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Microalgae: Potential precursors of CO_2 adsorbents

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ABSTRACT

With faster growth rates and higher photosynthetic efficiencies than other terrestrial plants, microalgae biomass could be considered as a green, low-cost, alternative carbon source. This paper explores the potential use of various species of microalgae as activated carbon precursors. *Chlorella* and *Spirulina* were evaluated both as freeze-dried microalgae and in fresh paste form, while *Acutodesmus Obliquus* and *Coelastrella sp.* were studied only as paste.

Activated carbons were produced using the selected species of microalgae as well as mixtures of pine sawdust and microalgae. Two different preparation routes were compared: with and without hydrothermal carbonization pretreatment before physical activation with CO_2 in a single step. All samples were conformed into pellets prior to CO_2 activation.

The CO_2 adsorption capacity of the microalgae derived carbons was assessed in conditions representative of a flue gas (10.5 vol.% CO_2 at atmospheric pressure and 50 °C). Significant differences in terms of CO_2 adsorption capacity, carbon yield and pellet density were obtained among the species studied. These preliminary results showed that activated carbons produced from microalgae mixed with pine sawdust and directly activated with CO_2 are among the most promising adsorbents to capture CO_2 from flue gas.

1. Introduction

Microalgae have attracted a lot of interest in the last few years due to their potential use in a wide range of fields [1]. Research has mainly focused on the production of biodiesel and other biofuels (bioethanol, biomethane and biohydrogen) and obtaining heat and electricity [2]. Other applications study the development of high added value products from microalgae in fields like nutrition and human health, aquaculture, cosmetics and biofertilizers [3]. In addition, biological capture of carbon dioxide by using microalgae has shown promising, as microalgae fix CO_2 during their growth [4,5].

However, scientific literature related to the use of microalgae as a sorbent is relatively scarce. In this area of application, microalgae have been foremost used as biosorbents for metal decontamination of liquid streams and, particularly, for removal of heavy metals from wastewater [6].

Adsorptive capture of CO_2 from flue gas streams is a promising technology for greenhouse gas mitigation. The success of CO_2 capture using solid sorbents is greatly dependent on the development of a low cost, regenerable sorbent with high CO_2 adsorption capacity [7]. Many commercial activated carbons are produced from agriculture and forestry biomass resources [8]. Microalgae could be a potential low-cost precursor due to their high carbon content and fast growth rate that guarantees availability. Furthermore, their cultivation requires CO_2 thus leading to a negative carbon dioxide emission process. In fact, biofixation of CO_2 by microalgae is being extensively investigated as part of the greenhouse gas reduction strategy [9–11]. Carbon dioxide from the atmosphere or from flue gases can be used to boost microalgae growth. Several studies have shown that microalgae have better CO_2 fixation ability (10–50 times more) than terrestrial plants [12,13].

Microalgae are an extremely diverse collection of organisms including prokaryotic cyanobacteria and eukaryotic microalgae. They can occur in highly diverse habitats and grow under strongly varying environmental conditions. The chemical composition of algal cells can vary over a wide range; nevertheless, the main components are carbohydrates, lipids and proteins. Compared to lignocellulosic biomass, microalgae are too small, cultures are much diluted and it is necessary to spend a lot of energy to recover the biomass. Alternative routes for microalgae biomass exploitation are then sought to lessen the production costs.

Hydrothermal carbonization (HTC) is a process in which biomass is heated in water under pressure to create a product called hydrochar. HTC, also referred to as wet torrefaction, is a thermochemical process that converts organic feedstocks into a high carbon rich solid product. HTC is performed in a low temperature range of 180–280 °C during which wet biomass is heated in a confined vessel under pressure (26

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MPa) for 5–240 min. Usually the reaction pressure is not controlled in the process, it is autogenic with the saturation vapor pressure of water (subcritical-water) corresponding to the reaction temperature. The HTC process results in the formation of three main products: solid (hydrochar), liquid (bio-oil mixed with water) and small fractions of gases (mainly CO_2) [14,15].

Hydrochar represents the main product of the process and it has attracted much attention due to its potential application in environmental and energy related fields. A broad range of lignocellulosic materials such as agricultural residues (corn cobs, olive husks, rice husks), herbaceous crops (switchgrass), forestry residues and waste paper have been subjected to HTC [16–18]. Most of the studies have focused on producing hydrochar pellets for fuelstock [19–22]. The resulting solid presents considerably higher energy density compared to the raw feedstock. Besides the utilization for heat and power production, hydrothermal carbonization has also been studied as a way to prepare porous carbons for contaminants removal in aqueous solution [23,24] or for CO_2 adsorption [25,26]. The procedure consists of two-steps: firstly, the feedstock is hydrothermally carbonized and then the char is further activated physically or chemically.

Green and blue-green microalgae are not lignocellulosic in composition, the chemistry is entirely different and involves proteins, lipids and carbohydrates. Thus, algal materials require much milder conditions in HTC compared to lignocellulosic feedstocks: treatment temperatures between 180–220 °C, time < 1 h and pressure < 2 MPa [27]; microalgae can then be converted in an energy efficient manner into an algal char product [28].

The potential of microalgae as CO_2 adsorbents is to be explored. In this study, activated carbons intended for CO_2 capture were prepared using selected species of microalgae as precursors as well as mixtures of pine sawdust (PS) and microalgae. Two synthesis methodologies were evaluated: with and without hydrothermal carbonization pretreatment prior to physical activation with CO_2 in a single step.

2. Materials and methods

2.1. Materials

Different species of microalgae, supplied by Neoalgae Microseaweeds® in the framework of the ReCO_2very project [29], were studied. First, two species widely used in other applications, *Chlorella* and *Spirulina*, were evaluated, both freeze-dried microalgae and microalgae paste. Later, two other species were studied, all in paste form, such as *Acutodesmus Obliquus* and *Coelastrella* sp.

Ultimate analysis was carried out in order to determine the chemical composition of the carbons (see Table 1). The carbon, hydrogen and nitrogen contents were determined in a LECO CHNS-932 analyzer and the oxygen content in a LECO VTF-900 analyzer. In addition, the moisture and ash content of the samples were determined by means of a thermogravimetric analyzer. Microalgae pastes needed to be dried and ground before analysis.

Table 1
Analysis results for the microalgae studied.

Microalgae	Humidity (wt.%)	Ash (wt.%, db)	Ultimate analysis (wt.%, db)				
			C	H	N	S	O
Freeze-dried *Chlorella* sp.	4.97	8.01	47.55	6.52	7.97	0.29	30.52
Freeze-dried *Spirulina*	6.66	7.45	49.57	6.70	11.71	0.47	24.66
Chlorella paste	8.61	13.89	46.62	6.56	7.52	0.98	28.98
Spirulina paste	5.82	10.00	46.15	6.51	9.87	0.00	28.32
Acutodesmus obliquus	3.58	10.94	46.16	6.41	7.23	0.00	29.15
Coelastrella sp.	3.18	16.85	43.34	5.84	6.63	0.00	29.19

db: dry basis.

As it can be seen in Table 1, the studied species present different humidity and ash contents. Water content values are lower than 9 wt.% in all microalgae while ash content reaches up to 17 wt.% for *Coelastrella*. Low ash content is highly desirable for the development of carbon materials since ash is inactive during the porosity formation in the carbonaceous matter.

All varieties analyzed show similar carbon (around 50 wt.%) and hydrogen contents. Sulfur content in all of them is less than 1 wt.% and they all show high oxygen contents between 25 and 30 wt.%. *Spirulina* has higher nitrogen content as a consequence of the relatively high fraction of proteins [30]; however it is worth to note the differences in carbon, nitrogen and oxygen composition between the sample in paste form and that freeze-dried (≈ 2–3 wt.%). No significant deviations were observed in elemental composition between freeze-dried and paste of *Chlorella*.

2.2. Adsorbent preparation

Activated carbons were prepared using the selected species of microalgae as precursor as well as mixtures of pine sawdust (PS) and microalgae. Two synthesis methodologies were evaluated: with and without hydrothermal carbonization pretreatment before physical activation with CO_2 in a single step (see scheme in Fig. 1).

The objective of the hydrothermal carbonization (HTC) pretreatment is to increase the global carbon yield, especially when processing biomass with high water content. Biomass does not need to be dried, and the associated energy input is then eliminated. The HTC process takes place effectively in water media, is exothermic and proceeds spontaneously. The biomass in aqueous solution (i.e., paste) is heated up to 180–220 °C in an auto-pressurized vessel.

In order to increase the carbon-to-oxygen ratio (commonly referred to as “carbonization”), dehydration rather than splitting off carbon dioxide is pursued [14]. This mechanism is undesirable because, with loss of carbon dioxide, carbon and oxygen are depleted and formation of gas products causes even greater reaction pressures that in turn increase the complexity and cost of the required equipment. The non-cellulosic carbohydrate composition of microalgae may allow dehydration to occur at relatively moderate temperatures similarly to soluble biomass substrates, e.g., glucose.

During hydrothermal carbonization, feedstock decomposition is dominated by reaction mechanisms similar to those in dry pyrolysis, which include hydrolysis, dehydration, decarboxylation, aromatization and recondensation. Decomposition of biomass into CO_2 or methane plays only a minor role as it is shifted to dehydration reactions and coalification instead of hydrid transfer and decarboxylation [31,32].

2.2.1. Physical mixture and conformation of samples

All samples were conformed into pellets prior to CO_2 activation. Freeze-dried microalgae powder was directly conformed into cylindrical pellets of 4.1 mm in diameter by uniaxial compression in a single punch table press machine. Microalgae paste required to be dried and ground before conformation into pellets. Pine sawdust and microalgae blends were prepared in a 1:1 mass ratio and pelletized similarly to the individual cases.

2.2.2. Single-step CO_2 activation

All samples were activated with CO_2 following a single step procedure by means of a thermogravimetric analyzer (Setaram TGA 92). Program settings were as follows: feed flow rate of 50 cm^3/min of CO_2, heating rate of 5 °C/min up to the set point activation temperature (800 °C) and soaking time of 1 h at this temperature. The samples were dried in situ at 100 °C for 1 h prior to the activation tests. The yield of the activation process was calculated as: