Simulating the pyrolysis process of sludge-lignin with the production of active carbons

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Abstract Using the method of the planned experiment, mathematical models that establish a relationship between the technological parameters of the pyrolysis process of sludge-lignin with the characteristics of a porous surface of the synthesized active carbons are obtained. The nature of the influence of temperature and duration of the pyrolysis, the dosage of activating agent on the yield of carbon, the volume and specific surface of the pores are determined. The optimal conditions for obtaining adsorbents from sludge-lignin are established; the specific BET surface area was about 2000 m²/g.

1. Introduction
Active carbons (AC) are used in various fields of human activity: medicine and pharmaceuticals, treated water production and wastewater treatment, electronics, food, chemical and other industries. Along with wood, technical lignins formed at wood processing and pulp and paper industries (PPI) can be used as raw materials for AC production: hydrolysis [1–3] and sulfate lignin [3–7], lignosulfonates [8, 9], black liquor [10, 11].

The raw material for the synthesis of carbon adsorbents can also be lignin sludge, a precipitate formed in the processes of coagulation treatment of lignin-containing wastewater and water treatment [12]. Pyrolysis of sludge-lignin is the most effective way of processing it to produce a marketable product – activated carbons [8], it will contribute to a wider implementation of local coagulation systems for waste water treatment of pulp and paper industry and, as a result, will improve the environmental situation.

An urgent task in the production of activated carbons is the synthesis of adsorbents with desired properties and characteristics, which should include in the first place the parameters that determine the porous structure of adsorbents: volume and specific surface. This problem can be solved by developing mathematical models that connect the characteristics of activated carbon (AC) with the conditions for obtaining it. The modeling of the pyrolysis process of technical lignins can be carried out using the methods of the planned experiment [2, 13]; similar work has not been carried out in relation to pyrolysis of sludge-lignin.

The purpose of the work is to obtain mathematical models that establish the dependence of the characteristics of activated carbons from sludge-lignin with the pyrolysis conditions by the method of
the planned experiment, as well as a comparative analysis of the characteristics of AC from sludge-lignin with the characteristics of adsorbents from other types of technical lignins.

2. Research objects and research methods

Sludge-lignin was obtained in laboratory conditions by treating lignin-containing wastewater with aluminum oxychloride, based on the optimal conditions and operating parameters established by us earlier [14], dried to an air-dry state, and subjected to pyrolysis. Pyrolysis was carried out by thermochemical activation, the advantage of which is the production of carbons with high characteristics of porous surface [15]. Sodium hydroxide was used as an activating agent, as an effective reagent for the pyrolysis of carbon materials having an disordered structure [3].

Previous studies have established that an experimental study of the pyrolysis process can be carried out using a three-factor rotatable central compositional plan of the second order [1, 2]. This plan was used by us to simulate the pyrolysis process of sludge-lignin. The regression equation describing the experimental data in accordance with the specified plan has the following form:

\[ y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 \]

For the experiment, the most significant thermochemical activation factors were selected: \( X_1 \) is the pyrolysis temperature (T, °C), \( X_2 \) is the duration of the pyrolysis (\( \tau \), min), and \( X_3 \) is the dosage of the activating agent (D, %). The following characteristics were used as output parameters: coal yield (Y, %); micropore volume calculated according to the Dubinin-Radushkevich equation of micropore volumetric filling theory (V_{DR}, cm³/g); micropore volume (V_{BET}, cm³/g), total pore volume (V_{Σ}, cm³/g) and the specific BET surface (S_{BET}, m²/g) calculated according to the Brunauer-Emmett-Teller (BET) equation of the theory of polymolecular adsorption; Mesopore volume determined by the Barrett-Joyner-Halenda method (V_{BJH}, cm³/g); specific surface of meso- and macropores determined by the t-plot method (S_{M}, m²/g).

The characteristics of the porous structure of active carbons were determined by low-temperature nitrogen adsorption (at a temperature of 77 K) using the ASAP 2020MP automated system (Micromeritics).

Based on the results of preliminary studies, we determined the levels of variation of the experimental factors (table 1) and, in accordance with the chosen plan, compiled a planning matrix (table 2).

| Table 1. Factor variation levels. |
|----------------------------------|
| Factors                          | Factor levels |
|                                  | −1.682        | −1  | 0  | 1  | 1.682 |
| Pyrolysis temperature            | 650           | 670 | 700 | 730 | 750   |
| Pyrolysis duration               | 30            | 42  | 60  | 78  | 90    |
| Sodium hydroxide dosage          | 120           | 144 | 180 | 216 | 240   |

| Table 2. Experiment planning matrix. |
|--------------------------------------|
| Experiment №                      | Coded notations | Actual values |
|                                     | \( X_1 \)  | \( X_2 \)  | \( X_3 \)  | \( X_1 \)  | \( X_2 \)  | \( X_3 \)  |
| 1                                   | −1      | −1      | −1      | 670     | 42      | 144     |
| 2                                   | 1       | −1      | −1      | 730     | 42      | 144     |
| 3                                   | −1      | 1       | −1      | 670     | 78      | 144     |
| 4                                   | 1       | 1       | −1      | 730     | 78      | 144     |
| 5                                   | −1      | −1      | −1      | 670     | 42      | 216     |
3. Results and discussion

We conducted experimental studies, the obtained data we used to calculate the coefficients of the regression equations and the development of statistical models. Models were checked according to the Fisher criterion: all models adequately describe the processes under study, since for all the equations obtained, the calculated value of the Fisher criterion does not exceed the tabulated one (at a significance level of 0.05). Using the equations of mathematical models, we constructed response surfaces that clearly demonstrate the influence of experimental factors on the output characteristics.

Mathematical models:

\[
Y = 19.8 - 2.0X_3 - 3.5X_1X_3 - 3.1X_1^2 + 2.6X_3^2
\]

(1)

\[
V_{DR} = 0.31 + 0.13X_3 - 0.06X_1X_2 + 0.06X_1X_3 + 0.02X_2^2
\]

(2)

\[
V_{BET} = 0.36 + 0.15X_3 - 0.06X_1X_2 + 0.07X_1X_3
\]

(3)

\[
V_{BJH} = 0.08 + 0.07X_3 + 0.03X_1X_3 + 0.05X_3^2
\]

(4)

\[
V_S = 0.45 + 0.23X_3 - 0.08X_1X_2 + 0.1X_1X_3 + 0.08X_3^2
\]

(5)

\[
S_{BET} = 788 + 374X_3 - 138X_1X_2 + 162X_1X_3 + 41X_2X_3 - 88X_1^2 + 69X_2^2 + 86X_3^2
\]

(6)

\[
S_M = 145 - 45X_2 + 119X_3 - 55X_1X_2 + 87X_1X_3 + 63X_2^2 + 38X_3^2
\]

(7)

The dosage of sodium hydroxide negatively affects the AC output; the mutual influence of the pyrolysis temperature and alkali dosage is also negative; the coefficient at \(X_1^2\) is negative, and at \(X_3^2\) is positive, this means that the response surface will be convex with respect to the pyrolysis temperature and concave with respect to the dosage of sodium hydroxide (1). This generally agrees with the data of previous studies [1], but the amount of coal output from sludge-lignin is somewhat lower and amounted to 20–30%, which is associated with the presence of a larger amount of inorganic substances (aluminum compounds) in the composition of the initial sludge-lignin.

The mathematical models obtained for the micropore volume calculated by the Dubinin-Radushkevich (2) and BET (3) equations are almost identical; the presence of a quadratic coefficient in equation (2) gives some curvature of the response surface relative to factor \(X_2\) — the duration of the pyrolysis (figure 1b). The dependences of these parameters on the pyrolysis conditions are of a similar nature: the factor that has the most significant positive effect is the dosage of the activating agent; at temperatures below 700°C, with an increase in the duration of pyrolysis, the micropore volume increases, and at higher temperatures it decreases (figure 1a, figure 2a). At a constant pyrolysis
temperature (figure 1b, figure 2b) with increasing $\tau$, the micropore volume decreases slightly. In general, the micropore volume of the obtained AC samples reaches 0.8 cm$^3$/g.

Figure 1. $V_{DR}$ versus AC production conditions: at a constant dosage of NaOH (a) and at a constant pyrolysis temperature (b).

Figure 2. The dependence of $V_{BET}$ on the conditions for obtaining AC: at a constant dosage of NaOH (a) and at a constant pyrolysis temperature (b).

The dosage of sodium hydroxide has a positive effect on the mesopore volume at values of the latter 160% and higher; in this interval, the response surface has a significant degree of curvature (figure 3b), which is due to the quadratic coefficient $b_{33}$ in equation (4). The duration of the pyrolysis process does not affect $V_{BJH}$; with an increase in the pyrolysis temperature, the volume of mesopores increases linearly in the entire temperature range (figure 3a). The value of $V_{BJH}$ reaches 0.2–0.3 cm$^3$/g.

The dependences constructed for the total pore volume (figure 4) and micropore volume (figure 1, figure 2), in general, have a similar character. This is due to the fact that a significant proportion of the pore volume (up to 80%) falls on micropores. Thus, the adsorbents we synthesized from sludge-lignin have mainly a microporous surface structure.
Figure 3. The dependence of $V_{\text{BJH}}$ on the conditions for obtaining AC: at a constant dosage of NaOH (a) and at a constant pyrolysis temperature (b).

Figure 4. The dependence of $V_{\Sigma}$ on the conditions for obtaining AC: at a constant dosage of NaOH (a) and at a constant pyrolysis temperature (b).

The specific surface of $S_{\text{BET}}$ has a significant degree of curvature due to the presence of quadratic effects coefficients in the equation, the dosage of sodium hydroxide has a major and positive effect, therefore, the mutual effects of the pyrolysis temperature and alkali dosage and the duration of pyrolysis and alkali dosage also have a positive effect, and the mutual influence of temperature and the duration of the pyrolysis process is negative (6).

From the presented data (figure 5), it is possible to establish the optimal conditions for the pyrolysis of sludge-lignin, based on the fact that the obtained samples of activated carbon have a developed microporous structure: temperature – 700 °C, duration – 80 min, dosage of sodium hydroxide – 200%. The specific surface area was about 2000 m$^2$/g.

The specific surface of meso- and macropores under optimal conditions was about 500 m$^2$/g (figure 6). The size of this parameter is positively affected by the dosage of alkali and negatively by the duration of the pyrolysis process (7).
**Figure 5.** The dependence of $S_{\text{BET}}$ on the conditions for obtaining AC: at a constant dosage of NaOH (a) and at a constant pyrolysis temperature (b).

**Figure 6.** The dependence of $S_M$ on the conditions for obtaining AC: at a constant dosage of NaOH (a) and at a constant pyrolysis temperature (b).

**Table 3.** Active carbons of thermochemical activation with sodium hydroxide.

| Raw material                  | $V_{\text{BET}}$, cm$^3$/g | $S_{\text{BET}}$, m$^2$/g |
|-------------------------------|-----------------------------|----------------------------|
| Sludge-lignin                 | 0.8                         | 2000                       |
| Sludge-lignin [12]            | –                           | 98–112                     |
| Hydrolytic lignin [16]        | –                           | 1300                       |
| Sulphate lignin [5]           | 1.2                         | 2400                       |
| Sulphate lignin [7]           | 0.8–1.08                    | 1900–2430                  |
| Sulphate lignin [17]          | –                           | 800–2000                   |
| Sulphate lignin [18]          | 0.75                        | 1440                       |
Considering the generally accepted characteristics of adsorbents – the volume and the specific BET surface area, it can be noted that the samples of coal from sludge-lignin synthesized by us are practically inferior, and in some cases, superior to ACs obtained from various types of technical lignins by the method of thermochemical activation with sodium hydroxide (table 3).

4. Conclusion
For the implementation of specific tasks requires activated carbons with certain characteristics. First of all, they include the characteristics of the porous surface – volume and specific surface. By changing the technological parameters of the pyrolysis process, one can obtain adsorbents with desired properties and characteristics.

Our mathematical models link the conditions for the synthesis of AC from sludge-lignin with their characteristics and allow one to simulate the pyrolysis process, while receiving adsorbents with pre-predicted properties.

It was found that the dosage of the activating agent (sodium hydroxide) has the most significant effect on all the output parameters that we studied: in all models, except the AC output equation, this factor is positive. Thus, increasing the dosage of alkali, it is possible to obtain coals with a highly developed porous structure, however, their output will decrease. The temperature and duration of pyrolysis have a smaller effect on the characteristics of activated carbons from sludge-lignin. At the same time, a simultaneous increase in these factors leads to a slight decrease in V_BET and S_BET and an increase in S_M. Using the effect of the mutual influence of T and τ, we can to some extent change the ratio of the parameters of micropores and mesopores.

Based on the ratio of the volumes of micropores and mesopores and the specific surfaces of S_BET and S_M, it was concluded that the structure of the obtained AC is mainly microporous.

According to the nature of the influence of experimental factors on the S_BET value, the optimal operating parameters of the sludge-lignin pyrolysis were established: T – 700 ºC, τ – 80 min, D – 200 %. Active carbons obtained under optimal conditions have high porous surface characteristics (S_BET = 2000 m²/g) and, in general, are not inferior in their properties to adsorbents synthesized from other types of technical lignins by thermochemical activation with sodium hydroxide.

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