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Preparation and characterization of porous carbon material from post-extracted algal residue by a thermogravimetric system

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ABSTRACT

Post-extracted algal residue (AR), a processing by-product from a *Chlorella* production enterprise, was evaluated as a novel feedstock for preparing porous carbon material. Using a thermogravimetric system at the heating rate of 10 °C/min in this work, a combined carbonization–activation process using nitrogen-carbon dioxide (N_2-CO_2) gases was used to prepare the carbon products at the activation temperature of 900 °C and different holding times from 0 to 60 min. The pore properties of the resulting activated products were investigated by means of nitrogen adsorption–desorption isotherms and scanning electron microscopy (SEM). Based on the pore properties, activation temperature at around 900 °C with longer holding time seemed to be preferred for the production of highly microporous carbon material, where its optimal BET surface area and *t*-plot micropore area were around 800 and 640 m^2/g, respectively. This micropore characterization was also shown in the analyses of nitrogen isotherms and pore size distribution. More consistently, the pore volume of the resulting activated products increased with holding time ranging from 0 to 60 min. On the other hand, we clearly observed the porous structures of the resulting carbon products by SEM as compared to its precursor (i.e., AR).

1. Introduction

Lignocellulosic biomass has been considered to be a carbon-neutral and renewable resource mainly due to the environmental benefits associated with the mitigation of greenhouse gas emissions. It can be transformed into a variety of biomass energy products such as electricity, heat and fuels (i.e., syngas, bio-oil and charcoal), and even into chemical feedstocks [1]. In this respect, both micro- and macro-algae have received much attention recently because these waterborne plants are promising biomass sources with several advantages over terrestrial plants. Some of these advantages include higher productivity and energy yields in carbon fixation, use of nonproductive land without requiring arable land, and reuse of waste/wastewater nutrients while avoiding direct competition with food crops for fertilizers [2,3]. On the other hand, because of its high nutritional contents like protein and lipid, algae, especially the microalgae are economically important biomass feedstocks for food, biodiesel production, livestock/aquaculture feeds, soil additives, neutraceuticals, pigments, cosmetics, and so on [4–8].

In order to extract the valuable components of microalgae, many cell disruption methods have been exploited to break the rigid cell wall. Some of these methods include bead milling, ultrasonication, freeze fracturing, microwave radiation, enzymatic treatment, cell homogenizer and high-pressure cell disruption [9,10]. Inevitably, the so-called post-extracted algae residue (PEAR) is produced after the extraction process. To lower the total production cost, the effective use of algal biomass residue would also be a valuable long-run component of co-product revenue [7,11]. This situation is important, especially in biodiesel production because microalgae are among the biomass feedstocks being explored as the new or third generation energy sources [8,12]. However, very few studies have focused on the utilization of algal biomass residue after extraction, or investigated an approach for raising its value [10].

It is well known that the chemical composition of microalgal biomass with regard to lipids, proteins and carbohydrates (polysaccharides) will greatly determine its nutritional value. Like other green plants, most microalgae possess robust cell walls with the main structural contents of cellulose [5], one of the polysaccharides. To open the rigid structure, cell disruption is often necessary for recovering intracellular components from microalgae, such as lipids for biodiesel production and proteins for manufacturing value-added products. As a result, most of these polysaccharides are expected to be present in the algal residue after extraction. In addition, small amounts of valuable components, such as proteins and lipids will also remain in the algal residue due to the limited efficiency of cell wall disruption. Because of its high organic contents such as carbohydrate, protein, and fiber, microalgae or its leftover biomass was traditionally suitable for human nutrition,

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animal (livestock) feed, soil conditioner, or organic fertilizer [4,7]. In addition, by using various biochemical and thermochemical approaches, it can be further reused as a potential feedstock to produce useful energy forms, such as syngas [13], biomethane [14], bioethanol [15], bio-oil and/or biochar [16–18]. In previous studies [19,20], dried algal biomass was directly used as a low-cost biosorbent for removal of cationic adsorbates (e.g., malachite green and methylene blue) mainly due to the nature of the cell wall constituents and functional groups [21].

Many studies have reported the utilization of algal biomass as a precursor of porous carbon material like activated carbon [22–29]. However, all of these researches focused on the use of marine macroalgae as a precursor for preparing porous carbon adsorbent. Thus, the main objective of this work was to use the dried *Chlorella*-based residue, a post-extracted residue from a *Chlorella* production enterprise, as a novel precursor of microporous carbon material via a combined carbonization–activation process in a thermogravimetric heating system. Therefore, a series of activated carbon products derived from algal residue were prepared at 900 °C (activation temperature) with a holding time ranging from 0 to 60 min under CO_2 atmosphere. Furthermore, the resulting products were analyzed to observe their variations on pore properties by means of nitrogen adsorption–desorption isotherms and scanning electron microscopy (SEM).

2. Materials and methods

2.1. Materials

The exhausted algal residue (AR) studied in this work was obtained from a local *Chlorella*-based biotechnology workshop in the Pingtung County (Taiwan). The spray-dried biomass material was a by-product generated from a patented cell expansion–disruption processing of fresh microalgae of the genera *Chlorella*. A Taiwan patented method of bursting cell wall (Patent No. 542699 issued on Jul. 21, 2003; title: Method for bursting cell wall), a special solvent-free process for bursting *Chlorella* cell wall by the instantaneous cycle operation units (pressurization, heating, depressurization, and drying), was used to vaporize the moisture inside the cell without damaging the cell wall, while maintaining its functional ingredients. The microalgal residue was first stored carefully in glass bottles. Prior to thermochemical characterization and carbonization–activation experiments, the as-received sample was dried at about 100 °C for at least 24 h.

2.2. Thermochemical characteristic analyses of exhausted microalgal residue

2.2.1. Thermogravimetric analysis

Thermogravimetric analysis (TGA) is often used to observe the thermal stability of biomass by measuring weight loss as a function of temperature or time under a controlled atmosphere. In this work, the dried microalgal residue was examined by the thermogravimetric analysis (TGA) in this work to observe its thermal decomposition behavior prior to the carbonization–activation experiments. TGA was carried out in a thermal analyzer (Model: TGA-51; Shimadzu Co., Japan) under dynamic nitrogen (N_2) atmosphere as purge gas, with a flow rate of 20 cm^3/min. The sample (about 30 mg) was placed into a cylindrical crucible made of quartz and then heated with a constant heating rate of 10 °C/min from ambient temperature to 1000 °C. The information on dynamic residual weight and derivative thermogravimetry (DTG) with temperature was recorded and analyzed to determine the decomposition reaction mechanism and thermal stability.

2.2.2. Proximate analysis

The method used for the proximate analysis was based on the American Society for Testing and Materials (ASTM) Standard Test Methods for determining the contents of moisture, volatile matter, ash, and fixed carbon in the as-received biomass sample. The percent moisture of the sample was determined by weighing about 1 g of the sample on a pre-weighed dish and then drying the sample in an oven at 105 °C for 24 h. The volatile matter content was determined by placing the pre-weighed sample (about 1 g) into a covered crucible in a muffle furnace at 105 °C, which was then heated to 950 °C for 7 min. Finally, the ash content was obtained by using the uncovered crucible where the pre-weighed sample (about 1 g) was heated to 670 °C for holding 1 h. The fixed carbon content was determined by the difference of subtracting the percent contents of moisture, volatile matter and ash from 100%. In order to evaluate the precision of measurement, each sample was repeatedly analyzed twice.

2.2.3. Ultimate (elemental) analysis

The ultimate analysis gives the organic elements of the biomass in wt.% of carbon (C), hydrogen (H) and oxygen (O) as well as sulfur (S) and nitrogen (N). The analyses of the dried microalgal sample (about 3 mg) were conducted by using an elemental analyzer (Model: vario EL III; Elementar Co., Germany). For each analysis, the standard samples (i.e., sulfanilic acid and benzoic acid) were first analyzed for checking the experimental error within ±1% for C/H/N/S elements (i.e., 41.60/4.07/8.09/18.50%) and O element (26.20%), respectively.

2.2.4. Calorific value analysis

The calorific value of the dried algal biomass was determined by burning a pre-weighed sample in an oxygen bomb calorimeter (Model: CALORIMETER ASSY 6200; Parr Instrument Co., USA) under controlled conditions. In the experiments, about 0.5 g of the dried sample was analyzed in the calorimeter to measure the constant volume of heat released by the complete combustion of the biomass with pure oxygen.

2.3. Carbonization–activation experiment

Basically, there are two different processes for the preparation of activated carbon or porous carbon material. These include physical activation and chemical activation. Due to the environmental considerations of the chemical agent added (e.g., zinc chloride or phosphoric acid) and its derived wastewater treatment in the chemical activation process, physical activation process has been widely used in commercial production [30]. This process involves the carbonization of a carbonaceous precursor followed by activation (or gasification) of the resulting char in the presence of activating gases (e.g., carbon dioxide or water vapor steam) at 850–950 °C to further develop micropores and/or porosity by selective gasification, thus obtaining a well-developed carbon structure.

A series of carbonization–activation experiments with different holding times ranging from 0 to 60 min at an activation temperature of 900 °C was conducted and each was replicated twice. The experiments for preparing porous char products were carried out in a thermal analyzer (Model: TGA-51; Shimadzu Co., Japan) under a dynamic atmosphere of nitrogen (N_2) and carbon dioxide (CO_2) at a flow rate of 50 cm^3/min as purge gas and activating gas, respectively. About 0.2 g of the dried microalgal residue was put in a quartz holder and housed at the center of the reaction system. A sweep gas (N_2) from a cylinder regulated (using a mass flow controller) was precisely metered into the system. Based on the thermal decomposition behavior shown by the TAG results, the experimental condition in the carbonization stage was performed at a fixed heating rate of 10 °C/min from ambient temperature to 500 °C. An additional residence time of 3 min was applied when the carbonization temperature reached 500 °C. The resulting char was then followed by an activation treatment using CO_2 gas and further heated from 500 to 900 °C. Several activated chars were thus produced under different holding times (0 to 60 min). The resulting carbon product (after cooling for about 30 min) was taken out of the reaction system to weigh its mass and finally store in an oven for subsequent pore property characterization. The resulting activated carbon products