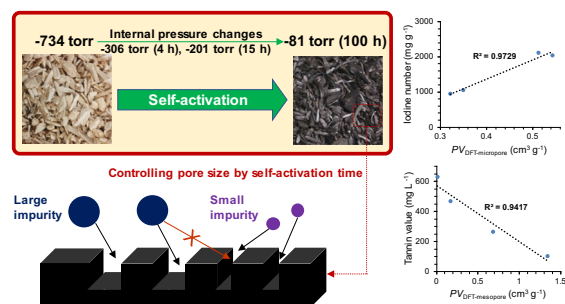


## Regular Article

## Controlling pore size of activated carbon through self-activation process for removing contaminants of different molecular sizes

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## GRAPHICAL ABSTRACT



## ARTICLE INFO

## Article history:

Received 8 December 2017

Revised 31 January 2018

Accepted 5 February 2018

Available online 7 February 2018

## Keywords:

Self-activation

Activated carbon

Surface area

Pore volume

Chemical adsorption

## ABSTRACT

Self-activation was employed for the manufacturing of activated carbon (AC) using kenaf core fibers, which is more environmentally friendly and cost-effective than the conventional physical/chemical activations. It makes the use of the gases emitted from the thermal treatment to activate the converted carbon itself. The mechanism was illustrated by the Fourier transform infrared spectroscopy and mass spectrometry analysis of the emitted gases, showing that CO<sub>2</sub> served as an activating agent. The AC from self-activation presented high performance, for instance, the Brunauer-Emmett-Teller surface area was up to 2296 m<sup>2</sup> g<sup>-1</sup>. Using the Density Functional Theory (DFT), the pore volume (PV) was determined to be 1.876 cm<sup>3</sup> g<sup>-1</sup>. Linear relations of  $PV_{DFT-micropore}$ /iodine number, and  $PV_{DFT-mesopore}$ /tannin value were established, indicating a strong relationship between the pore structure of AC and its adsorbing preference. Adsorption results for copper (II) and rhodamine 6G also indicated that the pore size of AC should be designed based on the molecular size of the contaminants.

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## 1. Introduction

Driven by the societal concerns, anthropogenic changes of the ecosystem have become an important part of the political agenda [1]. In this context, green process engineering is greatly attracting the public interests [2]. Traditionally, the manufacturing methods

of activated carbon (AC) can be sorted to two categories, i.e. physical and chemical activations [3]. The physical activation process uses gases presenting mild oxidation, for instance, carbon dioxide (CO<sub>2</sub>, a greenhouse gas), steam, air, etc. [4], to eliminate the volatile matters, followed by partial gasification with thermal treatment, at the expense of raising environmental issues [5–8]. Besides, chemical activation process introduces chemicals, e.g. ZnCl<sub>2</sub>, KOH, and H<sub>3</sub>PO<sub>4</sub>, into the activation processes [9–11]. The removal of those activating chemicals after the activation might introduce hazardous chemical wastes [9,12–14]. For instance, strong acids (e.g.

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HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>) are normally used to eliminate the zinc compound formed during the ZnCl<sub>2</sub> activation, which creates hazardous waste chemicals. Hence, both the conventional activation processes are accompanied by hazardous wastes, which needs the additional disposal and brings environmental bearings.

As well-known, tremendous volume of gases will be released from biomass during the thermal decomposition processes, e.g. pyrolysis and gasification. It was reported that those gases from high-temperature decomposition of biomass mainly contained H<sub>2</sub>, CO<sub>2</sub>, CO, CH<sub>4</sub>, H<sub>2</sub>O, etc. [15,16], in which, CO<sub>2</sub> and H<sub>2</sub>O have been greatly utilized as activating agents for producing AC [3,17]. Consequently, the CO<sub>2</sub> and H<sub>2</sub>O emitted from the biomass thermal decomposition may serve as the agents during the activation process, so that no additional gas needs to be imported [18], which might revolutionarily solve the environmental issues during the activation processes. This activation process employing the emitted gases from thermal decomposition of biomass as activation agents was defined as self-activation process, which has been developed rapidly [15,18–20].

Recently, apart from the conventional activation processes, Wang et al. categorized self-activation as the third type of activation methods in a review article [21]. In addition to the advantages of the more environmental-friendly and cost-effective compared with the conventional activation approaches, the performance of ACs from self-activation process was very competitive with that of the traditional ACs. For instance, the surface areas (SAs) of ACs from physical and chemical activation processes were 1926 m<sup>2</sup> g<sup>-1</sup> (coconut shell-based) and 1720 m<sup>2</sup> g<sup>-1</sup> (cotton stalk-based), respectively [4], while the SAs from the self-activated ACs were 2738 m<sup>2</sup> g<sup>-1</sup> (pine-based), 2602 m<sup>2</sup> g<sup>-1</sup> (cellulose-based), and 2432 m<sup>2</sup> g<sup>-1</sup> (kenaf core-based) [15,18,20].

Kenaf, as a porous material and mainly composed of C, H and O, has been demonstrated to be an excellent feedstock for manufacturing ACs [18,22–24]. For instance, Soheil et al. prepared fiber-like AC from kenaf fiber using K<sub>2</sub>HPO<sub>4</sub> activation for adsorbing phenolic contaminants [22]. Chowdhury et al. prepared AC from kenaf fiber for removing copper from waste water [23]. In this work, self-activation was successfully applied to fabricate kenaf core fibers (KCFs)-based AC (KAC), and its mechanism was investigated. The performance of ACs from self-activation were evaluated by SAs, pore volumes (PVs), iodine numbers, tannin values, etc. It was found that the ACs' pore structures owned a great effect on their performance of absorbing impurities with different molecular sizes. Commonly, the pore size can be sorted into three ranges in according with the definition from International Union of Pure and Applied Chemistry (IUPAC), i.e. micropore width less than 2 nm, macropore larger than 50 nm, and mesopore size at the range of 2 to 50 nm. The ACs with different pore structures could exhibit diverse adsorption preferences. Hence, the association between pore structure of AC and its adsorption capacity was investigated in this study.

## 2. Materials and methods

### 2.1. Self-activation process

KCFs (3 – 30 meshes) from Biotech Mills Inc., Snow Hill, NC, USA, were selected for producing AC through the self-activation process. The dried KCFs own 49.0% of cellulose, 29.7% of hemicellulose, and 19.2% lignin. The results from proximate analysis and ultimate analysis of the dried KCFs, KAC-1, KAC-2, and KAC-3 are shown in Table 1. The chemical composition of KCFs from the proximate analysis ultimate analysis was similar to the reported values [25]. The fixed carbon (proximate analysis) and the carbon content (ultimate analysis) of the KACs were decreased with the activation

time increase, because of the increased amount of inorganic ash content (Table 1). The oxygen contents of the KACs presented very low values, compared with AC prepared by chemical activation [26]. The low oxygen of AC might benefit to its adsorption of specific chemicals, e.g. surfactant [27].

The detail processes of self-activation were described in our previous work [18]. Briefly, the self-activation process was conducted in the Sentro Tech Corp. STY-1600C box furnace that has vacuum capability. After placing 200 g KCFs (179 g dried mass and 21 g moisture) into the chamber in the air atmosphere, the furnace was pumped down to an approximate pressure of -734 torr (the absolute vacuum pressure is approximate -760 torr) and then all the valves were switched off. The furnace was kept in the state as a closed system (no mass transfer between the surrounding air and furnace) during the entire process. Then, the self-activation process was conducted by following three stages: (a) ramping (1 0 °C min<sup>-1</sup>) the furnace temperature to 1000 °C; (b) dwelling at 1000 °C for 4, 15, and 100 h, respectively; and (c) cooling down (≤10 °C min<sup>-1</sup>). Finally, the as-produced KACs were obtained and denoted as KAC-1 (4h), KAC-2 (15 h), and KAC-3 (100 h), respectively.

In addition to the three groups of KACs from self-activation process, a commercial granular AC (8 × 16 meshes) from Calgon Carbon Corp. (CAC) was used as a comparison in this study. Prior to the tests of iodine number determination, the tannin value test, copper (II) and rhodamine 6G adsorptions, all four groups of ACs were grinded into the particle sizes of not less than 90% at 325 mesh, 95% at 200 mesh, and 99% at 100 mesh. This particle size requirement of AC is defined in the American Water Works Association (AWWA) B600-10 standard, which is a standard designed for powdered AC used in drinking water purification.

### 2.2. Surface area and pore volume

The Micromeritics Instrument Corp. 3Flex 3500 surface area and pore size analyzer was employed for determining the SAs and PVs of the ACs. The N<sub>2</sub> gas adsorption at 77 K was used to analyze the gas adsorption capabilities of the ACs. Prior to the tests, the Micromeritics Instrument Corp. VacPrep 061 degasser was employed for vacuum-degassing the ACs at 350 °C for ~4 d. After being transferred to the analyzing ports, the ACs were *in situ* vacuum-degassed by the Edwards EXT75DX 63CF turbo pump at 350 °C for 20 h. The SAs of ACs were calculated from the isothermal plots through the instrumental software (3Flex Version 1.02) by means of the Brunauer-Emmett-Teller (BET) model. The PVs and pore size distribution of the ACs were investigated depending on the Density Functional Theory (DFT).

### 2.3. Fourier transform infrared spectroscopy

The Fourier transform infrared spectroscopy (FT-IR) was employed to examine the concentration changes of CO<sub>2</sub> and CO for the self-activation processes with different dwelling times. A Thermo-Fisher Nicolet 6700 FT-IR analyzer with a 20-mL Pike flow cell was employed. Three gas samples were collected by 1-L Tedlar bags containing the emitted gases after the self-activation processes at 1000 °C for 4 h, 15 h, and 30 h, respectively.

### 2.4. Iodine number determination

The iodine number is a parameter to represent the adsorbing capacity of AC, which is an important characteristic for the chemical adsorption evaluation of AC. The iodine numbers of the powdered ACs were established using the sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) volumetric method in accordance with the ASTM D4607 standard [28]. The iodine number can be used as an approx-

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