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Habib, Khairul

Interdisciplinary Graduate School of Engineering Sciences, Kyushu University

Saha, Bidyut Baran

Interdisciplinary Graduate School of Engineering Sciences, Kyushu University

El-sharkawy, Ibrahim Ibrahim

Interdisciplinary Graduate School of Engineering Sciences, Kyushu University

Chakraborty, Anutosh

Interdisciplinary Graduate School of Engineering Sciences, Kyushu University

他

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Adsorption Characteristics of Methane, HFC-134a and R507A on Highly Porous Activated Carbon

Khairul HABIB*¹ Bidyut Baran SAHA*^{1,†} Ibrahim Ibrahim El-SHARKAWY*¹
Anutosh CHAKRABORTY*¹ Kandadai SRINIVASAN*¹ and Shigeru KOYAMA*¹
†E-mail of corresponding author: *bidyutb@cm.kyushu-u.ac.jp*

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We have measured adsorption isotherms of methane, HFC-134a and R507A on highly porous activated carbon namely Maxsorb III, by using desorption method. The adsorption isotherms of methane, HFC-134a and R507A on Maxsorb III specimen are measured experimentally over a temperature ranging from 5 to 70°C. The pressure variation for methane + Maxsorb III and HFC-134a + Maxsorb III systems is from 2 to 20 bar. However, for R507A + Maxsorb III system the pressures are being varied from 2 to 13 bar. The experimentally measured isotherm data are fitted with Dubinin-Astakhov (DA), and Tóth isotherm models and these data matched well within the acceptable uncertainty limits. The experimental data for methane have been extrapolated up to 25 bar. Furthermore, the isosteric heat of adsorption data of the assorted pairs are also measured as a function of temperature, pressure and uptake.

Key words: *Activated carbon, Adsorption isotherms, Desorption method, HFC-134a, Methane, R507A*

1. Introduction

Thermally powered adsorption cycle is considered as one of the most prominent cycles for adsorbed natural gas (ANG) storage and adsorption cooling applications¹⁻⁴. However, for designing of an ANG storage or adsorption cooling system the adsorption characteristics data of the assorted adsorbent + adsorbate pair is inevitable.

Several researchers have measured the physical adsorption of methane on activated carbon⁵⁻¹³. Methane which is the main ingredient of natural gas has the edge as a dominant fossil fuel over other gases as it plays a vital role in maintaining a clean environment. It remains clean during burning and after burning no ash particles are left. Natural gas has a relatively lower emissions of sulphur, carbon and nitrogen. In the transport sector, adsorbed natural gas can be used more effectively than compressed natural gas (CNG). Because the operating pressure is very high for CNG which results in higher costs. But, ANG can operate at significantly lower pressure, which can contribute substantially in the

reduction of gas storage cylinder cost. The physical adsorption characteristics of methane into activated carbon are the deciding factor of the performance of the ANG. A perfect adsorbent is necessary to maximize methane uptake per storage and should have higher micropore volume and surface area. Activated carbon namely Maxsorb III specimen possesses the above qualities.

In order to save stratospheric ozone layer damaged by chlorofluorocarbons (CFCs), HFC-134a (1,1,1,2-tetrafluoroethane) has been introduced for the purpose of refrigeration. The use of CFCs has been substantially reduced after the Montreal protocol. HFC-134a is currently regarded as an excellent replacement for refrigeration due to its no ozone depletion potential (ODP) and global warming potential (GWP). Another problem of CFCs affecting the environment adversely is disposal. Since, CFCs' contain highly stable organic compounds (chlorine or bromine), their safe disposal is not easy. Incineration or chemical destruction are the methods applied to dispose CFCs safely. But chemical destruction of CFCs results in generation of chlorinated or brominated compounds which causes severe air pollution.

*1 Interdisciplinary Graduate School of Engineering Sciences

Adsorption cycle is considered as one of the most promising environmental-friendly cooling system. Several researches have been carried out adsorption experiments of HFC-134a on activated carbon¹⁴⁻¹⁸).

The refrigerant R507A is an azeotropic blend consisting of 50% R125 (pentafluoroethane) and 50% R143a (1,1,1-trifluoroethane) by weight. The refrigerants R125 and R143a are hydrofluorocarbons and they do not contribute to the stratospheric ozone layer. It has relatively smaller GWP compared with the CFCs and the ODP is zero. It is also non-flammable and the level of acidity is significantly small (below 1.0 ppm). Adsorption of R507A on activated carbon has been carried out by the authors of the present study¹⁹⁻²⁰).

Methane has been selected as one of the assorted adsorbates in the present study for measuring adsorption parameters for gas storage application. For cooling application, HFC-134a and R507A are selected as the assorted adsorbates. Adsorption characteristics of methane, HFC-134a and R507A on Maxsorb III have been measured by the desorption method, which is based on the principle of amount desorbed between two equilibrium states. The experimental results are fitted with Dubinin-Astakhov and Tóth isotherm models and found to be fairly consistent with the experimental errors.

2. Experimental Sections

2.1 Materials

The activated carbon (Maxsorb III specimen) labeled as MSC-30 has been supplied by the Kansai Coke Co. Ltd. It has a Brunauer-Emmet-Teller (BET) surface area of 3,140 m²/g and a micropore volume of 1.7 cc/g. The mean particle diameter of Maxsorb-III specimen is 72 μm, ash content less than 0.1%, moisture of no more than 0.8% and pH is 4.1. The SEM photograph at a magnification ratio of 370,000 is shown in the Fig. 1.

3.2 Experimental setup

The schematic diagram of the experimental test rig is shown in Fig. 2. The Maxsorb III specimen which has a mass of 65.66 g and net packing density of 0.31 g/cc is kept inside a

cylindrical-shaped adsorption cell. The internal diameter of the cylinder is 30 mm with a depth of 300 mm and volume of 212 cm³. The cell is designed to tolerate pressure of 50 bar at a temperature of 150°C. The external plumbing is made of nominal stainless steel having thickness (t) of 0.635 mm and inner diameter of 4.35 mm, and the total volume of the internal plumbing is estimated to be 13.1 cc. All valves are of Swagelok SS 304 type. To stop the migration of the activated carbon during evacuation and desorption, a filter of 2 micron stainless steel fine mesh was fitted in the plumb line at the exit of the cell. Detail description of the experimental setup can be found elsewhere⁴).

3.3 Instrumentation

The instrumentation consists of: (a) a mass flow regulator of type Kojima-Kofloc-5100 having 10 standard liters per minute (at 20°C and 1.013 bar), (b) a pressure transducer of type Kyowa-PGS-50KA 50 bar with an uncertainty in measurement of ±1% of full scale (1.67 cm³/s), (c) a series of K type thermocouples (supplied by Chino Corp., Japan), (d) a Keithly 2700 data acquisition system connected to a computer, (e) a set of Swagelok fittings and stainless steel tubes, (f) a constant temperature water bath (TBN302DA) in which the adsorption cell is immersed inside, and (g) a water circulator (CTO 3000) which controls the temperature of the water bath.

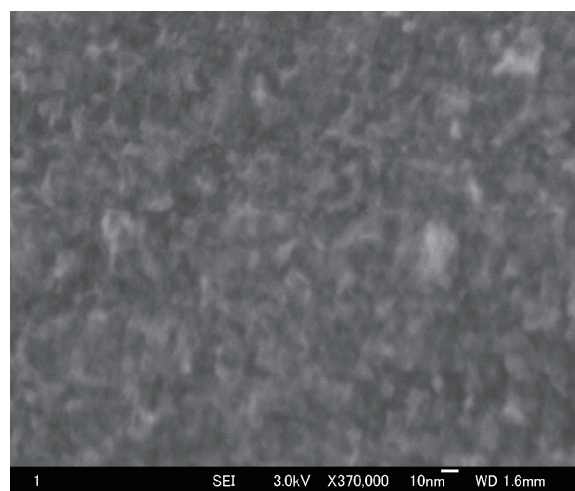
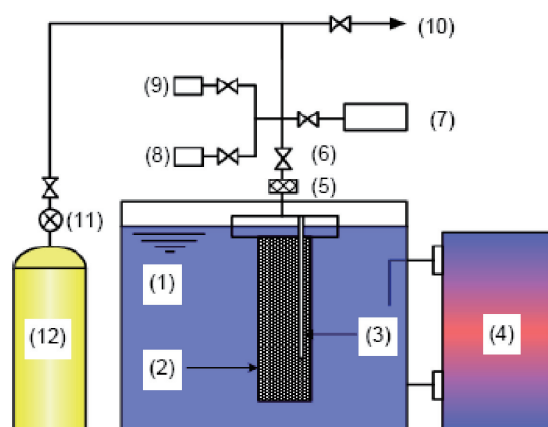


Fig. 1 SEM photograph of Maxsorb III specimen.

3.4 Experimental procedures

Using the desorption test rig, adsorption characteristics of methane, HFC-134a and R507A has been evaluated. Prior to each experiment, evacuation is needed to remove any residual gases remaining in the system. For this reason, degassing is performed for 3 to 5 days using a vacuum pump until the pressure in the adsorption cell reaches at 25 Pa or even lower, and at the same time the cell temperature is raised at 75°C in the water bath. The assorted adsorbate was flushed in the adsorption cell and degassed at heated condition. The adsorbate was charged again at 5°C and then evacuated while the cell temperature was raised from 5 to 75°C. This process of flushing and degassing were continued several times to ensure that the remaining gas is only the assorted adsorbate.



1: Water bath, 2: Adsorption cell, 3: Thermocouple well, 4: Water circulator, 5: Fine mesh, 6: Valve, 7: Mass flow controller, 8: Vacuum gauge, 9: Pressure transducer, 10: Towards the vacuum pump, 11: Pressure regulator, 12: Refrigerant cylinder

Fig. 2 Schematic diagram of the experimental setup.

Figure 3 depicts the sequence of experimental operation. Experiments for the assorted adsorbate were conducted in two ways. Firstly, the adsorbate is charged slowly into the adsorption cell at a temperature of 5-10°C (T_a). When equilibrium attains, the temperature of the cell is raised isothermally to the desired temperature. As a result, both pressure and temperature are increased and are collected to obtain isosteric heat of adsorption. When the cell achieves equilibrium at the desired temperature, the pressure at that point is referred as initial pressure (p_i) before

desorption. Desorption is then started by opening the valve just above the adsorption cell and the valve near the mass flow regulator. As a result, pressure started to decrease. When the flow rate reaches at a value where errors are like to occur, both valves are closed. Therefore, the pressure inside the adsorption cell is raised. When pressure is stabilized, another bout of experiment is started. This is repeated several times to get the gas out as much as possible. When flow is no longer measurable, the process is stopped. After desorption, the pressure of the cell is raised again and achieves equilibrium which is referred as final pressure (p_f). In the second way, methane is adsorbed in the cell at a given temperature and after reaching equilibrium desorption was started at that temperature.

For HFC-134a and R507A, the charging pressure is always less than the saturation pressure corresponding to the temperature of the adsorption cell to ensure that no condensation is occurred. The experimental procedure for HFC-134a and R507A was same as methane.

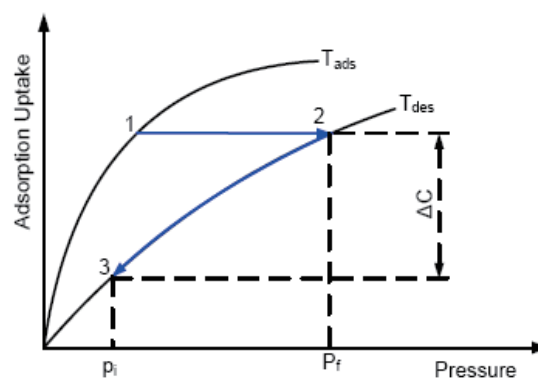


Fig. 3 Sequence of experimental operation.

3.5 Data reduction

The primary data are the time dependent flow rate through the mass flow regulator, the adsorption cell temperature (T_{cell}) and ambient temperature (T_a) and the initial and final pressures (p_i and p_f). The flow data are directly reduced to standard liters desorbed by numerical integration of the flow record and converted to total mass desorbed using standard conditions specified by the flow meter manufacturer. This desorbed mass is required to be corrected for the void volume in the

adsorption cell²¹). There are two types of void, one is for cell void and other for pipeline void. Void volume is calculated by assuming that adsorption occurs in the micropores of the assorted adsorbent and can be expressed as:

$$V_{void} = V_{cell} - m_{ac} / \rho_s - m_{ac} V_{micropore} \quad (1)$$

Therefore the desorbed mass can be written as:

$$\Delta m_{void} = V_{void} (\rho_i(p_i, T_d) - \rho_f(p_f, T_d)) \quad (2)$$

$$\Delta m_{pipe} = V_{void} \left[\begin{array}{l} \rho_i(p_i, (T_d + T_a)/2) \\ - \rho_f(p_f, (T_d + T_a)/2) \end{array} \right] \quad (3)$$

The density data of methane, HFC-134a and R507A are collected from the NIST database.

4. Theoretical Analysis

In this study, the experimental data are fitted with DA and Tóth isotherm equations.

DA isotherm equation can be expressed as⁴,

$$W = W_o \exp \left[- \left\{ \frac{RT}{E} \ln \left(\frac{p_s}{p} \right) \right\}^n \right] \quad (4)$$

where W is the volumetric uptake, W_o is the maximum volumetric uptake (m^3/kg), E is the characteristic energy (kJ/kg), R denotes universal gas constant ($8.314 \text{ J}/\text{mol}\cdot\text{K}$) and n represents heterogeneity constant. Adsorption uptake can be calculated by,

$$C = W/V_a \quad (5)$$

Where, V_a is the adsorbed phase volume which can be expressed as,

$$V_a = V_b \exp[\mathcal{Q}(T_d - T_b)] \quad (6)$$

For methane, \mathcal{Q} is the isosteric coefficient of expansion and has been assumed as $1/T$ in this study⁴.

The experiments are performed in the super critical range, so we have used a pseudo-relation to obtain the saturation

pressure p_s at the desired desorption temperature²²,

$$P_s = (T_d/T_c)^2 P_c \quad (7)$$

For HFC-134a and R507A, \mathcal{Q} can be written as¹⁵,

$$\mathcal{Q} = \ln(b/V_b)/(T_c - T_b) \quad (8)$$

For HFC-134a, $T_b = 246.78\text{K}$, $T_c = 374.21\text{K}$, $V_b = 7.2643 \times 10^{-4} \text{ m}^3/\text{kg}$ and Van der Waals volume $b = RT_c/8P_c$, P_c for HFC-134a is 40.59 bar, yielding $b = 9.39 \times 10^{-4} \text{ m}^3/\text{kg}$. The saturation vapor pressure is calculated from NIST.

For R507A, $T_c = 343.8\text{K}$, $T_b = 226.4\text{K}$, $V_b = 7.59 \times 10^{-4} \text{ m}^3/\text{kg}$, $b = 9.75 \times 10^{-4} \text{ m}^3/\text{kg}$. The saturation vapor pressure is calculated from NIST.

Tóth isotherm equation can be written as¹⁹,

$$\frac{C}{C_0} = \frac{KP}{\{1 + (KP)\}^{1/t}} \quad (9)$$

where, K is the Henry's law coefficient which can be written as,

$$K = k_0 \exp \left(\frac{Q_{st}}{RT} \right) \quad (10)$$

Here, k_0 is the pre-exponential coefficient, t is the Tóth constant and Q_{st} stands for isosteric heat of adsorption.

One form of Tóth equation used for methane experiments⁴,

$$\frac{C}{C_0} = \frac{P}{\left[\frac{k_0 \sqrt{MT}}{\exp \left(\frac{Q_{st}}{RT} \right)} + P^t \right]^{1/t}} \quad (11)$$

The equations (Eqs. 4,9 and 11) can be expressed to the following for desorption at a given temperature between initial and final pressures (p_i and p_f):

$$\Delta C_d = \frac{W_0}{V_a} \left[\left\{ \exp\left(-\frac{RT_d}{E} \ln\left(\frac{p_s}{p_i}\right)\right)^n \right\} - \left\{ \exp\left(-\frac{RT_d}{E} \ln\left(\frac{p_s}{p_f}\right)\right)^n \right\} \right] \tag{12}$$

$$\Delta C_d = C_0 \left[\frac{Kp_i}{\left\{1 + (Kp_i)^t\right\}^{1/t}} - \frac{Kp_f}{\left\{1 + (Kp_f)^t\right\}^{1/t}} \right] \tag{13}$$

$$\Delta C_d = C_0 \left[\frac{p_i}{\left(\frac{k_0 \sqrt{MT_d}}{\exp\left(\frac{Q_{st}}{RT_d}\right)} + p_i^t \right)^{1/t}} - \frac{p_f}{\left(\frac{k_0 \sqrt{MT_d}}{\exp\left(\frac{Q_{st}}{RT_d}\right)} + p_f^t \right)^{1/t}} \right] \tag{14}$$

5. Results and Discussion

Fig. 4 depicts the adsorption isotherms of methane on Maxsorb III specimen when pressures are varying from 1 to 20 bar at three different temperatures of 20, 40 and 60°C. The DA isotherm model has been used to fit the experimental data. It can be observed from Fig. 4 that the maximum uptake of methane on Maxsorb III specimen using DA model is around 0.13 kg/kg.

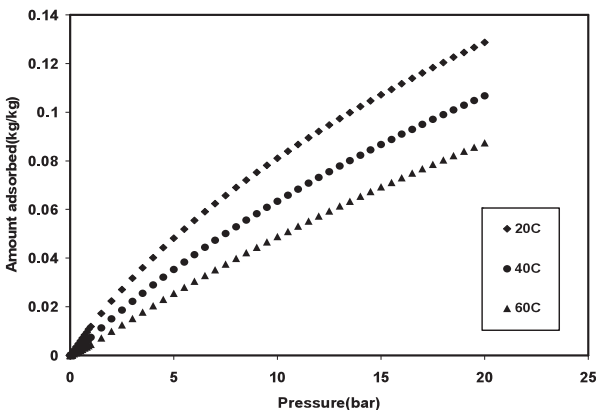


Fig. 4 Adsorption isotherms of methane on Maxsorb III using DA model.

The adsorption isotherms of methane on Maxsorb III using Tóth isotherm model is shown in the Fig. 5 when pressures are varying from 1 to 20 bar at three different temperatures of 20, 40 and 60°C. It can be observed from Fig. 5 that the maximum uptake of methane on Maxsorb III specimen using the Tóth model is around 0.12 kg/kg thus shows good agreement between the two assorted isotherm models.

The adsorption isotherms of HFC-134a on Maxsorb III specimen is shown in Fig. 6 where pressures are ranging from 2 to 18 bar and temperatures are varying from 20 to 60°C. DA isotherm model has been used to fit the experimental data. It can be seen from Fig. 6 that the maximum uptake of HFC-134a on Maxsorb III using the DA model is about 2.14 kg/kg.

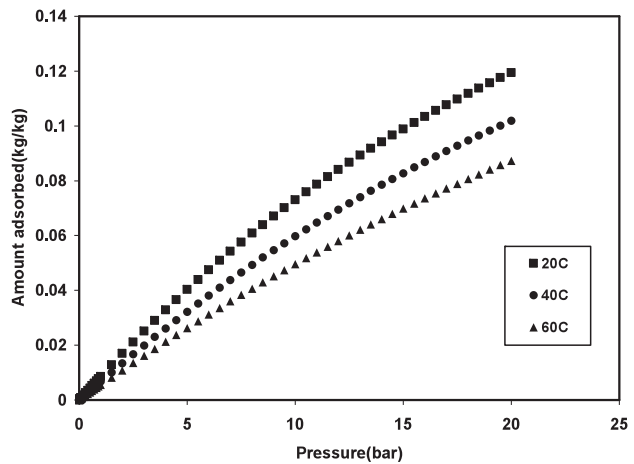


Fig. 5 Adsorption isotherms of methane on Maxsorb III using Tóth model.

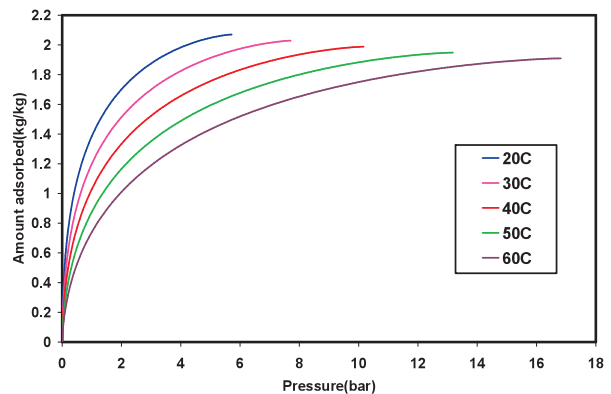


Fig.6 Adsorption isotherms of HFC-134a on Maxsorb III.

Fig. 7 shows a comparison of adsorption isotherms of R507A on Maxsorb III specimen between DA and Tóth isotherm fittings when

pressures are varying from 2 to 13 bar at three different temperatures of 5, 30 and 60°C. It can be seen from Fig. 7 that the maximum uptake of R507A on Maxsorb III specimen using DA and Tóth models are around 1.38 and 1.4 kg/kg, respectively. It can be seen from Fig. 7 that both the isotherm fittings match closely with each other. However, the DA isotherm fitting is about 3-5% higher as compared to the Tóth isotherm fittings.

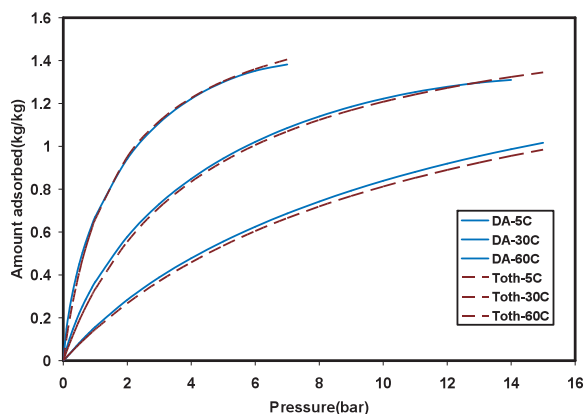


Fig. 7 Adsorption isotherms of R507A on Maxsorb III.

The parameters of DA and Tóth isotherm models for methane, HFC-134a and R507A on Maxsorb III system are regressed from our experimental data and these are furnished in Table 1, 2 and 3 respectively.

Table 1 Adsorption parameters of methane for DA and Tóth models.

Parameters	DA	Tóth
Limiting uptake W_0 [m^3/kg] for DA C_0 [kg/kg] for Tóth	1.17×10^{-3}	0.248
Characteristic Energy E [kJ/kg]	319.8	
Heterogeneity constant n [-]	1.42	
Pre-exponential coefficient k_0 [-]		3.1×10^{-8}
Isosteric heat of Adsorption Q_{st} [kJ/kg]		677.5
Tóth constant t [-]		1.3

Table 2 Adsorption parameters of HFC-134a for DA and Tóth models.

Parameters	DA	Tóth
Limiting uptake W_0 [m^3/kg] for DA C_0 [kg/kg] for Tóth	1.65×10^{-3}	2.32
Characteristic Energy E [kJ/kg]	79.4	
Heterogeneity constant n [-]	1.41	
Pre-exponential coefficient k_0 [-]		6.78×10^{-7}
Isosteric heat of Adsorption Q_{st} [kJ/kg]		244.6
Tóth constant t [-]		0.77

Table 3 Adsorption parameters of R507A for DA and Tóth models.

Parameters	DA	Tóth
Limiting uptake W_0 [m^3/kg] for DA C_0 [kg/kg] for Tóth	1.15×10^{-3}	1.77
Characteristic Energy E [kJ/kg]	58.04	
Heterogeneity constant n [-]	1.47	
Pre-exponential coefficient k_0 [-]		2.1×10^{-5}
Isosteric heat of Adsorption Q_{st} [kJ/kg]		237.2
Tóth constant t [-]		0.93

6. Conclusions

Adsorption characteristics of methane, HFC-134a and R507A on Maxsorb III specimen have been evaluated by using the desorption

method. Dubinin-Astakhov (DA), and Toth isotherm models are applied to fit the experimental data and the fitted values are found to be fairly consistent within the experimental errors. The present isotherm data of methane on activated carbon are useful in designing effective gas storage systems and the isotherm data of HFC-134a and R507A are useful in designing environmental friendly high pressurized bed adsorption cooling systems.

Nomenclature

V_{void}	void volume	m^3
V_{cell}	cell volume	m^3
m_{ac}	mass of activated carbon	kg
ρ_{s}	solid density	kg/m^3
$V_{\text{micropore}}$	micropore volume	m^3/kg
Δm_{void}	mass of void cell	kg
Δm_{pipe}	mass of pipe void	kg
ρ_{i}	initial cell density	kg/m^3
ρ_{f}	final cell density	kg/m^3
T_{d}	temperature at desorption	$^{\circ}\text{C}$
T_{a}	ambient temperature	$^{\circ}\text{C}$
Q_{st}	isosteric heat of adsorption	kJ/kg
R	universal gas constant	$\text{kJ}/\text{kg}\cdot\text{K}$
k_{o}	pre-exponential coefficient	
M	molecular weight	kg/kmol
T_{c}	critical temperature	$^{\circ}\text{C}$
t	Toth constant	-
E	activation coefficient	kJ/kg
P_{c}	critical pressure	bar
P_{s}	saturation pressure	bar

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