Effect of bio-based surfactant on wettability of low-rank coal surface and its mechanism

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Abstract
In this study, the effect of a bio-based environment-friendly surfactant, cardanol polyoxyethylene ether (BGF), on the wettability of the surface of low-rank coal (LRC) and its mechanism were studied. The adsorption experiment showed that the adsorption of the surfactant conformed to the Langmuir adsorption model and the pseudo-second-order kinetic model. The adsorption was mainly affected by hydrogen bonding, and the adsorption rate was affected by intraparticle diffusion and liquid film diffusion. The wettability experiment showed that the influence of BGF on the wettability of the surface of LRC followed the given order: BGF-7 > BGF-10 > BGF-15. The investigation of adhesion work showed that the adhesion work and the stability of the coal–water system decreased after adsorption. Fourier transform infrared and X-ray photoelectron spectroscopy analyses showed that after adsorption, the peak strength of vinyl ether, the content of elemental carbon, and the content of C–C/C–H groups increased.

Keywords Low-rank coal · Cardanol polyoxyethylene ether · Adsorption · Wettability

Introduction
Continuous exploitation of coal has caused an increase in the proportion of low-rank coal (LRC) in total coal reserves throughout the globe. The proven reserves of LRC in China account for 58.13% of its total proven reserves (Zhang et al. 2020). Owing to the low metamorphic degree of LRC, its surface contains a large number of hydrophilic groups, resulting in poor wettability and poor natural floatability of the LRC surface. This causes problems for subsequent large-scale industrial processing and utilization. Therefore, effective modification of the surface of LRC to reduce the number of hydrophilic groups on its surface and improve its surface wettability is imperative to promote the efficient upgradation and utilization of LRC (Xin et al. 2019).

To achieve effective regulation of the surface wettability of LRC, scholars around the world have conducted a significant amount of research on the subject. Zhao et al. (Zhao et al. 2021) studied the wettability of LRC surfaces with different surfactants and observed that it could significantly improve the wettability of coal dust. Yan et al. (Yan & Huang 2020) studied the dehydration of fine LRC by using a method of compounding inorganic salts and surfactants and observed that the existence of surfactants improved the surface wettability of LRC. Li et al. (Li et al. 2021a, 2021b) used a surfactant as a dispersant to study the paddle characteristics of LRC water slurry and observed that the wettability of the LRC surface changed after the addition of the surfactant. Liu et al. (Liu et al. 2020) found the wettability change of a LRC surface after adding fatty alcohol polyoxyethylene ether carboxylate (AEC) using molecular simulation and experiment and observed that after adding the surfactant, its wettability decreased at first and then increased...
with the concentration of the surfactant. The above studies show that surfactants have good effects on the regulation of the surface wettability of LRC. However, most traditional surfactants are not easily degraded, and large-scale industrial production can easily cause environmental pollution (Ivanković and Hrenović 2010). Therefore, finding new environmentally friendly surfactants to regulate the surface wettability of LRC has become important for the improvement and utilization of LRC.

Cashew phenol polyoxyethylene ether is a nonionic surfactant derived from cashew shell liquid. Compared with traditional petroleum ether surfactants, it is biodegradable and renewable, and is an environmentally friendly surfactant. Zhao et al. (Zhao et al. 2017b) studied the surface activity of cardanol polyoxyethylene ether 10 (BGF-10) and observed that BGF-10 had good surface properties and strong salt resistance to monovalent inorganic salts. However, the surface activity increased with an increase in the concentration of divalent inorganic salts. Zhu et al. (Zhu et al. 2013) compared the degradation performance of three different surfactants and observed that the degradation rate of BGF was above 95%. Tyman and Bruce (2004) compared the biodegradability of nonylphenol polyoxyethylene ether, BGF, and glucose, and observed that the biodegradability of BGF was equivalent to that of glucose. Zhao et al. (Zhao et al. 2017a) synthesized saturated BGF and observed that it has good emulsifying properties and is a good alternative to nonylphenol polyoxyethylene ether. Wang et al. (Wang et al. 2017) prepared a deinking agent by compounding BGF with other common surfactants for office waste paper and observed that it had good compounding performance with most surfactants. The above research shows that BGF exhibits good surface properties, rapid degradation, high degradation rate, and good compounding performance, making it a good choice to replace nonylphenol polyoxyethylene ether.

In this study, the surfactants BGF 7, 10, and 15 (BGF-7/10/15) were selected as to study their adsorption characteristics and wettability on the surface of LRC. The results about the study provide theoretical support for finding new environmentally friendly surfactants to improve the quality and utilization of LRC.

### Materials and methods

#### Analysis of raw coal properties

The coal samples selected for this study were low-rank lump coal from the mining area of the Shenhua Shendong Group. The industrial and elemental analyses are presented in Table 1.

As shown in Table 1, the air-dried basis ash (A_d) of the coal sample is 7.53%, which represents low ash coal. Air-dried basis moisture (M_d) is 7.55%, which represents low total moisture coal. The air-dried basis volatile matter (V_daf) is 32.21%, which represents a highly volatile coal. The air-dried basis fixed carbon (FC_daf) content is 52.71%, which represents a low fixed carbon coal. According to the GB/T 17,607–1998 Coal seam classification in China, the sample belonged to long flame coal.

#### Test reagents

Pure BGF-7 and BGF-10 reagents were purchased from Shandong Yousuuo Chemical Technology Co., Ltd., and BGF-15 was purchased from Shanghai Gubang New Materials Technology Co., Ltd. The molecular diagram is shown in Fig. 1.

#### Test method

##### Adsorption experiment

A series of BGF-7/10/15 solutions with different concentrations were prepared. Coal samples (0.50 g) were weighed and placed in a conical flask. Then, 50 mL of the prepared solution was added and stirred continuously in a conical flask to completely mix the coal samples with the surfactant solution. The mixed solution was placed in a THZ-82
constant-temperature water bath oscillator for 12 h and then removed. The SHK-IIIS circulating water multi-purpose vacuum pump was used to filter the solution at a pressure of 0.1 MP. The filtrate was measured using an SP-756 ultraviolet–visible spectrophotometer, and the adsorption isotherms at different temperatures were determined. In addition, time is a variate in the adsorption kinetics experiments. In adsorption kinetics, the concentration of the BGF solution was 0.1 g/L, and the adsorption temperature was set to 35 °C. The tests with BGF-7/10/15 were effectuated during 60, 120, 240, 480, 720, 960, 1200, and 1440 min.

Analysis and characterization

1) Contact angle analysis.
A 769YP 30 T manual powder tablet press was used to press for 300 s under a pressure of 15 MPa to prepare low-rank coal flake samples. The contact angle of the LRC samples after adsorbed was analyzed using a DSA30 optical contact angle measuring instrument (Kruss DSA30). The contact angle measurement range was 0–180°, and the interfacial tension measurement range was 0.1–2000 mN/m.

2) FTIR analysis.
 Fourier transform infrared (FTIR) spectroscopy analysis of the coal surface before and after adsorption was performed within the wavenumber range of 4000–400 cm⁻¹. A Nicolet iS50 FT-IR spectrometer was used to collect the data. The samples for the analysis were prepared using the KBr tablet method at a pressure of 10 MPa for a duration of 1 min (Table 2).

3) XPS analysis.
X-ray photoelectron spectroscopy (XPS) was used to determine the surface elemental composition of raw and dehydrated coal by wide scanning of the C, O, N, and Si elements. An ESCAL-AB250Xi was used to collect the spectral data. The test excitation source was an aluminum monochrome anode target (AlKα). The spot size of the beam was 500 μm, and the vacuum of the analysis chamber was $5 \times 10^{-8}$ Pa. The wide-range scanning energy was 50 eV, and the resolution was 1 eV.

Table 2 Fitted adsorption parameters for BGF on coal samples

| Surfactant | $T$, °C | LIAE | FIAE |
|------------|---------|------|------|
|            | $q_e$, mg/g | $K$, L/g | $R^2$ | $n$ | $K_f$ | $R^2$ |
| BGF-7      |         |      |      |      |      |      |
| 25         | 18.63   | 20.19 | 0.99 | 4.46 | 16.94 | 0.60 |
| 35         | 26.46   | 24.35 | 0.99 | 4.05 | 26.10 | 0.75 |
| 45         | 38.72   | 28.35 | 0.99 | 4.18 | 35.96 | 0.72 |
| BGF-10     |         |      |      |      |      |      |
| 25         | 17.29   | 13.86 | 0.99 | 3.92 | 15.47 | 0.61 |
| 35         | 24.07   | 15.04 | 0.99 | 3.97 | 21.78 | 0.70 |
| 45         | 36.60   | 17.85 | 0.99 | 3.69 | 33.78 | 0.71 |
| BGF-15     |         |      |      |      |      |      |
| 25         | 17.05   | 10.32 | 0.99 | 4.87 | 12.77 | 0.52 |
| 35         | 22.96   | 11.27 | 0.99 | 3.89 | 19.62 | 0.62 |
| 45         | 34.08   | 12.93 | 0.99 | 3.54 | 30.62 | 0.65 |

Fig. 2 Curve of BGF adsorption on LRC surface over time

Results and discussion

Adsorption test

Adsorption time

The test results of the adsorption time of BGF on the surface of LRC are shown in Fig. 2. The gradient of the adsorption curve was large during the initial stage, indicating that the adsorption rate was high. With enhanced time, the slope about the adsorption curve gradually decreased and finally tended to be flat. Comparing the adsorption capacities of the three surfactants over a duration of 60 min, the adsorption capacity of BGF-7 was found to be the highest. Therefore, BGF with a smaller degree of polymerization is more likely to be adsorbed on surface.
Adsorption isotherms

The isothermal adsorption curves of BGF on the surface of LRC at different temperature are shown in Fig. 3.

With an increase in the equilibrium adsorption concentration, the quantity of BGF adsorbed on surface also enhanced. Figure 3 shows that when it reaches a certain concentration, the curve tends to become flat and represents a type I isotherm. The maximum equilibrium adsorption capacity of BGF increases gradually with an enhanced temperature, signifying that increasing the temperature is beneficial to its adsorption on the surface of LRC. At a constant temperature, an enhanced polymerization degree leads to a gradual lessening about the equilibrium adsorption amount. For example, at 35 °C, the maximum equilibrium adsorption amounts of BGF-7, BGF-10, and BGF-15 were 26.46 mg/g, 24.07 mg/g, and 22.96 mg/g, respectively. This might be because a continuous increase in the degree of polymerization would increase the likelihood of BGF with a higher degree of polymerization to interact with water (Sis and Chander 2003).

Isothermal adsorption

To better explain the adsorption behavior, the Langmuir isothermal adsorption equation (LIAE) and Freundlich isothermal adsorption equation (FIAE) were used to fit the adsorption process, and the adsorption behavior was determined.

The LIAE is given in Eq. (1):

$$q_e = \frac{K_L q_m c_e}{1 + K_L c_e}$$  \hspace{1cm} (1)

After the expression is uniformly rearranged, the linear form of the mathematical line can be obtained in Eq. (2):

$$\frac{c_e}{q_e} = \frac{c_e}{q_m} + \frac{1}{K_L q_m}$$  \hspace{1cm} (2)

The mathematical expression of FIAE is given in Eq. (3):

$$q_e = K_F c_e^{1/n}$$  \hspace{1cm} (3)

After the expression is rearranged, its linear expression can be obtained in Eq. (4):
lnq_e = \frac{1}{n} \ln c_e + \ln K_F \quad (4)

For BGF, the LIAE performed better than the FIAE. The $R^2$ fitted by the LIAE was greater than 0.99. The counterpoise adsorption capacity about the three surfactants enhanced with an increase in temperature. This was mainly due to the molecular movement in the structure of BGF, which enhanced with an enhanced in temperature, making it easier to be adsorbed. However, a comparison of the three surfactants at the same temperature (25 °C) showed that the equilibrium adsorption capacities of BGF-7, BGF-10, and BGF-15 were 18.63 mg/g, 17.29 mg/g, and 17.05 mg/g, respectively. The equilibrium adsorption capacity decreased with an increase in the degree of polymerization. With an increase in the chain length of polyoxyethylene, the molecular force between the polyoxyethylene group and water was enhanced (Sis and Chander 2003). This caused an increase in the interaction between the polymer chain and water, and therefore, the equilibrium adsorption amount was reduced.

**Adsorption thermodynamics**

Based on the experimental data of BGF adsorption, the Gibbs free energy ($\Delta G$), enthalpy change ($\Delta H$), and entropy change ($\Delta S$) of BGF adsorption on the surface of LRC were calculated. The formulae used to calculate $\Delta G$, $\Delta H$, and $\Delta S$ are given below. $\Delta G$ can be obtained using the Van’t Hoff equation given in Eq. (5):

$$\Delta G = -RT \ln K$$

$\Delta H$ can be calculated using the Clausius–Clapeyron equation. The specific formula is given in Eq. (6):

$$\frac{d \ln K}{d(1/T)} = -\frac{\Delta H}{R}$$

From the Gibbs function given in Eq. (7), we can get.

$$\Delta G = \Delta H - T \Delta S$$

where $R$ is the molar gas constant (8.314 J/mol K), $T$ is the absolute temperature (K), and $K$ is the equilibrium constant calculated using the Langmuir adsorption equation.

As shown in Table 3, $\Delta G$ of the adsorption of the three different surfactants is negative, indicating that the adsorption process does not require additional external energy. A comparison of the adsorption of the same surfactant at different temperatures indicates that the absolute value about $\Delta G$ enhances with an enhancement in temperature. For example, $\Delta G$ of BGF-7 from low to high temperature is $-6.23$ kJ/mol, $-6.92$ kJ/mol, and $-7.55$ kJ/mol, respectively. In addition, the absolute value of $\Delta G$ increases, indicating that adsorption is more likely to occur with an increase in temperature. This implies an enhancement about the adsorption capacity with enhancing temperature.

The thermodynamic calculation shows that at the same temperature, such as 25 °C, $\Delta G$ of BGF-7, BGF-10, and BGF-15 is $-6.23$ kJ/mol, $-5.78$ kJ/mol, and $-5.69$ kJ/mol, respectively. With an increase in the degree of polymerization, $\Delta G$ of the three surfactants decreased gradually, indicating that the adsorption of BGF-7 on the surface of LRC was relatively easier than that of the other two surfactants. BGF-10 was second in terms of ease of adsorption, and BGF-15 was the least likely to adsorb on the surface of LRC. By calculating the entropy change, it can be seen that $\Delta S$ is positive. Therefore, the adsorption of the three surfactants on the surface of LRC results in an increase in entropy.

Because the adsorption is completed at atmospheric pressure, it can be considered that the adsorption heat is approximately equal to the standard adsorption enthalpy ($\Delta H$). Generally, the adsorption heat of physical adsorption is 0–40 kJ/mol, and that of chemical adsorption is 80–400 kJ/mol. The adsorption heat of BGF-7, BGF-10, and BGF-15 on the surface of LRC were 13.39 kJ/mol, 9.93 kJ/mol, and 9.82 kJ/mol, respectively. Therefore, the adsorption mechanism about the three surfactants was physical adsorption (Estrada et al. 2021).

| Surfactant | $T$, °C | $\Delta G$, kJ/mol | $\Delta H$, kJ/mol | $\Delta S$, J·K$^{-1}$·mol$^{-1}$ |
|-----------|---------|---------------------|-------------------|-------------------------------|
| BGF-7     | 25      | -6.23               | 13.39             | 65.82                         |
|           | 35      | -6.92               | 13.39             | 65.92                         |
|           | 45      | -7.55               | 13.39             | 65.82                         |
| BGF-10    | 25      | -5.78               | 9.93              | 52.71                         |
|           | 35      | -6.19               | 9.93              | 52.30                         |
|           | 45      | -6.84               | 9.93              | 52.72                         |
| BGF-15    | 25      | -5.69               | 9.82              | 52.03                         |
|           | 35      | -6.11               | 9.82              | 51.70                         |
|           | 45      | -6.67               | 9.82              | 51.84                         |

Table 3  Thermodynamic parameters

Electrostatic adsorption, van der Waals forces, and hydrophobic and hydrogen bonds are generally considered to be the main driving forces for the physical adsorption of surfactants at the solid/liquid interface. Since BGF is a bio-based nonionic surfactant, it has negligible ionization in water and, therefore, exhibits little electrostatic attraction. The heat absorption of the general van der Waals force is 4–10 kJ/mol, the absorption heat of the hydrophobic force is approximately 5 kJ/mol, and the absorption heat of the hydrogen bond is 2–40 kJ/mol. By comparing the absorption heat ranges of different forces, it can be seen that the adsorption of the three surfactants on the surface of LRC is mainly affected by hydrogen bonds (Von Ooepen et al. 1991).
Adsorption kinetics

A pseudo-first-order kinetic equation (PFKE) and a pseudo-second-order kinetic equation (PSKE) were used to analyze the adsorption kinetics to investigate the effect of adsorption time on the adsorption behavior of the three surfactants on the surface of LRC.

The linear expression of the PFKE (Taty-Costodes et al. 2003) is given in Eq. (8):

\[
\ln(q_e - q_t) = \ln q_e - K_1 t
\]

and the linear expression of the PSKE (Vadivelan and Kumar 2005) is given in Eq. (9):

\[
\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}
\]

The fitting of the PFKE and PSKE for the adsorption about the surfactants is shown in Figs. 4 and 5.

It can be seen from Figs. 4 and 5 that at a same temperature of 35 °C, the adsorption of three surfactants is fitted by PFKE and PSKE. The value of the correlation coefficient $R^2$ obtained using the PSKE for depicting the adsorption of the three surfactants on the surface of LRC was greater than 0.99, which is far better than the correlation coefficient obtained using the PFKE. This indicates that the PSKE was more fit for describing the process about the three surfactants (Table 4).
To further describe the adsorption kinetics of the three surfactants, the intraparticle diffusion model (IDM) and liquid film diffusion model (LFDM) were used to further process the adsorption kinetics data.

The mathematical expression of IDM is given in Eq. (10):

\[ q_t = K_{id} t^{0.5} + I \tag{10} \]

The mathematical expression of LFDM is given in Eq. (11):

\[ \ln(1 - F) = -K_f t + A \tag{11} \]

The fitting results of the IDM and LFDM of the three surfactants adsorbed are shown in Figs. 6 and 7.

By fitting the IDM and the LFDM, the IDM about the three surfactants on LRC conforms to two-stage fitting. However, the line of fit representing the equation of IDM does not pass through the origin, indicating that the adsorption about the three surfactants is controlled by mechanisms other than intraparticle diffusion. According to the IDM fitting, the slope during the first stage is large, which indicates that BGF is rapidly adsorbed in beginning. The mechanism of adsorption during the first stage is mainly liquid film diffusion. In the second stage, the slope of the curve begins to decline and tends to be flat, indicating that the adsorption process began to slow down with an increase in adsorption time and that this stage was mainly dominated by intraparticle diffusion.

The fitting results of the LFDM show that the simple LFDM cannot adequately explain the adsorption kinetics about BGF. However, because the fitting line does not pass through the origin, it indicates that the adsorption is controlled by mechanisms other than liquid film diffusion. Therefore, the adsorption mechanism of the three surfactants is a combination of both liquid film diffusion and intraparticle diffusion.
through the origin, it indicates that the IFDM is also a limiting factor for the adsorption rate. Therefore, the kinetic process of BGF adsorption on the surface of LRC is not dominated solely by intraparticle diffusion or liquid film diffusion, but by a combination of the two effects.

**Wettability**

To explore the effect of BGF on the wettability of the surface of LRC, we measured the change in the surface contact angle after adding the three surfactants, as shown in Fig. 8.

After adding the three types of surfactants, the contact angle of the LRC surface first increased and then decreased after reaching a certain concentration. After the action of the three surfactants, the maximum contact angles of the coal samples treated with BGF-7, BGF-10, and BGF-15 were 68.96°, 67.69°, and 66.76°, respectively. These values were significantly higher than that of raw coal (52.66°), and the contact angles for BGF-7, BGF-10, and BGF-15 were increased by 30.95%, 28.54%, and 26.77%, respectively. By comparing the concentrations of the three surfactants at the highest contact angle values, it can be observed that when the polymerization degree is small, a lower concentration can make the surface contact angle of LRC maximum, and its maximum angle is also different. With an increase in the degree of polymerization, the maximum contact angle gradually decreased. Studies regarding the adsorption thermodynamics showed that at constant temperature, an increase in the degree of polymerization of BGF resulted
in a gradual decrease in the equilibrium adsorption amount. Based on the contact angle and adsorption thermodynamics, it can be concluded that the adsorption of BGF has an effect on the wettability of the LRC. The three surfactants affected the wettability of the LRC in the following order: BGF-7 > BGF-10 > BGF-15.

To further explain the influence of BGF on the wettability of the LRC surface, we calculated its adhesion work. Through the analysis of the change in adhesion work, it can be seen the stability of the coal–water system before and after adsorption.

The first-order linear expression of Dupre equation (Griffiths et al. 2021) is given in Eq. (12):

\[ \gamma_{sl} = \gamma_{sg} + \gamma_{lg} - W_{sl} \]

(12)

The first-order linear expression of Young equation (Shalel-Levanon and Marmur 2003) is given in Eq. (13):

\[ \gamma_{sg} = \gamma_{sl} + \gamma_{lg} \cos \theta \]

(13)

The first-order linear expression of the adhesion work can be obtained by combining the two formulae:

\[ W_{sl} = \gamma_{lg}(1 + \cos \theta) \]

The changes in the adhesion work of the three surfactants on LRC surfaces are shown in Fig. 9.

The minimum value of adhesion work usually refers to the minimum energy required for coal–water interface separation. The lower the adhesion work is, the more unstable the coal–water combination is. From the change in adhesion work, it can be seen that after adding BGF, the adhesion work of the LRC surface first decreased and then increased. When the concentration of BGF-7 was 1.00 × 10^{-3} mol/L, the value of adhesion work reached a minimum of 98.94 mJ/m^2. When the concentration of BGF-10 was 1.25 × 10^{-3} mol/L, the minimum value of adhesion work was 100.44 mJ/m^2. When the concentration of BGF-15 was 1.75 × 10^{-3} mol/L, the minimum value of adhesion work was 101.53 mJ/m^2. Within a certain concentration range, BGF effectively reduced the work per unit area required for the separation of water from the surface of LRC. After the addition of the surfactant, the adhesion work of the coal–water system decreased, indicating that the surfactant reduced the energy required for the separation of LRC from water. The stability of the coal–water system decreases, and the separation of LRC from water becomes easier, which is favorable for controlling the wettability of the surface of LRC.

FTIR analysis

The adsorption spectra of BGF on the surface of LRC are shown in Fig. 10.

The absorption peaks at 3391.89 cm^{-1} are the stretching vibration peaks of alcohol and phenolic –OH. The absorption peak at 2921.27 cm^{-1} is –CH_{2} antisymmetric stretching vibration. The absorption peak at 2852.69 cm^{-1} is –CH_{3} stretching vibration of naphthenic or aliphatic hydrocarbons. The absorption peak at 1598.87 cm^{-1} is –O– substituted C–C stretching vibration, –C=O and –OH hydrogen bond resonance, and –C=O stretching vibration. The absorption peak at 1440.10 cm^{-1} is aromatic C=C, –CH_{2}, and –CH_{3} stretching vibration (aromatic skeleton vibration). The absorption peak at 1221.91 cm^{-1} is the C–O vibration of acid, phenol, ether, ester, and alcohol. The three absorption peaks between
971 cm\(^{-1}\)–710 cm\(^{-1}\) correspond to aromatic C–H stretching vibration.

**XPS analysis**

XPS is an important method for studying the surface element distribution of LRC. XPS wide-range scanning was used to analyze the coal sample, and the coal sample after adsorption of BGF is shown in Fig. 11. The elemental changes are listed in Table 5.

The XPS wide-sweep energy spectrum results of BGF showed that the elemental carbon content in the adsorbed coal samples increased significantly after the addition of the three surfactants. The elemental carbon content in the coal samples with added BGF-7 increased from 73.71 to 75.53%. In the coal samples treated with BGF-10, the carbon content increased from 73.71 to 74.81%. The carbon content of the coal samples treated with BGF-15 increased from 73.71 to 74.53%, which proved that some BGF was adsorbed on surface after the addition of the surfactants, thus changing its surface wettability (Table 6).

It can be proved that BGF was successfully adsorbed on surface, thereby changing its surface wettability. To intuitively study the changes in the oxygen-containing functional groups on the surface of the coal samples after adding BGF, XPS narrow sweep analysis was carried out. The results of the analysis are shown in Fig. 12.

Comparing the XPS narrow scan data before and after adsorption, it can be seen that after the addition of BGF, the content of C–C/C–H groups in coal samples increases to varying degrees, while the content of C–O, C = O, O = C–O, and other groups decreases significantly. This corresponds to the increase of elemental C in XPS wide scan. The adsorption results of the three surfactants in combination with LRC showed that BGF-7 is easier to combine with the surface. An increase in polyoxyethylene ether group results in a gradual decrease in the content of elemental C on the surface of BGF-7, which corresponds to an increase in polyoxyethylene ether group in the adsorption isotherm and a decrease in the adsorption capacity. It can be seen from the wettability data that the wettability change is caused by a decrease in the number of oxygen-containing functional groups on the surface and the enhancement of surface hydrophobicity after the adsorption of BGF.

**Conclusions**

1. The analysis of the adsorption thermodynamic data shows that the adsorption of BGF conforms to the Langmuir adsorption equation and follows spontaneous physical adsorption, which is mainly affected by hydrogen bonding. As the chain length of polyoxyethylene increased, the water–chain interaction increased and the equilibrium adsorption capacity decreased. The adsorption kinetics data show that the pseudo-second-order kinetics can better explain the surfactants’ adsorption behavior on the surface of LRC, and the adsorption rate step is affected by the combined effect of intraparticle diffusion and liquid film diffusion.

2. The wettability test showed that after adding BGF, the contact angle of the coal samples first increased, then decreased, and then increased again at a certain concentration. A comprehensive contact angle and adsorption thermodynamics study indicated that the adsorption of

| Sample     | Element content, % | C1s | O1s   | S2p | N1s |
|------------|--------------------|-----|-------|-----|-----|
| Coal       | 73.71              | 24.20 | 0.39  | 1.70|
| Coal/BGF-7 | 75.35              | 22.93 | 0.35  | 1.37|
| Coal/BGF-10| 74.81              | 23.39 | 0.39  | 1.41|
| Coal/BGF-15| 74.53              | 23.71 | 0.40  | 1.36|

**Table 5** XPS wide sweep analysis

| Sample     | Content, % | C–C/C–H | C–O  | C = O | O = C–O |
|------------|------------|---------|------|-------|---------|
| Coal       | 69.50      | 18.98   | 2.80 | 8.71  |
| Coal/BGF-7 | 74.05      | 17.30   | 2.61 | 6.04  |
| Coal/BGF-10| 72.52      | 17.88   | 2.51 | 7.09  |
| Coal/BGF-15| 71.45      | 18.40   | 2.45 | 7.71  |

**Table 6** Contents of carbon groups in coal samples
BGF has an effect on the wettability of LRC. The three surfactants affected the wettability of the LRC in the following order: BGF-7 > BGF-10 > BGF-15. By calculating the adhesion work, it was observed that after adding BGF, the adhesion work decreased to varying degrees, and the stability of the coal–water system decreased.

(3) FTIR and XPS studies showed that after adding BGF, the characteristic peak intensity of vinyl ether in coal was significantly improved, the content of elemental C in coal increased, and the content of C–C/C–H and other groups increased, which changed the wettability of its surface.

**Author contribution** LL: conceptualization, methodology, writing—reviewing and editing; ML: data curation, writing—original draft preparation; JL: investigation, visualization; XL: investigation, visualization; CM: investigation, visualization; MH: investigation, visualization; QW: investigation, visualization; YH: oversight and leadership responsibility for the research activity planning and execution; XY: acquisition of the financial support for the project leading to this publication.

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**Availability of data and materials** The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Declarations**

**Ethics approval and consent to participate** Not applicable.

**Consent for publication** Not applicable.

**Competing interests** The authors declare no competing interests.
References

Estrada A, Lozano FC, Díaz R (2021) Thermodynamics and kinetic studies for the adsorption process of methyl orange by magnetic activated carbons. Air, Soil and Water Research 14:117862212110133

Griffiths S, Wedi A, Schmitz G (2021) Work of adhesion and reactive wetting in SnPb/Cu, Ni and SnBi/Cu, Ni soldering systems. Mater Charact 178:111–304

Ivanković T, Hrenović J (2010) Surfactants in the environment. Arh Hig Rada Toksikol 61:95–110

Li L, Ma C, Lin M, Liu M, Yu H, W Q, Cao X, You X (2021b) Study of sodium lignosulfonate prepare low-rank coal-water slurry: experiments and simulations. Chin J Chem Eng 29:344–353

Li L, Ma C, Hu S, He M, Yu H, Wang Q, Cao X, You X (2021a): Effect of the benzene ring of the dispersant on the rheological characteristics of coal-water slurry: experiments and theoretical calculations. International Journal of Mining Science and Technology

Liu Z, Zhou G, Li S, Wang C, Jiang W (2020) Molecular dynamics simulation and experimental characterization of anionic surfactant: influence on wettability of low-rank coal. Fuel 279:118–323

Shalel-Levanon S, Marmur A (2003) Validity and accuracy in evaluating surface tension of solids by additive approaches. J Colloid Interface Sci 262:489–499

Sis H, Chander S (2003) Adsorption and contact angle of single and binary mixtures of surfactants on apatite. Miner Eng 16:839–848

Taty-Costodes VC, Fauduet H, Porte C, Delacroix A (2003) Removal of Cd (II) and Pb (II) ions, from aqueous solutions, by adsorption onto sawdust of Pinus sylvestris. J Hazard Mater 105:121–142

Tyman J, Bruce IE (2004) Surfactant properties and biodegradation of polyethoxylates from phenolic lipids. J Surfactants Deterg 7:169–173

Vadivelan V, Kumar KV (2005) Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk. J Colloid Interface Sci 286:90–100

Von Oepeb B, Kördel W, Klein W (1991) Sorption of nonpolar and polar compounds to soils: processes, measurements and experience with the applicability of the modified OECD-Guideline 106. Chemosphere 22:285–304

Wang F, Long Z, Chen J, Wang B, Zhang F (2017) Preparation and application of cardanol polyoxyethylene ether compounded deinking agent. Chem Indus for Prod 37:95–100

Xin F, Xu H, Tang D, Yang J, Chen Y, Cao L, Qu H (2019) Pore structure evolution of low-rank coal in China. Int J Coal Geol 205:126–139

Yan Y, Huang L (2020) Effect of inorganic salts and surfactants on dewatering performance of fine low-rank coal slime. Clean Coal Technology 26:106–112

Zhang H, Zhu XD, Lang XC, Liu HB (2020) Distribution of low rank coal and development prospect in Shanxi Province. MINERAL EXPLORATION 11:106–113

Zhao X, Wang L, Huang Z, Kang W, Che F (2017a) Surface performance testing of cardanol polyoxyethylene ether and its application in detergent. China Detergent & Cosmetics 2:63–69

Zhao X, Huang Z, Kang W, Wang L, Che F, Zhai Z (2017b) Study on the surface performance of cardanol polyoxyethylene ether. China Surfactant Detergent & Cosmetics 047:492–496

Zhao L, Zhang L, Wen X, Jia Y, Shu H (2021) Wetting ability of surfactants on low-rank coal and wetting mechanism. Journal of xi’an University of Science and Technology 41:323–330

Zhu H, Zeng Y, Yang M (2013) Properties of cashew phenol polyoxyethylene ether and its application in laundry detergents. DETERGENT & COSMETICS 36:27–31

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