Adsorption Mechanism between Corn Stalk Fiber and Asphalt

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Abstract: Corn stalk fibers are produced by physical and chemical means. To prove that corn stalk fibers can adsorb asphalt, the adsorption process of asphaltenes was studied. There are four main components in asphalt, and this study used asphaltenes as an adsorbate in an asphalt solution. The corn stalk fibers were characterized by scanning electron microscopy and Brunauer-Emmett-Teller (BET) analysis, which indicated that the corn stalk fibers were composed of macroporous and mesoporous structures, with uneven surfaces. The amount of asphaltenes adsorption was found to increase with the weight of the corn stalk fiber, the initial concentration of asphaltenes and the adsorption time. The asphaltenes adsorption gradually slowed with time. The Redlich-Peterson model can describe the adsorption process better than the Freundlich and Langmuir models. The pseudo-second-order model presented better suitability for adsorption equilibrium data than the pseudo-first-order model. The adsorption process can be separated into three parts: film diffusion, both film diffusion and intraparticle diffusion, and intraparticle diffusion through the Weber and Morris model. The Boyd model found that film diffusion is the rate-limiting step. The high-temperature performance of corn stalk fiber asphalt increased with increasing mass ratio of fibers and increasing asphaltenes adsorption rate. Finally, the corn stalk fibers were proven to adsorb the asphalt effectively.

Keywords: corn stalk fiber; asphalt; adsorption; high-temperature performance

1. Introduction

As the quickly development economy, the quality of people’s living has continued to improve, which has led to a significant increase in the amount of traffic [1]. Therefore, people have imposed higher requirements for the performance of asphalt pavement. Consequently, researchers have improved the performance of asphalt pavement by adding fibers to asphalt mixtures [2,3], such as stone mastic asphalt and fiber asphalt concrete. At present, the fiber materials commonly used in asphalt pavement are polymer fiber [4,5], basalt fiber [6–8], glass fiber [9,10] and lignin fiber [11,12]. Polymer fiber improves the performance of asphalt mixtures, but it has the disadvantages of high cost and insufficient high-temperature stability. Due to the poor adhesion of glass fiber to asphalt, this material is now rarely used. At present, mineral fiber is widely used. Due to its good tensile strength, it has a good effect on improving the mechanical properties of asphalt mixtures, but the production of mineral fibers consumes a large amount of energy. Lignin fibers are widely used in SMA (Stone Mastic Asphalt) asphalt mixtures due to their good asphalt adsorption. However, the use of lignin fibers consumes wood resources.

Due to human consumption, Earth’s limited resources are constantly decreasing, and with increasing awareness of environmental protection, people are beginning to recognize the value of plant fibers. Due to the good physical and mechanical properties of plant fiber, it can be added to the base material as a reinforcing material to form a reinforced composite material. Therefore, some researchers have begun to use different plant fibers to make composite materials, such as straw stalk fiber, wheat stalk fibers, cotton stalk fibers, barley shell fibers and coconut bell fibers [13–16].
China produces hundreds of millions of tons of crops each year. If crop stalks, which are agricultural by products, are not handled properly, such as by incineration and accumulation, they will cause serious environmental pollution [17]. If the corn stalks are abandoned in the field or roadside, they will gradually decompose after long-term exposure to the sun and rain, so that the nutrients including nitrogen, phosphorus, potassium and trace elements will enter the surface and underground water system with the rain, resulting in the eutrophication of water resources. However, the open burning of corn stalks will cause regional intermittent air pollution. The burning of corn stalks will produce a large amount of CO, CO$_2$, NO, NO$_2$ and other gases, and will also lead to the increase of fine particulate matter (PM2.5) in the air, which will cause harm to the atmospheric environment and human body. If corn stalk is made into a fiber material and applied to asphalt material to become composite materials, it will not only improve the mechanical performance of the asphalt material but also solve the problem of environmental pollution.

In asphalt pavement SMA (Stone Mastic Asphalt) structure, it is necessary to add the lignin fiber material. The lignin fiber material is derived from wood, and its extensive use will damage the ecological environment. The application of corn stalk fiber in asphalt pavement can alleviate this problem, thus also solving the environmental pollution problem caused by corn stalk storage or burning. The corn stalk fiber has a rough surface and a large amount of pore structures [18,19], and its physical properties are basically the same as those of lignin fiber. The lignin fiber plays a role in adsorbing the asphalt [20]. The ability of corn stalk fiber to adsorb asphalt will affect the mechanical properties of asphalt-based fiber composites. The physical and mechanical properties of corn stalk fiber asphalt binder have been studied [21], but its adsorption mechanism has rarely been studied.

There are four main components in asphalt, namely, asphaltenes, resin, saturates and aromatics. This study used asphaltenes as an adsorbate, which is typical of asphalt. This aim of this study was to investigate the adsorption process of asphaltenes from an asphalt solution on corn stalk fibers. The corn stalk fiber would be used as adsorbent, and the structural characteristics of corn stalk fiber were analyzed using scanning electron microscopy (SEM), nitrogen adsorption-desorption Brunauer-Emmett-Teller (BET) tests. The adsorption process were analyzed by researching the adsorption isotherms, kinetics and mechanism of asphaltenes on the prepared corn stalk fiber. The adsorption isotherms models were Langmuir, Freundlich and Redlich-Peterson models [22–24]. The adsorption kinetics models were the pseudo-first-order and pseudo-second-order models [25,26]. The adsorption mechanism models were the Weber and Morris intraparticle diffusion model and the Boyd film diffusion models [27,28]. Then, corn stalk fibers were mixed into asphalt, and the high-temperature performance was evaluated by dynamic shear rheological tests. This study can provide useful information to prove that corn stalk fiber can adsorb asphalt.

2. Materials and Methods

2.1. Corn Stalk Fiber Preparation

The corn stalk fiber preparation procedure was described in our previous work [18]. First, some mold-free, undamaged and dry corn stalks were collected. After that, the marrow in the corn stalk was removed by using a skin-marrow separation instrument. Then, the corn stalk skin was washed with water. After cleaning, the corn stalk skin was dried in an oven at 60 °C. Next, the corn stalk skin was cut into strips with a size of 0.5–1.5 × 3–5 cm, and the corn stalk strips were crushed and comminuted by a WKF250 crusher instrument and a high-speed multifunction machine for 3.5 min. In a sixth step, the corn stalk fiber was put into a sodium hydroxide solution for chemical treatment. Here, the weight ratio of corn stalk fibers, sodium hydroxide particles and water was 8:1:200. During this chemical treatment process, a magnetic stirrer was used in which the speed was set at 2100 rpm, the temperature was set at 80 °C, and the time was set at 30 min. Finally, the corn stalk fibers were washed with deionized water and then dried in an oven at 100 °C. The preparation of corn stalk fibers is shown in Figure 1.
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2.2. Asphalt

Asphalt contains four main components: asphaltenes, resin, saturates and aromatics. To analyze the adsorption process of corn stalk fiber in asphalt, asphaltenes were used as an adsorbate in asphalt. Five different types of asphalt materials were selected as solutions, which meant five different concentrations of asphaltene asphalt solutions were used for this research. Anda-50, Anda-70 and Anda-90 asphalt materials were produced in Panjin City, Liaoning Province, China, and SK-70 and SK-90 asphalt materials were produced by the SK Asphalt Plant in South Korea.

Thin-layer chromatography with flame ionization detection was used to detect the mass ratios of the four components in the five different types of asphalt. The measurement of the four components of asphalt was as follows: the sample was unfolded and separated on a special chromatographic rod. The chromatographic rod was passed through a hydrogen flame at a constant speed. The separated organic material on the thin layer of the chromatographic rod was ionized by energy from the hydrogen flame, and the hydrogen flame ion detector monitored the current generated by these ions. Since the current intensity was proportional to the amount of each substance entering the flame zone, quantitative monitoring was achieved. As shown in Figure 2, there were four very obvious peaks, which, from left to right, correspond to asphaltenes, resins, aromatics and saturates. By calculating the area ratio of these four peaks, the content of the four components in asphalt was obtained.

Then, the mass ratios were used to calculate the concentrations of asphaltenes in different types of asphalt. The concentrations of asphaltenes are presented in Table 1.
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| Asphalt Type   | Concentration of Asphaltenes (g/L) |
|----------------|------------------------------------|
| Anda-50        | 57.3                               |
| Anda-70        | 67.8                               |
| Anda-90        | 90.3                               |
| SK-70          | 102.9                              |
| SK-90          | 149.0                              |

### 2.3. Characterization of Corn Stalk Fibers

Scanning electron microscopy (Zeiss, SUPRA55, Jena, Germany) was used to obtain micrographs of the pore structure and surface of corn stalk fibers at an acceleration voltage of 20 kV. Before the test, the surfaces of the samples were sprayed with gold for 10 min.

The surface area and pore size of the corn stalk fibers were measured using a Micromeritics ASAP 2020 (Micromeritics Instrument CORP, Norcross, GA, USA) surface area analyzer by the nitrogen adsorption-desorption method. The corn stalk fibers were degassed under N$_2$ flow at 150 °C for 10 h before adsorption isotherms were generated by N$_2$ at 77 K.

### 2.4. Batch Equilibrium Adsorption Studies

Batch equilibrium tests were carried out for the adsorption of asphaltenes on the prepared corn stalk fibers. The effects of the initial asphaltene concentration in the asphalt solution and the weight of corn stalk fibers on the adsorption uptake were investigated. The amount of asphaltenes adsorbed per gram of corn stalk fibers at equilibrium, $q_e$ (g/g), can be calculated according to Equation (1).

$$q_e = \frac{(C_0 - C_e) \times V}{m}$$

where $C_0$ and $C_e$ (g/L) are the initial and equilibrium liquid-phase concentrations of the asphaltenes, respectively. $V$ (L) is the volume of the asphalt solution. $m$ (g) is the weight of the dried corn stalk fiber.

#### 2.4.1. Effect of Initial Asphaltene Concentration

The effect of the initial asphaltene concentration on the adsorption process was studied by selecting different types of asphalt solutions with Anda-50 (57.3 g/L), Anda-70 (67.8 g/L),...
Anda-90 (90.3 g/L), SK-70 (102.9 g/L), and SK-90 (149.0 g/L). First, the five types of asphalt materials were heated to 135 °C in an oven to become liquid. A series of 400 mL asphalt solutions with five initial asphaltene concentrations were prepared in 800 mL beakers. Corn stalk fibers weighing 8 g were added into each beaker, and 50 µm sieve baskets were used to separate the fibers from the asphalt solution in each beaker. Next, the beakers were placed in a magnetic isothermal oil bath shaker with a rotation speed of 100 rpm for 60 min at 135 °C to attain equilibrium. Figure 3 shows the flowchart of the adsorption experiment.

The mass ratios of asphaltenes before and after adsorption in the supernatant solutions were measured using thin-layer chromatography with flame ionization detection. Finally, we could calculate the concentration of asphaltenes from the density of asphalt. The adsorption rate of asphaltenes on corn stalk fibers was calculated based on the following Equation (2).

\[
\text{Adsorption (\%) = } \frac{(C_0 - C_e)}{C_0}
\]

where \(C_0\) (g/L) and \(C_e\) (g/L) are the initial and equilibrium concentrations of asphaltenes in asphalt, respectively.

2.4.2. Effect of the Weight of Adsorbent

To study the effect of the weight of the adsorbent on the adsorption uptake, corn stalk fibers weighing 4 g, 8 g, 12 g, 16 g and 20 g were blended into Anda-70 (67.8 g/L) asphalt. Other operating parameters, such as rotation speed, time and temperature, remained constant without any adjustment. The method used to obtain the concentration of asphaltenes was the same as that used in the previous study.

2.5. Batch Kinetic Studies

The kinetic studies were performed according to a similar procedure for batch equilibrium adsorption studies. However, the concentrations of asphaltenes in an asphalt solution were measured at different times. The method to determine the concentration of
asphaltenes was the same as in a previous study. The amount of asphaltenes at time \( t \), \( q_t \) (g/g), could be obtained by the following Equation (3).

\[
q_t = \frac{(C_0 - C_t) \times V}{m}
\]  

(3)

where \( C_0 \) (g/L) and \( C_t \) (g/L) are the liquid-phase concentration of asphaltenes at the initial and any time \( t \) (min), respectively. \( V \) (L) is the volume of the solution. \( m \) (g) is the weight of the corn stalk fibers.

3. Results
3.1. Characterization of Corn Stalk Fibers
3.1.1. Scanning Electron Micrograph Analysis

The morphologies and porous structure of the corn stalk fiber were determined by scanning electron microscopy. Figure 4a shows that the surface of the corn stalk fiber was uneven and rough. Figure 4b shows that the inner tubular structure of corn stalk fiber was exposed, which can improve the adsorption capacity of fiber for asphaltenes. A previous study observed that the uneven and rough surface of corn stalk fiber was caused by chemical treatment [18].

![Figure 4. Scanning electron micrographs of corn stalk fiber: (a) the surface of the corn stalk fiber was uneven and rough; (b) the inner tubular structure of corn stalk fiber.](image)

3.1.2. Brunauer-Emmett-Teller (BET) Analysis

The \( N_2 \) adsorption-desorption isotherms at 77 K for corn stalk fibers are shown in Figure 5. The surface characteristic parameters of corn stalk fibers are presented in Table 2. The overall shape of the isotherm curve of the corn stalk fibers exhibited behaviors of both type II and type IV isotherms. The adsorption isotherm curve demonstrated a slow increase in the low \( P/P_0 \) range and a sharp increase at a high relative pressure (\( P/P_0 \)). The type II isotherm reflected the typical physical adsorption process on nonporous or macroporous adsorbents [29–31]. According to the scanning electron microscopy images, the corn stalk fibers were adsorbents with a macroporous structure. Then, the adsorption-desorption isotherm curve of corn stalk fibers presented a hysteresis loop, which was similar to that of the type IV isotherm. Therefore, it can be concluded that there were also mesoporous structures in corn stalk fibers.
Figure 5. The N₂ adsorption-desorption isotherm of corn stalk fibers.

Table 2. Characteristics of corn stalk fibers evaluated by N₂ adsorption isotherms at 77 K.

| Parameters                      | Corn Stalk Fibers |
|--------------------------------|-------------------|
| BET surface area (m²/g)        | 5.84              |
| Langmuir surface area (m²/g)   | 7.75              |
| Micropore area (m²/g)          | 5.45              |
| External surface area (m²/g)   | 0.39              |
| Total pore volume (cm³/g)      | 2.86 × 10⁻³       |
| Micropore volume (cm³/g)       | 2.52 × 10⁻³       |
| Average pore size (Å)          | 19.57             |

3.2. Effect of Weights of Corn Stalk Fibers on Asphaltene Adsorption

Figure 6 shows the effects of corn stalk fiber weights on the asphaltene adsorption process, and the adsorbent weights were 4 g, 8 g, 12 g, 16 g and 20 g for 400 mL of Anda-70 asphalt solution (67.8 g/L). It can be seen from Figure 6a that the adsorption rate increased with increasing adsorbent weight, as the higher weight of the corn stalk fibers more effectively provided vacant surface sites for asphaltenes [32]. However, Figure 6b illustrates that the capacity of the corn stalk fibers decreased as the weight of the adsorbent increased, which indicates that the excessive vacant surface areas of adsorption were not fully used [33].

Figure 6. Effect of corn stalk fiber weight on asphaltene adsorption: (a) the change of the adsorption rate; (b) the change of qₑ.
3.3. Effect of Initial Asphaltene Concentrations on Adsorption

Figure 7 demonstrates that the adsorption of asphaltenes increased with increasing time and reached a constant value that fluctuated slightly with increasing time, indicating that the corn stalk fibers did not further adsorb asphaltene from the asphalt solution. This constant value was the dynamic equilibrium point of asphaltene adsorption and illustrated the maximum adsorption capacity of the corn stalk fibers. The adsorption curves of asphaltenes increased quickly at the beginning of the contacting phases, after which the increasing rate of the curve decreased until the value of the curve barely grew. The high rate of adsorption at the initial stage occurred because the adsorption of asphaltenes was caused by the exterior surface area of corn stalk fibers. When the exterior surface of adsorbents reached saturation, the asphaltene entered the porous structure of the corn stalk fibers and were adsorbed by the interior surface areas of the adsorbents [34]. This situation also indicated that many effectively vacant surface areas could be occupied by asphaltenes on the corn stalk fibers during the early period, and thereafter, the remaining vacant surface areas were hard to occupy because of repulsive forces between the asphaltenes on the corn stalk fibers and on the asphalt solutions [35].

![Figure 7](image_url)

**Figure 7.** Effect of initial asphaltene concentrations on adsorption.

In this study, it can be seen from Figure 7 that the values of \( q_e \) at equilibrium increased from 1.64 g/g to 3.1 g/g with an increase in the initial concentration of asphaltenes from 57.3 g/L to 149.0 g/L. This was due to an increase in the number of asphaltenes transferred to the electively vacant surface and interior areas. Figure 7 also shows that the contact time to reach equilibrium for asphaltene adsorption increased with increasing initial asphaltene concentration. This phenomenon was illustrated by the following facts about adsorbate adsorption. First, the asphaltenes were subject to the influence of the corn stalk fiber boundary layer, after which they entered the surface areas and ultimately diffused into the pores of the corn stalk fibers [36]. Therefore, the adsorption process of higher initial asphaltene concentrations required a longer contact time to reach equilibrium because more asphaltenes were adsorbed by corn stalk fibers.

3.4. Adsorption Isotherm Models

In this study, to optimize the asphaltene adsorption process, it would be necessary to set up a suitable correlation for the adsorption equilibrium data. Three models were used to suit the data of adsorption equilibrium: Langmuir, Freundlich and Redlich-Peterson.

The Langmuir model has three assumptions: first, the surface of the adsorbent is homogeneous; second, the free energy is constant; and finally, the adsorbed substance
would not migrate on the adsorbent [37]. The Langmuir model can be written as the Equations (4) and (5).

\[
\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{q_m K_L}
\]

\[
R_L = \frac{1}{1 + K_L C_0}
\]

where \(C_e \text{ (g/L)}\) is the equilibrium concentration of the asphaltenes in the liquid phase. \(q_e \text{ (g/g)}\) is the weight of asphaltenes adsorbed per gram of corn stalk fibers at equilibrium. \(q_m\) and \(K_L\) are Langmuir parameters, which reflect the adsorption capacity and the free energy of adsorption, respectively. The Langmuir parameters can be obtained from linear regression analysis by the adsorption data curve of \(C_e/q_e\) against \(C_e\). \(R_L\) is the separation factor of the Langmuir isotherm. \(C_0 \text{ (g/L)}\) is the initial concentration of the asphaltenes.

The Freundlich model is based on the hypothesis that adsorption is caused by the heterogeneous surface area of the adsorbent, which means different adsorption capacities in the surface areas of the adsorbent [36]. It is shown as the Equation (6).

\[
\ln q_e = \frac{1}{n} \ln C_e + \ln K_F
\]

where \(q_e \text{ (g/g)}\) is the weight of asphaltenes adsorbed per gram of corn stalk fiber at equilibrium. \(C_e \text{ (g/L)}\) is the equilibrium concentration of the asphaltenes. \(K_F \text{ ((g/g)} (L/g)^{1/n})\) is the Freundlich parameter, which represents the adsorption capacity of corn stalk fibers. \(n\) is also a Freundlich parameter, as a heterogeneous factor of the adsorbent, which indicates the level of adsorption. The values of the Freundlich parameters were generated from linear regression analysis, using the plots of \(\ln q_e\) against \(\ln C_e\).

The Redlich-Peterson model combines three parameters in this model [38]. It is written as the Equation (7).

\[
q_e = \frac{XC_e}{1 + YC_e^\alpha}
\]

Because this model has three parameters, it is impossible to perform linear regression analysis. Therefore, this study transformed this formula into a logarithmic formula [31,39], which is written as the Equation (8).

\[
\ln\left(\frac{XC_e}{q_e} - 1\right) = \alpha \ln C_e + \ln Y
\]

where \(C_e \text{ (g/L)}\) is the equilibrium concentration of the asphaltenes in the liquid phase. \(q_e \text{ (g/g)}\) is the weight of asphaltenes adsorbed per gram of corn stalk fibers at equilibrium. \(X \text{ (L/g)}\), \(Y \text{ (L/g)}\) and \(\alpha\) are three parameters from Equation (8). The Redlich-Peterson parameters can be acquired from the pseudolinear plots of \(\ln (XC_e/q_e - 1)\) against \(\ln C_e\) regression analysis. The values of \(X\) and \(R^2\) are chosen to be the most optimized.

Figure 8 shows that the Langmuir, Freundlich and Redlich-Peterson adsorption isotherms of asphaltenes on corn stalk fibers are related to \(q_e\) and \(C_e\) at 135 °C. All the correlation coefficients (\(R^2\)) and parameters of the three isotherm models are presented in Table 3. The \(R^2\) value of the Redlich-Peterson model was the highest (0.979), indicating that the adsorption process of asphaltenes on corn stalk fibers was best described by the Redlich-Peterson model. The next best model was the Freundlich model (0.976), and the last was the Langmuir model (0.952). This phenomenon illustrated that the adsorption process of asphaltenes was more likely to be caused by the heterogeneous surface of corn stalk fibers and involved with multilayer adsorption [40].
Figure 8. Langmuir, Freundlich and Redlich-Peterson isotherms for asphaltenes at 135 °C.

Table 3. Langmuir, Freundlich and Redlich-Peterson isotherm model parameters of asphaltene adsorption.

| Isotherms          | Parameters          | Corn Stalk Fibers |
|--------------------|---------------------|-------------------|
| Langmuir           | $q_m$ (g/g)         | 9.337             |
|                    | $K_L$ (L/g)         | 0.020             |
|                    | $R^2$               | 0.952             |
| Freundlich         | $K_F$ ((g/g) (L/g)$^{1/n}$) | 0.712             |
|                    | $1/n$               | 0.478             |
|                    | $R^2$               | 0.976             |
| Redlich-Peterson   | $X$ (L/g)           | 2.871             |
|                    | $Y$ (L/g)$^\alpha$  | 3.620             |
|                    | $\alpha$            | 0.537             |
|                    | $R^2$               | 0.979             |

The curve of the separation factor ($R_L$) from different asphaltene initial concentrations at 135 °C is shown in Figure 9. The $R_L$ value can be calculated from the Langmuir model parameter and indicates the shape of the adsorption isotherm. The adsorption process was unfavorable when $R_L > 1$, linear when $R_L = 1$, and irreversible when $R_L = 0$, and the adsorption process was favorable when the value of $R_L$ was between 0 and 1 [41,42]. From Figure 9, the values of $R_L$ were all between 0 and 1, illustrating that the adsorption process of asphaltenes on the corn stalk fibers was favorable. The values of $R_L$ decreased with increasing asphaltene initial concentration, demonstrating that the adsorption capacity of corn stalk fibers increased with increasing initial asphaltene concentration because of the driving forces generated by the concentration gradient. The value of $1/n$ from the Freundlich model was between 0 and 1 [32,42], which also represented the favorable adsorption process of asphaltenes and the heterogeneous surface of corn stalk fibers.
3.5. Adsorption Kinetic Models

The kinetics of adsorption can be used to investigate the interaction between asphaltenes and the surface of corn stalk fibers and characterize the rate of asphaltene adsorption on corn stalk fibers. The pseudo-first-order and pseudo-second-order models were used to describe the behavior of the adsorption process.

The equation of the pseudo-first-order model is written as the Equation (9) [43].

$$\ln(q_e - q_t) = -k_1 t + \ln q_e$$  \hspace{1cm} (9)

where \(q_t\) (g/g) and \(q_e\) (g/g) are the adsorption weights of asphaltenes per gram of corn stalk fibers at any time \(t\) (min) and equilibrium, respectively, and \(k_1\) (1/min) is the adsorption rate parameter of the pseudo-first-order model. The adsorption rate constant can be obtained from the slope of the linear regression analysis between the plots of \(\ln(q_e - q_t)\) versus \(t\). The intercept of the linear regression analysis can be the value of \(\ln q_e\), and the calculated \(q_e\) is the predicted adsorption weight of asphaltenes per gram of corn stalk fiber at equilibrium.

The equation of the pseudo-second-order model is given as the Equation (10) [44].

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2}$$ \hspace{1cm} (10)

where \(q_t\) (g/g) and \(q_e\) (g/g) are the adsorption weights of asphaltenes per gram of corn stalk fiber at time \(t\) (min) and at equilibrium and \(k_2\) (g/g min) is the adsorption rate parameter in the pseudo-second-order model. The value of the adsorption rate parameter is generated from the slope of the linear regression analysis using the plots of \(t/q_t\) against \(t/q_e\). The predicted adsorption weight of asphaltenes at equilibrium can be acquired by calculating the intercept of the linear regression analysis.

The calculated values of \(q_e\), \(k_1\) and correlation coefficient \(R^2\) from pseudo-first-order and pseudo-second-order models are shown in Table 4. The linear regression analyses of pseudo-first-order and pseudo-second-order models are presented in Figures 10 and 11, respectively. The correlation coefficients \(R^2\) of the pseudo-second-order models (0.996–0.998) were higher than those of the pseudo-first-order models (0.767–0.993) at asphaltene concentrations from 57.3 g/L to 149.0 g/L. This indicated that the pseudo-second-order model was a better description of the adsorption process of asphaltenes on corn stalk fibers, and then the values of \(q_e\) calculated from the pseudo-second-order model were closer to the experimental values of \(q_e\) than those of the pseudo-second-order model. This phenomenon illustrated that the adsorption process of asphaltenes on corn stalk fibers could not only be physical adsorption but also be related to chemical adsorption [45].
Table 4. The parameters of pseudo-first-order and pseudo-second-order models for asphaltene adsorption on corn stalk fiber at 135 °C.

| Asphaltene Concentration (g/L) | \( q_{e, \text{exp}} \) (g/g) | Pseudo-First-Order Model | Pseudo-Second-Order Model |
|-------------------------------|-----------------------------|--------------------------|---------------------------|
|                              | \( q_{e, \text{cal}} \) (g/g) | \( k_1 \) (1/min) | \( R^2 \) | \( q_{e, \text{cal}} \) (g/g) | \( k_2 \) (g/min) | \( R^2 \) |
| 57.3  | 1.640 | 1.054 | 0.088 | 0.767 | 1.804 | 0.114 | 0.997 |
| 67.8  | 1.885 | 1.370 | 0.078 | 0.946 | 2.121 | 0.078 | 0.996 |
| 90.3  | 2.135 | 1.773 | 0.095 | 0.993 | 2.339 | 0.091 | 0.998 |
| 102.9 | 2.400 | 2.304 | 0.101 | 0.962 | 2.699 | 0.057 | 0.998 |
| 149.0 | 3.100 | 2.685 | 0.081 | 0.966 | 3.364 | 0.053 | 0.998 |

Figure 10. Pseudo-first-order model for asphaltenes adsorbed on corn stalk fibers at 135 °C.

Figure 11. Pseudo-second-order model for asphaltenes adsorbed on corn stalk fibers at 135 °C.
3.6. Adsorption Mechanism

It was necessary to predict the rate-limiting step in the adsorption process, which was controlled by the adsorption mechanism. To analyze the adsorption mechanism and determine the rate-limiting step, the intraparticle diffusion model of Weber and Morris and the film diffusion model of Boyd were used to differentiate between film diffusion and intraparticle diffusion in the adsorption process of asphaltenes on corn stalk fibers.

The equation of the Weber and Morris intraparticle diffusion model is presented as the Equation (11) [42].

\[ q_t = k_{pi} t^{0.5} + C \]  

where \( q_t \) (g/g) is the weight of asphaltenes adsorbed at any time \( t \) (min). \( k_{pi} \) (g/g min) is the rate constant of intraparticle diffusion. \( C \) is the constant of boundary layer thickness. The value of the rate constant can be obtained from the slope of the linear regression analysis using the plots of \( q_t \) against \( t^{0.5} \), and the intercept is the value of the constant of the boundary layer thickness.

The model of the Boyd film diffusion model is written as the Equations (12) and (13) [46]:

\[ \ln(1 - \frac{q_t}{q_e}) = -\frac{D\pi^2}{a^2} t + C \]  

\[ B = \frac{D\pi^2}{a^2} \]  

where \( q_t \) (g/g) and \( q_e \) (g/g) are the adsorption weights of asphaltenes per gram of corn stalk fiber at any time \( t \) (min) and at equilibrium, respectively. The values of the parameters \( B \) and \( C \) are generated from the slope and intercept of the linear regression analysis by the plots of \( \ln(1 - \frac{q_t}{q_e}) \) against \( t \), respectively.

Figure 12 shows the Weber and Morris intraparticle diffusion model of asphaltene adsorption on corn stalk fibers at 135 °C, and Table 5 presents the values of the parameters of this model. The intraparticle diffusion model was divided into three parts. The slope of the first part (\( k_{p1} \)) was highest, and the highest rate constant indicated rapid asphaltene adsorption on the external surface of corn stalk fibers because there were many adsorption sites and low competition for asphaltene. This phenomenon also indicated that the first part was caused by film diffusion [47]. The second part was a transitional stage of boundary diffusion and intraparticle diffusion. The third part was mainly controlled by intraparticle diffusion. These stages illustrated that the asphaltenes diffused from the external surface to the internal surface of corn stalk fibers. The adsorption rates of the three parts gradually decreased over time until adsorption equilibrium was reached due to the reduction in concentration driving forces [48]. The slope of the second part was closer to that of the third part at asphaltene concentrations from 57.3 g/L to 149.0 g/L, which indicated that the time of the transitional stage was shorter as the asphaltene concentration increased. The value of the intercept of the intraparticle model can be used to evaluate the adsorption contribution of the corn stalk fiber surface in the rate-controlling step [49]. As seen in Figure 12, the adsorption contribution was best in the first part, followed by the second part and finally the third part.

The Boyd film diffusion model for asphaltene adsorption on corn stalk fibers at 135 °C and the values of the parameters for this model are shown in Figure 13 and Table 6, respectively. The plots did not pass through the origin for \( C \) values from 57.3 g/L to 149.0 g/L, which illustrated that asphaltene adsorption on the corn stalk fibers corresponded to film diffusion. This diffusion was the rate-limiting step [46]. The adsorption mechanisms of asphaltene on corn stalk fiber are shown in Figure 14.
Figure 12. Weber and Morris intraparticle diffusion model for asphaltenes adsorbed on corn stalk fibers at 135 °C.

Table 5. The parameters of the Weber and Morris intraparticle diffusion model for asphaltene adsorption on corn stalk fibers at 135 °C.

| Asphaltenes Concentration (g/L) | Weber and Morris Intraparticle Diffusion Model |
|---------------------------------|-----------------------------------------------|
|                                 | \( k_{p1} \) (g/g min)  | \( C_1 \)  | \( R_1^2 \) | \( k_{p2} \) (g/g min)  | \( C_2 \)  | \( R_2^2 \) | \( k_{p3} \) (g/g min)  | \( C_3 \)  | \( R_3^2 \) |
| 57.3                            | 0.377                          | 0          | 0.982        | 0.225                  | 0.548        | 1          | 0.023                  | 1.474        | 0.511              |
| 67.8                            | 0.409                          | 0          | 0.969        | 0.256                  | 0.556        | 1          | 0.056                  | 1.491        | 0.722              |
| 90.3                            | 0.504                          | 0          | 0.981        | 0.209                  | 0.886        | 1          | 0.102                  | 1.424        | 0.863              |
| 102.9                           | 0.508                          | 0          | 0.976        | 0.260                  | 0.864        | 1          | 0.121                  | 1.532        | 0.884              |
| 149.0                           | 0.678                          | 0          | 0.970        | 0.259                  | 0.721        | 1          | 0.180                  | 1.761        | 0.940              |

Figure 13. Boyd film diffusion model for asphaltenes adsorbed on corn stalk fibers at 135 °C.
Table 6. The parameters of the Boyd film diffusion model for asphaltene adsorption on corn stalk fibers at 135 °C.

| Asphaltene Concentration (g/L) | Boyd Film Diffusion Model |
|-------------------------------|---------------------------|
|                               | B  | C    | R²   |
| 57.3                          | 0.084 | 0.570 | 0.738 |
| 67.8                          | 0.108 | 0.117 | 0.997 |
| 90.3                          | 0.093 | 0.240 | 0.996 |
| 102.9                         | 0.101 | 0.054 | 0.956 |
| 149.0                         | 0.783 | 0.054 | 0.968 |

Figure 14. The adsorption mechanisms of asphaltene on corn stalk fiber.

3.7. Effect of Asphaltene Adsorption Rate on Corn Stalk Fiber Asphalt Performance

Corn stalk fibers weighing 4 g, 8 g, 12 g, 16 g and 20 g were mixed into Anda-70 asphalt, and then the high-temperature performance was evaluated by dynamic shear rheological (DSR) testing. The test procedure was that corn stalk fiber asphalt was first placed on the test plate. Then, the instrument automatically adjusted the distance between the oscillating plate and the test plate. Finally, the rutting factor parameters were obtained by rotating and shearing the corn stalk fiber asphalts at 70 °C to account for the high temperature performance.

Figure 15a shows that the values of the rutting factors increased as the mass ratio of corn stalk fiber increased, and the mass ratio of corn stalk fibers also affected the adsorption rate of the asphaltenes. From Figure 15b, it can be seen that the values of the rutting factors also increased as the adsorption rate of asphaltene increased. This explains why corn stalk fibers have a good effect on the high temperature of asphalt, and corn stalk fibers can adsorb asphalt.
Figure 15. The rutting factors of corn stalk fiber asphalts: (a) the values change of the rutting factors as the mass ratio of corn stalk fiber increased; (b) the values change of the rutting factors as the adsorption rate of the asphaltenes increased.

4. Conclusions

The adsorption process of asphaltenes on corn stalk fibers was studied. Scanning electron microscopy illustrated that the corn stalk fibers had rough surfaces and pore structures. Brunauer-Emmett-Teller (BET) analysis showed that the corn stalk fibers had macroporous and mesoporous structures. The amount of asphaltenes adsorption on the corn stalk fibers increased as the weight of the corn stalk fibers, the initial concentration of asphaltene and time increased. The Redlich-Peterson model best described the asphaltene adsorption process and explained the favorable adsorption process of asphaltenes. The adsorption process of asphaltenes was more likely to be caused by the heterogeneous surface of corn stalk fibers and involved with multilayer adsorption. The parameters of the kinetic model indicated that the pseudo-second-order model is a better description of the asphaltene adsorption process than the pseudo-first-order model, which indicated that the adsorption process involved not only physical adsorption but also chemical adsorption. The Weber and Morris intraparticle diffusion model showed that the adsorption process was first film diffusion, followed by the transition stage and finally, intraparticle diffusion. The Boyd film diffusion model illustrated that the rate-limiting step of the adsorption process was film diffusion. The rutting factors of corn stalk fiber asphalt increased as the mass ratio of fibers and the adsorption rate of asphaltene increased. Finally, the corn stalk fibers were proven to adsorb the asphalt effectively.

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