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Characterization of activated carbon prepared from chlorella-based algal residue

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HIGHLIGHTS

- The activated carbons derived from microalgal residue have significant nitrogen contents, which make them lower carbon contents.
- Activation temperature is a determining process factor that has the significant effect on the textural development of the resulting activated carbons.
- The pore properties of the resulting activated carbons were characterized by their microporous features based on the type I isotherm.

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ABSTRACT

The chlorella-based microalgal residue (AR) was tested as a novel precursor for preparing activated carbons. A combined carbonization-activation process with flowing N_2 and CO_2 gases was used to prepare the carbon materials at the activation temperatures of 800–1000 °C and the residence times of 0–30 min in this work. The elemental contents, pore properties and scanning electron microscopy (SEM) observations of the resulting activated carbons have been performed. The results showed that activation temperature may be the most important parameter for determining their pore properties. The maximal Brunauer–Emmett–Teller (BET) surface area and total pore volume of the resulting activated carbon, which was produced at the activation temperature of 950 °C with the residence time of 30 min, were 840 m^2/g and 0.46 cm^3/g, respectively. More interestingly, the resulting activated carbons have significant nitrogen contents of 3.6–9.6 wt%, which make them lower carbon contents (i.e., 54.6–68.4 wt%) than those of commercial activated carbons.

1. Introduction

Renewable biomass, especially in lignocellulosic materials, has been considered to be an important feedstock in the predominant carbon-neutral sources of biofuels and organic chemicals. This transition for returning to biorenewable resource utilization is mainly due to the factors, including environmental quality, national security, agricultural production, and rural development (Brown and Brown, 2014). In this respect, microalgae have received much attention recently because these microscopic photosynthetic organisms are promising biomass sources, which have several advantages over land-based plants, including higher yields in both lipid production and carbon dioxide (CO_2) sequestration, use of marginal crop land without requiring arable land, and utilization of nutrients from waste/wastewater with avoiding direct competition for fertilizers with food crops (Brune et al., 2009; Lane et al., 2014). On the other hand, microalgae are economically important to provide feedstocks for health-care foods, biofuels, animal/aquacultural feeds, soil additives, nutraceuticals, pigments, and cosmetics (Spolaore et al., 2006; Williams and Laurens, 2010; Fenton and O'hUallachain, 2012; Vanthoor-Koopmans et al., 2013; Yen et al., 2013), because they are rich in nutritional contents like protein, lipid, carbohydrate and minerals.

After the extraction of lipid and/protein from the microalgal biomass for the production of biodiesel and/or essential amino acids, a considerable amount of the so-called post-extracted algae residue (PEAR) will be produced as a co-product biomass. To lower the downstream production cost, the effective use of the microalgal residue would be critical to the economically feasible production of algal biofuels (e.g., biodiesel) (Gao et al., 2012). Currently, the utilization of PEAR as a livestock feed likely represents the most important long-run component of co-product revenue (Bryant et al., 2012). On the other hand, recent studies also focused on the utilization of the microalgal biomass for the production of

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biohydrogen, biogas (methane), bio-crude and biochar by fermentation, anaerobic digestion, liquefaction and pyrolysis, respectively (Yang et al., 2011; Zhu et al., 2013; Wang et al., 2013; Alzate et al., 2014; Cheng et al., 2014; Ramos-Suarez and Carreras, 2014). Due to its chemical constituents with polysaccharides, the dried PEAR was directly reused as a low-cost biosorbent for removal of cationic adsorbates (e.g., malachite green and methylene blue) from the aqueous solution in the previous studies (Tsai and Chen, 2010; Tsai et al., 2011).

As described above, the chemical components, including polysaccharides, proteins and lipids, will be also remained in the algal biomass residue after the cell wall disruption and lipid extraction applied. It could be thus pyrolyzed for bio-oil and biochar production. Compared to the pyrolysis of macroalgal biomass, few studies focused on the pyrolysis of microalgal biomass or its lipid-extracted residue (Wang et al., 2013). In spite of some reports on the use of the marine macroalgae biomass as a precursor for preparing activated carbon by chemical activation method (El-Sikaily et al., 2007, 2011; Aravindhan et al., 2009; Zhang et al., 2010; Rathinam et al., 2011), the studies on the physical activation of this microalgal residue for preparing porous carbon material have been scarcely found in the literature. Thus, the main objective of the present work was to use the dried chlorella-based residue, a post-extracted residue from a chlorella production enterprise, as a novel precursor of producing microporous carbon material via a combined carbonization-activation process in a thermogravimetric heating system. Variables such as the temperature of activation with CO_2 gas and holding time were studied to be in connection with their variations on the elemental compositions and pore properties of the resulting products by means of elemental analysis, nitrogen adsorption–desorption isotherms, and scanning electron microscopy (SEM).

2. Methods

2.1. Material

The exhausted algal residue studied in this work was obtained from the chlorella-based biotechnology workshop, Taiwan. This microalgal biomass was a co-product generated from the patented processes of combining the cell expansion-disruption with spray-drying. This microalgal residue was first closely stored in glass bottles. Prior to the carbonization-activation experiments, the as-received sample was dried at about 100 °C for at least 24 h. Its characterization has been described in detail in the previous work (Tsai and Chen, 2010; Tsai et al., 2011), showing that this dried biomass comprises a large percentage of organic matter with low surface area (<0.5 m^2/g), and high contents of carbon (~51%), hydrogen (~8%) and nitrogen (~11%).

2.2. Carbonization-activation experiment

Two carbonization-activation experiments (first, different activation temperatures of 800–1000 °C at a residence time of 0 min; second, different activation temperatures of 800–950 °C at a residence time of 30 min) were conducted and each was replicated twice. Herein, the residence time was defined as the additional time for passing an oxidizing gas (i.e., carbon dioxide) at a specific activation temperature. The experiments for preparing activated carbon products from the microalgal residue were carried out using a thermogravimetric analyzer (Model No.: TGA-51; Shimadzu Co., Japan) under dynamic atmosphere of flowing nitrogen (N_2) and carbon dioxide (CO_2) with 20 cm^3/min as inert/purge gas and physically activating gas, respectively. These gases from a cylinder regulated (using a mass flow controller) were precisely metered into the TGA system. For each experiment, about 0.2 g of the dried microalgal residue in a quartz holder was paced into the reaction chamber. According to the preliminary analysis using the TAG results, the carbonization condition was performed at a fixed heating rate of about 10 °C/min from ambient temperature to 500 °C. In order to switch the gas flow from N_2 to CO_2, an additional residence time of 3 min was applied when the carbonization temperature reached to 500 °C. The resulting char was subsequently followed by the gasification treatment using CO_2 gas and further activated from 500 °C to prescribed activation temperatures with two different residence times (i.e., 0 and 30 min). The resulting activated carbon products (after cooling for about 30 min) was taken out of the TGA system to weigh its mass and finally stored in an oven for subsequent pore property characterization. The yields were calculated by difference in mass before and after carbonization-activation. The resulting activated carbons produced at 800, 850, 900, 950, and 1000 °C for a residence time of 0 min were labeled as AR-800-0, AR-850-0, AR-900-0, AR-950-0, and AR-1000-0, respectively. Those carbon products produced at 800, 850, 900, and 950 for a residence time of 30 min were labeled AR-800-30, AR-850-30, AR-900-30, and AR-950-30, respectively.

2.3. Elemental analysis of microalgae-derived carbon product

Due to the chemical compositions of microalgal residue rich in organic components such as cellulose and protein, the elemental analyses of AR and its resulting activated carbons (about 3 mg for each analysis) were conducted using an elemental analyzer (Model: vario EL III; Elementar Co., Germany) in terms of its basic elements of carbon (C), hydrogen (H) and nitrogen (N). In order to evaluate the precision of measurement, each sample was repeatedly carried out in duplicate. The standard compound (i.e., sulfanilic acid) was also analyzed for checking the experimental error within ±1% for C/H/N elements (i.e., 41.60/4.07/8.09 wt%).

2.4. Pore property analysis of microalgae-derived carbon product

The pore characterization of the AR-derived CO_2-activated carbons relating to surface area, pore volume and pore size distribution was carried out by measuring nitrogen (N_2) adsorption–desorption isotherms at −196 °C on an automatic apparatus (Model No.: ASAP 2020; Micromeritics Co., USA). The data on N_2 isotherms were employed to calculate the specific surface area (S_{BET}) based on the BET theory in the region of relative pressures (0.05–0.35) near completed monolayers (Lowell and Shields, 1991). Also, total pore volume (V_t) was obtained at a relative pressure of *ca.* 0.95 where the pores are filled with liquid adsorbate (i.e., nitrogen) at saturated vapor pressures. The micropore surface area (S_{mp}) and micropore volume (V_{mp}) were estimated on the basis of *t*-plot method (Lowell and Shields, 1991), a plot of the statistical thickness (*t*) versus the relative pressure. The pore size distribution was measured using the differential pore volumes of Barrett–Joyner–Halenda (BJH) desorption branch based on the Kelvin equation. Before the N_2 adsorption–desorption measurements, the samples were first outgassed under vacuum (0.03 mmHg) at 60–90 °C for 1–2 h to remove any adsorbed moisture and/or gases.

2.5. Scanning electron microscopy (SEM) observation of microalgae-derived carbon product

In order to observe the variations on the surface morphologies of AR-derived CO_2-activated carbons with different activation conditions, these samples were examined using a high-resolution scanning electron microscopy (Model No.: S-3000N; Hitachi Co., Japan), which was operated at a 15 kV accelerating potential. Prior