Hydrothermal carbonization synthesis and KOH activation of porous carbons from waste marigold flowers

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Abstract. Marigold flower-derived porous carbons were synthesized via hydrothermal carbonization (HTC) and KOH activation. The effect of HTC and KOH activation on the change in morphology, chemical functional group, and surface area were studied and discussed based on the results of scanning electron microscopy, Fourier transform infrared spectroscopy, and N2 sorption analysis, respectively. Both HTC and KOH activation were found to play critical roles in changing morphology and enhancing surface area. Without HTC and KOH activation, carbons had low surface area and lacked porosity. In contrast, with both HTC and KOH activation, a sponge-like morphology with a large specific surface area of 1825 m2/g was obtained. The results serve as a useful guideline for further development and synthesis of porous carbons in certain specific applications.

1. Introduction
Porous carbons with a high surface area and porosity have recently received considerable attention as potential materials for a broad range of applications, such as electrode in electrochemical energy devices [1], wastewater treatment adsorbents [2], and carbon dioxide captures [3]. Currently, several kinds of agricultural wastes are widely used as a carbon source precursor to prepare porous carbons, since their chemical structure typically consists of lignin, cellulose, and hemicellulose [4]. Over the past several years, most researchers reported the preparation of porous carbons from several agricultural waste products available in their local area, including rice husk [5], cornstalks [6], and palm empty fruit bunches [7]. In addition to agricultural waste products, a number of plant biomasses continue to require investigation and understanding. In our previous work, waste marigold flower was used as a carbon source precursor for the synthesis of porous carbon, since they are usually discarded as waste after religious ceremonies in sacred places and temples in Thailand. The synthesis was performed using hydrothermal carbonization (HTC) at different treatment times, followed by a pyrolysis process [8]. We found that the specific surface area of porous carbons derived from marigold flower increased in accordance with longer HTC time from 118 to 281 m2/g, owing to the development of microporosity. However, the specific surface area and porosity were still low and insufficient for use as absorbents or electrodes in supercapacitors. Typically, carbon materials with relatively large surface areas can easily be prepared by either physical or chemical activation processes. Physical activation is usually achieved...
by heat treatment in an inert atmosphere under the presence of CO$_2$ or steam [9]. Meanwhile, chemical activation necessarily requires a chemical agent for activation, such as H$_3$PO$_4$, KOH, or NaOH [10].

Herein, we report the synthesis of porous carbons from marigold flower via HTC and KOH activation. The effects of HTC and KOH activation on the change in morphology, chemical functional group, and surface area of porous carbons were studied and discussed based on three characterization techniques, including scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and N$_2$ adsorption–desorption isotherm analysis, respectively.

2. Experimental

2.1. Preparation of raw materials
Marigold flowers were collected from Three Musketeers' Kaset Monument at Kasetsart University. They were washed by deionized water followed drying at 80 °C for 24 h in a hot-air oven. Dried marigold flowers were cut into small pieces using a blender machine and then ground into a fine powder using a mortar and pestle, followed by sieving with a 0.79 mm-screen mesh.

2.2. Synthesis of porous carbon from marigold flowers
10 g of the fine powder and 50 mL of deionized water were mixed together and then added into a Teflon-lined stainless-steel autoclave. HTC was performed at 180 °C for 24 h in a hot-air oven (Memmert, UN55, Germany). The products obtained after HTC were washed with deionized water, followed by drying at 80 °C for 24 h. The dried products were mixed with KOH at a weight ratio of 1:1 and then heated in a ceramic tube furnace (Chavachote, Thailand) at 800 °C for 1 h at a heating rate of 10 °C/min under Ar gas flow (0.2 L/min). The samples after HTC with and without KOH activation were designated as MHAC and MHC, respectively. For comparison, marigold flowers were directly pyrolyzed under the same condition both with and without KOH activation, which were designated as MAC and MC, respectively. The sample names and the experimental conditions are summarized in Table 1.

### Table 1. Sample names and the corresponding experimental conditions in this study.

| Sample name | HTC temperature/time | Pyrolysis temperature/time | Hydrochar:KOH |
|-------------|----------------------|----------------------------|---------------|
| MC          | -                    | 800 °C / 1 h               | 1:0           |
| MHC         | 180 °C / 24 h        | 800 °C / 1 h               | 1:0           |
| MAC         | -                    | 800 °C / 1 h               | 1:1           |
| MHAC        | 180 °C / 24 h        | 800 °C / 1 h               | 1:1           |

2.3. Characterization
The morphology of the samples was examined using a field-emission scanning electron microscope (JEOL, JSM-7600F, Japan) at an acceleration voltage of 3 kV. Transmittance spectra were recorded using Fourier transform infrared spectrometer (Bruker, Alpha II, Germany). Textural properties were determined from the N$_2$ adsorption–desorption isotherms at 77 K, which were acquired with a surface area analyser (Micromeritics, 3Flex, USA).

3. Results and discussion
Figure 1 shows the SEM images of porous carbons prepared under different conditions. An clear morphological change is clearly observed for each sample, indicating the significant effect of HTC and KOH activation. As can be seen, MC exhibited smooth with wavy lines on the surface with remaining morphology similar to a raw marigold flower (Figure 1a). The MHC sample had a rougher and more
ruptured surface. This implies that the HTC process resulted in the deterioration of lignocellulosic structure of marigold flower. In contrast, for the samples with KOH activation, MAC and MHAC showed a sponge-like morphology with a continuous pore-network structure. However, the MHAC structure was finer and more uniform than the MAC pore structure. This was likely due to a rougher and more ruptured surface of hydrochars which allowed a uniform interaction with KOH during activation. From the SEM observation, it can be concluded that HTC and KOH activation strongly affected the morphology of the carbons derived from marigold flowers.

Figure 1. SEM images (5000×) of (a) MC, (b) MHTC, (c) MAC, and (d) MHTAC.

The FTIR spectra of all the samples are shown in Figure 2a. No obvious absorption peaks were detected for MC and MH due to the decomposition of lignocellulosic structure during HTC and pyrolysis. For KOH activation, the absorption band of OH stretching was observed at about 3400 cm⁻¹ for both MAC and MHAC. The presence of absorption peaks at 1404 and 1003 cm⁻¹ of MAC were assigned to OH bending and C–O stretching, respectively. For MHAC, the absorption peaks at 1560 and 1080–1208 cm⁻¹ were attributed to aromatic C=C stretching and C–O–C stretching, respectively [11]. The FTIR result suggests that the KOH activation at high temperatures created the oxidation on carbon surface, as reflected by the presence of oxygen functional groups for MAC and MHAC.

Figure 2. (a) FTIR spectra and (b) N₂ adsorption–desorption isotherms of MC, MHC, MAC, and MHAC.

Furthermore, the measurements of N₂ adsorption–desorption isotherms were used to elucidate the specific surface area and pore structure of carbons, as shown in Figure 2b. The specific surface area of MC, MHC, MAC, and MHAC determined using the Brunauer–Emmett–Teller (BET) method were 7, 281, 1416, and 1825 m²/g, respectively. A small specific surface area of MC indicates a lack of porosity. This result is consistent with the morphology observed by SEM as previously discussed. For further information about the pore structure, the type of isotherm was analyzed based on the IUPAC classification. MHC and MAC were found to show type I isotherm with no difference between
adsorption and desorption, which is the characteristic isotherm of micropore. However, a combination of type I and IV characteristics were observed for MHAC. The hysteresis loop at the relative pressure of 0.45–0.99 indicated the presence of mesopore. The t-plot was also used to determine the surface area contributed by micropores. The proportion of micropore in MHC, MAC, and MHAC was 83%, 38%, and 36%, respectively. The average pore size of MHC, MAC, and MHAC was determined from desorption isotherm using the Barrett-Joyner-Halenda (BJH) theory, and were about 2–3 nm. It can be concluded that HTC and KOH activation are important processes to enhance surface area through the formation of nanoporous formation. Moreover, KOH activation plays an important role in creating mesopores in the samples. Textural parameters of all the samples discussed above are listed in Table 2.

### Table 2. Textural properties of MC, MHC, MAC, and MHAC.

| Sample | BET surface area (m²/g) | Micropore area (m²/g) | External surface area (m²/g) | Pore volume (cm³/g) | Micropore volume (cm³/g) |
|--------|------------------------|----------------------|-------------------------------|--------------------|------------------------|
| MC     | 7                      | 2 (29%)              | 5 (71%)                       | 0.0108             | 0.0011                 |
| MHC    | 281                    | 237 (84%)            | 44 (16%)                      | 0.1629             | 0.1243                 |
| MAC    | 1416                   | 550 (39%)            | 866 (61%)                     | 0.7711             | 0.2843                 |
| MHAC   | 1825                   | 675 (37%)            | 1150 (63%)                    | 1.0801             | 0.3588                 |

### 4. Conclusions

HTC and KOH activation were found to be necessary for the synthesis of porous carbon from marigold flowers with a large surface area. Direct pyrolysis without HTC and KOH activation resulted in MC having a very small surface area due to a lack of porosity. The MHAC with both HTC and KOH activation exhibited a sponge-like structure and had the largest surface area with a meso/macropore contribution of 63%. KOH activation also led to the surface oxidation of carbons. The preliminary results obtained in this study are highly useful for further maximizing surface area with controllable porosity by adjusting the activation temperature and KOH amount. The porous carbons derived from marigold flowers can be used as electrodes in supercapacitors or as adsorbents.

### 5. References

[1] Hu C, Xiao Y, Zou Y and Dia L 2018 *Electrochem. Energy Rev.* 1 84.
[2] Wong S, Ngadi N, Inuwa IM and Hassan O 2018 *J. Cleaner Prod.* 20 361.
[3] Creamer AE and Gao B 2016 *Environ. Sci. Technol.* 50 7276.
[4] Deng J, Li M and Wang Y 2016 *Green Chem.* 18 4824.
[5] Kim J, Yi Y, Peck DH, Yoon SH, Jung DW and Park HS 2019 *Environ. Sci.: Nano* 6 916.
[6] Yu H, Zhang W, Li T, Dang L, Liu Z and Lei Z 2017 *RSC Adv.* 7 1067.
[7] Guntagerg K, Panomsuwan G and Eiad-ua A 2018 *Walailak J. Sci. Technol.* 15 779.
[8] Chaiaamart N, Wongcharoen S, Eiad-ua A, Ishizaki T and Panomsuwan G 2019 *Key Eng. Mater.* 824 23.
[9] Zhou J, Luo A and Zhao Y 2017 *J. Air Waste Manage. Assoc.* 68 1269.
[10] Hunsom M and Aauthanit C 2013 *Chem. Eng. J.* 229 334.
[11] Siipola V, Tamminen T, Källi A, Lahtti R, Romar H, Rasa K, Keskinen R, Hyvälouma J, Hannula M and Wikberg H 2018 *BioResources* 13 1.

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