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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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Chemosphere

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--

Manuscript Number:	CHEM91505R1
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Keywords:	pyrolysis; gasification; filtration media; PAH and PCB release; metal release; drinking water plant
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	Massimo Del Bubba
Abstract:	Maria Concetta Bruzzoniti, PhD
	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.
Opposed Reviewers:	



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Turin, 07th October 2021

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

Dear Editor,

please find enclosed the revised version of the manuscript CHEM91505 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.

The paper was carefully revised in consideration of the reviewer’s comments (see attached file) and improved with the literature references suggested.

We hope that you will favourably welcome the revised manuscript for publication in *Chemosphere*.

We thank you in advance for your cooperation.

Best regards.

Prof. Dr. Maria Concetta Bruzzoniti



Turin, 7th October 2021

REPLIES TO THE COMMENTS FROM EDITORS AND REVIEWERS

Dear Editor and Reviewers,

We would like to thank you for the time and the efforts for improving the quality of our manuscript.

Each comment was carefully considered, and the replies are reported hereafter.

Reviewer #1:

In this work, the authors have compared the adsorption capacity of 3 analytes into 7 biochars, and what is more important, they have also compared them with 3 commercial activated carbons used in their country. First, the chars were characterized and then the most suitable were selected and their adsorption capacities were compared.

In my opinion, the authors do more work than necessary, as they fully characterize chars that they know will not be able to be used. Nevertheless, this information could be used for other authors in the field and a good reflection is made of the reasons that lead to the results obtained for all the parameters studied.

ANSWER – We would like to thank the Reviewer #1 for her/his positive comment on the general quality of the manuscript.

I only have 2 general comments related to the conclusions of the paper.

General comments

1. After summarizing and evaluating the results obtained during the characterization, the authors come to the conclusion that only BC6 and BC7 are the most suitable for the following analyzes. However, taking into account what is stated in section 3.1.1. "only BC2, BC3, and as previously mentioned BC7, are allowed to be used as sorbent materials in potabilization facilities." BC6 should not be selected. In my opinion, it makes no sense to study a biochar for possible use in water treatment plants if it is already known that it will not be able to be used.

ANSWER – We fully agree with Reviewer #1 that the biochar labelled as BC6 should not be selected for studying the sorption capacity based on its content of ash. However, the materials were subjected to a very complete characterization, which includes the pH of the zero point charge (pH_{pzc}), the surface area and the study of the porosity distribution. All these parameters combine to determine the sorbent properties of the material. For example, comparing the pH_{pzc} values of BC6 and BC7, it appears evident that once placed in contact with water having a pH around neutrality, the first, unlike the second, has a positive surface charge that makes it more suitable for the sorption of the anion diiodoacetic acid. Paradoxically, with our results we demonstrate that a parameter such as the ash content, although considered mandatory by the legislation, may not be decisive *per se* for the sorption performance. In fact, it should be remembered that the sorption properties of a given material are the result of a set of characteristics, all together contributing to the sorption ability, as evidenced by the multivariate analyses developed in this research. Following the comment of Reviewer #1, the conclusion section was modified, underlying the importance of the multivariate approach (see lines 510-512 of the revised manuscript).

2. It is concluded that BC7 has a much lower adsorption capacity than BC6, which, due to the ash content, could not be used. In fact, it is established that the BC5 and BC6 biochars are



the most similar to commercial activated carbon and it seems that their use is promoted, but it could not be. So, the conclusion I can draw from the work is that biochars that could be used because they are compliant with regulations have a much lower efficiency than commercial activated carbon

ANSWER – As reported in the previous reply, the biochar sorption efficiency is the result of a set of characteristics that certainly include but are not limited to the ash content. By the way, many of these features (e.g. pH_{pzc} and specific surface area) are not regulated. The lower removal capacity observed for biochars compared to activated carbons is therefore the multivariate result of a very large number of material properties. One of the results of this study is precisely having highlighted the importance of a multivariate approach instead of the evaluation of individual characteristics, even if they are regulated by legislation. According to the Reviewer #1 comment, the conclusions have been improved (see lines 515-517 of the revised manuscript).

Reviewer #2

In this manuscript, the authors systematically characterized seven biochars (BCs) and three commercial activated carbons (ACs, that was commonly used in drinking water treatment plants for removing diiodoacetic acid, benzene and 1,2-dichlorobenzene. Various parameters including ash contents, iodine and methylene blue adsorption indexes, pore volume distribution, etc., were compared. In general, BCs may or may not share some physical and chemical properties to ACs. The performances of BCs were less competitive than ACs, but they gave acceptable removals towards organic pollutants, indicating they might be promising adsorption media in future drinking water treatment. I would recommend the acceptance of the manuscript after a moderate revision. Below are some comments for the authors' consideration.

ANSWER – We would like to thank the Reviewer #1 for her/his positive comment on the general quality of the manuscript.

Lines 60-63, it should be noted that recent research also reported granular activated carbon can readily remove many halogenated disinfection byproducts (DBPs), especially aromatic halo-DBPs in drinking water treatment (ES&T 2017, 51, 3435; 2020, 54, 1646). As the authors investigated the removal of DBPs using carbon materials in this manuscript, it would be good to mention the recent studies in the introduction to strengthen the background of this research.

ANSWER – According to the Reviewer's suggestion, the references were included in the introduction section at line 66 of the revised manuscript.

Lines 104-113, it would be good to mention the adverse effects of the monitored organic pollutants. For instance, DBPs are reported to be cytotoxic, genotoxic, developmentally toxic and growth inhibitory (ES&T 2021, 55, 5906; 2018, 52, 10552).

ANSWER – According to the Reviewer's suggestion, the references were included in the introduction section at lines 64-65 of the revised manuscript, modifying the related paragraph, as well.

Line 145, it was unclear how to prepare or collect seven BCs. Please clarify it.

ANSWER – The biochars were donated by different companies, which produce the biochars for commercial scopes (BC3 and BC4 from PYREG GmbH; BC5 and BC6 from Romana Maceri Centro Italia S.r.l.; BC7 from Agrindustria Tecco S.r.l.) or for internal use (BC1 and BC2 from Sea Marconi s.a.s.). In all cases, the materials were not the result of an occasional production, but were conversely obtained according to well-established procedures, that for BC3, BC4, BC5, and BC6 are even patented, as mentioned at lines 244-246 of the original version of the manuscript. It should also be noted that the production characteristics of the



biochars used in this study were fully reported in Table 1 of the original manuscript. However, we agree with the Reviewer #2 that more information about the origin of the material must be provided in the revised version of the manuscript, since in the original version (i.e. at line 145), we reported only that the seven biochars were donated. Accordingly, for the sake of clarity we have now specified that the biochars were produced through well-established production protocols (see lines 148-150 of the revised version, paragraph 2.2). The companies that donated the biochars were mentioned in the acknowledgements.

Sections 2.2-2.6, was the sample prepared in duplicate? Please briefly introduce the quality control and quality assurance of the measurements.

ANSWER – We are not sure to have correctly understood the issue arisen by the Reviewer #2 regarding the sample preparation. If the Reviewer #2 refers to the biochar preparation, as mentioned in the previous reply, the char samples used in this study belong to tracked lots of production of the companies and are therefore fully representative of bulk samples. Regarding the quality assurance/control of the measurements performed, it should be noted that standard methods were used when available for the characterization of biochars and activated carbons, i.e. for the determination of ash, iodine and methylene blue indexes, extractable substances (PCB, PAH, and metals). Adsorption isotherms were performed using standard methods, as well. Hence, the only measure that was conducted without the availability of official protocols was the pH of the zero-point charge, the determination of which was however done based on a previously published method. Moreover, as mentioned in the original version of the manuscript, we included in the study one virgin and one regenerated activated carbon, which have been supplied by a potabilization plant. This potabilization plant buys the activated carbons through a contract specification, which includes the compliance with various parameters, such as specific surface area, iodine index, ash content, and release of PAHs and metals. Our measurements were in accordance with the values provided by the supplier of the activated carbons in the contract specification and with the analyses commissioned by the potabilization plant to an external certified laboratory for the verification of these parameters. A short paragraph describing the use of virgin and regenerated activated carbons as quality control was introduced in the revised version of the manuscript (new paragraph 2.3.6).

Sections 3.1 and 3.2, it seemed that the authors have compared various physical and chemical properties of BCs and ACs and selected BC6 (with features the closest to AC) and BC7 (with features the farthest to AC) for further comparison. It was unclear whether BC1-BC5 can behave better than BC7 and worse than BC6 in removing organic pollutants. Please briefly discuss this.

ANSWER – Our study aimed precisely at the in-depth characterization of the seven BCs and the three ACs and the subsequent multivariate analysis of the results of this characterization, in order to select the materials, which are respectively closest and farthest to the characteristics of ACs, which are considered the sorbents of choice in the drinking water plants. These materials were BC6 and BC7. Therefore, we do not have any information regarding the sorption ability of the other BCs. However, the sorption performances obtained for BC6 and BC7 compared to those achieved for AC1 and AC2 (see Table 3 of the original version of the manuscript), are in agreement with the characterization measurements and multivariate analyses performed for these materials and therefore suggest intermediate sorption performances for the other BCs. This last consideration was included in the conclusion section (lines 520-521 of the revised manuscript).

Sections 3.3 and 3.4, the authors compared the adsorption of various pollutants using adsorption isotherm tests. The application of different chars under real drinking water treatment scenarios



might not be well considered. The carbon dose (4 g/L) might be very high, as ppm levels of particle activated carbon are dosed into the water treatment plants. Besides, the pollutants concentration (20 ppb) might also be very high. Please briefly comment on this.

ANSWER – As mentioned at lines 473-475 of the original version of the manuscript, the removal tests were performed in order to highlight possible competitive effects exhibited by the matrix compared to data obtained in ultrapure water. Accordingly, we chose concentrations of chars and pollutants within the ones tested in sorption isotherm experiments. Honestly, we did not care to use a char dosage and pollutant concentrations simulating the real ones. However, as regards the concentrations of DIAA used in these tests, i.e. 20 ppb, real effluents from the dynamic separation basin and the pre-sedimentation tank of the facility considered here, have recently shown concentrations of haloacetic acids as high as 10-15 ppb. Moreover, the limit set by the European Directive 2020/2184 for these compounds is 60 ppb.

We hope that you will favourably welcome the revised version for publication.

Best regards

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:

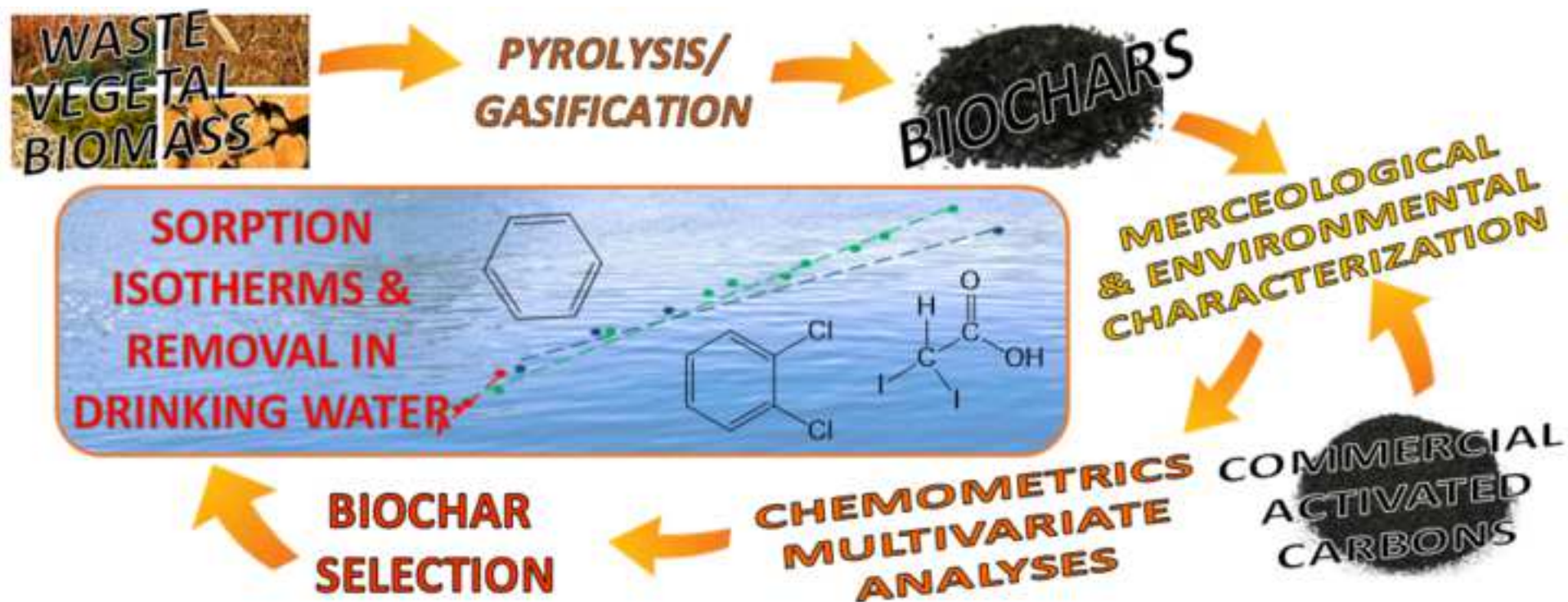
Torino, 23 August 2021

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



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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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48

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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 routinely integrated in drinking water
61 production, for the removal of toxic micropollutants organic and inorganic contaminants from
62 occurring in raw waters (Ali and Gupta, 2006) for the removal of micropollutants occurring per se in
63 raw waters and/or as a result of generated that is routinely integrated in drinking water production by
64 disinfection processes, thereby eliminating the toxicity induced by these molecules in treated water
65 (Han and Zhang, 2018; Han et al., 2021). Within this context, adsorption is generally based on the
66 use of activated carbon (Jiang et al., 2017; Perrich, 2018; Jiang et al., 2020), even though innovative
67 sorbents, such as mesoporous silica (Kyzas and Matis, 2015; Rivoira et al., 2016) or other waste-
68 derived ceramic materials (Jana et al., 2016; Bruzzoniti et al., 2018) have been proposed as alternative
69 adsorption media. Low-cost materials like biochar (BC) have recently received attention for their
70 physicochemical characteristics including the porous structure, which is similar to that of activated
71 carbons. Biochar is the solid by-product of the thermal conversion of a wide range of feedstocks, such
72 as agricultural wastes (Ali and Gupta, 2006; Colantoni et al., 2016), wood residues (Wang et al.,
73 2013), manure (Cao and Harris, 2010), and sludge (Méndez et al., 2017).

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

77 Internationally recognized standards detailing the physicochemical characteristics of biochars to be
78 used for agricultural applications have been recently released (European Biochar Foundation (EBC)).
79 Similar standards have not yet been established on the characteristics required for biochars to be used
80 in water purification. However, international standards are available that require compliance with
81 specific limits for certain physical and chemical parameters in adsorbent materials (Comite Europeen
82 de Normalisation (CEN), 2004), and particularly in activated carbons (Comite Europeen de
83 Normalisation (CEN), 2009), used for the treatment of drinking water.

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

97 Based on the considerations mentioned above, the aim of this research was to investigate the
98 physicochemical properties, the regulated leachable substances, and the removal performances of
99 seven biochars (commercially available or synthesized for the purpose), obtained from pyrolysis or

gasification of vegetal biomass, in comparison with three commercially available vegetal ACs used in an Italian drinking water facility, at different age of operation. Data obtained were chemometrically treated through principal component analysis, allowing for selecting the most promising biochars to be further investigated by adsorption tests. In a first phase of this study, adsorption capabilities were 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), 2,2',4,4',5,5'-hexachlorobiphenyl (PCB 153), 3,3',4,4',5,5'-hexachlorobiphenyl (PCB 169), 2,2',3,4,4',5,5'-heptachlorobiphenyl (PCB 180), 2,3,3',4,4',5,5'-heptachlorobiphenyl (PCB 189); and dioxin-like PCBs: 3,4,4',5-tetrachlorobiphenyl (PCB 81), 2,3',4,4',5-pentachlorobiphenyl (PCB 118), 2',3,4,4',5-pentachlorobiphenyl (PCB 123), 2,3',4,4',5,5'-hexachlorobiphenyl (PCB 167). Labelled isotope compounds for PCBs (2 mg L⁻¹) and for PAHs (5 mg L⁻¹), Wellington Laboratories (Ontario, Canada), were used as internal and surrogate standards in order to obtain calibration curves and extraction recoveries, respectively. The ¹³C surrogate solutions of PAHs contained: [¹³C₆]benzo(a)anthracene [¹³C₆-BaA], [¹³C₆]chrysene [¹³C₆-Chr], [¹³C₆]benzo(b)fluoranthene [¹³C₆-BbFl], [¹³C₆]benzo(k)fluoranthene [¹³C₆-BkFl], [¹³C₄]benzo(a)pyrene [¹³C₄-BaP], [¹³C₆]indeno(1,2,3-cd)pyrene [¹³C₄-Ind], [¹³C₆]dibenzo(a,h)anthracene [¹³C₆-DBA], and [¹³C₁₂]benzo(g,h,i)perylene [¹³C₁₂-BP]. The ¹³C surrogate solution of PCBs contained: ¹³C₁₂-PCB28, ¹³C₁₂-PCB52, ¹³C₁₂-PCB118, ¹³C₁₂-PCB153, and ¹³C₁₂-PCB180. Volatile organic compounds, namely benzene (100 µg L⁻¹ in methanol), and 1,2-dichlorobenzene (100 µg L⁻¹ in methanol), were purchased from Ultra Scientific Italia (Bologna, Italy). DIAA was supplied by Chemical Research (Rome, Italy). Ultrapure water was obtained by an EMD Millipore Milli-Q Direct Water Purification System (Millipore, Bedford, MA, USA).

2.2 Biochar and activated carbon samples

The seven BCs considered in this study were donated for the purpose [by different companies, which produce the materials for commercial scopes or for their internal use through well-established procedures](#). The three ACs were supplied by a local potabilization plant at different age of operation:

151 AC1: new activated carbon; AC2: regenerated activated carbon; AC3: regenerated activated carbon
152 in use at the plant. The status of operation, and the characteristics of the feedstock and the thermal
153 process used to produce the ten chars are summarized in **Table 1**.

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

156 2.3 Biochar and activated carbon characterization

157 The chars investigated in this study were physicochemically characterized through the determination
158 of ash content, pH of the point of zero-charge (pH_{pzc}), physisorption analysis, iodine and methylene
159 blue adsorption indexes (I_2In and MBIn), as well as for water-extractable substances of environmental
160 concern. The procedures adopted for the aforementioned determinations are briefly described below,
161 whilst full details are provided in the *Supplementary Material* section. [For the determination of the](#)
162 [parameters described below, standard methods were used when available.](#)

163
164
165
166

167 2.3.1 Ash content

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

170 2.3.2 Water-extractable substances

171 Metals (namely Sb, As, Cd, Cr, Pb, Hg, Ni and Se), PAHs and PCBs were extracted according to the
172 EN 12902 standard (Comite Europeen de Normalisation (CEN), 2004). After extraction, metals were
173 determined by an Elan 6100 ICP-MS (Perkin Elmer, Waltham, Massachusetts, USA), whereas PAHs
174 and PCBs were preconcentrated by solid-phase extraction (SPE) and analysed by GC-MS, as
175 elsewhere described (Bruzzoniti et al., 2019a; Rivoira et al., 2019). Quality controls were performed

176 to verify the recovery efficiency of PAHs and PCBs during the preconcentration step, using labelled
177 standards, as specified in the *Supplementary material* (see **Tables S1** for BCs and **S2** for ACs).

178 2.3.3 pH of the point of zero charge

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

181 2.3.4 Adsorption indexes

182 The determination of I_2/In and MB/In was performed according to the definitions indicated by CEFIC
183 for ACs (Conseil Européen des Fédérations de l'Industrie Chimique (CEFIC), 1986).

184 2.3.5 Physisorption analysis

185 Physisorption analysis of biochars and ACs was performed via nitrogen adsorption and desorption
186 experiments using a Porosity Analyser Thermo Fisher Scientific (Milan, Italy) model
187 SORPTOMATIC 1990 according to the American Society for Testing and Materials specifications
188 (American Society for Testing and Materials, 2012, 2017). In further detail, the specific surface area
189 (SSA) and micropore surface area (MiSSA) were determined respectively by the Brunauer–Emmett–
190 Teller (BET) method and by t-plot method, whereas mesopore surface area (MeSSA) was measured
191 by the Barrett-Joyner-Halenda (BJH) method applied to desorption data.

192 [2.3.6 Quality control of biochar and activated carbon characterization](#)
193 [Quality control of char characterization measurements was carried out by comparing the results here](#)
194 [obtained for AC1 and AC2 with those reported in the technical specifications of the two commercial](#)
195 [materials.](#)

197 2.4 Adsorption studies on DIAA and VOCs

198 Adsorption tests were performed on DIAA and VOCs in ultrapure water ($\text{pH} = 6.5 \pm 0.1$) using the
199 micro-isotherm technique for adsorbates at ppb concentrations, as established by ASTM D5919-96
200 standard (American Standard Test Method (ASTM), 1996). Aliquots of 40 mL and 100 mL,
201 containing fixed amounts of DIAA and VOCs, respectively (DIAA: $5 \mu\text{g L}^{-1}$ for BCs and $20 \mu\text{g L}^{-1}$

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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 different amounts of BCs/ACs varying approximately between 0.02 and 0.5 g. The mixture was stirred in an orbital shaker for 24 hours. The solution was then filtered through a mixed cellulose ester membrane (0.45 µm). Control experiments using the same aforementioned concentrations of target analytes were also conducted without the addition of the adsorbent materials, in order to estimate their removal due to mechanisms other than sorption (e.g. volatilization and degradation). Experimental data were fitted by the Freundlich isotherm model (Foo and Hameed, 2010):

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

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

2.5 Analytical determination of DIAA and VOCs

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

2.6 Water sample collection and characterization

Water samples were withdrawn from two potabilization plants located in the Piedmont region (North Italy) which treat the same raw water. One sample (labelled as DSB) was taken at the outlet of the dynamic separation basins for the removal of slurry from clarified waters (in which coagulant, hypochlorite and chlorine dioxide solutions are dosed), before entering the activated carbon beds. The other sample (labelled as CB) was taken at the outlet of a clarification basin (in which coagulant only is added), before entering the activated carbon beds. The water samples were characterized for pH and total organic carbon (TOC). TOC was determined using a Shimadzu TOC-V-CSH analyser, by

the differential method, i.e. analysing both total carbon (TC) and total inorganic carbon (TIC) through separate measurements and calculating TOC by subtracting TIC from TC.

2.7 Data analysis

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

3 Results and discussion

3.1 Characterization of chars

3.1.1 Ash content

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

The data obtained here can be interpreted based on the characteristics of biomass and thermal 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

252 contact time (slow pyrolysis) (Inyang and Dickenson, 2015). Hence, it is evident that, if the same
253 feedstock is used, the ash concentration will be higher in gasification processes than in pyrolysis
254 (Fryda and Visser, 2015). Moreover, increasing ash percentages will be obtained with increasing
255 temperature (Rafiq et al., 2016) and higher ash concentrations will be found under fast pyrolysis
256 conditions (Brewer et al., 2009). Based on these considerations, it makes sense that BC2, BC3, and
257 BC7, all deriving from slow pyrolysis processes (**Table 1**), showed ash percentages much lower than
258 BC5 and BC6, which were conversely obtained under gasification conditions using a same patented
259 process and plant. The very high ash concentration found in BC4 (about 29%) compared to BC3, both
260 produced with the patented PYREG® pyrolysis process under the same experimental conditions,
261 could be attributed to the different nature of the feedstocks employed, i.e. non woody vegetal biomass
262 for BC4 and woody waste biomass for BC3 (**Table 1**). Finally, the unexpected high ash content of
263 BC1 probably depends on the peculiar characteristics of the woody waste used as feedstock, which
264 derives from the cutting of a forest planted for the phytoremediation of a soil contaminated by
265 different chemicals, including heavy metals. Virgin activated carbon (AC1) showed a lower ash
266 content (7%), in agreement with the high standard quality requested by the potabilization plant in its
267 specifications. Higher ash percentages were obviously found in regenerated and in-use ACs (i.e. AC2
268 and AC3).

269 *3.1.2 Water-extractable substances*

270 The thermal conversion process that transforms biomasses into chars may lead to the formation of
271 unwanted organic and inorganic hazardous species, depending on the original composition of the
272 feedstocks. Among them, PAHs (Wang et al., 2017), PCBs (European Biochar Foundation (EBC))
273 and heavy metals (Lievens et al., 2009) can be present in biochars, thus introducing possible limitation
274 in the use of the chars themselves. The EN 12915-1 normative regulates the presence of water
275 extractable pollutants in materials to be applied for water treatments, setting a threshold concentration
276 limit for the sum of six PAH compounds (i.e. fluoranthene, benzo(b)fluoranthene,
277 benzo(k)fluoranthene, benzo(a)pyrene, benzo(g,h,i)perylene and indeno-(1,2,3-cd)-pyrene) at 0.02

278 $\mu\text{g L}^{-1}$. In addition, the EN standard imposes limits to the presence of As ($10 \mu\text{g L}^{-1}$), Cd ($0.5 \mu\text{g L}^{-1}$), 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
 279 $^{-1}$), 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
 280 regards PCBs, no limit is currently established by the EN standard. However, it should be mentioned
 281 that PCB concentrations are regulated in biochars to be used for soil conditioning and feed additives
 282 (European Biochar Foundation (EBC); International Biochar Initiative, 2015).
 283 Results obtained for leachable PAHs showed that all the chars fulfil the limits set by EN 12915-1
 284 regulation. In detail, the regulated PAHs were detected in BC1, BC2, BC3, BC4, and BC7 (all
 285 deriving from pyrolysis), with the sum of their concentrations ranging from 1.6 ng L^{-1} (BC4) to 13.3
 286 ng L^{-1} (BC7). Conversely, for ACs and the other BCs, the concentrations of PAHs included in the EN
 287 standard were below detection limits (**Table S3** of the *Supplementary material*).
 288 EPA PAHs other than the ones included in the EN standards were also determined (see **Table S3**),
 289 highlighting that PAHs with 2-3 aromatic rings were generally more abundant than those with higher
 290 molecular weight, as also observed elsewhere (Lyu et al., 2016). BC7, which was produced under
 291 pyrolysis at the lowest temperature (450°C), was the material providing by far the highest total
 292 leachable PAH concentration (826 ng L^{-1}), while biochars obtained under gasification conditions
 293 showed the lowest PAHs release ($11\text{-}12 \text{ ng L}^{-1}$). These BCs were also the ones providing respectively
 294 the highest and the lowest benzo(a)pyrene equivalent concentrations (BaPy_{eq}), based on toxic
 295 equivalence factors (TEFs) available in literature (Berardi et al., 2019). PAHs occurrence in BCs can
 296 be explained based on re-polymerization phenomena of the radical hydrocarbon fragments formed
 297 during the thermal process, which are favoured by the absence of oxygen. Moreover, the presence of
 298 PAHs depends also on the conversion temperature adopted, which plays a main role in PAH
 299 formation up to about 500°C , but also in their degradation beyond this value (Parker et al., 2014; Lyu
 300 et al., 2016). An influence of the biomass composition in the presence of leachable PAHs can also be
 301 evidenced from the comparison of BC3 (321 ng L^{-1}) and BC4 (26 ng L^{-1}), which were obtained under
 302 exactly the same pyrolysis conditions, but with completely different feedstocks.

303 The concentrations of extractable PCBs found in the BCs and ACs leachate are reported in **Table S4**
304 of the *Supplementary material*. BC1 was the only char exhibiting the presence of all the PCBs
305 investigated in its leachate, with total concentration of about 96 ng L⁻¹. Conversely, all the other BCs
306 showed PCB15 as the only leachable chlorinated biphenyl, the concentration of which was in the low
307 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-
308 29 ng L⁻¹) in BC5 and BC6. PCBs occurrence in the BC leachate could be ascribed to the thermal
309 transformation of chloride, originally contained in feedstocks (Reed) and in this regard, it should be
310 recalled that BC1 has been prepared with wood waste deriving from a multi-contaminated soil. To
311 the best of our knowledge, this is the first study investigating PCBs in BC leachates, thus preventing
312 any comparison with literature data.

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

320 *3.1.3 pH of the point of zero charge*

321 The values of pH_{pzc} were characterized by a high variability (7.0-12.0), in agreement with the wide
322 range of the production conditions, including the type of feedstock that, as already reported in
323 literature, significantly influence this property (Ippolito et al., 2020). For BCs, a significant linear
324 correlation with positive slope was found by plotting ash concentrations as a function of pH_{pzc} values
325 ($R^2 = 0.780$, $P < 0.05$). This correlation can be ascribed to the ash composition typically reported in
326 literature (Ippolito et al., 2020), which mainly consists in metals present in the hydroxide form, thus
327 promoting the increase of the pH in solution. ACs did not follow this trend, as the higher the amount
328 of ash, the lower the pH_{pzc} observed. This finding is in agreement with the increasing amount of

chemicals other than organic carbon adsorbed by ACs during operation, which however do not influence the alkalinity of material surfaces.

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

3.1.4 Adsorption indexes of chars

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

I_2In is commonly considered as related to the presence in the structure of micropores (average diameter less than 2 nm) and should be therefore informative for the removal efficiency of small-size organic water pollutants (Del Bubba et al., 2020). Conversely, $MBIn$ should be associated to the 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 I₂In (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 I₂In 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 area (Liu et al., 2010; Ahmad et al., 2014), since BC5/BC6 and BC7 were obtained by the highest and lowest conversion temperature, respectively (**Table 1**). Indeed, very good linear correlations ($R^2 = 0.981-0.984$, $P < 0.05$) were observed between SSA and adsorption indexes (see **Figures S2-A** and **S2-B** of the *Supplementary material*), even excluding ACs from the regression ($R^2 = 0.781-0.904$, data not shown).

In general, BCs showed a higher percentage of macroporosity than ACs. However, it should be noted that BC3 and BC4, produced with the same patented PYREG® pyrolysis system, had a very small microporosity, comparable to that observed in ACs. The relative percentages of microporosity and

mesoporosity were comparable in all materials, with the exception of AC1, which was strongly characterized by microporosity. Moreover, high correlations were found between MiSSA and I₂In ($R^2 = 0.972$, $P < 0.05$), as well as between the MeSSA and MBIn ($R^2 = 0.922$, $P < 0.05$) (**Figs. S2-C and S2-D**). However, similarly to findings observed for the correlation between adsorption indexes, also these relationships were mainly driven by the presence of ACs, since their exclusion strongly lowered the determination coefficients, making null the significance of the correlation (data not shown).

Differently from adsorption indexes, SSA is often reported as fundamental parameter for the characterization of sorption properties of BCs. In order to understand the overall significance of SSA data obtained here, it is therefore interesting to compare them with the values reported in literature for the numerous biochars obtained from vegetal feedstocks. However, the kind of conversion process, its temperature and time, as well as the type of biomass used, strongly affects the SSA of BCs. Accordingly, this comparison was restricted to biochars obtained from woody vegetal feedstocks, which represent the main type of biomass used for the production of BCs here investigated, obtaining SSA values in the range 2-637 m² g⁻¹ (Chen et al., 2016; Hansen et al., 2016; Chen et al., 2019; Grojzdek et al., 2021). Therefore, the SSA values between 136 and 309 m² g⁻¹ measured in this study are fully in the range reported in the literature.

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, I₂In, 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, I₂In, 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 (intermediate value for BC1 and the highest one for BC7), and total metals (the highest in BC1 and the lowest in BC7), which strongly contributed to these PCs.

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

carbon (AC1) and the regenerated ones (AC1 and AC2), which exhibited a very low degree of similarity (about 20%).

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

3.3 Adsorption studies on DIAA and VOCs

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

3.3.1 DIAA

As regards DIAA, at 5 µg/L, both ACs exhibited a quantitative removal for all the char concentrations tested, since target analyte was not detected in water solutions after 24 h of contact. Conversely, removal in the ranges of 18.8-70.8 % and 5.1-28.4% were observed for BC6 and BC7, respectively (**Table 3**). The different adsorption performances exhibited by BC6 and BC7 should be ascribed not only to the different surface area, but also to the surface charge, as derived by pH_{pzc} measures. In fact, pH_{pzc} tests indicated a significantly higher positive surface charge for BC6 ($pH_{pzc}=11.0$) than BC7 ($pH_{pzc}=7.0$) at the working pH value (pH=6.5), which is responsible for electrostatic interactions between biochar and DIAA (Inyang and Dickenson, 2015).

As no detectable DIAA concentrations were found for ACs at 5 µg L⁻¹, adsorption isotherm experiments were repeated using an initial concentration of 20 µg L⁻¹. With this concentration, the removal percentage of the two ACs remained quite similar, ranging approximately from about 89 % to 100 % in both cases (**Table 3**). As illustrated by **Figure 3**, adsorption data were fitted by the linearized Freundlich equation, observing in all cases determination coefficients ≥ 0.925 and statistically significant models based on ANOVA (P -values $\ll 0.05$). Values of K_F (**Table 3**) for BCs

were about three orders of magnitude lower than those for ACs. Hence, BCs provided a poor adsorption ability compared to those determined for materials routinely used in water treatment plants. In more detail, based on the K_F values, BC6 exhibited sorption ability about 3 times higher than BC7. A similar efficiency ratio was observed for AC1 vs. AC2, in accordance with the fact that the former is a virgin material, while the latter is a regenerated char. Slope ($1/n$) values of the regression lines (**Fig. 3**) were in all cases < 1 (from 0.432 for BC7 to 0.736 for AC1), following the order $BC7 \approx BC6 < AC2 < AC1$. The values determined for slopes suggest an L-type isotherm behaviour (European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC), 2013) for the adsorption of DIAA on the investigated chars, notwithstanding the pseudo-linear aspect of the experimental equilibrium concentration data (i.e. X/M vs. C_e), which is probably related to the quite high concentrations of material and their narrow range tested here (i.e. about one order of magnitude). This means that when DIAA concentration increases, the relative adsorption decreases due to the saturation of adsorption sites available to DIAA, resulting in relatively less intense adsorption, with increasing the amount of chemical adsorbed onto the material, as commonly observed for the sorption of organic compounds on chars.

3.3.2 VOCs

Adsorption isotherm experiments on VOCs showed a not negligible variability of data, probably due to the high vapour pressure and low water solubility of these analytes (Henry constants of $5.5 \cdot 10^{-4}$ 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 should be noted that control experiments evidenced losses of both the investigated VOCs (about 15-25%). Accordingly, adsorption isotherms were not calculated for VOCs. However, it is possible to state that both BCs showed good adsorption properties, since, at both 20 and 5 $\mu\text{g/L}$ the removal percentage was almost quantitative for ACs and BC6, and approximately equal to 60-70% and 70-80%, for BC7 towards benzene and 1,2-dichlorobenzene, respectively.

3.4 Removal tests in water samples collected in drinking water plants

483 The removal capabilities of BC6 and BC7 were additionally tested in two water samples (i.e. DSB
484 and CB) collected from the drinking water plant treatment train (before entering the final refinement
485 stage with activated carbon beds) and compared with those of commercial AC1. These tests were
486 performed by putting in contact for 24 h 0.4 g of chars with 100 mL of DSB and CB spiked with 20
487 $\mu\text{g L}^{-1}$ of DIAA or VOCs. In such a way, the possible competitive effects exhibited by the matrix can
488 be assessed and results obtained from adsorption experiments in ultrapure water eventually
489 confirmed. To better explain possible competitions mechanisms, Total Organic Carbon (TOC) was
490 initially measured in the two samples, obtaining TOC values of 4.3 mg L^{-1} and 2.4 mg L^{-1} for CB and
491 DSB, respectively. The lower TOC value observed for DSB should be ascribed to the disinfection
492 stage operated in this treatment train. The results obtained in these removal tests are summarized in
493 **Table 4**. As a general consideration, the use of water samples collected within the treatment train of
494 the potabilization plants did not alter the performance of the BCs, even though the lower
495 performances of biochars compared to the activated carbon were confirmed. Results obtained in real
496 water samples fully support the design of column experiments to assess accurately the removal
497 capacity and exhausting time of BCs, with particular reference to BC6.

498 **4 Conclusions**

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

502 In this paper, seven BCs obtained from gasification or pyrolysis processes of waste vegetal biomass,
503 were characterized in depth for numerous parameters, in comparison with a virgin commercial AC, a
504 freshly regenerated AC, and a regenerated AC in use at a potabilization facility. The characterization
505 included the evaluation of “environmental concern” parameters (e.g. PAHs and metals release), for
506 which mandatory limits are provided at European level for materials intended as sorbents for drinking
507 water filtration, but seldom evaluated elsewhere. Most BCs met these limits, whilst the “sorption
508 performance parameters” regulated in the European standard (i.e. I_2/In and ash in the UNI EN 12915-

509 1) were in almost all cases outside the acceptance thresholds, suggesting lower efficiencies compared
510 to ACs. However, the sorption ability of a given material towards a specific molecule is the result of
511 a set of characteristics, which all contribute together to the overall removal efficiency, thus suggesting
512 the importance of following a multivariate approach.

513 Indeed, multivariate analyses performed in this work (i.e. PCA and CA) allowed for easily
514 identifying the materials with the closest (BC5 and BC6) or the farthest (BC1 and BC7) characteristics
515 to those of ACs. Accordingly, and the multivariate approach is use should be promoted in the field
516 of exploration of data deriving from material characterization, rather than the evaluation of individual
517 characteristics, even if they are regulated by legislation.

519 Adsorption tests towards DIAA and VOCs carried out in ultrapure water highlighted the much lower
520 sorption ability of BC7 compared to BC6. These results were in agreement with findings of
521 multivariate analyses, therefore suggesting intermediate sorption performances for BC1-BC5.
522 Interestingly, removal tests in waters withdrawn from potabilization plants did not evidence any
523 significant decrease of the sorption ability of BC6 and BC7s towards the investigated contaminants
524 compared to tests in ultrapure water, thus supporting the implementation of column experiments for
525 establishing the maximum loading capacity of the materials in experimental conditions more similar
526 to the real scale.

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

532 Even if ashes are a regulated parameter, our results suggest that this could not be a limiting parameter
533 for the adsorption of organic molecules.

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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 (C_e , 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 , $\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$). 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	0.00484
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	
BC7 (5 µg L ⁻¹)				
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	
AC1 (20 µg L ⁻¹)				
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	
AC2 (20 µg L ⁻¹)				
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 100 mL-aliquots of 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

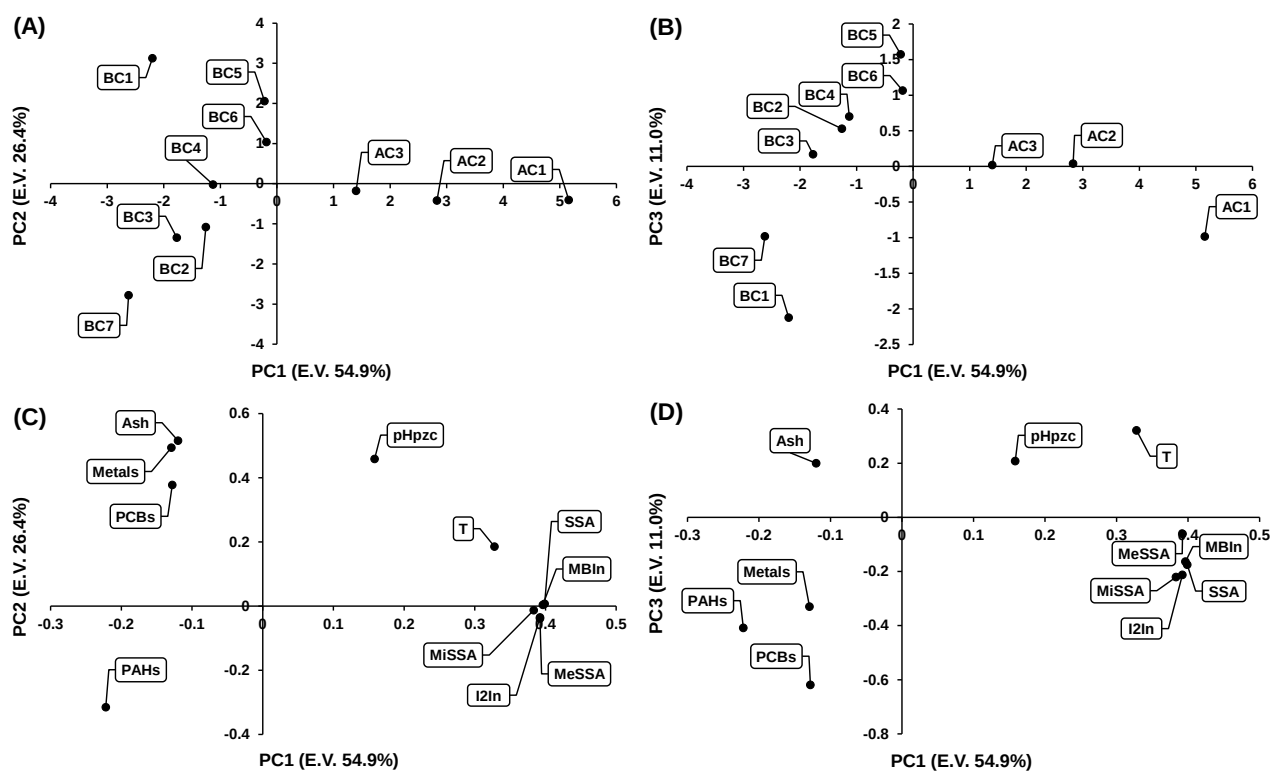


Figure 1 – Score (A-B) and loading (C-D) plots of PC1 versus PC2 and PC1 versus PC3, representing a percentage of explained variance (E.V.) of 81.3% and 65.9%, respectively. PCA values were calculated using the autoscaled values determined for the eleven original variables in the ten char samples. Note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

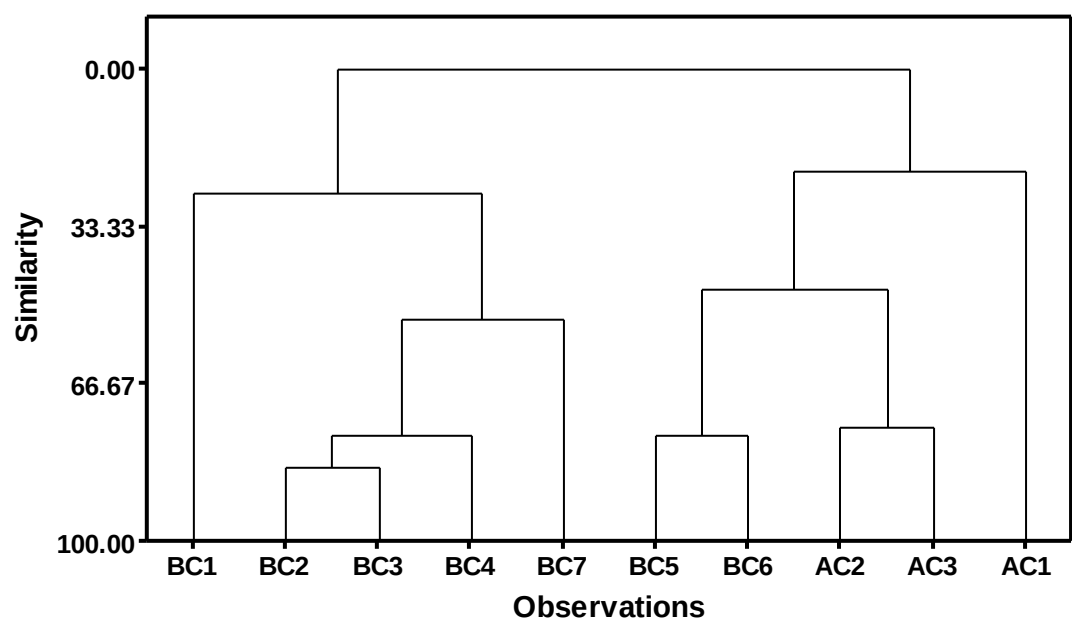


Figure 2 – Dendrogram of similarity of the ten investigated char samples, calculated through the complete linkage method on the basis of Euclidean distances of the autoscaled values of the eleven original variables.

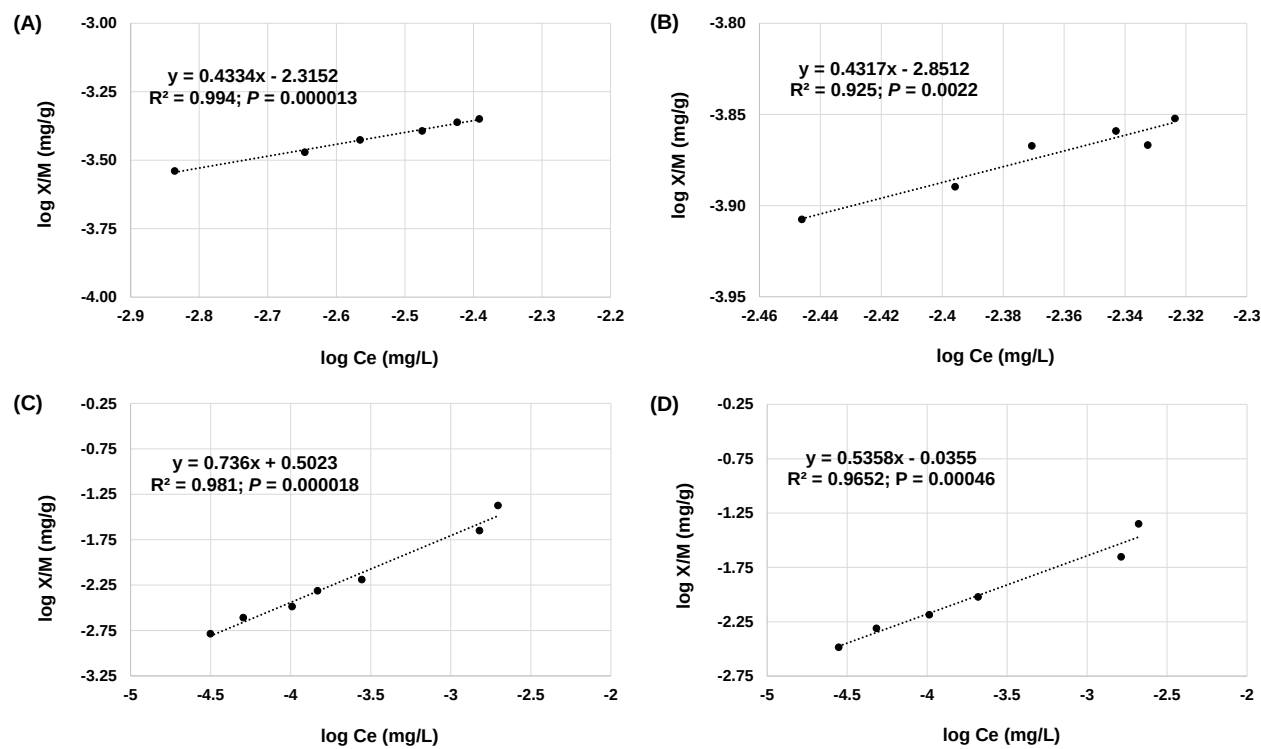


Figure 3 – Plots of linearized Freundlich isotherms obtained for BC6 (A), BC7 (B), AC1 (C), and AC2 (D).

**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

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 routinely integrated in drinking water
61 production (Ali and Gupta, 2006) for the removal of micropollutants occurring *per se* in raw waters
62 and/or as a result of disinfection processes, thereby eliminating the toxicity induced by these
63 molecules in treated water (Han and Zhang, 2018; Han et al., 2021). Within this context, adsorption
64 is generally based on the use of activated carbon (Jiang et al., 2017; Perrich, 2018; Jiang et al., 2020),
65 even though innovative sorbents, such as mesoporous silica (Kyzas and Matis, 2015; Rivoira et al.,
66 2016) or other waste-derived ceramic materials (Jana et al., 2016; Bruzzoniti et al., 2018) have been
67 proposed as alternative adsorption media. Low-cost materials like biochar (BC) have recently
68 received attention for their physicochemical characteristics including the porous structure, which is
69 similar to that of activated carbons. Biochar is the solid by-product of the thermal conversion of a
70 wide range of feedstocks, such as agricultural wastes (Ali and Gupta, 2006; Colantoni et al., 2016),
71 wood residues (Wang et al., 2013), manure (Cao and Harris, 2010), and sludge (Méndez et al., 2017).
72 Due to its properties, biochar has found application as animal feed additives (McHenry, 2010) and
73 soil amenders (Singh et al., 2010), as well as for the adsorption of micropollutants from aqueous
74 matrices (Palansooriya et al., 2020).

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

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

95 Based on the considerations mentioned above, the aim of this research was to investigate the
96 physicochemical properties, the regulated leachable substances, and the removal performances of
97 seven biochars (commercially available or synthesized for the purpose), obtained from pyrolysis or
98 gasification of vegetal biomass, in comparison with three commercially available vegetal ACs used
99 in an Italian drinking water facility, at different age of operation. Data obtained were chemometrically
100 treated through principal component analysis, allowing for selecting the most promising biochars to

101 be further investigated by adsorption tests. In a first phase of this study, adsorption capabilities were
102 tested in ultrapure water, whereas afterwards the sorption capacity was evaluated on a restricted group
103 of biochars in water samples collected at intermediate treatment stages of a potabilization plant. In
104 all cases ACs were also tested as reference comparative materials.

105 Diiodoacetic acid (DIAA), benzene, and 1,2 dichlorobenzene, were selected as model pollutants
106 commonly monitored in drinking water facilities. Specifically, DIAA is a model emerging
107 disinfection by-product (Bruzzoniti et al., 2019b) never investigated before for its sorption by
108 biochars. Moreover, 1,2 dichlorobenzene can also originate from disinfection treatments during the
109 potabilization process (Lahaniatis et al., 1994; Hou et al., 2012) and its monitoring in tap water is
110 recommended by the World Health Organization guidelines (taste threshold value $1 \mu\text{g L}^{-1}$) (World
111 Health Organization, 2017), while benzene is regulated by the Directive 2020/2184 regarding the
112 quality of water intended for human consumption ($1 \mu\text{g L}^{-1}$). It should also be noted that benzene and
113 1,2 dichlorobenzene are volatile organic carbons (VOCs) still detected in some industrial districts
114 (Martínez et al., 2002) and are therefore also important from the wastewater treatment viewpoint.

115 **2 Materials and methods**

116 **2.1 Reagents**

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

123 For the determination of extractable polycyclic aromatic hydrocarbons (PAHs), the 16 compounds
124 listed by EPA were purchased from Sigma Aldrich (Darmstadt, Germany). For the analysis of
125 extractable polychlorinated biphenyls (PCBs), the compounds were purchased from LGC Standards
126 (Milan, Italy). They were non dioxin-like PCBs: 3,3'-dichlorobiphenyl (PCB 11), 4,4'-

127 dichlorobiphenyl (PCB 15), 2,4,4'-trichlorobiphenyl (PCB 28), 2,2',5,5'-tetrachlorobiphenyl (PCB
 128 52), 2,2',4,5,5'-pentachlorobiphenyl (PCB 101), 2,2',3,4,4',5-hexachlorobiphenyl (PCB 138),
 129 2,2',4,4',5,5'-hexachlorobiphenyl (PCB 153), 3,3',4,4',5,5'-hexachlorobiphenyl (PCB 169),
 130 2,2',3,4,4',5,5'-heptachlorobiphenyl (PCB 180), 2,3,3',4,4',5,5'-heptachlorobiphenyl (PCB 189);
 131 and dioxin-like PCBs: 3,4,4',5-tetrachlorobiphenyl (PCB 81), 2,3',4,4',5-pentachlorobiphenyl (PCB
 132 118), 2',3,4,4',5-pentachlorobiphenyl (PCB 123), 2,3',4,4',5,5'-hexachlorobiphenyl (PCB 167).
 133 Labelled isotope compounds for PCBs (2 mg L⁻¹) and for PAHs (5 mg L⁻¹), Wellington Laboratories
 134 (Ontario, Canada), were used as internal and surrogate standards in order to obtain calibration curves
 135 and extraction recoveries, respectively. The ¹³C surrogate solutions of PAHs contained:
 136 [¹³C₆]benzo(a)anthracene [¹³C₆-BaA], [¹³C₆]chrysene [¹³C₆-Chr], [¹³C₆]benzo(b)fluoranthene [¹³C₆-
 137 BbFl], [¹³C₆]benzo(k)fluoranthene [¹³C₆-BkFl], [¹³C₄]benzo(a)pyrene [¹³C₄-BaP],
 138 [¹³C₆]indeno(1,2,3-cd)pyrene [¹³C₄-Ind], [¹³C₆]dibenzo(a,h)anthracene [¹³C₆-DBA], and
 139 [¹³C₁₂]benzo(g,h,i)perylene [¹³C₁₂-BP]. The ¹³C surrogate solution of PCBs contained: ¹³C₁₂-PCB28,
 140 ¹³C₁₂-PCB52, ¹³C₁₂-PCB118, ¹³C₁₂-PCB153, and ¹³C₁₂-PCB180.
 141 Volatile organic compounds, namely benzene (100 µg L⁻¹ in methanol), and 1,2-dichlorobenzene
 142 (100 µg L⁻¹ in methanol), were purchased from Ultra Scientific Italia (Bologna, Italy). DIAA was
 143 supplied by Chemical Research (Rome, Italy). Ultrapure water was obtained by an EMD Millipore
 144 Milli-Q Direct Water Purification System (Millipore, Bedford, MA, USA).
 145 **2.2 Biochar and activated carbon samples**
 146 The seven BCs considered in this study were donated for the purpose by different companies, which
 147 produce the materials for commercial scopes or for their internal use through well-established
 148 procedures. The three ACs were supplied by a local potabilization plant at different age of operation:
 149 AC1: new activated carbon; AC2: regenerated activated carbon; AC3: regenerated activated carbon
 150 in use at the plant. The status of operation, and the characteristics of the feedstock and the thermal
 151 process used to produce the ten chars are summarized in **Table 1**.

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

154 2.3 Biochar and activated carbon characterization

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

161 2.3.1 Ash content

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

164 2.3.2 Water-extractable substances

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

172 2.3.3 pH of the point of zero charge

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

175 2.3.4 Adsorption indexes

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

178 2.3.5 *Physisorption analysis*

179 Physisorption analysis of biochars and ACs was performed via nitrogen adsorption and desorption
180 experiments using a Porosity Analyser Thermo Fisher Scientific (Milan, Italy) model
181 SORPTOMATIC 1990 according to the American Society for Testing and Materials specifications
182 (American Society for Testing and Materials, 2012, 2017). In further detail, the specific surface area
183 (SSA) and micropore surface area (MiSSA) were determined respectively by the Brunauer–Emmett–
184 Teller (BET) method and by t-plot method, whereas mesopore surface area (MeSSA) was measured
185 by the Barrett-Joyner-Halenda (BJH) method applied to desorption data.

186 2.3.6 *Quality control of biochar and activated carbon characterization*

187 Quality control of char characterization measurements was carried out by comparing the results here
188 obtained for AC1 and AC2 with those reported in the technical specifications of the two commercial
189 materials.

190 2.4 Adsorption studies on DIAA and VOCs

191 Adsorption tests were performed on DIAA and VOCs in ultrapure water (pH = 6.5±0.1) using the
192 micro-isotherm technique for adsorbates at ppb concentrations, as established by ASTM D5919-96
193 standard (American Standard Test Method (ASTM), 1996). Aliquots of 40 mL and 100 mL,
194 containing fixed amounts of DIAA and VOCs, respectively (DIAA: 5 µg L⁻¹ for BCs and 20 µg L⁻¹
195 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
196 different amounts of BCs/ACs varying approximately between 0.02 and 0.5 g. The mixture was
197 stirred in an orbital shaker for 24 hours. The solution was then filtered through a mixed cellulose ester
198 membrane (0.45 µm). Control experiments using the same aforementioned concentrations of target
199 analytes were also conducted without the addition of the adsorbent materials, in order to estimate
200 their removal due to mechanisms other than sorption (e.g. volatilization and degradation).

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

202
$$\log \frac{X}{M} = \log K_F + \frac{1}{n} \log C_e$$

203 Where X/M is the ratio of the amount of analyte adsorbed per mass unit of sorbent (mg g^{-1}), K_F is the
204 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
205 the equilibrium concentration (mg L^{-1}), and $1/n$ is the exponent of non-linearity.

206 2.5 Analytical determination of DIAA and VOCs

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

211 2.6 Water sample collection and characterization

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

221 2.7 Data analysis

222 Least squares regressions and related analyses of variance (ANOVA) were performed with Excel
223 2016 (Microsoft, Redmond, WA, USA). Principal component analysis (PCA) and cluster analysis
224 (CA) were carried out using the Minitab statistical software package, version 17.1.0 (Minitab Inc.,
225 State College, PA, USA). All data plots were performed using Excel 2016.

226 3 Results and discussion

227 3.1 Characterization of chars

228 3.1.1 Ash content

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

235 The data obtained here can be interpreted based on the characteristics of biomass and thermal
236 conversion processes through which the chars were obtained. According to literature, ash
237 concentration of chars is mainly influenced by the type of feedstock, being woody biomass the one
238 providing a lower ash content, compared to other feedstocks, such as non-woody vegetal biomass and
239 animal waste (Tomczyk et al., 2020). However, the type of thermal conversion process (i.e. pyrolysis
240 or gasification) and the temperature and contact time conditions adopted in the process may also play
241 a role in determining the ash concentration, which obviously depends on the amount of char obtained.
242 In this regard, it should be remarked that biochar yield is a function of the type of thermal conversion
243 process (i.e. pyrolysis or gasification) and the temperature and contact time conditions adopted in the
244 process, being the highest yields obtained with pyrolysis conducted at low temperature and high
245 contact time (slow pyrolysis) (Inyang and Dickenson, 2015). Hence, it is evident that, if the same
246 feedstock is used, the ash concentration will be higher in gasification processes than in pyrolysis
247 (Fryda and Visser, 2015). Moreover, increasing ash percentages will be obtained with increasing
248 temperature (Rafiq et al., 2016) and higher ash concentrations will be found under fast pyrolysis
249 conditions (Brewer et al., 2009). Based on these considerations, it makes sense that BC2, BC3, and
250 BC7, all deriving from slow pyrolysis processes (**Table 1**), showed ash percentages much lower than
251 BC5 and BC6, which were conversely obtained under gasification conditions using a same patented
252 process and plant. The very high ash concentration found in BC4 (about 29%) compared to BC3, both
253 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).

3.1.2 *Water-extractable substances*

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

Results obtained for leachable PAHs showed that all the chars fulfil the limits set by EN 12915-1 regulation. In detail, the regulated PAHs were detected in BC1, BC2, BC3, BC4, and BC7 (all deriving from pyrolysis), with the sum of their concentrations ranging from 1.6 ng L^{-1} (BC4) to 13.3

279 ng L⁻¹ (BC7). Conversely, for ACs and the other BCs, the concentrations of PAHs included in the EN
280 standard were below detection limits (**Table S3** of the *Supplementary material*).

281 EPA PAHs other than the ones included in the EN standards were also determined (see **Table S3**),
282 highlighting that PAHs with 2-3 aromatic rings were generally more abundant than those with higher
283 molecular weight, as also observed elsewhere (Lyu et al., 2016). BC7, which was produced under
284 pyrolysis at the lowest temperature (450°C), was the material providing by far the highest total
285 leachable PAH concentration (826 ng L⁻¹), while biochars obtained under gasification conditions
286 showed the lowest PAHs release (11-12 ng L⁻¹). These BCs were also the ones providing respectively
287 the highest and the lowest benzo(a)pyrene equivalent concentrations (BaPy_{eq}), based on toxic
288 equivalence factors (TEFs) available in literature (Berardi et al., 2019). PAHs occurrence in BCs can
289 be explained based on re-polymerization phenomena of the radical hydrocarbon fragments formed
290 during the thermal process, which are favoured by the absence of oxygen. Moreover, the presence of
291 PAHs depends also on the conversion temperature adopted, which plays a main role in PAH
292 formation up to about 500°C, but also in their degradation beyond this value (Parker et al., 2014; Lyu
293 et al., 2016). An influence of the biomass composition in the presence of leachable PAHs can also be
294 evidenced from the comparison of BC3 (321 ng L⁻¹) and BC4 (26 ng L⁻¹), which were obtained under
295 exactly the same pyrolysis conditions, but with completely different feedstocks.

296 The concentrations of extractable PCBs found in the BCs and ACs leachate are reported in **Table S4**
297 of the *Supplementary material*. BC1 was the only char exhibiting the presence of all the PCBs
298 investigated in its leachate, with total concentration of about 96 ng L⁻¹. Conversely, all the other BCs
299 showed PCB15 as the only leachable chlorinated biphenyl, the concentration of which was in the low
300 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-
301 29 ng L⁻¹) in BC5 and BC6. PCBs occurrence in the BC leachate could be ascribed to the thermal
302 transformation of chloride, originally contained in feedstocks (Reed) and in this regard, it should be
303 recalled that BC1 has been prepared with wood waste deriving from a multi-contaminated soil. To

304 the best of our knowledge, this is the first study investigating PCBs in BC leachates, thus preventing
305 any comparison with literature data.

306 The concentrations of metals determined in BC leachates are illustrated in **Table S5** of the
307 *Supplementary material*, where the limits set by UNI EN 12915-1 are also reported. BCs generally
308 complied with the release limits set by the aforementioned regulation, with the only exception of
309 BC1, which exceeded the limit for Cr, with an observed concentration ($17.3 \mu\text{g L}^{-1}$) three times higher
310 than this limit, in agreement with the considerations previously reported. As regards ACs, only AC3
311 exceeded limit for Se ($5 \mu\text{g L}^{-1}$ versus $3 \mu\text{g L}^{-1}$, see **Table S5**), suggesting that a possible saturation
312 of adsorption sites occurred during service.

313 3.1.3 *pH of the point of zero charge*

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

324 The measurement of the pH_{pzc} values allowed us to make some considerations about the net surface
325 charge of the chars, which mainly depends on the surface functional groups of the material and is
326 extremely useful to explain the adsorption behaviours of BCs towards ionized or ionisable
327 compounds. Most BCs (with the only exception of BC7) exhibited pH_{pzc} higher than pH values of
328 drinking water collected before entering AC filters of the aforementioned potabilization plants, which
329 ranged between 7.6 and 7.7. Hence, BC1-BC6 are expected to exhibit positively charged surfaces

330 when they were applied to the treatment of these waters, whereas BC7 is supposed to be negatively
331 charged (Li et al., 2017).

332 3.1.4 Adsorption indexes of chars

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

335 I_2In is commonly considered as related to the presence in the structure of micropores (average
336 diameter less than 2 nm) and should be therefore informative for the removal efficiency of small-size
337 organic water pollutants (Del Bubba et al., 2020). Conversely, $MBIn$ should be associated to the
338 abundance of mesopores (average diameter in the range 2-50 nm) and thus considered as a useful
339 indicator of adsorption capacity towards medium-large sized organic pollutants (Del Bubba et al.,
340 2020). For BCs, the I_2In was found in the range 77-197 mg I_2 g⁻¹, with BCs obtained from gasification
341 (i.e. BC5 and BC6) showing the highest values (156-197 mg I_2 g⁻¹), while the lowest ones (77-88 mg
342 I_2 g⁻¹) were exhibited by materials produced under pyrolytic conditions (i.e. BC3 and BC7). The range
343 determined for I_2In in BCs was about five times lower than that determined in virgin and regenerated
344 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.
345 AC2 after some use in the potabilization plant) was lower than that of AC2 (438 mg I_2 g⁻¹), in
346 agreement with the progressive pore saturation phenomena occurring during operation.

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

355 can be explained by the general differences in micro, meso, and macroporosity distributions of BCs
356 due to the different experimental conditions adopted for their production.

357 3.1.5 Physisorption analysis

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

360 As expected, ACs exhibited much higher values of the SSA ($561\text{-}1053\text{ m}^2\text{ g}^{-1}$) than BCs ($136\text{-}309\text{ m}^2$
361 g^{-1}), being the latter group characterized by a data trend similar to those observed for adsorption
362 indexes. To elaborate, BC5 and BC6, in addition to showing greater values of the adsorption indexes,
363 also exhibited the highest SSA, whereas BC7 had the lowest values of the aforementioned parameters.
364 These findings can be explained by the well-recognized role of temperature in increasing the surface
365 area (Liu et al., 2010; Ahmad et al., 2014), since BC5/BC6 and BC7 were obtained by the highest
366 and lowest conversion temperature, respectively (**Table 1**). Indeed, very good linear correlations (R^2
367 $= 0.981\text{-}0.984$, $P < 0.05$) were observed between SSA and adsorption indexes (see **Figures S2-A** and
368 **S2-B** of the *Supplementary material*), even excluding ACs from the regression ($R^2 = 0.781\text{-}0.904$,
369 data not shown).

370 In general, BCs showed a higher percentage of macroporosity than ACs. However, it should be noted
371 that BC3 and BC4, produced with the same patented PYREG® pyrolysis system, had a very small
372 microporosity, comparable to that observed in ACs. The relative percentages of microporosity and
373 mesoporosity were comparable in all materials, with the exception of AC1, which was strongly
374 characterized by microporosity. Moreover, high correlations were found between MiSSA and I_2/In
375 ($R^2 = 0.972$, $P < 0.05$), as well as between the MeSSA and MBIn ($R^2 = 0.922$, $P < 0.05$) (**Figs. S2-C**
376 **and S2-D**). However, similarly to findings observed for the correlation between adsorption indexes,
377 also these relationships were mainly driven by the presence of ACs, since their exclusion strongly
378 lowered the determination coefficients, making null the significance of the correlation (data not
379 shown).

Differently from adsorption indexes, SSA is often reported as fundamental parameter for the characterization of sorption properties of BCs. In order to understand the overall significance of SSA data obtained here, it is therefore interesting to compare them with the values reported in literature for the numerous biochars obtained from vegetal feedstocks. However, the kind of conversion process, its temperature and time, as well as the type of biomass used, strongly affects the SSA of BCs. Accordingly, this comparison was restricted to biochars obtained from woody vegetal feedstocks, which represent the main type of biomass used for the production of BCs here investigated, obtaining SSA values in the range 2-637 m² g⁻¹ (Chen et al., 2016; Hansen et al., 2016; Chen et al., 2019; Grojzdek et al., 2021). Therefore, the SSA values between 136 and 309 m² g⁻¹ measured in this study are fully in the range reported in the literature.

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, I₂In, 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, I₂In, 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 (intermediate value for BC1 and the highest one for BC7), and total metals (the highest in BC1 and the lowest in BC7), which strongly contributed to these PCs.

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

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

3.3 Adsorption studies on DIAA and VOCs

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

436 3.3.1 DIAA

437 As regards DIAA, at 5 µg/L, both ACs exhibited a quantitative removal for all the char concentrations
438 tested, since target analyte was not detected in water solutions after 24 h of contact. Conversely,
439 removal in the ranges of 18.8-70.8 % and 5.1-28.4% were observed for BC6 and BC7, respectively
440 (**Table 3**). The different adsorption performances exhibited by BC6 and BC7 should be ascribed not
441 only to the different surface area, but also to the surface charge, as derived by pH_{pzc} measures. In fact,
442 pH_{pzc} tests indicated a significantly higher positive surface charge for BC6 ($pH_{pzc}=11.0$) than BC7
443 ($pH_{pzc}=7.0$) at the working pH value ($pH=6.5$), which is responsible for electrostatic interactions
444 between biochar and DIAA (Inyang and Dickenson, 2015).

445 As no detectable DIAA concentrations were found for ACs at 5 µg L⁻¹, adsorption isotherm
446 experiments were repeated using an initial concentration of 20 µg L⁻¹. With this concentration, the
447 removal percentage of the two ACs remained quite similar, ranging approximately from about 89 %
448 to 100 % in both cases (**Table 3**). As illustrated by **Figure 3**, adsorption data were fitted by the
449 linearized Freundlich equation, observing in all cases determination coefficients ≥ 0.925 and
450 statistically significant models based on ANOVA (P -values $\ll 0.05$). Values of K_F (**Table 3**) for BCs
451 were about three orders of magnitude lower than those for ACs. Hence, BCs provided a poor
452 adsorption ability compared to those determined for materials routinely used in water treatment
453 plants. In more detail, based on the K_F values, BC6 exhibited sorption ability about 3 times higher
454 than BC7. A similar efficiency ratio was observed for AC1 vs. AC2, in accordance with the fact that
455 the former is a virgin material, while the latter is a regenerated char. Slope ($1/n$) values of the
456 regression lines (**Fig. 3**) were in all cases < 1 (from 0.432 for BC7 to 0.736 for AC1), following the
457 order $BC7 \approx BC6 \ll AC2 < AC1$. The values determined for slopes suggest an L-type isotherm

behaviour (European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC), 2013) for the adsorption of DIAA on the investigated chars, notwithstanding the pseudo-linear aspect of the experimental equilibrium concentration data (i.e. X/M vs. C_e), which is probably related to the quite high concentrations of material and their narrow range tested here (i.e. about one order of magnitude). This means that when DIAA concentration increases, the relative adsorption decreases due to the saturation of adsorption sites available to DIAA, resulting in relatively less intense adsorption, with increasing the amount of chemical adsorbed onto the material, as commonly observed for the sorption of organic compounds on chars.

3.3.2 VOCs

Adsorption isotherm experiments on VOCs showed a not negligible variability of data, probably due to the high vapour pressure and low water solubility of these analytes (Henry constants of $5.5 \cdot 10^{-4}$ 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 should be noted that control experiments evidenced losses of both the investigated VOCs (about 15-25%). Accordingly, adsorption isotherms were not calculated for VOCs. However, it is possible to state that both BCs showed good adsorption properties, since, at both 20 and 5 $\mu\text{g/L}$ the removal percentage was almost quantitative for ACs and BC6, and approximately equal to 60-70% and 70-80%, for BC7 towards benzene and 1,2-dichlorobenzene, respectively.

3.4 Removal tests in water samples collected in drinking water plants

The removal capabilities of BC6 and BC7 were additionally tested in two water samples (i.e. DSB and CB) collected from the drinking water plant treatment train (before entering the final refinement stage with activated carbon beds) and compared with those of commercial AC1. These tests were performed by putting in contact for 24 h 0.4 g of chars with 100 mL of DSB and CB spiked with 20 $\mu\text{g L}^{-1}$ of DIAA or VOCs. In such a way, the possible competitive effects exhibited by the matrix can be assessed and results obtained from adsorption experiments in ultrapure water eventually confirmed. To better explain possible competitions mechanisms, Total Organic Carbon (TOC) was initially measured in the two samples, obtaining TOC values of 4.3 mg L^{-1} and 2.4 mg L^{-1} for CB and

DSB, respectively. The lower TOC value observed for DSB should be ascribed to the disinfection stage operated in this treatment train. The results obtained in these removal tests are summarized in **Table 4**. As a general consideration, the use of water samples collected within the treatment train of the potabilization plants did not alter the performance of the BCs, even though the lower performances of biochars compared to the activated carbon were confirmed. Results obtained in real water samples fully support the design of column experiments to assess accurately the removal capacity and exhausting time of BCs, with particular reference to BC6.

4 Conclusions

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

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_2 In and ash in the UNI EN 12915-1) were in almost all cases outside the acceptance thresholds, suggesting lower efficiencies compared to ACs. However, the sorption ability of a given material towards a specific molecule is the result of a set of characteristics, which all contribute together to the overall removal efficiency, thus suggesting the importance of following a multivariate approach. Indeed, multivariate analyses performed in this work (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. Accordingly, the multivariate approach should be promoted in the exploration of data deriving from material characterization, rather than the evaluation of individual characteristics, even if they are regulated by legislation.

510 Adsorption tests towards DIAA and VOCs carried out in ultrapure water highlighted the much lower
511 sorption ability of BC7 compared to BC6. These results were in agreement with findings of
512 multivariate analyses, therefore suggesting intermediate sorption performances for BC1-BC5.
513 Interestingly, removal tests in waters withdrawn from potabilization plants did not evidence any
514 significant decrease of the sorption ability of BC6 and BC7 towards the investigated contaminants
515 compared to tests in ultrapure water, thus supporting the implementation of column experiments for
516 establishing the maximum loading capacity of the materials in experimental conditions more similar
517 to the real scale.

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

523 Even if ashes are a regulated parameter, our results suggest that this could not be a limiting parameter
524 for the adsorption of organic molecules.

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Author Contribution Statement

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

Michele Castiglioni: Formal analysis and Writing – original draft; Luca Rivoira: Supervision, Data curation and Visualization; Irene Ingrando: Formal analysis and Visualization; Lorenza Meucci: Methodology, Resources and Visualization; Rita Binetti: Methodology, Resources and Visualization; Martino Fungi: Methodology, Resources and Visualization; Ayoub El-Ghadraoui: Formal analysis and Visualization; Zaineb Bakari: Formal analysis and Visualization. Massimo Del Bubba: Data curation, Software, Writing – review & editing; Maria Concetta Bruzzoniti: Conceptualization, Supervision, Writing – review & editing, Funding acquisition, Project administration.



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Supplementary Material

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