Effect of Dextrin on the Adsorption Behavior and Surface Characteristics of Sub-Bituminous Coal and Silica

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ABSTRACT: Dextrin is a derivative of starch produced by partial thermal degradation under acidic conditions, which is usually used as a depressant in the mineral processing industry. Dextrin can also effectively depress coal particles in the reverse flotation process. To study the effect of dextrin on the flotation behavior of both coal and gangue mineral in coal reverse flotation, this research compared the adsorption behavior difference between sub-bituminous coal and silica as well as the surface property change of both sub-bituminous coal and silica after being treated by dextrin. The result illustrates that the adsorbing capacity of sub-bituminous coal on dextrin is much higher than that of silica under different initial concentrations and different interaction times. The isoelectric points of both sub-bituminous coal and silica increase after being treated by dextrin. But the increasing ζ-potential value of silica is larger than that of sub-bituminous coal. Dextrin could enhance the hydrophilicity of sub-bituminous coal and weaken the hydrophilicity of silica slightly according to the result of surface wetting rate tests. Reverse flotation using dextrin as a depressant indicates that good performance could be obtained with the addition of dextrin. Larger dextrin dosage might deteriorate silica flotation slightly.

1. INTRODUCTION

Dextrin is one kind of starchy polysaccharide reagent, which is a derivative of starch produced by partial thermal degradation under acidic conditions. Dextrin has higher branched polymeric carbohydrates and is composed of dextrose units. The structure of dextrin is shown in Figure 1.1,2 This starchy reagent is one common flotation depressant in mineral processing industrial engineering. It has been used in phosphate and gangue mineral flotation in 1931 for the first time, as well as the flotation of sulfide ores, oxidized ores, saline minerals, natural element minerals, other nonmetal minerals, etc.3 The adsorption of dextrin on mineral surface could be in different ways, such as chemisorption, hydrophobic-hydrophobic interaction, hydrogen-bond interaction, electrostatic interaction, etc. During the reverse flotation of rutile and hematite, dextrin used as a depressant interacted with minerals through chemical interaction.4 In 1974, Wie and Fuerstenau researched about the effect of dextrin on molybdenite and proposed that the adsorption of dextrin on a molybdenite surface might be hydrogen-bond interaction for the first time.5 Miller et al. found that dextrin only has strong interaction on the hydrophobic surface of mineral but has weak interaction on the hydrophilic mineral surface such as pyrite. When pyrite is associated with coal or has been treated by xanthate, the adsorption capacity of dextrin strengthens, which proves that the adsorption of dextrin on the pyrite surface is hydrogen-bond interaction further.6 X-ray photoelectron spectroscopy and Auger electron spectroscopy were used to test the mineral surface property change before and after adsorbing dextrin.7 It was found that the Auger parameter change of Ba element on the surface of barite was obvious (−0.75 eV), which meant that the interaction of dextrin on the barite surface is chemisorption. While the Auger parameter change of Ba element on the surface of barite before and after adsorbing dextrin was very weak (−0.20 eV), which was more likely to be physical, such as hydrogen-bond interaction.7

Dextrin is also usually used as a depressant in coal reverse flotation, during which process coal is depressed and gangue mineral is floated.8–10 In the complex pulp system of coal reverse flotation process, the co-adsorption of dextrin on minerals would affect the performance of reverse flotation. Therefore, it is very necessary to study the adsorption behavior difference between coal and gangue mineral on dextrin, as well as the surface characteristic change rule of coal and gangue

Figure 1. Structure diagram of the dextrin molecule.
mineral after adsorbing dextrin. This research result might provide theoretical guidance for coal reverse flotation.

2. MATERIALS AND METHODS

2.1. Experimental Materials. The coal sample used in this study was sub-bituminous coal collected from the Powder River coal basin of the U.S. The coal sample after sampling was crushed to below 200 μm by a hammer mill. The particle size fractions of the sample were obtained by sieving using lab vibrating screens, and the result is shown in Table 1. The proximate analysis of sub-bituminous coal is as follows: moisture 27.72%, ash dry 8.63%, volatile 46.62%, fixed carbon 16.85%, and sulfur 0.72%. The particle size fractions of the silica sample (ASTM quartz c-778 purchased from eBay, purity 98.8%) is as follows: 10%, 1.53 μm; 50%, 7.24 μm; 90%, 26.71 μm; mean size, 10.87 μm.

2.2. Chemical Reagents. The chemical formula of dextrin (Fisher Scientific) used in this research is \((C_6H_{10}O_5)_n\) and the molecular weight is 162.067 g/mol. Dextrin was used as 1% solution. The preparation steps are as follows: first, 1 g of dextrin powder was taken in a 100 mL volumetric flask and deionized water was added to make it 100 mL. Then, the bottle plug was screwed and the volumetric flask was moved up and down several times. Finally, the volumetric flask was put into a 60 °C thermostatic water bath to dissolve the contents faster. Dextrin solution should be made everyday to prevent biological decomposition. The complex cationic ammonium salt, Lilaflot D817M (AKZO NOBEL), was used as a collector in this study.\(^1\)\(^9\)\(^10\) It was also used as a 1% solution. Distilled water was used throughout the tests.

2.3. Experimental Methods. 2.3.1. TOC Test. For the test, 1 g/100 mL dextrin solution was diluted to 10−500 mg/L in a test tube. For this, 20 mL of diluent was added to the test tube. A TOC analyzer was used to measure the total carbon content in dextrin solution at different concentrations to obtain the linear relation curve between the dextrin solution concentration and the total carbon content. The linear relation curve would be taken as a standard curve.

The adsorption capacity of dextrin on minerals was obtained by calculating the difference of the total carbon content in dextrin solution before and after being adsorbed by samples. The test steps are as follows: first, 1 g of sub-bituminous coal or silica was measured and added to a 100 mL beaker containing 100 mL dextrin solution at different concentrations. The sample was agitated to disperse sufficiently using a glass bar successively. Afterward, the beaker was placed on a magnetic stirrer for 5 min to obtain sufficient adsorption. When it reaches the adsorption equilibrium after 3 h of standing, the pulp was poured into a pressure filter. After filtering using low-speed qualitative filter paper, the filtrate was obtained. Then, 20 mL of the filtrate was taken into a test tube, and the content of total carbon in dextrin solution was measured using a TOC analyzer. Finally, the test result was compared with the standard curve to get the difference value, which is the adsorbing capacity.

2.3.2. ζ-Potential Test. Both the coal sample and silica used in the ζ-potential test were ground to −30 μm using an agate pestle. HCl (25.00% v/v) and NaOH (99.99% grade) were used for pH adjustment. The 10^{-3} M KCl solution was used as the supporting electrolyte. The concentration of dextrin is 0.057 g/L. The ζ-potential analyzer used in this research was manufactured by Brookhaven Instruments Corporation. All of the measurements were performed following the steps in the instruction manual. Distilled water was used in the whole process.

2.3.3. Surface Wetting Rate Test. After adsorbing sufficient in the reagent solution at 180 and 50 mg/L concentrations, respectively, the sub-bituminous coal sample and silica sample for the surface wetting rate were obtained after filtration and low temperature drying. The surface wetting rate of minerals was measured using surface tension apparatus (Tesiometer K100). The process steps are conducted following the procedures described in the instruction manual.

3. RESULTS AND DISCUSSION

3.1. FTIR Analysis of Sub-Bituminous Coal. FTIR (NEXUS) was used to evaluate the functional groups on the coal surface. The FTIR spectrum of sub-bituminous coal is shown in Figure 2. The absorbance peak at about 3342 cm^{-1} is for −OH and the high peak around 3600 cm^{-1} means that it has high moisture content.\(^1\)\(^3\) The absorbance peak at 1605 cm^{-1} is for −COOH and those between 1150 and 1380 cm^{-1} are for C−O and O−H in phenoxy groups.\(^1\)\(^2\)\(^−\)\(^1\)\(^5\) All of these peaks are very high, indicating that there are high contents of oxygen-containing functional groups on the surface of sub-bituminous coal. The oxygen-containing functional groups on the surface of sub-bituminous coal would interact with water and increase its surface hydrophilicity.\(^1\)\(^1\)\(^5\)

3.2. Results of Adsorption Test. The samples used in the adsorption test are sub-bituminous coal and silica with a whole size range. The adsorption formula of sub-bituminous coal and silica on dextrin is as follows

\[
q_c = \frac{(C_0 - C_x) \times V}{m}
\]

\(1\)

where \(q_c\) is the equilibrium adsorption capacity (mg/g), \(C_0\) is the initial concentration of dextrin (mg/L), and \(C_x\) is the

| particle size/μm | yield/% | ash dry/% |
|-----------------|---------|-----------|
| 150−200         | 15.71   | 6.42      |
| 120−150         | 12.92   | 6.96      |
| 74−120          | 15.3    | 7.05      |
| 53−74           | 10.52   | 7.3       |
| 38−53           | 3.51    | 8.7       |
| <38             | 42.04   | 11.3      |
| total           | 100.00  | 8.81      |

Table 1. Particle Size Distribution of Sub-Bituminous Coal
equilibrium concentration (mg/L), \( v \) is the volume of the solution (L), and \( m \) is the sample quality (g).

The relationship between the total carbon content and the concentration of dextrin is shown in Figure 3. The standard curve of dextrin solution is as follows

\[
y = 0.4045x + 1.9278
\]

(2)

The correlation coefficient is \( R^2 = 0.99932 \). The effective concentration range of dextrin is 10−300 mg/L.

3.2.1. Adsorption Property of Sub-Bituminous Coal and Silica on Dextrin at Different Initial Concentrations. The adsorption property of sub-bituminous coal on dextrin at different initial concentrations is shown in Figure 4. It can be seen from Figure 4 that during the whole tested dextrin concentration range (0−250 mg/L), the adsorbing capacity of dextrin on sub-bituminous coal is much higher than that on silica. The equilibrium adsorption capacity of dextrin on sub-bituminous coal increases with the increase of dextrin concentration, and the increase speed is higher than that on silica. When dextrin concentration is larger than 50 mg/L, the adsorption speed of dextrin on silica decreases, reaching adsorption equilibrium; the equilibrium adsorption capacity is about 2.3 mg/g. When the initial concentration of dextrin is larger than 180 mg/L, the adsorption speed of sub-bituminous coal also decreases, and the equilibrium adsorption capacity is about 4.56 mg/g.

3.2.2. Adsorption Property of Sub-Bituminous Coal and Silica on Dextrin at Different Adsorption Times. The dextrin concentrations were set when sub-bituminous coal and silica reach adsorption equilibrium, which are 180 and 50 mg/L, respectively, as the initial concentrations to explore the adsorption kinetics of sub-bituminous coal and silica. The adsorption time was set as follows: 10, 20, 40, 60, 90, 120, and 180 min. The adsorption capacity was obtained by comparing the result with the standard curve. Figure 5 illustrates the adsorption property of dextrin on sub-bituminous coal and silica at different adsorption times. It could be seen that the adsorption rate of dextrin on sub-bituminous coal is very fast within 60 min and reaches equilibrium (4.53 mg/g) at about 120 min. While the adsorption rate of dextrin on silica decreases gradually after 40 min and reaches adsorption equilibrium (2.00 mg/g) at about 60 min. This is because dextrin concentration is very large at the beginning, and there are also many active sites on the surface of particles, which lead the adsorption rate faster at the beginning relatively. Comparing the adsorption curve of dextrin on sub-bituminous coal and silica at different adsorption times, it can be seen that the adsorption rate of dextrin on sub-bituminous coal is higher than that on silica at the initial 120 min. But during the whole process, the adsorption capacity of dextrin on sub-bituminous coal is always higher than that on silica. This means that during

![Figure 3. Total carbon content in dextrin solution with different concentrations (standard curve).](image)

![Figure 4. Adsorption rule of sub-bituminous coal and silica on dextrin at different initial concentrations.](image)

![Figure 5. Adsorption kinetic curves of sub-bituminous coal and silica on dextrin.](image)
the process of reverse flotation, dextrin has better selectivity to the goal mineral, sub-bituminous coal.

3.3. Influence of Dextrin on the Surface Property of Sub-Bituminous Coal and Silica. 3.3.1. Effect of Dextrin on the \( \zeta \)-Potential of Minerals. Figure 6 shows the effect of dextrin on the \( \zeta \)-potential of sub-bituminous coal after adsorbing dextrin. It can be seen that the isoelectric point of sub-bituminous coal increases from pH 3 to about pH 3.3 after the adsorption of dextrin. With the increase of pH, the electronegativity enhances gradually. During the whole test range, the \( \zeta \)-potential value of sub-bituminous coal after being treated by dextrin is a little higher than that before adsorbing dextrin.

The \( \zeta \)-potential change law of silica before and after adsorbing dextrin is shown in Figure 7. It could be seen that the isoelectric point of silica before adsorbing dextrin is at about pH 2. With the increase of pH, the electronegativity enhances gradually. After the adsorption of dextrin, the isoelectric point of silica increases to about pH 3.2. During the whole test range, the \( \zeta \)-potential value of silica after being treated by dextrin is also a little higher than that before the adsorption of dextrin.

3.3.2. Effect of Dextrin on the Wettability Rate of Minerals. Figures 8 and 9 illustrate the wettability curves of sub-bituminous coal with deionized water and normal hexane, respectively. It can be seen that the wettability rate of sub-bituminous coal after adsorbing dextrin is higher (0.0015 g2/s) than that before adsorbing dextrin (0.0009 g2/s) when using deionized water as the wetting liquid. When the wetting liquid is changed to normal hexane, the wettability rate of sub-bituminous coal after adsorbing dextrin is lower (0.0031 g2/s) than that before adsorbing dextrin (0.0045 g2/s) when using deionized water as the wetting liquid. The wettability rate of silica after adsorbing dextrin increases slightly (0.0024 g2/s) than that before adsorbing dextrin (0.0021 g2/s) when the wetting liquid is changed to normal hexane. This indicates that the hydrophilicity of silica weakens and the hydrophobicity enhances slightly after adsorbing dextrin.

Figure 6. Effect of dextrin on the surface \( \zeta \)-potential of sub-bituminous coal.

Figure 7. Effect of dextrin on the surface \( \zeta \)-potential of silica.

Table 2 illustrates the surface wetting rate results of sub-bituminous coal (deionized water) and silica before and after adsorbing dextrin. It can be known that dextrin could enhance the hydrophilicity of sub-bituminous coal as a depressant in coal reverse flotation. However, dextrin weakens the surface hydrophilicity of silica. Therefore, excessive dextrin might deteriorate the flotation of silica.

Figure 8. Effect of dextrin on the surface wettability rate of sub-bituminous coal (deionized water).
3.4. Reverse Flotation Test. Reverse flotation with artificial mixed flotation feed was conducted referring to the previous research. The ratio of sub-bituminous coal to silica is 7:3. Dextrin and ammonium salt Lilaflot D817M were used as a depressant and collector, respectively. The effect of dextrin on reverse flotation results is shown in Figure 12. As can be seen that the combustible matter recovery increases from 74.12 to 86.87% when dextrin dosage increases from 0 to 1 kg/t, indicating that more coal particles are depressed. The separation efficiency also increases significantly, from 62.70 to 71.45%, after 1 kg/t dextrin was added. This means that the addition of a depressant could enhance coal reverse flotation performance very well. With the increase of dextrin dosage, the separation efficiency increases slightly. The ash content of the concentrate increases from 7.58 to 8.23% after the addition of 1 kg/t dextrin, indicating that more dextrin would affect the recovery of silica in the froth product. The ash content of the concentrate increases slightly when dextrin dosage changes from 1 to 4 kg/t. It is concluded that low dextrin dosage (1 kg/t) would be the best for coal reverse flotation to obtain relatively good separation efficiency.

Table 2. Surface Wetting Rate of Sub-Bituminous Coal and Silica before and after Adsorbing Dextrin (20 °C)

| sample                     | wetting rate, k (g²/s) | deionized water | n-hexane |
|----------------------------|------------------------|-----------------|----------|
| sub-bituminous coal        | 0.0009                 | 0.0030          |          |
| sub-bituminous coal + dextrin | 0.0015               | 0.0015          |          |
| silica                     | 0.0045                 | 0.0021          |          |
| silica + dextrin           | 0.0031                 | 0.0024          |          |

Figure 9. Effect of dextrin on the surface wettability rate of sub-bituminous coal (n-hexane).

Figure 10. Effect of dextrin on the surface wettability rate of silica (deionized water).

Figure 11. Effect of dextrin on the surface wettability rate of silica (n-hexane).

Figure 12. Effect of dextrin on reverse flotation performance (pulp concentration 40 g/L, collector Lilaflot D817M 2 kg/t, frother MIBC 20 ppm, conditioning time 0 min, and conditioning speed 1000 rpm).
4. CONCLUSIONS

Dextrin is usually used as a depressant in mineral processing, especially in coal reverse flotation. The adsorption behavior difference of dextrin on sub-bituminous coal and silica was compared. It is found that the adsorption capacity of dextrin on sub-bituminous coal is always higher than that on silica under different conditions. Dextrin could increase the isoelectric point of both sub-bituminous coal and silica. The hydrophilicity of sub-bituminous coal after being treated by dextrin enhances while that of silica weakens slightly according to the result of surface wetting rate tests. The addition of low dosage dextrin (1 kg/t) could help in obtaining good reverse flotation performance.

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The author declares no competing financial interest.

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