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Determination of effective diffusion coefficient of methane adsorption on activated carbon

Alireza Azimi*, Masoomeh Mirzaei
Department of Chemical Engineering, Mahshahr branch, Islamic Azad University, Mahshahr, (IRAN)
E-mail: alireza_azimi550@yahoo.com; mirzaei_fateme@yahoo.com
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ABSTRACT

Experimental data of adsorption of methane on two types of microporous activated carbon with different pore volume carried out at pressure up to 35 bar and ambient temperature. Adsorption equilibrium and kinetics data at high pressure were measured using volumetric method. Parameters of Longmuir equilibrium relation and effective diffusion coefficient were calculated from experimental data. The theoretical model was solved using the measured equilibrium data and diffusion coefficient as input parameters. A good agreement was observed between experimental data and modeling results. Storage capacity of activated carbons with high micropore volume was higher but diffusion coefficient and adsorption rate was lower than carbons with low micropore volume.

KEYWORDS

ANG;
Methane;
Adsorption;
Effective diffusion coefficient;
Activated carbon.

INTRODUCTION

Microporous solids are widely used in gas adsorption process. To describe this process isotherm data of gas on adsorbents and also kinetics results must be determined. Uptake data is applied to calculate diffusion coefficient of gas in solids. ANG (Adsorbed Natural Gas) is one of the applications of gas adsorption on microporous solids. ANG technology, based on adsorption of natural gas in porous materials at relatively low pressures 3.5-4 MPa and ambient temperature, are preferred compared to LNG (Liquid Natural Gas) and CNG (Compressed Natural Gas) applications[8]. Activated carbons, because of the great micropore volume they may contain, have shown to be an appropriate material, for adsorption hydrocarbons[1,3,4,6,9].

Description of the charge and discharge cycle dynamics of an ANG reservoir has been the subject of several studies in recent years[2,5,7,10].

In this work, a volumetric method is designed to measure the isotherm data and diffusion coefficient of methane on activated carbon. An accurate mathematical model is presented to calculate the uptake data and results of model and experiments are compared.

THEORETICAL MODEL

In this study an accurate model has been presented to calculate the uptake data of gas adsorption on microporous adsorbents. In this model diffusion resistance in micropores has been considered.

The continuity equation was written in the bed in axial direction (x).

$$\varepsilon\frac{\partial C}{\partial t}+(1-\varepsilon)\rho_s\frac{\partial \bar{q}}{\partial t}=-u\frac{\partial C}{\partial x} \quad (1)$$

Initial and boundary conditions for this equation has been

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presented as follow:

$$\begin{cases} \forall t = 0 \quad \text{for all } x \quad C = 0 \\ \forall x = 0 \quad \text{for all } t \quad C = C_0 \end{cases}$$

Diffusion equation in spherical pellet:

$$\frac{\partial q}{\partial t} = \frac{1}{r^2} D_{eff} \frac{\partial}{\partial r}\left(r^2 \frac{\partial q}{\partial r} \right) \qquad (2)$$

$$\begin{cases} \forall t = 0 \quad \text{for all } r \quad q = 0 \\ \forall r = 0 \quad \text{for all } t \quad \dfrac{\partial q}{\partial r} = 0 \\ \forall r = r_p \quad \text{for all } t \quad q_s(r_p, t) = \dfrac{q_m bP}{1 + bP}, \; P = ZCRT \end{cases}$$

Isotherm parameters at the last boundary condition will be achieved from experimental data.

$$\bar{q} = \frac{3}{r_p^3} \int_0^{r_p} q.r^2 .dr \qquad (3)$$

To obtain the uptake data of system in each kind of adsorbent particle, Eq. 2 is used and analytical solutions of these equations are presented below:

$$\frac{\bar{q}}{q_s} = \frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(- \frac{Dn^2 \pi^2 t}{r_p^2} \right) \qquad (4)$$

Where M_t is the total mass of the diffusing species that has adsorbed in the particle at time t, and M_∞ is the total adsorbed mass, so M_t / M_∞ is the fraction approach to equilibrium. At 70% uptake a plot of $ln\,(1 - M_t / M_\infty)$ versus t should be linear with slop $-\pi^2 Deff / r_p^2$.

Implicit finite difference method was applies to solve the set of equations. Iteration was used to obtain the, mean gas adsorbed and uptake data in the bed achieved as functions of time.

EXPERIMENTAL

Materials

Two granular microporous activated carbons, PK (PK1-3, steam activated carbon, from Norit) and AC (commercialized by Merck, Ref.:102514) with 1.5 mm diameters were selected in this study. Textural properties have been shown in TABLE 1. Methane and helium purities were 99.5% vol.

TABLE 1 : Specific Surface area (S_{BET}), total pore volume (V_t), micropore volume (V_{micro}) and bulk density (ρ_{bulk}) of activated carbons.

Carbon	S_{BET} (m^2/g)	V_t (cm^3/g)	V_{micro} (cm^3/g)
PKN[11]	696	0.47	0.23
ACM[12]	974	0.546	0.42

Apparatus

The experimental set-up for investigation of methane adsorption on activated carbon at the ambient temperature and 3.5 MPa pressure is shown in Figure 1. It consists of a cylindrical vessel which fills with activated carbon, a loading cell to supply gas during the experiments with pressure and temperature sensors with division scale of 0.01 bar and 0.01 K, a pressure control valve and vacuum pump. Temperature and pressure data are measured and sent to the computer to record the data in each second. The vessel and loading cell volume are 200 cc and 1710cc respectively.

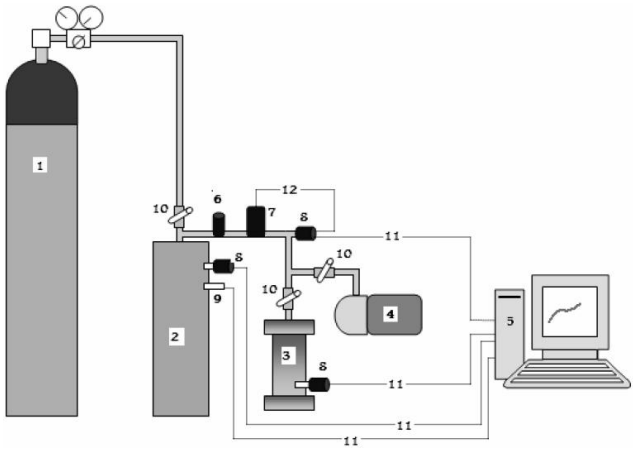

Figure 1 : Experimental set up, (1) methane, (2) Loading cell, (3) Vessel, (4) Vacuum pump, (5) PC, (6) Metering valve, (7) Pressure control valve, (8) Pressure sensors, (10) Valves, (11) Electronically signal to computer, (12) Signal to Pressure control valve

Procedure

Adsorption isotherms

Adsorption isotherms data were determined with the volumetric method. The vessel was filled with specified weight of activated carbon and then heated up to 80°C for 2 hours and vacuumed with vacuum pump simultaneously. Loading cell was pressurized with methane in the range of 1 to 50 bar at the different discreet values. In each initial pressure of loading cell, the exit valve of loading cell, metering valve, control valve and entrance valve of vessel were opened. Loading cell pressure was decreased until equilibrium was reached

and the pressure of the vessel was equal to loading cell pressure. According to the initial and final pressure of loading cell, amount of gas adsorbed on activated carbon was calculated from the following equation:

$$n_{ads} = \frac{P_0 V_{L-C}}{Z_0 RT} - \frac{P_f (V_{L-C} + V_c + V_{AC})}{Z_f RT},$$

$$Q = \frac{1000 \times n_{ads}}{W_0} (mmole/g) \quad (5)$$

Peng-Robinson equation was used to evaluate compressibility factor.

$$Z^3 - (1-B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0 \quad (6)$$

Adsorption isotherm curves were reached from plotting adsorbed amount of methane *(Q)* versus initial pressure for two activated carbons. For each activated carbon storage capacity can be determined as follow.

$$Storage\,Capacity = \frac{n_{ads} \times 83.14 \times 273.15}{V_{vessel}} \left(V/V\right) \quad (7)$$

Adsorption kinetics

The effective diffusion coefficient of methane to activated carbon was determined from uptake data. To measurement these data after heating and vacuum the activated carbon, loading cell pressurized to 50 bar with methane. The pressure control valve was set on 35 bar to keep the vessel entrance pressure at this value. The exit valve of loading cell was opened and gas pressure in the line was increased to 35 bar so control valve was closed automatically then entrance valve of vessel was opened and gas was entranced to the vessel and the pressure in the line decreased, in this condition control valve was opened immediately, so the pressure in the line was reached 35 bar again. During this process loading cell pressure was decreased and this behavior was repeated until reaching constant pressure in the loading cell. It means that methane cannot be more adsorbed on the activated carbon in this condition. Temperature and pressure of loading cell were recorded and in each second amount of methane adsorbed was calculated from these data due to the equation of $M_t = 16 \times n_{ads}$.

RESULTS AND DISCUSSION

Adsorption isotherms

Longmuir equilibrium relation has two parameters as it has been shown in Eq. 8.

$$Q = \frac{Q_m b P}{1 + b P} \quad (8)$$

The equilibrium adsorption data measured for methane on PKN and ACM are shown in Figure 2. They were plotted according to the linearized form of the Longmuir equation. The data obtained from experiments fit into a straight line quite well. Isotherm parameters were calculated from illustrated linear regression lines.

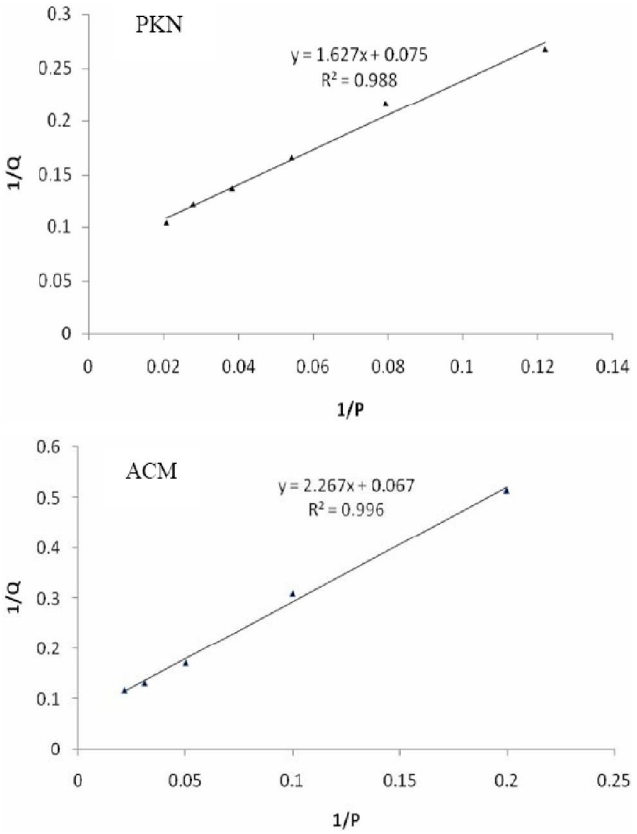

Figure 2 : Longmuir equation for adsorption isotherms of methane on PKN and ACM

Figure 3 shows the equilibrium isotherms obtained experimentally (points) as compared to each Longmuir equation with adjusted parameters. The adjusted parameters (Q_m *and* b) are shown in TABLE 2.

By comparison of two isotherms it can be seen that, in the same pressure, ACM shows more adsorbed methane than PKN. It can be due to higher pore volume and micropore volume of ACM than PKN.

Adsorption kinetics

Methane was charged into the vessel according to the procedure previously described. Uptake data cal-

culated as mentioned in section Procedure.

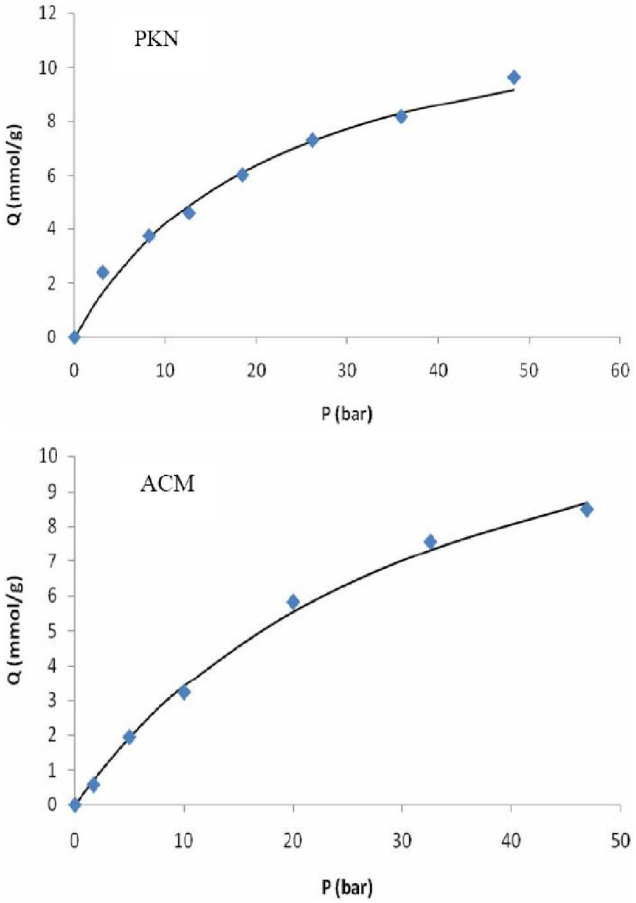

Figure 3 : Adsorption isotherms of methane, lines represent the longmuir fit to experimental data

In Figure 4, *ln (1-M$_t$/M$_\infty$)* has been plotted versus *t* for ACM and PKN. Effective diffusion coefficients of two activated carbons were determined from slop of straight line. These values are listed in TABLE 2.

TABLE.2 : Comparison of PKN and ACM

Carbon	Qm (mmol/g)	b (1/bar)	Storage capacity (v/v)	D_{eff} (cm^2/s)
PKN	13.33	0.046	59.75	1.25×10^{-5}
ACM	14.92	0.0295	84.1	4.6×10^{-6}

Physical properties and model input parameters have been shown in TABLE 3.

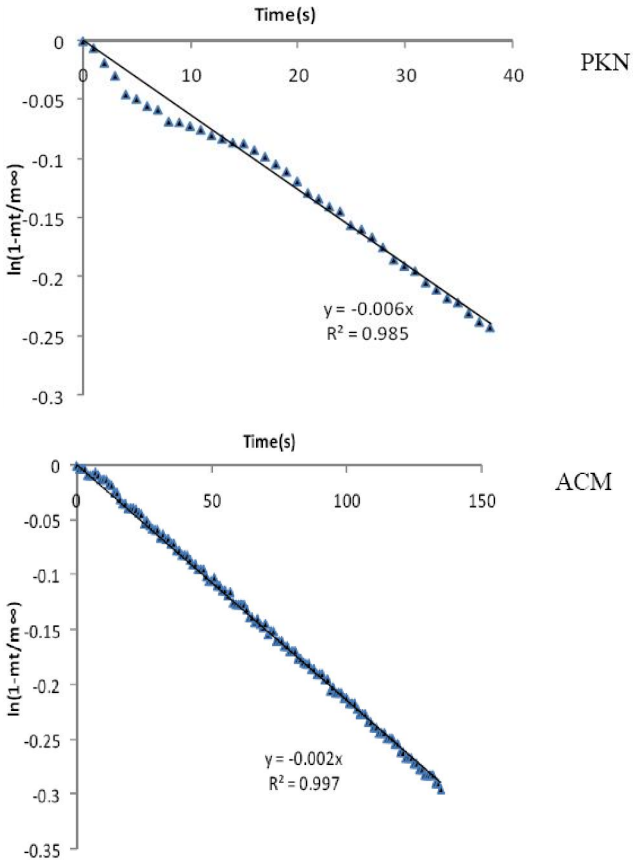

Figure 4 : Straight line achieved from plotting *Ln (1-mt/M")* versus *t*

Longmuir parameters and also effective diffusion coefficients are used in the model as input data to calculate uptake data from simulation. The experimental data and model results of uptake rate measurement for two activated carbons are shown in Figure 5.

Figure 5 shows the good adjustment between the model results and experimental data for two activated carbons with different properties, so this model can be used to determine effective diffusion of gas on the porous solids with high accuracy. Because in presents model diffusion resistance in micropore has been considered and this term has important effect in kinetic of gas adsorption on microporous adsorbents.

According to Figure 5, at the beginning of the process rate of adsorption is high, and then decreased and

TABLE 3 : Model input parameters

Parameter	value	Parameters	value	Parameters	value
L	10 (cm)	Co	0.01808 (g/cm3)	Q_m (ACM)	14.92 (mmol/g)
D	4.5 (cm)	Q_m (PKN)	13.33 (mmol/g)	b (ACM)	0.0295 (1/bar)
r_p	1.5 (mm)	b (PKN)	0.046 (1/bar)	D_{eff} (PKN)	1.25×10-5(cm2/s)
D_{eff} (ACM)	4.6×10-6 (cm2/s)	Δz	1 (cm)	Δt	1 (s)

finally reached to the maximum value. This trend has been achieved for two carbons, but for ACM the maximum value reached after the longer time. It can be due to the higher micropore volume of this carbon. The higher micropore volume caused higher amount of methane adsorption as mentioned before. As a result, it can be seen that activated carbon with more micropore volume, has higher storage capacity but lower rate of adsorption.

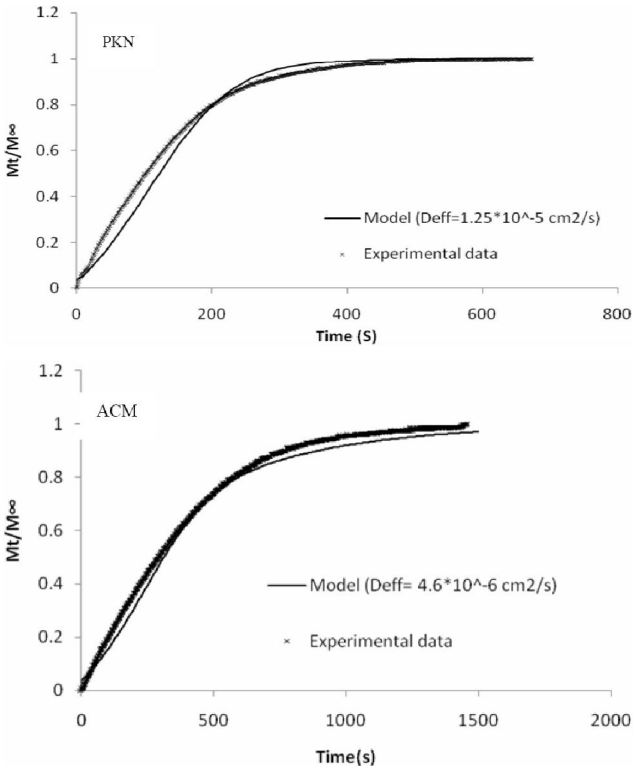

Figure 5 : Experimental data and modeling results of uptake data

CONCLUSIONS

Experimental and theoretical study of methane adsorption on two types of activated carbon performed in a cylindrical vessel filed with microporous carbon. Equilibrium and kinetics data were measured using a volumetric method. Longmuir equilibrium parameters and effective diffusion coefficients were determined and used in the model as input parameters. Experimental data and modeling results indicated good adjustment. Activated carbons with different micropore volume were selected in this study. As a result, Activated carbon with higher micropore volume has been shown higher storage capacity but lower adsorption rate and diffusion coefficient.

NOMENCLATURE

C	:	Gas density (g/cm^3)
q	:	Adsorbed gas(-)
u	:	Gas velocity (cm/s)
C_o	:	Inlet concentration (g/cm^3)
$\bar{q}$	:	Mean gas adsorbed (g/g)
x	:	Length coordinate of vessel (cm)
D_{eff}	:	Effective diffusivity (cm^2/s)
r	:	Radius coordinate in particle (cm)
Z	:	Compressibility factor
P	:	pressure (Pa)
R_o	:	Outer radius of vessel (cm)
B, q_m	:	Longmuir constant
r_p	:	Particle radius (mm)
z	:	Axial coordinate in particle (cm)
t	:	Time(s)
L	:	Length of vessel (cm)
Q	:	Adsorbed gas (mmol/g)
P_0	:	Initial pressure of loading cell (bar)
P_f	:	Final pressure of loading cell (bar)
V_{L-C}	:	Loading cell volume (cm^3)
V_{AC}	:	Avoid volume of vessel (cm^3)
n_{ads}	:	Adsorbed gas (mole)
W_0	:	Adsorbent weight (g)
V_c	:	Conectors volume (cm^3)

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