

# Study on removal performance of Fe<sup>3+</sup> by biomass-based activated carbon and Liquefaction of Poplar Sawdust catalyzed by ferro activated Carbon

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**Abstract:** The adsorption experiment of iron ions on biomass based nut shell activated carbon was conducted to explore the adsorption capacity of iron ions on biomass based activated carbon and the key influencing factors: pH value, initial concentration of solution and adsorption time on the adsorption effect of activated carbon. The preparation of supported catalyst of activated carbon iron and its influence on the effect of catalytic liquefaction of poplar sawdust were investigated. The results showed that the optimal pH value of Fe<sup>3+</sup> solution adsorbed by activated carbon was 5.0. The adsorption rate of activated carbon decreased with the increase of initial ion concentration, and the adsorption equilibrium of activated carbon reached at 250min. The optimum concentration of poplar sawdust liquefaction catalyzed by iron supported on activated carbon is between 6mg/L and 10mg/L.

**Keywords:** Biomass; Activated carbon; Heavy metal ions; Adsorb.

## 1. Introduction

Biomass energy is the energy provided by living plants in nature. These plants use biomass as a medium to store solar energy, which is a renewable energy. It has been calculated that the energy stored in biomass is twice as large as the world's current total energy consumption.

Catalysts are needed in biomass conversion process, among which carbon-based catalysts are one of the commonly used catalysts. The adsorption capacity of activated carbon is an important factor affecting the metal loading capacity and catalytic performance of the catalyst. Activated carbon treatment of heavy metals is mainly by adsorption. Activated carbon adsorption mechanism of heavy metal ions is: heavy metal ions and activated carbon surface ion exchange adsorption. The adsorption of heavy metals by activated carbon is the ion exchange between heavy metal ions and ions on the surface of activated carbon. Another reason is the adsorption of pores on the surface of activated carbon, as well as the anion reaction between metal cations and the surface of activated carbon. The adsorption of heavy metals by activated carbon can be described by the surface complexation mode. The group on the surface of activated carbon reacts with the metal ions in the solution to form the surface complexation and produce the adsorption effect.

This paper focuses on the adsorption performance of activated carbon and its application in biomass liquefaction conversion process. Activated carbon iron supported catalyst was prepared to investigate its effect on catalytic liquefaction of poplar sawdust.

## 2. Experiment part

### 2.1. Instruments and reagents

Flame atomic absorption spectrophotometer (TAS-990F), blast drying oven (Model 101-1AB), volumetric flask and conical flask.

Fe<sup>3+</sup> solution (1mg/mL), coal activated carbon, nut shell activated carbon, concentrated hydrochloric acid (analytically

pure), sodium hydroxide standard solution (1mol/L), deionized water.

### 2.2. Removal of Fe<sup>3+</sup> from biomass-based activated carbon

Weigh enough activated carbon particles, wash them with hydrochloric acid and distilled water, add distilled water and boil them for 20min, then cool them to room temperature, put them in a drying oven, and dry them at 105°C for 24h. Take 2mL of 1mg/mL Fe<sup>3+</sup> solution into a 100mL volumetric flask and add deionized water for constant volume. Then 5 Fe<sup>3+</sup> solutions of 0.4mg/L, 1mg/L, 2mg/L, 3mg/L and 4mg/L were prepared according to the ratio of the solution, and then by atomic absorption spectrophotometer measured the absorbance values of the solubility (analysis instrument parameters for: line: 271.9 nm, lamp current: 8 mA, slit width: 0.1 mm, burner height: 5 mm, air flow: 1.4 L/min, acetylene flow rate: 1.1 L/min), and draw the standard curve.

Take 10mL of 1mg/mL Fe<sup>3+</sup> solution into a 100mL volumetric flask, add the constant volume of deionized water, and set aside.

### 2.3. The influence of different conditions on the adsorption effect of activated carbon

The influence of different pH values on the adsorption effect of activated carbon: with the prepared standby solution, 100mL of 5mg/L Fe<sup>3+</sup> containing solution was prepared respectively. In each solution, 2g of pre-treated activated carbon was added, and then 1mol/L of sodium hydroxide standard solution was used to adjust the pH value of the solution. The pH values of 5 parts of Fe<sup>3+</sup> solution were adjusted to 2.0, 3.0, 5.0, 6.0 and 8.0 respectively. Finally, the heavy metal ion solution with the adjusted pH value was oscillated at 20°C (normal temperature) for 4h, and then filtered. The obtained filtrate was then measured with atomic absorption spectrophotometer for ionic solubility, and then the adsorption effect of activated carbon on Fe<sup>3+</sup> was observed.

The influence of different initial solubility on the

adsorption effect of activated carbon: Based on the previous experimental results, the temperature of 20°C (normal temperature) and pH value (Fe<sup>3+</sup> is 5.0) were selected. The prepared standby solution was used to prepare 5 parts of 100mL Fe<sup>3+</sup> solution with the solubility of 2mg/L, 4mg/L, 6mg/L, 8mg/L and 10mg/L, and the pH value was adjusted to 5.0. 2g of pretreated activated carbon was added to each solution, and then filtered after 4h oscillation, and the ionic solubility of the obtained filtrate was determined by atomic absorption spectrophotometer.

The influence of different adsorption time on the adsorption effect of activated carbon: According to the previous experimental results, the initial solubility of the heavy metal ion solution was 10mg/L at 20°C (normal temperature), pH value (Fe<sup>3+</sup> was 5.0). With the prepared standby solution, 100mL of 5 Fe<sup>3+</sup> containing solutions with a solubility of 10mg/L were prepared respectively, and 2g of pre-treated activated carbon was added into each solution. The adsorption time was 50min, 100min, 150min, 200min and 250min, respectively. The filtrate was filtered and the ionic solubility was determined by atomic absorption spectrophotometer.

#### 2.4. Preparation and characterization of ferric activated carbon supported catalyst

At pH=5, different Fe<sup>3+</sup> concentration solutions were prepared for activated carbon adsorption, with a duration of 50min. A certain amount of activated carbon adsorbed Fe<sup>3+</sup> was placed in a tubular furnace, nitrogen was injected, the temperature was raised to 550 °C, and calcined for 3h to prepare the required Fe/C supported catalyst. The Fe/C catalyst was characterized by X-ray diffraction (XRD). Test condition is: the tube voltage of 40 KV, is 40 mA tube current, scan velocity 10°/min, the scanning range is 2θ=5~80°.

#### 2.5. Activated carbon iron supported catalyst catalyzes liquefaction of poplar sawdust

Before the experiment, the hydrothermal synthesis reactor was cleaned and dried. Weigh 1 g of poplar sawdust, 0.1 g of catalyst and 10 ml of ethanol, and place them in the tank of the reactor. Put the tank of the reactor into the ultrasonic cleaner for 3 min and then take it out. Then put it in the oven at 180 °C, reaction for 2 h, and take it out of the oven after the temperature drops to room temperature. After the reactor is cooled, the reactor is opened after pressure relief, all the reaction products in the reactor are collected in the beaker, the inner wall of the reactor is repeatedly cleaned with ethanol solution, and then the solids and liquids are separated through filtration. The residue is put into the oven for drying for 12 hours and then weighed to obtain the residue quality. Use rotary evaporator to concentrate filtrate, remove ethanol, transfer to sample bottle, weigh and reserve.

GC/MS was used to analyze the composition of liquid products. GC/MS conditions were set as follows: the inlet temperature was 300 °C; The chromatographic column was a capillary column TC-1701 (GL Sciences, Co. Ltd., 60 m in length, 0.25 mm in diameter). The column temperature was set as follows: after being kept at 40 °C for 5 min, the temperature was raised to 250 °C at 4 °C/min, and was kept at 250 °C for 20 min. The range of mass charge ratio detected by mass spectrometry was 50-650 AMU. Chromatographic peaks were determined by matching with NIST standard database. The relative peak area content of each substance is calculated, as shown in Formula (1).

$$y_i = \frac{A_i}{A_{all}} * 100\% \quad \text{Formula} \quad (1)$$

$y_i$  is the content of product  $i$ ;  $A_i$  refers to the peak area corresponding to the  $i$  th product;  $A_{all}$  refers to the total peak area of all peaks.

### 3. Results and Discussion

#### 3.1. Study on adsorption of Fe<sup>3+</sup> solution by activated carbon

A standard curve was drawn according to the absorbance of Fe<sup>3+</sup> and the concentration of Fe<sup>3+</sup> solution, as shown in Figure 1(a). The significance of the standard curve: to describe the relationship between the ion concentration of Fe<sup>3+</sup> and the absorbance value; The elements of the standard curve: R<sup>2</sup> -- representing the exponent; The curve equation is a first order function; The straight line in Figure 1 is the trend line.

The pH value has a great influence on the adsorption effect of activated carbon, and the adsorption effect of different pH on activated carbon is not the same. In general, activated carbon adsorption of heavy metal ions in acidic conditions of the adsorption effect is higher, with the increase of the pH value of heavy metal ions solution, activated carbon adsorption of metal ions also improved. However, for different heavy metal ions, their optimal adsorption pH is also different. The specific adsorption of Fe<sup>3+</sup> by activated carbon is shown in Figure 1 (b)

According to Figure 1 (b), the optimal pH value of activated carbon adsorption Fe<sup>3+</sup> solution was 5.0. Under acidic conditions, with the increase of pH value, the concentration of heavy metal ions in Fe<sup>3+</sup> solution decreases, that is to say, the adsorption capacity of activated carbon to Fe<sup>3+</sup> increases, the adsorption effect improves, and the adsorption rate rises. However, under the alkaline condition, activated carbon has a poor adsorption effect on heavy metal ions, which is mainly because activated carbon in the alkaline solution will occur peptizing phenomenon, resulting in a low adsorption effect. However, when the pH value is greater than 5.0, the adsorption effect of activated carbon on Fe<sup>3+</sup> gradually weakens. This is because, although under acidic conditions, Fe<sup>3+</sup> will hydrolyze in water and produce iron hydroxide precipitation due to the chemical reaction of OH in water, resulting in the decrease of the adsorption amount and adsorption rate of activated carbon. Therefore, in summary, activated carbon has a stronger adsorption capacity for heavy metals under acidic conditions than under alkaline conditions, but the optimal adsorption pH value of Fe<sup>3+</sup> is 5.0.

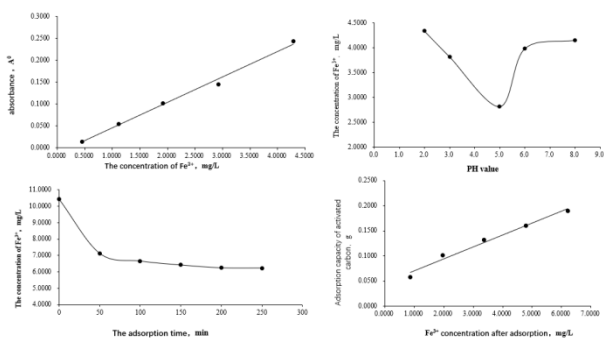
In order to find the equilibrium time of activated carbon adsorption, we selected 5 parts of Fe<sup>3+</sup> solution with the ionic solubility of 10mg/L, and then added 2g of activated carbon which had been pretreated. The adsorption time was selected as 50min, 100min, 150min, 200min and 250min, respectively. After the time is up, the filtrate is filtered successively, and the ionic solubility is measured by atomic absorption spectrophotometer. Observe the adsorption effect of activated carbon. The specific adsorption of Fe<sup>3+</sup> solution by activated carbon is shown in Figure 1 (c).

It can be seen from Figure 1 (c) that when activated carbon adsorbs Fe<sup>3+</sup> solution, when the amount of activated carbon added is a constant value, the concentration of Fe<sup>3+</sup> in the solution decreases rapidly in the first 50min. The adsorption capacity of activated carbon increases rapidly, mainly

because there are many pores on the surface of activated carbon, which can rapidly adsorb  $\text{Fe}^{3+}$ . But with the increase of the adsorption amount of activated carbon, the adsorption rate of activated carbon began to slow down, this is because the adsorption amount of activated carbon is fixed, so with the increase of the adsorption amount, the adsorption rate of activated carbon slows down. Finally, with the increase of adsorption time, the adsorption capacity of activated carbon reaches the maximum, and the concentration of  $\text{Fe}^{3+}$  in the solution slowly decreases until the adsorption equilibrium is reached. The time to reach equilibrium is about 250min.

Activated carbon adsorbed  $\text{Fe}^{3+}$  solutions with ionic solubility of 2mg/L, 4 mg/L, 6 mg/L, 8 mg/L and 10 mg/L, respectively. The removal efficiency of activated carbon was calculated by comparing the adsorbed ion solubility with the initial ion solubility. The specific situation of removal of  $\text{Fe}^{3+}$  by activated carbon is shown in Figure 1(d).

It can be seen from Figure 1(d) that when activated carbon adsorbed  $\text{Fe}^{3+}$ , when the amount of activated carbon added was a constant value, with the increase of initial ion solubility, the removal efficiency of activated carbon to  $\text{Fe}^{3+}$  gradually decreased. This is because the adsorption capacity of activated carbon is fixed, and the position of the adsorption point on the surface of activated carbon is also fixed, so when the initial solubility of heavy metal ions increases, the adsorption effect of activated carbon to heavy metal ions also decreases. When the solubility of  $\text{Fe}^{3+}$  solution was lower than 4mg/L, the removal efficiency of  $\text{Fe}^{3+}$  solution by activated carbon was about 60%. However, when the concentration of  $\text{Fe}^{3+}$  solution adsorbed by activated carbon was higher than 8mg/L, the removal efficiency of  $\text{Fe}^{3+}$  by activated carbon was only about 40%.

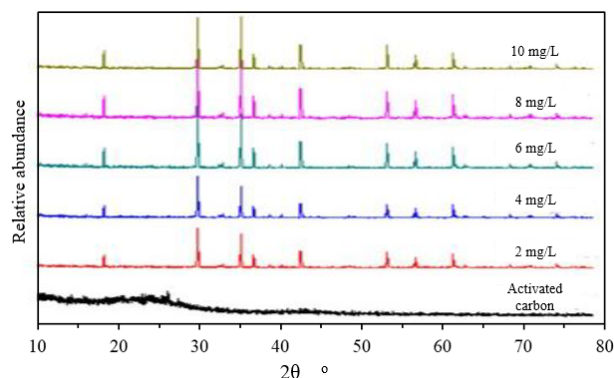


**Figure 1.** Adsorption capacity of  $\text{Fe}^{3+}$  on activated carbon and its key influencing factors  
(a) The standard curve; (b) PH value; (c) Time; (d) initial concentration

### 3.2. Effects of different conditions on the adsorption effect of $\text{Fe}^{3+}$ catalyzed liquefaction of poplar sawdust by activated carbon

Figure 2 shows the characterization diagram of carbon-based iron catalysts obtained by different impregnation concentrations. We can clearly observe that there are very strong diffraction peaks around  $2\theta = 18.32^\circ, 30.12^\circ, 35.44^\circ, 37.12^\circ, 44.10^\circ, 53.4^\circ, 57.1^\circ$  and  $62.56^\circ$ . After comparison with ASTM diffraction data card, we find that this is a crystal plane diffraction peak of ferric oxide, and it can be determined that the iron oxide loaded on activated carbon is ferric oxide. Under the condition that the peak width is similar, we can judge by the peak height and peak width. When the

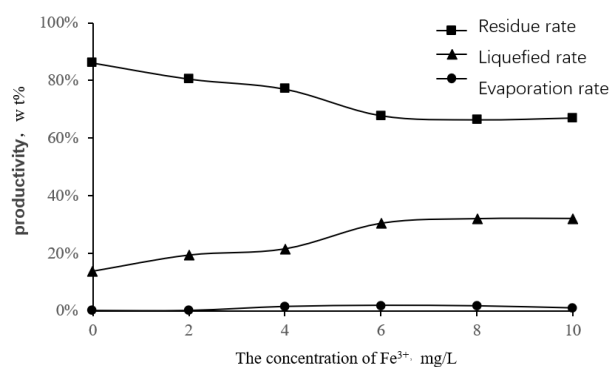
immersion concentration is 8mg/L, ferric tetroxide has the best crystallinity and dispersity on activated carbon. Under the condition of close dispersion, the better crystallinity, the better performance of catalyst. When the impregnation solution exceeds the optimal concentration, the crystallinity of ferric oxide on activated carbon will decrease instead.



**Figure 2.** XRD characterization of activated carbon after  $\text{Fe}^{3+}$  adsorption

FIG. 3 shows the yield of poplar sawdust products catalyzed by iron supported on activated carbon. It can be seen from the figure that when the concentration of  $\text{Fe}^{3+}$  rose from 4mg/L to 6mg/L, the liquefaction rate of catalytic poplar sawdust suddenly increased by about 10%, and the residue rate also decreased by 10%. When the concentration of  $\text{Fe}^{3+}$  was increased again, the liquefaction rate and residue rate of catalytic poplar sawdust did not change much.

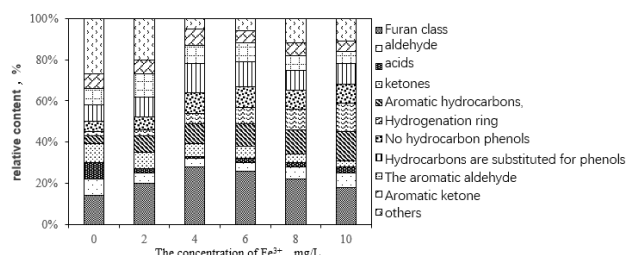
From this, we conclude that the appropriate concentration of activated carbon supported iron catalyzed liquefaction of poplar sawdust is between 6mg/L and 10mg/L. The optimum concentration of  $\text{Fe}^{3+}$  should be selected in combination with the saving of raw materials and other influencing conditions.



**Figure 3.** Yield of poplar sawdust products catalyzed by iron supported on activated carbon

FIG. 4 shows the component distribution diagram of the group of products from the catalytic liquefaction of Yang wood chips with different concentrations of  $\text{Fe}^{3+}$  supported by activated carbon. It can be seen from the figure that when the concentration of  $\text{Fe}^{3+}$  is from 4mg/L to 6mg/L, the component content of furan products is greatly increased, while the source of furan products is cellulose and hemicellulosic in the raw materials. When the concentration of  $\text{Fe}^{3+}$  is 0, the proportion of acids and ketones in the product is greater than that of other catalytic products; when the concentration of  $\text{Fe}^{3+}$  is greater than 8mg/L, the proportion of aromatics and hydrogenation ring components in the product is greater than that of other catalytic products.

When the concentration of  $\text{Fe}^{3+}$  is greater than 2mg/L, the proportion of hydrocarbon-free phenolic components in the product becomes higher and basically remains unchanged. When the concentration of  $\text{Fe}^{3+}$  is between 4mg/L and 6mg/L, the proportion of hydrocarbon-substituted phenolic components is the highest, while the phenols in the product are derived from lignin in the raw material. The proportion of aryl aldehydes and aryl ketones varied and had no significant relationship with the concentration of  $\text{Fe}^{3+}$ .



**Figure 4.** Distribution of group components of aspen sawdust liquefaction products

## 4. Conclusions

The optimal pH value of  $\text{Fe}^{3+}$  solution adsorbed by activated carbon was 5.0.

When activated carbon adsorbed  $\text{Fe}^{3+}$ , when the amount of activated carbon added was a constant value, with the increase of initial ion solubility, the adsorption efficiency of activated carbon to  $\text{Fe}^{3+}$  gradually decreased.

When activated carbon adsorbs  $\text{Fe}^{3+}$  solution, the equilibrium time is about 250min.

When the immersion concentration was 8mg/L, the crystallinity and dispersion of ferric oxide on activated carbon were the best.

The optimum concentration of poplar sawdust liquefaction catalyzed by iron supported on activated carbon is between 6mg/L and 10mg/L.

When the concentration of  $\text{Fe}^{3+}$  ranged from 4mg/L to 6mg/L, the component content of furan products increased, which was derived from cellulose and hemicellulose in raw materials. When the concentration of  $\text{Fe}^{3+}$  is greater than 2mg/L, the proportion of non-hydrocarbon phenolic components becomes higher. When the concentration of  $\text{Fe}^{3+}$  is between 4mg/L and 6mg/L, the proportion of hydrocarbon

substituted phenolic components is the highest, which is derived from lignin in raw materials.

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