Carbon dioxide adsorption on shale: a comparative study of isotherm models across diverse samples and temperatures

Zaheer Hussain 1,2* and Dr. Dzeti Farhah 1

1Department of Petroleum Engineering Universiti Teknologi Petronas Seri Iskandar Perak, Malaysia
2Mehran University of Engineering and Technology, SZAB Campus Khairpur, Pakistan

Abstract. In order to address one of the most serious environmental concerns of our day, reducing carbon footprints, the globe has turned its attention to carbon dioxide (CO$_2$) storage as a potential solution. Because of its unique features, shale is one of the most intriguing options in this area. Adsorption is the method through which CO$_2$ is stored in shale, particularly in its supercritical condition. Adsorption isotherm models can be used to deduce the behaviour and mechanisms of this adsorption. Langmuir, Freundlich, Dubinin-Astakhov (D-A), and Brunauer-Emmett-Teller (BET) models are among the many available for CO$_2$ modelling on shale. We attempted to fit these models to experimental data gathered from literature sources in this study, concentrating on four separate shale samples from various places in China. Among these samples are LMX1 and LMX2 from the Silurian Longmaxi Formation, WF1 from the Ordovician Wufeng Formation in the Sichuan Basin, and YC from the Ordos Basin’s Yanchang Formation. The total organic carbon (TOC) content of these shales, three marine and one continental, ranged from 3.19 to 4.27. The experimental data used to fit the model was obtained at three different temperatures: 35, 45, and 55°C. The Langmuir and D-A models offered the best fit for the data across all samples and temperature. $R^2$ values 0.93429 (for YC rock at 35°C) to 0.99287 (for WF1 at 35°C) for Langmuir and 0.88879 to 0.99201 LMX1 at 35°C. The theoretical underpinnings of these models, which account for the physical properties and adsorption dynamics of supercritical CO$_2$ on shale, are responsible for their performance. Finally, this study adds to our understanding of CO$_2$ adsorption on shale, giving useful insights for future research and potential practical uses in CO$_2$ storage. More research is needed, however, to completely understand the mechanisms and influencing factors of CO$_2$ adsorption in various types of shale, as well as to develop the models used to forecast this behaviour.

*Corresponding author: zaheer-22006297@utp.edu.my
1 Introduction

More and more consideration is being given to shale deposits, in particular as possible CCS storage sites. Shale is fine-grained sedimentary rock made up of Minerals, clay, and muck. Its ultralow permeability, intricate pore structure, and high organic content make it an especially appealing option for CO$_2$ adsorptive storage [5–7]. For long-term storage systems, the Shale’s low permeability is essential since it guarantees that there will be little or no CO$_2$ leakage back into the environment. CO$_2$ reaches the supercritical state during sequestration in deep formations, when temperatures and pressures may rise above 31.1 °C and 7.38 MPa, respectively. According to the CO$_2$ phase transition diagram (Fig. 1), the deep geological environment can provide the conditions needed for the phase transition. The physio-chemical characteristics of supercritical carbon dioxide (scCO$_2$) are unique in that it has a high density similar to a liquid and a low viscosity like a gas [8–10]. Because of this, scCO$_2$ is regarded as the perfect non-aqueous fracturing fluid that can result in a denser fracture network. Compared to its gas or liquid phases, supercritical CO$_2$ has unique characteristics. Shale’s surface is excellent adsorbent to this particular type of CO$_2$ [11].

Fig. 1. The phase transition diagram of carbon dioxide [12].
To numerically or analytically describe the adsorption behavior of different gases and shale samples, adsorption usually relies on an isotherm. Various adsorption isotherm models can be used to model and understand the process of adsorption on shale. Among multiple available isotherms model for different material Langmuir, Freundlich, Dubinin-Astakhov (D-A), and Brunauer-Emmett-Teller (BET) are prominent models [13,14]. Understanding these models is essential for maximizing storage capacity and guaranteeing the stable storage of CO$_2$ over the long run. The focus of numerous studies has been on simulating the adsorption of CO$_2$ and other gases on shale using different isotherms. To estimate CO$_2$ adsorption, scientists used a variety of models and assessed how effective they were. The simplest Langmuir and Dubinin-Radushkevich models were found to be the best suitable for modelling single component adsorption on coal and shale [15]. Jin, examined the dissolved molecules of organic substances and find that the traditional Langmuir model could not adequately represent the behavior of the fluid in the porous medium with pore sizes greater than 10 nm, they adopted a cubic equation of state [16]. Lu, developed a novel model that is entirely based on a numerical producer combined with Artificial Neural Network Technology in order to calculate the amount of gas lost throughout the coal production process Le, has developed a new computational model to predict the flow of methane in the matrix of cracked shale, based on the averaging of mass conservation equations [17]. Yu, employed the BET isotherm rather than the Langmuir isotherm to model gas adsorption in the Marcellus Shale. Studies have demonstrated that in certain Marcellus shale samples, the Langmuir isotherm is not a good model for adsorption [18].

The current study compares four commonly used isotherm models in order to develop our understanding and improve knowledge of CO$_2$ adsorption on shale. We concentrate specifically on shale samples from three geologically distinct formations in China: the Yanchang Formation in the Ordos Basin, the Ordovician Wufeng Formation in the Sichuan Basin, and the Silurian Longmaxi Formation. To take into consideration the impact of temperature on adsorption dynamics, measurements were carried out at temperatures of 35 $^\circ$C, 45 $^\circ$C and 55 $^\circ$C. This study also sheds light on the mechanics underlying CO$_2$ adsorption on shale, although more research is required. It is essential to have a deeper comprehension of the mechanisms and variables influencing CO$_2$ adsorption in different kinds of shale. Furthermore, for more precise forecasts and excellent storage options, ongoing improvement of the current isotherm models is essential.

2 Materials and Methods

2.1 Sample Preparation

Sample preparation was carried out using a FRITSCH Mortar Grinder to obtain shale particles in size of less than 20 μm. Powdered samples were then preserved in airtight plastic bags to avoid any physical and chemical changes due to oxidation as shown in (Fig. 2).
Fig. 2. Representative shale samples from various formations: (a)-(c) Longmaxi Formation, Silurian Basin; (d) Wufeng Formation, Sichuan Basin; (e) Yanchang Formation, Ordos Basin.

Before sending samples for adsorption experiments, samples were sent for Total organic carbon (TOC) and X-ray diffraction (XRD) analysis. The shale samples TOC contents were measured using the TOC analyzer HT13000/Multi NC 3100 and mineral were identified using XRD-Powder Diffraction (Xpert3 Powder) [19]. Through an analytical run using the quantity of CO2 generated during burning, the devices calculated the individual or organic and inorganic carbon [20]. In order to eliminate any carbonate traces from the sample, 37% hydrochloric acid (HCL) was applied to it prior to testing [21]. To get rid of any remaining traces of extra HCL, the samples were rinsed with distilled water and allowed to dry in the oven for the entire night. Compared to marine shale, continental shale often contains more clay and less quartz. All samples vary in their TOC content ranges from 3.19 to 4.27 and mineralogical composition as shown in Table 1 [22,23].

Table 1. TOC Content and Mineralogical composition of shale Sample.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mineralogical composition in percentage</th>
<th>TOC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Quartza</td>
<td>Carbonata</td>
</tr>
<tr>
<td>LMX 1</td>
<td>42.4</td>
<td>37.8</td>
</tr>
<tr>
<td>LMX 2</td>
<td>53.3</td>
<td>15.5</td>
</tr>
<tr>
<td>WF 1</td>
<td>49.2</td>
<td>28.8</td>
</tr>
<tr>
<td>YC</td>
<td>28.9</td>
<td>14.6</td>
</tr>
</tbody>
</table>

2.2 Adsorption Experiment

Using a Shale adsorption device, the CO2 adsorption experiment was carried out volumetrically on shale. Figure displays the unit's schematic diagram. It is made up of two cylinders made of stainless steel, a set of high-pressure valves, and a 0.1% accurate high-precision pressure transducer. A heater that was positioned next to the cells and had a temperature control accuracy of 0.1 °C was used to maintain a constant temperature throughout the experiment because shale's adsorption capability is temperature sensitive. Samples of dry powdered shale were used for the adsorption tests. To eliminate any remaining moisture, all of the shale samples were dried in a vacuum oven for 12 hours at 110 °C. Within a cell were dried samples. The actual adsorption experiment was started at 1000 Psia after a leakage test. Helium expansion was used to compute the void volume (Vvoid). V_void can be calculated by the (eq:1):
\[ V_{\text{void}} = \frac{pV_{\text{He}}}{ZT_C} c \]

Where,

Subscripts \( R \) and \( S \) indicate the conditions in a reference cell and samples cell, respectively, while \( V_{\text{He}} \) is the volume of helium injected. The compressibility factors of helium are \( Z_1 \) and \( Z_2 \). The sample cell's pre- and post-he helium injection circumstances are denoted by the underscores 1 and 2, respectively.

Fig. 3. Schematic of the adsorption unit (reproduced from [23]).

The adsorption of \( \text{CO}_2 \) was measured after the determination of the \( V_{\text{void}} \). It was decided to let the \( \text{CO}_2 \) gas expand into the sample cell and adsorb onto the shale. Until equilibrium pressure was reached, the arrangement was left in place. Once equilibrium was reached, the pressure was measured, and the adsorbed gas volume was computed. To determine the adsorbed volume at each pressure level, the identical procedure was done multiple times with increasing pressure. Experiments were carried out at three distinct temperatures 35°C, 45°C, and 55°C at seven different pressure values form 1-8 MPa to better understand the significance of temperature in the adsorption process as shown in Table 2.

Table 2. Equilibrium Pressure and Absolute Adsorption of \( \text{CO}_2 \) on Shale Samples at Temperatures of 35°C, 45°C, and 55°C.
<table>
<thead>
<tr>
<th>LMX 2</th>
<th>0.78105</th>
<th>1.24201</th>
<th>0.582405</th>
<th>1.53512</th>
<th>0.621623</th>
<th>1.30021</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.17811</td>
<td>2.1242</td>
<td>0.952978</td>
<td>2.00934</td>
<td>1.15654</td>
<td>1.9329</td>
</tr>
<tr>
<td></td>
<td>3.10336</td>
<td>2.46782</td>
<td>2.06096</td>
<td>2.88295</td>
<td>2.09911</td>
<td>2.49116</td>
</tr>
<tr>
<td></td>
<td>4.49708</td>
<td>3.21663</td>
<td>3.12599</td>
<td>3.44241</td>
<td>3.16361</td>
<td>2.97219</td>
</tr>
<tr>
<td></td>
<td>5.80078</td>
<td>3.69779</td>
<td>4.10912</td>
<td>3.96185</td>
<td>4.06403</td>
<td>3.33396</td>
</tr>
<tr>
<td></td>
<td>6.51348</td>
<td>3.87237</td>
<td>5.13226</td>
<td>4.36404</td>
<td>5.08691</td>
<td>3.69693</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>WF 1</th>
<th>0.709832</th>
<th>1.06666</th>
<th>0.671463</th>
<th>0.819643</th>
<th>0.748201</th>
<th>0.725071</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.13189</td>
<td>1.42942</td>
<td>1.03597</td>
<td>1.16315</td>
<td>1.247</td>
<td>1.10719</td>
</tr>
<tr>
<td></td>
<td>2.01439</td>
<td>2.15513</td>
<td>2.09113</td>
<td>1.73777</td>
<td>2.14868</td>
<td>1.52919</td>
</tr>
<tr>
<td></td>
<td>3.10791</td>
<td>2.91982</td>
<td>3.10791</td>
<td>2.16032</td>
<td>3.16547</td>
<td>1.87579</td>
</tr>
<tr>
<td></td>
<td>4.10552</td>
<td>3.72202</td>
<td>4.16307</td>
<td>2.67799</td>
<td>4.1247</td>
<td>2.31705</td>
</tr>
<tr>
<td></td>
<td>5.1223</td>
<td>4.41039</td>
<td>5.1223</td>
<td>3.21419</td>
<td>5.16067</td>
<td>2.60678</td>
</tr>
<tr>
<td></td>
<td>6.17746</td>
<td>5.06097</td>
<td>6.13909</td>
<td>3.75066</td>
<td>6.08153</td>
<td>2.87697</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>YC</th>
<th>0.748201</th>
<th>0.725071</th>
<th>0.836044</th>
<th>0.314743</th>
<th>0.832066</th>
<th>0.14239</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.247</td>
<td>1.10719</td>
<td>1.25725</td>
<td>0.566908</td>
<td>1.36782</td>
<td>0.358317</td>
</tr>
<tr>
<td></td>
<td>2.14868</td>
<td>1.52919</td>
<td>2.37966</td>
<td>1.20488</td>
<td>2.13983</td>
<td>0.812003</td>
</tr>
<tr>
<td></td>
<td>3.16547</td>
<td>1.87579</td>
<td>3.31633</td>
<td>1.79397</td>
<td>3.1648</td>
<td>1.22733</td>
</tr>
<tr>
<td></td>
<td>4.1247</td>
<td>2.31705</td>
<td>4.34409</td>
<td>2.32995</td>
<td>4.46659</td>
<td>1.63841</td>
</tr>
<tr>
<td></td>
<td>5.16067</td>
<td>2.60678</td>
<td>5.50747</td>
<td>2.74315</td>
<td>5.39451</td>
<td>1.84833</td>
</tr>
<tr>
<td></td>
<td>6.08153</td>
<td>2.87697</td>
<td>6.50857</td>
<td>3.12436</td>
<td>6.4155</td>
<td>2.0913</td>
</tr>
</tbody>
</table>
2.3 Fitting of Adsorption Isotherms

This work intends to clarify the adsorption kinetics of supercritical CO₂ on shale by employing these isotherm models, each of which provides distinct benefits and viewpoints based on its theoretical foundation. The experimental data was fitted using four well-known adsorption isotherm models: Langmuir, Freundlich, Dubinin-Astakhov (D-A) and Brunauer-Emmett-Teller (BET). Based on their different theoretical underpinnings and presumptions, each of these models provides a distinctive perspective on the adsorption behavior of supercritical CO₂ onto shale.

2.3.1 Langmuir Isotherm Model

\[ q_e = \frac{Q_m \times K \times C_e}{\Delta k \times C_e} \]

Where, \( q_e \) is the amount of adsorbate per unit weight of adsorbent at equilibrium, \( Q_m \) is the maximum amount of adsorbate that can be adsorbed, \( K \) is the Langmuir constant, and \( C_e \) is the equilibrium concentration of the adsorbate.

2.3.2 Freundlich Isotherm Model

\[ q_e = K_f \times C_e^n \]

Where, \( q_e \) is the equilibrium concentration of adsorbate/absolute adsorption, \( K_f \) is the Freundlich constant, and \( n \) is an empirical parameter indicative of the intensity of adsorption.

2.3.3 Dubinin-Astakhov (D-A) Isotherm Model

\[ q_e = Q_m \times k \times e^{-\epsilon} \]

Where, \( q_e \) is the amount adsorbed per unit weight, \( Q_m \) is the theoretical saturation capacity, \( K \) is the D-A constant, and \( \epsilon \) is the Polanyi potential.
2.3.4 Brunauer-Emmett-Teller (BET) Isotherm Model

The BET theory extends the Langmuir theory to multilayer adsorption. While the Langmuir model describes monolayer adsorption (i.e., only one molecular layer thick), the BET model considers that gas molecules can adsorb onto solid surfaces in multiple layers. It is provided by and frequently utilized for gases adsorbed onto solid surfaces [27]. The equation for BET model is:

\[
\frac{C_e}{q_e \times Q_m - q_e} = \frac{C_e \times K}{Q_m} + \frac{C_e \times K}{Q_m}
\]

Where, \(C_e\) is the equilibrium concentration of adsorbate, \(q_e\) is the amount of adsorbate adsorbed at equilibrium, \(Q_m\) is the monolayer capacity, and \(K\) is the BET constant.

2.4 The goodness of Fit

These isotherm models were fitted to the experimental data by non-linear least squares regression methods. To measure the goodness of fit, the coefficient of determination (R²) was employed. For predicting CO₂ adsorption in shale formations, the most durable and dependable models are those that yield the best match across all samples at varying conditions. The models that most closely matched the experimental findings under various sample and temperature circumstances were the best-fitting ones. This replication gave important insight into possible storage processes by offering a comprehensive way for evaluating how well different isotherm models described CO₂ adsorption on shale.

3 Results and Discussion

The different CO₂ adsorption capabilities of samples LMX1, LMX2, WF1, and YC appear to be impacted by their individual mineral compositions and organic content. Quartz is generally recognized for low CO₂ adsorption, although LMX2 has noteworthy adsorption capabilities despite its high quartz content. This implies that additional elements, such as its high organic content or the other minerals present, are important. However, LMX1, which has a high carbonate content, also shows substantial CO₂ adsorption, suggesting that carbonates may have a beneficial impact in adsorption. Interestingly sample YC is unique because of its high concentration of clay, a material known for having good CO₂ adsorption properties. YC is good at storing CO₂, especially in colder conditions. But because YC has little organic carbon, it might not store as much CO₂ as possible. Moreover, the influence of temperature is noticeable in every sample. The adsorption capacity of these samples often declines with increasing temperature (fig 4), which is important to take into account for real-world applications like oil recovery and carbon storage. Predicting the CO₂ adsorption behavior of shale samples is crucial for energy and environmental applications, and it essentially requires an understanding of the particular mineral and organic makeup of the samples.
In Fig 4 samples LMX1, LMX2, WF1, and YC, shows the absolute adsorption \( (q_e) \) in terms of \( \text{cm}^3/\text{g} \) in relation to the equilibrium pressures \( (P_{eq}) \), measured in MPa. Adsorption behavior is recorded at three different temperatures 35 °C, 45 °C, and 55 °C. For sample LMX1, there is a discernible drop in adsorption at lower equilibrium pressures as the temperature increases from 35 °C to 55 °C. However, the adsorption values tend to stabilize at pressures more than 2 MPa at 55 °C, suggesting that LMX1 has a higher affinity for adsorption under these circumstances. LMX2 operates differently, adsorption increases progressively at temperatures of 35 °C and 45 °C as pressure increases. In contrast, LMX2 exhibits comparatively constant adsorption at 55°C across the pressure range, with a discernible increase at 4 MPa. These results suggest that this sample is susceptible to temperature variations in this range (45 °C to 55 °C) at similar pressures. In general, the adsorption for sample WF1 rises with pressure. However, when the temperature increases from 35 °C to 55 °C, there is a discernible decrease in adsorption capacity. For instance, the adsorption at 35 °C is significantly higher than that at 55 °C at an equilibrium pressure of about 6 MPa. This suggests that WF1 adsorption efficiency might decrease at higher temperatures. Sample YC shows a distinct pattern. The greatest adsorption values for all pressures occur at 35°C, with 45°C trailing closely behind. Observations at 55 °C often exhibit the lowest adsorption capabilities, which are particularly noticeable at pressures lower than 4 MPa. This suggests that when temperature rises, YC adsorption effectiveness decreases. The effect of temperature on adsorption differs throughout samples; each exhibits enhanced adsorption with rising equilibrium pressures. While LMX2 exhibits temperature sensitivity, WF1 appears to prefer colder settings, YC functions best at 35 °C across the tested pressures, and LMX1 is rather stable between 35 °C and 45 °C. When choosing materials for certain adsorption applications, this knowledge might be crucial, particularly in situations where temperature is a factor.

The primary objective of this research was to assess the suitability of various isotherm models, including Langmuir, Freundlich, Dubinin-Astakhov (D-A), and Brunauer-Emmett-Teller (BET), for characterizing the adsorption of CO\(_2\) on shale samples that range in temperature and organic content. The experimental data was fitted in models. The Langmuir and D-A models were shown to be the most accurate predictors of CO\(_2\) adsorption on shale samples throughout a range of temperatures, according to the data shown in Figure 3. The goodness-of-fit of the models is assessed statistically using the \( R^2 \) values. The Langmuir model showed \( R^2 \) values varying from 0.99316 for the WF1 sample to 0.99287 for the YC rock sample at 35 °C. These strong \( R^2 \) values imply that the Langmuir model accurately captures the kinetics of CO\(_2\) adsorption onto shale shown in (Fig: 5).
The D-A model highest R² values for WF1 at 35 °C that is 0.99201 and Lowest R² values at 0.88879 for the LMX1 sample at 35 °C. The D-A model is a dependable method for describing the nuances of CO₂ adsorption on shale, as supported by the high R² values. The experimental data revealed a significant finding: all samples showed a decrease in CO₂ adsorption rates as temperature increased. Important ramifications for CCS operations stem from this temperature sensitivity. Optimizing settings that maximize carbon storage in shale deposits requires an understanding of the thermal dynamics of CO₂ adsorption; the Langmuir and D-A models stand out for their ability to account for the distinct physical properties and adsorption dynamics of supercritical CO₂ on shale. Their strong R² values suggest that they can be used as trustworthy models for both practical and upcoming research. When developing and evaluating the viability of CCS techniques in diverse geological formations, these models may prove especially beneficial.

4 Conclusion
By doing this, they close a significant information gap regarding the storage of CO₂ in sedimentary rock formations such as shale. All of the shale samples in the investigation showed a significant decrease in CO₂ adsorption rates with increasing temperatures. Because it explains how changes in geology and climatic factors can affect the efficiency of CO₂ storage, this thermal sensitivity is crucial to the development of CCS technology. It is essential to comprehend these thermal dynamics in order to develop CCS solutions that are more reliable and effective.

Even if the results are significant, this study is more of a steppingstone than a definitive response. To completely understand the mechanisms underlying CO₂ adsorption in different kinds of shale formations, further thorough research is required. Predictive models also need to be progressively improved and modified in order to increase the efficacy and efficiency of CCS technologies. It is envisaged that subsequent investigations will expand on the results of this study, deepening our comprehension of the intricate relationship between CO₂ and shale, and consequently advancing environmentally friendly technologies.

References


