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REVIEW PAPER

Fe (III) reduction strategies of dissimilatory iron reducing bacteria

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Abstract−Advances in applied and industrial microbial biotechnology have opened up many new avenues for application of several microorganisms. A group of certain metal reducers such as the dissimilatory iron reducing microorganisms possess an inherent potential to reduce oxidized metals under strict anaerobic/facultative anaerobic condition, thereby opening possibilities to combat environmental pollution. This unique property has invited researchers towards understanding the metabolic regulatory pathways that enables the microbes to thrive under extreme environmental conditions. Currently, dissimilatory iron reducing bacteria (DIRB) is in the focus of researchers to elucidate the specific mechanisms responsible for microbial metal reduction. The recent advances towards understanding the metabolism of iron reduction in *Shewanella* and *Geobacter*, the model DIRB has been covered in this review. It is believed that the metabolic insights into the Fe (III) reduction systems of the model DIRB; *Shewanella* and *Geobacter* (as discussed in the review) can be a basis for metabolic engineering to provide improved practical applications. With the advancement of our existing knowledge on the metabolic processes of the model iron reducers, applications ranging from laboratory to field scale practices can be carried out. DIRB has gained immense interest for its application in the field of bioremediation, electrobiosynthesis, and bioelectronics in this decade. It can therefore be anticipated that the forthcoming years will see more applications of microbial iron reducers based on the existing as well as advanced metabolic informations available in open source literature.

Keywords: Dissimilatory Iron Reducing Bacteria, *Shewanella*, *Geobacter*, Metabolism, Applications

INTRODUCTION

Iron is the second most redox-active metal on the earth existing in two oxidation states: ferrous (Fe (II)) and ferric (Fe (III)). At circum-neutral pH, Fe (II) rapidly oxidizes to Fe (III) and forms solid phase Fe (III) minerals like goethite, akagenite, hematite or magnetite [1]. In contrast, the reduction of Fe (III) to Fe (II) is comparatively slower and occurs mostly in sub/deep-surface anoxic environments. Previously, Fe (III) reduction was considered to be the result of an abiotic phenomenon until the discovery of microorganisms that were capable of enzymatically reducing Fe (III) in the 19^{th} century. These microbes play a major role in mineral formation via metal reduction during the biogeochemical cycling of iron, carbon, nitrogen, sulphur and phosphate [2-4]. Such a group of microorganisms, namely the iron reducing bacteria (IRB) reduce or transform crystalline and amorphous Fe (III) oxides under anaerobic conditions [5-7]. The role of IRB can be traced back to the Pre-Cambrian Age that led to banded iron formation [8].

Microbial metal reduction is a respiratory process that generates energy for its metabolism, cell growth and reproduction by the reduction of an extracellular metallic terminal electron acceptor in absence of oxygen as terminal electron acceptor. Dissimilatory iron reducing bacteria (DIRB) conserve energy by the oxidation of organic acids/H_2 coupled to reduction of a solid phase as terminal electron acceptor [9]. This strategy of growth by electron transfer in DIRB has been termed as 'extracellular respiration' [10]. Much of the work related towards understanding microbial iron reduction has revolved around IRB such as *Geobacter* and *Shewanella* and are thus considered to be the model iron reducers.

With the advent in scientific research towards exploring some of the processes in which the iron reducers derive their energy to carry out the reduction process, further profound research is essential towards elucidating the underlying mechanisms for a possible industrial application. The present review focuses on providing the details of recent advances on the metabolic strategy adopted by the model iron reducers, *Geobacter* and *Shewanella*, with emphasis on possible future applications in biomineral processing.

DIRB-MINERAL INTERACTION

Before moving into the details of the metabolic pathways and iron reduction strategies, it is desirable to understand the microbe-mineral interactions. The close association between the iron reducers and solid Fe (III) rich surface necessary for an efficient metabolic interaction is mediated by the formation of a biofilm [11,12]. This biofilm is formed by the clustering of microbial cells within its exudate for adhesion, which is majorly composed of EPS (extra polymeric substance) matrix. EPS is a requisite for electron transfer in *G. sulfurreducens* as it forms a scaffold for anchoring the electron transport proteins and helps in conductivity of the biofilm [13]. The conductive nanowires in case of *Geobacter* are also seen to play a vital role in biofilm formation [14]. Deletion of the gene respon-

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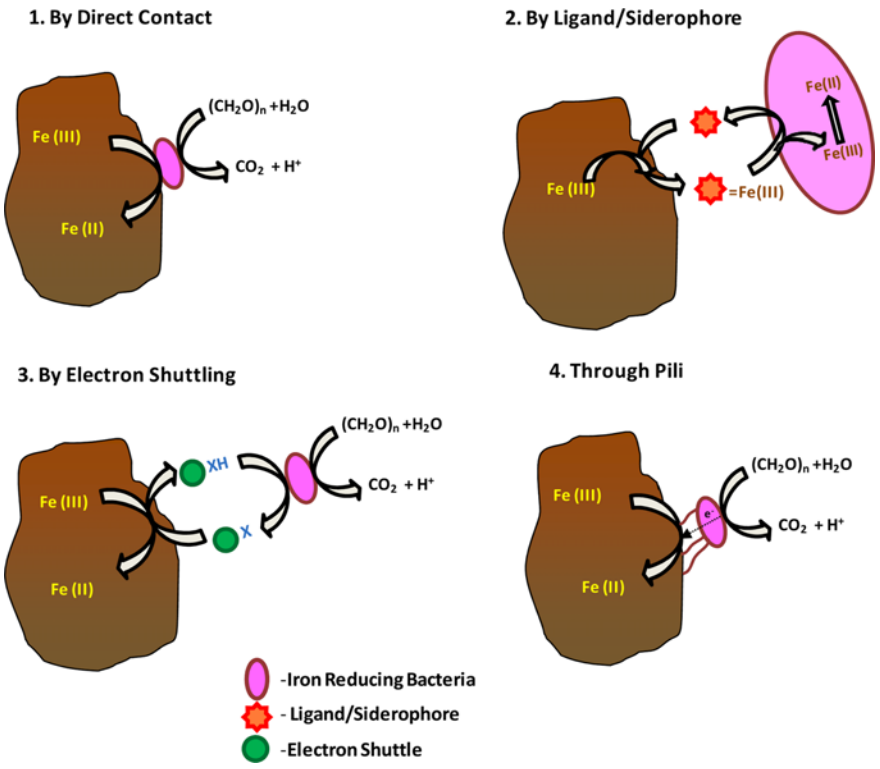

Fig. 1. Schematic illustrating solid phase Fe (III)-DIRB electron transfer mechanisms.

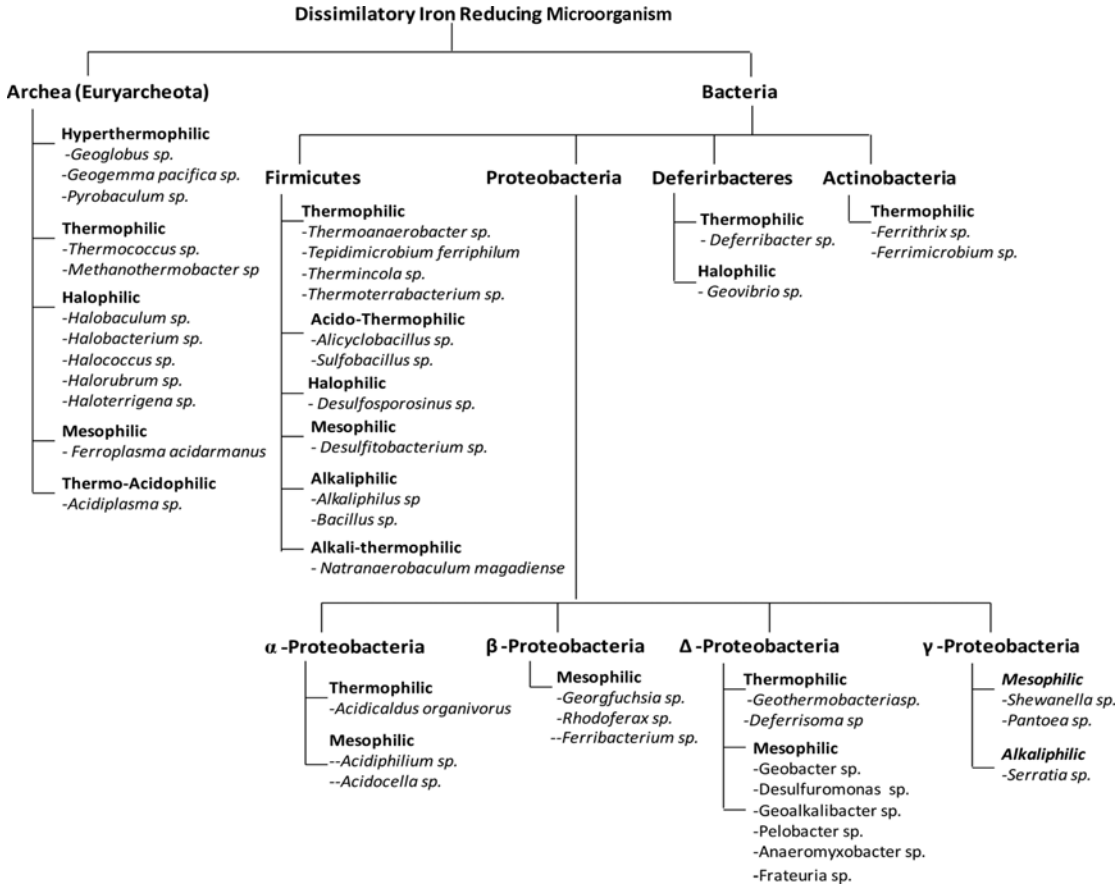

Fig. 2. Classification of Dissimilatory Iron Reducing Microorganism.

sible for EPS formation has been seen to result in a loss of its ability to reduce Fe (III) compounds with thin EPS formation having low cytochrome content [15]. In the case of *Shewanella*, infra-red spectroscopy and proteomics studies on *Shewanella* biofilms indicated the EPS teemed with 20 redox-active proteins out of the 58 proteins identified, which could contribute to the metal reduction and biofilm conductivity in microbial fuel cells (MFC) [16].

In view of the fact that EPS plays a major role in electron transfers, four mechanisms have been conceptualized for the electron transfer between the bacterial cell and Fe (III) surface: (i) direct contact of bacterial cell surface redox-active compounds to Fe (III) surface; (ii) through ligands (chelators/siderophores) which solubilize Fe (III) by complex formation; (iii) by redox cycling of electron shuttle between the bacterial cell and Fe (III) surface; and (iv) contact mediated by pili, also known as 'protein nanowires' between bacteria and Fe (III) surface [17]. These mechanisms are schematically described in Fig. 1.

CLASSIFICATION OF DISSIMILATORY IRON REDUCING MICROORGANISMS (DIRM)

Numerous DIRM have been identified belonging to various taxa of bacteria and archaea. Both bacteria and archaea consist of thermophilic, halophilic iron reducers. Most of the archaeal iron reducers belong to euryarcheota taxa, while the bacterial iron reducers find themselves belonging to different taxa of Firmicutes, Proteobacteria, Deferribacteres, Thermotogae, Actinobacteria. Fig. 2 shows various iron reducers categorized under different taxa. Iron reducers belonging to archea thrive mostly under extreme conditions such as *Geoglobus* sp., *Geogemma pacifica* sp., *Pyrobaculum* sp. which are hyper-thermophilic, *Thermococcus* sp., *Methanothermobacter* sp. are thermophilic, *Acidiplasma* sp. is thermo-acidophilic, *Ferroplasma acidarmanus* is an mesophile while *Halobaculum* sp., *Halobacterium* sp., *Halococcus* sp., etc are halophiles. Under bacteria, the taxa firmicutes consist of a range of extremophiles. *Thermoanaerobacter* sp., *Tepidimicrobium ferriphilum*, *Thermincola* sp. are thermophilic while *Alicyclobacillus* sp., *Sulfobacillus* sp., thermoacidophiles. Halophilic, mesophilic, alkaliphilic and alkali-thermophilic iron reducers too exist in this taxonomy. Deferribacteres consist of thermophilic and halophilic iron reducers, while actinobacteria are mostly thermophilic. The iron reducers under the taxa Proteobacteria are distributed in different classes of α-, β-, Δ- and γ-proteobacteria. The most extensively studied model iron reducers, *Shewanella* and *Geobacter* belong to Δ-proteobacteria and γ-proteobacteria, respectively. The existence of a number of species belonging to the genus *Shewanella* and *Geobacter* are widely distributed in our eco-

Table 1. Nutrition and distribution of some DIRB strains

S. No	Bacterial strain	Electron donor	Electron acceptor	Conditions	Habitat & geographical source	Reference
1.	*Pelosinus fermentans*[*]	Fermentable substrate	Fe(III) and AQDS	Mesophilic	Subsurface primary kaolin deposits in Russia.	[20]
2.	*Geoglobus acetivorans* sp. nov.	Acetate, formate, pyruvate, fumarate, malate, propionate, butyrate, succinate,	Fe(III) oxide and Fe(III) citrate	Thermophilic	World Ocean Hydrothermal field, Ashadze Field, Mid-Atlantic Ridge	[21]
3.	*Geothrix fermentans* gen. nov., sp. nov[*]	Propionate, palmitate, lactate, fumarate or succinate	Fe (III), Mn(IV), nitrate, 2,6-anthraquinone disulfonate or fumarate	Mesophilic	Petroleum-contaminated aquifer, Hanahan, USA	[22]
4.	*Geoalkalibacter subterraneus* sp. nov.	Formate, acetate, malonate, propionate, pyruvate, lactate, butyrate, isobutyrate, succinate, fumarate, valerate	Fe(III), Mn(IV), nitrate, elemental sulfur and trimethylamine N-oxide	Mesophilic	Production water of Rewash Oilfield, USA	[23]
5.	*Deferribacter thermophilus*	Hydrogen, acetate, malate, citrate, pyruvate, lactate, succinate, and valerate	Fe(III), Mn (IV), and nitrate	Thermophilic	Beatrice Petroleum Reservoir, North Sea	[24]
6.	*Bacillus subterraneus*[*]	Yeast extract, glucose, sucrose, fructose, maltose, xylose, starch, glycerol, ethanol or lactate	Amorphous Fe(III), Mn(IV), Nitrate, Nitrite and Fumarate	Mesophilic	Subterranean Thermal waters of the Great Artesian Basin of Australia	[25]
7.	*Acidiphilium cryptum* JF-5[*]	Glucose, Cellobiose, Hydrogen	Fe(III)	Meso-acidophilic	Acidic Coal mine lake, East Central Germany	[26]
8.	*Bacillus pseudormus* MC02	Sucrose, lactate, glucose and glycerol	Fe (III), AQDS, Humic acids	Meso-alkaliphilic	Sludge-fed microbial fuel cell	[27]

[*]Type strains

Table 2. Nutrition and distribution of *Shewanella* strains

Sl. No	Bacterial strain	Electron donor	Electron acceptor	Conditions	Habitat & geographical source	Reference
1.	*Shewanella amazonensis* sp. nov.*	Acetate, succinate, fumarate and citrate	Fe (III) oxide, Manganese oxide, Sulphur	Mesophilic	Amazonian Shelf-muds, Brazil	[28]
2.	*S. putrefaciens* IR-1	Lactate, Pyruvate	Insoluble Fe (III) (FeOOH) and soluble Fe (III) citrate	Mesophilic	Paddy Fields, Seoul	[29]
3.	*Shewanella* sp. HN-41	Lactate, formate, pyruvate	Fe (III), As(V), U(VI), Se(IV)	Mesophilic	Tidal flats in Haenam Jeollanam-do, Southwest coast of Republic of Korea	[30]
4.	*S. putrefaciens* CN-32	Lactate	Fe (III), Mn(IV), nitrate, Oxygen, U(VI), fumarate	Mesophilic	Sub-surface of shale sandstone, Albuquerque, New Mexico	[31]
5.	*S. oneidensis* MR-1*	Lactate	Fe(III)-citrate, Mn(IV), Nitrate, Fumarate, TMAO, DMSO	Mesophilic	Anaerobic sediments of Lake Oneida, New York	[28]
6.	*S. baltica* W3-6-1	Lactate	Fe(III), oxygen, nitrate	Psychrotolerant	Deep Pacific Ocean marine sediments, USA	[32]
7.	*Shewanella* sp. PV-4	Lactate, formate, pyruvate, hydrogen	Fe(III)-citrate, O_2, Fe(III), Co(III), Cr(VI), Mn(IV), U(VI), fumarate	Psychrotolerant	Hydrothermal vent of Loihi Seamount, Pacific Ocean	[31]
8.	*S. peizotolerans* WP3	Lactate	Hydrous Fe (III) Oxide (HFO)	Psychrotolerant, Peizotolerant	West Pacific deep-sea sediments	[33]
9.	*S. decolorationis*	Lactate, Acetate	Nitrate, Iron oxide and Thiosulfate	Mesophilic	Activated sludge of textile-printing waste-water, Guangzhou, China.	[34]
10.	*S. frigidimarina**	Sodium lactate, Sodium acetate	Fe (III) compounds, nitrate, TMAO	Psychrotropic	Antarctic sea ice	[35]
11.	*S. gelidimarina**	Sodium lactate, Sodium acetate	Fe (III) compounds, nitrate, TMAO	Psychrophilic	Antarctic sea ice	[35]
12.	*S. loihica*	Lactate	Fe (III) citrate MnO_2, Akaganeite, Uranyl carbonate, HFO, TMAO	Psychrotolerant	Iron-rich microbial mats of Loihi Seamount, Hawaii, Pacific Ocean	[36]
13.	*S. pealeana**	Lactate	Iron, Nitrate, Fumarate, Manganese, TMAO, Thiosulfate and elemental sulfur	Mesophilic, Psychrotolerant	Accessory nidamental gland of the squid *Loligo pealei*	[37]

*Type strains

system according to the available electron acceptors and donors for their growth and sustenance. The nutritional requirement and distribution of most *Shewanella*, *Geobacter* species and other iron reducing species are tabulated in Tables 1, 2 and 3, respectively, for a direct comparison.

IRON REDUCTION STRATEGY IN *Shewanella*

Shewanella sp. are facultative anaerobes capable of partial oxidation of lactate coupled to reduction of soluble electron acceptors as well as solid mineral phases [46]. They have a versatile respiratory system to utilize diverse electron acceptor, including several metal oxides and organic compounds such as Fe (III), Mn (IV), S^o, sulfite, nitrate, O_2, Cr (VI), and U (VI), DMSO, and trimethylamine-N oxide, but have narrow capacity to utilize simple carbon source like acetate, lactate, formate, glucose as electron donor [47-49]. The following sections discuss the electron transport systems in *Shewanella* genera.

1. Direct Electron Transfer Via the Mtr Pathway

S. oneidensis MR-1 is considered as a model organism of this genus as its complete genome sequence is available [50] to understand the biochemistry behind this 'extracellular respiration'. *S. oneidensis* MR-1 has an extraordinary branched electron transport system that includes more than 40 multi-haem c-type cytochromes, quinones, dehydrogenases and Fe-S proteins [51-54]. Extensive studies have been performed to identify the specific cytochromes and

Table 3. Nutrition and distribution of *Geobacter* strains

S. No	Bacterial strain	Electron donor	Electron acceptor	Conditions	Habitat & geographical source	Reference
1	*Geobacter bemidjiensis* sp. nov.*	Lactate, pyruvate, acetate, malate, succinate, ethanol	Fe(III), fumarate, AQDS, malate and manganese(IV) oxide	Mesophilic	Sub-surface Aquifer in Bemidji, MN, USA	[38]
2.	*G. psychrophilus* sp. nov.	Acetate, butanol, ethanol, formate, lactate, malate, pyruvate, succinate	AQDS, Fe(III) citrate, Fe(III) oxide, Fe(III) pyrophosphate, Fe(III) NTA, fumarate, malate, manganese(IV) oxide and graphite electrodes	Psychrotolerant	Sub-surface Aquifer in Bemidji, MN, USA	[38]
3.	*G. bremensis* sp. nov.*	Formate, acetate, propionate, butyrate, pyruvate, lactate, malate, succinate, fumarate	Fe(III), Mn(IV), S^o, fumarate and malate	Mesophilic	Sediments of Freshwater ditches in Bremen, Germany	[39]
4.	*G. pelophilus* sp. nov.*	Hydrogen, Formate, Acetate, Propionate, Pyruvate, Malate, Succinate, Fumarate,	Fe(III), Mn(IV), S^o, fumarate and malate	Mesophilic	Sediments of Freshwater ditches in Bremen, Germany	[39]
5.	*G. daltonii*	Fumarate, acetate	Fe(III) citrate, elemental sulfur, malate and fumarate Fe(III)-oxyhydroxide	Mesophilic	Oakridge shallow subsurface containing mixed waste of U (IV) and aromatic hydrocarbons	[40]
6.	*G. lovleyi* sp. nov. strain SZ*	Acetate, Pyruvate, and Hydrogen	Nitrate, soluble and insoluble forms of Fe (III), manganic, sulfur, fumarate, malate, and U(VI)	Mesophilic	Freshwater sediment collected from Su-Zi Creek, South Korea	[41]
7.	*G. metallireducens**	Shortchain fatty acids, alcohols, and monoaromatic compounds acetate	Poorly crystalline Fe (III), Mn(IV), U(VI), and nitrate	Mesophilic	Freshwater sediments of the Potomac River, Maryland	[5]
8.	*G. luticola*	Acetate, lactate, pyruvate and succinate	Fe(III)-NTA, Fe (III) citrate, amorphous iron (III) hydroxide and nitrate	Mesophilic	lotus field mud in Aichi prefecture, Japan	[42]
9.	*G. pickeringii*	Methanol, ethanol, butanol, glycerol, acetate, lactate, butyrate, pyruvate, succinate and valerate	Fe(III) citrate, Fe(III) NCA, Fe(III) pyrophosphate, MnOOH, elemental sulfur, AQDS, fumarate and malate	Mesophilic	Sedimentary kaolin strata in Georgia, USA	[43]
10.	*G. argillaceus*	Ethanol, butanol, glycerol, acetate, lactate, butyrate, pyruvate and valerate	Fe(III) citrate, Fe(III) NCA, Fe(III) pyrophosphate, MnOOH, elemental sulfur and nitrate	Mesophilic	Sedimentary kaolin strata in Georgia, USA	[43]
11.	*G. sulfurreducens**	Acetate, Hydrogen	Fe(III) PP1, Fe (III) oxyhydroxide, Fe (III) citrate, elemental sulfur, Co(III)-EDTA, fumarate, malate	Mesophilic	Surface sediments of a hydrocarbon-contaminated ditch in Norman, Okla	[44]
12.	*G. uraniireducens*	Acetate, lactate, pyruvate, ethanol	Fe(III), Mn(IV), AQDS, malate, fumarate	Mesophilic	Subsurface sediment undergoing uranium bioremediation at Old Rifle	[45]

*Type strains

other biomolecules involved for further elucidation of the biochemical pathways involved in electron transfer during Fe (III) reduction [55,56]. Electron transfer for reduction of metals and electrodes in *Shewanella* sp. is known to occur through a group of proteins

spanning the cell membrane forming the Mtr pathway [57,58]. Four multi-heme cytochromes CymA [59], MtrA [60], MtrC [61] and OmcA [62] along with a non-heme protein MtrB [63] are believed to constitute the Mtr pathway that transfers electrons from the menaquinone pool to the cell surface [58]. Until recently, after gaining deeper insight into this Mtr pathway, this microbe-mineral interaction in *Shewanella* has been descriptively renamed as 'porin-cytochrome' model, as the MtrB behaves like a pore and in association with the other cytochromes helps in electron transfer across the membrane [64]. OmcA and MtrC are the outer membrane cytochromes that can interact directly with Fe (III) or redox-active flavins that indirectly reduce Fe (III) [65].

CymA, a tetraheme cytochrome c, is a member of the NapC/NirT family of quinol dehyrogenases that has been reported to be indispensable for the respiratory versatility of the bacteria [66,67]. CymA recycles the QH_2 pool of the inner membrane and transfers electrons to MtrA cytochrome of outer membrane via numerous small molecules such as tetra-heme cytochromes (STC), fumarate reductase (Fcc_3) and monohaem cytochromes c_5 (ScyA) [68-70]. Lack of interactions among these cytochromes in the periplasmic space has indicated the existence of two separate pathways from CymA to MtrA: one involving STC and the other involving Fcc_3 [71]. Mutation in the gene encoding CymA resulted in a Fe (III) reduction deficient strain [72]. Further investigation proposed the ability of SirC, a Fe-S protein and SirD, a hydroquinone dehydrogenase to functionally replace CymA through transfer of electrons by an alternative pathway, due to expression of insertion sequence (IS) genes [73].

MtrA transfers the electrons to OmcA/MtrC through a porin protein MtrB. *mtrA* deficient cells are unable to transfer electrons due to the instability of the MtrABC complex caused by absence of MtrA cytochrome [74,75]. MtrA-MtrB-OmcA/MtrC complex forms a conductive channel for electron transfer from periplasm to outer surface [10,75].

MtrB is a β-barrel protein spanning the outer membrane connecting the periplasmic MtrA and outer membrane cytochrome MtrC [63,77]. MtrC and OmcA are the terminal reductases of Mtr respiratory pathway [56]. Though both these c-type cytochromes contain ten heme proteins with broad redox potentials [55,74], several studies using UV-visible spectropotentiometric titrations and electron paramagnetic resonance (EPR), scanning tunneling microscopy and tunneling spectroscopy consistently highlight their different electron transfer properties [78-80]. Lower et al. [81] found that there exists a direct interaction (electron transfer) of purified MtrC and OmcA with hematite, an iron oxide by atomic force microscopy measurements [81]. Their findings show that the binding strength of OmcA-hematite is twice the binding strength of MtrC-hematite, while the binding frequency of MtrC-hematite is twice the binding frequency of OmcA-hematite [81-83]. They also reported that both MtrC and OmcA possess hematite binding motif of Thr-Pro-Ser/Thr using phage display technology, and concluded that the apparent rate constant of electron transfer between the outer membrane cytochromes and hematite was quite low [83,84] which agrees with the observation of Hansel et al. [85] that the Fe (III) reduction rate is slow in *Shewanella* [85]. However, Fe (III) reduction was observed to be enhanced on addition of flavins, suggesting its shuttling role during MtrC/OmcA-mediated electron transfer [86]. The role of MtrC in electron transfer to solid phases with OmcA playing larger role in attachment was further studied and confirmed by Coursolle and Gralnick [58]. The role of these cytochromes in the Fe (III) reduction has been discussed in many recent reviews [17,55,56,87]. The bioenergetics of iron metabolism has been reviewed by Bird et al. [88].

2. Indirect Electron Transfer

Indirect electron transfer refers to the 'electron shuttling mechanism' wherein the redox-active compounds shuttle the electrons from cell surface to Fe (III) source [10,17]. Soluble redox-active shuttles are responsible for indirect electron transfer in *Shewanella*. These electron shuttles can be exogenous like humic substances and sulfur compounds [89,90] or endogenous as those secreted by the organism itself. *Shewanella* has been found to produce endogenous electron shuttle molecules like riboflavin [91] and riboflavin mononucleotide (FMN) [92]. Seven protein encoded genes responsible for flavin biosynthesis are found in 23 genome sequenced *Shewanella* species with exception of *Shewanella denitrificans* which lack the ribB gene and the Mtr respiratory pathway genes, making it incapable of reducing metal oxides and electrodes [17]. The exact mechanism by which the synthesized flavins traverse the inner membrane is unkown. The riboflavin (RF) transport genes were not found in *Shewanella* unlike other bacteria. Covington et al. [93] found that FAD is the form that can enter the periplasmic space [93]. FAD secretion serves two purposes: (i) Incorporation in fumarate reductase (FccA). FccA is the most prominent cytochrome present in the periplasm when grown anerobically under Fe (III) reducing conditions. It contains an N-terminal tetraheme domain and a flavin domain with non-covalently bound FAD. Schuetz et al. [70] provided evidence that FccA is a transient energy storage protein which allows the use of carbon and electron source even if electron acceptor is absent, by itself acting as an e-acceptor [70]. (ii) Hydrolysis of unbound FAD by UshA to be utilized as electron shuttles. UshA is a predicted periplasmic 5′ nucleotidase.

MtrF, MtrD, and MtrE are homologues of MtrC, MtrA, and MtrB. The *mtrDEF* operon is highly expressed during biofilm growth. An X-ray crystal structure of MtrF was proposed as a model of electron transfer [76]. The trifurcated structure of MtrF gives molecular insight into the possible mechanism of insoluble Fe (III) reduction in the cell surface. A 3.2 Å resolved crystal structure with ten hemes spatially arranged in a crossed confirmation is explained to understand electron conduit for reduction of insoluble substrates, soluble substrates and redox cytochromes. The exact mechanism of indirect electron transfer by Fe (III) complexing ligands and the soluble Fe (III) complexes is still unknown. But some organic Fe (III) complexes have been observed in *Shewanella putrefaciens* 200 as studied by Taillefert et al. [94].

3. Direct Electron Transfer Via Pili

Direct electron transfer mediated by pili has been reported for *Shewanella* sp. Pili are the non-flagellar polypeptide structures found to be electrically conductive and are also known as bacterial nanowires [95,96]. Msh and Pil are the two major Type IV pilin secretion systems in *Shewanella* sp. Fitzgerald et al. [97] studied the role of *msh* biosynthetic system in electron transfer of *S. oneidensis* MR-1. Using a bioinformatics tool, they predicted 16 Msh pilin proteins.

A comparative study of hypothetical *S. oneidensis* MR-1 Msh pilin complex in wild type and mutants towards current output was made. The results indicated that Msh biosynthetic pilin expression system proteins (base) are more important to electron transfer than the actual extracellular structural pilin proteins (nanofilaments). Msh pili proteins are also capable of direct electron transfer in *S. oneidensis* MR-1 [97].

IRON REDUCTION STRATEGIES IN *Geobacter*

Geobacter metallireducens is the first isolated species of *Geobacter* genus [9] and the first *Geobacter* species to find application in bioremediation and bioelectrochemical systems [2,98]. However, the genome of *G. sulfurreducens* has been completely sequenced [99], and with the availability of a genetic system [100] it is considered the model organism for this genus. In contrast to *Shewanella*, *Geobacter* species is a strict anaerobe which can completely oxidize the carbon source coupled to the reduction of Fe (III).

Studies on the electron transfer mechanism from *Geobacter* cells to solid Fe (III) oxide have concluded that *G. metallireducens* lack electron shuttling or iron chelating compounds and are incapable of solubilizing Fe (III), but addition of Fe (III) chelating compounds has stimulated the solubilization and hence Fe (III) reduction [101-103]. Hence, electron transfer to Fe (III) in *Geobacter* sp. has been suggested to mostly occur by direct contact at the outer cell surface [103-106]. The genome of *G. sulfurreducens* has 111 putative genes for c-type cytochromes, with at least 30 of them being outer membrane (OM) cytochromes. But only four (OmcB, OmcS, OmcE, OmcZ) of the OM cytochromes are reported to play a role in Fe (III) reduction. The exact pathway of electron transfer from periplasm to OM is still not clearly understood [107], but a soluble triheme cytochrome PpcA seems to serve as intermediary electron transferring protein which is the best studied protein to date [108, 109]. OmcB is known to be the most important protein involved in reduction of insoluble Fe (III) and Fe (III) citrate. OmcE and OmcS are identified to be loosely attached to the OM and can be easily released on shearing. They are proposed to take the role of electron transfer directly to the Fe (III) surface, similar to MtrC and OmcA of *S. oneidensis* MR-1. OmcS was found to be aligned along the pili, enabling the transfer of electrons to Fe (III) oxides [110]. OmcS also has been suggested to function as capacitors, i.e., temporarily store electrons during cell transition between Fe (III) sources [111].

The exopolysaccharide (EPS) matrix in *Geobacter* has been reported to be rich in OmcZ, an octaheme c-type cytochrome that plays a significant role in electron transfer and is essential for high density current in a microbial fuel cell (MFC). Mutants with deleted *omcZ* gene lack the ability to utilize solid electron acceptors [112]. Deletion of the *omcZ* gene decreases current production in fuel cells drastically and irreversibly [113]. Deletion of *omcB*, *omcS*, and *omcE* genes impedes current generation and gets adapted by increased OmcZ redox mediators [114]. The electron transfer process in *Geobacter* biofilms is described as 'electron superexchange' for their superior catalytic activity on anodes [115]. This exclusive ability of DIRB is exploited in microbial fuel cells for generation of current. The expression level of the *omcZ* gene is similar in the inner and outer sections of the anode biofilm in MFCs [116].

It has also been reported that outer membrane proteins (Omp) apart from c-type cytochromes are essential for electron transfer during Fe (III) reduction [104,107,117-119]. Afkar et al. [117] identified a novel outer membrane protein: OmpJ that is specific to *Geobacteraceae* family, which is a putative porin responsible for reduction of soluble and insoluble Fe (III) indirectly. It maintains the integrity of the periplasmic space for proper folding and functioning of other periplasmic and outer membrane components. OmpJ shares 21% identity and 51% similarity with amino acids of the Omp35 of *S.oneidensis* MR-1 which is a porin-like protein involved in indirect metal reduction.

Mehta et al. [118] first reported a multicopper oxidase protein OmpB with a competent Fe (III) binding site and fibronectin motifs, suggesting the possible role of OmpB in accessing Fe (III) oxides [118]. OxpG, a psuedopilin involved in type II secretion system, is responsible for exporting the OmpB across outer membrane, which remains loosely associated with outer surface [120]. To evaluate the *ompB* expression patterns in different metabolic states of *Geobacter* sp., Holmes et al. [119] identified another multicopper outer membrane protein, OmpC, a homologue of OmpB which is a requisite for optimal Fe (III) oxide reduction [119]. Putative multicopper proteins have been identified in other metal-reducing bacteria, signifying their role in Fe (III) reduction.

1. Electron Transfer through Pili

Geobacter is essentially known to interact with solid Fe (III) oxide using Type IV pilin filaments, also known as 'bacterial nanowires' [107,121]. These filaments constitute multiple copies of PilA proteins. Deletion of the *pilA* gene failed to produce pili in the DL-1 strain of *G. sulfurreducens* [107] and in *G. metallireducens* [122], leading to loss of growth on Fe (III) oxide and elimination of high density current production capacity [113,123,124]. But complementation of mutation with a functional copy of the *pilA* gene intrans restored its capacity to produce pili and hence Fe (III) oxide reduction. Hence, PilA is required for long-range electron transfer and is expressed at equivalent levels in the outer and inner layers of mature biofilm [116], which when correlated with the electrochemical data confirms that PilA protein is the electron transfer mediator between cells of a thick biofim and at cell/electrode interface [125]. High electrical conductivity of *Geobacter* pili was observed by conductive probe of AFM, while no conductance was observed in the pili of other IRB like *Shewanella,* as reported by Reguera et al. [107]. However, about the same time, Gorby et al. [95] stated the electrical conductance along the diameter of *Shewanella* pili grown in electron-acceptor limited conditions, when examined under scanning tunneling microscopy (STM) [95]. El-Naggar et al. [96] demonstrated the electron transport along the pili of *Shewanella* under the same deficit conditions, serving as strategic extracellular electron transport system [96]. Deeper investigation into the nanowires of *Shewanella* confirmed them to exhibit p-type, tunable electronic behavior comparable to synthetic organic semiconductors [126]. Production of pili by *G. sulfurreducens* was localized to one side of the cell [103] and occurred only during growth on Fe (III) oxide and not on soluble Fe (III), highlighting its need for electron transfer while growth on a solid phase.

Much extensive research has been done to date to understand

Table 4. Comparsion of the characteristic features in *Shewanella* sp. and *Geobacter* sp.

Feature	*Shewanella* sp.	*Geobacter* sp.
Oxygen requirement	Facultative anaerobe	Strict anaerobe
Carbon source	Use lactate preferentially as electron donor and is incompletely oxidized to acetate	Use acetate preferentially as electron donor and is completely oxidize acetate to CO_2
Mode of Fe (III) reduction	No physical contact is necessary for Fe (III) reduction	No Fe(III) reduction takes place without physical contact
Secretion of electron shuttles	Secrete soluble cytochromes like flavins as electron shuttles	Do not secrete flavins or other soluble chelators or e^- shuttles
Conserved sequence	MtrA is conserved in the sequence	OmcE and OmcS are not conserved in the sequence
Electron transfer pathway	Have a mechanistic pathway for electron transfer	Limited information available and hence lack a mechanistic explanation for electron transfer via pilin proteins

the mechanism of electron transfer via pili. An emphasis towards elucidating the structure of the pili has been made [127,128]. Malak et al. [129] reported that electrons hop through a chain of amino acids along peptides till they reach the electron acceptor [129]. This electron-hopping model favors long-range electron transfer though requiring intermediate aromatic amino acid stations to harbor the electrons for short duration [130]. Thus, PilA subunit of *Geobacter* pili has been suggested to transfer electrons using this electron-hopping model and intense efforts are being made to identify the amino acids of mature PilA and their role in insoluble Fe (III) oxide reduction. Toward this end, as investigated by Reardon et al. [128] the carboxyl terminus of *Geobacter* PilA is the region that most differs from pilA of other microbes and has five aromatic residues [128]. Vargas et al. [131] constructed an Aro-5 strain of *G. sulfurreducens* by substituting the five aromatic acids of PilA with alanine, which hence produced pili of diminished conductivity [131]. The conductivity of Aro-5 biofilms was ten-fold lower than control strains with graphite anode as electron acceptor, though it still served as a scaffold for the cytochromes. Aro-5 strain lacked the ability to reduce insoluble Fe (III) oxide, demonstrating that OmcS associated pili [110] does not suffice for Fe (III) reduction; pili should be conductive too. Aro-5 strains produced relatively thicker biofilms than *pilA* deficient strains [111,124], indicating that the presence of PilA supports better cell cohesion in biofilms. This study confirms the hypothesis of Malvankar et al. [132] that aromatic amino acids are required for tunable metallic-like conductivity of *G. sulfurreducens* pili [132].

Richter [133] identified an amino acid Tyrosine at position 32 of the C-terminal of mature PilA to be posttranslationally modified with a glycerolphosphate molecule [133]. Strains with point mutation of Tyrosine of PilA with phenylalaine produced a mutant incapable of Fe (III) reduction and current generation, suggesting the significant role of the glycerolphosphate moiety in the pilus surface chemistry for reduction by attachment and electron transfer to Fe (III).

Though numerous studies on physiological functions and mechanisms have been done using *G. sulfurreducens*, it lacks many physiological features of *G. metallireducens* [122]. *G. metallireducens* has been reported to reduce Fe (III) oxide 17 times faster than *G. sulfurreducens* [134], which may be credited to the flagella expression by *G. metallireducens* [104] in comparison with the non-motility of *G. sulfurreducens* [44]. *G. metallireducens* synthesize specific appendages to contact the Fe (III) phase only when they sense its need by chemotaxis.

DIVERGENCE IN Fe (III) METABOLISM AND CHARACTERISTICS IN *Shewanella* AND *Geobacter*

Shewanella and *Geobacter* have diverse mechanism of Fe (III) metabolism. Though c-type outer membrane cytochromes (OMCs) play a relatively vital role in Fe (III) metabolism of both *Shewanella* and *Geobacter*, the mechanisms vary and are tabulated in Table 4.

ADSORPTION OF BIOGENIC Fe (II): CAUSE OF DECELERATED BIO-REDUCTION OF Fe (III) BY DIRB OVER EXTENDED TIME

The rate and extent of Fe (III) oxide bio-reduction by DIRB is majorly influenced by its crystallinity, surface chemistry (specific surface area), surface area, and particle size. The available literature provides evidence that the rate of bio-reduction was higher for amorphous Fe (III) than crystalline Fe (III) in the order: amorphous Fe (III), i.e., Hydrous Fe (III) Oxide>Goethite>Hematite [135]. Also, smaller particle size with increased surface area resulted in higher Fe (III) oxide bio-reduction activity. Studies with a continuum of Fe (III) oxide particle types provide explicit evidence for the linear relationship of surface area with Fe (III) bio-reduction rate [135,136].

The decrease in the rate of Fe (III) oxide bio-reduction over extended time may be attributed to the adsorption/precipitation of accumulated biogenic Fe (II) blocking the reactive dissolution sites of Fe (III) oxide such as kinks [135] and decreased thermodynamic driving force, due to accretion of biogenic products at interface or decreased biologically available reaction potential [137]. Formation of secondary Fe (II) precipitates like Fe_2O_3, $FeCO_3$, and $Fe_3(PO_4)_2$, on Fe (III) oxide surface is also suggested to be an important agent in cessation of Fe (III) bio-reduction [138]. Several studies have considered the speciation of Fe (II), especially in batch cultures to establish its crucial role in the rate and extent of Fe (III) oxide reduction activity [139].

Delay or retardation in sorption/precipitation of aqueous biogenic Fe (II) can activate the Fe (III) oxide bio-reduction over extended time. Attempts were made toward this by addition of Fe

(II) complexants and ligands like citrate, EDTA and NTA, which either complexed with Fe (III) followed by its solubilization at the oxide surface or complexed with biogenic Fe (II), retarding its sorption on DIRB cells/Fe (III) oxide surface [101,102,139].

Addition of natural organic matter like humic acids, riboflavin, AQDS, ferrozine, methyl viologen and methylene blue enhanced Fe (III) oxide bio-reduction through electron shuttling abiotically via their quinone functional groups [137,140,141]. The retarded reduction activity was also found to be revived on addition of fresh media and inoculum [138]. Removal of Fe (II) ion in semicontinous cultures [39] and continuous flow column reactors via advective transport attained a greater degree of Fe (III) oxide bio-reduction over extended time compared to batch experiments [142]. The presence of other solid phase compounds like alumina, kaolin, quartz, layered silicates has been found to behave as Fe (II) sinks which draw away the biogenic Fe (II), decelerating the surface passivation on DIRB cells/Fe (III) oxide surface, thereby enhancing the Fe (III) bio-reduction activity [139,143].

High concentrations of phosphate (≥4 mM) in culture media diminshed Fe (III) bio-reduction activity by formation of precipitates with excess biogenic Fe (II) such as $Fe_3(PO)_4$, mineralogically identified as vivianite [138,140,144], although some studies state the lack of phosphate influence on Fe (III) bio-reduction when around 30 μM was used in the growth medium [137].

Apart from the speciation of biogenic Fe (II) influencing the extent of Fe (III) bio-reduction as discussed above, numerous other factors appear to regulate the activity such as type and concentration of electron donor, medium composition, post-bioreduction geochemical reactions, structural, thermodynamic and surface physico-chemical properties of solid phase oxide and other physiological factors such as metabolic status and growth of DIRB [144].

APPLICATIONS OF DISSIMILATORY IRON REDUCING BACTERIA (DIRB)

1. Application of DIRB in Biomineral Processing

In biomineral processing, microorganisms play a vital role in extraction of valuable metals from their ores and mineral wastes. Several heterotrophic microorganisms like *Aspergillus* sp., *Penicillium* sp., *Bacillus* sp., etc. and chemolithotrophs like *Acidithiobacillus*, *Leptospirillum*, and *Sulphobacillus* have been reported to be actively involved in biomineral processing [145]. These leaching microbes carry out a bio-oxidation process which is not successful in leaching iron oxidic minerals, as the solubility of oxidized Fe (III) is lower than Fe (II) [146]. To overcome such a problem associated with the oxidic based ores, a process of reductive bioleaching may contribute to dissolution/reduction of iron, providing a platform to release certain associated metals that are otherwise difficult to leach in their original form. Such an attempt is very scarce in the literature where few studies have emphasized the role of DIRB in reductive leaching. DIRB has been found efficient in bio-beneficiation of bauxite [147], kaolin [148], silica [149] contaminated with iron impurities. DIRB reduced the Fe (III) in the ore matrix to soluble Fe (II), which can be easily removed, thereby refining the ore. Further, few studies have focused on the application of DIRB in bioleaching of iron bearing ores. Eisele studied the removal of iron from low-grade magnetite under continous conditions in column using IRB which released around 1.8 g/l iron over an extended time of 300 days [150]. Pradhan et al. [151] first observed the mineral transformation of chromite overburdens (COB) from goethite [Fe (III)] to magnetite and hematite [Fe (II)] by the action of enriched DIRB, resulting in the release of the goethite embedded nickel alongwith cobalt dissolution from COB of Sukinda Valley, India. Further to this study, efficient bio-reduction of COB prior to acid leaching has been conferred to DIRB for enhanced recovery of nickel and cobalt [152]. However, extensive studies towards application of DIRB towards metal recovery using a more appropriate bioleaching (bioreduction using DIRB+leaching)-solvent extraction-electrowinning route is still not practiced. Such biohydrometallurgical application to recover metal values using DIRB is expected to provide new insights into the the application of mineral reducers in the biomineral processing area.

2. Application of DIRB for Downstream Processing for Metal Recovery

A more appropriate use of biohyrdometallurgical application using DIRB can be expected to provide an efficient alternative for recovering metals from oxidic based ores. In such a case, the bioleached liquor, either generated during bio-reduction or direct leaching of a bio-reduced ore, containing varying concentrations of different metals can be subjected to the unit operations involving solvent extraction and electrowinning (SX-EW) to recover pure metal [153, 154]. In solvent extraction, each metal is stripped to a pure solution at a suitable pH to obtain pure metallic solutions. These pure metal solutions are further subjected to chemical precipitation or electrowinning to obtain pure metal.

In the conventional electrowinning process, electricity is consumed, which increases the economic cost of the biological process. To circumvent this downside, a novel bioelectrochemical method using metallurgical microbial fuel cells (MMFC) has been proposed [155] as potential environment bioremediation technology. MMFC can efficiently replace electrowinning to produce pure metals by microbial utilization of organic wastes coupled to production of electricity. Alternatively, the green electricity produced from the microbial fuel cell (MFC) can be used for electrowinning.

In this process, oxidation of organic matter occurs by the bacteria (DIRB) attached to the anode while the cathode reduces the dissolved metals of leachate using electrons produced at anode. This method has been successful in recovery of cobalt from spent $LiCoO_2$ [156] using a two-chambered MFC separated by a cation exchange membrane, in copper recovery from metallurgical waste streams [155] using a bipolar membrane MMFC for pH maintenance, and for removal of cadmium and zinc from industrial wastewater [157] using a single chamber air-cathode MFC. Table 5 summarizes a few MMFC with modified operational modes to enhance the extraction of metal with simultaneous higher current generation.

Although MMFC has proved to be profitable, a thorough investigation towards the development of appropriate anodes and suitable substrates for cathodes with optimal working conditions is still in progress for full-fledged application.

3. Potential Applications of the Model Iron Reducers other than Iron Reduction

3-1. Application of *Shewanella* sp.

The metabolic versatility of *Shewanella* sp. to reduce numerous

Table 5. Metal recovery using different operational modes of microbial fuel cell

Metal recovery	Leachate type	Operational mode	Power density	Reference
Cobalt	Spent Lithium batteries	Two-chambered MFC separated by a cation exchange membrane	E_a of 30.6 KJ/mol	[155]
Copper	Metallurgical waste streams	Two-chambered MFC with bipolar membrane for pH maintenance	0.8 W/m^2	[154]
Vandium & Chromium	Wastewater	Two-chambered MFC	0.970±0.60 W/m^2	[157]
Chromiun	Chromium VI contaminated water	Dual Chambered Salt Bridge Microbial Fuel Cell	0.207 W/m^2	[158]
Silver	Wastewater	Two-chambered MFC with batch-fed cathode and continuous-fed anode system	4.25 W/m^2	[159]
Mercury	Wastewater		0.433 W/m^2	[160]
Silver	Wastewater	Two-chambered MFC separated by an anion exchange membrane	1.93 W/m^2	[161]
Cadmium & Zinc	Industrial wastewater	Single chamber air-cathode MFC	3.6 W/m^2	[156]

elements has drawn attention for various applications. It is a potential bio-tool for the efficient clean-up of contaminated environment and has found use in bioremediation of pollutants. *Shewanella* sp. has been reported to reduce radionuclides like Co^{60} [163], Tc^{99} [164, 165], actinides like U (VI) [47,166], Pu (IV) [167,168], Np (V) [166] and fission products of Tc (VII) [169]. It helps in detoxifying heavy metals like mercury [170], chromium [171], and arsenic [46]. It anaerobically degrades aromatic pollutants of nitramines [172], azo and anthraquinone dyes [173], pyridine [174], paint [175]. It competently produces silver and uraninite nanoparticles [176,177], arsenic-sulfide nanotubes [178], gold nanoplates and nanorods [179,180], palladium nanoparticles [181], selenium nanoparticles, nanowires and nanoribbons [182,183]. It reductively transforms tetrachloromethane [184] and carbon tetrachloride [185]. And it also plays an active role in electricity generation via microbial fuel cells (MFC) [95,186].

3-2. Applications of *Geobacter* sp.

Geobacter sp. is of profound importance for mineral and nutrient cycling in the ecosystems and has found numerous applications in bioremediation of toxic heavy metals like uranium [2,20,187], vanadium [188], selenium [189], reduction of actinides and fission products like technetium (VII) [166-168]. It is used in energy production via bacterial fuel cells from various organic sources like bug juice [190], organic matter [191], aquatic sediments [192], seafloor [193], animal waste [194], and marine sediments [98]. It plays a significant role in environmental restoration by anaerobic degradation of aromatic hydrocarbons [195], anaerobic benzene degradation [196], and anaerobic phenol degradation [197]. It helps in electricity generation [114,198] and is used in microbial fuel cells [199].

FUTURE PROSPECTS AND CONCLUSION

The current scenario of microbial research aiming towards several biotechnological applications is encouraging. Over the past few years, the area of applied microbal biotechnology has found numerous applications, majorly focusing on the environmental aspects. Microbial applications are gaining much popularity these days due to their advantages over some of the conventional methodologies. Most of the studies on DIRB are related to the fundamental aspects. A deeper understanding and insight into the metabolism of DIRB can broaden our understanding for better and wider applications. Revealing much of the information through bioinformatic means can help us predict many new avenues. Bioinformatic application can put better insights into some of the genomic information and predict accurate models of iron metabolism under diverse environmental conditions using diverse metal reducers apart from *Shewanella* and *Geobacter* sps. In addition, compiling all of the genomic information in one place using bioinformatics can also help in the development of a novel bacterial consortium that can be tested for either metal reduction for metal extraction or in bioremediation programs [200]. Further, scale up studies, say for example in large scale bioreactors or heaps, can be carried out using such novel consortiums that can open up new doors to the area of microbal biotechnology. It is believed that the coming years will find new application of DIRB to the field of various industrial or hazardous waste treatment.

In addition, the tunable conducting behavior of DIRB nanowires, especially those of electron acceptor starved *Shewanella* strains, opens new avenues for its application in the field of bioelectronics to produce cheap biosemiconductors, although some extended investigations are required pertaining to its huge production, nanoscale integration, etc.

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