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Research

Keywords: Global Warming, Flue Gas, Adsorption, Unmineable Coal, Adsorption Models

Posted Date: October 29th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-1019889/v1>

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Modelling of pure CO₂ and flue gas sorption data on South African coals using Langmuir, Freundlich, Temkin, and Extended Langmuir isotherm models

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Abstract

Greenhouse gases (GHGs) have sharply increased over the past four decades due to intensifying industrial activities; as a result, the earth has been faced with global warming in which the major contributor is the anthropogenic carbon dioxide (CO₂) emissions. Carbon sequestration in unmineable coal seams has been proposed as one of the most attractive technologies to mitigate CO₂ emissions in which CO₂ is stored in the microporous structure of the coal matrix in an adsorbed state. The CO₂ 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 adsorption isotherm models were employed including Langmuir, Freundlich, and Temkin for pure CO₂ adsorption data, and the Extended-Langmuir model for multicomponent, such as flue gas mixture-adsorption data as investigated in this research work. The adsorption data was acquired from a high-pressure volumetric sorption system (HPVSS) experiment involving two South African coal samples from Ermelo and Somkhele coalfields with pure CO₂ and synthetic industrial flue gas to simulate emissions that are representative of a typical coal-fired power plant (12% CO₂, 5.5% O₂, 82% N₂, 0.38% SO₂, and 0.12% NO₂). The adsorption data was measured on 10 g samples with a mean size of 2 mm at temperatures ranging from 30 °C to 60 °C and pressure up to 9.0 MPa using the HPVSS. The statistical evaluation of the goodness-of-fit was done using three (3) statistical data analysis methods including correlation coefficient (R²), standard deviation (σ), and standard error (SE). The Langmuir isotherm model conventionally fits the pure CO₂ gas experimental data better than Freundlich and Temkin. The Extended Langmuir gives best experimental data fit for the flue gas.

Keywords: Global Warming; Flue Gas; Adsorption; Unmineable Coal; Adsorption Models

1 Introduction

Considering the rising quantities of carbon dioxide (CO₂) in the atmosphere resulting in global warming, a systematic plan for developing cost-effective and energy-efficient technologies to reduce CO₂ 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). CO₂ emissions from burning fossil fuels have been reported as a significant contributor to elevated anthropogenic levels of CO₂ 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 CO₂ emissions, with coal-fired power plants contributing 30% of the total (IEA 2019).

Anthropogenic CO₂ reportedly accounts for over 63% of all contributors to climate change in the atmosphere. The rate of CO₂ emissions since 2000 was higher than the rate of CO₂ 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 CO₂ emissions when burning fossil fuels. This alternative involves disposal methods, such as injection of CO₂ into deep saline aquifers, unmineable coal seams, and depleted gas and oil reservoirs. CO₂ 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 CO₂, 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 CO₂ 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 optimizing the pathways of the adsorption mechanism, and the design of adsorption systems (Chen 2015). 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).

This research paper presents the comprehensive theoretical modelling of the adsorption data generated by Mabuza et al. (2017), in which pure CO₂ 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 CO₂ 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 (R²), 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 Experimental adsorption data

The experimental adsorption data was acquired through a series batch tests using a high-pressure volumetric sorption system (HPVSS) at temperatures ranging from 30 °C to 60 °C and pressures up to 9.0 MPa. Details of the experimental methodology are outlined by Mabuza et al. (2017) in their work on sorption of flue gas mixtures on South African Bituminous (Coal EML) and Anthracite coals (Coal SML). 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).

2.2 Non-linear and linear forms of the isotherm models

Three (3) well-known empirical adsorption isotherm models were employed for sorption verification in this study to model the sorption of pure CO₂ on two South African coals (Coal EML and Coal SML). Those isotherm models included:

- Langmuir model;
- Freundlich model; and
- 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:

$$N_s = \frac{K_L P N_{sm}}{1 + K_L P} \quad (1)$$

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:

$$\frac{P}{N_s} = \frac{P}{N_{sm}} + \frac{1}{K_L N_{sm}} \quad (2)$$

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

$$q_e = K_F P_e^{1/n} \quad (3)$$

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

$$\log q_e = \log K_F + (1/n) \log P_e \quad (4)$$

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 $(\ln P_e)$ (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 (Haghsersht and Lu 1998).

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

$$q_e = \frac{RT}{b_T} \ln(A_T P_e) \quad (5)$$

The linear form of this expression is:

$$q_e = B_T \ln A_T + B_T \ln P_e \quad (6)$$

where

$$B_T = \frac{RT}{b_T} \quad (7)$$

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):

$$n_i(T, P, y) = \frac{N_{m,i} B_i y_i P}{1 + \sum_{j=1}^{n_c} B_j y_j P} \quad (8)$$

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

2.3 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:

$$\Delta Q(\%) = \sqrt{\frac{\sum [(Q_{\text{exp}} - Q_{\text{calc}})/Q_{\text{exp}}]^2}{(N-1)}} \times 100\% \quad (9)$$

where $S(\%)$ is the normalized standard deviation, Q is the number of moles, the subscripts 'exp' and 'cal' 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 (equations 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:

$$\Delta n = |n_{\text{cal}} - n_{\text{exp}}| \quad (10)$$

$$R = \Delta n / n_{\text{exp}} \times 100\% \quad (11)$$

3 Results and discussion

3.1 Pure CO₂ 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. Fig. 1 and Fig. 2 illustrate pure CO₂ 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 CO₂ experimental data with a minimal average relative. This means that Langmuir isotherm model can describe the present pure CO₂ 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.

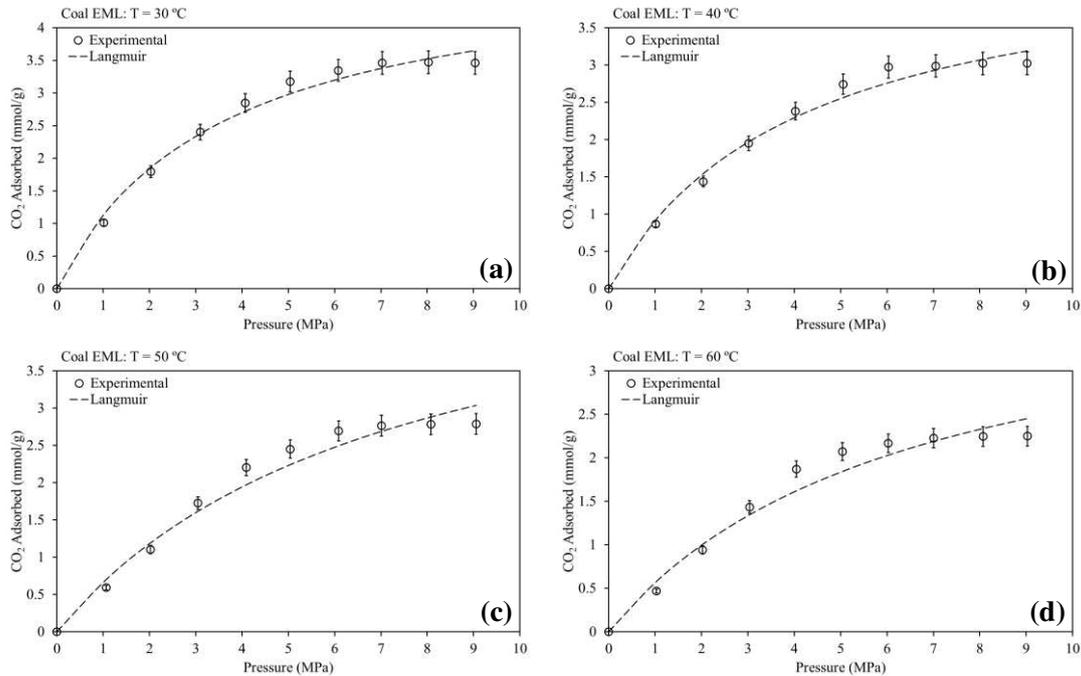


Fig. 1 Langmuir isotherm model fit for pure CO₂ sorption on Coal EML at (a) 30 °C, (b) 40 °C, (c) 50 °C, and (d) 60 °C.

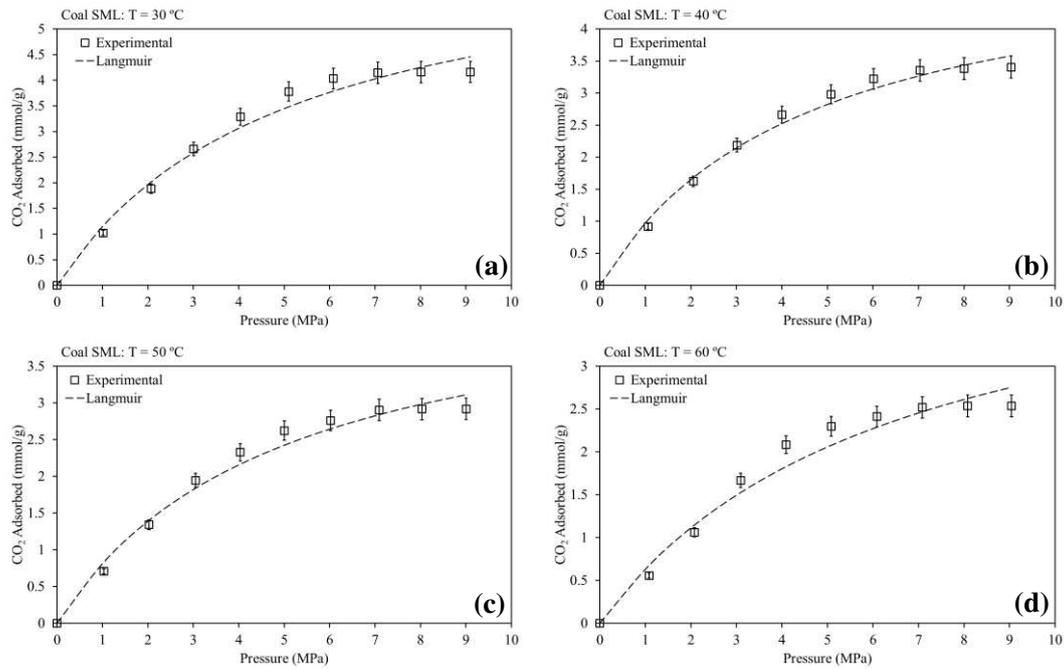


Fig. 2 Langmuir isotherm model fit for pure CO₂ sorption on Coal SML at (a) 30 °C, (b) 40 °C, (c) 50 °C, and (d) 60 °C.

The Freundlich model was applied to estimate the adsorption intensity, $1/n$, of the CO₂ on the coal surface. Fig. 3 and Fig. 4 show pure CO₂ 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 CO₂ experimental data, this is more evident beyond the subcritical pressures (> 6.0 MPa). This behaviour could be attributed to the sorption sites having the same energies of sorption, which is contrary to the assumption made by Freundlich (1906) on this sorption isotherm model. This behaviour suggests that the Freundlich isotherm model cannot be used to describe or represent the current pure CO₂ adsorption experimental data; consequently, the adsorption intensity, $1/n$, of CO₂ on the coal surfaces cannot be accurately estimated using the Freundlich equation.

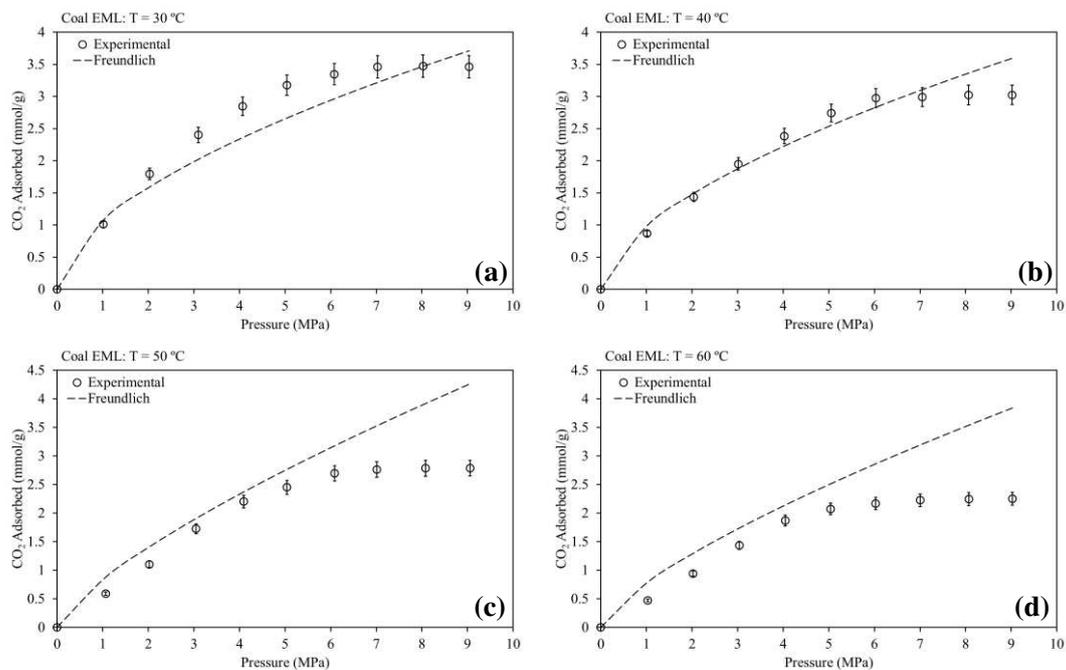


Fig. 3 Freundlich isotherm model fit for pure CO₂ sorption on Coal EML at (a) 30 °C, (b) 40 °C, (c) 50 °C, and (d) 60 °C.

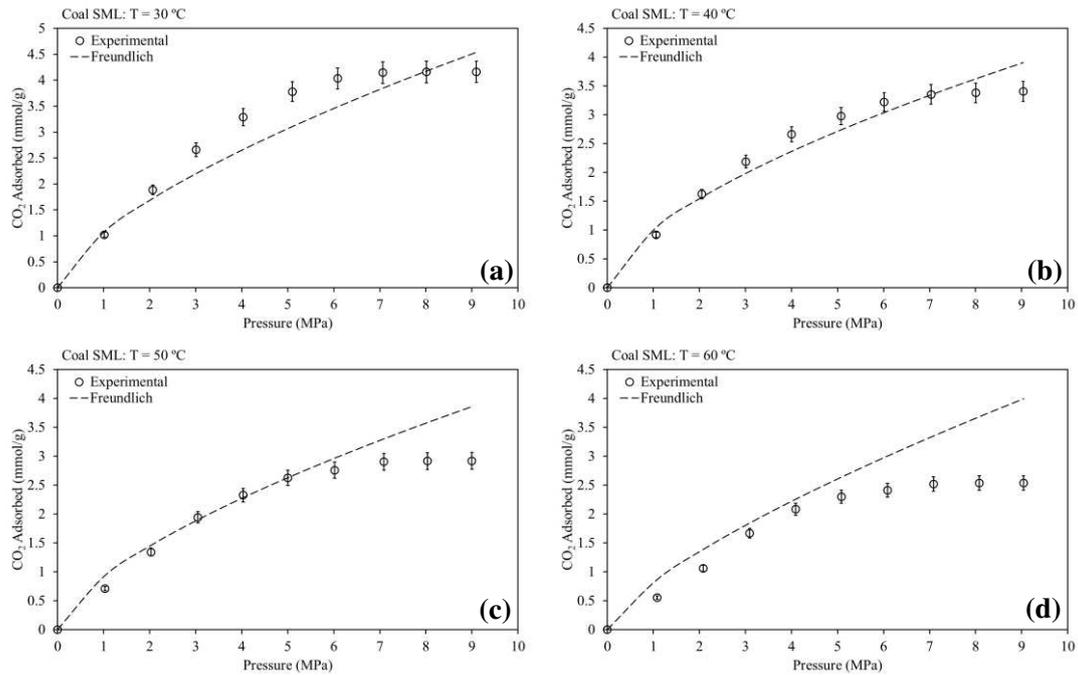


Fig. 4 Freundlich isotherm model fit for pure CO₂ sorption on Coal SML at (a) 30 °C, (b) 40 °C, (c) 50 °C, and (d) 60 °C.

The Temkin adsorption isotherm model was applied to evaluate the adsorption potential, b_T , of the CO₂ on the coal surface. Fig. 5 and Fig. 6 present pure CO₂ 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 CO₂ sorption experimental data measured under the conditions of temperature and pressure probed; as a result, the adsorption potential, b_T , of CO₂ on the coals surfaces cannot be accurately estimated using the Temkin equation.

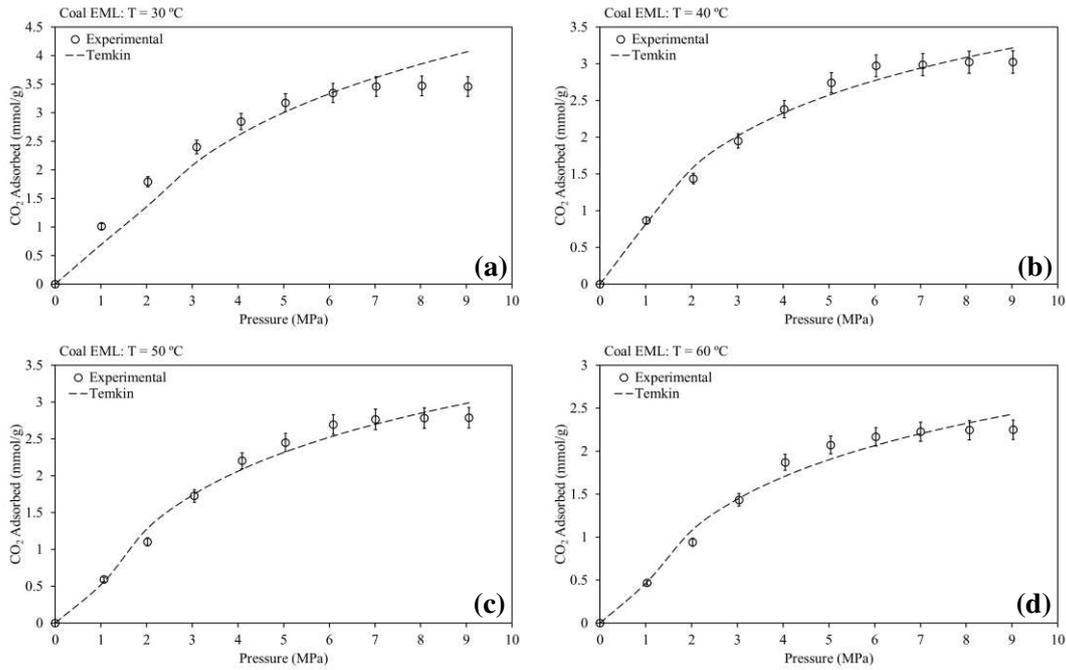


Fig. 5 Temkin isotherm model fit for pure CO₂ sorption on Coal EML at (a) 30 °C, (b) 40 °C, (c) 50 °C, and (d) 60 °C.

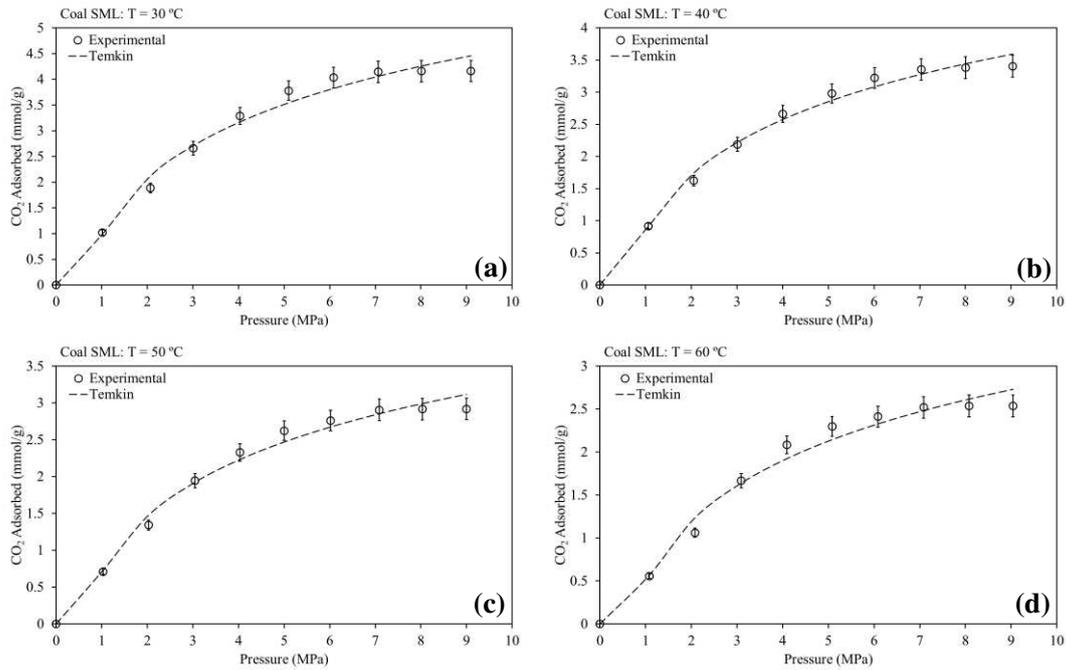


Fig. 6 Temkin isotherm model fit for pure CO₂ sorption on Coal SML at (a) 30 °C, (b) 40 °C, (c) 50 °C, and (d) 60 °C.

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 °C to 40 °C) and below 0.9 at high temperatures (50 °C and 60 °C) 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 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.

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

		Temperature (°C)							
		Coal EML				Coal SML			
Model	Parameter (Units)	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
	a (MPa ⁻¹)	0.284	0.245	0.137	0.155	0.197	0.221	0.202	0.153
	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 (dimensionless)	1.762	1.690	1.353	1.374	1.526	1.623	1.530	1.388
	$1/n$ (dimensionless)	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
Temkin	Standard Error (SE)	0.304	0.294	0.432	0.423	0.398	0.322	0.344	0.412
	B_T (dimensionless)	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 (MPa ⁻¹)	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

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 CO₂ 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 CO₂ on the coals as reported by Mabuza et al. (2017). The standard deviation is less than ± 1.6 for Coal EML and less than ± 1.2 for Coal SML for the entire temperature range.

Fig. 7 compares the experimental and theoretical maximum sorption capacity of CO₂ on Coal EML and Coal SML at 30 °C, 40 °C, 50 °C, and 60 °C. 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 CO₂ 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.

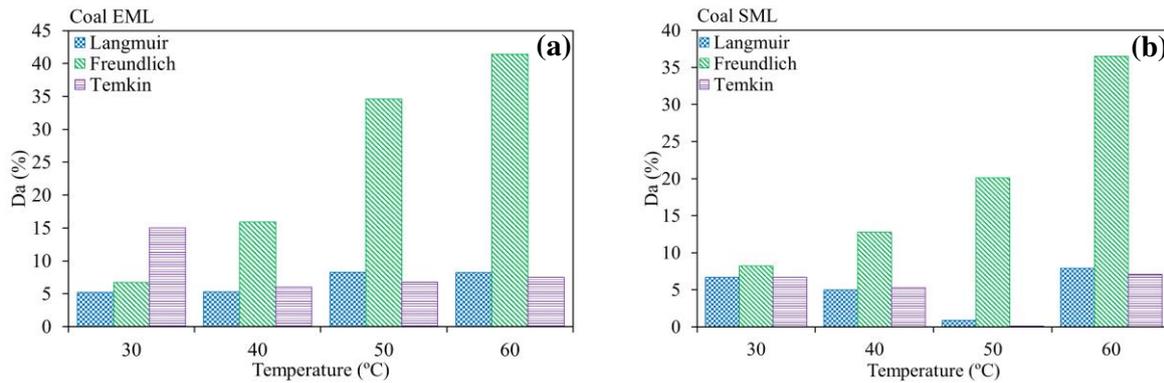


Fig. 7 Statistical comparison of experimental and theoretical maximum CO₂ sorption capacity for (a) Coal EML and (b) Coal SML at 30 °C, 40 °C, 50 °C, and 60 °C.

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 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. Fig. 8 and Fig. 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.

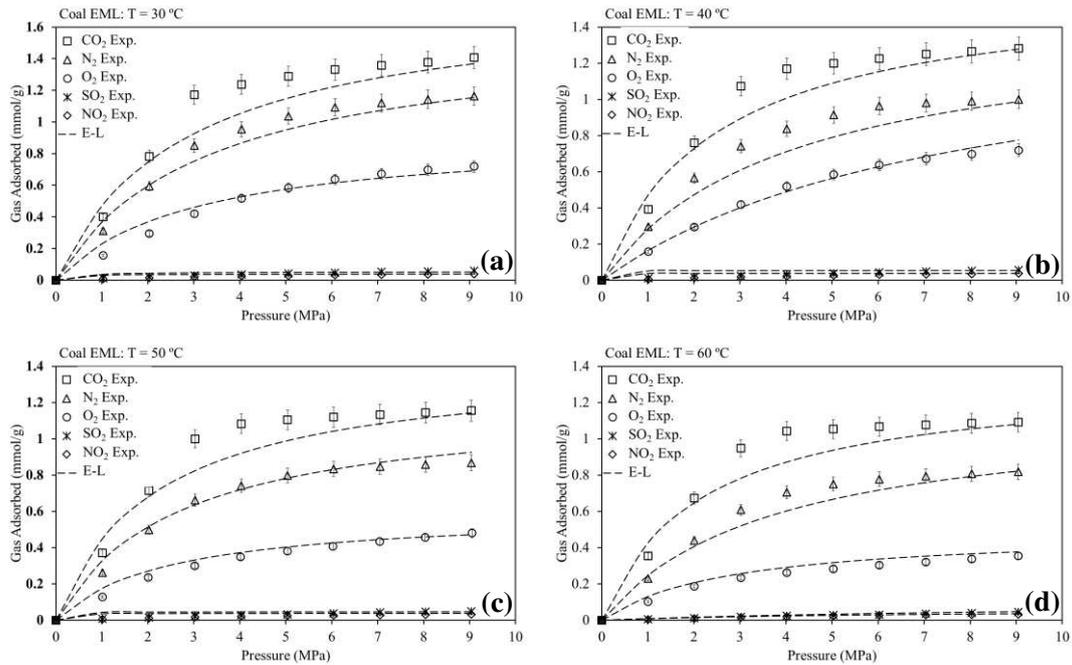


Fig. 8 Extended-Langmuir model fit for flue gas sorption on Coal EML at (a) 30 °C, (b) 40 °C, (c) 50 °C, and (d) 60 °C.

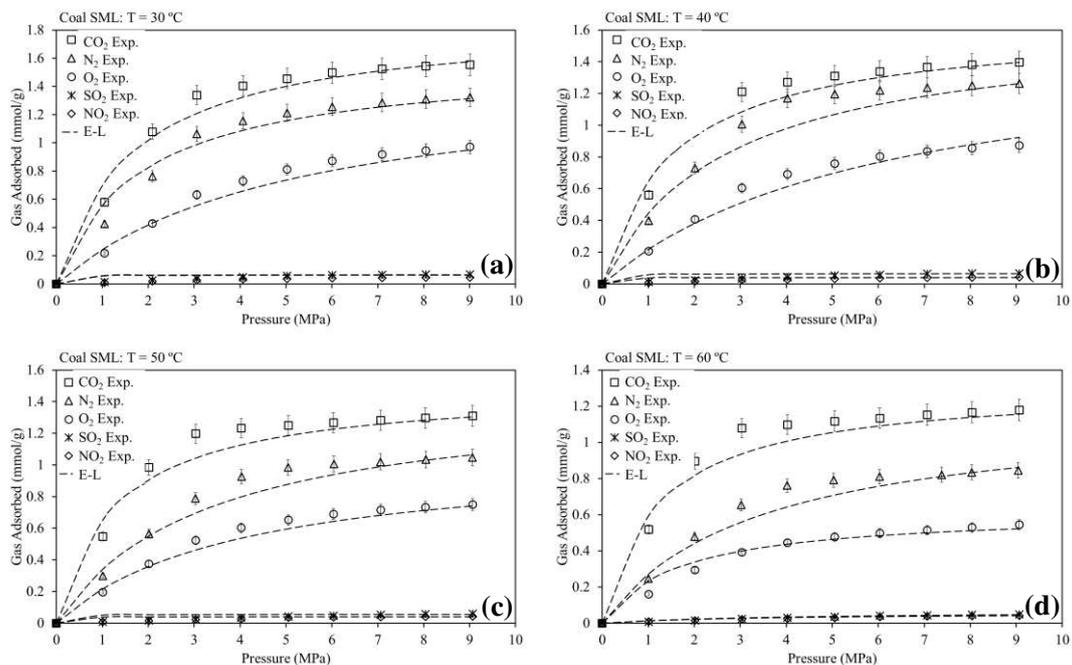


Fig. 9 Extended-Langmuir model fit for flue gas sorption on Coal SML at (a) 30 °C, (b) 40 °C, (c) 50 °C, and (d) 60 °C.

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, with an exception of Coal SML at 30 °C recording a relative deviation close to 10% as shown in Fig. 10. 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.

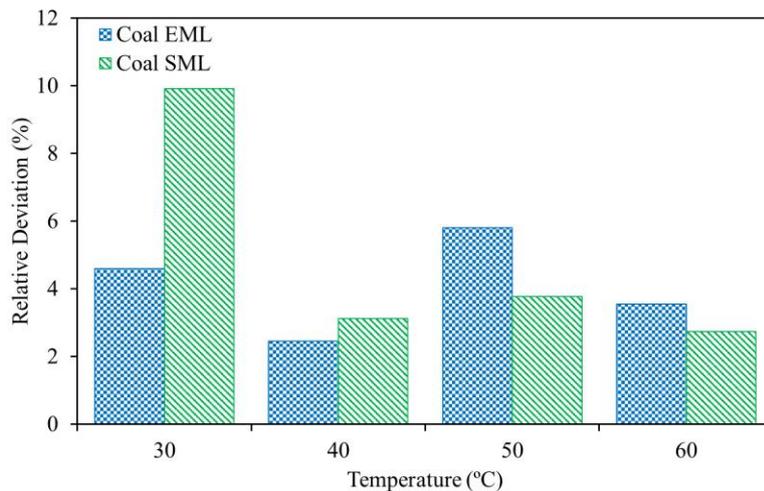


Fig. 10 Statistical comparison of experimental and theoretical maximum flue gas sorption capacity for (a) Coal EML and (b) Coal SML at 30 °C, 40 °C, 50 °C, and 60 °C.

4 Conclusions

The pure CO₂ 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 CO₂ 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: CO₂ > N₂ > O₂ > SO₂ > NO₂ on molar basis. This indicates that the coals have a preferential sorption for CO₂. Langmuir adsorption isotherm model was found to describe the pure CO₂ 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.

Availability of data and materials

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

Conflict of interest

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.

Acknowledgements

The authors acknowledge the National Research Foundation (NRF) of South Africa for the financial support provided to undertake this research successfully. The findings and conclusions expressed in this publication are solely those of the authors and do not necessarily reflect the views of the Foundation.

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