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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
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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

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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

1   **Biochars intended for water filtration: a comparative study with activated carbons of their**

2   **physicochemical properties and removal efficiency towards neutral and anionic organic**

3   **pollutants**

4

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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:
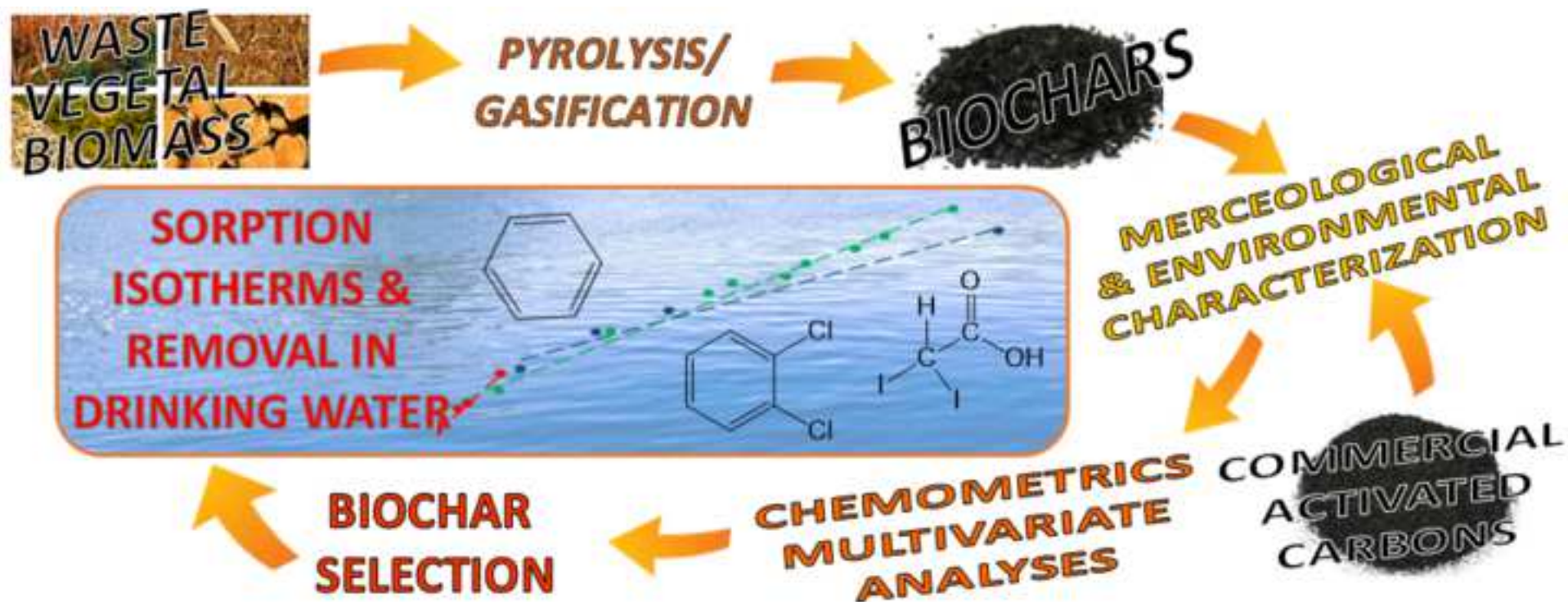
Torino, 23 August 2021
Signed
Professor Maria Concetta Bruzzoniti

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

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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.

Keywords: pyrolysis, gasification, filtration media, PAH and PCB release, metal release, drinking water plant

2

1 Introduction

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

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

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

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

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

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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 absorbent 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

4

102 of biochars in water samples collected at intermediate treatment stages of a potabilization plant. In

103 all cases ACs were also tested as reference comparative materials.

104 Diiodoacetic acid (DIAA), benzene, and 1,2 dichlorobenzene, were selected as model pollutants

105 commonly monitored in drinking water facilities. Specifically, DIAA is a model emerging

106 disinfection by-product (Bruzzoniti et al., 2019b) never investigated before for its sorption by

107 biochars. Moreover, 1,2 dichlorobenzene can also originate from disinfection treatments during the

108 potabilization process (Lahaniatis et al., 1994; Hou et al., 2012) and its monitoring in tap water is

109 recommended by the World Health Organization guidelines (taste threshold value 1 μg L^{-1}) (World

110 Health Organization, 2017), while benzene is regulated by the Directive 2020/2184 regarding the

111 quality of water intended for human consumption (1 μg L^{-1}). It should also be noted that benzene and

112 1,2 dichlorobenzene are volatile organic carbons (VOCs) still detected in some industrial districts

113 (Martínez et al., 2002) and are therefore also important from the wastewater treatment viewpoint.

114 **2   Materials and methods**

115 2.1   Reagents

116 For the determination of adsorption indexes, the following reagents, supplied by Merck (Kenilworth,

117 NJ, USA), were used: iodine solution (0.1 N), sodium thiosulfate solution (0.1 N), zinc iodide starch

118 solution, hydrochloric acid (37%), potassium hexacyanoferrate (>99%), methylene blue, anhydrous

119 acetic acid (>99.8%). Ammonia solution (28%), dichloromethane and 2-propanol were from VWR

120 International (Radnor, PA, USA). For the evaluation of extractable metals, an ICP multi-element

121 standard solution IX (100 mg L^{-1} of As, Be, Cd, Cr (VI), Ni, Pb, Se, Tl) from Merck was used.

122 For the determination of extractable polycyclic aromatic hydrocarbons (PAHs), the 16 compounds

123 listed by EPA were purchased from Sigma Aldrich (Darmstadt, Germany). For the analysis of

124 extractable polychlorinated biphenyls (PCBs), the compounds were purchased from LGC Standards

125 (Milan, Italy). They were non dioxin-like PCBs: 3,3'-dichlorobiphenyl (PCB 11), 4,4'-

126 dichlorobiphenyl (PCB 15), 2,4,4'-trichlorobiphenyl (PCB 28), 2,2',5,5'-tetrachlorobiphenyl (PCB

127 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 ^{13}C surrogate solutions of PAHs contained:

135 [$^{13}C_6$]benzo(a)anthracene [$^{13}C_6$-BaA], [$^{13}C_6$]chrysene [$^{13}C_6$-Chr], [$^{13}C_6$]benzo(b)fluoranthene [$^{13}C_6$-

136 BbFl], [$^{13}C_6$]benzo(k)fluoranthene [$^{13}C_6$-BkFl], [$^{13}C_4$]benzo(a)pyrene [$^{13}C_4$-BaP],

137 [$^{13}C_6$]indeno(1,2,3-cd)pyrene [$^{13}C_4$-Ind], [$^{13}C_6$]dibenzo(a,h)anthracene [$^{13}C_6$-DBA], and

138 [$^{13}C_{12}$]benzo(g,h,i)perylene [$^{13}C_{12}$-BP]. The ^{13}C surrogate solution of PCBs contained: $^{13}C_{12}$-PCB28,

139 $^{13}C_{12}$-PCB52, $^{13}C_{12}$-PCB118, $^{13}C_{12}$-PCB153, and $^{13}C_{12}$-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

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

2.3.1   Ash content

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

2.3.2   Water-extractable substances

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

2.3.3   pH of the point of zero charge

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

2.3.4   Adsorption indexes

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

2.3.5   Physisorption analysis

Physisorption analysis of biochars and ACs was performed via nitrogen adsorption and desorption experiments using a Porosity Analyser Thermo Fisher Scientific (Milan, Italy) model 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 (pH = 6.5±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 μg L^{-1} for BCs and 20 μg L^{-1}

188 for ACs; VOCs: 5 μg L^{-1} or 20 μg L^{-1} for BCs and 20 μg 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 μm). 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
$$\log \frac{X}{M} = \log K_F + \frac{1}{n} \log C_e$$

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 ($mg^{1-1/n}$ $L^{1/n}$ 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

concentration of chars is mainly influenced by the type of feedstock, being woody biomass the one providing a lower ash content, compared to other feedstocks, such as non-woody vegetal biomass and animal waste (Tomczyk et al., 2020). However, the type of thermal conversion process (i.e. pyrolysis or gasification) and the temperature and contact time conditions adopted in the process may also play a role in determining the ash concentration, which obviously depends on the amount of char obtained. In this regard, it should be remarked that biochar yield is a function of the type of thermal conversion process (i.e. pyrolysis or gasification) and the temperature and contact time conditions adopted in the process, being the highest yields obtained with pyrolysis conducted at low temperature and high contact time (slow pyrolysis) (Inyang and Dickenson, 2015). Hence, it is evident that, if the same feedstock is used, the ash concentration will be higher in gasification processes than in pyrolysis (Fryda and Visser, 2015). Moreover, increasing ash percentages will be obtained with increasing temperature (Rafiq et al., 2016) and higher ash concentrations will be found under fast pyrolysis conditions (Brewer et al., 2009). Based on these considerations, it makes sense that BC2, BC3, and BC7, all deriving from slow pyrolysis processes (**Table 1**), showed ash percentages much lower than BC5 and BC6, which were conversely obtained under gasification conditions using a same patented process and plant. The very high ash concentration found in BC4 (about 29%) compared to BC3, both produced with the patented PYREG® pyrolysis process under the same experimental conditions, could be attributed to the different nature of the feedstocks employed, i.e. non woody vegetal biomass for BC4 and woody waste biomass for BC3 (**Table 1**). Finally, the unexpected high ash content of BC1 probably depends on the peculiar characteristics of the woody waste used as feedstock, which derives from the cutting of a forest planted for the phytoremediation of a soil contaminated by different chemicals, including heavy metals. Virgin activated carbon (AC1) showed a lower ash content (7%), in agreement with the high standard quality requested by the potabilization plant in its specifications. Higher ash percentages were obviously found in regenerated and in-use ACs (i.e. AC2 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 $\mu g\ L^{-1}$. In addition, the EN standard imposes limits to the presence of As (10 $\mu g\ L^{-1}$), Cd (0.5 $\mu g\ L^{-1}$

265 $^{-1}$), Cr (5 $\mu g\ L^{-1}$), Hg (0.3 $\mu g\ L^{-1}$) Ni (15 $\mu g\ L^{-1}$), Pb (5 $\mu g\ L^{-1}$), Sb (3 $\mu g\ L^{-1}$) and Se (3 $\mu g\ L^{-1}$). 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 (11-12 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

11

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.

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

332   indicator of adsorption capacity towards medium-large sized organic pollutants (Del Bubba et al.,

333   2020). For BCs, the I_2In was found in the range 77-197 mg I_2 g^{-1}, with BCs obtained from gasification

334   (i.e. BC5 and BC6) showing the highest values (156-197 mg I_2 g^{-1}), while the lowest ones (77-88 mg

335   I_2 g^{-1}) were exhibited by materials produced under pyrolytic conditions (i.e. BC3 and BC7). The range

336   determined for I_2In in BCs was about five times lower than that determined in virgin and regenerated

337   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.

338   AC2 after some use in the potabilization plant) was lower than that of AC2 (438 mg I_2 g^{-1}), in

339   agreement with the progressive pore saturation phenomena occurring during operation.

340   The MBIn showed a trend within the BCs and ACs clusters, and among them, similar to that described

341   for I_2In (e.g. higher values for ACs than BCs and for BC5 and BC6 compared to the other BCs).

342   Accordingly, as illustrated by **Figure S1** of the *Supplementary material*, the two indexes showed a

343   very good linear correlation (R^2 = 0.945, *P*<<0.05), in agreement with findings observed elsewhere

344   for different types of ACs and BCs (Del Bubba et al., 2020), even though a lower determination

345   coefficient was observed by excluding ACs from the correlation (R^2= 0.534, *P*=0.062). The much

346   lower correlation was mainly ascribable to the opposite trend observed for some pairs of materials,

347   such as BC5 and BC6, the latter exhibiting lower MBIn but higher I_2In than the former. These findings

348   can be explained by the general differences in micro, meso, and macroporosity distributions of BCs

349   due to the different experimental conditions adopted for their production.

350   *3.1.5 Physisorption analysis*

351   **Table 2** illustrated the results obtained for the porosimetry analyses (i.e. BET SSA, t-plot MiSSA and

352   BJH desorption cumulative MeSSA) of the investigated BCs and ACs.

353   As expected, ACs exhibited much higher values of the SSA (561-1053 m^2 g^{-1}) than BCs (136-309 m^2

354   g^{-1}), being the latter group characterized by a data trend similar to those observed for adsorption

355   indexes. To elaborate, BC5 and BC6, in addition to showing greater values of the adsorption indexes,

356   also exhibited the highest SSA, whereas BC7 had the lowest values of the aforementioned parameters.

357   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

To summarize the wide group of information discussed above, deriving from the determination of the several characterization parameters in the ten char samples, a multivariate elaboration of the autoscaled original data was performed by means of PCA. In more detail, PCA elaboration included the following eleven parameters: conversion temperature (T), the seven parameters reported in **Table 2** (i.e. ash, pH_{pzc}, SSA, MiSSA, MeSSA, I_2In, and MBIn), total PAHs (expressed as BaPy TEF concentrations), total PCBs, and total metals. Three principal components (PCs), characterized by eigenvalues > 1 and accounting for percentages of explained variances (E.V.) of 54.9%, 26.4%, and 11.0%, were obtained (total E.V. = 92.3%). **Figure 1** illustrates the plots of scores (**Fig. 1A-B**) and loadings (**Fig. 1C-D**) of PC1 versus PC2 and PC1 versus PC3, which represent E.V. of 81.3% and 65.9%, respectively. The contributions of each variable to the three significant PCs were not always well differentiated, even though most original variables showed remarkably different absolute values of loadings among the three components. In more detail, SSA, MiSSA, MeSSA, I_2In, and MBIn contributed mainly in PC1, pH_{pzc} and above all ash were mainly represented on PC2, whilst total PCBs exhibited by far the highest loading on PC3. Conversely, T was represented in PC1 and PC3 to the same extent, whereas total PAHs and metals contributed almost equally to PC2 and PC3. Among the ten investigated chars, ACs clustered in both score plots, mainly due to their peculiar characteristics in terms of adsorption indexes and physisorption data. BC5 and BC6, which derived from the same gasification process, also clustered in both score plots mostly because of the particularly high values of ash and very low leachable concentrations of total PAHs. Actually, BC6 was the closest char to the AC cluster, suggesting interesting adsorption properties. This consideration points out that PCA is a valuable tool to select the best sorbents for adsorption measurements, when one or more reference materials are included in the unsupervised multivariate analysis as comparators. BC2, BC3, and BC4 identified a further cluster in both score plots. Conversely, BC1 and BC7 behaved as outliers, being they quite distant from the other BCs and the farthest from ACs, due to their peculiar values of the coordinates on PC2 and PC3. In fact, their scores, were mainly 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 (pH$_{pzc}$=7.0) at the working pH value (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 µg L^{-1}, adsorption isotherm

439 experiments were repeated using an initial concentration of 20 µg 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 $\geq$ 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 BC7$\approx$BC6$\ll$AC2<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. Ce), 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 5.5·10^{-4}

462 and $2.3 \cdot 10^{-3}$ atm·m^3 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 µg/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 µg 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.

19

In this paper, seven BCs obtained from gasification or pyrolysis processes of waste vegetal biomass, were characterized in depth for numerous parameters, in comparison with a virgin commercial AC, a freshly regenerated AC, and a regenerated AC in use at a potabilization facility. The characterization included the evaluation of "environmental concern" parameters (e.g. PAHs and metals release), for which mandatory limits are provided at European level for materials intended as sorbents for drinking water filtration, but seldom evaluated elsewhere. Most BCs met these limits, whilst the "sorption performance parameters" regulated in the European standard (i.e. I_2In and ash in the UNI EN 12915-1) were in almost all cases outside the acceptance thresholds, suggesting lower efficiencies compared to ACs.

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

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

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

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659

Table 1

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

Table 2 – Ash (%), pH of the point of zero charge (pH_{pzc}), specific surface area (SSA, BET method, m^2 g^{-1}), surface area of micropores (MiSSA, t-plot method, m^2 g^{-1}), surface area of mesopores (MeSSA, BJH model – desorption cumulative surface area, m^2 g^{-1}), iodine index (I_2In, 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_2In	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

Table 3

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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.

M	Ce	R	X/M	K_F
BC6 (5 µg L^{-1})				
0.490	0.00146	70.8	0.00029	
0.324	0.00226	54.8	0.00034	
0.243	0.00272	45.6	0.00038	0.00484
0.163	0.00335	33.0	0.00040	
0.113	0.00377	24.6	0.00044	
0.084	0.00406	18.8	0.00045	
BC7 (5 µg L^{-1})				
0.459	0.00358	28.4	0.00012	
0.304	0.00402	19.6	0.00013	
0.218	0.00426	14.8	0.00014	0.00141
0.133	0.00454	9.2	0.00014	
0.103	0.00465	7.0	0.00014	
0.072	0.00475	5.1	0.00014	
AC1 (20 µg L^{-1})				
0.486	0.000032	99.8	0.00164	
0.323	0.000051	99.7	0.00247	
0.244	0.000102	99.5	0.00326	
0.163	0.000147	99.3	0.00487	3.18
0.122	0.000278	98.6	0.00647	
0.033	0.001510	92.5	0.02241	
0.017	0.001970	90.2	0.04242	
AC2 (20 µg L^{-1})				
0.244	0.000028	99.9	0.00327	
0.163	0.000048	99.8	0.00489	
0.122	0.000103	99.5	0.00652	0.922
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

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-dichlororbenzene (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

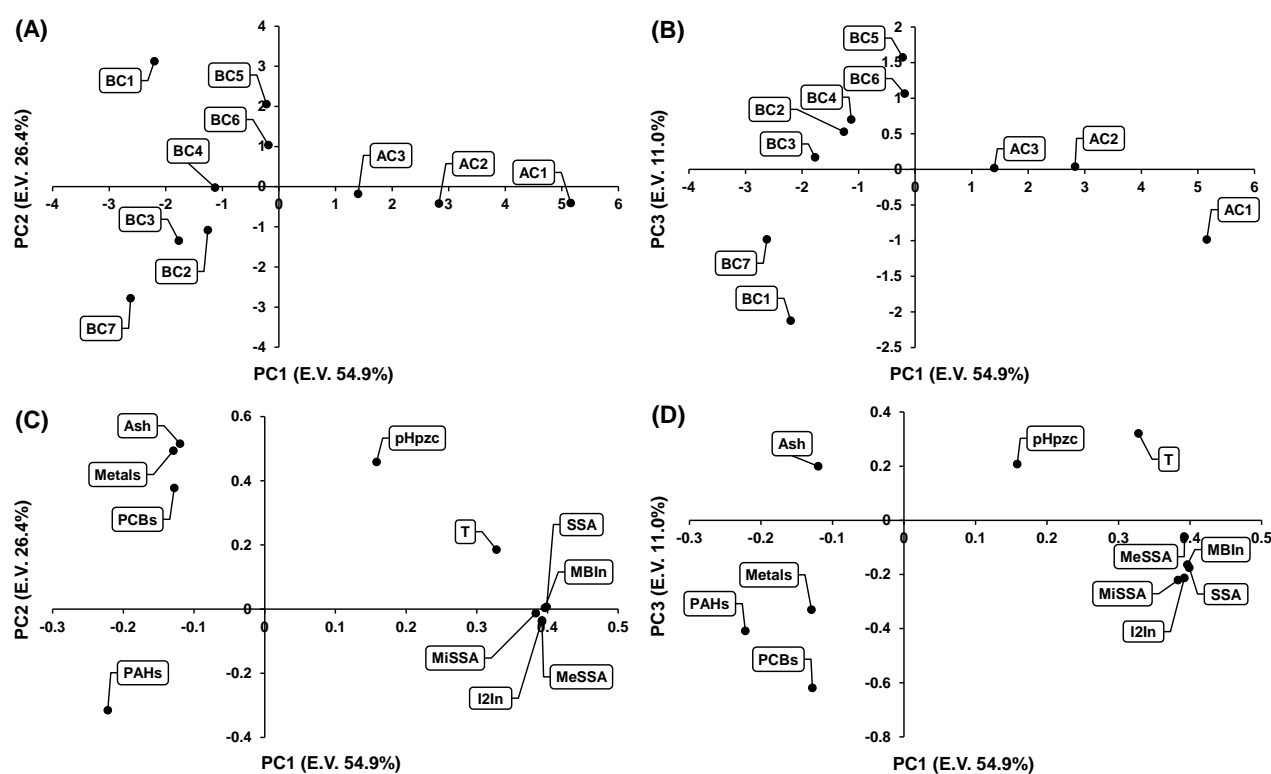Click here to access/download;Figure;Figure 1.docx ⬇

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.
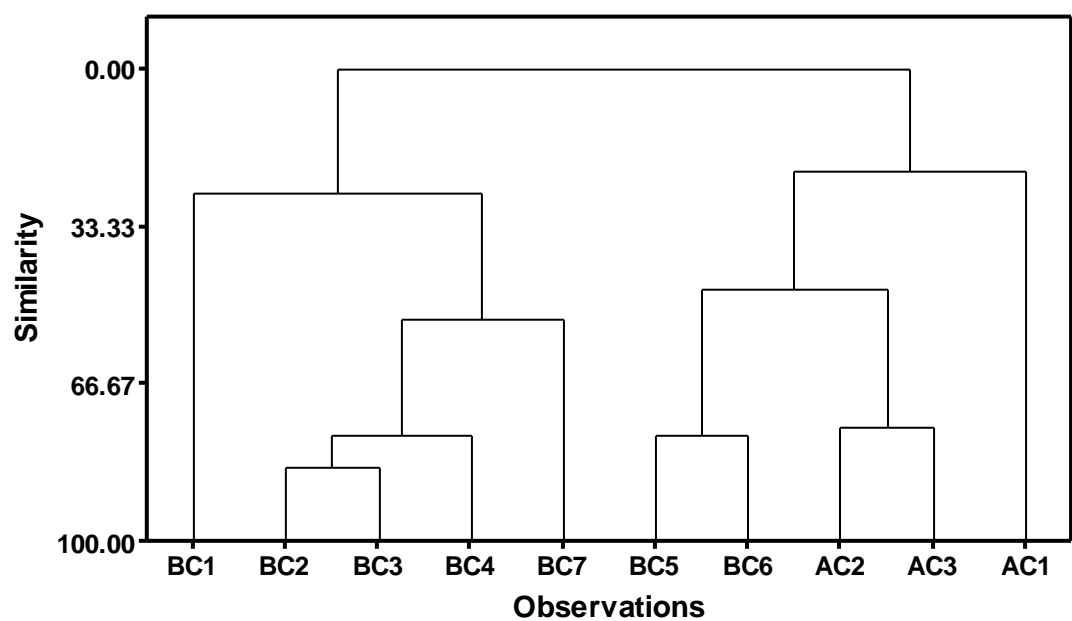
Figure 2

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.
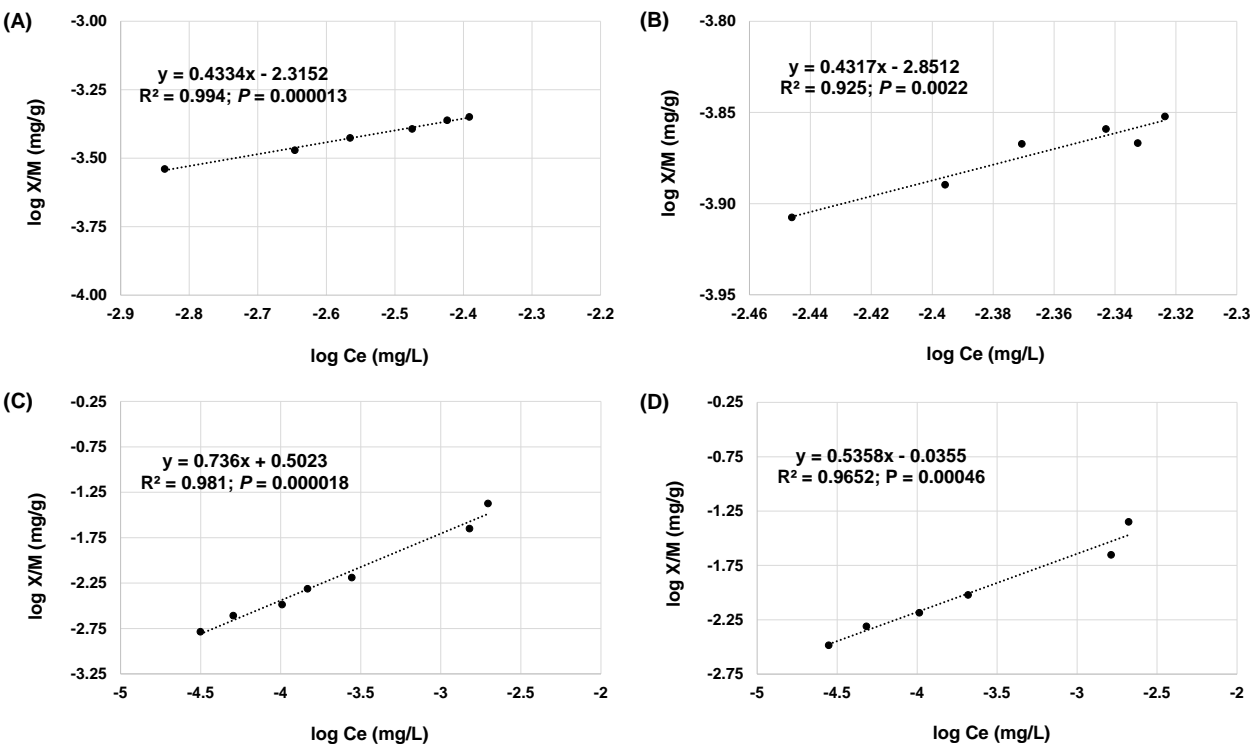
Figure 3   Click here to access/download;Figure;Figure 3.docx ⬇

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

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