INTRODUCTION

Geological storage of CO₂ in deep unmineable coal deposits for enhanced CH₄ recovery (CO₂-ECBM) has long been considered an option for decreasing greenhouse gas emissions, while concurrently increasing natural gas production.¹⁻⁶ Compared to other CO₂ containment mechanisms, adsorption containment performs enigmatically in porous coal networks due to its preferential attraction toward the coal matrix.⁷⁻⁹ Recent investigations determined that CO₂ adsorption is larger compared to methane absorption at all pressure ranges.¹⁰⁻¹² This is primarily why CO₂...
injection can effectively improve CH4 recovery. It should be noted that the temperature and pressure of unmineable coals suitable for CO2 sequestration are commonly above the CO2 critical point 13,14; therefore, assessment of deep coal CO2 sequestration potential should be based on observations of supercritical CO2 adsorption.

In order to assess supercritical CO2 adsorption capacity, a reliable supercritical adsorption model should be established according to isotherm adsorption experiments. However, frequently used adsorption models, such as the monolayer Langmuir, multilayer Brunauer-Emmett-Teller ( BET), and volume-filling Dubinin-Radushkevich (D-R) models, not only misinterpret supercritical CO2 molecule state and its adsorption behavior, but also fit poorly with isotherm results.15,16 Sakurovs et al17 proposed a supercritical adsorption model based on D-R pore filling model that accurately represents adsorption data covering a wide range of temperatures and pressures.13,18

Gas sorption causes swelling of the coal matrix, and CO2 penetration causes more swelling compared to CH4 and N2 19 A large number of experimental studies have shown that injection of CO2 into a coal seam will cause the coal seam to expand and deform, causing primary fractures in the coal seam to close, thus affecting methane migration.20,21 However, the supercritical D-R adsorption model indicates that swelling changes the estimated supercritical CO2 adsorption capacity corrected for by less than 1%.22 At high pressures, swelling ceases, but adsorption continues. In addition, the moisture in pores reduces coal matrix swelling because adsorption sites are occupied by water molecules.23

A number of previous studies have argued that adsorption mechanisms are dependent on coal properties, temperature, pressure, and pore structure.24-29 A crossover of adsorption curves at different temperatures is clearly illustrated, but its interpretations are still controversial, although some scholars consider the adsorption temperature dependence to be attributable to the tendency of a gas molecule to cling to pore surfaces in pores of different sizes.30,31 In addition, significant variation of supercritical CO2 density can be observed at elevated temperatures and is expressed as a change in CO2 density as a free phase relative to the adsorbed phase, which can also result in a thermodynamic change in adsorption capacity.8,26 Many previous studies have performed CH4 adsorption experiments at different pressure-temperature conditions and discussed CO2 injection implementations in the Qinshui Basin.5,32-35 However, supercritical CO2 adsorption in the Qinshui anthracite and the effect of CO2 density-temperature on reservoir conditions are not well understood.

In this study, three sets of CO2/ScCO2 adsorption experiments on moisture-equilibrated coal were conducted using a manometric procedure. We then applied the revised Dubinin-Radushkevich (D-R) model identified by Sakurovs et al17 to fit the adsorption data and account for the effects of supercritical CO2 density and temperature on adsorption. Finally, according to the critical point for sub-supercritical CO2 and a transition temperature from supercritical isochore to fully supercritical CO2, we discerned distinct adsorption stages under a range of pressure-temperature conditions and further considered their significance for supercritical CO2 injection in deep unmineable coal reservoirs in the southern Qinshui Basin. The aim of this study is to interpret the effect of dramatic changes in CO2 density near the supercritical point on CO2 adsorption and determine the maximum storage capacity of coal reservoirs in the Qinshui Basin.

2 | GEOLOGICAL SETTING

The Qinshui Basin, located in Shanxi Province in central China (Figure 1A), is of critical significance for understanding geological storage of CO2 in deep coal. The basin supports a major commercial coalbed methane (CBM) industry and has been the site of multiple CO2-injection pilots for enhanced CBM recovery.5,35-38 The Qinshui Basin underwent a range of heterogeneous, vertical tectonic movements since the Hercynian, and ultimately evolved into a fault-bound basin during the late Paleozoic. The Qinshui Basin contains a NNE-trending synclinorium with essentially symmetric flanks and minor faults. Coal-bearing strata, which were deposited during the late Carboniferous to the early Permian, include the Benxi Formation, Taiyuan Formation, and Shanxi Formation in ascending order. The coals occur mainly in the Taiyuan Formation, which was deposited in a marine carbonate platform environment, and in the Shanxi Formation, which was deposited in a shoal-water delta environment.39 Variations in sedimentary environments contribute to the diversity in the Shanxi and Taiyuan coals, which further affects adsorption-desorption characteristics.40,41

Generally, during the late Paleozoic, multiple marine transgressions contributed to extensive peat development on the stable North China Craton, producing multiple coal-bearing successions.39,40 However, most of the coal seams are thin and unmineable. The main coal seams, which could be targets for CO2 storage, are the #3 coal in the Shanxi Formation and the #15 coal in the Taiyuan Formation. The #3 coal ranges in thickness from 5 to 6 m in the entire southern Qinshui Basin. Within the synclinorium, the #3 coal has greater depth in the central basin (>1000 m) than on the flanks (<500 m, Figure 1B). In contrast, the #15 coal formed in a marginal marine environment, has high sulfur content, low porosity, and major fractures are commonly filled with calcite or clay minerals.31 Therefore, due to the lower porosity and permeability of the #15 coal, the #3 coal, which has relatively higher gas content, porosity, and permeability, is expected to be more commercially feasible for CO2 injection.
and ECBM recovery. Coal samples analyzed in this study were collected from the Shanxi Formation. The geothermal gradient in the #3 coal reservoir is 3.53°C/100 m, and a zone of constant temperature zone is 20 m below the surface with the temperature of 9°C. The lithostatic pressure gradient is approximately 1 MPa/100 m in the southern Qinshui Basin.42,43

3 | METHODS AND THEORY

3.1 | Sample preparation

One low-volatile bituminous coal sample (YW) and two anthracite samples (CZ and SH) were collected from the #3 coal in the Shanxi Formation in the southern part of the Qinshui basin (Figure 1B). Maceral analyses were performed using a MPV-III microphotometer at the China University of Mining and Technology in accordance with China Standard GB/T 15589-2013. Vitrinite reflectance was measured using a Zeiss Axio Imager microspectrophotometer using a point counting procedure with a minimum of 100 point counts. Prior to moisture equilibration, coal samples (as-received) were crushed to a sieve size range of 60 to 80 mesh (0.18-0.25 mm) according to China Standard GB/T 19560-2008. This coal size has been widely used in high pressure adsorption experiments.7,11,14

The results of vitrinite reflectance, proximate analysis, and macerals of the three Qinshui coal samples are shown in the Table 1. The macerals show that as vitrinite reflectance increases, the vitrinite content also increases, and the inertinite and minerals decrease. These three coal samples have similar ash content, but the YW samples have twice the volatile content of the other samples, and the CZ samples have 2-2.5 times moisture content.

Sample moisture equilibration was conducted in accordance with the Standard Test Method for Equilibrium Moisture of Coal at 96 to 97 Percent Relative Humidity and 30°C (ASTM D 1412-93). After moisture equilibration, samples were immediately placed into a sample cell and then into the manometric apparatus for CO2 adsorption testing. The detailed moisture equilibration procedure was reported by Mavor et al44 and Krooss et al24 We used an average geothermal gradient of 3.53°C/100 m and an average pressure gradient of 1.0 MPa/100 m to estimate the

| Samples | $R_o/%$ | $M_{ad}/%$ | $A_{ad}/%$ | $V_{daf}/%$ | Vitrinite/% | Inertinite/% | Minerals/% |
|---------|---------|------------|------------|-------------|-------------|-------------|------------|
| YW      | 2.18    | 1.10       | 11.98      | 13.44       | 73.66       | 23.16       | 3.18       |
| CZ      | 2.97    | 2.71       | 12.18      | 6.94        | 75.80       | 21.40       | 2.80       |
| SH      | 3.37    | 1.48       | 13.12      | 6.32        | 79.84       | 18.36       | 1.80       |

Ad- air-dried basis, daf- dry ash-free basis, YW- low-volatile bituminous coal sample, CZ and SH- anthracite samples
temperature and pressure of the coal reservoirs, which are deeper than 800 m. Accordingly, the testing temperatures were 45°C, 62.5°C, and 80°C, and the maximum pressures are 10 MPa, 15 MPa, and 20 MPa, which represent reservoir conditions at depths of 1000 m, 1500 m, and 2000 m, respectively.

3.2 | Set-up and procedure

The manometric method is widely used for determining coal gas adsorption capacity.15,46–49 A schematic diagram of the apparatus is shown in Figure 2. Prior to each gas adsorption experiment, a helium expansion procedure was conducted to determine the void volume of the sample cell at each temperature. The reference cell and sample cell were kept at a constant temperature (using a water bath) ± 0.1°C. All gas adsorption experiments were isothermal and conducted at 45°C, 62.5°C, and 80°C, corresponding to final pressures of 10, 15, and 20 MPa, respectively. Six, nine, and twelve pressure steps were used to define isotherms at each final pressure. Pressures were measured using DG2113-B-401B/B high-pressure transducers manufactured by Senex. The pressure range of the transducers is 0 to 40 MPa with an accuracy of 0.05%.

Excess adsorption of coal at each pressure, $n_{\text{exc}}$, is the difference between the volume of gas that has been transferred into the sample cell, up to a given pressure, and the “nonsorption” reference volume, which is:

$$n_{\text{exc}} = \frac{1}{M} \sum_{i=1}^{N} V_{\text{ref}}(\rho_{g}^{i} - \rho_{g}^{i-1}) - V_{0}(\rho_{g}^{N})$$

(1)

where $M$ is the molar mass of CO₂, 44 g/mol; $V_{\text{ref}}$ is volume of gas in the sample cell in the free phase, cm³; $V_{0}$ is accessible volume in the sample cell, cm³; $N$ is the measurement step; $\rho_{g}$ is the CO₂ free phase density as a function of temperature and pressure, g/cm³.

Absolute adsorption, $n_{\text{abs}}$, is the volume of gas adsorbed by the coal at a given temperature and pressure. The calculation procedure for $n_{\text{exc}}$ and $n_{\text{abs}}$ is as follows:

$$n_{\text{exc}} = (1 - \frac{\rho_{g}}{\rho_{a}})n_{\text{abs}}$$

(2)

where $n_{\text{abs}}$ is the absolute adsorption capacity of the coal; $\rho_{g}$ is the CO₂ free phase density; $\rho_{a}$ is the adsorbed phase density of CO₂ and was taken as 1278 kg/m³ based on the works of Busch & Gensterblum and Yee et al. Mavor et al52 The bulk density of fluid as a function of temperature and pressure was calculated using the NIST REFPROP V8 software, and the equation of state of CO₂ is recommended by Span & Wagner.53

3.3 | Error analysis

To evaluate the reliability of the adsorption data, multivariate error propagation was used. The error analysis of adsorption isotherms determined using the manometric method was reported by Mohammad et al54 The amount of excess adsorbed gas is defined as the difference between the transferred amount and the unabsorbed amount. For wet coals, the dissolved gas amount should also be considered. Therefore, the error in the adsorbed gas amount is:

$$\sigma_{n_{\text{exc}}}^2 = \sigma_{n_{\text{tra}}}^2 + \sigma_{n_{\text{unads}}}^2 + \sigma_{n_{\text{sol}}}^2$$

(3)

where $\sigma_{n_{\text{exc}}}$ is the error in the amount of excess absorbed gas; $\sigma_{n_{\text{tra}}}$ is the error in the transferred gas from the reference cell to sample cell; $\sigma_{n_{\text{unads}}}$ is the error in the unabsorbed gas amount; $\sigma_{n_{\text{sol}}}$ is the error in the dissolved gas amount.
3.4 | Supercritical D-R model

Previous work has demonstrated that a revised D-R model can successfully fit high pressure CO\textsubscript{2} adsorption data if gas pressure is replaced by gas density.\textsuperscript{13,17,18} Using CO\textsubscript{2} density overcomes a discrepancy where there is no saturated vapor pressure under supercritical conditions, and also reduces the error in adsorption capacity resulting from moisture and volume expansion. Accordingly, this model was applied to interpret high pressure CO\textsubscript{2} adsorption on high rank coals from the southern Qinshui Basin. The revised D-R model is as follows:

\[ n_{\text{exc}} = n_0 \left( 1 - \frac{\rho_g}{\rho_a} \right) e^{-D[\ln(\rho_g/\rho_a)]^2} + k \rho_g \]  

(4)

where D is a constant, which is a function of both the heat of adsorption and the affinity of the gas for coal; and k is a constant related to Henry's Law. However, k is an adsorption capacity revision induced by involvement of moisture or volume expansion.\textsuperscript{22}

3.5 | Swelling of coal

CO\textsubscript{2} exposure to coal can cause a volumetric swelling ranging from 1% to 5%, and swelling increases with decreasing coal rank.\textsuperscript{20,55} Previous works using the supercritical D-R model indicate that this model could accurately estimate CO\textsubscript{2} adsorption capacity at high pressure without a swelling correction, and this swelling correction had negligible effects on the calculated sorption capacity.\textsuperscript{20,56} In addition, the presorbed moisture significantly reduced coal swelling when exposed to CO\textsubscript{2}, due to adsorption sites being occupied by water molecules.\textsuperscript{23} Clearly, swelling affects the gas transport properties of coal seams during CO\textsubscript{2}-ECBM; however, the investigation of coal swelling is related to rock mechanics, which is beyond the scope of this study. Therefore, there is no swelling correction for adsorption capacity in this study, which is similar to the procedure in the previous studies.\textsuperscript{14,28}

4 | RESULTS

4.1 | Isotherms results

Results of high-pressure CO\textsubscript{2} adsorption experiments performed on the moisture-equilibrated coal samples (as-received) are illustrated in Figure 3. Excess adsorption displays a non-Langmuir-like trend and reaches maximum values near critical pressure (7.4 MPa). However, absolute adsorption shows different extensions at and above critical pressure. For a better understanding of the adsorption capacity of high rank coal, we compared the difference between excess adsorption and absolute adsorption (Figure 3).

CO\textsubscript{2} excess adsorption isotherms of high rank coal samples at all three temperatures increase up to pressures near 7 MPa, and then decrease (Figure 3). Interestingly, low temperature isotherms peak near 6 MPa, whereas higher temperature isotherms are more erratic in their behavior. The highest excess adsorption values for the three moisture-equilibrated coal samples are 31.46, 28.14, and 30.08 cm\textsuperscript{3}/g and are observed at 45°C. However, absolute adsorption displays a different trend, indicating that CO\textsubscript{2} density near the supercritical isochore has a significant influence on adsorption capacity (>7.3 MPa). From Eq. (1), the increase in free CO\textsubscript{2} density increases the difference between absolute and excess adsorption capacity at pressures above the critical pressure. Absolute adsorption shows a pronounced increase up to 7 MPa and then increases slightly or shows a slight decline, and a Langmuir-like trend could not be discerned with increasing pressure. In general, excess adsorption and absolute adsorption show similar increases in adsorption capacity at low pressures (<7 MPa) but show opposing trends resulting from decreasing CO\textsubscript{2} density between the adsorbed and free gas phases under supercritical conditions.

4.2 | Error analysis results

The reference cell and sample cell volumes for both methods were 250 and 500 cm\textsuperscript{3}, respectively, and 100 g of coal was used. In the error propagation for both methods, the following experimental uncertainties were used: 0.1°C in temperature, 0.012 MPa in pressure, 0.01% for the void in volume as determined by helium expansion, 0.02 cm\textsuperscript{3} for the reference cell volume, and 0.01 g in the amount of coal. The compressibility factor and its derivatives with respect to pressure and temperature were obtained from the equation of state given by Span and Wagner.\textsuperscript{53}

Because the experimental device and procedure were the same for all three coal samples, we took excess adsorption amount of SH coals at 80°C as an example to display the experimental uncertainties. Results show that the maximum error accounts for 40% of the excess adsorption amount at 20 MPa, and the average experimental error in the excess adsorbed amount is 23% (Figure 4). Higher pressures correlate to higher experimental uncertainties. These large experimental uncertainties at higher pressures are caused mainly by the uncertainty in the transferred amount.

4.3 | Fit results

To better understand the phase transition from subcritical to supercritical CO\textsubscript{2}, the relationships between CO\textsubscript{2} density and adsorption capacity are illustrated in Figure 5. In general, the effect of pressure on CO\textsubscript{2} adsorption capacity is similar to that of density because a higher concentration per unit area requires increased gas density. The highest excess adsorption values for
the three moisture-equilibrated coal samples occur at a density of 0.1-0.2 g/cm³, and the peak excess adsorption value at each temperature is consistent. Decreasing excess adsorption above a gas density of 0.2 g/cm³ is a result of the free CO₂ density approaching the absorbed CO₂ density, and the absolute adsorption data for YW coal follow the Langmuir-like shapes of the adsorption isotherms shown in Figure 5 up to a density of 0.6 g/cm³. Whereas, the absolute adsorption data of the CZ...
and SH coal samples show slight to significant decreases at densities ranging from 0.15 to 0.2 g/cm³.

The revised D-R model did fit the experimental data for the three coal samples at the three temperatures extremely well, with coefficients of determination ($R^2$) ranging from 0.83 to 0.98 (Table 2 and Figure 6). $R^2$ values for the data obtained at 45°C are higher than those obtained at the other two temperatures. Figure 7 shows the wave-like deviations between the experimental data and the best fit regression function using the revised D-R model. The maximum deviation extent exhibits some positive correlation with coal rank ($-1 < Y_W, R_o = 2.18\% <1; -2.5 < CZ, R_o = 2.97\% <2; -2.5 < SH, R_o = 3.37\% <2.5$), indicating that in this study the fitting results for bituminous coal are better than that of anthracite.

## DISCUSSION

### 5.1 Isotherm anomalies related to rank and temperature

Clearly, CZ coal (vitrinite reflectance = 2.97%) displays a higher adsorption capacity than the higher rank SH coal (vitrinite reflectance = 3.37%). This may be a discrepancy in our regular recognitions related to coal rank effect on adsorption capacity. Numerous studies have found a significant relationship between sorption and rank. Although, this rank dependence does not always facilitate an increase in CO₂ adsorption capacity.\(^{13,59,60}\) Therein, an explanation for rank dependence of CO₂ adsorption may result from the increasing micropore volume and specific surface area used for gas molecule absorption.\(^{61}\)

Specific surface area and total pore volume in CZ coal are both approximately 2.5 times that in SH coal according to low-temperature nitrogen adsorption tests,\(^{42}\) which explains higher adsorption capacity in these samples.

In addition, the 45°C excess adsorption data from CZ and SH are equivalent to the 62.5°C excess adsorption data at approximately 10 MPa (Figure 3), indicating that the temperature dependence on adsorption is more complex under supercritical conditions. These results in relation to supercritical CO₂ adsorption were also observed by previous workers.\(^{26,28,62}\) Previous studies state that temperature affects adsorption capacity, but the temperature dependence of supercritical CO₂ adsorption is seldom related to fluid density.\(^{51,63-65}\) The crossover at lower supercritical temperatures may be the result of a dramatic change of supercritical CO₂ density with a small pressure change, which could be the supercritical isochore. There is a max density difference between 45°C isotherm and 62.5°C isotherm at a step between 9 and 10 Ma (Figure 8).

Adsorption isotherms all initially significantly increase and then decrease with increasing density. This is because significant adsorption occurs in micropores, which causes a rapid increase in adsorption at low densities. However, higher pressures cannot cause more absolute adsorption because the adsorption approaches a maximum absolute amount. The larger free density increase causes a larger decline in the excess adsorption isotherm compared to the absolute adsorption isotherm according to Eq. 2. The 45°C isotherm shows a larger decline, resulting in crossover with the 62.5°C isotherm. However, at higher temperatures, this crossover may disappear.

### 5.2 Density effects on excess and absolute adsorption

As the free CO₂ density approaches adsorption density, the difference between absolute and excess capacity increases significantly, but temperature has a negative effect on this increase (Figure 9), which has also been investigated by Zhou et al.\(^{66}\) For CO₂, it is difficult to identify the boundary between the adsorbed and free phrases because there is no condensation of CO₂ under supercritical conditions. Hence, supercritical CO₂ can cause the number of CO₂ molecule layers to increase and further contribute to increasing adsorption capacity compared to subcritical CO₂ adsorption.\(^{31}\)

The highest CO₂ density at each successive temperature shows a significant decrease with increasing pressure, because nonideality for CO₂ becomes increasingly pronounced as temperature decreases (Figure 10). However, at supercritical conditions, there are two distinct CO₂ density changes between low and high temperature. At a higher temperature, for example 400K, CO₂ density shows a linear growth, similar to the subcritical phrase. In contrast, at lower supercritical temperatures, density rapidly increases near the critical pressure. Nevertheless, under subsurface conditions, temperature and pressure tend to increase with the increasing of depth, and CO₂ density changes accordingly. In the temperature-pressure diagram of CO₂ with a typical gradient in the Qinshui Basin (Figure 10A), there is a cross point between supercritical
isochore and typical gradient, suggesting that there are two density changes under supercritical conditions. It should be noted that pressure increases during CO₂ injection into in situ coals, and injected CO₂ and coalbed methane production can cause dramatic temperature changes. During CO₂-ECBM, the pressure-temperature field can considerably...
change. Therefore, the plots of adsorption capacity vs CO2 density, which are a result of temperature and pressure, may be more appropriate during an investigation of supercritical CO2 adsorption as part of CO2-ECBM.

Excess adsorption or Gibbs adsorption is defined as the net amount of gas adsorbed on a sorbent without gas of free density. Absolute adsorption is excess adsorption plus the free gas occupying adsorption space.30 When supercritical CO2 adsorption occurs, CO2 density shows a progressive increase at elevated pressures, and the trend transforms into a linear increase at higher temperatures (Figure 10B). As a result, CO2 can maintain a free phase that approaches the density of adsorbed phase. Therefore, increasing free gas density contributes to an increasing difference between absolute adsorption and excess adsorption (Figure 9). Overall, the $R^2$ values of difference vs density are significantly higher than those compared to pressure, indicating the CO2 density is more appropriate for interpreting supercritical CO2 adsorption. The functional relationship between excess and absolute adsorption is formulated below:

$$n_{\text{abs}} - n_{\text{exc}} = V_\text{ad} \times \rho_g$$  \hspace{1cm} (5)

Accordingly, the difference between absolute adsorption and excess adsorption demonstrates a clear linear relationship with gas density (Figure 9). The gradients of all lines for the different coal samples and temperatures represent the adsorption space according to Eq. 5.69 The decrease in gradients with increasing temperature in the three coal samples points to shrinking adsorption space (the volume occupied by the adsorbed CO2 molecule), which further results in a decrease in adsorption capacity.

The difference illustrates a lower gradient at higher temperature, indicating that excess adsorption values approach absolute adsorption as temperature increases under supercritical conditions (Figure 11). In contrast, the difference between excess and absolute adsorption in the supercritical CO2 adsorption phase accounts for nearly half of the absolute adsorption. In addition, as CO2 density increases, the difference between excess adsorption and absolute adsorption linearly increases. The above results suggest that assessment of geological storage of supercritical CO2 cannot simply rely on excess adsorption because excess adsorption capacity alone provides an incomplete view of the total adsorption capacity of coal. Nevertheless, excess adsorption or net adsorption is a truer indication than absolute adsorption of the volume of CO2 that adheres to pore walls by van Der Waals forces.70

### 5.3 Thermodynamics of supercritical CO2 adsorption at different temperatures

For an improved interpretation of the temperature dependence of supercritical CO2 adsorption, we refer to the heat of adsorption, which reflects the affinity between the sorbing gas molecule and the coal substrate (Table 3). In the revised D-R model, the term D can be expressed as: $D = (RT/βE)^2$, where R is the gas constant, T is the temperature, $E$ is the heat of adsorption, and $β$ is a coefficient relating to the affinity of the gas to the substrate. Using the above equation and a value of 0.35 for $β$,16 $E$ yields a range of heats of adsorption from 32.83 to 40.9 kJ/mol with an average of 37.76 kJ/mol, which is consistent with previous observations (36 kJ/mol, Day et al71), but higher than those obtained by Ozdemir et al16 and Goodman et al71 Additionally, when 0.39 is used for $β$, values ranging from 29.46 to 37.2 with an average of 33.89 kJ/mol are calculated. This result is similar to those determined by Wood.72 The differences in the heat of adsorption values reported in the literature are attributed to experimental conditions.16,71 Therefore, it can be clearly concluded that the inner surface of the coal matrix can adsorb more supercritical than subcritical CO2 molecules, which is reflected in the increasing free phase CO2 density.31

Because the gas is supercritical, there is apparently no obvious boundary between the adsorbed phase and free phase, resulting in an enlargement of the pore width for multilayer adsorption as the temperature and pressure increase. However, a maximum pore width exists even at high pressure.30,31 Free CO2 density in micropores increases toward pore surfaces, facilitating effective multilayer adsorption until the two adsorbed layers in opposite pore interfaces encounter each other, ultimately forming complete CO2 molecule filling.32 Namely, the maximum

### Table 2 Fitting parameters of the revised D-R model

| Parameter | Temperature/°C | CZ | YW | SH | Average |
|-----------|----------------|----|----|----|---------|
| $n_0$     | 45             | 43.049 | 39.378 | 40.742 |
|           | 62.5           | 40.031 | 29.359 | 32.588 |
|           | 80             | 31.256 | 29.989 | 31.165 |
| $D$       | 45             | 0.041 | 0.053 | 0.038 |
|           | 62.5           | 0.05  | 0.038 | 0.037 |
|           | 80             | 0.047 | 0.057 | 0.046 |
| $k$       | 45             | -0.007 | -0.001 | -0.005 |
|           | 62.5           | -0.003 | 0 | 0.001 |
|           | 80             | -0.005 | -0.006 | -0.008 |

### Table 3 Heat of supercritical CO2 adsorption with different β values

| Parameter | Temperature/ K | CZ | YW | SH | Average |
|-----------|----------------|----|----|----|---------|
| $E (β = 0.35)/$kJ/mol | 318.15 | 37.32 | 32.83 | 38.77 | 37.76 |
|          | 335.65 | 35.66 | 40.90 | 41.45 |
|          | 353.15 | 38.69 | 35.14 | 39.11 |
| $E (β = 0.39)/$kJ/mol | 318.15 | 33.50 | 29.46 | 34.79 | 33.89 |
|          | 335.65 | 32.00 | 36.71 | 37.20 |
|          | 353.15 | 34.73 | 31.53 | 35.10 |
pore width for complete gas infilling appears when free CO$_2$ density in the center of pores approaches the adsorbed density. However, density growth is limited in actual reservoirs, and a temperature increase could cause a significant decrease in adsorption capacity. At higher temperatures, the adsorbed phase, which completely fills some
micropores, transforms into a coexisting state coupled with the free and adsorbed phases. Multilayer adsorption tends toward Langmuir-like monolayer adsorption, and ultimately contributes to a reduction in the adsorption capacity. A more significant the gas density variations results in a greater the difference between the multilayer adsorption and monolayer adsorption, which further affects the pore width which could be completely filled. Therefore, there is monolayer adsorption, multilayer adsorption, free storage, and transitional multilayer systems, with a change in temperature, pressure and free CO₂ density.

In regard to the above hypothesis, at a temperature at the cross point above the critical temperature in the underground environment, a slight increase in free CO₂ density will no longer cause an enlargement of pore width for forming more multilayer adsorption, and alternatively a negative effect on adsorption. This results from the negative effect of temperature on adsorption, and finally contributes to a decrease in adsorption capacity.⁴⁰ for example, there is an approximate difference of 5 cm³/g between 45°C and 62.5°C but 10 cm³/g between 62.5°C and 80°C at high density in our supercritical absolute adsorption. This interpretation appropriately matches the high pressure CH₄ or CO₂ adsorption as a function of temperature-pressure conditions, which has a maximum CH₄ or CO₂ adsorption capacity at critical depths in different coal-bearing basins.⁴⁷,⁷³,⁷⁴

5.4 | CO₂ adsorption from subcritical to supercritical condition in subsurface environments

CO₂ density is a function of temperature and pressure, therefore CO₂ adsorption displays nonlinear variations at
increased depths. The subsurface temperatures, pressures, and corresponding CO$_2$ densities in the Qinshui Basin suggest that CO$_2$ goes through three density stages with increasing depth, as follows: (I) subcritical CO$_2$; (II) supercritical isochore characterized by a rapid increase in supercritical CO$_2$ density; and (III) fully supercritical CO$_2$ showing no or a slight increase in density (Figure 12A,B). The boundary temperature between stage II and III is approximately 50°C (Figure 5A). In stage II, the CO$_2$ shows a vapor-like nature and therefore has a significant compressibility. In
stage III, the CO$_2$ has a slight or no density increase due to its liquid-like nature. In a large porous system, such as meso- to macropores in coals, density gradually decreases away from a monolayer due to the weaker attraction between coal and gas. However, subcritical CO$_2$ displays a Langmuir-like monolayer adsorption, which can be distinguished from the adsorption isotherm at low pressures and temperatures. The increase in density causes more CO$_2$ molecules adhere to the surface and further contributes to multilayer adsorption, completely infilling pores with CO$_2$ (Figure 12C).

Particularly in the subcritical stage, free CO$_2$ density remains significantly different from adsorbed CO$_2$ density with increasing pressure. With the transition from the subcritical to supercritical phase, the rapid density change that occurs in the supercritical isochore results in more free CO$_2$ molecules falling to successively move into the adsorbed phase. The adsorbed phase transforms from monolayer adsorption to multilayer adsorption in response to the sharp increase in CO$_2$ density, thus the observed supercritical adsorption capacity increases at elevated temperatures. Finally, at a certain temperature-pressure condition, free CO$_2$ density in the center of the pores is close or equal to the adsorbed phase density, which suggests that the boundary between adsorbed and free CO$_2$ becomes indistinguishable. Above this condition, increasing temperature has a negative effect on supercritical CO$_2$ adsorption processes in the subsurface.

### 5.5 Implication for CO$_2$ geological storage in deep coals

For assessment of CO$_2$ storage capacity in deep, unmineable coal reservoirs, free gas storage capacity should not be neglected because of its high density. However, the amount of dissolved CO$_2$ in water is almost negligible compared to the adsorption capacity. Therefore, the amounts of free CO$_2$ and adsorbed CO$_2$ could represent an ultimately acceptable CO$_2$ storage capacity for geological sequestration in deep coal reservoirs after CO$_2$ injection into deep coals. According to the revised D-R model, we calculated the absolute adsorption capacity and amount of free CO$_2$ at different temperatures and pressures, as summarized in Table 4. It is evident that absolute adsorption capacities decrease in response to increasing temperature-pressure conditions, implying that temperature has a predominantly negative effect on supercritical CO$_2$ adsorption in deep underground environments. CO$_2$ capacity has either no or only slight decreases from 1000 to 1500 m, and significant decreases from 1500 to 2000 m, suggesting that there is probably a maximum CO$_2$ storage capacity existing between the supercritical isochore and fully supercritical CO$_2$ conditions (Stage II, III in Figure 12).

Our study on CO$_2$ density-temperature dependence of adsorption and the division of the three types of adsorption behavior related to subcritical, supercritical isochore, and fully supercritical conditions, can help identify target depths for CO$_2$ injection in deep, unmineable coal reservoirs. Many workers have acknowledged that various coals have a greater adsorption potential for supercritical CO$_2$ than for subcritical CO$_2$ due to its peculiar physicochemical properties. However, it should be noted that there is a maximum pore width constrained by temperature and free gas density for

| Samples | T/°C | P/MPa | MD/m | AC/cm$^3$/g | FC/cm$^3$/g | TC/cm$^3$/g | FC/TC |
|---------|------|-------|------|-------------|-------------|-------------|-------|
| CZ      | 45   | 10    | 1000 | 36.75       | 6.17        | 42.92       | 14.38% |
|         | 62.5 | 15    | 1500 | 28.67       | 7.17        | 35.84       | 20%   |
|         | 80   | 20    | 2000 | 22.34       | 7.35        | 29.69       | 24.76% |
| YW      | 45   | 10    | 1000 | 35.31       | 5.78        | 41.09       | 14.07% |
|         | 62.5 | 15    | 1500 | 32.90       | 6.71        | 39.61       | 16.94% |
|         | 80   | 20    | 2000 | 21.46       | 6.89        | 28.35       | 24.3%  |
| SH      | 45   | 10    | 1000 | 35.79       | 6.84        | 42.63       | 16.055 |
|         | 62.5 | 15    | 1500 | 35.62       | 7.95        | 43.57       | 18.25% |
|         | 80   | 20    | 2000 | 24.86       | 8.16        | 33.02       | 24.71% |

T-temperature, P-pressure, MD-modeled depth, AC-adsorption capacity, FC-free gas capacity, TC-total capacity. The porosity of each coal was derived from Sun and the average gas saturation of the #3 coal in the southern Qinshui basin is 70.53%.

Table 4: Calculated absolute adsorption capacity using the revised D-R model and related free and CO$_2$ capacity according to the modeled depth.
complete infilling by supercritical CO\textsubscript{2}. Once the transition temperature is passed, increasing temperatures will have a significant negative effect on adsorption capacity. Therefore, the potential depth of CO\textsubscript{2} storage in high porosity and permeability deep coal reservoirs for maximum supercritical CO\textsubscript{2} adsorption should be preferentially targeted. The calculation of total CO\textsubscript{2} storage capacity also indicates a potential depth of 1100 to 1200 m for maximum CO\textsubscript{2} storage capacity in the Qinshui Basin. The temperature and pressure in deep, unmineable coals in the southern Qinshui Basin, which are suitable for geological storage of CO\textsubscript{2}, are well beyond the CO\textsubscript{2} critical point, and injected CO\textsubscript{2} can potentially be stored in a supercritical state over geological time. The potential target depth should be confined near the transition temperature where coals have a maximum adsorption capacity for supercritical CO\textsubscript{2} storage.

6 | CONCLUSIONS

1 The revised D-R model was used to fit CO\textsubscript{2}/ScCO\textsubscript{2} adsorption data at three temperatures, which are generally representative of depths of 1000 m, 1500 m, and 2000 m in the deep coal reservoirs. Crossovers were observed between adsorption isotherms derived at 45°C and 62.5°C, indicating that supercritical CO\textsubscript{2} adsorption is dependent on a rapid change in CO\textsubscript{2} density in the supercritical isochore.

2 Passing from the sub- to supercritical phase, CO\textsubscript{2} adsorption shows three stages resulting from changes in CO\textsubscript{2} density and temperature in coal reservoir environments. Above the CO\textsubscript{2} critical point, there is a transition from monolayer adsorption to multilayer adsorption, resulting in the increasing of supercritical CO\textsubscript{2} adsorption capacity.

3 CO\textsubscript{2} density is a function of temperature and pressure, which displays a ladder-like track in the southern Qinshui Basin. The density-temperature effect on supercritical CO\textsubscript{2} adsorption suggests that the preferred coal reservoirs targeted for CO\textsubscript{2} sequestration occur near the depth of the boundary between the supercritical isochore and fully supercritical CO\textsubscript{2} stages.

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