

# Applications of biochar in redox-mediated reactions

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## HIGHLIGHTS

- A first-time comprehensive overview on the role of biochar in redox applications.
- Biochar is chemically more reduced and reactive than the original feedstock.
- Graphite, functional groups and redox-active metals contribute to redox capacity.
- Biochar impacts microbial electron shuttling and solute transformation.
- Redox reactions of biochar can be manipulated to manage contaminants and nutrients.

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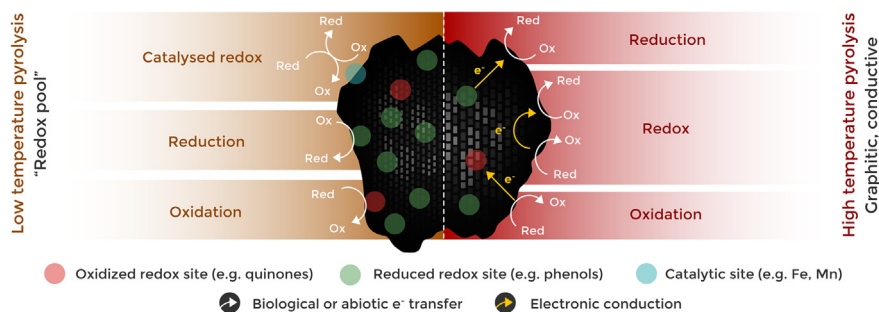
Redox reactions

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## GRAPHICAL ABSTRACT



## ABSTRACT

Biochar is chemically more reduced and reactive than the original feedstock biomass. Graphite regions, functional groups, and redox-active metals in biochar contribute to its redox characteristics. While the functional groups such as phenolic species in biochar are the main electron donating moieties (i.e., reducers), the quinones and polycondensed aromatic functional groups are the components accepting electrons (oxidants). The redox capacity of biochar depends on feedstock properties and pyrolysis conditions. This paper aims to review and summarize the various synthesis techniques for biochars and the methods for probing their redox characteristics. We review the abiotic and microbial applications of biochars as electron donors, electron acceptors, or electron shuttles for pollutant degradation, metal(loid)s (im)mobilization, nutrient transformation, and discuss the underlying mechanisms. Furthermore, knowledge gaps that exist in the exploration and differentiation of the electron transfer mechanisms involving biochars are also identified.

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## 1. Introduction

Biochar is produced by pyrolysis of biomass such as crop residue, manure, and solid wastes (Ok et al., 2015). Traditionally biochar is used for carbon sequestration due to its stability in soils. Biochar has been extensively studied to enhance nutrient availability in soils (Schulz and Glaser, 2012) and plant growth (Hussain et al., 2017). There is increasing interest in the potential of biochar in sorption of contaminants and their subsequent immobilization in relation to remediation of contaminated soil and groundwater (Ahmad et al., 2014; Rajapaksha et al., 2016). Biochar has high surface area and favourable pore architecture characteristics enabling high efficiency in the retention of contaminants, including metal (loid)s and organic pollutants in soils (Mohan et al., 2014; Ahmed et al., 2016; Li et al., 2017).

The mobility and bioavailability of contaminants and nutrients including heavy metal(loid)s and organic compounds in soils, sediments, and groundwater are affected by both adsorption and redox reactions in soil-biochar systems (Adriano, 2001; Beiyuan et al., 2017; Cho et al., 2017). Redox reactions influence the speciation and mobility of metal(loid)s. Metals are generally less soluble in their higher oxidation state, whereas the solubility and mobility of metalloids depend on both the oxidation state and the ionic form (Ross, 1994). Redox reactions play a key role in the transformation of toxic heavy metal(loid)s, especially arsenic (As), chromium (Cr), mercury (Hg), and selenium (Se), in soils and sediments (Gadd, 2010; Rajapaksha et al., 2013). Redox reactions also impact the bioavailability of plant nutrients, especially nitrogen, sulfur, iron, and manganese in soils. For example, reduction of nitrate resulted in the release of nitrous oxide, which is an important greenhouse gas (Saggar et al., 2015; Mandal et al., 2016). Similarly, the biodegradation of many organic contaminants (e.g., trichloroethane) is mediated through redox reactions (Graber et al., 2007). Thus, a deeper understanding of the redox reactions involving biochars will help in developing *in situ* bioremediation technologies that are environmentally compatible.

Redox reactions of contaminants and nutrients in soil, sediments, and groundwater are affected by the physicochemical characteristics of the medium (e.g., moisture content, pH, and temperature), solute characteristics (concentration and speciation), and biological factors (e.g., plant and microbial activity). The redox reactions can also be manipulated through the addition of organic and inorganic amendments such as composts, biosolids, and biochar (Park et al., 2011; Bolan et al., 2013; Beiyuan et al., 2017). For example, the addition of organic matter-rich soil (electron donor) enhances the reduction of metal(loid)s such as Cr

and Se (Park et al., 2011; Rajapaksha et al., 2013). Biochar is chemically more reduced than the original feedstock and hence participates in redox reactions in soil and aquatic systems. The redox capacity of biochar depends on the nature of feedstock materials, pyrolysis conditions, and modification of the biochar.

Several comprehensive reviews describe the potential value of biochar in the immobilization of metal(loid)s and organic contaminants (Mohan et al., 2014; Ahmed et al., 2016; Rizwan et al., 2016). However, the impact of redox reactions of biochar on the mobility and bioavailability of environmental contaminants and nutrients has not been extensively studied yet (Cho et al., 2017). This review paper aims to: (i) identify the components of biochar contributing to its redox reactions; (ii) describe the factors affecting the redox reactions involving biochars; and (iii) provide case studies examining the influence of biochar-induced redox-mediated reactions on microbial electron shuttling, organic pollutant degradation, and inorganic contaminant (im)mobilization.

## 2. Synthesis of biochar

Biochar can be produced from various plants, woody biomass, crop residues, animal litter, and various solid wastes by using thermochemical processes including pyrolysis, slow pyrolysis, fast pyrolysis, torrefaction, microwave assisted pyrolysis, and hydrothermal carbonization (Van Poucke et al., 2016; Igalavithana et al., 2017). Pyrolysis is an inexpensive and robust technology, which can result in the thermochemical decomposition of organic matter into non-condensable syngases, condensable bio-oil, and a solid residual co-product, biochar or charcoal. The end product of pyrolysis can be controlled by optimizing the pyrolysis parameters such as temperature and residence time. For example, increasing the pyrolysis temperature increases gas yield and decreases biochar production. Thus, optimized and advanced pyrolysis systems have been used recently to control biochar quality (Lee et al., 2017).

Slow pyrolysis is a low-temperature pyrolysis (<700 °C) in which feedstocks, not finely crushed, is subjected to a low heating rate and long residence time to produce a high quantity of biochars (Manyà, 2012). It has been well established that biochars derived from slow pyrolysis at low temperatures are high in surface acidity and polarity but low in hydrophobicity and aromaticity. Generally, a biochar yield between 25–35% can be reproducibly produced under slow pyrolysis. The yields of biochar and acid functional groups (i.e. –COOH and –OH) decrease with increasing pyrolysis temperature, whereas those of the basic functional groups and ash content increase (Zhang and Liu, 2015). On the contrary, in fast

pyrolysis, the feedstock, usually finely ground to allow fast heat transfer, is subjected to a moderate temperature with shorter residence time to produce a high-quality biochar. Due to short residence time, the production of biochar is considerably less during fast pyrolysis compared to slow pyrolysis (Bridgwater and Grassi, 1991). A biochar yield of nearly 12% of the total biomass can be achieved from fast pyrolysis.

Hydrothermal carbonization (HTC) is an exothermic process in which feedstock is subjected to elevated temperatures in aqueous media (water) in a confined system (Bridgwater and Grassi, 1991). HTC offers significant advantages for biochar production including high conversion efficiency and relatively low operation temperature (i.e., 150–250 °C), and it lacks an energy-extensive drying process. HTC generates liquid (bio-oil), gaseous, and solid products (biochar). The distributions of these product streams are strongly dependent on treatment conditions. Depending on the treatment temperature, biochar, bio-oil, and gaseous products are the main products of a hydrothermal process below 250 °C, at 250–400 °C, and above 400 °C, respectively. The composition and structure of the biochar (hydrochar) from HTC differs substantially from pyrolysis biochars. The chemical structure of hydrochar closely resembles natural coal with higher H/C and O/C ratios than the biochars from pyrolysis (Libra et al., 2011).

Torrefaction is a modified pyrolysis technique in which biomass is slowly heated within a specified temperature range and retained there for a particular time interval to remove moisture, carbon dioxide, and oxygen contained in feedstocks in an inert or limited oxygen environment at 200–300 °C (Van Poucke et al., 2016). Torrefaction temperature is the most important parameter to influence the biomass weight loss and the chemical and thermophysical properties of biochars. The torrefied biomass has properties in-between that of raw biomass and biochar, because torrefaction is just the beginning of the pyrolysis process and the torrefied biomass still contains some volatile organic compounds (Kambo and Dutta, 2015). Microwave assisted pyrolysis (MAP) is based on microwave heating of feedstock by “dielectric heating” or “molecular friction”, in which dipolar polarization and ionic conduction are the two main mechanisms (Kappe, 2004). In MAP, the heat reaches the entire volume with a fast rate, because the heat is generated in the bulk of the material. This produces a homogeneous biochar at a faster rate and lower energy cost compared to conventional methods (Clark and Sutton, 1996). Besides, the MAP technique increases biochar yield and quality by negating undesirable secondary reactions among volatile compounds. However, the yields of MAP biochar are lower compared to those obtained by slow pyrolysis in a similar temperature range.

### 3. Characteristics of biochar

Physical and chemical properties of biochar are affected by feedstock types and production conditions such as pyrolysis temperature (Supplementary Data).

#### 3.1. Physical characterization

Surface area (SA) and porosity of biochar are key parameters controlling the magnitude of interactions between biochar and nutrients/contaminants. Beesley and Marmiroli (2011) showed that large SA of hardwood biochar favoured the sorption of Cd and Zn, which reduced concentrations of the metals in leachates from a contaminated soil by 300 and 45-fold, respectively. In addition to the feedstock types, the SA and porosity of biochar are affected by temperature, gas flow, and the presence of air/CO<sub>2</sub>/N<sub>2</sub> (Lee et al., 2017). For example, by increasing the pyrolysis temperature, the volatile matter present in the biochar pore-infillings is

released by producing biochars with maximum SA and microporosity (Mukherjee et al., 2011). Pore sizes <2 nm, 2–50 nm, and >50 nm are termed as micro-, meso-, and macro-pores, respectively. The relative distribution of these pores impacts interactions between biochar and the environmental solutes including contaminants and nutrients. For example, micropores (<2 nm) have high adsorptive capacities for small molecules such as gases and common solvents (Lehmann and Joseph, 2009).

#### 3.2. Chemical characterisation

Elemental composition, cation exchange capacity, surface functional groups, pH, and Eh of biochars are important chemical properties that control the interactions between biochar and contaminants and nutrients. Biochar is made up of elements such as C, H, S, P, O, and N, as well as minerals in its ash component. The elemental compositions of a biochar also depend upon its production conditions and feedstock types. Elemental molar ratios such as H/C and O/C of biochar are used to measure the aromaticity and maturation of biochar. Aromaticity is defined as the fraction of C in biochar that forms aromatic bands. Biochar with dense aromatic structures is more resistant to oxidation and microbial degradation. Therefore, the degree of aromatic condensation in biochar is related to its recalcitrance in the environment (Spokas, 2010). Low-temperature biochars are likely to have lower aromaticity than high-temperature biochars (Keiluweit et al., 2010). Biochar is typically an alkaline material, which depends on the original feedstock materials and the preparation conditions. The pH of biochar is related to the ash content in which a higher ash content results in a higher pH (Lehmann, 2007). Functional groups such as carboxylic and phenolic groups in biochar determine its surface charge and redox properties, and play an important role in the retention of cations and anions in soil and aqueous environments. Retention of metal(loid)s by biochars can also be explained by their precipitation as (hydr)oxide, carbonate, or phosphate compounds.

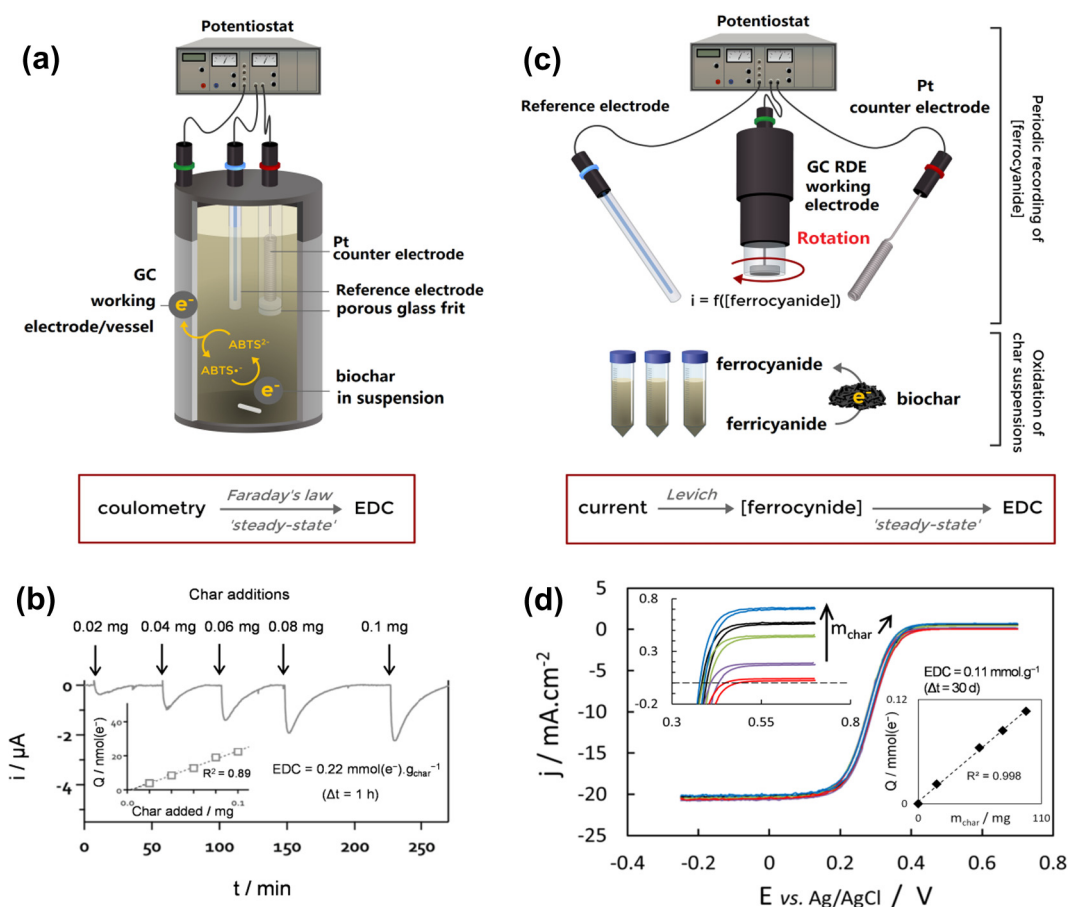
#### 3.3. Redox characteristics

Biochars can donate, accept, or transfer electrons in their surrounding environments, either abiotically or via biological pathways (Klöpffel et al., 2014; Saquing et al., 2016). The reducing power of biochar is currently quantified by the maximum amount of electrons that it can donate (electron donating capacity (EDC), expressed in mmol(e<sup>-</sup>) g<sub>char</sub><sup>-1</sup>), while the maximum amount of electrons that can accept a char is the electron accepting capacity (EAC). These abilities of biochars to reduce (or oxidize) their environment strongly vary with the nature of the feedstock and the pyrolysis conditions, particularly with the highest treatment temperatures (HTTs) and the residence time at HTT (Klöpffel et al., 2014; Prévotau et al., 2016). The redox moieties of the biochar are believed to be transformation products generated by the pyrolysis of lignin and cellulose (note that non-pyrolyzed powder of synthetic lignin already has high EDC (Prévotau et al., 2016)). Oxygen-containing functional groups are probably forming most of this “redox pool”. A certain fraction of these compounds can be reversibly oxidized and reduced, giving the biochars the property of a redox buffer (Klöpffel et al., 2014). The electron donating moieties (i.e., reducers) from the biochars are likely phenolic species, while the compounds accepting electrons (oxidants) are believed to be quinones and polycondensed aromatic structures (Klöpffel et al., 2014). These redox moieties undergo proton-coupled electron exchange (Aeschbacher et al., 2011), and the acidity level of the surrounding environment will modify the redox properties of a biochar. At circumneutral pH, the EAC of biochar from wood or grass-based feedstock typically increases with the

HTT (up to a maximum around 400–500 °C) before decreasing, likely because of the initial generation of quinoid structures followed by their consumption at higher HTT. Similarly, the EDCs of biochars appear to increase at low HTTs, reaching a maximum around 400 °C before decreasing sharply at higher HTTs (Klöpffel et al., 2014; PrévotEAU et al., 2016). This fast decrease likely corresponds to the important decline in hydroxyl functions induced by the dehydration of lignin-derived phenols and alcohols, coupled with the onset of aromatization of the biochars occurring around 450–550 °C (Harvey et al., 2012). The extent of this aromaticity is also crucial with respect to the redox interaction of the biochar with its environment, since it increases its electronic conductivity. Below an HTT of 600 °C, this conductivity is typically unsubstantial (Xu et al., 2013). At higher HTTs, the growth of graphitic structures enhances the conductivity of the carbon matrix, which can allow delocalized redox reactions (such as in an electrochemical cell in short-circuit condition) (Sun et al., 2017). This delocalized redox reaction could happen either between: (i) two abiotic components; (ii) two microorganisms (a so-called “direct” interspecies electron transfer (Chen et al., 2014); or (iii) a couple that has a microbial and an abiotic process. The abiotic redox components could be from the intrinsic redox pool of the biochar (e.g., phenols, quinones) or from the surrounding environment. Increasing the HTT also increases the porosity of the biochar (Keiluweit et al., 2010), which likely enhances the reachability of the redox moieties by

dissolved exogenous redox compounds. Furthermore, the pores probably need to be sufficiently hydrated to allow a percolation of ionic conduction reaching the inner redox compounds; this is indeed required for these redox compounds to be involved in delocalized redox reactions across a sufficiently conductive biochar (i.e., for “closing the electrochemical cell”). The size of char particles would also modify the rate and possibly the extent of the redox reactions.

The possible occurrence of the two phenomena (intrinsic “redox pool” and long distance electron transfer) and their possible coupling should be kept in mind before concluding what redox process is taking place when a sufficiently conductive biochar is involved. Overall, proper selection of feedstock and its charring temperature could allow tuning the redox properties of biochar in order to perform target applications involving electron exchanges (Ok et al., 2015). For this purpose, values of EAC and EDC should be adequately recorded. Recognition of the significant redox impact of biochar is only recent; hence the reports of EAC and EDC recordings are scarce and recent. Fig. 1 illustrates two different techniques reported for quantifying these parameters. Both techniques make use of a three-electrode system but substantially differ in their principle, acquisition time, and results. For the sake of simplicity and to avoid redundancy, only the recordings for EDC are represented and discussed below. The first method makes use of mediated electrochemical oxidation (MEO, Fig. 1a) (Klöpffel et al.,



**Fig. 1.** Two different techniques reported for recording the EAC and EDC of biochars (here only illustrated for EDC). (a) Mediated electrochemical oxidation and (b) corresponding chronoamperogram generated by successive additions of char suspensions (note that the negative current is here an oxidation reaction). The amount of charge exchanged is obtained by integration of the current signal (coulometry). (c) Hydrodynamic electrochemical techniques with rotating disc electrode, with (d) cyclic voltammograms recorded in suspension of increasing mass of char. The amount of charge exchanged is proportional to the concentration of ferrocyanide (itself determined with the anodic plateau current (zoom on top inset) via the Levich equation). The good proportionality between the amount of charge exchanged and the mass of char analyzed is shown on inset for both techniques. Panels (b) and (d) are adapted from (Klöpffel et al., 2014) and (PrévotEAU et al., 2016), respectively.



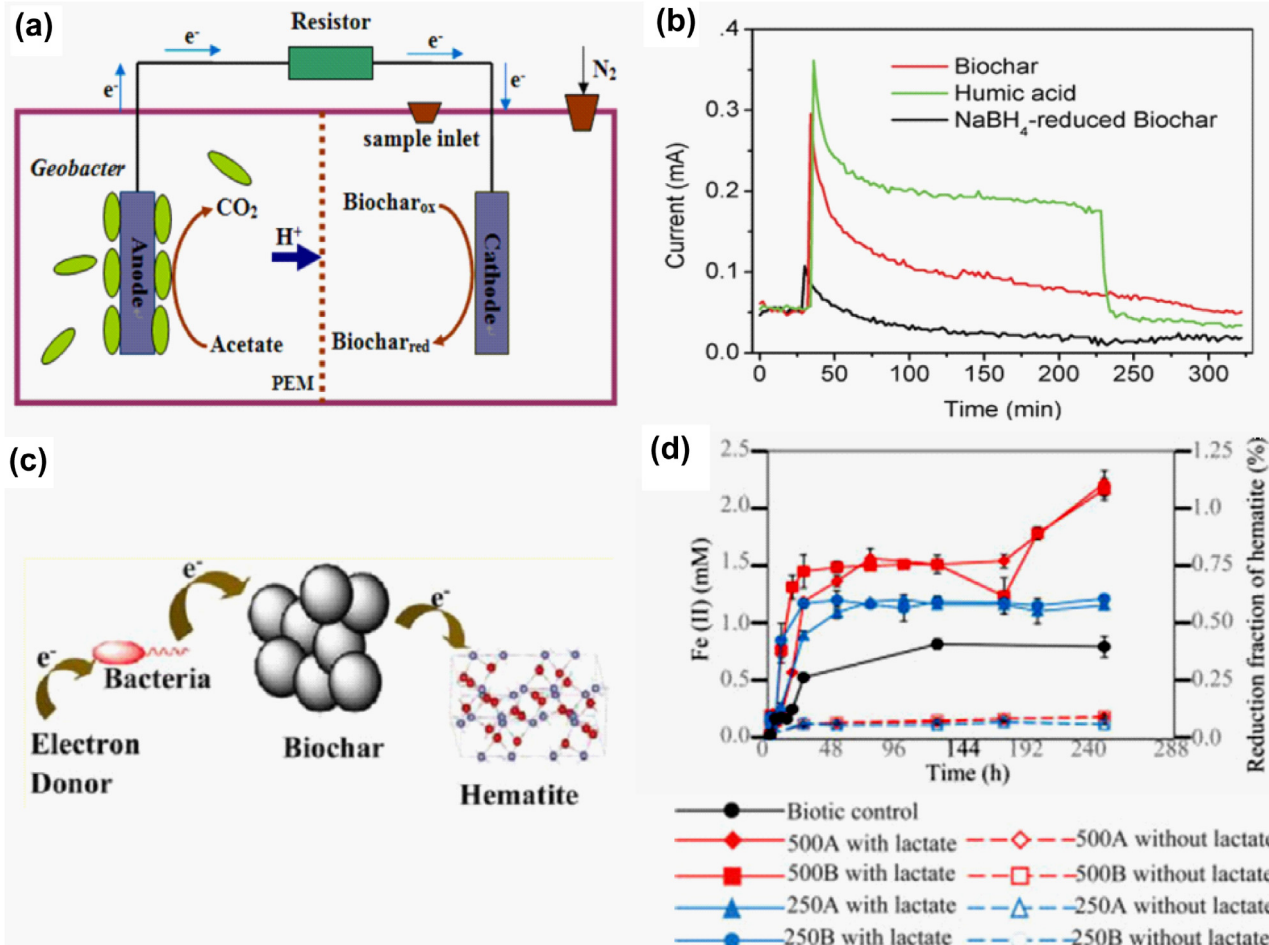
2014). A conductive vessel (glassy carbon) serves as the working electrode (poised at a constant high potential) and contains a dissolved redox mediator sufficiently oxidated (high  $E^0$ , here the radical form of 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid), ABTS $^{\cdot-}$ ). When a biochar suspension is added to the solution, electrons flow from the biochars to the working electrode by using the redox mediator as an electron shuttle. The integration of the current provides the total amount of charge transferred (chronocoulometry) resulting from each biochar addition, which provides the EDC value via a Faraday law (Fig. 1b). The method is simple to operate, fast ( $\leq 1$  h per sample), and can be performed with very small amounts of biochar ( $\leq 0.1$  mg). Furthermore, by performing recordings at different electrode potentials (which match the potential of the solution ( $E_h$ ) at a final, apparent steady-state), one could obtain a distribution of redox potentials of the different redox moieties present in a biochar (Aeschbacher et al., 2011). The second technique is also straightforward and presented in Fig. 1c (PrévotEAU et al., 2016). Biochar suspensions react with a solution of oxidant (here ferricyanide), and the amount of electrons donated by the biochar to the solution is punctually recorded by classic hydrodynamic electrochemical techniques (cyclic voltammetry (CV, see Fig. 1d) or chronoamperometry) using a rotating disc electrode (RDE). The EDC is obtained when a quasi-steady state is reached. An advantage of recording hydrodynamic CVs is the ability to follow over time the respective concentrations of the oxidized and reduced forms of the dissolved compound (PrévotEAU et al., 2015), which allows excluding their substantial adsorption on the biochar or their putative instability.

In two different reports, both aforementioned techniques provided very similar EAC values for similar biochars (pine wood-biochars of similar particle size and pyrolyzed at identical HTTs ranging from 400 to 600 °C), in the interval 0.05–0.5 mmol(e $^-$ ).g $^-1$ .char. Oppositely, the EDCs recorded with the RDE-method were at least one order of magnitude higher than with the MEO (up to 7 mmol (e $^-$ ).g $^-1$ .char for an HTT of 400 °C). When determining these EDCs, the MEO reached an apparent redox steady-state in only 1 h (Klöpffel et al., 2014), while the biochars were monitored donating electrons to the solution for 2 months with the RDE-method (PrévotEAU et al., 2016). The rate of electron donation by the biochar very quickly decreased once the biochar was added in the oxidative solution (as seen in the current response on Fig. 1b). It has therefore been suggested that the much slower electron donation by the biochar (i.e., after 1 h) may go unnoticed by continuous MEO – whose current signal is proportional to the rate of biochar oxidation; while it could still be quantified by successive punctual measurements with the RDE – whose current is proportional to the total extent of biochar oxidation (PrévotEAU et al., 2016). These discrepancies stress the need for further investigations of the redox mechanisms involving biochars at different time-scales. In particular, they raise the question of the definition of EDC itself. The latter should be intrinsic to the biochar and method-independent. Accordingly, a standardized method should ideally be developed to record pertinent values of EAC and EDC, and to allow relevant comparisons between different biochars and studies. This 'standard' EDC could either favour the quantification of a fast, rather reversible oxidation of the biochar taking place at the initial stage; it also include, to a certain extent, the contribution of more sluggish oxidation processes (for example, involving more recalcitrant or less accessible redox compounds); some oxidative mineralization to CO $_2$  (Hilscher et al., 2009); or some putative oxidative polymerization of phenolic compounds (Kobayashi et al., 2014; PrévotEAU et al., 2016). It is also essential to compare these values obtained under laboratory conditions (i.e., maximizing the oxidation) with the extent of redox reactions induced by the biochars in specific applications and at different time scales.

## 4. Application of biochar in redox-mediated reactions

### 4.1. Microbial electron shuttling

Van der Zee and Cervantes (2009) defined electron shuttles, also referred to as redox mediators, as organic molecules that can be reversibly oxidized and reduced, thereby conferring the capacity to serve as an electron carrier in multiple redox reactions. Similarly, some soil organic matters are redox-active and can act as terminal electron acceptors in anaerobic microbial respiration (Beiyuan et al., 2017). Their ability to re-oxidize during aeration of temporarily anoxic systems, such as wetlands and soils, has been well demonstrated (Klöpffel et al., 2014). Researchers have suggested that biochar also may facilitate microbial electron shuttling processes as they exhibit some functional characteristics similar to soil redox-active organic matter (Graber et al., 2014). Biochar-mediated microbial extracellular electron transfer has been considered as a very important electron transfer process involved in many important biogeochemical reactions. Yu et al. (2016) studied a bioelectrochemical system to prove the possibility of biochar to take up extracellular electrons from a model exoelectrogen *Geobacter sulfurreducens*. As shown in Fig. 2a, the bioelectrochemical system consisted of an anode compartment that was inoculated with *G. sulfurreducens* in the absence of a dissolved electron acceptor and a cathode compartment with biochar suspension, both compartments separated by a Nafion membrane. In such a system, the current generation demonstrated the capability of biochar to take up electrons from *G. sulfurreducens* (Fig. 2b). The electron uptake capacity of biochar may be as much as that of humic substances depending on the feedstock materials and pyrolysis temperatures (Klöpffel et al., 2014). Biochar could not only function as an electron acceptor for exoelectrogens but also as an electron donor to facilitate the reduction Fe(III) minerals. Kappler et al. (2014) have found that highly concentrated biochar suspensions stimulated both the rate and extent of microbial reduction of poorly crystalline Fe(III) oxyhydroxide ferrihydrite by *Shewanella oneidensis* MR-1. Furthermore, Xu et al. (2016) have found that biochar could also promote the microbial reduction of crystalline Fe(III) oxide such as hematite (Fig. 2c and d). They demonstrated that both biochar particles and leachate could facilitate the microbial reduction of hematite, through electron shuttling as well as aqueous Fe(II) binding. Semiquinone functional groups of biochar particles or leachate were likely involved in the reduction of hematite. A study reported that wood derived biochar could act as a rechargeable reservoir of bioavailable electrons under anaerobic conditions (Saquing et al., 2016). According to the research findings, acetate oxidation by *G. metallireducens* was enabled by biochar acting as the only electron acceptor for the microorganism. The reduced biochar could then act as an electron donor for *G. metallireducens* and enhance the biological denitrification. The authors estimated that the biochar's bioavailable electron storage capacity for *G. metallireducens* was 0.85 and 0.87 mmol $_e$ .g $^-1$  based on the acetate oxidation and nitrate reduction, respectively. Furthermore, biochar has been reported to promote the extracellular electron transfer from bacterial cell to bacterial cell, which was termed as direct interspecies electron transfer (DIET). Chen et al. (2014) carried out laboratory incubation experiments using defined co-cultures of *G. metallireducens* and *G. sulfurreducens* in a medium with ethanol as electron donor and fumarate as electron acceptor. They found that biochar could accelerate electron transfer from *G. metallireducens* to *G. sulfurreducens*, promoting their growth. The authors concluded that biochar promotes interspecies electron exchange via a conduction-based mechanism, in which electrons migrate through the biochar from electron-donating to electron accepting cells. This mechanism is significantly different from the mecha-



**Fig. 2.** Biochar-facilitated microbial extracellular electron transfer: (a) a bioelectrochemical system consists of an anode compartment with *G. sulfurreducens* bacterial cells and a cathode compartment with biochar suspension, which is used to evaluate the electron accept capacity of biochar; (b) the corresponding current produced from the bioelectrochemical system with biochar and humic acid as the electron acceptors, respectively, indicating that biochar could accept extracellular electrons generated from *G. sulfurreducens*; (c) and (d) indicated that biochar could mediate the extracellular electron transfer from *S. oneidensis* to hematite for iron (III) reduction. Panels (a) and (b) are adapted from (Yu et al., 2016); panels (c) and (d) are adapted from (Xu et al., 2016).

**Table 1**  
Biochar-mediated redox reactions for degradation of organic pollutants.

Feedstock	Production condition	Contaminants	Removal capacity	References
Sucrose	Pyrolysis at 800 °C (pretreated at 300 °C)	Nitrobenzene	100%	Liu et al. (2017)
Oak wood	Pyrolysis at 550 °C	DDT	/	Ding and Xu (2016)
Fisher activated carbon	Pyrolysis at 440 °C	RDX	100%	Kemper et al. (2008)
Rice straw and polymers	Pyrolysis at 550 °C	DNT	100%	Oh and Seo (2016)
Poultry litter	Pyrolysis at 400 °C	Pendimethalin	95%	Oh et al. (2013)
Poultry litter	Pyrolysis at 400 °C	Trifluralin	50%	Oh et al. (2013)
Poultry litter	Pyrolysis at 400 °C	DNT	91%	Oh et al. (2013)
Wastewater biosolids	Pyrolysis at 400 °C	Pendimethalin	92%	Oh et al. (2013)
Wastewater biosolids	Pyrolysis at 400 °C	Trifluralin	45%	Oh et al. (2013)
<i>Spartina alterniflora</i>	Hydrothermal carbonization at 240 °C	Methylene blue	99.2%	Xu et al. (2014)
Red oak wood	Pyrolysis at 600–900 °C	RDX	/	Xu et al. (2013)
Rape-straw	Pyrolysis at 350 °C	PCP	100%	Tong et al. (2014)
Rice straw	Pyrolysis at 500 °C	PCP	29.7%	Yu et al. (2015)
Rice straw	Pyrolysis at 900 °C	PCP	85.1%	Yu et al. (2015)

nisms used by other electron shuttles, such as humic substances, but similar to those proposed for granular activated carbon (Liu et al., 2012). However, some researchers highlighted that the electron transfer mechanism of biochar significantly depended on the pyrolysis temperatures, since they modify the conductivity of the char (Yu et al., 2015; Sun et al., 2017). Studies should not exclude the possibility for the char to act as a redox pool (via its redox moieties) before concluding on a possible DIET, especially for chars of

low conductivities (pyrolysis below ~700 °C). Meanwhile, it has been reported that biochar could also promote the DIET that occurred in a complex up-flow anaerobic sludge blanket (UASB) (Zhao et al., 2015). In this case, biochar significantly stimulated the enrichment of 16S rRNA gene sequences closely related to *Geobacter* and *Methanosaeta* species known to participate in DIET, resulting in accelerating the conversion of organic wastes to methane in UASB.

Conventionally, organic contaminants sorbed onto biochar have been considered to be chemically and biologically inert. However, recent studies disclosed the ability of biochar to catalyze the chemical and biological transformation of organic contaminants, such as military explosives, precursors for pesticides, and starting materials for antibiotics, leading to the degradation of these contaminants (Table 1). Oh et al. (2013) reported that biochar stimulated chemical reduction of nitro herbicides and explosives by shuttling electrons between reductants (e.g., dithiothreitol) and organic contaminants (i.e., pendimethalin, trifluralin, 2,4-dinitrotoluene and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)). Ding and Xu (2016) showed that biochar in the presence of sulfide can foster the degradation of persistent organic pollutants including 1,1-trichloro-2,2-di(4-chlorophenyl)ethane and 1,1-dichloro-2,2-bis(4-chlorophenyl)-ethane and 1,1-dichloro-2,2-bis(4-chlorophenyl)ethylene. The redox properties of biochar (surface-oxygenated functional groups and conductivity) are proposed to be responsible for the facilitated transformation of organic contaminants through either reduction or nucleophilic substitution, depending on the chemical structure of the contaminants. After applying chemical treatments to modify biochar surfaces, Yu et al. (2011) demonstrated that the reduction rate of nitrobenzene by sulfide correlated with the prevalence of oxygenated functional groups on the biochar surfaces. However, Xu et al. (2013) indicated that the enhanced chemical transformation rates of contaminants were assigned to the electrical conductivity ( $\pi$ - $\pi$  electron network associated with conductive graphite regions) of biochar rather than the surface-oxygenated functional groups. In this case, the graphite regions in biochar could directly transfer electrons from electron donors to contaminants accepting electrons. Besides, because of the complex compositions of biochar, Oh et al. (2013) mentioned that redox-active metals (i.e., Fe, Cu, and Mn) of biochar could also be involved in the enhanced reduction of nitro herbicides. A biochar-nanoscale zero-valent iron composite acted as a green oxidizing system for the degradation of trichloroethylene (TCE) by persulfate (Yan et al., 2015). It was revealed that  $-\text{COOH}$  and  $-\text{OH}$  groups on the biochar surface acted as electron mediators, accelerating the formation of  $\text{SO}_4^{\cdot-}$  and the subsequent degradation of TCE in water. In addition, these oxygenated functional groups may activate the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  redox action in persulfate solution further enhancing the TCE degradation. Moreover, Fang et al. (2014) found that biochar may contain persistent free radicals (PFRs), formed during the thermal decomposition process. The PFRs catalyzed  $\text{H}_2\text{O}_2$  decomposition producing hydroxyl radicals ( $\cdot\text{OH}$ ) that facilitate efficient degradation of polychlorinated biphenyls (PCBs). The catalytic ability of biochar on persulfate activation for the degradation of PCBs has been well documented (Fang et al., 2015). Persulfate was activated by biochar depending on the concentration and type of PFRs, in order to produce  $\text{SO}_4^{\cdot-}$ , resulting in effective PCB degradation. These studies show that biochar can stimulate the generation of reactive oxygen and degrade organic contaminants efficiently. Thus, biochar applications to contaminated environments may be an excellent remediation approach to act as a mediator for the reductive transformation of organic contaminants.

Similar to the role of biochar in chemical transformation of contaminants, biochar-mediated extracellular electron transfer could also promote the biotransformation of organic contaminants. For example, Tong et al. (2014) demonstrated that biochar could enhance the extracellular electron transfer in soils to promote pentachlorophenol (PCP) transformation by stimulating the growth and metabolism of microorganisms in the soils. However, the authors did not give direct evidence for the biochar mediated electron transfer from bacterial cells to PCP due to the use of a complex

microcosm with the mixed culture. In this regard, Yu et al. (2015) carried out incubation experiments using pure culture *G. sulfurreducens* as model microorganism and biochar produced at various temperatures as the mediators to identify the role of biochar in the biodegradation of PCP (Supplementary Data). The biodegradation of PCP was significantly accelerated in the presence of biochar. The PCP degradation efficiencies highly depended on the electrical conductivity (resulting from polycondensed aromatic structures) and electron exchange capacity (surface redox-active groups). Three pathways coexisted for PCP degradation in the presence of biochar: (i) direct reduction of PCP by *G. sulfurreducens*; (ii) electron transfer involving biochar via its surface redox-active groups; and (iii) electron transfer involving biochar via its conductive graphite regions. A mathematic model revealed that the different processes respectively accounted for 3%, 56% and 41% of the PCP degradation for a biochar produced at 900 °C.

#### 4.3. Inorganic contaminant (im)mobilization

Metal(loid)s, including As, Cr, Cd, Fe, Mn, Hg, and Se, are commonly subjected to redox reactions in natural environments, thereby influencing their speciation and mobility (Bolan et al., 2014). It has been reported that biogeochemistry of metals is influenced by dissolved organic matter (DOM), as DOM can act as both electron donor and acceptor (Wittbrodt and Palmer, 1997). Redox processes of biochar also impact the immobilization of inorganic contaminants. Dong et al. (2014) revealed that DOM extracted from biochar acted as both electron donor and acceptor, reducing Cr(VI) and oxidizing As(III). It was suggested that the DOM extracted from biochar was a better reductant than oxidant since it was more effective in Cr(VI) reduction in comparison with As(III) oxidation. Using XPS analysis, the authors confirmed that biochars are rich in  $\pi$  electrons due to surface functional groups and they may act as electron donors for the above-mentioned reduction reactions. Using electron spin resonance and Fourier transform infrared analysis, the authors confirmed that semiquinone radicals in the DOM were involved in As(III) oxidation, and carboxylic groups in the DOM participated in both Cr(VI) reduction and As(III) oxidation. The reduction of aqueous toxic Cr(VI) into less toxic Cr(III) by carboxylic and hydroxyl groups on biochar surfaces has been well studied. This reduction can also be performed by  $\pi$  electrons donated from the disordered polycyclic aromatic hydrocarbons sheets (Wang et al., 2010). Furthermore, mobile and toxic As(III) in water can be oxidized into less mobile and less toxic As(V) by oxidants such as  $\text{FeO}(\text{OH})$ ,  $\text{MnOOH}$ ,  $\text{MnO}_2$ , or  $\text{NO}_3^-$  (Joseph et al., 2010; Rinklebe et al., 2016). Also, some biochars can contain nanoparticles of redox active mineral phases of Fe and Mn (Joseph et al., 2013). They could either act as catalysts for redox reactions, or be reduced or oxidized depending on their formal potential and the surrounding environment (Petter and Madari, 2012). Cascade redox reactions can also take place. For example, Mn(IV) (MnO<sub>2</sub> in biochar) can first be reduced to Mn(III) creating the intermediate product MnOOH\* (a combination of Mn(III), hydroxyl, and H<sub>2</sub>O) which oxidizes in turn As(III) to As(V) (Herath et al., 2016). Iron can exist in different oxidized forms in biochar, such as  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ , or  $\text{FeOOH}$ . Their concentrations in biochar depend on feedstocks, pyrolysis conditions, and interactions of an alkali metal with organic molecules during the pyrolysis process (Joseph et al., 2013). The oxidation of As(III) to less toxic As(V) and its adsorption on iron oxide has been investigated by several research groups (Wilkie and Hering, 1996; Dixit and Hering, 2003). The pH of the media can significantly impact the extent and rate of the redox reactions (Dixit and Hering, 2003). The removal of Cr and As in water environments using different types of biochar is summarized in Table 2.



**Table 2**

Removal of aqueous chromium and arsenic by different types of biochar in aqueous medium.

Contaminant	Biochar type	Production conditions	pH	Maximum removal (mg g <sup>-1</sup> )	Reference
Cr	Wheat straw	Pyrolysis at 250 °C (pretreated using H <sub>3</sub> PO <sub>4</sub> )	1.8–3.1	188.10	Liu and Li (2015)
	Woodchips	Pyrolysis at 700 °C	2	1.71	Hyder et al. (2014)
	Walnut shell	Pyrolysis at 600 °C (and modified using chitosan)	2	206	Huang et al. (2016)
	Wheat residue	Open air burning	1	21.34	Wang et al. (2010)
	Wheat straw	Thermal decomposition from 350 °C to 650 °C	2	24.60	Tytlak et al. (2015)
	Wicker	Thermal decomposition from 350 °C to 650 °C	2	23.60	Tytlak et al. (2015)
	Sugar beet tailing	Pyrolysis at 300 °C	2	123	Dong et al. (2011)
	Municipal wastewater sludge	Pyrolysis at 400 °C	2	0.21	Zhang et al. (2013)
	Ramie residues	Pyrolysis at 300 °C	2	82	Zhou et al. (2016b)
	As	Municipal solid waste	Pyrolysis at 400 °C	6	24
Municipal solid waste		Pyrolysis at 500 °C	6	25	Jin et al. (2014)
Municipal solid waste		Pyrolysis at 600 °C	6	28	Jin et al. (2014)
Empty fruit bunch		Pyrolysis at 700 °C	5	5.1	Samsuri et al. (2013)
Rice husk		Pyrolysis at 700 °C	6	7.1	Samsuri et al. (2013)
Rice husk		Pyrolysis at 300 °C	6.7–7	0.002	Agrafioti et al. (2014)
Sewage sludge		Pyrolysis at 300 °C	6.7–7	0.004	Agrafioti et al. (2014)
Solid waste		Pyrolysis at 300 °C	6.7–7	0.003	Agrafioti et al. (2014)
Rice husk		Pyrolysis at 500 °C	9.5	0.35	Sari et al. (2014)

#### 4.4. Nutrient transformation

Nitrogen (N) is an essential nutrient for primary productivity in terrestrial and aquatic ecosystems. Numerous studies have shown that biochar has potential to impact N cycling through modulation of primary N transformation processes (N<sub>2</sub> fixation, mineralization, immobilization, denitrification, and ammonia volatilization) (Taghizadeh-Toosi et al., 2012; Cayuela et al., 2014; Zhou et al., 2016a). The existing body of research offers mixed results regarding the impact of biochar on denitrification and anaerobic ammonium oxidation, and the results depend on the C and N status of soil. The decrease in soluble NH<sub>4</sub><sup>+</sup> concentration with increasing input of wood-based biochar was apparently responsible for the decreased nitrification rates in biochar-amended soils (Taghizadeh-Toosi et al., 2012). Several laboratory and field studies have reported that biochar exerts a substantial control on denitrification and could mitigate from 50% to 90% of N<sub>2</sub>O soil emission (Cayuela et al., 2014; Ameloot et al., 2016). Cayuela et al. (2013) carried out laboratory incubation experiments using a range of soils and different biochars produced at 500 °C. They reported that no N<sub>2</sub>O was emitted from soil under abiotic conditions both in the presence and absence of biochar, which demonstrated that biochar did not induce abiotic N<sub>2</sub>O formation through catalytic reactions with hydroquinones, metal ions, or radicals present in biochar. However, they found biotic N<sub>2</sub>O production and a consistent decrease in the N<sub>2</sub>O/N<sub>2</sub> ratio after biochar application. They hypothesized that biochar enhances the last step of denitrification (i.e., the reduction of N<sub>2</sub>O to N<sub>2</sub>) by acting as an 'electron shuttle' that facilitates the transfer of electrons to denitrifying microorganisms. Anaerobic ammonium oxidation coupled to iron (III) reduction, termed Feammox, is a newly discovered N cycling process. Zhou et al. (2016a) reported that biochars act as electron shuttles to facilitate the transfer of electrons from NH<sub>4</sub><sup>+</sup> to solid Fe(III) (oxyhydr)oxides in the presence of Feammox bacteria, ultimately leading to an increase in N loss from the system (Supplementary Data). The extent of the Feammox process was further increased when biochar was combined with soluble electron mediators (i.e., AQDS). Overall, the role of biochar in redox-regulated nitrogen cycling could be explained by the following mechanisms: (i) biochar enhances soil aeration by reducing bulk density and increasing porosity and thereby depresses the nitrification potential (Albuquerque et al., 2015; Gul et al., 2015); (ii) biochar could overexpress the nosZ gene of denitrifiers (Cayuela et al., 2013;

Harter et al., 2014), increasing the synthesis of nitrous oxide reductase responsible for catalyzing the reduction of N<sub>2</sub>O to N<sub>2</sub>; (iii) biochar could enhance microbial NO<sub>3</sub><sup>-</sup> immobilization and plant uptake (Zheng et al., 2013); and (iv) it also elevates soil pH, increasing N<sub>2</sub>O reductase activity which promotes N<sub>2</sub> formation and higher N<sub>2</sub>/N<sub>2</sub>O ratios (Cayuela et al., 2014; Gul et al., 2015).

Phosphorus (P) is another limiting plant macro-nutrient in agricultural systems. Redox-mediated phosphorus transformations have gained particular significance during episodic soil flooding and drainage events. During soil flooding microbial respiration results in reductive dissolution of Mn(III, IV) and Fe(III) (oxyhydr)oxides in soils that leads to release of P adsorbed to minerals and thereby enhances P availability (Peretyazhko and Sposito, 2005; Chacon et al., 2006). On the contrary, the oxidizing condition developed during soil drainage or intermittent flooding promotes the oxidative precipitation of Fe (oxyhydr)oxides, leading to the reduction of P solubility and bioavailability. Wisawapipat et al. (2017) have shown that oil palm derived biochar has the potential for increasing available P pools in paddy soils during flooding and oxygenic conditions through minimization of the reactive surfaces of Fe/Al (hydr)oxides for P adsorption. Their study showed that biochar amendment has the potential for increasing dissolved P from the residual pool due to electron shuttling of biochar with Fe(III) minerals.

#### 5. Future research directions

Two important issues need to be addressed when applying biochar-based redox reactions to manage contamination and control the bioavailability of nutrients. First, the implementation of bioremediation methods should be done with caution, because many sites contain multiple contaminants, including metal(loid)s and organic compounds, and organisms that affect the output of bioremediation approaches. Therefore, the remediation of contaminated sites usually requires a combination of many different approaches. Second, bioremediation rarely restores an environment to its original condition. Often, the residual contamination remaining after treatment is strongly sorbed and not available to microorganisms for degradation. Over a long period, these residuals can be slowly released, generating additional pollution. There is little research on the fate and potential toxicity of such released residuals; therefore, both public and regulatory agencies



continue to be concerned about the possible deleterious effects of residual contamination.

However, research on biochar-mediator reactions is in its infancy. Further investments in research are needed to understand the impact of biochar in redox processes and the corresponding mechanisms. Pre. An ultimate goal would be to finely tailor the redox (and other physico-chemical) characteristics of biochars by well-controlled synthesis and post-treatments in order to use them in specific target applications. Future research directions in relation to the redox properties of biochars include:

- Production of biochars with high redox activity by introducing more redox functional groups with suitable pyrolysis and post-treatments.
- Exploration and differentiation of the electron transfer mechanisms involving biochars, which result from their surface-redox functional groups (donating or accepting electrons) and/or from their electrical conductivity (transferring electrons between two (bio)chemical entities).
- Application of biochar-mediated redox reactions for treating real industrial effluents of complex mixtures and containments in natural environments to promote commercial-scale applications in remediation.
- Examination of the long-term stability of biochar in relation to redox-mediated immobilization and bioavailability of contaminants and nutrients.

## 6. Conclusions

In this review we discussed the redox characteristics of biochars and the corresponding biogeochemical impacts with their surrounding environment. Biochar can be used as an environmentally-sustainable electron donor, acceptor, or mediator. It can enhance the reduction of oxidized contaminants and participate in elemental cycling in terrestrial, groundwater, or waste water ecosystems. We illustrated that it is possible to tailor the redox characteristics of the biochar by selecting specific feedstocks, pyrolysis temperatures, and post-treatments. Further understanding of the factors impacting these redox properties will allow production of biochars for specific redox applications.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.biortech.2017.06.154>.

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