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Research on adsorption characteristics of H$_2$S, CH$_4$, N$_2$ in coal based on Monte Carlo method

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In order to study the adsorption characteristics of H$_2$S, CH$_4$ and N$_2$ by coal under different conditions, the new macromolecular structure model of Dongqu No. 2 was constructed, and the grand canonical Monte Carlo (GCMC) method was used to simulate the adsorption process of three types of gases in coal. The dependence of adsorption capacity of coal on its temperature, pressure and moisture content was analyzed. The results show that with the increase of pressure and temperature, adsorption isotherms of all the three gases follow Langmuir model. For pressure greater than 2 MPa, the influence of temperature on adsorption capacity was greater than that of pressure. With rise in temperature, the decrease in rate of H$_2$S adsorption was least and drops in the heat of adsorption of H$_2$S most. This indicates that the adsorption of H$_2$S on coal is more stable than those of CH$_4$ and N$_2$. As the water content of coal increased, its adsorption capacity for the present three gases decreased linearly, and the capacity for H$_2$S (1.77 mmol/g) changed the most. The reduction of free volume linearly and preferential occupation of adsorption sites by water molecules are the main reasons for the highest change in the adsorbed amount of H$_2$S gas.

In the mining of high-sulfur coal, the escape of a toxic and harmful H$_2$S gas threatens the safety of health and life of coal miners[1,2]. It is reported that inhaling by human being of H$_2$S gas at a concentration level 1 g/m^3 can cause death within seconds[3–5]. More than 10 deaths due to poisoning by H$_2$S gas have been reported in our country in the present century. With gradual exhaustion of earth's fossil resources of energy, the depth of coal mining is expected to increase, and consequently H$_2$S is going to become a major concern of safety in coal production[6–8]. Therefore, understanding of adsorption characteristics of coal for H$_2$S gas is of significance currently.

The origin of H$_2$S gas in coal is a subject of research globally[9–11]. It is believed currently that the gas existing with coal has come from three processes: biochemical including biodegradation and microbial sulfate reduction (BSR); thermochemical, including thermochemical decomposition (TDS) and thermochemical sulfate reduction; and Magma. The toxic nature of H$_2$S, limits experimental studies on it. The main factors influencing adsorption of H$_2$S on coal are: pores, microscopic components, moisture, pressure, degree of coalification etc[12]. Based on identical experiments carried out on isothermal adsorption of H$_2$S, CH$_4$ and N$_2$ on coal. He et al.[13] reported that highest adsorption capacity of coal is for H$_2$S (among the present three gases) and the lowest for N$_2$. Liang et al.[14] simulated the adsorption of H$_2$S, CO$_2$, CH$_4$, and N$_2$ gas molecules on the coal surface by quantum chemical methods, and reported that the adsorption capacity for H$_2$S is lowest, and the presence of H$_2$S in the coal seam enhances its ability to adsorb CH$_4$. Xue et al.[15] studied the interaction between functional groups present on coal and H$_2$S molecules using molecular simulation, and found that between hydroxyl group and H$_2$S the interaction is strongest. Xue et al.[16] studied adsorption of H$_2$S gas on different types of coal samples and used adsorption models suited to them. The results have shown that adsorption capacity of coal for H$_2$S increases with the degree of coalification, and Langmuir model is the best fit. Many research groups globally, have studied in detail adsorption of CH$_4$ and N$_2$ on coal[17–22], and therefore CH$_4$ and N$_2$ have been selected in the present work as controls to analyze the data of adsorption of H$_2$S on coal. Monte Carlo method applied to understand adsorption of various gases on coal in the recent past has been used here for calculations[23–26].

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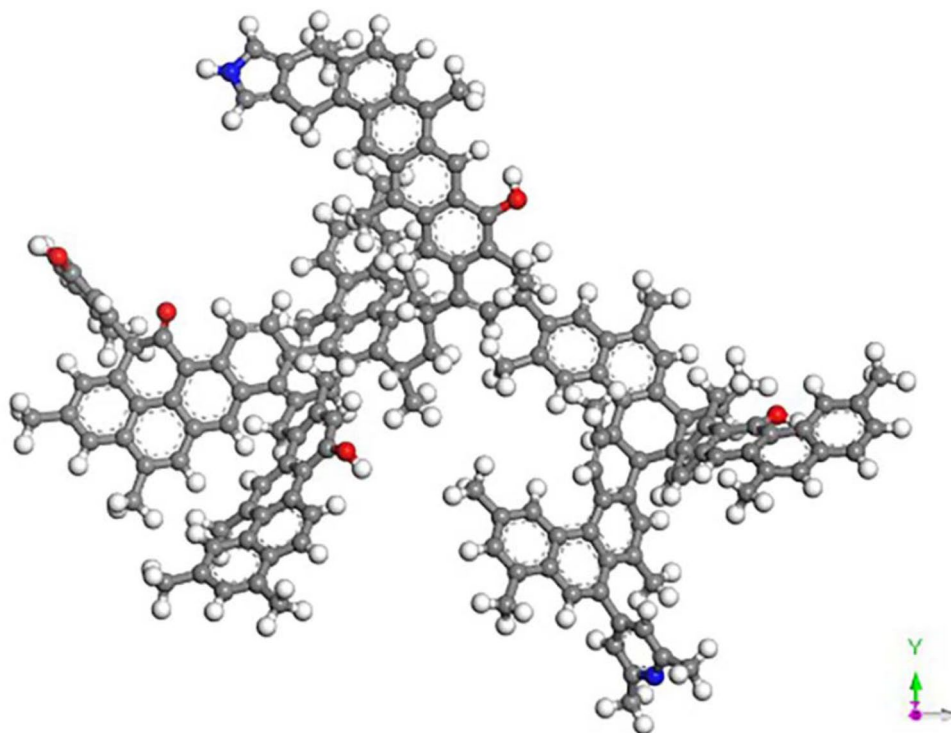
Figure 1. Molecular model of Dongqu No.2.

From the above research, we can find that the previous research is mainly based on experiments. The adsorption experiments only measure and analyze the adsorption phenomenon at a macro level, and cannot describe the microscopic process of adsorption. The computational methods simulating adsorption on coal are not disturbed by the external environment. The experimental research has laid undoubtedly some theoretical basis to discuss adsorption of H_2S on coal but the adsorption characteristics of H_2S are scantly analyzed from a microscopic point of view. The effect of water associated with coal on adsorption of H_2S also has not been studied. The level of water content in coal is an important factor that affects the amount of H_2S adsorbed. In the present paper, the adsorption characteristics of coal for H_2S gas are studied from the perspective of macromolecular organic structure of coal, and the adsorption characteristics of CH_4 and N_2 are used as a control to analyze the difference in the adsorption capacity of coal for the present three single-component gases. This paper uses molecular simulation methods to study adsorption of H_2S, CH_4 and N_2 (as a single-component gas) on coal, Dongqu No. 2, use of which eliminates the influence of different geological conditions on the inorganic contents of coal. The effect of different pressures (up to10MPa), temperatures (298, 318, 338, 358 and 378 K) and water contents (0, 1.18, 2.31, 3.42, and 4.51%) on the adsorption isotherm curve, isosteric heat of adsorption and energy of adsorption are reported. Thus, a theoretical basis is provided for control of H_2S in coal seams.

Dongqu No. 2 coal model and simulation method

The molecular structure model of Dongqu No. 2 (Fig. 1) proposed by Li Yaogao[27] for coal was adopted in the present paper. The aromatic skeleton of this model is mainly anthracene ring, and it contains phenolic hydroxyl, carboxyl, pyridine and pyrrole functionalities. Its molecular formula is $C_{174}H_{148}O_5N_2$. The molecular model constructed for coal has used the "Forcite" module to optimize its geometry and energy. The lowest energy of the molecular model is shown in Fig. 1. It uses the module Amorphous Cell to put thirteen molecules of coal in the box, and COMPASS force field is selected for geometric optimization of the constructed three-dimensional structure, annealing, and molecular dynamics[28]. As the constructed coal model has a periodic structure, the electrostatic interactions are all Ewald and van der Waals type and are based on atom. The molecular dynamics parameter settings are shown in Table 1. The final model is shown in Fig. 2.

Based on the coal structure model constructed (Fig. 2), the Sorption modules were used to calculate at fixed pressure (0.01, 2, 6, and 8 MPa) adsorption isotherms (298, 318, and 338 K). The Sorption Locator module was used to build coal structure models with different moisture content. Thereafter to simulate the gas adsorption Sorption module was used. The average loading (Eq. 1) is the amount adsorbed. Its unit is N/uc, and conversion formula for the unit is:

$$\text{uptake/(mmol/g)} = \frac{\text{average loading}}{M} \times 10^3 \tag{1}$$

M is the relative molecular mass of the adsorbent (g/mol).

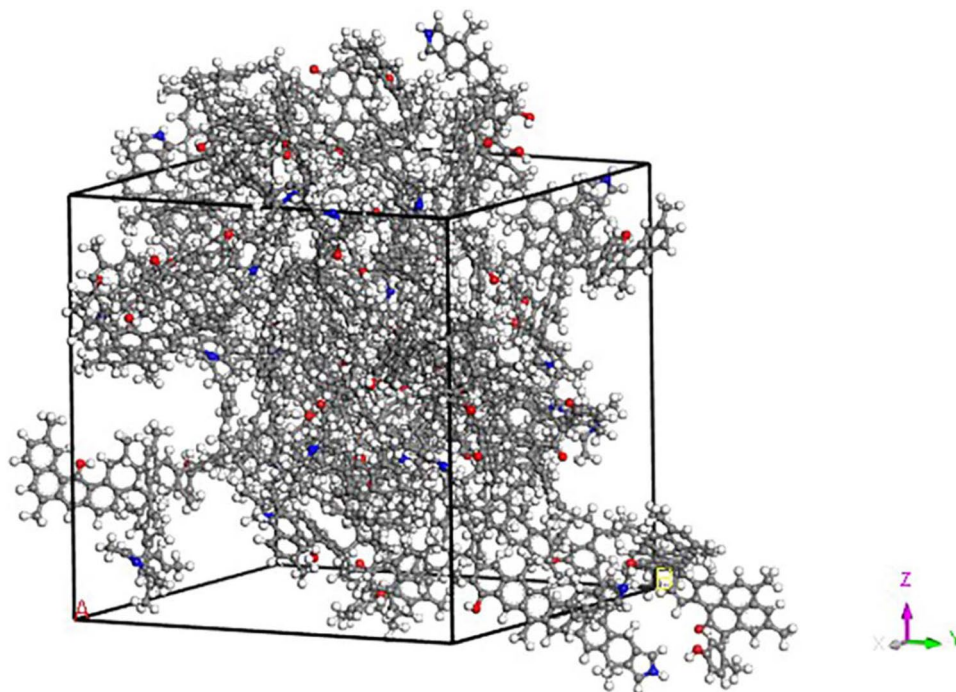| Force field	COMPASS[28]	Charges	Use current
Electrostatic	Ewald[29]	Production	10^6
Van der Waals	Atom based[30]	Step size/fs	1
Canonical ensemble	NPT[31]	Steps total time/ps	1000
Temperature	Nose[32]	Quality	Fine

Table 1. Parameters of molecular dynamics.

Figure 2. Model of coal structure.

Results and analysis

Adsorption isotherm. The adsorption isotherms of coal molecules at temperatures 298, 318, and 338 K for H_2S, CH_4 and N_2 are shown in Fig. 3. It reveals that pressure has a very large effect on the adsorption capacity of coal for the three gases. With the increase in pressure, the adsorption capacity of coal for the three gases first increases rapidly and then slowly. At different temperatures, the adsorption curves of the three gases show similar trend. The temperature affects only the quantity of gas adsorbed, and does not change the trend of its adsorption. Langmuir model (Eq. 2) is followed by adsorption of each gas (Fig. 3)

$$Q = \frac{abp}{1 + bp} \tag{2}$$

Here Q: is adsorption capacity for gas (mmol/g); a, maximum adsorption capacity of coal sample (mmol/g); b, adsorption constant, (MPa^{-1}); p, pressure of gas adsorbed, (MPa).

The fitting constants and correlation coefficients of three gases at different temperatures are shown in Table 2.

Figure 3 shows that at some pressure, the adsorption capacity of coal for H_2S, CH_4 and N_2 decreases with increase in temperature. It can be seen from the above figure, the influence of pressure in the range 0–2 MPa on the adsorption capacity of coal for H_2S, CH_4 and N_2 is greater than influence of temperature on adsorption.

At a pressure of 10 MPa, average reduction rate of adsorption of H_2S, CH_4, and N_2 on coal with rise in temperature is 13, 14, and 20%, respectively. The adsorption of N_2 is most affected by temperature, followed by CH_4 and H_2S. This may be correlated to their critical temperatures which are 212.75, 111.65, and 77 K for H_2S, CH_4 and N_2 respectively. The gas with high critical temperature liquefies easily and is adsorbed on coal matrix[33]. At a particular temperature, repulsion between molecules of H_2S is least and capacity of coal for its adsorption is highest in comparison to those of two other gases investigated here.

In order to analyze the effect of temperature on the adsorption capacity of coal for the three gases, considered Fig. 3. In the initial stage of adsorption, the pressure (up to 2 MPa), shows a large effect on the adsorption capacity
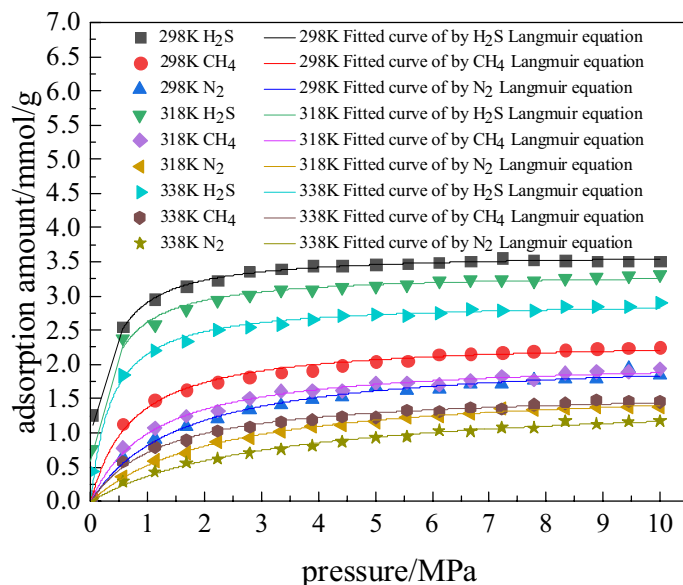
Figure 3. Adsorption isotherms of H$_2$S, CH$_4$ and N$_2$ at different temperatures.

Temperature	298 K			318 K			338 K		
	a	b	R^2	a	b	R^2	a	b	R^2
H$_2$S	3.4521	3.9335	0.9911	3.3149	3.3955	0.9571	2.9157	2.4730	0.9741
CH$_4$	2.3681	1.3745	0.9910	2.0831	0.9086	0.9925	1.6199	0.7844	0.9903
N$_2$	2.1303	0.6227	0.9915	1.7203	0.4394	0.9973	1.5386	0.3120	0.9925

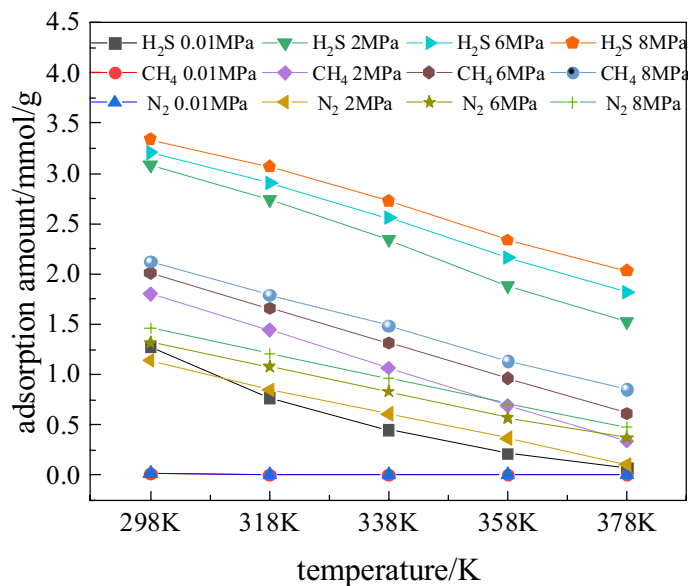**Table 2.** Langmuir parameters of adsorbed gases at different temperatures.

Figure 4. Adsorption capacity of H$_2$S, CH$_4$ and N$_2$: variation with temperature at different pressures.
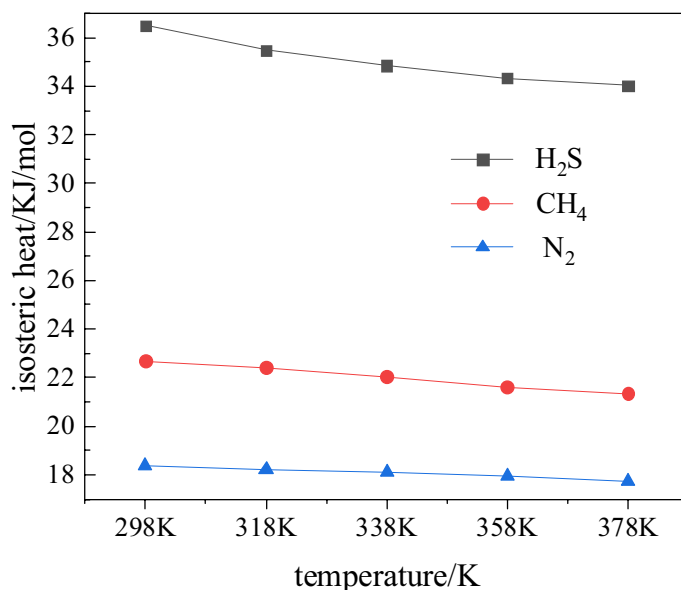
Figure 5. Adsorption heat of H_2S, CH_4 and N_2: Variation with temperature.

Pressure	Van der Waals			Electrostatic energy		
	H_2S	CH_4	N_2	H_2S	CH_4	N_2
0	0	0	0	0	0	0
0.01	265.55	11.50	4.06	36.91	0	0
0.1	482.95	92.24	35.64	66.86	0	0
1	631.27	185.60	103.74	75.37	0	0
2	639.68	247.13	122.13	80.87	0	0
3	653.34	287.69	139.00	82.58	0	0
4	661.94	301.63	147.95	83.06	0	0
5	673.40	308.99	175.25	84.45	0	0
6	695.14	317.50	198.04	86.95	0	0
7	701.58	320.59	205.52	90.40	0	0
8	703.50	325.37	210.41	99.01	0	0
9	707.98	334.87	220.42	100.21	0	0
10	716.17	345.59	227.08	103.91	0	0

Table 3. Van der Waals and electrostatic energy of adsorption of each gas at different pressure.

of the gases, but the effect of temperature on adsorption capacity of coal for the three of gases is not regular. Therefore, the relationship between adsorption capacity and temperature was analyzed at fixed pressures 2, 6 and 8 MPa (Fig. 4). As shown in Fig. 4, in the temperature range 298–378 K and pressure at 2 MPa, the adsorption capacity (mmol/g) of coal for H_2S, CH_4 and N_2 drops by 1.55, 1.43 and 1.04 respectively. At 8 MPa, and in the same temperature range, the capacity (mmol/g) for H_2S, CH_4 and N_2 drops by 1.30, 1.26 and 0.98 respectively. In the pressure range 2-8 M Pa, and at temperature 378 K, adsorption capacity of coal changes by 0.51 mmol/g for H_2S; 0.48 mmol/g for CH_4, and 0.38 mmol/g for N_2. Thus, the temperature also has a high influence on the adsorption capacity of coal for the three gases at pressure beyond 2 MPa.

Isometric heat of adsorption. The heat of adsorption indicates the strength of adsorption. In the adsorption process, gas molecules move towards the surface of coal, and the speed of their molecular motion is reduced greatly, and thus heat is released[34,35]. The relationship between heat of adsorption of H_2S, CH_4 and N_2 with temperature is shown in Fig. 5. The heat decreases with increase in temperature. The average gradients of decrease for H_2S, CH_4 and N_2 are 0.44/20 K, 0.27/20 K, 0.13/20 K, respectively. At 298 K, the heat of adsorption on coal for the three gases H_2S, CH_4 and N_2 is highest, 36.49, 22.67, and 18.38 kJ/mol respectively. As all the heats are less than 42 kJ/mol, the adsorption of H_2S, CH_4 and N_2 on coal is of physical type, which is consistent with the earlier results[14]. From the average gradient of the drop of adsorption heat for the three gases, it can be inferred that the
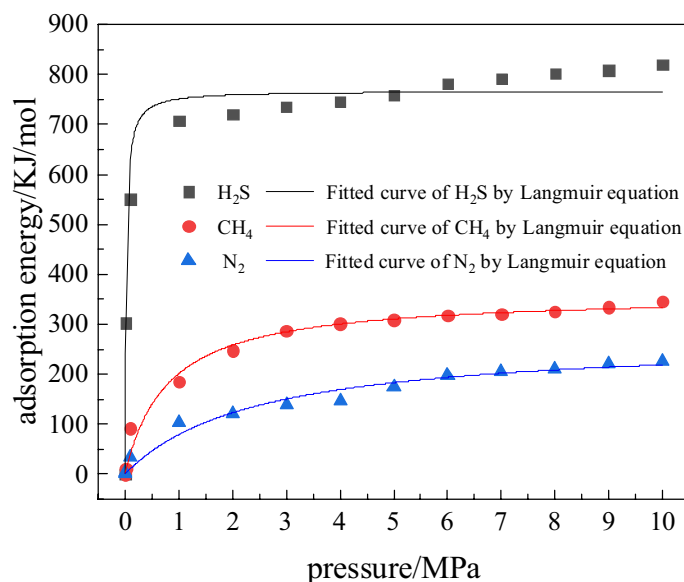
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Figure 6. Adsorption energy of H_2S, CH_4 and N_2: variation with pressure.

	a	b	R^2
H_2S	767.2742	36.1554	0.9661
CH_4	359.6122	1.2760	0.9807
N_2	272.1298	0.4131	0.9721

Table 4. Langmuir parameter of adsorption energy at 298 K.

adsorption heat of H_2S decreases the most as the temperature rises. The amount of H_2S adsorbed is least affected by temperature, thus its adsorption would release more heat than CH_4 and N_2, making adsorption more stable.

Adsorption energy. The adsorption energy referred in this paper includes van der Waals, electrostatic, and intramolecular energies. The intramolecular energy is too small and has been ignored. The van der Waals and electrostatic energy obtained by the simulation are both negative. The numerical value is considered when analyzing the energy strength, thus the absolute value is taken for analysis. Table 3 shows the variation of van der Waals energy and electrostatic energy of adsorption of H_2S, CH_4, and N_2 on coal with pressure at 298 K, and in Fig. 6 also the variation of corresponding adsorption energy with pressure is shown.

It can be seen from Table 3 that with the increase of pressure, van der Waals energy undergoes significant change. When, the pressure increases from 0 to 10 MPa, the van der Waals energy of H_2S, CH_4 and N_2 adsorption on coal increases by 716.17, 345.59 and 227.08 kJ/mol, respectively. Adsorption of H_2S on coal releases small electrostatic energy, while such energy released for CH_4 and N_2 is 0. This is because H_2S and coal (due to functional groups) are polar, and force between them is directional. The CH_4 and N_2 are non-polar molecules, and the force between them and coal depends on dispersion and inducing.

The fitting constants and correlation coefficients of three gases at different pressures are shown in Table 4. It can be seen from Fig. 6 that as the pressure increases the adsorption energy of H_2S, CH_4, and N_2 first increases rapidly, and then tends to flatten. They all follow the Langmuir adsorption model. When the pressure is 0–2 MPa, the adsorption energy shows a rapid growth and is affected most by the pressure. In the pressure range from 2 to 8 MPa, the energy increases slowly. In slow growth stage, the pressure has little effect on the adsorption energy. This is because the pores on the surface of coal matrix are covered by a large amount of gas, and the gas molecules compete with each other for the remaining vacancies, so that the adsorption capacity increases slowly with the pressure, resulting in slow increases in the adsorption energy. At 8–10 MPa pressure, the adsorption tends to get saturated, i.e. equilibrium stage for adsorption is reached, and the pressure has almost no further effect on the adsorption energy. In this pressure range, the adsorption energy of H_2S is highest, followed by CH_4 and N_2, indicating that the adsorption capacity of coal for H_2S is highest. In the pressure range of 0–2 MPa, the adsorption energy of H_2S increases significantly, (by 820.08 kJ/mol), indicating that the pressure has the maximum impact on adsorption of H_2S at its low value.

Effect of water content of coal. The capacity of coal structure model with moisture content of 0, 0.50, 1.18, 2.31, 3.42 and 4.51% for adsorption of H_2S, CH_4 and N_2 has been calculated at 298 K and 8 MPa pressure respectively, using the following formula (Eq. 3) for water content calculation:
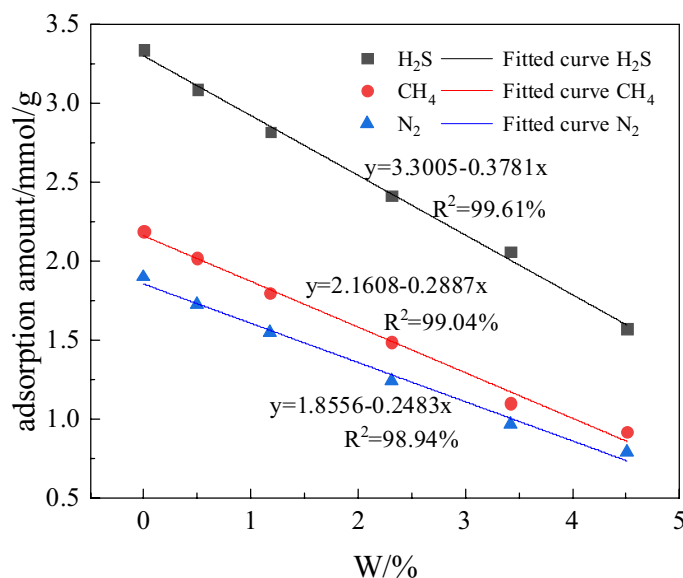
Figure 7. Adsorption of H_2S, CH_4 and N_2: correlation with water present in coal.

$$W = \frac{M_{H_2O}}{M_{coal} + M_{H_2O}} \times 100\% \qquad (3)$$

In the formula, M_{H2O} is the molar mass of water (g/mol); M_{coal} is the molar mass of theoretical coal molecule (g/mol).

When analyzing the influence of water content on gas adsorption capacity, the number of water molecules added to the simulated coal is 0, 9, 20, 40, 60 and 80. The relationship between the adsorption capacity of coal for the three gases and the moisture content is shown in Fig. 7. It can be seen from the Figure that the adsorption capacity of coal for the three gases decreases with increase in its moisture content. After linear curve fitting, it was found that within the given water content range, the adsorption capacity of coal for H_2S, CH_4 and N_2 decreases linearly with the increase in water content. Linear fitting is 99.61, 99.04 and 98.94%, respectively for H_2S, CH_4 and N_2. It is calculated that, 26.61% of free volume of coal structure model is without water, 25.87% with 9 water molecules, 25.29% with 20 water molecules, 24.14% with 40 water molecules, 22.79% with 60 water molecules and 21.56% with 80 water molecules. The increase in the number of water molecules is accompanied by decrease of free volume in coal, which is the main reason for the decrease in adsorption of gas. In the range of water content 0–4.51%, the adsorption capacity of coal for H_2S drops from 3.34 mmol/g at 0% water to 1.57 mmol/g at 4.51% of water. The adsorption capacity for CH_4 drops from 2.19 mmol/g at 0% water to 0.92 mmol/g at 4.51% water, and for N_2 the drop for the same water content range is from 1.90 to 0.79 mmol/g. The amount of H_2S adsorbed is reduced the most. Figure 8 reflects the relationship between the free volume of coal and the moisture content after adsorption of gas. It can be seen from Fig. 8 that the free volume of the coal after adsorption of H_2S is least affected by moisture. Since positions for adsorption of H_2S and water molecules in coal are the same, water replaces H_2S from positions of its adsorption. Therefore, the reduction of free volume and the preemption of adsorption sites by water molecules are the main factors causing reduction in adsorption of H_2S on coal. For CH_4 and N_2, as number of water molecules increases, they occupy free volume, which promotes the competitive adsorption of CH_4 and N_2. Since the radius of the CH_4 molecule is larger than that of water, the coal shows a high adsorption capacity for water due to its molecular structure and water occupies the space meant for adsorption of CH_4, but cannot enter in the space of adsorbed N_2, which has a smaller radius than that of water molecule. Consequently, $\Delta Q_{(CH4)}$ is greater than $\Delta Q_{(N2)}$.

In order to intuitively understand the influence of moisture in coal on its adsorption capacity for the present three gases, Fig. 9 shows the density distribution of the three gases when the pressure is 8 MPa and the water content is 1.18 or 4.51%. When the water content is 1.18%, N_2 is adsorbed sporadically in the coal pores. The H_2S forms more cluster structures in the pores of coal, compared to CH_4, indicating high density of adsorption. The number of coal molecules adsorbing H_2S, CH_4, and N_2 are 90, 60, and 46, respectively. When the water content is 4.51%, N_2 is more dispersed in the coal pores, and H_2S and CH_4 are scattered in the pores, indicating that density of adsorption is reduced. At this time, the number of coal molecules adsorbing H_2S, CH_4, and N_2 are 57, 32, and 27, respectively. It can be concluded that as the water content increases, the adsorption density of the three types of gases decreases. The relationship of adsorption capacity $H_2S > CH_4 > N_2$ is always maintained.

Conclusions

Based on the results of Monte Carlo method applied to study the adsorption characteristics of H_2S, CH_4 and N_2 in the organic structure of coal under different conditions, the following conclusions can be made:
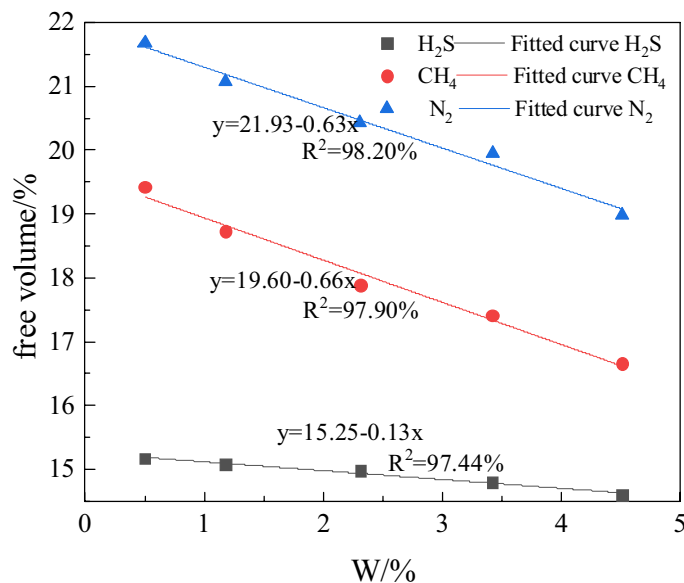
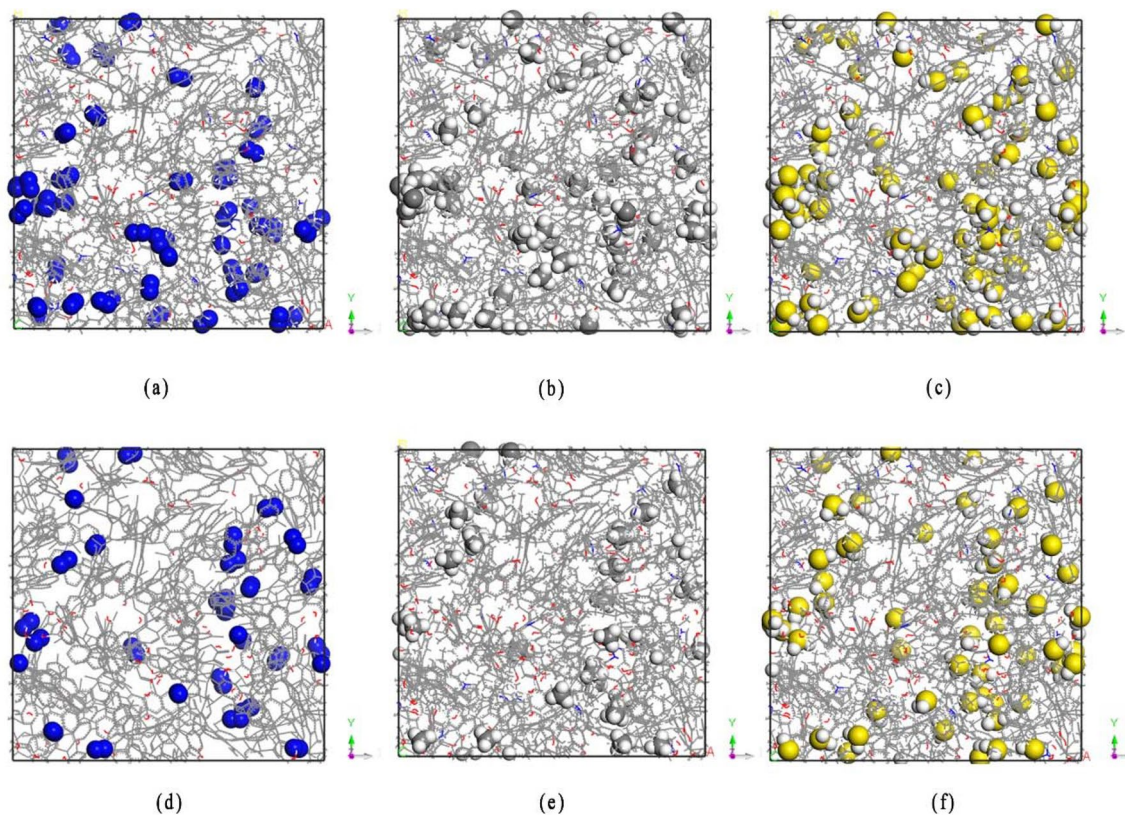**Figure 8.** Free volume in coal of varying moisture content after adsorbing gas.

Figure 9. Density distribution of the gases, when content of water in coal is 1.18 or 4.51%. (**a**) N_2,1.18%, (**b**) $CH_4$1.18%, (**c**) H_2S, 1.18%, (**d**) N_2, 4.51%, (**e**) CH_4, 4.51%, (**f**) H_2S, 4.51%.

1. The adsorption isotherms of H_2S, CH_4 and N_2 follow Langmuir model. If pressure is in the range 0-2 MPa, the adsorption capacity of coal for the three gases is more influenced by pressure than temperature. Beyond 2 MPa, the temperature exerts greater influence on the adsorption capacity of coal for these gases than the pressure. When the pressure is the same, the adsorption capacity of coal for the three gases decreases with increase in temperature. The influence of temperature on the adsorption capacity of coal is maximum for N_2, followed by CH_4 and H_2S.

2. The heat of adsorption of the three gases decreases with the increase in temperature, and for H_2S it drops the most. The amount of H_2S adsorbed changes the least with the increase in temperature, indicating that the H_2S adsorbed coal is stable. At 298 K, the heat of adsorption of H_2S, CH_4, and N_2 respectively are 36.49, 22.67 and 18.38 kJ/mol.

3. In the pressure range ~ 0–10 MPa, the adsorption energy of H_2S is followed by that of CH_4 and N_2. The low pressure has the greatest impact on the adsorption energy of H_2S.

4. At a fixed pressure and temperature, as the number of H_2O molecules increases, the free volume in the coal decreases proportionally and linearly. The adsorption capacity of coal for the three gases also decreases linearly. The change in the amount of H_2S adsorbed is 1.77 mmol/g. The linear decrease in the free volume and preferential occupation of adsorption sites by water molecules are the main reasons for the largest change in the amount of H_2S gas adsorbed.

References

1. Fu, X. H., Liu, A. H., Wang, K. X. & Shen, J. Prevention and origin of exceptional deleterious gas compositions in coal mine. *Procedia Eng.* **26**, 424–430 (2011).
2. Deng, P., Cheng, B., Yang, S. & Peng, M. H. Research progress on the determination method of hydrogen sulfide content in underground coal seams. *Coal Mine Saf.* **50**(5), 172–175 (2019).
3. Zhang, S. N. Talking about the formation mechanism and comprehensive prevention measures of hydrogen sulfide in coal mines. *Energy Energy Conserv.* **3**, 67–68 (2017).
4. Mao, D. Q. & Hu, C. Y. The cause and prevention technology of hydrogen sulfide in coal mines. *Sci. Technol. Inf.* **24**, 264–269 (2008).
5. Liu, M. J. *et al.* Discussion on the genetic types of hydrogen sulfide gas in coal mines. *J. China Coal Soc.* **36**(6), 978–983 (2011).
6. Deng, Q. G. *et al.* Research advances of prevention and control of hydrogen sulfide in coal mines. *Sci. World J.* **18**, 8719260 (2019).
7. Deng, Q. G., Liu, M. J., Cui, X. F. & Wen, J. J. Research on the genesis of hydrogen sulfide gas in coal mines in the southeastern margin of Junggar Basin. *Earth Sci. Front.* **24**(5), 395–401 (2017).
8. Tang, W. S. Study on comprehensive treatment technology of hydrogen sulfide in Longmenxia North Mine. *China Coal* **42**(12), 111–114 (2016).
9. Machel, H. G., Krouse, H. R. & Sassen, R. Products and distinguishing criteria of bacterial and thermochemical sulfate reduction. *Appl. Geochem.* **10**(4), 373–389 (1995).
10. Cai, C. F. *et al.* Distinguishing Cambrian from Upper Ordovician source rocks: evidence from sulfur isotopes and biomarkers in the Tarim Basin. *Org. Geochem.* **40**(7), 755–768 (2009).
11. Zhu, G. Y., Zhang, S. C., Liang, Y. B. & Dai, J. X. The origin and prediction of high H_2S content in natural gas. *Chin. J. Geol.* **4**(1), 152–157 (2006).
12. He, Y., Fu, X. H. & Lu, L. Analysis of factors affecting the adsorption of H_2S by different coal ranks. *Coal Mine Saf.* **46**(11), 149–151 (2015).
13. He, Y., Fu, X. H. & Lu, L. Analysis of the difference in the adsorption of H_2S, CH_4 and N_2 by coal. *Chin. Sci. Technol. Pap.* **11**(15), 1775–1777 (2016).
14. Liang, B., Qu, R., Sun, W. J., Jia, L. F. & Shi, Z. S. Quantum chemical analysis of H_2S gas adsorption characteristics on coal surface. *J. Liaoning Tech. Univ.* **35**(11), 1193–1197 (2016).
15. Xue, J. Z., Fu, X. H., Wu, J. H. & Ding, Y. M. Adsorption characteristics of H_2S gas in coal mine gas and its influence on governance. *Geol. Prospecting* **53**(3), 609–614 (2017).
16. Xue, J. Z., Fu, X. H., Fan, C. J. & Song, D. Y. The adsorption difference and adsorption model of H_2S gas by different coal rank coals. *Coal Field Geol. Explor.* **44**(6), 75–78 (2016).
17. Skoczylas, N., Pajdak, A., Kudasik, M. & Braga, L. T. P. CH_4 and CO_2 sorption and diffusion carried out in various temperatures on hard coal samples of various degrees of coalification. *J. Nat. Gas Sci. Eng.* **81**, 103449 (2020).
18. Hou, J., Wu, J. & Zhou, K. Distinct performance characters and inducing mechanisms of CO_2 and N_2 enhanced coalbed methane recovery. *Int. J. Oil Gas Coal Technol.* **11**(2), 204–227 (2016).
19. Gao, D. M., Hong, L., Wang, J. R. & Zheng, D. Molecular simulation of gas adsorption characteristics and diffusion in micropores of lignite. *Fuel* **269**, 117743 (2020).
20. Ma, L., Li, Z. B., Deng, J., Li, B. & Hu, A. P. Study on the adsorption characteristics of N_2/CO_2/CH_4 single component gas by coal under normal pressure. *J. Saf. Environ.* **15**(2), 64–67 (2015).
21. Wu, S. Y., Deng, C. B. & Wang, X. F. Molecular simulation of flue gas and CH_4 competitive adsorption in dry and wet coal. *J. Nat. Gas Sci. Eng.* **71**, 102980 (2019).
22. Wu, S. Y., Jin, Z. X. & Deng, C. B. Molecular simulation of coal-fired plant flue gas competitive adsorption and diffusion on coal. *Fuel* **239**, 87–96 (2019).
23. Gao, D. M., Wang, J. R., Hong, L. & Zheng, D. The characteristics of gas adsorption in micropores and its influence on coal and gas outburst. *Fresenius Environ. Bull.* **28**(12), 9443–9451 (2019).
24. Zhang, S. J., Li, C. W., Ding, C. & Zhang, H. Coal surface molecular fragment model and gas adsorption molecular mechanics simulation. *Mining Res. Dev.* **30**(1), 88–91 (2010).
25. Xiang, J. H., Zeng, F. G., Liang, H. Z., Li, B. & Song, X. X. Molecular simulation of the adsorption of CH_4/CO_4/H_2O in the molecular structure of coal. *Sci. China Earth Sci.* **44**(7), 1418–1428 (2014).
26. Gao, D. M., Hong, L., Wang, J. R. & Zheng, D. Adsorption simulation of methane on coals with different metamorphic grades. *AIP Adv.* **9**, 095108 (2019).
27. Li, Y. G. Coal HRTEM image processing technology based on neural network. *Coal Technol.* **38**(8), 167–170 (2019).
28. Zhang, K. F. *et al.* Molecular simulation of the adsorption characteristics of methane in Zhaozhuang 3# coal. *Chin. Sci. Technol. Pap.* **15**(1), 94–99 (2020).
29. Li, S. G. *et al.* Molecular simulation of adsorption of gas in coal slit model under the action of liquid nitrogen. *Fuel* **255**, 115775 (2019).
30. Karasawa, N. & Goddard, W. A. Force fields, structures, and properties of polyvinylidene fluoride crystal. *Macromolecules* **25**, 7268 (1992).
31. Li, S. G. *et al.* Molecular dynamics study of CO_2 sorption and transport properties in coal. *Fuel* **177**, 53–62 (2016).
32. Nosé, S. Constant temperature molecular dynamics methods. *Prog. Theor. Phys. Suppl.* **103**, 1 (1991).
33. Jin, S. Q. *et al.* H_2S management in 15 # coal seam of Fenghuangshan coal mines. *Procedia Eng.* **26**, 1490 (2011).

34. Liu, Z. X. & Feng, Z. C. Theoretical study on adsorption heat of methane in coal. *J. China Coal Soc.* **37**(4), 647–653 (2012).
35. Zhou, F. *et al.* Effects of coal functional groups on adsorption microheat of coal bed methane. *Energy Fuels* **29**, 150218104145002 (2015).

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Competing interests
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