Preparation of Cotton Straw-Based Activated Carbon by Microwave Charring and Its Adsorption Characteristics on Ni\textsuperscript{2+}

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Abstract: In this study, cotton stalks from Xinjiang Alar were used as raw materials. Preparation of modified cotton straw-based activated carbon by microwave-assisted pyrolysis using H\textsubscript{3}PO\textsubscript{4} as activator. The effects of different impregnation ratios, microwave power and irradiation time on the yield of cotton straw carbon and its adsorption performance on Ni\textsuperscript{2+} in the simulated wastewater were investigated by using Lagergren’s quasi primary and secondary adsorption kinetic equations. The experimental results showed that the adsorption performance of the modified cotton straw-based activated carbon was best under the conditions of 100 mL of simulated wastewater, Ni\textsuperscript{2+} mass concentration of 30 mg/L, pH=6.5, impregnation ratio of 1.5, microwave power of 600W and irradiation time of 7 minutes, and the adsorption kinetics of Ni\textsuperscript{2+} was in accordance with Lagergren quasi-secondary kinetic equations. The BET surface area and total pore volume of the modified cotton straw-based activated carbon were 1334 m\textsuperscript{2}/g and 0.918 m\textsuperscript{3}/g, respectively, which were 112 and 29 times higher than those of the direct pyrolysis activated carbon.

Keywords. Cotton straw, activated carbon, nickel, microwave, kinetic equation

1. Introduction

With the rapid development of my country’s industry, the problem of heavy metal pollution in water has become increasingly serious, which has become the main factor restricting the sustainable development of society and economy. Heavy metal wastewater has the characteristics of high toxicity, carcinogenicity and non-biodegradability, and has been paid much attention \cite{1, 2}. At present, the treatment methods of heavy metal wastewater mainly include chemical precipitation, ion exchange, flocculation and coagulation, and membrane separation technology. However, the adsorption method has the advantages of wide adaptability, high purification efficiency, and reusable adsorbents. It is one of the most effective and fast methods to remove heavy metal pollutants in water.

Activated carbon, as a porous, high-quality adsorbent material with large specific surface area and rich surface functional groups, is widely used in water purification, environmental protection and other fields \cite{3}. Most of the traditional industrial production of activated carbon in China uses coal, petroleum and trees as raw materials, which are very prone to environmental damage and other problems, so how to prepare activated carbon in a green way and efficiently use its adsorption properties has

\textsuperscript{1} Corresponding Author, Ying YANG, School of Data Science and Intelligent Engineering, Xiamen Institute of Technology, Xiamen 361021, Fujian, China; Email: 591908603@qq.com.
become one of the current problems. China is the world’s largest producer of cotton, with a national cotton production of 5.9 million tons in 2020 [4], which produces a large amount of straw waste every year but the utilization rate is less than 10% of the total straw volume. How to efficiently use these cotton straw resources and improve their added value has become a hot spot of widespread concern.

The preparation of activated carbon from biomass is one of the ways to increase the value-added utilization of crop straw, and scholars at home and abroad have carried out a lot of research on this. Guo [5], etc. used \( \text{H}_3\text{PO}_4 \) as an activator to prepare activated carbon, which can remove moisture from biomass materials and undergo cross-linking reaction with lignocellulose in biomass at high temperature. Peng [6], etc. using wood chips as raw materials, the activated carbon prepared by microwave-zinc chloride activation method can reach the national first-class standard. On the basis of relevant literature research, using cotton stalk as raw material, this paper systematically studies the influence and mechanism of modified activated carbon prepared by microwave-assisted and phosphoric acid as activator on its adsorption performance, in order to provide a theoretical basis for the combination of microwave and chemical modifier. The industrial production of modified activated carbon and the treatment of heavy metal sewage provide theoretical basis and technical support.

2. Materials and Methods

2.1. Experimental Materials

The cotton straw waste was selected from the long-staple cotton base in Alar, Xinjiang, washed and dried after removing the debris, placed in a muffle furnace, the temperature was adjusted to 110°C and dried for 24 hours. The cotton straw waste was crushed with a pulverizer and passed through a 40-mesh sieve and set aside. The chemical reagents used in the experiments were analytically pure, and the solutions were prepared by deionized water.

2.2. Experimental Equipments

JF-2000 type intelligent muffle furnace 8023, CTL-K4 type Granville microwave oven, Quanta 200 type environmental scanning electron microscope, VERTEX70 Fourier transform micro infrared spectrometer, Shimadzu-uv2700 ultraviolet visible spectrophotometer, GZX-9140MBE type electric thermostatic blast oven, A1004 type analytical electronic balance, JJ200B type one thousandth electronic balance, static nitrogen adsorption instrument, etc.

2.3. Preparation of Cotton Straw-Based Activated Carbon

- Optimization of direct pyrolysis process of cotton straw

Cotton straw-based activated carbon was prepared under direct pyrolysis conditions, and the experimental factors and levels in Table 1 were used to study the adsorption capacity, influencing factors and level optimization of this activated carbon for heavy metals \( \text{Ni}^{2+} \) in simulated wastewater. The raw materials for the preparation of activated carbon were accurately weighed at 50g each, placed in a muffle furnace, and
the N₂ gas was always kept in the charring process at a rate of 400 cm³/ min. The test data of each group were recorded accurately.

<table>
<thead>
<tr>
<th>LevelsA: Pyrolysis temperature (℃)</th>
<th>B: Pyrolysis time (min)</th>
<th>C: Pyrolysis temperature rise rate (℃/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>300</td>
<td>90</td>
</tr>
<tr>
<td>2</td>
<td>350</td>
<td>120</td>
</tr>
<tr>
<td>3</td>
<td>400</td>
<td>150</td>
</tr>
<tr>
<td>4</td>
<td>450</td>
<td>180</td>
</tr>
</tbody>
</table>

Based on the experimental factors and levels of the orthogonal test, the optimal adsorption conditions of cotton straw-based activated carbon prepared by direct pyrolysis carbonization on simulated wastewater Ni²⁺ were determined. Through the analysis of orthogonal experimental data, the maximum adsorption amount of Ni²⁺ by the activated carbon sample is used as the evaluation index, and the order of the primary and secondary factors affecting the preparation of activated carbon from cotton stalk is determined by Extremely poor size to determine: pyrolysis temperature > pyrolysis heating rate > pyrolysis time [7] Based on the calculation of the mean value k, the optimal preparation conditions for the preparation of cotton straw-based activated carbon were obtained by combining the best levels of each experimental factor: A3C4B4, i.e. pyrolysis temperature of 400°C, pyrolysis heating rate of 15°C/min, and pyrolysis time of 180 minutes.

- Preparation of modified cotton straw-based activated carbon with phosphoric acid as activator and microwave assistance

The optimum preparation conditions were 400°C, 150 minutes for pyrolysis, 15°C/min of pyrolysis heating rate, and 400 cm³/min of N₂ gas inflow during the carbonization process to prepare cotton straw-based activated carbon. The activated carbon was repeatedly rinsed with hydrochloric acid and distilled water until the pH of the washing solution was 6.5, and then impregnated with H₃PO₄ solution at different impregnation ratios (H₃PO₄/activated carbon: 0.25, 0.5, 0.75, 1, 1.5, 2, 3) for 24 hours. The activated carbon was then dried in an oven with the temperature adjusted at 110°C. The activated carbons with different impregnation ratios were reprocessed at microwave power of 100-800W and irradiation time of 3-10 minutes to become microwave-assisted phosphoric acid modified cotton straw-based activated carbons. The carbon yield of the modified cotton straw-based activated carbon reaction process was defined as the mass of modified cotton straw-based activated carbon (GXT) produced per unit mass of initial activated carbon (AC) [8].

2.4. Experimental Data Processing Methods

In this study, Origin 8.5 software was used to analyze and graph the experimental data.

- Determination of pyrolysis activated carbon yield

The mass of cotton straw before and after preparation of activated carbon was compared to calculate the carbon rate. According to equation (1).

$$\rho = \frac{m_1}{m_2} \times 100\%$$
where $\rho$—activated carbon yield (%); $m_1$—charring product mass (g); $m_2$—quality of raw materials (g).

- Experimental method of adsorption performance

A 250mL conical flask was selected as the reaction vessel, 100mL of Ni$^{2+}$ simulated wastewater solution with a concentration of 30mg/L was added, and 0.2g of modified cotton stalk-based activated carbon samples treated by microwave with different irradiation power and irradiation time were added, and the cone The shaped bottle was placed in a constant temperature water shaker with a temperature of 25°C, and the shaking speed was 180rpm. Samples were taken at different times for analysis, and the mass concentration of Ni$^{2+}$ in the solution was measured using a u2700UV-Vis spectrophotometer, and the adsorption amount of Ni$^{2+}$ by cotton stalk-based activated carbon was calculated according to equation (2).

$$q_t = \frac{V(C_0 - C_t)}{m}$$

where:
- $q_t$ is the adsorption amount of Ni$^{2+}$ by cotton straw-based activated carbon at time $t$(mg/g);
- $C_0$ and $C_t$ are the concentrations of Ni$^{2+}$ ions in the simulated wastewater at the initial moment and the adsorption $t$ time(mg/L);
- $V$ is the volume of simulated wastewater Ni$^{2+}$ solution being adsorbed(mL);
- $m$ is the amount of modified cotton straw-based activated carbon added(g).

- Adsorption kinetics

To describe the kinetic behavior of microwave-assisted modified activated carbon for the adsorption of heavy metals Ni$^{2+}$ in simulated wastewater, the Lagergren quasi-primary adsorption kinetic equation and the Lagergren quasi-secondary adsorption kinetic equation were used for linear fitting.

The linear expression of Lagergren’s quasi-primary adsorption kinetic equation [9] is shown in equation (3).

$$\ln(q_e - q_t) = \ln q_e - k_1t$$

The linear expression of the Lagergren quasi-secondary adsorption kinetic equation is shown in equation (4).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{t}{q_e}$$

where, $t$ is the adsorption reaction time(min); $q_t$ is the adsorption volume at adsorption equilibrium(mg/g); $q_e$ is the amount of adsorption at time t(mg/g); $k_1$ is the Lagergren quasi primary adsorption rate constant(g/(mg·min)); $k_2$ is the Lagergren quasi-secondary adsorption rate constant(g/(mg·min)).
3. Results and Analysis

In the following experiments, the initial experimental conditions were chosen to simulate wastewater containing Ni^{2+} at a mass concentration of 30 mg/L, a volume of 100 ml, simulated wastewater pH=6.5, temperature control at 25°C, and an oscillation speed of 180 rpm.

3.1. Effect of Impregnation Ratio on Char Yield and Adsorption Capacity

The effects of different impregnation ratios on the carbon yield and Ni^{2+} adsorption capacity were investigated when the microwave power was 350W and the irradiation time was 5 minutes. As shown in Figure 1, with the increasing impregnation ratio, the adsorption capacity of phosphoric acid-activated cotton stalk-based activated carbon on Ni^{2+} increased from 15.12 mg/g to 24.89 mg/g, and the carbon yield increased from 73.1% to 86.7%. When the ratio was 1.5, the adsorption capacity of Ni^{2+} reached the highest, and then the adsorption capacity decreased slowly with the increase of the impregnation ratio. The main reason for the analysis is that there is a high content of lignin in the cotton stalk. Under the strong action of microwave, the cellulose in the cotton stalk has a chemical reaction with phosphoric acid. There is a significant effect, and the prepared activated carbon has a more developed pore structure. However, rapid microwave heating releases the volatile substances in the cotton stalk to achieve a good pore-forming effect [10].

![Figure 1](image)

Figure 1. Effect of impregnation ratio on carbon yield and adsorption capacity.

3.2. Effect of Microwave Irradiation Power on Carbon Yield and Adsorption Amount

The effect of different microwave irradiation power on char yield and Ni^{2+} adsorption was investigated at an impregnation ratio of 1.5 and an irradiation time of 5 minutes. As shown in Figure 2, the phosphoric acid-activated cotton straw-based activated carbon showed a significant effect on the adsorption of Ni^{2+}, with the adsorption amount increasing from 16.52 mg/g to 26.53 mg/g and the carbon yield reaching up to 90.8%. Experimentally, with the gradual increase of irradiation power, the irradiation power in the 200-400W on Ni^{2+} adsorption increased the most, and the adsorption amount was the largest when it reached 600W, which is due to the rapid increase of activated carbon temperature after the microwave effect, high temperature to further
expand the internal void of activated carbon, and phosphoric acid activation process generated pyrophosphate can react with the cellulose of cotton straw to generate oligophosphate compounds. This series of reactions makes the activated carbon have more abundant functional groups, which is consistent with the results of Rockstraw [11].

![Graph](image)

**Figure 2.** Effect of microwave radiation power on carbon yield and adsorption capacity.

### 3.3. Effect of Microwave Irradiation Time on Carbon Yield and Adsorption Amount

The effect of different microwave irradiation times on the carbon yield and Ni\(^{2+}\) adsorption was investigated at an impregnation ratio of 1.5 and an irradiation power of 600W. The experimental results in Figure 3 showed that different irradiation times had some effects on the carbon yield and adsorption amount. The increase of irradiation time from 4 minutes to 7 minutes increased the adsorption amount of Ni\(^{2+}\) from 18.83 mg/g to 26.91 mg/g, and the highest carbon yield reached 89.1%. This is mainly due to the increase in irradiation time, which led to the increase in reaction temperature, more adequate reaction and better pore structure. At the same time, the adsorption capacity of activated carbon was the highest when the local high temperature time reached 7 minutes under microwave irradiation. The adsorption capacity of activated carbon decreased slightly when the irradiation time exceeded 7 minutes. The reason for this phenomenon is that the increasing irradiation time caused sintering and adhesion between adjacent pores of activated carbon, lowering the specific surface area and destroying the pores, reducing the active sites and causing a decrease in adsorption capacity, which is consistent with the study of Ning [12] and others using activated carbon a microwave treatment of typical organic simulated wastewater.

### 3.4. Adsorption Equilibrium Experiments

The adsorption patterns of modified activated carbon on Ni\(^{2+}\) solution with different mass concentrations of Ni\(^{2+}\) at 20 mg/L, 30 mg/L, 40 mg/L and 50 mg/L were studied by selecting activated carbon produced by the impregnation ratio of 1.5, irradiation power of 600W and irradiation time of 7 minutes. The experimental results are shown in Figure 4: the adsorption amount increased with the increase of adsorption time, and the adsorption reached equilibrium after 180 minutes, and the maximum adsorption amount reached 48.13 mg/g for the simulated wastewater.
containing Ni\(^{2+}\) at a concentration of 50 mg/L. The reason was analyzed that with the increase of adsorption amount, the activated carbon voids were gradually filled and saturated, and the adsorption amount increased slowly until it no longer increased.

Figure 3. Effect of microwave irradiation time on carbon yield and adsorption capacity.

Figure 4. Effects of different initial mass concentrations and adsorption time on adsorption capacity.

3.5. Microwave-Assisted Modified Activated Carbon Microstructure Characterization

The results of scanning electron microscopy tests are shown in Figure 5. The surface morphological characteristics of the cotton straw-based activated carbon produced by direct pyrolysis, different microwave powers, different treatment times and different impregnation ratios of phosphoric acid modification were investigated, respectively. As can be seen in Figure 5-AC1, the cotton straw-based activated carbon obtained under direct pyrolysis conditions maintained the basic morphological characteristics of cotton straw after pyrolysis, and the surface pore structure was relatively regular; Figure 5 shows the cotton straw-based activated carbon modified by microwave-assisted phosphoric acid with different power (200W, 600W, 800W). With the increase of microwave power, the basic structure of cotton straw-based activated carbon remains unchanged, the microscopic pores increase and the voids become larger; however, the
power is not the greater the better, and the outer layer of cotton straw carbon corrodes to a certain extent with the microwave power of 800W, and a certain adhesion bonding phenomenon occurs and the voids are destroyed.

![Figure 5. SEM image of cotton stalk charcoal.](image)

The pore structure characteristics of the activated carbon (AC) obtained by direct pyrolysis and the modified activated carbon (GXT) treated with optimal impregnation ratio, microwave power and microwave irradiation time were tested by nitrogen adsorption and are shown in Table 2. As seen from the table, the BET surface area of the modified activated carbon after combined treatment with activator and microwave is a 112-fold increase in the surface area of the activated carbon by direct pyrolysis and a 29-fold increase in the total pore volume. This indicates that the combined treatment of activator and microwave can substantially increase the microstructure of activated carbon, which is also consistent with the adsorption experimental results.

<table>
<thead>
<tr>
<th>Items</th>
<th>AC</th>
<th>GXT</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET surface area (m²·g⁻¹)</td>
<td>11.89</td>
<td>1334</td>
</tr>
<tr>
<td>Micropore area (m²·g⁻¹)</td>
<td>3.67</td>
<td>565</td>
</tr>
<tr>
<td>Specific surface area of external pores (%)</td>
<td>30.8</td>
<td>42.4</td>
</tr>
<tr>
<td>Total pore volume (m³·g⁻¹)</td>
<td>0.032</td>
<td>0.918</td>
</tr>
<tr>
<td>Microporous volume (m³·g⁻¹)</td>
<td>0.0153</td>
<td>0.342</td>
</tr>
</tbody>
</table>

3.6. Adsorption Kinetic Model Study

The results of the fitting analysis of the experimental data according to OriginPro8.5 are shown in Table 3. The correlation coefficient of the fitted curve of Lagergren quasi-secondary kinetic equation was 0.998, and the calculated value of equilibrium adsorption was closer to the equilibrium value of adsorption obtained from the experiment. This indicates that the Lagergren quasi-secondary kinetic equation can better describe the adsorption process. The Lagergren quasi-secondary kinetic model also showed that the equilibrium maximum equilibrium adsorption of Ni²⁺ by the produced cotton straw-based activated carbon was 48.13 mg/g at a concentration of 50 mg.L⁻¹. The correlation coefficient reached 99%. 
Table 3. Quasi-primary Kinetics and Quasi-secondary Kinetics equations and parameters.

<table>
<thead>
<tr>
<th>Simulation of the initial concentration of wastewater (mg.L⁻¹)</th>
<th>Quasi-primary Kinetics</th>
<th>Quasi-secondary Kinetics</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calculated equilibrium adsorption capacity (mg.g⁻¹)</td>
<td>Adsorption rate constant/k (1/min⁻¹)</td>
</tr>
<tr>
<td>20</td>
<td>19.64</td>
<td>3.11</td>
</tr>
<tr>
<td>30</td>
<td>29.19</td>
<td>4.25</td>
</tr>
<tr>
<td>40</td>
<td>38.6</td>
<td>5.20</td>
</tr>
<tr>
<td>50</td>
<td>48.05</td>
<td>8.73</td>
</tr>
</tbody>
</table>

4. Conclusion

In the combined preparation of cotton straw-based activated carbon by microwave-assisted-phosphoric acid activation method, it had a good adsorption effect on the heavy metal Ni²⁺ in the simulated wastewater, which reached equilibrium after 180 min of adsorption under the optimal experimental conditions, and the maximum adsorption amount reached 48.13 mg/g for the simulated wastewater containing Ni²⁺ at a concentration of 50 mg/L. The BET specific surface area of the modified activated carbon was 112-fold increase in surface area of directly pyrolyzed activated carbon and 29-fold increase in total pore volume, indicating that the microstructure of activated carbon could be substantially improved after combined microwave-phosphoric acid activator treatment.

The adsorption kinetics of the modified cotton straw-based activated carbon prepared by the combined microwave-assisted-phosphoric acid activation method on the heavy metal Ni²⁺ in the simulated wastewater was in accordance with the quasi-secondary adsorption kinetic model, and the correlation coefficient of the fitted curve was 0.998. The calculated equilibrium adsorption amount was closer to the experimental equilibrium adsorption amount value. This indicates that the adsorption process of heavy metal Ni²⁺ in simulated wastewater by cotton straw-based activated carbon is a dynamic chemisorption process with the combined effect of several processes.

References


