Environmental Technology & Innovation xxx (xxxx) 101358

Contents lists available at ScienceDirect

Environmental Technology & Innovation

journal homepage: http://ees.elsevier.com

Use of plant-based sorbents and mycodegradation for the elimination of endocrine disrupting chemicals from soil: A novel facile and low-cost method

Elisabetta Loffredo [1,*], Marco Parlavecchia

Dipartimento di Scienze del Suolo, della Pianta e degli Alimenti, Università degli Studi di Bari Aldo Moro, Via Amendola 165/A, 70126 Bari, Italy

ARTICLE INFO

Article history:
Received 19 July 2020
Received in revised form 24 December 2020
Accepted 4 January 2021
Available online xxx

Keywords:
Soil decontamination
Pesticide
Endocrine disruptor
Biosorbent
Adsorption
Ligninolytic fungi
Biodegradation
Bioremediation

ABSTRACT

Soil contamination is a worldwide emergency that requires prompt, economical and eco-compatible solutions. This work explored an innovative approach consisting of sequential adoption of plant-based adsorbents and mycodegradation to remediate a multi-contaminated soil. Wood biochar (BC) and hydrochar (HC) samples, and spent coffee grounds (CG) were used to remove from the soil two well-known endocrine disrupting chemicals (EDCs), 4-tert-octylphenol (OP) and bisphenol A (BPA), and two suspected EDCs, the fungicide boscalid and the herbicide metribuzin, each at a concentration of 1 mg L^{-1}. The adsorbents were spread on a layer of tissue–non-tissue and overlaid to the soil. After 2, 4 and 7 d of exposure to the polluted soil, the adsorbents were removed. The percentages of OP, BPA, boscalid and metribuzin adsorbed in just 2 d onto BC were, respectively, 80, 62, 34 and 50%. whereas they were lower on HC and much lower on CG. At the two successive times, the amounts of EDCs removed increased, following the same trend OP > BPA > metribuzin > boscalid for all materials and all samplings. The materials removed from the soil after 7 d were inoculated with the fungi *Trametes versicolor* and *Pleurotus eryngii*, separately, and incubated for 7 and 14 days. After 7 d, the maximum degradation was observed for OP in any material, being averagely 70 and 74% by *T. versicolor* and *P. eryngii*, respectively. After 14 d, averagely, and with slight differences among treatments, *P. eryngii* degraded 83, 75, 68 and 63% of OP, BPA, boscalid and metribuzin, respectively, while *T. versicolor* was slightly less effective. Plant assays clearly showed a noticeable reduction of soil phytotoxicity after the remediation treatment with the adsorbents, especially BC. The overall results obtained encourage to study in deep this strategy that allows both the remediation of soil and the elimination of pollutants with a very facile and inexpensive procedure.

1. Introduction

In recent years, the widespread pollution of soils has become a global emergency. Agricultural, industrial and urban activities are not only utilizing the soil but also declining its quality. The discharge of wastewaters and sludges, the incorporation of biomass of dubious quality can introduce into the soil a dangerous load of mineral and organic pollutants. It arouses much concern because of the potential movement of pollutants in ground- and surface water.

Among the contaminants present in the soil, there is a large class of compounds known as endocrine disrupting chemicals (EDCs), which include plant protection products, pharmaceuticals, surfactants, wood preservatives, dyes and other industrial products and by-products (EC, 2020; EPA, 2015). These compounds, even at low concentrations, can interfere with the normal functioning of the endocrine system of humans and animals, especially aquatic. As EDCs mimic or inhibit endogenous hormones and alter hormone receptors, they are responsible of the onset of several dysfunctions and pathologies to the reproductive and cardiovascular systems (Calafat et al., 2008; Diamanti-Kandarakis et al., 2009).

EDCs are currently widespread in the environment, consumer products and even food (Campbell et al., 2006; Calafat et al., 2008). These compounds may enter the soil through agricultural practices, and the application of urban and industrial effluents, sludges and

* Corresponding author.
E-mail address: elisabetta.loffredo@uniba.it (E. Loffredo)
[1] Submitter author.

https://doi.org/10.1016/j.eti.2021.101358
2352-1864/© 2021

other wastes. One of the main risks associated with EDCs is their mobility and leaching potential, especially for those with low hydrophobicity like some pesticides, thus being able to contaminate natural waters and sediments (Ying et al., 2003). The dynamics of some EDCs in environmental systems has been extensively investigated in the last years (Campbell et al., 2006; Sharma et al., 2009).

The 4-tert-octylphenol [4-(2,4,4-trimethyl-2-pentanyl)phenol, OP] originates by microbial breakdown of the surfactants octylphenol polyethoxylates (OPEOs) used in the formulation of plastics, paints, detergents and pesticides (Sharma et al., 2009). OP is persistent and has ascertained oestrogenic properties on animals and humans (Calafat et al., 2008). Bisphenol A [2,2-(4,4 dihydroxydiphenyl) propane, BPA] is one of the chemicals produced in the largest quantity in the world (about 3 million tons each year) to obtain polycarbonates, epoxy resins, flame retardants, and is also adopted as a stabilizer for polyvinyl chloride and in the manufacture of food and drink packaging (Calafat et al., 2008; Sharma et al., 2009). It possesses oestrogenic activity as well as antiandrogenic effects (Calafat et al., 2008). BPA is widely occurrent in the environment, including soil, where it is recalcitrant.

Boscalid [2-chloro-N-(4′-chlorobiphenyl-2-yl)-nicotinamide] is a broad-spectrum fungicide largely used worldwide for the protection of fruit and horticultural plants. It is persistent in soil (Chen and Zhang, 2010). Metribuzin (4-amino-6-tert-butyl-3-methylsulfanyl-1,2,4-triazin-5-one) is a selective triazinone herbicide used extensively to control broadleaf annual weeds. Because of its low hydrophobicity, metribuzin has been included into the group of pesticides having the greatest potential for leaching into groundwater (USEPA Office of Water Report, 2003). Both boscalid and metribuzin are suspected EDCs (EC, 2016; EPA, 2015).

The progressive reduction of organic matter content in many soils has enhanced the risk of contaminants leaching. Furthermore, the rapid increase of anthropic activities has generated huge quantity of waste biomass. Therefore, specialists have developed technologies that recycle biomass to produce C-rich materials used mainly as soil amendments, such as biochar (BC) and hydrochar (HC). BC is obtained from the pyrolysis of biomass at temperatures ranging from 300 to 800 °C (Lehmann and Joseph, 2015). It has proven to be useful in improving soil quality and for remediation purposes because of the effective retention of water, nutrients and also mineral and organic pollutants. (Lehmann and Joseph, 2015). HC is a carbonaceous material produced from the hydrothermal carbonization of raw biomass, at temperatures ranging from 180 to 250 °C, under high pressure. The presence of oxygenated functional groups and the mesoporous structure makes HC efficient as adsorbent of organic pollutants (Yu et al., 2020).

Recently, some researchers have demonstrated the decontamination potential of low-cost and easily available biosorbents having cellulose- and lignin-based nature, such as unmodified and modified wastes from agriculture and food industries (Bhatnagar and Sillanpää, 2010). Worldwide consumption of coffee generates globally about 6.5 million tons per year of spent coffee grounds (CG) (ICO, 2019). Either unprocessed or activated CG have proven to be an effective adsorbent for a wide range of pollutants, such as metal ions and dyes (Dai et al., 2016; McNutt and He, 2018), EDCs and pesticides (Loffredo and Taskin, 2017; McNutt and He, 2018). BC, HC and CG have high carbon content, small pore size, large specific surface area, numerous functional groups, chemical composition fairly steady, noticeable sorption capacity and a certain biodegradability (Bhatnagar and Sillanpää, 2010; Taskin et al., 2019b).

The ability of white rot fungi to degrade organic pollutants, such as agrochemicals, EDCs, dyes and pharmaceuticals, has increasingly gained the interest of scientists who have tried to exploit this process for bioremediation purposes (Jing et al., 2011; Yang et al., 2013; Spina et al., 2018). In nature, these fungi are primary decomposers of recalcitrant lignocellulosic material through their extensive hyphal network and enzymes. In addition, white rot fungi are capable to degrade xenobiotic molecules, especially phenol-type that by chemical structure resemble lignin (Yang et al., 2013). Mycoremediation has proven successful towards various EDCs, polycyclic aromatic hydrocarbons and pesticides with low water solubility (Loffredo et al., 2012; Yang et al., 2013). Degradation of EDCs by ligninolytic fungi occurs by means of a unique set of extracellular oxidative enzymes with low substrate specificity, which includes laccase, Mn-dependent peroxidases and lignin peroxidases (Cajthaml et al., 2009; Yang et al., 2013). These enzymes have proven effective in degrading numerous phenolic and non-phenolic contaminants, such as phenylureas, phenylamides and s-triazines (Bending et al., 2002; Jing et al., 2011; Yang et al., 2013). Furthermore, these fungi produce low molecular weight exudates which, acting as redox-active mediators, promote the decomposition and enlarge the spectrum of degradable contaminants (Yang et al., 2013).

Despite the great potential and low cost, mycoremediation is still poorly understood, especially in the case of EDCs, and recent studies mainly concern decontamination of liquid matrices (Cajthaml et al., 2009; Loffredo et al., 2012; Sadiq et al., 2015; Spina et al., 2018). Scarce information can be found in the literature so far about the use of fungi to remediate soil (Spina et al., 2018) and limited concerning the combined use of sorbents and mycodegradation for the removal of EDCs (Loffredo et al., 2016).

Therefore, this study aims to investigate a novel simple and inexpensive methodology for removing and eliminating four EDCs from a multi-contaminated soil. In a first phase, we compare the effectiveness of two wood chars and spent coffee grounds, spread on the soil surface, in removing the EDCs after different times. In a successive phase, we test the potential of the fungi *Trametes versicolor* and *Pleurotus eryngii* to degrade the chemicals absorbed by the materials over time. Finally, plant assays evaluate the possible reduction of phytotoxicity of the soil following the remediation treatment.

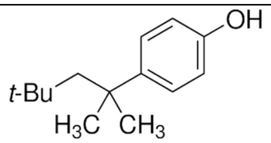
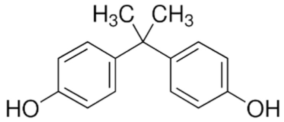
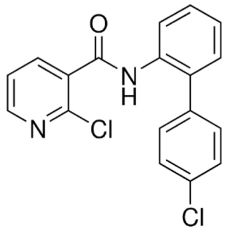
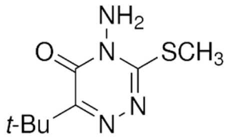
2. Materials and methods

2.1. Chemicals, soil, adsorbents and fungi

The 4-tert-octylphenol (OP) at 99.5% purity, bisphenol A (BPA) and boscalid, both at 99% purity, and metribuzin at 98% purity were purchased from Sigma-Aldrich s.r.l., Milano, Italy. Chemical structures and some properties of the compounds are shown in Table 1. All other chemicals of extra pure grade were obtained from commercial sources and used without further purification.

The loamy soil was collected at 0–20 cm depth at an experimental station located in Valenzano, Italy (41° 1’ N, 16° 54’ E). The air-dried soil was sieved with a 2-mm sieve. Some soil characteristics were: 24.4 g kg^{-1} of total organic C, 31.7 g kg^{-1} of total carbonates, pH value of 7.6 and EC of 0.26 dS m^{-1} (Ferrara et al., 2012).

Table 1
Some properties of the compounds.

Compound	Chemical structure	Molecular weight (g mol $^{-1}$)	Water solubility (mg L $^{-1}$) at 25 °C	log Kow
4-tert-Octylphenol		206.32	5.1	5.25
Bisphenol A		228.29	300	3.32
Boscalid		343.21	4.6	2.96
Metribuzin		214.29	1200	1.70

Data from PubChem (2020).

The adsorbents used were biochar (BC), hydrochar (HC) and spent coffee grounds (CG). The BC sample, supplied by Blucomb S.r.l., Udine, Italy, was obtained from grapevine pruning residues through a process of micro-gasification or slow pyrolysis with a thermal maximum of 550 °C and a residence time of 3 h, followed by dry cooling. The HC sample, provided by Ingelia Italia S.r.l., Lucca, Italy, was produced from urban pruning residues through hydrothermal carbonization operating at temperature between 180 and 210 °C, pressure ranging between 10 and 20 bars and residence time of 8 h. The CG were collected after the preparation of espresso coffee. Soluble and coloured components of CG were removed by repeated washing with distilled water until the filtrate was transparent, whereas volatile compounds were removed by heating at a temperature of 105 °C overnight. Some properties of these materials are shown in Table 2. All the three air-dry adsorbents were ground, 0.5-mm sieved and autoclaved at 121 °C for 15 min.

Trametes versicolor (L.:Fr.) Pilàt (CBS 114372) isolate was purchased from the Centraal Bureau voor Schimmelcultures (CBS-KNAW), Utrecht, The Netherlands. The isolate of *Pleurotus eryngii* (DC.) Quél. (ITEM 13681) was provided by the fungal culture collection of the Institute of Sciences of Food Production (ITEM Collection, http://www.ispa.cnr.it/Collection/), Bari, Italy. Both fungi were grown on potato dextrose agar (Oxoid, 4% w/v, PDA) in Petri dishes in the dark at 20 °C ± 1 °C. The fungal inoculum was a 2-mm radius PDA disk overgrown by 9-day mycelium collected from the growing margin of the colony.

2.2. Adsorption of the contaminants onto the materials

An aliquot of 120 g of soil in plexiglass pot (7-cm diameter and 5-cm height) was added with the four EDCs in ethanol solution to obtain an individual concentration of 1 μg per g of dry soil. The soil was accurately mixed to obtain a homogeneous contamination. Then, a piece of porous and water-repellent tissue–non-tissue (TNT) was overlaid to the soil. Preliminary experiments showed that no adsorption of the four molecules occurred on TNT. A suspension of 1.2 g of individual BC, HC and CG in 50 mL of water (only 50 mL of water in the control sample) was added to the TNT, in order to restore the field capacity of soil and favour the movement of the

Table 2
Some properties of the adsorbents.

Adsorbent	Moisture (%)	Ash (%)	pH [a]	C [b] (%)	EC [a] (dS m $^{-1}$)
BC	4.5	9.9	9.9	75.5	2.23
HC	7.0	12.5	6.6	61.5	1.03
CG	1.3	1.4	6.2	47.0	0.32

Data of BC and HC from Taskin et al. (2019b).
Data of CG from Loffredo et al. (2016).
[a] 1:10 (w/v) in double distilled water.
[b] Total organic carbon on dry and ash free basis.

products in the capillary water up to the adsorbent. The TNT allowed the passage of water but not that of the adsorbent. Every 48 h, a volume of 15 mL of water was added to maintain adequate soil moisture. The experiments were conducted into a Phytotron chamber (FDM, F.lli Della Marca S.r.l., Roma, Italy) simulating greenhouse conditions, i.e., 10-h photoperiod, 60% air humidity and a temperature of 20 ± 1 °C. All experiments were done in triplicates.

After 2, 4 and 7 days, an aliquot of 0.4 g of EDCs-contaminated adsorbent was collected, added with 10 mL of methanol and kept under mechanical shaking at 350 rpm for 16 h. Then, the suspension was centrifuged (Kendro Heraeus Biofuge Stratos, mod. D-37520, Hamburg, Germany) at 10,000×*g* for 10 min, the supernatant solution was filtered through 0.45 μm Millipore™ cellulose acetate filters and finally analysed by high performance liquid chromatography (HPLC) to quantify adsorbed EDCs, as described in Section 2.4.

At each sampling, an aliquot of 20 g of soil was extracted with 50 mL of methanol for 16 h on a mechanical shaker at 350 rpm and filtered. Then, an aliquot of 20 mL of the methanol extract was centrifuged at 10,000×*g* for 10 min, filtered through 0.45 μm Millipore™ cellulose acetate filters, and residual EDCs in the supernatant solution were quantified by HPLC (see Section 2.4). Recovery percentages of OP, BPA, boscalid and metribuzin, at individual concentration of 1 μg g^{-1}, from soil were, respectively, 91.1 ± 2.01, 92.4 ± 0.7, 96.0 ± 1.61 and 92.2 ± 1.61% (n = 3).

2.3. Degradation of the contaminants by the fungus

The EDCs-contaminated adsorbents collected after 7 days were used in the mycodegradation experiments. An aliquot of 0.25 g of each EDCs-contaminated adsorbent was poured in a 9-cm Petri dish and 15 mL of cooling PDA at 50 °C was added. The pH values of BC-medium, HC-medium and CG-medium were 8.6, 6.6 and 6.7, respectively. After solidification at room temperature under a vertical laminar flow hood (ASAL S.r.l., Cernusco sul Naviglio, Italy) the medium was not inoculated (control) or inoculated in the centre with the fungus *T. versicolor* or *P. eryngii* and stored in an incubator (Velp Scientifica™ S.r.l., mod. FOC 215I, Usmate Velate, Italy) in the dark at a constant temperature of 23 ± 1 °C. All experiments were done in triplicates.

After 7 and 14 days, the plates were removed and each medium, without (control) or with the fungus, was lyophilized, ground in a mortar, and extracted twice with methanol (50 + 50 mL) for 3 h on a mechanical shaker. Finally, an aliquot of 20 mL of the methanol extract was centrifuged at 10,000×*g* for 10 min, and the supernatant solution was analysed by HPLC (see Section 2.4).

2.4. Chromatographic analysis

The concentration of EDCs in solution was measured using a HPLC apparatus (Thermo Electron Corporation, San Jose, CA, USA) equipped with a Spectra System ™ pump, a Rheodyne® 7125 injector valve fitted with a 20–μL loop, and a Supelcosil ™ LC-18 chromatographic column (250 mm × 4.6 mm × 5 μm). The mobile phase was a mixture of water (A) and acetonitrile (B) flowing at 0.8 mL min^{-1}. The gradient elution adopted was: 0–4 min, 50% B; 4–8 min, from 50 to 70% B; 8–14 min from 70 to 90% B. The retention times of metribuzin, boscalid, BPA and OP were about 4.0, 6.2, 9.2 and 13.6 min, respectively. OP and BPA were quantified by a fluorescence detector Spectra SystemFL3000 operating at wavelengths of 230-nm excitation and 310-nm emission. Boscalid and metribuzin were detected using a Spectra System UV6000LP™ diode array detector at wavelengths of 207 nm and 294 nm, respectively. All compounds were quantified using the external standard method.

2.5. Plant assays

To test the residual phytotoxicity of the soil after the treatments, early growth assays were conducted using lettuce (*Lactuca sativa* L.). This plant is often used as dicotyledon target species in standard phytotoxic bioassay for its sensitive and prompt response. Sets of 10 seeds of lettuce were placed on filter paper in 9-cm Petri dishes, 3 mL of distilled water was added to it and it was left to germinate for 3 d. Afterwards, 6 healthy seedlings uniformly sized were transplanted in the EDCs-contaminated soil samples untreated (control) and treated with the adsorbents for 7 days. Pots with plants in not contaminated (NC) soil were also prepared for comparison. All pots were kept at room temperature (20–22 °C) and natural light for 15 d. Then, root and shoot lengths of seedlings and fresh and dry weight (overnight at a temperature of 70 °C) were measured. All experiments were done in triplicates and all data obtained were statistically analysed by one-way analysis of variance (ANOVA) and the means separated by the least significant difference (LSD) test using the Microsoft Excel spreadsheet software version 2016.

3. Results and discussion

3.1. Adsorption of the contaminants onto the materials

In the samples where only the TNT tissue covered the soil (control), residual EDCs ranged between 77 and 84%, with minor differences among the contaminants and the samplings (Fig. 1). These results indicated a fairly good stability of the four molecules in such conditions. Ying and Kookana (2005) found that the degradation of OP and BPA in soil was highly dependent on aeration, moisture content and microbial density of soil, being quite fast in an acidic sandy soil but almost absent in sterilized soil and under anaerobic conditions. Boscalid dissipation in soil was found to be slow having a half-life of about 17 days (He et al., 2020). Studying metribuzin dissipation in a silty loam soil, Mehdizadeh et al. (2019) found a half-life of 119 d.

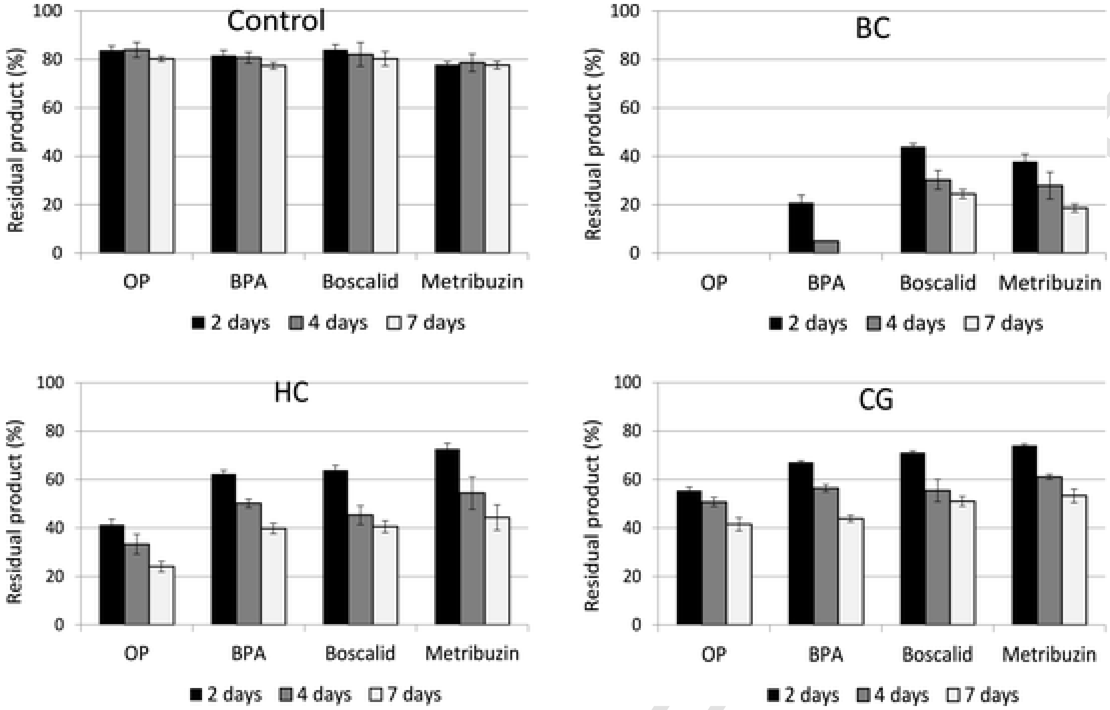


Fig. 1. Residual products in the soil untreated (control) and treated with the adsorbents for 2, 4 and 7 days.

When the soil was surmounted by the sorbents, a much lower quantity of each compound was found in the soil after just 2 d and, especially, after 7 d, indicating a remarkable sorption of the products onto the materials that followed the order BC > HC > CG (Fig. 1). In particular, after only 2 d, in the treatment with BC, the most hydrophobic OP was completely absent in the soil, whereas BPA, boscalid and metribuzin were 21, 44, and 38% of the initial amount added (Fig. 1). Although significant amounts of the EDCs disappeared in soil also with HC treatment, this material needed more time to reduce the contamination level of the soil. After 7 d, HC treatment of the soil reduced OP, BPA, boscalid and metribuzin levels down to 24, 40, 40 and 44%, respectively, of the initial amount added. When CG was used to retain the contaminants, after 7 d, residual OP, BPA, boscalid and metribuzin in soil were 41, 44, 51 and 53%, respectively, of the initial amount added, indicating a less efficacy but still appreciable. In all treatments, residual EDCs decrease over time, generally with a more relevant difference between the sampling at 2 and 4 d (Fig. 1). The disappearance of the contaminants in the soil after the treatments was reasonably due mostly to the diffusion of the molecules from the soil to the sorbents through the TNT layer and adsorption on the materials, and also, to a lesser extent, some microbiological degradation occurred in the non-sterile soil.

The amounts of the EDCs adsorbed on each material at the three times are reported in Fig. 2. Compared to the other materials, BC showed a much greater adsorption capacity, and, at 2 d, was able to retain up to 80 μg g^{-1} of OP and 62 μg g^{-1} of BPA. Except in the case of OP on BC, whose adsorption did not increase over time, the adsorption of the other molecules generally increased at the successive samplings, although scarcely when the exposure of the materials was extended from 4 to 7 d (Fig. 2). This indicates that sorption on BC is rapid and almost complete in few days. Since we used a sorbent:soil ratio of 1:100 and the initial dose of each product was 1 μg g^{-1}, the values reported in Fig. 2 represent also the percentages of products adsorbed. Although there was not a significant direct relationship between the amounts of products adsorbed by BC and the corresponding log Kow of the products, it was evident that the maximum retention was achieved with the most hydrophobic molecules, i.e., OP and BPA. There are many studies in the literature demonstrating the excellent sorption capability of BC towards a wide range of organic molecules, including pesticides and other types of EDCs. However, most of the studies concern the use of BC to adsorb compounds from water and other aqueous media or to sequester them after the incorporation of BC in soil. Hurtado et al. (2017) showed that the bioavailability of BPA decreased significantly in soil after amendment with BC. Loffredo and Taskin (2017) demonstrated the high efficiency of BC to adsorb OP from aqueous media. Mukherjee et al. (2016) reported that the retention of boscalid in soil increased considerably with the addition of BC. Essandoh et al. (2017) used a BC from switchgrass to adsorb metribuzin from aqueous media reporting high BC sorption capacity. The same BC used in this work showed a relevant sorption capacity towards metribuzin in aqueous media (Loffredo et al., 2019a,b).

In most of those studies, the sorption capacity of BC was higher than that found in this study. It should be noted that the quantity of product adsorbed depends on various factors, such as the substrate/solution ratio, the concentration of the contaminant, the pH and so on. On the basis of results present in the literature, it can be reasonably expected that even in the case of a more severe contamination of the soil, in the conditions of this study, BC can adsorb all or almost all the amount of OP, and perhaps also BPA, present in the soil. Further studies will clarify this aspect. The relevant sorption capacity of BC can be undoubtedly attributed to the properties of this material that allow for interaction with a wide range of organic contaminants through chemical and physical interactions.

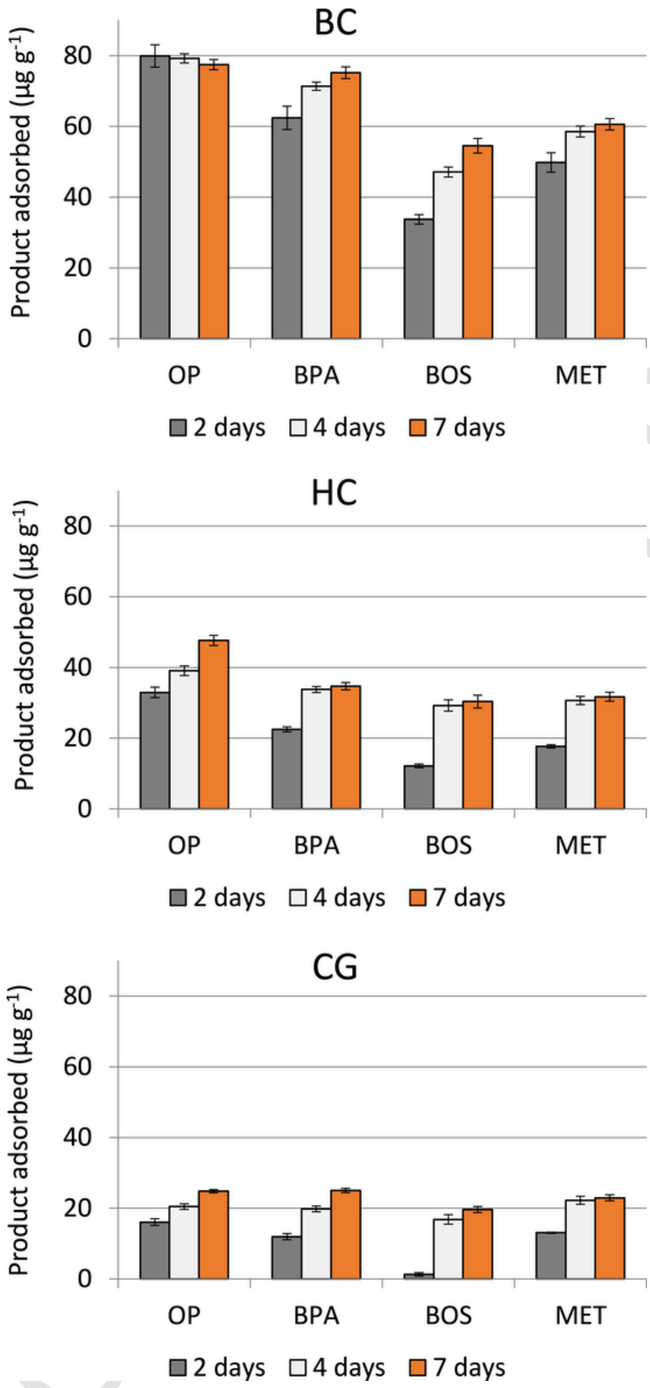


Fig. 2. Amounts of products adsorbed onto the materials after 2, 4 and 7 days.

The low H/C (~0.02) and high C/N (~142) ratios of this material indicate a high degree of aromaticity, a highly condensed aromatic structure and a high degree of carbonization (Taskin et al., 2019b). Moreover, BC has a high surface area and numerous functional groups that make this material an excellent sorbent for both mineral and organic pollutants (Zhang et al., 2019). Sorption mechanisms may include π-π bonding, hydrogen bond, electrostatic and hydrophobic interactions. Finally, SEM image of this BC sample revealed a porous structure (most pores larger than 10 µm) originating from the quick release of small volatile molecules, such as CO, CO_2, CH_4 and H_2O, during the thermal conversion process (Taskin et al., 2019a,b). BC porosity is an extremely important contribution to the sorbent capacity of this material, especially when it is used for decontamination purposes.

Compared to BC, HC adsorbed lower amounts of the EDCs, and, except for OP, no significant differences were observed between the amounts of compounds adsorbed after 4 d and those adsorbed after 7 d of exposure (Fig. 2). Nonetheless, HC showed a good sorbent capacity of the four molecules, especially towards OP. Fang et al. (2018) demonstrated that HC was a good sorbent of organic pollutants and, therefore, useful in remediation applications. The same authors also reported a scarce porosity in HC due to a pore blockage caused by products originating during the hydrothermal carbonization process (Fang et al., 2018). It is known that HC, in particular wood HC, compared to BC, has a lower C content because of the lower dehydration and decarboxylation occurring during the hydrothermal carbonization process. Moreover, the H/C (~0.10) and C/N (36) ratios of the HC used in this study denote less aromaticity than BC (Taskin et al., 2019b). The presence on the surface of acid groups, oxygenated functional groups and also hydrophobic sites make HC adequate for the retention of products of high or moderate hydrophobicity. All these along with the lower porosity of HC, compared to BC, and the pore blockage caused by an abundance of microparticles generated during the thermochemical process (Taskin et al., 2019a,b) can account for the lower sorption of the EDCs onto HC observed in this study. Recently, the HC sample used here demonstrated a noticeable retention of metribuzin, however, it was lower than that of BC (Loffredo et al., 2019a).

The CG was the least effective among the materials tested, even if the adsorption of the four molecules was not negligible. After 4 and 7 d of exposure, the retention on this adsorbent was quantitatively similar for the four compounds and increased only slightly with time (Fig. 2). The micromorphology of CG explored by SEM technique showed a rough surface and diffuse porosity, with edges and pores of different size, possibly originated during coffee roasting (Loffredo et al., 2019b) Little information is present in the literature concerning the use of spent coffee grounds as sorbent of organic pollutants, such as dyes (Dai et al., 2016), and very few about sorption of EDCs. CG showed a good capacity to adsorb OP from water, while its efficiency was lower with less hydrophobic compounds (Loffredo and Taskin, 2017). Unfortunately, as far as we know, the adsorption of BPA, boscalid and metribuzin on CG was not previously investigated at all, and that do not allow a discussion.

The novelty of this study concerns the technique adopted to remove the EDCs, that is without the incorporation of the sorbent into the soil. The addition of the sorbent directly to soil can be effective in the retention of pollutants, however, this procedure allows only a temporary sequestration/immobilization of pollutant. Hence, when dilution occurs either during rainfall or irrigation, the contaminants will likely desorb from the sorbent and become bioavailable, thus becoming toxic. Using the methodology presented here, the contaminants can be removed from the soil in a really eco-compatible and inexpensive way.

3.2. Degradation of the contaminants by the fungi

After 7 and, especially, 14 d, about 20%–30% of the amounts of contaminants adsorbed was not found in the media (EDCs-contaminated materials plus PDA) stored without fungal inoculation (Fig. 3). Based on the visual contamination of the control plates, the disappearance of the EDCs might be reasonably due to degradation by microorganisms present in the not sterilized soil. After 7 days from the preparation of the plates, the average percentages of OP, BPA, boscalid and metribuzin degraded were not statistically different from each other (Fig. 3). At 14 d, averagely for the three materials, the amounts of OP, BPA, boscalid and metribuzin degraded were 22%, 27%, 29% and 24%, respectively, and these were found to be statistically different (Fig. 3).

Both fungi grew well in all media tested demonstrating a remarkable tolerance to the pollutants and a very good competition with the other microorganisms present in the plates. Both fungi were very effective in degrading the four compounds on each material (Table 3). After only 7 d of incubation, averagely for the materials, *T. versicolor* was able to degrade a large fraction of the EDCs adsorbed, with highly significant ($P \leq 0.01$) differences among the molecules that followed the order OP > BPA > boscalid > metribuzin. After 14 d, the amount of product degraded by *T. versicolor* increased for any contaminant, following the same trend previously observed ($P \leq 0.05$). Results obtained suggested that a large amount of the contaminants were degraded rapidly, and the degradation process was continuous two weeks after fungal inoculation.

The fungus *P. eryngii* was very efficient in the degradation of all compounds, both after 7 and 14 d from inoculation, with highly significant differences among the compounds. Even in the presence of this fungus, the disappearance of the pollutants in the media followed the trend OP > BPA > boscalid > metribuzin ($P \leq 0.01$) (Table 3). The fungicide boscalid was not toxic for both fungi that degraded noticeable amounts of it in all media. These findings were in agreement with a previous study that demonstrated the ability of the white rot fungi *Bjerkandera adusta* and *Irpex lacteus* to degrade various pollutants, including OP (Loffredo et al., 2016).

Comparing the degrading potential of the two fungi, *P. eringii*, at both samplings, demonstrated a slightly higher efficacy than the other fungus. Both fungi are able to produce the main lignin modifying enzymes, namely lignin peroxidase (LiP), manganese-dependent peroxidase (MnP) and laccase (Yang et al., 2013). Furthermore, some fungi, like *T. versicolor*, may combine extracellular oxidoreductases with intracellular cytochrome P450 system which can be crucial for the degradation of some pollutants (Yang et al., 2013). The slightly lower efficiency of *T. versicolor*, compared to the other fungus, might depend on the different activity of the enzymes and/or the different redox potential of specific oxidative enzymes (Yang et al., 2013).

Compared to BC, the presence of HC and CG significantly ($P \leq 0.01$) increased the degrading activity of both fungi in all treatments (Table 3). Similarly, OP degradation by two white rot fungi was higher in the presence of CG, compared to BC (Loffredo et al., 2016). In a recent study, Taskin et al. (2019a) found that both BC and, especially, HC were able to stimulate the mycelial growth and the activity of laccase of *T. versicolor* and, especially, *P. eringii*. The different composition of the two materials, in particular the higher contents of easily degradable compounds and mineral elements of HC, compared to BC, can account for the greater degradation in HC-medium, compared to BC-medium. Another possible explanation is the different pH values of the two media. Differently from BC-medium that has an alkaline pH (8.6), HC-medium has a pH close to neutrality (6.6) that is more suitable for fungal growth. Studying the degradation of BPA by laccase, Kim and Nicell (2006) found that the optimal pH for BPA degradation by fungal laccase was 5.

The trend of degradation of the four compounds by the fungi seems to indicate that the rate of product elimination is directly and positively related to its hydrophobicity. Certainly, the chemical structure of the compound and its physico-chemical properties have an important role in the oxidative enzymatic process of degradation. Furthermore, even biosorption of the compound onto the fungal wall might have a role in the elimination of the pollutant, although of secondary importance. Yang et al. (2013) reported that pheno-

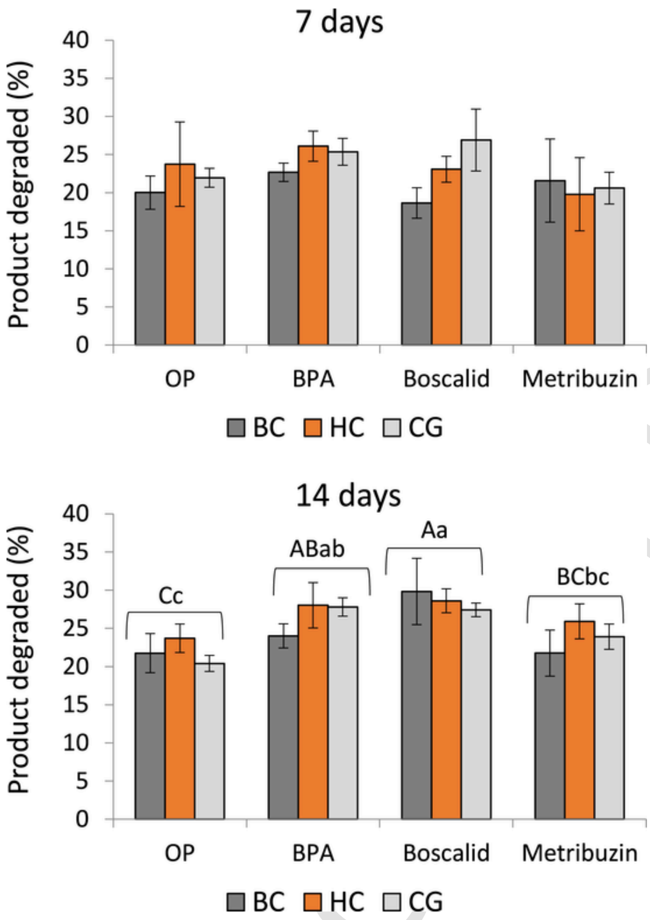


Fig. 3. Amounts of products degraded in not inoculated medium (control) after 7 and 14 days, compared to the amount initially adsorbed (100%). Data were statistically analysed by two-ways analysis of variance (ANOVA). Significant differences between means of contaminants are shown by different letters according to the Duncan's multiple range test at $P \leq 0.05$ (lower-case letters) and $P \leq 0.01$ (upper-case letters).

lic compounds, such as OP and BPA, are more susceptible to oxygenase activity because of their strong electron donating functional groups, such as hydroxyl group. Conversely, the presence of electron withdrawing functional groups, such as the amide group and halogens of boscalid or the triazine ring of metribuzin, generates an electron deficiency that renders the molecule less susceptible to oxidative breakage (Yang et al., 2013). Wang et al. (2012) found a very high removal capacity of five EDCs, among which OP and BPA, in a reaction mixture containing LiP from *Phanerochaete sordida*. A recent investigation showed that same white rot fungi, including *T. versicolo*r, were able to degrade metribuzin both alone and in combination with other herbicides (Gouma et al., 2019). In that study, the authors reported that *T. versicolor* was not inhibited by 30 mg L^{-1} of metribuzin and, in 21 d, was able to degrade 37% of the herbicide spiked in the growth medium at 10 mg L^{-1} (Gouma et al., 2019). In the conditions of our study, the same fungus eliminated a maximum of about 70% of boscalid in both HC- and CG-medium after 14 d from inoculation.

Although several studies demonstrated the effectiveness of white rot fungi in degrading phenolic and non-phenolic pollutants, usually individually applied, most of these works were conducted in model liquid media. In such media, the presence of individual compounds, optimal temperature, pH correction, addition of nutrients, and the absence of other interfering organic and mineral contaminants, allows fungi to perform optimally and promotes the degradation process to the highest levels, but are not predictive with real matrices. Our medium, i.e., EDCs-contaminated material plus PDA, was different from the optimal fungal growth medium, because it included soil components and various microorganisms that were resident in the soil used. It is presumable that, aside from the EDCs, the adsorbents, especially BC, removed from the soil numerous other molecules and mineral elements that were transferred to the fungal medium. Kim and Nicell (2006) found that the presence in the medium of heavy metals, such as Cu, Zn, Fe and Mn, could reduce BPA degradation acting unfavourably on fungal laccase.

In this work, our intention was to create and study in laboratory a facile system that could be scaled-up for an effective elimination of the pollutants without sophisticated and expensive protocols. Furthermore, the multi-contaminated soil here considered might better mimic the condition of soils, especially greenhouse soil, that received long-term treatments with pesticides. Sometimes these soils also receive contaminated sewage sludges and low-quality amendments that dramatically reduce soil quality and compromise the integrity of agricultural produce.

Table 3
Effects of the adsorbent, the compound and their interaction on the percentage of product degraded by the fungus.

Adsorbent compound	BC	HC	CG	Average
T. versicolor 7 days				
OP	71.4	70.4	68.3	70.1 Aa
BPA	60.2	64.9	68.5	64.5 Bb
Boscalid	49.7	60.2	61.5	57.1 Cc
Metribuzin	41.5	53.9	54.1	49.8 Dd
Average	55.7 Bb	62.4 Aa	63.1 Aa	
T. versicolor 14 days				
OP	78.0	78.2	79.0	78.4 Aa
BPA	68.8	73.0	78.9	73.5 Ab
Boscalid	54.5	69.6	69.4	64.5 Bc
Metribuzin	51.2	62.7	61.8	58.6 Cd
Average	63.1 Bb	70.9 Aa	72.3 Aa	
P. eringii 7 days; *0.05P*: 7.0 [a]; *0.01P*: 10.1 [b]				
OP	78.3	73.9	70.2	74.1 Aa
BPA	61.2	65.7	70.0	65.6 Bb
Boscalid	53.3	61.5	59.4	58.1 Cc
Metribuzin	40.8	52.1	59.7	50.8 Dd
Average	58.4 Bb	63.3 Aa	64.8 Aa	
P. eryngii 14 days				
OP	81.1	84.0	84.1	83.3 Aa
BPA	71.9	73.4	80.8	75.4 Bb
Boscalid	63.3	70.0	70.9	68.1 Cc
Metribuzin	57.5	64.6	67.7	63.3 Cd
Average	68.5 Bb	73.0 Aa	76.1 Aa	

Note: Percentage was calculated compared to the contaminant adsorbed (100%). Data were statistically analysed by two-ways ANOVA. Significant differences between means of contaminants are shown by different letters according to the Duncan's multiple range test at $P \leq 0.05$ (lower-case letters) and $P \leq 0.01$ (upper-case letters).

[a] LSD for the interaction adsorbent × contaminant at $P \leq 0.05$.

[b] LSD for the interaction adsorbent × contaminant at $P \leq 0.01$.

3.3. Evaluation of the residual phytotoxicity of the remediated soil

Residual phytotoxicity of the contaminated soil was tested using lettuce plants. This plant generally gives a sensitive and timely response to toxic compounds or conditions. Plant growth results obtained for the control (EDCs-contaminated soil kept untreated for 7 d), treated soil and uncontaminated soil (NC-soil) are shown in Fig. 4. As expected, compared to NC-soil, the control soil caused deleterious effects on lettuce, dramatically reducing root and shoot elongation and biomass of seedlings (Fig. 4). After the soil treatment for 7 d with the three materials, significant increases of the biometric parameters were observed in the order BC > HC > CG. The treatment of the soil with BC almost completely eliminated the soil toxicity due to the contaminants present, resulting lettuce growth very similar to that in NC-soil. Compared to the control (100%), BC treatment increased root and shoot lengths and fresh and dry biomass up to 128, 172, 293 and 232% ($P \leq 0.01$ in all cases), respectively (Fig. 4). The evident soil detoxification caused by the treatments with the materials can be attributed primarily to the removal of the EDCs but possibly also to some soluble and stimulant components of the sorbents leached in the soil during their permanence over the soil, and/or to the retention by the adsorbents of some other phytotoxic components of the soil, aside from the EDCs. To the best of our knowledge, similar studies are not present in the literature and that does not make a comparison possible.

Conclusions

This study presents a novel methodology to remove and eliminate four EDCs, namely OP, BPA, boscalid and metribuzin, from an artificially contaminated soil. Results obtained demonstrated that BC, HC and spent coffee grounds overlaid on the soil through a layer of tissue–non-tissue were effective in adsorbing relevant amounts of each pollutant, especially the two phenolic compounds. When the contaminated adsorbents were removed from the soil and inoculated with the white rot fungi *T. versicolor* and *P. eringii*, a considerable quantity of each compound was degraded by any fungus. Plant assays evidenced a significant soil detoxification after the treatments with the adsorbents, especially BC. The overall results obtained are encouraging, and we believe that the strategy proposed might be helpful in removing and eliminating a wide range of contaminants from the soil, in a way that is eco-compatible, facile and very inexpensive.

CRediT authorship contribution statement

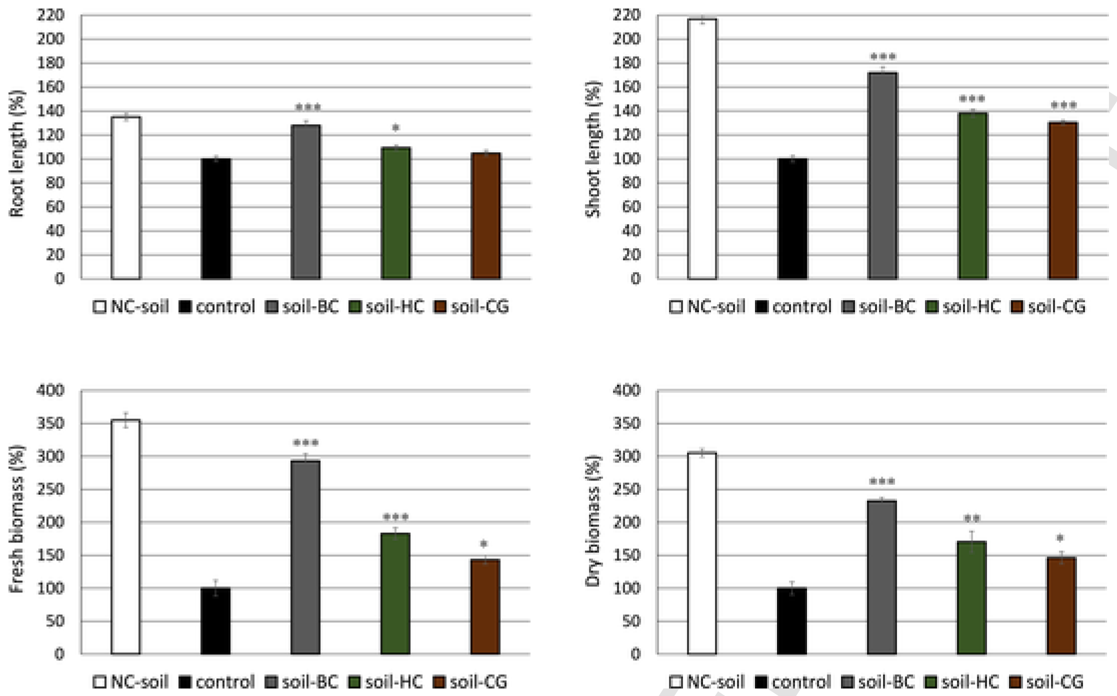


Fig. 4. Lettuce growth data obtained in not contaminated soil (NC-soil), contaminated soil not treated (control) and contaminated soil treated for 7 d with BC (soil-BC), HC (soil-HC) and CG (soil-CG). The vertical line on each bar indicates the standard error (n = 3). Data were statistically treated with one-way ANOVA and the means of the treatments were compared to the control by the LSD test. $*P \leq 0.05$; $**P \leq 0.01$; $***P \leq 0.001$.

Elisabetta Loffredo: Conceptualization, Methodology, Formal analysis, Writing - review & editing, Funding acquisition. **Marco Parlavecchia:** Investigation, Data curation, Formal analysis.

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.

Acknowledgements

This work was supported by the University of Bari Aldo Moro, Italy . The authors thank Dr. Claudio Altomare of CNR-ISPA, Bari, Italy, for providing the isolate of *P. eryngii*, and Ingelia Italia S.p.a. for providing the hydrochar sample used in this study. The authors are grateful to the anonymous reviewers for their valuable comments and suggestions.

References

Bending, G.D., Friloux, M., Walker, A., 2002. Degradation of contrasting pesticides by white rot fungi and its relationship with ligninolytic potential. FEMS Microbiol. Lett. 212, 59–63. doi:10.1111/j.1574-6968.2002.tb11245.x.

Bhatnagar, A., Sillanpää, M., 2010. Utilization of agroindustrial and municipal waste materials as potential adsorbents for water treatment - a review. Chem. Eng. J. 157, 277–296. doi:10.1016/j.cej.2010.01.007.

Cajthaml, T., Koesinova, Z., Svobodova, K., Moder, M., 2009. Biodegradation of endocrine-disrupting compounds and suppression of estrogenic activity by ligninolytic fungi. Chemosphere 75, 745–750. doi:10.1016/j.chemosphere.2009.01.034.

Calafat, A.M., Ye, X., Wong, L.Y., Reidy, J.A., Needham, L.L., 2008. Exposure of the U.S. population to bisphenol A and 4-tertiary-octylphenol: 2003-2004. Environ. Health Perspect. 116, 39–44. doi:10.1289/ehp.10753.

Campbell, C.G., Borglin, S.E., Green, F.B., Grayson, A., Wozei, E., Stringfellow, W.T., 2006. Biologically directed environmental monitoring, fate, and transport of estrogenic endocrine disrupting compounds in water: a review. Chemosphere 65, 1265–1280. doi:10.1016/j.chemosphere.2006.08.003.

Chen, L., Zhang, S., 2010. Dissipation and Residues of Boscalid in Strawberries and Soils. Bull. Environ. Contam. Toxicol. 84, 301–304. doi:10.1007/s00128-010-9934-y.

Dai, Y., Zhang, K., Zhang, D., Chen, Y., 2016. Kinetic and equilibrium studies of neutral red adsorption onto spent ground coffee from aqueous solution. J. Chem. Soc. Pak. 38, 836–842.

Diamanti-Kandarakis, E., Bourguignon, J.P., Giudice, L.C., Hauser, R., Prins, G.S., Soto, A.M., Zoeller, R.T., Gore, A.C., 2009. Endocrine-disrupting chemicals: an Endocrine Society scientific statement. Endocr. Rev. 30, 293–342. doi:10.1210/er.2009-0002.

European Commission (EC), 2016. Defining criteria for identifying endocrine disruptors in the context of the implementation of the plant protection products regulation and biocidal products regulation. https://ec.europa.eu/transparency/regdoc/rep/10102/2016/EN/SWD-2016-211-F1-EN-MAIN-PART-6.PDF (accessed 1 July 2020).

European Commission (EC), 2020. Endocrine Disruptors. https://ec.europa.eu/environment/chemicals/endocrine/index_en.htm (accessed 1 July 2020).

Environmental Protection Agency (EPA), 2015. Endocrine Disruptor Screening Program Tier 1 Screening Determinations and Associated Data Evaluation Records. https://www.epa.gov/endocrine-disruption/endocrine-disruptor-screening-program-tier-1-screening-determinations-and (accessed 1 July 2020).

Essandoh, M., Wolgemuth, D., Pittman, C.U., Jr., Mohan, D., Mlsna, T., 2017. Adsorption of metribuzin from aqueous solution using magnetic and nonmagnetic sustainable low-cost biochar adsorbents. Environ. Sci. Pollut. Res. 24, 4577–4590. doi:10.1007/s11356-016-8188-6.

Fang, J., Zhan, L., Ok, Y.S., Gao, B., 2018. Minireview of potential applications of hydrochar derived from hydrothermal carbonization of biomass. J. Ind. Eng. Chem. 54, 15–21. doi:10.1016/j.jiec.2017.08.026.

Ferrara, G., Farrag, K., Brunetti, G., 2012. The effects of rock fragmentation and / or deep tillage on soil skeletal material and chemical properties in a Mediterranean climate. Soil Use Manage. 28, 394–400. doi:10.1111/j.1475-2743.2012.00423.x.

Gouma, S., Papadaki, A.A., Markakis, G., Magan, N., Goumas, D., 2019. Studies on Pesticides Mixture Degradation by White Rot Fungi. J. Ecol. Eng. 20, 16–26. doi:10.12911/22998993/94918.

He, Y., Meng, M., Yohannes, W.K., Khan, M., Wang, M., Abd EI-Aty, A.M., Hacımüftüoğlu, F., He, Y., Gao, L., She, Y., 2020. Dissipation pattern and residual levels of boscalid in cucumber and soil using liquid chromatography-tandem mass spectrometry. J. Environ. Sci. Heal. B 55, 388–395. doi:10.1080/03601234.2019.1706374.

Hurtado, C., Cañeras, N., Domínguez, C., Price, G.W., Comas, J., Bayona, J.M., 2017. Effect of soil biochar concentration on the mitigation of emerging organic contaminant uptake in lettuce. J. Hazard. Mater. 323A, 386–393. doi:10.1016/j.jhazmat.2016.04.046.

International Coffee Organization (ICO), 2019. Historical data on the global coffee trade. http://www.ico.org/new_historical.asp?section=Statistics (accessed 1 July 2020).

Jing, D.J., Huang, J.B., Yang, Z.P., Hu, R., Cheng, Z.Z., Huang, Q.M., 2011. Induce of laccase from *Trametes gallica* and its degradation on neutral dyes and organophosphorus pesticides. J. Appl. Ecol. 22, 3300–3306.

Kim, Y.J., Nicell, J.A., 2006. Impact of reaction conditions on the laccase-catalyzed conversion of bisphenol A. Bioresour. Technol. 97, 1431–1442. doi:10.1016/j.biortech.2005.06.017.

Lehmann, J., Joseph, S., 2015. Biochar for Environmental Management: Science and Technology. second ed. Earthscan, London, UK.

Loffredo, E., Castellana, G., Taskin, E., 2016. A two-step approach to eliminate pesticides and estrogens from a wastewater and reduce its phytotoxicity: adsorption onto plant-derived materials and fungal degradation. Water Air Soil Pollut. 227 (6), 188. doi:10.1007/s11270-016-2883-2.

Loffredo, E., Parlavecchia, M., Perri, G., Gattullo, R., 2019a. Comparative assessment of metribuzin sorption efficiency of biochar, hydrochar and vermicompost. J. Environ. Sci. Heal. B 54 (8), 728–735. doi:10.1080/03601234.2019.1632643.

Loffredo, E., Scarcia, Y., Parlavecchia, M., 2019b. Removal of ochratoxin A from liquid media using novel low-cost biosorbents. Environ. Sci. Pollut. Res. 27, 34484–34494. doi:10.1007/s11356-020-09544-z.

Loffredo, E., Taskin, E., 2017. Adsorptive removal of ascertained and suspected endocrine disruptors from aqueous solution using plant-derived materials. Environ. Sci. Pollut. Res. 24, 19159–19166. doi:10.1007/s11356-017-9595-z.

Loffredo, E., Traversa, A., Senesi, N., 2012. Biodecontamination of water from bisphenol A using ligninolytic fungi and the modulation role of humic acids. Ecotoxicol. Environ. Saf. 79, 288–293. doi:10.1016/j.ecoenv.2012.01.013.

McNutt, J., He, Q.S., 2018. Spent coffee grounds: a review on current utilization. J. Ind. Eng. Chem. 71, 78–88. doi:10.1016/j.jiec.2018.11.054.

Mehdizadeh, M., Izadi-Darbandi, E., Yazdi, M.T.N.P., Rastgoo, M., Malaekeh-Nikouei, B., Nassirli, H., 2019. Impacts of different organic amendments on soil degradation and phytotoxicity of metribuzin. Int. J. Recycl. Org. Waste Agric. 8, S113–S121. doi:10.1007/s40093-019-0280-8.

Mukherjee, S., Tappe, W., Weihermueller, L., Hofmann, D., Köppchen, S., Laabs, V., Schroeder, T., Vereecken, H., Burauel, P., 2016. Dissipation of bentazone, pyrimethanil and boscalid in biochar and digestate based soil mixtures for biopurification systems. Sci. Total. Environ. 544, 192–202. doi:10.1016/j.scitotenv.2015.11.111.

PubChem Open Chemistry Database At the National Institutes of Health (NIH), 2020. U. S. National Library of Medicine https://pubchem.ncbi.nlm.nih.gov/compound/8814 (accessed 1 July 2020).

Sadiq, S., Inam ul Haq, M., Ahmad, I., Ahad, K., Rashid, A., Rafiq, N., 2015. Bioremediation potential of white rot fungi, *Pleurotus Spp* against organochlorines. J. Bioremed. Biodeg. 6 (5), 308. doi:10.4172/2155-6199.1000308.

Sharma, V.K., Anquandah, G.A.K., Yngard, R.A., Kim, H., Fekete, J., Bouzek, K., Ray, A.K., Golovko, D., 2009. Nonylphenol, octylphenol, and bisphenol-A in the aquatic environment: A review on occurrence, fate, and treatment. J. Environ. Sci. Heal. A 44, 423–442. doi:10.1080/10934520902719704.

Spina, F., Gecchi, G., Landinez-Torres, A., Pecoraro, L., Russo, F., Wu, B., Cai, L., Liu, X.Z., Tosi, S., Varese, G.C., Zotti, M., Persiani, A.M., 2018. Fungi as a toolbox for sustainable bioremediation of pesticides in soil and water. Plant Biosyst. 152 (3), 474–488. doi:10.1080/11263504.2018.1445130.

Taskin, E., Branà, .M.T., Altomare, C., Loffredo, E., 2019a. Biochar and hydrochar from waste biomass promote the growth and enzyme activity of soil-resident ligninolytic fungi. Heliyon 5, e02051. doi:10.1016/j.heliyon.2019.e02051.

Taskin, E., de Castro Bueno, C., Allegretta, I., Terzano, R., Rosa, A.H., Loffredo, E., 2019b. Multianalytical characterization of biochar and hydrochar produced from waste biomasses for environmental and agricultural applications. Chemosphere 233, 422–430. doi:10.1016/j.chemosphere.2019.05.204.

USEPA Office of Water Report, 2003. Candidate contaminant list regulatory determination support document for metribuzin. https://www.epa.gov/sites/production/files/2014-09/documents/support_cc1_metribuzin_ccl_regdet.pdf (accessed 1 July 2020).

Wang, J., Majima, N., Hirai, H., Kawagishi, H., 2012. Effective removal of Endocrine-Disrupting Compounds by Lignin Peroxidase from the White-Rot Fungus *Phanerochaete sordida* YK-624. Curr. Microbiol. 64, 300–303. doi:10.1007/s00284-011-0067-2.

Yang, S., Hai, F.I., Nghiem, L.D., Price, W.E., Roddick, F., Moreira, M.T., Magram, S.F., 2013. Understanding the factors controlling the removal of trace organic contaminants by white-rot fungi and their lignin modifying enzymes: a critical review. Biores. Technol. 141, 97–108. doi:10.1016/j.biortech.2013.01.173.

Ying, G.-G., Kookana, R.S., 2005. Sorption and degradation of estrogen-like-endocrine disrupting chemicals in soil. Environ. Toxicol. Chem. 24, 2640–2645. doi:10.1897/05-074R.1.

Ying, G.-G., Kookana, R.S., Dillon, P., 2003. Sorption and degradation of selected five endocrine disrupting chemicals in aquifer material. Water Res. 37 3785–379 doi:10.1016/S0043-1354(03)00261-6.

Yu, J., Zhu, Z., Zhang, H., Guanglan, D., Qiu, Y., Yin, D., Wang, S., 2020. Hydrochars from pinewood for adsorption and nonradical catalysis of bisphenols. J. Hazard. Mater. 385, 121548. doi:10.1016/j.jhazmat.2019.121548.

Zhang, Z., Zhu, Z., Shen, B., Liu, L., 2019. Insights into biochar and hydrochar production and applications: a review. Energy 171, 581–598. doi:10.1016/j.energy.2019.01.035.