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REVIEW ARTICLE

Reactivity of Pyrogenic Carbonaceous Matter (PCM) in mediating environmental reactions: Current knowledge and future trends

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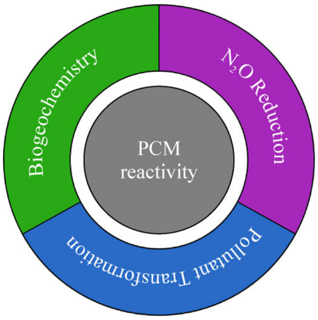
HIGHLIGHTS

- Pyrogenic Carbonaceous Matter (PCM) promotes both chemical and microbial synergies.
- PCM-enhanced abiotic transformation pathways of organic pollutants are discussed.
- Conjugated microporous polymers (CMPs) can mimic the performance of PCM.
- CMPs offer a platform that allows for systematic variation of individual properties.

GRAPHIC ABSTRACT



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ABSTRACT

Pyrogenic Carbonaceous Matter (PCM; e.g., black carbon, biochar, and activated carbon) are solid residues from incomplete combustion of fossil fuel or biomass. They are traditionally viewed as inert adsorbents for sequestering contaminants from the aqueous phase or providing surfaces for microbes to grow. In this account, we reviewed the recently discovered reactivity of PCM in promoting both chemical and microbial synergies that are important in pollutant transformation, biogeochemical processes of redox-active elements, and climate change mitigation with respect to the interaction between biochar and nitrous oxide (N_2O). Moreover, we focused on our group's work in the PCM-enhanced abiotic transformation of nitrogenous and halogenated pollutants and conducted in-depth analysis of the reaction pathways. To understand what properties of PCM confer its reactivity, our group pioneered the use of PCM-like polymers, namely conjugated microporous polymers (CMPs), to mimic the performance of PCM. This approach allows for the controlled incorporation of specific surface properties (e.g., quinones) into the polymer network during the polymer synthesis. As a result, the relationship between specific characteristics of PCM and its reactivity in facilitating the decay of a model pollutant was systematically studied in our group's work. The findings summarized in this account help us to better understand an overlooked environmental process where PCM synergistically interacts with various environmental reagents such as hydrogen sulfide and water. Moreover, the knowledge gained in these studies could inform the design of a new generation of reactive carbonaceous materials with tailored properties that are highly efficient in contaminant removal.

1 Motivation

Pyrogenic carbonaceous matter (PCM) refers to the solid pyrolysis products of fresh or fossilized biomass. Broadly, it includes environmental black carbon — i.e., fossil fuel soot and chars resulting from natural and deliberate-set fires — and engineered carbons such as biochar and activated carbon (AC) (Pignatello et al., 2017). Traditionally, PCM is considered a passive adsorbent in sequestering pollutants from the aquatic environment or providing microbes with a surface to grow (Luthy et al., 1997; Jonker and Koelmans, 2002; Koelmans et al., 2006; Cho et al., 2009; Ghosh et al., 2011; Simon, 2015; Payne et al., 2019). As a result, PCM in the form of activated carbon has been

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widely used as an adsorbent, with applications that include, but are not limited to, the decontamination of public drinking water (Zhou and Xie, 2002; Karanfil, 2006), the removal of micropollutants from wastewater (Boehler et al., 2012), and the sequestration of organic pollutants (such as polycyclic aromatic hydrocarbons (PAHs) from contaminated soils and sediments (Cho et al., 2009; Simon, 2015; Fan et al., 2017; Payne et al., 2019).

Recently, a small but growing body of literature has reported that PCM is intrinsically reactive and can participate in a suite of environmental reactions that are critical to biogeochemical processes (Kappler et al., 2014; Xu et al., 2016), climate change (Lehmann et al., 2011; Cayuela et al., 2014), and the fate of contaminants (Xu et al., 2013; Chen et al., 2014b; Fang et al., 2014; Xu et al., 2015; Ding and Xu, 2016; Ding et al., 2018; Qin et al., 2018; Ding et al., 2019; Zhao et al., 2020). We will review these abiotic and biotic reactions in this account with a focus on the reaction mechanisms.

Specifically, our research group has shown that there are synergistic interactions between naturally existing environmental reagents in the subsurface environment, such as between PCM and hydrogen sulfide (H_2S/HS^-) (Xu et al., 2013; Xu et al., 2015; Ding and Xu, 2016; Ding et al., 2019; Zhao et al., 2019), or between PCM and water (Ding et al., 2018; Li et al., 2019). Hydrogen sulfide can present at relatively high concentrations as a product of sulfate-reducing bacteria in the subsurface environment (Lippa and Roberts, 2002). Although hydrogen sulfide can act as a nucleophile or reductant for the abiotic transformation of dihalomethanes, chloroazines, and hexachloroethane, it is ineffective in reacting with more persistent halogenated contaminants (e.g., 1,1,1-trichloro-2,2-di(4-chlorophenyl) ethane (DDT)) under environmental conditions close to neutral pH (Curtis and Reinhard, 1994; Lippa and Roberts, 2002; Loch et al., 2002). However, our group demonstrated that PCM can promote the abiotic degradation of DDT by hydrogen sulfide, resulting in lower toxicity products including chloride (Ding and Xu, 2016; Ding et al., 2019). Recently, we discovered that dichloroacetamide safeners can undergo complete dechlorination by PCM and sulfide, forming sulfur substituted products that are less mobile than the parent compounds (Xu et al., 2020). Furthermore, even at neutral pH, we found that PCM can promote hydrolysis of nitroaromatics (e.g. 2,4,6-trinitrotoluene (TNT) and 2,4-dinitroanisole (DNAN)), forming Meisenheimer complexes that are less stable than parent compounds (Ding et al., 2018). We will discuss the reaction pathways of these reactions in detail here.

Another aspect of our group efforts involves understanding what properties of PCM confer its reactivity. Although PCM is ubiquitous in sediments, the amount of PCM that is present, its redox status, and its surface functionalities often vary significantly. All of these properties are critical to PCM's ability to promote contaminant transformation. As a result, abiotic processes mediated by PCM are not observed across sediments consistently (Quensen et al., 1998; Hale et al., 2009). For instance, values for percent sedimentary organic carbon accounted for by black carbon (one type of PCM) can range from 0.1% to above 50% in marine sediments (Masiello, 2004), where little reactivity would be expected at the lower range, despite comparable carbon content. Due to this inherent heterogeneity in the PCM-system, it is difficult to predict the degree of contaminant transformation occurring in natural or engineered systems. Therefore, to define the conditions necessary for these abiotic processes to occur, we need to delineate the heterogeneity of the PCM-system so that the contributions of individual properties of PCM can be studied. Our group has pioneered this work, employing a PCM-like polymer network that resembles the key attributes of PCM (Li et al., 2019). By selecting different monomers, we can control the functionality of PCM-like polymers via a bottom-up synthesis. This approach is well-poised to elucidate the currently poorly understood mechanisms affecting the reactivity of PCM. We will review this line of research and discuss future research directions in this account.

Upon gaining a comprehensive understanding of the relationship between the properties and reactivity of PCM, we can better predict the fate of pollutants in natural or engineered systems. Moreover, this knowledge can be translated toward the engineering of tailored materials that confer high reactivity in promoting the detoxification of contaminants. All the work outlined here will lay the groundwork for developing ecologically and economically sound contaminant removal solutions that address the shortcomings of current technologies. This will ultimately improve health outcomes by reducing human exposure to these contaminants.

2 Structure of PCM

PCM is an amorphous solid without long-range order. It is highly porous and contains micropores (< 2 nm), mesopores (2–50 nm), as well as larger pores (Fig. 1B) (Pignatello et al., 2017). The surface of PCM contains various surface functional groups, including carboxyl, hydroxyl, and heterocyclic amine groups that could serve as active sites for interaction with ionizable compounds (Fig. 1A) (Pignatello et al., 2017). The large surface area, high porosity, and diverse surface functional groups of PCM all contribute to its effectiveness as an adsorbent of hydrophobic organic pollutants, ionizable organic contaminants, and metal ions (Jonker and Koelmans, 2002; Kah et al., 2017). As pyrolysis temperature increase in the production of char, H/C and O/C ratios decrease. At low temperatures, chars are rich in oxygenated functional groups (e.g., carboxylic acids, esters, phenols, and methoxy groups), which can form complexes with metals (Inyang et al., 2016). As temperatures become higher these groups are lost in favor of a gain in aromatic carbons (Cao et al., 2012), which increases the conductivity of the chars and consequently, resulting redox activity (Pignatello et al., 2017). Surface oxygen functionalities, especially quinone, are believed to confer redox behavior to PCM (Klupfel et al., 2014). PCM also contains polyaromatic ring clusters in its amorphous solid phase (graphitic regions), which contribute to the electrical conductivity and reactivity of PCM (Cao et al., 2012; Xu et al., 2013). These conductive graphitic regions are formed during the heat-induced condensation reaction during the production of PCM, which are three-dimensional, aromatic structures with conjugation and π bonds that facilitate electron delocalization. The higher pyrolysis temperature leads to the formation of larger polyaromatic ring clusters, which makes the PCM more conductive (Fig. 1C) (Cao et al., 2012; Xu et al., 2013).

3 Role of PCM as a passive adsorbent

Black carbon, one form of PCM, is ubiquitous in soils and sediments. It constitutes 3% to 6% of the sedimentary organic matter in coastal regions, and over 50% in the deep ocean. In soils, values ranging from 2% to 30% have been reported (Masiello, 2004). Due to the strong affinity of black carbon toward contaminants (e.g., PAHs and polychlorinated biphenyls (PCBs)), soils and sediments serve as important sinks for pollutants, substantially reducing their bioavailability to benthic organisms. This topic has been extensively reviewed elsewhere (Luthy et al., 1997; Jonker and Koelmans, 2002). Most contaminants bind to PCM via Van der Waals interactions or surface complexation (Luthy et al., 1997; Jonker and Koelmans, 2002). π-π Interactions, which include electron donor-acceptor interactions, are the dominant force through which nonpolar aromatic contaminants (e.g., TNT (Zhu and Pignatello, 2005) and PAHs (Jonker and Koelmans, 2002)) associate with the graphitic regions of PCM. Polar aromatic compounds can also engage in π-π interactions (Xiao and Pignatello, 2015). For instance, cationic aromatic compounds can participate in π +-π interactions with PCM (Pignatello et al., 2017). Polar compounds can form hydrogen bonds with functional groups of PCM. The hydrogen bond is particularly strong (charge-assisted H-bond) when sorbates contain functional groups with proton affinities approaching identical values to those of groups on the carbonaceous surface (Li et al., 2015; Pignatello et al., 2017). Ionic contaminants (e.g., nitrite) are expected to associate with anion or cation exchange sites on PCM (Padhye, 2017). Contaminants adsorbed on PCM have been assumed to be passively sequestered from the aqueous phase without undergoing chemical reaction.

The addition of engineered carbons (e.g., AC or biochar) into contaminated sediments to extract pollutants from the sediment matrix has been successfully demonstrated at the pilot scale as an alternative technology for sediment stabilization and cleanup (Cho et al., 2009; Payne et al., 2019). Engineered carbons are made by heating woody feedstock under controlled conditions of temperature, time, and headspace gas composition, usually at low or zero oxygen concentration (Pignatello et al., 2017). The addition of colloidal or granular AC into contaminated groundwater (e.g., chlorinated solvents and petroleum hydrocarbons) and sediments as a passive adsorbent to sequester aqueous phase pollutants has been successfully demonstrated at full-scale (Simon, 2015; Fan et al., 2017). PCM is also frequently used as a delivery vehicle to transport microorganisms to contaminated sites (Payne et al., 2019). According to these investigations, porewater concentration of PAHs, PCBs, and DDT have been reduced up to 99% in sediment where AC amendment had been added at a range of 1 to 5% (Simon, 2015; Fan et al., 2017). However, while adsorption significantly reduces the toxicity of contaminants (in those cases, toward benthic organisms), it only redistributes contaminants between the aqueous and solid phases but does not actually destroy them. Consequently, upon desorption, pollutants can still

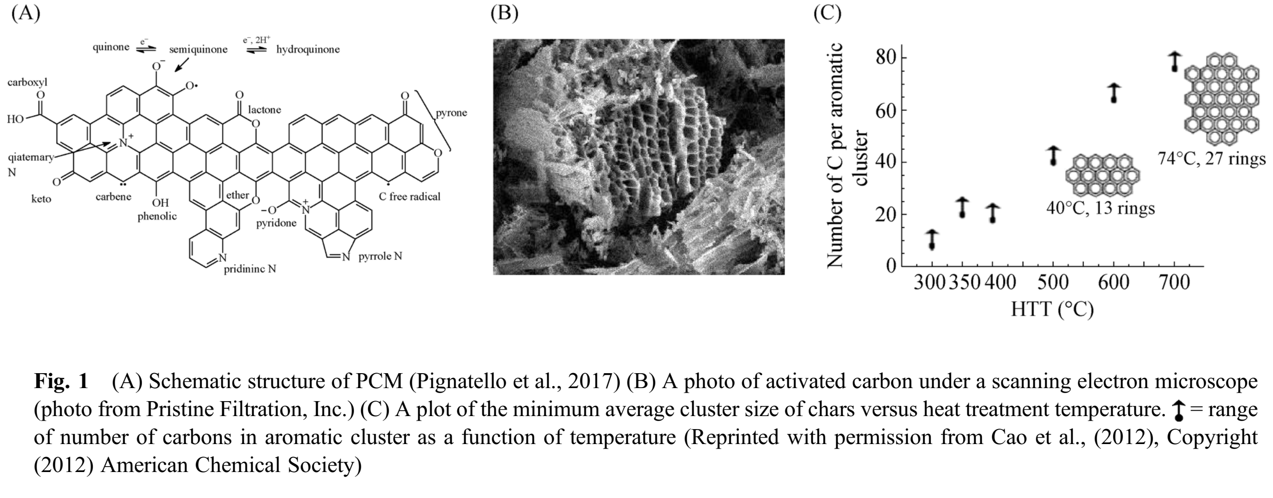


Fig. 1 (A) Schematic structure of PCM (Pignatello et al., 2017) (B) A photo of activated carbon under a scanning electron microscope (photo from Pristine Filtration, Inc.) (C) A plot of the minimum average cluster size of chars versus heat treatment temperature. ↥ = range of number of carbons in aromatic cluster as a function of temperature (Reprinted with permission from Cao et al., (2012), Copyright (2012) American Chemical Society)

enter groundwater or surface runoff, and their associated risks are not eliminated. Therefore, long-term monitoring is often required.

In addition to this in situ treatment using engineered carbons, PCM has been used in water and wastewater treatment processes to remove recalcitrant contaminants. For instance, biological activated carbon (BAC) has been widely applied in water treatment to remove haloacetic acids (HAAs), a group of disinfection byproducts that are formed during disinfection (Zhou and Xie, 2002). Moreover, granular activated carbon (GAC) has shown promising performance in removing perfluoroalkyl substances (PFAS) in water and wastewater treatment. It is particularly effective for long-chain PFAS compounds, such as perfluorooctane sulfonate (PFOS), where the removal efficiencies from batch studies with GAC can be achieved above 80% (McCleaf et al., 2017).

4 Reactivity of PCM

PCM contains a range of oxygenated functional groups, particularly hydroquinone/quinone pairs, that can catalyze redox reactions (Fig. 1A) (Pignatello et al., 2017). It is postulated that phenolic groups contribute to the electron-donating capacity (EDC) while quinones, as well as conductive graphitic regions, account for the electron-accepting capacity (EAC) of PCM (Klupfel et al., 2014). Meanwhile, research suggests that the π-conjugated system of PCM could help stabilize the unpaired electrons of free radicals, resulting in the formation of persistent free radicals (PFRs) that can last for days or even months. These PFRs can either directly react with a contaminant or further promote the formation of reactive oxygen species (ROS), thereby facilitating redox reactions (Fang et al., 2014; Qin et al., 2018). Taken together, these redox-active properties of PCM enable them to participate in a range of environmental reactions, both biotically and abiotically.

4.1 PCM-facilitated biotic reactions

Traditionally, PCM was assumed to be inert, simply providing a surface for bacteria to grow. It is assumed that pollutant-degrading bacteria are sessile and, thereby, prefer to grow on surfaces rather than in water (Simon, 2015). Interestingly, recent studies suggest that PCM can promote microbial synergies, possibly due to its redox-active properties discussed above. This process is particularly important for Methanogenic archaea (*Methanosarcina*), *Geobacter*, and certain organo-halide respiring bacteria (OHRB), which utilize surface-mediated electron transfer processes (Liu et al., 2012; Chen et al., 2014a; Shrestha and Rotaru, 2014). For example, investigators have observed increases in ethanol oxidation and the reduction of fumarate in response to the addition of GAC to cocultures of *Geobacter metallireducens* and *Geobacter sulfurreducens* (Liu et al., 2012). PCM can also affect the structure of microbial communities. For example, the effects of biochar on soil microbial communities in temperate soils were monitored by phospholipid fatty acid analysis, in which the structure of the microbial community is determined by examining the chemical composition of the phospholipid fatty acid biomarkers of the organisms within the community. Biochar was found to affect the composition of microbial communities without affecting the overall biomass (Anders et al., 2013).

In addition to promoting microbial synergy, PCM mediates the biodegradation of a suite of contaminants, including chlorinated solvents, pentachlorophenol (PCP), PCBs, and tetrabromobisphenol A (TBBPA) (Kjellerup et al., 2014; Simon, 2015; Yu et al., 2015; Lefèvre et al., 2018). For instance, a study showed that biochar can function as an electron shuttle in the reductive dechlorination of PCP by *Geobacter sulfurreducens*. The authors observed, through the examination of different biochars, that the ability of biochar to accelerate this reaction depends on its electron-exchange capacity and its electrical conductivity (Yu et al., 2015). According to another investigation, AC and biochar accelerated the decay of TBBPA in wastewater sludge, resulting in a nearly complete transformation of TBBPA ~20 days earlier in reactors containing PCM as compared to controls in which PCM was absent (Lefèvre et al., 2018). AC was also able to enhance the decay of PCBs in field studies, produce less chlorinated congeners that more readily undergo aerobic degradation to achieve complete mineralization, and even cause microbial community shifts to putative OHRB phylotypes (Kjellerup et al., 2014).

PCM can also transfer electrons between microbes (e.g., *Geobacter* and *Shewanella* bacteria) and minerals (e.g., goethite and ferrihydrite), resulting in the reductive dissolution of minerals and affecting the biogeochemical cycle of redox-active elements (e.g., Fe) (Kappler et al., 2014; Xu et al., 2016). Moreover, it has been postulated that PCM could donate electrons to soil denitrifying bacteria and thereby promote the reduction of nitrous oxide (N_2O) to nitrogen (N_2) (Singh et al., 2010). Notably, N_2O has a global warming potential (GWP) 300 times that of carbon dioxide (CO_2). However, conflicting results in field studies have been reported and the underlying mechanism still warrants further investigation (Cayuela et al., 2014). Despite all these interesting observations, an understanding of how the properties of PCM shape the activities, functions, and structures of microbial community networks requires additional study.

4.2 PCM-facilitated abiotic reactions

4.2.1 Reduction and oxidation reactions

Several features of PCM could be important in mediating redox reactions, including quinone/hydroquinone pairs, persistent free radicals (PFRs) that are stabilized on PCM surfaces, and polyaromatic ring clusters (illustrated in Fig. 2A). Quinone moieties can activate persulfate to produce sulfate radicals, resulting in faster PCB decay by 10-fold (Fang et al., 2013). Moreover, AC was found to mediate the reduction of azo dye (i.e., hydrolyzed Reactive Red 2) using both volatile fatty acids and sulfide as electron donors. Since quinones had previously been shown to accelerate the reduction of azo dyes by sulfide in abiotic systems, this and other earlier studies support the hypothesis that quinones associated with AC play a role in the AC-catalyzed degradation of the azo dye (Van Der Zee et al., 2003). Similarly, graphene oxide (GO) and multi-walled carbon nanotubes (CNT) can enhance the rate of reductive dichlorination of hexachloroethane by sulfide by factors of four and two, respectively. Since GO and CNT are also rich in quinone groups, the roles of these moieties as electron shuttles may explain these results. Nevertheless, the authors of this study observed an increased reaction rate in the presence of bulk graphite (which lacks functionalities) as well, prompting them to propose additional mechanisms that include electron transfer via the graphitic region and activation of the C-Cl bonds of hexachloroethane by carbons at the edges and defects (Fu et al., 2014). Reactions involving PFRs associated with PCM have been reviewed elsewhere (Qin et al., 2018). Table 1 provides a summary of the abiotic reactions discussed herein, which includes the type(s) of PCM involved and the important structural features of PCM that have been proposed to participate in the reactions.

In addition to quinone moieties, the polyaromatic ring clusters in PCM (associated with conductivity) are important in facilitating electron transfer between chemical reagents, resulting in the reduction of nitroglycerin and 1,1-dichloro-2,2-bis(4-chlorophenyl) ethylene (DDE) (Xu et al., 2010; Ding and Xu, 2016). This has been demonstrated through electrochemical cell experiments (Fig. 2B), where contaminants and hydrogen sulfide were physically separated in cathodic and anodic cells, respectively. Cells were connected via an insulated copper wire attached to graphite sheet electrodes and the electrical circuit was completed by a salt bridge. As a result, any destruction of contaminants in the cathodic cell could only be attributed to the reduction pathway where electrons are transferred from hydrogen sulfide in the anodic cell. The presence of PCM accelerated the decay of both nitroglycerin and DDE; the half-life for nitroglycerin was shortened from 5.8 to 3.7 h, whereas DDE exhibited a half-life of 55.1 d, as compared to no evidence of reaction in the absence of PCM (Ding and Xu, 2016). Moreover, the presence of PCM facilitated the transformation of reaction intermediates, such as 1,2- and 1,3-dinitroglycerin, which otherwise will persist (Xu et al., 2010).

4.2.2 Nucleophilic substitution and hydrolysis

Hydrogen sulfide (the sum of H_2S, HS^-, S^{2-}), produced biologically by sulfate-reducing bacteria, is a strong nucleophile in addition to its role as a reducing agent discussed above. This compound often coexists with black carbon in subsurface environments, providing potential synergies in contaminant transformation. To this end, we have demonstrated that PCM could (illustrated in Fig. 3): (I) react with sulfide, forming a surface-bound nucleophile that subsequently attacks contaminants (Ding and Xu, 2016); and/or (II) oxidize sulfide into various reactive sulfur species, such as S_n^{2-}, which are more nucleophilic than HS^- during reactions with contaminants (Lippa and Roberts, 2002; Loch et al., 2002). Notably, more than one of these pathways could occur concurrently. Herein, we will review each operational pathway and the contaminants that are susceptible to the specific pathway.

Several studies have postulated the formation of surface intermediates via a reaction between sulfide and PCM, which serve as stronger nucleophiles than sulfide in facilitating contaminant transformation. For instance, both hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) (Xu et al., 2013) and DDT (Ding and Xu, 2016) were observed to undergo transformation in the presence of graphite that was pre-exposed to hydrogen sulfide. The pre-treated graphite

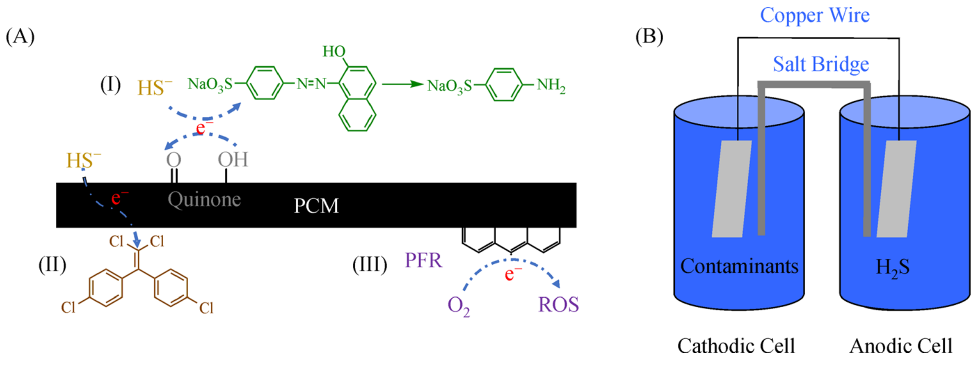


Fig. 2 (A) (I) Quinone/hydroquinone pairs, (II) polyaromatic ring clusters, (III) persistent free radicals (PFRs) of PCM in facilitating redox reactions. (B) Electrochemical cell set up.

Table 1 PCM-facilitated abiotic reactions for pollutant transformation

Type of PCM	Proposed important feature of PCM	Contaminant undergoing decay	Type of reaction	Reference(s)
SA-4 (steam activated carbon) and SX-4 (acid washed,steam activated carbon	Quinones	Azo dye (hydrolyzed Reactive Red 2)	Reduction	Van Der Zee et al., (2003)
Graphene Oxide, graphite, multi-walled carbon nanotubes	Quinones, graphitic carbon	Hexachloroethane	Reduction	Fu et al. (2014)
Graphite (sheet and powder)	Graphitic carbon	Nitroglycerin, DDE	Reduction	Xu et al. (2010); Ding and Xu (2016)
Red oak wood chars, activated carbon, graphite	Surface bound intermediate as nucleophile (sulfide)	RDX, DDT	Nucleophilic substitution	Xu et al. (2013); Ding and Xu (2016)
Multi-walled carbon nanotubes and various types of PCM	Oxidized sulfide, forming reactive sulfur species at surface	Azo dye, (di)chloroacetamide safeners, chloroacetamide herbicides	Nucleophilic substitution	Zhao et al. (2019); Xu et al. (2020)
Graphite powder	Surface bound sulfite, thiosulfate	DDT	Nucleophilic substitution	Ding et al. (2019)
Carbon nanotubes	-NH_2 and-OH groups acting as strong base	1,1,2,2-tetrachloroethane (TeCA)	hydrolysis	Chen et al. (2014b)
Graphite, biochar	-OH groups	TNT, DNAN	hydrolysis	Ding et al. (2018)

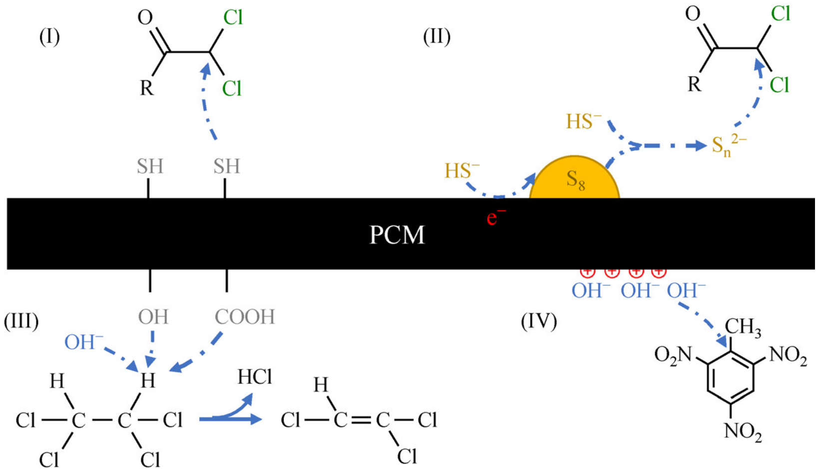


Fig. 3 Schematic illustration of the nucleophilic substitution and hydrolysis pathways in which PCM could participate to promote contaminant transformation.

was rinsed thoroughly to remove any adsorbed sulfur species, allowing for the isolation of the nucleophilic substitution pathway associated with surface-bound intermediates. Results indicate that the half-life of RDX was 0.87 h (and that of DDT was 8.7 d). No decay of RDX or DDT by sulfide was observed in the absence of PCM. The extent of decay in the sulfide-pretreated graphite system was comparable to that of batch reactors that encompass all possible reaction pathways, suggesting the importance of such surface-bound nucleophiles (Xu et al., 2013; Ding and Xu, 2016).

Recently, a novel reaction pathway that involves the formation of polysulfide was found to be responsible for the enhanced decay of azo dye (Zhao et al., 2019), as well as (di)chloroacetamide safeners and herbicide (Xu et al., 2020). The lag phase of azo dye decolorization by sulfide was shortened from 64.3±7.0 to 13.3±6.1 min after the addition of PCM (Zhao et al., 2019). Our group investigated the ability of PCM to enhance the transformation of dichloroacetamide safeners (AD-67, benoxacor, and dichlormid) and two chloroacetamide herbicides (metolachlor and acetochlor) by sulfide. Complete dechlorination was observed for all three dichloroacetamide safeners. Furthermore, the presence of (multi)sulfur-bridged dimers and trimers, along with cyclization products, was observed, suggesting that nucleophilic reaction likely took place. The electron-accepting capacity (EAC) of various types of PCM showed a positive correlation with respect to the decay rates for contaminants. As a result, we postulated that S_n^{2-} contributed to the accelerated decay of (di)chloroacetamides in batch reactors containing both black carbon and sulfide. The formation of S_n^{2-} can be ascribed to a reaction between bisulfide and S_8 (reaction 1), where S_8 is postulated to form from the oxidation of bisulfide by black carbon (Xu et al., 2020). In addition to S_n^{2-}, our group reported that other sulfur species, sulfite (SO_3^{2-}) and thiosulfate ($S_2O_3^{2-}$), generated by sulfate-reducing bacteria (SRB) could promote the degradation of DDT in the presence of PCM following a similar pathway, indicating a potential synergistic effect between PCM and SRB under environmentally relevant conditions (Ding et al., 2019).

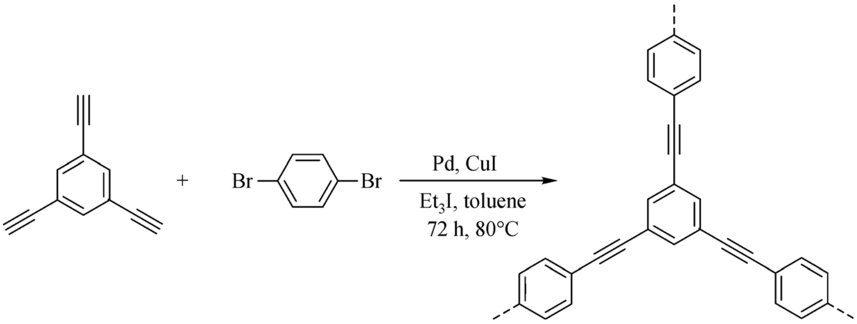
$$HS^- + \frac{n-1}{8}S_8 \rightleftharpoons H^+ + S_n^{2-} \tag{1}$$

In addition to nucleophilic substitution, PCM can also facilitate contaminant decay via alkaline hydrolysis (see Fig. 3). For instance, a previous study reported that carbon nanotubes can catalyze the dehydrochlorination of 1,1,2,2-tetrachloroethane (TeCA) in a pH-dependent manner. The authors proposed that functional groups (e.g., $-NH_2$ or $-OH$) act as base by abstracting a proton from TeCA, resulting in the formation of trichloroethylene (TCE) (Chen et al., 2014b). Furthermore, our group reported that PCM (i.e., graphite and biochar) can promote the decay of explosive nitroaromatics such as TNT and DNAN at pH 7, where no reaction occurs without PCM. The observed reactions proceeded via base-catalyzed hydrolysis, where the decay of TNT accompanied the formation of a Meisenheimer complex as an intermediate and released nitrite. Moreover, the addition of tetramethylammonium cation ($(CH_3)_4N^+$) was shown to enhance TNT decay, most likely due to the strong binding affinity of $(CH_3)_4N^+$ to the PCM surface, which allows for an increased local concentration of hydroxide, thereby promoting the hydrolysis of TNT (Ding et al., 2018). Our group is currently looking more closely at DNAN hydrolysis and other insensitive munitions, 3-nitro-1,2,4-triazol-5-one (NTO) and nitroguanidine (NQ). These compounds are more polar and water-soluble, therefore posing a greater risk for groundwater and surface water contamination than legacy explosives. The findings that PCM could promote alkaline hydrolysis at neutral pH conditions have profound implications for in situ remediation due to the easy implementation of such technologies. Moreover, alkaline hydrolysis can be advantageous compared to reduction or oxidation of nitrogenous compounds, which could produce toxic nitroso-intermediates (Ding et al., 2018).

5 PCM-like polymer platform

As previously described, the heterogeneity of the PCM-system makes it difficult to delineate the contribution of individual properties to the observed reactivity, which hinders our ability to harness the reactivity of PCM for engineering applications. For instance, both physical (surface morphology, pore size, and surface area) and chemical properties (electron-donating or-accepting capacities, redox potential, and functionalities) of the PCM vary depending on the precursor materials and post-pyrolysis treatment, resulting in variations in PCM performance (Cao et al., 2012; Klupfel et al., 2014; Pignatello et al., 2017). To enhance its reactivity, previous studies modified PCM through the application of various wet-chemical treatment approaches (e.g., ozonation, nitric acid treatment) (Valdés et al., 2002; Langley and Fairbrother, 2007). However, these studies could not pin down the critical properties of PCM that are responsible for its observed reactivity because multiple PCM characteristics were altered simultaneously (e.g., surface area, pore distribution, and oxygenated functional groups).

One way to overcome this hurdle is to simplify the PCM-system with a polymer surrogate. We have demonstrated (Li et al., 2019) that PCM-like polymers, namely conjugated microporous polymers (CMPs), can be synthesized via a bottom-up approach using the Sonogashira-Hagihara coupling reaction (reaction (2)) and connecting a 1,4-dibromobenzene linker to 1,3,5-triethynylbenzene. Like PCM, CMPs are (1) highly conjugated and amorphous with no long-range molecular order, (2) contain micropores and large surface areas (e.g., ~1000 $m^2\ g^{-1}$), and (3) have a high affinity toward organic contaminants. Different from PCM, however, selected properties can be systematically tuned during the polymer synthesis process (illustrated in Fig. 4) (Jiang et al., 2008; Dawson et al., 2009; Li et al., 2019). For instance, to introduce different functional groups, the linker, 1,4-dibromobenzene, can be substituted with 2,5-dibromohydroquinone and 2,5-dibromoquinone to incorporate hydroxyl and quinone functional groups into synthesized polymers, respectively, following the same synthetic route. To fine-tune the porosity of synthesized polymers, different strut lengths of the monomers can be selected to increase or decrease the pore size. Previous research suggested that smaller strut length could result in smaller pore size with an increase in both surface area and total pore volume (Jiang et al., 2008), which provides a systematic approach for manipulating the porosity for the subsequent tasks. Lastly, conductivity can be altered by carbonizing samples at different temperatures in the absence of oxygen. Similar to PCM, it is expected that an increase in the carbonization temperature will increase the size of ring clusters in carbonized samples and therefore, increase the conductivity (Cao et al., 2012; Xu et al., 2013; Li et al., 2019).



(2)

In our previous work (Li et al., 2019), we demonstrated that CMPs can mimic the surface of PCM in contaminant adsorption and transformation and as a result, can be used as PCM analogs to provide insights into PCM reactivity. Specifically, attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) and solid state ^{13}C multi-CP/MAS Nuclear Magnetic Resonance (NMR) Spectroscopy were used to characterize the CMPs, confirming that cross-coupling between aryl halides and terminal alkynes had occurred and that polyaromatic clusters (a key structural feature of PCM) were produced as a result of pyrolysis. Moreover, the results obtained using a Brunauer–Emmett–Teller (BET) surface analyzer showed high surface area, microporosity, and mesoporosity for all of the CMPs and carbonized CMPs produced, confirming their comparability to PCM in terms of both surface area and pore structures (Li et al., 2019). Whereas some of the CMPs promoted the decay of a model pollutant trichloronitromethane, there was no evidence of reaction in the absence of CMPs. We further proposed that the transformation of trichloronitromethane occurred via reductive dechlorination. The rate-limiting step is probably the first dissociative electron transfer from the CMP, which functions as a reducing agent. The key role of interfacial electron transfer kinetics was underscored by the positive correlation between the kinetics of CMP-mediated trichloronitromethane decay and conductivity (not electron-donating capacity) of CMPs (Li et al., 2019).

This line of research provides a tunable platform for controlled variation of individual surface properties and porosity during the polymer synthesis process, which allows us to address important knowledge gaps concerning how PCM surface attributes (e.g., redox-active properties) support chemical and microbial synergies. Understanding the effect of nanoconfinement on contaminant decay could help us design novel materials to serve as nanoreactors that effectively remove contaminants by utilizing hydrolysis or other reactions that are widely accessible. Furthermore, we could tailor the PCM to optimize the activities of microbial communities that are responsible for pollutant degradation, providing a sustainable alternative for in situ clean up. A new generation of highly efficient carbon materials can be engineered and applied to simultaneously retain and degrade contaminants in situ.

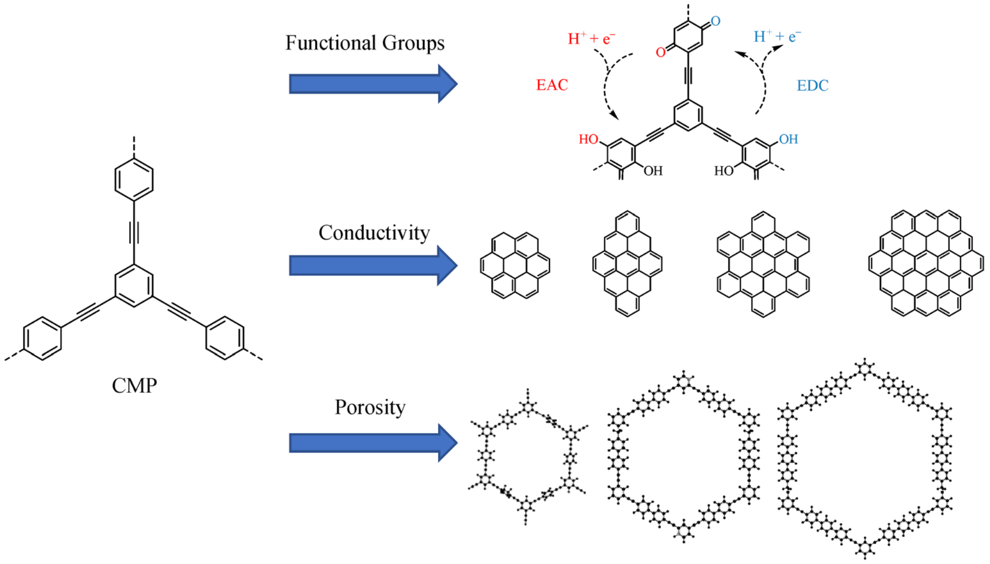


Fig. 4 The PCM-like polymer platform, CMP, allows for systematic variation of functional groups, conductivity, and porosity.

6 Future directions

Despite the wealth of knowledge generated in understanding the reactivity of PCM, several areas still require further investigation. First, what is the mobility and toxicity of transformation products for contaminants that undergo PCM-enhanced degradation in the environment? For instance, we observed the formation of sulfur-substituted products that are less polar than their parent compounds during the degradation of dichloroacetamide safeners in the presence of PCM and sulfide, suggesting that these products may be more readily sequestered through adsorption processes by soil particles. However, what about other contaminants? The ecological endpoints for these transformation products need to be assessed in the environment. Moreover, how do chemical structures of contaminants dictate the PCM-mediated reaction pathways that they undergo? What emerging contaminants are susceptible to the PCM-enhanced transformation either abiotically or biotically? More importantly, how do we utilize the information we have obtained to aid in chemical design, ensuring further development of chemicals containing structural moieties that render them susceptible to natural attenuation, thereby reducing their persistence once they enter the environment?

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References

Anders E, Watzinger A, Rempt F, Kitzler B, Wimmer B, Zehetner F, Stahr K, Zechmeister-Boltenstern S, Soja G (2013). Biochar affects the structure rather than the total biomass of microbial communities in temperate soils. Agricultural and Food Science, 22(4): 404–423

Boehler M, Zwickenpflug B, Hollender J, Ternes T, Joss A, Siegrist H (2012). Removal of micropollutants in municipal wastewater treatment plants by powder-activated carbon. Water Science and Technology, 66(10): 2115–2121

Cao X, Pignatello J J, Li Y, Lattao C, Chappell M A, Chen N, Miller L F, Mao J (2012). Characterization of wood chars produced at different temperatures using advanced solid-state ^{13}C NMR spectroscopic techniques. Energy & Fuels, 26(9): 5983–5991

Cayuela M L, Van Zwieten L, Singh B P, Jeffery S, Roig A, Sanchez-Monedero M A (2014). Biochar's role in mitigating soil nitrous oxide emissions: A review and meta-analysis. Agriculture, Ecosystems & Environment, 191: 5–16

Chen S, Rotaru A E, Shrestha P M, Malvankar N S, Liu F, Fan W, Nevin K P, Lovley D R (2015). Promoting interspecies electron transfer with biochar. Scientific Reports, 4(1): 5019–5025

Chen W, Zhu D, Zheng S, Chen W (2014b). Catalytic effects of functionalized carbon nanotubes on dehydrochlorination of 1,1,2,2-tetrachloroethane. Environmental Science & Technology, 48(7): 3856–3863

Cho Y M, Ghosh U, Kennedy A J, Grossman A, Ray G, Tomaszewski J E, Smithenry D W, Bridges T S, Luthy R G (2009). Field application of activated carbon amendment for in-situ stabilization of polychlorinated biphenyls in marine sediment. Environmental Science & Technology, 43(10): 3815–3823

Curtis G P, Reinhard M (1994). Reductive dehalogenation of hexachlorethane, carbon-tetrachloride, and bromoform by anthrahydroquinone disulfonate and humic-acid. Environmental Science & Technology, 28(13): 2393–2401

Dawson R, Laybourn A, Clowes R, Khimyak Y Z, Adams D J, Cooper A I (2009). Functionalized conjugated microporous polymers. Macromolecules, 42(22): 8809–8816

Ding K, Byrnes C, Bridge J, Grannas A, Xu W (2018). Surface-promoted hydrolysis of 2,4,6-trinitrotoluene and 2,4-dinitroanisole on pyrogenic carbonaceous matter. Chemosphere, 197: 603–610

Ding K, Duran M, Xu W (2019). The synergistic interaction between sulfate-reducing bacteria and pyrogenic carbonaceous matter in DDT decay. Chemosphere, 233: 252–260

Ding K, Xu W (2016). Black carbon facilitated dechlorination of DDT and its metabolites by sulfide. Environmental Science & Technology, 50(23): 12976–12983

Fan D, Gilbert E J, Fox T (2017). Current state of in situ subsurface remediation by activated carbon-based amendments. Journal of Environmental Management, 204: 793–803

Fang G, Gao J, Dionysiou D D, Liu C, Zhou D (2013). Activation of persulfate by quinones: free radical reactions and implication for the degradation of PCBs. Environmental Science & Technology, 47(9): 4605–4611

Fang G, Gao J, Liu C, Dionysiou D D, Wang Y, Zhou D (2014). Key role of persistent free radicals in hydrogen peroxide activation by biochar: Implications to organic contaminant degradation. Environmental Science & Technology, 48(3): 1902–1910

Fu H, Guo Y, Chen W, Gu C, Zhu D (2014). Reductive dechlorination of hexachloroethane by sulfide in aqueous solutions mediated by graphene oxide and carbon nanotubes. Carbon, 72: 74–81

Ghosh U, Luthy R G, Cornelissen G, Werner D, Menzie C A (2011). In-situ sorbent amendments: a new direction in contaminated sediment management. Environmental Science & Technology, 45(4): 1163–1168

Hale S E, Tomaszewski J E, Luthy R G, Werner D (2009). Sorption of dichlorodiphenyltrichloroethane (DDT) and its metabolites by activated carbon in clean water and sediment slurries. Water Research, 43(17): 4336–4346

Inyang M I, Gao B, Yao Y, Xue Y, Zimmerman A, Mosa A, Pullammanappallil P, Ok Y S, Cao X (2016). A review of biochar as a low-cost adsorbent for aqueous heavy metal removal. Critical Reviews in Environmental Science and Technology, 46(4): 406–433

Jiang J X, Su F, Trewin A, Wood C D, Niu H, Jones J T, Khimyak Y Z, Cooper A I (2008). Synthetic control of the pore dimension and surface area in conjugated microporous polymer and copolymer networks. Journal of the American Chemical Society, 130(24): 7710–

7720

Jonker M T, Koelmans A A (2002). Sorption of polycyclic aromatic hydrocarbons and polychlorinated biphenyls to soot and soot-like materials in the aqueous environment: Mechanistic considerations. Environmental Science & Technology, 36(17): 3725–3734

Kah M, Sigmund G, Xiao F, Hofmann T (2017). Sorption of ionizable and ionic organic compounds to biochar, activated carbon and other carbonaceous materials. Water Research, 124: 673–692

Kappler A, Wuestner M L, Ruecker A, Harter J, Halama M, Behrens S (2014). Biochar as an electron shuttle between bacteria and Fe(III) minerals. Environmental Science & Technology Letters, 1(8): 339–344

Karanfil T (2006). Interface Science and Technology. Amsterdam: Elsevier,345–373

Kjellerup B, Naff C, Edwards S, Ghosh U, Baker J, Sowers K (2014). Effects of activated carbon on reductive dechlorination of PCBs by organohalide respiring bacteria indigenous to sediments. Water Research, 52: 1–10

Koelmans A A, Jonker M T, Cornelissen G, Bucheli T D, Van Noort P C, Gustafsson Ö (2006). Black carbon: The reverse of its dark side. Chemosphere, 63(3): 365–377

Langley L A, Fairbrother D H (2007). Effect of wet chemical treatments on the distribution of surface oxides on carbonaceous materials. Carbon, 45(1): 47–54

Lefèvre E, Bossa N, Gardner C M, Gehrke G E, Cooper E M, Stapleton H M, Hsu-Kim H, Gunsch C K (2018). Biochar and activated carbon act as promising amendments for promoting the microbial debromination of tetrabromobisphenol A. Water Research, 128: 102–110

Lehmann J, Rillig M C, Thies J, Masiello C A, Hockaday W C, Crowley D (2011). Biochar effects on soil biota: A review. Soil Biology & Biochemistry, 43(9): 1812–1836

Li X, Gámiz B, Wang Y, Pignatello J J, Xing B (2015). Competitive sorption used to probe strong hydrogen bonding sites for weak organic acids on carbon nanotubes. Environmental Science & Technology, 49(3): 1409–1417

Li Z, Mao J, Chu W, Xu W (2019). Probing the surface reactivity of pyrogenic carbonaceous material (PCM) through synthesis of PCM-like conjugated microporous polymers. Environmental Science & Technology, 53(13): 7673–7682

Lippa K A, Roberts A L (2002). Nucleophilic aromatic substitution reactions of chloroazines with bisulfide (HS^-) and polysulfides (S_n^{2-}). Environmental Science & Technology, 36(9): 2008–2018

Liu F, Rotaru A E, Shrestha P M, Malvankar N S, Nevin K P, Lovley D R (2012). Promoting direct interspecies electron transfer with activated carbon. Energy & Environmental Science, 5(10): 8982–8989

Loch A R, Lippa K A, Carlson D L, Chin Y P, Traina S J, Roberts A L (2002). Nucleophilic aliphatic substitution reactions of propachlor, alachlor, and metolachlor with bisulfide (HS^-) and polysulfides (S_n^{2-}). Environmental Science & Technology, 36(19): 4065–4073

Luthy R G, Aiken G R, Brusseau M L, Cunningham S D, Gschwend P M, Pignatello J J, Reinhard M, Traina S J, Weber W J, Westall J C (1997). Sequestration of hydrophobic organic contaminants by geosorbents. Environmental Science & Technology, 31(12): 3341–3347

Masiello C A (2004). New directions in black carbon organic geochemistry. Marine Chemistry, 92(1–4): 201–213

McCleaf P, Englund S, Östlund A, Lindegren K, Wiberg K, Ahrens L (2017). Removal efficiency of multiple poly-and perfluoroalkyl substances (PFASs) in drinking water using granular activated carbon (GAC) and anion exchange (AE) column tests. Water Research, 120: 77–87

Sumaraj, Padhye L P (2017). Influence of surface chemistry of carbon materials on their interactions with inorganic nitrogen contaminants in soil and water. Chemosphere, 184: 532–547

Payne R B, Ghosh U, May H D, Marshall C W, Sowers K R (2019). A pilot-scale field study: in situ treatment of PCB-impacted sediments with bioamended activated carbon. Environmental Science & Technology, 53(5): 2626–2634

Pignatello J J, Mitch W A, Xu W (2017). Activity and reactivity of pyrogenic carbonaceous matter toward organic compounds. Environmental Science & Technology, 51(16): 8893–8908

Qin Y, Li G, Gao Y, Zhang L, Ok Y S, An T (2018). Persistent free radicals in carbon-based materials on transformation of refractory organic contaminants (ROCs) in water: A critical review. Water Research, 137: 130–143

Quensen J F III, Mueller S A, Jain M K, Tiedje J M (1998). Reductive dechlorination of DDE to DDMU in marine sediment microcosms. Science, 280(5364): 722–724

Shrestha P M, Rotaru A E (2014). Plugging in or going wireless: strategies for interspecies electron transfer. Frontiers in Microbiology, 5: 237–244

Simon J A (2015). Editor's perspective—An in situ revelation: First retard migration, then treat. Remediation Journal, 25(2): 1–7

Singh B P, Hatton B J, Singh B, Cowie A L, Kathuria A (2010). Influence of biochars on nitrous oxide emission and nitrogen leaching from two contrasting soils. Journal of Environmental Quality, 39(4): 1224–1235

Valdés H, Sánchez-Polo M, Rivera-Utrilla J, Zaror C (2002). Effect of ozone treatment on surface properties of activated carbon. Langmuir, 18(6): 2111–2116

van der Zee F P, Bisschops I A, Lettinga G, Field J A (2003). Activated carbon as an electron acceptor and redox mediator during the anaerobic biotransformation of azo dyes. Environmental Science & Technology, 37(2): 402–408

Xiao F, Pignatello J J (2015). Interactions of triazine herbicides with biochar: Steric and electronic effects. Water Research, 80: 179–188

Xu S, Adhikari D, Huang R, Zhang H, Tang Y, Roden E, Yang Y (2016). Biochar-facilitated microbial reduction of hematite. Environmental Science & Technology, 50(5): 2389–2395

Xu W, Dana K E, Mitch W A (2010). Black carbon-mediated destruction of nitroglycerin and RDX by hydrogen sulfide. Environmental Science & Technology, 44(16): 6409–6415

Xu W, Pignatello J J, Mitch W A (2013). Role of black carbon electrical conductivity in mediating hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) transformation on carbon surfaces by sulfides. Environmental Science & Technology, 47(13): 7129–7136

Xu W, Pignatello J J, Mitch W A (2015). Reduction of nitroaromatics sorbed to black carbon by direct reaction with sorbed sulfides. Environmental Science & Technology, 49(6): 3419–3426

Xu X, Sivey J D, Xu W (2020). Black carbon-enhanced transformation of dichloroacetamide safeners: Role of reduced sulfur species. Science of the Total Environment: 139908

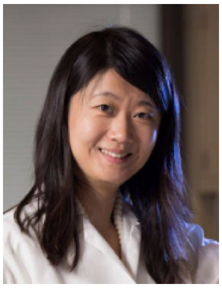
Yu L, Yuan Y, Tang J, Wang Y, Zhou S (2015). Biochar as an electron shuttle for reductive dechlorination of pentachlorophenol by *Geobacter sulfurreducens*. Scientific Reports, 5(1): 16221–16230

Zhao H Q, Huang S Q, Xu W Q, Wang Y R, Wang Y X, He C S, Mu Y (2019). Undiscovered mechanism for pyrogenic carbonaceous matter-mediated abiotic transformation of azo dyes by sulfide. Environmental Science & Technology, 53(8): 4397–4405

Zhao W, Lian L, Jin X, Zhang R, Luo G, Hou H, Chen S, Zhang R (2020). In situ electron-induced reduction of NO_x via CNTs activated by DBD at low temperature. Frontiers of Environmental Science & Engineering, 14(2): 20

Zhou H, Xie Y F (2002). Using BAC for HAA removal. Part 1: Batch study. Journal- American Water Works Association, 94(4): 194–200

Zhu D, Pignatello J J (2005). Characterization of aromatic compound sorptive interactions with black carbon (charcoal) assisted by graphite as a model. Environmental Science & Technology, 39(7): 2033–2041



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