

Investigation of Diffusion and Adsorption of Acetone in Building Materials by Dynamic Method

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Abstract

In this study, diffusion and adsorption behavior of volatile organic compound of acetone on building materials such as perlite plaster, thermal isolation plate plaster and machine plaster were investigated by using one-sided single pellet moment technique. Experimental studies were conducted in a one-sided single pellet Wicke Kallenbach type diffusion/adsorption cell under isobaric conditions. The amount of acetone in the gas phase was measured by GC technique. The zeroth moment analyses showed that the adsorption of acetone on all gypsum plasters used was found to be reversible. The results indicated that the adsorption degree of acetone on the thermal insulation plaster was the lowest value. The acetone adsorption decreased with increasing temperature while the effective diffusivities of acetone increased with increasing temperature in the gypsum plasters. Moreover, the studies revealed that the adsorption process was physical adsorption process and exothermic.

Keywords: Adsorption, Effective Diffusivity, Acetone, Gypsum Plaster, Dynamic Method

Asetonun Yapı Malzemelerindeki Difüzyon ve Adsorpsiyonunun Dinamik Metotla İncelenmesi

Özet

Bu çalışmada plaster alçı, ısı yalıtım sıvası ve makine sıvası gibi yapı malzemeleri üzerine asetonun difüzyon ve adsorpsiyon davranışı tek taraflı pellet moment tekniği kullanılarak araştırılmıştır. Deneysel çalışmalar, izobarik şartlar altında tek taraflı pelet Wicke Kallenbach tipi difüzyon / adsorpsiyon hücresinde yürütülmüştür. Gaz fazındaki aseton miktarı GC tekniği ile ölçülmüştür. Sıfır moment analizleri, asetonun kullanılan tüm sıva örneklerindeki adsorpsiyonunun tersinir olduğunu ortaya koymuştur. Deneysel sonuçlar, asetonun ısı yalıtım sıvası üzerindeki adsorpsiyon derecesinin en düşük değer olduğunu ortaya koymuştur. Aseton adsorpsiyon katsayısı sıcaklık artışıyla azalırken, asetonun etkin difüzyon katsayısının plaster alçıda sıcaklık artışıyla artmıştır. Deneysel çalışmalar, adsorpsiyon işleminin fiziksel adsorpsiyon ve ekzotermik olduğunu ortaya koymuştur.

Anahtar Kelimeler: Adsorpsiyon, Etkin Difüzyon Katsayısı, Aseton, Plaster Alçı, Dinamik Metot

1. Introduction

Volatile Organic Compounds (VOCs) are one of the main sources of the indoor air contaminants. VOCs including acetone, toluene and methanol in building materials such as adhesives, sealants, paints, solvents, stains, carpets, vinyl flooring, wallboard and engineered woods can act to indoor air quality due to their toxic effect. For this reason, these compounds emitted by building materials are considered as a rising problem for productiveness, comfortable and healthy life [1-4]. Short-term exposure to VOCs which is potentially the most hazardous threat may lead to health problems such

as eye and respiratory irritations, headaches, fatigue, and asthmatic symptoms. Long-term exposure may also lead to cancers [5]. In addition to VOCs that negatively affect indoor air quality, these compounds such as aromatic hydrocarbons and chlorinated hydrocarbons used as dry washing solvents in the chemical industry lead to soil and water pollution [2]. Therefore, the diffusion and adsorption behaviors of VOCs, which recognized as potentially dangerous to humans and living organisms in indoor or outdoor environment, are important to predict the VOC emission.

Gypsum plasters or boards are widely used to cover the interior walls or ceilings of the

residential buildings because of their properties such as aesthetics, easily workable, low density, and insulating behavior. One of the most properties of gypsum plasters is a highly porous material [6]. The diffusion and adsorption of many compounds including moisture and low molecule weight vapors found in indoor environment can cause through this property. The effective diffusivity of the compounds is a key parameter to understand the transport and/or adsorption phenomena in porous media.

In order to calculate the effective diffusivities of diffusing components in porous solids, many experimental methods are available in the literature [6-10]. The single pellet moment technique improved by Dogu and Smith due to put out of action of the interpellet mass transfer and the axial dispersion effects [11,12]. The developed this technique is a very fast and reliable technique for determination of effective diffusivities and adsorption equilibrium constant of tracers in the porous solids.

The objective of this present work is to investigate the diffusion and adsorption behavior of acetone, onto various gypsum plasters (perlite plaster, thermal isolation plate plaster and machine plaster) in the one-sided single pellet at different temperature and isobaric conditions.

2. Materials and Methods

The one-sided single pellet studies were executed by using the pellets prepared from perlite, thermal isolation plate and machine plasters. The gypsum plaster samples were obtained from Arslanlı Corporation which is manufactured in Elazığ-Turkey. The BET surface area and the mean pore diameter of the gypsum plasters used in experimental studies were calculated on a Micromeritics® ASAP 2020.

The true density of the gypsum plaster samples was measured by using helium pycnometer (Quantachrome MVP-1). Some physical properties of the gypsum plasters used in this work are given in Table 1. Acetone (Reidel, 99% purity) are used as VOC in the experiments. The dynamic studies of the adsorption and diffusion of acetone in gypsum plasters were performed in the dynamic diffusion/adsorption apparatus called Wicke-Kallenbach shown in Fig. 1. The pellet holder made of stainless steel with 0.013 m in diameter and 0.003 m in length was used to prepare the gypsum plaster pellets. In order to prepare the gypsum plaster pellets, firstly, the gypsum plasters were mixed with water at weight ratios of 10:2.8 for thermal isolation plate plaster, and 10:6 for perlite and machine plasters. The prepared gypsum plaster pellets were dried to constant weight first at room temperature and in the oven at temperature of 40 °C. Then the plasters were stored in desiccators for further use. The prepared pellets were placed in the diffusion/adsorption cell shown in Fig 1. To prevent gas leakage in the prepared pellets, Teflon O-ring was placed on the upper side of the pellet. Finally, the diffusion/adsorption cell was mounted in GC (SRI 8610) oven with constant temperature controlling unit. TCD was used as detector in GC. The carrier gas passing through the upper face of the pellet was Nitrogen. The experiments performed under isobaric conditions (i.e. 1 atm) were carried out at flow rates ranging from 50-175 ml/min and at different temperatures ranging from 25 to 60 °C. 2 µL pulses of the diffusing and adsorbing tracers were then injected into the carrier gas stream by using a syringe, in order to flow past the upper face of the pellet. The response peaks obtained by GC were analyzed by the moment technique. Then, the experimental data of the moments were computed by the Simpson numerical integration rule.

Table 1. Some physical properties of the gypsum plasters pellets used in this study

Building materials	Solid density, ρ_s , g/cm ³	Apparent density, ρ_p , g/cm ³	Total porosity, $\varepsilon_p = 1 - (\rho_p / \rho_s)$	Mean pore diameter, d , µm	BET surface area, S_g , m ² /g
Perlite plaster	2.34	1.47	0.38	0.014	8.4
Thermal isolation plate plaster	2.65	2.20	0.17	0.021	1.6
Machine plaster	2.36	1.64	0.31	0.021	4.2

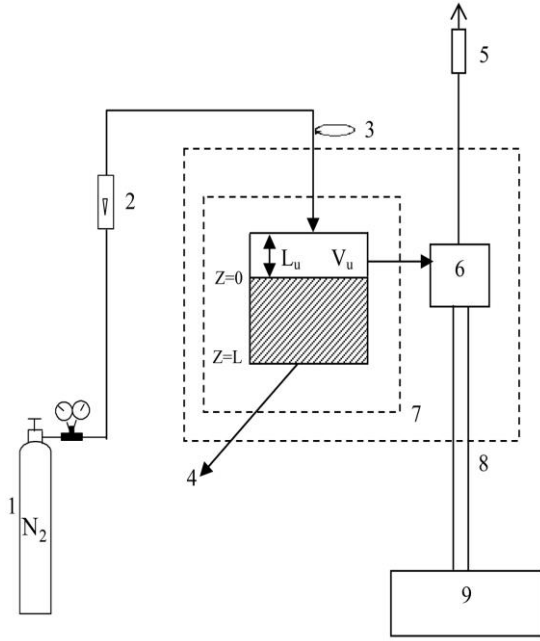


Figure 1. Experimental setup. (1) Carrier gas tube, (2) Rotameter, (3) Sample inlet, (4) Diffusion/adsorption pellet cell, (5) Soap bubble meter, (6) TCD detector, (7) Oven, (8) GC, and (9) Recorder.

2.1. Theory of the one-sided single pellet diffusion/adsorption cell

For adsorption and transport parameters of experimental measurements, theoretical expressions for the distribution of the adsorbing and diffusing tracers in the gypsum plaster pellet and the upper chamber of the diffusion/adsorption cell were used. The species conservation equation for the tracer within the one-sided diffusion/adsorption cell pellet is given by Eq. 1.

$$\varepsilon_p \frac{\partial C_s}{\partial t} = D_e \frac{\partial^2 C_s}{\partial z^2} - N'_s \quad (1)$$

where D_e is the effective diffusivity (m^2/s), ε_p is the pellet porosity, C_s is the tracer concentration in the pores of the pellet ($kmol/m^3$), z is axial coordinate (m), t is time (s) and N'_s is the adsorption rate ($kmol/m^3s$) [12,13].

$$N'_s = \rho_p K_a \frac{\partial C_s}{\partial t} \quad (2)$$

where $\rho_p K_a$ is the overall adsorption constant. Substitution of Eq. 2 into Eq. 1 results in Eq. 3 being obtained as:

$$\varepsilon_p \frac{\partial C_s}{\partial t} = D_e \frac{\partial^2 C_s}{\partial z^2} - \rho_p K_a \frac{\partial C_s}{\partial t} \quad (3)$$

The species conservation equation applied to the upper chamber of the pellet is then given by Eq. 4:

$$-FC_u + D_e \left(\frac{\partial C_s}{\partial z} \right)_{z=0} A = V_u \frac{dC_u}{dt} \quad (4)$$

where F is the carrier gas flow rate (mL/min), C_u is the tracer concentration in the upper chamber ($kmol/m^3$), A is the cross-sectional area of the pellet (m^2) and V_u is the volume of the upper chamber of the diffusion/adsorption cell (m^3).

The initial and boundary conditions of a finite single pellet for Eqs 3 and 4 are explained by Eqs 5 to 8:

$$C_s = 0 \quad (\text{at } t = 0 \text{ for } 0 \leq z \leq L) \quad (5)$$

$$C_s = C_u \quad (\text{at } z = 0 \text{ for all } t) \quad (6)$$

$$\frac{\partial C_s}{\partial z} = 0 \quad (\text{at } z = L \text{ for all } t) \quad (7)$$

$$C_u = C_0 \quad (\text{at } t = 0) \quad (8)$$

The estimation of the adsorption equilibrium constant and effective diffusivity can be performed by solving Eqs 3 and 4. The solutions of these equations have been previously reported in the literature [14,15]. The equations (Eqs 9 to 11) have shown below represent summary of single pellet moment expressions.

$$m_0 = C_0 \tau \quad (9)$$

$$\mu_1 = \frac{m_1}{m_0} = \tau + \frac{AL}{F} (\varepsilon_p + \rho_p K_a) \quad (10)$$

$$\mu_2 = \frac{m_2}{m_0} - \mu_1^2 = \left[\tau + \frac{AL}{F} (\varepsilon_p + \rho_p K_a) \right]^2 + \frac{2}{3} \left(\frac{AL^3}{FD_e} \right) (\varepsilon_p + \rho_p K_a)^2 \quad (11)$$

where m_n is n^{th} moment about the origin, μ_1 is first absolute moment (s), μ_2 is second central moments (s^2), L is pellet length (m) and τ is retention time of tracer at the upper chamber of the diffusion/adsorption cell (s^{-1}).

The top chamber (upper surface of the pellet being covered with an impermeable teflon plate) moment expressions are summarized by Eqs 12 to 14, as follows:

$$m_{0u} = C_0 \tau \quad (12)$$

$$\mu_{1u} = \tau \quad (13)$$

$$\mu_{2u} = \tau^2 \quad (14)$$

where C_0 is initial concentration of tracer in the upper chamber ($kmol/m^3$), μ_{1u} is first absolute moment at the upper chamber of the diffusion/adsorption cell (s) and μ_{2u} is second central moment at the upper chamber of the diffusion/adsorption cell (s^2).

The corrected moment expressions are as shown below:

$$m_{0c} = \frac{m_0}{m_{0u}} = 1 \quad (15)$$

$$\mu_{1c} = \mu_1 - \mu_{1u} = \frac{AL}{F} (\varepsilon_p + \rho_p K_a) \quad (16)$$

$$\frac{\mu_{2c}}{\mu_{1c}^2} = 1 + \frac{2V_u}{AL(\varepsilon_p + \rho_p K_a)} + \left(\frac{2L}{3D_e A} \right) F \quad (17)$$

where μ_{1c} is corrected first absolute moment (s) and μ_{2c} is corrected second central moment (s^2).

The value of the adsorption equilibrium constant, $\rho_p K_a$, can be evaluated from the slope of μ_{1c} vs. $1/F$ data. Also, the calculation of the effective diffusivity, D_e , may be found from slope of the line by plotting (μ_{2c}/μ_{1c}^2) against F .

3. Results and Discussion

The one-sided single pellet moment data were evaluated by using the areas of chromatographic peaks under isobaric conditions, different flow rates and temperatures. Fig. 2 shows a sample of zeroth moment values obtained with

(m_{0u}) and without (m_0) the Teflon plate covering the top surface of the machine plaster pellet at 25 °C. As seen from Fig. 2, both tracers are very close together. Similar results have been obtained in other plaster pellets and other temperature (figure not shown). These results introduce that having reversible adsorption process for the adsorption of acetone onto the gypsum plaster pellets [16,17].

The corrected first absolute moments for acetone onto perlite plaster pellets at temperatures ranging from 25 to 60 °C are given in Fig. 3 as a typical graph. The corrected first absolute moments, μ_{1c} , shown in the graph calculated from the differences μ_1 and μ_{1u} values. According to Fig. 3, the corrected first absolute moment values of perlite plaster pellets for acetone used as a tracer decrease with increasing temperature. The values of the adsorption equilibrium constant, $\rho_p K_a$, of the gypsum plaster pellets used this study found from slope of the line by plotting μ_{1c} against $1/F$. For example, Fig. 4 is represented for all gypsum

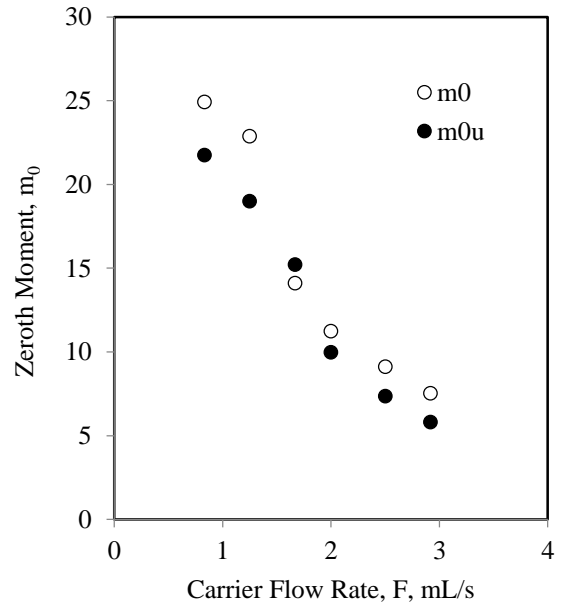


Figure 2. Zeroth moment data for acetone in machine plaster at 25 °C.

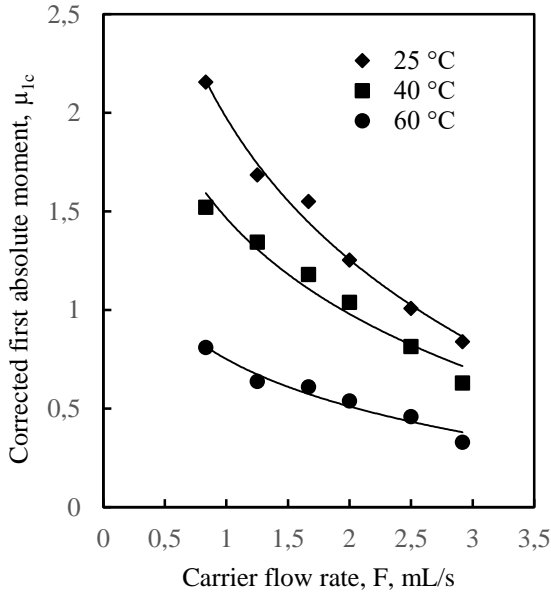


Figure 3. The corrected first absolute moment values of acetone for perlite plaster in the temperature range of 25-60 °C

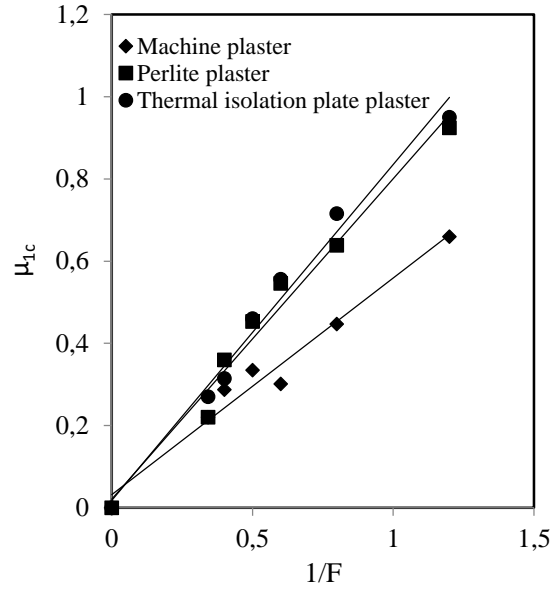


Figure 4. The plot of μ_{1c} against $1/F$ in all gypsum plasters at 60 °C

plaster pellets at 60 °C. The adsorption equilibrium constants of acetone used for the all gypsum plaster pellets was also utilized in the same manner and the results are listed in Table 2. As shown in Table 2, the adsorption equilibrium constant values of acetone in all gypsum pellets are decreased with the increasing temperature. This is a typical characteristic of physical adsorption in the literature [6,10,16]. The values of $\rho_p K_a$ of acetone tracer decreased in the order of thermal isolation plate < perlite < machine plaster. The adsorption of volatile organic compounds in the building material is generally dependent on the type of building material, porosity, specific surface area, and the type of volatile organic compound and vapor pressure.

It can be also said that the adsorption of machine and perlite plaster is higher than thermal isolation plate plaster because the porosity and the surface area of the perlite and machine plaster are higher than thermal isolation plate plaster. Similar results are available in the literature [18-21].

The theoretical temperature dependency of adsorption heat for all the gypsum plaster pellets in which acetone is used can be calculated from the Van't Hoff equation (Eq. 18).

Table 2. Adsorption equilibrium constants of acetone in the gypsum plaster pellets at different temperatures

Building materials	$\rho_p K_a$		
	25 °C	40 °C	60 °C
Perlite plaster	4.44	3.17	2.36
Machine plaster	4.59	3.25	2.41
Thermal isolation plate plaster	3.87	2.93	2.11

$$\ln(\rho_p K_a) = \Delta S - \frac{\Delta H}{RT} \quad (18)$$

The adsorption heat values (ΔH) and entropy changes (ΔS) of the gypsum plaster pellets can be found from the slope and intercept of the line by plotting $\ln(\rho_p K_a)$ against $1/T$ (Fig. 5). The results calculated by Eq. 18 and obtained from the slope and intercept of the curves shown in Fig. 5 are listed in Table 3a. As can be seen in Table 3, these amounts of acetone onto the gypsum plaster pellets revealed that the adsorption process was physical adsorption process. Moreover, the negative value of ΔH introduced that the adsorption process is exothermic. Furthermore, Gibbs free energy changes (ΔG) of the gypsum plaster pellets can be calculated by Eq. 19.

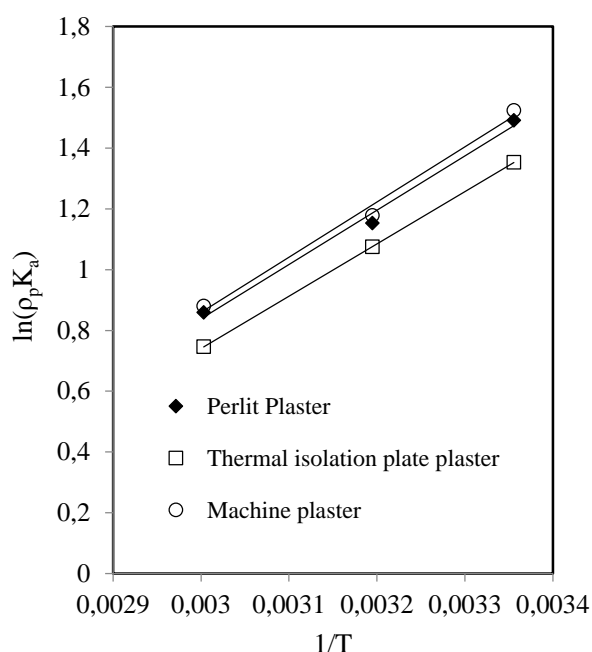


Figure 5. Effect of temperature on adsorption the equilibrium constant of acetone in the gypsum plaster pellets

$$\Delta G = \Delta H - T\Delta S \quad (19)$$

The results calculated by using Eq. 19 for ΔG are given in Table 3b. The negative ΔG value indicated that the adsorption process is spontaneous and feasible. In addition, the negative ΔS value means that the randomness at the solid/solution interface has decreased during adsorption.

The effective diffusivities of acetone in gypsum plaster pellets can be evaluated from the slope of (μ_{2c}/μ_{1c}^2) vs. F data, in Fig. 6 as a sample graph in machine plaster at 60 °C. The obtained effective diffusivity data listed in Table 4. As seen in Table 4, the effective diffusivities of acetone in all gypsum plaster pellets increased with increasing temperature. Also, the effective diffusivities of the thermal isolation plate plaster for acetone were the lowest according to the others. Similar observations were reported in the literature [18-21].

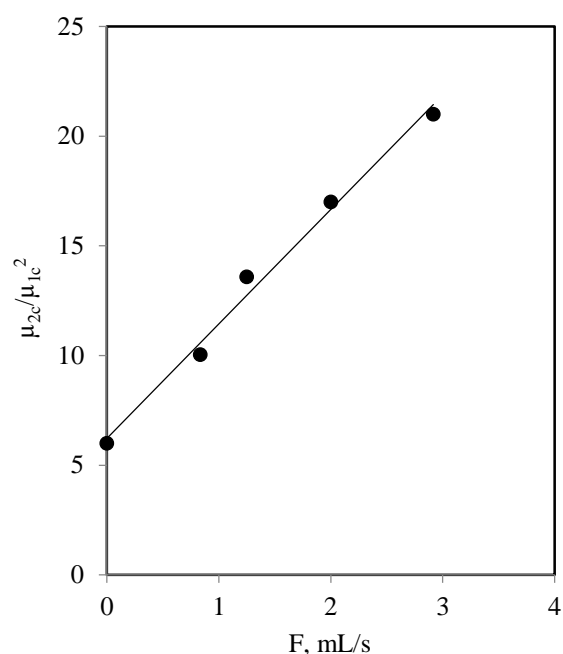


Figure 6. Variation of μ_{2c}/μ_{1c}^2 vs. F in machine pellets at 60 °C for acetone

Table 3. The thermodynamic parameters for acetone in the gypsum plaster pellets a) The values of ΔH and ΔS b) The values of ΔG

Building materials	-ΔH kcal/gmol		-ΔS kcal/gmol	
	25 °C	40 °C	25 °C	40 °C
Perlite plaster	3.544	3.416	8.966	8.778
Thermal isolation plate plaster	3.416	3.605	8.778	9.108
Machine plaster	3.605	3.605	9.108	9.108

Building materials	-ΔG kcal/gmol		
	25 °C	40 °C	60 °C
Perlite plaster	0.872	0.738	0.559
Thermal isolation plate plaster	0.801	0.669	0.494
Machine plaster	0.891	0.755	0.572

Table 4. Effective diffusivities of acetone in the gypsum plaster pellets at different temperatures

Building materials	D _e , cm ² /s		
	25 °C	40 °C	60 °C
Perlite plaster	0.109	0.118	0.183
Thermal isolation plate	0.041	0.067	0.091
Machine plaster	0.056	0.093	0.125

4. Conclusions

In this work, the diffusion and adsorption of acetone in various building materials at different temperatures were investigated by dynamic method. The results indicated that acetone was reversibly adsorbed in gypsum plaster pellets. Physical adsorption was observed when the adsorption heat values were examined. The acetone adsorption decreased with increasing temperature while the effective diffusivities of acetone in the gypsum plasters increased with increasing temperature. Moreover, the reasons such as testing of different volatile organic compounds from acetone, moisture effect on VOC diffusion and adsorption in gypsum plaster samples and binary or multi-component diffusion and adsorption can be recommended for further investigation.

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