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RESEARCH

Modelling and thermodynamic properties of pure CO_2 and flue gas sorption data on South African coals using Langmuir, Freundlich, Temkin, and extended Langmuir isotherm models

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Abstract
Carbon sequestration in unmineable coal seams has been proposed as one of the most attractive technologies to mitigate carbon dioxide (CO_2) emissions in which CO_2 is stored in the microporous structure of the coal matrix in an adsorbed state. The CO_2 adsorption process is hence considered one of the more effective methodologies in environmental sciences. Thus, adsorption isotherm measurements and modelling are key important scientific measures required in understanding the adsorption system, mechanism, and process optimization in coalbeds. In this paper, three renowned and reliable adsorption isotherm models were employed including Langmuir, Freundlich, and Temkin for pure CO_2 adsorption data, and the extended-Langmuir model for multicomponent, such as flue gas mixture-adsorption data as investigated in this research work. Also, significant thermodynamics properties including the standard enthalpy change ($\Delta H°$), entropy change ($\Delta S°$), and Gibbs free energy ($\Delta G°$) were assessed using the van't Hoff equation. The statistical evaluation of the goodness-of-fit was done using three (3) statistical data analysis methods including correlation coefficient (R^2), standard deviation (σ), and standard error (SE). The Langmuir isotherm model accurately represent the pure CO_2 adsorption on the coals than Freundlich and Temkin. The extended Langmuir gives best experimental data fit for the flue gas. The thermodynamic evaluations revealed that CO_2 adsorption on the South African coals is feasible, spontaneous, and exothermic; and the adsorption mechanism is a combined physical and chemical interaction between the adsorbate and the adsorbent.

Keywords Global warming · Flue gas · Adsorption · Unmineable coal · Adsorption models

1 Introduction

Considering the rising quantities of carbon dioxide (CO_2) in the atmosphere resulting in global warming, a systematic plan for developing cost-effective and energy-efficient technologies to reduce CO_2 emissions is urgently needed (Wang et al. 2013). About 80% of global commercial energy needs come from fossil fuels, including coal, oil, and gas (Gadonneix et al. 2013). CO_2 emissions from burning fossil fuels have been reported as a significant contributor to elevated anthropogenic levels of CO_2 in the atmosphere (Shojai Kaveh et al. 2012; Wang et al. 2013). In 2019, fossil fuels and industry accounted for over 80% of the overall global CO_2 emissions, with coal-fired power plants contributing 30% of the total (IEA 2019).

Anthropogenic CO_2 reportedly accounts for over 63% of all contributors to climate change in the atmosphere. The rate of CO_2 emissions since 2000 was higher than the rate of CO_2 emissions expected by most fossil-fuel-intensive scenarios established by the Intergovernmental Panel on Climate Change in the late 1990s (IPCC 2020). Carbon capture and storage (CCS) can potentially reduce atmospheric CO_2 emissions when burning fossil fuels. This alternative involves disposal methods, such as injection of CO_2 into

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deep saline aquifers, unmineable coal seams, and depleted gas and oil reservoirs. CO_2 injected into a coal reservoir flows through the cleat network, diffuses through the carbon matrix and is stored on the microporous surfaces of the coal in a sorbed state (Shojai Kaveh et al. 2012). In the context of the geological storage of CO_2, a few studies (Mabuza and Premlall 2014; Mazumder et al. 2006; Pini et al. 2009; Shojai Kaveh et al. 2012; Syed et al. 2013; Zhang et al. 2016; Lukhele et al. 2017) consider the direct injection of flue gases from power plants or other flue gas emitting industries.

The sorption capacity of CO_2 or flue gas on coal can be measured through adsorption isotherm data, which was collected through a series of repeated laboratory experimental tests to ensure validation of results. The modelling of adsorption isotherm data has become an essential and useful methodology for predicting adsorption performance, which is critical for understanding the pathways of the adsorption mechanism, and the design of adsorption systems (Chen 2015). Proper interpretation and understanding of adsorption isotherms are critical to improving adsorption mechanism pathways and effective design of adsorption system. As such, regression analysis has been one amongst the foremost applied tools for outlining the best fitting adsorption models because it quantifies the distribution of adsorbates, analyses the adsorption system, and verifies the consistency of theoretical assumptions of adsorption isotherm model (Ayawei et al. 2017). The Langmuir, Freundlich, and Temkin, are two-parameter isotherm models that are commonly used in modelling the adsorption data for pure gases at constant temperature, with the Extended-Langmuir used in modelling the adsorption data for multicomponent gases (Dada et al. 2012). The modelled experimental adsorption isotherm generates a non-linear curve that describes the adsorption process; and the mathematical correlation described in the modelling analysis is essential for operational design and practical applications of the adsorption system (Foo and Hameed 2010).

Recently, many researchers have further explored the adsorption and transportation of gases on coals with different degrees of maturity. Wang et al. (2020) found that coal has a high adsorption capacity as well as strong adsorption potential, especially for CO_2. In a multicomponent gas containing CO_2, CH_4, N_2, and He, Zhou et al. (2020) found that the adsorption capacity decreased in the following order: $CO_2 > CH_4 > N_2, > He$, with the CO_2 adsorption having the noticeable negative effect on the strength of the coal, while the He has negligible effect on coal strength due to its non-adsorptive nature (Wang et al. 2014). Furthermore, the diffusivity of CO_2 on high rank coals is higher than low rank coals, suggesting a positive CO_2 diffusivity corelation with increased coal maturity, more especially in vitrinite rich coals (Keshavarz et al. 2017). In addition to this, gas adsorption on coals from the view of thermodynamics aspects provides significant information related to the mechanism of adsorption of gases on coal surfaces (Tang and Ripepi 2017). Thermodynamic properties including the standard enthalpy change ($\Delta H°$), Gibbs free energy change ($\Delta G°$), the entropy change ($\Delta S°$), and isosteric heat of adsorption give adequate physical insight to interpret the sorption process (Yan et al. 2019). Hao et al. (2021) evaluated the thermodynamic properties of $CH_4/CO_2/N_2$ adsorption on Zaozhuang anthracite coal and showed that the gas adsorption is exothermic physisorption ($\Delta H° < 40$ kJ/mol), thermodynamically spontaneous ($\Delta G° < 0$), and the gas molecules are highly ordered ($\Delta S° < 0$) on the coal surface. Raganati et al. (2018) reported that adsorption systems which have standard enthalpy change in the range $20 < \Delta H° < 40$ kJ/mol are attributed to a combined nature of physisorption and chemisorption mechanism.

This research paper presents the comprehensive theoretical modelling of the adsorption data generated by Mabuza et al. (2018), in which pure CO_2 and a flue gas representative mixture of a typical SA coal-fired power plant has been used to evaluate the sorption on the microporous coal surface for CO_2 storage in unmineable coal seams at isothermal temperatures of 30 °C, 40 °C, 50 °C, and 60 °C and pressure up to 9.0 MPa. The accuracy in parameters prediction for the isotherm models were compared and are discussed accordingly. The statistical evaluation of the goodness-of-fit was done using the correlation coefficient (R^2), standard deviation (σ), and standard error (SE). The results of modelling this adsorption data are expected to expand on the theoretical basis of gas–solid adsorption in carbon capture and storage for environmental protection.

2 Methodology

2.1 Origin of the coal samples and preparation

The coal samples examined were collected from two different South African coalfields located in Mpumalanga (Ermelo—Coal EML) and KwaZulu-Natal (Somkhele—Coal SML). A report by Viljoen et al. (2010) has described these coalfields as potential CO_2 storage sites in the future. The samples were sealed in airtight zip-lock bags and placed in the refrigerator (under 3 °C temperature condition) after being flushed with nitrogen gas. This coal storage practise was conducted to avoid spontaneous oxidation and excessive exposure to the atmosphere, and it is a practise recommended by Ören and Şensöğüt (2018). Coal EML is classified as medium rank C (bituminous C) while Coal SML is high rank C (Anthracite C). Coal EML is inertinite-rich (74.2 vol%, inc. mm), while Coal SML is vitrinite-rich (84.0 vol%, inc. mm). Details of the petrography of the two coals may be acquired from Mabuza et al. (2020). Each sample was obtained as 50 mm lumps that were divided using the coning and quartering method in accordance with the ISO 14780—solid biofuels—sample preparation (2017). It was then crushed with a TENCAN—XPC jaw crusher to an average grain size of 2 mm. These samples were used for pure CO_2 and flue gas sorption experiments.

2.2 Experimental sorption data

The experimental high-pressure sorption data for pure CO_2 and flue gas (at nominal molar feed composition of 12 mol% CO_2, 5.5 mol% O_2, 82 mol% N_2, 0.38 mol% SO_2, and 0.12 mol% NO_2) sorption on Coal EML and Coal SML at temperatures ranging from 30 ℃ to 60 ℃ and pressures up to 9.0 MPa was acquire through a series of batch tests using a high-pressure volumetric sorption system (HPVSS). Details of the experimental setup and experimental procedures to generate the sorption data are given by Mabuza et al. (2018) in their work on low–high temperature flue gas direct injection in south African bituminous and anthracite coals: sorption capacity assessment.

The adsorbed-phase density is usually assumed to be constant across the experimental range (Kim et al. 2011). In this study the value of 22.6 mmol/cm^3 for CO_2 was adopted since it has been found to be a reasonable estimation and was previously successfully applied by numerous other authors (Fitzgerald et al. 2005; He et al. 2010; Kim et al. 2011). The adsorbed-phase density estimates do, however, affect the calculated absolute adsorption isotherm (Fitzgerald et al. 2005).

2.3 Non-linear and linear forms of the isotherm models

Three well-known empirical adsorption isotherm models were employed for sorption verification in this study to model the sorption of pure CO_2 on two South African coals (Coal EML and Coal SML). Those isotherm models included (1) Langmuir model, (2) Freundlich model, and (3) Temkin model.

These isotherm models are typically represented as two parameter models. As reported by Ho et al. (2002), the simplest method to determine isotherm constants for two parameter isotherms is to transform the isotherm variables so that the equation is converted to a linear form and then to apply linear regression.

In the Langmuir adsorption model, the adsorbed amount, N_s, is correlated to the monolayer coverage, N_{sm}, as follows:

$$N_s = \frac{K_L P N_{sm}}{1 + K_L P} \tag{1}$$

where P is the system pressure and K_L is Langmuir constant and highly depends on the energy of adsorption. This expression can be reorganized as follows:

$$\frac{P}{N_s} = \frac{P}{N_{sm}} + \frac{1}{K_L N_{sm}} \tag{2}$$

For the experimental data, P/N_s versus P can be plotted. The plot will be linear, and the slope is equal to $1/N_{sm}$ (Birdi 2017). The Langmuir constants (K_L and N_{sm}) are fundamental factors that determine the field development of coal reservoirs. Langmuir monolayer coverage (N_{sm}) is a direct indicator of the gas storage capacity and is positively related to coal rank. The affinity of a gas for a solid surface as well as the energy stored in a coal formation are both related to the Langmuir constant K_L which is inversely related to coal rank (Yang et al. 2019). N_{sm} is proportional to the number of sorption sites available and is also dependent on the coal composition and surface complexity (Cai et al. 2013).

The Freundlich isotherm equation is given by the following expression (Al-Wahbi and Dammag 2011; Dada et al. 2012):

$$q_e = K_F P_e^{1/n} \tag{3}$$

Linearization of the above equation via logarithmic plot yields (Dada et al. 2012):

$$\log q_e = \log K_F + \left(1/n\right) \log P_e \tag{4}$$

where K_F is Freundlich isotherm constant, $1/n$ is the adsorption intensity, P_e is the equilibrium pressure, and q_e is the amount of gas adsorbed at equilibrium pressure. The Freundlich coefficients n and K_F are acquired from the plots of (ln q_e) versus (In P_e) (Oladoja et al. 2008). The magnitude of exponent (n) provides an indication of the capacity and favourability of the adsorbate/adsorbent system (Al-Wahbi and Dammag 2011). According to Treybal (1980) values of n between 1 and 10 represent favourable adsorption. When the slope ($1/n$) ranges between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. While a value below unity indicates chemisorption process where $1/n$ over one is an indication of cooperative adsorption (Haghseresht and Lu 1998).

The Temkin isotherm model equation is generally applicable in the following form (Temkin and Pyzhev 1940):

$$q_e = \frac{RT}{b_T} \ln \left(A_T P_e\right) \tag{5}$$

The linear form of this expression is:

$$q_e = B_T \ln A_T + B_T \ln P_e \tag{6}$$

where

$$B_T = \frac{RT}{b_T} \tag{7}$$

where T is the absolute temperature, R is the universal gas constant, A_T is the equilibrium binding constant corresponding to the maximum binding energy, b_T is Temkin isotherm constant and the constant B_T is related to the heat of adsorption (dimensionless) (Al-Wahbi and Dammag 2011).

The Extended-Langmuir (EL) adsorption isotherm model was used to correlate the measured flue gas sorption data. According to Reeves and Koperna (2008), the EL model predictions require single-component isotherm measurements. The EL adsorption isotherm model has a semi-empirical nature and it is given by (Kapoor et al. 1990). By applying the Langmuir isotherm to a N component mixture and assuming no interaction among the adsorbate molecules, the EL model is:

$$n_i(T,P,y) = \frac{N_{m,i}B_iy_iP}{1+\sum_{j=1}^{n_c}B_jy_jP} \tag{8}$$

where $N_{m,i}$ is the maximum amount of adsorption of component i, Bi is the Langmuir constant at a specified temperature for component i, P is the pressure, and yi being the molar fraction of component i in the gas phase (Wei et al. 2007).

2.4 Statistical evaluation of the adsorption isotherm models goodness-of-fit

Several hundred papers are published yearly reporting liquid–solid and gas–solid adsorption data. In general, the data is analysed using a variety of standard models such as the Langmuir, Freundlich, Temkin, and extended Langmuir. The validity of these models is often assessed empirically via their ability to fit the data, independently of their physicochemical soundness (Douven et al. 2015). For Langmuir, Freundlich, and Temkin models, a common error function often used is called the normalized standard deviation of sorption models (Song et al. 2016). The normalized standard deviation describes the variation in experimental measurements in comparison with the calculated values. This function is expressed as:

$$\Delta S(\%) = \sqrt{\frac{\sum\left[\left(Q_{\mathrm{exp}}-Q_{\mathrm{calc}}\right)/Q_{\mathrm{exp}}\right]^2}{(N-1)}} \times 100\% \tag{9}$$

where $S(\%)$ is the normalized standard deviation, Q is the number of moles, the subscripts 'exp' and 'calc' are the experimental and calculated values, respectively, and N is the number of data points (Wu et al. 2009).

For Extended-Langmuir model, an error function known as the absolute (Δn) and relative deviations error (R) analyses (Eqs. (10) and (11)) are often used to measure the deviations between the flue gas sorption experimental data and the Extended-Langmuir model data. The functions are expressed as follows:

$$\Delta n = \left|n_{\mathrm{cal}} - n_{\mathrm{exp}}\right| \tag{10}$$

$$R = {}^{\Delta n}/_{n_{\mathrm{exp}}} \times 100\% \tag{11}$$

2.5 Adsorption thermodynamic properties

Thermodynamic parameters including the standard enthalpy change ($\Delta H°$), Gibbs free energy change ($\Delta G°$), and the entropy change ($\Delta S°$) are evaluated for adsorption systems to establish the nature of adsorption (i.e., adsorbate-adsorbent interactions), either physisorption or chemisorption (Raganati et al. 2018). Physisorption arises from van der Waals forces due to weak interactions, while chemisorption is characterized by strong chemical interactions due to chemical bonding as a consequence of electrons transfer between the adsorbate and adsorbent (Peköz and Donadio 2016). The theoretical data obtained from the Langmuir isotherm models is combined with thermodynamic laws to determine these thermodynamics parameters by applying the following equations (Kumar Singh and Anil Kumar 2018; Wilson and Handan Tezel 2021):

$$\Delta G° = -RT\ln K_{\mathrm{L}} \tag{12}$$

$$\Delta G° = \Delta H° - T\Delta S° \tag{13}$$

where R is the universal ideal gas constant, T is the absolute temperature, and K_{L} is the Langmuir constant. Substituting Eq. (12) into Eq. (13) results in the van't Hoff equation:

$$\ln K_{\mathrm{L}} = \left(\frac{\Delta S°}{R}\right) - \left(\frac{\Delta H°}{RT}\right) \tag{14}$$

This linear equation is used to construct the van't Hoff plots, where $\ln K_L$ represents the y-axis and $1/T$ the x-axis. The parameters $\Delta H°$ and $\Delta S°$ are determined from the slope and intercept, respectively, while $\Delta G°$ may be calculated directly from Eq. (13).

The standard enthalpy change ($\Delta H°$) determines whether the adsorption process is exothermic or endothermic by a negative or positive value, respectively. In an exothermic adsorption process, energy is released to the surroundings in form of heat, this is alluded while in an endothermic process energy is absorbed from the surroundings. Furthermore, for a physisorption process, the value of $\Delta H°$ is less than 20 kJ/mol, and it is greater than 40 kJ/mol for a chemisorption process (Ahmed et al. 2019). With reference to $\Delta S°$, the value is indicative of the order (organization) of adsorbate at the solid–gas interface during the adsorption process. Such that, when $\Delta S° < 0$ the adsorbate is less random (highly ordered) on the solid surface, and for $\Delta S° > 0$ the adsorbate is more random (less ordered). For Gibbs free energy change ($\Delta G°$), the adsorption process is said to take place spontaneously and feasible when the value is less than zero (i.e., $\Delta G° < 0$). Otherwise for ($\Delta G° > 0$), the process is non-spontaneous and non-feasible (Du et al. 2021).

3 Results and discussion

3.1 Pure CO_2 sorption isotherms modelling

The Langmuir isotherm model was applied to estimate maximum adsorption capacity corresponding to complete monolayer coverage, N_{sm}, on the coal surface. Figures 1 and 2 illustrate pure CO_2 experimental sorption isotherms for Coal EML and Coal SML with Langmuir isotherm model regression at the various temperatures. It is observed that there is a good correlation between experimental and Langmuir theoretical (calculated) data, this is validated by the Langmuir isotherm model regression fitting well with the CO_2 experimental data with a minimal average relative. This means that Langmuir isotherm model can describe the present pure CO_2 sorption data of the two coal samples. Moreover, this good correlation between experimental and theoretical data suggests that the maximum sorption capacity corresponding to complete monolayer coverage, N_m, on the coal surfaces can be accurately estimated using the Langmuir equation.

The Freundlich model was applied to estimate the adsorption intensity, $1/n$, of the CO_2 on the coal surface. Figures 3 and 4 show pure CO_2 experimental sorption isotherms for Coal EML and Coal SML with Freundlich isotherm model regression. It is observed that there is a poor correlation between the experimental and Freundlich theoretical data. The Freundlich isotherm regression does not fit well with the pure CO_2 experimental data, this is more evident beyond the subcritical pressures (> 6.0 MPa). This behaviour is attributed to the limitations of the isotherm model at high pressure of the gas. According to Kumar et al. (2010), under high pressure gas experimental applications, the experimental isotherm deviates from the Freundlich isotherm model while approaching the saturation or while approaching the limiting pressure conditions. This means that the Freundlich isotherm cannot explain the sorption behaviour at high pressure regions.

The Freundlich equation, experimentally, was previously shown that the amount of adsorption changes directly with pressure until saturation is attained. Beyond that point, even when a higher pressure is applied, the rate of adsorption saturates (Kang et al. 2014). Thus, adsorbents produce

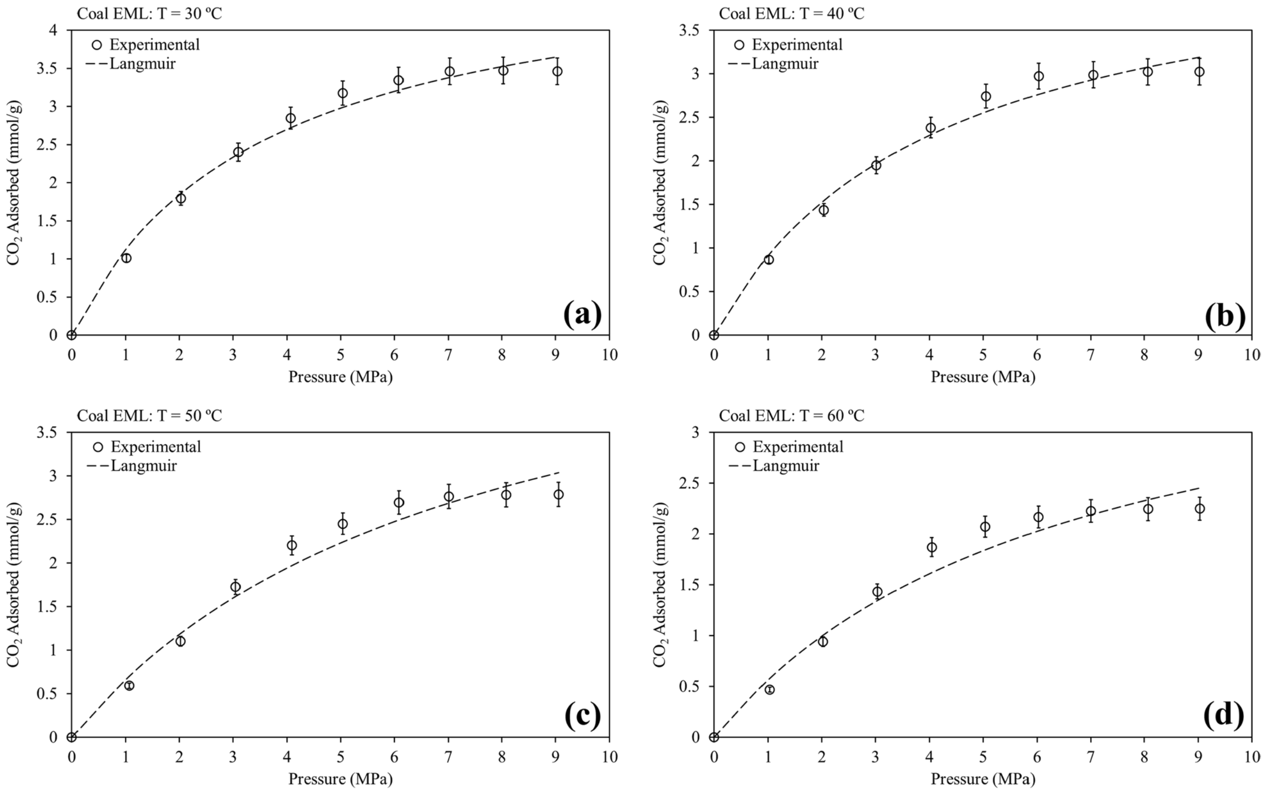

Fig. 1 Langmuir isotherm model fit for pure CO_2 sorption on Coal EML at **a** 30 °C, **b** 40 °C, **c** 50 °C, and **d** 60 °C

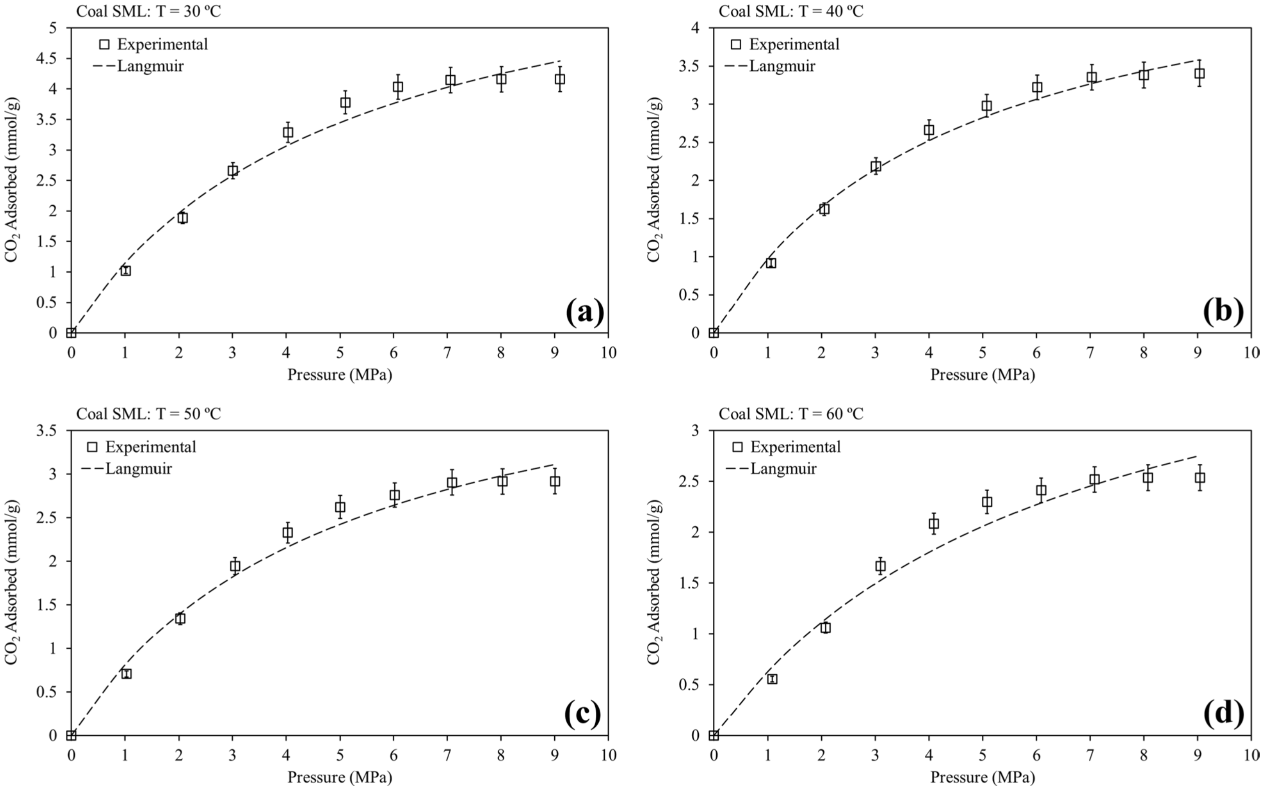

Fig. 2 Langmuir isotherm model fit for pure CO_2 sorption on Coal SML at **a** 30 ºC, **b** 40 ºC, **c** 50 ºC, and **d** 60 ºC

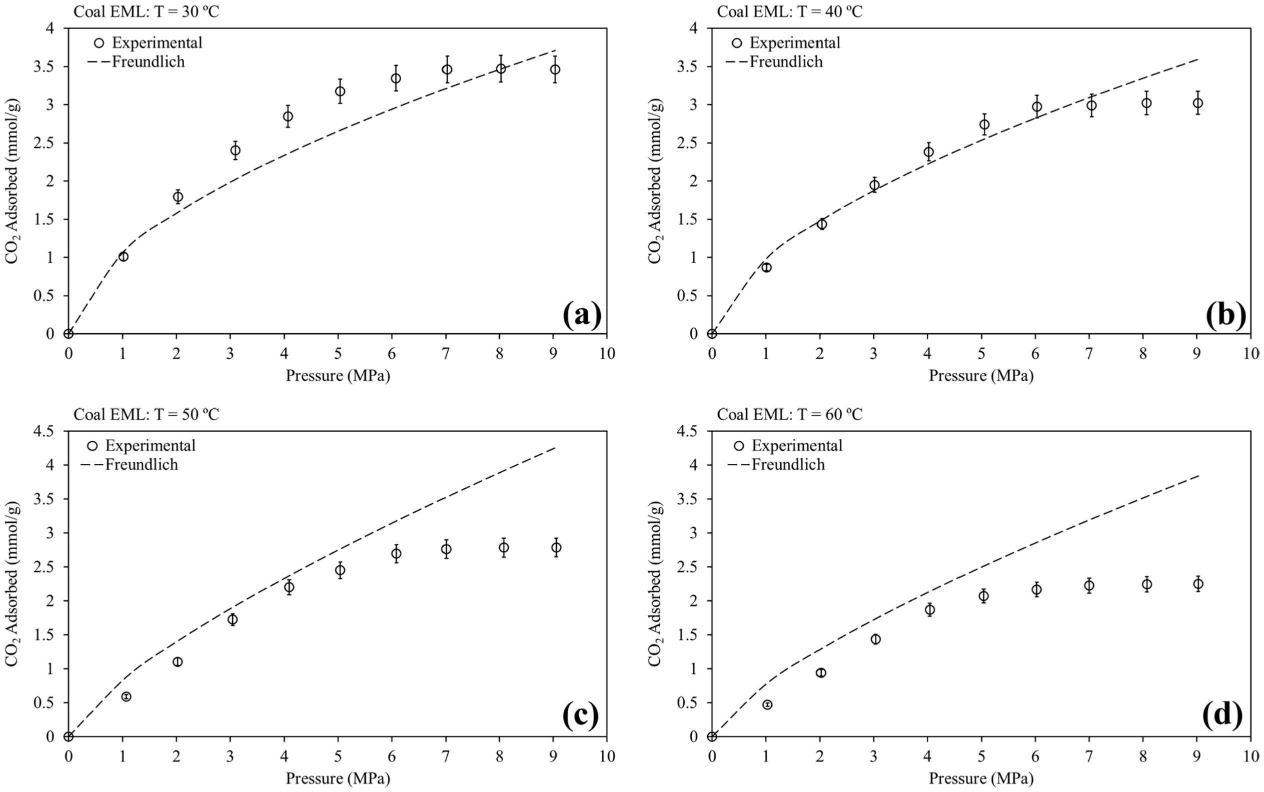

Fig. 3 Freundlich isotherm model fit for pure CO_2 sorption on Coal EML at **a** 30 ºC, **b** 40 ºC, **c** 50 ºC, and **d** 60 ºC

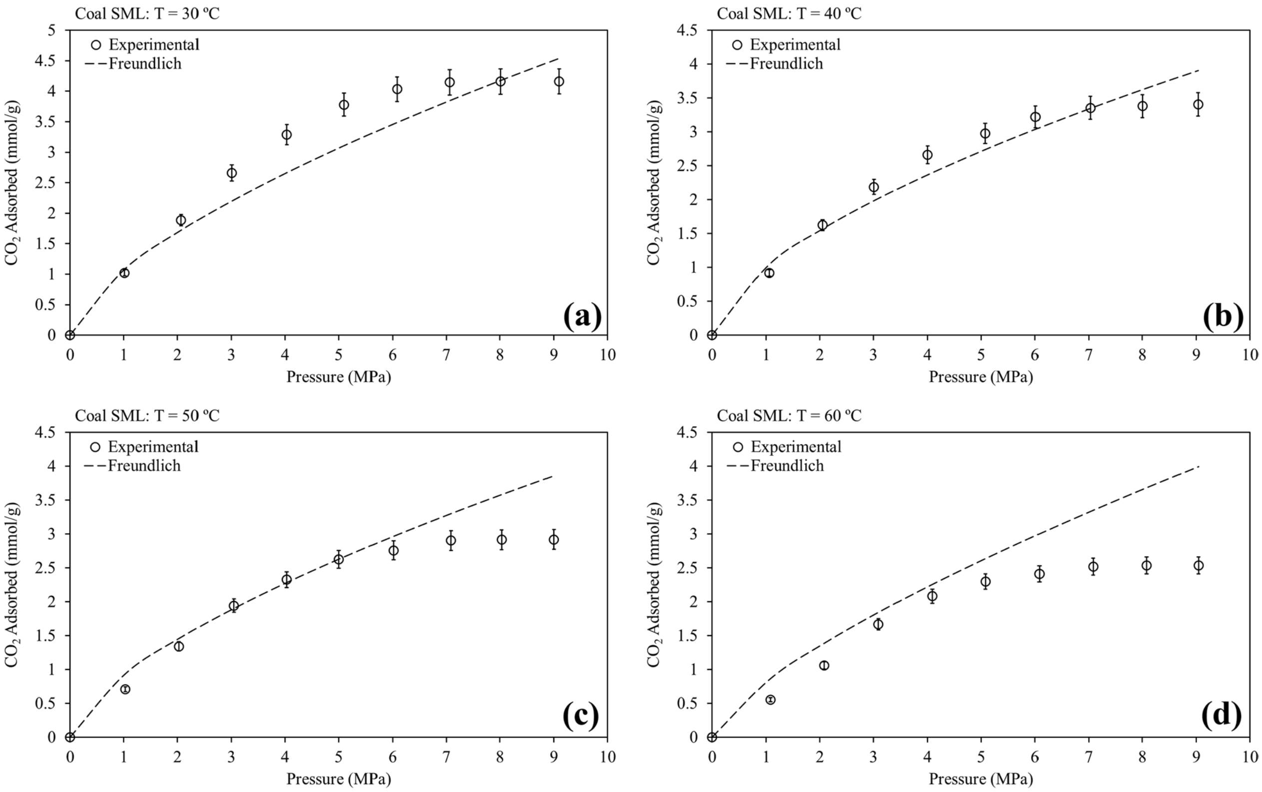

Fig. 4 Freundlich isotherm model fit for pure CO_2 sorption on Coal SML at **a** 30 ºC, **b** 40 ºC, **c** 50 ºC, and **d** 60 ºC

isotherms that satisfy the Freundlich equation in the low to intermediate pressure range, but the agreement is frequently poor at high pressures (Adelodun et al. 2017). The Freundlich isotherm model, unlike the Langmuir model, does not approach a limiting adsorptive capacity as the pressure approaches infinity, hence, resulting in these limitations. This indicates that there is no saturation limit for the Freundlich isotherm model (Raganati et al. 2018). Consequently, the Freundlich isotherm model tend to fail at higher pressures. This behaviour suggests that the Freundlich isotherm model cannot be used to describe or represent the current pure CO_2 adsorption experimental data; consequently, the adsorption intensity, $1/n$, of CO_2 on the coal surfaces cannot be accurately estimated using the Freundlich equation.

The Temkin adsorption isotherm model was applied to evaluate the adsorption potential, b_T, of the CO_2 on the coal surface. Figures 5 and 6 present pure CO_2 experimental sorption isotherm of Coal EML and Coal SML, respectively, with Temkin isotherm model regression. As was the case with the Freundlich isotherm model, there is a poor correlation between the experimental and Temkin theoretical data. This phenomenon is mostly observed at pressures close to supercritical (> 7.39 MPa). This behaviour is in complete contrast with literature, according Kim et al. (2004) as well as Foo and Hameed (2010), Temkin equation is excellent for predicting the gas phase equilibrium on solids (when organization in a tightly packed structure with identical orientation is not necessary); however, conversely complex adsorption systems including the liquid-phase adsorption isotherms are usually not appropriate to be represented. This contrast indicates that the Temkin isotherm model cannot be used to describe the pure CO_2 sorption experimental data measured under the conditions of temperature and pressure probed; as a result, the adsorption potential, b_T, of CO_2 on the coals surfaces cannot be accurately estimated using the Temkin equation.

3.2 Statistical evaluation and model parameters for Langmuir, Freundlich, and Temkin

Table 1 presents the Langmuir, Freundlich, and Temkin models constants, parameters, and correlation coefficients for Coal EML and Coal SML for the temperature range under investigation. The table also presents the statistical analysis including the normalized standard deviation, and standard error for the two coals. For the Langmuir model, the coefficient of correlation, R^2, is above 0.9 at low temperatures (30 ºC to 40 ºC) and below 0.9 at high temperatures (50 ºC and 60 ºC) this means that the measured sorption data fitted the linear regression better at low temperatures than at high temperatures. The standard deviation, σ, for Coal EML does not exceed ± 0.85 and for Coal SML exceeds ± 0.85

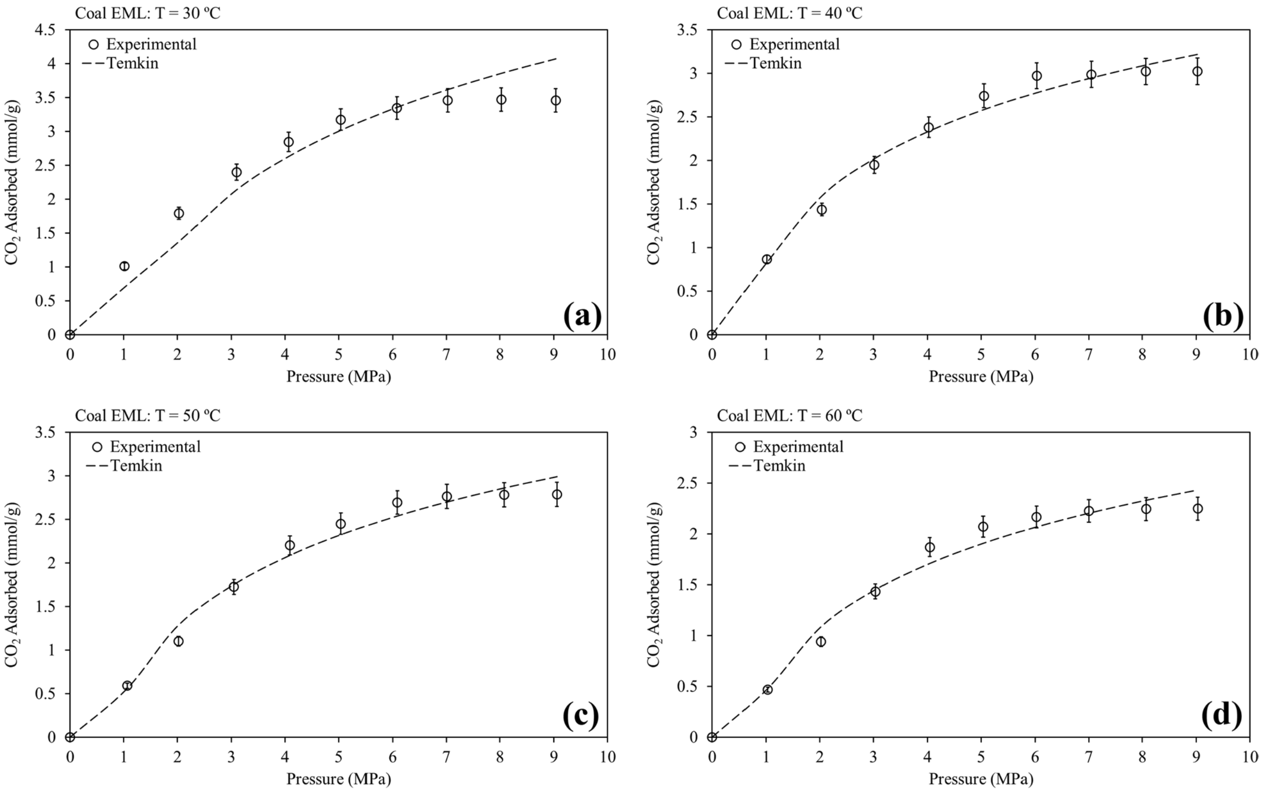

Fig. 5 Temkin isotherm model fit for pure CO_2 sorption on Coal EML at **a** 30 ºC, **b** 40 ºC, **c** 50 ºC, and **d** 60 ºC

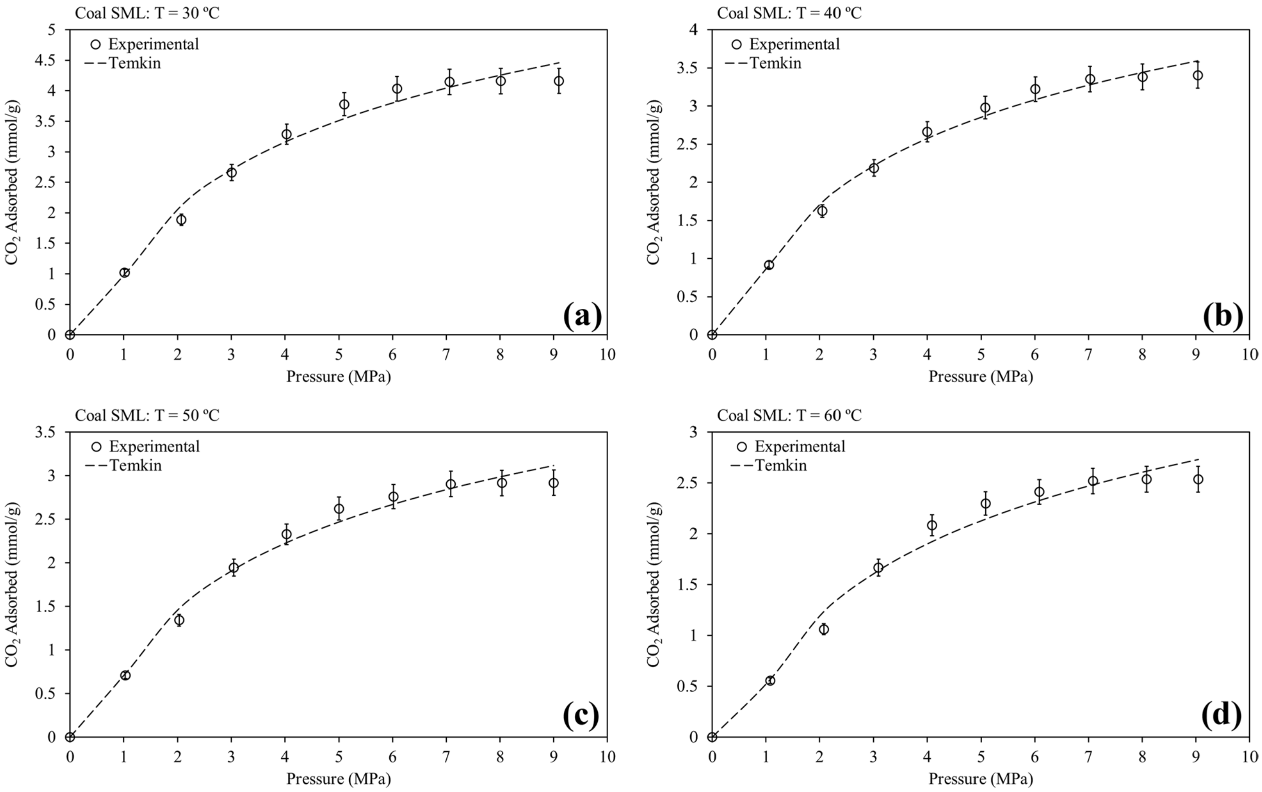

Fig. 6 Temkin isotherm model fit for pure CO_2 sorption on Coal SML at **a** 30 ºC, **b** 40 ºC, **c** 50 ºC, and **d** 60 ºC

Table 1 Langmuir, Freundlich, and Temkin isotherm model parameters obtained by linear fitting for Coal EML and Coal SML at 30 ºC, 40 ºC, 50 ºC, and 60 ºC

		Temperature (ºC)							
		Coal EML				Coal SML			
Model	Parameter	30	40	50	60	30	40	50	60
Langmuir	N_{sm} (mmol/g)	5.071	5.485	4.638	4.209	6.944	5.382	4.819	4.742
	K_L (1/MPa)	0.284	0.255	0.157	0.115	0.297	0.241	0.152	0.101
	R^2	0.9766	0.970	0.8649	0.8533	0.9441	0.9722	0.9444	0.866
	Standard deviation (σ)	±0.839	±0.762	±0.796	±0.635	±1.107	±0.863	±0.769	±0.705
	Standard error (SE)	0.280	0.254	0.265	0.212	0.369	0.288	0.256	0.235
Freundlich	n	1.762	1.690	1.353	1.374	1.526	1.623	1.530	1.388
	$1/n$	0.567	0.592	0.739	0.728	0.655	0.616	0.654	0.720
	K_F (mmol/g MPa)(MPa)$^{1/.n}$	1.064	0.978	0.836	0.775	1.068	1.006	0.918	0.818
	R^2	0.9421	0.9559	0.9413	0.9246	0.9462	0.9527	0.9378	0.9272
	Standard deviation (σ)	±0.911	±0.882	±1.296	±1.268	±1.194	±0.965	±1.03	±1.235
	Standard error (SE)	0.304	0.294	0.432	0.423	0.398	0.322	0.344	0.412
Temkin	B_T	1.806	1.137	1.093	0.900	1.583	1.252	1.103	1.019
	b_T (kJ/mol)	1.395	2.363	2.382	3.076	1.592	2.079	2.440	2.718
	A_T (1/MPa)	1.054	2.104	1.535	1.653	1.841	1.957	1.880	1.615
	R^2	0.9769	0.972	0.9735	0.9631	0.9737	0.9847	0.9789	0.9683
	Standard deviation (σ)	±1.154	±0.783	±0.801	±0.641	±1.132	±0.881	±0.784	±0.711
	Standard error (SE)	0.385	0.261	0.267	0.214	0.377	0.294	0.261	0.237

but less than ± 1.107 for all the temperature range. While the standard error, SE, for Coal EML is less than 0.3 and in excess of 0.3 but less than 0.4 for Coal SML. This means that there is less variation or dispersion of the experimental values when compared to the theoretical values.

The correlation factor acquired from the Freundlich model regression is above 0.9 for both coals throughout the entire temperature range. The corresponding adsorption intensity, $1/n$, ranges between 0.567 to 0.739 for Coal EML, and between 0.616 to 0.720 for Coal SML. It is observed that the adsorption intensity increases with an increase in temperature for both coals. According to Ghazi et al. (2013) adsorption intensity value greater than 1.0 implies weak bond between the adsorbate and the adsorbent. This means that there is a stronger bond between the CO_2 and the coal since adsorption is less than 1.0 throughout the temperature range. However, this bond is the strongest at low temperatures and tend to weaken at higher temperatures. This means that more energy is required for adsorption at higher temperatures. This phenomenon aligns well with the gas–solid adsorption theory that adsorption is an exothermic process. Since the adsorption process exothermic, low temperatures allow the process to take place favourably by increasing the gas–solid bond strength. The standard deviation is less than ± 1.268 for both coals for the entire temperature range.

The correlation factor obtained from the Temkin model regression is also above 0.9 for both coals for the entire temperature range. The Temkin constant related to the heat of adsorption (amount of energy that is released), b_T, ranges between 1.395 kJ/mol and 3.076 kJ/mol for Coal EML and between 1.592 kJ/mol and 2.718 kJ/mol for Coal SML. This heat of adsorption increases with an increase in temperature. The positive values ($b_T = \Delta Q = -\Delta H$) means that the adsorption process is exothermic for the entire temperature range. However, the increase in temperature favours the reverse process; hence, a decrease in the adsorption capacity of CO_2 on the coals as reported by Mabuza et al. (2017). The standard deviation is less than ± 1.6 for Coal EML and less that ± 1.2 for Coal SML for the entire temperature range.

Figure 7 compares the experimental and theoretical maximum sorption capacity of CO_2 on Coal EML and Coal SML at 30 ºC, 40 ºC, 50 ºC, and 60 ºC. This comparison is important to distinguish the degree of discrepancies (Da) between the experimental and theoretical sorption capacity in order to validate the reliability of the adsorption models used. Viljoen et al. (2010) only reported the maximum potential CO_2 that can be stored in various coal seams in South Africa; however, they did not specify how much can be stored in an adsorbed state. Thus, experiments and models were necessary to estimate and predict the maximum amount that can be stored in an adsorbed state.

From the graphs presented in Fig. 7, the percentage discrepancy for Langmuir and Temkin isotherm models values when compared to the experimental values is less than 10% for both coals and across the entire temperature range. However, similar comparison yielded discrepancies in excess of

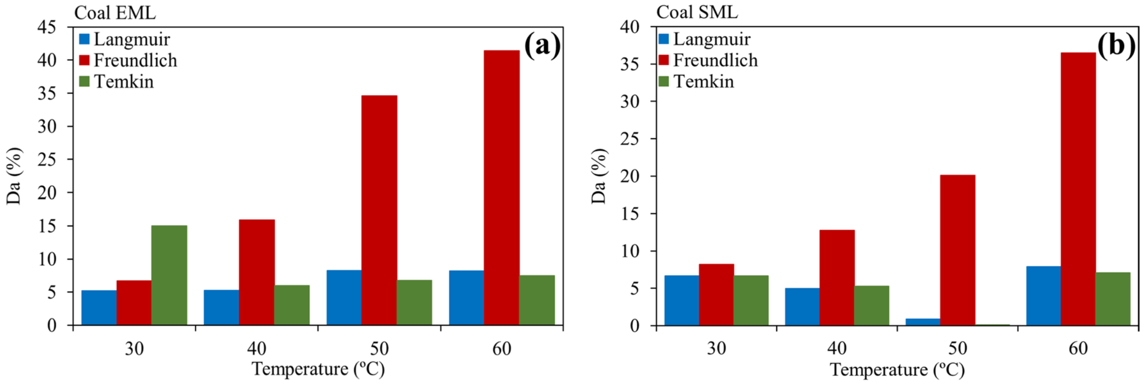

Fig. 7 Statistical comparison of experimental and theoretical maximum CO_2 sorption capacity for **a** Coal EML and **b** Coal SML at 30 °C, 40 °C, 50 °C, and 60 °C

10% for the Freundlich isotherm model at 40 °C, 50 °C, and 60 °C. According to de Myttenaere et al. (2016) there is no upper limit on a "mean absolute percent error" in statistical and scientific studies. There is only the necessary (human) judgment on whether the data referred to can be useful or not. As such, a Da value more than 10% was considered high in this study, the basis of this deduction is both experiential and was also adopted from literature (Guang et al. 1995; McKay et al. 2014). Thus, Freundlich isotherm model may not be used to describe the experimental data for both coals, especially at elevated temperatures.

3.3 Flue gas sorption modelling

The Extended-Langmuir (EL) adsorption isotherm model was used to correlate the measured flue gas sorption data. According to Reeves and Koperna (2008), the EL model predictions require single-component isotherm measurements. The EL adsorption isotherm model has a semi-empirical nature. Figures 8 and 9 present the flue gas experimental sorption isotherms with EL isotherm model regression for Coal EML and Coal SML, respectively, at 30 °C, 40 °C, 50 °C, and 60 °C. The EL theoretical data fits well on the experimental data with a calculated average relative deviation, R, of less than 10% for both coal samples. This suggests that the EL isotherm model can fairly describe the flue gas sorption behaviour on the coals.

Figure 10 presents the relationship of the Extended Langmuir isotherm model parameters for the various flue gas species obtained by linear fitting for Coal EML with temperature at 30 °C, 40 °C, 50 °C, and 60 °C. Similar trends were acquired for and Coal SML for the same relationship. In the 30–60 °C range, the maximum adsorption amount of the two coal samples decreases with an increase in temperature as shown in Fig. 10a. The most credible explanation for this negative effect is that adsorption is an exothermic process. Since the adsorption process is exothermic, low temperatures allow the process to take place favourably by increasing the gas–solid bond strength due to increased adsorbed phase volume (Krooss et al. 2002). However, the variation of the Langmuir adsorption constant with temperature is complicated and non-monotonic as shown in Fig. 10b. Chen et al. (2011) observed similar trends when modelling adsorption data of Chinese Changcui and Qinan coals and concluded that the relationship between the maximum adsorption amount, $N_{m,i}$, and temperature, is described by an exponential function.

The relative deviation between the experimental and theoretical maximum flue gas sorption capacity for Coal EML and Coal SML is less than 6% for most temperatures investigated, except for Coal SML at 30 °C recording a relative deviation close to 10% as shown in Fig. 11. This indicates that there is minimal difference between the experimental and the theoretical values; thus, the Extended-Langmuir adsorption isotherm model may be used to predict the flue gas sorption isotherms at temperatures of 30 °C, 40 °C, 50 °C, and 60 °C, and at pressures ranging from 1.0 MPa to 9.0 MPa.

3.4 Adsorption thermodynamic properties

Figure 12 shows the van't Hoff plot generated from CO_2 adsorption data for Coal EML and Coal SML at temperatures ranging from 30 °C to 60 °C. The standard enthalpy change ($\Delta H°$), the entropy change ($\Delta S°/R$), and Gibbs free energy change ($\Delta G°$) values were calculated from the van't Hoff plot slope ($\Delta H°/R$), the intercept ($\Delta S°/R$), and the Eq. (13), respectively, these parameters are listed in Table 2. The $\Delta G°$ is negative at all the investigated adsorption temperature range, this indicates that the CO_2 adsorption process on Coal EML and Coal SML occurs spontaneous and feasible. The $\Delta G°$ magnitude decreases with an increase in temperature (i.e., $\Delta G°$ approaches zero or becomes less negative), this means that the adsorption process is more

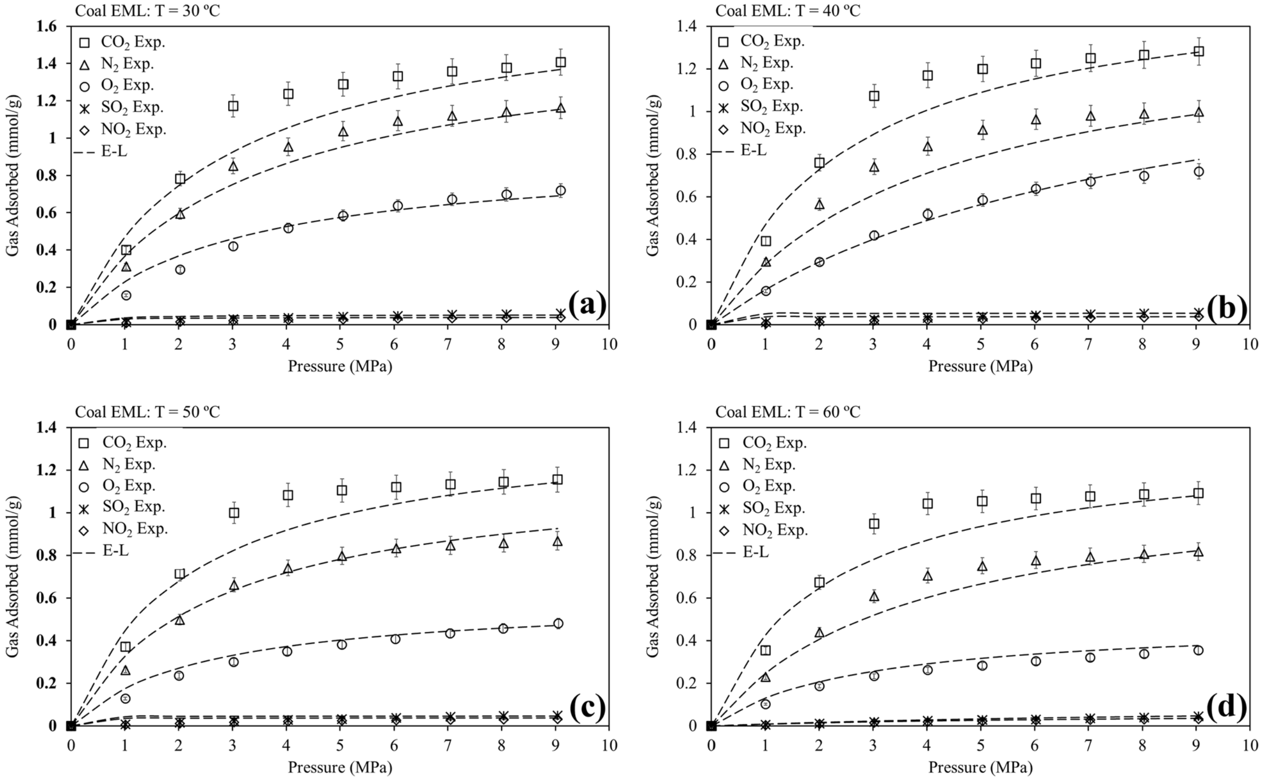

Fig. 8 Extended-Langmuir model fit for flue gas sorption on Coal EML at **a** 30 ºC, **b** 40 ºC, **c** 50 ºC, and **d** 60 ºC

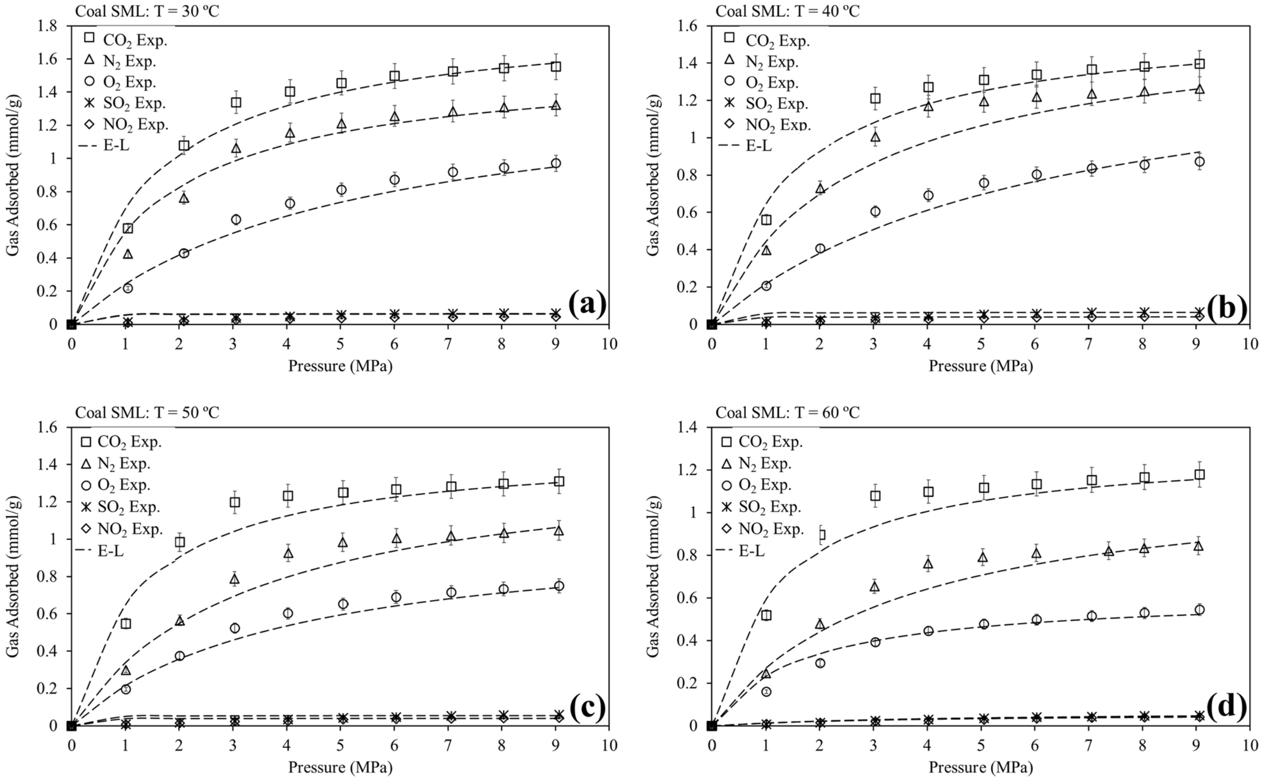

Fig. 9 Extended-Langmuir model fit for flue gas sorption on Coal SML at **a** 30 ºC, **b** 40 ºC, **c** 50 ºC, and **d** 60 ºC

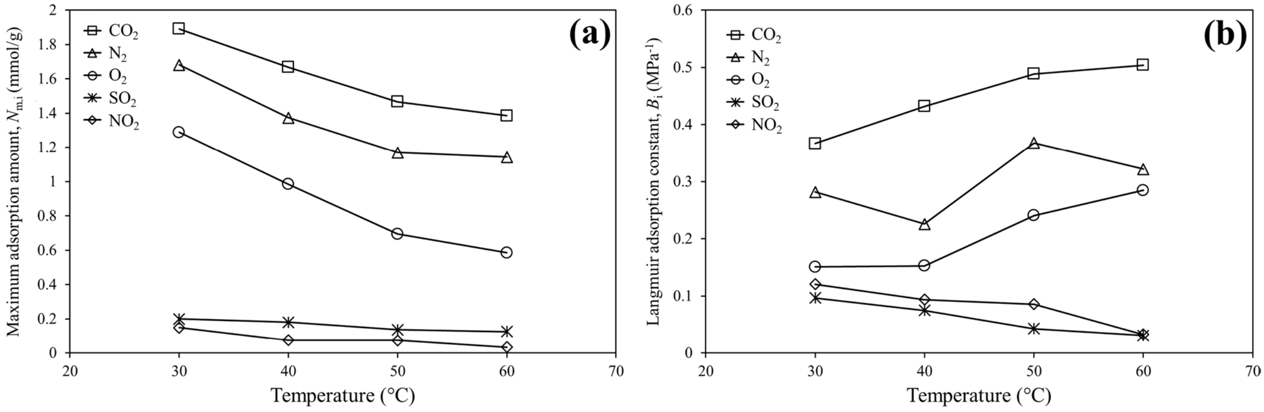

Fig. 10 Change curves of extended Langmuir parameters with temperature: **a** Maximum adsorption amount; **b** Langmuir adsorption constant for Coal EML

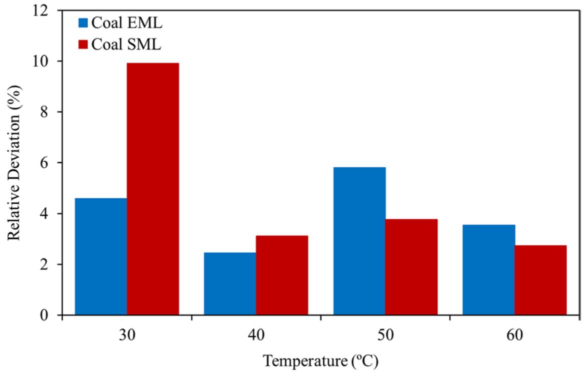

Fig. 11 Statistical comparison of experimental and theoretical maximum flue gas sorption capacity for **a** Coal EML and **b** Coal SML at 30 °C, 40 °C, 50 °C, and 60 °C

favourable at low temperatures. This is attributable to the fact that at higher temperatures, the physical bonds between the adsorbent and CO$_2$ molecules weaken, and the opposite of adsorption (i.e., desorption) is favoured. This implies that the equilibrium shifts in the reversal direction (i.e., from adsorption to desorption) (Ammendola et al. 2020). Furthermore, CO$_2$ molecules have higher kinetic energy at higher temperatures which result in reduced physical interaction with the coals surfaces (Yu et al. 2018).

The standard heat change ($\Delta H°$) reveals that the adsorption process is exothermic for both the coals since the values are negative. The $-\Delta H°$ values are larger than 20 kJ/mol but less than 40 kJ/mol; thus, the adsorption systems are neither within a well-defined physisorption region ($\Delta H° < 20\,\text{kJ/mol}$) nor the chemisorption region ($\Delta H° > 40\,\text{kJ/mol}$). This implies that the CO$_2$ adsorption processes have a dual nature of physical and chemical adsorption on the two coals investigated. Gabruś et al. (2021) also made similar findings on Polish hard coals in the Upper Silesia Coal Basin. They alluded that the combined adsorption nature is due to the heterogeneous morphology of coal texture, as well as the extreme coal bed seam conditions. Lastly, the negative standard entropy change ($\Delta S°$) suggests that the magnitude of randomness of the CO$_2$ molecules decreased (i.e., became more ordered) during the

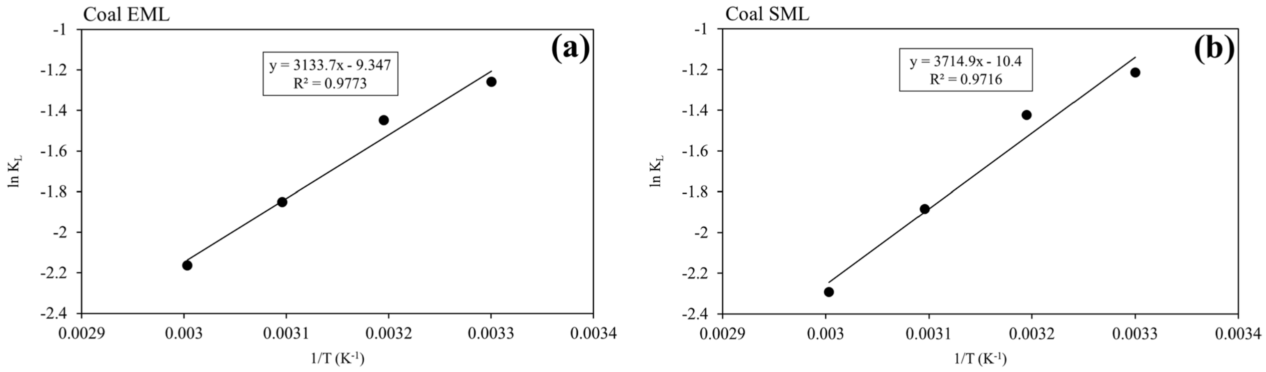

Fig. 12 van't Hoff plots for **a** Coal EML and **b** Coal SML

Table 2 Thermodynamic parameters for CO_2 adsorption on Coal EML and Coal SML

Coal ID	Temperature (°C)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/mol K)
Coal EML	30	−2.541	−26.054	−0.078
	40	−1.765		
	50	−0.989		
	60	−0.213		
Coal SML	30	−4.5553	−30.886	−0.087
	40	−3.6863		
	50	−2.8173		
	60	−1.9483		

adsorption process. This is alluded to the reduced freedom of movement of the CO_2 molecules as they adhere to the surface of the coals. In principle, CO_2 molecules transform from random state (in gaseous phase) to an organized state (solid-like phase on the surface of an adsorbent) during the adsorption process.

4 Conclusions

The pure CO_2 experimental data was fitted on three conventional adsorption isotherm models (Langmuir, Freundlich, and Temkin) and the flue gas experimental data was fitted on Extended-Langmuir adsorption isotherm model. There is a negative effect of temperature on sorption capacity of pure CO_2 and flue gas on the coal samples. This suggests that the sorption process was exothermic; as a result, decreasing the sorbed phase volume with increasing temperature. Generally, the maximum sorption capacity of the coals with respect to the flue gas individual components decreased in the following order: $CO_2 > N_2 > O_2 > SO_2 > NO_2$ on molar basis. This indicates that the coals have a preferential sorption for CO_2. Langmuir adsorption isotherm model was found to describe the pure CO_2 sorption process better than Freundlich and Temkin adsorption isotherm models. This is an indication of the occurrence of the monolayer coverage adsorption mechanism. Extended Langmuir adsorption isotherm model was found to describe the flue gas sorption process on both the coal samples, and the maximum amount adsorbed decreases with temperature. However, the variation of Langmuir adsorption constant with temperature in non-monotonic. The thermodynamic study showed that the CO_2 adsorption on the coals is feasible, spontaneous, and exothermic; also, the adsorption mechanism is dual in nature with physical and chemical interactions taking place.

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Author contributions All authors read and approved the final manuscript.

Availability of data and materials The raw data that support the findings of this study may be made available by the corresponding upon request.

Declarations

Competing interests We assert that none of the information in the paper has been published or is being considered for publication elsewhere, and that there are no competing interests.

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