

ANAEROBIC DIGESTION OF HYDROTHERMAL LIQUEFACTION WASTEWATER AND BIOCHAR FROM SPENT COFFEE GROUNDS

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Abstract

Purpose

Spent coffee grounds (SCG) are an underused lignocellulosic residue generated by the instant coffee industry. Hydrothermal liquefaction (HTL) is an alternative thermochemical process applied to high-water-content and renewable biomasses, such as SCG, to produce biocrude oil along with solid residues, bio-char and a high-organic-content wastewater. These last two HTL co-products were investigated associated to anaerobic digestion process. This research aimed at the soluble organic content reduction and the methane recovering from the post hydrothermal liquefaction wastewater (PHWW) of SCG through the anaerobic digestion process enhanced by the addition of activated carbon and biochar, the co-product of the HTL process, as adsorbents.

Methods

The HTL of SCG process was carried out at literature selected conditions in a laboratory scale batch reactor to recover PHWW and solid residues. The solid residue was cleaned and activated prior to be used as adsorbent during the anaerobic digestion assay. PHWW was characterized and stored to be further anaerobically digested with activated solid residue (ASR) and activated granular carbon (GAC) for comparison.

Results

The PHWW and ASR association enhanced the anaerobic digestion of the PHWW organic compounds, increasing phenols removal efficiency from 36 % (PHWW-AD) to 45 % (PHWW-AD with ASR) and Methane Yield in 62 %. Furthermore, the ASR addition to the PHWW-AD process has contributed to increase methane production rate in 40 %.

Conclusion

The results also indicated that PHWW digestion in presence of ASR potentially reduced inoculum acclimatization periods to the recalcitrant PHWW compounds, thus, it is operationally practical and economically feasible.

Keywords: bioadsorption, toxic wastewater, biomethane, anaerobic digestion.

1. Introduction

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40 The growing trend of the global demand for energy brings to light the need for investigating conversion technologies
41 to produce biofuels using different renewable biomasses as feedstock. Solid residues from industrial processes are more
42 readily available as feedstock for bio-based conversions. Thus, studying the integration of waste management and energy
43 production is therefore paramount. This integration contributes to diversify the energy matrix and to prevent negative
44 impacts on the environment. Spent coffee grounds (SCG) are an underused lignocellulosic residue generated in large
45 amounts by the instant coffee industry. It is estimated that 6 million tons of this residue is annually disposed of in landfills
46 [1]. The SCG is majorly composed by lignin, hemicellulose, cellulose, high levels of lipids and proteins. It presents a
47 small particle size and a high moisture content, being studied as feedstock when performing hydrothermal liquefaction
48 (HTL) processes aiming at biocrude oil and biochar production for some authors [2,3].

49 Hydrothermal liquefaction is a thermochemical process carried out at temperatures from 220°C to 370°C and high
50 pressures (6–15MPa), which converts solid biomasses of high water-content, such as SCG, into biocrude oil and biochar
51 of higher high heating values, with no need for previous drying. The conversion occurs by breaking solid biopolymeric
52 structures and repolymerizing them according its affinity [4-6].

53 One of the hydrothermal liquefaction bottlenecks is the high quantity of generated wastewater, also called as PHWW
54 (post hydrothermal wastewater) [7,8]. This PHWW presents high soluble organic matter and it is composed by some
55 recalcitrant compounds, such as polyphenols [9,10]. Some authors have associated the HTL process followed by the
56 anaerobic digestion (AD) of the wastewater produced from the HTL itself. This cascade approach is interesting, since the
57 AD of the PHWW reduces the organic content of the generated aqueous fraction at the same time that contributes to
58 recovery energy from the converted biomass by producing methane from the solubilized organic fraction. However, the
59 high organic load of the PHWW [13] associated with its recalcitrance potentially inhibits methanogenesis [14-16]. Thus,
60 a variety of methods has been investigated aiming at enhancing the AD of such effluents, including biomass
61 acclimatization and adsorbents use [17,18]. Regarding PHWW, the recent literature lacks more researches on AD
62 enhancing techniques to avoid or to attenuate toxic effects on methanogenesis.

63 In order to mitigate the presence of such toxics, the use of activated carbon is an interesting alternative, since its
64 porous structure allows the adsorption of recalcitrant and toxic compounds, such as ammonia and phenols, decreasing
65 these compounds concentration in the reaction medium and their inhibitory effect [17,18]. Moreover, when associating
66 activated carbon in anaerobic digestion systems, a desorption effect can be observed after adsorption induced by the
67 concentration gradient between the liquid medium and the adsorbent. Therefore, adsorbents can operate as a buffer,
68 temporarily storing compounds from the wastewater, that may cause inhibition due its high concentration, and slowly
69 releasing them to microorganisms, and thus contributing to higher methane yields and higher conversion rates even in the
70 presence of potentially toxic compounds [11].

71 Even though activated carbon is considered one of the best adsorbent options, the energy expenditure for its
72 production makes the treatment processes more expensive and, thus, unfeasible. Under these circumstances, the
73 development of low-cost adsorbents, produced from residues from fruit processing, straw, coconut residues, coffee
74 residues, vegetable peels, sludge, draws attention [19]. The novelty of this work is to combine two HTL co-products,
75 solid residues and PHWW, in a biological process. The combination allowed investigating HTL solid residues as an
76 adsorbent associated to with the anaerobic treatment of PHWW which is a recalcitrant wastewater, as above-mentioned.

77 78 **2. Methods**

79 80 *2.1 HTL of SCG*

Spent coffee grounds (SCG) from instant coffee production was kindly provided by Nestlé Brasil Ltd (Araras, SP, Brazil). Just after its collection, the material was stored at -4 °C prior to use. The HTL of SCG was carried out according to [2], more precisely, at an initial pressure of 0.5 MPa, at a temperature ramped up to 275 °C, and keeping the reaction happening for 10 min at this final temperature. The reaction was performed in a Parr Reactor 4552 with 4 L of reaction volume, with a water-to-feedstock ratio of 20:01 (in mass). The products, wastewater (PHWW), solid residues and crude oil, were previously separated by density difference and then by filtration using a 0,45-mesh pore size membrane.

2.2 Characterization of PHWW

The PHWW was characterized in terms of its: carbon oxygen demand (COD), total nitrogen and ammoniac nitrogen [20]; total suspended solids (TSS) [21]; phenols [22]; alkalinity and acidity [23]; pH using a pH-meter.

2.3 Biochar preparation and activation

The solid residue collect after the HTL process were mixed with acetone in the proportion of 2:5 (in mass) for 24 hours and then rinsed with water. After dried at 105 °C for 24 h, the activation step was carried out using NaOH-0.1M and HCl-0.1 M in the proportion 1:5 and then, rinsed with water, according to [24], adapting the mass ratio.

2.4 Adsorption capacity of ASR

The adsorption capacity experiment was carried out for 24 hours at 37 °C, under constant agitation of 100 rpm in the presence of 2 g·L⁻¹ of adsorbent and 10 mL of “raw” PHWW. The adsorbents used in this assay were ASR and GAC. The removal efficiency was calculated according to Equation 1; while the adsorption capacity was evaluated according to Equation 2, both were reported for COD and phenolic compounds.

$$\%R = \frac{(C_i - C_f)}{C_i} \cdot 100 \quad \text{Equation (1)}$$

$$q_e = \frac{(C_i - C_f) \cdot V}{m} \quad \text{Equation (2)}$$

Whereas: %R is removal efficiency, q_e is adsorption capacity (mg·g⁻¹), c_i is initial concentration (mg·L⁻¹), c_f is final concentration (mg·L⁻¹), v is nominal volume (L) and m is mass of adsorbent (g).

2.5 Anaerobic digestion

The inoculum was originally pulled from an Upflow Anaerobic Sludge Blanket (UASB) reactor used for effluent treatment of a poultry slaughterhouse. Previous the AD assay, the inoculum, was exposed to progressive concentrations of PHWW organic content in terms of COD of 1.0 g·L⁻¹ and 2.3 g·L⁻¹, in sequencing batch cycles of 10 days of incubation period each at mesophilic condition (37 °C). AD was carried out in 120 mL serum bottles with 40% of headspace, at an inoculum concentration of 8 g SSV·L⁻¹. The substrate was the previously collected PHWW diluted to 3,9 gCOD·L⁻¹ and supplemented with macro and micronutrient solution according to [25]. Thus, the F/M ratio (food to microorganism ratio) was 0.5, approximately. The incubation temperature was maintained at 37 °C. Three conditions were set up for AD, one

123 with no adsorbent addition (Condition 1), one with 2 g·L⁻¹ of ASR addition (Condition 2) and one with 2 g·L⁻¹ of GAC
 124 (Condition 3). The methane was measured using the alkali liquid displacement, in accordance with [26]. The experimental
 125 data for the accumulates methane profile collect during the incubation period were evaluated using the modified Gompertz
 126 equation [27].

127

$$128 \quad P_{CH_4}(t) = P_{CH_4} \cdot \exp \left\{ -\exp \left[\frac{k \cdot e}{P_{CH_4}} (\lambda - t) + 1 \right] \right\} \quad \text{Equation (7)}$$

129

130 Where $P_{CH_4}(t)$ (NL CH₄) is the methane produced at any time (t), P_{CH_4} maximum methane cumulated potential (mL
 131 CH₄), k is the maximum rate of methane production (NL·h⁻¹), λ is the lag phase time constant (h) and t is the incubation
 132 period (h).

133

134 3. Results and Discussion

135

136 3.1 Characterization of PHWW

137 **Table 1** presented all parameters measured for characterizing the PHWW.

138

Table 1. PHWW characterization

Parameter	Content
Chemical oxygen demand (COD) (mg L ⁻¹)	12611.0 ± 0.26
Total solid suspended (TSS) (mg L ⁻¹)	46.5 ± 0.70
Alkalinity (mg L ⁻¹)	n/a
Acidity (mg L ⁻¹)	233.15 ± 8.98*
Total nitrogen (mg L ⁻¹)	379.31 ± 13.69
Ammoniac nitrogen (mg L ⁻¹)	133.27 ± 12.91
Phenols (mg L ⁻¹)	1101 ± 0.004**
pH	4.3 ± 0.01

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* acetic acid equivalent;

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** gallic acid equivalent.

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142 3.2 Adsorption capacity of ASR

143 ASR presented the capacity of removing COD and phenols from the PHWW by adsorption. ASR showed an
 144 adsorption capacity in COD terms of 56% of the total GAC capacity of adsorbing COD from the PHWW at the same
 145 operational conditions, as it can be seen in **Table 2**. Moreover, it can be noticed that phenols efficiency removal ASR
 146 represented 47% of GAC phenols efficiency removal. Thus, the adsorption capacity of ASR can be potentially
 147 investigated as an alternative to the GAC use as adsorbent when treating PHWW.

148

Table 2. Adsorption capacity

	ASR		GAC	
	Efficiency removal (%)	q_e (mg. g ⁻¹)	Efficiency removal (%)	q_e (mg. g ⁻¹)
COD	7.3 ± 0.7	443.3 ± 61,2	12.1 ± 2.7	79.,9 ± 175.1
Phenols	7.0 ± 5.2	33.2 ± 24,5	15.0 ± 6.2	71.0 ± 29.3

149

150 This behavior showed that the ASR adsorption process was primarily governed by the concentration gradient of the
 151 PHWW compounds presented in the liquid solution, and most likely, these compounds established a covalent interaction

152 with the active sites of the adsorbent [28] and the solid residue generated by the HTL of SCG has functional adsorbent
 153 groups of C=C [29] and C-H type [30].

154 To comprehend the difference between de adsorption capacity when comparing GAC and ASR is necessary to point
 155 out that the adsorption process is a superficial phenomenon. The extent of adsorption is proportional to the adsorbent
 156 specific surface area, that is, the portion of the total area available for adsorption, where active sites interact with the
 157 target compounds [31]. Thus, the greater the presence of active sites in the adsorbent, the greater the volume of matter
 158 collected in its structure, which makes the adsorption process faster in the initial stages [32]. This implies that the GAC
 159 has more active sites available for adsorption than ASR, indicating that further investigation is requested on the ASR
 160 production in order to increase its adsorption capacity equivalent to the CAG one.

161 3.3 Anaerobic digestion

162 **Table 3** shows an increase in the phenol's removal efficiency from the first exposition to the third one of 7 %, for
 163 the first, to up to 16 %, for the second, and 36 %, for the third exposition. Even though no significant increase in the COD
 164 efficiency removal was observed, COD efficiency removal did not decrease with the feed's COD level increasing from 1
 165 to up to 3.9 gCOD·L⁻¹, for the first and the third exposure, respectively. The organic matter content and phenolic
 166 compounds were also measured after 15 minutes of incubation during the third exposition, i.e. 3.76±0.30 gCOD·L⁻¹ and
 167 349.3±47.04 mg phenol·L⁻¹ for the batch with GAC, 4.88±0.43 gCOD·L⁻¹ and 390.21 ± 49.67 mg phenol·L⁻¹ for the batch
 168 with ASR.

169
 170 **Table 3.** COD and total phenols values measured during the incubation period. AD is anaerobic digestion, GAC is
 171 activated carbon and ASR is activated solid residue

Studied AD condition	Adsorbent addition	COD (g·L ⁻¹)		COD efficiency removal (%)	Phenols (mg·L ⁻¹)		Phenols efficiency removal (%)
		Affluent	Effluent		Affluent	Effluent	
First Exposition	No	1.43 ± 0.07	0.67 ± 0.01	53.06	66.9 ± 0.0	62.1 ± 5.3	7.18
Second Exposition	No	2.21 ± 0.01	1.21 ± 0.01	45.16	198.7 ± 30.0	165.1 ± 6.2	16.90
	No		2.42 ± 0.26	54.24		262.39 ± 9.13	36.05
Third Exposition	GAC	5.29 ± 1.69	1.59 ± 0.04	69.84	410.34 ± 15.28	156.18 ± 3.27	61.94
	ASR		2.23 ± 0.23	57.78		224.06 ± 10.57	45.40

172
 173 As observed by Dias et al. [33], the progressive increase of PHWW COD level in consecutive batches enabled the
 174 consortium acclimatization to the PHWW of SCG toxic compounds. The hypothesis debated is that the consortium present
 175 in the inoculum capable of degrading and consuming the organic compounds of the PHWW have prevailed with the
 176 progressive increase in the PHWW addition and the elapsed time of experimentation. This is supported by several authors,
 177 such as Saady [34] who attributes the inhibitory effects due to the lack of biomass adaptability period to the concentration
 178 of toxic compounds, in which in the AD process imply that some of the metabolic routes of the mixed inoculum are
 179 inhibited or displaced, causing an influence on the selection of the microorganisms. There is a huge variety of inhibitors
 180 compounds in the studied PHWW but main inhibitors are furanic (sugar monomer degradation products) such as furfural
 181 and 5-hydroxymethylfurfural (HMF), from dehydration of pentoses and hexoses, and also phenolic compounds such as

182 syringaldehyde and vanillin originating from the degradation of lignin polymers [35-37], which is one of the SCG
 183 structural compounds [2].

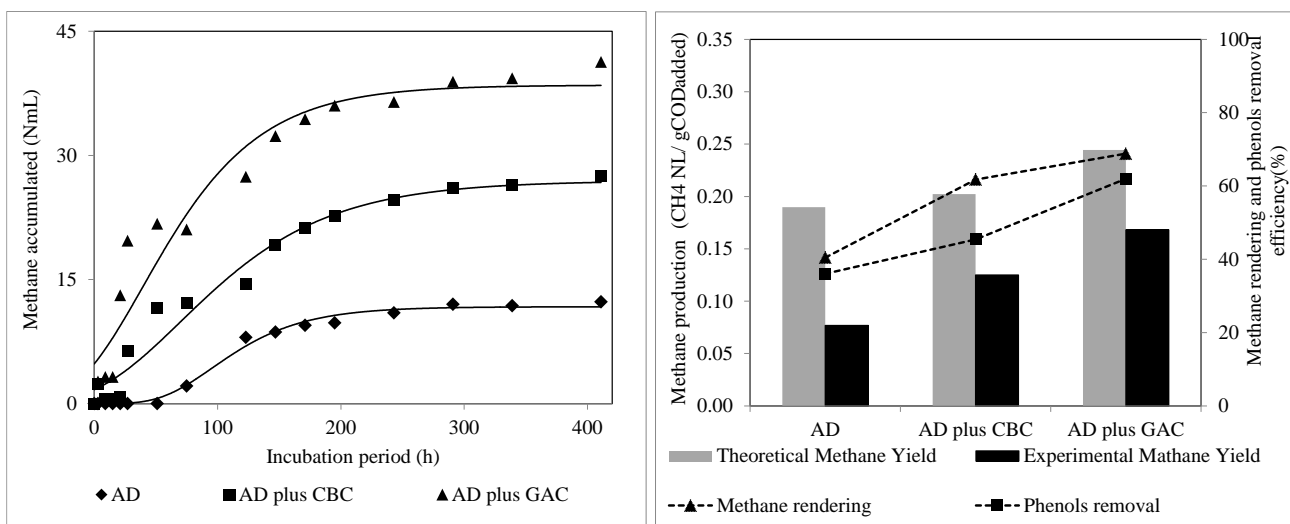
184 Even though the adaptation proved to increase COD degradation when working with recalcitrant compounds, its
 185 disadvantage is the time that this operational system requires to achieve efficient removal of the toxic compounds.
 186 Regarding this study, the third exposition enabled the comparison between both techniques acclimatization and use of
 187 adsorbents. It can be observed that using ASR as adsorbent in the AD assay managed a phenols removal efficiency of 45
 188 % during the third operational exposure. This removal efficiency was also achieved by Dias et al (2021) when anaerobic
 189 digesting PHWW of SCG in a similar system operation. However, Dias et al. [33] acclimatization technique required a
 190 longer adaptation period (seven consecutive batches) when in comparison to this study (three consecutive batches) to
 191 achieve similar phenols removal efficiency (around 45 %).

192 The phenol removal efficiency of 36 %, observed in the third exposure, represented an increase of 113 % when in
 193 comparison to the second exposure result. Regarding to the third exposure in the presence of ASR and GAC, the increase
 194 for the same parameter were, respectively, 169 % and 266 % when comparing to second exposure result. It can be
 195 concluded that adsorbents using, both the more traditional GAC and the economically viable ASR, can reduce
 196 acclimatization periods when working with recalcitrant wastewaters such as PHWW of SCG.

197 Regarding the third exposition, the COD removal efficiency values were 54 %, 58 %, and 70 % for, respectively,
 198 PHWW-AD itself, PHWW-AD plus ASR, and PHWW-AD plus GAC (**Table 3**). For the GAC and the ASR assays, a
 199 remarkable decrease in the COD was noticed due to instant adsorption (first 15-minutes of incubation). **Figure 1** shows
 200 that the maximum methane production was 12.3 ml, 27.6 ml, and 41.3 ml of CH₄ for PHWW-AD itself, PHWW-AD plus
 201 ASR, and PHWW-AD plus GAC, respectively, indicating that using ASR was beneficial and probably have contributed
 202 to increase methane production. However, no significant increase in the COD removal efficiency was observed when
 203 adding ASR. These results showed that biochar input increased methane rendering from 40 % to 60 %. In comparison,
 204 the GAC input has increased methane rendering from 40 % to 70 %, as indicates the results shown in **Table 4**.

205

206 Figure 1: (A) Methane production profile experimental data and exponential equation adjust. (B) Accumulated methane
 207 experimental potential and the theoretical methane potential (maximum)



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209

210

211 **Table 4.** Methane Yield and rendering, COD and phenols efficiency removal values for AD (Anaerobic digestion), AD
 212 plus ASR (AD plus biochar) and AD plus GAC (activated char) experimental sets

Experimental set	CH ₄ Yield (mLCH ₄ ·g ⁻¹ COD)	Theoretical CH ₄ Yield (mLCH ₄ ·g ⁻¹ COD)	CH ₄ rendering (%)	Modified Gompertz		
				k (NL·d ⁻¹)	Total CH ₄ (NmL)	lag (d)
AD	76.83	189.84	40.47	2.47	11.7	2.24
AD plus ASR	124.91	202.24	61.76	3.45	26.93	0.0489
AD plus GAC	168.18	244.44	68.80	6.28	38.48	-0.61

213
 214 Barakat et al. [36] found that syringaldehyde, HMF, furfural and vanillin at concentrations greater than 1 g L⁻¹ were
 215 inhibitory to methanogenesis activity, leading to an increment on the “lag” phase. Thus, the methane yield improvement
 216 can be related to the inhibition effect of some recalcitrant compounds diminishing, such as the phenols. Phenols removal
 217 efficiency increased from 36 % to 45 % and 62 % for the ASR and GAC assays. Likewise, Wang et al. [38] assessed the
 218 anaerobic digestion of municipal sludge PHWW and observed a boost in the methane produced potential when removing
 219 phenolic compounds from the aqueous phase throughout biochar detoxification. Accordingly, Torri and Fabbri [39] found,
 220 when anaerobically digesting aqueous fraction from pyrolysis, that the presence of biochar in the system decreased
 221 inhibition effects of recalcitrant compounds on methanogenesis and doubled methane yield from 34 ± 6% of the
 222 theoretical potential to 60 ± 15 % of the theoretical potential. In this study the methane yield went from 76.83 (40.5 % of
 223 theoretical) to 124.91(61.7 % of theoretical).

224 Regarding to the methane produced profile considering the incubation period, the same improvement trend
 225 observed for the methane yield, phenols and COD efficiency removals can be observed when comparing the values of k
 226 and λ (Modified Gompertz parameters) for the different assays. In the third exposition, k values resulted from the curve
 227 fitting were 2.47, 3.45, 6.28 NL·d⁻¹ for the PHWW-AD itself, PHWW-AD plus ASR, and PHWW-AD plus GAC assays.
 228 The “lag time”, λ is also shorter for the same assays (PHWW-AD plus ASR, and PHWW-AD plus GAC) when in
 229 comparison to the λ value of the AD assay with no adsorbent addition. The short lag phase of AD associated with
 230 adsorbents can also be attributed to its previous adaptation using lower concentrations of affluent and due to quick
 231 adsorptions of organic compounds by the adsorbents shown in **Table 4** and corroborated with Zhou et al. [13] results.

232 Many factors can influence toxicity during AD processes, including specific toxic concentrations (levels of
 233 inhibitory concentration vary widely for each toxic substance), biomass concentration, time of exposure to toxic
 234 substances, cell age, dietary pattern, acclimatization and temperature [16]. The inhibitors adsorption, the increasing
 235 buffering, the nutrient retention and the microbial immobilization are some of the biochar capacities and mechanisms that
 236 can be applied to overcome AD challenges. According to Pan et al. [40], the biochar addition to the chicken manure AD
 237 system contributed to accelerate the hydrolyze step. Furthermore, the authors reported that the organic matter and acid
 238 removal rates were increased by biochar Zhang et al. [41] observed that biochar addition relieved VFAs accumulation in
 239 the thermophilic pilot-scale CSTR when anaerobically digesting food wastes. According to Cai et al. [42] the higher
 240 degradation rate of VFAs, preventing VFAs accumulation can be associated to biochar ability to accelerate the
 241 development of electrical connections for direct transfer of electrons between species DIET. In the same way a wide range
 242 of authors reported a substantially VFA accumulation subdued/alleviated after biochar supplement [43].

243 Zhou et al. [13] also describes the adsorbent role as a buffer which holds a significant part toxic compounds,
 244 giving the opportunity to the microorganisms break down these compounds in a lower concentration and due to the
 245 difference of concentration created, gradually the adsorbent releases this to the aqueous. In addition, the adsorbent can

246 adsorb intermediate compounds such as volatile acids [44] in order to maintain the balance between acidogenesis-
247 acetogenesis and methanogenesis [45].

248 The biochar may also promote DIET, which is recognized by the transfer of electrons between microorganisms
249 without interfering with electron corridors, such as hydrogen in the process of anaerobic digestion. The DIET mechanism
250 has been shown to be more efficient in relation to energy analysis and methane production reaction times compared to
251 ordinary electron carriers [46,47]. In this way, the DIET mechanism facilitates the direct exchange of electrons between
252 syntrophic microbial communities of bacteria and methanogenic arteries, reducing the latency phase and improving the
253 production of methane, both in the quantity and quality of the biogas.

254 **Table 5** shows some adsorbents applicability to different wastewater and improvement regarding, where: (a)
255 maximum methane produced volume, (b) yield production, (c) “lag time” and (d) COD efficiency removal. All mentioned
256 studies in **Table 5** reported an improvement on biogas production. Even though there were differences in the biochar
257 (concentrations input, sources and activation process) and in the AD system (inoculums and main substrate), the PHWW-
258 AD facilitated by the ASR input showed improvements comparable to similar studies in the literature, being the ASR one
259 of the few originated from HTL as a residue.

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264
265**Table 5.** Anaerobic digestion of different complex wastewater enhanced by adsorbents addition, where (a) maximum methane produced volume, (b) yield production, (c) “lag time” and (d) COD efficiency removal.

Wastewater	AD conditions	Parameter (k)	Biochar Origin	Biochar input	Methane Yield	Improvement	Refs
Food wastes	37 °C, ISR of 0,8	0.040±0.002 mLCH ₄ /gVS/d	Pyrolysis of fruit woods at 800–900 °C	0.2 g/g waste	490.2±7.1 mL/gVSadded	33.3% (a); up to 54% (c)	[42]
Food waste	35 °C and pH of 7	156 mLCH ₄ /L/d	Pyrolysis of pine sawdust at 650 °C for 20 min.	8.3 g/L	1136 mL/ L	41.6% (a); 10% (b); 41 (c)	[48]
Activated sludge and food waste	35 °C and S/I at 1.5	9.4 mLCH ₄ /d	Pyrolysis of sawdust at 500 °C for 1.5 h.	6 g/L	116.2 mL	40.3% (a); 42.9% (b)	[49]
Lab-made with glucose	37 °C and pH of 7.8	-	Pyrolysis of ashes juniper at 400 °C for 30 min	10 g/L	330 ± 2 mL/gCOD	71%(b); 15% (d)	[50]
Algae-PHWW	37 °C and pH of 7.8	-		10 g/L	296 ± mL/gCOD	from 24 to 296 % (b)	
Lab-made with sucrose	UASB (15 kgCOD (m ³ ·d)	-	Pyrolysis of rice straw at 500 °C	4 g/L	-	from 89.6% to 98.2% (d); 28.6% (c)	[51]
beer lees	AD-Dry of 35 °C and I/S at 1:3	7386 ± 134 mL CH ₄ /d	Pyrolysis of cow manure at 500 °C for 4 hours	10 g/L	310.4 ± 9.2 mL/gVS	46.8% (b)	[52]
citrus peel wastes	37 °C o and I/S at 1:1	14.27 ± 0.28 LCH ₄ /kgSV/d	Production from vineyard prunings	10 g/L	196.87 ± 2.95 L/kgSV	33% (b)	[53]
citrus peel wastes	37 °C and I/S at 1:1	14.15 ± 0.28 LCH ₄ /kgSV/d		30 g/L	280.99 ± 4.21 L/kg SV	56% (b)	
Food wastes	55 °C of sludge to substrate 3.13	123.7 mL CH ₄ /gVS/d	Gasification of waste wood pellets from sawmill at 700–800 °C	6 g/L	786 mL/gVS	36% (a); 31% (b) e 33% (c)	[41]
Food waste and sludge (1:4)	35 °C	12.6 mLCH ₄ /d	Pyrolysis of sawdust waste at 300 °C	15 g/L	167.2 mL	66% (a); 6% (b); 25% (c)	[54]
Dry chicken manure	35 °C and CSTR reactor	-	Pyrolysis of discarded fruitwood at 550 °C	50 g/L	0.19 L/gVSadded	12% (b)	[43]
Mono-cardboard	-	-	Pyrolysis of sawdust at 500 °C for 1h	0.77 g/gTS	89.28 mL/gVS	40.6% (a)	[55]
Chicken manure	35 °C semi-continuous	-	Pyrolysis of orchard waste wood at 550 °C	-	-	33% (b)	[40]
PHWW of SCG	37 °C	3.45 LCH ₄ /h	Hydrothermal liquefaction of SCG at 275 °C for 10 min	2 g/L	124.91 mL	130,17% (a); 60% (b); 97,82%(c); 6,53% (d)	This study

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267

268 **4. Conclusion**

269 ASR showed the capacity of removing 443.3 ± 61.2 mgCOD g⁻¹ASR (56% of CAG removal capacity) and 33.2
 270 ± 24.5 mg phenols g⁻¹ASR (47% of GAC removal capacity) from the PHWW by adsorption. The ASR adsorption
 271 capacity proved to be potentially interesting as an alternative to the GAC use as adsorbent when anaerobic digesting
 272 PHWW. Both the ASR and the PHWW were co-produced by HTL process and their association, which is operationally
 273 practical and economically feasible, enhanced the anaerobic digestion of the PHWW soluble organic compounds,
 274 increasing COD removal efficiency from 54% (PHWW-AD) to 58% (PHWW-AD with ASR); increasing phenols
 275 removal efficiency from 36% (PHWW-AD) to 45% (PHWW-AD with ASR) and increasing Methane Yield from 77
 276 mLCH₄ gCOD⁻¹ (PHWW-AD) to 125 mLCH₄ gCOD⁻¹ (PHWW-AD with ASR). Furthermore, the ASR addition to the
 277 PHWW-AD process has contributed to the increase in the modified Gompertz parameter of methane production maximum
 278 rate in 40%. It was also concluded that PHWW and ASR co-digestion can potentially reduce inoculum acclimatization
 279 periods to the recalcitrance compounds of the PHWW.

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284

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