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Research on the Optimization for Acidification Modification Scheme Considering Coal's Wettability Based on the AHP−TOPSIS Method

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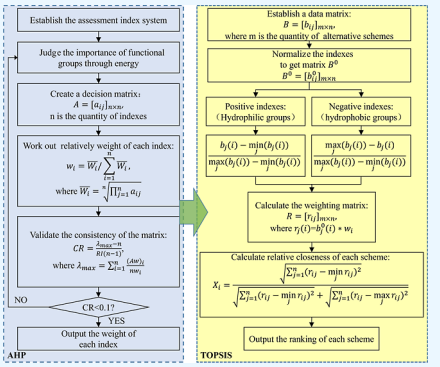
ABSTRACT: Acidification technology is an important measure for enhancing the extraction of coalbed methane from seams with low permeability and abundant minerals, and the acidification scheme is the key to the success of acidification treatment. To determine the optimal acidification modification scheme, an improved AHP−TOPSIS method is proposed to decide on the optimal conditions for wettability modification. This method constructs an evaluation index system, taking the wettability of coal as the target layer and the pro/hydrophobic functional groups in coal as the index layer. Meanwhile, it innovatively takes the adsorption energy of each functional group when absorbing a single water molecule as the basis for assigning weights to the evaluation indexes. Then, nine acidification modification schemes are evaluated and selected by the improved AHP−TOPSIS method based on the test results of different schemes to get the optimal one. The optimal scheme selected by the AHP−TOPSIS method is validated by water adsorption tests and isothermal adsorption tests. The results showed that the significance of each evaluation index is ranked as follows: aromatic structures > hydroxyl groups > aliphatic functional groups > oxygen-containing functional groups. The optimal acidification modification scheme is selected by the AHP−TOPSIS method with a HF concentration of 4% and a reaction time of 6 h. The ranking of acidification modification schemes obtained by the AHP−TOPSIS method is in high agreement with the ranking of water adsorption tests. When compared with raw coal, the coal samples treated with the optimal scheme have lower adsorption capacity for gas, which indicates that the aforementioned method could be used to evaluate and select the optimal acidification modification scheme, and the selected optimal scheme has the potential to increase the output of coalbed methane.



1. INTRODUCTION

Coalbed methane (CBM) is an unconventional natural gas found in abundant reserves in China and is regarded as both a kind of harmful gas which may lead to gas accidents in coal mines and a clean energy with a high calorific value.[1−4] Realizing efficient extraction of CBM is one of the ways to prevent gas accidents and guarantee diversified energy supply. However, coal seams in China generally have characteristics such as poor permeability, low porosity, and complex geological conditions, which make the extraction of CBM difficult.[5−8] Therefore, how to improve the permeability of seams has been the key factor to enhance the extraction of CBM in China.

In the past decades, physical permeability improvement measures, such as hydraulic fracturing, hydraulic punching, and hydraulic slitting, had been widely used in CBM mining, and they all played a positive role in increasing the permeability of seams and reducing impact ground pressure.[9−12] However, in long-term practice, it is found that hydraulic permeability enhancement measures are difficult to form cross-link networks in rich-mineral seams with low permeability and cannot deal with the minerals filled in seams.[13,14] Acidification technology, which could improve the permeability of reservoirs through injecting acid solvent to dissolve minerals, has been widely used in the field of oil and shale gas to increase their production.[15−17] Drawing on the application of acidification technology in other fields, some researchers did some acidification experiments in the field of CBM extraction and found that acidification technology could be used in seams to dissolve minerals, unblock the pore fracture, and convert the structure of coal, thereby changing its physical and chemical properties. Zha et al.[18] treated coal samples with different acid solvents and found that the content of minerals in coal reduced substantially and the permeability increased after acidification. Balucan et al.[19] treated coal with HCl and found that the acid solution could dissolve minerals, thereby improving the porosity and permeability of coal and making the flow paths of gas smoother. Zhang et al.[20] found that the active organic part in coal could react in acid solvent, thereby changing the surface chemical properties of

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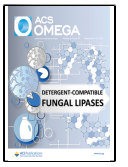

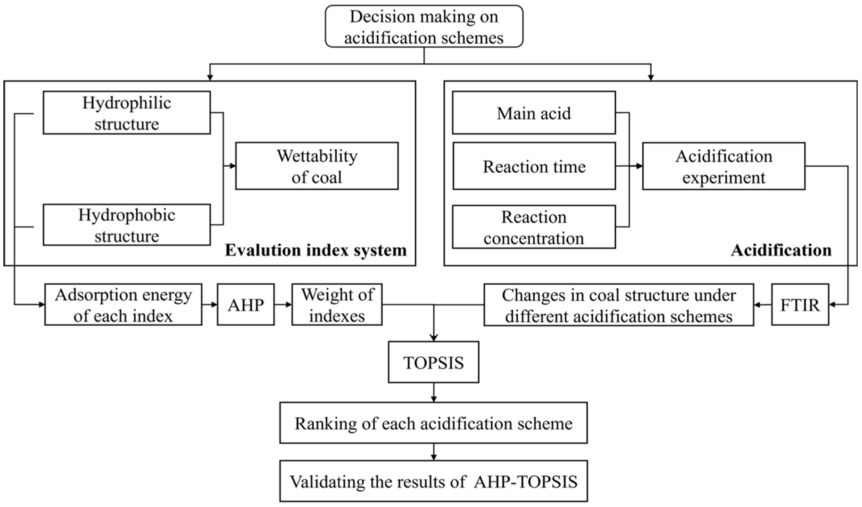

Figure 1. Analysis process of the improved AHP−TOPSIS method.

coal, improving the wettability of coal, and inhibiting the adsorption of methane.

Nevertheless, studies showed that acidification technology in seams depends on the acidification scheme and using acidification technology blindly may harm the seams.[21,22] An acidification scheme that matches the geological conditions of the reservoir could improve permeability and enhance production while an inappropriate acidification scheme may lead to reservoir damage, which will result in seepage channel blockage and even output reduction.[23,24] In recent years, the determination of optimal acidification conditions generally relies on pore measurement tests in laboratory to obtain the pore structure parameters of coal samples under different acidification schemes. Therefore, these schemes can be evaluated and selected by comparing their effects on the pore structure of coal samples. Wang et al.[25] tested the changes of pore structures in coal samples before and after acidification and then selected the optimal acidification conditions through the pore parameters. Xun et al.[26] reported the changes of microstructures in coal samples under the acid−heat coupling conditions with the help of piezometric mercury and scanning electron microscopy-energy dispersive spectrometry and then selected the optimal acidification conditions according to the results of experiments. Yu et al.[27] determined the optimal acidification concentration and reaction time by observing the changes in surface morphology on coal samples under different acidification conditions. Yet, the measures mentioned above for determining the optimal acidification scheme are difficult, time-consuming, and not able to show the effects of acidification fully, which may result in deviating from the ideal scheme.

Multi-attribute decision making methods are widely used in energy, environmental protection, healthcare, and other fields. It could use the mathematical comparison logic to integrate and analyze multiple attributes that are difficult to measure and create conflict with each other so that the alternative schemes could be evaluated and ranked.[28,29] Li et al.[30] transformed experts' judgment on the safety risks of coal mine into the weights for the evaluation indexes related to coal mine safety using the fuzzy analytic hierarchy process (FAHP) and then used these indexes and their weights to evaluate the safety risks of the local coal mine. Khojastehmehr et al.[31] analyzed the oil production enhancement technologies in different situations and selected the best one using the technique for order preference by similarity to ideal solution (TOPSIS) method. To sum up, using multi-attribute decision making methods correctly could simplify the steps of optimization and transform complex parameters into an intuitive index for the decision-makers to choose a scheme.

To solve these problems discussed above, an improved AHP−TOPSIS method is proposed in this paper to select the optimal acidification wettability modification scheme. This method constructs an evaluation index system on the basis of functional groups affecting the wettability of coal and weighs all indexes based on their adsorption energies of adsorbing a single water molecule using the AHP method. Finally, it comprehensively evaluates each scheme using the TOPSIS method to get the optimal scheme. In this paper, we validate the feasibility and potential of the selected optimal scheme through experiments. This research analyzes the effects of acid on functional groups in coal with Fourier transform infrared spectroscopy (FTIR) tests and explores the mechanism of functional groups affecting the wettability of coal. Moreover, it provides a new method to determine the optimal acidification modification scheme, which is relatively quick and accurate.

2. TESTS AND METHODS

2.1. Coal Samples' Collection and Preparation. The experimental coal samples are one-third coking coal taken from 12# coal seam on the upper part of the 11,202 back mining face of the Zhongzhichang coal mine in Panzhou city, Guizhou Province, China. The pieces of coal were wrapped with a cling film and sent to the laboratory for crushing and screening immediately after being taken from the fresh exposed mining face. Then the coal samples with particle sizes ranging from 0.18 to 0.25 mm were selected for isothermal adsorption experiment. Besides, the coal samples used in the X-ray diffraction (XRD) and FTIR analyses required them to be less than 0.078 mm in size.

2.2. Scheme Selection Method. To get the optimal acidification wettability modification scheme, an improved AHP−TOPSIS method is proposed to analyze and evaluate these schemes. The analytical process is shown in Figure 1.

2.2.1. Evaluation Indexes. Wettability is an inherent physicochemical property of coal, which not only shows the hydrophilicity of coal but also reflects the occurrence and migration of CBM in seams.[32] Therefore, the wettability of coal

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ACS Omega 2023, 8, 32667−32676

is picked up as the target layer of the evaluation index system. It is universally acknowledged that the function of things is determined by its structure, so the wettability of coal is determined by the distribution of functional groups in its surface.[33] Therefore, the contents of pro/hydrophobic functional groups, which have huge influence on the wettability of coal, were picked up as positive/negative evaluation indexes with reference to previous studies. The former includes hydroxyl and oxygen-containing functional groups, and the latter includes aromatic structures and aliphatic functional groups.[34−36] The evaluation index system is shown in Figure 2.

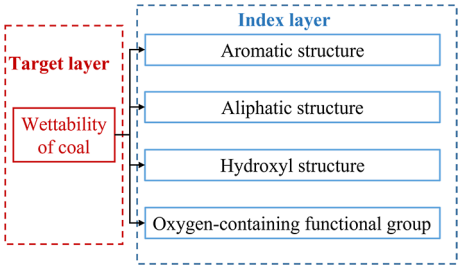

Figure 2. Evaluation index system.

2.2.2. Steps of the AHP−TOPSIS Method. AHP method is a mathematical model created by Saaty et al. in the 1970s, which is often used in the decision-making process.[37] The AHP method is based on pairwise comparisons and could express the importance of each index numerically through scale table (Table 1).[38]

Table 1. Scale and Its Meaning in Judgment Matrix

Scale	Linguistic scale of importance
1	A_i is as important as A_j
3	A_i is slightly more important than A_j
5	A_i is more important than A_j
7	A_i is strongly more important than A_j
9	A_i is absolutely more important than A_j
2,4,6,8	intermediate value of the two adjacent scales above

TOPSIS, created by Hwang and Yoon originally, is a widely used method in multi-attribute decision making.[39] The TOPSIS method is based on a distance idea and can evaluate the alternative schemes according to their distance. It requires the optimal scheme to be the nearest to the positive ideal solution (PIS) and the farthest from the negative ideal solution (NIS). Therefore, alternative schemes can be evaluated and ranked using the TOPSIS method. The steps of the improved AHP−TOPSIS method are shown in Figure 3.

In Figure 3, the final score $X_i = \frac{d_i^-}{d_i^- + d_i^+}$ is the score of the ith scheme, and the higher the score, the better the evaluation scheme; d_i^- and d_i^+, respectively, represent the Euclidean distance between the ith scheme and the positive/negative ideal solution; RI is the random consistency index, and its values for matrices of order 1−10 are shown in Table 2.[40] The consistency is considered to be passed when CR < 0.1, otherwise the decision matrix needs to be designed again.

The hydrophilic/hydrophobic functional groups in coal are the key factors affecting the wettability of coal and can illustrate the effects of acidification wettability modification. To reduce the deviation caused by subjective judgment when using the AHP method, the adsorption energies of functional groups adsorbing a single water molecule are innovatively taken as the quantitative basic to judge the significance of each functional group.

Since it is difficult to get the adsorption energy through experiments, we mean to calculate the adsorption energy using the Guassian 09W program. Considering the complexity of the coal structure, it is too hard to calculate the adsorption energy of all functional groups in coal, so the calculation and analysis processes need to be simplified. For this reason, functional groups, which have huge influence on the wettability of coal, are summarized and divided into four parts mentioned above. Additionally, the four main parts are further simplified and symbolized with a kind of specific and typical functional group. In this process, the graphite lamellae, which is commonly used as a simplified coal molecular model for simulation, is further simplified to benzene, and each functional group is considered to connect with benzene directly.[41,42] Besides, previous studies showed that the methyl group is the most important structure factor among aliphatic functional groups affecting the wettability of coal, so the aliphatic functional groups are simplified to the methyl group.[43]

Density functional theory (DFT) was used in the Gaussian 09W program to simulate the adsorption of water molecules by the functional groups, and the equilibrium configurations and the adsorption energy were analyzed and calculated at the B3LYP/6-311G++(d,p) level. The adsorption energy calculation equation is shown below.[44,45]

$$E_{ad} = E_{B\text{-}R} + E_{water} - E_{System} \quad (1)$$

where E_{ad} is the adsorption energy (kcal/mol); $E_{B\text{-}R}$ is the total energy of coal structure(kcal/mol); E_{water} is the energy of a single water molecule (kcal/mol); and E_{System} is the energy of the whole adsorption system(kcal/mol). The higher the abs(E_{ad}), the stronger the adsorption capacity of this thing is.

2.3. Experimental Methods. XRD experiment was carried out to get the mineral content in coal and then determine the main acid according to the reaction mechanism between minerals and acid solution. Next, different acidification modification schemes were carried out on coal samples after washing and drying them. Then, FTIR experiments were carried out to obtain the changes of functional groups so that the effects of different acidification modification schemes on wettability can be revealed and analyzed. Finally, water adsorption and isothermal adsorption experiments were conducted to validate the improvement of wettability and the enhancement potential of gas extraction under the selected scheme. The process of these experiments is shown in Figure 4.

2.3.1. XRD Test. XRD tests were performed using an X'Pert PRO X-ray diffractometer produced by Panaco, the Netherlands. During the measurement process, the voltage and the current were 40 kV and 200 mA, respectively, and the scanning speed was set to 10°/min (range 10 to 80°).

The result of the XRD test was imported into the MDI jade 6.0 program to obtain the spectra of raw coal, as shown in Figure 5. Then phase search and semiquantitative analyses were carried out on the spectra of coal samples to get the minerals content, as shown in Table 3.

2.3.2. Acidification on Coal Samples. According to Table 3, the silicate mineral content of the coal sample is relatively high, accounting for about 94.7%, while the carbonate mineral content is relatively low, accounting for about only 5.3%.

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ACS Omega 2023, 8, 32667−32676

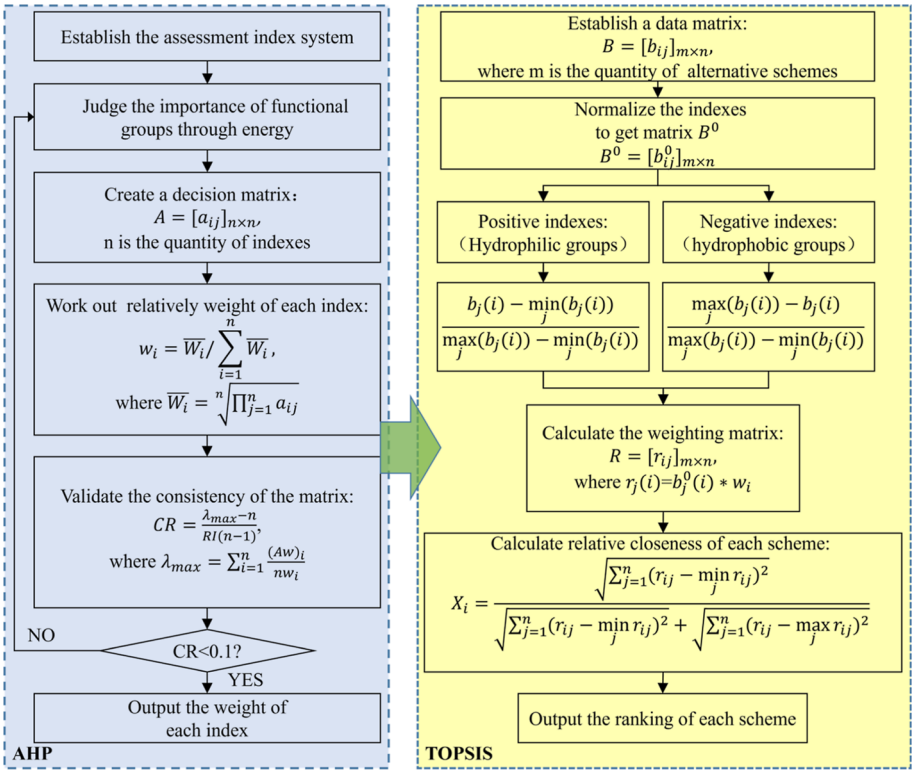

Figure 3. Steps of the AHP−TOPSIS method.

Table 2. Values of the Random Consistency Index

n	1	2	3	4	5	6	7	8	9	10
RI	0	0	0.58	0.9	1.12	1.24	1.32	1.41	1.45	1.49

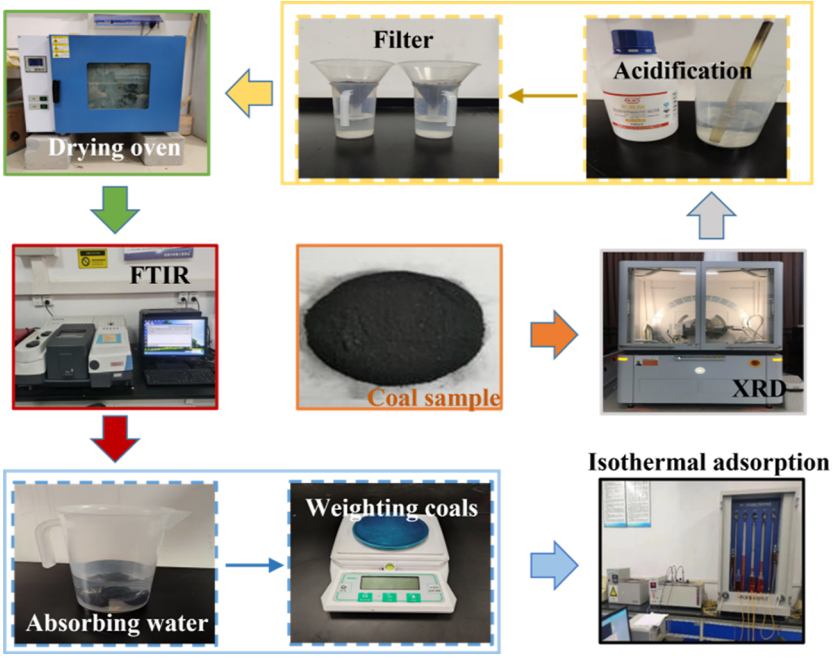

Figure 4. Experimental process.

Therefore, it is recommended to use HF as the main acid for acidification experiments.

Both acid concentration and reaction time are the key factors that affect the wettability of coal in the acidification process, and they are convenient to control. Thus, we focused on the two factors to pick up the optimal acidification modification scheme in this paper. The concentration is set to 2, 4, and 6%,

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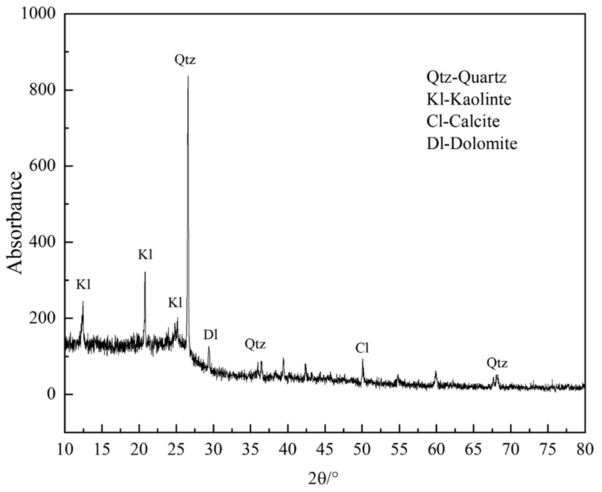

Figure 5. XRD spectrum of raw coal.

Table 3. Mineral Components of Coal Samples

Mineral type	Quartz	Kaolinite	Calcite	Dolomite
Relative content (%)	64.8	29.9	5.2	0.1

respectively, and the reaction time is set to 6, 12, and 24 h in sequence.

To represent each scheme intuitively, the coal samples under different schemes were numbered in the form of acid concentration−reaction time. The designed acidification schemes are shown in Table 4.

2.3.3. FTIR Tests. FTIR tests were performed using a Nicolet 6700 Fourier transform infrared spectrometer, as shown in Figure 4. In this process, the coal particles were mixed with dried KBr in a homogeneous ratio of 1:100, and then the mixture was pressed into flakes at 12 MPa. Finally, the flaky coal samples were placed in the instrument for measurement.

This instrument has a scanning wavelength range of 400−4000 cm^{-1} with a working resolution of 4 cm^{-1}, and 32 scans are accumulated per measurement.

2.3.4. Water Adsorption Test. To validate the results of the AHP−TOPSIS method, saturated water adsorption of coal samples was measured separately to represent wettability of coal samples under different acidification schemes by referring to Part V Measurements of Water Adsorption of Coal and Rock in the national standard GB/T 23561. In this process, three coal samples were measured in a single water adsorption test, and the average value was taken as the final saturated water adsorption rate. The calculation equation of saturated water adsorption rate is shown in eq 2.

$$\omega = \frac{M_0 - M_1}{M_0} \quad (2)$$

where ω is the saturated water adsorption rate, %; M_0 is the mass of the dry coal samples, g; M_1 is the mass of the saturated coal samples, g.

2.3.5. Isothermal Adsorption Test. The isothermal adsorption experiments were conducted using an HCA-1 high-pressure volumetric gas adsorption device to validate the enhancement potential of the optimal scheme. The test temperature was 303.15 K, and the adsorbate was 99.99% methane gas. There are six equilibrium pressure points in this test, and it is considered to be the adsorption equilibrium when the methane pressure does not change by more than 0.01 MPa within 0.5 h.

3. RESULTS AND DISCUSSION

3.1. Results and Analysis of FTIR Tests. The results of FTIR tests under different acidification schemes are shown in Figure 6.

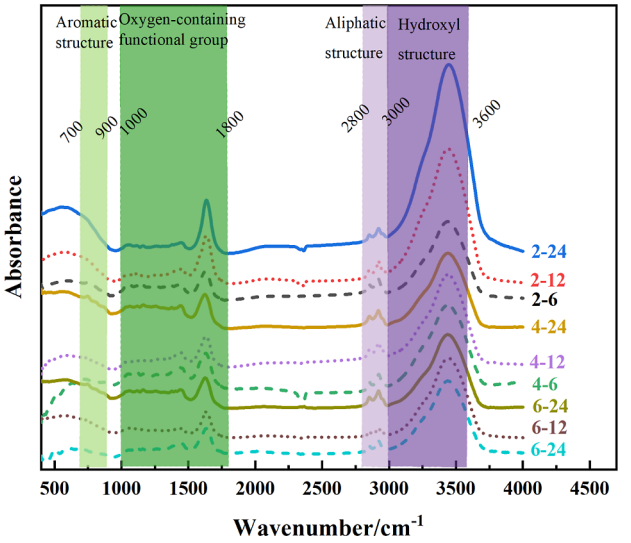

Figure 6. Infrared spectra of experimental coal samples under different acidification schemes.

As shown in Figure 6, we can see that the positions of adsorption peaks in FTIR spectra under different acidification conditions are almost identical while the shapes of those peaks are different, which implies that acidification could affect the wettability of coal by controlling the contents of functional groups.

To further explore the changes of the four functional groups affecting the wettability greatly, the FTIR spectra of coal samples were divided into four parts based on the attribution of functional groups: aromatic adsorption region (700−900 cm^{-1}), oxygen-containing functional group adsorption region (1000−1800 cm^{-1}), aliphatic functional group adsorption region (2800−3000 cm^{-1}), and hydroxyl structure adsorption region (3000−3600 cm^{-1}).[46,47] Then, the Peakfit v4.12 program was used to calculate the peak area ratio of each functional group, and the results are shown in Table 5.

3.2. AHP−TOPSIS Analysis. *3.2.1. Weight Calculation.* The water molecule structure and benzene ring structure (B) were constructed in the GaussView program, and the typical functional group (−CH_3, −OH, −COOH, −CHO, and

Table 4. Acidification Schemes' Design

Scheme	2−6	2−12	2−24	4−6	4−12	4−24	6−6	6−12	6−24
Concentration	2%	2%	2%	4%	4%	4%	6%	6%	6%
Time	6 h	12 h	24 h	6 h	12 h	24 h	6 h	12 h	24 h

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Table 5. Proportion of Corresponding FTIR Absorption Peak Areas of Functional Groups in Coal Samples under Different Acidification Schemes

Scheme	2−6	2−12	2−24	4−6	4−12	4−24	6−6	6−12	6−24
Aromatic structure	10.84%	5.24%	6.21%	3.30%	5.91%	8.89%	13.19%	3.80%	6.13%
Aliphatic functional group	18.64%	26.19%	16.80%	22.46%	40.94%	12.36%	27.35%	20.40%	22.28%
Hydroxyl structure	45.34%	45.01%	52.34%	57.03%	65.20%	66.40%	48.67%	54.48%	62.07%
Oxygen-containing functional group	25.18%	23.56%	24.65%	17.21%	28.90%	12.36%	10.79%	21.32%	9.52%

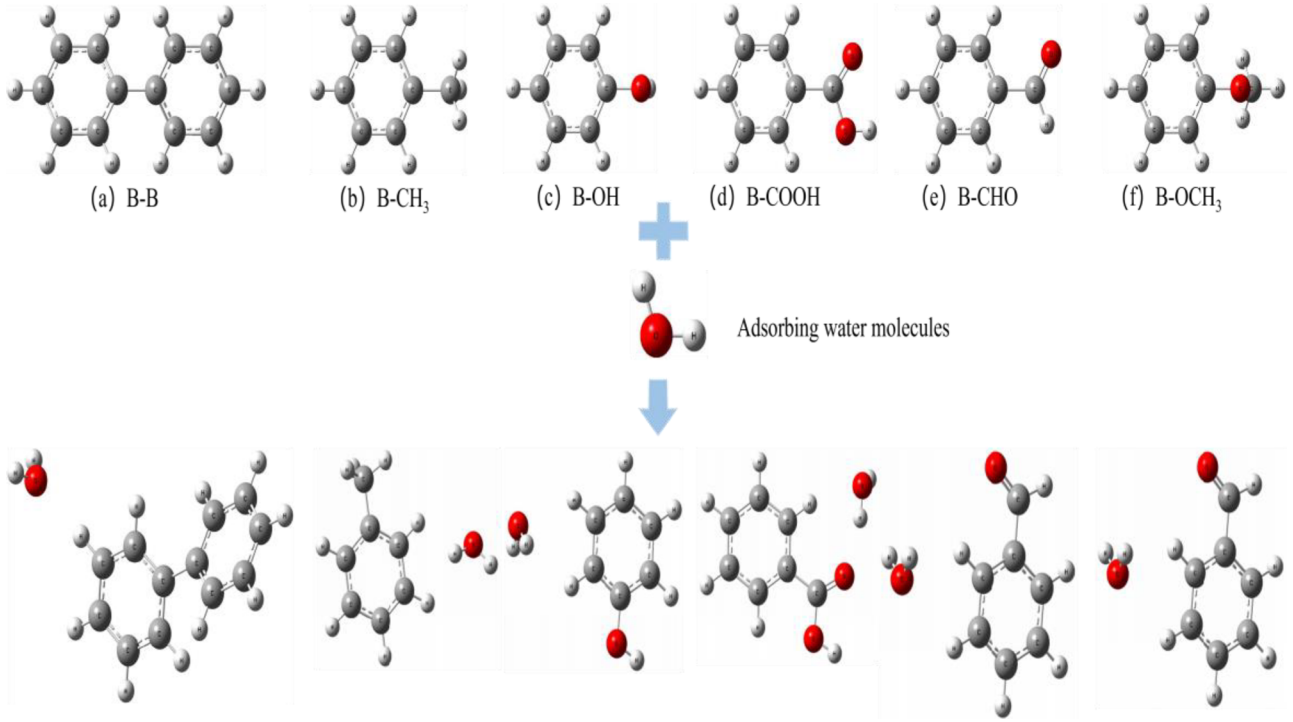

Figure 7. Equilibrium configuration of functional groups when adsorbing water molecules.

Table 6. Energy of Functional Groups When Adsorbing Water Molecules in Equilibrium

Coal structure	$E_{B\text{-}R}$/(kcal/mol)	E_{water}/(kcal/mol)	E_{System}/(kcal/mol)	E_{ad}/(kcal/mol)
B−B	−290727.68	25426.48	−338688.82	−22534.73
B−CH_3	−170408.85	25426.48	−218364.10	−22528.70
B−OH	−192932.03	25426.48	−240891.29	−22532.78
B−COOH	−264062.25	25426.48	−312024.14	−22535.42
B−CHO	−216845.02	25426.48	−264731.99	−22460.49
B−OCH_3	−217593.89	25426.48	−265552.27	−22531.90

Table 7. Judgment Matrix of the Paired Comparison Indicator

Project	Oxygen-containing functional group	Aliphatic structure	Hydroxyl structure	Aromatic structure
Oxygen-containing functional group	1	1/7	1/8	1/9
Aliphatic structure	7	1	1/3	1/4
Hydroxyl structure	8	3	1	1/2
Aromatic structure	9	4	2	1

−OCH_3) was attached to the benzene ring to obtain biphenyl (B−B), methylbenzene (B−CH_3), phenol (B−OH), benzoic acid (B−COOH), benzaldehyde (B−CHO), and anisole (B−OCH_3). Furthermore, those structures were put into the Gaussian 09W program to obtain the equilibrium configurations shown in Figure 7.

By putting the energy data calculated by Gaussian 09W into eq 1, the adsorption energy of each coal structure can be obtained, as shown in Table 6.

As can be seen in Table 6, the adsorption energies of functional groups are different when they are in equilibrium with a single water molecule. Besides, the oxygen-containing functional groups (including the ether bond, carboxyl group, and aldehyde group) are regarded as a whole in this paper, so the average of these three is taken as the adsorption energy of oxygen-containing functional groups, which is −22509.19(kcal/mol).

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ACS Omega 2023, 8, 32667−32676

Table 8. Final Score Values of Different Acidification Schemes

Project	2−6	2−12	2−24	4−6	4−12	4−24	6−6	6−12	6−24
d_i^+	0.4924	0.3403	0.2561	0.1503	0.1993	0.2826	0.5690	0.1843	0.1683
d_i^-	0.1686	0.4077	0.3895	0.5372	0.4747	0.4123	0.0894	0.5043	0.4470
X_i	0.2551	0.5450	0.6033	0.7813	0.7044	0.5933	0.1358	0.7324	0.7265

The adsorption energy difference between two functional groups is considered as the basis for deciding a matrix in this paper, and the rules for judging the importance are as follows: the importance of each functional group compared with itself is regarded as 1 and then the minimum value of adsorption energy difference among functional groups is taken and set as t. Therefore, the importance of the functional group with a larger energy value relative to the smaller one is 1+abs(ΔE)/t. The importance of the functional group with smaller energy relative to the larger one is 1/[1+abs(ΔE)/t]. According to the rules above, the decision matrix can be obtained, as shown in Table 7.

According to Table 7, AHP analysis was performed to obtain the weights of functional groups (aromatic structure, hydroxyl group, aliphatic functional group, and oxygen-containing functional group), which are 0.4972, 0.3177, 0.1492, and 0.0360, respectively. Then the consistency test was carried out, as shown in Table 7, and the value of CR is 0.0641 (<0.1), which indicates the passing of consistency test.

3.2.2. Acidification Scheme Evaluation. By putting the weights and FTIR data of each functional group into the AHP−TOPSIS method shown in Figure 3, the weighted matrix can be obtained, as shown in eq 3.

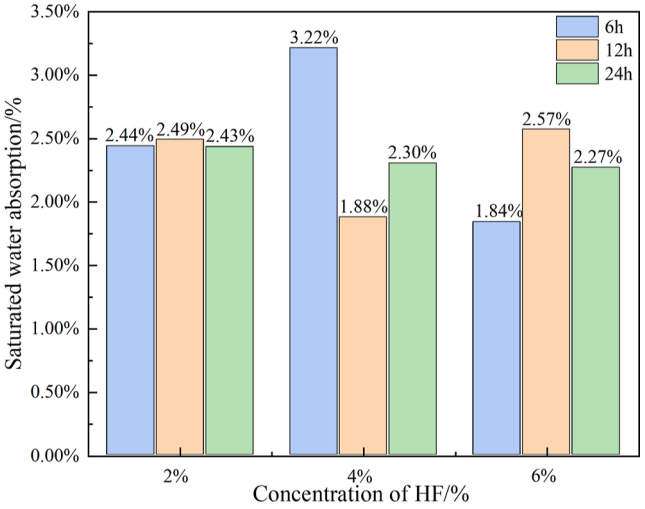

Figure 8. Saturated water adsorption of coal samples under different acidification schemes.

$$R = \begin{bmatrix} 0.1184 & 0.3995 & 0.3509 & 0.4972 & 0.3663 & 0.2163 & 0 & 0.4718 & 0.3551 \\ 0.0050 & 0 & 0.1090 & 0.1786 & 0.2998 & 0.3177 & 0.0544 & 0.1406 & 0.2534 \\ 0.1161 & 0.0770 & 0.1260 & 0.0965 & 0 & 0.1492 & 0.0710 & 0.1072 & 0.0974 \\ 0.0291 & 0.0261 & 0.0281 & 0.0143 & 0.0360 & 0.0053 & 0.0024 & 0.0219 & 0 \end{bmatrix}^{\mathrm{T}} \quad (3)$$

First, the maximum and the minimum values of each row in eq 3 were selected to form the positive/negative ideal solutions, which is D^+ = [0.4972, 0.3177, 0.1492, 0.0360], and D^- = [0,0,0,0], respectively. Next, the positive/negative ideal solutions and the weighted matrix R were brought into the calculation steps shown in Figure 3 to get the Euclidean distance sums (d_i^- and d_i^+) and final scores (X_i) of each scheme, as shown in Table 8. According to Table 8, the superiority ranking of each acidification scheme is 4−6 > 6−12 > 6−24 > 4−12 > 2−24 > 4−24 > 2−12 > 2−6 > 6−6, so the optimal scheme selected by the AHP−-TOPSIS method is 4−6.

3.3. Water Adsorption Tests. Saturated water adsorption is one of the most direct ways to represent the wettability of coal. So, the water adsorption tests were conducted to explore the difference in wettability of coal samples under the nine acidification modification schemes in this paper. The measurement results of this tests are shown in Figure 8.

As can be seen in Figure 8, the saturated water adsorption of coal samples varies under different acidification modification schemes. The saturated water adsorption is the highest when the HF concentration is 4% with a reaction time of 6 h, and the saturated water adsorption is the lowest when the HF concentration is 6% with a reaction of 6 h. In addition, the saturated water adsorption of coal samples changed very slightly at 2% HF when the reaction time went on, indicating that the reaction time had little effect on the wettability of coal samples at this concentration.

To compare the difference between the analysis results calculated by the AHP−TOPSIS method and the actual results measured by water adsorption tests, the superiority ranking of coal samples' wettability obtained by these two means are shown in Table 9.

As can be seen in Table 9, the optimal acidification wettability modification scheme determined by the AHP−TOPSIS method and water adsorption tests is the same one, indicating that the AHP−TOPSIS method could accurately select the optimal acidification conditions. Moreover, the ranking of acidification schemes obtained by AHP−TOPSIS had consistent ranking with the ranking obtained by water adsorption tests on 2nd, 5th, 6th, and 9th. In addition, the AHP−TOPSIS method also shows high coincidence with the results of water adsorption tests in some situations, such as 6−X (X = 6,12,24) and Y−6 (Y = 2,4,6), which demonstrates that the AHP−TOPSIS method matches well with the experimental results and have the potential to further optimize acidification schemes.

3.4. Isothermal Adsorption Tests. To validate the potential of the optimal acidification modification scheme for improving the production of CBM, the isothermal adsorption tests were conducted on raw coal and coal samples treated with scheme (4−6) to explore the change of their adsorption

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ACS Omega 2023, 8, 32667−32676

Table 9. Ranking of Coal Samples' Wettability Obtained by the AHP−TOPSIS Method and Water Absorption Tests

Project	2% 6 h	2% 12 h	2% 24 h	4% 6 h	4% 12 h	4% 24 h	6% 6 h	6% 12 h	6% 24 h
AHP−TOPSIS	8	7	5	1	4	6	9	2	3
Water adsorption tests	4	3	5	1	8	6	9	2	7

capacity. The fitting curves and adsorption constants a and b are shown in Figure 9.

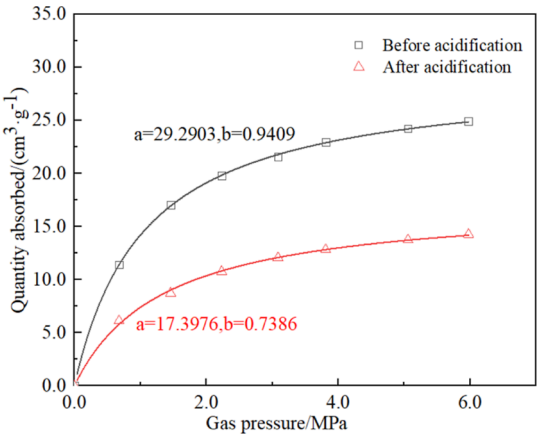

Figure 9. Isothermal adsorption curves of coal samples before and after acidification.

The adsorption constants a and b are significant physical parameters for researching the adsorption capacity of coal.[48] The smaller the values of a and b, the weaker the ultimate adsorption quantity and rate of coal for CBM. As can be seen in Figure 9, the values of a and b decrease by 40.60 and 21.50% after acidification, which indicates that the adsorption capacity of coal samples for gas decreases greatly after acidification and the optimal scheme selected by the AHP−TOPSIS method has the potential to promote the output of CBM.

Generally speaking, the core of acidification technology is to inject acid solution into seams to dissolve minerals in a reservoir and react with the active organic components so as to change the physical and chemical properties and realize the extraction enhancement of CBM. Wettability is a comprehensive reflection of the hydrophilic/hydrophobic ability of coal which could reflect the gas−water competition adsorption and gas migration in seams and is also closely related to the pore and fissure structure of coal.[49,50] Therefore, the effects of acidification can be evaluated by analyzing the changes of wettability of coal samples before and after acidification. In this paper, the wettability of coal is picked up as the basis for optimization, and then the optimal scheme was selected from nine acidification modification schemes by the AHP−TOPSIS method. In addition, the water adsorption test showed that the optimal scheme selected by the AHP-TOPSIS method is consistent with the actual measure results. The coal sample's adsorption capacity for gas is apparently reduced after acidification, which illustrates that this selected optimal scheme has the potential to promote the production of CBM to some extent. To sum up, this research indicates that the improved AHP−TOPSIS method used in this paper is feasible for selecting the optimal acidification wettability modification scheme and could do some good for the production enhancement of CBM with acidification and gas accident prevention.

4. CONCLUSIONS

To address the issues of cumbersome operation, time-consuming, and limited evaluation in conventional methods for determining the acidification conditions, an improved AHP−TOPSIS method based on the wettability of coal is proposed in this paper. Above all, this method calculates the adsorption energies of functional groups in coal when adsorbing a single water molecule with the help of the Gaussian 09W program and then assigns weights to each evaluation index using the AHP method. Next, the optimal acidification conditions were picked up based on the weights and content changes of functional groups using the TOPSIS method. The main conclusions are as follows:

(1) The calculation results show that the energy ranking of coal structures when adsorbing a single water molecule is benzene > B−COOH > B−OH > B−OCH_3 > B−CH_3 > B−CHO. The weights of the wettability evaluation index based on this ranking order given above are 0.4972, 0.3177, 0.1492, and 0.0360, respectively.

(2) The results of the AHP−TOPSIS method are validated by water adsorption tests, which indicates that this method could select the optimal acidification wettability modification scheme. Besides, the rankings obtained by the AHP-TOPSIS method and water adsorption tests are consistent on the 2nd, 5th, 6th, 9th, 6−X (X = 6,12,24) and Y−6 (Y = 2,4,6).

(3) The gas extraction enhancement potential of the optimal scheme selected by the AHP-TOPSIS method is validated using isothermal adsorption tests. The adsorption constants a and b decrease by 40.60 and 21.50% after acidification, which implies that the adsorption capacity of coal samples for gas reduces after acidification and the selected optimal scheme has the potential to promote the production of CBM.

(4) The mechanism of functional groups affecting the surface chemical properties and the gas affinity of coal need to be studied further using more advanced molecular simulation technology for improving the application of acidification in seams and the accuracy of the AHP−TOPSIS method.

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Notes

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