Synthesizing activated carbon from coconut shells and evaluating its electrochemical characteristics for supercapacitors

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ABSTRACT

Activated carbon derived from coconut shells underwent successful synthesis employing three distinct chemical activators: NaOH, H_3PO_4, and $ZnCl_2$. Harvested from highland regions with freshwater environments, coconut shells were solar thermally dried prior to carbonization at 600°C for 3 hours, followed by thorough activation. Characterization of the samples encompassed X-Ray Diffraction (XRD), Fourier Transform Infrared (FTIR), to discern crystal structure, functional groups, surface area, and morphology. XRD analysis revealed the formation of an amorphous phase with carbon graphite as the predominant constituent, while impurities such as hydrogen, oxygen, nitrogen, potassium, sodium, phosphorus, calcium, and magnesium were identified. FTIR spectroscopy indicated no significant discrepancies across the three activating agents, affirming successful activation through the presence of –OH, C=O, and C-O functional groups. These findings collectively endorse the potential applicability of coconut shell-based activated carbon in water purification treatments. The compacted activated carbon underwent cyclic voltammetry testing across varied scan rates ranging from 20 mV/s to 100 mV/s, within a potential window of 0.05 to 0.8. Specific capacitance values were recorded at each scan rate: 602.19 F/g, 299.78 F/g, 378.31 F/g, 374.13 F/g, and 286.92 F/g, respectively. Notably, the highest specific capacitance of 600.89 F/g and an energy density of 45.64 Wh/kg were achieved at a scan rate of 20 mV/s. Comparative analysis with prior research indicated that the synthesized activated carbon electrodes in this study exhibited the highest specific capacitance observed to date.

Keywords: Stereotactic Body Radiotherapy (SBRT), Dice Similarity Coefficient (DSC), Geographical Miss Index (GMI) and Discordance Index (DI), Four-Dimensional Computed Tomography (4-DCT) images

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INTRODUCTION

Activated carbon stands as a cornerstone in the chemical industry, prized for its exceptional physicochemical properties such as high surface area and stability, rendering it versatile in various applications like water purification, gas filtration, supercapacitor electrodes, and catalyst support [1-3]. The activation of carbon can be achieved through two primary methods: physical activation via pyrolysis under an inert atmosphere and chemical activation involving impregnation with agents like KOH, NaOH, $ZnCl_2$, or acids [4-7]. Chemical activation, often preferred for its lower temperature and shorter activation time, hinges on factors like concentration, temperature, and activation duration, influencing its efficacy in inhibiting formation and enhancing surface area. Such activation methods offer diverse avenues for tailored physicochemical characteristics in activated carbon, crucial for its performance as an adsorbent [8-11].

The surging demand for activated carbon underscores the pivotal role of precursor carbon materials in its fabrication. Chemical activation, particularly, garners interest due to its ability to yield activated carbon with high specific surface area, pore volume, and tunable porosity, critical for diverse applications spanning air and water purification, pollutant adsorption, gas separation, and catalysis. However, the cost associated with activated carbon derived from high-carbon, low-inorganic content precursors prompt exploration into low-cost alternatives, notably biomass wastes like coconut shells, prized for their abundance and affordability.

In regions abundant in coconut production like South Sulawesi province, Indonesia, harnessing coconut shell waste for activated carbon fabrication emerges as a promising endeavor [12-15].

By employing various activating agents such as NaOH, alkali earth metal salts, $ZnCl_2$, and H_3PO_4, researchers aim to optimize the utilization of coconut shell waste. Previous studies have highlighted the efficacy of different activating agents in enhancing surface area, micro porosity, and adsorption capacities of activated carbon.

In this study, the influence of activating agents on coconut shell-based activated carbon will be scrutinized using an array of analytical techniques including XRD for crystal structure analysis, FTIR for functional group analysis, in this study, we fabricated activated carbon electrodes derived from coconut shells employing a novel two-stage chemical activation process

involving H_2SO_4 and KOH. Our investigation focused on evaluating the porous structure and energy storage capabilities of these electrodes [16-21]. The novelty lies in the utilization of a two-stage chemical activation approach, distinguishing it from previous methodologies which predominantly relied on either physical activation followed by chemical activation or vice versa.

MATERIAL AND METHOD

Preparation of activated carbon

Sourcing and preparation of raw material:

Local coconut shells were obtained and dried before being crushed into approximately 5 mm pieces. This process aimed to enhance the efficacy of subsequent pyrolysis by maximizing the surface area available for carbonization. The crushed shells underwent washing and filtering to remove dust particles and other solid impurities. Subsequently, the coconut shells were heated at 100°C for 2 hours in an electric oven [22].

Pyrolysis of crushed material:

The dried and crushed coconut shell samples were introduced into a medium-sized reactor, specifically a tightly lidded crucible within a vacuum electric furnace for pyrolysis. Each batch underwent heating at 600°C for 12 hours to facilitate pyrolysis [23-25]. Following pyrolysis, the resultant lumps were transferred to a ball mill for milling for approximately 2 hours. The milled samples underwent sieving, and any oversized particles were reground until the entire batch reached the desired -300 μm size range.

Two-stage chemical activation (Acid-Alkali):

The sieved pyrolyzed carbon particles were placed into beakers containing $1M\ H_2SO_4$ for the first stage of activation. The mixture was stirred and left to soak for 2 hours. Subsequently, the acid-activated carbon material underwent multiple rinses with distilled water before being transferred to beakers containing 1M KOH solution for the second (alkali) stage of activation. After stirring and soaking for 2 hours, the material was once again rinsed with distilled water and finally dried at 100°C in the oven for 2 hours [23].

Fabrication of activated carbon super capacitor electrode

Following activation, the activated carbon underwent milling for approximately 1 hour in a ball mill. The resulting activated carbon samples were sieved to a size less than 106 μm. Polyvinyl Alcohol (PVA) was chosen as the binder due to its mechanical strength, wettability, and capacitance properties, surpassing those of Polyvinylidene Fluoride (PVDF). A solution was prepared by mixing 1g of PVA with 75 ml of distilled water, which was stirred for approximately 20 minutes at room temperature. Subsequently, 30 g of activated carbon was added to the solution and stirred for 2 hours. The resulting paste was then coated and mounted into a castable polymer material, allowing the carbon electrode to dry there after [25-29].

Structural characterization

The acid-alkali activated carbon electrodes were subjected to structural characterization to elucidate their elements, functional groups, and overall structure. This analysis utilized X-Ray Diffraction (XRD). XRD analysis was employed to identify non-carbon compounds still present on the electrode surface following the activation process [24]. The sample underwent examination using a Rigaku D/Max-III C X-ray diffractometer. Diffraction patterns were generated at a scanning rate of 2°/min within the range of 2°C to 50°C at room temperature, utilizing Cu-Kα radiation set at 40 kV and 20 mA.

Electrochemical evaluation

Cyclic voltammetry:

Cyclic voltammetry was conducted to evaluate the charge storage and supercapacitor properties of the acid-alkali activated coconut shell carbon electrode. Each sample, affixed with copper conductors, was cold-mounted onto a polyester base to securely hold the conductor in place. Subsequently, the samples were immersed in a three-electrode electrochemical cell, comprising the mounted sample, a Ag/AgCl reference electrode, a platinum counter electrode, and a 1 M H_2SO_4 solution serving as the electrolyte. The electrodes were then connected to a Versastatm 4 potentiostat. The cyclic voltammetry tests comprised three cycles, ranging from 0.05 V to 0.8 V potential window, at scan rates of 20 mV/s, 40 mV/s, 60 mV/s, 80 mV/s, and 100 mV/s, respectively. Following the tests, charge storage parameters including Specific Capacitance (C_{sp}) and Energy density (E) were determined.

RESULTS AND DISCUSSION

Ultra violet spectroscopy

UV spectroscopy was employed to examine the optical absorbance of the synthesized activated carbon, recorded within the wavelength range of 200 nm-800 nm, as depicted in figure 1. The broad optical wavelength of the activated carbon was observed at 267 nm, indicating the presence of π-π^* transitions resulting from van der waals forces occurring between the carbon layers of the fused carbon hexagonal structure within the substance. This transition is attributed to the delocalization of extra electrons within the carbon ring during UV light absorption, affirming the presence of C=C bonds within the prepared material and confirming the formation of activated carbon in its pure form. Previous literature reports a similar optical band observed at 270 nm for activated carbon derived from coconut shells.

Fourier transforms infrared spectroscopy

FT-IR spectroscopy was employed to identify functional groups present in the synthesized activated carbon, with transmittance spectra recorded within the range of 4000 cm^{-1}-600 cm^{-1}, as shown in figure 2. The spectrum revealed distinct peaks at 645.07 cm^{-1}, 750.17 cm^{-1}, and 873.59 cm^{-1}, indicating the presence of CH bonds within the sample. A sharp peak observed at 1022.09 cm^{-1} corresponds to the strong stretching vibration of C-O bonds, likely attributable to the presence of acid groups originating from natural sources. Additionally, a prominent stretching band at 1582.31 cm^{-1} confirms the presence of C=C bonds within aromatic rings. Another narrow band observed at 1698.65 cm^{-1} signifies the presence of C=O stretching bands of carbonyl groups, potentially originating from organic compounds such as ketones, lactones, aldehydes, and carboxylic acids inherent in the material due to its natural source. Notably, a broad band spanning the range of 3440.79 cm^{-1}-3862.15 cm^{-1} indicates the presence of O-H bonds characteristic of hydroxyl functional groups in phenolic across

aromatic rings. Furthermore, two narrow peaks observed at 2904.27 cm⁻¹ and 2949.59 cm⁻¹ correspond to the out-of-plane bending vibration of CH bonds within aromatic rings. The FT-IR analysis concluded that no impurities were detected in the synthesized activated carbon.
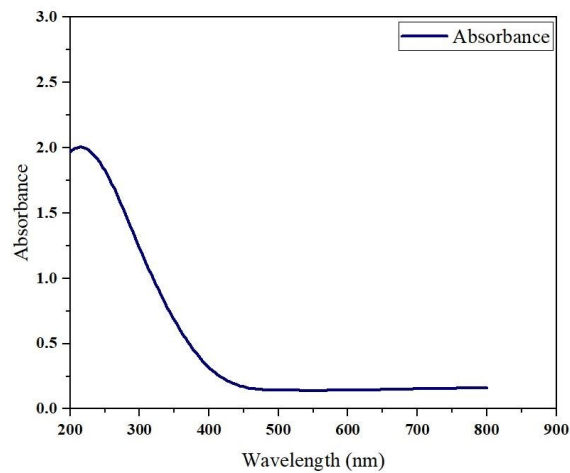

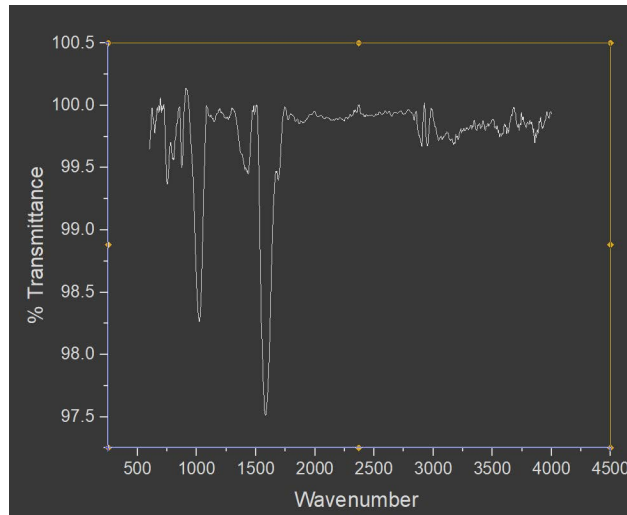**Fig. 1.** UV plot for activated carbon

Fig. 2. Fourier Transform Infrared Spectroscopy (FTIR)

Elemental analysis

Figure 3 presents the XRD pattern revealing the composition of the activated carbon electrode synthesized from coconut shells. These compounds exist in simple, double, and/or complex oxide and sulfide forms. Their presence may be attributed to residual substances remaining in the starting materials post-activation process.

These impurities could potentially induce localized action when the electrode interacts with an electrolyte, thereby contributing to internal resistance. The two-stage activation process notably reduces the proportion of non-carbon elements in the electrode, affirming the efficacy of the acid-alkali chemical activation method.
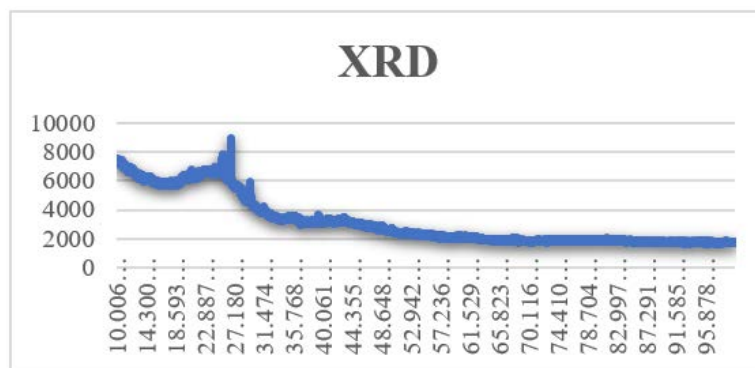

Fig. 3. XRD pattern of coconut shell derived activated carbon

Cyclic voltammetry

The Cyclic Voltammograms (CV) depicted in figure 4 showcase the performance of the developed acidic-alkali activated carbon electrode derived from coconut shells across various scan rates ranging from 20 mV/s to 100 mV/s within a potential window of 0.05 V-0.8 V (Ag/AgCl). Remarkably, the CV curves maintain a consistent shape even at higher scan rates, suggesting a uniform electrolytic reaction regardless of the scanning speed. This uniformity hints at an enhanced stability in charge transfer within the device. Notably, the CV plots predominantly exhibit quasi-rectangular/hysteretic structures, indicative of robust charge storage and capacitive prowess, a desirable trait in electrode materials [26]. The spikes observed in the curves could be attributed to electrical noise or the occurrence of multiple intermediate reactions during the charging/storage and discharge phases of the electrolytic cell, with the electrode subjected to a scan rate of 60 mV/s displaying this phenomenon most prominently. Moreover, the near-closure of the CV curves at both ends suggests the electrode's capability for complete reversibility between charging and discharge, a characteristic particularly evident with the 20 mV/s and 40 mV/s electrodes. This observation underscores the stability of the developed electrode throughout the cycling process.
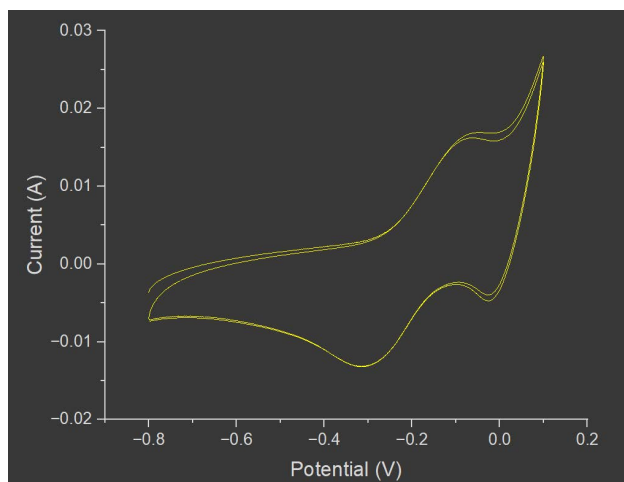

Fig. 4. CV graphs of the activated carbon obtained at different scan rates

CONCLUSION

This study effectively showcased the production of high-performance porous activated carbon material through the pyrolysis and chemical activation (using KOH and H_2SO_4 in a two-stage acid-alkali process) of coconut shells, an abundant resource in numer-ous developing nations. The resultant activated carbon electrodes demonstrated remarkable charge storage capacities, reaching up to 602.19 F/g, along with energy densities of up to 45.64 Wh/kg. These electrodes exhibited favorable stability across moderate charging and discharging cycles. Our findings suggest that carbon derived from coconut shells holds great promise for enhancing the performance of supercapacitor devices. Overall, coconut shell-derived activated carbon exhibits favorable electrical properties and high capacitance, making it a promising precursor material for supercapacitor electrode production. The acid-alkali chemical activation process proved effective in achieving optimal electrode properties.

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