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Study on adsorption characteristics of CO_2 and CH_4 in shale based on Langmuir model and artificial neural network

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ABSTRACT

CO_2-enhanced shale gas recovery technology (CO_2-ESGR) is one of the most potential carbon capture, storage and utilization (CCUS) technologies to mitigate the greenhouse effect and achieve the goal of carbon neutrality. The adsorption characteristics of CO_2 and CH_4 in shale are the key factors for CO_2-ESGR, and fast and accurate prediction of adsorption capacity is still challenging, especially for the mixture of CO_2 and CH_4. This paper conducted a prediction study of CO_2 and CH_4 adsorption in shale in a large range of temperatures, pressures and total organic carbon (TOC) by employing the Langmuir model and the back propagation artificial neural network (BP-ANN) method. The key parameters of Langmuir model, saturation adsorption capacity Q_0 and Langmuir pressure P_L, were optimized for improving the prediction accuracy of CO_2 and CH_4 adsorption capacity in shale, and the determination coefficient of the improved model was R^2=0.9691. In addition, the activation function, number of hidden layer neurons, learning efficiency and other key parameters of the BP-ANN were optimized by using data normalization method. The determination coefficients R^2 of the BP-ANN prediction to experimental data for pure CH_4 and pure CO_2 were 0.9921, 0.9867 , respectively, a little better than the improved Langmuir model. The improved Langmuir model and BP-ANN method proposed in this study can accurately predict the adsorption characteristics of CO_2 and CH_4 in shale, which can provide theoretical support for CO_2-ESGR.

Keywords: CO_2 and CH_4, shale, adsorption, Langmuir model, artificial neural network, CCUS

NONMENCLATURE

Abbreviations	
CO_2-ESGR	CO_2-enhanced shale gas recovery
CCUS	Carbon Capture, Utilization and Storage
BP-ANN	back propagation artificial neural network
TOC	total organic carbon
Symbols	
N_{ab}	absolute adsorption capacity
Q_0	saturated adsorption capacity
P	experimental pressure
P_L	Langmuir pressure
T	tempture

1. INTRODUCTION

In recent years, with the improvement in living standards, people's demand for natural gas resources has been increasing. Besides conventional natural gas resource development, scientists focus on the exploration and development of unconventional natural gas resources,such as shale gas, coalbed methane, tight gas and natural gas hydrate. For shale gas reservoirs, the main component, methane is usually distributed in shale micropores and fractures in the form of adsorption, dissociation and dissolution. With the sharply increased emissions of carbon dioxide, the greenhouse effect caused serious harm to the global ecological environment. CCUS is regarded as one of the most important measures to achieve large-scale reduction of CO_2 emissions for the goal of carbon neutrality.

At present, significant achievements have been made in the study of the adsorption performance of CH_4

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and CO_2 gases in shale [1-14].In shale, CO_2 gas has stronger adsorption capacity than methane (CH_4) gas [5], [6], [12]. This is one of the important theoretical basis for injecting CO_2 gas into shale reservoirs to enhance CH_4 recovery rate technology. CO_2-enhanced shale gas recovery (CO_2-ESGR) is an efficient and economical technology, which can not only improve the recovery of CH_4, but also store CO_2, thus achieving a win-win situation of economic and environmental benefits. The CO_2-ESGR involves physical processes such as the diffusion and adsorption of CH_4 and CO_2 on shale, which have a significant impact on the displacement effect of CH_4 and the safe storage of CO_2. Therefore, in CO_2-ESGR, it is crucial to master the adsorption characteristics of CH_4 and CO_2 in shale, to understand the competitive adsorption between CH_4 and CO_2, and to establish a accurate prediction model for adsorption.

This paper collected a large number of experimental data on gas adsorption of shale samples from major shale gas resource rich areas in China, for summarizing the changing law of gas adsorption characteristics.The adsorption characteristics of CO_2 and CH_4 in shale were studied by employing the improved Langmuir adsorption model and BP-ANN model.

2. MATERIAL AND METHODS

2.1 Experimental data collection

This paper counts the experimental data of CO_2 and CH_4 gas adsorption in shale samples from major shale gas resource rich areas in China published in the past 10 years [11],[14],[15-23].The shale samples used in the adsorption experiment mainly come from the Sichuan Basin, Qaidam Basin, and Ordos Basin, with the largest number of shale samples selected from the Sichuan Basin.

2.2 Langmuir model

The Langmuir adsorption model is a single-molecule layer adsorption theoretical model proposed by American physical chemist Irving Langmuir in 1916, based on molecular dynamics theory, for the low-pressure adsorption of gas molecules onto solid surfaces. Langmuir adsorption model has the characteristics of easy solution and high precision, so this equation is widely used to describe the adsorption characteristics of shale gas. Langmuir adsorption isotherm equation is shown in Eq. (1) [19].

$$N_{ab} = Q_0 \frac{P}{P + P_L} \tag{1}$$

where N_{ab} is the absolute adsorption capacity, mmol/g; Q_0 is the saturated adsorption capacity, which is the maximum adsorption capacity at a specific temperature, mmol/g; P is pressure, MPa; P_L is the Langmuir pressure, the gas pressure at which the absolute adsorption capacity is equal to 1/2 of Q_0, in MPa.

With fitting Q_0 and P_L by the collected adsorption experimental data, this work improved the Langmuir model through establishing the functional relationships of its key parameters with temperature and TOC for prediction of the adsorption characteristics of CO_2 and CH_4 in shale.

2.3 BP neural network model

Artificial Neural Network (ANN) [24], whose basic principle comes from neural networks in biology, has the ability of autonomous learning. It can analyze the internal relationship through a batch of corresponding input and output data provided by the designer, and finally form a complex nonlinear function. ANN is widely used in various scientific engineering applications.

This paper employed BP-ANN for gas adsorption prediction. The collected experimental data is classified and stored according to input and output variables. Before training, the data is divided into a training set (85% of the total data) and a testing set (15% of the total data) according to a certain proportion.The data is normalized to eliminate errors caused by orders of magnitude. After training is completed, the prediction results are de normalized. Finally, performance evaluation is conducted by comparing the average absolute percentage error (MAPE), mean square error (MSE), root mean square error (RMSE), and determination coefficient (R^2) between the predicted and experimental values.

3. RESULTS AND DISCUSSION

3.1 Langmuir model fitting results

3.1.1 Fitting of the key parameters of Langmuir model

The fitting curve of Langmuir model for CH_4 and CO_2 single component gas is shown in Fig.1. As the temperature increases, the adsorption capacity of CH_4 and CO_2 gases gradually decreases, and the adsorption capacity of CH_4 and CO_2 gases gradually increases as the pressure increases. The average R^2 of model fitting is 0.9921, indicating a high fitting accuracy.

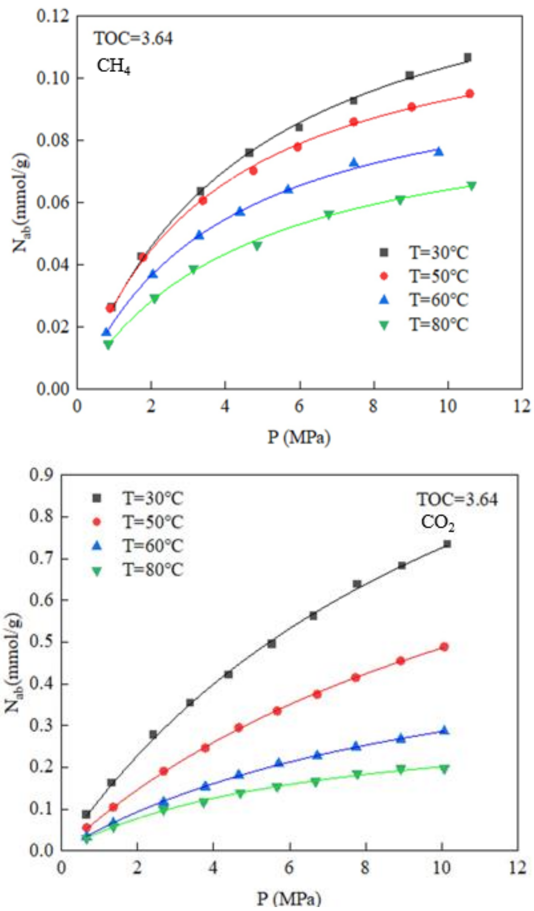


Fig. 1. Langmuir model fitting curve

3.1.2 Improved Langmuir model considering key parameters fitting

By fitting the adsorption experimental data , a series of key parameters Q_0 and P_L of the Langmuir model under different temperatures and TOC were obtained. A quantitative analysis was conducted to study the influence of TOC and temperature on the key parameters Q_0 and P_L of the Langmuir model. The relationship between key parameters and temperature under the conditions of various TOC is shown in Fig.2.For both CH_4 and CO_2, the adsorption capacity of shale becomes weaker with increasing temperature. The saturated adsorption capacity Q_0 gradually decreases with increasing temperature, showing a linear decrease relationship. R^2 is 0.9821 and 0.9915 for CH_4 and CO_2, with a good linear correlation. The Langmuir pressure P_L gradually increases with the increase of temperature, showing a linear increase relationship. R^2 is 0.9809 and 0.9929 for CH_4 and CO_2, with also a good linear correlation.

The effect of TOC on Q_0 and P_L of Langmuir for CH_4 and CO_2 single component gases is shown in Fig.3.

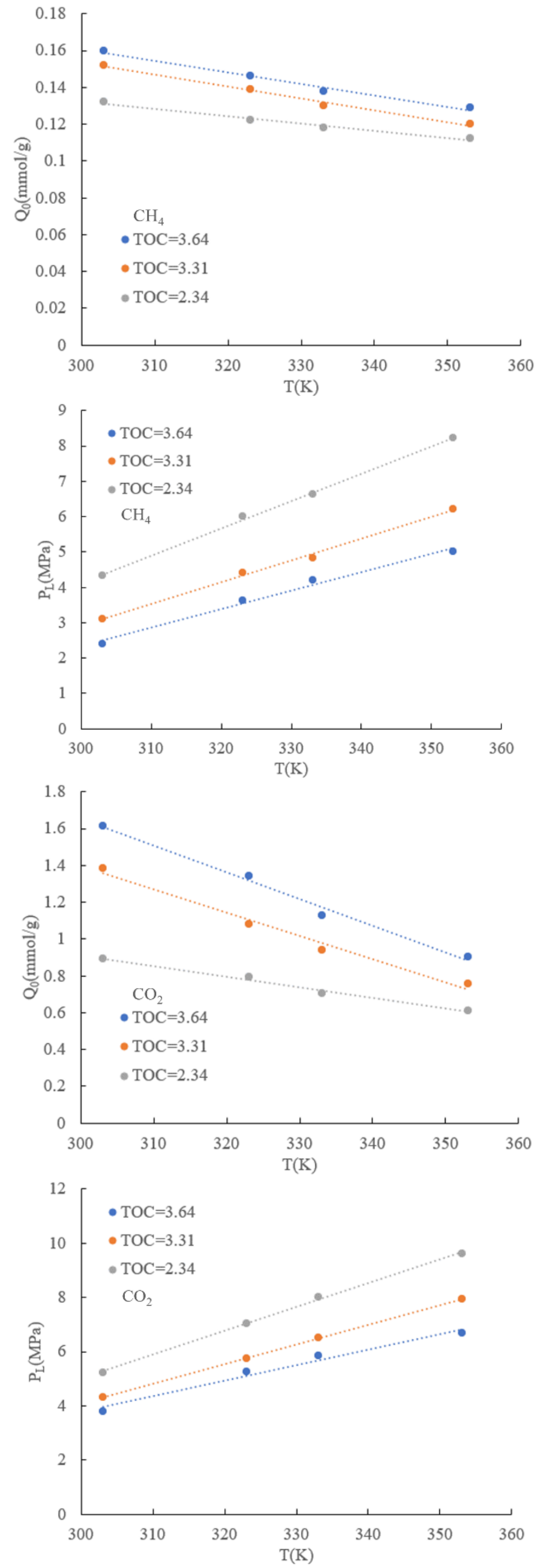


Fig. 2. The relationship between Q_0, P_L and temperature

In Fig.3, it can be seen that whether it is CH_4 or CO_2 gas, the higher the TOC, the stronger the adsorption capacity of shale. Q_0 gradually increases with the increase of TOC, showing a good linear relationship with

R^2 of 0.9803 and 0.9928. P_L gradually decreases with the increase of TOC, showing a good linear relationship with R^2 of 0.9834 to 0.9914.

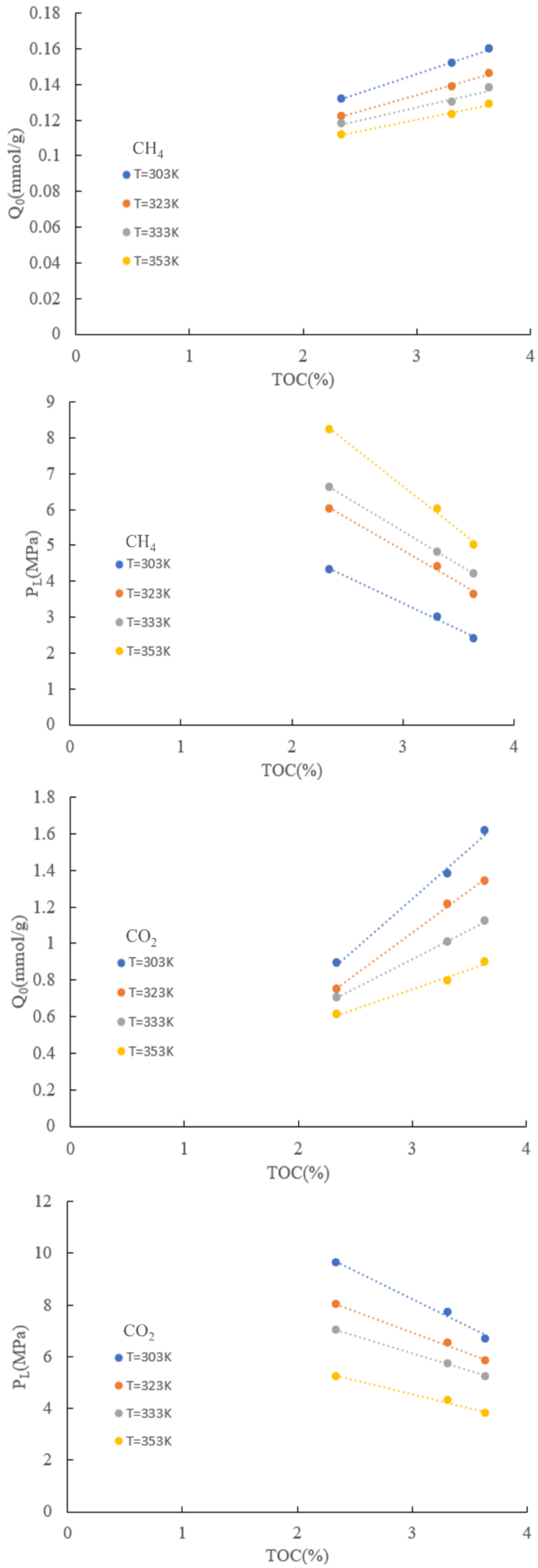


Fig. 3. The relationship between Q_0, P_L and TOC

It can be seen from Fig.2 and Fig.3 that the key parameters Q_0 and P_L are linear with temperature and TOC.I It can be assumed that Q_0 and P_L are binary linear function of temperature and TOC. Then, a linear regressive function for the relationship of Q_0 and P_L with temperature and TOC were proposed as follows.

CH_4:

$$Q_0 = -0.000941T + 0.0213TOC + 0.37 \quad (2)$$

$$P_L = 0.0477T - 1.6483TOC - 5.3181 \quad (3)$$

CO_2:

$$Q_0 = -0.0244T + 0.1853TOC + 8.2013 \quad (4)$$

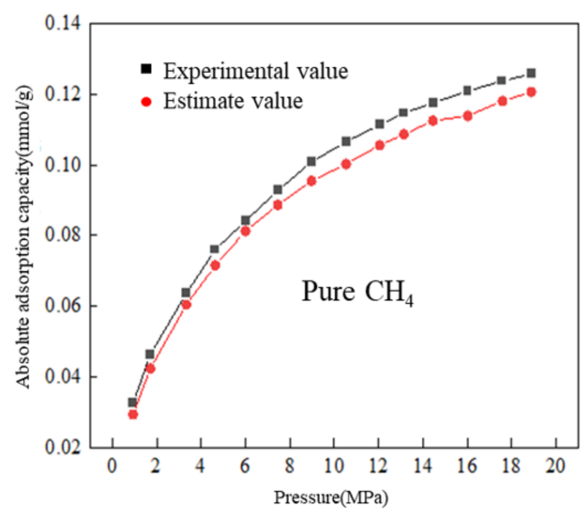
$$P_L = -0.0645T - 1.6698TOC + 32.6167 \quad (5)$$

The R^2 of the functions of Q_0 and P_L with temperature and TOC is 0.9482, 0.9576, 0.9692 and 0.9699, indicating a high fitting accuracy. Through establishing the relationship function between Q_0 and P_L with temperature and TOC, an improved Langmuir model for predicting the absolute adsorption capacity of CH_4 and CO_2 single component gases is obtained.

3.1.3 Validation of the improved Langmuir model

The adsorption experimental data of CH_4 and CO_2 single component gases on shale samples with T=303 K and TOC=3.64% were selected for the validation of the improved improved Langmuir model. The comparison between the model fitting results and experimental values is shown in Fig. 4.

From Fig. 4, the overall difference between the absolute adsorption capacity fitted by the model and the experimental measurement is not significant. The trend of the isothermal adsorption curve is basically consistent, and the average R^2 is 0.9548 and 0.9583. It can be seen that the improved Langmuir model can fit the adsorption behavior of CH_4 and CO_2 single component gases in shale with good accuracy.



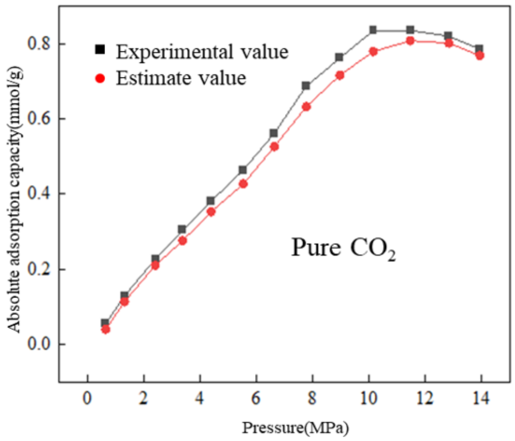


Fig. 4. Comparison between predicted and experimental values

3.2 BP neural network model fitting results

The adsorption characteristics of CO_2 and CH_4 in shale were also predicted by BP-ANN. The prediction results of the neural network model are shown in Fig. 5.

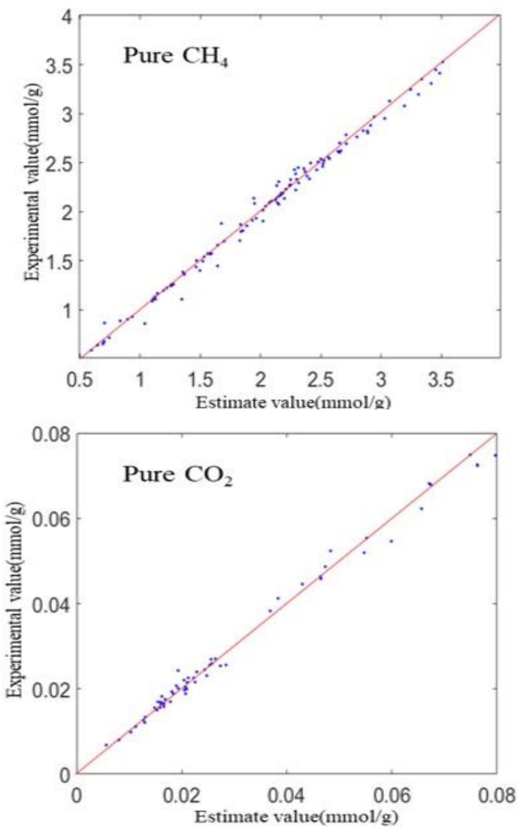


Fig. 5. Comparison between model prediction results and experimental values

From Fig. 5, it can be seen that the predicted values of the neural network model have a good linear correlation with the experimental values. The errors of the model fitting results are within the expected error range, with an average R^2 of 0.9836 and 0.9946 for CH_4 and CO_2, respectively. The model fitting accuracy is relatively high. The specific error values of the model prediction results are shown in Fig. 6. The average MAPE, MSE and RMSE of the two experiments were 0.0253, 0.000435 and 0.0203.

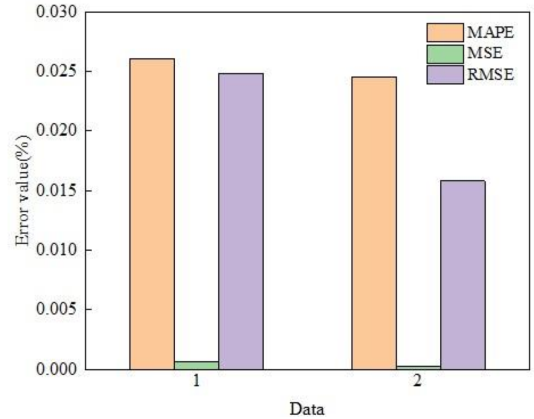


Fig. 6. Model fitting error

4. CONCLUSIONS

Through the collection and analysis of experimental data on CO_2 and CH_4 gas adsorption in shale samples from major shale gas resource rich areas in China, this paper studied the adsorption characteristics of CH_4 and CO_2 in shale Based on Langmuir model and BP-ANN model. The finding of this work will provide theoretical support for CO_2-ESGR application in China. The main conclusions are as follows:

(1) The Langmuir adsorption model was used to analyze the effects of temperature and TOC on the its key parameters and on the CO_2 and CH_4 adsorption performance in shale. The saturated adsorption capacity decreases with the increase of temperature, and increases with the increase of TOC; Langmuir pressure increases with increasing temperature and decreases with increasing TOC. The Langmuir model was improved based on key parameters related to temperature and TOC and can accurately predict the adsorption behavior of CO_2 and CH_4 in shale, the average R^2 is 0.9691.

(2) The experimental data of shale gas adsorption are trained by BP-ANN model. The predicted results of the model are basically consistent with the measured values, with an average R^2 greater than 0.9, indicating a relatively high fitting accuracy of the model.

DECLARATION OF INTEREST STATEMENT

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. All authors read and approved the final manuscript.

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