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Fabrication of spherical biochar by a two-step thermal process from waste potato peel

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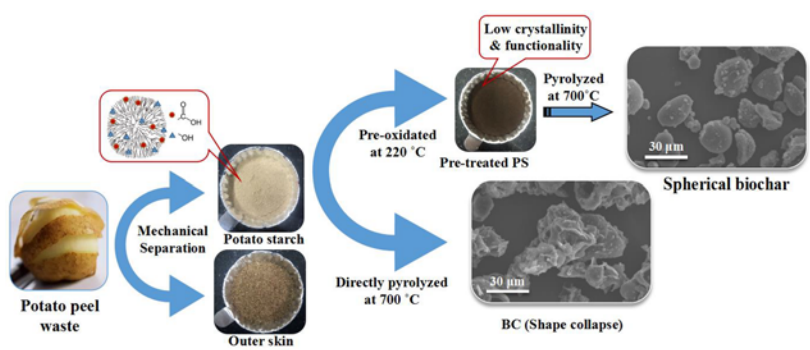
HIGHLIGHTS

- Potato starch (PS) derived from potato peel waste (PPW) has highly regular spherical shape.
- PS morphology was retained with pre-oxidation process after pyrolysis.
- PS's spherical shape affords great homogeneity to the produced biochar.
- Mechanism of shape maintenance was studied via various spectral characterizations.

GRAPHICAL ABSTRACT



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ABSTRACT

The aim of this study was to develop a new approach for the preparation of spherical biochar (SBC) by employing a two-step thermal technology to potato peel waste (PPW). Potato starch (PS), as a carbon-rich material with microscale spherical shape, was separated from PPW as a precursor to synthesizing SBC. The synthesis process comprised (1) pre-oxidization (preheating under air) of PS at 220 °C and (2) subsequent pyrolysis of the pretreated sample at 700 °C. Results showed that the produced SBC successfully retained the original PS morphology and that pre-oxidization was the key for its shape maintenance, as it reduced surface tension and enhanced structural stability. The SBC possessed excellent chemical inertness (high aromaticity) and uniform particle size (10–30 μm). Zero-cost waste material with a facile and easy-to-control process allows the method to be readily scalable for industrialization, while offering a new perspective on the full use of PPW.

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1. Introduction

Conversion of biowastes to biochar, a stable carbon-rich product from thermal decomposition of organic material in the absence of O_2, is a promising strategy for energy recovery (i.e., bio-oil and biogas production), environmental remediation, advanced material preparation, and biocomposite engineering (Chintagunta et al., 2015; Frank et al., 2014; Kim et al., 2011a). Potato, as the fourth main crop after rice, wheat, and maize, plays a crucial role in human diets worldwide. Potato production is increasing, with >380 million metric tons produced in 2014 (USDA, 2016). This has created an unavoidable need for rational utilization of the industrial by-product, potato peel waste (PPW), which accounts for approximately 6–10% of potato production as uneatable through typical peeling losses (dos Santos et al., 2016; Liang et al., 2014; Mader et al., 2009). The PPW, the major by-product of potato processing plants, has abundant carbon-rich components (i.e., starch, non-starch polysaccharides, proteins, and lipids) and nutritive fractions (e.g., K, Ca minerals), which make it a promising new precursor for manufacturing materials that possess antioxidant, antibacterial, and chemopreventive properties (Camire et al., 1997). However, PPW produced from potato processing has not been used effectively to date; it is either discarded directly in landfills or converted to low-value livestock feed or fertilizer (Camire et al., 1997). Hence, novel and value-added conversion of this carbon-rich resource will benefit the environment while helping to avoid resource wastage.

To endow biochar with specific properties, the synthesis of carbonaceous materials from wastes should be well designed in order to proceed along a proper route. In contrast to biochar that originates from conventional biomass, the physicochemical properties of shaped biochar, such as its intrinsic microstructure, chemical composition, and surface capacities, can be effectively controlled by the utilization of talented precursors and choice of carbonization conditions including heating temperature, rate, and holding time. As a subclass of spherical carbon (SC), biochar with microscale size and spherical shape, has gained increasing interest because such a material has widespread application in ionization cells, catalysis, gas storage, and functionalized composites. It shows greater performance owing to its fascinating and unique electrical, optical, and thermal properties (Choi et al., 2012; Lv et al., 2011; Wickramaratne and Jaroniec, 2012; Zhai et al., 2011). These characteristics allow for a high surface-to-volume ratio, excellent biocompatibility, a tunable porous structure, thermal insulation, and physicochemical stability (Sun et al., 2014; Wang et al., 2015; Wickramaratne and Jaroniec, 2013).

To date, a number of strategies for synthesis and use of SC have been reported. For example, N-containing hollow SC was synthesized using a template method for sodium-ion batteries, which demonstrated high reversible discharge capacity (114 mAh g^{-1}) even at high current density (10 A g^{-1}) (Qu et al., 2016). Ultrahigh-surface-area spherical hydrochar (3350 m^2/g) was derived from starch via CO_2 activation; accordingly, it exhibited high uptakes for CH_4 (10.7 mmol/g, 298 K), CO_2 (21.2 mmol/g, 298 K), and H_2 (6.4 wt%, 77 K) (Li et al., 2016). Magnetic-activated SC was developed as a high-performance adsorbent to remove dye from wastewater with effective solid–liquid separation afterward (Yang et al., 2016). However, major challenges remain. The SC preparation from most of the current synthesis strategies has an ungreen and uneconomical feedstock, low yield, moderate to high manufacturing costs, and complicated control of reaction conditions and releases toxic materials. To facilitate the development of SC in the biochar arena, selecting renewable and widely available starting materials, such as biomass waste with spherical shape by nature, and employing simple, green, and facile synthesis routes have emerged as new foci in this field (Hoheisel et al., 2010; Zhao et al., 2009).

In the present work, great emphasis was placed on SC fabrication by taking advantage of the naturally spherical shape of potato starch (PS) collected from PPW. A novel two-step thermal treatment strategy was employed to synthesize SC from separated PS. This approach demonstrated to be feasible for large-scale production because of its green route and lack of chemical involvement. A pre-oxidization process (i.e., preheating the samples before thermal decomposition via pyrolysis) was conducted to ensure the samples underwent the structural transition reaction at a mild and steady rate. The SC obtained from this sustainable biomass was designated spherical biochar (SBC).

Advanced spectroscopic techniques were applied to describe the controlling mechanism of SBC and to assess the SBC's performance. To date, no complete and accurate studies exist that focus on biochar with specific shape. Thus, it is important to acquire a better knowledge of the relationship between the micromorphology and performance of biochar. The strategy developed in this study will ultimately offer better insights into the efficient conversion of agricultural wastes into value-added products.

2. Materials and methods

2.1. Sample collection

PPW was obtained from a food processing company located in Gangwon province, Korea. All the soils and impurities on the PPW were removed by rinsing with water. The PS fraction from the raw potato peels was prepared as follows: raw PPW was dried in an oven at 105 °C for 24 h, ground using an electrical grinder, and then filtered through a 250 μm sieve. The filtered starch-rich sample (<250 μm) was designated PS.

2.2. Synthesis of SBC from PS

The PS fraction was subjected to thermal pretreatment at 220 °C for 12 h in ambient atmosphere using an air-blowing thermostatic oven (OF-22GW, JEIO TECH, Korea). The pretreated PS was placed into a muffle furnace (N11/H, Nabertherm GmbH, Germany), pyrolyzed from ambient temperature to 700 °C at a ramping rate of 2 °C/min, and then held at 700 °C for 1 h. The samples were cooled down to ambient temperature naturally, marked as SBC. The PS directly pyrolyzed at 700 °C was also produced, marked as BC. Three replicates were conducted in each step to ensure the reliability and reproducibility.

2.3. Characterization of materials

Thermogravimetry (TG, SDT Q600, TA instruments, USA) was used to investigate the thermal behavior of the raw PS. Biomass and pyrolyzed products were characterized via scanning electron microscopy (SEM, S4300, Hitachi, Japan) equipped with energy dispersive X-ray spectrometry (EDX), Fourier-transform infrared spectroscopy (FTIR, Frontier, PerkinElmer, United Kingdom), X-ray diffraction (XRD, X'Pert PRO MPD, PANalytical, Netherland), Raman spectroscopy (ARAMIS, Horiba Jobin, Japan), and X-ray photoelectron spectroscopy (XPS, K-Alpha, ThermoFisher, USA). The N_2 adsorption method was adopted to understand the porous structure of the pyrolyzed samples by a surface area analyzer (Gemini VII, Micromeritics, USA). The sample was degassed at 300 °C for 6 h before analysis. The detailed procedures were provided in SI. Properties including contents of moisture, volatile matter, fixed carbon, and ash residual were investigated, following the methodology reported by Ahmad et al. (2013). The total carbon, hydrogen, oxygen, nitrogen, and sulfur contents of samples were measured using an elemental analyzer (EuroEA 3000, Eurovector, Italy). Sample pH and electrical conductivity (EC) were analyzed using a 1:20 (w/v) solid/deionized water suspension through a benchtop multiparameter meter (Orion VSTAR93, ThermoFisher, USA).