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ORIGINAL PAPER

# Formation of persistent free radicals in sludge biochar by hydrothermal carbonization

Zheng Tang[1] · Song Zhao[2] · Yajie Qian[1] · Hanzhong Jia[2] · Pin Gao[1,3] · Yanming Kang[1] · Eric Lichtfouse[4,5]

**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 ºC 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 $47.2\times10^{15}$ spins/g for 220 ºC, 2 h heating, and 40%w solid ratio. Moreover, low temperature of about 160 ºC favors the production of oxygen-centered radicals, whereas higher temperature of 220 ºC 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

✉ Pin Gao
pingao@dhu.edu.cn

1 College of Environmental Science and Engineering, Donghua University, 2999 North Renmin Road, Songjiang District, Shanghai 201620, China

2 College of Resources and Environment, Northwest A & F University, Yangling 712100, Shaanxi, China

3 National-Regional Joint Engineering Research Center for Soil Pollution Control and Remediation in South China, Guangdong Key Laboratory of Integrated Agro-Environmental Pollution Control and Management, Guangdong Institute of Eco-Environmental and Soil Sciences, Guangdong Academy of Sciences, Guangzhou 510650, China

4 CNRS, IRD, INRAE, Coll France, CEREGE, Aix-Marseille Univ, 13100 Aix en Provence, France

5 State Key Laboratory of Multiphase Flow in Power Engineering, Xi'an Jiaotong University, Xi'an 710049, China

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 •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 •OH, sulfate radical anion $SO_4^{\bullet-}$, 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 •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 •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 ºC 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 ºC 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 ºC 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 ºC 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 $19.7\times10^{15}$ spins/g at 160 ºC for 0.5 h to $47.2\times10^{15}$ spins/g at 220 ºC 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

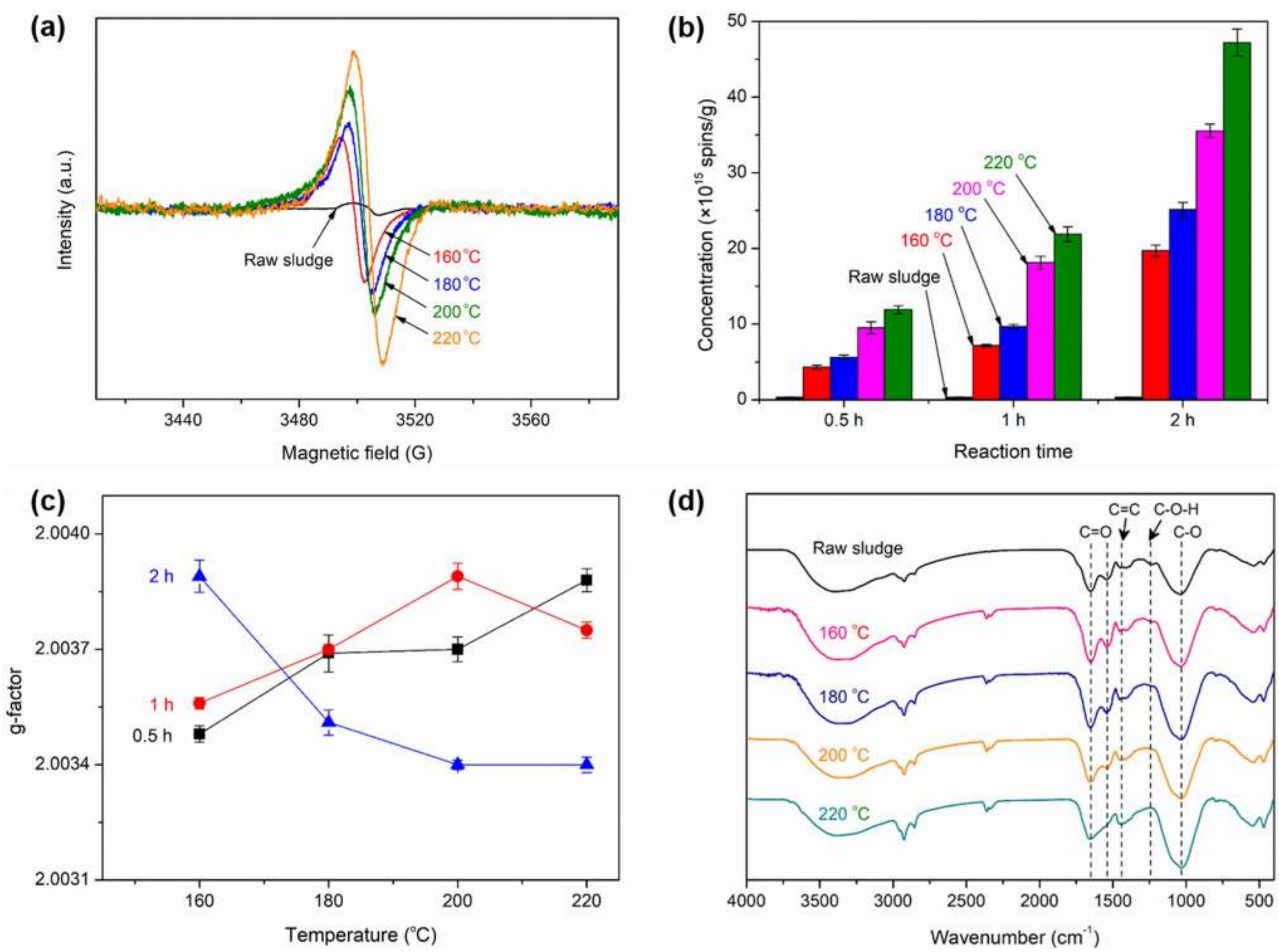


**Fig. 1** Effect of temperature on the formation of persistent free radicals (PFRs) in biochars produced by hydrothermal conversion of waste sludge with a weight ratio of 40%w. **a**–**c** electron paramagnetic resonance (EPR) and **d** Fourier transform infrared spectrometry (FTIR)

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 ºC. 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 $11.9 \times 10^{15}$ to $47.2 \times 10^{15}$ spins/g with reaction time from 0.5 to 2 h at 220 °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 °C or decrease sharply at 180–220 °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 °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 °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 $29.5 \times 10^{15}$ to $47.2 \times 10^{15}$ spins/g when the weight ratio increases from 10%w to 40%w at 220 ºC 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.

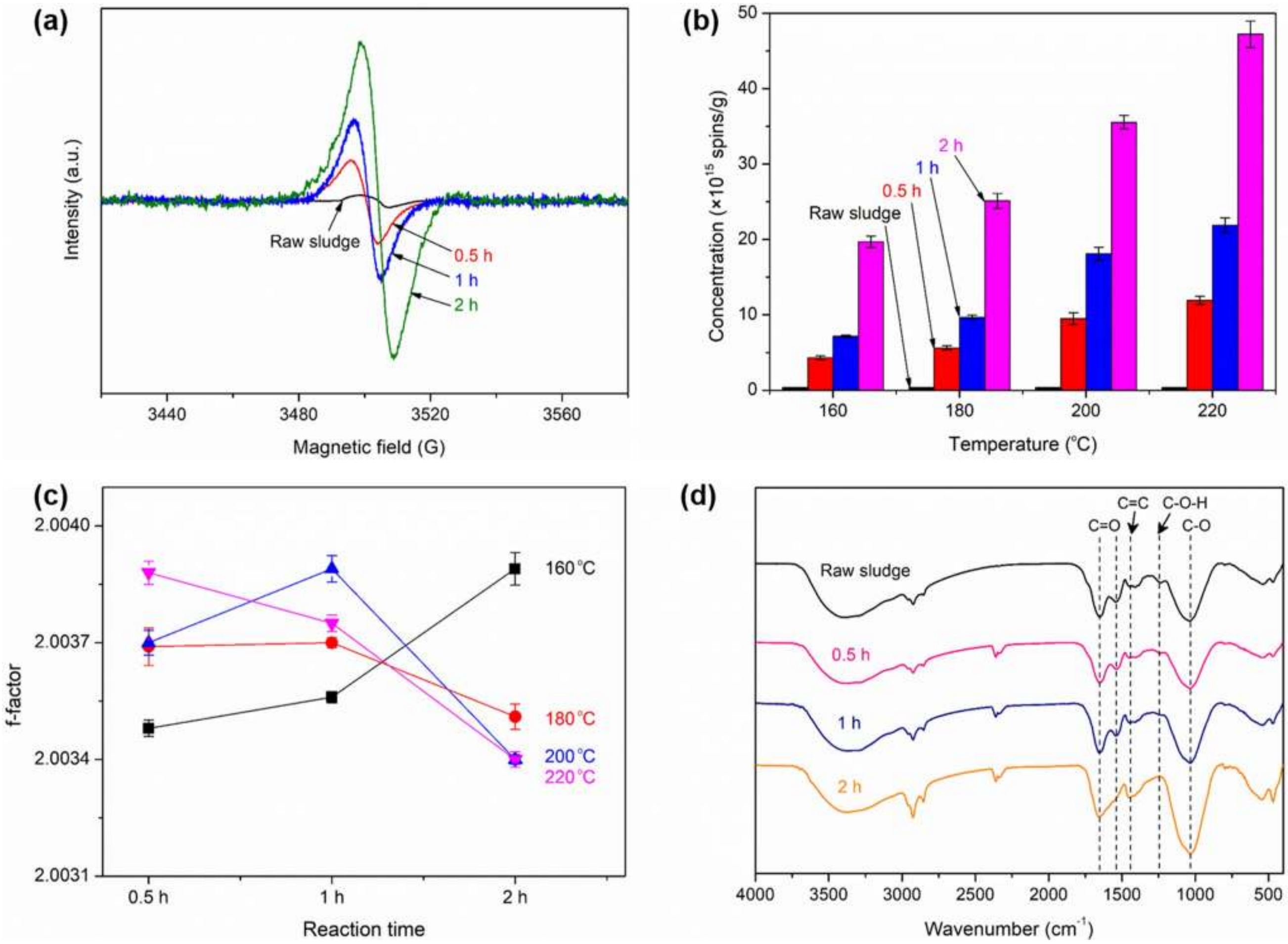


**Fig. 2** Effect of reaction time on the formation of persistent free radicals (PFRs) in biochars produced by hydrothermal conversion of waste sludge with a weight ratio of 40%w. **a**–**c** electron paramagnetic resonance (EPR) and **d** Fourier transform infrared spectrometry FTIR

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 ºC 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 ºC), reaction time (0.5–2 h), and weight ratio (10%w–40%w). A lower temperature of 160 ºC facilitated the formation of oxygen-centered radicals, whereas a relatively higher temperature at 220 ºC 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).

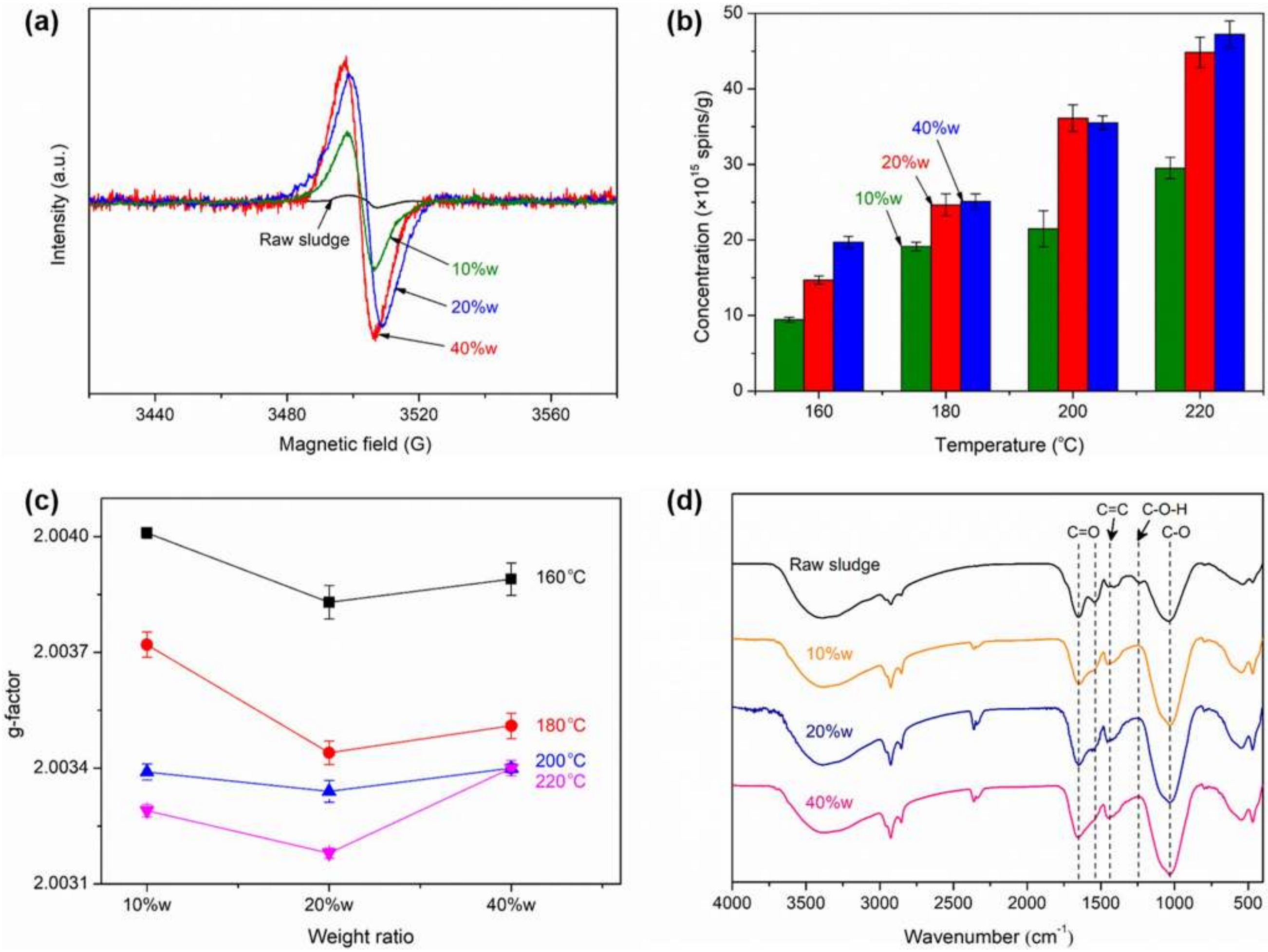


**Fig. 3** Effect of solid weight ratio on the formation of persistent free radicals (PFRs) in biochars produced by hydrothermal conversion of waste sludge with a reaction time of 2 h. **a**–**c** electron paramagnetic resonance (EPR) and **d** Fourier transform infrared spectrometry (FTIR)

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## Compliance with ethical standards

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

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