Formation of persistent free radicals in sludge biochar by hydrothermal carbonization

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Abstract

The uses of biochar as soil fertilizer can offset global warming and reduce dependence on limited mineral resources in the future circular economy, yet biochar may contain contaminants that can ultimately enter the food chain. In particular, persistent free radicals are emerging contaminants previously detected in biochar but underlying mechanisms of radical formation are not yet established. Here we studied radical generation during hydrothermal carbonization of waste sludge at 160–220 °C for 0.5–2 h with solid weight ratios of 10%w–40%w using electron paramagnetic resonance and Fourier transform infrared spectrometry. Results reveal that radical concentration increases with temperature, reaction time, and weight ratio in sludge biochars, reaching a content of 47.2×10^{15} spins/g for 220 °C, 2 h heating, and 40%w solid ratio. Moreover, low temperature of about 160 °C favors the production of oxygen-centered radicals, whereas higher temperature of 220 °C produces carbon-centered radicals. Our findings imply that biochar ecotoxicity should be assessed prior applications to prevent adverse health effects.

Keywords Persistent free radicals · Waste sludge · biochar · Hydrothermal carbonization

Introduction

Waste sludge is the byproduct produced from wastewater treatment process, containing organic matter, minerals, and various contaminants (Gao et al. 2016a, b; Lichtfouse et al. 2005; Raheem et al. 2018). In China, the production of waste

sludge is increasing sharply and reaching approximately 56.6 million tons with a moisture of 80% in 2018 (GEP Research 2018). Recycling waste sludge for recovery of resources and energy is favorably recommended by the Chinese government and is actively studied (Peccia and Westerhoff 2015). Waste sludge is commonly valued as soil fertilizer or adsorbent (Devi and Saroha 2017; Seleiman et al. 2020). Waste sludge has been recently upgraded as biochar by hydrothermal carbonization for energy recovery (Coronella et al. 2017), yet its environmental consequences are still discussed (Tasca et al. 2019; Xu and Jiang 2017). In particular, owing to the presence of organics and metals in sludge, radicals are expected to be formed during hydrothermal conversion, but this fact has not been established (Khachatryan et al. 2011). Temperature and other factors were reported to influence radical formation during hydrothermal carbonization of sewage sludge (Zhu et al. 2019), but little information on their influencing patterns and mechanisms is available for biochar.

Persistent free radicals (PFRs) have been identified as emerging contaminants (Vejerano et al. 2018) in various environmental matrix including contaminated soils (dela Cruz et al. 2012; Jia et al. 2017), sediments (dela Cruz et al. 2014), aerosol particles (Arangio et al. 2016; Yang et al. 2017; Xu et al. 2019), and fly ashes (Zhao et al. 2019). These

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radicals are of increasing concern owing to their strong durability and potential toxicity. Indeed, several studies suggest that PFRs produce reactive oxygen species (ROS) that can damage biological systems and cause adverse effects on infant health (Lieke et al. 2018; Reed et al. 2015; Saravia et al. 2013). Radicals are known to be primarily generated during heat treatment such as thermal decomposition of biomass during high-temperature pyrolysis and relatively low-temperature hydrothermal carbonization (Dellinger et al. 2007; Qin et al. 2018; Volpe et al. 2019). Ruan et al. (2019) summarized sources, formation, and characteristics of PFRs in biochars produced by pyrolysis and hydrothermal carbonization. Temperature controls the hydrolysis degree of raw materials and formation of final products during hydrothermal process (Brindhadevi et al. 2021; Zhang et al. 2019).

Although biochar radicals are less active than ROS such as the hydroxyl radical $\bullet\text{OH}$, they can act as electron donors and carriers to promote electron transfer in chemical reactions (He et al. 2019; Wang et al. 2019). In particular, biochar generates ROS such as $\bullet\text{OH}$, sulfate radical anion $\text{SO}_4^{\bullet-}$, hydrogen peroxide H_2O_2 , and ozone O_3 , thus enhancing decomposition of organic contaminants (Chen et al. 2017; Qin et al. 2017). For example, biochar radicals have increased the production of $\bullet\text{OH}$ and H_2O_2 under daylight irradiation and, in turn, have enhanced the degradation of sulfadimidine (Chen et al. 2017). Similarly, Qin et al. (2017) observed that biochar radicals acted as electron donors for Fe(III) reduction, thus promoting $\bullet\text{OH}$ generation and alachlor degradation. PFRs are usually sorted as carbon- and oxygen-centered radicals (dela Cruz et al. 2011), of which the oxygen-centered radicals appeared to be more reactive than carbon-centered radicals (Zhang et al. 2020). Thus, the concentration and type of radicals influence their catalytic ability and, in turn, the transformation of contaminants, yet knowledge of radical formation is limited (Fang et al. 2015; Wang et al. 2019).

Practical applications suggested that a temperature range of 180–210 °C is suitable for hydrothermal carbonization of sewage sludge in terms of performance and profitability (HTCycle 2021). Therefore, here we studied the concentration, abundance, and type of PFRs during hydrothermal conversion of waste sludge at 160–220 °C for 0.5–2 h with solid weight ratio of 10%w–40%w, using electron paramagnetic resonance (EPR) and Fourier transform infrared spectrometry (FTIR).

Experimental

Materials and chemicals

Waste sludge was collected from a municipal sewage treatment plant located at Songjiang in Shanghai. The

raw sludge was first precipitated for 24 h for solid–liquid separation. The resulting residues were centrifuged at 4000 rpm, then freeze-dried for 24 h with a LGJ-10E from Sihuan, Beijing, China. Dried solids were ground into powder, passed through a 40-mesh sieve, then stored in an amber glass bottle at 4 °C prior to use. Potassium bromide (KBr) was purchased from Sinopharm Chemical Reagent Co., Shanghai, China. 2, 2-diphenyl-1-picrylhydrazyl (DPPH) from Sigma-Aldrich was used as a stable radical standard.

Hydrothermal preparation of sludge biochar

The apparatus and procedures for sludge biochar have been previously reported (Gao et al. 2016b, 2018). Typically, the preparation was performed in a para-polyphenylene (PPL) lined 100-mL stainless steel autoclave at a stirring speed of 800 rpm with the aid of magnetic stirrer. The samples were heated at 160, 180, 200, and 220 °C for 0.5, 1 h, and 2 h, with solid weight ratios of 10%w, 20%w, and 40%w. After completion of the reaction, the reactors were allowed to cool down to room temperature. The solid residues were washed with ethanol and deionized water several times, followed by centrifuging and freeze-drying.

Characterization

Persistent free radical (PFRs) formation in biochar samples was measured at room temperature with a Bruker EMX micro-6/1/P/L EPR instrument (Karlsruhe, Germany). Approximately 50 mg of each sample was transferred into a 4-mm-inner-diameter electron paramagnetic resonance (EPR) quartz micro-tube. The micro-tube was sealed with grease at one tip and placed in the EPR instrument for measurement. Free radical signals were continuously recorded. EPR running parameters were microwave frequency 9.8 GHz (X-band), central field 3504.3 G, microwave power of 0.5024 MW, modulation frequency 1.0 G, scanning width 80 G, time constant 0.01 ms and scanning time 30 s. Then, radical concentrations were obtained using the Bruker's Xenon program and comparison with standard based on the quantitative theory of spin calculation. Fourier transform infrared spectrometry (FTIR) spectra were recorded with a Bruker Tensor 27 spectrometer, Ettlingen, Germany. Approximately 3 mg of each biochar sample was mixed with 300 mg of KBr, ground uniformly with an agate mortar, and compressed for scanning over wavelength range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1} . Metal contents in raw sludge and biochar samples were measured by an inductive coupled plasma emission spectrometer (ICP-OES) Prodigy from Leeman Labs, USA.

Statistical analysis

Averages and standard deviations of data for PFRs were calculated by Microsoft Excel 2016. Statistical analyses were performed using SPSS 19.0 from SPSS Inc., Chicago, IL, USA, and significance was accepted at p below 0.05. All plots were generated with OriginPro 9.0 software from OriginLab Corporation, USA.

Results and discussion

We studied the concentration, abundance, and type of persistent free radicals (PFRs) during hydrothermal conversion of municipal waste sludge at 160–220 °C for 0.5–2 h with solid ratios of 10%w–40%w, by electron paramagnetic resonance (EPR) and Fourier transform infrared spectrometry (FTIR). Data is given in Table S1.

Effect of temperature

Figure 1 shows the effect of heating sludge at 160–220 °C. Figure 1a displays a single signal between 3480 and 3520 G for the raw sludge and sludge biochars. The weak signal of the raw sludge is most probably due to the presence of iron at 35.2 mg/g and aluminum at 5.4 mg/g (Table S2, Dellinger et al. 2007). The concentration of radicals increases sharply from 19.7×10^{15} spins/g at 160 °C for 0.5 h to 47.2×10^{15} spins/g at 220 °C for 2 h (Fig. 1b). This increase is tentatively explained by the hydrolysis of sludge cellulose at high temperature, which induces the formation of functional groups bearing free radicals (Gao et al. 2012). Other reactions are likely to generate radicals. For instance, it has been shown that C–C and C-heteroatom bonds are broken by catalysis and oxidation in the presence of subcritical water (Hu et al. 2014). Then, as temperature and time increase, reactions such as dehydration, decarboxylation, condensation, polymerization, and aromatization take place and could

Fig. 1 Effect of temperature on the formation of persistent free radicals (PFRs) in biochars produced by hydrothermal conversion of waste sludge with a weight ratio of 40%w. **a–c** electron paramagnetic resonance (EPR) and **d** Fourier transform infrared spectrometry (FTIR)

generate radicals (Demirbaş 2000). Noteworthy, similar reactions involving free radicals occur over geological ages during the formation of coal and petroleum (Rouxhet and Robin 1978; Tissot and Welte 1984; Lichtfouse et al. 1994).

Figure 1c shows that g-factors are in the range of 2.0030–2.0040 and vary with temperature. This implies the coexistence of oxygen- and carbon-centered radicals (Jia et al. 2017). The sharp decrease of g-factor with temperature for the longest time treatment of 2 h is likely to result from declining oxygen-centered radicals and rising carbon-centered radicals because the latter are more stable at high temperature.

In Fig. 1d, peaks at around 1050 cm^{-1} , attributed to C–O stretching vibrations of phenolic groups according to Ishizaki and Martí (1981), are rising with temperature. Whereas peaks at around 1240 cm^{-1} due to C–O–H bend according to Zhang et al. (2018) are declining then almost disappear above $180\text{ }^{\circ}\text{C}$. This suggests that C–O–H groups are transformed into phenoxyl radicals at elevated temperatures. Moreover, single-molecule free radicals can be formed from the cleavage of some weak chemical bonds such as β -O-4 (Sabio et al. 2016). The increase of newly-formed phenolic C–O structures may also represent potential precursors of phenoxyl radicals (Fig. 1d). Peaks at 1550 – 1670 cm^{-1} related to carboxyl, quinonyl, and aldehyde C=O are weakened with increasing temperature, which suggests the formation of oxygen- and carbon-centered radicals in the presence of transition metals (Zhu et al. 2019). Last, the presence of aromatic rings is suggested by the presence of a C=C infrared peak at around 1440 cm^{-1} (Fig. 1d). Indeed, such a peak has been attributed to C=C in aromatic and heterocyclic rings (He et al. 2013), suggesting that aromatic radicals were possibly generated by electron migration in the presence of metal oxides (Fang et al. 2014; Jia et al. 2016). Overall, our findings show an increase of radical concentration with temperature, which is likely to result from various chemical reactions such as formation of phenoxyl radicals then carbon-centered radicals at higher temperature.

Effect of reaction time

Figure 2 shows the effect of reaction time from 0.5 to 2 h on PFRs formation during hydrothermal conversion of waste sludge into biochar. The results show that radical concentrations increase highly with reaction time at any temperature (Fig. 2a,b). Specifically, radical concentration increases from 11.9×10^{15} to 47.2×10^{15} spins/g with reaction time from 0.5 to 2 h at $220\text{ }^{\circ}\text{C}$. Previous studies revealed that, on the contrary, the concentration of biochar radicals declined continuously from 1 to 6 h of reaction time (Gao et al. 2018; Lu et al. 2013). This opposite trend is probably due to different raw materials and reaction conditions, such as rice straw under hydrothermal conditions, the radical concentration of

which reduced rapidly when reaction time increased (Gao et al. 2018). Different raw materials and reaction conditions may change the nature of chemical reactions, inducing in particular formation of precursors such as phenolic and polycyclic compounds.

Figure 2c shows that g-factors rise or decrease slightly from 0.5 to 1 h reaction time. Then g-factors either increase sharply at $160\text{ }^{\circ}\text{C}$ or decrease sharply at 180 – $220\text{ }^{\circ}\text{C}$ for 2 h of reaction time. These findings support the stepwise formation of oxygen-centered radicals then carbon-centered radicals. Indeed, we speculate that the lowest temperature of $160\text{ }^{\circ}\text{C}$ induces generation of oxygen-centered radicals, but is not high enough to raise the proportion of carbon-centered radicals within 2 h, whereas, carbon-centered radicals become predominant at 180 – $220\text{ }^{\circ}\text{C}$.

Figure 2d displays the evolution of biochar infrared spectra with reaction time. The results show that peaks of C–O–H, around 1240 cm^{-1} , and quinonyl C=O, around 1550 cm^{-1} , are weakened, while peaks associated with phenolic C–O and aromatic C=C are enhanced. These trends thus partly explain the increase of radical concentrations. The increase of aromatic C=C peak at about 1440 cm^{-1} supports the formation of carbon-centered radicals, according to Fang et al. (2014). Overall, our findings reveal the increase of PFRs with reaction time in biochars from hydrothermal treatment of sludge, and strengthen the stepwise formation of oxygen-centered radicals followed by carbon-centered radicals.

Effect of solid weight ratio

Figure 3 shows the effect of solid weight ratio from 10%w to 40%w on the production of PFRs during hydrothermal conversion of waste sludge into biochar. The results show a gradual increase of radical concentration with solid weight ratio (Fig. 3a,b). Specifically, radical concentration increases from 29.5×10^{15} to 47.2×10^{15} spins/g when the weight ratio increases from 10%w to 40%w at $220\text{ }^{\circ}\text{C}$ during 2 h of reaction time. This result indicates that the higher weight ratio results in higher abundance of PFRs in biochars. Normally, a higher weight ratio provides more active moieties for PFRs formation from the cleavage of bonds in sludge components, and also weakens interactions between water molecules and sludge components. By contrast, a lower weight ratio facilitates complete hydrolysis of sludge components owing to the solvent and catalytic effects of subcritical water, promoting saturation of PFR-forming compounds by donation of sufficient hydrogen ions and enhancing recombination of PFRs (Sabio et al. 2016). Moreover, water protons can promote ring-opening of heterocycles under subcritical conditions (Ogunsola and Berkowitz 1995), thus reducing formation of PFRs in biochars.

Fig. 2 Effect of reaction time on the formation of persistent free radicals (PFRs) in biochars produced by hydrothermal conversion of waste sludge with a weight ratio of 40%w. **a–c** electron paramagnetic resonance (EPR) and **d** Fourier transform infrared spectrometry FTIR

Figure 3c shows slight decreases of g-factors when the solid weight ratio increases from 10%w to 20%w, then slight increases when the weight ratio increases to 40%w. A higher solid weight ratio may cause insufficient carbonization of sludge, while a lower ratio should result in generation of more oxygen-centered radicals, because more oxygen-containing moieties are likely to be formed. The g-factors exhibit a variation in the range of 2.0032–2.0034 at 200–220 $^{\circ}\text{C}$ for 2 h of reaction time. This indicates the dominance of carbon-centered radicals at high temperatures.

Figure 3d displays the evolution of biochars infrared spectra with solid weight ratio. Results show that peak of aromatic C=C at about 1440 cm^{-1} is enhanced, while peak associated with quinonyl C=O at around 1550 cm^{-1} is weakened and almost disappear when the weight ratio is 40%w. This suggests the formation of carbon-centered radicals. Overall, our findings indicate that weight ratio also has an effect on the abundance and type of PFRs in biochars from hydrothermal treatment of sludge.

Conclusion

The formation of persistent free radicals (PFRs) in biochars from hydrothermal carbonization of municipal waste sludge was investigated. The results showed that PFRs formation in biochars depends on temperature, reaction time, and weight ratio. Radical concentration increased with increasing temperature (160–220 $^{\circ}\text{C}$), reaction time (0.5–2 h), and weight ratio (10%w–40%w). A lower temperature of 160 $^{\circ}\text{C}$ facilitated the formation of oxygen-centered radicals, whereas a relatively higher temperature at 220 $^{\circ}\text{C}$ produced carbon-centered radicals. These finding can provide a new route for recycling of waste sludge to produce valuable PFRs-containing biochars, which can be used as an alternative for transformation of environmental contaminants.

Supplementary Information The online version contains supplementary material available at (<https://doi.org/10.1007/s10311-021-01198-8>).

Fig. 3 Effect of solid weight ratio on the formation of persistent free radicals (PFRs) in biochars produced by hydrothermal conversion of waste sludge with a reaction time of 2 h. **a–c** electron paramagnetic resonance (EPR) and **d** Fourier transform infrared spectrometry (FTIR)

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Compliance with ethical standards

Conflicts of interests The authors declare that they have no conflict of interest.

References

- Arangio AM, Tong H, Socorro J, Pöschl U, Shiraiwa M (2016) Quantification of environmentally persistent free radicals and reactive oxygen species in atmospheric aerosol particles. *Atmospheric Chem Phys* 16(20):13105–13119. <https://doi.org/10.5194/acp-16-13105-2016>
- Brindhadevi K, Anto S, Rene ER, Sekar M, Mathimani T, Chi NTL, Pugazhendhi A (2021) Effect of reaction temperature on the conversion of algal biomass to bio-oil and biochar through pyrolysis and hydrothermal liquefaction. *Fuel* 285:119106. <https://doi.org/10.1016/j.fuel.2020.119106>
- Chen N, Huang Y, Hou X, Ai Z, Zhang L (2017) Photochemistry of hydrochar: reactive oxygen species generation and sulfadimidine degradation. *Environ Sci Technol* 51(19):11278–11287. <https://doi.org/10.1021/acs.est.7b02740>

- Coronella C, Hiibel SR, Vahed Qaramaleki S, Román S, Silva N (2017) Hydrothermal carbonization of wastes for simultaneous nutrient recovery and energy capture. AIChE Annual Meeting, Sustainable Engineering Forum. <https://www.aiche.org/conferences/aiche-annual-meeting/2017/proceeding/paper/314a-hydrothermal-carbonization-wastes-simultaneous-nutrient-recovery-and-energy-capture>
- dela Cruz AL, Cook RL, Dellinger B, Lomnicki SM, Donnelly KC, Kelley MA, Cosgriff D (2014) Assessment of environmentally persistent free radicals in soils and sediments from three Superfund sites. *Environ Sci Process Impacts* 16(1):44–52. <http://doi.org/https://doi.org/10.1039/c3em00428g>
- dela Cruz AL, Cook RL, Lomnicki SM, Dellinger B (2012) Effect of low temperature thermal treatment on soils contaminated with pentachlorophenol and environmentally persistent free radicals. *Environ Sci Technol* 46(11):5971–5978. <https://doi.org/10.1021/es300362k>
- dela Cruz AL, Gehling W, Lomnicki S, Cook R, Dellinger B (2011) Detection of environmentally persistent free radicals at a superfund wood treating site. *Environ Sci Technol* 45(15):6356–6365. <http://doi.org/https://doi.org/10.1021/es2012947>
- Dellinger B, Lomnicki S, Khachatryan L, Maskos Z, Hall RW, Adoukpe J, McFerrin C, Truong H (2007) Formation and stabilization of persistent free radicals. *Proc Combust Inst* 31(1):521–528. <https://doi.org/10.1016/j.proci.2006.07.172>
- Demirbaş A (2000) Mechanisms of liquefaction and pyrolysis reactions of biomass. *Energ Convers Manag* 41:633–646. [https://doi.org/10.1016/S0196-8904\(99\)00130-2](https://doi.org/10.1016/S0196-8904(99)00130-2)
- Devi P, Saroha AK (2017) Utilization of sludge based adsorbents for the removal of various pollutants: A review. *Sci Total Environ* 578:16–33. <https://doi.org/10.1016/j.scitotenv.2016.10.220>
- Fang G, Gao J, Liu C, Dionysiou DD, Wang Y, Zhou D (2014) Key role of persistent free radicals in hydrogen peroxide activation by biochar: implications to organic contaminant degradation. *Environ Sci Technol* 48(3):1902–1910. <https://doi.org/10.1021/es4048126>
- Fang G, Liu C, Gao J, Dionysiou DD, Zhou D (2015) Manipulation of persistent free radicals in biochar to activate persulfate for contaminant degradation. *Environ Sci Technol* 49(9):5645–5653. <https://doi.org/10.1021/es5061512>
- Gao Y, Wang X-H, Yang H-P, Chen H-P (2012) Characterization of products from hydrothermal treatments of cellulose. *Energy* 42(1):457–465. <https://doi.org/10.1016/j.energy.2012.03.023>
- Gao P, Xu W, Sontag P, Li X, Xue G, Liu T, Sun W (2016a) Correlating microbial community compositions with environmental factors in activated sludge from four full-scale municipal wastewater treatment plants in Shanghai. *China Appl Microbiol Biot* 100(10):4663–4673. <https://doi.org/10.1007/s00253-016-7307-0>
- Gao P, Zhou Y, Meng F, Zhang Y, Liu Z, Zhang W, Xue G (2016b) Preparation and characterization of hydrochar from waste eucalyptus bark by hydrothermal carbonization. *Energy* 97:238–245. <https://doi.org/10.1016/j.energy.2015.12.123>
- Gao P, Yao D, Qian Y, Zhong S, Zhang L, Xue G, Jia H (2018) Factors controlling the formation of persistent free radicals in hydrochar during hydrothermal conversion of rice straw. *Environ Chem Lett* 16(4):1463–1468. <https://doi.org/10.1007/s10311-018-0757-0>
- GEP Research (2018). Research reports on the sludge treatment and disposal industry (in Chinese). <http://www.gepresearch.com/99/view-767612-1.html>. Accessed 2 Nov 2020
- He C, Giannis A, Wang J-Y (2013) Conversion of sewage sludge to clean solid fuel using hydrothermal carbonization: hydrochar fuel characteristics and combustion behavior. *Appl Energy* 111:257–266. <https://doi.org/10.1016/j.apenergy.2013.04.084>
- He J, Xiao Y, Tang J, Chen H, Sun H (2019) Persulfate activation with sawdust biochar in aqueous solution by enhanced electron donor-transfer effect. *Sci Total Environ* 690:768–777. <https://doi.org/10.1016/j.scitotenv.2019.07.043>
- HTCycle. Hydrothermal carbonisation for a clean-running world. Retrieved January 21, 2021. https://htcycle.ag/en/process_40
- Hu J, Shen D, Wu S, Zhang H, Xiao R (2014) Effect of temperature on structure evolution in char from hydrothermal degradation of lignin. *J Anal Appl Pyrol* 106:118–124. <https://doi.org/10.1016/j.jaap.2014.01.008>
- Ishizaki C, Martí I (1981) Surface oxide structures on a commercial activated carbon. *Carbon* 19(6):409–412. [https://doi.org/10.1016/0008-6223\(81\)90023-3](https://doi.org/10.1016/0008-6223(81)90023-3)
- Jia H, Nulaji G, Gao H, Wang F, Zhu Y, Wang C (2016) Formation and stabilization of environmentally persistent free radicals induced by the interaction of anthracene with Fe(III)-modified clays. *Environ Sci Technol* 50(12):6310–6319. <https://doi.org/10.1021/acs.est.6b00527>
- Jia H, Zhao S, Nulaji G, Tao K, Wang F, Sharma VK, Wang C (2017) Environmentally persistent free radicals in soils of past coking sites: distribution and stabilization. *Environ Sci Technol* 51(11):6000–6008. <https://doi.org/10.1021/acs.est.7b00599>
- Khachatryan L, Vejerano E, Lomnicki S, Dellinger B (2011) Environmentally persistent free radicals (EPFRs). 1. Generation of reactive oxygen species in aqueous solutions. *Environ Sci Technol* 45:8559–8566. <https://doi.org/10.1021/es201309c>
- Lichtfouse E, Albrecht P, Behar F, Hayes JM (1994) A molecular and isotopic study of the organic matter from the Paris basin, France. *Geochim Cosmochim Acta* 58:209–221. [https://doi.org/10.1016/0016-7037\(94\)90458-8](https://doi.org/10.1016/0016-7037(94)90458-8)
- Lichtfouse E, Sappin-Didier V, Denaix L, Caria G, Metzger L, Amellal-Nassr N, Schmidt J (2005) A 25-year record of polycyclic aromatic hydrocarbons in soils amended with sewage sludges. *Environ Chem Lett* 3:140–144. <https://doi.org/10.1007/s10311-005-0010-5>
- Lieke T, Zhang XC, Steinberg CEW, Pan B (2018) Overlooked risks of biochars: persistent free radicals trigger neurotoxicity in *Caenorhabditis elegans*. *Environ Sci Technol* 52(14):7981–7987. <https://doi.org/10.1021/acs.est.8b01338>
- Lu X, Pellechia PJ, Flora JR, Berge ND (2013) Influence of reaction time and temperature on product formation and characteristics associated with the hydrothermal carbonization of cellulose. *Bioresour Technol* 138:180–190. <https://doi.org/10.1016/j.biortech.2013.03.163>
- Ogunsola OM, Berkowitz N (1995) Removal of heterocyclic S and N from oil precursors by supercritical water. *Fuel* 74:1485–1490. [https://doi.org/10.1016/0016-2361\(95\)00099-Q](https://doi.org/10.1016/0016-2361(95)00099-Q)
- Peccia J, Westerhoff P (2015) We should expect more out of our sewage sludge. *Environ Sci Technol* 49(14):8271–8276. <https://doi.org/10.1021/acs.est.5b01931>
- Qin Y, Zhang L, An T (2017) Hydrothermal carbon-mediated fenton-like reaction mechanism in the degradation of alachlor: direct electron transfer from hydrothermal carbon to Fe(III). *ACS Appl Mater Int* 9(20):17115–17124. <https://doi.org/10.1021/acsami.7b03310>
- Qin Y, Li G, Gao Y, Zhang L, Ok YS, An T (2018) Persistent free radicals in carbon-based materials on transformation of refractory organic contaminants (ROCs) in water: a critical review. *Water Res* 137:130–143. <https://doi.org/10.1016/j.watres.2018.03.012>
- Raheem A, Sikarwar VS, He J, Dastiyar W, Dionysiou DD, Wang W, Zhao M (2018) Opportunities and challenges in sustainable treatment and resource reuse of sewage sludge: a review. *Chem Eng J* 337:616–641. <https://doi.org/10.1016/j.cej.2017.12.149>
- Reed JR, dela Cruz ALN, Lomnicki SM, Backes WL (2015) Inhibition of cytochrome P450 2B4 by environmentally persistent free radical-containing particulate matter. *Biochem Pharmacol* 95:126–132. <https://doi.org/https://doi.org/10.1016/j.bcp.2015.03.012>
- Rouxhet and Robin (1978) Infrared study of the evolution of kero-gens of different origins during catagenesis and pyrolysis. *Fuel* 57(9):533–540. [https://doi.org/10.1016/0016-2361\(78\)90038-8](https://doi.org/10.1016/0016-2361(78)90038-8)

- Ruan X, Sun Y, Du W, Tang Y, Liu Q, Zhang Z, Doherty W, Frost RL, Qian G, Tsang DCW (2019) Formation, characteristics, and applications of environmentally persistent free radicals in biochars: a review. *Bioresour Technol* 281:457–468. <https://doi.org/10.1016/j.biortech.2019.02.105>
- Sabio E, Alvarez-Murillo A, Roman S, Ledesma B (2016) Conversion of tomato-peel waste into solid fuel by hydrothermal carbonization: influence of the processing variables. *Waste Manag* 47:122–132. <https://doi.org/10.1016/j.wasman.2015.04.016>
- Saravia J, Lee GI, Lomnicki S, Dellinger B, Cormier SA (2013) Particulate matter containing environmentally persistent free radicals and adverse infant respiratory health effects: a review. *J Biochem Mol Toxic* 27(1):56–68. <https://doi.org/10.1002/jbt.21465>
- Seleiman MF, Santanen A, Mäkelä PSA (2020) Recycling sludge on cropland as fertilizer: advantages and risks. *Resour Conserv Recy* 155:104647. <https://doi.org/10.1016/j.resconrec.2019.104647>
- Tasca AL, Puccini M, Gori R, Corsi I, Galletti AMR, Vitolo S (2019) Hydrothermal carbonization of sewage sludge: a critical analysis of process severity, hydrochar properties and environmental implications. *Waste Manage* 93:1–13. <https://doi.org/10.1016/j.wasman.2019.05.027>
- Tissot BP, Welte DH (1984) Diagenesis, catagenesis and metagenesis of organic matter. In: *Petroleum formation and occurrence*. Springer, Berlin. https://doi.org/10.1007/978-3-642-87813-8_6
- Vejerano EP, Rao G, Khachatryan L, Cormier SA, Lomnicki S (2018) Environmentally persistent free radicals: insights on a new class of pollutants. *Environ Sci Technol* 52(5):2468–2481. <https://doi.org/10.1021/acs.est.7b04439>
- Volpe R, Bermudez Menendez JM, Ramirez Reina T, Volpe M, Messineo A, Millan M, Titirici M-M (2019) Free radicals formation on thermally decomposed biomass. *Fuel* 255:115802. <https://doi.org/10.1016/j.fuel.2019.115802>
- Wang H, Guo W, Yin R, Du J, Wu Q, Luo H, Liu B, Sseguya F, Ren N (2019) Biochar-induced Fe(III) reduction for persulfate activation in sulfamethoxazole degradation: Insight into the electron transfer, radical oxidation and degradation pathways. *Chem Eng J* 362:561–569. <https://doi.org/10.1016/j.cej.2019.01.053>
- Xu X, Jiang E (2017) Treatment of urban sludge by hydrothermal carbonization. *Bioresour Technol* 238:182–187. <https://doi.org/10.1016/j.biortech.2017.03.174>
- Xu M, Wu T, Tang Y, Chen T, Khachatryan L, Rameshlyer P, Guo D, Chen A, Lyu M, Li J, Liu J, Li D, Zuo Y, Zhang S, Wang Y, Meng Y, Qi F (2019) Environmentally persistent free radicals in PM_{2.5}: a review. *Waste Dispos Sustain Energy* 1:177–197. <https://doi.org/10.1007/s42768-019-00021-z>
- Yang L, Liu G, Zheng M, Jin R, Zhu Q, Zhao Y, Wu X, Xu Y (2017) Highly elevated levels and particle-size distributions of environmentally persistent free radicals in haze-associated atmosphere. *Environ Sci Technol* 51(14):7936–7944. <https://doi.org/10.1021/acs.est.7b01929>
- Zhang K, Sun P, Faye MCAS, Zhang Y (2018) Characterization of biochar derived from rice husks and its potential in chlorobenzene degradation. *Carbon* 130:730–740. <https://doi.org/10.1016/j.carbon.2018.01.036>
- Zhang Z, Zhu Z, Shen B, Liu L (2019) Insights into biochar and hydrochar production and applications: a review. *Energy* 171:581–598. <https://doi.org/10.1016/j.energy.2019.01.035>
- Zhang Y, Yin M, Sun X, Zhao J (2020) Implication for adsorption and degradation of dyes by humic acid: Light driven of environmentally persistent free radicals to activate reactive oxygen species. *Bioresour Technol* 307:123183. <https://doi.org/10.1016/j.biortech.2020.123183>
- Zhao S, Gao P, Miao D, Wu L, Qian Y, Chen S, Sharma VK, Jia H (2019) Formation and evolution of solvent-extracted and nonextractable environmentally persistent free radicals in fly ash of municipal solid waste incinerators. *Environ Sci Technol* 53(17):10120–10130. <https://doi.org/10.1021/acs.est.9b03453>
- Zhu Y, Wei J, Liu Y, Liu X, Li J, Zhang J (2019) Assessing the effect on the generation of environmentally persistent free radicals in hydrothermal carbonization of sewage sludge. *Sci Rep* 9(1):17092. <https://doi.org/10.1038/s41598-019-53781-3>