Synthesis of Nanoporous Carbon from Water Hyacinth via Hydrothermal Carbonization Process Assisted Acid Activation

Nattaya Suksai[1], Sirayu Chanpee[1], Napat Kaewtrakulchai[1], Sutee Chutipaijit[1], Masayoshi Fuji[2], Apiluck Eiad-ua[1*]

[1] College of Nanotechnology, King Mongkut's Institute of Technology, Bangkok, Thailand 10520.
[2] Advanced Ceramic Center, Nagoya Institute of Technology, Tajimi, Gifu 507-0033, Japan.

* Corresponding author. Tel.: +66-89-781-5665; email: apiluck.ei@kmitl.ac.th
Manuscript submitted December 10, 2019; accepted April 21, 2020.
doi: 10.17706/ijmse.2020.8.2.52-57.

Abstract: Water hyacinth (WHs), which is a crucial waste material from agriculture in Thailand. It consists of hemicellulose, cellulose and lignin that has a potential for carbon material production. In this research, carbon material was prepared from Water hyacinth via hydrothermal Carbonization (HTC) by study the effect of hydrothermal temperature 200 °C, reaction time (4-24 h) and using H_3PO_4 activation to develop porosity and surface area. The sample have been characterized chemical-physical properties of carbon nanoporous materials through a scanning electron microscope (SEM), fourier transformer Infrared spectroscopy (FT-IR), X-ray diffraction (XRD). The results revealed that carbon content of nanoporous carbon materials from water hyacinth were increased with higher HTC temperature and time. Performing HTC at 200 °C for 12 h and using H_3PO_4 activation catalyst shows porosity increased on char surface is the optimum condition to synthesis of precursor materials for good adsorbent.

Key words: Water hyacinth, hydrothermal carbonization, nanoporous carbon, adsorbent.

1. Introduction

Water hyacinth is one of environment problems in Thailand due to its rapid spread in natural water sources. Its uncontrollable spread also causes problems in water transportation and drainage systems. In the other hand, water hyacinth is one of interesting water hyacinth is a biomass composed of cellulose, hemicellulose, lignin and ash biomass options that can be transformed to more valuable products [1]. It also helps to reduce the amount of waste that must be eliminated. There are some ways to make use of water hyacinth such as using as an adsorbent which is the purpose of this study. Water hyacinth has an interesting potential to use as raw material for porous absorbent material [2]. In this study used hydrothermal carbonization process- a type of biomass conditioning process that uses mild operating conditions (low temperature) (<300 °C) and it performs a high production yield [3]. The HTC mechanism provided water molecules, heat and pressure to decompose bonding of biomass polymer, cellulose, hemicellulose and lignin result in increasing of porosity and surface area compared to other processes [4]-[9]. These processes obtained at 200 °C for 4-24 h, which can add acidic or base catalyst for development of the pore structure and surface area.

In this research, the study temperature and time control of hydrothermal carbonization process that

affects the properties carbon and revealed the effect of acid catalyst H_3PO_4 on the morphology, surface area and porosity of produced carbon material from water hyacinth via hydrothermal carbonization process. Which can be observed from the morphological structure and surface characteristics using scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD). Carbon materials then applied by organic substances adsorption such as methylene Blue, methyl orange, methyl red, phenol red, and methyl violet.

2. Experimental Procedure

2.1. Raw Material

Water hyacinth (WHs) has derived from Ladkrabang, Bangkok, Thailand. Structure consists of hemicellulose, lignin and ash. Previous to HTC process, water hyacinth was dried in oven at 90°C to remove moisture and consecutively weighted until no further weight loss and crushed using a blender to obtain a powder was used to produce the hydrochars by the HTC process.

2.2. Method

Synthesize of porous carbon materials from water hyacinth via hydrothermal process (HTC) starts from drying collected raw water hyacinth by sun exposure to expel moisture and grind it into raw powder. Prepare of biomass 30 g of raw powder with 90 mL. The mixture was sealed into a Teflon vessel and then inserted in the autoclave, the reaction occurs in the range of 200 °C and 4-24 h. The best hydrochar sample obtained from hydrothermal process was selected via FT-IR analysis to find the best temperature. The hydrochar was chemical activating with a saturated solution of H_3PO_4 at concentration 4M after hydrothermal treatment, the product was dried at 90°C for overnight.

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. Analyze the crystal structure of the compound contained in the sample by X-ray diffraction (XRD).

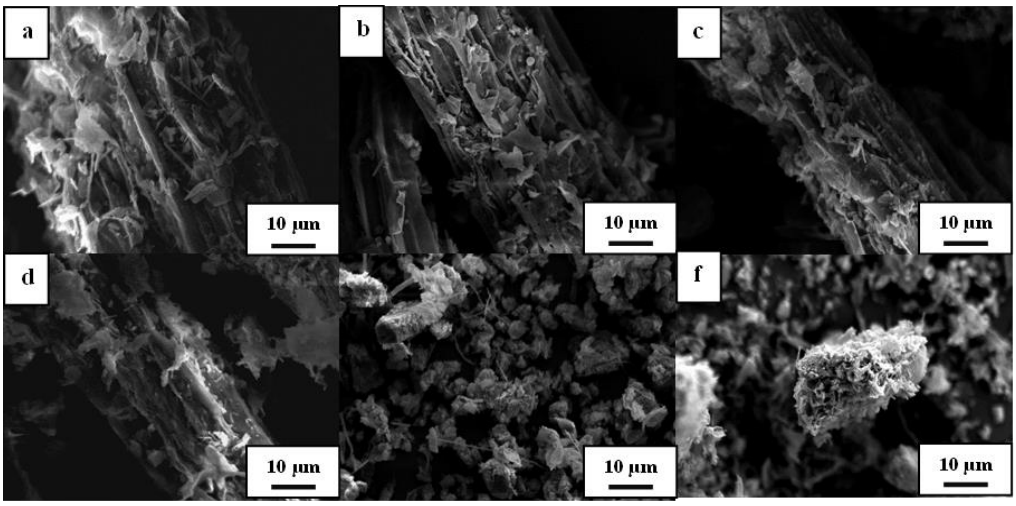

Fig. 1. SEM images (500x) of Water hyacinth through hydrothermal process at (a) Water hyacinth, (b) HTC200-4, (c) HTC200-8, (d) HTC200-12, (e) HTC200-24, and different co-solvent treatment (f) H_3PO_4.

3. Results and Discussion

3.1. Scanning Electron Microscope (SEM)

Scanning electron micrographs of the surface morphology of the feedstock and different reaction temperatures 200°C for (4, 8, 12 and 24 h) and co-solvent treatment H_3PO_4. The SEM analysis of the surfaces images (500x) of Water Hyacinth through hydrothermal process at 200 °C for 4-12 h. In Fig. 1(a-d), after hydrothermal 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 times of 12 h showed that the hemicellulose were destroyed significantly surface area of the sample compared that has a large increase in porosity and been treated found that the surface has rugged. Fig. 1(f), shows the surface area of the sample treated found that the surface has rugged By Water Hyacinth activation with 4M of H_3PO_4 will have a surface area more porous than hydrochars via hydrothermal carbonization.

3.2. Fourier Transforms Infrared (FT-IR)

The hydrothermal of Water hyacinth at 200 ºC with vary reaction time (4, 8, 12 and 24 h) are studied and FT-IR spectra of produced hydrochars are displayed in Fig. 2. 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 CH_2 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 [10], [11]. 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 CH_2 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. The hydrothermal of water hyacinth at 200 °C with vary reaction time (4, 8, 12 and 24 h) are studied and FT-IR spectra of produced hydrochars are displayed in Fig. 2. Compared with the starting Water hyacinth, the hydrochars composed of complex aromatics with oxygen-containing, while alkane content decreased. It can be indicated that decomposition of hemicellulose, cellulose and some lignin increase when hydrothermal for a longer time. The solvent, including H_3PO_4 are used as co-solvent in hydrothermal process of Water hyacinth at 200 °C for 12 h. The effect of co-solvent to functional group of hydrochars are shown in Fig. 2, the solvent, including (f) H_3PO_4. The effect of co-solvent to functional group of hydrochars. It can be observed that the FT-IR spectra at OH, aliphatic C-H, aromatic ring (1600 cm^{-1} and 1512 cm^{-1}) and C-O linkage are less remained when compared with hydrochars without co-solvent. The FT-IR results are not clear to decide the effect of co-solvent. The detected functional groups may be of original cellulose, hemicellulose, lignin and or new compound and even the co-solvent. However, hydrochar at 200 °C for 12 best choice of activate with H_3PO_4 for hydrothermal reaction.

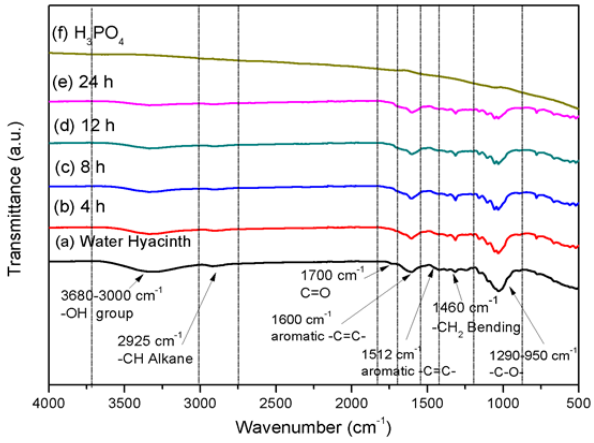

Fig. 2. FTIR spectra of Water hyacinth hydrothermal at 200°C for (a) Water hyacinth, (b) 4 h, (c) 8 h, (d) 12 h, (e) 24 h and co-solvent treatment (f) H_3PO_4.

3.3. X-Ray Diffraction (XRD)

The XRD measurement was investigated to examine the phase structure of carbon materials, as shown in Fig. 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 [12]. For these activated carbons, the diffraction profiles exhibited broad peaks at around 24 and 42° which are assigned to the reflection from (002) and (10) planes, respectively. The occurrence of broad peaks at these 2θ indicates an increasing regularity of crystal structure and resulting in better layer alignment.

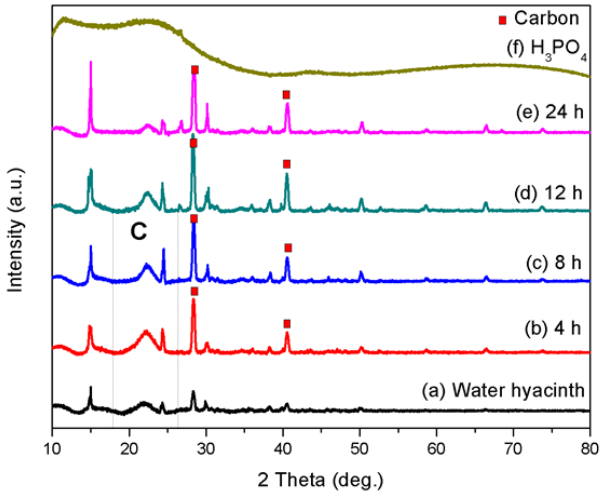

Fig. 3. XRD of (a) Water hyacinth through hydrothermal process at 200 °C for (b) 4 h, (c) 8 h, (d) 12 h, (e) 24 h, and co-solvent treatment (f) H_3PO_4.

4. Conclusions

The hydrothermal time and co-solvent treatment are mainly effects on the morphology of hydrochar. Higher hydrothermal temperature and time can more decompose of hemicellulose and cellulose. However, carbon nanoparticles have been successfully synthesized via hydrothermal at 200 °C for 12 h. Activated chemical activation of H_3PO_4. Carbon nanoparticle produced may be used to produce various applications such as used as a catalyst support or may be used to absorbent dye. in the other hand, the base used must be the appropriate concentration and time that will cause porosity on the carbon surface lest causing damage to the porous structure.

Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

Nattaya Suksai Experiment and wrote the paper, Sirayu Chanpee Concuted the research, Napat Kaewtrakulchai Analyzed the data, Sutee Chutipaijit Thesis Advisor, Masayoshi Fuji, Thesis Advisor, Apiluck Eiad-ua Thesis Advisor

Acknowledgments

The authors are thankful to the College of Nanotechnology, King Mongkut's Institute of Technology Ladkrabang for supporting this work.

References

[1] Ausavasukhi, A., Kampoosaen, C., & Kengnok, O. (2016). Adsorption characteristics of Congo red on carbonized leonardite. *J. Clean. Prod., 134*, 506-514

[2] Islam, M. A., Ahmed, M. J., Khanday, W. A., Asif, M., & Hameed, B. H. (2017). Mesoporous activated coconut shell-derived hydrochar prepared via hydrothermal carbonization-NaOH activation for methylene blue adsorption. *J ENVIRON MANAGE., 203*, 237-244.

[3] Xiao, J., Zhang, J., Lv, W., Song, Y., & Zheng, Q. (2017). Multifunctional graphene/poly(vinyl alcohol) aerogels: In situ hydrothermal preparation and applications in broad-spectrum adsorption for dyes and oils, *CARBON, 123*, 354-363

[4] Berge, N. D., Ro, K. S., Mao, J., Flora, J. R., Chappell, M. A., & Bae, S. (2011). Hydrothermal carbonization of municipal waste streams. *J ENVIRON SCI, 45(13)*, 5696-5703.

[5] Erabee, I. K., Ahsan, A., Zularisam, A. W., Idrus, S., R. *et al.* (2017). A new activated carbon prepared from sago palm bark through physiochemical activated process with Zinc Chloride. *Eng. J., 21(5)*, 1-14.

[6] Liu, Z., Quek, A., Hoekman, S. K., & Balasubramanian, R. (2013). Production of solid biochar fuel from waste biomass by hydrothermal carbonization. *FUEL., 103*, 943-949.

[7] Purnomo, C., Castello, D., & Fiori, L. (2018). *Granular Activated Carbon from Grape Seeds Hydrothermal Char APPL SCI-BASEL, 8(3)*, 331.

[8] Sevilla, M., & Fuertes, A. B. (2009). The production of carbon materials by hydrothermal carbonization of cellulose. *Carbon, 47(9)*, 2281-2289.

[9] Zhang, L., Wang, Q., Wang, B., Yang, G., Lucia, L. A., & Chen, J. (2015). Hydrothermal carbonization of corncob residues for hydrochar production. *ENERG FUEL., 29(2),* 872-876.

[10] Guo, S., Dong, X., Wu, T., Shi, F., & Zhu, C. (2015). Characteristic evolution of hydrochar from hydrothermal carbonization of corn stalk. *J ANAL APPL PYROL, 116*, 1-9.

[11] Schwan, J., Ulrich, S., Batori, V., Ehrhardt, H., & Silva, S. R. P. (1996). Raman spectroscopy on amorphous carbon films. *J. Appl. Phys., 80(1)*, 440-447

[12] Kartika, D., Indraswati, N. Y., & Ismadji, S. (2008). Activated carbon from jackfruit peel waste by H_3PO_4 chemical activation: Pore structure and surface chemistry characterization. *CHEM ENG J*.

Nattaya Suksai is a bachelor degree student. She is with the College of Nanotechnology, King Mongkut's Institute of Technology Ladkrabang (KMITL). She joined in Nonoporous Material Laboratory since 2019. Her present research interest is on application of nanoporous carbon for adsorbent.

Sirayu Chanpee is a bachelor degree student. He is with the College of Nanotechnology, King Mongkut's Institute of Technology Ladkrabang (KMITL). He joined in Nonoporous Material Laboratory since 2019. His present research interest is on application of nanoporous carbon for adsorbent.

Napat Kaewtrakulchai was born in Bangkok, Thailand in 1993. He studied nanomaterial engineering at the King Mongkut's Institute of Technology Ladkrabang, KMITL from 2011 to 2014, and master of engineering program in energy technology and management at the King Mongkut's University of Technology Thonburi, KMUTT from 2016–2017. He becomes a Ph.D. candidate of nanoscience and nanotechnology at the King Mongkut's Institute of Technology Ladkrabang, KMITL from 2018. His current research focuses on porous materials and biomass conversion technology, as well as the application of heterogeneous catalysts to the synthesis of biofuels.

Sutee Chutipaijit is an assistant professor in the College of Nanotechnology and vice president for Students Development, King Mongkut's Institute of Technology Ladkrabang (KMITL). He received the bachelor degree in biotechnology from KMITL in 2004, the bachelor degree in occupational health and safety from Sukhothai Thammathirat Open University in 2007, and doctor degree in biotechnology from KMITL in 2008, respectively. He had experience to work in Faculty of Science, Srinakharinwirot University in 2008. He joined KMITL with present research interest on nanobiotechnology and application of nanomaterials in plant since 2009.

Masayoshi Fuji is an assistant professor in Advanced Ceramic Center, Nagoya Institute of Technology, Tajimi, Gifu. He graduated from Tokyo Metropolitan University, Faculty of Engineering, Department of Industrial Chemistry in 1989, he also got the doctor degree from Tokyo Metropolitan University. He had experiences to work in Univ. of Florida as a researcher.

Apiluck Eiad-ua is an assistant professor in the College of Nanotechnology, King Mongkut's Institute of Technology Ladkrabang (KMITL). He received the bachelor degree in chemical engineering from Prince of Songkla University in 2001, master degree in chemical engineering from Chulalongkorn University in 2004, and doctor degree in frontier material from Nagoya Institute of Technology in 2011, respectively. He had experiences to work in National Institute of Advanced Industrial Science and Technology (AIST), Japan for 2 years and National Metal and Material Technology Center (MTEC) for 10 months. He joined KMITL with present research interest in synthesis and application of nanoporous materials since 2011.