Effect of soil organic matter-mediated electron transfer on heavy metal remediation: Current status and perspectives

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HIGHLIGHTS

- Pros and cons of microbial extracellular electron transfer pathways were evaluated.
- The role of soil organic matter-mediated electron transfer in the remediation of heavy metals have been discussed.
- The main factors affecting organic matter-mediated electron transfer were analyzed.
- Perspectives and suggestions for future on electron transfer in the remediation of soil heavy metals are provided.

GRAPHICAL ABSTRACT
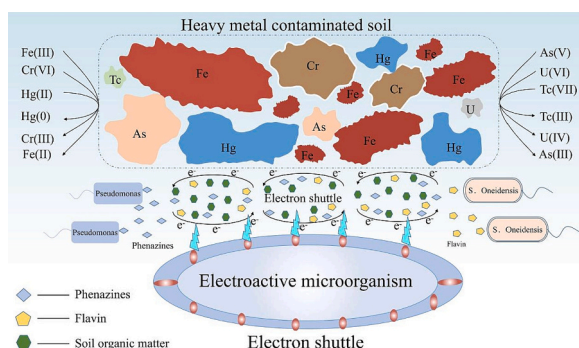
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ABSTRACT

Soil contamination by heavy metals poses major risks to human health and the environment. Given the current status of heavy metal pollution, many remediation techniques have been tested at laboratory and contaminated sites. The effects of soil organic matter-mediated electron transfer on heavy metal remediation have not been adequately studied, and the key mechanisms underlying this process have not yet been elucidated. In this review, microbial extracellular electron transfer pathways, organic matter electron transfer for heavy metal reduction, and the factors affecting these processes were discussed to enhance our understanding of heavy metal pollution. It was found that microbial extracellular electrons delivered by electron shuttles have the longest distance among the three electron transfer pathways, and the application of exogenous electron shuttles lays the foundation for efficient and persistent remediation of heavy metals. The organic matter-mediated electron transfer process, wherein organic matter acts as an electron shuttle, promotes the conversion of high valence state metal ions, such as Cr(VI), Hg(II), and U(VI), into less toxic and morphologically stable forms, which inhibits their mobility and bioavailability. Soil type, organic matter structural and content, heavy metal concentrations, and environmental factors (e.g., pH, redox potential, oxygen conditions, and temperature) all influence organic matter-mediated electron transfer processes and bioremediation of heavy metals. Organic matter can more effectively mediate electron transfer for heavy metal remediation under anaerobic conditions, as well as when the heavy metal

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content is low and the redox potential is suitable under fluvo-aquic/paddy soil conditions. Organic matter with high aromaticity, quinone groups, and phenol groups has a stronger electron transfer ability. This review provides new insights into the control and management of soil contamination and heavy metal remediation technologies.

Abbreviations

SOM	Soil organic matter
HS	Humic substances
HA	Humic acid
FA	Fulvic acid
DOM	Dissolved organic matter
SPOM	Solid-phase organic matter
SPHS	Solid phase humic substances
EDC	Electron donating capacity
EAC	Electron accepting capacity

1. Introduction

Soil heavy metal pollution is an important obstacle that restricts the sustainable development of agriculture and the safe production of food crops (Liu et al., 2023). According to the soil pollution survey communique by the Ministry of Environmental Protection of China and the Ministry of Land and Resources in 2014, >16.0 % of all surveyed sites soil had contaminated, with heavy metals being an important source of soil contamination (EPC, 2014). Industrial, agricultural, and commercial activities have been shown to be the primary sources of heavy metal pollution, and these include fossil fuel combustion, sewage irrigation, mining, smelting, pesticide application, and fertilizer application (Brusselen et al., 2020; Tan et al., 2018; Zhang et al., 2015). In order to achieve efficient remediation of heavy metals in soil, researchers have proposed surface covering, soil replacement, thermal remediation, electrokinetic remediation, chemical stabilization, chemical leaching, phytoremediation, and microbial remediation (Gong et al., 2018; Kumar et al., 2021). However, some technical bottlenecks, repair costs, and effects limit the scale application of the above remediation technologies (Wu et al., 2021). For example, thermal remediation has high energy consumption, chemical stabilization and leaching technologies have the risk of secondary pollution, while plant and microbial remediation technologies have a longer cycle (Borggaard et al., 2019; Gong et al., 2018).

Soil organic matter (SOM) is an important carrier that sustains the global carbon cycle, as well as a key factor affecting soil pollution processes and remediation (Ochoa et al., 2016). SOM is a major player in multiple reactions in various physical, chemical, and biological processes in the soil microenvironment (Che et al., 2021; Kopecký et al., 2021; Markiewicz et al., 2018). Electron transfer is an important function of SOM, and it affects the deposition of contaminants in the soil (Rendon et al., 2016; Zhu et al., 2019). This function is mainly attributed to the abundant redox groups in SOM, such as quinone and phenolic hydroxyl groups. These groups can accept electrons from electron donors and transfer the electrons gained to surrounding electron acceptors. They can mediate electron transfer in the environment and thus affect the redox process of organic pollutants and heavy metals (Pham et al., 2012; Wang et al., 2022a). The speciation and valence of heavy metals may change when they enter the soil depending on the mineral composition and organic matter structure of the soil, and this affects the environmental behavior of heavy metals and the effectiveness of remediation techniques. The speciation and valence of heavy metals are the main factors affecting their mobility and toxicity. For example, after

uranium is reduced from hexavalent to tetravalent results in a significant decrease in bioavailability (Lovley et al., 1991). The cytotoxicity of pentavalent arsenic is significantly lower than that of trivalent arsenic (Moe et al., 2016). In general, the electron transfer processes mediated by organic matter can affect the stability and bioavailability of heavy metals by altering their speciation and valence, and this has implications for heavy metal remediation. Since the organic matter and extracellular respiratory microorganisms involved in the reaction are all original soil components. Therefore, the organic matter-mediated microbial electron transfer process, as a clean, safe, low-disturbance, and low-cost effective way, compensates for the limitations of traditional physical, chemical, and biological remediation technologies.

Previous studies have shown that both dissolved and solid-phase organic matter in soils have electron transfer functions, which accelerate the electron transfer process and promote redox reactions of heavy metal ions (Tan et al., 2019a; Lovley et al., 1996). Wittbrodt et al. found that dissolved organic matter (DOM) has a strong reducing capacity for heavy metals by modelling the process of interaction between DOM and heavy metals in natural environments (Wittbrodt and Palmer, 1995). DOM facilitates the extracellular respiration of microorganisms and the redox of metal minerals by mediating electron transfer (Jiang and Kappler, 2008). In contrast, solid-phase organic matter (SPOM) in the soil is not highly accessible to microorganisms, and they can affect their intrinsic connection with microorganisms through mechanisms such as physicochemical protection, which leads to difficulties in performing the electron shuttling function of certain redox-active functional groups in solid-phase organic matter (Tan et al., 2019a, 2020; Roden et al., 2010). To facilitate the remediation of heavy metal-contaminated soils, whether interactions between different types of organic matter and heavy metals affect the transport and transformation of heavy metals needs to be determined. In addition, the mobility and biotoxicity of different forms and valence states of heavy metals are affected by the type of heavy metal. Therefore, the role of electron transfer processes involving organic matter in the remediation of different types of heavy metals requires consideration.

Existed studies about heavy metal remediation have focused on conventional physical, chemical, and biological remediation techniques. In particular, there have been few reports about the influence of organic matter-mediated electron transfer on the transport and transformation of heavy metals in soil. Meanwhile, this process is extremely complex, and it is affected by many environmental factors. Our lack of knowledge of the effects of these factors limits our understanding of the positive and negative bidirectional effects of organic matter in heavy metal remediation. Here, we provide an overview of the microbial extracellular electron transfer pathways and common electron shuttles, highlight the main role of the SOM electron transfer function in the soil heavy metal remediation process, and analyze the main influencing factors. We also conducted a systematic search of the literature and summarized the application potential of major organic substances-mediated electron transfer in different heavy metal remediation.

2. Electron transfer pathways and common electron shuttles

Microorganisms that perform extracellular respiration can release electrons by oxidizing intracellular organic matter, and these electrons are passed through the intracellular respiratory chain to extracellular electron acceptors to sustain their growth (Zhou et al., 2023). Microbial extracellular electron transfer may be coupled with the reduction of heavy metals. Heavy metals act as terminal electron acceptors and undergo redox reactions, changing their occurrence state in the soil and

reducing their toxicity and mobility. Organic matter mainly receives electrons from microbial growth and metabolism under natural conditions and passes them to heavy metals (Klüpfel et al., 2014; Lovley et al., 1996; Tan et al., 2019a). As an extracellular redox mediator, it facilitates electron shuttling between microorganisms and heavy metals and accelerates redox reactions (Hu et al., 2023). In the reduction of heavy metal ions by microorganisms, the key issue is how electrons are transferred from the cell and accepted by the heavy metal ions. Given that cell membranes do not conduct electricity, electron transfer proteins, cytochromes, and electron shuttles in cell membranes play important roles in the transfer of electrons across membranes (Jiang and Kappler, 2008; Logan et al., 2019).

2.1. Electron transfer pathways

Electron transfer can be direct and indirect depending on the pathway and distance of electron transfer. Direct electron transfer involves physical contact by electroactive microorganisms using cytochrome *c* on the outer cell membrane or nanowire structures attached to the cell surface. Indirect electron transfer involves the transfer of electrons from a microorganism to an extracellular terminal receptor utilizing an electron shuttle (Glasser et al., 2017; Light et al., 2018; Reguera et al., 2005).

2.1.1. Cytochrome-mediated proximity direct electron transfer

Cytochrome c (c-type cytochromes) is widely distributed on the inner, periplasmic, and outer cell membranes. It is a protein-like substance with an electron transfer function composed of several iron-containing hemoglobins. Microorganisms can reduce extracellular terminal electron acceptors by direct physical contact between cytochrome *c* on the outer cell membrane and extracellular electron acceptors (Kumar et al., 2017; Logan et al., 2019; Pérez-Mejías et al., 2022). The complete electron transport chain formed between cytochromes is a prerequisite for the extracellular transport of electrons by microorganisms. The pathway of intracellular electron transfer to iron-containing minerals in *Shewanella oneidensis* MR-1 is the most well-studied extracellular electron transfer process, and it involves at least seven multiple heme-containing cytochrome molecules: CymA, Fcc3 (FccA), MtrA, MtrB, MtrC, OmcA, and STC (Fonseca et al., 2013; Schuetz et al., 2009; Shi et al., 2016). During the intracellular breakdown of organic molecules, *S. oneidensis* MR-1 first passes electrons to the coenzyme NAD or FAD to become the reduced coenzyme NADH or FADH. In the process of electron transfer along the respiratory chain, NADH and FADH pass electrons to quinone (Q) through a series of processes, and quinone (Q) receives electrons and becomes hydroquinone (QH2) (Kerscher et al., 2008; Light et al., 2018) (Fig. 1). CymA is an *S. oneidensis* MR-1 quinone pool dehydrogenase that oxidizes electrons from the quinone pool and transports them to the periplasmic cytochromes STC and Fcc3 (Beblawy et al., 2018; Marritt et al., 2012). The cytochrome molecules in turn

transfer electrons to the MtrA, MtrB, and MtrC complexes to further transfer electrons from the periplasm to the cell surface (Rehnlund et al., 2022). Finally, the pigment proteins OmcA and MtrC on the cell surface interact (MtrC is primarily responsible for electron transfer, whereas OmcA primarily facilitates the attachment of the bacteriophage to the mineral surface) (Coursolle et al., 2010) and transfer electrons to the receptor via soluble ferrous hemoglobin (Hartshorne et al., 2009) (Fig. 1). Electron transfer involving cytochromes also couples the reduction of heavy metals. Lovley et al. demonstrated that cytochrome *c* acts as a hexavalent chromium reductase for the reduction of Cr(VI) at a rate 40 times faster than the previously reported maximum reduction of Cr(VI) by *P. ambigua* (Lovley and Phillips, 1994; Suzuki et al., 1992).

2.1.2. Nanowire-mediated long-range direct electron transfer

The cilia-like appendages with electrical conductivity are known as "nanowires." It was first discovered on the cell surface of *Geobacter sulfurreducens* by Reguera et al. (2005). Nanowires are the most common way by which *Geobacter sulfurreducens* contacts electron acceptors for long-range extracellular electron transfer (Malvankar et al., 2011; Malvankar and Lovley, 2014; Summers et al., 2010). Subsequent research has revealed that nanowire-like structures are present in other genera, such as *S. oneidensis* MR-1 and *Cyanobacterium* (Gorby et al., 2006). There is some disagreement regarding the composition, structure, and potential conduction mechanisms of nanowires. Scientists have proposed two different theories to explain the ultra-high conductivity of nanowires. Malvankar et al. suggested that the electron delocalization formed by the staggered stacking of aromatic groups in nanowires is the main reason for electron transfer (Malvankar et al., 2011, 2015; Shi et al., 2016). A recent study has shown that OmcS is an important component of the conductive hairs of *G. sulfurreducens*. The Π-Π interactions of heme greatly enhance the interconnection between two adjacent OmcS internal subunits, allowing direct electron transfer between hemes in close proximity (3.5–6.0 A) (Wang et al., 2019a). The composition of the nanowires differs among genera; the nanowires of *S. oneidensis* MR-1 cells are an extension of the outer membrane MtrC-OmcA fusion protein unlike in the conductive pilus of the genus *Geobacter*. The surface of *S. oneidensis* MR-1 cells is densely packed with cytochromes, and electron hopping between cytochromes allows electrons to pass along the wires and interact with the vesicle structure of the outer membrane, which has been referred to as a multi-step electron hopping conduction mechanism (Pirbadian and El-Naggar, 2012; Pirbadian et al., 2014) (Fig. 2). Michelson et al. used a 1.4 μm thick microfluidic reactor containing approximately 200 nm pores to physically separate *G. sulfurreducens* from aqueous sodalite. During the reaction, Mn(VI) mineral birnessite was found to be reduced 15 μm away from the bacterium, with a length close to that of the nanowire (Michelson et al., 2017). The irreplaceable role of nanowire-mediated electron transfer in heavy metal reduction has thus been verified.

2.1.3. Electron shuttle-mediated long-range indirect electron transfer

Microorganisms can also achieve electron transfer through redox-active electron shuttles. The reciprocal transition between its own oxidized and reduced states is the main principle of electron shuttle-mediated electron transfer (Glasser et al., 2017; Light et al., 2018). Electron shuttles offer a variety of possibilities for electron transfer due to differences in their redox properties (Glasser et al., 2017). The electron shuttle was previously thought to be soluble and diffusible. However, subsequent research has shown that solid-phase organic matter and biochar play an important role in the electron transfer process (Roden et al., 2010; Tan et al., 2019a). Environmental electron shuttles can be classified according to their origin into two main categories: endogenous (secreted by microorganisms) and exogenous (naturally occurring or synthetic) (Hernandez and Newman, 2001). Known endogenous electron shuttles include phenazine and flavin; humic substances (HS) and quinone are the main exogenous electron shuttles (Fig. 3) (Cai et al., 2020; Light et al., 2018; Liu et al., 2022).
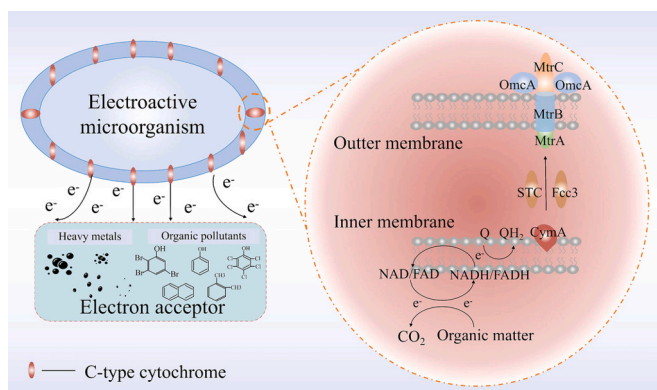

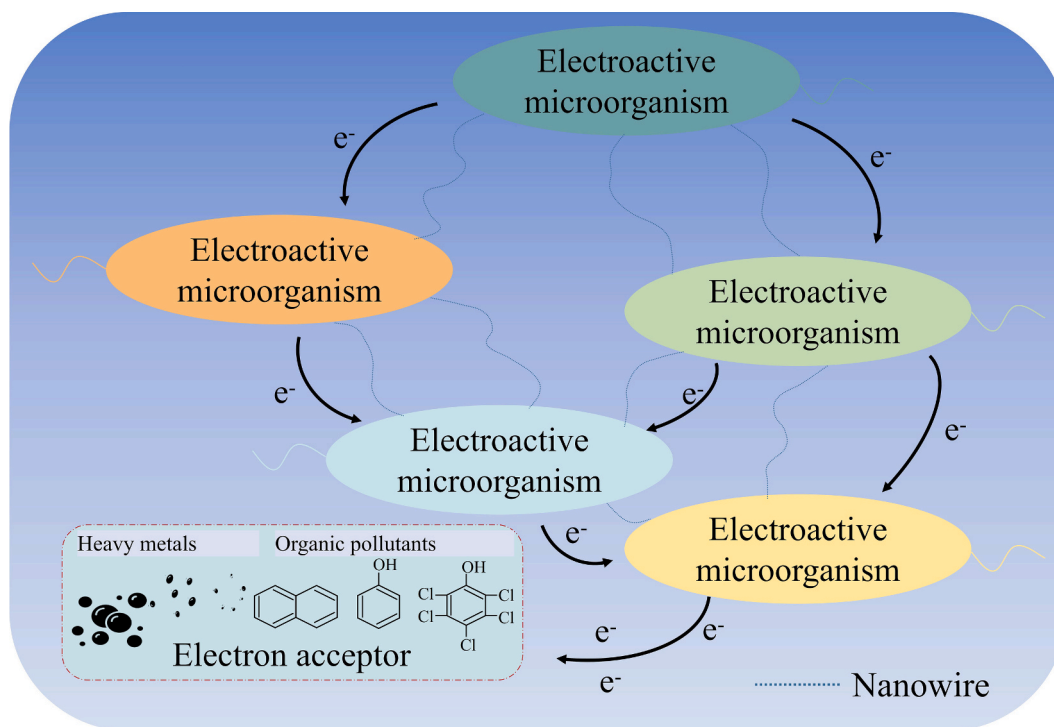**Fig. 1.** Cytochrome-mediated proximity direct electron transfer.

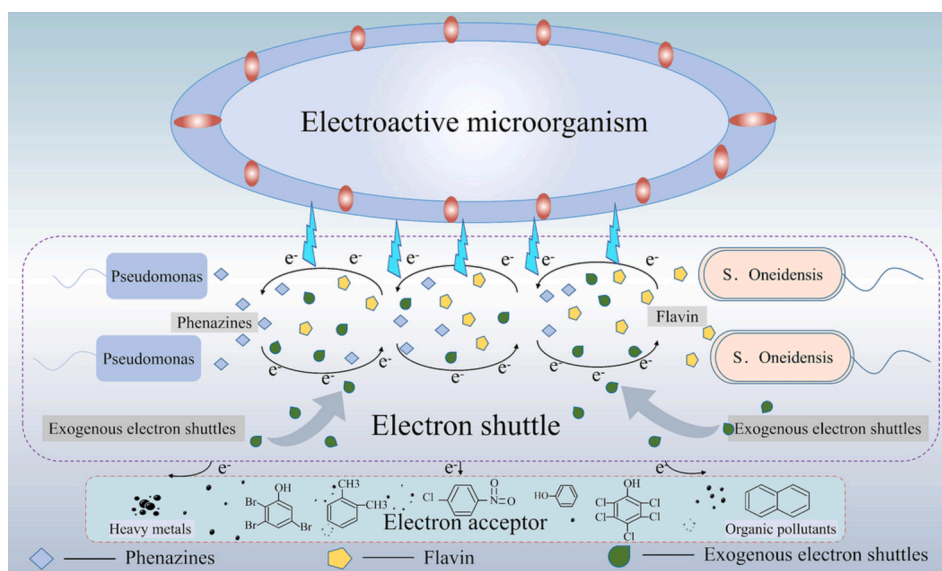**Fig. 2.** Nanowire-mediated long-range direct electron transfer.

Fig. 3. Electron shuttle-mediated long-range indirect electron transfer.

In sum, cytochrome *c* is distributed on some structures of microbial cells, so it can only mediate electron transfer over very short distances (Shi et al., 2009). Nanowires can transport electrons from microorganisms across membranes to distances thousands of times the length of the bacteria (Lovley, 2011; Michelson et al., 2017; Pfeffer et al., 2012). Since the above two pathways require contact with extracellular electron acceptors through microbial functional proteins or nanowires. Therefore, their electron transfer rate is faster, but the electron transfer distance is shorter (Jiang et al., 2023). Compared with the cytochrome *c* and nanoconductor pathways, the electron shuttle-mediated long-range electron transfer process breakthrough the obstacle of contact with electron acceptors, effectively improving the distance and efficiency of microbial extracellular electron transfer (Glasser et al., 2017). The

electron transport chain and the expression of related genes in microorganisms might differ significantly under different electron acceptors. Thus, different electron transport methods might be used in the reduction reaction (Bretschger et al., 2007; Rosenbaum et al., 2012).

2.2. Electron shuttle

2.2.1. Endogenous electron shuttle

(1) Flavin

Flavin is a redox-active organic compound secreted by *S. oneidensis* (Kotloski and Gralnick, 2013). Flavin (riboflavin (RF) and flavin

mononucleotide (FMN)) can act as an electron shuttle to mediate extracellular electron transfer (Fig. 3) (Brutinel and Gralnick, 2012; Canstein et al., 2008; Marsili et al., 2008). Previous studies have shown that the removal of flavin from supernatants with electrode-bound biofilm systems results in a loss of microbial current of approximately 70 % (Marsili et al., 2008). The addition of trace amounts of RF to *S. oneidensis*-based microbial fuel cells results in an almost 10-fold increase in the number of electrons transferred (Coursolle et al., 2010). On the one hand, free flavin as a redox mediator can directly mediate the two-electron reaction (Okamoto et al., 2013). On the other hand, flavin is an OM enzyme cofactor that can interact with OmcA and MtrC to provide electrons to the electron acceptor through direct contact in a single-electron reaction mode (Okamoto et al., 2014a, 2014b). In the mutant *S. oneidensis* lacking MtrC, flavin-mediated reduction reactions are impaired (Coursolle et al., 2010). Removal of flavin bound to MtrC reduced reductase activity by three orders of magnitude (Ross et al., 2009). The cofactor-bound redox process provides more favorable electron transfer kinetics than the free state flavin-mediated electron shuttle mechanism. The electron transfer rate of this process is approximately 10^3–10^5 times higher than that of the electron shuttle mechanism. This suggests that the one-electron reaction is the primary pathway for the flavin-mediated electron transfer process (Okamoto et al., 2013; Okamoto et al., 2014c). Meanwhile, flavin accelerated the bioreduction of heavy metals. Suzuki demonstrated that in the medium with 0.05 mM flavin, *Shewanella putrefaciens* increased the reduction efficiency of U (VI) by 1.08 times within 2 h (Suzuki et al., 2010).

(2) Phenazine

Phenazines are a group of secondary metabolites with a unique heterocyclic aromatic ring structure secreted by bacteria of the genus *Pseudomonas* (Simoska et al., 2018). Phenazine derivatives differ in their physicochemical properties, and this variation is associated with differences in the functional groups on the nitrogen-based heterocycles. The position and nature of the different functional groups can affect the redox potential (standard redox potential: NHE_{PYO} = -34mv; NHE_{PCA} = -177mv; NHE_{PCN} = -115mv; $NHE_{1-OH-PHZ}$ = -172mv), stability, and polarity of phenazines, and this affects their biological activity (Price-Whelan et al., 2006). Phenazine plays a key role in balancing the NADH/NAD^+ ratio in bacteria and regulating the expression of related genes (Dietrich et al., 2008; Graef et al., 1999). This has also been confirmed by the findings of Wang et al. showing that *Pseudomonas aeruginosa* PA14 with an intact phenazine synthesis gene survives longer than PA14 with a mutated phenazine synthesis gene; the addition of other oxides structurally similar to phenazine does not extend the life of the mutant (Wang et al., 2010). Phenazine can cycle back and forth between the bacterium and the mineral to transfer electrons, thereby accelerating the reduction of Fe—Mn oxides by *Pseudomonas* (Rhodes et al., 2021). Rabaey et al. showed that the exogenous addition of phenazine increases the electron transfer rate in microbial fuel cells (Rabaey and Verstraete, 2005; Rabaey et al., 2005). *P. aeruginosa* can affect the synthesis of phenazine by regulating the biosynthetic pathway. The specific role of the different species in the electron transfer process remains unclear due to the variation and structural complexity of phenazines; thus, the intrinsic mechanism by which phenazines function as electron mediators requires further study.

2.2.2. Exogenous electron shuttles

(1) HS

HS is a class of macromolecular organic compounds produced by the long-term physical, chemical, and biological transformation of plant and animal residues (Stevenson, 1982; Zaiets and Poch, 2016). The electron-shuttling ability of HS mainly stems from the presence of functional groups such as quinone and phenol (Aeschbacher et al., 2012; Tan et al.,

2017; Walpen et al., 2016). Meanwhile, many nitrogenous and sulfur functional groups in HS contribute to their electron transfer ability; they can even account for 21–56 % of the total electron transfer capacity of HS (Ratasuk and Nanny, 2007; Xi et al., 2018). The ability of HS to act as electron shuttles is a widespread microbial electron transfer mechanism, and it is an important pathway for electron transfer in anoxic environments, such as soil and sediment (Klüpfel et al., 2014; Zhang and Weber, 2009). Lovley et al. first identified HS as electron acceptors in the extracellular respiration of *Geobacter metallireducens*, and this work has provided a foundation for the development of organism electron transfer in the field of pollutant remediation (Lovley et al., 1996). Early studies on the mechanism by which HS acts as electron shuttles to mediate the reduction of heavy metals have focused on dissolved HS, such as humic acid (HA) and fulvic acid (FA) (Alberts et al., 1974; Skogerboe and Wilson, 1981; Sunda and Kieber, 1994). HS is involved in the repair process of heavy metals by mediating electron transfer (Lovley and Blunt-Harris, 1999; Pham et al., 2012). Huang et al. showed that the addition of 2 mg L^{-1} HA increased the reduction rate of Cr(VI) by 3.38 times in *Aeromonas hydrophila* (Huang et al., 2019). In addition to natural HS, exogenous HS can also be used as electronic shuttles. Previous studies have shown that composting humus plays a key role in mediating electron transfer and that this ability to mediate electron transfer is largely influenced by the composting process (Xiao et al., 2019; Yuan et al., 2017; Zhao et al., 2019). Yuan et al. demonstrated that the increase in quinone group content, aromaticity, molecular weight, and humification of HS during composting was the main reason for the increase in electron transfer capacity (Yuan et al., 2018a, 2018b). Solid-phase humic substances (SPHS) is the most dominant constituents of HS in soils and sediments, and they can also mediate electron transfer (Keller and Takagi, 2013; Roden et al., 2010). Close physical contact between microorganisms, SPHS, and metal oxides is important for the ability of SPHS to mediate electron transfer. However, the intrinsic associations of SPHS with microorganisms can be affected by mechanisms such as physicochemical protection. This impedes the electron shuttle function of certain redox-active functional groups in SPHS (Tan et al., 2019a, 2019b). Thus, the extracellular electron transfer process in SPHS depends not only on its chemical structure but also on the surrounding soil environment (Tan et al., 2019a, 2020). Tan et al. used physical soil fractionation and electrochemical measurements to assess the extent of the microbial reduction of SPHS in mineral soils under different protection mechanisms. The results indicate that the degree of microbial reduction of SPHS decreases as the size of soil aggregates decreases (Tan et al., 2020). The extracellular electron transfer process of SPHS is largely controlled by its physicochemical conservation.

(2) Quinones

The transfer of electrons from *G. metallireducens* to the humus is accompanied by a significant increase in the concentration of semi-quinone in the humus, demonstrating that the main electron acceptors in the humus are quinones (Scott et al., 1998). In addition, Nurmi et al. found that the characteristic peaks of six model quinones are similar to those of natural humus samples by cyclic voltammetry (Nurmi and Tratnyek, 2002). Therefore, some small molecule quinones have been widely used as templates for functional groups of HS in studies of microbial extracellular electron transfer processes to better understand the electron-shuttling ability of HS (Cervantes et al., 2003; Liu et al., 2019), such as anthraquinone-2,6-disulfonate (AQDS), NQSA (1,2-naphthoquinone-4-sulphonate), BQ (1,4-benzoquinone), NQ (1,4-naphthoquinone), AQCA (anthraquinone-2-carboxylate), AQS (anthraquinone-2-sulfonic acid sodium), and AQC (anthraquinone-2-carboxylic acid) (Nopawan and Nanny, 2007; Wolf et al., 2009). A recent study has shown that extracellular electron transfer distances mediated by AQDS can reach the centimeter level (Bai et al., 2020). Quinones are reduced to hydroquinone by accepting intracellular electrons from extracellular respiratory bacteria; they subsequently pass the

electrons to extracellular electron acceptors (e.g., iron/manganese oxides) and become oxidized, transforming to semi-quinone and finally quinone. This process can occur when the AQDS concentration reaches 0.01 mM (Cutting et al., 2009; Lan et al., 2019). Quinones are involved in the extracellular electron transfer and heavy metal repair process by cyclic conversion between oxidation/reduction states (Chen et al., 2011; Hong et al., 2012). Han et al. showed that the addition of AQDS as a mediator significantly increased the reduction rate of organic arsenic compounds by *Shewanella putrefaciens* CN32 by 119 % (Han et al., 2017). The activation energy of AQS-mediated Cr (VI) reduction by *Ochrobactrum intermedium* BCR400 was reduced by 1.1 times (Kavita and Keharia, 2012).

The concentration of endogenous electron shuttles secreted by microorganisms tends to be low and the ability to secrete them is closely related to microbial metabolism and vital activities, so the continuity of their mediated electron transfer processes is weak. Yang et al. showed that the concentration of flavin naturally secreted by wild-type *S. oneidensis* Mr-1 was lower than 1 µM, which limits its extracellular electron transfer efficiency, particularly at the interface from OMc-cyts to electron acceptors (Yang et al., 2015). The highly pathogenic nature of *P. aeruginosa* limits the application of phenazine as an electron shuttle in microbial electrochemical systems (Rhodes et al., 2021; Venkataraman et al., 2011). Therefore, the development of approaches for enhancing endogenous flavin and phenazine production in microorganisms should be a goal of future research on endogenous electron shuttle mediated indirect electron transfer processes in the extracellular electron transfer network of *S. oneidensis* and *P. aeruginosa*. Compared with flavin and phenazine, the source of exogenous electron shuttles is abundant and extensive. The electron transfer process mediated by organic matter such as HA and FA from peat, compost, and soil has been widely studied (Huang et al., 2021; Li et al., 2023; Xie et al., 2017, 2018). The discovery and utilization of such electron shuttles open up new avenues for microbial electricity production as well as for the migration and transformation of heavy metals.

3. The role of organic matter-mediated electron transfer in Fe/Mn oxides reduction and other heavy metal remediation

The accumulation capacity and biotoxicity of heavy metals in soil systems are not only related to their total concentrations but also the speciation change and valence distribution. The environmental impacts and bioavailability of heavy metals vary among different speciations and valences (Cai et al., 2021; Li et al., 2021). For example, the reduction of uranium (U) from hexavalent to tetravalent can result in the formation of insoluble mineral precipitates, which reduces the ability of U to migrate in the environment (Lovley et al., 1991). The reduction of hexavalent Cr (Cr(VI)) to trivalent Cr (Cr(III)) significantly reduces its biological toxicity, and studies have shown that Cr(VI) is 100 times more hazardous than Cr(III) (Azeez et al., 2021; Tabaraki and Heidarizadi, 2018). Therefore, the regulation of the speciation and valence state of heavy metal ions plays a key role in the management of heavy metal pollution. Redox reactions are the main way in which the toxicity and mobility of heavy metals can be affected through changes in their speciation and valence state.

Soil organic matter is the main indicator for evaluating soil fertility and safety. It contains a large number of reducing groups and can directly reduce heavy metals under anoxic conditions (Chen et al., 2003). In addition, small molecule organic matter can play a role in microbial extracellular respiration by acting as an electron shuttle to facilitate the conversion of heavy metals from highly toxic and soluble oxidized forms to less toxic and insoluble reduced forms, which accelerates the remediation of toxic metals (He et al., 2014; Rush et al., 2021). Since Organic matter and microorganisms are important bearers of this heavy metal remediation process, as well as important components of the soil. Therefore, the microbial electron transfer process mediated by organic matter has great application potential in the remediation of heavy metals in soil in the future as an effective way of safety, small disturbance to soil, low cost, and no secondary pollution. Various oxidized heavy metals are present in the soil environment, such as Fe(III), Mn(IV) As(V), Hg(II), and Cr(VI). Although their solubility in the soil is extremely low and they are strongly kinetically limited in redox reactions, they are still important electron acceptors in the natural soil environment (Fig. 4) (Kavita and Keharia, 2013; Wang et al., 2021; Zhang et al., 2021).

3.1. Reduction of Fe/Mn oxides

Soil Fe/Mn oxides have surface properties such as large specific surface area, low surface charge, and high affinity for metals, which to some extent influence the mobility and bioavailability of pollutants in soil (Li et al., 2022; Lu et al., 2022). In addition, Fe(III) and Mn(IV) are abundant and the predominant electron acceptor in anaerobic soils. Studies have confirmed that electron transfer of organic matter can reduce iron minerals to Fe (II), and Fe (II) as an active electron mediator can further mediate the reduction of other heavy metals, while Mn acts more as a final electron acceptor (Nyman et al., 2002; Roden et al., 2010). However, ensuring that Fe(III)/Mn(IV) oxides that cannot diffuse to the cell surface can be accessed has become a major problem for the reduction of Fe(III)/Mn(IV) by microorganisms. Lovley's early research provided new insights into these questions. Lovley found that HA was less effective in solubilizing Fe(III) than other heavy metal insoluble salts. The difference is that the reaction rate of HA as an extracellular electron acceptor for microbial respiration to mediate the reduction of Fe(III) is significantly higher than that of other heavy metal insoluble salts (Lovley et al., 1996). The transfer of electrons via microbial oxidation processes to Fe/Mn is not limited to iron-reducing microorganisms. Subsequent studies have shown that organic matter plays an important role in the reduction of Fe(III))/Mn(IV) oxides as an electron acceptor for the cellular respiration of fermenting bacteria, sulfate-reducing bacteria, halobacteria, methanogenic bacteria, and thermophilic microorganisms (Cervantes et al., 2002; Xi et al., 2018). The ability of these microorganisms to indirectly reduce Fe(III))/Mn(IV) may be much greater than that of iron-reducing bacteria (Kappler et al., 2004; Merino et al., 2021). Organic matter is an electron shuttle that significantly increases the rate of extracellular electron transfer, and this has an important effect on the reduction of Fe(III)/Mn(IV) oxides in soil. Jiang et al. found that the rate of electron transfer from *G. sulfurreducens* to dissolved HS (617 µmol min^{-1}) is approximately 27 times higher than that to solid-phase Fe(III) (23 µmol min^{-1}) minerals, and the rate of iron oxide reduction using dissolved humus as an electron shuttle is approximately seven times higher than the rate of direct microbial iron oxide reduction (Jiang and Kappler, 2008). AQDS has been shown to accelerate the reduction of Mn(IV) (Li et al., 2007). In addition to reducing heavy metals by mediating electron transfer, HS contains
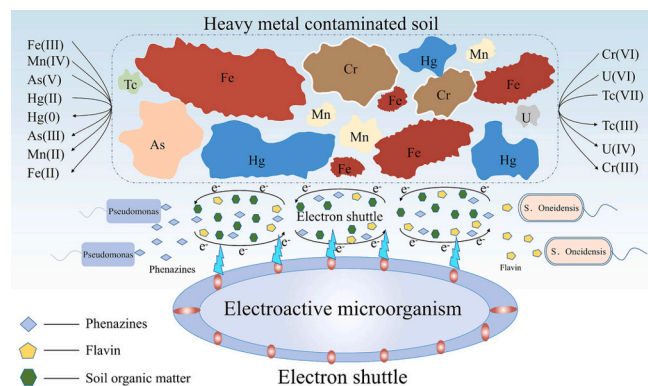

Fig. 4. Electron transfer pathway and its application in heavy metal remediation process.

abundant reductive active groups that play a key role in heavy metal remediation (Meunier et al., 2005; Voelker et al., 1997). Meunier et al. found that HS, aside from mediating the microbial reduction of heavy metals, can directly reduce Fe(III) to Fe(II) in an abiotic environment (Meunier et al., 2005). Organic matter can also stimulate the reduction of Fe(III) by microorganisms through complexation with Fe(III) or Fe(II). The microbial accessibility of Fe(III) is enhanced by the complexation of organic matter with Fe(III). The Fe(II) complexation reaction reduces the concentration of free Fe(II), which increases the thermodynamic driving force for Fe(III) reduction (Kappler et al., 2004; Urrutia et al., 1999).

The extracellular electron transfer process mediated by organic matter may affect the crystallographic transformation of the iron reduction products, which contributes to the formation of iron minerals with different crystal structures (Bae and Lee, 2013). This effect may in turn be counteracted to some extent by redox reactions. Previous studies have found that the extent of electron transfer from organic matter to Fe(III) compounds depends on the crystallinity and solubility of Fe(III) (Bonneville et al., 2004; Shi et al., 2012). As solubility increases, more electrons are transferred from reduced HS to Fe(III). Bauer et al. quantified the electron transfer from HS to goethite and hematite and compared it with ferrihydrite and Fe(III) citrate in the dissolved state. The degree of reduction of Fe(III) by HA was highest for Fe(III) citrate (621 ± 36 µeq (g HA)$^{-1}$), followed by ferrihydrite (521 ± 25 µeq (g HA)$^{-1}$), goethite (169 ± 10 µeq (g HA)$^{-1}$), and hematite (102 ± 29 µeq (g HA)$^{-1}$) (Bauer and Kappler, 2009). Furthermore, given that the organic matter-mediated iron reduction process usually occurs on the surface of iron oxides, the exposure surface may affect the interfacial reaction of iron oxides. Hu et al. investigated AQDS-mediated bioreduction processes with different exposure surfaces of hematite ({001} and {100}). The results revealed that electrons are more readily transferred from the cell or AQDS to the surface of hematite {001} than in the hematite {100}-AQDS system (Hu et al., 2021). This mainly stems from the higher surface charge of hematite {001}, which adsorbs more AQDS and AH$_2$QDS by electrostatic attraction and provides more reactive sites for AQDS or AH$_2$QDS (Li et al., 2020; Lv et al., 2018). The addition of AQDS reduces the surface resistance of the hematite and increases electrical conductivity. Compared with hematite {100}, hematite {001} has a higher electrical conductivity and a higher positive redox potential, which confers a higher electron transfer rate (Hu et al., 2021).

3.2. Cr(VI) reduction

In the soil environment, Cr is mainly present in the oxidized forms of Cr(VI) and Cr(III). Cr(VI) is a highly mobile, highly toxic carcinogenic substance, and some of the main forms include $Cr_2O_7^{2-}$, $HCrO_4^-$, and CrO_4^{2-} (Kang et al., 2022; Zhang et al., 2022). Cr(III) is usually less soluble, has a strong affinity for soil, and is easily adsorbed on soil particles as $Cr(OH)_3$ (Kang et al., 2022; Sarkar et al., 2013). Therefore, the reduction of Cr(VI) to the less toxic Cr(III) has become a strategy for the remediation of Cr-contaminated soils (Meng et al., 2018). Organic matter-mediated electron transfer can use Cr(VI) as an electron acceptor to facilitate the reduction of Cr(VI) to Cr(III), reducing its bioavailability and reactive toxicity (Sathishkumar et al., 2017; Xia et al., 2021; Zheng et al., 2015). Gu et al. found that the addition of a small amount of HA to the Cr(VI) reduction system of *Shewanella putrefaciens* CN32 significantly increases the rate of Cr(VI) reduction (Gu and Chen, 2003). Kavita et al. found that quinones significantly increases the reduction efficiency of Cr(VI) by *Bacillus* sp. BT1. The rate of Cr(VI) reduction by *Bacillus* sp. BT1 increased by 5.45, 2.51, and 40.0 times at the original concentrations of 100, 200, and 300 mg L^{-1} of Cr(VI), respectively, with the addition of 1 mmol L^{-1} of AQS. The activation energy for AQS-mediated Cr(VI) reduction is 2.1-fold lower than that for direct Cr(VI) reduction by *Bacillus* sp. BT1 (Kavita and Keharia, 2013). Zhang et al. found that the rate constant for Cr(VI) reduction using *S. putrefaciens* and flavin (0.053 h^{-1}) was approximately 29.44 times higher than that when

S. putrefaciens was used alone (0.0018 h^{-1}). The efficiency of Cr(VI) reduction by *S. putrefaciens* alone was only 24.10 %. The combination of *S. putrefaciens* and flavin increases the Cr(VI) reduction efficiency to 100 % (Zhang et al., 2022). Thus, organic matter not only accelerates the rate of bioreduction of Cr(VI) but enhances the microbial reduction of Cr(VI).

In addition to directly mediating the microbial reduction of Cr(VI), organic matter can mediate the reduction of Cr(VI) through the reduction of Fe(II) generated from iron minerals (Li et al., 2009; Roden et al., 2010). Some studies have found that this indirect reduction rate of Cr(VI) by Fe(II) may be several orders of magnitude faster than the direct bioreduction of Cr(VI) (Nyman et al., 2002). In addition, Fe(III) has a catalytic effect on the organic matter-mediated reduction of Cr(VI). On the one hand, the presence of Fe(III) increases the rate of direct reduction of Cr(VI) by organic matter. For example, Deng et al. found that metal oxides such as α-FeOOH and TiO$_2$ can accelerate the rate of Cr(VI) reduction by mandelic acid (Deng and Stone, 1996). In recent years, Zhang et al. have demonstrated a 5-fold increase in the ability of tartaric acid to reduce Cr(VI) in short periods (Zhang et al., 2019a). This mainly stems from the fact that the complexation of organic matter with Fe(III) reduces the electrostatic repulsion between the two negatively charged reactants and facilitates their contact. The adsorption of Fe(III) onto organic matter and Cr(VI) results in a change in the relative positions of the two, which facilitates electron transfer between them (Stumm, 1992; Zhang et al., 2019a). Fe(III) minerals and organic matter have a synergistic effect on the bioreduction of Cr(VI). Meng et al. evaluated the effect of iron-bearing clay minerals (nontronite NAu-2), ferrihydrite, goethite, and AQDS on Cr(VI) bioreduction. The direct reduction rate of Cr(VI) by MR-1 was 0.035 ± 0.003 h^{-1}, and AQDS increased the bioreduction rate of Cr(VI) to 0.191 ± 0.001 h^{-1} (Meng et al., 2018). The addition of nontronite NAu-2 and ferrihydrite increased the rate of AQDS-mediated Cr(VI) reduction by 2.4 and 2.1 times, respectively (Meng et al., 2018). The synergistic mechanism of bioreduction of Cr(VI) by Fe(III) minerals and organic matter may be attributed to two factors: (I) the binding of iron ions by soil organic matter can reduce the redox potential of iron ions, thus enhancing their ability to participate in the reaction (Jiang et al., 2019). (II) The presence of Fe(III) increases the reduction pathway for Cr(VI) and reduces the activation energy required for the reaction. The contribution of iron minerals to the bioreduction of Cr(VI) is affected by factors such as Fe(III) species, crystallinity, and surface area. Compared with nontronite NAu-2 and ferrihydrite, goethite has higher crystallinity and a smaller surface area, and some of the active sites are encapsulated within the crystals, which reduces the strength of the synergistic effect of goethite on the AQDS-mediated bioreduction process of Cr(VI).

3.3. Hg(II) reduction

Hg is a non-essential toxic element for living organisms, and the chemical form of Hg greatly influences its toxicity and mobility. Hg in the soil environment can be classified as inorganic (Hg(II), Hg(0), etc.) and organic (methylmercury, ethylmercury, etc.). Compared to inorganic mercury, methylmercury interacts weakly with soil components and is more neurotoxic and mobile in the environment (Parks et al., 2013; Si et al., 2015; Tsui et al., 2019). Soil organic matter-mediated redox cycling can have a significant effect on Hg transformation and bioavailability (Alberts et al., 1974; Lovley, 1993). It reduces Hg(II) to Hg (0), which is a major way for reducing microbial availability of methylated Hg (Siciliano et al., 2002). Reductive quinones are the main functional group causing the reduction of Hg(II). Thiol-involved physicochemical adsorption and ligand-induced oxidative complexation reactions promote the oxidation of Hg(0) (Gu et al., 2011; Hu et al., 2013; Zheng et al., 2012, 2013). Lee et al. reported a 2-fold increase in the rate of reduction of Hg(II) by *S. oneidensis* Mr-1 when HA was added to the reaction system (Lee et al., 2017). Electron transfer from microorganisms to organic matter is the rate-limiting step in the organic matter-

mediated Hg(II) reduction reaction (Zheng et al., 2012).

Organic matter plays a dual role in the redox reaction of Hg. The soil organic matter concentration (DOC to Hg(II) molar ratio) has a significant effect on the redox reaction of Hg. When the concentration of organic matter is low, the reduction reaction is dominant. Organic matter facilitates the reduction of Hg(II) by mediating the microbial shuttling of electrons; this process removes bioavailable Hg and limits Hg methylation. When the concentration of organic matter is high, the oxidation reaction is dominant. Thiols oxidize Hg(0) to Hg(II), which is readily bound to organic matter, thus facilitating the methylation of Hg by microorganisms (Gu et al., 2011; Lee et al., 2017; Zheng et al., 2012, 2013). Gu et al. found that up to 70 % of Hg(II) is reduced to Hg(0) when the HA concentration was 0.2 mg L^{-1}. When the HA concentration was increased (>0.2 mg L^{-1}), the reduction of Hg(II) was inhibited. When the HA concentration was >5 mg L^{-1}, the reduction reaction of Hg(II) ceased (Gu et al., 2011). The main reason for this pattern is that the thiol functional groups and the Hg(0) content increase and the thiol-induced oxidation reaction becomes increasingly dominant as the concentration of HA increases. The different sources and types of organic matter contain different levels and activities of redox groups, which significantly affect the redox process of Hg (Wang et al., 2022b). For example, the rate of oxidation of Hg(0) by mercaptoacetic acid is significantly higher than that of glutathione, and this mainly stems from differences in the molecular configuration and neighboring functional groups of thiol compounds (Zheng et al., 2012).

3.4. Reduction of other metallic minerals

Organic matter-mediated redox reactions play an equally important role in the remediation of other heavy metals. For example, FA will reduce Cu(II) in both aerobic and anoxic environments. Under anoxic conditions, Cu(II) is rapidly reduced to Cu(I), and the rate of the Cu(II) reduction reaction decreases as the reaction time increases. Oxygen and FA concentrations significantly affect the slow phase of the reduction reaction (Pham et al., 2012). Myers et al. showed that menaquinone and cytochrome are prerequisites for V reduction by *S. oneidensis* MR-1 (Myers et al., 2004). Organic matter-mediated electron transfer plays an important role in controlling the morphology and mobility of radioactive elements such as uranium (U) and technetium (Tc) (Fredrickson et al., 2000a, 2000b; Gu et al., 2005a). Gu et al. added a small amount of natural HS to the system of U(VI) reduction by *S. putrefaciens* CN32 and found that the reduction rate of U(VI) was increased by almost 10 times (Gu et al., 2005b). Fredrickson et al. showed that *Deinococcus radiodurans* cannot directly reduce certain concentrations of Tc(VII) and U(VI) when AQDS is not present in the reaction system. The reduction of Tc(VII) and U(VI) by *D. radiodurans* can be as high as 95–100 % when 0.1 mmol L^{-1} AQDS was added to the reaction system at concentrations of 5–100 μmol L^{-1} Tc(VII) and U(VI) (Fredrickson et al., 2000a). As the concentration of Tc(VII) and U(VI) increased to 200 μmol L^{-1}, the reduction reaction rate decreased, and the reduction rates of *D. radiodurans* to Tc(VII) and U(VI) were 82 % and 89 %, respectively. This probably stems from the toxic effects of high concentrations of radioactive elements on microorganisms (Fredrickson et al., 2000a). In addition, Gu et al. found that HS not only increases the rate of microbial reduction of U(VI) but also reduces the inhibitory effect of elements such as Ca and Ni on U(VI) reduction (Gu et al., 2005b).

Given that Cd and Pb are non-variable valence heavy metals, the environmental risks of Cd and Pb in soil mainly depend on the composition of the Cd and Pb fractions (Filipović et al., 2018; Yang et al., 2022a; Zulfiqar et al., 2023). The reduction reaction involved in organic matter-mediated electron transfer might indirectly result in the immobilization of Cd and Pb via three pathways, which affects the bioavailability of Cd and Pb (Michálková et al., 2014; Yang et al., 2022b; Yuan et al., 2021). First, soil pH might be affected by organic matter when it serves as an electron donor in microbiologically mediated reduction reactions in soil. For example, the microbial reduction of Fe(III), Mn(IV),

and SO_4^{2-} to Fe(II), Mn(II), and H_2S, respectively, consumes protons and leads to an increase in soil pH, which promotes the formation of precipitates of Cd and Pb (Yuan et al., 2019, 2021). Second, the secondary iron minerals formed during iron reduction fix Cd and Pb by adsorption and co-precipitation. Luo et al. demonstrated that Cd can be re-adsorbed onto newly formed vivianite or incorporated into vivianite structures to increase the proportion of residual Cd during the HA- and FA-mediated microbial reduction of ferrihydrite (Luo et al., 2023). Zhou et al. found that organic matter can inhibit ferrihydrite transformation and limit Cd release, which favors the long-term stability of associated Cd in a reducing environment (Zhou et al., 2020). Finally, organic matter-mediated electron transfer processes promote the production of the sulfate reduction product H2S, which reacts with Cd and Pb to form insoluble CdS and PbS precipitates (Fulda et al., 2013). Among the three pathways of Cd and Pb immobilization by organic matter-mediated electron transfer, pH change had the strongest effect on Cd and Pb adsorption, followed by Fe reduction, and sulfate reduction, which had a weak effect on soil Cd and Pb fixation (Wang et al., 2019b; Yuan et al., 2019).

However, organic matter-mediated reduction reactions may have a negative effect on the As remediation process. Inorganic arsenate (As (V)) and arsenite (As(III)) are the two main forms of As present in the soil environment, and As(III) is more mobile and toxic (Cubadda et al., 2017; Kumarathilaka et al., 2018; Oremland and Stolz, 2003). Organic matter-mediated electron transfer has a significant reducing effect on As(V), which contributes to its conversion to As(III) (Palmer et al., 2006; Tongesayi and Smart, 2006). Palmer et al. found that the reduction of arsenate by HA can be as high as 20–60 % (Palmer et al., 2006). Yamamura et al. showed that AQDS and flavin are common exogenous and endogenous electron shuttles, respectively, and that both compounds significantly enhance As(V) reduction (Yamamura et al., 2017). In addition, the reduction of iron minerals is accelerated when organic matter acts as an electron shuttle. This process may release As adsorbed on the surface of iron minerals, which increases the biological effectiveness of As as well as its environmental risks (Hwang et al., 2014; Qiao et al., 2019). This was confirmed by the study of Hwang et al. After 52 days of reaction with AQDS, an electron shuttle for As/Pb-contaminated soil, approximately 2000 mg L^{-1} Fe(III) was reduced in the reaction system, whereas approximately 500 mg L^{-1} As(V) was reduced to As(III) and released into the reaction system (Hwang et al., 2014).

4. Factors affecting organic matter-mediated electron transfer

4.1. Structure and content of organic matter

The aromaticity, type of substituent, and position of the organic matter are the main factors affecting their electron transfer capacity. The electron transfer capacity of organic matter depends on its aromaticity (Klüpfel et al., 2014; Ratasuk and Nanny, 2007). Electron accepting capacity (EAC) and electron donating capacity (EDC) are positively correlated with the content of quinone and phenol groups in organic matter, respectively (Nurmi and Tratnyek, 2002; Tan et al., 2017; Zhang et al., 2019b). Soil HS are more aromatic due to their relatively complex structure compared with aquatic HS. Furthermore, soil humus has a higher content of precursors (lignin) than aqueous humus. Lignin has a high content of quinone groups and a low content of phenolic groups (Argyropoulos and Zhang, 1998; Peretyazhko and Sposito, 2006). These structural differences result in soil humus with high EAC and low EDC (Aeschbacher, 2011; Klüpfel et al., 2014). He et al. found that increasing the fulvic-like and humic-like substance content, oxygenated aliphatic carbon content, lignin-derived aromatic carbon content, molecular weight, and the N and S content of DOM increased its electron transfer capacity (He et al., 2014). HS are operationally classified as fulvic acids (FA), humic acids (HA), and humins, which are very different in terms of their chemical properties and molecular structures. FA contains

molecules with lower molecular weights and higher oxygen content, whereas HA contains more polyaromatic hydrocarbons and heterocyclic hydrocarbons (Han et al., 2022). HA and FA from the same source have different electron transfer capacities, and HA has a higher EAC than FA (EAC_{HA} = 920–1960, EAC_{FA} = 490–1050 µmole-g^{-1}) (Klüpfel et al., 2014; Wolf et al., 2009). In addition, the soil organic matter content may also constrain electron transfer and thus affect heavy metal remediation. High concentrations of organic matter and UVC humic acid-like may increase the environmental risk of arsenic by facilitating electron shuttling between bacteria (Gustave et al., 2019). In sum, organic matter with a high degree of aromaticity and a high content of quinone and phenol groups is more capable of electron transfer.

4.2. Soil types

Soil is a heterogeneous multiphase system, and soil type affects the rate of electron transfer reactions. Wang et al. concluded that the microbial-catalyzed electron transfer process in fluvo-aquic soil shows higher removal efficiency of Cr(VI) compared with red soil (Wang et al., 2016). Red soil is rich in electron acceptors (e.g., Fe(III)), and these acceptors compete with Cr(VI) in the reduction process; the high clay content in red soil has a strong adsorption effect on Cr(VI), thus hindering the interaction of Cr(VI) with electron acceptors (Sun et al., 2022). In addition, Zhang et al. evaluated the copper removal efficiency of microbial fuel cells in red soil, black soil, and paddy soil. Paddy soil had the best power generation performance and copper removal efficiency under a micro-electric field (Zhang et al., 2020). Therefore, we suggest that organic matter-mediated electron transfer processes are more capable of removing heavy metals in fluvo-aquic soil and paddy soil.

4.3. Environmental conditions

4.3.1. pH

pH has a major effect on the redox activity of organic matter (Yuan et al., 2014). There is some disagreement regarding the mechanism of the effect of pH on the electron transfer capacity of organic matter. Some studies have found that the rate of heavy metal reduction reactions mediated by organic matter is higher at low pH. Zhilin et al. showed that the reduction rate of Cr(VI) by humus of mineral origin accelerated as the pH decreased, and the reduction ability of the humus was lost when the pH was >9.2 (Zhilin et al., 2004). Gu and Chen showed that the reduction ability of DOM was high at pH 3, and the reduction efficiency of Cr(VI) was negligible when the pH increased to 7, which mainly stemmed from the change in the Cr form in the solution under neutral conditions (Gu and Chen, 2003). By contrast, Bauer et al. obtained the electron transfer capacity of two humic substances between pH 4.5 and 8.0, demonstrating that the electron supply capacity of humic substances increased with pH (Bauer et al., 2007). This conclusion was confirmed by Struyk et al. The electron transfer capacity of humic acids from three different sources was determined at 25 °C and pH 5 and 7. The results showed that the oxidizing capacity of HA ranged from 1.09 to 6.5 molc kg^{-1} at pH 5 and from 3.3 to 11.5 molc kg^{-1} at pH 7 (Struyk and Sposito, 2001). The relationship between pH and the electron transfer capacity of organic matter is affected by the source and composition of the organic matter. We hypothesize that there are two main reasons for this phenomenon. First, pH affects the redox potential of heavy metal redox electron pairs, which directly affects the ease of electron transfer from organic matter. Second, the redox groups and aromatic components of organic matter change with increasing pH, thus affecting the reducing capacity of the organic matter.

4.3.2. Redox potential

Organic matter functions as an electron shuttle within a specific redox potential range. The redox potential range in the environment determines the role that organic matter plays in the electron transfer

process. For organic matter to participate in the reaction, the redox potential of the reducing state of organic matter must be lower than that of the pollutant. The electron shuttle can be re-reduced by microorganisms after oxidation by the pollutant (Klüpfel, 2009). This reversible electron transfer capacity of organic matter thus plays a key role in the continuous redox cycle (Childers et al., 2002).

4.3.3. Oxygen conditions

Generally, the microbial reduction of heavy metals by organic matter-mediated electron transfer occurs under anaerobic conditions. This is because molecular oxygen has a higher redox potential than most organic matter and acts preferentially as an electron acceptor (Yuan et al., 2014). Therefore, a high oxygen content will inhibit the reduction of heavy metals by organic matter-mediated electron transfer. However, reducing functional groups are present in HS in the presence of oxygen. This means that even in the presence of oxygen, some of the reducing groups of HS tend to mediate electron transfer and thus the reduction of heavy metals (Bauer and Kappler, 2009; Visser, 1964). This conclusion was demonstrated by Zhilin et al. who showed that humic samples from both limonite and peat reduced hexavalent chromium under acidic aerobic conditions (Zhilin et al., 2004).

4.3.4. Temperature

Temperature is also an important factor that affects the electrons in organic matter. The increase in temperature is favorable to the reaction. Tan et al. reported that increased temperature promotes the oxidative degradation and transformation of HS in soil, thus potentially facilitating the transformation of electron donor phenol molecules and electron acceptor quinone molecules in the structure of HS, which ultimately improves the EAC of HS (Tan et al., 2017). Wittbrodt et al. investigated the temperature dependence of Cr (VI) reduction by HS. Reactions were conducted with the temperature of 277–328 K at pH 2.0, the increase in temperature greatly accelerated the rate of Cr(VI) reduction by HS (Wittbrodt and Palmer, 1996).

4.4. Heavy metal concentrations and species

High concentrations of heavy metals may have toxic effects on microorganisms, which constrains heavy metal reduction by microorganisms (Liu et al., 2016; Meng et al., 2018). In general, soil microbial metabolic activity was inhibited at Cr(VI) concentrations >200 mg kg^{-1} in soil (Jeyasingh and Philip, 2005). The intermediate *Ochrobactrum intermedium* BCR400 isolated by Kavita and Keharia from chromium-contaminated soil completely reduced Cr(VI) within 52 h, with an initial reduction rate of 1.98 mg (L h)$^{-1}$ at a cadmium concentration of 100 mg L^{-1}. As the concentration of Cr(VI) increased from 100 mg L^{-1} to 500 mg L^{-1}, the reduction rate of Cr(VI) decreased significantly (Kavita and Keharia, 2012). Mohamed et al. investigated the kinetics and mechanism of Cr(VI) reduction in the presence of HA using *S. oneidensis* Mr-1. The rate of Cr(VI) reduction by Mr-1 decreased significantly as the initial chromate concentration increased. At an initial Cr(VI) concentration of 0.5 mmol L^{-1}, Cr(VI) was completely reduced by Mr-1 within 1 h. At initial Cr(VI) concentrations of 1.0, 1.5, and 2.0 mmol L^{-1}, Mr-1 reduced to 65 %, 42 %, and 29 % of the total Cr(VI) after 8 h, respectively (Mohamed et al., 2020). Therefore, organic matter-mediated microbial reduction processes are more suitable for the ecological remediation of sites contaminated with low concentrations of heavy metals. In addition, heavy metal species also affected the reduction reaction mediated by organic matter. The microbial reduction of U(VI) by NOM fractions was found to be very slow under the same conditions as used for the bioreduction of Cr(VI) (Gu and Chen, 2003).

5. Conclusion and perspectives

Industrialization and modernization accelerate heavy metal pollution in the soil environment, and this poses a major threat to human and

soil health. Electroactive microorganisms achieve synergy between their growth and heavy metal remediation while releasing electrons through extracellular respiration. Electron shuttles mediate electron transfer over longer distances and more efficiently than cytochrome and nanowire pathways. Organic matter is an important electron shuttle in the soil environment, and its ability to mediate electron transfer plays a key role in the remediation of heavy metal-contaminated soil. Some of its advantages include its cleanliness, safety, and low cost. It is found that organic matter-mediated soil redox reaction promotes the transformation of heavy metals such as Cr (VI), Hg (II), V (V), U (VI), and Tc (VII) from their unstable and highly toxic oxidation forms to relatively insoluble and less toxic reduction forms, which inhibits the migration of the heavy metals and significantly accelerates the remediation of various toxic heavy metals and radioactive elements. For example, organic matter can lead to a 100 % microbial reduction efficiency of Cr (VI), which contributes to a 2- to 40-fold increase in the rate of Cr(VI) reduction. The structure and content of organic matter, soil type, heavy metal concentration, and environmental factors such as pH, redox potential, temperature, and oxygen conditions are the main factors affecting the electron transfer of organic matter. Specifically, a suitable redox potential is essential for the effectiveness of organic matter as an electron shuttle. Organic matter with a high aromaticity, quinone group, and phenol group can effectively mediate electron transfer. Under anaerobic conditions, organic matter has a greater opportunity to participate in the electron transfer process as an electron acceptor. Organic matter is more equipped to mediate electron transfer conditions in fluvo-aquic/paddy soils than in red soil and black soil. In addition, high concentrations of heavy metals reduce extracellular electron production by inhibiting the metabolism of electroactive microorganisms. Analysis of the mechanisms underlying the interactions between organic matter and heavy metals is important for ensuring the efficient remediation and biogeochemical cycling of heavy metals. However, the following research topics relating to organic matter and heavy metals have yet to be investigated.

(1) The reversible electron transfer capacity of organic matter as shuttles is the key to the continuous redox cycle. Quantitative descriptions of the ability of organic matter to act as an electron shuttle are still lacking. In addition, the electron shuttle may be adsorbed by soil particles or degraded by microorganisms during release and diffusion. Therefore, the quantification of the electron shuttle cycling capacity is important for furthering our understanding of organic matter-mediated heavy metal remediation processes in the natural environment.
(2) Most studies to date have examined organic matter-mediated electron transfer-coupled heavy metal reduction using indoor experiments. However, research on the extent of organic matter-mediated remediation of heavy metals in natural soil environments is lacking.
(3) Organic matter-mediated redox reactions of heavy metals are significantly affected by variations in the source, composition, structure, and properties of organic matter. A large number of studies have focused on the role of individual components of organic matter (e.g., HA, FA) in heavy metal remediation. However, soil organic matter is a complex system comprising various subcomponents. Therefore, more studies are required to clarify how the mechanisms observed in contaminated sites explain the results of previous studies. To elucidate the mechanisms by which organic matter participates in heavy metal remediation, the interactive effects of various subcomponents of organic matter on heavy metal remediation require further study.
(4) Heavy metal remediation processes involving organic matter do not only include redox reactions due to electron transfer. Meanwhile, organic matter is rich in reactive functional groups, and the processes of complexation, chelation, and adsorption in which it is directly involved are also important pathways that

affect the speciation and bioavailability of heavy metals. Thus, clarifying the interrelationships between the reactions and revealing the extent to which organic matter-mediated redox reactions affect their participation in the overall reaction is important for enhancing the efficiency of the remediation of soil heavy metal pollution.
(5) Previous major reports on the factors influencing organic matter-mediated electron transfer have examined only a single or very few factors, and the process descriptions show a certain degree of fragmentation. However, the combination and interaction of multiple factors are the actual factors affecting the organic matter-mediated electron transfer in the soil environment. The impact of this process on heavy metal remediation is more than worth exploring, and the details related to the mechanism of impact should also be given further attention.

CRediT authorship contribution statement

Bing Kou: Writing – review & editing, Writing – original draft, Visualization, Conceptualization. **Ying Yuan:** Writing – review & editing, Supervision, Project administration, Funding acquisition. **Xiaoli Zhu:** Writing – original draft, Visualization, Resources, Investigation. **Yuxin Ke:** Writing – review & editing, Resources. **Hui Wang:** Writing – review & editing, Resources. **Tingqiao Yu:** Writing – review & editing. **Wenbing Tan:** Writing – review & editing.

Declaration of competing interest

The authors declare no competing interests.

Data availability

No data was used for the research described in the article.

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Not applicable.

Consent for publication

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