Study on the application of KOH to produce activated carbon to realize the utilization of distiller’s grains

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Abstract. The distiller’s grains in a liquor factory are selected as the main material to study the preparation of activated carbon with KOH activation. The solid-to-liquid ratio \textit{A}, KOH concentration \textit{B}, activation temperature \textit{C}, activation time \textit{D} are regarded as variables to produce single factor experiment. The results show that the best preparation conditions of various factors are: 50\% KOH concentration, solid-liquid ratio of 1:4, activation temperature of 750\textdegree C, activation time of 2.0h. The L9 (3\textsuperscript{4}) orthogonal experiment is carried out by selecting three levels from each single factor, showing that the importance order of the factors is: \textit{B} > \textit{A} > \textit{C} > \textit{D}. In addition, when KOH solution concentration is 60\%, the solid-liquid ratio is 1:5, activation temperature is 700\textdegree C, and activation time is 2.0h, the performance of the preparation of activated carbon is the best.

1. Introduction
Many plants are widely used as materials for the preparation of activated carbon, for example, corncob, coconut, almond shell, peanut shell, bamboo, etc. Huang Lihua\textsuperscript{[1]} used residual activated sludge to prepare activated carbon, studied the effect of preparation conditions on the adsorption performance and yield of activated carbon by using different activated method to prepare activated carbon. Song Lei\textsuperscript{[2]} used waste tea to prepare activated carbon, studied the best preparation conditions and the control of pore structure. Xie Xinping\textsuperscript{[3]} used phosphoric acid activating eucalyptus chips to prepare activated carbon and so on.

The lees are the main byproducts of the brewing industry. In addition to the consumption of carbohydrates after fermentation, protein, fat, vitamins, organic acids, amino acids, nucleic acids and many other substances content all be increased\textsuperscript{[4-5]}. Therefore, the lees are usually used to make animal feed and its additives\textsuperscript{[6-7]}, pit mud fermentation nutrient, cultivation of edible fungus\textsuperscript{[8]}, brewed soy sauce and vinegar\textsuperscript{[9-11]}, fertilizer\textsuperscript{[12]} and so on.

China is a big producer of liquor. As a subsidiary products with a large amount, lees will rot if they are not treated timely. It will not only be a waste of resources, but also will seriously pollute the environment. Therefore, using lees for the preparation of activated carbon can realize "ecological" to the enterprise and have a vital significance for China’s resources recycling and environmental protection.

2. Materials and methods

2.1. Experimental materials
Distiller's grains: the main raw material of distiller's grains from a liquor factory in Chengdu, the main ingredients are shown in Table 1. The lees from Maotai flavor liquor, its'organic compounds are relatively high, and the lowest content of rice husk.

Table 1. The material content of distiller's grains (%)

| Items      | Maotai flavor liquor | Luzhou flavor liquor | Fen flavor liquor |
|------------|----------------------|----------------------|------------------|
| Starch     | 14.8~15.6            | 4.6~6.2              | 2.8~3.2          |
| Protein    | 9~10                 | 2.7~3.5              | 1.5~2.6          |
| Fat        | 3.5~4.3              | 0.9~1.8              | 0.6~1.3          |
| Rice husk  | 8~12                 | 56~68                | 65~76            |

KOH: analytical pure, HCl: analytical pure, Nitrogen: high purity nitrogen 99.999%

2.2. Experimental equipment
SK Tubefurnace 2.5-13, TU-1901 UV spectrophotometer (Beijing Puxi), BPG-9070A Precision blast drying box, THZ-82B Gas bath thermostat (Jin Yi), BS-124-S Electronic balance etc.

2.3. Experimental methods
In this experiment, KOH activation method was used to prepare activated carbon, the main influencing factors of activated carbon’s final yield and quality are as follows: (1) the concentration of KOH—A; (2) solid-liquid ratio of distiller's grains and KOH solution—B; (3) the activation temperature —T; (4) activation time—t.

Through the investigation of each influence factor, we can find out a data range can meet the orthogonal experiment, and finally get the best method of the preparation of activated carbon by orthogonal experiment. The experimental procedure is shown in figure 1.

Figure 1. The flow chart of the experiment.

3. Experimental results

3.1. The influence of preparation conditions on activated carbon

3.1.1 Effect of KOH solution concentration on activated carbon. Under the conditions of solid-liquid ratio of 1: 4, activation temperature of 750 ℃ and activation time of 2h, the concentration of KOH solution was 10%, 20%, 30%, 40%, 50% and 60% to prepare activated carbon.

It can be seen from Figure 2 that with the increase of the concentration of KOH solution, the adsorption value of iodine and methylene blue of the activated carbon increased and then decreased, and reached the highest yield of 24.48% at the concentration of 40%, the maximum iodine adsorption value and the highest methylene blue adsorption value of 1521.94mg / g and 21.28 (10mL / g) at the concentration of 50%. The purpose of KOH activation is to activate the mesopores and micropores of activated carbon. In the internal pore structure of activated carbon, the more developed micropores, the higher the adsorption value of iodine and methylene blue. When the concentration of KOH is less than 40%, the degree of activation of distillers is low, but with the increase of KOH concentration, the micropores are more developed in the internal void structure of activated carbon. When the concentration of KOH reaches 50%, the pore structure is the most developed. When the concentration of KOH is higher than 50%, due to excessive activation, the internal structure of activated carbon is destroyed, part of the microporous turn into large pores.
In the case of comprehensive consideration of the yield and the adsorption value, the three levels of KOH solution concentration, which have a great influence on the preparation of activated carbon, were selected as follows: 40%, 50%, and 60%.

### 3.1.2 Effect of solid-liquid ratio on activated carbon

Under the condition of KOH solution concentration of 50%, activation temperature of 750 °C and activation time of 2h, the solid-liquid ratio of the control lees and KOH solution was 1: 1, 1: 2, 1: 3, 1: 4, 1: 5, 1: 6 to prepare activated carbon.

It can be seen from Figure 3 that with the increase of dosage of KOH, the adsorption value of iodine and methylene blue of the activated carbon increased first and then decreased. The highest yield
and the highest iodine adsorption value were obtained when the solid-liquid ratio was 1:4, and the highest adsorption value of methylene blue (10mL/g) was obtained at the solid-liquid ratio of 1:5. When the solid-liquid ratio is greater than 1:4, the charred distiller's grains are not completely immersed in the KOH solution and cannot be fully contacted with the KOH, so the degree of activation of the distiller's grains is low. With the increase in the amount of KOH, distiller's grains and KOH solution are in full contact, so the activation degree is improved and the pores tend to develop. When the solid-liquid ratio reached 1:4, it achieves the best activation state. When the solid-liquid ratio is less than 1:4, the specific surface area of the activated carbon is relatively reduced due to excessive excess of KOH.

In the case of comprehensive consideration of the yield and the adsorption value, the three levels of solid-liquid ratio, which have a great influence on the preparation of activated carbon, were selected as follows: 1:4, 1:5, 1:6.

3.1.3 Effect of activation temperature on activated carbon. Under the condition of KOH solution concentration of 50%, solid-liquid ratio of 1:4 and activation time of 2h, the activation temperature of the control variable was controlled at the activation temperature of 600 °C, 650 °C, 700 °C, 750 °C, 800 °C, 850 °C to prepare activated carbon.

![Figure 4. Effect of activation temperature on properties of activated carbon](image)

It can be seen from Figure 4 that with the increase of calcination temperature, the adsorption value of iodine and methylene blue of the activated carbon increased first and then decreased, but the final yield has been decreasing. The maximum adsorption value is reached at the activation temperature of 750°C. Distiller's grains and activator KOH can react at high temperature. With the increase of temperature, the reaction speed is accelerated, so the activation is accelerated. When the temperature is over 750°C, the temperature is too high, resulting in uneven activation of activated carbon and decreased adsorption performance.

In the case of comprehensive consideration of the yield and the adsorption value, the three levels of calcination temperature, which have a great influence on the preparation of activated carbon, were selected as follows: 700°C, 750°C, and 800°C.
3.1.4 Effect of Activation Time on Activated Carbon. Under the condition of KOH solution concentration of 50%, solid-liquid ratio of 1: 4 and activation temperature of 750 ℃, the activation time of the control variable was 0.5h, 1.0h, 1.5h, 2.0h, 2.5h, 3.0h to prepare activated carbon.

![Graph showing the effect of activation time on activated carbon properties](image)

**Figure 5.** Effect of activation time on properties of activated carbon

As can be seen from Figure 5, with the increase of activation time, the iodine adsorption value and methylene blue adsorption value of activated carbon increased first and then decreased, and the maximum value was obtained at 2 hours, but the yield of activated carbon shew a decreasing trend. With the increase of time, the reaction between KOH and the lees is more and more abundant, and the pore structure is more and more developed, so the quality of activated carbon is reduced. When the reaction time reaches 2 hours, it reaches the peak of the micro- and mesopore structure, and the adsorption performance is the best. When the activation time is more than 2 hours, with the increase of time, the reaction is still continuing, so the micro hole is destroyed, the pore becomes larger, and the adsorption performance decreases.

In the case of comprehensive consideration of the yield and the adsorption value, the three levels of calcination time, which have a great influence on the preparation of activated carbon, were selected as follows: 1.5h, 2.0h, 2.5h.

3.2. Determination of the optimum preparation conditions of orthogonal experiment

3.2.1 Establishment of orthogonal experiment. Based on the above investigation of each influencing factor, 4 factors were determined in this experiment: A: concentration of KOH solution; B: solid-liquid ratio of distiller's grains and KOH solution; C: activation temperature; D: activation time. The three levels of each factor were selected, and the level of experimental factors were shown in Table 2, orthogonal experiment was carried out by L9 (3^4) orthogonal table.

| Number of factors | A: concentration of KOH solution | B: solid-liquid ratio of distiller's grains and KOH solution | C: activation temperature | D: activation time |
|-------------------|----------------------------------|-------------------------------------------------------------|--------------------------|-------------------|

Table 2. Factors affecting the performance of activated carbon.
3.2.2 Results and analysis of orthogonal experiment. Results of orthogonal experiment were shown in Table 3.

### Table 3. Results of orthogonal experiment.

| Serial number | A  | B  | C  | D  | yield (%) | adsorption value of iodine (mg/g) | adsorption value of methylene blue (10mg/g) |
|---------------|----|----|----|----|-----------|----------------------------------|---------------------------------------------|
| 1             | 1  | 1  | 1  | 1  | 25.32     | 1060.3                           | 20.1                                        |
| 2             | 1  | 2  | 2  | 2  | 1          | 944.5                            | 15.5                                        |
| 3             | 1  | 3  | 3  | 3  | 24.2       | 1003.2                           | 16.52                                       |
| 4             | 2  | 1  | 2  | 3  | 17.77      | 1100.1                           | 20                                           |
| 5             | 2  | 2  | 3  | 1  | 18.64      | 1124.8                           | 22.22                                       |
| 6             | 2  | 3  | 1  | 2  | 24.17      | 810.4                            | 18.25                                       |
| 7             | 3  | 1  | 3  | 2  | 18.06      | 1115.5                           | 20.55                                       |
| 8             | 3  | 2  | 1  | 3  | 24.71      | 1183.7                           | 23.22                                       |
| 9             | 3  | 3  | 2  | 1  | 16.22      | 899.7                            | 18.32                                       |

Analysis of results was shown in Table 4.

### Table 4. Analysis of results.

| Items                      | Serial number | A: concentration of KOH solution | B: solid-liquid ratio of distiller's grains and KOH solution | C: activation temperature | D: activation time |
|----------------------------|---------------|---------------------------------|------------------------------------------------------------|---------------------------|-------------------|
| yield (%)                  |               |                                 |                                                            |                           |                   |
|                            |               | K1j/3                           | 24.84                                                      | 20.38                     | 24.73             | 20.06             |
|                            |               | K2j/3                           | 20.19                                                      | 22.78                     | 19.66             | 22.41             |
|                            |               | K3j/3                           | 19.66                                                      | 21.53                     | 20.3              | 22.23             |
|                            |               | Rj                              | 5.18                                                       | 2.4                       | 5.07              | 2.35              |
| best solution              |               | A1                              |                                                            |                           |                   |                   |
|                            |               | K1j/3                           | 1002.7                                                     | 1092                      | 1018.1            | 1028.1            |
|                            |               | K2j/3                           | 1011.8                                                     | 1084.3                    | 981.4             | 956.8             |
|                            |               | K3j/3                           | 1066.3                                                     | 904.4                     | 1081.2            | 1095.7            |
|                            |               | Rj                              | 63.6                                                       | 187.6                     | 99.8              | 138.9             |
| best solution              |               | A3                              |                                                            |                           |                   |                   |
| adsorption value of iodine (mg/g) |       | K1j/3                           | 17.37                                                      | 20.22                     | 20.52             | 20.21             |
|                            |               | K2j/3                           | 20.16                                                      | 20.31                     | 17.94             | 18.1              |
|                            |               | K3j/3                           | 20.7                                                       | 17.7                      | 19.76             | 19.91             |
|                            |               | Rj                              | 3.33                                                       | 2.61                      | 2.58              | 2.11              |
| best solution              |               | A3                              |                                                            |                           |                   |                   |
| adsorption value of methylene blue (10mg/g) |       | K1j/3                           | 17.37                                                      | 20.22                     | 20.52             | 20.21             |
|                            |               | K2j/3                           | 20.16                                                      | 20.31                     | 17.94             | 18.1              |
|                            |               | K3j/3                           | 20.7                                                       | 17.7                      | 19.76             | 19.91             |
|                            |               | Rj                              | 3.33                                                       | 2.61                      | 2.58              | 2.11              |
| best solution              |               | A3                              |                                                            |                           |                   |                   |
| Importance of factors      |               |                                 |                                                            |                           |                   | B>A>C>D           |

Note: Kij---- the average value of all test results of leval(i) of factor(j).

The data of yeild show that, the variance is A > C > B > D, iodine adsorption value is B > D > C >
A, methylene blue adsorption value is A > B > C > D. But after considering the yield and adsorption values, the variance is A > B > C > D, that is to say, the maximum impact on the performance of activated carbon is the concentration of KOH, followed by the solid-liquid ratio of distiller's grains and KOH solution, and then the activation temperature, the activation time is minimal.

The best solution from the yield is A1B2C1D2, the adsorption value of iodine is A3B1C3D3, the adsorption value of methylene blue is A3B2C1D1. Above all, the best solution is A3B2C1D. Because the preparation time is 2 hours, so the best solution is A3B2C1D2, that is, the concentration of KOH is 60%, the solid-liquid ratio is 1 to 5, the activation temperature is 700 ℃, the activation time is 2 hours, achieving the best performance of activated carbon.

4. Analysis and discussion

The preparation process of activated carbon is various, but carbonization and activation are the key factors affecting the quality of activated carbon.

4.1. Carbonization

In addition to containing carbon, which is the main component of the preparation of activated carbon, but also contains a small amount of water, nutrients, oxygen, hydrogen, sulfur and other elements. Carbonization is the process of reducing the carbon composition by heating the lees. In this experiment, the carbonization temperature is 450 ℃, and with the increase of temperature, the distiller's grains are dehydrated and acid. When the temperature reaches 400 ℃, the oxygen is precipitated in the form of H2O, CO, CO2 and so on, so as to facilitate the subsequent activation reaction.[14]

4.2. Activation

After the contact with the KOH, the distiller's grains were activated at a high temperature, the carbon between the crystallites was burned by chemical reaction to form pores. However, if the activation time is too long and the temperature is too high, the micropores will be destroyed, the pore size becomes larger, and the yield decreases. In the activation process, the main reaction occurred [15]:

\[
4 \text{KOH} + \text{C} \rightarrow \text{K}_2\text{CO}_3 + \text{K}_2\text{O} + 2 \text{H}_2
\]

The carbon is eroded by KOH, releasing hydrogen, leaving voids on the carbon frame. At 500 degrees below, Dehydration(2) may occur due to the presence of potassium oxide, which can catalyze the occurrence of water gas (3) and transformation reaction (4), then the carbon dioxide and potassium oxide can produce potassium carbonate according to (5). Therefore, the main products are mainly hydrogen, as well as a small amount of carbon monoxide, carbon dioxide, etc.

\[
\begin{align*}
2 \text{KOH} & \rightarrow \text{K}_2\text{O} + \text{H}_2\text{O} \\
\text{C} + \text{H}_2\text{O} & \rightarrow \text{H}_2 + \text{CO} \\
\text{CO} + \text{H}_2\text{O} & \rightarrow \text{H}_2 + \text{CO}_2 \\
\text{K}_2\text{O} + \text{CO}_2 & \rightarrow \text{K}_2\text{CO}_3
\end{align*}
\]

5. Conclusion

(1) With the increase of KOH solution, the adsorption value and final yield of activated carbon were increased firstly and then decreased. At the concentration of 50%, the highest adsorption value was achieved, and the highest yield and the highest iodine adsorption value were reached at the solid-liquid ratio of 1: 4, the highest methylene blue adsorption value was obtained at the solid-liquid ratio of 1: 5.

(2) With the increase of the activation temperature and activation time, the adsorption value of the activated carbon increased first and then decreased, and the maximum adsorption value achieved at 750 ℃ and 2 hours. Because of the increase of pore structure, the yield has been decreasing.

(3) The maximum impact on the performance of activated carbon is the concentration of KOH, followed by the solid-liquid ratio of distiller's grains and KOH solution, and then the activation temperature, the activation time is minimal.

(4) When the concentration of KOH solution is 60%, the solid to liquid ratio is 1: 5, the activation
temperature is 700℃, the activation time is 2 hours, the activated carbon has the best performance.

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