



Production of high surface area mesoporous activated carbons from waste biomass using hydrogen peroxide-mediated hydrothermal treatment for adsorption applications



Akshay Jain^a, Rajasekhar Balasubramanian^b, M.P. Srinivasan^{a,*}

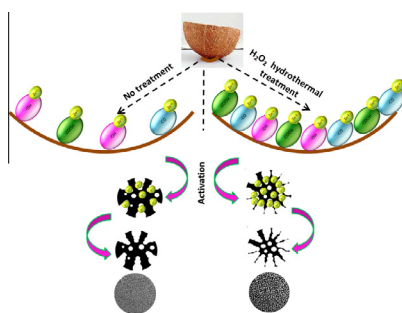
^a Department of Chemical and Biomolecular Engineering, National University of Singapore, Singapore 117585, Singapore

^b Department of Civil and Environmental Engineering, National University of Singapore, Singapore 117585, Singapore

HIGHLIGHTS

- High mesopore area obtained by improved chemical activation with ZnCl_2 .
- Hydrothermal treatment of biomass with H_2O_2 enhanced the chemical activation.
- Up to 100% increase in mesopore area is achieved by employing H_2O_2 pre-treatment.
- OFG in biomass/precursor and mesopore area in the carbon are strongly correlated.
- High dye uptake capacity of 714 mg/g is achieved.

GRAPHICAL ABSTRACT



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ABSTRACT

High-surface area mesoporous activated carbons were prepared from biomass by incorporating H_2O_2 as an oxidizing agent during hydrothermal pre-treatment of the raw material (coconut shell). Use of H_2O_2 led to enhanced formation of OFGs in the hydrochar precursor and resulted in activated carbons possessing high mesopore and BET surface areas. A strong interdependence is observed between the extent of formation of oxygenated functional groups (OFGs) in the hydrochars obtained from the hydrothermal pre-treatment and mesopore area in corresponding carbons. The mesoporous carbons showed high adsorption capacity for Rhodamine B up to 714 mg/g.

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1. Introduction

Porous carbon-based materials serve as the material of choice in many applications such as gas separation [1–3], water and air purification [4–6], catalysis [7,8], chromatography [9], energy storage [10–12], electrode materials [7,13–18], hydrogen storage [19,20].

In particular, mesoporous carbon materials are critical for applications which involve large molecules, such as substrates for immobilizing biomolecules, electrodes for Li-ion batteries and biosensors [21] and adsorbents for dyes [22–26]. Many studies have explored the use of agricultural wastes such as coconut shells, coffee beans, sugar cane bagasse, oil-palm stone to produce activated carbons [27–38]. Coconut shells are popular as they possess high hardness [39], high volatility and low ash content [39–42] and

* Corresponding author.

can yield high specific surface areas. However, synthesis of mesoporous carbon is a resource-intensive process. In particular, zinc chloride (ZnCl_2) and phosphoric acid (H_3PO_4) are extensively used as chemical activating agents [43–47] for the production of mesoporous activated carbon from biomass, and excess quantities of the activating agents are required for formation of high mesoporosity and surface area [23,48,49].

Chemical activation has been shown to be influenced by the presence of oxygenated functional groups (OFGs) comprising carboxylic, lactonic and phenolic moieties in the precursor [20,50,51]. Biomass and pure carbohydrates have been hydrothermally carbonized to improve the chemical characteristics of hydrochar products for various applications by bestowing OFGs and reducing the degree of aromatization [20,27,32,52–54]. Liu et al. reported a 340% increase in OFG content in hydrothermally treated pinewood compared to that observed in pinewood char obtained by pyrolysis. Higher Cu adsorption on the former was attributed to the presence of higher OFG content, thereby demonstrating the importance of OFGs in adsorption of cationic species [55]. However, it is well-known that the hydrochars thus produced possess significantly low surface areas compared to activated adsorbents [13,14]. Thus, in the absence of further processing, hydrothermal carbonization as a stand-alone process is not sufficient for efficient deployment of biomass as an adsorbent. Sevilla et al. validated hydrochar as a suitable precursor for microporous activated carbon synthesis when activated with KOH [27].

Formation of activated carbon from biomass typically demands use of activating agents in excess. Ahmadpour et al. obtained activated carbon with a BET surface area of $2500 \text{ m}^2/\text{g}$ and a total pore volume of $1.95 \text{ cm}^3/\text{g}$ from coconut shell by employing ZnCl_2 as the activating agent (ZnCl_2 :shell ratio = 5:1) [46]. Recently, Ma et al. reported a total pore volume of $2.727 \text{ cm}^3/\text{g}$ and a BET surface area of $1297 \text{ m}^2/\text{g}$ by activating glucose with activating agent (mixture of ZnCl_2 and KCl):glucose ratio of 6:1 [56]. The use of activating agents in high excess to create mesoporosity makes such processes uneconomical and thus alternative processes that can deliver mesoporous carbon with reduced resource usage are clearly needed.

We have reported recently that hydrothermal pre-treatment of biomass (coconut shell) in presence of ZnCl_2 to obtain hydrochar leads to extensive dehydration and increase in OFG content compared to the hydrothermal treatment in the absence of it as ZnCl_2 eases the breakage of glycosidic linkages. High OFG content in the hydrochar makes it more suitable for chemical activation and thus results in an increase in the mesopore area of the activated carbons [57,58]. It can be expected that oxidative surface modification of raw lignocellulosic biomass with an oxidizing agent may result in enhanced formation of OFGs, thereby leading to improved activation. Indeed, Zeronian et al. have shown that cellulose oxidized to oxy-cellulose upon treating with H_2O_2 which might also lead to formation of carboxylic groups [59]. In this work, we have employed H_2O_2 as an oxidative agent to induce formation of OFGs on the precursor during pre-treatment of raw coconut shell which is expected to increase the affinity of the chemical activating agent (ZnCl_2) to the precursor surface during the ensuing activation process. Amarasekara et al. have proposed that Zn^{2+} exists as hydration shells in solution and the coordinated water molecules act as nucleophiles [60]. These nucleophiles are expected to be attracted to the free electron pairs of the O atoms in the OFGs, thereby giving Zn^{2+} greater access to the precursor surface which leads to better dehydration of lignocellulosic biomass. Thus, the OFGs promote chemical activation by ZnCl_2 , leading to higher mesopore area and volume. While ZnCl_2 is deployed as a catalyst in hydrothermal pre-treatment and also as the activating agent during pyrolysis in this work, most of it can be recovered and reused [36,46,61–63] and hence its use does not impose limitations in terms of environmental issues.

H_2O_2 was presented to the raw biomass by refluxing and hydrothermal treatment and the ensuing product was subjected to activation with ZnCl_2 . Use of H_2O_2 in resulted in improved mesopore area and in particular, its use in the hydrothermal environment resulted in increase in mesopore area up to 100% ($1208 \text{ m}^2/\text{g}$ vs $606 \text{ m}^2/\text{g}$ in the absence of H_2O_2). This enhancement in mesopore area resulted in the large adsorption capacity of Rhodamine B (tracer dye) up to 714 mg/g . The relation between functional property of the starting material and surface characteristics of carbon is manifested as a strong interdependence between OFGs in the precursor and mesopore area in the corresponding carbon. The study underscores the utility of simple pre-treatment protocols that extract even higher value from an established biomass source by understanding and exploiting the role of surface functional groups.

2. Materials and experimental procedure

Coconut shells (*Cocos nucifera*) were obtained from Malaysia. ZnCl_2 , reagent grade (Scharlab), H_2O_2 (30% GR, Merck), blackstrap molasses (Nature's glory), Na_2HPO_4 (>99%, Sigma Aldrich), H_3PO_4 (85%, Mallinckrodt), sodium hydroxide (Merck, EMSURE, >99%), Rhodamine B (Sigma Aldrich, India) and hydrochloric acid (37%, Panreac) were used as received.

2.1. Preparation of activated carbon precursors

The coconut shells (after trimming the fibers) were dried at 105°C for 24 h, crushed using a commercial laboratory blender (Waring) and then ground and sieved into coarse granules (10–20 mesh). ZnCl_2 and CO_2 were used as chemical and physical activating agent, respectively and H_2O_2 was used as an oxidizing agent. Fig. 1 depicts the various treatments applied to raw biomass to obtain the precursors. Precursors were prepared via following pre-treatments:

- (1) ZnCl_2 soaking at 105°C (denoted by ZS).
- (2) Reflux with H_2O_2 (HR).
- (3) Hydrothermal treatment with H_2O_2 (HHT).
- (4) Hydrothermal treatment without H_2O_2 (control sample for determining effect of H_2O_2 treatment) (HT).
- (5) Hydrothermal treatment with ZnCl_2 (ZHT).

2.2. ZnCl_2 soaking (ZS)

The samples (coconut shell granules or precursors) were mixed with ZnCl_2 solution with a ZnCl_2 :raw shell ratios of 1:1, 2:1 or 3:1 and dried at 105°C for 12 h.

2.3. Reflux with H_2O_2 (HR)

A mixture of coconut shell granules and H_2O_2 (15 g shell in 90 mL H_2O_2 (10% by weight)) was refluxed for 1 h at 100°C . The solids were separated by filtration and washed thoroughly with de-ionized water. The product was then dried at 105°C for 12 h.

2.4. Hydrothermal treatment (HT)

2.4.1. Hydrothermal treatment with H_2O_2 (HHT)

The coconut shell granules– H_2O_2 mixture (same quantities as used in Section 2.3) was subjected to hydrothermal treatment in a Parr 4848 autoclave at 200°C for 20 min. The reactor was then cooled to room temperature and the products were dried at 105°C for 12 h. 200°C was chosen as the preferred treatment temperature since it delivered the hydrochar with high OFG content. A

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