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Iron oxide nanoparticles in geomicrobiology: from biogeochemistry to bioremediation

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Iron oxides are important constituents of soils and sediments and microbial iron reduction is considered to be a significant anaerobic respiration process in the subsurface, however low microbial reduction rates of macroparticulate Fe oxides in laboratory studies led to an underestimation of the role of Fe oxides in the global Fe redox cycle. Recent studies show the high potential of nano-sized Fe oxides in the environment as, for example, electron acceptor for microbial respiration, electron shuttle between different microorganisms, and scavenger for heavy metals. Biotic and abiotic reactivity of iron macroparticles differ significantly from nano-sized Fe oxides, which are usually much more reactive. Factors such as particle size, solubility, ferrous iron, crystal structure, and organic molecules were identified to influence the reactivity.

This review discusses factors influencing the microbial reactivity of Fe oxides. It highlights the differences between natural and synthetic Fe oxides especially regarding the presence of organic molecules such as humic acids and natural organic matter. Attention is given to the transport behavior of Fe oxides in laboratory systems and in the environment, because of the high affinity of different contaminants to Fe oxide surfaces and associated co-transport of pollutants. The high reactivity of Fe oxides and their potential as adsorbents for different pollutants are discussed with respect to application and development of remediation technologies.

Nano-sized minerals in global biogeochemistry

Iron (Fe) is one of the most abundant elements of the earth's crust and therefore ubiquitous in many biogeochemical compartments. Fe oxides occur in the atmosphere, pedosphere, biosphere, hydrosphere, and lithosphere in a great diversity of morphologies, minerals, and associations [1,2]. They appear as anhydrous forms like hematite (α-Fe_2O_3) and maghemite (γ-Fe_2O_3), mixed-valent oxides like magnetite (Fe_3O_4) and wuestite ($Fe_{1-x}O$), and oxyhydroxides with the common formula FeOOH (goethite, lepidocrocite, akaganeite). More hydrated forms such as ferrihydrite with variable water contents are often described as $Fe(OH)_3$ [3] (referred to as Fe oxides in this review).

Like many environmental minerals, Fe oxides also occur as nanoparticles. Nanoparticles have a size of one to several tens of nanometers (but smaller than 1 μm) in three dimensions [4]. Stably dispersed in a medium such as water, nanoparticles are defined as colloids [5]. According to the DLVO theory, aggregation is inhibited if electrostatic repulsion forces dominate over van der Waals attraction [6,7]. Owing to brownian movement, colloids do not sediment. When Fe oxide minerals form by precipitation from ferrous solutions, their primary nucleation sites are within the nanometer range. Ferrihydrite, as an exceptional Fe oxide, is a nanomineral that only exists in nanometer-sized crystallites [4]. Those crystallites form aggregates of 100–300 nm (nanoaggregates) [8] which may have colloidal properties. Ferrihydrite macroaggregates larger than 1 μm are formed by agglomeration of nanoaggregates and do not form stable suspensions but precipitate

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in aqueous solutions. For other Fe oxides, the nanoparticle stage is naturally a transitory phase to macroparticle agglomeration [4]. However, the growth process can be interrupted by for example, depletion of the ferrous source or complexation of ferric or ferrous Fe with organic matter, leading to a decrease of the mineral saturation index [9]. Solid, bulk minerals by contrast are exposed to shearing, straining, weathering, and a multitude of other dissolutive reactions [10], also yielding nanoparticles. Therefore, a fraction of the global pool of environmental Fe minerals is constantly present as nanoparticles [11]. A study with sediment from the Mediterranean Sea revealed an abundance of nano-sized goethite of 7–30% of the total Fe in dependence of sampling site and depth [12].

In soils and aquifers, chemical or physical perturbation of the ambient groundwater conditions can lead to mobilization of already existing nano-sized minerals [13]. This raises questions on the reactivity of this fraction in global biogeochemistry.

The reactivity and the role of Fe oxides in the environment might have been underestimated until now because at particle sizes within the nanometer range minerals show variations in their crystal structure as compared to their macroparticulate counterparts. With particle size decreasing to the nanometer-range, physical, chemical, and magnetic properties can change [1,14,15]. Several studies indicate that these effects have an impact on the reactivity of nanominerals in microbial redox reactions. Anaerobic microbial oxidation of pyrite (FeS_2) by *Thiobacillus denitrificans* was observed with pyrite nanoparticles but not with larger crystals [16], indicating that minerals which do not react as macroparticles may become reactive in nanoparticulate forms. Another example showed that the oxidation of Mn^{2+} on hematite surfaces was up to 1.5 orders of magnitude faster for 7.3-nm hematite relative to 37-nm hematite, resulting in a faster formation of Mn oxides [17]. In the environment, the fast mineralization of Mn induced by Fe oxide nanoparticles probably leads to a much faster increase of available adsorption surface sites for heavy metal uptake than previously assumed. Furthermore, the thermodynamic stabilities of Fe oxides relative to the formation of other Fe oxides were shown to be a function of surface area and therefore particle size [3].

High reactivity of iron oxide nanoparticles in geomicrobiological reactions: the role of solubility, surface area, and ferrous iron

Factors controlling microbial Fe oxide reduction were intensively studied during the past decades and several key factors for Fe oxide reactivity were identified. Maximum microbial reduction rates by *Shewanella putrefaciens* were positively correlated with the solubility of Fe oxides in the order amorphous Fe(III) oxide (2-line ferrihydrite) $\geq$ 6-line ferrihydrite $\gg$ nanohematite = lepidocrocite $\gg$ goethite $>$ macroparticulate hematite [18–20]. According to the modified Kelvin equation, the solubility of minerals increases exponentially with decreasing particle size to the nanometer-scale [15,21]:

$$\frac{S}{S_0} = e^{2\gamma V/RTr} \quad (1)$$

where S is the solubility (mol kg^{-1}) of fine grains with the radius r (m), S_0 is the solubility of the bulk material. γ is the surface free energy (mJ m^{-2}), V is the molecular volume (m^3 mol^{-1}), R is the universal gas constant (mJ mol^{-1} K^{-1}), and T is the temperature (K). This indicates in conclusion that decreasing particle size enhances solubility, which in turn increases microbial reduction rates.

However, it is not known how generally applicable this is for all minerals. Some minerals such as hydroxyapatite became less soluble with particle sizes decreasing to a crucial value [22]. The crucial value depended on the size of pits on the crystallite surface which induced the dissolution of hydroxyapatite. When the crystallite sizes were in the same order as the formed pits, dissolution became self-inhibiting.

In general, one should distinguish between large crystal sizes and aggregates of smaller particles. The solubility, mostly tested under acidic conditions and thereby leading to disaggregation (e.g. [20,23]), is dependent on the crystal size and largely independent on the aggregate size of precipitated nanoparticles [20,24].

A study by Roden [23] showed that the rate-limiting steps of abiotic reductive dissolution by ascorbate for a wide set of amorphous, nanoparticulate and highly crystalline, macroparticulate Fe oxides were different from microbial reduction by *S. putrefaciens*. Comparison of the specific surface areas of different Fe oxides with their reduction rates showed an approximately linear relationship for microbial reduction whereas the relationship for abiotic reduction was logarithmic (Fig. 1). This logarithmic behavior was attributed to differences in the thermodynamic properties (e.g. crystal order) which are correlated with the specific surface area and the Fe(II) detachment from Fe oxide surfaces during reduction. The linear relationship between microbial reduction rates and the specific surface area indicated that the rate-limiting step in microbial Fe oxide reduction was the rate of electron transfer from the cell to the Fe oxide surface. By contrast to abiotic reduction, microbial reduction led to an Fe(II) coating on the Fe oxide surfaces. Outliers showing a low reactivity compared to specific surface area (Fig. 1) were most probably caused by strong aggregation [23]. Recent studies investigated the abiotic dissolution behavior of hematite nanoparticles in the size-range between 7 and 40 nm [21,24]. Initial reduction rates of 7 and 8 nm-hematites were triggered by dispersed and rapidly dissolved particles and exceeded initial reduction rates of 30 and 40 nm particles by 2- to 10-fold. Here, reduction was mainly initiated by internal defects and nanoscale surface steps. This indicates that not only the specific surface area and the Fe(II) detachment from the surface, but also structural defects and surface roughness control the initial reduction rates. Especially the reduction rates of environmental nanoparticles are most probably underestimated. They precipitate in the presence of ions and organic molecules and are therefore characterized by defect structures [25] (Fig. 2).

In accordance with both findings, the microbial reduction rates of differently sized hematite nanoparticles by *Geobacter sulfurreducens* decreased in the order 30 nm $>$ 10 nm $\gg$ 50 nm due to stronger aggregation of the 10 and 50 nm particles compared to the 30 nm particles [26] (Fig. 2). Aggregation diminished the specific surface area and therefore the number of available Fe(III) centers at the Fe oxide surfaces available for the electron issuing sites of the cell membranes [23]. Direct Fe(III) reduction by microorganisms requires attachment of the cells to the nanoparticles [18,19,27], but reduction kinetics of larger aggregates might subsequently be controlled by crystal properties [21,28]. The latter

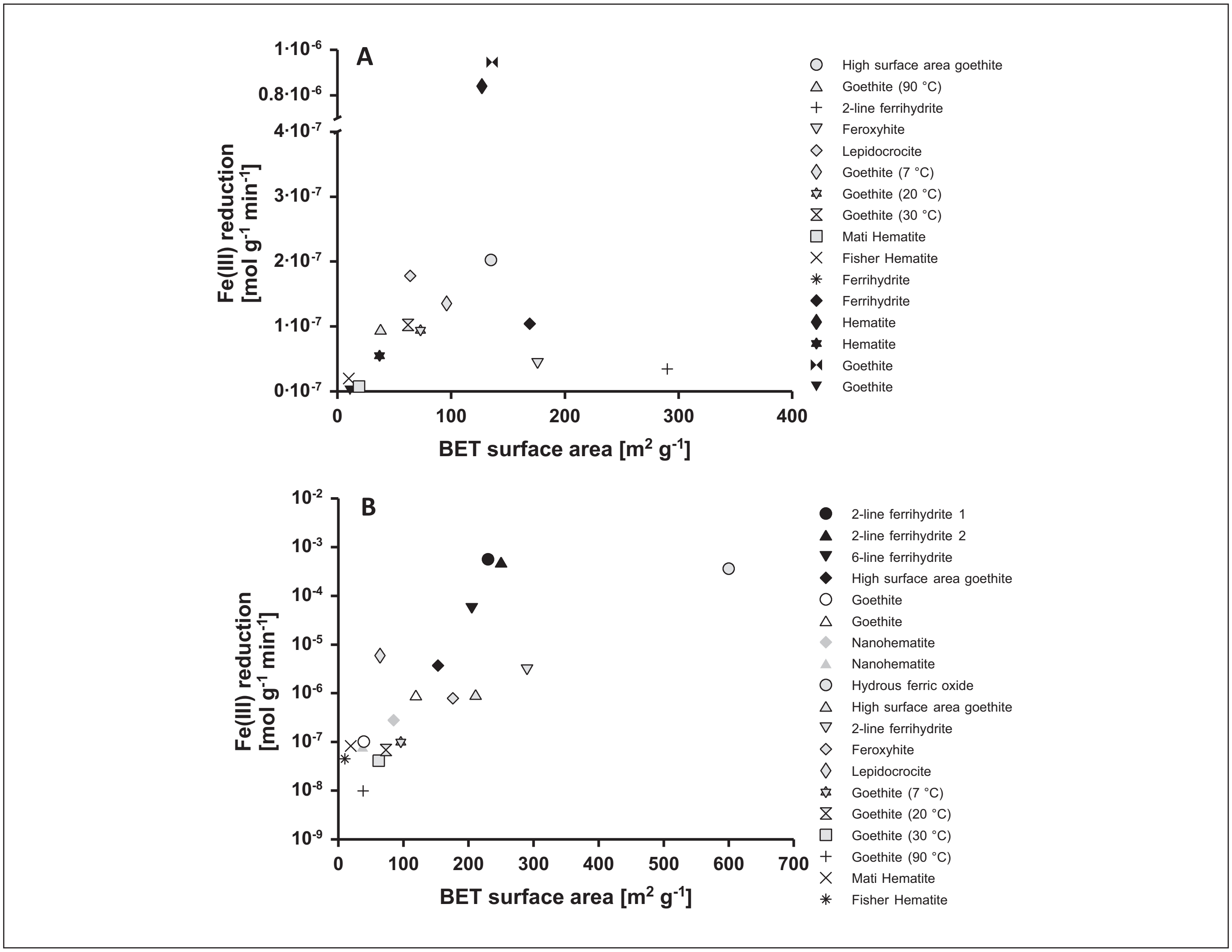

FIGURE 1

Relationship between oxide surface area and initial microbial **(a)** and abiotic reduction rates **(b)**. Different experimental procedures in respective studies (e.g. different microorganisms or reducing agents) cause different slopes. Approximately linear and logarithmic correlations are discernible for biotic and abiotic reduction, respectively.
Data taken from Roden [23] and Table 1.

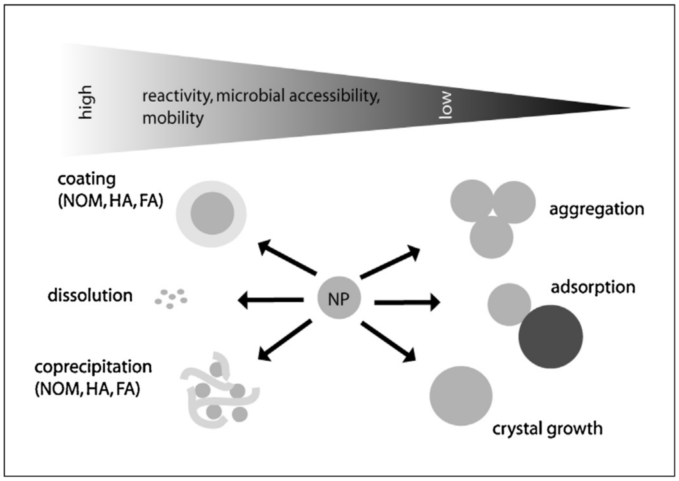

FIGURE 2

Possible interactions of nanoparticles in the environment or laboratory systems. NOM, natural organic matter; HA, humic acids; FA, fulvic acids. Modified from Delay and Frimmel [123].

studies observed no influence of the aggregation behavior of hematite nanoparticles on microbial reduction rates. Initial reduction rates of 30 and 43 nm particles were similar to rates of 500 nm aggregates, even though the large aggregates presented less surface area for cell contact. Thus, not only particle size but also particle morphology, shape, and the degree of aggregation seem to determine both the contact between Fe oxides and cells and the reduction mechanism (e.g. direct or indirect electron transfer) used by *Shewanella oneidensis*.

However, higher microbial reduction rates of colloidal Fe oxides compared to their macroparticulate counterparts have been observed [29,30]. The microbial reduction of different Fe oxide colloids by *G. sulfurreducens* was up to two orders of magnitude faster compared to the macroparticulate oxides of the same mineral (Table 1 and Fig. 3). Surprisingly, all colloidal Fe oxides were almost totally reduced, to extents of 78–100% [30]. The high biotic reactivity of different Fe oxide nanoparticles was also proven with soil microbial communities grown in electrochemical cells [31]. Amendment of Fe oxide nanoparticles to the electrochemical

TABLE 1

Comparison of initial biotic and abiotic reduction rates of different Fe oxides from literature

Fe oxide	Particle/aggregate size [nm]	Specific surface area [m^2 g^{-1}]	Reducing agent	Abiotic reduction rate [mol m^{-2} min^{-1}]	Microorganism	Cell density [cells mL^{-1}]	Biotic reduction rate [mol m^{-2} min^{-1}]	Source
2-Line ferrihydrite 1	3.29	230	Ascorbic acid	2.46E−06	–	–	–	Larsen and Postma [20]
2-Line ferrihydrite 2	3.03	250	Ascorbic acid	1.98E−06	–	–	–	Larsen and Postma [20]
6-Line ferrihydrite	3.70	205	Ascorbic acid	2.70E−07	–	–	–	Larsen and Postma [20]
High surface area goethite	10.67	153	Ascorbic acid	2.40E−08	–	–	–	Larsen and Postma [20]
Goethite	(1006 ± 55)[a] × (43 ± 7)[b]	39 ± 2	HNO_3	2.61E−09	–	–	–	Rubasinghege *et al.* [124]
Goethite	(75 ± 20)[a] × (10 ± 3)[b]	119 ± 3	HNO_3	7.70E−09	–	–	–	Rubasinghege *et al.* [124]
Nanohematite	6.8 ± 0.8	84.7[c], 117.5[d]	Ascorbic acid	3.27E−09	–	–	–	Echigo *et al.* [21]
Nanohematite	30.5 ± 3.5	37.1[c], 39.1[d]	Ascorbic acid	2.15E−09	–	–	–	Echigo *et al.* [21]
Hydrous ferric oxide	1.3	600	Ascorbate	6.05E−07	*Shewanella putrefaciens* CN32	2.0E+08	3.97E−09	Roden [23]
High surface area goethite	7.7	211	Ascorbate	4.92E−09	*Shewanella putrefaciens* CN32	2.0E+08	1.21E−09	Roden [23]
Goethite (90 °C)	43.4	38	Ascorbate	2.59E−10	*Shewanella putrefaciens* CN32	2.0E+08	2.52E−09	Roden [23]
Ferrihydrite	336 ± 40	275 ± 0.6	–	–	*Geobacter sulfurreducens*	2.1E+08	5.49E−08	Bosch *et al.* [29,30]
Ferrihydrite	70 200 ± 30%	169 ± 0.3	–	–	*Geobacter sulfurreducens*	2.1E+08	6.17E−10	Bosch *et al.* [29,30]
Hematite	123 ± 4	127 ± 1.1	–	–	*Geobacter sulfurreducens*	2.1E+08	6.62E−09	Bosch *et al.* [29,30]
Hematite	27 600 ± 30%	37 ± 0.9	–	–	*Geobacter sulfurreducens*	2.1E+08	1.48E−09	Bosch *et al.* [29,30]
Goethite	64 ± 3	136 ± 0.5	–	–	*Geobacter sulfurreducens*	2.1E+08	6.95E−09	Bosch *et al.* [29,30]
Goethite	11 900 ± 30%	11 ± 0.1	–	–	*Geobacter sulfurreducens*	2.1E+08	1.33E−10	Bosch *et al.* [29,30]
Soil effluent ferrihydrite	281 ± 146	n.d.	–	–	*Geobacter sulfurreducens*	4.8E+07	160 μM h^{-1}	Fritzsche *et al.* [60]
Soil effluent ferrihydrite	100 ± 43	n.d.	–	–	*Geobacter sulfurreducens*	4.8E+07	93 μM h^{-1}	Fritzsche *et al.* [60]

[a] Length.

[b] Width.

[c] Degassed for 4 hours at 120°C under N_2 flow before measurement.

[d] Degassed for 4 hours at 90°C under N_2 flow before measurement.

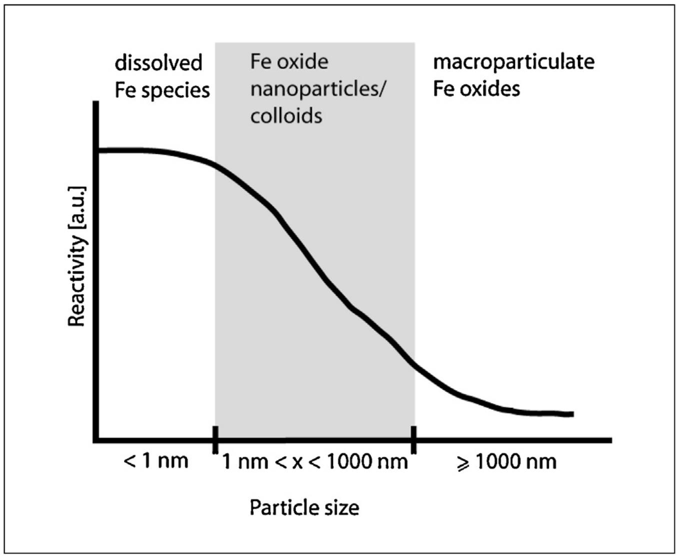

FIGURE 3

Generalized trend of Fe oxide reactivity in dependency of particle size. Modified from Wigginton *et al.* [125].

cells led to an >30-fold increase in current production, probably caused by constructed electrically conductive networks between microbial cells, Fe oxide nanoparticles, and electrodes. The authors assumed that probably nanoparticles alone can take this role because larger crystals cannot diffuse into the intercellular spaces of microbial assemblages to form electron conduits. Furthermore, the ability of electrically conductive nano-magnetite to facilitate electron transfer between *G. sulfurreducens* to *Thiobacillus denitrificans* was recently shown [32]. These findings indicate the important and diverse functions of Fe oxide nanoparticles as electron acceptor and electron mediator in nature due to their high bioavailability.

Impact of organic matter on reactivity of synthetic and environmental iron oxide nanoparticles

The mechanisms of microbial Fe oxide reduction as discussed above were investigated with synthetic Fe oxides in artificial laboratory systems. In nature, not only Fe oxides but also many other minerals are commonly associated with organic molecules [33–35]. This leads to the question whether this association limits or accelerates microbial reduction rates of naturally occurring Fe oxides.

Humic acids, extracts of natural organic matter at strong alkaline conditions, were reduced by Fe-reducing organisms belonging to the family of the *Geobacteraceae* with acetate as sole electron donor [36–38]. The electron accepting capacity of humic acids and especially their quinone moieties seemed to enable humic substances to enhance microbial reduction of Fe oxide macroparticles via electron shuttling between cells and minerals. This was observed with dissolved and solid-state humic acids [39].

The abiotic electron transfer from reduced organic molecules to Fe oxides is essential for this mechanism. Chen *et al.* [40] proved that polyphenylic-rich and carbohydrate-rich fractions of aquatic natural organic matter from a wetland pond, and soil humic acids were able to partly reduce dissolved Fe(III) and an amorphous Fe(III) precipitate abiotically at acidic ($pH < 4$) but also at neutral pH values. Electron transfer from microbially reduced humic acids to ferrihydrite turned out to be at least 7-fold faster than the electron transfer from *G. sulfurreducens* to ferrihydrite macroaggregates [41] (Fig. 2). Redox potentials of quinones are a controlling factor in electron shuttling-mediated Fe oxide reduction, with redox potentials of most effective quinones in a range of -137 to -225 mV versus standard hydrogen electrode at pH 7 [42].

In aquatic systems, small fulvic compounds (0.8–3 nm) adsorb on inorganic colloids and prevent aggregation by electrostatic and steric repulsion. Thus, Fe oxide nanoparticles can be stabilized in suspension in the environment [43–45]. By contrast, adsorption of large rigid biopolymers (consisting of structural and fibrillar polysaccharides with total lengths up to 1 μm) destabilized colloids due to formation of larger aggregates [43,44]. Biopolymers acted as long distance bridges between single colloids and formed loose aggregates of large dimensions. Smaller polymers also adsorbed on colloidal Fe oxide surfaces. However, charge neutralization of the Fe oxides led to the collapse of colloids rather than polymer bridging [43]. A stabilizing effect was also observed for goethite colloids coated with tannic and polygalacturonic acid whereas colloids coated with dissolved organic matter formed large aggregates [46]. In summary, stabilization of nanoparticles by electrostatic repulsion as well as aggregation by polymer bridging affects the specific surface areas of the nanoparticles and therefore also their reactivity.

In natural systems, Fe oxide colloids generally form in the presence of natural organic matter, leading to distorted crystal structures [47–49]. For example, complexation of Fe(II) and Fe(III) inhibited hydrolysis and therefore Fe oxide formation [50–53]. Coprecipitation experiments of Fe(III) nitrate solutions with different hydroxybenzoic acids showed that especially the position rather than the number of phenol groups of the respective acid controlled the interaction with Fe(III) and was therefore decisive for the formed crystallite sizes [52]. Two-line ferrihydrite macroaggregates coprecipitated with microbial exopolysaccharides revealed no changes of Fe(III) coordination, but a slightly reduced crystallite size and crystallinity [54]. Water extractable natural organic matter from a forest topsoil interfered strongly with the crystal growth of synthetic ferrihydrite during coprecipitation [55]. Even small amounts led to smaller ferrihydrite crystallites, increased lattice spacings, and more distorted $Fe(O,OH)_6$ octahedra. Furthermore, not only organic ligands such as citrate and oxalate, but also humic acids and natural organic matter increased the solubility of Fe oxides [56–58]. In a structural study of natural ferrihydrite from an acid mine drainage environment, increasing Al, Si, and organic matter contents caused decreasing crystallite size, while an increase of structural disorder occurred [25]. Aluminum substituted Fe^{3+} while Si and organic matter coprecipitated with ferrihydrite inhibited Fe polymerization and particle growth. This led to additional structural disorder. Coprecipitation of ferrihydrite macroaggregates with acid polysaccharides affected the surface reactivity of ferrihydrite due to the increase of accessible surface area for additionally dissolving present ligands such as citrate. Coprecipitation therefore controlled ligand-promoted dissolution at neutral pH [59].

All the discussed factors and heterogeneities occurring in nature have the potential to accelerate microbial Fe oxide reduction. Natural ferrihydrite colloids, derived from a soil column experiment were precipitated in the presence of natural organic matter and applied to microbial reduction experiments [60]. Microbial reduction rates of natural colloids exceeded reduction rates of synthetic ferrihydrite macroaggregates in literature by about two orders of magnitude and were almost similar to dissolved ferric Fe species like ferric citrate. The fast reduction stemmed from the increased solubility of ferrihydrite induced by incorporated natural organic matter. Furthermore, complexed Fe(III) was readily bioavailable for microbial cells and enhanced initial microbial reduction [61]. Similar results with synthetic lepidocrocite nanoparticles precipitated in presence and absence of humic and fulvic acids were obtained by Pédrot *et al*. [57]. Here, microbial reduction with *S. putrefaciens* led to an 8-times faster reduction of the coprecipitated lepidocrocite compared to the pure lepidocrocite. Furthermore, natural organic molecules increase the potential of abiotic photochemical reduction of Fe oxides by the generation of highly reactive intermediates (e.g. organic radicals) and reactive oxygen species (e.g. singlet oxygen, hydrogen peroxide, hydroxyl radicals) [9,62].

Redox cycling of iron

The production of biogenic dissolved Fe(III) or colloidal Fe oxides by Fe(II)-oxidizing bacteria and its depletion by Fe(III)-reducing bacteria occur simultaneously within the same sediment layer [63,64]. A sustained Fe redox cycling was already proposed for different redox interfacial habitats such as hot springs and hydrothermal vents [65,66], at sediment–water interfaces in aquatic ecosystems under circumneutral [63,64] and acidic conditions [67], plant roots [68,69], and groundwater Fe seeps [70]. Synthetic Fe oxides inoculated with cocultures of Fe(II)-oxidizing and Fe(III)-reducing microorganisms [63] or enrichment cultures of freshwater sediment microorganisms [71,72], showed repeated reduction of goethite nanoparticles or ferrihydrite aggregates. This was observed in co-occurrence with Fe(II) oxidation at oxic-anoxic interfaces. These findings were supported by Bloethe and Roden [70] who could show the rapid Fe oxide reduction and the subsequent Fe(II) oxidation in freshly collected, anaerobic seep material. A conceptual model for the bacterial Fe redox cycling is based on the close juxtapositioning of Fe(II)-oxidizing bacteria and Fe(III)-reducing bacteria in cocultures within the Fe(II)-O_2 reaction zone [63,64]. Here, clumping of Fe(II)-oxidizing and Fe(III)-reducing bacteria around Fe oxide aggregates suggested that Fe(III)-reducers take advantage of anaerobic micro zones within the aggregates. These microzones are generated by O_2-scavenging during microbial Fe(II) oxidation, leading to 'ultramicrogradients' of O_2 at the surface of the aggregates. Anoxic conditions at the aggregate surface allow proceeding Fe(III) reduction within a bulk aerobic environment.

The higher reactivity of Fe oxide nanoparticles compared to their macroparticulate counterparts suggests that the efficiency of Fe redox cycling strongly depends on their availability. Recently a field site study proved Fe redox cycling within a floating puffball structure. The authors assumed, based on a former scanning electron microscopy study from the same site [73] that nanometer-sized amorphous Fe oxide particles are the ferric Fe source in this process [74]. Therefore, probably the nanoparticulate Fe oxides are a driving force in the Fe redox cycling process in the environment due to their high reactivity.

Transport of iron oxide colloids

Organic and inorganic colloids have a significant impact on pollutant, trace element, heavy metal, and radionuclide mobilization in soils and groundwater due to adsorption or incorporation [13,75–78]. During the past decades many laboratory studies were conducted to get insights into mechanisms and factors controlling mobility of colloids [79–83] and the concomitant co-transport of trace elements and pollutants [84–88]. Experiments with columns filled with quartz sand and Fe oxide colloids [76] or with natural soil [75,89] demonstrated the strong association of numerous elements (e.g. Ti, U, Pb, Ga, rare earth elements, Y, Cd, V, Sn) to Fe oxide colloids.

Chemical mobilization of colloidal Fe oxides and other minerals occurs mainly in response to decreasing ionic strength, increasing pH and increasing concentrations of dissolved organic carbon or surfactants. Infiltration of dilute precipitation water, irrigation or injection of fresh water for secondary oil extraction leads to the decrease of the ionic strength, an increase of repulsive electrostatic forces, and therefore to the mobilization of colloids. With pH values of 6–9, infiltrating water decreases the hydraulic conductivity of soils through clay dispersion. Introduction of surfactants to aquifers, for example, for the enhancement of oil recoveries or remediation of contaminated aquifers but also infiltration of organic matter-rich groundwater from swampy streams can cause colloid mobilization [13]. Colloid formation occurs very often in contaminant plumes. Here, high concentrations of organic acids, organic macromolecules, and reductants promote the mobilization of colloids [13]. Physical perturbation is mainly induced by increased flow velocities, for example, in fractured media or induced by pumping [13].

The stability of colloids against aggregation is essential for their transport and fate in porous media [6,7]. The stability of colloidal systems can be predicted by the DLVO theory based on repulsive electrostatic forces and attractive van der Waals forces. Strength of these forces depends mainly on ionic strength, pH, surface charge, and presence of adsorbed polymers. At high ionic strength ($\sim$100 mM) [90] the electric double layer shrinks and repulsive electrostatic forces diminish, leading to irreversible aggregation. Depending on the initial thickness of the electrical double layer, moderate ionic strength (10–30 mM) leads to an excess of van der Waals attraction. This results in the formation of a weaker secondary minimum where colloids can reversibly agglomerate to unstable aggregates [90]. Simulations have shown that an absolute value of surface potential, diffuse layer potential, and zeta potential of at least 25 mV stabilizes metal oxide nanoparticles over a huge range of ionic strengths [91]. Pure synthetic amorphous Fe oxide colloids are therefore predicted to be stable only in rainwater and in extreme pH river water because higher ionic strength causes immediate aggregation [92]. Coatings of natural organic matter prevented metal colloids effectively from aggregation because they induced a strongly negative surface charge [91] (Fig. 2).

Other factors controlling the mobility of colloids are heterodomains of attractive surface charge and roughness of the surfaces [93] as well as particle and pore sizes [94]. During the last decades, these interactions were mostly investigated in laboratory systems with glass beads and/or quartz sand as porous media and latex particles [90,94,95]. Apart from enhanced retention at high ionic strength, retention was increased at large colloid sizes relative to pore sizes [94]. Under unsaturated conditions, repulsive interactions between colloids and the liquid–gas interface (e.g. air bubbles) help to overcome repulsive forces between colloids and the porous medium [96]. Requirements for retention were thin water films of a thickness comparable to the colloid diameters. Transport behavior of synthetic ferrihydrite colloids in quartz sand depended on different ionic strengths and flow velocities. At low ionic strength (<5 mM) the influence of the flow rate on particle deposition was negligible, but became more important with increasing ionic strength [97]. The authors calculated travel lengths in clean groundwater (ionic strength $\sim$2–5 mM) of 10–20 m. Increasing ionic strength (up to 10 mM) resulted in a calculated travel distance of a few meters. These findings were in accordance with results on hematite colloids with and without coatings of natural organic matter [98]. Natural organic matter increased stabilization of colloids against aggregation in NaCl-containing solutions. No stabilizing effect was observed in presence of $CaCl_2$, according to the Schulze–Hardy rule. Furthermore, Ca^{2+} is well known to act as bridging agent between humic acids coated ferrihydrite colloids and therefore to promote aggregation [99].

Iron oxide-based remediation technologies

Recent and historical industrial and agricultural activities led to numerous sites with elevated contaminant concentrations in soils, sediments, surface-, and groundwater. In 2007 the European Environment Agency (EEA) estimated 250 000 contaminated sites where remediation was required [100]. Widespread contaminants are trace elements, metalloids, and aromatic, polyaromatic, and chlorinated organic compounds. During the last decades, Fe oxides were drawn into focus of the development of new remediation technologies due to their sorptive and reactive character [101]. *In situ* Fe based treatment methods are potentially cost-effective remediation options (Table 2) [102].

Permeable reactive barriers (PRB) are engineered zones below the water table. The intention is to remove dissolved groundwater contaminants by immobilization, by adsorption or transformation to less harmful products [103]. The materials within the barrier of PRBs depend on the respective contaminant. Iron oxides are used for the removal of, for example, U, Mo, and Cr by adsorption and the chemical reduction of nitroaromatics and dechlorinated aliphatics [103]. Iron oxides have a significant impact on the fate of organic contaminants via oxidative and reductive transformation processes [104]. Structural and mineral-bound Fe(II) reduces chlorinated hydrocarbons and nitroaromatic compounds [105–112]. Interestingly, no size-effect was observed for Fe(II)-mediated abiotic reduction of nitrobenzene with goethite nanoparticles between 7 and 670 nm after specific surface area normalization [113]. However, the authors explain this observation with aggregation of the particles and that the BET values should not be used for the determination of surface site densities of aggregated particles.

The dechlorination reaction of carbon tetrachloride by microbially formed nano-magnetite in a study of McCormick *et al.* [114] was estimated to be 260-fold faster than the enzymatic degradation by *Geobacter metallireducens*. Similar results were found by Tobler *et al.* [115]. Ferrous Fe, formed during the microbial oxidation of toluene with amorphous Fe oxides as electron acceptor by *G. metallireducens*, bound to highly crystalline, macroparticulate Fe oxide surfaces and led to abiotic reduction of 4-nitroacetophenone. Both results indicate the potential of ferrihydrite nanoaggregates as highly reactive material by coupling fast microbial Fe oxide reduction and abiotic Fe(II)-induced reduction of organic contaminants. Use of highly reactive nano-sized Fe oxides could putatively increase the efficiency of the aforementioned remediation technologies.

Arsenic is a widespread naturally occurring contaminant especially in inland or closed basins in arid or semi-arid regions, in strongly reducing aquifers, or in geothermal and mining areas [116]. Different Fe oxides were tested for their potential to remove As by adsorption, with amorphous Fe oxides as the most effective due to the high specific surface area [117,118]. High phosphate concentrations can reduce the sorption capacity of Fe oxides because phosphate competes for adsorption sites with As on hydrous ferric oxides and inhibits therefore As adsorption [102]. However, a study with ferrihydrite colloids derived from a soil column experiment revealed the strong binding of As to ferrihydrite surfaces via inner-sphere complexes which was not impeded by the presence of phosphate and polymerized silica [119].

Magnetite nanoparticles coated with SiO_2 [120] or organic molecules [121] or goethite [102] were shown to be highly efficient for metal ion removal (e.g. Cu^{2+}, Hg^{2+}, Pb^{2+}). Aggregation of Fe oxide nanoparticles decrease the sorption capacity of Cu^{2+} again [122], proving the high efficiency of nanoparticulate Fe oxides for metal ion removal. Those ‘assisted natural remediation’ treatments decrease metal concentrations in soil leachates and soil water and reduce microbial toxicity [102]. Therefore, highly reactive barriers could be easily implemented by using Fe oxide nanoparticles as these are mobile when injected as stable suspensions.

TABLE 2

Different Fe-based remediation technologies: stage of development, mode of application, and estimated costsModified from Cundy *et al.* [102]

Technology	Stage of development	*In situ* or *ex situ*	Remedial mechanism	Estimated cost (US $)
Assisted natural remediation	Laboratory and pilot field trials	*In situ*	Contaminant immobilization	Likely to be relatively low (<$50 per ton material treated)
Chemical reduction via addition of Fe(II)-containing solutions	Commercial systems available	*In situ* or *ex situ*	Reductive precipitation	Cost varies depending on surrounding conditions. $250 000–$300 000 per site
Permeable reactive barriers	Commercial systems available	*In situ*	Sorption or degradation in barrier	$60–$245 per ton material treated

Several Fe-based remediation technologies are still at an experimental or pilot stage and there is a need to verify their effective application in the large-scale field [102]. Widespread applied PRB systems revealed limitations, which include installation methods and the precipitation of minerals derived from reactions with groundwater over time and therefore the significant loss of porosity and permeability within the PRB system [102].

Alternatively, we propose a new *in situ* remediation technology for aquifers contaminated with aromatic hydrocarbons. Direct stimulation of microbial iron reduction seems feasible by injecting Fe oxide colloids into the plume. The fast microbial reduction of the Fe oxide colloids with contaminants as electron donor makes the development of a cost-effective remediation technology possible.

Conclusion and environmental implications

Iron oxide nanoparticles occur in a wide range of environmental compartments. Formed by precipitation from ferrous leachates or by dissolution of larger minerals, they are important agents of redox cycles. In association with organic matter, substitution of Fe^{3+} with other ions, and structural defects especially in natural Fe oxide nanoparticles reduce their crystallinity and increase their microbial availability. Nevertheless, laboratory studies with hardly reactive macroparticulate Fe oxides led to a general underestimation of Fe oxide reduction rates, and neglected the impact of ferric colloids. Yet during the last years more attention was paid to natural and synthetic nano-sized Fe oxides with respect to reactivity and transport behavior in porous media. Results imply an important role of nanoparticles in natural redox cycles. Furthermore, these recent findings indicate a huge potential for ferric nanoparticles in new remediation technologies for organic contaminants and as sorbents for heavy metals.

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