

# 1 **Biochar production from sewage sludge and microalgae combination: properties,** 2 **sustainability and possible role in a circular economy**

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6

## 7 **Abstract**

8 One possible destination for sewage sludge sustainable disposal is the production of biochar, that can  
9 be achieved by post-processing of the sludge itself, i.e. by pyrolysis. Biochar from sludge is  
10 considered one of the most interesting products in a wastewater treatment based circular economy, as  
11 proven by the multitude of possible uses so far tested in different areas. Recently, combined AS-  
12 microalgae systems have been proposed to recover both carbon and nutrients from wastewaters as  
13 alternative to conventional technologies such as those based on AS only. This could be efficient from  
14 the point of view of removal of mandatory components from wastewater effluents, but it adds  
15 potential issues to the problem of residue disposal. While in fact a consortium of microalgae and  
16 bacteria will prevail in the reactor as a function of the wastewater composition, environmental  
17 conditions, reactor design, and operation conditions, bacteria in the culture will oxidize the organic  
18 matter to inorganic compounds, consuming oxygen in this step, whereas microalgae use the light to  
19 uptake the inorganic nutrients that have been released by the bacteria and produce biomass, in turn  
20 releasing (some of) the oxygen required by bacteria for the oxidizing step. Although quite efficient  
21 for the liquid treatment stream side, such integrated systems seem to generate a residue that is  
22 apparently difficult to dispose of, as algae normally respond poorly to traditional, mechanical drying  
23 processes. In this study, alternative solutions for such disposal were investigated, by pyrolysis of  
24 a mixed sludge/bioalgae matrix under different conditions: in such way, not only landfillable residuals  
25 are practically eliminated, but a material with multiple possible end uses is generated. Starting  
26 materials (algae, sludge and combinations of both) and end-products (biochar and bio-oil) were  
27 physically and chemically characterized after pyrolysis under different conditions. Algae alone were  
28 also subject to preliminary solvent oil extraction to verify whether an increased biochar production  
29 would result from the modified process (which did, improving biochar generation by 25-33%). A  
30 comprehensive discussion on properties of end products as function of process design, possible  
31 applications and advantages of co-pyrolysis follows.

32

33 **Keywords**

34 Slow pyrolysis – Microalgae – *Chlorella* – Biochar analysis – Bio-oil – Sewage sludge disposal

35

36 **Introduction**

37 Sewage sludge is the final by-product of wastewater treatment in the integrated water cycle, its  
38 production is index of management efficiency of municipal and industrial wastewater treatment plants  
39 (WWTP). The volumes of excess sludge require additional treatment, disposal or final recovery in  
40 order to comply with current EU sanification objectives (Neczaj and Grosser, 2018). The cost of these  
41 processes has been estimated around 50% of the total cost of wastewater treatment (Callegari and  
42 Capodaglio, 2018). Italy, among the other EU countries, is required to improve quality of wastewater  
43 treatment effluents and update the facilities or proceed with the installation of new treatment plants  
44 where necessary, under penalty of EU sanctions. For this reason, in addition to the demographic  
45 growth, the production of sewage sludge is destined to increase. The problem of disposal is therefore  
46 a very important obstacle.

47 However, the alternatives for sludge disposal turn out to be limited, since the accumulation of heavy  
48 metals, organic pollutants and pathogens narrow the use of techniques such as direct shedding in  
49 agriculture, composting and anaerobic digestion (Mantovi et al., 2005).

50 An energy favouring and economically appealing alternative would be incineration, which, in  
51 addition to significantly reduce the quantities of waste to be disposed of, allows cogeneration (Herbert  
52 and Krishnan, 2016). However, incineration involves high costs due to gas effluent treatment, to  
53 reduce the concentration of pollutants in compliance with regulatory limits. Therefore, the  
54 researchers' interest has switched to other innovative technologies, such as pyrolysis and gasification,  
55 conducted in absence or depletion of oxygen, leading to a significant decrease in fumes production  
56 and volume (up to 50% in pyrolysis). Pyrolysis also provides for transformation of waste treated in a  
57 solid component called biochar, and a component liquid called bio-oil (Callegari and Capodaglio,  
58 2018).

59 These products can be used for different purposes, in particular biochar can be used as a fuel solid,  
60 as a soil conditioner for agricultural land, or can be applied in contaminated sites. Also, with the high  
61 temperatures of pyrolysis processes, the stability of metals present in sewage sludge is increased,  
62 reducing the possibility of potential leaks of these (Callegari and Capodaglio, 2018). About the  
63 energetic aspects, bio-oil and biochar can be used as fuels, meeting the increasing need for primary

64 energy, since the demographic increase has led to a sudden exploitation of the fossil fuels (Lakaniemi  
65 et al, 2013). Consequently, the alarming increase in the concentration of carbon dioxide and other  
66 greenhouse gases in the atmosphere have caused a global rise of temperatures (Solomon et al., 2009).  
67 Industrialization, demographic growth, urbanization and transport development are all based on  
68 intensive coal, oil and natural gas exploitation. Another important aspect to consider is the availability  
69 of these resources, which will tend to run out over the years (Chisti, 2008).

70 Studies on use of new non-exhaustive, economically advantageous and less impacting resources is  
71 becoming more and more central in researchers' interest, in particular biofuels derived from biomass  
72 (Bilgili et al., 2017).

73 In this context, microalgae emerge as third generation feedstock for biofuels production (Chen et al.,  
74 2011). Microalgae are unicellular photosynthetic microorganisms capable of fixing carbon dioxide  
75 performing photosynthesis, and present numerous characteristics that make them suitable to be  
76 applied for energy purposes (Ahmad et al., 2011,). Amongst them: (i) absence of competitiveness  
77 with the food market, (ii) high productivity with reduced cultivated surface (microalgae allow to  
78 obtain an oil production of about 70% by weight of dried biomass, furthermore is required only 0.1  
79 m<sup>2</sup> per year soil per kg of biodiesel), (iii) use of unusable surfaces for cultivation of different  
80 biomasses, not subtracting soil from food crops, (iv) the possibility of application with different types  
81 of water (fresh water, brackish water and wastewater). Microalgae present also a positive impact on  
82 carbon dioxide emissions, microalgal biomass contains about 50% of carbon over dry weight, which  
83 is derived mainly from CO<sub>2</sub>. To produce 100 tons of microalgae allows to fix about 183 tons of carbon  
84 dioxide (Sánchez et al., 2003).

85 The high reproduction speed and ease of cultivation makes them more appealing if compared with  
86 other biomasses, as they allow to reach high yields in terms of bio-oil and biochar, also thanks to their  
87 high lipid content e low ash content (Yu et al., 2017). Numerous studies have aimed to determine the  
88 oil yield for biodiesel production, and the results were very satisfactory (Chisti, 2007, Reen et al.,  
89 2018, Chaiwong et al., 2013). Growth and productivity of microalgae are strongly influenced from  
90 environmental and physiological factors such as temperature, pH, light intensity, nutrient availability  
91 and finally, on levels of carbon dioxide (Kumar et al., 2018).

92 Microalgae, if grown in wastewater, can recover directly the nutrients needed for their growth,  
93 obtaining the dual benefit of biomass production and wastewater treatment. Recently, combined AS-  
94 microalgae systems have been proposed to recover both carbon and nutrients from wastewaters as  
95 alternative to conventional technologies. The cultivation of microalgae in wastewater allows the  
96 recovery of nitrogen and phosphorus contained in them, producing up to 1 kg of dry biomass per m<sup>3</sup>  
97 of wastewater (Ficara et al., 2014). This technique has been proposed as an alternative to conventional

98 technologies, like the activated sludge treatment. Bacteria present tend to oxidize the organic  
99 substance contained in the wastewater into inorganic compounds consuming oxygen, while  
100 microalgae use sunlight to absorb inorganic nutrients released by bacteria, producing oxygen  
101 subsequently used by the bacteria for the oxidation.

102 The characteristics of the consortium can vary widely, depending on the conditions present in the  
103 reactor, but the fundamental element for growth appears to be the availability of light within the  
104 reactor. The process based on the use of microalgae consists of several phases: (i) effluent  
105 pretreatment, (ii) nutrient recovery and biomass production within photobioreactors, (iii) biomass  
106 collection, with recirculation or disposal of treated water and finally, (iv) transformation of the  
107 biomass into desired final products (Gabriel et al, 2018). Although quite efficient for the liquid  
108 treatment stream side, such integrated systems seem to generate a residue that is apparently difficult  
109 to dispose of, as algae normally respond poorly to traditional, mechanical separation and drying  
110 processes. The collection phase remains the phase more critical, since microalgae cells are small (2-  
111 20  $\mu\text{m}$ ), have a density similar to that of water, and a concentration in the wastewater rather low (0.5-  
112 0.3  $\text{g L}^{-1}$ ) (Gabriel et al, 2018).

113 The purpose of this paper is to evaluate biochar and bio-oil production through pyrolysis process  
114 starting from two initial materials: microalgae and sludge from wastewater treatment plants,  
115 determining which condition is more favourable to recovery of valuable products.

116

## 117 **2. Materials and methods**

118 Three different materials have been tested throughout the experiment, characterized and then  
119 pyrolyzed at two different temperatures. Both starter materials and solid products have been  
120 characterised using thermogravimetric analysis (TGA) and infrared spectroscopy (IR), HHV (higher  
121 heating value) in biochar samples has also been evaluated.

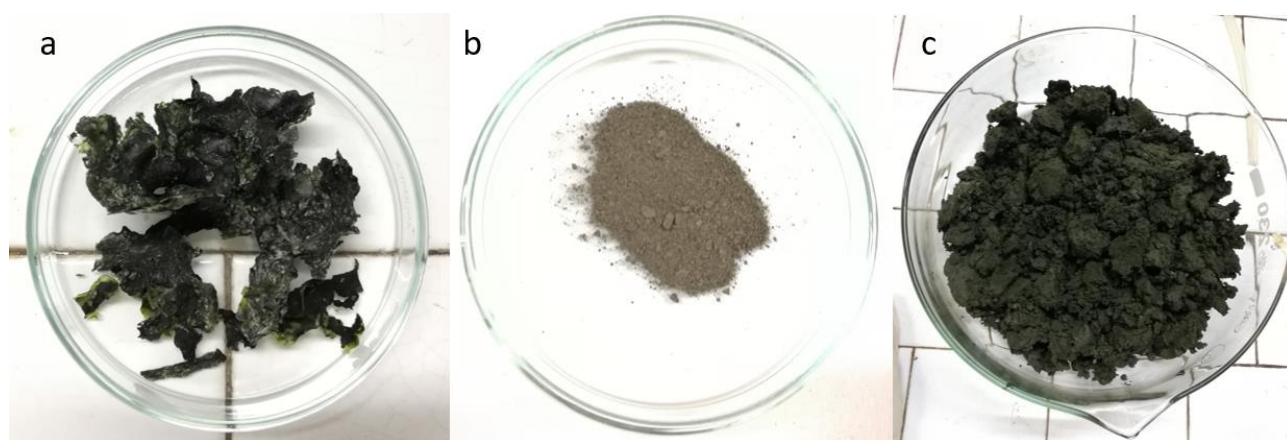
### 122 *2.1 Samples preparation and pretreatment*

123 A mixed culture of microalgae *Chlorella* has been cultivated in four lab-scale open reactors  
124 (0.35\*0.20\*0.10 cm) in a BG-11 medium, and kept at a constant high level of 3 cm. Air has been  
125 provided by a fishtank aerator to keep the microalgae suspended in the mixture, while light has been  
126 provided by a conventional warm light LED bulb (40 W) under light/dark ratio 16:8. Once the culture  
127 has reached stable growth, microalgae have been harvested and dried on nylon filters ( $\phi = 0.25 \mu\text{m}$ )  
128 for 12 h. The size of agglomerated dried microalgae has been reduced and uniformed using a mortar.

129 Sewage sludge (a mixture of primary and secondary sludge) has been collected from a nearby  
130 wastewater treatment plant, then dried in oven at 100°C for 12 hours and stored until use (humidity  
131 content below 10%).

132 The third material tested was a mixture of sludge and microalgae with high humidity content,  
133 collected from a phytoremediation plant in Spain (FCC Aqualia S.A.). Fresh material has been  
134 sparged in 2 cm high layers in crystallizers, and then put in the oven at 100°C for 12 hours.  
135 Subsequently the dried material has been shredded using a professional shredder, making the grain  
136 size as uniform as possible. The starting materials here presented are showed in Figure 1.

137



138

139 **Figure 1** – Starting materials operated in the experimentation. (a) microalgae *Chlorella* cultivated in  
140 laboratory; b) dried sludge collected from municipal sewage sludge treatment plant; c) mixture of  
141 microalgae and sludge from the phytoremediation plant.

142

## 143 2.2 Oil extraction from microalgae

144 To achieve better yields in biochar recovery, oil extraction from microalgae using solvents has been  
145 operated as reported in Kumar et al. (2018) as control using a chloroform-methanol ratio 2:1. For the  
146 two samples containing algae, 1 g of dried sample has been immersed in 20 mL of solvent solution  
147 in a flat-bottomed pyrex glass flask, and stirred with a magnetic stirrer for 25 minutes, then  
148 centrifuged for 20 mins at 4000 rpm. The liquid fraction has been filtrated to avoid solid presence in  
149 the bulk liquid, and finally evaporated in Rotovapor to remove the solvents and determine the weight  
150 of extracted oil.

## 151 2.3 Thermogravimetric analysis (TGA) and infrared spectroscopy (IR)

152 Initial materials such as sludge, a mixture of algae and deriving sludge from the Aqualia plant, and  
153 powdered algae were first subjected to a thermogravimetric analysis (25÷800 °C, heating speed 20  
154 °C min<sup>-1</sup>) in nitrogen in order to better identify the temperature at which the pyrolysis process begins,  
155 and later to a TGA in air, to determine the content of ashes and inorganic material. Both TGA in  
156 nitrogen and air were then carried out on the samples of solid residue deriving from the process of  
157 pyrolysis to verify the effective pyrolysis of the initial material, and for a comparison of the ash  
158 content. Subsequent thermogravimetric analysis in nitrogen were carried out on the residues of  
159 microalgae subjected to oil extraction with solvent, to compare such samples with untreated starting  
160 materials.

161 Infrared spectroscopy (IR) has been used to characterize starting materials and both liquid and solid  
162 residues from pyrolysis process, and to detect the presence of water in liquid samples.

#### 163 *2.4 Pyrolysis process and products recovery*

164 Substrates operated in the present experiment have been pyrolyzed through thermostatic sand bath S-  
165 70 (FALC instruments). A flat-bottomed pyrex glass flask has been immersed inside the heating body,  
166 containing 20.00 g of sample, in adhesion to the bottom of the sand-bath. The condition of absence  
167 of oxygen was guaranteed by a continuous flow of nitrogen regulated by a flow meter, blown directly  
168 inside the reactor. A three-way glass fitting was connected using a silicone tube, with a solvent trap  
169 containing acetone, immersed in crushed ice, used for the recovery of the oily fraction. The gases  
170 generated by the pyrolysis process pass through a silicone tube, they enter the trap where they are  
171 condensed. The experimentation was conducted at a temperature of 500 °C and 350 °C. For the  
172 samples subjected to the temperature of 500 °C the oven is kept at maximum operating temperature,  
173 and the temperature trend comes monitored by using a thermocouple inserted in the sand bath. Once  
174 the preset temperature was reached, it was kept constant for 30 minutes followed by switching off the  
175 heating device. As for the remaining samples, the use of a thermocouple allowed to monitor the  
176 temperature until it reaches 350 °C. This value was kept for about 30 minutes by acting on the  
177 thermoregulator of the oven itself. After this period, the device switched off. After cooling of the  
178 glass components, it was possible to recover the pyrolysis solid and liquid products. All experiments  
179 have been conducted in triplicates. Table 1 summarizes the samples analysed throughout the  
180 experimentation.

181

182 **Table 1** – Samples summary. Each sample has been tested in triplicates.

Sample ID	Substrate	Temperature
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1	Microalgae <i>Chlorella</i>	500 °C
2	Microalgae <i>Chlorella</i>	350 °C
3	Sludge from WWTP	500 °C
4	Sludge from WWTP	350 °C
5	Mix A+S	500 °C
6	Mix A+S	350 °C

183

184 Both solid (biochar) and liquid (bio-oil) fractions were recovered throughout the experiment. Gas  
 185 fraction hasn't been recovered as retained not necessary for the present work, but estimated by  
 186 difference. After pyrolysis process, all glass components and silicon tubes have been washed with  
 187 acetone to remove all solid and oil particles from the instrument. From this washing process a mixture  
 188 of biochar, bio-oil, acetone and, eventually, water is obtained, subjected to further treatment to  
 189 achieve separation of the components. To separate solid fraction, filtration using funnel Buchner was  
 190 operated. Every filter has been weighed before and after filtration to determine the fraction  
 191 successfully separated. Liquid fraction (a mixture of acetone and oil) was transferred in a balloon up  
 192 to  $\frac{3}{4}$  of volume, and then subjected to vacuum evaporation using Rotavapor R-100 (BUCHI) to  
 193 remove the solvent. The balloon has been weighed before and after use. If water was detected in the  
 194 sample during IR analysis, anhydrous  $\text{Na}_2\text{SO}_4$  was added to the solution, that was then filtrated and  
 195 evaporated.

196 Percentages of biochar and bio-oil successfully recovered have been calculated as it follows (Eq. (1)  
 197 and (2), respectively):

198 
$$\% \text{ biochar} = \frac{W_{\text{biochar}}}{W_i - W_{\text{H}_2\text{O}}} \cdot 100 \quad (1)$$

199 where  $W_{\text{biochar}}$  is the weight of biochar resulting from the test,  $W_i$  is the initial weight of the sample  
 200 (20 g for each test) and  $W_{\text{H}_2\text{O}}$  is the weight of water present in the initial sample, deduced from the  
 201 TGA analysis.

202 
$$\% \text{ bio - oil} = \frac{W_{\text{bio-oil}}}{W_i - W_{\text{H}_2\text{O}}} \cdot 100 \quad (2)$$

203 where  $W_{\text{bio-oil}}$  is the weight of bio-oil resulting from the test,  $W_i$  is the initial weight of the sample (20  
 204 g for each test) and  $W_{\text{H}_2\text{O}}$  is the weight of water present in the initial sample, deduced from the TGA  
 205 analysis.

206

## 207 3. Results

### 208 3.1 Starting material characterization

209 Each starting material has been characterized by performing TGA analysis in air (oxidative  
210 environment, reproducing the combustion process) and nitrogen (inert environment). In oxidative  
211 environment it is possible to evaluate the ashes content of the analysed material. TGA in inert  
212 environment was necessary to determine the pyrolysis temperature range suitable to the samples  
213 under examination. The thermochemical process in absence of oxygen leads to degradation of the  
214 volatile substances in the sample, leaving char as residue. Results of the TGA in air and nitrogen are  
215 summarized in Table 2.

216 Based on the percentage of ashes obtained from the TGA analysis, it has been estimated the  
217 percentage of microalgae and sludge in the sample from the real phytoremediation plant,  
218 corresponding to 15% and 85%, respectively. The ashes content in WWTP sludge sample is higher  
219 ( $30.2 \pm 1.8\%$ ) than the ones containing microalgae, meaning that adding a small amount (15%) of  
220 microalgae in the mixture positively contributes in reducing the amount of ashes produced by the  
221 process, improving its quality. As for the TGA in nitrogen, is relevant to see how the residues of the  
222 process for the sludge-microalgae mixture, composed by char and inorganic residues, is higher than  
223 that produced by the single matrix itself, theoretically leading to an increased solid material recovery.

224 **Table 2** – Amount of ashes (%) for the three samples based on TGA in air and nitrogen results.

Substrate	% ashes (800 °C)	% residues (char+ashes, 800 °C)
Microalgae <i>Chlorella</i>	$13.7 \pm 2.6$	$25.1 \pm 1.4$
Sludge WWTP	$30.2 \pm 1.8$	$36.2 \pm 2.1$
Mix A+S	$24.4 \pm 3.1$	$38.7 \pm 1.9$

225

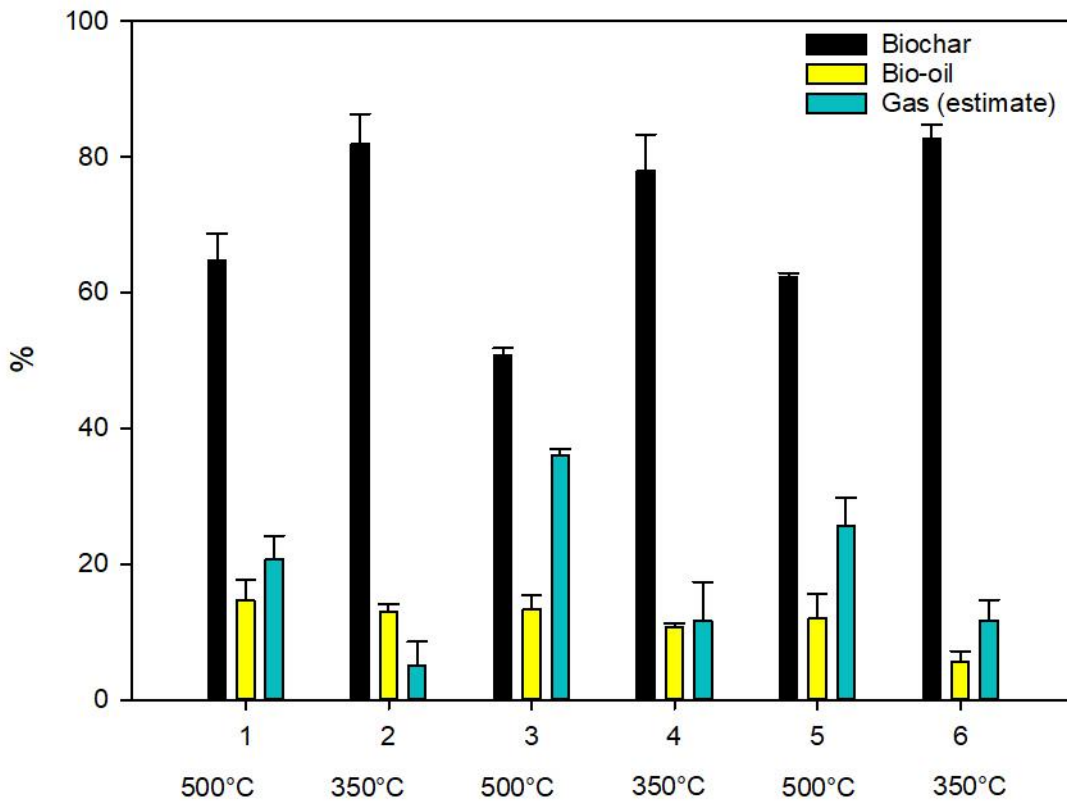
### 226 3.2 Biochar production and characterization

227 Pyrolysis tests have been conducted under two different temperatures, at 350°C and 500°C. The  
228 resulting pyrolysis products are solid residue (biochar) and liquid residue (bio-oil). After cleaning the  
229 components with acetone, to remove solid residues and liquid particles, and separating the fractions,  
230 the biochar has been weighed directly.

231 Figure 2 represents the products obtained from the pyrolysis of the samples previously described. For  
232 all matrix examined, pyrolysis at 350 °C produces the more relevant amount of solid residue  
233 (biochar), while higher temperatures (500 °C) are generally better performing in the production of



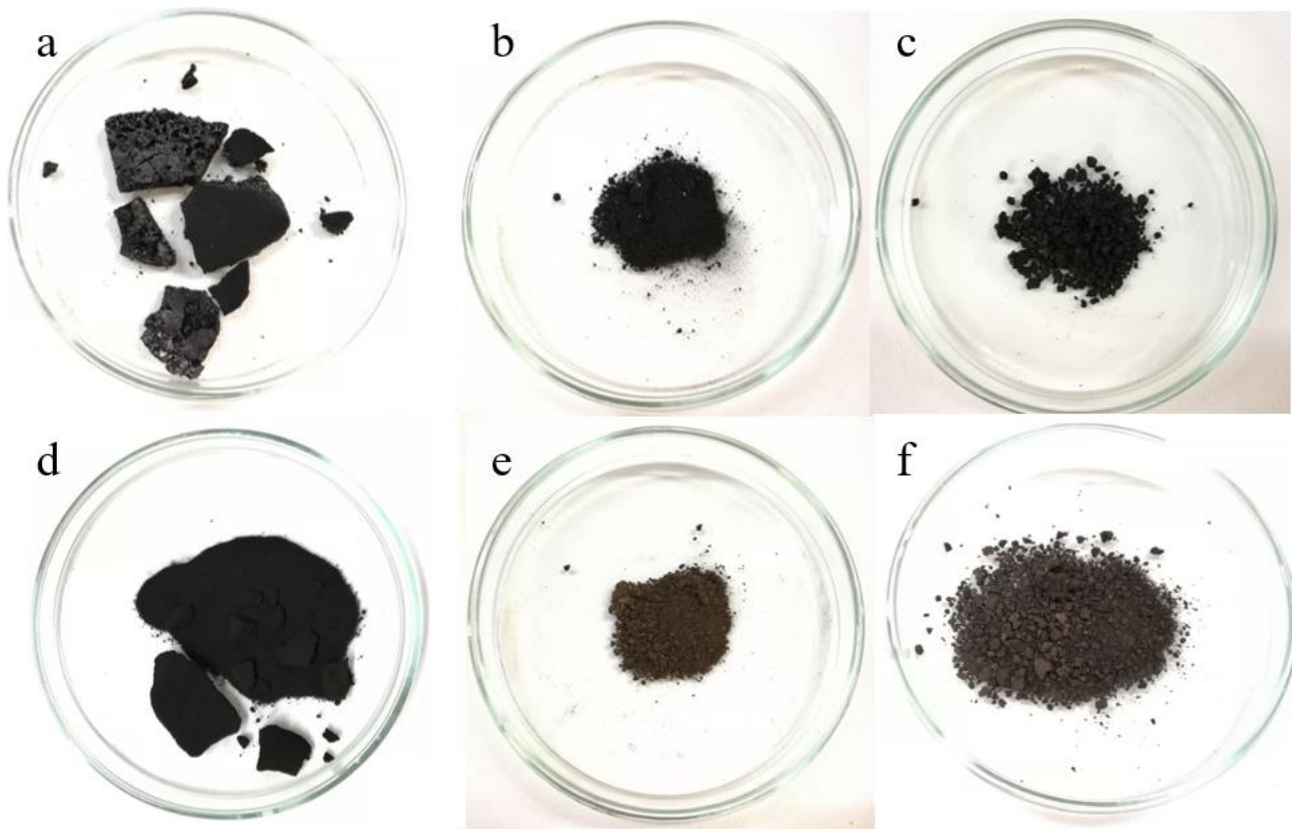
234 bio-oil. When considering only the broad production of biochar, WWTP sludge pyrolyzed at 350 °C  
 235 is the better performing ( $82.0 \pm 4.4$  %) along with the mixture solid residue at the same temperature  
 236 ( $82.7 \pm 2.1$ %). As for liquid residues, higher temperatures are usually reported to be better performing  
 237 than the ones operated in the present work (Atabani et al., 2013), but it can be stated that all samples  
 238 pyrolyzed at 500 °C produced  $13 \pm 3$ % of bio-oil.



239  
 240 **Figure 2** – Pyrolysis products: biochar (black), bio-oil (yellow) and gas (light blue, estimated). Error  
 241 bars represent variability of results between triplicates.

242 In the present work, only the solid residue has been fully characterized. Biochar samples obtained  
 243 from pyrolysis tests have been characterized through TGA, IR analysis and HHV (High Heating  
 244 Value, UNI EN 14918:2010). By visual analysis, all samples appeared different from one sample to  
 245 the other as function of temperature and starting material. Sample 2 and 4 from pyrolysis process at  
 246 350 °C (Figure 3 e, f) presented a fairer colour (brown) if compared to all the other samples (black).  
 247 In microalgae biochar samples 1 and 2 (Figure 3 a, d, respectively) no colour differences were  
 248 detectable, but they differed in consistence: sample 2 (Figure 3 d) was dusty, while sample 1 was in  
 249 solid state (Figure 3 a). TGA in air was performed to evaluate the ashes content of the biochar, while  
 250 TGA in nitrogen was used to evaluate the efficiency of the pyrolysis process, assessing the

251 supplemental weight loss for each sample. Results obtained from the analysis are reported in Table  
252 3.

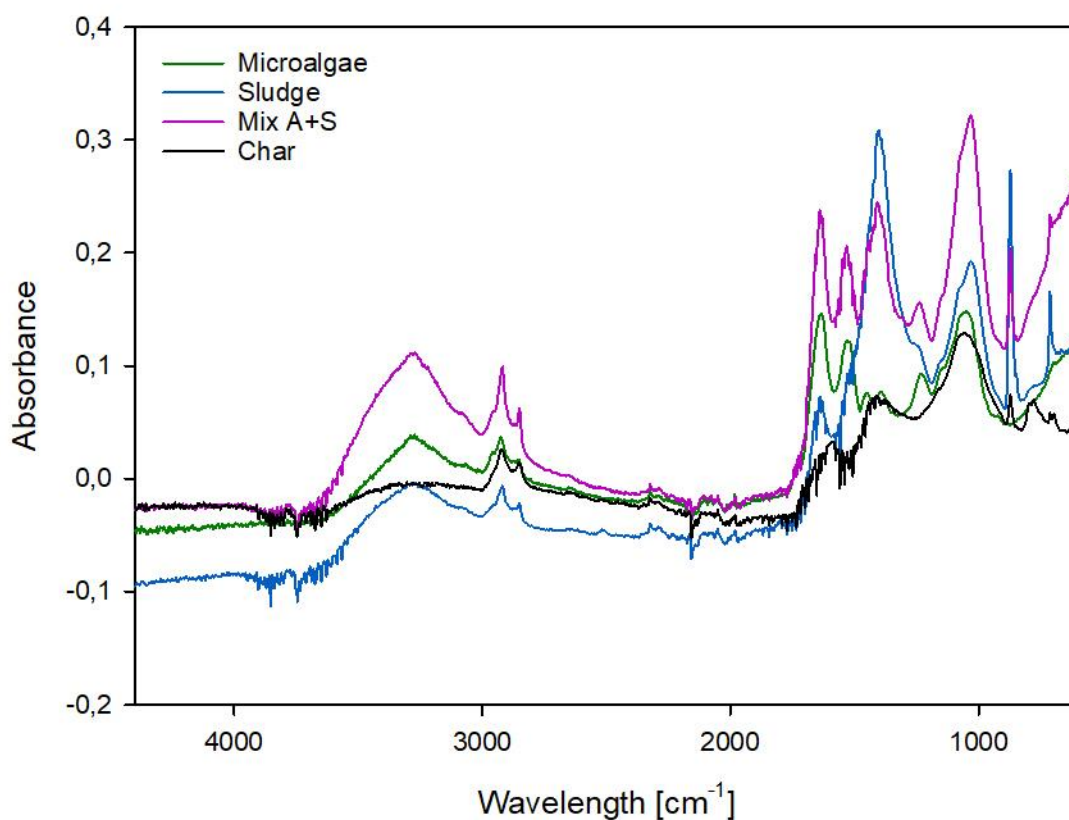


253

254 **Figure 3** – Samples from pyrolysis at 500 °C: a) microalgae *Chlorella*; b) sludge from WWTP; c)  
255 Mix M+S. Samples from pyrolysis at 350 °C: d) microalgae *Chlorella*; e) sludge from WWTP; f)  
256 Mix M+S

257 IR analysis was performed before and after pyrolysis to evaluate the variation of bonds composing  
258 the materials due to the process.

259 Infrared analysis makes it possible to determine the functional groups and bonds present in the  
260 material. Therefore, the most interesting areas are the wavelength representing water and the carboxyl  
261 groups present in the mixture (between  $3600$  and  $2500\text{ cm}^{-1}$ ), the C-C and C-H bonds wavelength  
262 ( $3300\text{ cm}^{-1}$ ); esters and fatty acids ( $1700\text{ cm}^{-1}$ ), and Si-O bonds present in the inorganic material ( $1100$   
263  $\text{cm}^{-1}$ ). By comparing the different spectrums, all samples analysed before pyrolysis are very similar  
264 to each other, although the relationships between the various components change. Instead, the  
265 pyrolyzed sample (only represented by one sample in the graph), shows the obvious removal of water  
266 and organic acids due to pyrolysis, and the reduction of many of the functional groups present.  
267 Obviously, the Si-O bonds are preserved as not involved in pyrolysis. This corresponds to formation  
268 of a compound with a high carbon content, even if they are present still C-C and C-H bonds.



270

271 **Figure 4** – IR analysis results. Absorbance curves for all the starting materials have been reported,  
 272 while only the solid residue (biochar) from Mix A+S at 350 °C has been printed.

273

274 HHV analysis shows that the biochar produced by microalgae has a higher heating value (sample 1  
 275 and 2), which decreases with decreasing pyrolysis temperature. As for the HHV of the remaining  
 276 samples, the result is less satisfactory, and this may suggest not to choose the combustion as the main  
 277 application (Table 3).

278

279 **Table 3** – Amount of ashes detected by TGA in air, weight loss (incomplete pyrolysis) from TGA  
 280 analysis in nitrogen, and HHV value of biochar obtained by the samples analysed (1-6).

Sample	Pyrolysis temperature [°C]	Ashes [%]	Weight loss [%]	HHV [kJ kg <sup>-1</sup> ]
1	500	41.6 ± 2.3	16.8 [250-800 °C]	29091

2	350	31.5 ± 1.7	67.5 [250-800 °C]	26951
3	500	50.1 ± 2.2	23.9 [200-800 °C]	16629
4	350	37.0 ± 1.9	28.5 [250-600 °C]	15648
			17.7 [600-800 °C]	
5	500	44.3 ± 2.7	7.9 [500-600 °C]	16245
			18.9 [600-800 °C]	
6	350	34.5 ± 3.0	49.3 [250 – 800 °C]	16671

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281

282 Oil extraction from microalgae by solvent has been conducted in order to verify whether this  
 283 treatment increased the production yield of biochar. To verify the effect of the pretreatment, the  
 284 sample of residue resulting from the extraction process has been subjected to TGA in nitrogen, and  
 285 then the result has been compared to the results achieved on the raw material.

286 The sample of microalgae showed significant results, if compared to the initial sample. The yield in  
 287 terms of biochar production increased from 25% to 33%. However, the mixture of microalgae and  
 288 sludges didn't show any benefit from the pretreatment (38% of biochar was produced in both cases).

289

#### 290 **4. Discussion**

291 This work aimed to verify if coupling sewage sludge and microalgae in the pyrolysis process would  
 292 be advantageous in terms of biochar production, as the sludge disposal problem is of major concern  
 293 nowadays. The analysis of the products operated didn't limit itself at observing the weight obtained  
 294 for each matrix, but also went thorough to determine the percentage of ashes present in the final  
 295 product, evaluating its quality. Different alternatives for coupling the two matrix together can be  
 296 operated: an option could be the separate cultivation of microalgae added to the sludge directly at the  
 297 time of pyrolysis, however, this strategy would be of little benefit if compared to the use of microalgae  
 298 already in the wastewater treatment chain. This type of process, in addition to allow the removal of  
 299 the nutrients present in the wastewater by the microalgae, produces a mixed biomass (sludge and  
 300 microalgae), which once pyrolyzed produces a solid residue with excellent characteristics, as herein  
 301 reported.

302

##### 303 *4.1 Possible applications of biochar*

304 Pyrolysis process conditions (temperature, speed of heating, type of biomass, etc.) are highly  
305 important to determine the end use of biochar, since they directly contribute to develop different  
306 intrinsic characteristics of the solid residue (Hossain et al., 2011). It is therefore important to analyze  
307 the starting material before the process, in order to establish which is the best performing use for the  
308 biochar that will be obtained at the end of the process. Given the results obtained from HHV analysis  
309 on biochar samples, if compared with the HHV of the hard coal that is around 30 MJ / kg, it is evident  
310 that biochar can also be used as a fuel. However, the use alternatives are known, a more  
311 interesting solution could be the use of biochar in agriculture as an adsorbent of pollutants, and  
312 secondly the combustion of this residue, in order to exploit its energy capacity.

313 The most interesting outcomes for this product are mostly related to a possible re-use and valorisation  
314 of the product, from the perspective of a circular economy. An appealing use of the solid residue of  
315 pyrolysis is in agriculture as soil improver, allowing to increase crop productivity, but also to reduce  
316 soil pollution (Arthur et al. 2015). The biochar itself has an excellent adsorbent capacity for organic  
317 and inorganic pollutants, and is also able to reduce the CO<sub>2</sub> in the atmosphere. For agricultural use  
318 the carbon content in biochar must be greater than 50% of the dry mass, the quantity of N and P  
319 should be between 1 and 45%, and the pH should not exceed 10. The specific surface should also be  
320 greater than 150 m<sup>2</sup>g<sup>-1</sup> (Santos and Pires, 2018). The effects of biochar on the physical-chemical  
321 characteristics of the soils depend strongly on the characteristics of the soil itself and of the biomasses  
322 used for the production of solid residue (Obia et al., 2016).

323 A recent study from Oliveira et al. (2017) stated that the low temperatures of pyrolysis (<500 °C),  
324 favour the partial carbonization, producing biochar with small pores, reduced surface area and high  
325 groups functional containing oxygen. These characteristics make biochar suitable for the removal of  
326 inorganic pollutants. On the contrary, a biochar produced at high temperatures (> 500 °C), could be  
327 applied for the removal of organic pollutants, due to the higher surface area, making it suitable for  
328 environmental bioremediation. Another interesting prospect for this solid residue could be in the  
329 wastewater treatment field, specifically for the removal of toxic compounds released by industries,  
330 or instead of the granular activated carbon in WWTP facilities (Ahmed et al. 2014). Finally, due to  
331 its carbon-rich properties, biochar could be suitable for use as electrode in bioelectrochemical systems  
332 (BES) Normally, the material used at the anode is granular graphite or activated carbon, both  
333 expensive, therefore the use of biochar would be an excellent advantage also in economic terms  
334 (Callegari and Capodaglio, 2018).

335

336 **Conclusions**

337 This work aimed to verify if coupling sewage sludge and microalgae in the pyrolysis process would  
338 be advantageous in terms of biochar production, as the sludge disposal problem is of major concern  
339 nowadays. Products analysis herein operated wasn't limited at observing the weight obtained for  
340 each matrix, but also went through to determine the percentage of ashes present in the final product,  
341 helping in evaluation of its quality. Experimental data showed that, the slow pyrolysis at a temperature  
342 of 350 °C of a mixture of sludge and microalgae, in percentages of 85 and 15%, respectively, allowed  
343 to obtain 80% biochar by weight of the initial sample, of which only 24% were ashes. Comparing this  
344 result to the data deriving from the pyrolysis of WWTP sludge at the same temperature, where the  
345 amount of biochar was 74% of the initial weight, but containing 30% ashes, the co-pyrolysis of  
346 sewage sludge and microalgae allowed to obtain a more valuable product with multiple uses.  
347 Moreover, it contributes to reduce the problem of disposal of waste deriving from wastewater  
348 treatment. In terms of circular economy, biochar is a valuable compound recovered from disposal  
349 material such as WWTP sludge, with multiple interesting outcomes to be further evaluated.

350

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354

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