Colloids and Surfaces A: Physicochem. Eng. Aspects 444 (2014) 104–113

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Methane adsorption characteristics on coal surface above critical temperature through Dubinin–Astakhov model and Langmuir model

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HIGHLIGHTS

- Methods for estimating pseudo-saturation vapor pressure were investigated.
- A procedure of determining the parameter, k, in $p_s = p_c(T/T_c)^k$ was proposed.
- The influence of the characteristic curve form on the prediction was investigated.
- A new form of the characteristic curve was proposed.

GRAPHICAL ABSTRACT

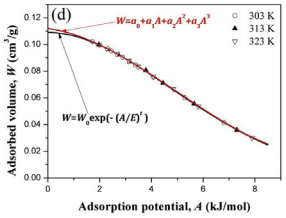

Fig. 5. Characteristiccurvesfor(d) Leiy-1#. The p_s was calculated by the modified Schwarz's method.

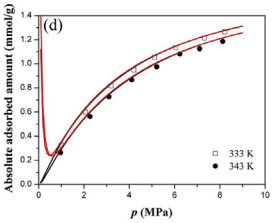

Fig. 6.Experimental *vs* predictive isotherms of methane on: (d) Leiy-1#. The red lines are predictive isotherms which based on Eq. (17) and the black lines are those which based on Eq.(14).

ARTICLE INFO

Article history:
Received 16 October 2013
Received in revised form
11 December 2013
Accepted 24 December 2013
Available online 3 January 2014

Keywords:
Coal
Methane
D–A equation
Pseudo-saturation vapor pressure
Characteristic curve

ABSTRACT

To acquire the required information of the adsorption system under supercritical conditions, four different rank coals were selected as studied samples. The textures of the coals were characterized through N_2 adsorption at 77 K. Their surface morphologies were analyzed by scanning electron microscopy (SEM). The high pressure adsorption data of methane on the coals were obtained at supercritical temperatures. The data were analyzed using the Dubinin–Astakhov (D–A) and Langmuir models. The methods for estimating pseudo-saturation vapor pressure were investigated. And the influence of the characteristic curve form on the D–A equation prediction was investigated. The results show that the constants derived by matching the experimental data to the Langmuir model might lack physical significance, though the Langmuir model was of the correct qualitative form to represent the isotherms of methane on coals. The method for estimating pseudo-saturation vapor pressures proposed by Schwarz failed to render the experimental data to fall onto one characteristic curve. A modified procedure of determining the value of parameter k in Schwarz's equation, i.e. $p_s = p_c(T/T_c)^k$ was proposed. It was found that the modified approach gave the most suitable temperature-independent characteristic curves with determination coefficient $R^2 > 0.9943$. The form of the characteristic curve could influence the D–A model prediction. Using cubic polynomial as characteristic curve form would result in an abnormal prediction i.e. the adsorption amount would increase with the pressure dropping when the pressure is less than approximately 0.9 MPa for Xingq-1–5# and Xujd-1#, 0.8 MPa for Qingh-2–3#, and 0.5 MPa for Leiy-1#. A new form of the characteristic curve deduced from D–A equation was proposed. The prediction uncertainty of D–A equation by using this new characteristic curve form is less than 2.43%.

1. Introduction

Adsorption phenomena are increasingly utilized to perform desired bulk separation or purification purposes [1–5]. Coal is porous material. Coalbed methane (CBM) is unconventional natural gas associated with coal. The key component of CBM is CH_4 (CH_4

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http://dx.doi.org/10.1016/j.colsurfa.2013.12.047

content being 88–98% [6]). CBM is retained in coal beds mainly in adsorbed state [7,8]. CBM is not only the major root of coal mine disaster and atmospheric pollution source, but also a valuable non-renewable energy [9]. The interest both in recovery of CH_4 from coal seam and in outburst hazards related to coal mining has led to extensive study of gas sorption in coal [7,9–12].

In recent years, increase in atmospheric CO_2 concentration has raised concern about climate change and led to worldwide efforts on reduction of CO_2 emissions [7,13–18]. Although several options for CO_2 sequestration are being considered, a potentially attractive approach is the storage of CO_2 in deep, unmineable coal beds [7,19]. Such coalbeds frequently contain large amounts of recoverable CH_4, and the recovery of this gas can be enhanced by injecting CO_2 into the coal beds [7,20]. The injection of CO_2 can serve dual purposes to sequester large amounts of CO_2 and to simultaneously provide an increased supply of CH_4. Consequently, some of the sequestration costs can be recovered in the value of the CH_4 produced [7,19].

The design of optimal recovery of CH_4 and CO_2 sequestration in coal beds relies greatly on the availability of high-pressure, supercritical adsorption data for gas sorption as well as reliable adsorption models that are capable of accurate predictions of adsorption phenomena [20]. To simulate reservoir conditions, laboratory sorption experiments are generally conducted at elevated temperature, usually between 293 and 323 K [7,11]. However, the coal bed temperature increases linearly with mining depth increasing [21].

Methane sorption isotherms in coal are commonly IUPAC type I [7]. The Langmuir model is widely used in the CBM industry because of its simplicity and providing a reasonable fit to most experimental data [7]. However, the assumption of an energetically homogeneous surface as proposed by Langmuir theory is not true for coal [11]. Furthermore, the Langmuir model cannot predict methane adsorption amount at different temperatures from one adsorption isotherm. This means that to obtain methane capacity at different temperatures there would be a lot of experiments to do.

The Dubinin–Astakhov (D–A) model has been commonly applied to the description of type I isotherms [22–24]. The D–A equation was mainly developed for the adsorption of vapors below the critical point [22]. However, experiments of gas adsorption on porous solids have shown that there is no abrupt change in the adsorption during the transition from sub-critical to super-critical conditions [22]. This suggests that the D–A equation can be empirically applied to super-critical gases as well [22]. The nice feature of using D–A equation for description of gas adsorption is that a single characteristic curve would be obtained if the characteristic energy is independent of temperature [22]. If the characteristic curve for an adsorption system is known, then adsorption uptake of the adsorbate at different temperatures could be predicted.

The problems of applying the D–A equation to supercritical fluids are [11,22,25]: (1) the estimation of the saturation vapor pressure, p_s. Above the critical temperature, T_c, the concept of saturation vapor pressure does not exist, hence the use of pseudo-saturation vapor pressures was proposed; (2) the density of the adsorbed phase at a given temperature. In order to obtain the volume of adsorbed phase, it is necessary to have a value of adsorbed phase density. The adsorbed phase density is not directly measurable and as a consequence, its value is approximated; and (3) the form of the temperature-invariant characteristic curve to be utilized. The influence of the methods for estimating pseudo-saturation vapor pressures on characteristic curves of activated carbon-methane adsorption systems has been reported [26]. However, to our knowledge, no study has been reported for coal-methane systems, and no study has been reported on the influence of the characteristic curve form on the D–A equation prediction too.

To avoid these problems above, Kim et al. [27] used gas density instead of gas pressure (and adsorbed phase density rather than pseudo-saturation vapor pressure) to modify the classic Dubinin–Radushkevich (D–R) equation, and then applied the modified D–R equation to the gases adsorption on coals under supercritical conditions. However, the modified D–R equation is not convenient to use in CBM industry for the gas density is not as intuitive as pressure.

In the present work, methane adsorption data on four different rank coals were obtained at supercritical temperatures. The D–A equation is applied to methane-coal isotherm data at elevated temperature. The purposes of the current study are: (1) to determine which empirical method presented in the literature to evaluate the pseudo-saturation vapor pressure is most suitable for analyzing the adsorption data above the T_c of methane. The criterion used in our analysis is that the data should be reduced to temperature-independent plots; and (2) to determine the form of the temperature-invariant characteristic curve. The criterion is prediction accuracy.

Table 1
Proximate and ultimate analysis of the coals.

Sample	Proximate analysis wt.%				Ultimate analysis wt.%			
	Ash	VM	FC	Moisture	C	H	O	N
Xingq-1–5#	8.40	29.83	71.17	0.80	77.42	6.58	14.60	1.40
Qingh-2–3#	1.66	21.47	78.53	0.68	84.66	6.47	7.08	1.79
Xujd-1#	11.71	11.66	88.34	0.67	88.70	3.56	4.35	3.39
Leiy-1#	18.45	5.55	94.45	0.15	90.98	1.26	5.53	2.23

Ash was calculated on a dry basis; Volatile matter (VM) and fixed carbon (FC) were calculated on a dried, ash-free basis.

2. Experimental

2.1. Materials

In this work, Xingqing coal (bituminous coal, Qinghai China, labeled as Xingq-1–5#), Qinghua coal (bituminous coal, Qinghai China, labeled as Qingh-2–3#), Xujiadong coal (bituminous coal, Hunan China, labeled as Xujd-1#),and Leiyang coal (anthracite, Hunan China, labeled as Leiy-1#) were used. The proximate analysis and ultimate analysis for the coals are given in Table 1. The oxygen content was determined by difference [28].The sulphur in the four coals was not detected. The coal samples were crushed to particles with size of 60–80 mesh.

2.2. Methods

2.2.1. 2.2.1. Characterization

Textural characterization of the coal samples was conducted using a NOVA1000e surface area and pore size analyzer (Quantachrome Company, USA) with N_2 (at 77 K) as adsorbate. Prior to analysis, samples were degassed at 383 K for 24 h [29]. The specific surface area was calculated by the multipoint BET method [30,31]; the micropore volume was determined by the D-R equation [31,32]; the total pore volume V_t was evaluated from the nitrogen adsorption at $p/p^0 = 0.98–0.99$ [33]; and the pore size distribution was calculated by the by the nonlocal density functional theory (NLDFT) method [31].

Surface morphology was investigated by scanning electron microscopy (SEM) (JEOL/EO JSM-5900, Japan).

2.2.2. Adsorption of methane

The adsorption isotherms were obtained through an equilibrium volumetric method. The detailed experimental method was presented elsewhere [29]. To avoid the influence of water in the coals on the calibration of the reference cell volume, the samples were dried in an oven overnight at 383 K before methane adsorption [29,32].