Microalgae: potential precursors of CO₂ 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 CO₂ in a single step. All samples were conformed into pellets prior to CO₂ activation.

The CO₂ adsorption capacity of the microalgae derived carbons was assessed in conditions representative of a flue gas (10.5 vol.% CO₂ at atmospheric pressure and 50°C). Significant differences in terms of CO₂ 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 CO₂ are among the most promising adsorbents to capture CO₂ 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 CO₂ 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 CO₂ from flue gas streams is a promising technology for greenhouse gas mitigation. The success of CO₂ capture using solid sorbents is greatly dependent on the development of a low cost, regenerable sorbent with high CO₂ 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 CO₂ thus leading to a negative carbon dioxide emission process. In fact, biofixation of CO₂ 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 CO₂ 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 (2-6 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 CO₂) [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 CO₂ 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 CO₂ adsorbents is to be explored. In this study, activated carbons intended for CO₂ 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 CO₂ in a single step.

2. Materials and methods

2.1. Materials

Different species of microalgae, supplied by Neoalgae Microseaweeds® in the framework of the ReCO₂very 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 <i>Chlorella sp</i>	4.97	8.01	47.55	6.52	7.97	0.29	30.52
Freeze-dried <i>Spirulina</i>	6.66	7.45	49.57	6.70	11.71	0.47	24.66
<i>Chlorella</i> paste	8.61	13.89	46.62	6.56	7.52	0.98	28.98
<i>Spirulina</i> paste	5.82	10.00	46.15	6.51	9.87	0.00	28.32
<i>Acutodesmus obliquus</i>	3.58	10.94	46.16	6.41	7.23	0.00	29.15
<i>Coelastrella sp.</i>	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 *Chlorella*. 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 ($\approx 2\text{-}3$ 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 Figure 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 $180\text{-}220$ °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].

Figure 1. Experimental procedure for the production of microalgae-based adsorbents.

2.2.1. Physical mixture and conformation of samples

All samples were conformed into pellets prior to CO₂ 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 CO₂ activation

All samples were activated with CO₂ following a single step procedure by means of a thermogravimetric analyzer (Setaram TGA 92). Program settings were as follows: feed flow rate of 50 cm³/min of CO₂, heating rate of 5 °C/min up to the set point activation temperature (800 °C) and soaking time of 1 hour 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:

$$CY_{\text{Activation}} (\%) = \frac{m_{fA}}{m_0} \times 100 \quad (1)$$

where m_{fA} represents the final mass of the sample at the end of the activation procedure, and m_0 is the mass of the sample at the end of the drying step.

2.2.3. Hydrothermal pretreatment

One of the main advantages of hydrothermal carbonization is that it allows direct use of microalgae paste, skipping the need of a previous drying step.

Hydrothermal carbonization was carried out using a Parr 45 cm³ acid digestion bomb made of PTFE. 10 g of microalgae paste were introduced in each experiment. Water content of microalgae pastes was different for each species, ranging from 73 to 88%.

The reactor was then heated to the desired temperature, 180 or 200 °C, and the reaction temperature was held for one hour. Afterwards the reactor was allowed to air cooling to room temperature. Then, the gas product was released to the atmosphere and the solid and liquid products were separated by filtration under gravity using 110 mm qualitative filter paper. The hydrochar was rinsed with water and it was dried for 4h at 100 °C in an air oven. It was observed that the HTC process facilitated the mechanical dewatering [33].

The carbon yield of the HTC pretreatment was calculated as follows:

$$CY_{HTC} (\%) = \frac{m_{fHTC}}{m_i} \times 100 \quad (2)$$

where m_i represents the initial mass of the sample introduced in the PTFE bomb calculated in dry basis, and m_{fHTC} is the mass of the dried hydrochar obtained.

Then, the produced hydrochar was conformed into cylindrical pellets and an activation step was carried out as explained in Section 2.2.2.

The overall yield was calculated from the yields of the HTC and activation steps to compare the results:

$$\text{Overall yield (\%)} = \frac{CY_{\text{Activation}}}{100} \times \frac{CY_{HTC}}{100} \times 100 = \frac{m_{fA}}{m_0} \times \frac{m_{fHTC}}{m_i} \times 100 \quad (3)$$

As for the microalgae paste-pine sawdust blends, a similar procedure was followed. However, in this case, the pine sawdust was directly mixed with the microalgae paste keeping a mass ratio of 1:1 (in dry basis). After one hour under agitation, the mixture was submitted to HTC followed by conformation and activation in CO₂.

2.3. Evaluation of CO₂ adsorption capacity: gravimetric adsorption tests

Gravimetric tests were conducted in a thermogravimetric analyzer (TGA/DSC1 STARe System from Mettler Toledo) to evaluate adsorption capacity on the basis of the increase in sample weight due to adsorption of a relevant gas, in this case a CO₂-N₂ gas mixture. Gases used were

supplied by Linde with a purity higher than 99.9% for CO₂ and higher than 99.9995% for N₂. The mixture CO₂/N₂ is prepared with a mass-flow gas controller, GC200, directly connected to the TGA. The adsorption behavior of the activated microalgae based carbon pellets, in conditions representative of a flue gas, was evaluated at 50 °C and atmospheric pressure using a total flow rate of 100 cm³/min of a mixture of 10.5 vol.% CO₂ and 89.5 vol.% N₂. The different steps of the experiment together with the expected mass uptake evolution are schematized in Figure 2. Further details on the experimental protocol can be found elsewhere [8].

Figure 2. Mass uptake profiles during the experiments in the thermogravimetric analyzer.

To gather information on the actual rate-controlling step the experimental CO₂ uptake data were further processed using the intra-particle diffusion model [34] in order to explain the diffusion mechanism during the CO₂ adsorption process [35,36]. The intra-particle diffusion model gives information about the steps involved in the adsorption process and is described by the following equation:

$$q_t = k_{id}t^{1/2} + C \quad (4)$$

where q_t is the amount adsorbed at any particular time (mol kg⁻¹), k_{id} is the intra-particle diffusion rate constant (mol kg⁻¹ min^{-1/2}) and C (mol kg⁻¹) gives an idea about the thickness of the boundary layer.

It is common to see multi-linearity on the q_t vs $t^{1/2}$ plot, which indicates that the adsorption mechanism consists of different stages. Most frequently, three steps in the intra-particle diffusion model can be identified, the first one corresponds to external diffusion adsorption or boundary layer diffusion, the second one to the gradual stage of adsorption (i.e., intra-particle diffusion, strictly speaking) and the third one to the final equilibrium stage. However, it is generally accepted that the third step is very rapid and does not represent the rate-limiting step. Generally, the slope of each linear stage is called the rate parameter $k_{id,i}$ (where i stands for the stage number) and the lowest slope identifies the rate-controlling step.

3. Results and discussion

Carbon yields and adsorption capacities at 50 °C, feeding a gas with 10.5 vol.% CO₂ (balance N₂), for all the microalgae samples are presented hereunder.

3.1. *Chlorella*

This species was evaluated as a freeze-dried powder and a paste. In both cases adsorbents prepared without and with a previous hydrothermal carbonization (at 220 °C for 1 hour) were compared. The results for a pine sawdust sample prepared under similar conditions are included as a reference. In addition, blends from *Chlorella* and pine sawdust were also studied.

Gravimetric tests conducted in the TGA/DSC1 STARE System from Mettler Toledo were repeated thrice. Standard deviations for the CO₂ adsorption capacities (CAC) are reported between brackets in Table 2. The uncertainty of the carbon yield (CY) during activation is mainly linked to the error in the TGA measurement; maximum error was estimated to be 0.001 mg.

Table 2. CO₂ adsorption capacities evaluated at 50 °C (CAC) and carbon yields (CY) for the adsorbents produced from *Chlorella* (HTC conditions: 220 °C, 1 h).

Samples	Microalgae content (wt.%)	without HTC		with HTC	
		CY (%)	CAC (wt.%)	CY (%)	CAC (wt.%)
Pine sawdust	—	14.6	2.29 (±0.02)	24.6	1.78 (±0.01)
<u>Freeze-dried <i>Chlorella</i></u>					
Freeze-dried <i>Chlorella</i>	100	26.8	1.55 (±0.01)	10.7	1.44 (±0.02)
Freeze-dried <i>Chlorella</i> -Pine (1:1)	50	23.2	2.43 (±0.04)	—	—
<u><i>Chlorella</i> paste</u>					
<i>Chlorella</i> paste	100	18.5	0.29 (±0.07)	15.8	0.49 (±0.03)
<i>Chlorella</i> paste-Pine (1:1)	50	—	—	21.3	1.68 (±0.03)

As it can be observed in Table 2, adsorbents prepared from *Chlorella*, both freeze-dried or as a paste, present modest adsorption capacity under flue gas conditions, lower than the pine sawdust. Nevertheless, freeze-dried *Chlorella* shows better performance than *Chlorella* paste. On the other hand, *Chlorella*-pine sawdust based samples turned out to be adsorbents with a significant capacity to adsorb CO₂, particularly the sample prepared from freeze-dried *Chlorella* without HTC pretreatment: 2.43 wt.% vs. 2.29 wt.% for the pine sawdust alone.

As carbon yield is concerned, it can be noticed that activation in a single step without hydrothermal carbonization pretreatment, results in considerable high yields, bearing in mind that in a conventional biomass based activated carbon production process, the yield usually

ranges between 12 and 15%. The HTC pretreatment causes an additional decrease in the carbon yield of the *Chlorella* based samples. However, the opposite occurs for the pine sawdust sample since a higher yield is obtained with HTC pretreatment at the expense of a reduction in adsorption capacity.

Carbon yield and adsorption capacity trends with microalgae content have been plotted in Figure 3. As it can be observed in Figures 3a) and 3c), CO₂ adsorption should decrease with microalgae content according to the additive rule; however, in the case of freeze-dried *Chlorella* mixed with pine sawdust, there is an enhancement in CO₂ adsorption capacity particularly when no HTC pretreatment is conducted. On the other hand, the addition of 50% *Chlorella* paste in conjunction with HTC pretreatment preserves the CO₂ adsorption capacity of the pine sawdust.

Figure 3. Evolution of adsorption capacity of CO₂ in flue gas conditions (50 °C, feed: 10.5 vol.% CO₂, balance N₂) and carbon yield vs. microalgae content for *Chlorella*-Pine sawdust mixtures: a) and b) samples without HTC, c) and d) samples with HTC. Dashed lines represent the expected trend according to the additive rule.

In the samples without HTC pretreatment the carbon yield increases with the *Chlorella* content and the carbon yield of the 1:1 mixture is higher than that predicted by the additive rule. The opposite trend was attained for the sample with HTC pretreatment, which showed a lowering of the carbon yield with the increase in *Chlorella* content. In this case the mixture with 50% *Chlorella*-Pine followed the theoretical estimation of the additive rule.

3.2. *Spirulina*

Spirulina was employed both freeze-dried and in paste form. Adsorbent pellets prepared from *Spirulina* paste, those as green pellets as well as those subjected to hydrothermal carbonization pretreatment, lacked of mechanical resistance and collapsed during the activation step. That behavior was only observed in this variety of microalgae, most likely related to the fact that *Spirulina* is a cyanobacteria. Therefore, it is a prokaryotic cell and does not have lignocellulosic cell wall.

Table 3 summarizes the results obtained for all the samples prepared from *Spirulina*, freeze-dried and paste, and pine sawdust. Hydrothermal carbonization pretreatment was carried out at 180 °C for 1 hour for all the samples of this series.

Table 3. CO₂ adsorption capacities evaluated at 50 °C (CAC) and carbon yields (CY) for the adsorbents produced from *Spirulina* (HTC conditions: 180 °C, 1 h).

Samples	Microalgae content (wt.%)	without HTC		with HTC	
		CY (%)	CAC (wt.%)	CY (%)	CAC (wt.%)
Pine sawdust	—	14.6	2.29 (±0.02)	13.1	2.24 (±0.01)
<u>Freeze-dried <i>Spirulina</i></u>					
Freeze-dried <i>Spirulina</i>	100	24.8	1.49 (±0.06)	—	—
Freeze-dried <i>Spirulina</i> (1:1)-Pine	50	23.7	2.73 (±0.03)	—	—
<u><i>Spirulina</i> Paste</u>					
<i>Spirulina</i> paste	100	14.8	0.00	7.4	0.23 (±0.12)
<i>Spirulina</i> paste-Pine (1:1)	50	21.1	4.02 (±0.02)	15.2	2.36 (±0.05)
<i>Spirulina</i> paste-Pine (2:1)	66.7	20.5	3.32 (±0.07)	—	—

Departing from *Spirulina* paste it was not possible to develop a CO₂ adsorbent while freeze-dried *Spirulina* without HTC delivered an adsorbent with a low CO₂ adsorption capacity, similar to that obtained from freeze-dried *Chlorella*. On the other hand, activated carbons prepared from blends of *Spirulina* and pine sawdust showed very competitive CO₂ uptakes (even greater than those produced from pine sawdust alone). In addition, carbon yields above 20% were obtained. The samples that stand out are the ones based on *Spirulina* paste mixed with pine sawdust at different mass ratios and without HTC that reached up to 4 wt.% CO₂ adsorption capacity at 50 °C and a CO₂ partial pressure of 10.5 kPa. It has to be noted that this is one of the highest values ever reported in literature at similar CO₂ adsorption conditions [37][38][39].

Figure 4 represents the carbon yield and CO₂ uptake trends with *Spirulina* microalgae content. In Figure 4a), 4c) and 4e), it is worth noting that there is an increase in adsorption capacity with addition of *Spirulina*, even greater than might be expected from the additive rule and particularly remarkable for *Spirulina* paste. Hydrothermal carbonization pretreatment reduces

the CO₂ uptake of the *Spirulina* derived samples. Nevertheless, the addition of *Spirulina* to pine sawdust has a synergetic effect on the CO₂ capture.

Figure 4. Evolution of adsorption capacity of CO₂ in flue gas conditions (50 °C, feed: 10.5 vol.% CO₂, balance N₂) and carbon yield vs. microalgae content for *Spirulina*-Pine sawdust mixtures: a), b), c) and d) samples without HTC, e) and f) samples with HTC. Dashed lines represent the expected trend according to the additive rule.

In terms of carbon yield, results showed different tendencies and the experimental values did not follow the additive rule. In the case of adsorbents from freeze-dried *Spirulina*, it can be observed a slight increase of carbon yield with microalgae content. Nevertheless, regarding the

adsorbents from *Spirulina* paste, the yields for the mixture of *Spirulina* paste-PS, with and without HTC pretreatment, significantly exceeded those of the single component samples, which is very positive for a prospective production process.

Due to the great potential of *Spirulina*-PS activated carbons, their dynamic behavior during the gravimetric adsorption tests was studied in order to evaluate mass transfer resistances controlling the CO₂ adsorption process. As it can be seen in Figure 5, CO₂ adsorption happens very fast at the beginning of the adsorption stage (1-2 min) and there is a sudden increase in mass uptake. As the adsorption continues the mass increase slows down because of mass transfer resistance.

In the case of the mixture *Spirulina* paste-PS (1:1) without HTC, a greater mass transfer resistance is noticed than for the other (1:1) blends evaluated. The second stretch of the curve shows a less steep slope that causes a slowdown when the CO₂ adsorption capacity is close to the maximum value at equilibrium. Figure 5 includes as well the mixture *Spirulina* paste-PS (2:1) and two adsorbents prepared from the mixture *Spirulina* paste-PS (1:1) subjected to a hydrothermal carbonization process at different temperatures, one at 180 °C and the other at 220 °C, for 1 hour in both cases.

Figure 5. Incremental mass uptake when the composition of the feed gas is changed from 100% N₂ to a mixture consisting of 90% N₂ and 10% CO₂ at 50 °C: a) full adsorption step and b) first 10 min of adsorption.

As it can be observed in Figure 5, samples with HTC pretreatment present a slower rate of adsorption during the first minutes than the samples without HTC. After this initial stage, a plateau is reached corresponding to the equilibrium of adsorption. On the other hand, a rise in the temperature of the hydrothermal carbonization process provokes a reduction of the CO₂ adsorption capacity.

Comparing mixtures 1:1 and 2:1 of *Spirulina* paste-PS without HTC, it can be noted that a higher content of microalgae translates into significant increase in mass transfer resistance, which hinders adsorption and also lessens the CO₂ adsorption capacity.

Assuming a diffusion based mechanism, the experimental data obtained in the thermogravimetric analyzer were fitted to the intra-particle diffusion model (eq. 4). The plots of q_t versus $t^{1/2}$ for the activated carbons from pine sawdust and *Spirulina* and pine sawdust blends are displayed in Figure 6. In the case of pine sawdust alone, only the sample without hydrothermal carbonization is displayed, since it was observed that the adsorption curves for this sample and for pine sawdust with HTC pretreatment at 180°C for 1 hour practically overlapped.

The initial points ($t^{1/2} < 0.5$) were disregarded as q_t was zero. Three sections can be identified: the first curved portion is usually attributed to boundary layer diffusion while the second linear portion responds to the effect of intra-particle diffusion. The third portion, where q_t is constant, is the final equilibrium stage. It can be noticed that after 60 minutes of CO₂ adsorption, equilibrium is not reached for all the samples represented in Figure 5a.

Figure 6. Intra-particle diffusion model plots for pine sawdust and *Spirulina*-PS mixtures.

Intra-particle diffusion model parameters were calculated to determine whether film diffusion or intra-particle diffusion is the rate limiting step. As it can be observed in Table 4, the values of $k_{id,1}$ are larger than those of $k_{id,2}$ for all the samples, indicating that film diffusion of CO₂ molecules towards the surfaces was relatively fast and therefore, intra-particle diffusion is the controlling step.

Table 4. Parameters from the linear fitting of the intra-particle diffusion model.

Samples	$k_{id,1}$ (mmol g ⁻¹ min ^{-1/2})	R_1^2	$k_{id,2}$ (mmol g ⁻¹ min ^{-1/2})	R_2^2
Pine sawdust w/o HTC	0.638	0.99	0.108	0.96
<i>Spirulina</i> paste-PS (1:1) w/o HTC	0.492	0.96	0.016	0.92
<i>Spirulina</i> paste-PS (2:1) w/o HTC	0.379	0.96	0.024	0.98
<i>Spirulina</i> paste-PS (1:1) HTC 180 °C 1h	0.243	0.96	0.035	0.90
<i>Spirulina</i> paste-PS (1:1) HTC 220 °C 1h	0.138	0.97	0.037	0.95
Freeze-dried <i>Spirulina</i> -PS (1:1) w/o HTC	0.435	0.95	0.027	0.92

Comparing mixtures 1:1 and 2:1 of *Spirulina* paste-PS without HTC, it can be observed that a higher content of microalgae implies a considerable increase in film diffusion resistance but a slight decrease in intra particle-diffusion.

Finally, the densities of the pellets of *Spirulina* samples were measured. Results corresponding to the geometric density (calculated from the dimensions and the weight of the pellet) are displayed in Figure 7.

As mentioned before, adsorbents prepared from *Spirulina* paste do not present mechanical resistance and lose their structure during the activation step. Pellets from *Spirulina*-Pine sawdust blends are significantly denser than those produced only from *Spirulina* or pine sawdust; however, it seems that an increase on the algae content does not cause a substantial change in density. On the other hand, it can be observed that the HTC treatment results in a densification of the biomass although it barely varies with the temperature of the HTC process.

Figure 7. Density of activated pellets from *Spirulina*.

3.3. *Acutodesmus obliquus* (A.o.)

This microalgae species was solely evaluated in paste form. Adsorbents were prepared with and without hydrothermal carbonization pretreatment. HTC process was carried out at 220 °C for 1 hour. Results are summarized in Table 5.

Table 5. CO₂ adsorption capacities evaluated at 50 °C (CAC) and carbon yields (CY) for the adsorbents produced from *Acutodesmus obliquus* (HTC conditions: 220 °C, 1 h).

Samples	Microalgae content (wt.%)	without HTC		with HTC	
		CY(%)	CAC (wt.%)	CY(%)	CAC (wt.%)
A.o.	100	28.9	1.28 (±0.01)	15.3	0.46 (±0.01)
A.o.-Pine (1:1)	50	25.7	1.67 (±0.02)	20.6	1.73 (±0.03)

Adsorbents obtained from *Acutodesmus obliquus*, single and mixed with pine sawdust, presented modest adsorption capacities, around 1.7 wt.%. The sample prepared from A.o. with HTC showed an adsorption capacity of less than 0.5 wt.%. However, carbon yields are as high as 29% for the sample prepared from A.o. without HTC.

Figure 8. Evolution of adsorption capacity of CO₂ in flue gas conditions (50 °C, feed: 10.5 vol.% CO₂, balance N₂) and carbon yield vs. microalgae content for *Acutodesmus obliquus*-Pine sawdust mixtures: a) and b) samples without HTC, c) and d) samples with HTC. Dashed lines represent the expected trend according to the additive rule.

Figure 8 shows the overall carbon yield and adsorption capacity trends with microalgae content. The mixture A.o.-PS with HTC pretreatment presents an adsorption capacity similar to pine sawdust, while its carbon yield follows the additive rule. The opposite effect was found for the A.o.-PS without HTC sample where the carbon yield increased and the CO₂ adsorption capacity followed linearity.

3.4. *Coelastrella* sp

Adsorption capacities and carbon yields for the adsorbents from *Coelastrella* sp. paste are presented in Table 6. Adsorbents were prepared without and with HTC pretreatment, which was carried out at 220 °C for 1 hour.

Table 6. CO₂ adsorption capacities evaluated at 50 °C (CAC) and carbon yields (CY) for the adsorbents produced from *Coelastrella* sp (HTC conditions: 220 °C, 1 h).

Samples	Microalgae content (wt.%)	without HTC		with HTC	
		CY (%)	CAC (wt.%)	CY (%)	CAC (wt.%)
<i>Coelastrella</i>	100	19.3	0.00	13.3	0.27 (±0.02)
<i>Coelastrella</i> -Pine (1:1)	50	11.0	0.00	—	—

Among all the species of microalgae evaluated, *Coelastrella* has shown the worst characteristics as adsorbent precursor for CO₂ adsorption. As it can be seen in Table 6 neither *Coelastrella* nor *Coelastrella*-Pine sawdust blends presented CO₂ adsorption. In the case of Pine-*Coelastrella* activated at 800 °C for 1 hour, the pellet broke or collapsed after activation. Another test was then conducted lowering the activation temperature to 700 °C and the pellet preserved its form. This sample had a discrete adsorption capacity of 1.85 wt.% with a carbon yield of 28.1%.

4. Comparison of results from microalgae species

Results presented in the previous section showed that, except from freeze-dried *Spirulina*, microalgae on their own are not suitable precursors of CO₂ adsorbents. However, blending microalgae with lignocellulosic biomass (e.g., pine sawdust) showed great potential and could be an interesting path to the production of activated carbons for CO₂ adsorption.

The most promising adsorbents, in terms of CO₂ adsorption capacity, obtained in this study are compared in this section. Carbon yield and pellet density are presented in Figure 9. Microalgae-pine sawdust blends present high carbon yields, generally between 21 and 28%, and noteworthy densities. In addition, comparing these values with those of the adsorbent

prepared from pine sawdust, substantial improvements are observed with the addition of microalgae.

All pellets prepared from microalgae and pine sawdust blends present high geometric density, almost twice that of pine sawdust alone. It must be borne in mind that a high density is desirable as it determines, together with the adsorption capacity which is generally expressed on a mass basis, the volume of the adsorbent required for a particular application. On the other hand, a good carbon yield means a better use of the precursor and therefore, a lower cost associated to the production of activated carbon.

Figure 9. Pellet density, carbon yield and adsorption capacity for the adsorbents prepared from microalgae and pine sawdust (1:1) without HTC pretreatment.

In scientific literature about CO₂ capture using low temperature solid sorbents, adsorption capacities are usually referred to the pure components, N₂ and CO₂, of the flue gas to treat. However, in this way the effect of co-adsorption of both gases is not taken into account. In addition, adsorption capacities are often reported at room temperature (~ 25 °C) and generally expressed on a mass basis.

CO₂ adsorption capacities at a CO₂ partial pressure of 10.5 kPa and temperatures of 30 and 50 °C, expressed on mass and volume basis, for the adsorbents prepared from microalgae and pine sawdust without HTC pretreatment are summarized in Table 7. As it could be expected, due to the exothermic nature of the adsorption process, capacities at 30 °C are higher than those at 50 °C. In order to determine the adsorption capacity on a volume basis, the geometric density of the pellets was employed; this value is comparable to the apparent density of the pellets. Commercial activated carbon Norit R2030 is included in Table 7 as reference material.

As it can be observed, adsorbents prepared from *Spirulina* or *Chlorella* mixed with pine sawdust present good CO₂ adsorption capacities, both on mass and volume basis, and even better than those of the commercial activated carbon and the adsorbent prepared from pine sawdust alone.

Table 7. Summary of CO₂ adsorption capacities at 30 and 50 °C and 10.5 kPa of CO₂.

Sample	CO ₂ adsorbed at 10.5 kPa			
	30°C		50°C	
	wt.%	mmol/cm ³	wt.%	mmol/cm ³
Norit R2030	3.09 (±0.02)	0.62	1.91 (±0.02)	0.38
Pine sawdust	3.41 (±0.10)	0.37	2.29 (±0.02)	0.24
<i>Spirulina</i> paste-Pine (1:1)	5.99 (±0.15)	1.20	4.02 (±0.02)	0.81
Freeze-dried <i>Spirulina</i> -Pine (1:1)	4.24 (±0.04)	0.77	2.73 (±0.03)	0.50
<i>Chlorella</i> -Pine (1:1)	4.05 (±0.07)	0.75	2.43 (±0.04)	0.45
<i>A.o.</i> -Pine (1:1)	2.83 (±0.06)	0.57	1.67 (±0.02)	0.34
<i>Coelastrella</i> -Pine (1:1)	2.89 (±0.08)	0.56	1.85 (±0.06)	0.36

It can be observed in Table 7 and Figure 10 the favorable effect of microalgae addition to pine sawdust on the properties of the CO₂ adsorbents; this is particularly relevant to adsorption capacities expressed on a volume basis (Figure 10). Regardless of the microalgae species evaluated, all pellets from microalgae-pine sawdust blends show higher CO₂ adsorption capacities than the pellets from pine sawdust. Compared to the commercial activated carbon Norit R2030, the greatest potential is observed for the samples prepared from *Spirulina* or *Chlorella* and in particular, the adsorbent obtained from *Spirulina* paste-pine sawdust without HTC pretreatment and activated at 800 °C during 1 hour.

Figure 10. Comparison of the adsorption capacities on a volume basis at 30 and 50 °C.

In order to compare the adsorption capacity of the samples prepared in this study, collected data from the literature regarding the performance of carbon-based materials in post-combustion capture conditions are reported in Table 8. It reveals that the CO₂ uptake capacity of *Spirulina* paste-pine sawdust is among the highest (6.0 wt.% at 30 °C and a CO₂ partial pressure of 10.5 kPa). Most of the biomass-derived activated carbons underperform this adsorbent in similar operating conditions and especially those that were produced by physical activation with CO₂.

Table 8. Comparison of CO₂ uptakes reported in literature for porous carbons derived from different biomass feedstocks.

Precursor	Activating agent	Adsorption temperature (°C)	CO ₂ pressure (kPa)	CO ₂ adsorption (wt.%)	Ref.
Coffee residue	CO ₂	25	15	3.5	[37]
		50	15	5.3	
Lignin	N ₂	25	15	5.2	[38]
Olive stones	CO ₂	25	15	3.5	[38]
Coconut shell	CO ₂	25	15	6.2	[40]
Empty palm fruit bunch	KOH	25	15	5.7	[41]
		50	15	3.2	
Pine cone	KOH	25	15	7.2	[42]
Macroalgae <i>E. prolifera</i>	KOH	25	15	6.1	[43]
Vine shoots	KOH	25	15	5.9	[44]
		25	10.5	4.6	
	CO ₂	25	15	5.3	
		25	10.5	4.4	
Grass cuttings	CO ₂	25	10	3.7	[26]
		50	10	2.2	
Macadamia nut shell	CO ₂	25	13.3	4.9	[45]
Rice husk	KOH	25	10	5.3	[46]
Corncob	NH ₃	25	10	4.8	[47]

5. Conclusions

The potential use of different species of microalgae for the production of activated carbon adsorbents of CO₂ was evaluated. Due to the lack of a carbonaceous structure, like the one encountered in lignocellulosic biomass, microalgae on its own turned out to hold poor characteristics as precursor of activated carbons. Regarding the two types of freeze-dried microalgae evaluated, *Chlorella* and *Spirulina*, CO₂ adsorption capacities (at 50 °C and pCO₂ = 10.5 kPa) of 1.55 and 1.49 wt.% were obtained, respectively. As far as the pastes of

microalgae evaluated are concerned, only *Acutodesmus obliquus* presented an adsorption capacity of 1.28 wt.%; all the remaining pellets either practically did not adsorb or their structure collapsed after the activation stage.

Therefore, mixtures of microalgae with lignocellulosic biomass (pine sawdust) were prepared and the effect of hydrothermal carbonization treatment prior to activation with CO₂ was evaluated. Microalgae-pine sawdust blends showed an increase in the CO₂ adsorption capacities, even higher than that expected according to the additive rule. Hydrothermal carbonization process did not improve the adsorption capacity of the materials but a positive densification effect was observed.

The most promising results, regarding the CO₂ adsorption capacity, were obtained for *Spirulina* mixed with pine sawdust and directly activated with CO₂. This sample presents an outstanding CO₂ adsorption capacity of 4 wt.% at 50 °C and a CO₂ partial pressure of 10.5 kPa. Some differences were observed between the fresh paste and freeze-dried microalgae. Hence, it can be concluded that not only the choice of the species of microalgae is important, but also the preservation and drying techniques used.

From the results presented in this preliminary study it can be concluded that mixtures of microalgae and pine sawdust hold enormous potential as precursors of CO₂ adsorbents and show CO₂ adsorption capacity values at 50 °C and 10.5 kPa that are among the highest reported in the literature.

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