



Review

Geobatteries in environmental biogeochemistry: Electron transfer and utilization

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ABSTRACT

The efficiency of direct electron flow from electron donors to electron acceptors in redox reactions is significantly influenced by the spatial separation of these components. Geobatteries, a class of redox-active substances naturally present in soil–water systems, act as electron reservoirs, reversibly donating, storing, and accepting electrons. This capability allows the temporal and spatial decoupling of redox half-reactions, providing a flexible electron transfer mechanism. In this review, we systematically examine the critical role of geobatteries in influencing electron transfer and utilization in environmental biogeochemical processes. Typical redox-active centers within geobatteries, such as quinone-like moieties, nitrogen- and sulfur-containing groups, and variable-valent metals, possess the potential to repeatedly charge and discharge. Various characterization techniques, ranging from qualitative methods like elemental analysis, imaging, and spectroscopy, to quantitative techniques such as chemical, spectroscopic, and electrochemical methods, have been developed to evaluate this reversible electron transfer capacity. Additionally, current research on the ecological and environmental significance of geobatteries extends beyond natural soil–water systems (e.g., soil carbon cycle) to engineered systems such as water treatment (e.g., nitrogen removal) and waste management (e.g., anaerobic digestion). Despite these advancements, challenges such as the complexity of environmental systems, difficulties in accurately quantifying electron exchange capacity, and scaling-up issues must be addressed to fully unlock their potential. This review underscores both the promise and challenges associated with geobatteries in responding to environmental issues, such as climate change and pollutant transformation. © 2024 The Authors. Published by Elsevier B.V. on behalf of Chinese Society for Environmental Sciences, Harbin Institute of Technology, Chinese Research Academy of Environmental Sciences. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction

Microbe-mediated redox reactions play a critical role in the intricate biogeochemical cycles of various elements in nature, including carbon (C), nitrogen (N), sulfur (S), iron (Fe), arsenic (As), chromium (Cr), and other trace elements that are sensitive to redox dynamics [1]. These reactions typically follow thermodynamic gradients, where microbes extract maximum energy from coupled oxidation and reduction reactions to sustain life [2,3]. Following

electron transfer from electron donors to the electron transport chain within cell membranes, microbes deliver electrons to extracellular terminal electron acceptors via a network of redox and structural proteins. This process constitutes the extracellular electron transfer process [4,5]. However, in the complex environmental landscape, electron donors and acceptors are not physically close or readily accessible in all cases. This spatial separation frequently leads to inefficient or inhibited microbial extracellular electron transfer processes.

Certain microbes have evolved to use extracellular electron mediators, such as geoconductors and geobatteries, to facilitate long-distance electron transfer. These mediators also drive electron transfer between different microbial species. In redox reactions, geoconductors (e.g., Fe oxides and carbon cloth) act as electron conduits to accelerate electron flow, given their high conductivity

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Abbreviations

NOM	Natural organic matter
PyC	Pyrogenic carbon
MMPs	Mixed-valent mineral phases
EAC	Electron-accepting capacity
EDC	Electron-donating capacity
EEC	Electron exchange capacity
CH ₄	Methane
CO ₂	Carbon dioxide
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
XRFI	X-ray fluorescence imaging
AFM	Atomic force microscope
XPS	X-ray photoelectron spectroscopy
AD	Anaerobic digestion

[6]. Differently, geobatteries refer to redox-active substances that function as intermediate electron carriers or reservoirs, bridging electron-releasing microbes with other terminal electron acceptors or microbes that are electrically and physically separated [5]. These substances include natural organic matter (NOM), pyrogenic carbon (PyC), mixed-valence mineral phases (MMPs), and even microplastics [7–10]. Modifications in electron flow pathways and utilization efficiencies by geobatteries inevitably affect the biogeochemical cycle and fate of elements. As a result, potential routes are created for environmental remediation strategies.

The redox activity inherent in a geobattery within nature can be activated and sustained through redox oscillations. These oscillations can be influenced by dynamic hydrological fluctuations, such as periodical water table fluctuations and tidal phenomena, particularly observed in intermittently anoxic soil systems [11,12]. Furthermore, the redox activity of specific geobatteries, such as PyC, can be enhanced through various modification technologies, including functional group modulation and the integration of conductive materials [13]. For instance, precise control of PyC's pyrolysis temperature within the low–medium range ensures the retention of abundant reversible redox-active functional groups. Consequently, its electron-accepting (EAC) and electron-donating capacities (EDC) are augmented [14,15]. Additionally, the coating of green rust [16] and magnetite [17], functioning as mixed-valence conductive Fe-containing minerals, improves the electron transfer capacity of geobatteries. To date, geobatteries have exerted significant impacts across diverse scientific domains, particularly in climate change mitigation [18–20], water and soil remediation [9,21–23], and waste management [17,24].

Considering the sustainable redox activity of geobatteries under natural conditions and their potential to be improved and tailored to maximize electron transfer efficiency in biogeochemical processes, this could broaden their environmental applications. However, our current understanding of geobattery-mediated electron transfer remains incomplete. Peiffer et al. [8] pioneered exploring how redox-active compounds impact the elemental biogeochemical cycle in hydrologically disturbed aquatic systems. Other studies also focused on individual geobattery components, such as PyC [25,26] and NOM [27], and their redox activity and environmental applications. However, a comprehensive review of these typical geobatteries remains insufficient. Thus, we address this gap and develop a comprehensive understanding of potential geobattery applications. Accordingly, this review presents the electron transfer mechanisms and characterization techniques of typical geobatteries and their current applications and latent prospects.

2. The geobattery concept

The concept of geobattery originates from geophysics and was

first introduced by Sato and Mooney in 1960 [28]. The term was initially used to describe self-potential anomalies in mineral exploration. Ore bodies, such as pyrite and graphite, serve as electron conductors, connecting deep anaerobic zones with shallow aerobic zones, resulting in upward electron flow. Subsequently, redox-related self-potential anomalies were observed in plumes of organic-rich contaminants. To explain this phenomenon, Revil and colleagues [29–33] proposed the concept of biogeobattery and defined conductors as bacterial biofilms and/or conductive minerals across redox gradients.

In 2021, Peiffer et al. [8] redefined the concept of biogeobattery in environmental science (Fig. 1). They characterized the concept as a series of redox-active substances with a wide range of redox potentials. These substances can store electrons from electron donors when other electron acceptors are not readily available and then donate them to other electron acceptors or microbes when conditions change [5]. They can reversibly accept, store, and donate electrons to promote electron flow in biogeochemical redox processes with minimal chemical composition and structure changes. This definition can be traced back to the work of Ratasuk and Nanny [34] in 2007, who discovered the potential for reversible electron transfer within NOM through abiotic pathways. Building on this concept, Klüpfel et al. [35] demonstrated that surface functional groups of NOM can play a key role in reversibly transferring electrons through biological pathways. Subsequent studies have successively unveiled the redox activity of PyC [36,37], MMPs [38,39], and microplastics [22] (Fig. 1). In this review, we refer to these redox-active substances as geobatteries, aligning with most of the literature [9,16,21,40,41]. It is worth noting that geobatteries naturally exist in soil–water systems and have been intentionally introduced into natural ecosystems (e.g., rice paddies) and engineered systems (e.g., wastewater treatment).

3. Electron transfer mechanisms of geobatteries

3.1. Natural organic matter

As the main redox-active component of terrestrial and aquatic ecosystems, NOM exhibits various redox potentials (from +150 to –300 mV at pH 7.0). This characteristic is due to the inclusion of different types, amounts, and redox states of redox-active functional groups. Thus, NOM often participates in redox reactions as an electron acceptor or donor [27,42]. Particularly, quinones or quinone-like moieties are the most common reversible redox-active functional groups within NOM molecules, and their redox cycling can account for more than 50% of the electron transfer capacity of NOM [43]. The repeatable charging/discharging property of quinones is mainly attributed to the resonance stabilization of semiquinone radical intermediates [44,45] (Fig. 2). Specifically, the π -electrons within the intermediate semiquinone are delocalized, that is, unpaired electrons are distributed on the ring structure rather than concentrated on a single atom. This structure reduces the system energy and allows quinone compounds to switch easily between oxidation and reduction states [46]. This property positions NOM as a classical geobattery with a reversible and sustainable electron transfer capacity, continuously participating in redox reactions as regenerated electron acceptors or donors [35,47].

The potential role of other non-quinone moieties in reversible redox reactions, such as organically bound S and N, should not be overlooked. Although NOM contains low S content (0.03–0.8 mol kg⁻¹) [48], diverse S-containing groups can be involved in redox reactions as potential electron acceptors (e.g., disulfide (0), sulfoxide (+2), and sulfone (+4)) or electron donors (e.g., thioether (–2) and thiols (–1)) [49]. The thiol group can also contribute up to 58% EDC of NOM [50]. Theoretically, the reversible

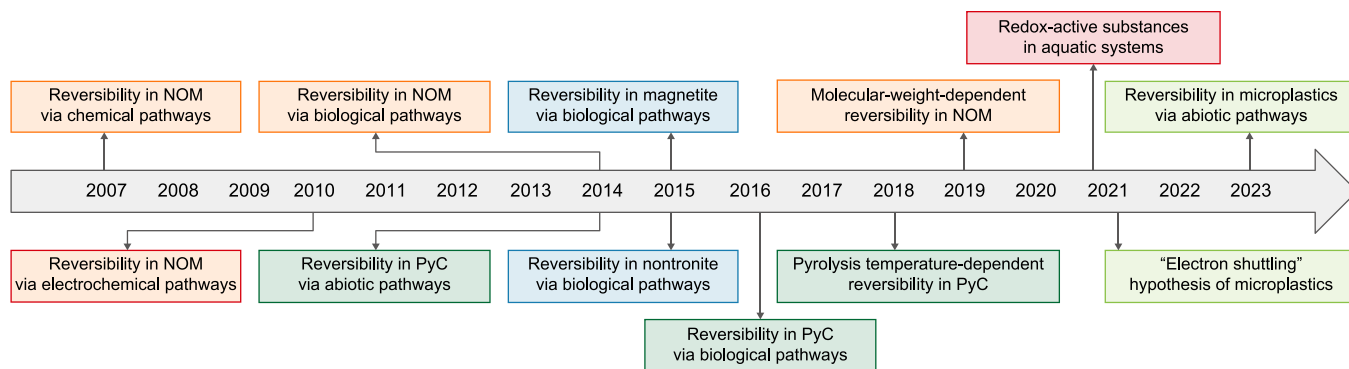


Fig. 1. Timeline of relevant research on the redox activity of geobatteries in the field of environmental science. Geobattery milestone: redox-active substances in aquatic systems proposed in 2021 with a red background [8]. Time points of natural organic matter (NOM) in 2007 [34], 2010 [99], 2014 [35], and 2019 [58] with orange backgrounds. Time points of pyrogenic carbon (PyC) in 2014 [36], 2016 [37], and 2018 [14] with dark green backgrounds. Time points of mixed-valent mineral phases (MMPs) in 2015 [38,39] with a blue background. Time points of microplastics in 2021 [173] and 2023 [22] with light green backgrounds.

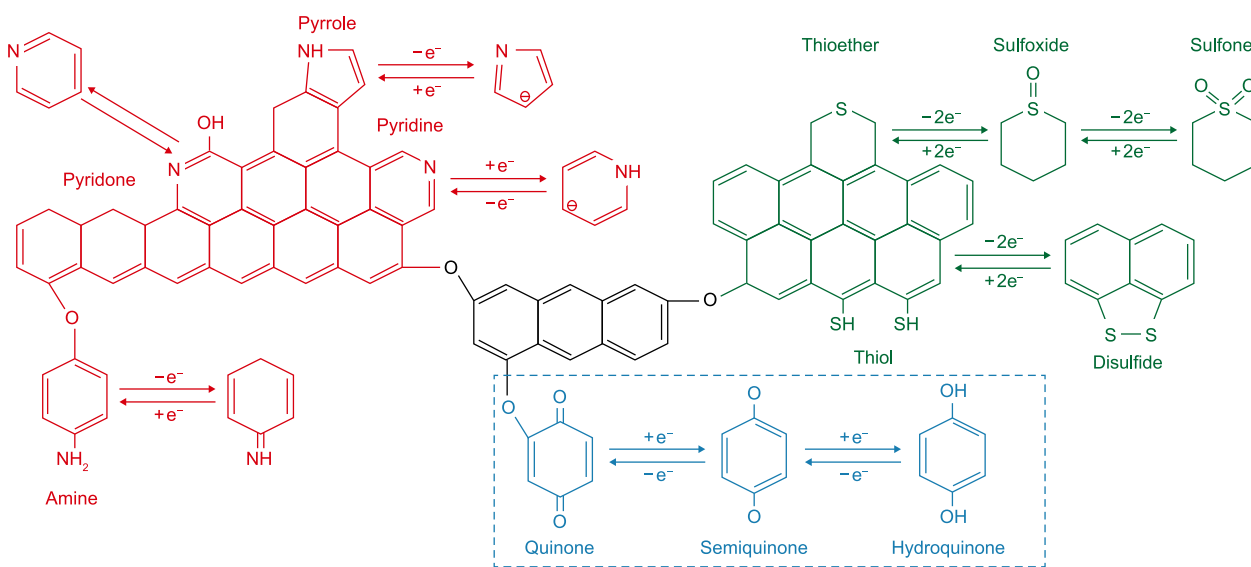


Fig. 2. The potential reversible redox reaction in natural organic matter (NOM).

redox reactions can occur between thioethers, sulfoxides, and sulfones [49,51] or between thiols, disulfides, and sulfoxides [34,52] (Fig. 2). This process is exemplified by the thiol/disulfide redox cycle that plays an important role in the regulation of the activity of many enzymes and proteins [53].

N-containing functional groups with multiple valence states (e.g., amine, amide, and heterocyclic nitrogen) have also been suggested as potential redox-active centers in NOM [49,54,55] (Fig. 2). However, investigations involving various N-containing model compounds revealed constrained electron transfer capacity [50]. This limitation can be attributed to the inherent instability of amine and amide N under environmental conditions (e.g., temperature, pH levels, presence of oxidizing agents, and humidity) and the relatively low concentration of heterocyclic N [45].

Notably, the compositional and chemical variations of NOM resulting from differences in age, geographical origin, and local climate conditions make it difficult to define a uniform molecular structure with molecular weights ranging from a few hundred to several million Daltons [56]. Thus, NOM exhibits different quantities of redox-active functional groups. For example, low-molecular-weight NOM can possess up to 27 times quinone-like functional

groups of bulk NOM. This molecular characteristic imparts low-molecular-weight NOM with an EAC of nearly 27 times greater than that of bulk NOM [57]. Furthermore, the proportion of redox-active functional groups involved in reversible redox reactions has shown a negative correlation with the average molecular weight of NOM. The complex spatial structure of large molecular sizes may mask specific redox-active functional groups, hindering their electron transfer capacity [58].

3.2. Pyrogenic carbon

PyC is a broad continuum with different reactivities ranging from slightly charred biomass to soot and microcrystalline graphite via incomplete combustion of organic matter [59,60]. PyC in soil–water systems can originate from different scenarios, such as wildfires [61], prescribed/controlled burnings [62], and anthropogenic applications for environmental management [63]. Here, certain typical carbon-based materials commonly recognized as geobatteries, including biochar [19], black carbon [64], and activated carbon [21], are products of natural or anthropogenic pyrolysis processes, hence collectively referred to as PyC. Similar to

NOM, quinone-like moieties constitute the main redox-active functional groups within PyC. These oxygen-containing functional groups in PyC predominantly result from the thermally induced transformation of lignin and cellulose [26]. This process stands in contrast to NOM, where the origin traces back to precursor biomolecules or emerges during diagenesis through an array of abiotic and biotic reactions transpiring at low temperatures [65]. In addition to the well-known quinone/hydroquinone pairs, other potentially reversible redox-active functional groups in PyC include anhydride [66], pyridinium [67,68], and phosphorus-containing functional groups [69]. Moreover, hydroxyl/carboxyl pairs on the branched carbon chain demonstrate the capacity for quasi-reversible redox reactions [70].

The geobattery function of PyC is most apparent within the domain of low–medium carbonization temperatures, typified below 650 °C [14,71]. At this temperature level, the charging and discharging of redox-active functional groups can contribute more than 78% of the total electron transfer in PyC [14]. However, as the carbonization temperature and duration increase, coupled with a slow heating rate, the amount of redox-active functional groups within PyC reduces. In parallel, the conjugated π -electron system bound to the condensation aromatic structure gradually forms and accumulates. This accumulation gradually gives rise to a graphite-like sheet structure, fostering the generation of a multitude of delocalized free electrons [71]. As a result, the electrical conductivity of PyC is enhanced, making it a geoconductor that can facilitate long-range electron transfer to allow delocalized redox reactions between abiotic components or microorganisms [26,72]. The direct electron transfer of PyC prepared at 650–800 °C as a geoconductor can account for above 87% of the total electron transfer [14]. The geoconductor and geobattery mechanisms in PyC-mediated redox reactions differ because the oxidation of reductants and reduction of oxidants mediated by the geoconductor mechanism occur simultaneously through electron transfer via the graphite-like sheet structure. In contrast, the electron storage function of the geobattery mechanism can enable the temporal and spatial decoupling of the redox half-reactions (Fig. 3).

Apart from temperature effects, feedstock differences, such as variations in biomass composition [73] and mineral content [49], also affect PyC's redox activity. However, establishing a general rule is challenging because results under different experimental conditions are difficult to compare. Additionally, various modification strategies have been employed to improve PyC's redox activity, such as chemical oxidation (e.g., nitric acid oxidation and hydrogen peroxide oxidation) [74,75], loading metals (e.g., Fe and manganese [Mn]) [76], and physical modifications (e.g., ball milling) [77]. For detailed information, refer to Zhou et al.'s review [78].

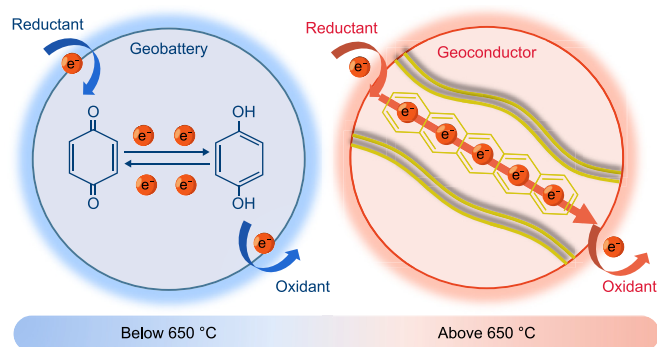


Fig. 3. Electron transfer mechanisms of geobattery and geoconductor in pyrogenic carbon (PyC).

3.3. Mixed-valent mineral phases

MMPs contain electroactive groups in at least two redox states, for example, Fe(II)/Fe(III) pairs in magnetite, green rust, and nontronite, Mn(II)/Mn(III) pairs in hausmannite, and Mn(III)/Mn(IV) pairs in birnessite [79]. Mobile charges can rapidly migrate between groups in different redox states, facilitated by intracrystalline electron hopping [10,80,81]. This property can endow MMPs with high electrical conductivity [82], enabling them to act as geoconductors and promote extracellular and intercellular electron transfer [5]. Electroactive groups in different redox states also allow MMPs to donate or accept electrons as geobatteries in the microbe-mediated redox cycle. Under oxic conditions, low-valent metal elements, for example, Fe(II) and Mn(II), in MMPs can serve as electron donors, whereas microbes fix carbon dioxide as an electron sink. Under anoxic conditions, the microbial reduction of high-valent metal elements, for example, Fe(III) and Mn(IV), in MMPs can act as an electron sink, whereas the microbial oxidation of organic matter functions as an electron source. Subsequently, the microbial oxidation of low-valent metal elements within MMPs can also serve as an electron source, with the microbial reduction of alternative electron acceptors (e.g., NO_3^- , SO_4^{2-} , As(V), and Cr(VI)) serving as an electron sink [38,83,84] (Fig. 4).

Specific MMPs, such as magnetite, can achieve their geobattery function through a discharge process during oxidation by the phototrophic Fe(II)-oxidizing bacterium *Rhodospseudomonas palustris* TIE-1. Subsequently, a charging process follows during reduction by the anaerobic Fe(III)-reducing bacterium *Geobacter sulfurreducens* [38]. Similarly, the reversible biological redox cycling of structural Fe in nontronite was demonstrated by coupling dissimilatory Fe(III)-reducing bacterium and nitrate-dependent Fe(II)-oxidizing bacterium [39]. Furthermore, after short-term oxidation, the structural Fe(II) in nontronite can also be regenerated during the subsequent anoxic phase by electron transfer from Fe(II) at the interior sites to Fe(III) at the edge sites without any exogenous electron acceptors [85]. Compared with magnetite and nontronite, green rust possesses higher contents of available surface Fe(II) and a weaker Fe(II) bonding environment, making it more reactive and susceptible to rapid oxidation in natural environments [81].

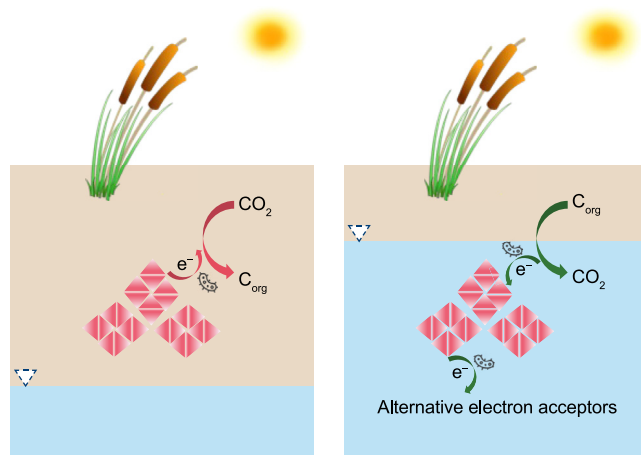


Fig. 4. Electron transfer mechanisms of mixed-valent mineral phases (MMPs) as geobatteries in soil–water systems. Adapted from Kappler et al. [84]. Copyright 2023. MSA Publication.

4. Redox-activity characterization in geobatteries

Various methodologies have emerged to characterize the redox activity in geobatteries (Fig. 5). Conventional qualitative techniques, including elemental analysis and spectroscopy, rapidly assess whether the target substance exhibits reversible electron transfer capabilities. Simultaneously, imaging techniques are deployed to pinpoint potential redox-active centers. Quantitative approaches, such as chemical, spectroscopic, and electrochemical methods, are employed to determine precisely the electron exchange capacity (EEC) of geobatteries. However, the aforementioned analytical methods are mainly conducted under laboratory conditions, with no apparent attempts at in situ measurement in the environment.

4.1. Qualitative characterization

To characterize qualitatively the redox activity in specific geobatteries such as PyC, elemental analysis serves as a rapid tool in determining the primary electron transfer pathway. The dominance of charging and discharging cycles of redox-active moieties is observed when the H/C and O/C molar ratios exceed 0.35 and 0.09, respectively. This dominance is observed over direct electron transfer driven by carbon matrices for PyC-related redox reactions [72].

The porous structure and large specific surface area of PyC can, however, pose challenges to identifying redox-active moieties accurately. Microbial accessibility to these moieties becomes crucial in influencing PyC-driven redox kinetics. Various imaging techniques, such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray fluorescence imaging (XRFI), and atomic force microscope (AFM), have been employed to localize these redox-active moieties. For example, the tracer Ag^+ was first dispersed in the fully reduced PyC to react with stored electrons, generating Ag^0 nanoparticles. Subsequently, SEM and TEM respectively revealed the densely covered nanoparticles on the PyC

surface and those dispersed within its structure (at a depth of ~500 nm from the surface) [86]. Similarly, the application of confocal micro-XRFI supplemented with micro-X-ray absorption near-edge structure and X-ray photoelectron spectroscopy (XPS) can map depth-dependent redox-active moieties within PyC (at a depth of ~250 μm from the surface) using Cr(VI) as a marker [87]. Additionally, conductive AFM enables simultaneous nanoscale physical and electrical property observations of PyC without markers, offering the potential to establish a direct link between the structure and redox-active moieties of PyC [88]. The conductive AFM, equipped with a conductive nanoscale probe tip, allows the acquisition of sample morphology by measuring the interaction force between the probe and sample surface and determining electrical properties by applying a voltage between the probe and sample surface.

On the spectroscopic front, Fourier transform infrared spectroscopy, XPS, synchrotron-based near-edge X-ray absorption fine structure, and ^{13}C nuclear magnetic resonance have been employed to discern reversible electron transfer pathways qualitatively by identifying redox-active moieties in organic geobatteries, such as PyC and NOM. The phenolic-OH group and quinoid C=O group emerge as the fully reduced and oxidized forms of the quinone moiety, playing a crucial role in the EDC and EAC of organic geobatteries, respectively [89]. In this context, identifying these functional groups becomes critical for recognizing the redox activity of geobatteries (Supplementary Material Tables S1–S4).

For inorganic geobatteries, that is, MMPs, spectroscopy is an important tool in analyzing their redox activity and associated electron transfer processes. For instance, when considering Fe-containing minerals, Mössbauer spectroscopy is a powerful technique for differentiating Fe(II) and Fe(III) and identifying their local coordination environment in these minerals [90]. This method helps to determine non-destructively the Fe(II)/Fe(III) ratio and characterize the degree of electron transfer during redox reactions within the mineral lattice [83]. Fe K-edge X-ray absorption spectroscopy is another useful tool for studying the electronic structure of Fe-containing minerals. It provides information about the oxidation state and coordination environment of structural Fe during redox reactions [91]. Additionally, XPS has been employed to determine the relative abundance of Fe(II) and Fe(III) species in Fe-containing minerals by measuring the binding energies of core electrons. However, its effectiveness is constrained by the detection depth and is limited to characterizing Fe in the near-surface region [83].

4.2. Quantitative characterization

Redox activities in geobatteries can be determined through chemical, spectroscopic, and electrochemical methods. The Boehm titration is a chemical approach that assesses acidic oxygen-containing functional groups in PyC, involving neutralization reactions with different bases. They include NaHCO_3 for carboxyls, Na_2CO_3 for carboxyls and lactones, and NaOH for carboxyls, lactones, and phenols [92]. This method provides a rough estimate of redox-active moieties, such as quinones and hydroquinones [25]. Moreover, redox titration with paired chemical reductants (e.g., titanium(III) citrate, dithionite, hydrogen sulfide, and metallic zinc) and oxidants (e.g., ferricyanide and dissolved oxygen) can measure the EAC and EDC of geobatteries [64,65,93,94]. The EEC reversibility of geobatteries can be further determined by the multiple redox cycles of reductant-oxidants.

Redox-active carbonyl groups (i.e., aromatic ketones/aldehydes and quinones) in NOM have been quantified by applying the fluorescence burst method. This method operates on the principle that the fluorescent signal experiences attenuation or bursts when the

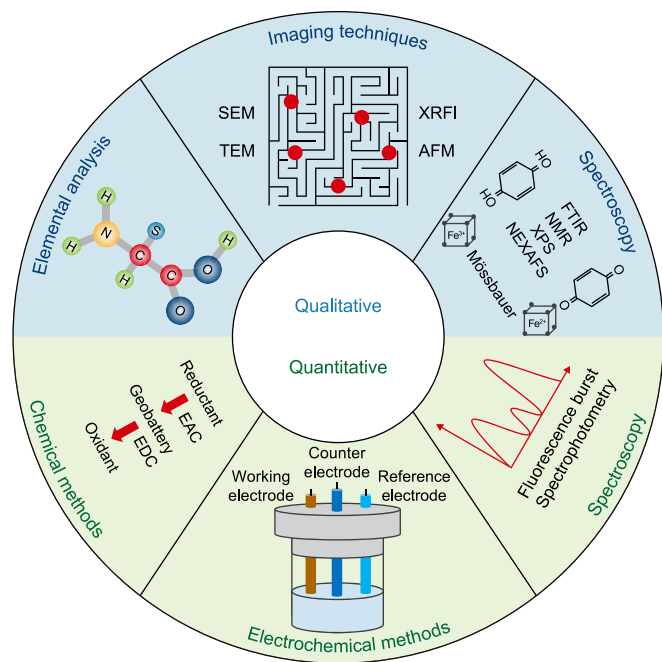


Fig. 5. Characterization techniques for redox activity of geobatteries. FTIR: Fourier transform infrared spectroscopy; NMR: Nuclear magnetic resonance; NEXAFS: Synchrotron-based near-edge X-ray absorption fine structure.

fluorophore interacts with specific molecules. For example, carbon quantum dots are introduced into pristine NOM, followed by complete reduction utilizing sodium borohydride. Then, the concentration of carbonyls is quantified by evaluating the degree to which the fluorescence intensity is restored in carbon quantum dots that were initially quenched by NOM [95]. Spectrophotometry can also be employed to quantify the electron transfer capacity of geobatteries. For instance, peat-derived NOM can be reacted with the reducing substance of the probe compound 4,4'-bipyridinium-1,1'-bis(2-ethylsulfonate), and its EAC is subsequently quantified by spectrophotometrically determining the concentration changes of the reducing substance [96].

Compared with purely chemical and spectroscopic methods, electrochemical methods are preferred due to their relatively higher sensitivity, accuracy, and real-time performance for assessing the redox activity of geobatteries. Electrochemical measurements involve subjecting geobatteries to controlled electrochemical conditions and monitoring the resulting current (i.e., amperometric techniques) or potential responses (i.e., potentiometric techniques). Amperometric techniques, including potentiodynamic (e.g., cyclic voltammetry) and constant potential techniques (e.g., chronoamperometry), have been widely employed to quantify EDC and EAC of NOM [97], PyC [25], and MMPs [98].

A typical electrochemical device involves a three-electrode system consisting of a glassy carbon working electrode, an Ag/AgCl, and an auxiliary electrode [99]. In the case of PyC, a four-electrode system is used to distinguish the geobattery and geoconductor behaviors of PyC, specifically by introducing a platinum working electrode [14]. Furthermore, direct electrochemical analysis, which relies on the direct physical contact between the analyte and the working electrode, may suffer from slow electron exchange kinetics, thus limiting sensitivity and accuracy. To overcome this issue, mediated electrochemical analysis employs dissolved redox mediators (e.g., diquat and ethylviologen) to facilitate electron transfer and redox equilibrium between the working electrode and geobattery in the electrochemical cell [36,99,100].

5. Environmental significance of geobatteries

5.1. Soil carbon cycle

The decomposition of soil organic carbon is critical in regulating global carbon cycle and climate change. Theoretically, microbial anaerobic respiration preferentially transfers electrons from organic carbon (electron donor) to various alternative electron acceptors (e.g., NO_3^- , Fe(III), Mn(IV), SO_4^{2-} , NOM, and PyC) that maximize chemical energy production, resulting in the release of carbon dioxide (CO_2). After depletion of the alternative electron acceptor pool, methane (CH_4) production occurs as the final step in organic carbon decomposition, implying that methanogenesis is competitively suppressed by the anaerobic CO_2 production.

Hydrological fluctuations can regulate alternative electron acceptor availability by changing soil redox conditions. In typical CH_4 -producing environments, such as peatlands [35,101], rice paddies [19,40], and coastal soils [12,102], the water table frequently changes due to periodic rainfall and droughts, extreme climate change-induced events, tidal influences, and human activities, such as drainage and rewetting/irrigation. Fluctuations in water tables below the ground surface signify transitions between anaerobic and aerobic conditions. This redox fluctuation can activate and maintain the dynamic charging and discharging properties of geobatteries, diverting electron and carbon flow away from methanogenesis to anaerobic CO_2 production processes (Fig. 6a). In the case of PyC, its multiple electron transfer mechanisms (including geobattery and geoconductor) can competitively

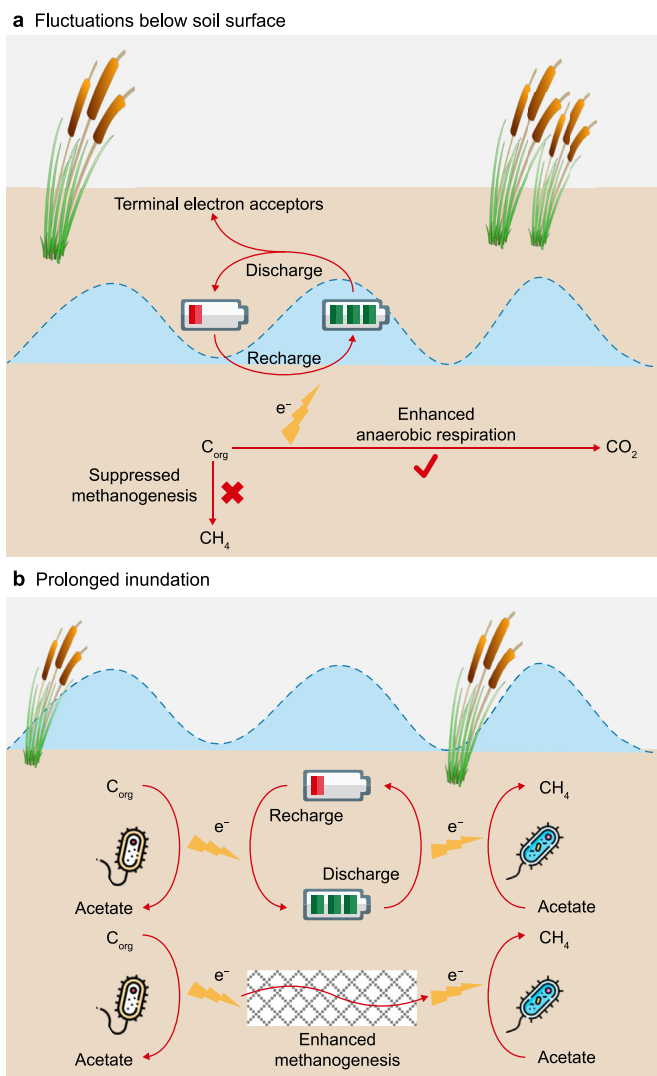


Fig. 6. The potential effect of geobatteries on soil organic carbon degradation. **a.** During natural hydrological fluctuations, they serve as electron acceptors in anaerobic respiration, suppressing methane emissions, or function as electron shuttles to transfer electrons to other alternative electron acceptors. **b.** Under prolonged inundation, especially when thermodynamically favorable alternative electron acceptor depletes, the redox cycling of geobatteries, as well as carbon matrices within pyrogenic carbon (PyC) (grid matrices), can promote direct interspecies electron transfer and thus enhance methane production.

suppress CH_4 production by 13–24% by promoting anaerobic CO_2 production [18]. However, if water levels remain above the ground surface despite fluctuations, continuous inundation occurs (Fig. 6b). Under this prolonged anaerobic conditions or thermodynamically favorable alternative electron acceptor depletion conditions [19], the abundant redox-active functional groups in low/medium-temperature PyC could increase CH_4 production by providing electrons to methanogens via electron-donating groups [40] or by promoting direct interspecific electron transfer between electron-donating microorganisms (e.g., *Geobacteraceae*) and methanogens (e.g., *Methanosarcina*) [20]. Carbon matrices that act as geoconductors in high-temperature PyC also promote this direct electron transfer [19,40].

NOM in peatlands has been repeatedly shown to act as a regenerable alternative electron acceptor for soil alternative microbial respiration, thereby competitively inhibiting CH_4 production [35,47,103,104]. This action is due to redox fluctuations driven

by periodic water table fluctuations or drainage-rewetting activities. The geobattery function of NOM can potentially reduce CH₄ fluxes from northern peatlands by up to 166% [35]. It also partly explains the high CO₂:CH₄ ratios observed in anoxic peat soils [105,106]. Given the higher global warming potential of CH₄ compared with CO₂, methanogenesis suppression can contribute to lowering the overall global warming potential of greenhouse gases emitted from peatlands. However, this NOM-methanogenesis suppression is more likely to be prevalent in ombrotrophic peatlands (i.e., bogs) rather than minerotrophic peatlands (i.e., fens) [101,106]. The reason is that the speed at which NOM is consumed as an electron acceptor is pivotal in determining the extent of CH₄ production suppression [101]. Compared to bogs with more refractory carbon, fens with more labile carbon (i.e., electron donors) can consume NOM more rapidly, leading to accelerated methanogenesis.

Fe turnover also strongly influences organic carbon remineralization in Fe-containing terrestrial and aquatic sediments [102] and stratified water columns [104,107]. For example, reactive oxygen species generated during the Fe(II) oxidation phase of Fe-containing minerals stimulate organic matter oxidation and CO₂ production. This process often leads to rapid organic carbon decomposition, frequently observed in tropical soils that experience frequent redox fluctuations [108]. Subsequently, Fe(III) reduction under anaerobic conditions can further promote anaerobic CO₂ production and suppress CH₄ emissions [109,110]. This process can contribute up to 44% of soil CO₂ respiration [109]. However, the charge/discharge cycling of Fe-containing minerals can link the processes of CH₄ oxidation and CO₂ reduction by accelerating electron transfer between CH₄-oxidizing and CO₂-reducing microorganisms. Consequently, greenhouse gas emissions can be significantly reduced [111]. Similar to Fe, Mn redox can also influence organic carbon decomposition [112]. In addition to changing electron flow pathways, the turnover of MMPs can indirectly affect the carbon cycle by influencing the availability of phosphorus via sorption/desorption. The reason is that phosphorus can act as a limiting nutrient for microbial metabolism [113].

The attendant consequence is that the geobattery-mediated biogeochemical cycle may significantly impact large-scale models of element cycling, particularly in predicting soil organic carbon degradation and greenhouse gas emissions. Traditional conceptual models, constrained by the limitations of thermodynamics and energetics on microbial activity, hold that wet environments restrict soil organic carbon decomposition, following the thermodynamically predicted “redox ladder” [114]. However, spatial heterogeneity in soil redox formed by hydrological fluctuations, coupled with the charging and discharging cycles of geobatteries, can lead to predicted reactions that may not align with empirical observations. Consequently, these predictive models may inaccurately estimate organic carbon decomposition and the corresponding greenhouse gas emissions in wet environments frequently affected by hydrological fluctuations. It has been shown that ignoring the redox cycling of Fe under water table fluctuations may lead soil carbon models to underestimate CO₂ emissions and overestimate CH₄ emissions [110]. This finding emphasizes the necessity for a deeper understanding of the role of geobattery-mediated redox reactions in large-scale models.

5.2. Anaerobic digestion

Anaerobic digestion (AD) plays a crucial role in the sustainable management of organic waste/wastewater while enabling energy recovery in CH₄. Methanogenesis during AD is primarily driven by obligate syntrophic interactions between fermentative bacteria and methanogenic archaea [115]. These interactions involve

interspecies electron transfer (IET), which creates thermodynamically favorable conditions for the continuous oxidation of organic compounds by fermentative bacteria [116]. Conventional wisdom suggests that this relationship is maintained by indirect IET (IIET) using electron shuttles, such as hydrogen or formate, but is often constrained by these shuttles' limited diffusion flux [117]. Direct IET (DIET) via conductive pili, c-type cytochromes, or conductive abiotic materials has been considered an alternative to IIET [17,116].

On the other hand, certain geobatteries, such as PyC [24,118–121], hydrochar [122,123], and magnetite, can also promote methanogenesis by promoting DIET (Table 1; Fig. 7). Magnetite achieves this process mainly through its high conductivity (10³–10⁶ S m⁻¹), alongside surface-enriched Fe-reducing bacteria driving dissimilatory Fe reduction [17]. The conductivity imparted by the carbon matrices of PyC can also serve as conduits to facilitate DIET, and the charge/discharge cycling of PyC's surface groups is another key pathway. For instance, the quinone moiety in geobatteries accepts electrons from organic matter oxidation by fermenting bacteria and is reduced to hydroquinone. Subsequently, hydroquinone is oxidized to the quinone moiety by transferring electrons to methanogenic archaea. This mechanism significantly increases CH₄ yield by up to 47% [24]. Hence, the redox-active functional groups within PyC, coupled with the highly conductive carbon matrices, can foster IET through the geobattery and geoconductor mechanisms [124].

Specific studies found that the redox cycling of functional groups within PyC can facilitate IET more effectively than the high conductivity of carbon matrices [118,119,125,126]. This phenomenon may be attributed to the comparatively lower electrical conductivity of PyC when compared with conventional conductive materials, such as granular activated carbon [127]. Another contributing factor is that the dominance of these two mechanisms depends on environmental conditions. For example, Lü et al. [128] compared the specific roles of PyC with rich redox-active functional groups and graphite with high electrical conductivity (i.e., graphite) in different stages of AD. The results showed that PyC performed better in hydrogenotrophic methanogenesis by facilitating IET, whereas graphite strongly recovered CH₄ production under high H₂ partial pressure via DIET. Furthermore, the doping of Fe, such as magnetite [17] and ferric chloride [129,130], can empower PyC with excellent geobattery and geoconductor mechanisms, thus promoting IET among syntrophic partners. Notably, the physical properties of PyC, for example, porous structure and surface charge, can also affect the efficiency of facilitated IET by influencing the adsorption to microorganisms [118,131]. Thus, when focusing on the effect of the geobattery mechanism of PyC on the IET, the effect of the geoconductor mechanism and other physicochemical properties of PyC on IET cannot be ignored.

5.3. Nitrogen removal

The main N loss pathways in anaerobic environments include anaerobic ammonium oxidation, denitrification, and denitrification-driven anaerobic CH₄ oxidation [132,133]. The unique electron transfer capacity of geobatteries positions them in crucial roles in these processes, acting as electron acceptors, donors, or shuttles.

Anaerobic ammonium oxidation coupled to Fe(III) reduction, known as Feammox, is a key pathway for N loss in terrestrial systems [134], biological N removal in wastewater treatment [132], and AD systems [135]. Despite the significance of Feammox, the low bioavailability of Fe(III) in its predominantly crystalline form hampers efficient electron transfer between ammonia and Fe(III) [135]. To overcome this limitation, electron shuttles, such as typical geobatteries including PyC [132,136,137] and NOM [132,135,138],

Table 1
Application of geobatteries in anaerobic digestion.

Geobatteries	Electron exchange capacity	Key electron transfer mechanisms	Substrate in anaerobic digestion	Performance enhancement	References
Corn stover PyC produced at 300 °C	EDC: 0.598 mmol e ⁻ g ⁻¹ EAC: 0.410 mmol e ⁻ g ⁻¹	Redox cycling of surface groups	Waste activated sludge	46.9% increase in cumulative methane production and 182% increase in maximum methane production rate	[24,128]
Swine manure PyC produced at 300 °C	EDC: 0.73 mmol e ⁻ g ⁻¹ EAC: 4.20 mmol e ⁻ g ⁻¹	Redox cycling of surface groups	Swine wastewater	21.5% increase in maximum methane production rate	[120]
Sawdust waste PyC produced at 500 °C	EEC: 6.67 μmol e ⁻ g ⁻¹	Redox cycling of surface groups	Food waste and sewage sludge	80.3% increase in maximum methane production rate	[118]
Digested sludge PyC produced at 516 °C	EDC: 12.8 -50.6 mmol e ⁻ g ⁻¹ EAC: 33.1 -180 mmol e ⁻ g ⁻¹	Redox cycling of surface groups	Sludge	48% increase in methane production	[121]
Corn straw PyC produced at 400 °C	-	Redox cycling of surface groups	Food waste	26.4% increase in removal efficiency of volatile suspended solid	[119]
Ashe juniper PyC produced at 400 °C	-	Redox cycling of surface groups	Glucose	71% increase in methane production	[174]
Switch grass PyC produced at 500 °C	-	Redox cycling of surface groups	Glucose	72% increase in methane production	[174]
Ashe juniper PyC produced at 400 °C	-	Redox cycling of surface groups	Aqueous phase of bio-oil	11.3 times increase in methane production	[174]
Peanut shell PyC produced at 500 °C	EDC: 0.10 mmol e ⁻ g ⁻¹ EAC: 0.13 mmol e ⁻ g ⁻¹	Redox cycling of surface groups	Glucose	21.7% increase in methane production	[175]
Pine sawdust PyC produced at 500 °C	-	Redox cycling of surface groups	Hydrothermal liquefaction aqueous phase	7.2% increase in cumulative methane production	[176]
Magnetite	-	Iron cycling and high electrical conductivity	Hydrothermal liquefaction aqueous phase	24.3% increase in cumulative methane production	[176]
Whiskey by-product PyC produced at 700 °C	-	Carbon matrices and redox cycling of surface groups	Whiskey by-product	5% increase in methane production	[124]
Magnetite loaded PyC produced at 800 °C	-	Iron cycling	Glucose	157% increase in methane production	[130]
Magnetic PyC produced at 500 °C	-	Redox cycling of surface groups in PyC and high electrical conductivity in magnetite	Waste activated sludge	22.1% increase in methane production	[177]
Corn stover PyC produced at 500 °C with nitric acid modification	-	Redox cycling of surface groups	Food waste	85.8% increase in maximum methane production rate	[74]
Corn straw hydrochar produced at 260 °C	-	Redox cycling of surface groups	Waste activated sludge	49.8% increase in maximum methane production rate	[123]
Sewage sludge hydrochar produced at 300 °C	EDC: 0.035 mmol e ⁻ g ⁻¹ EAC: 0.026 mmol e ⁻ g ⁻¹	Redox cycling of surface groups	Glucose	39% increase in methane production rate	[122]

Note: PyC: pyrogenic carbon; EDC: electron-donating capacity; EAC: electron-accepting capacity.

have effectively enhanced Feammox efficiency through reversible electron transfer (Fig. 8a). For example, Zhou et al. [132] reported that the addition of PyC or NOM could increase the potentially Feammox-mediated N loss by 17–340%.

In denitrification, electron transfer enhancement via geobatteries (Fig. 8b) is pivotal for improving microbial nitrate reduction efficiency. The high electron exchange activity conferred by quinone and hydroquinone pairs in low-temperature PyC can serve this purpose well [39,139–142] and improve nitrate removal by

415% [141]. For instance, Imhoff and Chiu [140] found that the biologically stored electrons in PyC obtained during the PyC-mediated oxidation of organic matter can be utilized for subsequent nitrate reduction. Therefore, PyC can be used as a rechargeable electron pool to improve nitrate removal efficiency. The biological redox cycling of Fe in nontronite can play a similar role to PyC during nitrate removal, and this Fe cycling is fully reversible without causing significant structural changes to nontronite [39].

Furthermore, NOM has been identified as an electron shuttle,

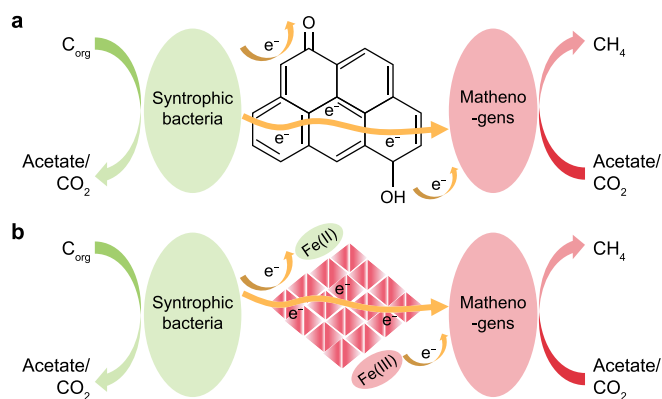


Fig. 7. Pathways of promoting electron transfer efficiency between methanogenic bacteria and methanogens in anaerobic digestion using typical geobatteries, such as pyrogenic carbon (PyC) (a) and magnetite (b).

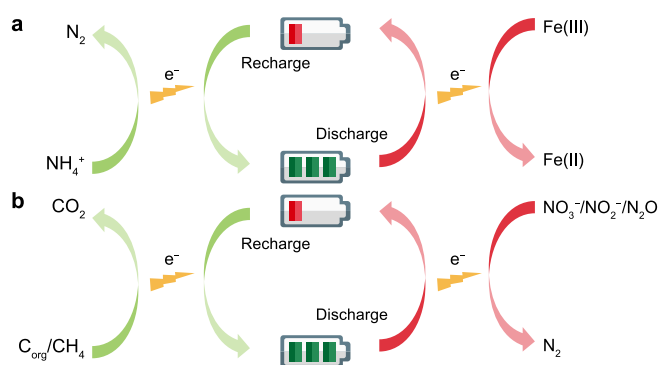


Fig. 8. Geobattery-mediated electron transfer mechanisms in anaerobic ammonium oxidation (a) and denitrification processes (b).

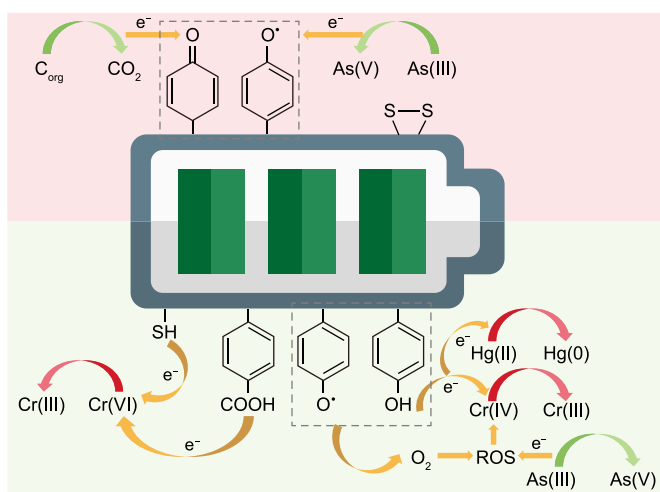


Fig. 9. Geobattery-mediated electron transfer mechanisms in the redox reactions of potentially toxic elements (PTEs). Yellow arrows represent electron transfer, green arrows represent oxidation processes, and red arrows represent reduction processes.

stimulating Fe(III)- [143] and Mn(IV)-dependent [144] anaerobic CH₄ oxidation, with its performance linearly correlated with its EEC [143]. This finding suggests the potential for geobatteries to mediate denitrifying anaerobic CH₄ oxidation, such as nitrate/nitrite-dependent anaerobic CH₄ oxidation, an approach offering

simultaneous CH₄ mitigation and N removal [145]. Moreover, NOM has been found to mediate nitrous oxide-dependent anaerobic CH₄ oxidation, presenting a novel pathway for the simultaneous biotransformation of CH₄ and nitrous oxide [146,147].

5.4. Transformation of potentially toxic elements

The transformations of potentially toxic elements (PTEs), particularly those with variable valence states such as Cr, As, and mercury (Hg), play a crucial role in determining their mobility, bioavailability, and fate within ecosystems. Geobatteries can directly act as electron donors or acceptors to facilitate the transformations of PTEs (Fig. 9) [148]. The carboxyl, phenolic-OH, and hydroquinone structural moieties in PyC and NOM [149,150], as well as the reduced organosulfur in NOM [151], can provide electrons to Cr(VI) reduction. The phenolic-OH and semiquinone-type persistent free radicals in PyC and NOM can also transfer electrons to oxygen, thereby forming reactive oxygen species for As(III) oxidation [89,152] and Cr(VI) reduction [153].

Furthermore, with the inherent reversible electron transfer capability of geobatteries, they can act as electron shuttles to promote PTE-related redox transformations (Fig. 9). For instance, NOM can mediate the biological reduction of Hg(II) to Hg(0), thereby potentially reducing the occurrence of Hg methylation in anoxic environments [154]. Redox-active groups in microplastics are also consistently mediate As(III) oxidation at hydrological fluctuation interfaces where frequent oxic/anoxic transitions occur [22]. Moreover, the redox cycling of redox-labile surface oxygen-containing functional groups in low-temperature PyC accelerates Cr(VI) reduction by organic carbon [23,155,156]. This phenomenon can significantly increase Cr(VI) reduction by 241%, showing a positive correlation with the EEC of PyC [23].

MMP-mediated electron transfer is also a critical pathway driving redox transformations in PTEs. For example, electron transfer between the Fe(II)/Fe(III) redox couple can oxidize As(III) to As(V) either catalytically under oxidizing conditions or through direct oxidation under anoxic conditions [157]. This phenomenon may be a key reason for the seasonal variation of As concentrations in groundwater. Additionally, reactive solid Fe(II) formed during the redox cycling of Fe-containing minerals can transfer electrons to Cr(VI) under aerobic conditions to facilitate its reduction [158]. Considering the prevalence of MMPs in different natural and contaminated ecosystems, they inevitably affect the fate of other redox-sensitive PTEs.

5.5. Degradation of emerging organic pollutants

Geobatteries can effectively promote chemical and biological degradation of emerging organic pollutants, such as pharmaceuticals (e.g., diclofenac and sulfamethoxazole), pesticides (e.g., imidacloprid), phenols (e.g., phenol, tribromophenol, and pentachlorophenol), and other compounds. The degradation mechanisms vary, with certain organic pollutants being degraded as electron donors [41,126,159] or acceptors [160], whereas others undergo degradation through reactive oxygen species (e.g., $\cdot OH$) induced via the charge/discharge cycle of geobatteries [16,161].

Quinone structures, typical redox-active centers found in PyC and NOM, play a crucial role as electron shuttles in the above processes. They mediate the electron transfer process between phenol-oxidizing bacteria (i.e., phenol as electron donor) and methanogens [41,126] and facilitate the dehalogenation process by halo-respiring bacteria using formate to reduce pentachlorophenol (i.e., electron acceptor) [160]. In addition, the redox cycling of Mn proves significant in enhancing the oxidation of diclofenac and sulfamethoxazole [159]. For instance, in a two-stage moving bed

biofilm reactor, Mn(IV) in the anaerobic reactor acted as an electron acceptor, driving the microbial oxidation of organic pollutants. The reduced Mn(II) was subsequently re-oxidized to Mn oxides in the aerobic reactor and periodically recycled to the anaerobic reactor for the next round of redox cycling.

The multiple electron transfer mechanisms of PyC can also promote Fe cycling via abiotic routes, thus accelerating the production of $\cdot\text{OH}$ for imidacloprid degradation in soils [161]. Similarly, NOM can receive electrons from green rust and then donate them to oxygen to produce $\cdot\text{OH}$ for tribromophenol degradation in groundwater [16].

6. Current challenges

The application of reversible electron transfer involving geobatteries holds significant promise in scientific research. A comprehensive understanding of the associated limitations and challenges is imperative for effective integration into environmental engineering practices. This section explores the various shortcomings hindering the application of reversible redox reactions.

(1) Complexity of environmental systems

Environmental systems inherently exhibit complexity, and the behavior of geobatteries can be influenced by various factors such as pH levels and the presence of other chemical species [162,163]. Under different pH conditions, redox-active moieties may undergo protonation or deprotonation reactions, thereby altering their redox properties [49]. Particularly, pH can impact the EEC of NOM by changing the molecule conformation [162]. At high pH levels, electrostatic repulsion between negatively charged groups within the NOM molecule increases, causing molecular swelling and increasingly exposing redox-active moieties. Conversely, low pH levels shrink NOM molecule, reducing accessibility to redox-active moieties [164]. In addition, co-existing species in the environment can compete with redox-active moieties for adsorption onto electrode surfaces/active sites or form complexes with redox-active moieties, thus impacting electron transfer kinetics. This phenomenon is evidenced by the potential influence of co-existing metal ions, ligands, and second metal oxides on the redox activity of MMPs [165].

(2) Difficulties in quantifying reversibility

Accurately quantifying the reversibility of electron transfer reactions in environmental matrices poses intricate challenges. Dynamic environmental conditions, subject to changes in temperature, pH levels, microbial activity, and various chemical species, introduce variability in electron transfer reactions over time. For instance, global warming changes the EAC and EDC of soil NOM by altering its chemical composition [166]. Fluctuations in pH levels or redox potential influence the equilibrium of reversible reactions [167], whereas the complex compositions of geobatteries lead to competitive adsorption, complexation reactions, and interference [97]. Concurrent side reactions, unwanted chemical transformations, and the involvement of reactive intermediates act as "electron traps," reducing observed reversibility [27,167]. Temporal and spatial variabilities within environmental samples further complicate accurate measurement, particularly when relying on point measurements. Detection challenges arise from small changes in geobattery species concentrations, specifically in samples with low analyte concentrations, limiting the precision of analytical techniques. A typical case is when the mediated electrochemical analysis is used to determine the electron transfer

capacity of geobatteries, multiple variables, such as temperature, pH levels, the chemical medium and its concentration, and reaction time, can affect the final results [49,96]. For example, fast reaction times may overlook slow electron transfer processes, as illustrated in the determination of the EDC of PyC. Prévotau et al. [168] found that the electron donation kinetics of PyC did not reach redox equilibria after 66 days, well beyond 1 h, as suggested by Klüpfel et al. [36]. Consequently, the difference in reaction times led to orders-of-magnitude differences in the estimated EDC of PyC. This finding highlights the contribution of the complexity of geobattery properties, environmental interferences, and measurement method variations to an ongoing variability in our understanding of the redox activity of geobatteries. Therefore, establishing a standard measurement for the EEC of different geobatteries remains challenging.

Another challenge is that laboratory samples cannot be analyzed using maximum oxidation or reduction rate, as we need to understand the true electron transfer capability of geobatteries in redox reactions [168]. Developing in situ measurement methods could be an alternative to avoid the artifacts arising from sampling and sample processing. However, the situation is not straightforward as these in situ measurement methods can be susceptible to numerous interfering factors in the field environment. Moreover, selectivity issues need to be considered due to the composite nature of geobatteries, particularly PyC and NOM.

(3) Scaling-up challenges

Although laboratory-scale studies may demonstrate reversible electron transfer under controlled conditions, scaling up these processes for practical applications introduces additional challenges. The recharge and discharge functions of geobatteries can be achieved through artificial redox oscillations and microbial activities, depending on specific objectives. For example, the discharge process of a geobattery may aim to enhance CH_4 yield by linking organic matter oxidation and CH_4 production in AD systems, promote N removal by linking organic matter oxidation and nitrate reduction in artificial wetlands or wastewater treatment, or reduce Cr toxicity by linking organic matter oxidation and Cr(VI) reduction. Thus, in these processes, sustainability relies on a sufficient electron donor during geobattery charging, eliminating the need for additional redox oscillation conditions. In this case, it is noteworthy that certain geobatteries may degrade over time due to factors such as chemical transformation, microbial activity, and environmental weathering [169]. Ensuring long-term stability is crucial for sustained and effective use in environmental engineering applications. Furthermore, the environmental impact of geobatteries and their by-products need a thorough evaluation. Unintended ecotoxicological effects arising from the use of these substances could pose risks to ecosystems, offsetting potential benefits. For instance, toxic substances, including polycyclic aromatic hydrocarbons and PTEs, can be released from PyC, affecting the application environment and organisms [170]. Therefore, we need to consider the precursor materials and formation/preparation conditions of geobatteries to minimize the toxic substances they carry.

In contrast, if the charging process is the objective, subsequent discharging processes require sufficient electron acceptors. Depletion of these acceptors necessitates artificial measures, such as providing oxygen, to regenerate the geobattery. This situation can be analogous to peatlands, where the regeneration of NOM leads to anaerobic respiration after the depletion of alternative electron acceptors such as Fe(III), NO_3^- , and SO_4^{2-} . As a result, CO_2 is produced, and CH_4 production is competitively inhibited. Therefore, forced water table fluctuations or intermittent aeration can suppress CH_4 generation in artificial wetlands or wastewater

treatment. Such forced redox oscillations can also regenerate geobatteries in anaerobic ammonium oxidation processes [9]. In this case, the amplitude and periodicity of artificially regulated redox fluctuations must be closely examined to avoid affecting the redox activity of geobatteries and the activity of microorganisms involved in the redox process [171,172].

7. Conclusions

Geobatteries demonstrate unique electron transfer mechanisms applicable in natural soil–water systems and other engineering systems. However, the exploration of their full potential is still in its infancy. Our comprehensive overview highlights the redox activity, characterization techniques, and the environmental and ecological significance of geobatteries. Overlooking geobattery-mediated biogeochemical cycles in soil–water systems can introduce significant biases into many large-scale models of element cycles, particularly the global carbon cycle. In addition, several challenges hinder their integration into environmental engineering. Environmental complexity influences the behavior of geobatteries, and the real electron transfer is difficult to quantify accurately because of dynamic conditions, side reactions, and detection limitations. Scaling up requires reasonable strategies tailored to specific environmental objectives, emphasizing the need for stability assessments and thorough environmental impact evaluations to balance benefits against potential ecotoxicological effects. With continued exploration, geobatteries promise to become practical tools in advancing environmental science and engineering solutions.

CRediT authorship contribution statement

Shihao Cui: Writing - Original Draft, Methodology, Investigation, Conceptualization. **Rui Wang:** Writing - Original Draft, Visualization. **Qing Chen:** Writing - Review & Editing, Supervision. **Lorenzo Pugliese:** Writing - Review & Editing. **Shubiao Wu:** Writing - Review & Editing, Supervision.

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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Appendix A. Supplementary data

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