Forum

Powering biological nitrogen removal from the environment by geobatteries

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Geobatteries are redox-active substances that can take up, store, and release electrons reversibly. Provided that their redox activity can be maintained by fluctuations of oxidizing and reducing redox conditions, geobatteries could also improve the performance of engineered systems, such as in biological nitrogen removal from wastewater or constructed wetlands.

Geobattery technology for nitrogen redox removal

Geobatteries [1] are natural redox-active substances covering a wide range of redox potentials which can reversibly donate, store, and accept electrons in biogeochemical redox processes without or with only minor changes in their chemical composition and structure [2]. Examples of geobatteries are carbon-based materials such as natural organic matter (NOM) and pyrogenic carbon (e.g., biochar) harboring both electron-donating (e.g., polyphenolic and hydroquinone moieties) and electron-accepting functional groups (e.g., quinone-like moieties) [1,3], as well as mixed-valent mineral phases such as magnetite and clays containing both ferrous iron [Fe(II)] and ferric iron [Fe(III)] [2]. Geobatteries inherently could even supply or accept electrons during biogeochemical cycling of nutrients and pollutants by involving internal redox reactions. As an illustrative example, N cycling can be fueled by NOM geobatteries serving as either an electron acceptor for oxidizing reduced N compounds [e.g., ammonium (NH_4^+)] or an electron donor for reducing oxidized N species [e.g., nitrate (NO_3^-), nitrite (NO_2^-), and nitrous oxide (N_2O)] [3]. Direct experimental evidence for a potentially reversible geobattery redox cycle coupled to microbial N cycling has only emerged in the past decade. While geobattery materials such as biochar and magnetite have been used as sorbents in remediation technologies [4,5], the role of redox-active compounds for removing excessive N from extant ecosystems has so far been underexplored. Recent innovative electrochemical approaches open new possibilities to unravel the mechanisms of microbial geobattery–N redox couplings [3] and the downstream application in (eco-)engineering systems. We advocate for using geobattery-based technologies for N removal from wastewater or constructed wetlands and propose strategies to activate and optimize the redox functioning of geobatteries.

Role of geobatteries in biological N removal

Geobatteries can support microbially mediated N removal processes by acting as either electron acceptors for ammonium oxidation or electron donors for N-oxide reduction (see Figure I in Box 1). Growing evidence has revealed redox couplings between compounds that can function as geobatteries and different nitrogen species under laboratory or environmental conditions (Box 1). For instance, on one hand, NOM and biochar can be electron sinks [serving as terminal electron acceptors or intermediary electron shuttles in Fe(III) reduction] for anaerobic microbial oxidation of ammonium to harmless dinitrogen (N_2) [6,7]. On the other hand, NOM and biochar in reduced states [8,9] as well as Fe(II) in magnetite and clays [10,11] can donate electrons for microbial reduction of nitrate. However, their function as geobatteries has not been well exploited so far in (eco-)engineering systems, including wastewater treatment plants or constructed wetlands. Some geobatteries can also function as geoconductors in microbial interspecies electron transfer. For example, the mineral magnetite can relay electrons from electron-donating to electron-accepting microbes and promote synergic metabolism involving nitrate reduction [12]. Although solid materials including biochar, magnetite, and clay minerals have been applied to remove nitrogen species from water, they are currently used predominantly as adsorbents rather than recyclable geobatteries for microbes.

Sustainability of geobatteries

Considering the microbial geobattery–N redox couplings outlined above, we conclude that geobatteries, unlike classical electron acceptors or donors, hold promise for continuously fueling biological N-removal processes in water treatment without being consumed. Geobatteries could minimize the demands of organic carbon (e.g., acetate) as electron sources. Present biological N-removal techniques include nitrification, denitrification, and anammox processes, along with combinations of these processes. To optimize charging and discharging processes of geobatteries for N removal, we propose techniques combining anaerobic oxidation of ammonium and reduction of N-oxides including nitrate (see Figure I in Box 1) in the same bioreactor or in a redox gradient of a constructed wetland. In this way, native geobatteries can be charged/recharged with electrons from ammonium oxidation (autotrophically) and the reduced geobatteries can subsequently be discharged by donating electrons for autotrophic or heterotrophic nitrate reduction. To combine ammonium oxidation and autotrophic nitrate reduction processes, geobatteries could be reduced during ammonium oxidation and then be oxidized in

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Box 1. Evidence of geobattery-driven microbial N redox cycling

The redox processes of microbial N cycling can be mediated by various geobattery materials. As geobatteries function as extracellular electron acceptors and donors, such processes mainly require the involvement of electroactive microbes capable of exchanging electrons with their extracellular environment. While Figure I illustrates the general principle of such redox couplings, some experimental evidence is detailed below.

NOM can act as terminal electron acceptor in microbial oxidation of ammonium to N_2 in marine sediments [6]. Anthraquinone-2,6-disulfonate (AQDS), an analog representing the main redox-active functional groups (quinones/hydroquinones) in humic substances and NOM, and biochar can function as electron shuttle in anaerobic ammonium oxidation coupled with Fe(III) reduction (Feammox) to produce N_2 [7]. Microbial reduction of AQDS and biochar were coupled to ammonium oxidation and subsequent chemical oxidation of reduced AQDS (AH_2QDS) and reduced biochar by ferrihydrite. Anaerobic ammonium oxidation coupled to the reduction of magnetite or clay geobatteries, however, has not yet been reported.

Humic substance reduced by the electroactive bacterium *Geobacter metallireducens* can be oxidized by the denitrifying bacterium *Paracoccus denitrificans* for nitrate reduction [8]. Chemically or microbially reduced biochar can serve as electron donor for microbial nitrate reduction by *G. metallireducens* [9]. Fe(II) in magnetite or in clays can serve as electron source for nitrate reduction by nitrate-dependent Fe(II)-oxidizing microorganisms [10,11]. Furthermore, reduced geobattery compounds can donate electrons for microbial reduction of nitrite and N_2O (possible intermediates of microbial nitrate reduction) as terminal electron acceptors [3].
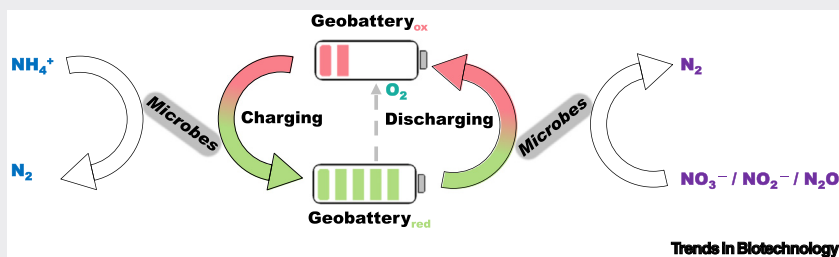

Figure I. Geobattery-powered microbial N cycling and biological N removal. The scheme illustrates not only the geobattery-dependent microbial pathways for anaerobic ammonium oxidation and N-oxide reduction, but also the principle of geobattery-based technologies for biological N removal as detailed in the main text. Abbreviations: ox, oxidized; red, reduced.

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autotrophic denitrification to harmless N_2, leading to decreases in both ammonium and nitrate levels. Coupling ammonium oxidation and heterotrophic nitrate reduction processes such as heterotrophic denitrification to N_2 requires less organic substrate because geobattery substances could serve as electron donors for denitrification, thereby alleviating the stress of organic carbon serving as an electron source in addition to a carbon source. Geobattery technologies, however, could be explored for not only the simultaneous removal of ammonium or N oxides but also the individual elimination of ammonium or N oxides. For ammonium removal, microbially reduced geobatteries resulting from anerobic ammonium oxidation could be discharged by abiotic oxidation with oxygen [13] (possibly with concomitant aerobic nitrification of any remaining ammonium) for the next redox cycle (see Figure I in Box 1). For N-oxide removal, native geobatteries could first be charged by chemical reductants or by microbes routing electrons from suitable electron donors to the geobattery, and then drive N-oxide reduction. Generally, the recyclable and durable nature of geobatteries should enable them to provide sustainable biological N removal. In practical applications, geobattery compounds with magnetic properties could be applied and fixed into magnetic carriers (e.g., magnetite itself) for use and follow-up recovery [5]. Consequently, geobattery-based technologies could reduce treatment costs compared to traditional

approaches based on continuous feeding of electron sources such as acetate.

Activating and maintaining the redox functioning of geobatteries

Redox fluctuations – alternation between oxidized and reduced conditions – may activate and maintain the functioning of geobatteries in N removal (Figure 1). In a recent landmark work, Peiffer and colleagues [2] propose that preserving the high reactivity of geobatteries in natural aquatic environments requires activation by redox fluctuations. They relate geobatteries to redox-active metastable phases. Ripening can increase their stability but decrease their reactivity for electron transfer reactions. Redox oscillations, however, interrupt the ripening process and regenerate the reactivity of geobatteries. They also argue that frequent hydrological oscillations in aqueous ecosystems at scales of meters to hundreds of meters could charge or discharge geobatteries, governing the nano- to micrometer scale element cycling. We propose to utilize this principle for N removal from wastewater or constructed wetlands. In particular, under such engineered settings, redox conditions can be readily manipulated and adjusted as needed (Figure 1). First, in anoxic environments, the repeated cycling between ammonium-oxidizing and nitrate-reducing conditions with appropriate frequencies is expected to enhance N removal in reactors or constructed wetlands. Second, oxygen is among the most powerful and accessible electron acceptors in nature, so periodic oxygen inputs [13] via air purging can rapidly discharge geobattery materials in reactors or constructed wetlands aimed only at anaerobic oxidation of ammonium. Third, with constructed wetlands, forced water table fluctuations are an alternative way to change the redox conditions by controlling the availability of electron acceptors (e.g., oxygen and sulfate) and donors (e.g., dissolved organic carbon) [2]. Together, (eco-)engineering systems could
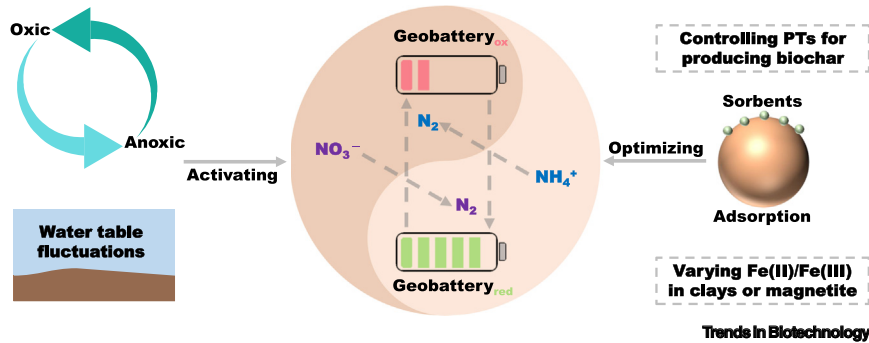
Figure 1. Strategies for activating and optimizing the redox functioning of geobatteries. Abbreviations: ox, oxidized; PTs, pyrolysis temperatures; red, reduced.

be exposed to alternating redox cycles to stimulate and maintain geobattery function for N redox removal.

Enhancing the redox functioning of geobatteries

We propose that the efficacy of geobatteries can be enhanced by tailoring its redox properties (Figure 1). Redox properties comprise redox capacity and redox state. Redox capacity refers to the total electron exchange capacity (EEC): the sum of the electron-accepting capacity (EAC) and electron-donating capacity (EDC) of a given geobattery substance. The ratio of EAC/EEC or EDC/EEC represents the redox state. Mediated electrochemical analysis (MEA) is an emerging tool for accurately determining the redox properties of geobattery materials [3,4].

The redox properties of geobatteries could be tailored by mixing them with sorbents. For example, the EDC and EEC of NOM are enhanced when present as a coating on redox-inert Al_2O_3, as evidenced by MEA [14]. Thus, modifying the electrochemical properties of geobatteries by adsorption, such as coating NOM on mineral surfaces, provides so-far unexplored opportunities to promote their ability to take up and release electrons in biological N transformations. In addition, the redox properties of biochar geobatteries can be tailored by the pyrolysis temperature. As an example, biochars produced at 400–

500°C showed the highest EDC, EAC, and EEC, as demonstrated by MEA [4]. Moreover, the redox properties of mixed-valent mineral phases can be tailored by varying the ratio of Fe(II) and Fe(III) in clays [15] or magnetite [5,10]. Clays or magnetite in more reduced redox states and more oxidized redox states may promote microbial N-oxide reduction and ammonium oxidation, respectively. Nevertheless, specific strategies for each geobattery material should be evaluated to enhance its redox capacity and reactivity.

Concluding remarks

Future technologies for improved biological N removal from wastewater or constructed wetlands may take advantage of geobattery compounds as durable and sustainable electron sinks and sources for microbial N-removal processes. Repeated oscillation between oxidizing and reducing conditions could activate and maintain the high reactivity of geobatteries in reactors or constructed wetlands. Suitable sorbents that can bind geobattery substances and maybe also capture N species could be applied to prime the redox capacity of geobatteries and to accumulate N species for subsequent redox removal. By choosing suitable conditions and composition, the redox capacity of geobatteries can be tailored to improve their ability to drive biological N removal.

Nonetheless, some challenges and uncertainties for deployment of geobattery

technologies remain. Sorption of biomass or phosphate in polluted water onto mineral-based geobatteries (such as magnetite) may also change their redox properties and accessibility and therefore affect their reactivity. Furthermore, it is unclear how the diversity and metabolic activities of electroactive and N-metabolizing microorganisms respond to multiple oxidation–reduction cycles of geobatteries and vice versa. More research is warranted to address these challenges and uncertainties for better management of geobatteries and microbe–geobattery interactions.

Declaration of interests

No interests are declared.

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