles. The mass transfer distance is assumed to be a quarter of the thickness of the carbon sheet. The diffusivity in the compartment is approximately taken as the diffusivity of the VOC and air.

The mathematical equation for the compartment will be

$$\frac{dc_i}{dt} = \sum_{j \neq i} \frac{k_{ij}}{V_i} (c_j - c_i) \tag{8}$$

The other compartment accounts for the activated carbon particles. The volume of the compartment is the total volume of the carbon particles, i.e. the volume of activated carbon sheet minus the volume of the interparticle voids. The contact area is equal to the total outer surface area of all carbon particles. The mass transfer distance is assumed to be one tenth of the diameter of the carbon particles, which follows a linear-driving-force approximation for diffusion in spherical particles with the form of $15D/r^2$ (Yang, 1987). It should be noted that the original linear-driving-force expression is derived for a pore diffusivity and a linear driving force based on the adsorbed phase concentration gradient (Yang, 1987), whereas in this study we use a pore diffusivity and a linear driving force based on the gas phase concentration gradient. The approximation we use would be equivalent to the original expression only when the adsorption isotherm was linear. The equation of mass balance for the compartment is dealt with slightly differently, because the adsorption equilibrium relation for activated carbon is not linear and cannot be properly expressed by Henry's Law.

Equation (1) is still applicable to this compartment. The term dc_{si}/dt in Equation (1) may be expressed as

$$\frac{dc_{si}}{dt} = \frac{dc_{si}}{dc_i} \frac{dc_i}{dt} \tag{9}$$

or

$$\frac{dc_{si}}{dt} = c_{si}' \frac{dc_i}{dt} \tag{10}$$

The mass balance equation for the compartment of the activated carbon particles can be expressed as

$$\frac{dc_i}{dt} = \sum_{j \neq i} \frac{k_{ij}}{V_i[\varepsilon_i + (1-\varepsilon_i)c_{si}']} (c_j - c_i) \tag{11}$$

where c_{si}' is a function of c_i, and it will be described further in a later section.

Mass Transfer between Bulk Air and Solid Surfaces

Mass transfer between the bulk gas phase and the solid surfaces depends on the concentration distribution in the gas phase and the gas flow pattern over the solid surface. In a room where air does not move, concentration in the gas phase is not uniform throughout the room, and the mass transfer occurs only by diffusion. When the air in the room is agitated by some source, e.g. ventilation, mass transfer will take place by bulk flow as well as by diffusion. Adjacent to the surface the gas moves with a laminar flow. Away from the surface the flow pattern gradually changes to turbulent. The mass transfer rate in a turbulent flow is higher than that in a laminar flow.

Mathematical description of the mass transfer between the bulk gas phase and the solid surface is often approximated by the film theory (Bird et al., 1960). According to this theory the molecules diffuse through a stagnant gas film over the solid surface. Outside the gas film the concentration is equal to that of the bulk gas phase (see Figure 3). The mass transfer rate in the gas film for a dilute binary system can be expressed as

$$N = \left(\frac{D}{\Delta x}\right)_{film} \frac{1}{M} (c_i - c_{int}) \tag{12}$$

where Δx is the gas film thickness.

For the overall resistance to mass transfer between the compartment i (bulk air) and the compartment j (any sorbing material in contact with the room air, including the flooring) the term $1/(D/\Delta x)_i$ in Equation (5) will be

$$\frac{1}{\left(\frac{D}{\Delta x}\right)_i} = \frac{1}{\left(\frac{D}{\Delta x}\right)_{film}} \tag{13}$$

The gas film thickness decreases with increasing air flow in the room. The air flow can be driven by a number of sources:

- natural convection due to outer walls and outer windows which have a different temperature from the room temperature;
- natural convection due to radiators in the room;
- ventilation;
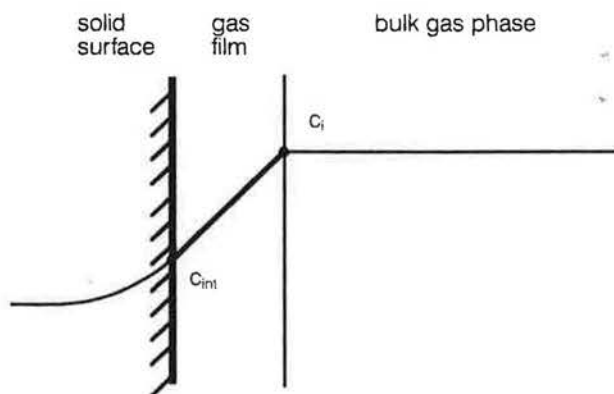- illuminators;
- human movement.

Fig. 3 Illustration of the film theory

The mass transfer coefficient concerning the first three causes above has been estimated (Yu and Neretnieks, 1991). The estimation indicates that the ventilation does not cause much air flow. A radiator has a small dimension compared with the room and hence will only cause local air flow. The main source of air flow will be the cool/warm wall effect, and the gas film thickness will be in the order of centimetres.

The Derivative for the Adsorption Equilibrium Relation

In Equation (11) there is a variable c_{si}', the derivative of the concentration of the VOC in the sorbed phase with respect to the concentration in the gas phase. The solution of the model equations requests a relationship between c_{si}' and c_i.

To express c_{si}' as a function of c_i, a mathematical relation for the adsorption equilibrium is needed. There are a number of mathematical correlation equations for single component adsorption equilibria. In this study the Tóth equation (Tóth, 1971) is chosen as it is one of the equations that works well for activated carbon and it approaches a constant value, as for Henry's Law, as the concentration goes to zero.

The Tóth equation can be written as follows

$$c_{si} = c_{sm} \frac{c_i}{(k + c_i^m)^{1/m}} \tag{14}$$

Then the derivative will be

$$c_{si}' = \frac{c_{sm} k}{(k + c_i^m)^{1+1/m}} \tag{15}$$

Results

The mathematical model is solved by using a standard numerical Stiff solver based on Gear's method. The solver makes use of the function SDRIV2 to solve n ordinary differential equations of the form $dy/dt = F(y,t)$, given the initial condition $\mathbf{y} = \mathbf{y0}$ (Kahaner et al., 1988).

The VOC used in the calculation is 2-ethylhexanol. Its molar mass is 0.1302 kg/mol. Its diffusivity in air is 7.90×10^{-6} m²/s. Its diffusivity and adsorption isotherm data in activated carbon particles at very low concentrations are not available. Its diffusivity in the micropores in the activated carbon particles is assumed to be 2.5×10^{-6} m²/s. This is estimated on the basis of the mass transfer coefficients for diffusion of methyl cyclohexane, toluene and isobutyl methyl ketone in activated carbon particles derived in earlier work (Yu, 1987). The adsorption equilibrium relationship of 2-ethylhexanol on activated carbon is assumed to follow a Tóth isotherm, which is similar to the isotherms for a few other organic components in a previous study (Yu and Neretnieks, 1990):

$$c_{si} = \frac{1.04 \times 10^4}{(1-\varepsilon_i)} \frac{c_i}{(0.16 + c_i^{0.075})^{1/0.075}} \tag{16}$$

The activated carbon sheet is assumed to be 5 m long, 2 m high, and 2 mm thick, consisting of spheric activated carbon particles of 1 mm in diameter. The porosity of the sheet is 0.4. The particle density including pore volume is 800 kg/m³.

The dimension of the room is assumed to be $5 \times 4 \times 2.4$ m³. A ventilation flow rate of 0.5 exchanges per hour is assumed, which corresponds to a flow rate of 6.67×10^{-3} m³/s.

The original emission source of 2-ethylhexanol is the PVC flooring, which has a dimension of $5 \times 4 \times 0.0019$ m³. Initially the total concentration of 2-ethylhexanol in the PVC flooring is 0.032 kg/m³. The other parts of the room contain no VOC.

The other data used in the calculations concerning the sorbing materials (dimension, sorption equilibrium coefficient, diffusivity, etc.) may be referred to elsewhere (Neretnieks et al., 1993).

The 23-Compartment Model

The model contains 23 compartments representing respectively the PVC flooring, the room air, the interparticle voids of the activated carbon sheet, the activated carbon particles in the sheet, and a num-
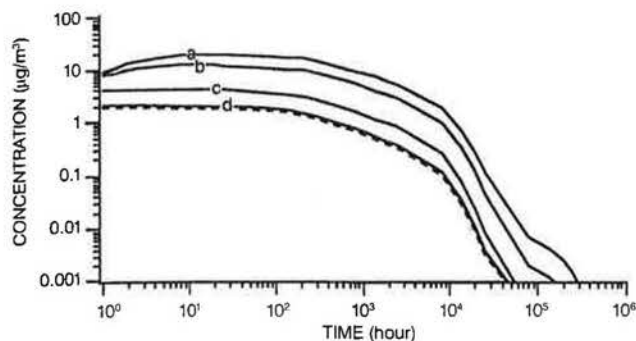
Fig. 4 The concentrations in the room air, calculated from the 21-compartment model (no carbon sheet) with $\Delta x = 10$ mm (-a-), the 23-compartment model with $\Delta x = 10$ mm (-b-), the 23-compartment model with $\Delta x = 1$ mm (-c-), the 23-compartment model with $\Delta x = 0.1$ mm (-d-), and the 23-compartment model without gas film resistance (---). Δx is the equivalent gas film thickness. The same value of Δx used for the activated carbon sheet has been used for all other objects in the room.

Fig. 5 The concentrations in the room air, calculated from the 21-compartment model (no carbon sheet) with $\Delta x = 10$ mm (-a-), the 22-compartment model (no void resistance) with $\Delta x = 10$ mm (-b-), the 23-compartment model with $\Delta x = 0$ for the activated carbon sheet (-c-), and the 22-compartment model (no void resistance) with $\Delta x = 0$ for the activated carbon sheet (-d-). In curves c and d, the film thickness Δx is assumed to be 10 mm for all other objects in the room.
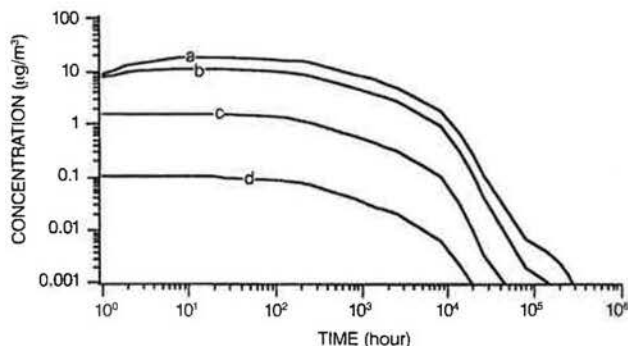
ber of building materials, furniture, and other sorbing objects that might be present in an ordinary room: ceiling, walls, a door, tables, bookshelves, drawers, books, binders, filing cabinets, curtains, and upholstered furniture. The concentration of 2-ethylhexanol in the room air versus time from the calculation is compared with that from a 21-compartment model which does not include any activated carbon sheet (Neretnieks et al., 1993), as presented in Figure 4.

The Effect of the Gas Film Resistance

The results for the film thickness of zero, 0.1 mm, 1 mm, 10 mm for the room air over all solid surfaces with the 23-compartment model have been calculated. The effect of the gas film resistance can be observed in Figure 4.

The Effect of the Resistance to Mass Transfer in the Interparticle Voids

Figure 5 shows the result from the assumption of zero void resistance and a 10 mm thick air film (curve b) and the result from the assumption of zero void resistance and zero air film resistance surrounding the activated carbon sheet but a 10 mm thick air film surrounding other objects (curve d), which are calculated by a 22-compartment model in which the compartment for the interparticle voids is excluded, and the compartment No. 22 accounts for the activated carbon particles. Figure 5 also shows the result from the calculation in which the void resistance is considered but the film thickness is zero for the activated carbon sheet and 10 mm for other

objects (curve c). In order to see the effect of the activated carbon sheet on reducing the concentration, the results are compared with the result from the calculation where no activated carbon sheet is used and the film thickness is assumed to be 10 mm (curve a).

Discussion and Conclusions

This is a preliminary investigation. A number of data values are assumed in the calculations. The results may not be exact, but the main trend is expected to be true. Experimental work regarding sorption equilibria and mass transport properties of the species and materials involved is needed for more accurate results.

From the results shown in Figure 4 one can see that the activated carbon sheet can reduce the concentration level of the VOC in the room air. However, the effect of the activated carbon sheet on controlling the concentration level of the VOC is considerably affected by the film resistance to mass transfer in the room air. The concentration level drops as the film resistance decreases. The concentration curve will approach to a limiting curve where the resistance to mass transfer in the activated carbon sheet dominates the mass transfer rate. If the limiting curve is compared with curve a in Figure 4, it turns out that the concentration level can be reduced by a factor of about 10. Based on this result, in order to enhance the effect of the activated carbon sheet, eliminating the resistance to mass transfer in the air surrounding the activated carbon sheet is important.

An analysis of the effects influencing the gas film mass transfer coefficient indicates that the mass transfer coefficient has a higher value when gas flows over a shorter surface, and hence the film resistance will be lower. Increase in gas flow velocity will also increase the mass transfer coefficient. Therefore it is advisable that the activated carbon sheet be divided into a number of smaller pieces and hung at some place where the air flow is relatively high. For example, the activated carbon sheets can be hung over a radiator where the local natural convection caused by the radiator will be higher than the air flow elsewhere in the room. The activated carbon sheets can also hang over and near places where people will move around. The geometric design of the activated carbon sheets may also affect the gas film mass transfer by varying the degree of movement.

In Figure 4, the room concentration of 2-ethylhexanol remains relatively constant over a long period of time. This could be partly due to the low but relatively constant emission rate from the PVC flooring and partly due to the fact that both the sorption rates onto the activated carbon sheet and other sorbing materials and the emission rate from the PVC flooring decrease synchronously.

Figure 5 reveals that the resistance to mass transfer in the interparticle voids of the activated carbon sheet is relatively low compared with the film resistance in the room air. The concentration curve b in Figure 5 is quite close to the curve b in Figure 4. This indicates that in this case, when the film thickness surrounding the activated carbon is 10 mm, the resistance to mass transfer in the interparticle voids has little effect on the controlling of the concentration level in the room air by the activated carbon sheet. Figure 5 also shows that when the film resistance surrounding the activated carbon sheet is eliminated, then the void resistance will considerably influence the concentration level, as one can see that the curve c is high above the curve d in the figure. The high resistance to mass transfer in the voids of the carbon sheet is attributed to the assumption in the modelling that the gas in the voids is stagnant. If the activated carbon sheet is made rather loose with high porosity which allows the gas flow through the voids, then the resistance to mass transfer in the voids may be reduced. Another approach to reduce the resistance to mass transfer in the interparticle voids is to use thinner activated carbon sheets, in which the mass transfer distance in the voids is shorter.

Figure 5 also reveals that if both the film resistance surrounding the activated carbon sheet and the resistance to mass transfer in the interparticle voids could be eliminated, the activated carbon sheet could effectively reduce the concentration level of the VOC in the room air. For example, the concentration could be reduced from 17 µg/m³ to 0.086 µg/m³, a factor of 200, after 100 hours had elapsed.

To sum up, we conclude that VOCs emitted from building materials can be controlled by thin activated carbon sheets. The elimination of the resistance to mass transfer in the air film surrounding the activated carbon sheets and in the interparticle voids of the sheets is important to enhance the efficiency of the sheets. The shape of the activated carbon sheets can be designed so as to reduce the film resistance and the void resistance as well as to meet decoration purposes, e.g. curtain-like sheets. After a period of time when most VOCs have emitted from building materials, the activated carbon sheets can be removed from the room.

Notation

A_{ij}	Contact area between compartment i and compartment j	m^2
c_i	Concentration in gas phase in compartment i	kg/m^3
c_{int}	Concentration in gas at solid surface	kg/m^3
c_{si}	Concentration in sorbed phase in compartment i	kg/m^3
c_{sm}	Parameter of the Tóth equation	kg/m^3
c_{si}'	Derivative of c_{si} with respect to c_i	
D	Diffusivity of volatile organic compound	m^2/s
F	Flow rate of ventilation	m^3/s
k	Parameter of the Tóth equation	
K_i	Equilibrium coefficient between gas and sorbed phase	
k_{ij}	Mass transfer coefficient	m^3/s
M	Molar mass of volatile organic compound	kg/mol
m	Parameter of the Tóth equation	
N	Mass transfer rate	$mol/(s \cdot m^2)$
r	Activated carbon particle radius	m
t	Time	s
V_i	Volume of compartment i	m^3
Δx	Mass transfer distance	m
ε_i	Porosity of sorbing material	

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