Review

Persistent free radicals in carbon-based materials on transformation of refractory organic contaminants (ROCs) in water: A critical review

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ABSTRACT

With the increased concentrations and kinds of refractory organic contaminants (ROCs) in aquatic environments, many previous reviews systematically summarized the applications of carbon-based materials in the adsorption and catalytic degradation of ROCs for their economically viable and environmentally friendly behavior. Interestingly, recent studies indicated that carbon-based materials in natural environment can also mediate the transformation of ROCs directly or indirectly due to their abundant persistent free radicals (PFRs). Understanding the formation mechanisms of PFRs in carbo-based materials and their interactions with ROCs is essential to develop their further applications in environment remediation. However, there is no comprehensive review so far about the direct and indirect removal of ROCs mediated by PFRs in amorphous, porous and crystalline carbon-based materials. The review aims to evaluate the formation mechanisms of PFRs in carbon-based materials synthesized through pyrolysis and hydrothermal carbonization processes. The influence of synthesis conditions (temperature and time) and carbon sources on the types as well as the concentrations of PFRs in carbon-based materials are also discussed. In particular, the effects of metals on the concentrations and types of PFRs in carbon-based materials are highlighted because they are considered as the catalysts for the formation of PFRs. The formation mechanisms of reactive species and the further transformation mechanisms of ROCs are briefly summarized, and the surface properties of carbon-based materials including surface area, types and number of functional groups, etc. are found to be the key parameters controlling their activities. However, due to diversity and complexity of carbon-based materials, the exact relationships between the activities of carbon-based materials and PFRs are still uncertain. Finally, the existing problems and current challenges for the ROCs transformation with carbon-based materials are also pointed out.

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1. Introduction

Environmentally persistent free radicals (PFRs) in airborne fine and ultrafine particulate matter have received considerable attentions during the last two decades (Assaf et al., 2016) because they cause pulmonary disease, cardiopulmonary dysfunction and cancer (Cormier et al., 2006; Pope et al., 2002; Xia et al., 2004). Different from traditional free radicals, PFRs are relatively stable. Their half-lives in the atmosphere are on the order of hours and days. The adverse health impacts are attributed to oxidative stress induced by environmentally PFRs through the formation of reactive oxygen species (ROS), including superoxide anion radicals ($O_2^{\bullet-}$), hydroxyl radicals ($^{\bullet}OH$), hydrogen peroxide (H_2O_2), etc. (Chung et al., 2006; Gehling et al., 2014; Squadrito et al., 2001).

Recent studies indicated that environmentally PFRs could also induce the formation of ROS in aqueous solutions (Khachatryan and Dellinger, 2011; Khachatryan et al. 2011, 2014). Dellinger and co-workers systematically investigated the formation of ROS in aqueous solutions with CuO/silica particles, and confirmed environmentally PFRs in CuO/silica particles could induce the formation of $O_2^{\bullet-}$, H_2O_2, and $^{\bullet}OH$ although failing to trap superoxide radicals in aqueous solutions (Khachatryan et al., 2011). Multiple studies have been established that environmentally PFRs were formed in the post-flame and cool-zone regions of combustion systems as well as other thermal processes (Gehling and Dellinger, 2013; Vejerano et al. 2011, 2012). The environmentally PFRs have been ubiquitously detected in the environment, such as in aqueous solution, soils and sediments, in addition to airborne particulate matter (dela Cruz et al., 2014; dela Cruz et al., 2011; Kiruri et al., 2013).

Likewise, carbon-based materials produced by thermal processes, such as biochar and hydrochar, also contained numerous PFRs (Chen et al., 2017; Mohan et al., 2014; Xiong et al., 2017; Yuan et al., 2017). These radicals may promote the formation of ROS, and thus influence the transformation of organic and inorganic contaminants in water. Fang et al. extensively studied the applications of biochar in the water remediation and found that biochar could activate O_2, H_2O_2 and persulfate to produce reactive species such as $^{\bullet}OH$ and sulfate radical ($SO_4^{\bullet-}$) to degrade organic contaminants (Fang et al. 2014a, 2014b, 2015a, 2015b; Lian and Xing, 2017; Zhu et al., 2017). Moreover, the abundant redox-active moieties on the surface of carbon-based materials like quinone, hydroquinone and phenolic moieties conjugated π-electron systems would provide plentiful redox sites for them because these moieties could act as electron donor and acceptor, simultaneously (Kappler et al., 2014; Klupfel et al., 2014; Sanroman et al., 2017; Yu et al., 2015). It has been demonstrated that both biochar and hydrochar can directly mediate the reduction of inorganic metal ions (such as Fe^{3+} or Cr^{6+}) (Dong et al., 2011; Fang et al., 2018; Hsu et al., 2009; Qin et al., 2017). Biochar can even induce the degradation of organic contaminants (p-nitrophenol) in water (Yang et al. 2016, 2017a).

As well-known, carbon-based materials have extensively been utilized in the elimination of various organic contaminants in soil and water due to their low cost, high sorption capacity, geological abundance, and environmental benignity (Gao et al., 2016; He et al., 2014; Lian et al., 2016; Liu et al., 2015; Mohan et al., 2006; Sarkar et al., 2018; Titirici et al., 2012). Numerous previous studies have been demonstrated that carbon-based materials possessing high surface areas and abundant functional groups exhibited promising adsorption capacity (Han et al., 2016; Shimabuku et al., 2016; Suhas et al., 2007; Tan et al., 2016; Vikrant et al., 2018). For example, Qiu et al. reported that straw biochar was an effective adsorbent for both cationic and anionic dyes (Qiu et al., 2009). Pine needles-derived biochar could adsorb nonpolar and polar organic contaminants, including naphthalene, nitrobenzene, m-dinitrobenzene and trichloroethylene (Ahmad et al., 2013; Chen et al., 2008). Fernandez et al. also indicated that orange peels-derived hydrochar was effective absorbent for the removal of diclofenac sodium and flurbiprofen (Fernandez et al., 2015).

However, the adsorption alone cannot fully destroy these organic contaminants, and the used carbon-based materials containing these adsorbed organic contaminants have to be treated as hazardous waste because these organic contaminants may cause serious threat to the health of humans and wildlife, and many of them are considered as toxicants, endocrine disruptors, and carcinogens even at very low concentrations (Ahmad et al., 2013; An et al., 2015; Watanabe et al., 2005). For these reasons, considerable attention has been recently paid to investigate the catalytic ability of carbon-based materials (Gao et al. 2014, 2015; Kimura and Miyamoto, 1994; Moreno-Castilla et al., 2010). During the last two decades, numerous studies have demonstrated the excellent ability of carbon-based materials to activate various oxidants, such as H_2O_2, O_3, and persulfate (including peroxymonosulfate and peroxodisulfate), to form ROS for the degradation of refractory organic contaminants (ROCs) (Georgi and Kopinke, 2005; Santos et al., 2009; Saputra et al., 2013). Since activated carbon, carbon nanotubes (CNTs, including multiwalled carbon nanotubes (MWCNTs) and single-walled carbon nanotubes (SWNTs)), and graphene have been well studied (Sarkar et al., 2018; Yang et al., 2017b), this review would not present these in details.

Carbon-based materials synthesized through the pyrolysis and hydrothermal carbonization of biomass are only emphasized in this review, and naturally occurring carbon-based materials are discussed. The first part focuses on the formation mechanisms of PFRs in the carbon-based materials with either hydrothermal or pyrolysis carbon-based materials. The second part provides a system view of the transformation mechanisms of ROCs in water mediating by in-situ produced PFRs from carbon-based materials.

The overarching objective of this paper is to provide a comprehensive review on the recent advances in the formation mechanisms and applications of PFRs in carbon materials and a better understanding of the potential roles of carbon-based materials in organic contaminants transformation mechanism as well as environmental remediation of ROCs in waters.

2. The PFRs formation in carbon-based materials

2.1. The formation mechanisms of PFRs in carbon-based materials

Currently, numerous carbon-based materials with different morphologies and structures including crystalline, porous, and amorphous carbon, have been synthesized with different kinds of techniques and precursors. Depending on operating conditions, precursors undergo different reactions to produce carbon-based materials with different properties. The formation mechanism of PFRs in different carbon-based materials, could thus be different from each other. Although PFRs have been found in cigarette smoke and coals date back to the 1950s (Ingram et al., 1954; Lyons et al., 1958), the formation mechanisms of PFRs in carbon-based materials are still not fully-understood because of the variety of synthesis methods and the high complexity of reaction processes. Therefore, this review will mainly focus on the hydrothermal and pyrolysis processes to illustrate the possible formation mechanisms of PFRs in carbon-based materials based on the limited documents.

2.1.1. The formation mechanism of PFRs during the hydrothermal process

Hydrothermal process is a thermochemical conversion process performed in hot water under elevated temperature and pressure. Depending on the reaction conditions, the main products of hydrothermal process include solid (hydrochar), liquid (bio-oil), and gases with different percentage distributions (Fang et al., 2018; Yan et al. 2009, 2010). Therefore, hydrothermal process could be classified into three main parts according to the final main products (Fig. S1) (Pavlovic et al., 2013): (1) hydrothermal carbonization (HTC) performed at the relatively low temperature ranges of 160—260 °C under autogenic pressure (2—6 MPa) corresponding the reaction temperature in water for hydrochar production (Liu and Balasubramanian, 2014), (2) hydrothermal liquefaction (HTL) carried out at about 200—370 °C with pressures between 4 and 20 MPa for heavy oil production (He et al., 2014), and (3) hydrothermal gasification (HTG) occurred at a near-critical temperatures for hydrogen rich gas production (Peterson et al., 2008). Though the main desired products in HTL and HTG processes are liquid and gaseous fuels instead of hydrochar, these processes (HTL and HTG) are also frequently utilized to synthesize MWCNTs, carbon films, carbon microspheres, and so on (Gogotsi and Yoshimura, 1994; Hu et al., 2010; Moreno and Yoshimura, 2001; Zheng et al., 2009). As shown in Fig. S1, HTC and HTL processes are carried out in subcritical conditions, and HTG process is performed in supercritical conditions. Hence, HTC and HTG processes are both taken as examples to elucidate the reaction mechanisms of hydrothermal processes.

HTC process, which is proposed to describe the natural coalification process by Friedrich Bergius in 1913 (Bach and Skreiberg, 2016; Ennis et al., 2012), has been widely applied in the synthesis of hydrochar (Funke and Ziegler, 2010; Kruse et al., 2013; Qin et al., 2017). As well-known, HTC process is dominated by ionic reactions at high concentration of hydronium ions (H_3O^+) and hydroxide ions (OH^-) generated by water autoionization in subcritical condition (Fang et al., 2018; Guo et al., 2010; Kalinichev and Churakov, 1999; Tekin et al., 2014). The H_3O^+ and OH^- catalyze the hydrolysis of high molecular weight organic compounds to form oligomers then to monomers (Fig. S2) (Kang et al., 2013; Sevilla and Fuertes, 2009; Wang et al., 2016b). Due to the complexity of biomass components and their properties, the hydrolysis degree and products are very different from each other. For example, the hydrolysis of hemicellulose and cellulose occurs at 180 °C and 200 °C, respectively, while only a small fraction of lignin could be decomposed during the HTC process (Table S1). Some weak linkage bonds such as C-C and C-X (X

represents heteroatomic) in the biomass and their hydrolysis products will cleave to form reactive monomeric radicals (Fig. 1) (Hu et al., 2014; Sabio et al., 2016). These radicals can abstract hydrogen to generate aromatic compounds, or undergo dehydration and fragmentation reactions to generate other intermediate products and radicals. Then, polymerization, condensation or aromatization take place to produce hydrochar as the final products (Jain et al., 2016; Kambo and Dutta, 2015). Meanwhile, some of the unpaired electrons in the radicals are stabilized by cyclic carbon π-system resulting in the formation of PFRs in hydrochar (Demir-Cakan et al., 2009).

On the other hand, water is easily dissociated to yield reactive $^\bullet OH$ and $^\bullet H$ in supercritical condition due to the decrease of water density (Akiya and Savage, 2002), and thus free-radical reactions dominate in the HTG process. Firstly, $^\bullet H$ produced by the dissociation of water reacts with oxygen to form peroxy radicals (Eq. (1)), resulting in the relatively high concentration of $^\bullet OH$ which could react with various kind of biomass due to its strong oxidizability (Ding et al., 1996). Then, radical chain reactions take place by breaking some weak linkage bonds and abstracting hydrogen (Eqs. (2) and (3)). Finally, homolytic hydroxylation (Eq. (4)) and condensation (Eq. (5)) reactions terminate the radical chain reactions. Phenol and quinone radicals, namely PFRs, formed during the reactions are not reactive enough to start a free radical chain reaction, but can interact with reactive free radicals to reduce the number of free radicals and inhibit free radical reaction chain. Moreover, the replacement of hydroxyl groups decreases the stability of benzene ring because π-electrons become delocalized (Guo et al., 2010). Therefore, further substitution and attack result in the ring cleavage reactions and the formation of relatively low-molecular weight compounds. The free radical scavenger is a stable free radical which is not reactive enough to start a free radical chain reaction. However, it can interact with reactive free radicals, thereby reducing the numbers of free radical and inhibiting the overall free radical reaction chain (He et al., 2014).

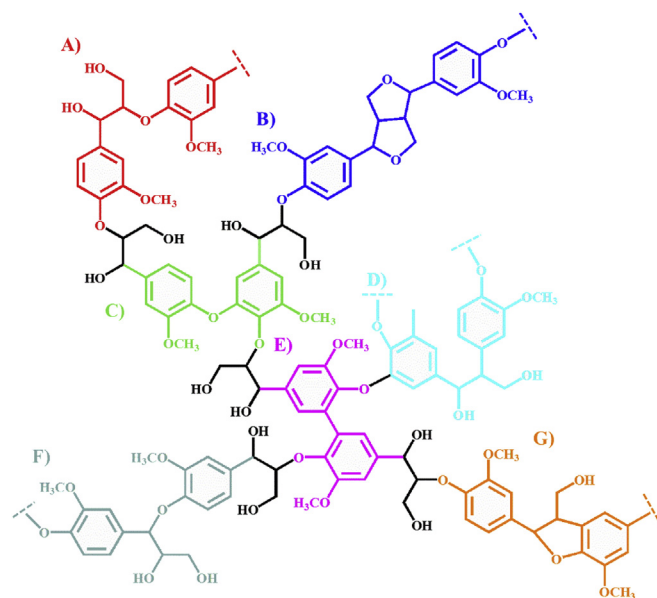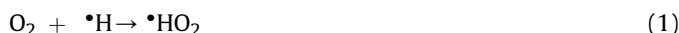$$O_2 + {^\bullet H} \rightarrow {^\bullet HO_2} \tag{1}$$

Fig. 1. Lignin fragment highlighting the linkages studied in this work: (A) β-O-4, (B) β-β, (C) 4-O-5, (D) β-1, (E) 5-5, (F) α-O-4, and (G) β-5 (Beste, 2014). Reprinted with permission from the American Chemical Society.

$$R - H + {}^{\bullet}H \rightarrow R^{\bullet} + H_2 \qquad (2)$$

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet} \qquad (3)$$

$$R^{\bullet} + OH \rightarrow ROH \qquad (4)$$

$$R^{\bullet} + R^{\bullet} \rightarrow R - R \qquad (5)$$

Although the hydrothermal process has been widely investigated, most of previous works have been focused on the formation mechanism of final products rather than the formation mechanism of PFRs. The generation process of PFRs in hydrochar is still not fully understood due to the variety of precursors, the complexity of underlying reactions and the serious lack of efficient characterization techniques for the in-situ detection of PFRs formation process. It is, therefore, of great significance to improve experimental and theoretical methods to investigate the PFRs formation mechanism.

2.1.2. The formation mechanism of PFRs during the pyrolysis process

Pyrolysis is one of main formation processes of black carbon in natural environment, which is an important natural constituent (Keiluweit et al., 2010; Pignatello et al., 2006) and significantly influences the migration and transformation of ROCs in natural environment (Cornelissen et al., 2005). Black carbon (such as activated carbon, graphite, CNTs, graphene oxide (GO), soot and biochar), produced by the incomplete combustion of fossil fuel, biofuel and biomass, has been found in oceanic and lacustrine sediments, soil organic matter, particulate matter in rivers and atmospheric particulates, accounting for about 4% of total soil carbon and 9% of organic carbon in aquatic sediments (Cornelissen et al., 2005; Koelmans et al., 2006; Kramer et al., 2004). At present, carbon-based materials produced from pyrolysis process have been recently utilized as catalysts in environment remediation due to their remarkable electron accepting capacities (Saquing et al., 2016; Xu et al., 2010). Although PFRs in carbon-based materials produced by pyrolysis have been found more than sixty years ago (Cormier et al., 2006; Uebersfeld et al., 1954) and play an important role in the catalytic processes, they have not received much attention until two decades ago (Assaf et al., 2016).

Depending upon the reaction temperature, time and heating rate, pyrolysis process could be divided into slow pyrolysis, fast pyrolysis and gasification (Onay and Kockar, 2003). In general, increasing reaction temperature leads to decrease of product yields (Nassini et al., 2016; Onay, 2007) with increase of carbon in carbon-based materials (Shen, 2015). Slow pyrolysis is regarded as a main process for the transformation of biomass to carbon-based materials due to the relatively high solid yields (25—35%) as compared with other pyrolysis processes (Liu et al., 2015; Mohan et al., 2006).

Slow-pyrolysis (around 300 °C) is believed to initiate a free-radical process by the homolytic cleavage of bonds. With further increase of reaction temperature (i.e. above 300 °C and below 500 °C), the decomposition of biomass mainly yields anhydrosugars (anhydroglucose), which are less reactive than the free radicals produced during bond cleavage (Le Brech et al., 2016). During the pyrolysis process, the main components of biomass (i.e., cellulose, hemicellulose and lignin) undergo their own reaction pathways, and the destructive pyrolysis temperatures of hemicellulose, cellulose and lignin are corresponding to 300 °C, 300—400 °C, and 350—450 °C, respectively (Di Blasi, 2009; Nzihou et al., 2013). The decomposition of hemicellulose and cellulose initiates by the depolymerization to produce oligosaccharides (Figs. S3 and S4) (Patwardhan et al., 2011; Shen and Gu, 2009; Shen et al., 2010; Zhang et al., 2013), and is followed by the formation of

their own monomers and monomeric radicals for the cleavage of glucosidic bond. The decomposition mechanism of lignin involving a series of free radical reactions (Kibet et al., 2012) is more complex than cellulose and hemicellulose due to its more complex structure (Jakab et al., 1997). Radicals are also formed in the first step of lignin pyrolysis by the homolytic cleavage of the α- and β-alkyl-aryl ether bonds, C-C and C-O linkage, which have lower bond dissociation energies, to form the corresponding radical (Fig. 2) (Kotake et al., 2014). These radical species can further generate the radical coupling products or abstract hydrogens from other molecules. Finally, a series of reactions, such as dehydration, decarboxylation, aromatization, and intramolecular condensation, are performed sequentially to form, so called, biochar (Collard and Blin, 2014). During the pyrolysis process at high temperature, abundant phenol or quinone moieties are also produced from the phenolic lignin in biomass and then could further transfer the electron to transition metals to form surface-bound PFRs in biochar (Fig. 3) (Fang et al., 2014a).

According to these works, the break of chemical bonds in precursors is likely the prime reason for the generation of PFRs in biochar and hydrochar, but the formation processes of PFRs in carbon-based materials produced by other methods such as chemical vapor deposition, laser ablation, and arc-discharge method, have been reported. Moreover, early studies have demonstrated that the PFRs in carbon-based materials could be classified into three types according to the different central atom of PFRs, carbon-centered PFRs without connected with other heteroatoms, carbon-centered PFRs connected with an adjacent oxygen atom, and oxygen-centered PFRs (Parshetti et al., 2013; Qin et al., 2017). However, the formation mechanisms of these different types of PFRs in carbon-based materials are still not attempted. In this regard, much efforts are needed to systemically investigate the formation mechanisms of PFRs in carbon-based materials produced by different technologies.

2.2. The effects of different influence factors on PFRs formation in carbon-based materials

Due to the variety of precursors and synthesis conditions, the factors affecting the concentrations and types of PFRs are extremely complex and have not been clearly elucidated. However, the relevant studies are very limited at this moment and most are focused on the optimization of different factors affecting the concentrations and types of PFRs in biochar. Thus, the detail advances on the influence of synthesis parameters and metal, precursors selection on the formation, concentrations, and types of PFRs in biochar are summarized in this section based on the limited available publications.

2.2.1. The analysis of PFRs in carbon materials

Previous studies have been demonstrated that the concentrations and types of PFRs in biochar were easy to detect due to their excellent resonance stabilities. There was a positive correlation between the ESR signal intensity and the concentrations of PFRs in carbon-based materials. Moreover, the spectral splitting factor of ESR spectra (g-factors) can be used to identify the types of carbon materials. For carbon-centered PFRs without connected to other heteroatoms, these g-factors were less than 2.0030. g-factors of carbon-centered PFRs connected with an adjacent oxygen atom were in the range of 2.0030—2.0040, while oxygen-centered PFRs have g-factors larger than 2.0040 (Hales and Case, 1981).

2.2.2. The influence of synthesized parameters on PFRs formation

As mentioned above, the cleavage of chemical bonds in precursors may be one of the critical step of PFRs formation process.
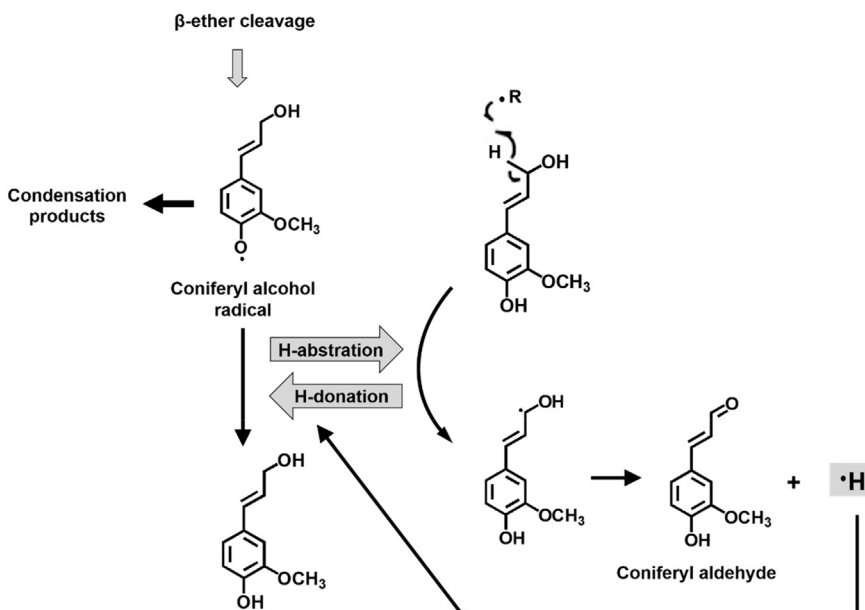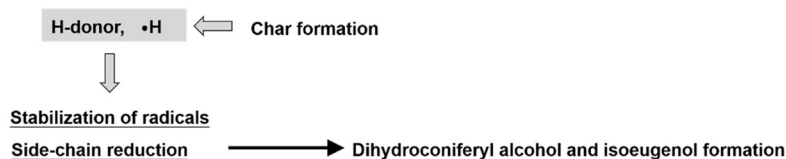
Fig. 2. A proposed role of the H-donor and H-radical in the formation of the monomeric guaiacols during the pyrolysis of Japanese cedar lignin (Kotake et al., 2014). Reprinted with permission from Elsevier.
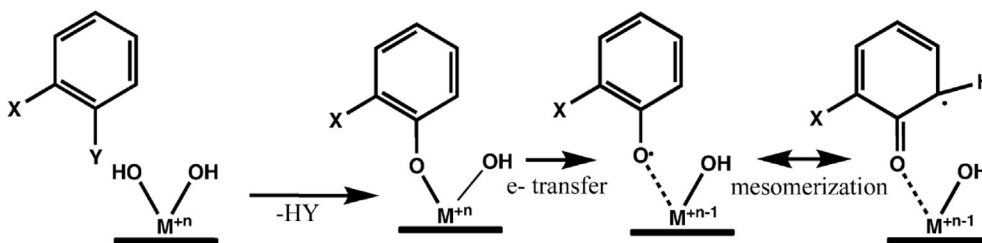

Fig. 3. Simplified model of PFRs formation from a substituted aromatic on a metal oxide surface via chemisorption and electron transfer (dela Cruz et al., 2011). Reprinted with permission from the American Chemical Society.

Therefore, pyrolysis temperature and time, which determine the break of chemical bonds, will significantly affect the types and concentration of PFRs in biochar (dela Cruz et al., 2012; Fang et al., 2015a, Vejerano et al., 2011).

Typically, the g-factors decreased clearly along with the increase of pyrolysis temperature and time (Table S1, Fig. 4C and D) (Fang et al. 2014a, 2015a; Liao et al., 2014), suggesting that the initially generated oxygen-centered PFRs were then mixed with carbon-centered free radicals. However, a sudden increase in the g-factor was observed by Liao et al. during the cooling process (120–150 min) in concert with the increase of ESR signal intensity (Liao et al., 2014). This is because the shrink of macromolecule structures at different directions and the breakdown of chemical bonds during the cooling process can result in the generation of additional free radicals (Sakaguchi et al., 2010). For example, the cleavage of C-O bonds or oxygen incorporation into broken C-C bonds may lead to the formation of oxygen-centered PFRs, thus resulting resulted in the sharp increase of PFRs concentrations (Maskos et al., 2005). With the increase of pyrolysis temperature from 300 °C to 600 °C, the concentrations of PFRs in biochar increased rapidly (Fang et al., 2015a; Liao et al., 2014; Yang et al., 2016), but then decreased markedly when the pyrolysis temperature increased to 700 °C (Figs. 4 and 5, and Table S1) (Fang et al. 2014a, 2015a; Yang et al., 2016). This may be attributed to the breakdown and reorganization of organic structures, which results in the disappearing of free radicals. Unfortunately, the limited
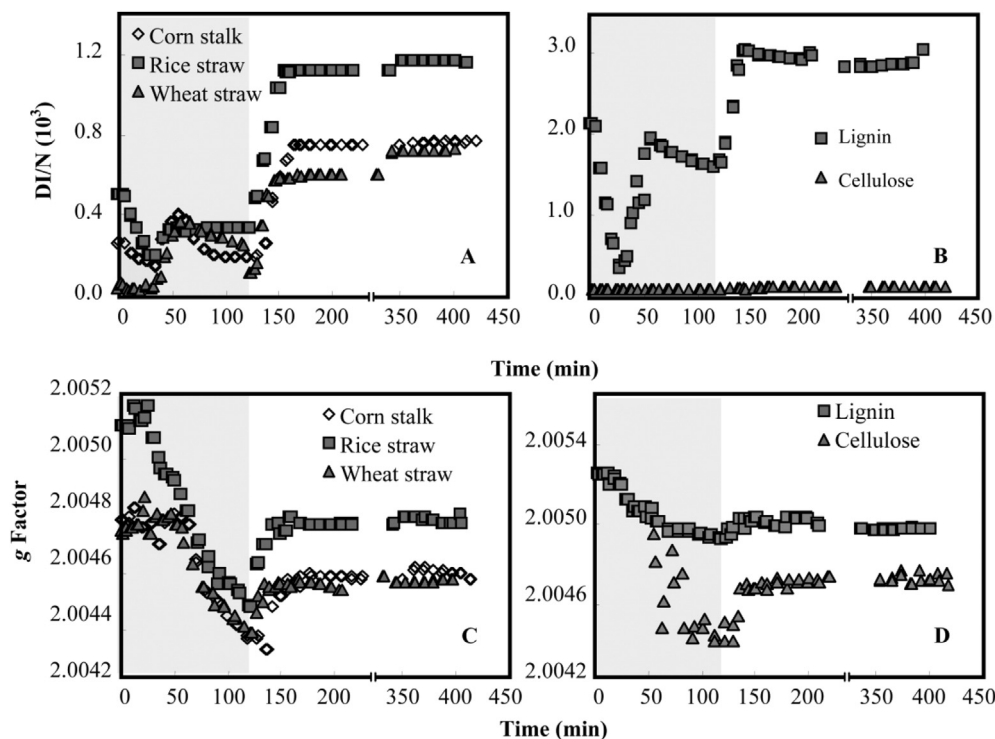
Fig. 4. An in-situ observation of ESR signals during biochar production at 200 °C when using biomass (A and C) and biopolymers (B and D). Normalized intensities (DI/N) (A and B) and g-factors (C and D) are presented. The grey area indicates the charring process and the white background during the cooling process (Liao et al., 2014). Reprinted with permission from the American Chemical Society.
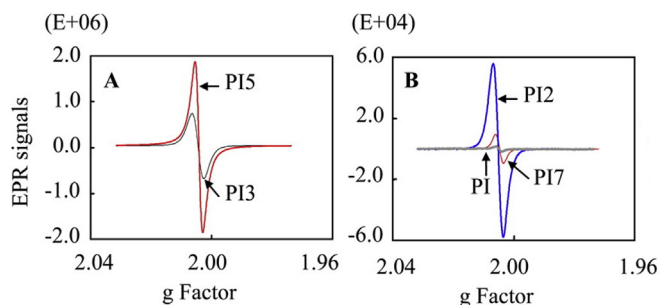

Fig. 5. ESR signals of pine wood (PI) and biochars produced at different temperatures (PI2, PI3, PI5 and PI7 for 200 °C, 300 °C, 500 °C, and 700 °C, respectively) in panels A and B (Yang et al., 2016). Reprinted with permission from the American Chemical Society.

numbers of publications could not provide more detailed information about the influences of pyrolysis temperature on the concentrations of PFRs in biochar (Fang et al. 2014a, 2015a; Yang et al., 2016).

The pyrolysis time is another complex parameter to influence the concentrations of PFRs in carbon-based materials. A recent study by Liao et al. indicated that the generation of free radicals in biochars contained several stages (Fig. 4A and B) (Liao et al., 2014). In the initial stage, the cleavage of some weak linkage bonds resulted in the formation of PFRs in biochar. Then, the outer-surface free radicals would rapidly react and dissipate, resulting in the decrease of PFRs concentration. Subsequently, the PFRs concentration further change with the increase of pyrolysis time. Plenty of free radicals may accumulate on the limited surface area of biochar, leading to the apparent decrease of ESR signals. In addition, the shrinkage of macromolecule structures at different directions and

the cleavage of chemical bonds during the cooling process of biochars can also result in the dominant formation of additional free radicals (Sakaguchi et al., 2010). However, the different stages of biochar produced by numerous precursors may require different times under different pyrolysis temperature. Therefore, the PFRs concentration in different kinds of biochar present different trends with the increase of pyrolysis time. For example, Fang et al. synthesized biochar with needles at 300 °C, 400 °C, 500 °C and 600 °C (denoted as P300, P400, P500 and P600, respectively), and found that the PFRs concentrations in P300 and P400 increased significantly with the pyrolysis time prolonged from 1 to 12 h, while decreased dramatically in P500 and P600 (Table S1) (Fang et al., 2015a). In fact, the PFRs concentrations in latter two carbon-based materials were even below the detection limit during the pyrolysis time at 2 or 12 h, respectively. Due to the complex synthesis conditions and structures of biochar, it is still difficult to completely clarify the dependence of the PFRs concentrations on the pyrolysis temperature and time.

2.2.3. The influence of precursors on PFRs in carbon-based materials

According to present research on the formation mechanisms of PFRs in carbon-based materials, organic compounds in precursors experience different reactions and then produce different free radical intermediates in the same pyrolysis condition. So, precursors are also important factors affecting the PFRs formation in carbon-based materials. Although some researchers have reported that biochar produced by different precursors at the same conditions exhibited the same type of PFRs with different g-factors and concentrations (Fig. 4 and Table S1) (Fang et al., 2014a; Liao et al., 2014), it was still difficult to thoroughly elucidate the influence mechanism of precursors on the types and concentrations of PFRs in carbon-based materials. Liao et al. compared the types and

concentrations of biochar synthesized with lignin and cellulose at 200 °C (Liao et al., 2014), and found that the PFRs concentration in biochar produced from lignin were 5 times higher than that of cellulose (Fig. 4), even though lignin is more stable than cellulose. Fang et al. reported that loading organic compounds also affected the concentrations of PFRs in biochar (Fang et al., 2015a). As shown in Fig. 6A and B, the PFR concentration rapidly increased when the hydroquinone, phenol, or catechol concentration increased from 0 to 5.0 mmol L^{-1}, but decreased with further increase of the concentration of organic compounds from 5.0 to 50 mmol L^{-1}.

Meanwhile, the g-factors of PFRs in biochar increased from 2.0042 to 2.0052, 2.0048 and 2.0048 when 1.0 mmol L^{-1} CT, PH or HQ was loaded, suggesting that the type of PFRs in biochar were still oxygen-centered PFRs. Although the type of PFRs in biochar kept unchanged, loading organic compounds of the biomass may also be an alternative to change types of PFRs in biochar because of their significant influence on the g-factors of PFRs.

In fact, many studies indicated that the addition of acid and base also can act as catalysts to accelerate the hydrothermal conversion of biomass to hydrochar (Jain et al., 2016; Jin and Enomoto, 2011). Small amounts of acids and base could catalyze the dehydration of biomass. Unfortunately, the concentrations and types changes of PFRs in hydrochar have not yet been attempted now. Further research is needed to investigate the roles of acids and base catalysts on the formation of PFRs in carbon-based materials synthesized with different methods.

2.2.4. The influence of external metals on the PFRs in carbon-based materials

It has been also reported that the phenol or quinone moieties formed during the pyrolysis processes of biomass can transfer electron to transition metals to produce surface-bound PFRs in biochar (Fang et al., 2014a). Therefore, it is of great importance to investigate the influences of metals in precursors on the PFRs in biochar. However, the kinds and concentrations of transition metals in precursors are still difficult to identify. Fang et al. investigated the effect of loaded transition metal ions (i.e., Fe^{3+}, Ni^{2+}, Cu^{2+} or Zn^{2+}) on pine needles to elucidate their effects on the formation PFRs in biochar (Fang et al., 2015a). They found that the PFR concentration increased sharply when 0.1 mmol L^{-1} of transition metal ions was loaded but decreased rapidly with further increase of the concentration from 0.1 to 2 mmol L^{-1} (Fig. 6C and D). This is because of the double-effect of transition metal ions on the formation of PFRs during the pyrolysis processes. At relatively low concentration, transition metal ions can accept electrons from phenol or quinone moieties and favor the formation of PFRs in biochar. On the other hand, excess amount of transition metal ions can also consume PFRs because PFRs can mediate electron transfer process to accelerate the reduction of transition metals such as Fe^{3+} and Cr^{6+} (Hsu et al., 2009; Xu et al., 2014), then resulting in the consumption of PFRs. With the loading of Fe^{3+}, Ni^{2+}, Cu^{2+}, or Zn^{2+} at a concentration of 0.1 mmol L^{-1}, the g-factors of PFRs in biochar decreased from 2.0042 to 2.0032, 2.0039, 2.0036 and 2.0040, indicating that
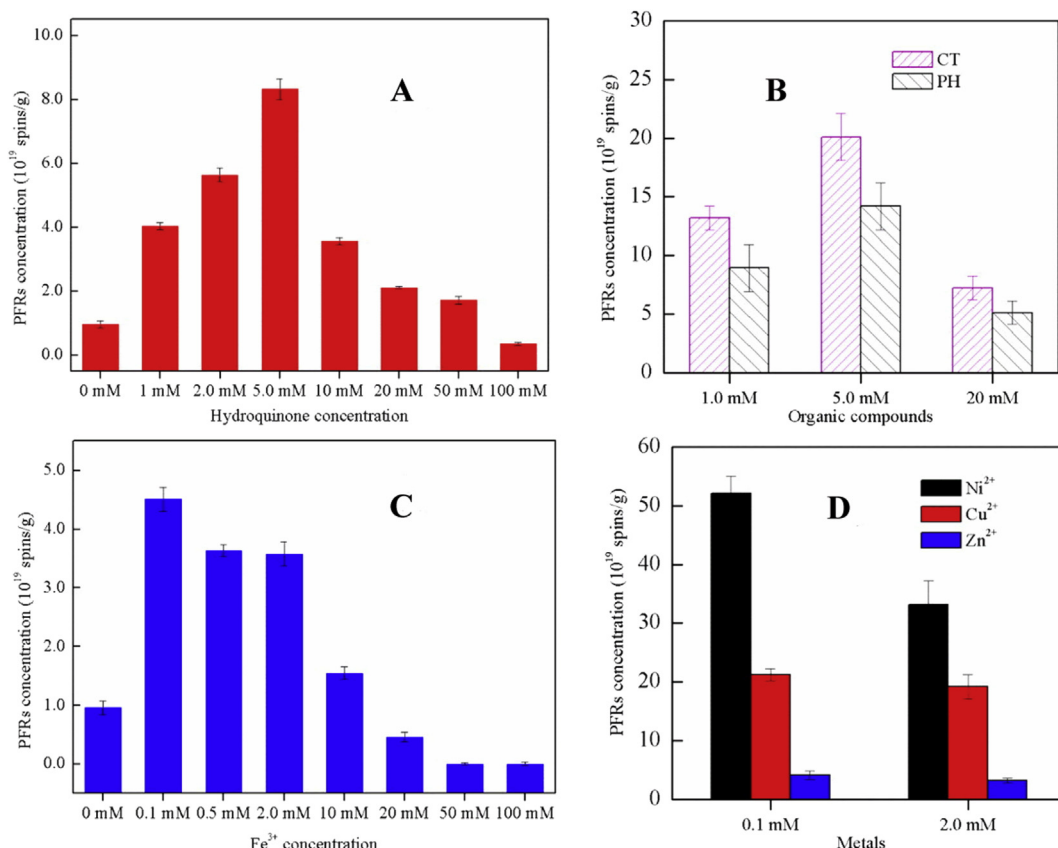
Fig. 6. Effect of organic and metal loading on the concentration of PFRs in biochar: (A) changes in PFR concentration as a function of HQ load concentration; (B) changes in PFR concentration as a function of catechol (CT) and phenol (PH) load concentration; (C) changes in PFR concentration as a function of Ni^{2+}, Cu^{2+}, and Zn^{2+} load concentration; and (D) changes in PFR concentration as a function of Fe^{3+} load concentration. Reaction conditions: $[HQ]_0 = 1.0-100$ mM; $[CT]_0 = [HQ]_0 = 1.0$ mM (5.0 and 20 mM); $[Fe^{3+}]_0 = 0.1-100$ mM; $[Ni^{2+}]_0 = [Cu^{2+}]_0 = [Zn^{2+}]_0 = 0.1$ mM (and 2.0 mM); pyrolysis temperature of 400 °C for 2 h (Fang et al., 2015a). Reprinted with permission from the American Chemical Society.

the types of PFRs in biochar converted form oxygen-centered PFRs to carbon-centered PFRs with an adjacent oxygen atom. This study indicated that metals can significantly influence the concentrations and types of PFRs in biochar, but the affecting mechanisms are still not so clear.

The influence of metals on the concentrations and types of PFRs in hydrothermal processes to form hydrochar has not been reported. But, one work confirmed that metals can promote the dehydration, condensation and carbonization step of biomass during the HTC process (Cui et al., 2006). Moreover, heavy metals in biochar significantly influence its qualities (eg. the heavy metals in biochar may release to environment and cause environmental pollution) when they are used as fertilizers to provide nutrients for plants (Liu et al., 2017; Major et al., 2010). Many studies also confirmed that biochar made from biomass with trace heavy metals may cause significant environmental risks, because they can increase the leaching of metals, reduce the bioavailability or mobility of metals, decrease the microbial activity, and affect the microbial community dynamics (Beauchemin et al., 2015; Jones and Quilliam, 2014). Therefore, more detailed work should be established to evaluate the role of metals in the formation of PFRs in carbon-based materials.

In summary, previous studies suggested that the types and concentrations of PFRs in biochar are influenced by many factors, including synthesis conditions, precursors, and so on. However, the underling mechanisms of these factors are still not fully-understood. Moreover, the influence factors of PFRs in carbon-based materials produced by other methods have not been reported. Therefore, more research is needed to better understand the role of various studies on the PFRs formation in carbon-based materials.

3. The transformation mechanism of ROCs mediated by PFRs in carbon-based materials

With the rapid growth of population and economy, numerous kinds of ROCs are continuously released to natural aquatic environment from their manufacture and application processes, and result in adverse effects on the public health as well as the aquatic ecosystems even at trace level. Carbon-based materials with abundant surface functional groups and high specific surface area have been frequently utilized as adsorbents for the removal of inorganic and organic contaminants in water for a long time (Upadhyayula et al., 2009). The adsorption mechanisms of inorganic and organic contaminants onto various kinds of carbon-based materials including hydrogen bond, π-π interactions, electrostatic attraction, and hydrophobic interaction (Ahmad et al., 2014; Upadhyay et al., 2014), have been well studied and already been summarized by many previous studies (Dabrowski et al., 2005; Inyang and Dickenson, 2015; Mohan et al., 2014). Thus, in this section, the degradation mechanisms of ROCs by ROS generated from carbon-based materials as well as the PFRs in carbon-based materials are reviewed in details hereafter. Furthermore, due to the high complexity of structure and components, the factor affecting the activity of carbon-based materials are also discussed.

3.1. The catalytic oxidation of ROCs by reactive free radicals from carbon-based materials

As well-known, carbon-based materials, such as C_3N_4 (Gu et al., 2014; Mamba and Mishra, 2016; Zheng et al., 2016), C_{60} (Arbogast et al., 1991; Lee et al. 2008, 2009; Yamakoshi et al., 2003) and C_{70} (Arbogast and Foote, 1991; Moor et al., 2015), have been highly regarded as effective heterogeneous photocatalysts for pollution abatement as they are more environmental friendly and avoid

metal leaching problems compared with metal-based catalysts (Li et al. 2015, 2016; Shi et al. 2013, 2014; Wang et al., 2017). Since the photocatalytic mechanisms have been well studied and already been summarized in many studies, this review would not present these in details. However, little knowledge has been reported on the photocatalytic properties of biochar and hydrochar (Chen et al., 2017; Fang et al., 2017), which widely exist in natural environment.

A recent study by Chen at al. systematically compared the sulfadimidine removal performances of biochar with hydrochar in the dark as well as under solar light irradiation (Chen et al., 2017). The authors suggested that the formation of ROS in the dark was dependent on the PFRs, while the oxygenated functional groups were responsible for the ROS generation under daylight irradiation. The PFRs concentration in biochar was much higher than that of hydrochar because hydrochar contained more oxygenated functional groups. Therefore, the sulfadimidine removal efficiency of biochar was obviously higher than that of hydrochar in the dark, but the yields of H_2O_2 and $^{\bullet}OH$, as well as the sulfadimidine degradation efficiency of biochar were significantly lower than that of hydrochar under daylight irradiation.

Carbon-based materials also exhibited excellent catalytic ability to activate oxidants, including O_3 (Beltrán et al., 2005; Gonçalves et al., 2012, 2013, Kasprzyk-Hordern, 2003), H_2O_2 (Huang et al. 2003a, b, Ribeiro et al., 2013) and persulfate (Duan et al., 2015a; Liu et al., 2014; Peng et al., 2013; Sun et al., 2013; Yang et al., 2011; Zhao et al., 2017), through the direct electron transfer process to produce ROS, such as $^{\bullet}OH$ and $SO_4^{\bullet-}$, for the degradation of ROCs (Fig. 7, Figs. S5 and S6). For example, Huang et al. prepared six kinds of biochar under different temperatures and evaluated their activation ability toward H_2O_2 for the degradation of sulfonamide antibiotic, sulfamethazine (Huang et al., 2016). The results indicated that all biochar exhibited excellent ability for the catalytic decomposition of H_2O_2 for sulfamethazine degradation. With the increase pyrolysis temperature from $300\,^{\circ}\mathrm{C}$ to $800\,^{\circ}\mathrm{C}$, the degradation efficiency increased from 93.4% to 100%, and the degradation rate constant increased from 0.0211 to 0.427 min^{-1}. Sun et al. performed a series studies on the persulfate activation with numerous kinds of carbon-based materials, including activated carbon (Saputra et al., 2013), mesoporous carbon (Tian et al., 2016), hydrochar (Wang et al., 2016c), graphene (Duan et al., 2016d; Indrawirawan et al., 2015a; Kang et al., 2016; Li et al., 2017; Wang et al., 2016a), CNTs (Duan et al. 2015b, 2015c, 2015d, 2016b; Sun et al., 2014), and nanodiamonds (Duan et al. 2016a, 2016c; Indrawirawan et al., 2015b), and demonstrated that these carbon-
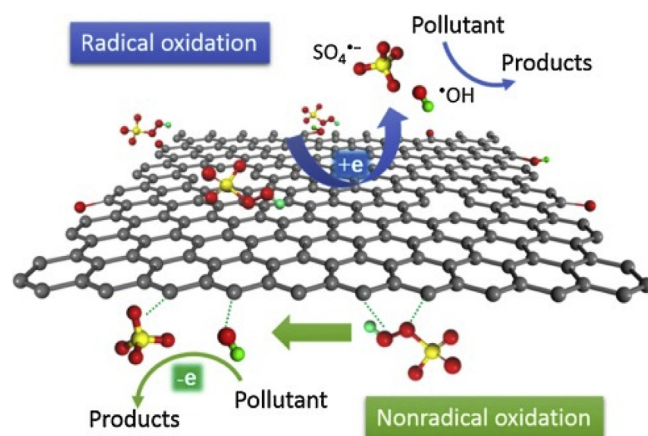

Fig. 7. The activation mechanism of peroxymonosulfate by carbon-based materials (Duan et al., 2016b). Reprinted with permission from Elsevier.

based materials can play promising roles in the catalytic degradation processes of ROCs. Even though, the catalytic decomposition of oxidants by carbon-based materials for the degradation of ROCs have been investigated and reviewed by few researchers, the activation mechanisms are still controversial. At present, one of the commonly accepted oxidant activation mechanisms by carbon-based materials was similar to the Fenton reaction and Haber-Weiss mechanism (Kimura and Miyamoto, 1994). Take the H_2O_2 activation by activated carbon as an example, the delocalized π-electrons on graphene layers transferred via electron donors/acceptors onto activated carbon surface to H_2O_2 then to produce $^\bullet OH$ as following Eqs. (6) and (7) (Kimura and Miyamoto, 1994; Moreno-Castilla et al., 2010):

$$Activated\ carbon + H_2O_2 \rightarrow Activated\ carbon^+ + OH^- + {}^\bullet OH \tag{6}$$

$$Activated\ carbon^+ + H_2O_2 \rightarrow Activated\ carbon + H_2O + H^+ \tag{7}$$
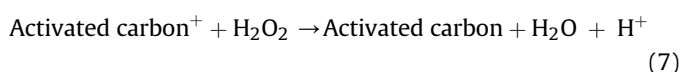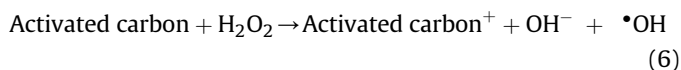
However, there was no direct evidence to prove the formation of activated carbon$^+$, even though the generation of ROS can be demonstrated by ESR. Moreover, two different reaction mechanisms including radical and nonradical reactions have been proposed to explain the persulfate activation process with carbon-based materials (Fig. 7) (Oh et al., 2016). But, the exact activation mechanisms are still unclear due to the lack of direct evidence to clarify the reaction processes although ESR has proved the generation of $^\bullet OH$, $SO_4^{\bullet-}$, and other kinds of reactive species. Moreover, recent studies by Fang et al. has been demonstrated that PFRs in carbon-based materials play key roles in affecting their catalytic activity (Fang et al. 2014a, 2014b, 2015a, 2015b), which have not been involved in most of previous studies. They suggested that carbon-based materials, such as activated carbon and several kinds of biochar, could effectively activate oxidants, including O_2, H_2O_2 or persulfate, via a single-electron transfer process from PFRs on carbon-based materials to oxidants to produce ROS for the degradation of ROCs (Figs. S5 and S6). The yields of ROS were positively linearly correlated with the PFRs concentrations in biochar, and increased with the increase of PFRs concentrations, indicating that PFRs were the main contributor to ROS formation. They also indicated that the oxygen-centered PFRs are more reactive than carbon-centered PFRs with adjacent oxygen toward persulfate for the generation of $SO_4^{\bullet-}$ (Fang et al., 2015a). After the activation processes, the PFRs concentration in carbon-based materials decreased significantly and thus inhibited the activity of carbon-based materials.

To improve the catalytic activity of carbon-based materials, surface modification, including physical and chemical activation (Duan et al., 2016d; Liu et al., 2014; Peng et al., 2013) and hetero-atom doping (Duan et al., 2015a; Indrawirawan et al., 2015a; Kang et al., 2016; Li et al., 2017; Liang et al., 2017; Sun et al., 2013; Wang et al., 2016a), were also utilized because they can (I) increase the specific area and surface functional of carbon-based materials, (II) improve π-electron mobility through the conjugation, (III) introduce new active sites and functional groups, (IV) alter the electron density in the local carbon atom, and thus enhance the activity of carbon-based materials. For example, although GO could not activate peroxymonosulfate or peroxodisulfate to degrade ROCs, the sulfachloropyridazine degradation efficiency still reached 65% and 100% within 3 h in the system of reduced graphene oxide (rGO) and N-rGO, respectively (Kang et al., 2016). The degradation rate in the system with N-rGO was 6.7 times higher than that of rGO, and even 2 times higher than that of the popular metal based-catalyst of

Co_3O_4. Similar results were also observed by Wang et al. during the peroxodisulfate activation process. Both GO and rGO could not activate peroxodisulfate to degrade endocrine disrupting compounds, bisphenol A and bisphenol F, but more than 97% of degradation efficiencies of bisphenols was obtained within 17 min (Wang et al., 2015). The apparent degradation rate constant of bisphenol A in the system of N-rGO even reached about 700 times higher than that of the system with N-free rGO. According to recent studies, the surface modification may also influence the types and concentrations of PFRs in carbon-based materials, and thus affected the catalytic activity of carbon-based materials. Fang et al. investigated the influence of HNO_3 treatment on the H_2O_2 activation ability of three kinds of activated carbon (Fang et al., 2014b). With the increasing treatment time of HNO_3, the H_2O_2 decomposition rates decreased obviously, but the yields of $^\bullet OH$ and the degradation rates of diethyl phthalate increased significantly. This is because HNO_3 treatment resulted in the decreas of acidic functional groups and the increase of PFRs concentrations in activated carbon. PFRs could transform H_2O_2 into $^\bullet OH$, while acidic functional groups can only catalyze the decomposition of H_2O_2.

These studies provided new insights into the environmental implications of carbon-based materials, but the knowledge on their catalytic activities are still relatively limited. According to current researches, both surface properties and the types and concentrations of carbon-based materials would influence the catalytic activities. However, the influence mechanisms of these factors are not fully understood. Moreover, there is little study on the relationships between the structures and PFRs amounts in carbon-based materials. The transformation of PFRs in biochar was not monitored even though some researches indicated that the concentration of PFRs in carbon-based materials decreased sharply (Fang et al. 2014a, 2014b). Furthermore, particular attention is also needed regarding the application of carbon-based materials in activating O_2 for $^\bullet OH$ generation to realize the degradation of ROCs, not only because of the strong oxidizability of $^\bullet OH$, but also due to the widespread of carbon-based materials and O_2 in natural environment.

3.2. The catalytic reduction of ROCs by ROS from carbon-based materials

As mentioned above, the PFRs in carbon-based materials are believed to exhibit semiquinone-type character, which could take up and release electrons through the conjugated π-electron systems (Montes-Morán et al., 2004). The quantitative analysis of biochar to reversibly donate and accept electrons was measured by Klüpfel et al. with electrochemical method and confirmed that biochar can accept or donate several hundred micromoles of electrons per gram depending on the precursors and the pyrolysis temperature (Klupfel et al., 2014). In fact, many previous studies have demonstrated that carbon-based materials can also act as a redox catalyst to promote the reduction of heterocyclic nitramines (such as hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)) (Kemper et al., 2008; Oh and Chiu, 2009; Oh et al., 2013a; Xu et al., 2010), nitroaromatic compounds (such as 2,4-dinitrotoluene and 3-bromonitrobenzene) (Fu and Zhu, 2013; Gong et al., 2016; Oh et al., 2013b; Xu et al., 2015; Yu et al., 2012), dinitroaniline herbicides (such as pendimethalin and trifluralin) (Gong et al., 2016; Oh et al., 2014), chlorinated aliphatic hydrocarbons (such as hexachloroethane and 1,1,2,2-tetrachloroethane) (Chen et al., 2014; Fu et al., 2014), etc. by accelerating the transfer of electrons from the reductants (such as dithiothreitol or H_2S) to target contaminants (Fig. 8). For example, Fu et al. reported that in the presence of GO, the reduction rate constant of nitrobenzene was raised by nearly 2 orders of magnitude (Fu and Zhu, 2013).

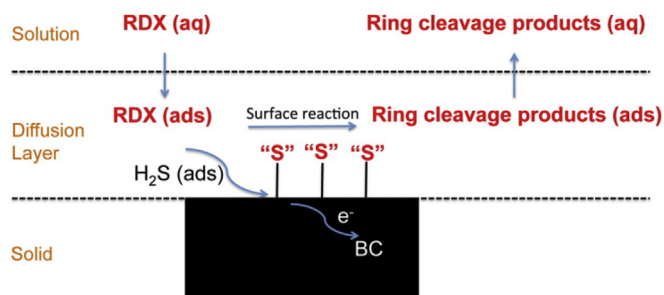However, the electron transfer mechanism from carbon-based

Fig. 8. Proposed reduction mechanisms of hexahydro-1,3,5-trinitro-1,3,5-triazine by black carbon and sulfides (Xu et al., 2013). Reprinted with permission from the American Chemical Society.

materials to target contaminants was still controversial. Some researchers have reported that the electron transfer ability of biochar was responsible for the promotion of RDX reduction rather than the surface functional groups (Xu et al., 2013, 2015). But, many others studies suggested that the surface functional groups played important roles in the electron transfer processes (Amezquita-Garcia et al., 2013; Gong et al., 2014). Oh et al. even stated that the electron transfer ability, surface functional groups and metals (including Fe, Cu, and Mn) in biochar were all found to be involved in the enhanced reduction of nitro compounds (Oh et al., 2013a). It is needed to clarify the dependence of the electron accepting and donating capacities on the structures and components of carbon-based materials.

In fact, ROCs can react directly with PFRs even though their reactivity are lower than ROS. Unfortunately, relevant reports are relatively limited even though some researchers observed a slow removal of ROCs in the presence of carbon-based materials without addition of other reductants. Recently, Yang et al. found that PFRs in biochar particles can directly degrade p-nitrophenol adsorbed onto the surface of biochar through the denitration process (Yang et al. 2016, 2017a), and the p-nitrophenol degradation rate was also found to be positively correlated with the PFRs concentration although biochar submerged in water. The produced ROS only resulted in about 20% of p-nitrophenol degradation, while 80% of p-nitrophenol directly reacted with the nonradical reactive sites of biochar. Unfortunately, due to the lack of literature, it is difficult to get a confirmed conclusion on the selectivity and reactivity of PFRs in carbon-based materials.

4. Conclusions and outlook

Carbon-based materials with different types and concentrations of PFRs have already been successfully synthesized and used in degradation of various ROCs. Due to the abundant precursors and environmental friendliness, carbon-based materials undoubtedly represent one of the most promising candidates to mediate the degradation of ROCs. In this review, the recent progress on the formation mechanisms of PFRs in carbon-based materials and the further applications in the degradation of various ROCs were summarized in detail. Compared with the traditional metal catalysts, carbon-based materials have many advantages (such as low-cost, the wide availability of the necessary feedstock, and so on) although there are still few concern about the biotoxicity of carbon nanoparticles as well as the release of absorbed organic compounds and heavy metals from carbon-based materials. Despite these shortcomings, there still remain many challenges and problem in application in the degradation of various ROCs. First, although many researchers have demonstrated that carbon-based materials possess the ability to medicate the transformation of ROCs, still only very little is known about the specific surface structure which determines the reactivity of carbon-based materials. Hence, further in-depth studies on the relationships between the structures and activities of carbon-based materials are urgently needed. Second, most studies are focused on the formation of ROS for the degradation of organic contaminants, but the transformation of PFRs in carbon-based materials has received only little attention. It is the PFRs in carbon-based materials which is widespread in environments that would interact with metal ions, minerals, inorganic and organic compounds and microorganism, and thus influence the migration and transformation of different organic and inorganic contaminants. In this regard, much effort is still needed to investigate the transformation of PFRs within carbon-based materials. Third, at present, most carbon-based materials applied in environment remediation are synthesized in the laboratory. Little research has been done in the activity of naturally occurring carbon-based materials, which may be the most promising candidates to mediate degradation of various organic contaminants due to their earth abundance, extremely low cost and environmental friendliness. Meanwhile, understanding the transformation mechanism of ROCs mediated by natural occurring carbon-based materials will be helpful in the applications of carbon-based materials in environment remediation.

Acknowledgements

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.watres.2018.03.012.

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