Supercritical-CO₂ Adsorption Quantification and Modeling for a Deep Coalbed Methane Reservoir in the Southern Qinshui Basin, China

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ABSTRACT: Accurate depiction of the adsorption capacity of supercritical CO₂ (ScCO₂) by existing adsorption models is an important focus for deep coal seams in CO₂-enhanced coalbed methane (CO₂-ECBM) recovery. To investigate the applicability of different adsorption models for the adsorption isotherms of ScCO₂, the validities of 10 different adsorption models were analyzed, based on analyses of the adsorption characteristics of ScCO₂ from deep coal seams of the Southern Qinshui Basin, China. These models include the Langmuir (L) model, two-parameter Langmuir (TL) model, Toth (T) model, Langmuir–Freundlich (LF) model, extended Langmuir (EL) model, double parameter Brunauer–Emmett Teller model, three-parameter BET (TBET) model, Dubinin–Radushkevich (D–R) model, Dubinin–Astakhov (D–A) model, and Ono–Kondo lattice (OK) model. These models were tested for both the excess and absolute adsorption capacities of ScCO₂ under various temperatures and pressures. The simulation accuracy of the different adsorption models was analyzed. The optimal models for the adsorption of ScCO₂ in deep coal seams were selected based on a comprehensive analysis of the simulation parameters, standard error, and residual sum of squares. There were obvious differences in the validity of the different adsorption models in terms of the excess adsorption capacity and absolute adsorption capacity of ScCO₂. The D–A and D–R models are the optimal adsorption models for the adsorption isotherms of the excess adsorption of ScCO₂ for the whole tested pressure range. The T, TL, and D–R models are the optimal adsorption models in simulation of the excess adsorption capacity of ScCO₂ when the equilibrium pressure is divided into two sections at the point of 8.13 MPa. In simulation of the absolute adsorption capacity of ScCO₂, the TBET and LF models are the optimal adsorption models among the selected models when the equilibrium pressure is less than or equal to 8.13 MPa. The linear, exponential, logarithmic, power function, and polynomial adsorption simulation all have good precision in the simulation of the absolute adsorption capacity of ScCO₂ when the pressure is beyond 8.13 MPa.

1. INTRODUCTION

Deep coalbed methane (CBM) is a clean energy source and is considered as one of the primary natural gas resources in China.¹,² Compared with shallow CBM reservoirs, deep-CBM formations have some unique reservoir properties because of the greater burial depth. For example, deep-CBM formations commonly have high gas content with high initial reservoir pressure, ultralow permeability, and high-stress conditions. These combined reservoir characteristics pose challenges for CBM exploration and development.²–⁴ Enhanced CBM production through sequestration of CO₂ in deep coal seams is one attractive alternative to increase gas recovery and simultaneously reduce greenhouse gas emission to the atmosphere.⁵–¹³ CO₂-enhanced CBM technology appears to be a “win–win” innovative technology for environmentally friendly energy production. However, there are key technical challenges to be solved before it can be commercially implemented, including injection optimization, methane–CO₂ counter-diffusion quantification, multicomponent gas adsorption and competitive adsorption, and phase modification of CO₂.
Models. For a wide pressure range of CO₂ adsorption, the L
studies were conducted to evaluate the accuracy of the various
needs to be investigated in detail for reservoir assessment and
N₂. Commonly, all adsorption models used to depict gas
including the Freundlich model, Langmuir (L) model, Brunauer–
model was found to be ine-
CO₂ adsorption because of the unique phase change behavior of
ff
The validity of di-
models used to depict gas
methane recovery with CO₂ injection (CO₂-ECBM).9,22
under in situ reservoir pressure and temperature conditions,
among others. Thus, supercritical CO₂ (ScCO₂) adsorption
behavior under the in situ conditions of deep coal seams needs
adsorption occurs on a
fl
at surface. The adsorption is local,
Because deep-CBM formations are normally associated with
high temperature and pressure, CO₂ usually exists in a
supercritical condition during injection. It is essential to
investigate the validity of the different adsorption models used
for modeling ScCO₂ adsorption in deep coal seams. The
Southern Qinshui Basin (SQB) in China is a mature CBM
development with a deep-CBM reservoir,39–41 with semianthracite and anthracite. In this study, 10 different models
were tested and compared based on semianthracite and
anthracite from the SQB. These models are the L model, two-
parameter Langmuir (TL) model, T eth (T) model, Langmuir–
Freundlich (LF) model, extended Langmuir (EL) model,
double parameter BET (DBET) model, three-parameter BET
(TBET) model, D–R model, D–A model, and OK model.
These models were used in simulation studies to investigate the
accuracy and reliability of adsorption modeling in reservoir
simulation results and to optimize the appropriate model for
ScCO₂ adsorption through comparative analysis. The obtained
results lay the foundation for deep-CBM reservoir development
and CO₂-enhanced CBM production optimization.

2. REVIEW OF ADSORPTION Isotherm MODELS

Table 1 summarizes all adsorption models used in this work. Each model is depicted in the following sections.

2.1. L Model and Its Derivative Models. The L model assumes that the surfaces of the adsorbent are homogeneous and
that adsorption occurs on a flat surface. The adsorption is local, specific, and occurs at a limited number of sites under
a monolayer of adsorbate, and each localized site can accom-

Table 1. Adsorption Model Equations and Simulation Parameters Used in This Study

| model name   | model equations | equation nos | simulation parameters |
|--------------|-----------------|--------------|-----------------------|
| L model      | \( V = V_0 \frac{p}{p_c + p} \) | (1)          | \( V_0, p_c \)        |
| TL model     | \( n_{\text{excess}} = \frac{p}{K_\text{L} + p} \left( 1 - \frac{V_{\text{L}}K_p}{1 + (K_p)^{1/n}} \right) \) | (2)          | \( n_{\text{excess}}, K_p \) |
| T model      | \( V = \frac{V_{\text{L}}K_p^{1/n}}{1 + (K_p)^{1/n}} \) | (3)          | \( V_{\text{L}}, K_p \) |
| LF model     | \( V = \frac{V_{\text{L}}K_p}{1 + \sqrt{K_p}p} \) | (4)          | \( V_{\text{L}}, K_p \) |
| EL model     | \( V = \frac{V_{\text{L}}K_p}{1 + K_p^{1/n}} \) | (5)          | \( V_{\text{L}}, K_p, n \) |
| DBET model   | \( V = \frac{V_{\text{C}}p}{(p^0 - p) \left[ 1 + (C - 1) \left( \frac{p}{p^0} \right)^C \right]} \) | (6)          | \( V_{\text{C}}, p^0 \) |
| TBET model   | \( V = \frac{V_{\text{C}}p}{(p^0 - p) \left[ 1 + (C - 1) \left( \frac{p}{p^0} \right)^C \right] \left( \frac{p}{p^0} \right)^{n+1}} \) | (7)          | \( V_{\text{C}}, p^0 \) |
| D–R model    | \( V = V_0 \exp \left[ -DL\ln \left( \frac{p}{p^0} \right) \right] \) | (9)          | \( V_0, D, n \) |
| D–A model    | \( V = V_0 \exp \left[ -DL\ln \left( \frac{p}{p^0} \right) \right] \) | (10)         | \( V_0, D \) |
| OK model     | \( \Gamma = \frac{2\Gamma_0 \left[ 1 - \exp \left( \frac{e}{RT} \right) \right]}{n_0 \rho_{\text{ad}} \left( \rho_{\text{vd}} - \rho_{\text{bb}} \right) + \rho_{\text{ad}} \exp \left( \frac{e}{RT} \right)} \) | (11)         | \( \Gamma_0, \frac{e}{RT} \) |
Table 2. Burial Depth, R_{\text{max}}, Maceral of Experimental Coal Samples

| sample ID | burial depth (m) | R_{\text{max}} (%) | vitrinite (%) | maceral mass fraction |
|-----------|------------------|---------------------|---------------|----------------------|
|           |                  |                     | telocollinite | desmocollinite       | inertinite (%)      | exinite (%) | mineral (%) |
| Yuwe      | 539              | 2.18                | 12.90         | 60.76               | 23.16               | 0           | 3.18        |
| Sihe      | 326              | 3.37                | 20.56         | 59.28               | 18.36               | 0           | 1.80        |
| Chenghuang| 457              | 2.97                | 19.80         | 56.00               | 21.40               | 0           | 2.80        |

*Note: R_{\text{max}} is the maximum vitrinite reflectance (%).*

modulate only one adsorbate.42 Based on the above assumptions, the L model can be derived as

\[ V = \frac{V_L}{K_L} \left(1 + \frac{\rho_{\text{CO}_2}(\rho_s, T)}{\rho_{\text{adsorbed}}}\right)^{-n} \]  

(1)

where \( V \) is the adsorption volume (cm\(^3\)/g), \( V_L \) is the Langmuir volume (cm\(^3\)/g), \( p \) is the pressure of adsorption equilibrium (MPa), and \( K_L \) is the Langmuir pressure (MPa).

The TL model was established by introducing the density of the free phase and density of the adsorbed phase in conjunction with the L model; the TL model can be defined as

\[ n_{\text{excess}} = n_{\text{id}} \frac{p}{K_L + p} \left(1 - \frac{\rho_{\text{CO}_2}(\rho_s, T)}{\rho_{\text{adsorbed}}}\right) \]  

(2)

where \( n_{\text{excess}} \) is the excess adsorption capacity (mmol/g), \( n_{\text{id}} \) is the absolute adsorption capacity when the pore surface is fully covered by CO\(_2\) (mmol/g), \( p \) is the pressure of adsorption equilibrium (MPa), \( \rho_{\text{CO}_2} \) is the density of the free phase (g/m\(^3\)), \( K_L \) is the Langmuir coefficient simulated by the adsorption model, and \( \rho_{\text{adsorbed}} \) is the density of the adsorption phase.43

The T, LF, and EL models were established by adopting three parameters: the binding constant \( K_L \), model parameter \( n \), and the Langmuir pressure \( P_L \), based on the L model.

Tóth formulated a three-parameter equation. Although the use of the Langmuir's isotherm implies a homogeneous surface, the choice of the isotherm suggests a heterogeneous surface if \( n \neq 1 \) (0 < \( n \) ≤ 1).44 The T model (eq 3), LF model (eq 4), and EL model (eq 5) can be derived, respectively, as

\[ V = \frac{V_L K_L p}{1 + (K_L p)^n} \]  

(3)

\[ V = \frac{V_L K_L p^n}{1 + K_L p} \]  

(4)

\[ V = \frac{V_L K_L p}{1 + K_L p + n \sqrt{K_L p}} \]  

(5)

where \( p \) is the pressure of adsorption equilibrium, MPa; \( P_L \) is the Langmuir pressure (MPa); \( V \) is the adsorption volume when the pressure reaches equilibrium (cm\(^3\)/g); \( V_L \) is the Langmuir volume (cm\(^3\)/g); \( K_L \) is the binding constant (m\(^3\)/[t · (MPa)]\(^{-n}\)); and \( n \) is a model parameter associated with the temperature and the distribution of coal pores.

2.2. BET Model. Brunauer et al. established poly-molecular layer theory based on the Langmuir adsorption theory by modifying the monolayer assumption into multilayer sorption potential.46 Following Brunauer et al.’s work, the DBET model (eq 6) and TBET model (eq 7) were derived, respectively, as

\[ V = \frac{V_{\text{id}} C_p}{(p^0 - p) \left[1 + (C - 1) \left(\frac{p}{p^0}\right)^n\right]} \]  

(6)

\[ V = \frac{V_{\text{id}} C_p}{(p^0 - p) \left[1 - (n + 1) \left(\frac{p}{p^0}\right)^n + n \left(\frac{p}{p^0}\right)^{n+1}\right]} \]  

(7)

In eq 7, \( p^0 \) can be obtained as follows

\[ p^0 = P_c \left(\frac{T_c}{T}\right)^2 \]  

(8)

where \( P_c = 7.38 \) MPa is the critical pressure of CO\(_2\); \( p^0 \) is the saturated vapor pressure (MPa); \( T_c = 304.25 \) K is the critical temperature of CO\(_2\); \( V_{\text{id}} \) is the adsorption capacity parameter of the monolayer (cm\(^3\)/g); \( C \) is a constant associated with the adsorption heat and the liquefied adsorbate; \( p \) is the pressure of adsorption equilibrium (MPa); and \( n \) is a model parameter associated with the temperature and the distribution of coal pores.

2.3. D–R Model and D–A Model. The D–R and D–A models were developed based on the adsorption potential theory.46,47 The D–R model can be derived as

\[ V = V_0 \exp\left[-D L n \left(\frac{P_0}{P}\right)^n\right] \]  

(9)

and the D–A model can be derived as

\[ V = V_0 \exp\left[-D L n \left(\frac{P_0}{P}\right)^n\right] \]  

(10)

where \( V_0 \) is the micropore volume (cm\(^3\)/g), \( D \) is a constant associated with the net adsorption heat, \( P^0 \) is the saturated vapor pressure (MPa), and \( n \) is a model parameter associated with the temperature and distribution of coal pores.

2.4. OK Model. The OK model is based on lattice theory and was originally proposed by Ono and Kondo and extended by Sudibandrio et al.46,49

\[ \Gamma = \frac{2 \Gamma_0 \left[1 - \exp(\epsilon_i/kT)\right]}{\rho_{\text{adsorbed}} / (\rho_{\infty} - \rho_{\text{inc}}) + \rho_{\text{inc}} \exp(\epsilon_i/kT)} \]  

(11)

where \( \Gamma \) is the total adsorption capacity of each phase (mmol/g), \( \Gamma_0 \) is the theoretical monolayer saturation adsorption density (mmol/g), \( \rho_{\infty} \) is the density of CO\(_2\) ontology phase (mmol/L), \( \rho_{\text{inc}} \) is the density of the adsorbed phase, taken as 23.3636 mmol/L, \( \epsilon_i \) is the contact potential energy between adsorbate molecules and the micropore surface (J), \( k \) is a constant of 1.38065 × 10\(^{-23}\) J/k, and \( T \) is the experiment temperature (K).
3. MATERIALS AND METHODS

3.1. Origin and Characteristics of Coal. The coal in the SQB is mostly semianthracite and anthracite. In this study, fresh coal samples from coal seam no. 3, named the Yuwu, Sihe, and Chengzhuang samples, were collected from the Yuwu, Sihe, and Chengzhuang coal mines in the SQB, respectively; the characteristics of these coal samples are shown in Table 2. The samples were collected by columnar sampling according to Chinese National Standard GB/T16773-2008 and were prepared into pulverized coal samples by crushing and screening fresh air-dried grains to the particle size range of 0.18–0.25 mm, according to Chinese National Standard GB/T475-2008.

Coal petrography, proximate analyses, and specific surface analyses were conducted according to Chinese National Standards GB/T8899-2013, GB/T212-2008, and GB/T21650-2008.52 Coal petrography, proximate analyses, and specific surface analyses were conducted according to Chinese National Standards GB/T8899-2013, GB/T212-2008, and GB/T21650-2008.52–54 An AXIO Imager M1m microspectrophotometer made by Zeiss, Germany, was used for coal petrography measurements (maceral composition and $R_{o, max}$), and a TriStar II3020 made by Micromeritics Instrument Corporation, USA, was used for measurement of specific surface area.

Mercury intrusion porosimetry (MIP) was conducted to analyze the pore size distribution for all coal samples, using the Autopore IV 9500 made by Micromeritics Instrument, USA, at pressure up to 60,000 psia (413.7 MPa) following ISO 15901-1-2016.38 The pore surface areas of all coal samples were analyzed by applying the BET theory, which is a multilayer adsorption theory.56 Micropore observations and mineral quantitative analyses of anthracite samples were performed on a ZEISS Sigma field emission-scanning electron microscope (FE-SEM operating at 20 kV, equipped with an energy dispersive spectrometer for analysis of minerals composition) and abided by Chinese Petroleum and Natural Gas Industry Standards SY/T 5162-2014 and SY/T 6189-1996, respectively.57,58

3.2. Experimental Apparatus. The $\text{CO}_2$ adsorption isotherm was measured using the volumetric method and we followed the recommended procedure of Chinese National Standard GB/T19560-2008.59 An independent high-pressure isothermal adsorption instrument DXF-II was developed in-house; the system is shown in Figure 1. The system includes a vacuum-pumping system, isothermal adsorption system, gas supercharging system, computer-control system, and a gas cylinder of $\text{CO}_2$. A schematic diagram of the experimental apparatus was previously reported in the corresponding research.60

![Figure 1. Schematic diagram of high-pressure isothermal adsorption instrument-DXF-II.](image)

3.3. Experimental Procedure and Measurement Conditions. In this study, pure $\text{CO}_2$ adsorption experiments were conducted at 45, 62.5, and 80 °C, respectively (Table 3).

| coal seam depth (m) | experimental temperature (°C) | pressure (MPa) |
|--------------------|-------------------------------|----------------|
| 1000               | 45.0                          | 10             |
| 1500               | 62.5                          | 15             |
| 2000               | 80.0                          | 20             |

The temperatures and pressures were selected according to the corresponding coal burial depths of 1000, 1500, and 2000 m. The adsorption isothermal experiment of $\text{ScCO}_2$ was carried out after equilibrium moisture treatment of all coal samples.

Helium as a reference gas is widely used to determine the free volume of sample cells in adsorption experiments, regardless of the low-pressure and high-pressure conditions, because helium is non-adsorbing and inert, according to published references internationally.32,61,62 A complete experiment for $\text{ScCO}_2$ adsorption consists of five consecutive steps: (1) checking system airtightness; system airtightness, including the reference cell, sample cell, and tubing, was checked with helium at 10 MPa. If the system pressure remained constant for 6 h, the system was regarded to have good airtightness.53 Then, the system was degassed under a high vacuum of $10^{-3}$ Pa for at least 24 h prior to beginning the measurements. (2) Setting experimental conditions; $\text{CO}_2$ and helium were injected into reference cells at high pressure (above 10 MPa). The temperature of the sample cell and gas reference cells was set to 45 °C. The confining pressure and the opening pressure of the liquid-displacement valve were set to 10 MPa using a Gilson pump. The equilibrium time for adsorption was beyond 12 h. After temperature and pressure equilibrium were achieved, tubing and sample cells were degassed once again. (3) Calibrating errors; measurements of free-space volume calibration and pore pressure-induced water displacement were conducted using helium at pressures between 2.0 and 9.5 MPa. (4) Adsorption measurements were run by increasing the $\text{CO}_2$ injection pressure in a step-wise manner to a maximum of 10 MPa. $\text{CO}_2$ was injected into the sample cell by a booster pump until the sample reached adsorption equilibrium. The variations of pressure and temperature of the sample cell and gas reference cells were continuously monitored by an online data acquisition system.

After measurement of $\text{ScCO}_2$ adsorption at the temperature of 45 °C, the same sample cell and pipelines were degassed once again. The experimental temperature was reset to 62.5 °C, $\text{CO}_2$ and helium were injected into the cells at high pressure (above 16 MPa), and the confining pressure and opening pressure of the liquid-displacement valve were set to 16 MPa using a Gilson pump. After the temperature and pressure of the apparatus reached equilibrium, the measurement procedures (3) and (4) were repeated. At 62.5 °C, the adsorption measurements were run to the final pressure of 16 MPa. After this, the temperature was increased to 80 °C, and the adsorption measurements were run by increasing the $\text{CO}_2$ injection pressure to 20 MPa.

3.4. Calculation of Adsorption Capacity. Adsorption capacity can be determined according to the manometric/volumetric method and the gravimetric method.32,38,41,61,62 The gravimetric method requires a very accurate balance to determine the amount of gas sorbed at a constant pressure, the volumetric method requires very accurate determination of cell
Table 5. Pore Structure Parameters of Different Coal Samples by MIP

| sample      | pore volume \(10^{-4}\) mL g\(^{-1}\) | volume fraction of PSD (%) |
|-------------|--------------------------------------|-----------------------------|
|             | \(V_1\) | \(V_2\) | \(V_3\) | \(V_4\) | \(V_5\) | \(V_1/V_1\) | \(V_2/V_1\) | \(V_3/V_1\) | \(V_4/V_1\) | \(V_5/V_1\) |
| Yuwu        | 24.70   | 21.16  | 110.09 | 190.76 | 346.71 | 7.12  | 6.10  | 31.75 | 55.03 |
| Sihe        | 29.18   | 9.28   | 86.12  | 200.02 | 324.60 | 8.99  | 2.86  | 26.53 | 61.62 |
| Chengzhuang | 37.49   | 16.45  | 101.50 | 228.36 | 383.80 | 9.77  | 4.28  | 26.45 | 59.50 |

Notes: \(V_1\)–\(V_5\) pore volume of macropore (>1000 nm in diameter), mesopore (100–1000 nm in diameter), and micropore (<10 nm in diameter), respectively; \(V_t\) total pore volume; \(V_1/V_1\) to \(V_4/V_1\), pore volume fraction from macropore, mesopore, transitional pore, and micropore in the total pore volume, respectively; \(\phi_{MIP}\), total porosity, %.

Table 6. Surface Area of Pores with Different Pore Radii from Coal Samples by MIP

| sample      | surface area \(m^2\) g\(^{-1}\) | percentage of PSD on surface area (%) |
|-------------|---------------------------------|--------------------------------------|
|             | \(S_1\) | \(S_2\) | \(S_3\) | \(S_4\) | \(S_5\) | \(S_1/S_1\) | \(S_2/S_1\) | \(S_3/S_1\) | \(S_4/S_1\) | \(S_5/S_1\) |
| Yuwu        | 0.002  | 0.05   | 2.11   | 15.72  | 17.87  | 0.011 | 0.263 | 11.79 | 87.94 |
| Sihe        | 0.001  | 0.02   | 1.80   | 16.66  | 18.49  | 0.005 | 0.108 | 9.75  | 90.13 |
| Chengzhuang | 0.002  | 0.03   | 2.10   | 19.03  | 21.17  | 0.009 | 0.142 | 9.93  | 89.92 |

Notes: \(S_1\)–\(S_5\), surface area of macropore (>1000 nm in diameter), mesopore (100–1000 nm in diameter), and micropore (<10 nm in diameter), respectively; \(S_t\), total surface area; \(S_1/S_1\) to \(S_5/S_1\), percentage of surface area from macropore, mesopore, transitional pore, and micropore in the total surface area, respectively.
Tables 5 and 6 show the pore volumes and their percentages for different types of the pores and the surface areas and their percentages for different types of the pores. According to Tables 5 and 6, the proportions of transitional pores and micropores in terms of the total pore volume and surface area are dominant, which indicates that transitional pores and micropores play the dominant role in gas adsorption. In addition, the pore volumes and surface areas from all coal samples indicate that the Chengzhuang sample has the highest values of pore volume and pore surface area, the Yuwu sample has the lowest value of surface area from transitional pores and micropores, and the Sihe sample has the lowest pore volume from transitional pores and micropores, which suggest that the growth of transitional pores and micropores in the Sihe sample is better than that in the Yuwu sample and will be beneficial to ScCO₂ adsorption. The genetic types of pores in coal from the SQB, China have been discussed in the relevant work⁶³,⁶⁴ and include gas pores, shrinkage-induced pores, and mineral-related pores. Figure 3 shows the pore types and mineral compositions in all coal samples. The pore types in all coal samples include gas pores (Figure 3a,d,e), shrinkage-induced pores (Figure 3b), and mineral-related pores such as intercrystalline pores and dissolution pores (Figure 3b,d,f); the types of minerals include kaolinite, pyrite, and barite (Figure 3b–d,f).

4.3. Experimental Results of CO₂ Adsorption. The excess adsorption isotherms of pure CO₂ from the Yuwu, Sihe, and Chengzhuang coal mines at temperatures of 45, 62.5, and 80 °C are plotted in Figure 4. As shown in Figure 4, the excess adsorption capacity generally increases with increase in pressure. However, the excess adsorption capacity starts to decrease after a certain pressure is reached for different temperature conditions, that is, the excess adsorption capacity exhibits a maximum around the critical pressure.⁶⁵,⁶⁶ The higher the operating temperature, the higher the pressure where the excess adsorption starts to decrease, as shown in Figure 4. This decrease of excess adsorption is expected as the adsorbed phase volume is not yet corrected.⁶⁷ Meanwhile, variation of the excess adsorption capacity under low pressure calculated based on the free volume determined with helium is different from the excess adsorption capacity under high pressure calculated based on the free volume determined with helium, and there is a negative adsorption phenomenon, that is, the excess adsorption capacity shows a decrease when the pressure reaches a peak, caused by the density of the adsorbed phase, based on the synthetic measurement of the free volume.⁶⁸ The cause of the negative adsorption is controversial, but it does not affect the work described in this paper.

Figure 5 presents the absolute adsorption capacities of pure CO₂ for the Yuwu, Sihe, and Chengzhuang coal mines at the temperatures of 45, 62.5, and 80 °C. As shown in Figure 5, the absolute capacity increases with the increase of pressure. Based on comparison with the excess adsorption capacities (Figure 4) and the absolute adsorption capacities (Figure 5) of ScCO₂, the absolute capacity of ScCO₂ is always higher than the excess adsorption capacity of ScCO₂ at all equilibrium pressures. The comparison results indicate that there are significant differences between the excess adsorption capacity of ScCO₂ and the absolute adsorption capacity of ScCO₂ for the tested deep coal samples. Moreover, the variation of the excess adsorption capacity of ScCO₂ or the absolute adsorption capacity of ScCO₂ has similar features at different temperatures. The different adsorption capacities of ScCO₂ from deep coal seams demonstrate that accurate adsorption modeling requires proper model screening.

4.4. Modeling of Coal Sorption with Different Models and Their Comparison. Taking the Sihe sample as an example, comparison of the experimental and modeled results at the temperatures of 45 °C (318 K), 62.5 °C (333.5 K), and 80 °C (349 K) is shown in Figures 6–8. Because the unit of adsorption capacity in the TL and OK models is mmol, which is different from the other adsorption models, the figures showing adsorption capacity are plotted separately (Figures 6–13). The R² and R of the simulation results from the different adsorption models are listed in Table 7.

As shown in Figures 6–8 along with data in Table 7, most of the adsorption models can describe the variational characteristics of the excess adsorption capacity of ScCO₂ and the simulation degree for the excess adsorption capacity of ScCO₂ at a relatively low temperature is higher than that at a relatively high temperature. At each temperature, the modeled results at low pressure are superior to the modeled results at high pressure. As shown in Figures 6–8, the modeled values of excess adsorption capacity deviate from the experimental values at a certain value of equilibrium pressure, and the trend becomes more obvious with the increase of the experimental pressure; the simulation accuracy in Table 7 also demonstrates this point, that is, that the regression coefficients R² and the correlation coefficients R of the simulation formula decrease with increase of the experiment temperature. There is an inflection point of the excess adsorption capacity when the equilibrium pressure is 8.13 MPa, the first value beyond the critical pressure 7.38 MPa.
the equilibrium pressure exceeds 7.38 MPa, the modeled results start to deviate from the experimental data and the deficiency increases with increased pressure. Based on 1, in the L, T, LF, EL, and DBET models, the excess adsorption capacity is a monotonous increasing function of equilibrium pressure. The excess adsorption capacity of ScCO₂ should always increase as the pressure increases, and no inflection points exist for the L, T, LF, EL, and DBET models. The excess adsorption capacities of ScCO₂ can show inflection points for the TL, D−R, D−A, TBET, and OK models, and this means that these models are capable of modeling excess adsorption capacity of ScCO₂. According to Figures 6–8, not all adsorption models can model
the excess adsorption capacity of ScCO₂ across all pressures and temperatures, especially high temperatures and pressures.

To analyze the validity of the adsorption models at low and high pressures, the Sihe sample at a temperature of 80 °C was used.

**Figure 8.** Comparison of experimental and different model simulation results of excess adsorption isotherms of ScCO₂ adsorption at the temperature of 80 °C (349 K) from Sihe coal mine; units of excess adsorption capacity are cm³/g (a) and mmol (b), respectively.

**Figure 9.** Comparison of experimental and different model simulation results of excess adsorption isotherms of ScCO₂ adsorption with the equilibrium pressure below 8.13 MPa and at the temperature of 80 °C (349 K) from Sihe coal mine; units of excess adsorption capacity are cm³/g (a) and mmol (b), respectively.

**Figure 10.** Comparison of experimental and different model simulation results of excess adsorption isotherms of ScCO₂ adsorption with the equilibrium pressure beyond 8.13 MPa and at the temperature of 80 °C (349 K) from Sihe coal mine; units of excess adsorption capacity are cm³/g (a) and mmol (b), respectively.

**Figure 11.** Comparison of experimental and different model simulation results of absolute adsorption isotherms of ScCO₂ adsorption at the temperature of 80 °C (349 K) from Sihe coal mine; units of absolute adsorption capacity are cm³/g (a) and mmol (b), respectively.
chosen as an example. Figures 9 and 10 demonstrate the comparison of the experimental and modeled results with equilibrium pressure less than or equal to 8.13 MPa and greater than 8.13 MPa, respectively. The \( R^2 \) and \( R \) values of the regression values are listed in Table 8.

As shown in Figures 9 and 10 and Table 8, when the equilibrium pressure is less than or equal to 8.13 MPa, the modeled results agree well with the experimental data for the excess adsorption capacity of Sc\( \text{CO}_2 \). When the equilibrium pressure is greater than 8.13 MPa, the results from most of the adsorption models agree reasonably with the experimental data. In contrast, the \( T, D_{-A}, T_L, \) and OK models have more deviations than the other adsorption models.

Based on analysis of Figures 4 and 5, the absolute adsorption capacity of Sc\( \text{CO}_2 \) is higher than the excess adsorption capacity of Sc\( \text{CO}_2 \). To simulate the absolute adsorption capacity of Sc\( \text{CO}_2 \), Figure 11 presents a comparison of the experimental and modeled results of the adsorption capacity of Sc\( \text{CO}_2 \) with Figure 12.

**Figure 12.** Comparison of experimental and different model simulation results of absolute adsorption isotherms of Sc\( \text{CO}_2 \) adsorption with the equilibrium pressure below 8.13 MPa and at the temperature of 80 °C (349 K) from Sihe coal mine; units of absolute adsorption capacity are cm\(^3\)/g (a) and mmol (b), respectively.

**Figure 13.** Comparison of experimental and different model simulation results of absolute adsorption isotherms of Sc\( \text{CO}_2 \) adsorption with the equilibrium pressure beyond 8.13 MPa and at the temperature of 80 °C (349 K) from Sihe coal mine; units of absolute adsorption capacity are cm\(^3\)/g (a) and mmol (b), respectively.

**Table 7.** Simulation Degree of Different Models for Excess Adsorption Capacity of Sc\( \text{CO}_2 \) at Different Temperatures

| temperature | simulation degree | L model | T model | LF model | EL model | TL model | DBET model | TBET model | D−R model | D−A model | OK model |
|-------------|------------------|---------|---------|----------|----------|----------|------------|------------|------------|-----------|-----------|
| 45 °C (318 K) | \( R^2 \)     | 0.98    | 0.99    | 0.99     | 0.98     | 0.96     | 0.98       | 0.99       | 0.99       | 0.94      |          |
|             | \( R \)       | 0.99    | 1.00    | 1.00     | 0.99     | 0.98     | 0.99       | 0.99       | 0.99       | 0.99      | 0.97      |
| 62.5 °C (333.5 K) | \( R^2 \) | 0.97    | 0.99    | 0.99     | 0.97     | 0.88     | 0.97       | 0.98       | 0.96       | 0.96      | 0.90      |
|             | \( R \)       | 0.99    | 1.00    | 1.00     | 0.99     | 0.94     | 0.99       | 0.99       | 0.98       | 0.98      | 0.95      |
| 80 °C (349 K) | \( R^2 \)     | 0.90    | 0.94    | 0.94     | 0.90     | 0.92     | 0.90       | 0.92       | 0.96       | 0.96      | 0.89      |
|             | \( R \)       | 0.95    | 0.97    | 0.97     | 0.95     | 0.98     | 0.95       | 0.96       | 0.98       | 0.98      | 0.94      |

**Table 8.** Simulation Degree of Different Models for Excess Adsorption Capacity of Sc\( \text{CO}_2 \) from the Sihe Sample at Different Equilibrium Pressures and Temperatures of 80 °C (349 K)

| equilibrium pressure (MPa) | simulation degree | L model | T model | LF model | EL model | TL model | DBET model | TBET model | D−R model | D−A model | OK model |
|---------------------------|-------------------|---------|---------|----------|----------|----------|------------|------------|------------|-----------|-----------|
| ≤8.13                     | \( R^2 \)       | 1.00    | 1.00    | 1.00     | 1.00     | 1.00     | 1.00       | 1.00       | 1.00       | 1.00      | 0.98      |
|                           | \( R \)         | 1.00    | 1.00    | 1.00     | 1.00     | 1.00     | 1.00       | 1.00       | 1.00       | 1.00      | 0.99      |
| >8.13                     | \( R^2 \)       | 0.91    | 3.8 × 10\(^{-3}\) | 0.95 | 0.91 | 0.06 | 0.96 | 0.94 | 0.66 | 0 | 0.05 |
|                           | \( R \)         | 0.96    | 0.06    | 0.97     | 0.96     | 0.25     | 0.98       | 0.97       | 0.81       | 0.21      |           |
Table 9. Simulation Degree of Different Models for Absolute Adsorption Capacity of ScCO₂ from the Sihe Sample at the Temperature of 80 °C (349 K)

| temperature | simulation degree | L model | T model | LF model | EL model | TL model | DBET model | TBET model | D−R model | D−A model | OK model |
|-------------|------------------|---------|---------|----------|----------|----------|------------|------------|------------|------------|---------|
| 80 °C       | $R^2$            | 0.93    | 0.97    | 0.98     | 0.93     | 0.87     | 0.93       | 0.98       | 0.61       | 0.50       | 0.81    |
|             | $R$              | 0.96    | 0.98    | 0.99     | 0.96     | 0.93     | 0.97       | 0.99       | 0.78       | 0.71       | 0.90    |

Table 10. Simulation Degree of Different Models for Absolute Adsorption Capacity of ScCO₂ from the Sihe Sample at Different Equilibrium Pressures and Temperatures of 80 °C (349 K)

| equilibrium pressure (MPa) | simulation degree | L model | T model | LF model | EL model | TL model | DBET model | TBET model | D−R model | D−A model | OK model |
|---------------------------|------------------|---------|---------|----------|----------|----------|------------|------------|------------|------------|---------|
| ≤8.13                     | $R^2$            | 1.00    | 1.00    | 1.00     | 1.00     | 1.00     | 1.00       | 1.00       | 1.00       | 1.00       | 0.98    |
|                           | $R$              | 0.96    | 0.97    | 0.99     | 0.96     | 0.97     | 0.99       | 0.99       | 0.98       | 0.05       | 0.21    |
| >8.13                     | $R^2$            | 1.00    | 1.00    | 1.00     | 1.00     | 1.00     | 1.00       | 1.00       | 1.00       | 1.00       | 0.99    |
|                           | $R$              | 0.98    | 0.98    | 1.00     | 0.98     | 0.98     | 1.00       | 0.99       | 0.00       | 0.05       | 0.21    |

Table 11. Results for Simulation Parameters with Different Models for Excess Adsorption Capacity of ScCO₂ from the Sihe Sample at Different Temperatures

| adsorption model | parameter | temperature | simulation results from different model |
|------------------|-----------|-------------|----------------------------------------|
| L model          | $V_{c}$  | 45 °C       | 27.32                                  |
|                  |           | 62.5 °C     | 22.37                                  |
|                  |           | 80 °C       | 20.0                                   |
| TL model         | $n_{d}$  | 2.50 $\times$ 10$^{-3}$ | 2.60 $\times$ 10$^{-3}$ |
|                  | $K_b$    | 3.07        | 5.28                                  |
|                  | $n$      | 110.90      | 4.17                                  |
| LF model         | $V_{c}$  | 29.40       | 25.36                                  |
|                  | $K_b$    | 3.06        | 0.41                                  |
|                  | $n$      | 41.62       | 3.41                                  |
| EL model         | $V_{c}$  | 74.05       | 55.02                                  |
|                  | $K_b$    | 74.05       | 55.02                                  |

different models at the temperature of 80 °C for the Sihe sample. The $R^2$ and $R$ of different models are listed in Table 9.

As shown in Figure 11 and Table 9, most of the adsorption models have relatively high precision for the absolute adsorption capacity of ScCO₂. However, there is relatively larger deviation for the D−R and D−A models. Because of the model assumptions and functional properties, the absolute adsorption capacities of ScCO₂ show a turning point when the TL, D−R, D−A, TBET, and OK models are adopted, which is inconsistent with the characteristics of increasing absolute adsorption capacity of ScCO₂ with the increase of equilibrium pressure.

To analyze the difference between the absolute adsorption capacity of CO₂ at low equilibrium pressure and that at high equilibrium pressure, a sectionalized simulation for the absolute adsorption capacity of ScCO₂ is shown in Figures 12 and 13. Table 10 presents the $R^2$ and $R$ of the regression results for various models and pressures.

As shown in Figures 12 and 13 and Table 10, most of the adsorption models have great precision for modeling absolute ScCO₂ capacity, but the D−A model is not suitable for modeling absolute adsorption.

Based on the above analysis, most of the adsorption models can be reasonably used to model the excess and absolute adsorption capacities of ScCO₂. It was found that these models are applicable for low pressure (≤8.13 MPa). A good match of the modeled and experimental results does not mean that the modeled results are valid; the model parameters obtained by a simulation must be analyzed further, and the suitability of the adsorption model must be thoroughly evaluated and assessed.

4.5. Comparison and Model Screening for ScCO₂ Sorption. An appropriate adsorption model should meet the following criteria: (1) the regressed parameter must have physical significance; (2) the modeled results must be in accordance with the adsorption characteristics of ScCO₂ for deep coal seams; (3) the modeling precision should be high enough for accurate prediction.

Based on the above criteria, in comparing the 10 adsorption models in the previous analyses, the regressed modeling parameters $V_{c}$, $P_c$, $n_d$, $K_b$, $n$, $\Gamma_0$, $V_{m}$, $C$, $V_{b}$, $D$, and $\Gamma_0$ must all have positive values. Moreover, $n$ in the exponential function, which appears in the T, LF, EL, TBET, and D−A models, must be a positive nonzero integer.

The results for the simulation parameters with different adsorption models for the excess adsorption capacities of ScCO₂ from the Sihe sample at the different temperatures are summarized in Table 11.

As shown in Table 11, the parameter $n$ simulated by the EL model and the parameters $V_{m}$ and $P_c$ simulated by the DBET
**Table 12. Results for Simulation Parameters with Different Models for Excess Adsorption Capacity of ScCO₂ from the Sihe Sample at the Temperature of 80 °C (349 K) and Different Ranges of Equilibrium Pressure**

| Adsorption Model | Parameter | ≤8.13 MPa | >8.13 MPa | Adsorption Model | Parameter | ≤8.13 MPa | >8.13 MPa |
|------------------|-----------|-----------|-----------|------------------|-----------|-----------|-----------|
| L model          | \( V_L \) | 32.84     | 18.64     | DBET model       | \( V_m \) | -0.07     | 610.93    |
|                  | \( P_L \) | 2.68      | -1.34     |                  | \( C \)   | 4697.61   | -0.03     |
| TL model         | \( n_{inf} \) | 2.00 \( \times \) 10⁻³ | 8.00 \( \times \) 10⁻³ |                  | \( P^0 \) | -2.37     | 7.54      |
|                  | \( K_n \) | 4.31      | 59.68     | TBET model       | \( V_m \) | 31.40     | 12.67     |
| T model          | \( V_L \) | 30.43     | 20.57     |                  | \( C \)   | 3.85      | -2.83     |
|                  | \( K_n \) | 0.34      | 15.49     |                  | \( P^0 \) | 1.06      | 1.71      |
|                  | \( n \) | 1.20      | 76.52     | D–A model        | \( V_0 \) | 24.50     | 20.56     |
| LF model         | \( V_L \) | 30.95     | 19.99     |                  | \( D \)   | 0.35      | -4.28 \( \times \) 10⁻⁴ |
|                  | \( K_n \) | 0.38      | -0.01     |                  | \( n \)   | 1         | 0         |
|                  | \( n \) | 1.12      | 3.41      | D–R model        | \( V_0 \) | 24.50     | 21.11     |
| EL model         | \( V_L \) | 0.13      | -0.35     |                  | \( D \)   | 0.23      | 0.13      |
|                  | \( K_n \) | 94.80     | 39.38     | OK model         | \( \Gamma_0 \) | 2.00 \( \times \) 10⁻³ | 2.30 \( \times \) 10⁻³ |
|                  | \( n \) | -1.99     | -2.04     |                  | \( \frac{\varepsilon}{K} \) | 484.74   | 390.88    |

**Table 13. Results for Simulation Parameters with Different Models for Absolute Adsorption Capacity of ScCO₂ from the Sihe Sample at the Temperature of 80 °C (349 K) and Different Ranges of Equilibrium Pressure**

| Adsorption Model | Parameter | 0–20 MPa | <8.13 MPa | >8.13 MPa | Adsorption Model | Parameter | 0–20 MPa | <8.13 MPa | >8.13 MPa |
|------------------|-----------|----------|-----------|-----------|------------------|-----------|----------|-----------|-----------|
| L model          | \( V_L \) | 58.03    | 44.45     | 276.65    | DBET model       | \( V_m \) | 2.43     | 0.04      | 6.76      |
|                  | \( P_L \) | 8.31     | 4.34      | 99.78     |                  | \( C \)   | -25.56   | -1079.90  | 1.66      |
| TL model         | \( n_{inf} \) | -0.01    | 3.90 \( \times \) 10⁻³ | -3.40 \( \times \) 10⁻³ |                  | \( P^0 \) | -10.53   | -4.35     | 38.41     |
|                  | \( K_n \) | -77.68   | 7.11      | -33.51    | TBET model       | \( V_m \) | -27.77   | 17.63     | -22.59    |
| T model          | \( V_L \) | 15.39    | 90.71     | 6.14 \( \times \) 10⁶ |                  | \( C \)   | 0.89     | 8.38      | 0.84      |
|                  | \( K_n \) | 0.11     | 0.25      | 1.48 \( \times \) 10⁻⁵ |                  | \( P^0 \) | -1.34    | 2.74      | -1.54     |
|                  | \( n \) | -1.13    | 0.48      | 0.12      | D–A model        | \( V_0 \) | 31.03    | 29.19     | 36.12     |
| LF model         | \( V_L \) | 12.96    | 67.09     | 14.92     |                  | \( D \)   | 2.2 \( \times \) 10⁻³ | 0.48      | -9.69 \( \times \) 10⁻⁴ |
|                  | \( K_n \) | -4.56    | 0.17      | -9.31     | D–R model        | \( V_0 \) | 33.93    | 28.45     | 28.65     |
|                  | \( n \) | -0.40    | 0.73      | -0.62     | OK model         | \( \Gamma_0 \) | 2.27 \( \times \) 10⁻⁵ | 6.03 \( \times \) 10⁻³ | -1.28 \( \times \) 10⁻³ |
| EL model         | \( V_L \) | 1.06     | 0.49      | 1.00      |                  | \( D \)   | 0.24     | 0.30      | -1.08     |
|                  | \( K_n \) | 6.57     | 20.97     | 2.76      |                  | \( \frac{\varepsilon}{K} \) | 55.45   | 216.47    | -1733.24  |

...model are less than 0 and thus have no physical significance; therefore, the EL and DBET models are not suitable to simulate the excess adsorption capacity of ScCO₂. In addition, the parameter \( V_L \) in the EL model for the different coal samples is obviously abnormal. When the TBET model is used to simulate the excess adsorption capacity of ScCO₂, the parameters \( C \) and \( P^0 \) are less than 0 for the Sihe sample at temperatures of 45 and 80 °C and thus have no physical significance. These results show that the stability of the TBET model is poor when it is used to simulate the excess adsorption capacity of ScCO₂ for a deep coal seam. Based on the above analyses, the L, TL, T, LF, D–A, D–R, and OK models are effective and may be used to model the adsorption isotherms of the excess adsorption of ScCO₂ in the scope of the whole equilibrium pressure range for deep coal seams.

Table 12 summarizes the results for the regression parameters with different adsorption models for the excess adsorption capacities of ScCO₂ from the Sihe samples at a temperature of 80 °C and different ranges of equilibrium pressure.

Based on Table 12, when the sectionalized simulation for the excess adsorption capacity of ScCO₂ is adopted, most of the parameters lose physical significance, such as \( P_L \) in the L model, \( K_n \) in the LF model, \( V_L \) and \( n \) in the EL model, \( V_{inf} \), \( C \), and \( P^0 \) in the DBET model, \( C \) in the TBET model, and \( D \) in the D–A model. In addition, \( V_L \) in the EL model is obviously abnormal. When the equilibrium pressure is lower than 8.13 MPa, most of the adsorption models have reasonable accuracy in modeling the excess adsorption capacity of ScCO₂, except the EL and DBET models. However, when the equilibrium pressure is higher than 8.13 MPa, most of the adsorption models are not applicable to describe the excess adsorption capacities of ScCO₂ except the TL, T, D–R, and OK models. Above all, the TL, T, D–R, and OK models are effective and can be used to simulate the excess adsorption capacity of ScCO₂ when sectionalized modeling for this capacity is adopted.

Table 13 demonstrates the results for the simulation parameters with different adsorption models for the absolute adsorption capacities of ScCO₂ from the Sihe sample at a temperature of 80 °C under different ranges of equilibrium pressure.

As shown in Table 13, when the equilibrium pressure varies from 0 to 20 MPa, the parameters \( n_{inf} \) and \( K_n \) in the TL model, \( n \) in the T model, \( K_n \) and \( n \) in the LF model, \( V_L \) and \( n \) in the EL model, \( C \) and \( P^0 \) in the DBET model, and \( V_m \) and \( P^0 \) in the TBET model are all less than 0 and thus lose physical significance. In addition, the parameter \( V_L \) in the EL model is obviously...
abnormal. According to the above analysis, the L model, D−A model, D−R model, and OK model are effective and can be used to model the adsorption isotherms of the absolute adsorption of ScCO₂ for the whole pressure range.

Figure 14. Simulation results of absolute adsorption isotherms of ScCO₂ adsorption using the linear function (a,b), the exponential function (c,d), the logarithmic function (e,f), the power function simulation (g,h), the polynomial function (i,j) with the equilibrium pressure beyond 8.13 MPa and at a temperature of 80 °C (349 K) from Sihe coal mine; units of absolute adsorption capacity adopted by cm³/g and mmol, respectively.

Based on Table 13, when the equilibrium pressure is less than or equal to 8.13 MPa, parameters such as n in the EL model and C and P₀ in the DBET model are all less than 0 and lose their physical significance. In addition, the parameters Vₓ in the T model and Vₓ in the EL model are obviously abnormal when the
From the Sihe Sample, the superiority of the models. In this paper, the standard error of the absolute adsorption capacity of ScCO₂ when the equilibrium pressure is higher than 8.13 MPa, a portion or all of the parameters in all adsorption models lose physical significance. In this work, the linear simulation, exponential simulation, logarithmic simulation, power function simulation, and polynomial simulation were conducted when the equilibrium pressure is lower than 8.13 MPa. However, when the equilibrium pressure is higher than 8.13 MPa, a portion or all of the parameters in all adsorption models lose physical significance. In this work, the linear simulation, exponential simulation, logarithmic simulation, power function simulation, and polynomial simulation were conducted when the equilibrium pressure is higher than 8.13 MPa. Figure 14 shows the modeled results from the linear simulation, exponential simulation, logarithmic simulation, power function simulation, and polynomial simulation for the absolute adsorption capacity of ScCO₂.

Figure 14 shows that the linear simulation, exponential simulation, logarithmic simulation, power function simulation, and polynomial simulation all have good precision; the $R^2$ values are 0.973, 0.9872, 0.9282, 0.9576, and 0.9959 respectively. The simulation results suggest that these five types of functions all can meet the needs for simulation of the absolute adsorption capacity of ScCO₂ when the equilibrium pressure is higher than 8.13 MPa. However, the results for $R^2$ show that the polynomial simulation, exponential simulation, and linear simulation are superior to the logarithmic simulation and power function simulation.

All selected models in this paper are nonlinear, so $R^2$ and $R$ cannot be used as effective standards for evaluating the superiority of the models. In this paper, the standard error $S$ (eq 12) and the residual sum of squares SSE (eq 13) are defined to evaluate the simulation effectiveness of the model simulations. Smaller $S$ and SSE indicate higher model accuracy.

$$S = \left[ \frac{1}{n} \sum_{i=1}^{n} (V_i - V_e)^2 \right]^{1/2}$$  \hspace{1cm} (12)$$

$$\text{SSE} = \sum_{i=1}^{n} (V_i - V_e)^2$$  \hspace{1cm} (13)

where $S$ is the standard error, SSE is the residual sum of squares, $n$ is the number of data points, and $V_i$ and $V_e$ are the experimental value and simulated value of the adsorption capacity of each pressure spot, respectively.

According to eqs 12 and 13, the units of the excess adsorption capacity in the TL model and OK model were converted to the same units of the excess adsorption capacity in the other adsorption models. The values of $S$ and SSE for the seven selected adsorption models were calculated for the excess adsorption capacity of ScCO₂; the results are shown in Table 14.

As shown in Table 14, when the experimental temperature was 45 °C, for the Sihe sample, the order of superiority of the seven types of adsorption model for the excess adsorption capacity of ScCO₂ is as follows: $T$ model = $LF$ model > $D$–$R$ model > $D$–$A$ model > $L$ model > $TL$ model > OK model. When the experimental temperature for the Sihe sample was 62.5 °C, the order of superiority of the seven types of adsorption models for excess adsorption capacity of ScCO₂ is as follows: $D$–$R$ model > $D$–$A$ model > $T$ model > $LF$ model > $L$ model > OK model > TL model. When the experimental temperature for the Sihe sample was 80 °C, the order of superiority for the seven types of adsorption model for the excess adsorption capacity of ScCO₂ is as follows: $D$–$R$ model > $D$–$A$ model > $T$ model > $LF$ model > $L$ model > OK model > TL model.

To verify the above results, the Yuwu sample was taken as a further example; the results of $S$ and SSE for the different adsorption models for the excess adsorption capacity of ScCO₂ at different temperatures are shown in Table 15.

As indicated in Table 15, for this sample, the order of the superiority of the seven types of the adsorption model for the excess adsorption capacity of ScCO₂ is as follows: $D$–$R$ model > $D$–$A$ model > $T$ model > $LF$ model > $L$ model > $TL$ model.

| temperature (°C) | L model | TL model | T model | LF model | D–A model | D–R model | OK model |
|-----------------|---------|----------|---------|----------|-----------|-----------|----------|
| 45              | 1.34    | 14.37    | 2.10    | 35.41    | 0.92      | 6.70      | 1.08     |
| 62.5            | 1.22    | 16.32    | 2.88    | 91.06    | 0.70      | 4.92      | 0.80     |
| 80              | 1.88    | 46.01    | 1.85    | 44.49    | 1.41      | 25.81     | 1.43     |

| temperature (°C) | L model | TL model | T model | LF model | D–A model | D–R model | OK model |
|-----------------|---------|----------|---------|----------|-----------|-----------|----------|
| 45              | 0.77    | 4.69     | 2.26    | 40.72    | 0.67      | 3.55      | 0.65     |
| 62.5            | 0.90    | 8.02     | 0.90    | 8.19     | 0.60      | 3.60      | 0.61     |
| 80              | 1.06    | 14.63    | 1.65    | 35.23    | 0.69      | 6.12      | 0.72     |

| temperature (°C) | L model | TL model | T model | LF model | D–A model | D–R model | OK model |
|-----------------|---------|----------|---------|----------|-----------|-----------|----------|
| 45              | 0.15    | 0.17     | 0.08    | 0.04     | 0.28      | 0.47      | 1.28     |
| 62.5            | 0.89    | 5.49     | 0.52    | 1.90     | 0.30      | 0.65      | 1.35     |
| 80              | 0.91    | 14.63    | 1.65    | 35.23    | 0.69      | 6.12      | 0.72     |

Table 14. Results for $S$ and SSE on Seven Adsorption Models for Excess Adsorption Capacity of ScCO₂ at Different Temperatures from the Sihe Sample

Table 15. Results for $S$ and SSE on Seven Adsorption Models for Excess Adsorption Capacity of ScCO₂ at Different Temperatures from the Yuwu Sample

Table 16. Results for $S$ and SSE on Four Adsorption Models for Excess Adsorption Capacity of ScCO₂ from the Sihe Sample at the Temperature of 80 °C (349 K) and Different Ranges of Equilibrium Pressure

| equilibrium pressure (MPa) | TL model | T model | D–R model | OK model |
|----------------------------|----------|---------|-----------|----------|
| $\leq 8.13$                | S        | SSE     | S         | SSE      |
| $>8.13$                    | $S$      | SSE     | $S$       | SSE      |

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Table 17. Results for S and SSE on Four Adsorption Models for Absolute Adsorption Capacity of ScCO₂ from the Sihe Sample at the Temperature of 80 °C (349 K) and Whole Range of Equilibrium Pressure

| equilibrium pressure | L model | D–A model | D–R model | OK model |
|----------------------|---------|-----------|-----------|----------|
| 0–20 MPa             | S       | SSE       | S         | SSE      | S        | SSE       |
|                      | 3.10    | 125.18    | 8.21      | 875.28   | 7.26     | 685.28    | 5.34     | 370.60 |

Table 18. Results for S and SSE on Seven Adsorption Model for Excess Adsorption Capacity of ScCO₂ from the Sihe Sample at the Temperature of 80 °C (349 K) and Equilibrium Pressure of Less Than or Equal to 8.13 MPa

| equilibrium pressure | L model | TL model | LF model | TBET model | D–A model | D–R model | OK model |
|----------------------|---------|----------|----------|------------|-----------|-----------|----------|
| ≤8.13 MPa            | S       | SSE      | S        | S          | S         | S         | S        |
|                      | 0.20    | 0.24     | 0.45     | 1.19       | 0.02      | 3.30 × 10⁻³ | 0.02     | 2.4 × 10⁻³ | 0.21    | 0.27    | 0.77   | 3.60   | 1.55   | 14.69   |

OK model, when the experimental temperature from the Yuwu sample was different.

Based on a combination of Tables 14 and 15, the D–R and D–A models had the best precision during the simulation of the excess adsorption capacity of ScCO₂ for the whole equilibrium pressure range. The T and LF models had moderate precision among the seven adsorption models, and the L, TL, and OK models had relatively low precision. Of these seven adsorption models, the D–R, D–A, TL, and OK models all can represent the inflection point of the excess adsorption capacity of ScCO₂. Therefore, the D–R and D–A models are the optimal adsorption models for simulation of the excess adsorption capacity of ScCO₂ for the whole equilibrium pressure range.

Table 16 shows the results of S and SSE for the four selected adsorption models for the excess adsorption capacity of ScCO₂ at a temperature of 80 °C and at different ranges of equilibrium pressure. As shown in Table 16, when the equilibrium pressure was less than or equal to 8.13 MPa, the order of priority of the efficiency of the four types of adsorption model was as follows: T model > TL model > D–R model > OK model. The order of priority of the efficiency of the four types of adsorption model in the simulation of the excess adsorption capacity of ScCO₂ when the equilibrium pressure was beyond 8.13 MPa is as follows: D–R model > T model > TL model > OK model. Moreover, the results for the priority of the four adsorption models are in accordance with the adsorption characteristics of ScCO₂ under different ranges of equilibrium pressure. Given the above, the T, TL, and D–R models are the optimal adsorption models for the sectionalized simulation of the excess adsorption capacity of ScCO₂ under different scopes of equilibrium pressure.

Table 17 shows the results of S and SSE for the four selected adsorption models in the simulation of the absolute adsorption capacity of ScCO₂ at the temperature of 80 °C and across the whole equilibrium pressure range. Table 18 shows the results of S and SSE for the seven selected adsorption models for the absolute adsorption capacity of ScCO₂ at the temperature of 80 °C and equilibrium pressure of less than or equal to 8.13 MPa.

As shown in Table 17, when the equilibrium pressure is the whole pressure with a range of 0–20 MPa, for the Sihe sample at a temperature of 80 °C, the order of superiority of the four types of adsorption model for the absolute adsorption capacity of ScCO₂ is as follows: L model > OK model > D–R model > D–A model. Moreover, the results for the order of priority of the four adsorption model are in accordance with the adsorption characteristics of ScCO₂ under different ranges of equilibrium pressure. When the equilibrium pressure is less than or equal to 8.13 MPa, the order of superiority of the seven types of adsorption model for the absolute adsorption capacity of ScCO₂ is as follows: L model > D–A model > D–R model > OK model.

5. CONCLUSIONS

This article investigates the sorption characteristics of ScCO₂ for deep coal seams of the SQB, China. Ten different adsorption models were considered to model the excess and absolute adsorption capacities of ScCO₂ under various temperatures and pressure ranges. The optimal adsorption models were selected by parametric comparison and analyses based on the standard error and the residual sum of squares. The conclusions can be summarized as follows:

1. The excess adsorption capacity of ScCO₂ has a common turning decline point at different pressures under different temperatures. The absolute capacity of ScCO₂ always increases with the increase of injection pressure. It is higher than the excess adsorption capacity of ScCO₂ at each equilibrium pressure.

2. Most of the adsorption models can describe adsorption characteristics and have good agreement with the experimental results when the pressure is less than 8.13 MPa for excess and absolute adsorption capacities. When the pressure is greater than 8.13 MPa, deviations of the modeled results are observed for most of the models.

3. The analytical results of the adsorption model parameters reveal that there is an obvious difference in the validity of the different adsorption models for the excess adsorption capacity and the absolute adsorption capacity of ScCO₂. The L, TL, T, LF, D–A, D–R, and OK models are effective in the simulation of adsorption isotherms for the excess adsorption of ScCO₂ in the scope of the whole equilibrium pressure range. The TL, T, D–R, and OK models are effective when sectionalized simulation is adopted. In representation of the absolute adsorption isotherms of ScCO₂, the L, D–A, D–R, and OK models are effective in the scope of the whole equilibrium pressure range.
pressure. The L, TL, LF, TBET, D−A, D−R, and OK models are effective when the equilibrium pressure is lower than or equal to 8.13 MPa. All adsorption models lose physical significance when the equilibrium pressure is higher than 8.13 MPa.

(4) The calculation results from the standard error S and the residual sum of squares SSE show that the D−R model and D−A model are the optimal adsorption models in the simulation of the excess adsorption capacity of ScCO2 with the condition of the whole equilibrium pressure range. The T, TL, and D−R models are the optimal adsorption models in the simulation of the excess adsorption capacity of ScCO2 in the selected adsorption model when the equilibrium pressure is divided into two sections at the point of 8.13 MPa. In the simulation of the absolute adsorption capacity of ScCO2, the TBET model and LF model are the optimal adsorption models for selection when the equilibrium pressure is less than or equal to 8.13 MPa. The linear simulation, exponential simulation, logarithmic simulation, power function simulation, and polynomial simulation all have good precision and can be used when the equilibrium pressure is beyond 8.13 MPa.

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