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CO_2 Adsorption of Geological Formation Mineral: A Review

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ABSTRACT

Greenhouse gases effect, particularly carbon dioxide (CO_2), has significantly resulted in an increase in climate change and global warming because of the uncontrolled combustion of hydrocarbon fuels. Carbon capture and storage (CCS) technology has been presented as an effective technique to mitigate CO_2 emissions by capturing and injecting back into subsurface geological formations for permanent storage. Geological formations consist of a diverse range of minerals such as olivine, pyroxene, amphibole, biotite and clays, among others, each with unique properties that influence their CO_2 adsorption capacity. This paper explores the carbon adsorption capacity of formation minerals, emphasizing clays, which plays a critical role in CCS. Minerals are categorized based on their crystal structure, chemical composition and physical characteristic originating from diverse geological environments, including magmatic, sedimentary, hydrothermal, and metamorphic systems. Understanding the physiochemical chemistry of these minerals is essential for evaluating their adsorption potential. This review highlights the significance of mineralogical diversity in influencing adsorption capacity and explains adsorption isotherms and kinetic models to aid in predicting adsorption behaviour. Aligned with Goal 13: Climate Action from the United Nations Sustainable Development Goals, this review advances sustainable development technologies to mitigate CO emission. By expanding the understanding of mineral-based CO_2 adsorption mechanisms, this review supports the advancement of CCS technologies that are pivotal in the global effort to tackle climate change and reduce atmospheric CO_2 concentrations. The findings underscore the potential of geological formations as viable long-term storage solutions, thereby promoting environmental sustainability and aiding in the conversion towards a low-carbon future.

Keywords: Carbon capture; CO_2 adsorption; clay minerals; geological formations; mineralogy diversity

INTRODUCTION

Greenhouse gases effect, particularly carbon dioxide (CO_2), has significantly resulted in an increase climate change and global warming because of the uncontrolled combustion of hydrocarbon fuels. The urgency to mitigate climate change through carbon emission has been addressed in Paris Agreement partied by 195 countries in the United Nations. One of the current methods to mitigate this problem is by capturing the emitted CO_2 and injecting it back underground into depleted reservoirs for permanent storage. The amount of CO_2 that can be stored in geological storage is affected by the adsorption capacity of the geological formation. Factors such as physical factors, geochemical factors, and mineral composition factors influencing the adsorption capacity. Additionally, equilibrium isotherms and kinetic models may assist in understanding and optimizing for the CO_2 adsorption processes.

The geological formation consists of various types of minerals including andalusite, actinolite, amphibole, biotite, garnet, oolite, olivine, plagioclase, pyroxene, and staurolite (Romaine 2020). These minerals are part of different geological environments such as magmatic, sedimentary, hydrothermal, and metamorphic systems (Best 2013; Bustillo Revuelta 2018). Additionally, advanced argillic minerals like alunite, kaolinite, dickite, pyrophyllite, and diaspore form in specific alteration environments due to various processes like vapor condensation, boiling of hydrothermal liquids, and supergene weathering (Hedenquist & Arribas 2022). The diversity of minerals distribution has evolved over time, with initial minerals being dominated by abundant elements and subsequent diversification occurring through fluid-rock interactions and biologically mediated processes (Hazen et al. 2023). This mineralogical diversity is crucial in shaping its geological formations and its capacity for carbon adsorption.

On this matter, the related literature of CCS technologies via geological storage is reviewed. Adsorption mechanism and their parameters that influence adsorption capacity including mineralogical properties are also to be described comprehensively. Furthermore, this article is to discuss the existing adsorption isotherms and kinetic models that are utilised to predict adsorption capacity. Therefore, the following section addresses the research gap and allows in designing an optimal strategy for CCS application.

CARBON CAPTURE AND STORAGE

PRINCIPLES OF CCS

The extensive utilization of hydrocarbon fuels from electricity generation, industrial activities, and transportation are releasing substantial amounts of greenhouse gases (GHG), primarily carbon dioxide, leading to the climate change and global warming. Over the preceding centuries, the CO level concentration in the atmosphere has expanded to 410 ppm, compared to a level of less than 300 ppm during pre-industrial period (Haley 2019). Therefore, mitigation strategies are required to prevent the CO_2 concentration from rising. CCS technology helps to mitigate the emission of CO_2 into the air. Many studies proved that CCS technology had the potential to effectively mitigate climate change by injecting CO_2 into geological formation (Ismail & Gaganis 2023; Rasool et al. 2023; Zapata et al. 2020).

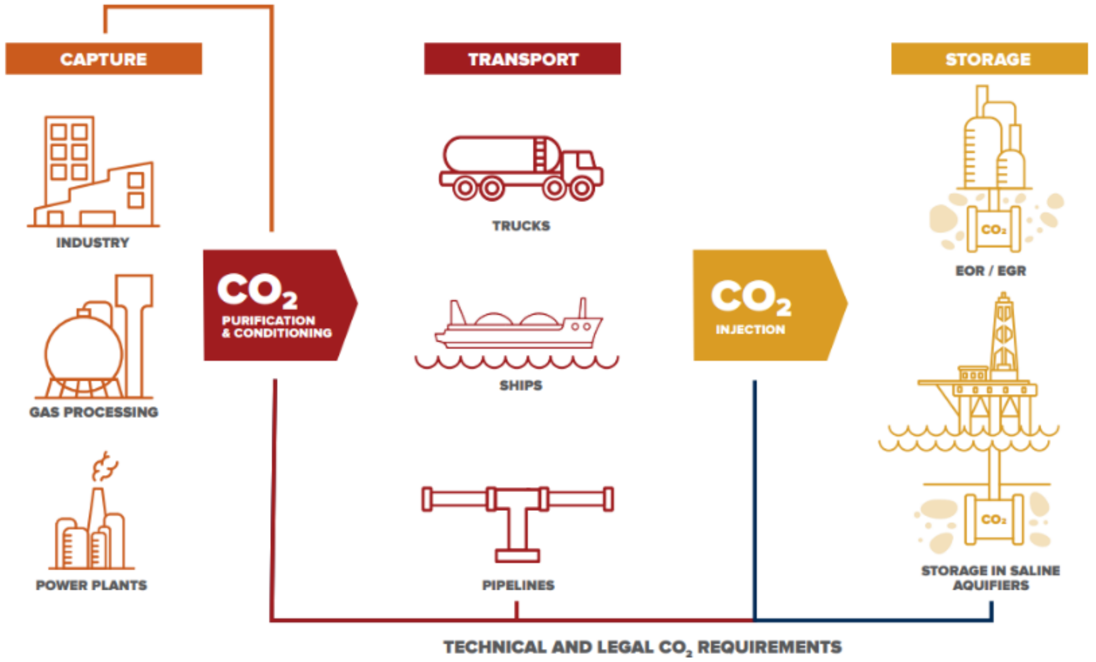

FIGURE 1. CCS Processes (Kearns et al. 2021)

Figure 1 provides an illustrated graphic representation of the overall processes involved in CCS. This technology captures CO_2 emission from industrial and energy sectors, compresses the CO_2, transports through pipelines to suitable storage sites and injects CO_2 into the rock formations for permanent storage. Possible storage mechanisms for CO_2 injection are into subsurface geological formations, deep ocean, or in inorganic carbonates (Shachi et al. 2019).

CARBON STORAGE IN DEPLETED RESERVOIR

CCS involves capturing and storing CO_2 in geological formations. This technology aims to permanently store CO_2 emission from large-scale point sources by injecting them into deep, porous, and permeable formations (Newell & Ilgen 2019). These geological formations must possess specific properties. For example, it is necessary for them to be located at a depth of at least 850 metres below the subsurface, and they must also be covered by one or more impermeable layers (known as caprock) to prevent the upward movement of CO_2 (Newell & Ilgen, 2019). Furthermore, the storage formation must possess high porosity and permeability for CO_2 storage (Feng et al. 2023)

Typically, CO_2 can be stored in several underground locations, including depleted reservoirs, deep saline aquifers, basaltic formations, coal seams, and clastic formations (Rasool et al. 2023). Saline aquifers possess the highest capacity for storing CO_2 among these storage locations (Luo et al. 2022). However, depleted gas reservoirs also make excellent CO2 storage locations due to various reasons. These reservoirs offer a larger pore volume, long-term hydrocarbon storage capabilities, and enhanced recovery of residual natural gas upon CO_2 injection (Hamza et al. 2021). Furthermore, their existing infrastructure and extensive knowledge of subsurface conditions provide significant advantages over saline aquifers. This allows for convenient CCS deployment by utilizing matured onshore fields and re-purposing existing infrastructures.

The mechanism of CO_2 storage in depleted reservoir is shown in Figure 2. Depleted reservoirs are geological formation that was previously utilized to extract hydrocarbon. The reservoir production and pressure reduction cause a larger pore size, which offer mechanism such as structural trapping to store natural gas, oil, or brines. The ability of storing hydrocarbons for many years indicates a safer option for CO_2 storage compared to other geological storage options. However, it requires a continuous monitoring to guarantee the durability of the CO_2 storage sites because due to various factors. Formation heterogeneity, geochemical and geomechanical parameters should be considered as it may leads to reservoir compaction and expansion (Hamza et al. 2021).

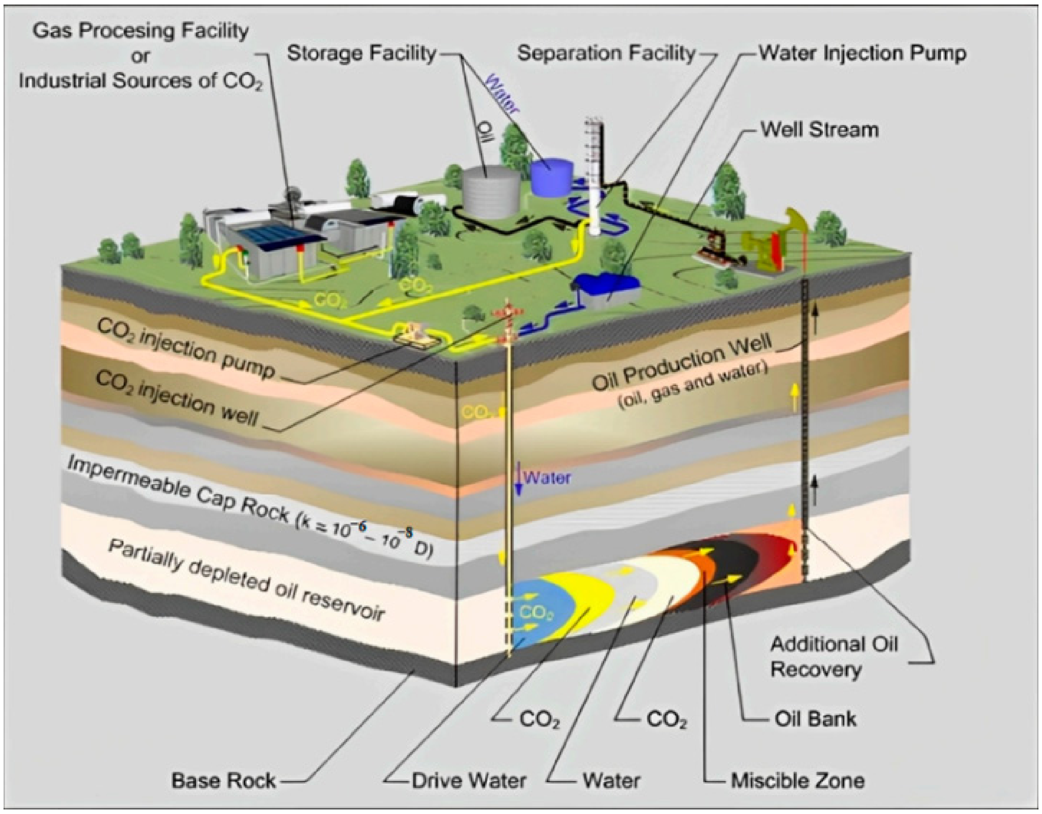

FIGURE 2. Mechanism of CO_2 storage in depleted reservoir (Ali et al. 2022)

ADSORPTION MECHANISM

Adsorption is a process where a mixture of gases or liquids, consisting of multiple components, attaches to the solid minerals surface. Adsorption is categorised into two, which are physical adsorption (physisorption) and chemical adsorption (chemisorption). Physisorption involves a London-van der Waals forces interactions between the solid and adsorbate, while chemisorption is a result of chemical bonding forces (Chiou, 2002). Both adsorption processes may occur to eliminate toxic substances and impurities in the air, which depends on the specific condition and the properties of the solid sorbent or storage medium. The criteria for physical adsorption and chemical adsorption can be clarified in Table 1.

Adsorption processes in the geological formation involve the use of natural minerals such as andalusite, actinolite, amphibole, biotite, garnet, oolite, olivine, plagioclase, pyroxene, and staurolite (Romaine, 2020). The effectiveness of the processes depends on the natural minerals, which needs to have a high adsorption capacity and efficient kinetics. These natural minerals possess outstanding CO_2 adsorption capacity that can assists in mitigating climate change economically at larger scale (Assen et al. 2021). The CO_2 adsorption capacity in the geological formation is influenced by internal and external factors. Internal factors including pore characteristics (specific surface area and pore volume), mineralogical properties (types and clay content), and organic matter characteristics are significantly impacting the adsorption capacity (Li et al. 2024). In addition, external factors such as adsorption temperature and pressure, moisture content, and CO_2 concentration also influence the adsorption capacity (Gunawardene et al. 2022).

TABLE 1. Difference between Physisorption and Chemisorption

Criteria	Physical Adsorption	Chemical Adsorption
Attraction Force	Van der Waal forces	Ionic or covalent bond
Specificity	Unspecific	Very specific
Nature of adsorption	Depend on nature of geological formation	Depend on nature of geological formation
Reversibility	Reversible or Partially Reversible process.	Mainly irreversible
Temperature	Not conducive under high temperatures.	Conducive under high temperature
Enthalpy	Low	High
Activation energy	Does not require high activation energy	Require high activation energy
Layer of adsorption of interfacial region	Multi layers	Mono layer

MINERALOGY DIVERSITY AFFECTING ADSORPTION

Minerals are formed through diverse geological environments. They are composed of various types of minerals including andalusite, actinolite, amphibole, biotite, garnet, oolite, olivine, plagioclase, pyroxene, and staurolite(Romaine, 2020). These minerals can be classified into several categories based on chemical composition, carbonates, silicates, sulphates, oxides and halides, sulfides, native elements, phosphates, and energetic minerals based on their chemical composition (Irannajad et al. 2019). The type of minerals can be determined form the chemical composition, crystal structure, and physical characteristics such as hardness, colour, and density (Ali et al. 2022). The diversity of minerals distribution has evolved over time, with initial minerals being dominated by abundant elements and subsequent diversification occurring through fluid-rock interactions and biologically mediated processes (Hazen et al. 2023; Hazen & Morrison, 2022). This leads to the formation of nano-sized pore structure and the heterogeneity of organic and non-organic composition within the geological formation. The minerals may indicate different pore characteristics such as pore volume and pore size distribution and indirectly influencing the surface area. Furthermore, the diverse minerals have correlated with Cation Exchange Capacity (CEC), which impacting the capability of adsorbing CO_2 (Mousalli et al. 2020). Clay minerals like montmorillonite, vermiculite, illite, and kaolinite, can significantly influence the CEC due to their pore structures and compositions. Other parameters include chemical composition, and hydroxyl groups also need to be considered. Therefore, the mineralogical diversity is to be studied as it significantly impacts the adsorption process.

Natural minerals are used to adsorb CO_2 as an alternative to CO_2 capture since they require less energy and have simpler operational conditions. A study to enhance the efficiency of CO_2 adsorption is conducted by analysing the mineralogy with relevant adsorption capacity and selectivity of CO_2. Recently, CO_2 capture has grown more difficult due to higher costs to prepare these materials in larger scale. In this context, clay minerals are being increasingly recognized as a viable option because of their non-toxic nature, global availability, affordability, and unique physicochemical characteristics such as large surface area, ion-exchange capacity, and catalytic attributes (Lazaratou et al. 2020).

PORE SIZE DISTRIBUTION

Each natural minerals provides a different particle size and pore volume, which significantly affecting the adsorption process. Nanoparticles size minerals with pore widths below 200 nm, such as clay minerals, has a high adsorption capacity due to their high surface area (Murugesu et al. 2019). Research on coal samples identified that adsorption capacity increases due to smaller particle size used (Li et al. 2022; Zhang et al. 2023). As a result, the surface area and the pore volume of the geological formation is inversely proportional to the particle size, leads to more interactions with the CO_2 molecules.

Clay minerals, such as phyllosilicates, tends to form smaller particle sizes through geological processes because of their crystal structure, including the order-disorder distribution of cation and crystal defects in the layered stacks, as proposed by the Periodic Bond Chains (PBCs) theory (Meunier, 2006). The formation of crystal defects obstructs crystal growth along specific axes, favouring nucleation over continued growth. As a result, numerous small crystals are formed than a larger one. Furthermore, abundant minerals can create nanosized crystals by deformational processes driven by tectonic evolution and geodynamics (Kazantseva, 2022). The contribution of these nano-scale particle size leads to higher surface area and pore volume, hence, increase overall adsorption sites.

MINERAL COMPOSITION

Geological formation contains complex clastic sedimentary rock with particles smaller than 62 μm, making up over 50% of its composition (PENG et al. 2022). It contains various minerals, primarily, siltstone, clay and minor quantities of biological silica minerals, endogenic carbonates, and phosphates (Lyu et al. 2019). Clay minerals in shale are typically believed to have several adsorption sites. The clay minerals, such as like montmorillonite, kaolinite, and illite, influence adsorption due to the mineralogy in the formation by the Cation Exchange Capacity (CEC) (Mousalli et al. 2020). The reason is that the different types of clay mineral provide a specific surface area and pore size distribution, hence, influence the adsorption capacity. The distribution of the minerals is essential for understanding on how they contributes to the formation's capacity to adsorb CO_2.

CHEMICAL COMPOSITION

Comprehending the chemical interactions among CO_2 molecules and geological formation is essential for optimizing CO adsorption. The interaction between geological formation minerals and CO_2 is mostly determined by their mineral composition, which in turn influences the chemical characteristics (Fatah et al. 2020). Furthermore, the chemical composition of CO_2 influences the dissolution and crystallization mechanisms and has a substantial impact on the pore structure (Du et al. 2020). Hydroxyl functional groups that represents in natural minerals, indicate the existence of clay materials such as kaolinite and illite. Higher clay contents can generate additional OH– ions, leading to a decrease in OH levels and hydroxyl functional groups (Fatah et al. 2021). They also stated that the changes in hydroxyl functional groups (groups with oxygen) may enhance CO_2 adsorption and impact the total storage capacity. The natural minerals-CO_2 interaction needs to be comprehensively reviewed, as it could occur changes in the mechanical, petrophysical, or petrochemical properties of geological formation.

CARBON STORAGE IN CLAY MINERALS

Adsorbents are widely used to adsorb pollutant due less energy required and simple operating conditions. It is vital to study the suitable adsorbent for CO_2 to achieve a cost-effective and sustainable processes in CCS. Clay minerals is an example of effective adsorbent. They are composed of kaolinite, smectite, illite and chlorite. Clay minerals are being increasingly recognized as a viable option because of their non-toxic nature, global availability, affordability, and unique physicochemical characteristics such as large surface area, ion-exchange capacity, and catalytic attributes (Lazaratou et al. 2020). Furthermore, clay minerals have an advantage over activated carbon in term of its carbon exchange capacity (CEC), swelling ability, microporosity and layered structure (Barakan & Aghazadeh 2021).

The physiochemical properties of various clay minerals significantly play a vital role in determining the amount of CO_2 adsorbed. The factors such as pore size and types of clay structure significantly influencing the adsorption capacity of the geological formations. Clay minerals provide a higher surface area because of the smaller particle size, micro to nanocrystalline material. A study found that kaolinite, illite and montmorillonite exhibit a different adsorption capacity for CO_2 and CH_4 (Hui et al. 2023). Montmorillonite shows the highest CO_2 adsorption capacity among others. Research confirms that the clay minerals, like smectites offer competitive adsorption capacity for CO_2 due to compact interlayer pore spaces and high-density adsorption sites (Bø Hunvik et al. 2021). In order to determine the mineral composition in the clay minerals, it is essential to analyse their structures, specifically how the tetrahedral and octahedral sheets connect and the different bonding arrangements between them. Therefore, geological formations with highest adsorption capacity minerals are the best option for CO_2 storage.

ADSORPTION ISOTHERM MODEL

Assessing CO_2 adsorption behaviours onto a natural mineral is crucial for better decision making in CCS project. Therefore, adsorption isotherm is applied to provide the amount of CO_2 adsorbed by the porous materials (Rani, Padmanabhan, et al. 2019). Research has introduced a novel method for predicting CO_2 adsorption capacity across various depths in geological storage using adsorption isotherm model (Han et al. 2023). However, it should be noted that the depleted reservoir comprises a various of natural minerals that could be challenging during prediction. Numerous adsorption isotherms have emerged to optimise adsorption phenomena, predict adsorption capacity, and design the adsorption systems (El-Khaiary, 2008; Garba et al. 2020). Freundlich's isotherm, Langmuir's isotherm, and BET's isotherm are a popular equation is quantifying CO_2 adsorption (Fakher & Imqam, 2020). However, a comprehensive review for other adsorption isotherms is required to determine the CO_2 adsorption behaviour in the heterogeneity of the geological formation. Various adsorption isotherm model is listed in Table 2.

TABLE 2. List of Adsorption Isotherm Model (Wang & Guo, 2020)

Adsorption Isotherm Model	Non-linear Expression
Langmuir	$q_e = q_m \frac{K_L C_e}{1 + K_L C_e}$
Freundlich	$q_e = K_F C_e^{1/n_F}$
BET	$q_e = \frac{q_m C\left(\frac{P}{P_0}\right)}{\left(1 - \frac{P}{P_0}\right)\left[1 + (C-1)\left(\frac{P}{P_0}\right)\right]}$
D-R	$q_e = q_m e^{-K_{DR}\varepsilon^2}$
D-A	$q_e = q_m e^{-\left(\frac{\varepsilon}{E_0}\right)^{n_{DA}}}$
Toth	$q_e = \frac{q_m K_T C_e}{\left(1 + K_T C_e^{n_T}\right)^{\frac{1}{n_T}}}$
Sips	$q_e = \frac{q_m K_S C_e^{n_S}}{1 + K_S C_e^{n_S}}$
R-P	$q_e = \frac{K_R C_e}{1 + a_R C_e^{n_R}}$

LANGMUIR ISOTHERM MODEL

The Langmuir model is versatile, describing both physisorption and chemisorption, and is commonly used for modelling CO_2 adsorption on shale rocks (J. Zhou et al. 2019). Although this model assumes a homogeneous formation, which contradicts the heterogeneous nature of shale pore walls (Duan et al. 2018), it remains popular for its simplicity and ease of use. This model is broadly employed to explain adsorption mechanism and effectively characterises the adsorption behaviour of formation under subcritical pressure and temperature (Yang et al. 2021). It struggles to match experimental data at elevated pressures (Shen et al. 2021; Song et al. 2018; Tian et al. 2016), often predicting higher volumes of adsorbed gas than observed. It became useless in supercritical condition. The assumptions of the Langmuir model such as homogeneous monolayer adsorption, same energy sites, and single-molecule adsorption (Alafnan et al. 2021; Ragadhita & Nandiyanto, 2021), may impact its accuracy, especially in unconventional reservoirs. Additionally, the Langmuir model shows deficiencies when applied to multicomponent mixtures. Therefore, empirical or semi-empirical correlations need to be incorporated for more accurate predictions.

FREUNDLICH ISOTHERM MODEL

The Freundlich model is an empirical equation often applied for heterogeneous formations such as silica, clays, metals, activated carbon, and polymers (Awad et al. 2019). Despite its broad applicability, it is limited to gases and ineffective at high pressures (Fakher & Imqam, 2020). Mabuza et al. (2022) applied the Freundlich isotherm to predict CO_2 adsorption on coal surfaces, finding it suitable for low-pressure conditions on shales but inaccurate at higher pressures. Given that CO_2 storage often involves supercritical conditions, the Freundlich isotherm is unsuitable for modelling real-field applications involving high pressures.

BRUNAUER–EMMETT–TELLER ISOTHERM MODEL

The BET isotherm model is a promising alternative for equilibrium gas-solid systems, though its complex equation can be challenging during simulations, often leading to insufficient data input. It is particularly suitable for describing physisorption, making it relevant for modelling CO_2 adsorption of geological formation. Commonly, it is used to calculate the surface area of solids from nitrogen or argon adsorption data (Mukhtar et al. 2020; Sinha et al. 2019). However, it has limitations, such as assuming gas molecules interact only with adjacent layers (Fakher & Imqam 2020). Xie et al. (2021) noted the applicability of the BET model for CO_2 adsorption on shale surfaces, achieving excellent results. However, these results were limited to temperatures between 30°C and 55°C. A modified model must be provided because the saturation vapour pressure (Po) in this equation is undefined in supercritical conditions (S. Zhou et al. 2019). Additionally, its application is more complex compared to other isotherms.

DUBININ-RADUSHKEVICH AND DUBININ-ASTAKHOV ISOTHERM MODEL

The D-R and D-A models, referred as a Dubinin-Polanyi (D-P) model, were originally designed to describe adsorption processes that follow a pore-filling mechanism and exhibit a Gaussian energy distribution. This approach considers the influence of the porous structure of adsorbents and can be employed to both homogeneous and heterogeneous surfaces (Alberti et al. 2012; Hu & Zhang, 2019). Harpalani et al. (2006) found the D-A isotherm is more accurate than the D-R isotherm when applied for CO_2 adsorption on coal samples. Rani, Prusty, et al. (2019) applied various isotherm models, including Langmuir, BET, D-R, and One-Kondo, to evaluate methane and CO_2 adsorption on shale formations. The D-A equation, with the lowest ARE and SSE, proved that it provides an accurate result for determining methane and CO_2 adsorption on tested shales. Additionally, the D-A isotherm model is effective for evaluating CO_2 adsorption across a wide temperature range due to their high adaptability toward temperature, making it suitable for $SubCO_2$ and $ScCO_2$ (Liu et al. 2019). Thus, this model is considered a good option than the BET isotherm model.

TOTH ISOTHERM MODEL

The Toth model is an experimental equation, which to improve upon the Langmuir equation and is particularly useful for explaining adsorption in heterogenous systems (Kumar et al. 2021). The three-parameter Toth isotherm, which assumes a quasi-Gaussian energy distribution, has been found to be highly capable in describing the adsorption of gases in heterogeneous systems at both low and high pressures. This makes it a competitive alternative to the D-A isotherm model. Despite its advantages, the Toth isotherm model often overestimates the CO_2 maximum adsorption capacity in many studies (Esfandian & Rezazadeh. M., 2020; Jacobs, 2021; Noorpoor & Nazari Kudahi, 2016). Additionally, in terms of range of temperatures and pressure, D-A isotherm model is an optimal adsorption model in CO2 adsorption capacity evaluation (Liu et al. 2019).

SIPS ISOTHERM MODEL

The Sips model is to predict adsorption in heterogeneous systems and overcome the limitations of the Freundlich isotherm at high concentrations of solids adsorbent. However, its potential is considered inferior to the D-A and Toth isotherm models. This is supported by (Serafin & Dziejarski, 2023), who found that the Toth isotherm model matches the experimental data a way better than the Sips isotherm model. Thus, it may not relevant choice to describe adsorption behaviour compared to D-A model. Nevertheless, the Sips model can still provide convincing results for homogenous and heterogeneous adsorbent.

REDLICH-PETERSON MODEL

The Redlich-Peterson (R-P) model, a hybrid of the Langmuir and Freundlich models, is widely used for both homogeneous and heterogeneous formation (Serafin & Dziejarski, 2023). This model is advantageous for a wide range of adsorbent concentrations in equilibrium due to its adaptability (Ehiomogue et al. 2022; Serafin & Dziejarski, 2023). However, the Toth isotherm model is preferred over the R-P model for evaluating isotherm data (Abunowara et al. 2016). Therefore, D-A isotherm model is the most suitable for predicting CO_2 adsorption capacity, as it effectively evaluates CO_2 adsorption across a wide temperature range and is adaptable to both subcritical and supercritical CO_2 conditions. Additionally, the D-A model specifically considers the pore size distribution as a factor that affecting CO_2 adsorption. Nevertheless, a limitation of all adsorption isotherm models is that no single equation can perfectly describe adsorption behaviour.

ADSORPTION KINETIC MODEL

Kinetic models are important in describing the adsorption behaviour on geological formation by estimating the rate of adsorption. These models including pseudo-first order -model, the pseudo-second order model, the Avrami kinetic model. The factors like temperature, initial CO_2 concentration, and gas flow rate are utilised for the prediction of CO_2 adsorbed rate onto the geological formations. Various models will be reviewed to evaluate the adsorption kinetics on solid surface. Hence, this model may improve the efficiency of CO_2 capture and storage methods by optimizing several parameters and advances the efficient strategies of CCS applications.

PSEUDO-FIRST ORDER MODEL

In 1898, Lagergren was presented a pseudo-first order kinetic model (Simonin, 2016). The model's underlying assumptions state that the rate of solute absorption over time is directly related to both the saturation concentration and the rate of solid uptake. Generally, it is fit over the initial stage of an adsorption process. The adsorption occurs though the diffusion at the interface follows this Lagergren model. This model can be expressed as below.

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{1}$$

The boundary conditions of Equation (1) state that: 1) $q_t = 0$ when $t = 0$; 2) $q_t = q_t$ when $t = t$. Integrate Equation (1) to derive the linear expression.

$$q_t = q_e(1 - e^{-k_1 t}) \tag{2}$$

PSEUDO-SECOND ORDER MODEL

The pseudo-second order kinetic model, was first proposed was by Ho and McKay in 1999 (Simonin, 2016), to explain the kinetics for heavy metal removal by natural zeolites. The adsorption rate in this scenario relies on the adsorption capacity instead of level of adsorbate concentration. The main benefit of using this model compared to Lagergren's model is that they may determine the equilibrium adsorption capacity, eliminating the necessity of experimental evaluation (Sahoo & Prelot, 2020). This model is proposed as follows:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{3}$$

Using the identical boundary parameters as previously mentioned, the expression can be derived by the integration of Equation (3).

$$q_t = \frac{1}{\frac{1}{k_2 q_e^2} + \frac{t}{q_e}} \tag{4}$$

ELOVICH KINETIC MODEL

The Elovich kinetic model is commonly employed to analyse adsorption kinetics and effectively represent second-order kinetics. It is applicable for gas-solid interaction. The equation is expressed as follows:

$$q_t = \frac{1}{\beta} ln(\alpha\beta) + \frac{1}{\beta} ln\, t \tag{5}$$

By plotting ln t versus q_t, the constants can be obtained from the slope and intercept of the plot. The desorption process can be seen when the value of β is equal to the desorption rate (Rashidi et al. 2013).

AVRAMI FRACTIONAL KINETIC MODEL

Avrami's fractional order model was a semi-empirical model, that initially developed in 1939 to explain particle nucleation (Whitehead & Finke, 2021). The Avrami's model can describe a complex adsorption kinetics mechanism successfully, as it accounts for both physisorption and chemisorption simultaneously, compared to pseudo-first order and pseudo-second order (Lin et al. 2023). The model is presented as follows:

$$q_t = q_e\left(1 - e^{-\frac{(k_a t)^n}{n}}\right) \tag{6}$$

INTRA-PARTICLE DIFFUSION MODEL

This model was developed by McKay and Poots in 1980, cited by Mousalli et al. (2020). Basically, intra-particle diffusion model describes the diffusion mechanism in adsorption. The model is expressed as follows:

$$q_t = k_p t^{\frac{1}{2}} + C \tag{7}$$

A plot of q_t against $t^{0.5}$ yield a straight line with a slope of k_p. The IP diffusion is not thought to be the only rate-limiting stage in the adsorption process if the plot does not pass through the origin.

CONCLUSION

With the rise in atmospheric CO_2 levels primarily due to fossil fuel combustion, effective strategies are necessary to curb this trend and mitigate climate change. CCS is a potential technology that captures CO_2 from industrial and energy sectors, compresses it, transports it via pipelines or ships, and stores it in suitable geological formations. These formation likes depleted petroleum reservoirs, offer a larger pore volume, long-term hydrocarbon storage capabilities, and enhanced recovery of residual natural gas upon CO_2 injection. It has a significant advantage over saline aquifers due to their existing infrastructure and extensive knowledge of subsurface conditions. This allows for convenient CCS deployment by utilizing matured onshore fields and re-purposing existing infrastructures. This paper underscores the importance of mineralogical diversity in enhancing CO_2 adsorption capacity. Clay minerals in geological formations, formed through various geological processes, contribute a highest adsorption capacity for CO_2. Adsorption mechanisms, alongside structural and residual trapping, contribute significantly to the effectiveness of CO_2 sequestration. Adsorption isotherm and kinetic models are essential for understanding and predicting CO_2 adsorption behaviors under different conditions. In conclusion, this approach known as CCS has significant promise for reducing greenhouse gas emissions and addressing climate change. The effectiveness of these efforts' hinges on a thorough insight of the mineralogical properties of storage formations and the development of robust adsorption models. This integrated approach is vital for optimizing CO_2 storage and ensuring the long-term stability of stored carbon.

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DECLARATION OF COMPETING INTEREST

None.

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