Nanoporous Carbon from Water Hyacinth Via Hydrothermal Carbonization

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Abstract. Nanoporous carbon materials have been successfully synthesized from water hyacinth via hydrothermal carbonization (HTC). This research was studied the effect of hydrothermal temperature from 160 - 200 °C and reaction time for 4 - 24 h. Afterwards, carbonization was carried out at the temperature of 600 - 900 °C for 2 h in N₂ atmosphere for developing porosity and even removing contaminants of hydrothermal char to obtain the porous carbon. The physico-chemical properties of nanoporous carbon materials were comprehensively characterized through Scanning electron microscope (SEM), Fourier transforms infrared spectroscopy (FT-IR), CHN elemental analysis, X-ray diffraction (XRD) and BET analysis. The adsorption capacity and carbon content of nanoporous carbon materials from water hyacinth were increased with increased hydrothermal carbonization temperature and time. Performing HTC at 200 °C for 12 h is the optimum condition to synthesis of precursor materials for good adsorbent.

1. Introduction

Agricultural wastes are generated as unused materials from harvesting, processing and storing activities. Corn cob, bagasse, and husk are examples of agricultural wastes called “biomass” [1]. Biomass mainly consists of three components- cellulose, hemicellulose, and lignin- which very ideal for producing carbon materials [2]. Latterly, these conventional biomasses were used as direct fuel, resulted in higher prices and scarcity. Therefore, alternative biomasses from aquatic plants such as water hyacinth is being considered. Water hyacinth (Eichhornia crassipes) is one of invaded species found in many countries in Southeast Asia. It spreads quickly and aggressively, leads to uncontrollable environmental problems- flow blockages, altering water tint and odor [3-7]. Water hyacinth is an interesting alternative to produce nanoporous carbon and has many uses such as capacitors or adsorbents. With nanoporous carbon production methods [8, 9] there are many ways to choose from to match nature of raw materials and properties of the desired nanoporous carbon. In this research, water hyacinths were used as precursors to produce adsorbents. By using the hydrothermal carbonization process [10, 11]. In a temperature range of 160 to 200 °C which is a carbonization method. It uses water molecules, heat, and pressure to break bonds in organic polymers. Water molecules will expand the pores [12-17]. It is an effective way to achieve high yield of carbon materials using less energy to
process. In this study, we studied the effect of temperature and the time it takes for HTC reaction, which can be observed from the morphological structure and surface characteristics using scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy, CHN elemental analyzer, BET analysis. Carbon materials then applied by organic substances adsorption such as paraquat and methylene blue.

2. Material and methods

2.1. Material
Water hyacinth were collected from natural canal in Ladkrabang, Bangkok, Thailand.

2.2. Method
Synthesize of porous carbon materials from water hyacinth starts from drying collected raw water hyacinth by sun exposure to expel moisture and grind it into raw powder. Prepare 30 g of raw powder with 90 mL of deionized water into Teflon canister and then installed in stainless steel reactor. Hydrothermal reaction was performed at different temperatures (160, 180, and 200 °C) and times (4, 8, 12, and 24 h). After finishing hydrothermal process, remove hydrochar s from the reactor and then dried in oven at 90 °C overnight. Dried hydrochars were carbonized in horizontal tube furnace at 500 – 900 °C for 2 h under constant nitrogen gas flow. Final products were analysed for chemical composition and morphology.

2.3. Characterization Techniques
The samples were characterized for surface morphology by Scanning Electron Microscope (SEM). Fourier Transform Infrared Spectroscopy (FT-IR) was used to determine the function group on surface of sample. Crystallinity was measure by using X-ray diffraction (XRD) and element was measure by using CHN elemental analyzer, respectively.

3. Results and discussion

3.1. Scanning Electron Microscope (SEM)
Morphology results from scanning electron microscope of hydrochars derived from HTC process are shown in Figure 1.

![SEM images](image_url)

**Figure 1.** SEM images (500×) of Water Hyacinth hydrothermally treated at (a) 200 °C for 12 h, HTC at different conditions: (b) 500 °C, (c) 600 °C, (d) 700 °C, (e) 800 °C, and (f) 900°C.
Scanning electron micrographs of the surface morphology of the feedstock and different reaction temperatures 200 °C for 12 h are given in Figure 1(a) Carbonization at 500 – 900 °C for 2 h under N₂. Figure 1(b-f) after HTC treatment significant changes on the surface morphology can be found at different temperature. When increase temperatures provide polymer bond are more break compared to the feedstock. At temperature of 200°C showed that the hemicellulose was destroyed significantly because water molecules can diffuse through the structure dramatically. This structure implies that the formation pathway of HTC may be attributed to hemicellulose hydrolysis followed by polymerization reaction since both stage temperatures are less than 230 °C. Therefore, at temperatures below 230 °C, most of the decomposition is hemicellulose, followed by cellulose and lignin, respectively. Temperature has a significant effect on the fracture structure over reaction time. At temperature 200 °C for 12 h and carbonization at 900 °C for 2 h under N₂ is optimum condition for surface improvement of HTC which result in increased surface area and porosity.

3.2. Fourier Transform Infrared Spectroscopy (FT-IR)
The FT-IR spectra of hydrochars derived from hydrothermal process are shown in Figure 2.

![Figure 2. FT-IR spectra of (a) Water hyacinth through hydrothermal process at 200 °C for 12 h and difference co-solvent treatment, (b) 500 °C, (c) 600 °C, (d) 700 °C, (e) 800 °C, and (f) 900 °C.](image)

A broad peak at around 3600 - 3000 cm⁻¹ confirms the presence alcohols from cellulose or phenols from lignin and hydroxyl or carboxyl groups. The peak at 2925 cm⁻¹ is due to CH₂ stretching vibrations of the aromatic methyl groups or aliphatic. Peaks around 1700 cm⁻¹ are attributed to the stretching vibration of C=O of from cellulose and lignin [18-19]. The peak at 1600 and 1512 cm⁻¹ is due to the vibration of the aromatic ring C=C stretching present in the lignin. The peak at 1460 cm⁻¹ is due to CH₂ bending vibrations of the C-H deformation in lignin and carbohydrates. The absorption band observed at 1290 - 950 cm⁻¹ is assigned to the stretching vibrations of C-O in aliphatic ethers and aliphatic alcohols.

3.3. CHN elemental analyzer
Elemental compositions of hydrochar and carbonization from water hyacinth at 200 °C for 4 h. and carbonization at 500 - 900 °C shown in Table 1. Carbon content in water hyacinth was about 32%, In the other head, Carbon content also increased with carbonization temperature for 45 – 48% Reductions in oxygen and hydrogen content for HTC products compared with those of water hyacinth were
observed. The reason may be that an intermolecular dehydration reaction of large molecules took place, transforming elemental hydrogen and oxygen to water.

Table 1. CHN elemental analyzer of hydrochar and carbonization samples.

| Sample               | Ultimate analysis (%) |
|----------------------|-----------------------|
|                      | C        | H        | N        | O        |
| Hydrothermal         |          |          |          |          |
| (200 °C, 12 h)       | 40.43    | 3.57     | 1.07     | 54.93    |
| HTC 500 °C           | 46.04    | 1.80     | 1.33     | 50.83    |
| HTC 600 °C           | 47.19    | 0.08     | 1.16     | 51.57    |
| HTC 700 °C           | 46.66    | -0.15    | 1.05     | 52.44    |
| HTC 800 °C           | 45.49    | -0.57    | 1.11     | 53.97    |
| HTC 900 °C           | 48.34    | -0.63    | 1.15     | 53.97    |

3.4. X-Ray Diffraction (XRD)

The XRD measurement was investigated to examine the phase structure of carbon materials [20], as shown in Figure 3. The broad diffraction at a 2θ angle around 19 - 26°, the broad characteristic feature indicates the major presence of amorphous phase. In addition, the peak is found at 2 theta positions of 28° and 40° was evidently noticed for all samples corresponding to the carbon [18].

Figure 3. XRD of (a) Water hyacinth through hydrothermal process at 200 °C for 12 h and difference co-solvent treatment, (b) 500 °C, (c) 600 °C, (d) 700 °C, (e) 800 °C, and (f) 900 °C

4. Conclusions

Nanoporous carbon were successfully prepared from water hyacinth via hydrothermal carbonization at 200 °C for 12 h and carbonization at 500 - 900 °C in nitrogen gas for 2 h to develop porous structure and carbon content. It was found that carbonized hydrochar at 900 °C exhibited the highest porosity.
and carbon content. The temperature are mainly affected the solid yield, the chemical and structural properties of HTC. With the increasing of reaction temperature HTC yield decreased. HTC derived from decomposition of hemicellulose, residual of cellulose and formation of amorphous carbonaceous compounds during HTC. While cellulose and lignin are thermally stable components. It decomposes when hydrothermal at higher temperatures. The influence of thermal decomposition process parameters improved product characteristics and provided HTC process a promising technology may be used for various applications.

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6. References
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