

# Influence of preparation conditions on the physical structure and surface properties of enteromorpha clathrate bio-char

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**Abstract.** Bio-char with rich pore structure was obtained by pyrolysis of enteromorpha clathrate (EC) and subsequent activation process. The effect of pyrolysis methods, KOH concentrations used in activation and heating rate was studied. A new method that combined pyrolysis and activation into one step was proposed. The bio-char obtained via slow pyrolysis at 450°C and 700°C had a certain pore structure. The bio-char obtained via fast pyrolysis had almost no effective pore structure and a large amount of organic matters still exist in the bio-char, while it had the largest specific surface area after activation by KOH at 800°C. Therefore, bio-char that is a kind of by-product in the process of making bio-oil by fast pyrolysis of EC is worthy of further exploration. As the KOH concentration of the impregnated solution increased, the specific surface area first increased and then decreased. The bio-char obtained via impregnation and activation with 3 mol/L KOH had the highest specific surface area (1128.85 m<sup>2</sup>/g) and pore volume (0.789 cm<sup>3</sup>/g). If the processes of pyrolysis and activation were combined into one step via mixing KOH and EC, the structure of cell tissue in the EC was reserved. The sample that prepared by mixing 2 g dried EC with 0.1 g KOH powder has the highest specific surface area (724.66 m<sup>2</sup>/g) and better pore structure. The best heating rate was 5°C/min for impregnation method and 2°C/min for one step method.

## 1. Introduction

Bio-char is a kind of carbon based material that has been attracting increasing attention because of its abundant raw materials and high adsorption capacity [1]. Among them, seaweed bio-char has a low price and contains active ions such as K and Na, which has great research values [2]. Enteromorpha clathrate (EC), as a kind of common marine green algae, is produced in the southeastern coastal areas of China. EC has a high efficiency in absorbing nutrients and a fast growth rate, which has a good auxiliary effect on the ecological restoration of the ocean. However, with the continuous marine pollution, the ocean eutrophication is becoming serious, leading to the increase of EC production. Meanwhile, with the developing of bio-oil production by pyrolysis of EC, a large amount of bio-char will be inevitably produced in this process [3]. Compared with activated carbon, this type of bio-char eliminates the carbonization process and then reduces costs in carbon production. If the bio-char from oil production is activated and applied to the field of industrial processes, it will be a very promising comprehensive utilization approach [4].

The operation conditions in the pyrolysis process have significant impacts on the characteristics of bio-char. Jian et al. [5] found that with the increase of pyrolysis temperature, the PH and ash content of bio-char tended to increase. Antal et al. [6] found that the bio-char yield and carbon content decreased as the heating rate increased. Bandosz et al. [7] found that the specific surface area and

pore volume of the bio-char decreased if the pyrolysis time was extended from 30 min to 1 h at 950°C.

The activation process is an important step in the modification of bio-char. The activation methods can be divided into physical activation and chemical activation. Ahmad et al. [8] used CO<sub>2</sub> and H<sub>2</sub>O as activating gas to treat bio-char from palm trees and the specific surface area of activated carbon prepared at 792-1079°C reached 1084 m<sup>2</sup>/g, 85.9% of which belonged to the micropores. The characteristics of bio-char after physical activation are related to the activated gas, reaction conditions, and the type of bio-char. Ghouma et al. [9] found that different bio-char (pine wood chips, walnut shells, etc.) produced under different activation conditions (time, temperature, etc.) was different in the adsorption capacity. After optimizing the conditions, the best bio-char had an adsorption capacity of 131 mg/g for NO<sub>2</sub>, while the worst was only 25.5 mg/g. Nabais et al. [10] used CO<sub>2</sub> and to activate the bio-char after pyrolysis and found that the use of water vapor as activating gas can make the bio-char have wider pore size distribution, while CO<sub>2</sub> can make the bio-char have larger pore volume. Rostamian et al. [11] used KOH as activator and the specific surface area of the activated bio-char reached 2201 m<sup>2</sup>/g. Compared with KOH, NaOH had less corrosiveness and lower price. However, the surface area of the bio-char activated by NaOH was less than 1 m<sup>2</sup>/g with less microporous. Zhao et al. [12] used CaCl<sub>2</sub> in activation to increase the number of basic groups on the surface, the degree of aromatization and the adsorption capacity. Sun et al. [13] used H<sub>3</sub>NO<sub>4</sub>

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as an activator and found that the prepared bio-char had a specific surface area of 1252 m<sup>2</sup>/g with more micropores. In this paper, we use EC to produce bio-char and study the influence of pyrolysis methods, KOH concentrations and heating rate on the physical and chemical properties of bio-char. The feasibility of explore bio-char from bio-oil production by fast pyrolysis is discussed.

## 2. Experimental

### 2.1 Preparation of bio-char

EC bio-char is prepared by two methods: fast pyrolysis and slow pyrolysis.

**Fast pyrolysis method:** The fast pyrolysis device is a stainless steel reactor. First, the reactor was heated to 550°C at a heating rate of 15°C/min, and then N<sub>2</sub> gas passed over the reactor at a flow rate of 1 L/min for 5 minutes. The flow rate was set to 200 mL/min and the dry EC powder was put into the reactor and maintained 15 minutes. After the reaction, the bio-char was collected and denoted as EC-FP.

**Slow pyrolysis method:** 5 g of dry EC powder was placed in a tubular furnace and passed 400 mL/min N<sub>2</sub> as a protective gas. After draining the air in the furnace, temperature of the tubular furnace was first raised to 100°C at a heating rate of 10°C/min and kept for 30 minutes at 100°C, then raised to 450°C or 700°C at 1°C/min and kept for 30 minutes. After cooling to room temperature, the sample was taken out and denoted as EC-450 and EC-700.

### 2.2 Activation of EC bio-char

2 g of bio-char prepared in section 2.1 was placed in KOH solution for 24 h and then filtered and dried at 110°C for 12 h. Then the sample was put into the tubular furnace with a N<sub>2</sub> flow at 400 mL/min as a protective gas. The activation is from room temperature to 800°C at a heating rate of 2°C/min or 5°C/min and maintained 30 minutes at 800°C. The cooled sample was taken out, washed with 1 mol/L hydrochloric acid solution and deionized water to pH=7, filtered and dried at 110°C for 12 h. The sample was denoted as EC-A-BM-C, A represents the pyrolysis method in section 2.1, B represents the mole of the KOH solution, and C represents the heating rate.

### 2.3 Preparation of EC bio-char by one-step activation method

2 g of dry EC powder mixed with KOH powder and put into a tubular furnace with 400 mL/min N<sub>2</sub>. The activation was from room temperature to 800°C at 1°C/min or 2°C/min and maintained 30 min at 800°C. The cooled sample was taken out and denoted as EC-2-D-C, D represents the quality of the KOH, and C represents the heating rate.

### 2.4 Characterization analysis

N<sub>2</sub> adsorption and desorption at liquid nitrogen temperature (77 K) was performed on the NOVA 3000e (Kangta). The pretreatment of the samples was at 200°C

for 3 hours. Fourier transform infrared (FTIR) spectrometer test was carried out in the Nicolet iS50 (USA Thermo Electron Corporation). The bio-char was mixed with KBr and pressed. The scanning range was 4000~400 cm<sup>-1</sup>, and the resolution was 4 cm<sup>-1</sup>. The scanning electron microscope (SEM) was obtained using the S-4800 (Hitachi).

## 3. Results and discussion

### 3.1 Influence of pyrolysis method

To study the structural characteristics of EC after different pyrolysis processes, the bio-char produced by fast pyrolysis and slow pyrolysis at 450°C and 700°C were analyzed. According to Table 1, the EC-FP obtained by the fast pyrolysis had no effective pore structure and EC-450 obtained by slow pyrolysis at 450°C had a low specific surface area, 84% of which was macropores. The specific surface area of EC-700 obtained by slow pyrolysis at 700°C was 43.48 m<sup>2</sup>/g, and 81% was microporous. It can be seen that the pyrolysis rate and temperature have a significant effect on the pore structure of the bio-char.

After being impregnated and activated with KOH at a concentration of 2 mol/L, the specific surface area of the bio-char was greatly improved. Although EC-FP had almost no pore structure, after activation, the specific surface area of EC-FP-2M-5 was the largest (801.99 m<sup>2</sup>/g), 79% of which was microporous. The specific surface area of EC-700-2M-5 and EC-450-2M-5 reached 560.42 m<sup>2</sup>/g (72% microporous) and 480.49 m<sup>2</sup>/g (88.2% microporous).

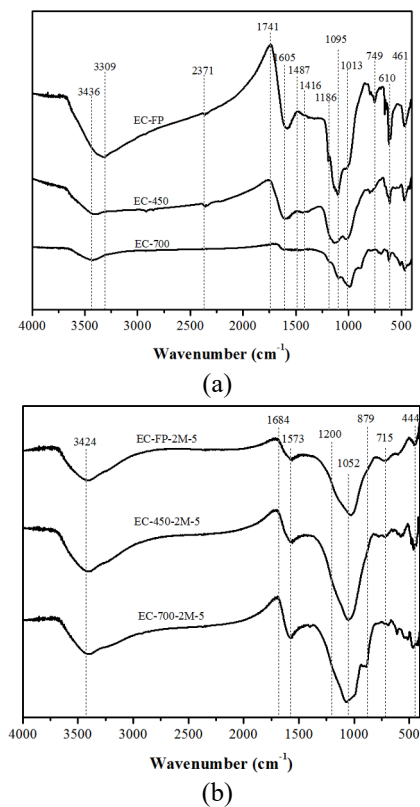
**Table 1.** Specific surface area (S<sub>BET</sub>) and pore parameters of the EC bio-char.

Samples	S <sub>BET</sub> (m <sup>2</sup> /g)	V(cm <sup>3</sup> /g)	S <sub>ms</sub> (m <sup>2</sup> /g)	S <sub>mes</sub> (m <sup>2</sup> /g)
EC-FP	~0	—	—	—
EC-450	1.96	0.003	0.32	1.64
EC-700	43.48	0.031	35.35	8.13
EC-FP-2M-5	801.99	0.605	631.18	170.82
EC-450-2M-5	480.49	0.311	424.03	56.46
EC-700-2M-5	560.42	0.434	400.94	159.47
EC-FP-1M-5	492.53	0.383	376.91	115.62
EC-FP-3M-5	1128.85	0.789	961.59	167.26
EC-FP-5M-5	1078.70	0.772	879.86	198.85
EC-FP-7M-5	912.43	0.641	740.68	171.75
EC-2-0.05-1	42.27	0.033	32.33	9.94
EC-2-0.1-1	594.24	0.451	433.67	160.58
EC-2-0.2-1	499.45	0.372	387.64	111.81
EC-FP-3M-2	883.98	0.647	709.74	174.24
EC-2-0.1-2	724.66	0.554	521.84	202.82
EC-2-0.1-5	589.17	0.469	417.56	171.60

Figure 1(a) shows the FTIR results of the bio-char prepared by different pyrolysis methods. It can be seen that the peak positions of EC-FP, EC-700 and EC-450 were same, indicating that the functional groups of the samples were same, including C–H, C–O, C=O, C=C, O–H, etc. The absorption intensity of EC-FP was the highest, followed by EC-450, and EC-700 was the weakest, indicating that EC-FP has a large number of surface functional groups because of incomplete pyrolysis. The peak at 700-1000 cm<sup>-1</sup> corresponds to C–H bond [14]. The prominent peaks at 1095 cm<sup>-1</sup> and 1013 cm<sup>-1</sup> correspond to C–O bonds; the other prominent peaks at 1741 cm<sup>-1</sup> and 1605 cm<sup>-1</sup> correspond to C=O of carboxyl or carbonyl groups [15, 16]. The tiny absorption peak at 2371 cm<sup>-1</sup>

corresponds to the C≡C bond; the absorption peaks at 3436 cm<sup>-1</sup> and 3309 cm<sup>-1</sup> correspond to the stretching vibration of the O–H bond [15, 17]. EC-FP and EC-450 had absorption peaks at 1487 cm<sup>-1</sup> and 1416 cm<sup>-1</sup> that correspond to aromatic bonds, while it was not observed for EC-700 [17].

After being impregnated and activated by KOH, the FTIR of bio-char tended to be consistent (Figure 1(b)), indicating that although the pre-pyrolysis methods were different, the types and proportions of surface functional groups after activation were similar. The peak corresponding to the C–O bond shifted to 1052 cm<sup>-1</sup>. Compared with the peaks of EC-450 and EC-700, the peaks of EC-450-2M-5 and EC-700-2M-5 had increased intensities, indicating the number of C–O functional groups on the surface of the bio-char increased after activation. The absorption peaks corresponding to the C=O bond shifted to 1684 cm<sup>-1</sup> and 1573 cm<sup>-1</sup>. The functional group corresponding to the aromatic bond disappears.



**Figure 1.** FTIR spectra of the bio-char (a) prepared by fast pyrolysis and slow pyrolysis at 450°C and 700°C, and (b) activated by 2 mol/L KOH after fast pyrolysis and slow pyrolysis.

### 3.2 Influence of KOH concentration in impregnation

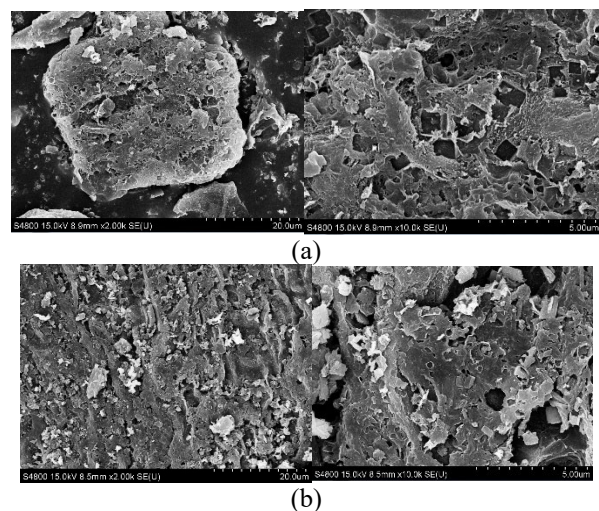
In order to study the effect of impregnation concentration on the surface properties of bio-char, the fast pyrolyzed bio-char was impregnated with 1-7 mol/L KOH solution and activated at 800°C. As the solution concentration increased, the specific surface area first increased and then decreased, and the pore volume was positively correlated with the specific surface area (Table 1). This is

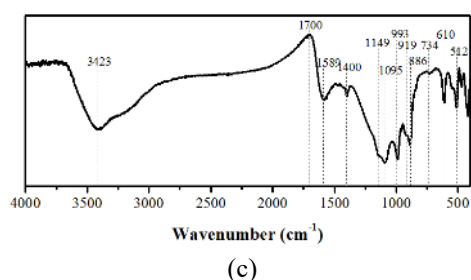
because when the concentration of the KOH solution was low, there was less KOH adhesion on the surface of the bio-char, and it was not fully etched when activated; as the solution concentration increased, the activation became more fully; but when the solution concentration was too high, the KOH condensed into agglomerates on the surface of the bio-char, resulting in a poor etching effect. The specific surface area and pore volume of the bio-char prepared by impregnation and activation with 3 mol/L KOH solution were the highest, reaching 1128.85 m<sup>2</sup>/g and 0.789 cm<sup>3</sup>/g, respectively, and 85% were micropores. Figure 2(a) is the SEM images of the sample EC-FP-3M-5. It can be seen that the sample had a layered structure with well-developed pores distributed inside.

### 3.3 One-step preparation method

During the experiments, we found that by mixing dry EC powder with KOH powder at different quality and then pyrolyzing it, bio-char with a high specific surface area can also be obtained. The specific surface area and pore structure of bio-char prepared with different mixing ratios of EC and KOH are shown in Table 1. When 0.05g KOH powder was mixed with EC, the specific surface area was only 42.27 m<sup>2</sup>/g, and the pore volume was only 0.033 cm<sup>3</sup>/g. When 0.1 g KOH powder was mixed with EC, the specific surface area increased to 594.243 m<sup>2</sup>/g with a pore volume of 0.451 cm<sup>3</sup>/g. However, when 0.2 g KOH powder was mixed with EC, its specific surface area and pore volume were reduced.

Figure 2(b) is SEM images of sample EC-2-0.1-1. The cell tissue structure of this sample was obvious with lamellar layers, and the surface was distributed with more circular pores, whose pore size was smaller than that EC-FP-3M-5. Figure 2(c) shows the FTIR spectrum of EC-2-0.1-1. Compared with EC-FP-3M-5, the absorption peaks were shifted to the left. There were many chaotic peaks before 734 cm<sup>-1</sup>, and these peaks are mainly C-H bonds of functional groups. In addition to the main absorption peaks of 1589 cm<sup>-1</sup>, 1149 cm<sup>-1</sup> and 1095 cm<sup>-1</sup>, there are also strong absorption peaks at 993 cm<sup>-1</sup> and 919 cm<sup>-1</sup>, representing the C–O bond. Bio-char prepared by one-step method has more abundant surface functional groups.





**Figure 2.** SEM images of (a) EC-FP-3M-5 and (b) EC-2-0.1-1; (c) FTIR spectra of EC-2-0.1-1.

### 3.4 The effect of heating rate

In order to study the effect of heating rates on EC bio-char, EC-FP-3M and EC-2-0.1 were prepared with different heating rates. It can be seen from Table 1, the pore characteristics of the sample prepared by impregnation with an activation heating rate of 5 °C/min was better than 2 °C/min. For the bio-char obtained by mixing and pyrolysis of EC powder and KOH powder, the sample prepared at a heating rate of 2 °C/min had the highest specific surface area, reaching 724.658 m<sup>2</sup>/g.

## 4. Conclusion

EC bio-char with abundant pore structure was obtained and effects of the pyrolysis method, activation method, impregnation concentration and heating rate on the physical and chemical properties of the bio-char was studied. The bio-char prepared by fast pyrolysis before activation had the highest specific surface area. Therefore, as a kind of by-products in producing bio-oil by fast pyrolysis of EC, bio-char can be used as raw material to prepare active carbon.

Before activation, the bio-char obtained by slow pyrolysis had a certain pore structure, while the bio-char obtained by fast pyrolysis had almost no effective pore structure. After KOH activation, the specific surface area of the bio-char had a great increase. The specific surface area and pore volume of bio-char prepared with 3 mol/L KOH solution and 5°C/min heating rate were the highest, reaching 1128.85 m<sup>2</sup>/g. Although the number and proportion of surface functional groups of bio-char obtained by different pyrolysis methods had a great difference, they got unanimity after activation.

EC bio-char can also be prepared by the one-step method, which has more abundant surface functional groups and obvious cell tissue structure. The bio-char prepared by mixing 2 g EC and 0.1 g KOH powder with 2°C/min heating rate had a higher specific surface area and a better pore structure.

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