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Insoluble carbonaceous materials as electron shuttles enhance the anaerobic/anoxic bioremediation of redox pollutants: Recent advances

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ABSTRACT

Carbonaceous materials can accelerate extracellular electron transfer for the biotransformation of many recalcitrant, redox-sensitive contaminants and have received considerable attention in fields related to anaerobic bioremediation. As important electron shuttles (ESs), carbonaceous materials effectively participate in redox biotransformation processes, especially microbially-driven Fe reduction or oxidation coupled with pollutions transformation and anaerobic fermentation for energy and by-product recovery. The related bioprocesses are reviewed here to show that carbonaceous ESs can facilitate electron transfer between microbes and extracellular substrates. The classification and characteristics of carbon-containing ESs are summarized, with an emphasis on activated carbon, graphene, carbon nanotubes and carbon-based immobilized mediators. The influencing factors, including carbon material properties (redox potential, electron transfer capability and solubility) and environmental factors (temperature, pH, substrate concentration and microbial species), on pollution catalytic efficiency are discussed. Furthermore, we briefly describe the prospects of carbonaceous ESs in the field of microbial-driven environmental remediation.

1. Introduction

Anaerobic biological treatment processes are considered important approaches to control recalcitrant organic or inorganic contaminants, *e.g.*, azo dyes, perchlorate and heavy metals, in municipal wastewater treatment plants (WWTPs). By 2018, China reached a sewage processing capacity of nearly 200 million m^3/d [1]. However, meeting increasingly strict national effluent quality standards is still a challenge because these recalcitrant chemicals are hard to biodegrade due to their complex aromatic structure, strong covalent bonds, *etc*. [2] Advanced oxidation technologies easily cause the problems of high cost, many toxic by-products and excess chemical sludge, but biotechnologies can make redox-sensitive pollutants discoloured, reduced and stabilized [3]. Nonetheless, the lower reaction rate and longer processing time of biotechnological approaches are still drawbacks in engineering applications, and the enhanced measures to accelerate biological reaction rates need further exploration.

Microbial respiration, including intracellular and extracellular respiration, utilizes biodegraded contaminants as metabolic substances to produce energetic ATP (Adenosine triphosphate). In microbial intracellular respiration process, the soluble or permeable matters, such as nitrate, carbonate or sulfate, are transferred into the cytoplasm and then reduced to N_2, CO_2, or H_2S, respectively. Different from that, extracellular respiration can utilize exocellular or insoluble compounds, *e.g.*, azo dyes, nitrobenzene, organochlorine pesticides, Mn(IV), Cr(VI), U(VI), As(V) and Fe(III), to accept or transfer electron for energy metabolism. The related remediation biotechnologies are frequently developed and evaluated to treat these pollutions. However, extracellular substances are generally redox sensitive and have variable toxicity, mobility and bioavailability depending on their existing states. The biochemical reaction rates are significantly limited by long-distance electron transportation [4]. For example, the produced electrical current had a low density in microbial electrolysis cells using ferric iron (Fe(III)) as an electron acceptor [5]. The reduction rate (k) of perchlorate was

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relatively low during an extracellular microbial reduction process [6].

Electron shuttles (ESs), also known as redox mediators, can participate in microbial extracellular respiration and accelerate extracellular electron transfer (EET) for contaminants removal and bioenergy production [7]. Various ES materials have partly resolved above problems *via* constructing fluent extracellular electron transport channels. Amongst ES materials, carbonaceous materials, including activated carbon, carbon nanotubes (CNTs) and biochar, have been widely applied in biological sewage treatment due to their high specific surface area, porous structure and strong redox capacity for the remediation of heavy metals or organic contaminants. The acceleration of electron transfer is attributed to the redox properties of surface oxygen- or nitrogen-containing groups, such as phenolic hydroxyl, carbonyl and quinonyl groups. The materials preparation sources, carbon morphology, carbonization activation method and environmental conditions have significant impacts on the electron transfer capacity. However, recent advances in carbonaceous materials and their application as ESs in the environmental remediation of redox pollutants have not been clearly summarized.

Although several comprehensive reviews have described the EET mechanisms and ESs applications of specific redox-sensitive contaminants [8–10], the development of carbonaceous ESs for aquatic environmental remediation has not been systematically focused on. In this article, the mediated redox applications of insoluble carbon materials and carbon-based immobilized ESs for pollutions control and their catalytic characteristics are summarized. The influencing factors on contaminants removal rate and efficiency, including carbonaceous materials properties and environmental conditions, are reviewed. Furthermore, the prospects of biochar-derived biotechnologies and carbon-based immobilized mediators are briefly described.

2. Redox-sensitive contaminants removal with ESs

2.1. ESs-mediated extracellular respiration mechanism

In extracellular respiration, microorganisms utilize a reduced substance to produce and transfer electrons along the cell respiratory chains to extracellular electron acceptors, thus providing bioenergy for microbial metabolism. According to the electron acceptors, extracellular respiration can be categorized as microbial electrogenic respiration, iron/manganese respiration, humic substance respiration, *etc*., which is generally coupled with the transformation of redox-sensitive contaminants (Table S1 in Supporting information). However, the bioavailability of insoluble substances and their reaction rates are severely limited. For example, an insoluble anode, as an electron acceptor, cannot penetrate the cytoplasm into cells; metal oxides are relatively difficult to transform and biodegrade.

The currently understood electron transfer mechanisms between microbes and extracellular solid substances mainly include i) direct contact by conductive proteins; ii) the nanowire theory; iii) the biological capacitor theory; and iv) the ES theory promoting electron transfer (Fig. S1 in Supporting information) [11,12]. Many redox proteins could mediate direct EET, such as membrane-bound NADH for acetogens and methanogens, surface-associated hydrogenases and formate dehydrogenases for *Methanococcus maripaludis* [13]. Nanowires are extensions of cells' outer membranes and responsible for direct electron transfer to solid metals or electrodes from microbes at a far distance. For the pili of *G. sulfurreducens*, the polymerized hexa-haem cytochromes OmcS could perform direct EET, and for *S. oneidensis*, the real conduits are cytochromes MtrABC and OmcA [14]. In the ES-mediated process, bacteria utilize endogenous or exogenous redox mediators to transfer electrons from cell's cytomembrane to a terminal extracellular acceptor, achieving a long-distance noncontact electron transport. For *Shewanella* sp. the self-excreted flavin mononucleotide (FMN) and riboflavin (RF) deliver electrons from c-type cytochromes to extracellular insoluble acceptors. Some artificial ESs, such as AQDS, methyl viologen, biochar, could play analogous roles in mediating the EET process.

2.2. Carbonaceous materials applications as ESs

In recent decades, the conventional ESs-catalysed biotransformation of recalcitrant contaminants has been widely studied, providing a new way to accelerate anaerobic treatment efficiency. Amounts of these ESs have been used in many fields and proven effective for the biodegradation of various pollutants, including azo dyes [15–22], nitrate [23–28], halogen compounds [6,29–32] and heavy metals [33–39] (Table 1). These ESs promoted the biological transformation and degradation rates of the target pollutants by one or more orders of magnitude. Therein, carbonaceous ESs have presented well catalysis efficiency and received increasing attentions. Not only have pristine activated carbon or biochar been alternative ES materials for efficient catalytic performance to the above pollutants, but also other carbon-based immobilized ESs could further be developed to various environmental remediation applications. More emerging studies have been extended to Fe catalyst and aerobic fermentative fields last several years.

2.2.1. Microbially-driven Fe reduction or oxidation

Iron is the fourth most prevalent element in the geochemical composition of the earth and can form a variety of iron oxide ores. Microbially-driven Fe(III)/Fe(II) transformation is a significant driving force for the biogeochemical cycling of C, O, P, S and N element to promote the biopurification of pollutants. Cultivating functional iron-oxidizing or reducing bacteria in actual aquatic or terrestrial environments could become a viable method for the bioremediation of organic compounds (petroleum aromatics, chlorinated ethane) or ammonium with carbonaceous ESs. In the microbial Fe(III) reduction process, electrons are generally transferred to oxidized iron ore with auto-secreted reduced flavin mononucleotide ($FMNH_2$) and FMN, but the external addition of redox mediators (activated carbon, 9,10-anthraquinone-2,6-disulfonate on activated carbon (AQDS@AC), natural organic matter on activated carbon (NOM@AC), *etc*.) (Fig. 1) or the immobilization of an iron-soluble chelating agent (ethylene diamine tetraacetic acid, polyphosphate, nitrilotriacetic acid, *etc*.) could result in a several-fold reduction rate, promoting Fe(III) ion dissolution and NH_4^+-N oxidation. Reduced graphene oxide (rGO) facilitated Fe(II) oxidation coupled with nitrite reduction by chemodenitrification *via* surface carboxyl groups during the nitrate-dependant iron denitrification process [40].

2.2.2. Anaerobic fermentation for resource recovery

Carbonaceous material-based bioaugmentation has recently emerged in anaerobic fermentation to produce energy gas (hydrogen and methane), volatile fatty acids (acetic acid, propionic acid and butyric acid) and solvents (ethanol and butanol). Atilano-Camino *et al.* found that the immobilized mediator of anthraquinone-2-sulfonate on activated carbon (AQS@AC) improved the yield rate of acetate, butyrate, ethanol, *etc*., by 36% compared with the control from glucose fermentation [41]. Activated carbon cloth (ACC) modified with HNO_3 improved the biotransformation efficiency of 4-nitrophenol by twofold due to the increase in acidic and basic functional groups on ACC and the supported biomass [42]. With ethanol as the substrate, rice straw and wood chip biochar could simulate electron syntrophy between methanogens and exoelectrogens with 10.7- and 12.3-fold higher

Table 1
Representative redox-sensitive contaminants removal mediated by soluble ESs and insoluble carbonaceous ESs.

Type of pollutant	Strain	Specific pollutant	Electron donor	Electron shuttle	Ref.
Azo dye	*Sphingomonas xenophaga* BN6	Amaranth	Glucose	AQS, Lawsone	[15]
	Pseudomonas aeruginosa	Reactive orange 16	Glucose	Phenazine	[16]
	Bacillus sp.	Methyl orange	Glucose	Magnetic HA	[17]
	Shewanella marisflavi BBL25	Reactive Red 120	Glucose	Biochar	[18]
	Novibacillus thermophiles SG-1	Orange I	Acetate	AQDS	[19]
	Enterobacteriaceae	Acid orange 7	Glucose	AQS	[20]
	Shewanella onediensis MR-1	Congo red	Sodium lactate	Methylene blue	[21]
	Geobacter sulfurreducens	Hydrolysed reactive red 2	Volatile fatty acids	Activated carbon	[22]
Nitrate	*Yersinia frederiksenii*	Nitrate	Glucose	ME, AQ, 1-AQ	[23]
	Shewanella oneidensis MR-1	Nitrate	Formate	HA	[24]
	Shewanella putrefaciens	Nitrate	Formate	HA	[25]
	Pseudomonas aeruginosa	Nitrate	Steel matrix (Fe^0)	Riboflavin, FAD	[26]
	Alcaligenes sp. *TB*	Nitrate	Ethanol	Pd-Fe/MWCNTs	[27]
	Proteobacteria	Nitrate	Glucose	Biochar	[28]
Halogen compounds	*Thaeura*	$KClO_4$	Acetate	HA, AQDS	[6]
	Proteobacteria	$KClO_4$	Sulfur	AQDS	[29]
	Shewanella oneidensis MR-1	Pentachlorophenol	Biowaste	HA	[30]
	Shewanella oneidensis MR-1	Pentachlorophenol	Lactate	HA	[31]
	Dehalobacter	BDE-47	H_2, Organic acid	Biochar	[32]
Heavy metals	*Brachymonas*	Cr(VI)	Glucose	HA	[33]
	Shewanella oneidensis MR-1	Hg(II)	Lactate	NOM	[34]
	Rhodobacter capsulatus	Te(IV), Te(VI)	Pyruvate	AQDS, Riboflavin	[35]
	Desulfitobacterium	As(V)	Acetate	AQDS-rGO	[36]
	Paenibacillus sp.	U(VI)	Ethanol	AQDS	[37]
	Geobacter sulfurreducens	Pd(II)	Acetate	AQDS	[38]
	Shewanella oneidensis MR-1	As(V)	Sodium lactate	Biochar	[39]

Abbreviations: 1-AQ, 1-Dichloroanthraquinone; BDE-47, 2,2′,4,4′-Tetrabromodiphenyl ether; FAD, Flavin adenine dinucleotide.

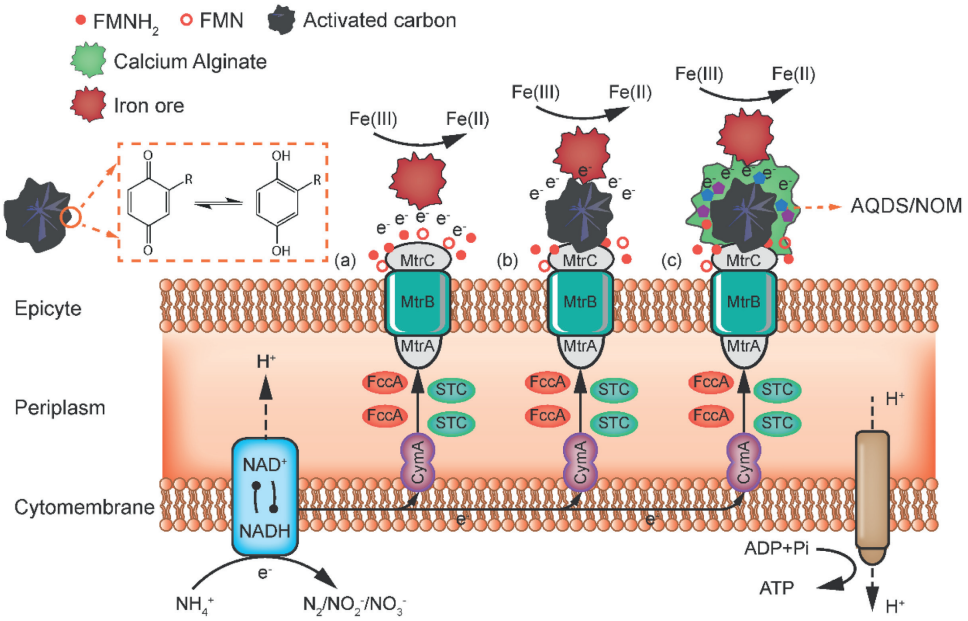

Fig. 1. Extracellular electron transportation model of Fe(III) reduction mediated by (a) endogenous $FMNH_2$/FMN; (b) exogenous ESs, such as activated carbon, and (c) immobilized ESs, such as AQDS and NOM. Reproduced with permission [7]. Copyright 2018, Elsevier.

methane production rates than those without biochar modulation [43]. In the hydrolysis-acidogenesis stage of anaerobic digestion (AD), the synergetic effect of nano-zero-valent iron (nano-ZVI) and activated carbon resulted in a higher ciprofloxacin degrading capability (72.41%) and volatile fatty acid yield (173.7%) than those in the blank group [44].

2.2.3. Emerging organic contaminants degradation

The discharge of emerging organic contaminants (EOCs), such as personal care products, pharmaceuticals, industrial chemicals, *etc*., in WWTPs is a growing global concern. The EOCs are toxic to both human and aquatic environment even at low concentrations. The structure of EOCs has different functional groups such as electron donating groups and electron withdrawing groups. In addition to wide advanced oxidation processes, more reports showed that extracellular respiration bacteria could be effective to degrade or abate EOCs. The functional dissimilatory metal-reducing bacterium (DMRB) could oxidize organic contaminants and then transfer the released electrons to metal ions-containing oxides, such as Fe(III) and Mn(IV). For example, the *Shewanella oneidensis* MR-1 biologically produced Fe(II) and H_2O_2, and then oxidized 2,2′,4,4′-tetrabrominated diphenyl ether *via* the Fenton reaction [45]. However, slow growth rate and low degradation activity make microorganisms impracticable for *in situ* remediations of contaminants. The carbonaceous ESs have been proved to be feasible to improve the aqueous phase removal of EOCs. An enzymatic membrane re-

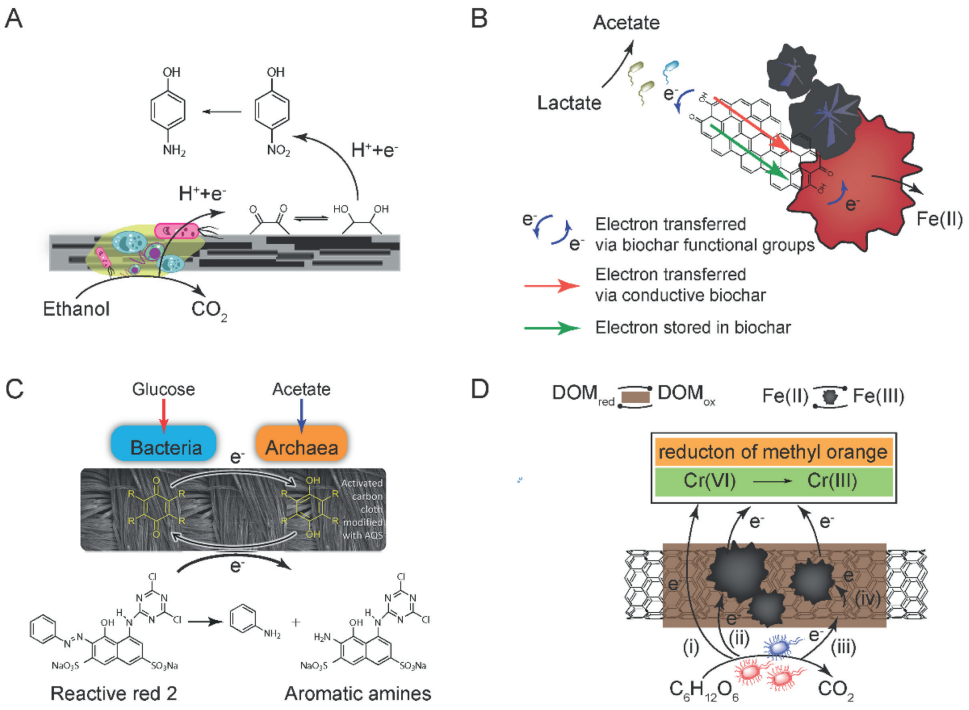

Fig. 2. Representative electron transfer pathways for microbial extracellular reduction processes mediated by carbonaceous ESs: (A) Anaerobic bioreduction of NP with ACF. Reproduced with permission [59]. Copyright 2016, Elsevier. (B) Microbial ferrihydrite reduction with redox-active biochar. Reproduced with permission [60]. Copyright 2020, Elsevier. (C) Azo dye biotransformation with AQS immobilized on ACC. Reproduced with permission [61]. Copyright 2019, Elsevier. (D) Bioremediation of azo dyes and Cr(VI) with NOM-modified magnetic CNTs. Reproduced with permission [62]. Copyright 2020, the Royal Society of Chemistry.

actor with a one-off addition of 3 g/L GAC was studied, and four recalcitrant EOCs' removal efficiency was consistently increased, namely carbamazepine, diclofenac, sulfamethoxazole and atrazine [46].

3. Carbonaceous ESs' classification and redox properties

Carbonaceous materials have high chemical reactivity due to their porous structure, specific surface area and abundant chemical groups. The surface of activated carbon or biochar has different proportions of amino, hydroxyl, quinonyl, aliphatic and aromatic functional groups, which can catalyse the biotransformation of the pollutants [47]. Moreover, activated carbon can simultaneously store and release electrons *via* double layer electrical capacitance and directly conduct electricity *via* electrical conductance [48]. In addition to activated carbon, newly developed materials, including CNTs and graphene oxide (GO), have been used as ESs to accelerate electron transfer [49]. Biochar can be explored as a natural ES to degrade contaminants and has a significant impact on biogeochemical cycling and element distribution. Carbon-based immobilized ESs enable the longer catalysis duration time and the high recovery efficiency from products. Representative electron transfer pathways mediated by carbonaceous materials or carbon-based immobilized ESs are shown in Fig. 2.

3.1. Activated carbon-like materials

Conventional activated carbon is a non-metallic material derived from coal, petroleum or their by-products after a series of carbonization and activation processes. According to size and shape, activated carbon can be classified as a powder (diameter < 0.175 mm), granules (> 0.175 mm) activated carbon fibre (ACF) and activated carbon felt, amongst others. Activated carbon felt is a 3D-structured porous material with randomly dispersed fibres and moderate hydrophilic properties and is often used as an electrode matrix modified by polypyrrole (PPy) or AQDS.

AD is an economic and feasible bioprocess for methane production from organic wastewater. Granular activated carbon (GAC) has been widely reported to benefit AD systems. In addition to mediated electron transfer, direct interspecies electron transfer (DIET) is an efficient pathway to donate electrons between species for CO_2 reduction. The indicator DIET microorganisms *Geobacter* and *Methanosarcina* were enriched in a self-fluidized GAC-amended upflow anaerobic sludge blanket (UASB) reactor to facilitate methane production [50]. The distinctive adsorption and conductive properties of GAC enhanced the degradation of phenol [51].

3.2. Graphene oxide and carbon nanotubes

Some emerging carbonaceous materials, including GO and CNTs, have received considerable interest due to their conductivity, redox properties and application potential as an ES support matrix. Graphene is a carbon allotrope with a one-atom-thick sheet structure and is constructed with sp^2-bonded carbon atoms. CNTs can be considered coiled graphene sheets and are generally classified as single- or multi-walled CNTs according to the number of coaxial sheets [52,53]. The bioaugmentation principle significantly differs for various bioprocesses. GO was chosen as an ES to provide a proper redox potential (50.8 mV) and increased the redox conversion rate of an azo compound (reactive red 2) and nitroaromatic compound (3-chloronitrobenzene) under methanogenic and sulfate-reducing conditions [54]. rGO was studied as a highly efficient matrix for enzyme immobilization of horseradish peroxidase, and its basal plane structure with quinone moieties acted as an ES to facilitate enzymatic turnover [55].

In addition to exhibiting redox moieties, graphene can behave as a conductive bridge to promote electron transfer to acceptors. The enhancement of Fe(III) reduction coupled with NH_4^+-N oxidation was observed in the presence of graphene in mangrove

Table 2
ESs classification schemes according to different properties.

Basis	Type	Examples
Chemical structure	Quinone	Benzoquinone, AQDS, Hydroquinone, *para*-Quinone
	Phenazine	Riboflavin, Neutral red
	Anthracene heterocycles	Methylene blue, Thionine, Resazurin
	Porphyrins	Protoheme, Zinc porphyrin, Cobalt porphyrin, Iron porphyrin
	Viologen	Methyl viologen, Benzyl viologen
Source	Natural	HA, FA, Humin, Sorgoleone, Juglone, Lawsone, Syringaldehyde
	Synthetic	AQDS, Carbon fibre, Phenazine, Porphyrins
Solubility	Soluble	Anthraquinone, Riboflavin, AQS, AQDS
	Insoluble	Activated carbon, Carbon fibre, CNTs, Graphene, Biochar, Immobilized redox mediators (1,2,5,8-Anthraquinone@Ca-alginate, 1,2-Naphthoquinone-4-sodium sulfonate@AER, HA@γ-Al_2O_3, AQS@GO, AQDS@ACF/PPy, AQS@ACC, nano-Fe_3O_4@GAC, Fe_2O_3@conductive carbon cloth)

sediment slurries [56]. Additionally, conducting CNTs favoured methane production by enhanced DIET for acetoclastic methanogenesis *via* acetate dismutation rather than conventional CO_2 reduction [57]. CNTs composites doped with 2% Fe (CNT@2% Fe) were prepared for the reduction of acid orange 10, and the highest efficiency was 79-fold that of non-ES systems owing to the magnetic conductive characteristics of the composites [58].

3.3. Biochar

Biochar is manufactured from the thermal pyrolysis of carbon-rich biomass under oxygen-limited conditions and has widespread preparation sources, including crop straw, corncobs, coconut shells, wood and rice husks. The mechanisms of electron transfer, including graphite region, functional groups and the modified redox metals, significantly differ to contribute to its redox properties and electrical conductivity in different cases. For example, methane production in the AD of waste activated sludge is mainly attributed to the electron-donating capacity (EDC) rather than bulk electrical conductivity [63]. In contrast to the above case, biochar conductivity enriched typical electroactive cells, simulating syntrophic phenol degradation by a potential DIET pathway [64]. Additionally, when using peanut shell biochar, both direct electron donation from the biochar and indirectly mediated redox reactions between organic acids and biochar contributed to Cr(VI) reduction [65].

3.4. Immobilized redox mediators

Common ESs have multiple classifications according to chemical structure, preparation source and solubility (Table 2). The chemical characteristics play important roles on electron transfer capacity. The corresponding electron transfer are dependant on the reversible conversion of functional groups and have different mechanisms in compounds of quinones, phenazines, anthracene heterocycles, porphyrins, viologens, *etc*. (Fig. 3) For example, Reduced hydroquinone can be oxidized to the intermediate semiquinone radical and para-benzoquinone. In addition, ES materials can be obtained from natural and artificial synthesis. Humic substrates are a form of macromolecular NOM with a molecular weight of 300 - 30,000 Da and include humic acid, humin and fulvic acid. Natural quinones include sorgoleone, juglone, lawsone and syringaldehyde, which can be extracted from plants and microbes. Artificially synthesized ESs mainly include quinone (AQDS and AQS), phenazine (riboflavin), porphyrins (protohaeme), *etc*. The diversity of this soluble ESs provides various options as functional groups for the ongoing development of carbon-based immobilized ESs.

According to solubility, ESs are classified as soluble and insoluble redox mediators. Although soluble ESs generally have high catalytic efficiency, favourable solubility and diffusivity, the loss of soluble ESs along with water-flow, the secondary pollution and the continuous addition still cause a series of problems for practical applications in WWTPs. Therefore, functional soluble ESs are immobilized on a solid matrix for material recovery. Soluble ESs, such as anthraquinone-2-sulfonate (AQS), AQDS, FMN and naphthoquinone (NQ), are immobilized on a functional matrix to achieve higher catalytic and mechanical stabilization. Immobilization of ESs provides a great solution to promote solid-liquid separation and maintain electron transfer efficiency in practical applications. Example matrices include barium/calcium alginate [66], polypyrrole [67], ion exchange resins [68] and macromolecular polymers [69], *etc*. However, calcium alginate would collapse as the number of use increase. Mass transfer efficiency could be low since ESs is embedded inside. Desorption of ESs in anion exchange resin should be considered for the reduced catalysis efficiency and secondary pollution with the stripping of ESs. Some applications of macromolecular materials possibly cause the risk of microplastic pollution and higher cost.

Carbonaceous materials have been chosen as a suitable matrix for immobilization due to their thermal and mechanical stability and large specific surface area. The covalent immobilization of AQS on activated carbon cloth improved the reductive decolorization of reactive red 2 [61]. The developing immobilization methods on carbonaceous materials include physic (embedment, adsorption, precipitation, resin exchange), chemical (covalence, surface amino modification, cross-binding) and electrochemistry (electropolymerization-doping) methods. Carbon mediators are a promising alternative for further catalysis. Organic ESs, *i.e*., oxalic acid, tartaric acid and hydroquinone, are combined on carbon materials to introduce more redox active moieties, yielding efficient immobilized ESs. The conduction band of semiconducting iron minerals can mediate electron transfer from Fe(II) to cytochrome *c*, simulating microbial Fe(II) oxidation system under dark and anoxic subsurface conditions [70]. The iron-doped AC could also facilitate mediating the EET in microbial remediation systems.

4. Influencing factors on carbonaceous ES catalysis

4.1. Properties of carbonaceous materials

4.1.1. Redox potential

The redox potential (E_0) indicates the relative strength of oxidants and reductants and determines the direction of the reaction. Theoretically, E_0 should be between those of the two redox half-reactions, and the rate-limiting step is greatly affected by E_0 [71]. If E_0 is two high, the limiting step is the reduction of high-valence contaminants due to the small ΔE_0 between the ES and the electron acceptor. Similarly, if the E_0 value is too small, the reduction of the oxidation-state ES will be correspondingly restricted. The redox potentials of typical pollutants and ESs are shown in Fig. 4. Various ESs have been successfully applied to the dissolution of iron minerals with a certain redox potential, but biochar generally

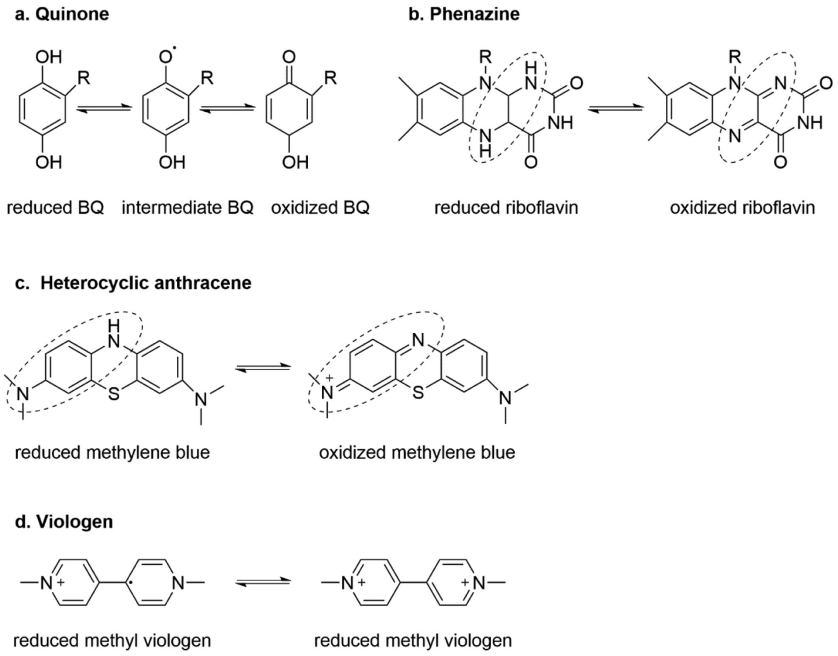

Fig. 3. Electron transfer mechanism for representative reduction- or oxidation-state ESs: (a) quinone, (b) phenazine, (c) heterocyclic anthracene and (d) viologen. The soluble functional groups can be immobilized to carbon matrices with certain immobilization methods. Reproduced with permission [76]. Copyright 2018, Elsevier.

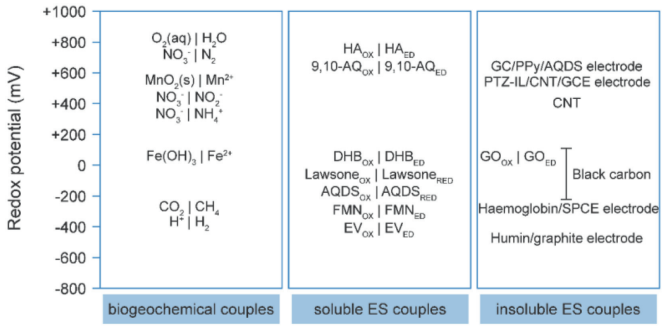

Fig. 4. Comparison of redox potential *vs.* SHE (E_0) of some biogeochemically relevant couples and soluble and insoluble ESs. Reproduced with permission [77]. Copyright 2013, American Chemical Society.

has a broad range of potentials (−0.35 to 0.15 V *vs.* SHE at pH 7) due to its diversity of redox-facile functional groups [72]. Gallocyanine, methylene blue and thionine were selected from nine compounds for the bioreduction of jarosite with a half-wave potential of 276–375 mV [73]. A similar simulated effect on haematite reduction was observed with a high content of indigenous pyrogenic carbon [74]. The redox potential of carbonaceous materials can be modulated by Fe-N doping, hydroquinone/*p*-phenylenediamine dual redox addition, pyrolysis temperature, *etc*. [75]

4.1.2. Electron transfer capability

The electron transfer capacity (ETC) refers to the number of electron equivalents that a unit of ES can send out or accept and includes the EDC and electron-accepting capacity (EAC) [64]. These properties are mainly attributed to the surface functional groups, radicals and redox-active metals of the material [78]. In biochar, phenolic -OH groups are mainly responsible for its EDC, and quinoid C=O groups are for its EAC. The evolution of oxygen-containing groups in the process of oxidation is generally as follows: 1) C–H/C–C → C–OH; 2) C–OH → C=O; 3) C=O → COOH; and 4) COOH → CO_2. Therefore, the oxidation extent should be controlled to form more functional moieties rather than excessive oxidation to obtain inactive COOH and even CO_2 [79]. Biochar derived from waste activated sludge pyrolysed at 600 °C had the best performance for acid orange 7 removal [80]. Biochar as an electron donor favours the reduction of organic pollutants, such as nitro herbicides and chlorinated organics. Three investigated biochars showed good reductive properties with EDC values of 0.18–1.83 mmol e^-/g biochar, phenolic groups acted as the mediation agent at low and intermediate heat-treatment temperatures (HTTs) (200–650 °C), and conjugated π-electrons associated with aromatic structures contributed to the reductive capacity at high HTTs due to their graphite-like structure [81].

The ETC test is helpful to evaluate the conductivity of ESs and prove the redox transformation processes of the studied substances. For quinone compounds, the EDC is close to the EAC, indicating the potential for reversible electron transfer. Some ESs, *e.g.*, 2-HNQ, 9,10-anthraquinone-2-carboxylic acid (AQC) and AQS, have a slightly higher EAC than EDC [82]. Wood-derived biochar reached a maximal EAC of 0.4 mmol e^-/g-char and an EDC reaching 7.0 mmol e^-/g-char at an HTT of 400 °C [83]. The transformation of Fe(II) to Fe(III) can be identified from two distinct anodic peaks in cyclic voltammetry (CV) testing in biochar-mediated ferrihydrite reduction systems [39].

4.1.3. Solubility and concentration

The degree of solubility of an ES has an effect on its transmembrane transport capability, thus affecting the conversion rate of contaminants. The effect of the concentration of soluble ES on the conversion rate of contaminants can be depicted with the Monod model. As the ES concentration increases, the bioconversion rate of pollutants greatly increases and then reaches a plateau [84]. However, solid primary carbon materials generally have a lower diffusivity and catalysis efficiency than exogenous soluble ESs in microbial reduction systems. In addition, due to the insoluble properties of carbonaceous ESs, the carbon particle size and the addition amount affect the catalytic performance. For example, smaller biochar sizes and higher biochar/ferrihydrite ratios promoted the aggregation of biochar, *Shewanella oneidensis* MR-1 cells and ferrihydrite, favouring electron transfer and microbial Fe(III) reduc-

tion by functional groups and the conductance and capacitance of carbon matrices [60]. The biochar addition significantly simulated both dissimilatory Fe(III) reduction and the production of methane, and powdered biochar amendment has higher catalysis efficiency than granulated biochar amendment in ferrihydrite enrichments [85].

4.1.4. Modification methods

Pristine carbonaceous ESs generally have a low redox capacity without pre- or post-modification, limiting the pollutant removal efficiency. Modification methods, which can be classified as physical, chemical and metal-loaded methods, have attracted increasing attention due to their ability to modify surface redox groups [86]. Amezquita-Garcia *et al.* compared the reduction efficiency of 4-nitrophenol (NP) using different ACFs as ESs, including unmodified (AW), HNO_3-treated (OX) and AQDS-immobilized ACFs (AQDS), and the results indicated that the content of redox moieties (carbonyl or quinone groups) was positively correlated with the NP biotransformation efficiency in the order OX > AQDS > AW [59]. Surface oxidation modifications using HNO_3, H_2O_2, O_3 and $(NH_4)_2S_2O_8$ increase the number of oxygen-containing acidic moieties and the EAC. In contrast, chemical reduction treatment by H_2, N_2, NH_3, aniline, *etc*. increases electron-rich alkaline groups with higher reduction ability. ACFs with 8 mol/L HNO_3 and 700 °C thermal treatment increased the concentration of quinone groups for nitroaromatic compound catalysis by 1.68 times compared to the control [87]. Moreover, mono- or bimetallic modification with Cu, Fe, Al, Ag, *etc*. could improve the catalytic properties and electrostatic attraction ability [88].

4.2. Environmental factors

4.2.1. Temperature

The preparation process of activate carbon (carbonization, activation and modification) can be significantly affected by temperature, determining the category and amount of functional groups. Moreover, the pyrolysis temperature affects the electrical conductivity of biochar and has a considerable impact on ETC and the ability to mediate the reduction of Cr(VI), nitrate, *etc*. [89,90] Three distinct biochars derived from corn stover at various pyrolysis temperature values (CS300, CS500 and CS800) were evaluated as additives in anammox systems, and CS300 enriched the abundance of *Candidatus Kuenenia* because the greater number of reduced moieties (phenolic and hydroquinone) in this biochar than in the other biochars facilitated the bioenergetics of anammox metabolism [60]. Similarly, the biochar prepared at lower 300 °C accelerated denitrifying rate the most, but denitrification was inhibited with CS800, indicating that the lower pyrolysis temperature made the biochar maintain a relatively high EDC [28]. When the pyrolysis temperature exceeded 600 °C, most functional moieties disappeared, and the charging and discharging capacity decreased, which is crucial for ESs in an AD system [91].

The incubation temperature also impacts the biological enzyme activity, reaction rate and chemical properties of ESs [92,93]. As temperature increases, the percentage of active molecules increases, resulting in a higher reaction rate constant k, as depicted in the Arrhenius model (Eq. 1) [94].

$$k = Ae^{-E_a/RT} \quad (1)$$

where k is the rate constant; R is the molar gas constant; T is the thermodynamic temperature; E_a represents the apparent activation energy; and A represents the frequency factor. Even at a relatively low T (10 °C), the rate and efficiency of denitrification were greatly improved with the addition of an ES [95,96]. Note that the greater E_a is, the higher the influence of temperature on k. Since the ES decreases the E_a value in ES-mediated anaerobic systems, the effect of T on k is smaller than that in non-ES systems [97].

4.2.2. pH

pH is one of the operational parameters that can modify ETC by changing functional moiety constituents, affecting the contaminant removal efficiency. The slow pyrolysis of biochar at a low temperature (< 700 °C) caused higher yields of biochar and acidic moieties (-COOH and -OH), biochar derived from peanut shells at 350 °C could act as both an electron donor and ES for Cr(VI) reduction. In contrast, fast pyrolysis increased the ash content, which generally resulted in a higher pH [98]. Moreover, lower pH 2 increased the electron donor moieties (−C−O and −C=O), making the biochar an electron donor, and at higher pH 4, the biochar tended to act as an ES with more O-centred radicals, *e.g*., semiquinone-type radicals [99]. At pH 8, the immobilization of humic acid (HA) and Fe(III) on CNTs (HA/Fe_2O_3@CNTs) demonstrated a high Cr(VI) and methyl orange reduction effectiveness, showing the excellent stability and reusability of nanotube catalysts [62].

The H^+ concentration has direct effects on the physiological properties of microorganisms and the existing forms of substrate species in ES-mediated reduction systems. The pH can change 1) the membrane potential, which affects selective permeability for ionic compounds; 2) the enzyme activity, which affects the reaction rate; and 3) the solubility and equilibrium of the substrate for microbial assimilation. For example, the solution pH has great impacts on the chemical structure and Gibbs free energy of reactions, such as the transformation of $(UO_2)_4(OH)_7^+$, $(UO_2)CO_3(OH)_3^-$ and $UO_2(CO_3)_3^{4-}$ with the same U(VI) valence state [100]. Arsenite exposure largely depends on its speciation, and the interconversion between As(III) and As(V) is affected by environmental pH and redox potential. In the normal pH range (< 8), arsenic typically presents as the arsenite oxyanion (H_3AsO_3) under anoxic conditions and dominates as $H_2AsO_4^-$ or $HAsO_4^{2-}$ in oxidizing soil or sediments [39].

4.2.3. Microbial species

Bacteria that perform extracellular respiration, including sulfate, carbonate and iron/manganese respiration, have different biological activities, reaction rates and selectivities for contaminants. The electrogenesis bacteria *Rhodopseudomonas* spp. have higher electrochemical activity than do *Citrobacter* spp. in the electron transfer process [101]. In nature, multispecies biofilms promote iron corrosion more than single-species biofilms do due to mutualism; for example, the riboflavin secreted by *S. oneidensis* can be utilized by *Bacillus licheniformis* to accelerate the oxidation of stainless steel [102]. Even with a similar process of reductive dechlorination of pentachlorophenol (PCP), the dominant species exhibited significant differences over time or in different humin or mangrove soils [103,104]. Carbon materials can provide suitable attached sites for microbes, generally resulting in high biodiversity and enrichment of functional microorganisms. Usman *et al.* found that hydrochars enriched *Geobacter* and certain methanogens to promote AD of hydrothermal liquefaction wastewater [105]. The supplement of nFe_3O_4 and CNT simulated the growth of electron-active bacteria such as *Syntrophomonas zehnderi* from 17% to 45%, thus increasing the yield of long chain fatty in AD system [106]. Granular activated carbon modified with nanoscale zero-valent iron increased genus *Methanothrix* (acetoclastic methanogens) by 13.32% to lead to a higher CH_4 production [107].

5. Perspectives for carbonaceous ESs

Bioaugmentation is a common strategy to attain stable resilient and robust performance in biological systems. Several physicochemical methods, such as biofilm or granular sludge construction

and the addition of functionalized metal oxides and oxytetracycline, are adopted to protect against environmental perturbations. Compared to those approaches, biochar is an inexpensive, low-ecotoxicology-risk and biocompatible alternative redox ES material for appropriate engineering applications. The preparation sources of biochar are derived from wide biomass types from agriculture, forestry, municipal sludge waste, *etc*., and the yield of crop straw could reach more than 700 million tons per year in China. The development and utilization of biochar as an ES could have positive effects on pollution control, reducing greenhouse gas emissions and alleviating the energy crisis and form an emerging study field. The biochar cost mainly includes collection and transportation fees of feedstock, preparation and handling, labour cost, *etc*., which varies in different countries. The cost-effectiveness could be improved by developing more efficient preparation and modification methods. Engineered biochar with enlarged surface area and abundant functional groups has significant commercial importance as a promising ES for environmental applications.

In addition to common ESs, such as quinone, flavin and phenazine, many new materials have been proven to have the properties of bio-catalytic EET. However, the issues of poor physical stability, easy peeling off from the matrix and a lower mass transfer rate remain unsolved in current research. Immobilized ESs technologies could efficiently facilitate the separation of the solid-liquid phase. Carbonaceous nanomaterials, including CNTs and GO, can be utilized as immobilized matrices or direct ESs to facilitate electron transfer. AD processes have been developed for decades, and their application areas have been expanded to include the decomposition of high-loading organic matter and recalcitrant matter and biological nitrogen removal. If carbon-based ESs are immobilized on reactor components or fixed carriers, the anaerobic biotransformation efficiency of contaminants will be further improved. Additionally, the integration of immobilized ESs with a membrane bioreactor (MBR) could significantly enhance ESs recovery and increase the treatment capacity. With the discovery of natural ESs compounds and convenient synthesis processes, various carbon-based immobilized ESs will arise, thus promoting the biodegradation of pollutants.

6. Conclusions

ES-mediated biotransformation provides a feasible method for the efficient biodegradation of recalcitrant redox-sensitive contaminants. The barrier of EET can be overcome by conventional or emerging carbonaceous ESs, including pristine carbon materials and immobilized redox mediators on a carbon matrix. Both the properties of the carbonaceous ESs and environmental factors can influence the catalytic efficiency for pollutants removal. Carbon materials are being rapidly updated, and biochar and carbon-based immobilized ESs have increasing prospects in practical applications. Further exploration of carbonaceous ES materials will favour anaerobic environmental remediation in biological wastewater treatment.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2021.06.064.

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