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Biochars intended for water filtration: A comparative study with activated carbons of their physicochemical properties and removal

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Biochars intended for water filtration: a comparative study with activated carbons of their physicochemical properties and removal efficiency towards neutral and anionic organic pollutants --Manuscript Draft--

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Abstract:	Seven biochars (BCs) obtained from pyrolysis or gasification of different vegetal feedstocks were thoroughly characterized in comparison with three commercial activated carbons (ACs) routinely used in drinking water treatment plants. BCs and ACs characterization included the determinations of ash, iodine and methylene blue adsorption indexes, and the release of metals and polycyclic aromatic hydrocarbons, which were performed according to international standards applied for adsorption media to be used in drinking waters. Total specific surface area, micropore and mesopore specific surface area, pH of the point of zero charge, and the release of polychlorinated biphenyls were also determined in all chars. Principal component analysis and cluster analysis were performed in order to summarize the complex set of information deriving from the aforementioned characterizations, highlighting the BC most similar (BC6 from high temperature gasification of woody biomass) and most different (BC7 from low-temperature pyrolysis of corn cob) from ACs. These BCs were studied for their adsorption in ultrapure water towards diiodoacetic acid (an emergent disinfection by-product), benzene, and 1,2-dichlorobenzene, in comparison with ACs, and results obtained were fitted by linearized Freundlich equation. Overall, BC6 showed higher sorption performances compared to BC7, even though both BCs were less performing sorbents than ACs. However, the sorption properties of BCs were maintained also in real water samples collected from drinking water treatment plants.
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Turin, 23 August 2021

**To the Attention of the Editor of
Chemosphere**

Dear Editor,

please find enclosed the manuscript entitled “*Biochars intended for water filtration: a comparative study with activated carbons of their physicochemical properties and removal efficiency towards neutral and anionic organic pollutants*” by M. Castiglioni, L. Rivoira, I. Ingrando, L. Meucci, R. Binetti, M. Fungi, A. El-Ghadraoui, Z. Bakari, M. Del Bubba, M.C. Bruzzoniti, which we would like to submit to *Chemosphere*.

The management of waste biomass to produce biochar (BC) as adsorbent for water treatment may be regarded as a “win-win” solution for pursuing circular economy principles.

The aim of our work is the in-depth characterization of seven BCs obtained from gasification or pyrolysis processes of waste vegetal biomass in comparison with a virgin commercial activated carbon (AC), a freshly regenerated AC, and a regenerated AC in use at a potabilization facility.

As a novel approach, the characterization for numerous parameters was accomplished according to international standards that require compliance for the treatment of drinking water (UNI-EN12915-1).

Worth to be mentioned that in the current literature it is not verified whether the BCs prepared in the various experimental conditions comply with the requirements set out in the UNI-EN12915-1. Finally, except in rare cases, no comparison with the adsorption capacity of standard ACs is provided by the literature. All these aspects represent obvious limitations in the reliable evaluation of the applicability of BCs for water treatment.

Specifically, all the BCs produced were characterized for adsorption parameters measuring iodine index as required by the UNI-EN12915-1 and methylene blue index as an additional indicator, only occasionally investigated by the current literature. Furthermore, the safety of BCs for being used in drinking water refinement processes, was assessed through the analysis of metals and PAHs in leachate as required by the UNI-EN12915-1, extending the analysis for the first time also to PCBs, which are pollutants not yet regulated by the standard, but which are possibly formed during the pyro-gasification processes.

Through a multivariate analysis the materials with the closest and the farthest characteristics to those of ACs were easily identified. The adsorption capabilities of the selected BCs were assessed towards model compounds of environmental interest. To elaborate, diiodoacetic acid (DIAA) was chosen as an emergent compound belonging to the haloacetic acids family (disinfection by-products of



potabilization plants); whereas benzene and 1,2-dichlorobenzene (volatile organic compounds, VOCs) were chosen since they are commonly monitored in drinking water facilities.

Despite the lower adsorption capacities of BCs in respect to ACs towards DIAA, BCs show good removal capabilities towards VOCs. Interestingly, for both DIAA and VOCs, the removal capabilities are not altered in the presence of real water withdrawn from the potabilization plant, supporting the design of column experiments for the achievement of a higher technology readiness level (TRL).

In our opinion the manuscript can address the interests of the readers of *Chemosphere* since it is targeted to a relevant issue with broad implications in *green/sustainable chemistry, toxic substances reduction and elimination, waste elimination and water management*.

The paper is not under consideration in any other journals.

Best regards

Prof. Dr. Maria Concetta Bruzzoniti

Biochars intended for water filtration: a comparative study with activated carbons of their physicochemical properties and removal efficiency towards neutral and anionic organic pollutants

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

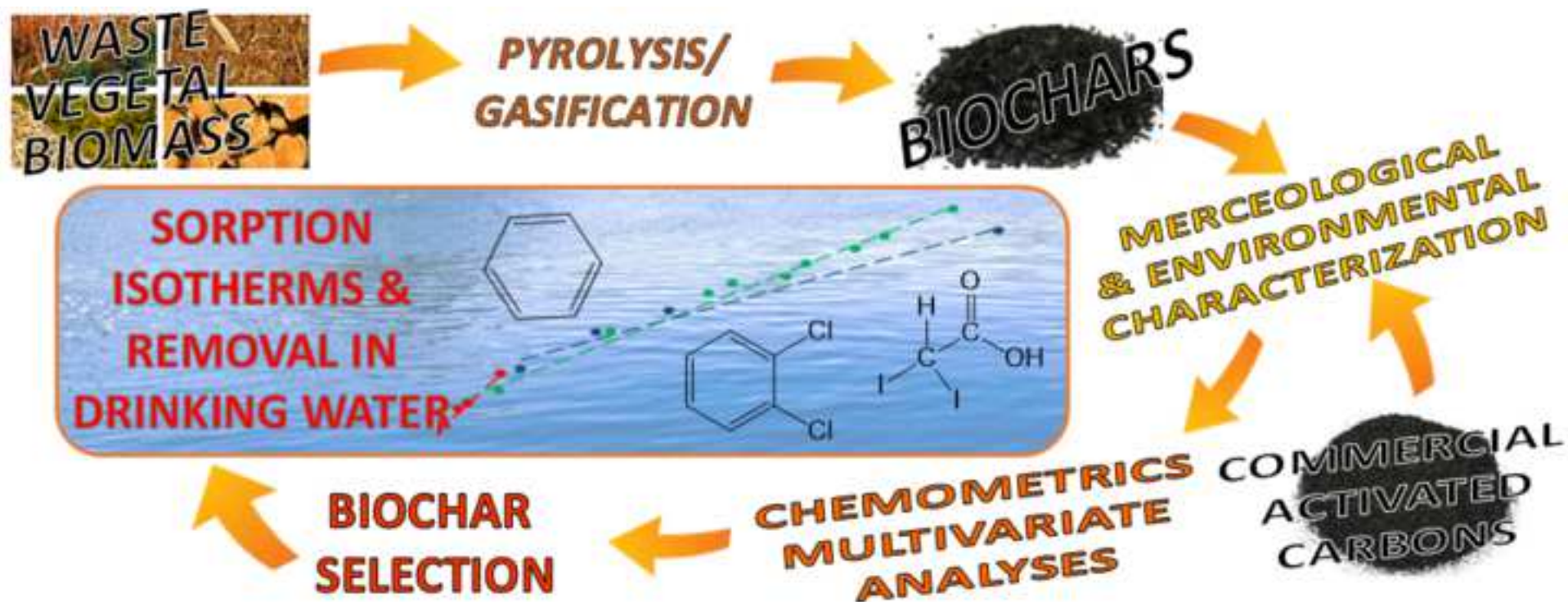
Torino, 23 August 2021

Signed

Professor Maria Concetta Bruzzoniti

Highlights (3 to 5 bullet points (maximum 85 characters including spaces per bullet point))

- Seven biochars (BCs) and three activated carbons (ACs) are characterized in depth
- Physicochemical and adsorption parameters of BCs and ACs were critically compared
- Ash, and metals and PAHs release of BCs are below the UNI EN 12915-1 Standard
- Multivariate chemometrics analyses are suitable for selecting the best BCs
- Hundreds ng/g diiodoacetic acid and low µg/g benzene/dichlorobenzene are removed



Biochars intended for water filtration: a comparative study with activated carbons of their physicochemical properties and removal efficiency towards neutral and anionic organic pollutants

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24 **Abstract**

25 Seven biochars (BCs) obtained from pyrolysis or gasification of different vegetal feedstocks were
26 thoroughly characterized in comparison with three commercial activated carbons (ACs) routinely
27 used in drinking water treatment plants. BCs and ACs characterization included the determinations
28 of ash, iodine and methylene blue adsorption indexes, and the release of metals and polycyclic
29 aromatic hydrocarbons, which were performed according to international standards applied for
30 adsorption media to be used in drinking waters. Total specific surface area, micropore and mesopore
31 specific surface area, pH of the point of zero charge, and the release of polychlorinated biphenyls
32 were also determined in all chars. Principal component analysis and cluster analysis were performed
33 in order to summarize the complex set of information deriving from the aforementioned
34 characterizations, highlighting the BC most similar (BC6 from high temperature gasification of
35 woody biomass) and most different (BC7 from low-temperature pyrolysis of corn cob) from ACs.
36 These BCs were studied for their adsorption in ultrapure water towards diiodoacetic acid (an emergent
37 disinfection by-product), benzene, and 1,2-dichlorobenzene, in comparison with ACs, and results
38 obtained were fitted by linearized Freundlich equation. Overall, BC6 showed higher sorption
39 performances compared to BC7, even though both BCs were less performing sorbents than ACs.
40 However, the sorption properties of BCs were maintained also in real water samples collected from
41 drinking water treatment plants.

42
43 **Keywords:** pyrolysis, gasification, filtration media, PAH and PCB release, metal release, drinking
44 water plant

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50 **1 Introduction**

51 Pollution by anthropic activities still affects the quality of water resources. According to the European
52 Water Framework Directive (2000/60/EU), waters must achieve good ecological and chemical status,
53 to protect human health, water supply, natural ecosystems and biodiversity (European Commission,
54 2010).

55 The accomplishment of the environmental objectives set by the European policies can be achieved
56 through proper integrated water management policies and technological approaches, which must be
57 sustainable from both environmental and economic points of view. Within this framework, water
58 treatments play significant and crucial roles in the supply of safe waters intended for human
59 consumption.

60 Adsorption is an effective and economically feasible approach for the removal of organic and
61 inorganic contaminants from waters (Ali and Gupta, 2006) that is routinely integrated in drinking
62 water production. Within this context, adsorption is generally based on the use of activated carbon
63 (Perrich, 2018), even though innovative sorbents, such as mesoporous silica (Kyzas and Matis, 2015;
64 Rivoira et al., 2016) or other waste-derived ceramic materials (Jana et al., 2016; Bruzzoniti et al.,
65 2018) have been proposed as alternative adsorption media. Low-cost materials like biochar (BC) have
66 recently received attention for their physicochemical characteristics including the porous structure,
67 which is similar to that of activated carbons. Biochar is the solid by-product of the thermal conversion
68 of a wide range of feedstocks, such as agricultural wastes (Ali and Gupta, 2006; Colantoni et al.,
69 2016), wood residues (Wang et al., 2013), manure (Cao and Harris, 2010), and sludge (Méndez et al.,
70 2017).

71 Due to its properties, biochar has found application as animal feed additives (McHenry, 2010) and
72 soil amenders (Singh et al., 2010), as well as for the adsorption of micropollutants from aqueous
73 matrices (Palansooriya et al., 2020).

74 Internationally recognized standards detailing the physicochemical characteristics of biochars to be
75 used for agricultural applications have been recently released (European Biochar Foundation (EBC)).

76 Similar standards have not yet been established on the characteristics required for biochars to be used
77 in water purification. However, international standards are available that require compliance with
78 specific limits for certain physical and chemical parameters in adsorbent materials (Comite Europeen
79 de Normalisation (CEN), 2004), and particularly in activated carbons (Comite Europeen de
80 Normalisation (CEN), 2009), used for the treatment of drinking water.

81 In the last years, biochars obtained from a very wide range of experimental conditions (e.g. feedstock,
82 thermo-chemical process and pretreatment of biomass and/or post-treatment of biochar) were
83 investigated as sorbent media for water purification issues, highlighting their promising adsorption
84 properties towards a large variety of organic and inorganic contaminants (Gwenzi et al., 2017; Wang
85 et al., 2020). However, it should be emphasized that, with few exceptions (Del Bubba et al., 2020) it
86 is not verified whether the biochars prepared in the various experimental conditions comply with the
87 requirements set out in the aforementioned standards, relating to the adsorbent materials intended to
88 be used for the filtration of drinking water. Moreover, in most cases, ultrapure water is used to
89 investigate sorption capabilities of biochars, whilst it would be advisable to perform these studies
90 using real aqueous matrixes. Last but not least, except in rare cases (Del Bubba et al., 2020), no
91 comparison has been made with the adsorption capacity of standard activated carbons (ACs). All
92 these aspects represent obvious limitations in the reliable evaluation of the applicability of biochars
93 for water treatment (Castiglioni et al., 2021).

94 Based on the considerations mentioned above, the aim of this research was to investigate the
95 physicochemical properties, the regulated leachable substances, and the removal performances of
96 seven biochars (commercially available or synthesized for the purpose), obtained from pyrolysis or
97 gasification of vegetal biomass, in comparison with three commercially available vegetal ACs used
98 in an Italian drinking water facility, at different age of operation. Data obtained were chemometrically
99 treated through principal component analysis, allowing for selecting the most promising biochars to
100 be further investigated by adsorption tests. In a first phase of this study, adsorption capabilities were
101 tested in ultrapure water, whereas afterwards the sorption capacity was evaluated on a restricted group

of biochars in water samples collected at intermediate treatment stages of a potabilization plant. In all cases ACs were also tested as reference comparative materials.

Diiodoacetic acid (DIAA), benzene, and 1,2 dichlorobenzene, were selected as model pollutants commonly monitored in drinking water facilities. Specifically, DIAA is a model emerging disinfection by-product (Bruzzoniti et al., 2019b) never investigated before for its sorption by biochars. Moreover, 1,2 dichlorobenzene can also originate from disinfection treatments during the potabilization process (Lahaniatis et al., 1994; Hou et al., 2012) and its monitoring in tap water is recommended by the World Health Organization guidelines (taste threshold value $1 \mu\text{g L}^{-1}$) (World Health Organization, 2017), while benzene is regulated by the Directive 2020/2184 regarding the quality of water intended for human consumption ($1 \mu\text{g L}^{-1}$). It should also be noted that benzene and 1,2 dichlorobenzene are volatile organic carbons (VOCs) still detected in some industrial districts (Martínez et al., 2002) and are therefore also important from the wastewater treatment viewpoint.

2 Materials and methods

2.1 Reagents

For the determination of adsorption indexes, the following reagents, supplied by Merck (Kenilworth, NJ, USA), were used: iodine solution (0.1 N), sodium thiosulfate solution (0.1 N), zinc iodide starch solution, hydrochloric acid (37%), potassium hexacyanoferrate (>99%), methylene blue, anhydrous acetic acid (>99.8%). Ammonia solution (28%), dichloromethane and 2-propanol were from VWR International (Radnor, PA, USA). For the evaluation of extractable metals, an ICP multi-element standard solution IX (100 mg L^{-1} of As, Be, Cd, Cr (VI), Ni, Pb, Se, Tl) from Merck was used.

For the determination of extractable polycyclic aromatic hydrocarbons (PAHs), the 16 compounds listed by EPA were purchased from Sigma Aldrich (Darmstadt, Germany). For the analysis of extractable polychlorinated biphenyls (PCBs), the compounds were purchased from LGC Standards (Milan, Italy). They were non dioxin-like PCBs: 3,3'-dichlorobiphenyl (PCB 11), 4,4'-dichlorobiphenyl (PCB 15), 2,4,4'-trichlorobiphenyl (PCB 28), 2,2',5,5'-tetrachlorobiphenyl (PCB 52), 2,2',4,5,5'-pentachlorobiphenyl (PCB 101), 2,2',3,4,4',5-hexachlorobiphenyl (PCB 138),

128 2,2',4,4',5,5'-hexachlorobiphenyl (PCB 153), 3,3',4,4',5,5'-hexachlorobiphenyl (PCB 169),
 129 2,2',3,4,4',5,5'-heptachlorobiphenyl (PCB 180), 2,3,3',4,4',5,5'-heptachlorobiphenyl (PCB 189);
 130 and dioxin-like PCBs: 3,4,4',5-tetrachlorobiphenyl (PCB 81), 2,3',4,4',5-pentachlorobiphenyl (PCB
 131 118), 2',3,4,4',5-pentachlorobiphenyl (PCB 123), 2,3',4,4',5,5'-hexachlorobiphenyl (PCB 167).
 132 Labelled isotope compounds for PCBs (2 mg L⁻¹) and for PAHs (5 mg L⁻¹), Wellington Laboratories
 133 (Ontario, Canada), were used as internal and surrogate standards in order to obtain calibration curves
 134 and extraction recoveries, respectively. The ¹³C surrogate solutions of PAHs contained:
 135 [¹³C₆]benzo(a)anthracene [¹³C₆-BaA], [¹³C₆]chrysene [¹³C₆-Chr], [¹³C₆]benzo(b)fluoranthene [¹³C₆-
 136 BbFl], [¹³C₆]benzo(k)fluoranthene [¹³C₆-BkFl], [¹³C₄]benzo(a)pyrene [¹³C₄-BaP],
 137 [¹³C₆]indeno(1,2,3-cd)pyrene [¹³C₄-Ind], [¹³C₆]dibenzo(a,h)anthracene [¹³C₆-DBA], and
 138 [¹³C₁₂]benzo(g,h,i)perylene [¹³C₁₂-BP]. The ¹³C surrogate solution of PCBs contained: ¹³C₁₂-PCB28,
 139 ¹³C₁₂-PCB52, ¹³C₁₂-PCB118, ¹³C₁₂-PCB153, and ¹³C₁₂-PCB180.

140 Volatile organic compounds, namely benzene (100 µg L⁻¹ in methanol), and 1,2-dichlorobenzene
 141 (100 µg L⁻¹ in methanol), were purchased from Ultra Scientific Italia (Bologna, Italy). DIAA was
 142 supplied by Chemical Research (Rome, Italy). Ultrapure water was obtained by an EMD Millipore
 143 Milli-Q Direct Water Purification System (Millipore, Bedford, MA, USA).

144 2.2 Biochar and activated carbon samples

145 The seven BCs considered in this study were donated for the purpose. The three ACs were supplied
 146 by a local potabilization plant at different age of operation: AC1: new activated carbon; AC2:
 147 regenerated activated carbon; AC3: regenerated activated carbon in use at the plant. The status of
 148 operation, and the characteristics of the feedstock and the thermal process used to produce the ten
 149 chars are summarized in **Table 1**.

150 Before being characterized and used in isotherm studies, all the char samples were repeatedly washed
 151 with ultrapure water according to the ASTM D-5919-96 method.

152 2.3 Biochar and activated carbon characterization

153 The chars investigated in this study were physicochemically characterized through the determination
154 of ash content, pH of the point of zero-charge (pH_{pzc}), physisorption analysis, iodine and methylene
155 blue adsorption indexes (I_2In and MBIn), as well as for water-extractable substances of environmental
156 concern. The procedures adopted for the aforementioned determinations are briefly described below,
157 whilst full details are provided in the *Supplementary Material* section.

158 2.3.1 Ash content

159 The ash content was determined according to the ASTM International D 2866-11 (American Standard
160 Test Method (ASTM), 2018), which refers to the analysis of ACs.

161 2.3.2 Water-extractable substances

162 Metals (namely Sb, As, Cd, Cr, Pb, Hg, Ni and Se), PAHs and PCBs were extracted according to the
163 EN 12902 standard (Comite Europeen de Normalisation (CEN), 2004). After extraction, metals were
164 determined by an Elan 6100 ICP-MS (Perkin Elmer, Waltham, Massachusetts, USA), whereas PAHs
165 and PCBs were preconcentrated by solid-phase extraction (SPE) and analysed by GC-MS, as
166 elsewhere described (Bruzzoniti et al., 2019a; Rivoira et al., 2019). Quality controls were performed
167 to verify the recovery efficiency of PAHs and PCBs during the preconcentration step, using labelled
168 standards, as specified in the *Supplementary material* (see **Tables S1** for BCs and **S2** for ACs).

169 2.3.3 pH of the point of zero charge

170 The pH of the point of zero-charge (pH_{pzc}) was determined using the pH drift method, widely adopted
171 for the evaluation of the surface charge of biochars and ACs (Del Bubba et al., 2020).

172 2.3.4 Adsorption indexes

173 The determination of I_2In and MBIn was performed according to the definitions indicated by CEFIC
174 for ACs (Conseil Européen des Fédérations de l'Industrie Chimique (CEFIC), 1986).

175 2.3.5 Physisorption analysis

176 Physisorption analysis of biochars and ACs was performed via nitrogen adsorption and desorption
177 experiments using a Porosity Analyser Thermo Fisher Scientific (Milan, Italy) model
178 SORPTOMATIC 1990 according to the American Society for Testing and Materials specifications

179 (American Society for Testing and Materials, 2012, 2017). In further detail, the specific surface area
180 (SSA) and micropore surface area (MiSSA) were determined respectively by the Brunauer–Emmett–
181 Teller (BET) method and by t-plot method, whereas mesopore surface area (MeSSA) was measured
182 by the Barrett-Joyner-Halenda (BJH) method applied to desorption data.

183 2.4 Adsorption studies on DIAA and VOCs

184 Adsorption tests were performed on DIAA and VOCs in ultrapure water ($\text{pH} = 6.5 \pm 0.1$) using the
185 micro-isotherm technique for adsorbates at ppb concentrations, as established by ASTM D5919-96
186 standard (American Standard Test Method (ASTM), 1996). Aliquots of 40 mL and 100 mL,
187 containing fixed amounts of DIAA and VOCs, respectively (DIAA: $5 \mu\text{g L}^{-1}$ for BCs and $20 \mu\text{g L}^{-1}$
188 for ACs; VOCs: $5 \mu\text{g L}^{-1}$ or $20 \mu\text{g L}^{-1}$ for BCs and $20 \mu\text{g L}^{-1}$ for ACs) were put in contact with
189 different amounts of BCs/ACs varying approximately between 0.02 and 0.5 g. The mixture was
190 stirred in an orbital shaker for 24 hours. The solution was then filtered through a mixed cellulose ester
191 membrane ($0.45 \mu\text{m}$). Control experiments using the same aforementioned concentrations of target
192 analytes were also conducted without the addition of the adsorbent materials, in order to estimate
193 their removal due to mechanisms other than sorption (e.g. volatilization and degradation).

194 Experimental data were fitted by the Freundlich isotherm model (Foo and Hameed, 2010):

$$195 \quad \log \frac{X}{M} = \log K_F + \frac{1}{n} \log C_e$$

196 Where X/M is the ratio of the amount of analyte adsorbed per mass unit of sorbent (mg g^{-1}), K_F is the
197 constant of the Freundlich isotherm equation ($\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$) related to adsorption capacity, C_e is
198 the equilibrium concentration (mg L^{-1}), and $1/n$ is the exponent of non-linearity.

199 2.5 Analytical determination of DIAA and VOCs

200 Residual DIAA concentrations were determined by ion chromatography coupled with triple-stage
201 quadrupole mass spectrometry as elsewhere described (Bruzzoniti et al., 2019b). Residual VOC
202 concentrations were determined by GC-MS after SPE. Details of both procedures are given in the
203 *Supplementary Material Section*.

204 2.6 Water sample collection and characterization

205 Water samples were withdrawn from two potabilization plants located in the Piedmont region (North
206 Italy) which treat the same raw water. One sample (labelled as DSB) was taken at the outlet of the
207 dynamic separation basins for the removal of slurry from clarified waters (in which coagulant,
208 hypochlorite and chlorine dioxide solutions are dosed), before entering the activated carbon beds. The
209 other sample (labelled as CB) was taken at the outlet of a clarification basin (in which coagulant only
210 is added), before entering the activated carbon beds. The water samples were characterized for pH
211 and total organic carbon (TOC). TOC was determined using a Shimadzu TOC-V-CSH analyser, by
212 the differential method, i.e. analysing both total carbon (TC) and total inorganic carbon (TIC) through
213 separate measurements and calculating TOC by subtracting TIC from TC.

214 2.7 Data analysis

215 Least squares regressions and related analyses of variance (ANOVA) were performed with Excel
216 2016 (Microsoft, Redmond, WA, USA). Principal component analysis (PCA) and cluster analysis
217 (CA) were carried out using the Minitab statistical software package, version 17.1.0 (Minitab Inc.,
218 State College, PA, USA). All data plots were performed using Excel 2016.

219 3 Results and discussion

220 3.1 Characterization of chars

221 3.1.1 Ash content

222 In biochars, ash percentages were found in the quite wide range of 6-49% (**Table 2**), with the lowest
223 value achieved for BC7, which derived from corn cob under pyrolysis treatment at 450°C (**Table 1**).
224 Ash content in materials intended for water filtration is regulated by EN 12915-1 standard, which sets
225 a limit of 15%, since a high ash content in filtering media is expected to reduce adsorption activity
226 (Inyang and Dickenson, 2015). Hence, as regards this parameter, only BC2, BC3, and as previously
227 mentioned BC7, are allowed to be used as sorbent materials in potabilization facilities.

228 The data obtained here can be interpreted based on the characteristics of biomass and thermal
229 conversion processes through which the chars were obtained. According to literature, ash

230 concentration of chars is mainly influenced by the type of feedstock, being woody biomass the one
231 providing a lower ash content, compared to other feedstocks, such as non-woody vegetal biomass and
232 animal waste (Tomczyk et al., 2020). However, the type of thermal conversion process (i.e. pyrolysis
233 or gasification) and the temperature and contact time conditions adopted in the process may also play
234 a role in determining the ash concentration, which obviously depends on the amount of char obtained.
235 In this regard, it should be remarked that biochar yield is a function of the type of thermal conversion
236 process (i.e. pyrolysis or gasification) and the temperature and contact time conditions adopted in the
237 process, being the highest yields obtained with pyrolysis conducted at low temperature and high
238 contact time (slow pyrolysis) (Inyang and Dickenson, 2015). Hence, it is evident that, if the same
239 feedstock is used, the ash concentration will be higher in gasification processes than in pyrolysis
240 (Fryda and Visser, 2015). Moreover, increasing ash percentages will be obtained with increasing
241 temperature (Rafiq et al., 2016) and higher ash concentrations will be found under fast pyrolysis
242 conditions (Brewer et al., 2009). Based on these considerations, it makes sense that BC2, BC3, and
243 BC7, all deriving from slow pyrolysis processes (**Table 1**), showed ash percentages much lower than
244 BC5 and BC6, which were conversely obtained under gasification conditions using a same patented
245 process and plant. The very high ash concentration found in BC4 (about 29%) compared to BC3, both
246 produced with the patented PYREG® pyrolysis process under the same experimental conditions,
247 could be attributed to the different nature of the feedstocks employed, i.e. non woody vegetal biomass
248 for BC4 and woody waste biomass for BC3 (**Table 1**). Finally, the unexpected high ash content of
249 BC1 probably depends on the peculiar characteristics of the woody waste used as feedstock, which
250 derives from the cutting of a forest planted for the phytoremediation of a soil contaminated by
251 different chemicals, including heavy metals. Virgin activated carbon (AC1) showed a lower ash
252 content (7%), in agreement with the high standard quality requested by the potabilization plant in its
253 specifications. Higher ash percentages were obviously found in regenerated and in-use ACs (i.e. AC2
254 and AC3).

255 3.1.2 Water-extractable substances

256 The thermal conversion process that transforms biomasses into chars may lead to the formation of
257 unwanted organic and inorganic hazardous species, depending on the original composition of the
258 feedstocks. Among them, PAHs (Wang et al., 2017), PCBs (European Biochar Foundation (EBC))
259 and heavy metals (Lievens et al., 2009) can be present in biochars, thus introducing possible limitation
260 in the use of the chars themselves. The EN 12915-1 normative regulates the presence of water
261 extractable pollutants in materials to be applied for water treatments, setting a threshold concentration
262 limit for the sum of six PAH compounds (i.e. fluoranthene, benzo(b)fluoranthene,
263 benzo(k)fluoranthene, benzo(a)pyrene, benzo(g,h,i)perylene and indeno-(1,2,3-cd)-pyrene) at 0.02
264 $\mu\text{g L}^{-1}$. In addition, the EN standard imposes limits to the presence of As ($10 \mu\text{g L}^{-1}$), Cd ($0.5 \mu\text{g L}^{-1}$),
265 Cr ($5 \mu\text{g L}^{-1}$), Hg ($0.3 \mu\text{g L}^{-1}$) Ni ($15 \mu\text{g L}^{-1}$), Pb ($5 \mu\text{g L}^{-1}$), Sb ($3 \mu\text{g L}^{-1}$) and Se ($3 \mu\text{g L}^{-1}$). As
266 regards PCBs, no limit is currently established by the EN standard. However, it should be mentioned
267 that PCB concentrations are regulated in biochars to be used for soil conditioning and feed additives
268 (European Biochar Foundation (EBC); International Biochar Initiative, 2015).

269 Results obtained for leachable PAHs showed that all the chars fulfil the limits set by EN 12915-1
270 regulation. In detail, the regulated PAHs were detected in BC1, BC2, BC3, BC4, and BC7 (all
271 deriving from pyrolysis), with the sum of their concentrations ranging from 1.6 ng L^{-1} (BC4) to 13.3
272 ng L^{-1} (BC7). Conversely, for ACs and the other BCs, the concentrations of PAHs included in the EN
273 standard were below detection limits (**Table S3** of the *Supplementary material*).

274 EPA PAHs other than the ones included in the EN standards were also determined (see **Table S3**),
275 highlighting that PAHs with 2-3 aromatic rings were generally more abundant than those with higher
276 molecular weight, as also observed elsewhere (Lyu et al., 2016). BC7, which was produced under
277 pyrolysis at the lowest temperature (450°C), was the material providing by far the highest total
278 leachable PAH concentration (826 ng L^{-1}), while biochars obtained under gasification conditions
279 showed the lowest PAHs release ($11\text{-}12 \text{ ng L}^{-1}$). These BCs were also the ones providing respectively
280 the highest and the lowest benzo(a)pyrene equivalent concentrations (BaPy_{eq}), based on toxic

281 equivalence factors (TEFs) available in literature (Berardi et al., 2019). PAHs occurrence in BCs can
282 be explained based on re-polymerization phenomena of the radical hydrocarbon fragments formed
283 during the thermal process, which are favoured by the absence of oxygen. Moreover, the presence of
284 PAHs depends also on the conversion temperature adopted, which plays a main role in PAH
285 formation up to about 500°C, but also in their degradation beyond this value (Parker et al., 2014; Lyu
286 et al., 2016). An influence of the biomass composition in the presence of leachable PAHs can also be
287 evidenced from the comparison of BC3 (321 ng L⁻¹) and BC4 (26 ng L⁻¹), which were obtained under
288 exactly the same pyrolysis conditions, but with completely different feedstocks.

289 The concentrations of extractable PCBs found in the BCs and ACs leachate are reported in **Table S4**
290 of the *Supplementary material*. BC1 was the only char exhibiting the presence of all the PCBs
291 investigated in its leachate, with total concentration of about 96 ng L⁻¹. Conversely, all the other BCs
292 showed PCB15 as the only leachable chlorinated biphenyl, the concentration of which was in the low
293 ng L⁻¹ range (0.56-2.8 ng L⁻¹) in BC2, BC3, and BC4 and about one order of magnitude higher (21.7-
294 29 ng L⁻¹) in BC5 and BC6. PCBs occurrence in the BC leachate could be ascribed to the thermal
295 transformation of chloride, originally contained in feedstocks (Reed) and in this regard, it should be
296 recalled that BC1 has been prepared with wood waste deriving from a multi-contaminated soil. To
297 the best of our knowledge, this is the first study investigating PCBs in BC leachates, thus preventing
298 any comparison with literature data.

299 The concentrations of metals determined in BC leachates are illustrated in **Table S5** of the
300 *Supplementary material*, where the limits set by UNI EN 12915-1 are also reported. BCs generally
301 complied with the release limits set by the aforementioned regulation, with the only exception of
302 BC1, which exceeded the limit for Cr, with an observed concentration (17.3 µg L⁻¹) three times higher
303 than this limit, in agreement with the considerations previously reported. As regards ACs, only AC3
304 exceeded limit for Se (5 µg L⁻¹ versus 3 µg L⁻¹, see **Table S5**), suggesting that a possible saturation
305 of adsorption sites occurred during service.

306 3.1.3 *pH of the point of zero charge*

307 The values of pH_{pzc} were characterized by a high variability (7.0-12.0), in agreement with the wide
308 range of the production conditions, including the type of feedstock that, as already reported in
309 literature, significantly influence this property (Ippolito et al., 2020). For BCs, a significant linear
310 correlation with positive slope was found by plotting ash concentrations as a function of pH_{pzc} values
311 ($R^2 = 0.780$, $P < 0.05$). This correlation can be ascribed to the ash composition typically reported in
312 literature (Ippolito et al., 2020), which mainly consists in metals present in the hydroxide form, thus
313 promoting the increase of the pH in solution. ACs did not follow this trend, as the higher the amount
314 of ash, the lower the pH_{pzc} observed. This finding is in agreement with the increasing amount of
315 chemicals other than organic carbon adsorbed by ACs during operation, which however do not
316 influence the alkalinity of material surfaces.

317 The measurement of the pH_{pzc} values allowed us to make some considerations about the net surface
318 charge of the chars, which mainly depends on the surface functional groups of the material and is
319 extremely useful to explain the adsorption behaviours of BCs towards ionized or ionisable
320 compounds. Most BCs (with the only exception of BC7) exhibited pH_{pzc} higher than pH values of
321 drinking water collected before entering AC filters of the aforementioned potabilization plants, which
322 ranged between 7.6 and 7.7. Hence, BC1-BC6 are expected to exhibit positively charged surfaces
323 when they were applied to the treatment of these waters, whereas BC7 is supposed to be negatively
324 charged (Li et al., 2017).

325 3.1.4 *Adsorption indexes of chars*

326 The adsorption efficiency of the BCs was evaluated in comparison with ACs through the
327 determination of I_2In and MBIn (**Table 2**).

328 I_2In is commonly considered as related to the presence in the structure of micropores (average
329 diameter less than 2 nm) and should be therefore informative for the removal efficiency of small-size
330 organic water pollutants (Del Bubba et al., 2020). Conversely, MBIn should be associated to the
331 abundance of mesopores (average diameter in the range 2-50 nm) and thus considered as a useful

indicator of adsorption capacity towards medium-large sized organic pollutants (Del Bubba et al., 2020). For BCs, the I_2In was found in the range 77-197 mg I_2 g⁻¹, with BCs obtained from gasification (i.e. BC5 and BC6) showing the highest values (156-197 mg I_2 g⁻¹), while the lowest ones (77-88 mg I_2 g⁻¹) were exhibited by materials produced under pyrolytic conditions (i.e. BC3 and BC7). The range determined for I_2In in BCs was about five times lower than that determined in virgin and regenerated ACs (i.e. AC1 and AC2), ranging between 540 and 1010 mg I_2 g⁻¹. As expected, the I_2In of AC3 (i.e. AC2 after some use in the potabilization plant) was lower than that of AC2 (438 mg I_2 g⁻¹), in agreement with the progressive pore saturation phenomena occurring during operation.

The MBIn showed a trend within the BCs and ACs clusters, and among them, similar to that described for I_2In (e.g. higher values for ACs than BCs and for BC5 and BC6 compared to the other BCs). Accordingly, as illustrated by **Figure S1** of the *Supplementary material*, the two indexes showed a very good linear correlation ($R^2 = 0.945$, $P < 0.05$), in agreement with findings observed elsewhere for different types of ACs and BCs (Del Bubba et al., 2020), even though a lower determination coefficient was observed by excluding ACs from the correlation ($R^2 = 0.534$, $P = 0.062$). The much lower correlation was mainly ascribable to the opposite trend observed for some pairs of materials, such as BC5 and BC6, the latter exhibiting lower MBIn but higher I_2In than the former. These findings can be explained by the general differences in micro, meso, and macroporosity distributions of BCs due to the different experimental conditions adopted for their production.

3.1.5 Physisorption analysis

Table 2 illustrated the results obtained for the porosimetry analyses (i.e. BET SSA, t-plot MiSSA and BJH desorption cumulative MeSSA) of the investigated BCs and ACs.

As expected, ACs exhibited much higher values of the SSA (561-1053 m² g⁻¹) than BCs (136-309 m² g⁻¹), being the latter group characterized by a data trend similar to those observed for adsorption indexes. To elaborate, BC5 and BC6, in addition to showing greater values of the adsorption indexes, also exhibited the highest SSA, whereas BC7 had the lowest values of the aforementioned parameters. These findings can be explained by the well-recognized role of temperature in increasing the surface

358 area (Liu et al., 2010; Ahmad et al., 2014), since BC5/BC6 and BC7 were obtained by the highest
359 and lowest conversion temperature, respectively (**Table 1**). Indeed, very good linear correlations (R^2
360 = 0.981-0.984, $P < 0.05$) were observed between SSA and adsorption indexes (see **Figures S2-A** and
361 **S2-B** of the *Supplementary material*), even excluding ACs from the regression ($R^2 = 0.781-0.904$,
362 data not shown).

363 In general, BCs showed a higher percentage of macroporosity than ACs. However, it should be noted
364 that BC3 and BC4, produced with the same patented PYREG® pyrolysis system, had a very small
365 microporosity, comparable to that observed in ACs. The relative percentages of microporosity and
366 mesoporosity were comparable in all materials, with the exception of AC1, which was strongly
367 characterized by microporosity. Moreover, high correlations were found between MiSSA and I_2In
368 ($R^2 = 0.972$, $P < 0.05$), as well as between the MeSSA and MBIn ($R^2 = 0.922$, $P < 0.05$) (**Figs. S2-C**
369 **and S2-D**). However, similarly to findings observed for the correlation between adsorption indexes,
370 also these relationships were mainly driven by the presence of ACs, since their exclusion strongly
371 lowered the determination coefficients, making null the significance of the correlation (data not
372 shown).

373 Differently from adsorption indexes, SSA is often reported as fundamental parameter for the
374 characterization of sorption properties of BCs. In order to understand the overall significance of SSA
375 data obtained here, it is therefore interesting to compare them with the values reported in literature
376 for the numerous biochars obtained from vegetal feedstocks. However, the kind of conversion
377 process, its temperature and time, as well as the type of biomass used, strongly affects the SSA of
378 BCs. Accordingly, this comparison was restricted to biochars obtained from woody vegetal
379 feedstocks, which represent the main type of biomass used for the production of BCs here
380 investigated, obtaining SSA values in the range 2-637 $m^2 g^{-1}$ (Chen et al., 2016; Hansen et al., 2016;
381 Chen et al., 2019; Grojzdek et al., 2021). Therefore, the SSA values between 136 and 309 $m^2 g^{-1}$
382 measured in this study are fully in the range reported in the literature.

383 3.2 Principal component analysis of the char characterization parameters

384 To summarize the wide group of information discussed above, deriving from the determination of the
385 several characterization parameters in the ten char samples, a multivariate elaboration of the
386 autoscaled original data was performed by means of PCA. In more detail, PCA elaboration included
387 the following eleven parameters: conversion temperature (T), the seven parameters reported in **Table**
388 **2** (i.e. ash, pH_{pzc}, SSA, MiSSA, MeSSA, I₂In, and MBIn), total PAHs (expressed as BaPy TEF
389 concentrations), total PCBs, and total metals. Three principal components (PCs), characterized by
390 eigenvalues > 1 and accounting for percentages of explained variances (E.V.) of 54.9%, 26.4%, and
391 11.0%, were obtained (total E.V. = 92.3%). **Figure 1** illustrates the plots of scores (**Fig. 1A-B**) and
392 loadings (**Fig. 1C-D**) of PC1 versus PC2 and PC1 versus PC3, which represent E.V. of 81.3% and
393 65.9%, respectively. The contributions of each variable to the three significant PCs were not always
394 well differentiated, even though most original variables showed remarkably different absolute values
395 of loadings among the three components. In more detail, SSA, MiSSA, MeSSA, I₂In, and MBIn
396 contributed mainly in PC1, pH_{pzc} and above all ash were mainly represented on PC2, whilst total
397 PCBs exhibited by far the highest loading on PC3. Conversely, T was represented in PC1 and PC3 to
398 the same extent, whereas total PAHs and metals contributed almost equally to PC2 and PC3. Among
399 the ten investigated chars, ACs clustered in both score plots, mainly due to their peculiar
400 characteristics in terms of adsorption indexes and physisorption data. BC5 and BC6, which derived
401 from the same gasification process, also clustered in both score plots mostly because of the
402 particularly high values of ash and very low leachable concentrations of total PAHs. Actually, BC6
403 was the closest char to the AC cluster, suggesting interesting adsorption properties. This consideration
404 points out that PCA is a valuable tool to select the best sorbents for adsorption measurements, when
405 one or more reference materials are included in the unsupervised multivariate analysis as
406 comparators. BC2, BC3, and BC4 identified a further cluster in both score plots. Conversely, BC1
407 and BC7 behaved as outliers, being they quite distant from the other BCs and the farthest from ACs,
408 due to their peculiar values of the coordinates on PC2 and PC3. In fact, their scores, were mainly
409 governed by the concentration values of ash (the highest in BC1 and the lowest in BC7), total PAHs

410 (intermediate value for BC1 and the highest one for BC7), and total metals (the highest in BC1 and
411 the lowest in BC7), which strongly contributed to these PCs.

412 In order to have a quantitative confirmation of the findings of PCA, CA was carried out, by using the
413 complete linkage method and the Euclidean distances on the autoscaled values of the aforementioned
414 eleven variables (**Figure 2**). The dendrogram confirmed the results of PCA, especially for BC2, BC3,
415 and BC4, for BC5 and BC6, and for AC1 and AC2, which were grouped in three clusters at similarity
416 percentages higher than 75%. It is also worth noting that BC5 and BC6 clustered with AC2 and AC3
417 with a similarity of about 50%. CA also highlighted the high distance between the virgin activated
418 carbon (AC1) and the regenerated ones (AC1 and AC2), which exhibited a very low degree of
419 similarity (about 20%).

420 Based on the results of the multivariate characterization of BCs and ACs and their summarising
421 picture obtained by PCA and CA, BC6 and BC7 were selected for the successive adsorption studies,
422 as the closest and the farthest materials to the ACs cluster, respectively. Within this latter group, the
423 virgin (AC1) and the regenerated (AC2) activated carbon were chosen as comparators.

424 3.3 Adsorption studies on DIAA and VOCs

425 Adsorption isotherm experiments were performed on BC6, BC7, AC1, and AC2, using the anion
426 DIAA and the neutral VOCs benzene and 1,2-dichlorobenzene in order to (i) hypothesize possible
427 retention mechanisms of BCs (Inyang and Dickenson, 2015) and (ii) estimate sorption capacity of
428 chars towards these pollutants, which are of environmental concern, *per se*.

429 3.3.1 DIAA

430 As regards DIAA, at 5 µg/L, both ACs exhibited a quantitative removal for all the char concentrations
431 tested, since target analyte was not detected in water solutions after 24 h of contact. Conversely,
432 removal in the ranges of 18.8-70.8 % and 5.1-28.4% were observed for BC6 and BC7, respectively
433 (**Table 3**). The different adsorption performances exhibited by BC6 and BC7 should be ascribed not
434 only to the different surface area, but also to the surface charge, as derived by pH_{pzc} measures. In fact,
435 pH_{pzc} tests indicated a significantly higher positive surface charge for BC6 ($pH_{pzc}=11.0$) than BC7

436 ($\text{pH}_{\text{pzc}}=7.0$) at the working pH value ($\text{pH}=6.5$), which is responsible for electrostatic interactions
437 between biochar and DIAA (Inyang and Dickenson, 2015).

438 As no detectable DIAA concentrations were found for ACs at $5 \mu\text{g L}^{-1}$, adsorption isotherm
439 experiments were repeated using an initial concentration of $20 \mu\text{g L}^{-1}$. With this concentration, the
440 removal percentage of the two ACs remained quite similar, ranging approximately from about 89 %
441 to 100 % in both cases (**Table 3**). As illustrated by **Figure 3**, adsorption data were fitted by the
442 linearized Freundlich equation, observing in all cases determination coefficients ≥ 0.925 and
443 statistically significant models based on ANOVA (P -values $\ll 0.05$). Values of K_F (**Table 3**) for BCs
444 were about three orders of magnitude lower than those for ACs. Hence, BCs provided a poor
445 adsorption ability compared to those determined for materials routinely used in water treatment
446 plants. In more detail, based on the K_F values, BC6 exhibited sorption ability about 3 times higher
447 than BC7. A similar efficiency ratio was observed for AC1 vs. AC2, in accordance with the fact that
448 the former is a virgin material, while the latter is a regenerated char. Slope ($1/n$) values of the
449 regression lines (**Fig. 3**) were in all cases < 1 (from 0.432 for BC7 to 0.736 for AC1), following the
450 order $\text{BC7} \approx \text{BC6} \ll \text{AC2} < \text{AC1}$. The values determined for slopes suggest an L-type isotherm
451 behaviour (European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC), 2013) for
452 the adsorption of DIAA on the investigated chars, notwithstanding the pseudo-linear aspect of the
453 experimental equilibrium concentration data (i.e. X/M vs. C_e), which is probably related to the quite
454 high concentrations of material and their narrow range tested here (i.e. about one order of magnitude).
455 This means that when DIAA concentration increases, the relative adsorption decreases due to the
456 saturation of adsorption sites available to DIAA, resulting in relatively less intense adsorption, with
457 increasing the amount of chemical adsorbed onto the material, as commonly observed for the sorption
458 of organic compounds on chars.

459 3.3.2 VOCs

460 Adsorption isotherm experiments on VOCs showed a not negligible variability of data, probably due
461 to the high vapour pressure and low water solubility of these analytes (Henry constants of $5.5 \cdot 10^{-4}$

462 and $2.3 \cdot 10^{-3} \text{ atm} \cdot \text{m}^3 \text{ mol}^{-1}$, for benzene and 1,2-dichlorobenzene, respectively). In this regard, it
463 should be noted that control experiments evidenced losses of both the investigated VOCs (about 15-
464 25%). Accordingly, adsorption isotherms were not calculated for VOCs. However, it is possible to
465 state that both BCs showed good adsorption properties, since, at both 20 and 5 $\mu\text{g/L}$ the removal
466 percentage was almost quantitative for ACs and BC6, and approximately equal to 60-70% and 70-
467 80%, for BC7 towards benzene and 1,2-dichlorobenzene, respectively.

468 3.4 Removal tests in water samples collected in drinking water plants

469 The removal capabilities of BC6 and BC7 were additionally tested in two water samples (i.e. DSB
470 and CB) collected from the drinking water plant treatment train (before entering the final refinement
471 stage with activated carbon beds) and compared with those of commercial AC1. These tests were
472 performed by putting in contact for 24 h 0.4 g of chars with 100 mL of DSB and CB spiked with 20
473 $\mu\text{g L}^{-1}$ of DIAA or VOCs. In such a way, the possible competitive effects exhibited by the matrix can
474 be assessed and results obtained from adsorption experiments in ultrapure water eventually
475 confirmed. To better explain possible competitions mechanisms, Total Organic Carbon (TOC) was
476 initially measured in the two samples, obtaining TOC values of 4.3 mg L^{-1} and 2.4 mg L^{-1} for CB and
477 DSB, respectively. The lower TOC value observed for DSB should be ascribed to the disinfection
478 stage operated in this treatment train. The results obtained in these removal tests are summarized in
479 **Table 4**. As a general consideration, the use of water samples collected within the treatment train of
480 the potabilization plants did not alter the performance of the BCs, even though the lower
481 performances of biochars compared to the activated carbon were confirmed. Results obtained in real
482 water samples fully support the design of column experiments to assess accurately the removal
483 capacity and exhausting time of BCs, with particular reference to BC6.

484 4 Conclusions

485 Within the actions pursued in a circular economy approach fostered by European Union for waste
486 management, the reuse of waste is promoted for the reduction of resources consumption. Biochar is
487 one successful example of valorisation of wastes.

488 In this paper, seven BCs obtained from gasification or pyrolysis processes of waste vegetal biomass,
489 were characterized in depth for numerous parameters, in comparison with a virgin commercial AC, a
490 freshly regenerated AC, and a regenerated AC in use at a potabilization facility. The characterization
491 included the evaluation of “environmental concern” parameters (e.g. PAHs and metals release), for
492 which mandatory limits are provided at European level for materials intended as sorbents for drinking
493 water filtration, but seldom evaluated elsewhere. Most BCs met these limits, whilst the “sorption
494 performance parameters” regulated in the European standard (i.e. I₂In and ash in the UNI EN 12915-
495 1) were in almost all cases outside the acceptance thresholds, suggesting lower efficiencies compared
496 to ACs.

497 Multivariate analyses (i.e. PCA and CA) allowed for easily identifying the materials with the closest
498 (BC5 and BC6) or the farthest (BC1 and BC7) characteristics to those of ACs, and their use should
499 be promoted in the field of exploration of data deriving from material characterization.

500 Adsorption tests towards DIAA and VOCs carried out in ultrapure water highlighted the much lower
501 sorption ability of BC7 compared to BC6, in agreement with findings of multivariate analyses.
502 Interestingly, removal tests in waters withdrawn from potabilization plants did not evidence any
503 significant decrease of the sorption ability of BCs towards the investigated contaminants compared
504 to tests in ultrapure water, thus supporting the implementation of column experiments for establishing
505 the maximum loading capacity of the materials in experimental conditions more similar to the real
506 scale.

507 Even though the sorption performances of BCs are much lower than those of ACs, it should be noted
508 that BCs did not undergo any physical or chemical activation process, which can surely improve their
509 removal capacity. Moreover, the management of waste biomass to produce biochar as adsorbent for
510 water treatment may be regarded as a “win–win” solution for pursuing circular economy principles
511 and protecting the environment.

512

513

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519

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659

Table 1 – Status of operation and production conditions of biochars (BC) and commercial activated carbons (AC); n.a. = not available

Sample	Status	Feedstock	Thermal treatment	Temperature (°C)	Contact time (min)
BC1	Virgin	Wood waste mixture ^a	Pyrolysis	550	10
BC2	Virgin	Wood waste mixture ^b	Pyrolysis	550	10
BC3	Virgin	Wood waste mixture ^b	Pyrolysis	550-600	15
BC4	Virgin	Herbal pomace	Pyrolysis	550-600	15
BC5	Virgin	Wood waste mixture ^c	Gasification	800-900	10
BC6	Virgin	Wood waste mixture ^d	Gasification	800-900	10
BC7	Virgin	Corn cob	Pyrolysis	450	30
AC1	Virgin	Coconut	Pyrolysis+physical activation	800-950	n.a
AC2	Regenerated	Coconut	Pyrolysis+physical activation	800-950	n.a
AC3	In use	Coconut	Pyrolysis+physical activation	800-950	n.a

^a Composition: 100% Poplar; ^b Unknown composition; ^c Approximate composition: Pine 60%, Beech 25%, Hazel 15%; ^d Approximate composition: Pine 40%, Beech 30%, Hazel 20%, Spruce 10%

Table 2 – Ash (%), pH of the point of zero charge (pH_{pzc}), specific surface area (SSA, BET method, m² g⁻¹), surface area of micropores (MiSSA, t-plot method, m² g⁻¹), surface area of mesopores (MeSSA, BJH model – desorption cumulative surface area, m² g⁻¹), iodine index (I₂In, mg g⁻¹), and methylene blue index (MBIn, mg g⁻¹), determined in biochars (BCs) and activated carbons (ACs). For the parameters tested by replicated analyses (n=3), mean and standard deviations (in bracket) are reported. Available limits set by European regulation EN 12915-1 are also reported; n.a. = not available.

Sample	Ash	pH _{pzc}	SSA	MiSSA	MeSSA	I ₂ In	MBIn
EN 12915-1	15	n.a.	n.a.	n.a.	n.a.	600	n.a.
BC1	42 (8)	10.5	253 (19)	81 (15)	53 (12)	129 (1)	4 (1)
BC2	12 (2)	8.6	243 (22)	43 (11)	63 (14)	144 (1)	4 (2)
BC3	14.1 (0.5)	8.4	153 (20)	65 (14)	76 (17)	88 (1)	1.4 (0.8)
BC4	29.2 (0.2)	9.1	222 (18)	92 (22)	117 (25)	124 (1)	4 (2)
BC5	49 (4)	12.0	302 (23)	121 (26)	97 (20)	156 (1)	6.0 (0.7)
BC6	25 (2)	11.0	309 (21)	80 (19)	136 (30)	197 (1)	4.1 (0.4)
BC7	6.2 (0.1)	7.0	136 (12)	33 (10)	40 (11)	77 (1)	2.2 (0.4)
AC1	7 (2)	10.9	1053 (88)	634 (118)	384 (81)	1010 (1)	20 (2)
AC2	13 (4)	9.9	714 (65)	300 (72)	359 (78)	540 (1)	15 (1)
AC3	21 (8)	8.1	561 (38)	205 (51)	273 (59)	438 (1)	11 (2)

Table 3 – Sorbent masses of chars (M, g) used in adsorption experiments of diiodoacetic acetic (DIAA), DIAA equilibrium concentrations (Ce, mg L⁻¹), DIAA removal (R, %), ratio of the amount of DIAA adsorbed per mass unit of sorbent (X/M, mg g⁻¹), and values of the Freundlich constant (K_F, mg^{1-1/n} L^{1/n} g⁻¹). Initial concentrations of DIAA tested for each char are reported in bracket.

Fig. 2. K_F and K_{SC} values for the initial concentrations of DHA tested for each oil are reported in bracket.				
M	Ce	R	X/M	K _F
<u>BC6 (5 µg L⁻¹)</u>				
0.490	0.00146	70.8	0.00029	0.00484
0.324	0.00226	54.8	0.00034	
0.243	0.00272	45.6	0.00038	
0.163	0.00335	33.0	0.00040	
0.113	0.00377	24.6	0.00044	
0.084	0.00406	18.8	0.00045	
<u>BC7 (5 µg L⁻¹)</u>				
0.459	0.00358	28.4	0.00012	0.00141
0.304	0.00402	19.6	0.00013	
0.218	0.00426	14.8	0.00014	
0.133	0.00454	9.2	0.00014	
0.103	0.00465	7.0	0.00014	
0.072	0.00475	5.1	0.00014	
<u>AC1 (20 µg L⁻¹)</u>				
0.486	0.000032	99.8	0.00164	3.18
0.323	0.000051	99.7	0.00247	
0.244	0.000102	99.5	0.00326	
0.163	0.000147	99.3	0.00487	
0.122	0.000278	98.6	0.00647	
0.033	0.001510	92.5	0.02241	
0.017	0.001970	90.2	0.04242	
<u>AC2 (20 µg L⁻¹)</u>				
0.244	0.000028	99.9	0.00327	0.922
0.163	0.000048	99.8	0.00489	
0.122	0.000103	99.5	0.00652	
0.083	0.000208	99.0	0.00954	
0.033	0.001630	91.9	0.02227	
0.016	0.002100	89.5	0.04475	

Table 4 – Mean values (n=3) and standard deviation (in bracket) of the removal performances of 0.4 g of BC6, BC7, and AC1 towards 20 µg/L of DIAA, benzene, and 1,2-dichlorobenzene (contact time 24 h) in two real water samples (DSB and CB) from a potabilization plant, in comparison with ultrapure water (UP). Tests were performed in triplicate. “Q” means quantitative removal, i.e. concentration of the contaminant at the end of the experiment below the detection limit.

	DIAA			Benzene			1,2-Dichlorobenzene		
	UP	DSB	CB	UP	DSB	CB	UP	DSB	CB
BC6	47 (1)	41 (3)	37 (2)	Q	Q	Q	Q	Q	Q
BC7	14 (2)	12 (3)	15 (3)	74 (10)	60 (12)	51 (9)	76 (9)	78 (11)	74 (10)
AC1	99 (1)	99 (4)	99 (3)	Q	Q	Q	Q	Q	Q

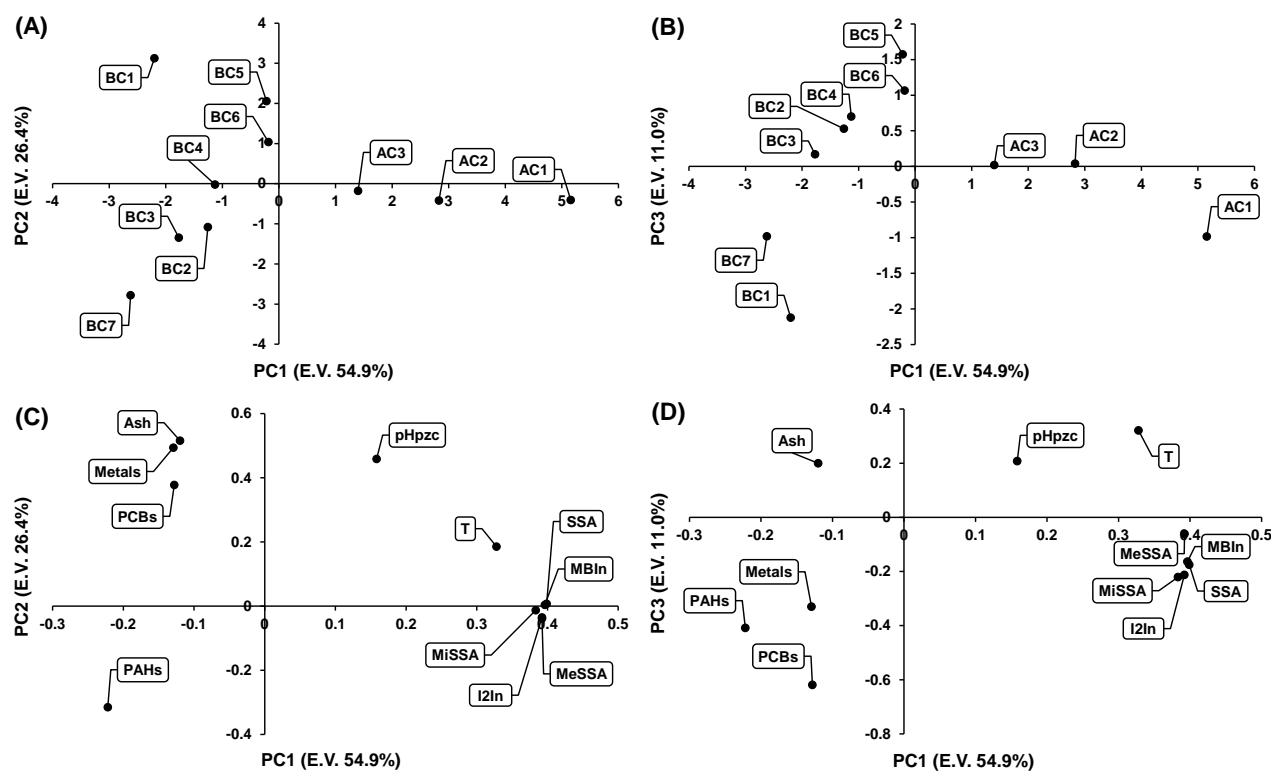


Figure 1 – Score (A-B) and loading (C-D) plots of PC1 versus PC2 and PC1 versus PC3, representing a percentage of explained variance (E.V.) of 81.3% and 65.9%, respectively. PCA values were calculated using the autoscaled values determined for the eleven original variables in the ten char samples. Note that the terms PAHs, PCBs, and Metals refer to their total leachable concentrations.

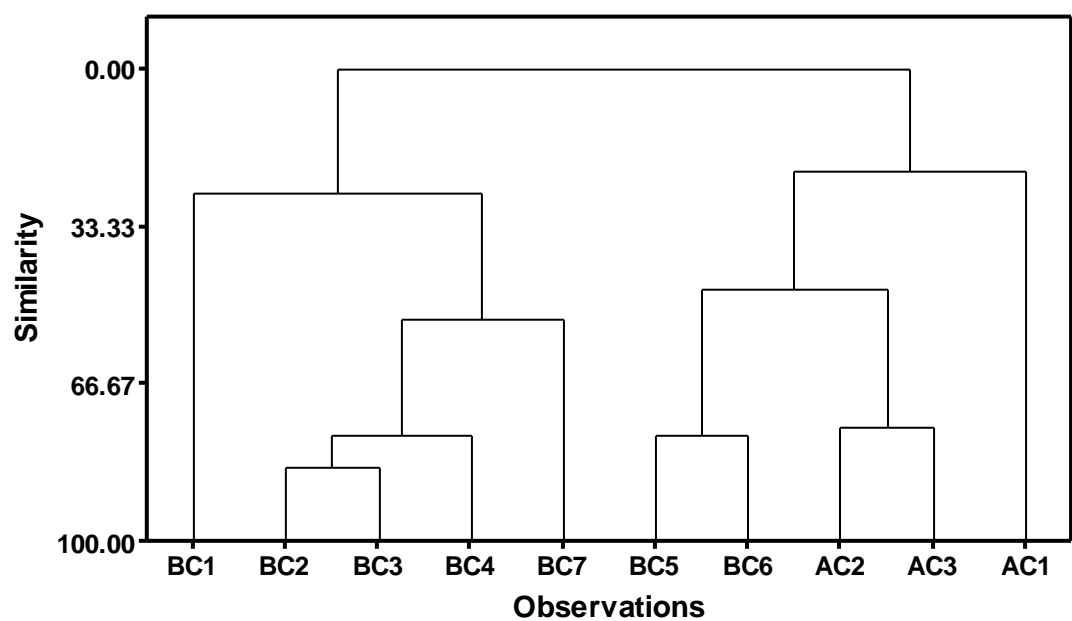


Figure 2 – Dendrogram of similarity of the ten investigated char samples, calculated through the complete linkage method on the basis of Euclidean distances of the autoscaled values of the eleven original variables.

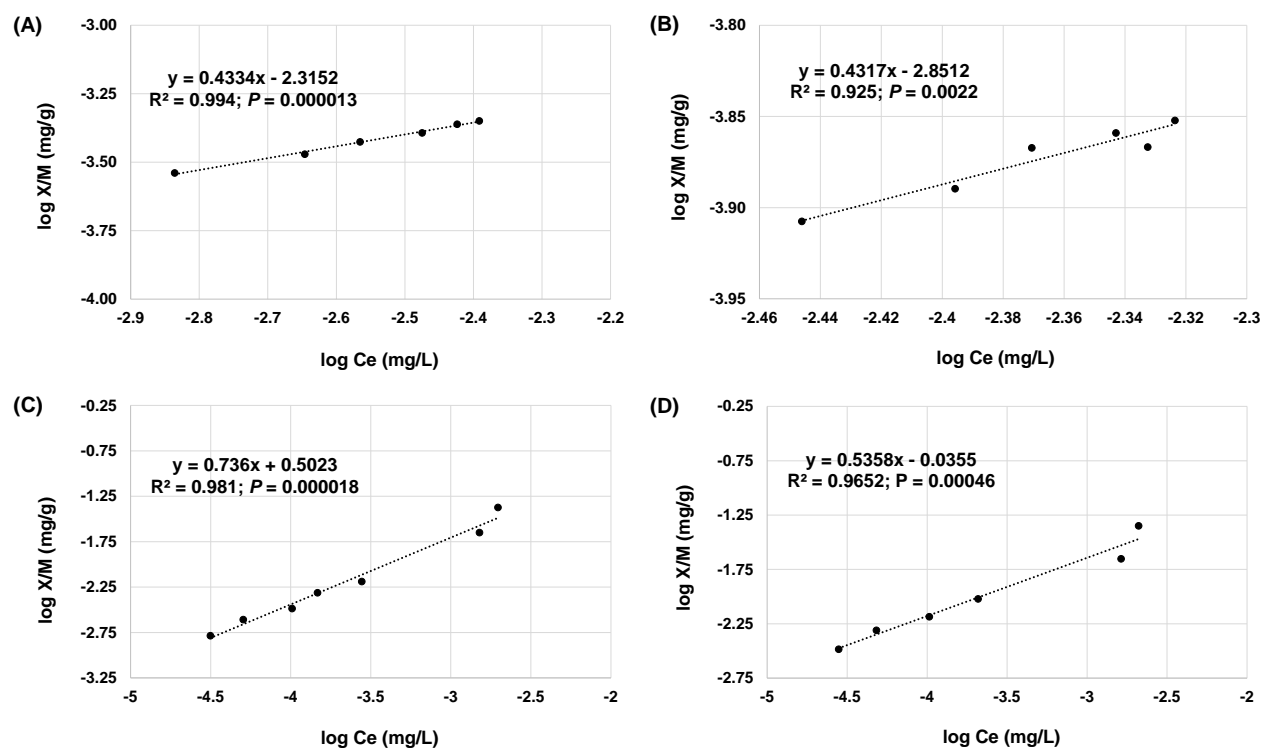



Figure 3 – Plots of linearized Freundlich isotherms obtained for BC6 (A), BC7 (B), AC1 (C), and AC2 (D).



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Supplementary Material

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