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

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HIGHLIGHTS

- 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.
- \bullet Hundreds ng/g diiodoacetic acid and low $\mu g/g$ benzene/dichlorobenzene are removed.

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ABSTRACT

Seven biochars (BCs) obtained from pyrolysis or gasification of different vegetal feedstocks were thoroughly characterized in comparison with three commercial activated carbons (ACs) routinely used in drinking water treatment plants. BCs and ACs characterization included the determinations of ash, iodine and methylene blue adsorption indexes, and the release of metals and polycyclic aromatic hydrocarbons, which were performed according to international standards applied for adsorption media to be used in drinking waters. Total specific surface area, micropore and mesopore specific surface area, pH of the point of zero charge, and the release of polychlorinated biphenyls were also determined in all chars. Principal component analysis and cluster analysis were performed in order to summarize the complex set of information deriving from the aforementioned characterizations, highlighting the BC most similar (BC6 from high temperature gasification of woody biomass) and most different (BC7 from low-temperature pyrolysis of corn cob) from ACs. These BCs were studied for their adsorption in ultrapure water towards diiodoacetic acid (an emergent disinfection by-product), benzene, and 1.2-dichlorobenzene, in comparison with ACs, and results obtained were fitted by linearized Freundlich equation. Overall, BC6 showed higher sorption performances compared to BC7, even though both BCs were less performing

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1. Introduction

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

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

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

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

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

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

water treatment (Castiglioni et al., 2021).

Based on the considerations mentioned above, the aim of this research was to investigate the physicochemical properties, the regulated leachable substances, and the removal performances of 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 μ 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 μ 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 multielement 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: [$^{13}C_6$]benzo(a)anthracene [$^{13}C_6$ -BaA], [$^{13}C_6$]chrysene [$^{13}C_6$ -Chr], [$^{13}C_6$]benzo(b)fluoranthene [$^{13}C_6$ -BbFl], [$^{13}C_6$]benzo(k)fluoranthene [$^{13}C_6$ -BkFl], [$^{13}C_6$]benzo(a)pyrene [$^{13}C_4$ -BaP], [$^{13}C_6$]benzo(k)fluoranthene [$^{13}C_6$ -BkFl], [$^{13}C_4$ -Ind], [$^{13}C_6$]dibenzo(a,h)anthracene [$^{13}C_6$ -DBA], and [$^{13}C_{12}$]benzo(g,h,i)perylene [$^{13}C_{12}$ -BP]. The ^{13}C surrogate solution of PCBs contained: $^{13}C_{12}$ -PCB28, $^{13}C_{12}$ -PCB52, $^{13}C_{12}$ -PCB118, $^{13}C_{12}$ -PCB153, and $^{13}C_{12}$ -PCB180.

Volatile organic compounds, namely benzene (100 μ g L⁻¹ in methanol), and 1,2-dichlorobenzene (100 μ g 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: AC1: new activated carbon; AC2: regenerated activated carbon; AC3: regenerated activated carbon in use at the plant. The status of operation, and the characteristics of the feedstock and the thermal process used to produce the ten chars are summarized in Table 1.

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

2.3. Biochar and activated carbon characterization

The chars investigated in this study were physicochemically characterized through the determination of ash content, pH of the point of

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	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%.

zero-charge (pH_{pzc}), physisorption analysis, iodine and methylene blue adsorption indexes (I₂In and MBIn), as well as for water-extractable substances of environmental concern. The procedures adopted for the aforementioned determinations are briefly described below, whilst full details are provided in the *Supplementary Material* section. For the determination of the parameters described below, standard methods were used when available.

2.3.1. Ash content

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

2.3.2. Water-extractable substances

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

2.3.3. pH of the point of zero charge

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

2.3.4. Adsorption indexes

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

2.3.5. Physisorption analysis

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

2.3.6. Quality control of biochar and activated carbon characterization

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

2.4. Adsorption studies on DIAA and VOCs

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

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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 contact time (slow pyrolysis) (Inyang and Dickenson, 2015). Hence, it is evident that, if the same feedstock is used, the ash concentration will be higher in gasification processes than in pyrolysis (Fryda and Visser, 2015). Moreover, increasing ash percentages will be obtained with increasing temperature (Rafiq et al., 2016) and higher ash concentrations will be found under fast pyrolysis conditions (Brewer et al., 2009). Based on these considerations, it makes sense that BC2, BC3, and BC7, all deriving from slow pyrolysis processes (Table 1), showed ash percentages much lower than BC5 and BC6, which were conversely obtained under gasification conditions using a same patented process and plant. The very high ash concentration found in BC4 (about 29%) compared to BC3, both produced with the patented PYREG® pyrolysis process under the same experimental conditions, could be attributed to the different nature of the feedstocks employed, i.e. non woody vegetal biomass for BC4 and woody waste biomass for BC3 (Table 1). Finally, the unexpected high ash content of BC1 probably depends on the peculiar characteristics of the woody waste used as feedstock, which derives from the cutting of a forest planted for the phytoremediation of a soil contaminated by different chemicals, including heavy metals. Virgin activated carbon (AC1) showed a lower

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)

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 $0.02 \ \mu g \ L^{-1}$. In addition, the EN standard imposes limits to the presence of As (10 μ g L⁻¹), Cd (0.5 μ g L⁻¹), Cr (5 μ g L⁻¹), Hg (0.3 μ g L⁻¹) Ni (15 μ g L⁻¹), Pb (5 μ g L⁻¹), Sb (3 μ g L⁻¹) and Se (3 μ 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 ng L⁻¹ (BC7). Conversely, for ACs and the other BCs, the concentrations of PAHs included in the EN standard were below detection limits (Table S3 of the *Supplementary material*).

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

The concentrations of extractable PCBs found in the BCs and ACs leachate are reported in Table S4 of the *Supplementary material*. BC1 was the only char exhibiting the presence of all the PCBs investigated in its leachate, with total concentration of about 96 ng L⁻¹. Conversely, all the other BCs showed PCB15 as the only leachable chlorinated biphenyl, the concentration of which was in the low ng L⁻¹ range (0.56–2.8 ng L⁻¹) in BC2, BC3, and BC4 and about one order of magnitude higher (21.7–29 ng L⁻¹) in BC5 and BC6. PCBs occurrence in the BC leachate could be ascribed to the thermal transformation of chloride, originally contained in feedstocks (Wilson and Reed, 2012) and in this regard, it should be recalled that BC1 has been prepared with wood waste deriving from a multi-contaminated soil. To the best of our knowledge, this is the first study investigating PCBs in BC leachates, thus preventing any comparison with literature data.

The concentrations of metals determined in BC leachates are

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

3.1.3. pH of the point of zero charge

The values of pH_{pzc} were characterized by a high variability (7.0–12.0), in agreement with the wide range of the production conditions, including the type of feedstock that, as already reported in literature, significantly influence this property (Ippolito et al., 2020). For BCs, a significant linear correlation with positive slope was found by plotting ash concentrations as a function of pH_{pzc} values (R² = 0.780, *P* < 0.05). This correlation can be ascribed to the ash composition typically reported in literature (Ippolito et al., 2020), which mainly consists in metals present in the hydroxide form, thus promoting the increase of the pH in solution. ACs did not follow this trend, as the higher the amount 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_2 In and MBIn (Table 2).

I₂In 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 I₂In was found in the range 77–197 mg I₂ 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 I₂In 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 I2In 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 ($R^2 = 0.945$, $P \ll 0.05$), 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 (R² = 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 (R² = 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* \ll 0.05), as well as between the MeSSA and MBIn ($R^2 = 0.922$, *P* \ll 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 feed-stocks. 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, 2019; Hansen et al., 2016; 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%). Fig. 1 illustrates the plots of scores (Fig. 1A and B) and loadings (Fig. 1C and 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



Fig. 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.

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 (Fig. 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 1,2dichlorobenzene 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 μ g L⁻¹, 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 μ g L⁻¹, adsorption isotherm experiments were repeated using an initial concentration of 20 μ g 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 Fig. 3, adsorption data were fitted by the linearized Freundlich equation, observing in all cases determination coefficients \geq 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

Table 3

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

М	Ce	R	X/M	K _F
BC6 (5 μ g 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 μ g 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	



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

0.736 for AC1), following the 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. Ce), 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 $2.3 \cdot 10^{-3}$ atm m³ 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 μ g L⁻¹ 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 μ 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

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 μ g L⁻¹ of DIAA, benzene, and 1,2-dichlororbenzene (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			Benzen	Benzene			1,2-Dichlorobenzene		
	UP	DSB	CB	UP	DSB	CB	UP	DSB	CB	
BC6	47	41	37	Q	Q	Q	Q	Q	Q	
	(1)	(3)	(2)							
BC7	14	12	15	74	60	51	76	78	74	
	(2)	(3)	(3)	(10)	(12)	(9)	(9)	(11)	(10)	
AC1	99	99	99	Q	Q	Q	Q	Q	Q	
	(1)	(4)	(3)							

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. I2In 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.

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

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

Author contribution statement

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.

Declaration of competing interest

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.

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Appendix A. Supplementary data

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