



Lignocellulosic biomass for ethanol production and preparation of activated carbon applied for supercapacitor



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ABSTRACT

To make full use lignocellulosic biomass resources, comprehensive utilization of this renewable energy resource was proposed. In this work, *Amygdalus pedunculata* shell served as typical lignocellulosic biomass was used for ethanol production and activated carbon preparation, and the maximum ethanol yield 0.0158 g g⁻¹ and activated carbon with maximum BET surface 2059 m² g⁻¹ were obtained. Additionally, the porous carbon was systematically characterized and applied as electrode material for supercapacitor which exhibits high specific capacitance of 358.4 F g⁻¹ at a current density of 0.5 A g⁻¹. After 1000 cycles, the capacitor still exhibited a stable performance with capacitance retention of 86.3% at a current density of 5 A g⁻¹. The conversion of *Amygdalus pedunculata* shell to bioethanol and activated carbon applied as electrode material in high performance supercapacitor offers significant potentials for comprehensive utilization of lignocellulosic biomass.

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1. Introduction

With the increasing demand for energy and excessive depletion non-renewable fossil fuels, lignocellulosic biomass offered as a vast renewable energy resource has attracted much attention during the past decade [1], especially for the sustainable bioethanol production. On the other hand, lignocellulosic material is also reported as precursors for the preparation of activated carbon which is used in a wide range of applications such as adsorbent, catalysts support and particularly electrode material for supercapacitor [2].

In the process of bioethanol production, there is a large proportion of unhydrolyzed solid residue which contains an ample amount of lignin and cellulose compounds. Meanwhile, in the carbonization process of the activated carbon preparation, there is a notable mass loss which was defined as the primary decomposition cellulose and hemicellulose [3,4]. To make full use of lignocellulosic biomass resources, we propose the comprehensive utilization of this material. Lignocellulosic biomass was used for ethanol production for the purpose of utilization of cellulose and hemicellulose and then the unused solid residue was used for the preparation of activated carbon applied as electrode material.

In this work, *Amygdalus pcdunculata* shell (APS) [5] served as typical lignocellulosic biomass was pretreated by sulfuric acid,

which is a pretreatment method with high potential for industrial applications [6], and then detoxified with liming and fermented by *saccharomyces cerevisiae*. Subsequently, the unhydrolyzed solid residue was activated by KOH which is widely used for obtaining porous carbon with high specific surface areas and well developed porosity [7]. Additionally, the porous carbon is systematically characterized and applied as electrode material for supercapacitor. The capacitive behavior of the electrodes and their supercapacitor performance were evaluated by electrochemical methods including cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvanostatic charge–discharge (GCD). Results were compared with published findings for activated carbons prepared from other lignocellulosic biomass resources. The present experimental study was carried out according to the flow diagram showed in Fig. 1.

2. Materials and methods

2.1. Raw materials and pretreatment

APS was collected from *Amygdalus pedunculata* plant which is a member of the family Rosaceae with high tolerance of drought, well-developed root system resisting and fixing sand, and greater adaptability to a wide range of soil types and a good candidate for desert reclamation. Prior to the experiment, the raw material was washed with distilled water to remove dust and other inorganic impurities and oven-dried for 24 h at 50 °C to reduce its moisture content. APS crushed to a 20-mesh size was pretreated

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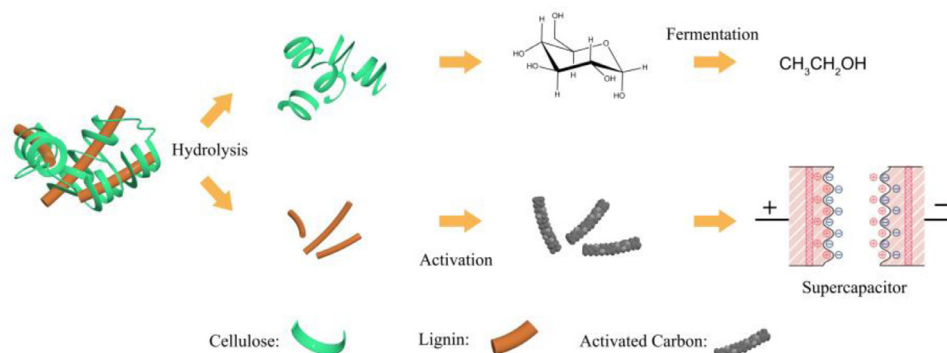


Fig. 1. Schematic process diagram of comprehensive utilization of lignocellulosic biomass from APS.

by suspending at 10% (w/v) solid loading in various concentrations of 100 mL H_2SO_4 solutions (0.2 M, 0.4 M, 0.6 M, 0.8 M and 1.0 M) within different contact time (15 min, 30 min, 45 min and 60 min) at 121 °C. After pretreatment, the resulting slurry were cooled down using tap water and centrifuged at 10,000 g for 10 min, the supernatant was harvested and the solid residue was washed with distilled water repeatedly to remove the residue H_2SO_4 until to pH 6–7 for further use.

2.2. Batch fermentation

The supernatant obtained was treated with calcium hydroxide to pH 10.0–10.5, and centrifuged at 10,000 g for 10 min to harvest the supernatant, which is the most commonly used method for removal of the inhibitors by precipitating at high pH values of 10.0–10.5 to reduce the effect of toxic components on ethanol production with microorganisms [8]. Subsequently, the supernatant harvested pH was adjusted with 1 mol L^{-1} H_2SO_4 to 4.5, a value suitable for fermentation, and supplemented with other nutrients [9], which was used as a medium for ethanol fermentation by *Saccharomyces cerevisiae* obtained from Cheng dong Ave. Yichang, Hubei, China. Prior to the process, the medium was purged by nitrogen gas for 5 min to maintain an anaerobic condition. Then, fermentation was performed in 250 mL cotton-plugged Erlenmeyer flasks containing 100 mL of fermentation medium with 1 g *Saccharomyces cerevisiae* at 30 °C and an agitation speed 180 rpm for 72 h.

The ethanol fermented was determined by gas chromatography (GC-14C, Shimadzu, Japan) via direct injection GC method coupling with an external standard for calibration. Before injection, the sample was centrifuged and the supernatant was filtered through a filter (organic membranes, 0.45 μm). A Rtx-Wax column (30 m \times 0.32 mm \times 0.25 μm) was employed at 120 °C, FID detector at 220 °C and nitrogen with a 0.5 MPa pressure carrier [10,11]. All analyses were carried out in duplicate and the average data were reported.

2.3. Preparation and characterization of activated carbon

Impregnation ratios and activation temperatures coupled with different activation times were employed to enlarge surface area of activated carbon (AC) from the solid residue. The washed solid residue was oven-dried at 105 °C for 12 h and then immersed in KOH solution, the mass ratio of KOH to solid residue ranging from 0.5 to 3.5. The mixture was dehydrated in an oven overnight at 105 °C. Subsequently, the treated sample was carbonized at 350 °C for 1 h in tubular furnace and activated at the desired temperatures (750 °C, 800 °C, 850 °C, 900 °C and 950 °C) for periods (60 min, 90 min, 120 min, and 150 min) under N_2 flow (100 mL min^{-1}) at a

heating rate of 5 °C min^{-1} . After being cooled, the resultant activated carbon was boiled with 0.1 M HCl 5 min and rinsed repeatedly with distilled water to remove the remaining chemicals until the filtrate reached neutral pH. The washed sample was dried in the oven at 105 °C for 24 h and ground in the mill used for textural and chemical characterization. The yield of the AC is defined as the equation: $Y (\%) = \text{mass of activated carbon} / \text{mass of dried solid residue} \times 100\%$.

Scanning electron microscope (HITACHI SU3500) was used to investigate the morphology of the solid residue and the AC at the accelerated voltage of 15 KV. The FTIR Spectra was recorded in a Bruker TENSOR 27 spectrophotometer using the KBr disk method operated in the range of 4000–400 cm^{-1} , resolution of 2 cm^{-1} and 32 scans. AC was characterized by powder X-ray diffraction (Bruker D8, equipped with Cu K α radiation, $\lambda = 1.5406 \text{ \AA}$) with a step size of 0.01°/s from 10° to 80°. The BET surface area and pore structure parameters of the produced carbons were assessed by nitrogen adsorption–desorption analysis (ASAP2020 porosimeter, Micromeritics, USA). Samples were degassed at 573 K for 24 h under vacuum prior to being analyzed and the data were recorded at liquid nitrogen temperature (77 K).

2.4. Electrode preparation and electrochemical measurements

The preparation method is to take the AC modified on the glass carbon electrode (GCE). Before the modification, a GCE electrode was polished with 0.05 μm $\alpha\text{-Al}_2\text{O}_3$ powder, and then ultrasonically rinsed by ethanol and deionized water, dried in N_2 at room temperature. 5 mg AC was dispersed in 2 mL N,N-Dimethylformamide and 0.1 mL Nafion (0.5%) using high power ultrasonic to form mixture dispersion. 20 μL AC suspensions were then dropped onto the GCE surface within three times. The electrode was subsequently dried under an infrared lamp to finish the modification.

Electrochemical measurements were performed on an electrochemical workstation (CHI 660D, CH Instruments, China) using a three electrode system. Platinum wire and Ag/AgCl electrode were used as the counter and reference electrode, respectively. Na_2SO_4 aqueous solution (1 M) was used as electrolyte. The cyclic voltammetry (CV) tests were conducted in the potential range from -1 V to 0 V at different scan rates ranging from 10 mV s^{-1} to 500 mV s^{-1} . Electrochemical impedance spectroscopy (EIS) analyses were recorded in a frequency range of 0.1 Hz to 1000 kHz with alternate current amplitude of 50 mV, and in an electrolyte solution of 0.1 M KCl containing 1 mM $[\text{Fe}(\text{CN})_6]^{4- / 3-}$. Galvanostatic charge-discharge (GCD) measurements were operated at different current densities ranging from 0.5 to 200 A g^{-1} with cutoff voltage of -1 to 0 V. The specific capacitance (C, F g^{-1}), energy density (E, Wh kg^{-1}) and power density (P, W kg^{-1}) of the symmetric

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