Chapter 2
Microbe–Mineral Interactions: Exploring Avenues Towards Development of a Sustainable Microbial Technology for Coal Beneficiation

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2.1 Introduction

Microbes are ubiquitous in nature, and their specific interactions with the surrounding environment play a key role in the functioning of several processes occurring in our day-to-day life. The numerous microbe–mineral interactions act as a link to understand the innate mechanisms of certain phenomena taking place in nature and assist to study the mineral surfaces and changes occurring in minerals with respect to time and action of microbial species (Mapelli et al. 2012). Over the past few years, the interactions of selected microorganisms for beneficiation and bioleaching of the low-grade minerals/mineral wastes have been reported (Baba et al. 2011; Erust et al. 2013; Esther et al. 2013; Panda et al. 2012a, b, 2013a, 2015) and gradually gaining lot of importance for providing eco-friendly methods of environmental reclamation.

Coal is one such fossilized mineral comprising mainly of carbon and is formed due to the burial and conversion of dead plant matter under high pressure and temperature conditions. For several years, coal has been used worldwide as a principal source of energy in the generation of heat, electricity, and in the refining

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of metals. The multiple advantages of coal and its applications in diverse fields have made it a suitable area of research in the current era. For efficient and judicious use of coal, it is essential to enhance the quality of coal and make it a better fuel for several industries. However, the usage of coal also has some environmental issues. By-products generated by combustion of coal have resulted in greenhouse effect and acid rain. Environmental pollutants such as sulfur dioxide, sulfuric acid, and hydrogen sulfide have their origin from high-sulfur coal combustion. The present law framed by the governments all over the world has deals to lower level of sulfur emissions from coal industries associated with coal burning.

Thus to enhance the quality of coal, one of the integral components like sulfur needs to be removed (Prayuenyong 2002). Many strategies have been adopted to enhance the quality of coal by removing its sulfur component. Some of the conventional chemical and physical methods adopted for removal of sulfur from coal are shown in Fig. 2.1. Although such methods have responded effectually toward removal of sulfur, the use of hazardous chemical and elevated operating temperatures make such processes unattractive and less eco-friendly. The present scenario of research is particularly focused on the development of eco-friendly techniques.

To achieve this objective, it is necessary to understand the complex structure of coal and the various stages of coal formation which determine the rank of coal. Microbe–mineral interactions are very pervasive in nature. Since coal is a chief source of energy for wide variety of industries, the importance of microbe–mineral interaction is indispensible for developing a sustainable microbial coal biotechnology. The underlying necessity of microbe–mineral interaction is also linked with acid mine drainage that is a universal environmental problem in iron- and sulfur-rich environments. In the view of the fact that microbes act as a storehouse of several novel biomolecules or enzymes, they can be used for bioprocessing on an industrial scale incorporating innovative ideas and advanced technologies.

This review highlights some of the important aspects related to coal and its types along with possible interactions occurring between microbes and the mineral phases associated with coal. In addition, the available biological methods for industrial application ranging from lab-scale experiments to commercial-scale ventures are summarized and discussed. Moreover, understanding the inherent

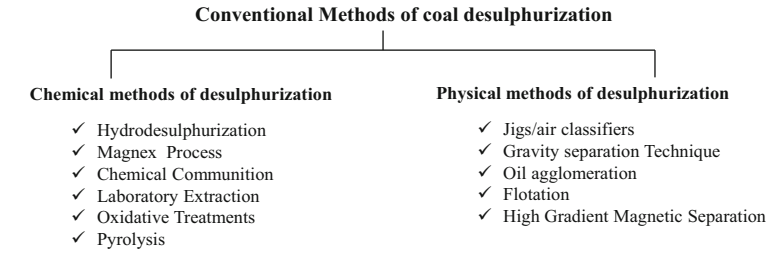


Fig. 2.1 A generalized flowchart depicting several conventional physicochemical methods adopted for desulfurization of coal (summarized from Soleimani et al. 2007; Kawatra and Eisele 2001, IPRO-346 report 2006)

mechanisms responsible in the microbe–mineral interactions would lead to the development of an efficient and eco-friendly technology toward the judicious use of natural resources and pave way toward a sustainable microbial coal biotechnology.

2.2 Types of Coal and Its Sulfur Content

Coal is a complex macromolecular structure that is formed by the combination of various biological and geological factors (Bhutto et al. 2013). Various organic and inorganic components constitute the complex structure. According to their stages of formation, different ranks of coal arise by the continuous burial of dead organic plant matter over time. The metamorphosis or the degree of alteration occurring during coal formation subsequently decides the so-called rank of a coal (Fakoussa and Hofrichter 1999). With increase in time, coal undergoes changes and passes through different ranks based on increase in burial pressure and temperature. High-rank coals have higher energy, lower volatile content, and shiny appearance than the low-rank coals. In general, most of the coals have a sulfur content varying from 0 to 4 %, but it can also go up to 10 % depending upon the region from which it has been extracted. In India, the sulfur content is also seen to vary in different regions of the state of Assam (Barooah and Baruah 1996). According to Soleimani et al. (2007), the average amount of sulfur in the USA coals ranges around 1.04–5.25 %. The organic sulfur of many coals may sometimes vary from 50 to 70 % of total sulfur content in coal (Soleimani et al. 2007). Since coal is a cheap and profuse source of energy, understanding the framework and composition of coal can assist in improving the energy value of coal. Some of the characteristic features of different ranks of coal are discussed below.

2.2.1 Peat

The process of coal formation begins with peat. Peat is considered to be the prerequisite for coal formation and is generally formed in water-logged regions like peat bogs, swamps, etc. (see http://en.wikipedia.org/wiki/Coal). It consists of various plant debris, decomposing plants, and plant products which undergo bacterial decay. Such materials experience continuous burial, supplemented with heat, time, and pressure leading to the formation of different ranks of coal. Basically, it is a decomposed fibrous material with typical content of volatile matter/weight percentage which is greater than 50 %. The typical weight percentage of carbon is 50–55 %, hydrogen 5–10 %, and oxygen 40 %. It acts as a useful absorbent for oil spills and has the ability to hold water and gradually release it which makes it a suitable conditioner (http://en.wikipedia.org/wiki/Coal). Seawater, freshwater, vegetation, and extraneous mineral matter can serve as an originating point for primary

sulfur (S). Although freshwater having 0–10 ppm S is continuously circulated through peat, it cannot donate much sulfur to coal (Ryan and Ledda 1997).

2.2.2 Lignite (Brown Coal: Immature)

Lignite is the lowest rank of coal formed during coalification of plant matter concomitant with loss of some water and volatile matter by the action of increasing pressure for a prolonged period of time. In other words, with increase in burial pressure and temperature, peat is metamorphosed into lignite. Lignite has a lower heat content, high moisture, and high volatile matter content. Basically, it contains woody material with hard blocky appearance. Typical content of volatile matter/weight percentage is about 50 %. The typical element analysis/weight percentage for carbon is 60 %, hydrogen 6 %, and oxygen 30 %. Lignite is mostly used as a fuel in the generation of electricity. But the transportation issues associated with lignite due to its high moisture content and spontaneous combustion property make it a less preferable fuel worldwide as compared to other high-rank coals (see http://en.wikipedia.org/wiki/Coal). Some lignite contains a sulfur percentage of less than 1 % (see http://energy.about.com/od/Coal/a/Lignite.htm; Fisher 1974). However, typical Indian lignite contains a high sulfur percentage of 1–7 % (Selvakumaran et al. 2013).

2.2.3 Subbituminous Coal

With increase in time, the increase in temperature and pressure converts the light weight and soft lignite into a more advanced form of coal, i.e., the dark subbituminous type. Subbituminous coal has high water content with properties varying from lignite to that of bituminous coal. Basically, it is a dark material with slight developing luster. Typical content of volatile matter/weight percentage is 45 %. The typical element analysis/weight percentage for carbon is 75 %, hydrogen 5 %, and oxygen 20 %. They are mainly employed for steam-electric power generation (see http://en.wikipedia.org/wiki/Coal). Most of the subbituminous coal found in different regions have low sulfur content than bituminous coal (discussed in the next section and may have less than 1–2 % of sulfur content (see http://energy.about.com/od/Coal/a/Sub-Bituminous-Coal.htm; http://www.britannica.com/EBchecked/topic/570576/subbituminous-coal).

2.2.4 *Bituminous Coal*

As the process of coal maturation continues, the subbituminous coal experiences physical and chemical changes which thereby convert it into a more hard coal—the bituminous type. Bituminous coal has a black and shiny appearance. It is of improved quality when compared with lignite and subbituminous coal but has lesser carbon content as compared to anthracite (discussed below). The major constituents of bituminous coal are macerals such as liptinite and vitrinite. Typical content of volatile matter/weight percentage is 35 %. The typical element analysis/weight percentage for carbon is 85 %, hydrogen 5 %, and oxygen 10 %. The application of bituminous coal in various areas is attributed to its distinctive grade of plasticity, volatility, and lower ash content specifically carbonate, phosphorus, and sulfur. Bituminous coals are mostly used for production of coking coal, in steel making, and for power generation (see http://en.wikipedia.org/wiki/Bituminous_coal). The sulfur content may vary from 0.7 to 4 % in this rank of coal.

2.2.5 *Anthracite Coal (Mature Coal)*

It is the highest rank of coal. Following a strong maturation of the bituminous variety, the anthracite coal forms the ultimate classification of coal. Anthracite coal or black coal is a hard mineral with metallic luster, high relative density, low volatile matter, and high fixed carbon content. Typical content of volatile matter/weight percentage is <10 %. The typical element analysis/weight percentage for carbon is 90 %, hydrogen 4 %, and oxygen 5 %. It is mainly used for metallurgical purpose as a replacement for coke in practices such as sintering and pelletizing. In many countries, anthracite is being used as a fuel for smelting of iron. In the present era, anthracite finds its major use as a domestic fuel in stoves and furnaces. This hard coal has a sulfur content of less than 1 % with high heating value and higher density. The latter interferes with its ignition properties (see http://energy.about.com/od/Coal/a/Anthracite-Coal.htm).

The summary of the formation of different ranks of coal is shown as a flowchart in Fig. 2.2.

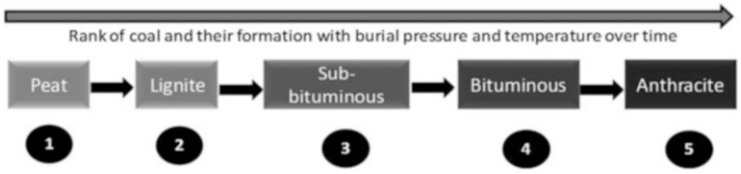


Fig. 2.2 A generalized flowchart for the formation of different ranks of coal with time

2.3 Microbes Reported for Beneficiation of Coal Through Desulfurization

Bacterial species belonging to the group α-, β-, γ-, and δ-proteobacteria have been found to predominate in the coal mine areas, while certain other bacterial lines of descent fall under the division *Nitrospira*, *Firmicutes*, and *Acidobacteria*. Similarly, archeal families comprising of *Thermoplasmatales* and *Sulfolobales* have been reported from the acid mine drainages (Siezen and Wilson 2009). Specific groups of microbes associate symbiotically with each other in order to fulfill their nutritional requirements and endure their growth and survival. However, few reports have additionally focused on the existence of eukaryotes in these sites (Baker and Banfield 2003). Majority of these microbial species employ essential enzymes required for various key transformations occurring in an acid mine drainage. Certain autotrophic groups are capable of oxidizing or reducing iron or sulfur to obtain their sole source of energy, whereas certain other heterotrophic groups are adept in utilizing organic compounds for their sustenance. Thus, most of the subsurface interactions occurring in the environment proceed through iron or sulfur oxidation, organic carbon oxidation, fixation of carbon or nitrogen, extracellular polymeric slime production, as well as iron and sulfur reduction.

Certain microorganisms are capable of modifying the structure of coal and degrading it. Both bacterial and fungal species have been found to disintegrate the coal structure and utilize the compounds present in coal as a source of carbon and sulfur to meet their nutrient requirements (Catcheside and Ralph 2002). Some bacterial species like *Pseudomonas fluorescens* release a very effective surfactant into the medium which lowers the surface tension of the medium, converts some coal into a more hydrophilic substance so that they become water soluble and can be easily taken up by the bacterial species to meet their nutrient requirement (Fakoussa 1981).

2.3.1 Organic S Removal

Initial efforts to remove organic sulfur from coal have been considered unsuccessful in view of the fact that the sulfur was not specifically removed from coal, and the calorific value of coal was also lost during the process. Most of the research works are focused on the degradation of dibenzothiophene present in coals, since it occupies a considerable portion of the organic sulfur. Several microbial species including *Rhodococcus erythropolis*, *Arthrobacter* spp., *Flavobacterium* spp., *Mycobacterium* spp., *Gordonia* spp., *Pseudomonas alcaligenes*, *Corynebacterium* spp., *Bacillus* spp., *Nocardia* spp., *Paenibacillus* spp., etc. are reported of having the capability to degrade various sulfur bearing organic compounds. Among these, certain species like *Microbacterium* ZD-M2 (Li et al. 2005; Soleimani et al. 2007),

Rhodococcus erythropolis IGTS8, *Rhodococcus erythropolis* D-1, *Mycobacterium* spp. G3, *Gordonia desulfuricans*, *Nocardia globerula* R-9 (Mingfang et al. 2003; Soleimani et al. 2007), and *Arthrobacter* species (Lee et al. 1995; Soleimani et al. 2007) could degrade dibenzothiophene via the 4S pathway or sulfur-specific pathway (discussed in Sect. 2.5.2.2). Other than these, certain thermophilic strains like *Bacillus subtilis* WU-S2B and *M. phlei* WU-F1 (Kirimura et al. 2004; Soleimani et al. 2007) and *Paenibacillus* spp. A11-2 (Ishii et al. 2000; Soleimani et al. 2007) also possessed the ability to remove sulfur from DBT via the sulfur-specific pathway. However, some other species such as *Pseudomonas alcaligenes*, *Pseudomonas putida* (Hartdegen et al. 1984; Monticello et al. 1985; Soleimani et al. 2007), *Brevibacterium* sp. DO (Nojiri et al. 2001; Dahlberg et al. 1993; Soleimani et al. 2007), and *Arthrobacter* K3b (Soleimani et al. 2007) were found to follow the carbon destructive pathway, i.e., the Kodama pathway of dibenzothiophene degradation (discussed in Sect. 2.5.2.1). Anaerobic strain like *Desulfovibrio desulfuricans* M6 have been efficient in degrading 96 and 42 % sulfur from benzothiophene and dibenzothiophene, respectively (Kim et al. 1990; Soleimani et al. 2007), by converting it to biphenyl and H_2S, while certain other species like *Desulfovibrio longreachii* and *Desulfomicrobium scambium* were found capable of degrading only 10 % dibenzothiophene dissolved in kerosene (Yamada et al. 2001; Soleimani et al. 2007). Strains of *Pseudomonas putida* were genetically modified to obtain better yield, since these strains are solvent tolerant and have a higher growth rate (Soleimani et al. 2007). Resting cells of genetically modified strain *Pseudomonas putida* A4 having solvent-tolerant capacity along with desulfurizing properties of *R. erythropolis* was able to degrade 86 % DBT in 10 % p-xylene in 6 h (Tao et al. 2006; Soleimani et al. 2007).

2.3.2 Inorganic S Removal

Inorganic sulfur mainly occurs in the form of sulfates and sulfides in coal. Since the sulfide particles exist as fine discrete crystals and are not bonded to the coal matrix, hence, they can be easily removed by physicochemical methods as well as biological methods, while sulfate sulfur easily gets dissolved and comes out when washed with water. Many sulfur-oxidizing microbes, namely *Acidithiobacillus ferrooxidans* (*A. ferrooxidans*), *Leptospirillum ferrooxidans* (*L. ferrooxidans*), *Beggiatoa*, *Sulfolobus, Acidithiobacillus thiooxidans* (*A. thiooxidans*) (Acharya et al. 2001; Masau et al. 2001), *Sulfolobus acidocaldarius* (*S. acidocaldarius*) (Kargi 1982), are reported of degrading sulfur compounds to form elemental sulfur or metal sulfides (Ryu et al. 1993). Among these, mesophiles such as *A. ferrooxidans*, *L. ferrooxidans*, and *A. thioxidans* are mostly involved in pyritic sulfur removal from coal as discussed by Prayuenyong (2002). Both *A. ferrooxidans* and *L. ferrooxidans* are capable of carrying out pyrite oxidation, whereas *A. thioxidans* is unable to utilize pyrite but can grow on sulfur released due to iron oxidation (Rawlings et al. 1999; Prayuenyong 2002). *A. ferrooxidans* is also

reported of removing a small amount of organic sulfur from coal along with pyritic sulfur removal (Chandra et al. 1980). *L. ferrooxidans* are more adapted to lower pH conditions and posses higher affinity for ferrous iron when compared to *A. ferrooxidans*. They are also more resistant toward inhibition by higher ferric iron concentration, which assists them in overriding *A. ferrooxidans* (Prayuenyong 2002). Certain thermophiles such as *Thiobacillus caldus*, *Metallosphaera sedula* (*M. sedula*), *Acidianus brierleyi* (*A. brierleyi*), and *S. acidocaldarius* are also reported of pyrite oxidation (Schippers et al. 1999). A thermophilic and acidophilic facultative autotroph, *S. acidocaldarius*, is also reported of removing pyritic as well as organic sulfur from bituminous coal (Kargi and Robinson 1986). Reports have shown that it was capable of removing 90 % pyritic and approximately 19% of organic sulfur from coal (Kargi and Robinson 1986). However, while going for a commercialization, mesophiles are more preferred over thermophiles, since they operate at a moderate temperature and provide higher output with lower residence time (Rossi 1993; Schippers et al. 1999).

2.4 Susceptibility of Coal to Microbial Action

In general, the coal is a highly complex structured material. These complex structures have been worked out, proposed, discussed, and reviewed by many researchers (Fakoussa and Hofrichter 1999; Levine et al. 1982). Sulfur accounts for one of the major impurities in coal and mainly occurs in the form of organic sulfur and inorganic sulfur. The inorganic sulfur is predominantly present as sulfides and sulfates. For example, pyrite (FeS_2), sphalerite (ZnS), galena (PbS), arsenopyrite (FeAsS), etc. constitute the sulfide minerals, and barite ($BaSO_4$, gypsum ($CaSO_4$. $2H_2O$), anhydrite ($CaSO_4$), and a number of iron sulfates constitute the sulfate minerals. On the other hand, the organic sulfur in coal exists in four different groups as reviewed by Prayuenyong (2002). They are the following:

(a) Aliphatic or aromatic thiols (mercaptans, thiophenols)
(b) Aliphatic, aromatic, or mixed sulfides (thioesthers)
(c) Aliphatic, aromatic, or mixed disulfides (dithioesthers)
(d) Heterocyclic compounds or thiophene type (dibenzothiophenes)

In case of the inorganic sulfur in coal, pyrite forms the major portion. It is very interesting to know that pyrite is randomly distributed throughout the coal. The percentage of inorganic sulfur in coal changes from 0.5 to 5 % depending on the type of coal. The inorganic sulfur usually exists in the form of discrete crystals and gets easily separated from the coal structure by the help of physicochemical techniques of sulfur removal (Kawatra and Eisele 2001). On the other hand, the organic sulfur is covalently bonded to the complex carbon matrix of coal which makes it very difficult to be removed by any physicochemical means.

Some coals are composed of a matrix which cannot be degraded by microbial action and are termed as hard coal, whereas a mobile phase in coal is composed of

nonoxidized compounds or volatile components like alkylated benzenes and alkanes and polyaromatic hydrocarbons which can be easily attacked by microbe. The mobile phase mostly includes phenols, benzoic acids, biphenyls, biphenyl ethers, n-alkenes, n-alkanols, and wax like aliphatics. Hard coals contain higher proportion of condensed aromatic rings and have a lower oxygen content and higher hydrophobicity due to which they are resistant to microbial attack (Hodek 1994). Fathoming the underlying relationship between the different aliphatic and aromatic hydrocarbons including other heteroatomic forms provides detail information about the coal chemistry and the possible chemical reactions it can undergo. The aromatic and naphthenic rings are interlinked to each other by aliphatic chains or heteroatomic bridges. Other polar groups like the hydroxyl group are also involved in the formation of a stable coal structure through electrostatic binding. The percentage of oxygen in coal plays an essential role in determining the coal structure and reactivity (Levine et al. 1982).

2.5 Microbial Coal Desulfurization

The following subsections discuss in details the microbe interactions with the inorganic and organic part of coal for sulfur removal. In addition, the details of the microbial systems for organic sulfur removal are also discussed.

2.5.1 Interaction Mechanisms for Inorganic Sulfur Removal

As already discussed in Sect. 2.4, pyrite forms the major portion of inorganic sulfur in coal. Certain group of chemolithoautotrophic meso-acidophilic bacteria has proved to be the correct answer to biodegradation of pyrite (Acharya et al. 2001). Such microorganisms utilize the iron source of pyrite for their growth and metabolism and are frequently used in bioleaching (Sand et al. 2001; Schippers and Sand 1999; Ciftci and Akcil 2010). The iron oxidizer *Acidithiobacillus ferrooxidans* (*A. ferrooxidans*) is considered to be the industrially important microorganism (Panda et al. 2012a; Pradhan et al. 2008). It is very important to note that *A. ferrooxidans* act as both an iron and sulfur oxidizer (under aerobic condition) and reducer under anaerobic conditions (Osorio et al. 2013). Different types of mechanisms have been proposed regarding the biological oxidation of pyrite by *A. ferrooxidans*, namely, the "*direct* (*contact*)" and "*indirect (noncontact*)" and "*cooperative*" bioleaching (Sand et al. 2001; Schippers and Sand 1999). Further, with the advance in the area bioleaching, two most coherent explanations are presently available for the indirect mechanisms, namely, the "*thiosulfate*" and "*polysulfide*" mechanisms (Schippers and Sand 1999; Schippers et al. 1996; Rohwerder et al. 2003). As shown in Fig. 2.3, the thiosulfate mechanism involves a ferric iron (Fe III) attack on the acid-insoluble metal sulfides, with thiosulfate

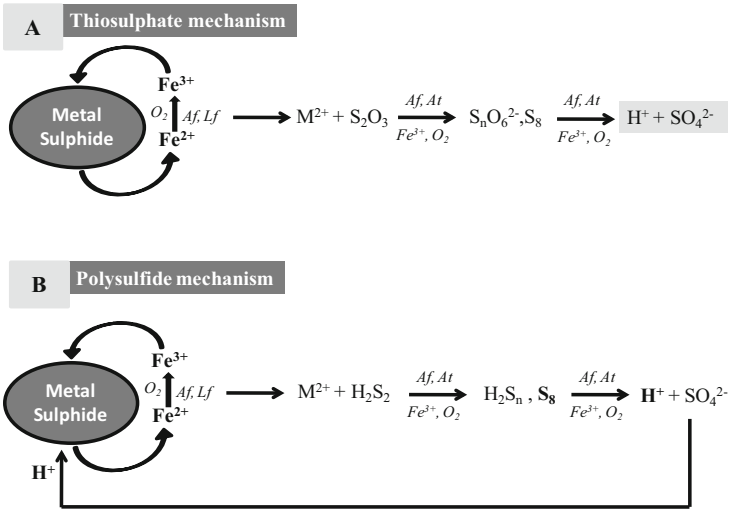


Fig. 2.3 Schematic comparison of two indirect mechanisms for metal sulfide (e.g., pyrite) degradation. (**a**) Thiosulphate mechanism and (**b**) polysulfide mechanism. M^{2+} - metal cations, *Af - Acidithiobacillus ferrooxidans, At - Acidithiobacillus thiooxidans*, and *Lf - Leptospirillum ferrooxidans* (Adapted from Schippers and Sand 1999)

being the main intermediate and sulfate being the main end product (Eqs. 2.1 and 2.2).

$$FeS_2 + 6Fe^{3+} + 3\,H_2O \rightarrow S_2O_3{}^{2-} + 7Fe^{2+} + 6H+ \tag{2.1}$$

$$S_2O_3{}^{2-} + 8Fe^{3+} + 5H_2O \rightarrow 2SO_4{}^{2-} + 8Fe^{2+} + 10H^+ \tag{2.2}$$

Similarly, in the polysulfide mechanism, the acid-soluble metal sulfide gets combined attack by ferric iron and protons, with elemental sulfur as the main intermediate. This elemental sulfur may be oxidized to sulfate by sulfur-oxidizing microbes (Fig. 2.3).

$$MS + Fe^{3+} + H^+ \rightarrow M^{2+} + 0.5H_2S_n + Fe^{2+}(n \geq 2) \tag{2.3}$$

$$0.5H_2S_n + Fe^{3+} \rightarrow 0.125S_8 + Fe^{2+} + H^+ \tag{2.4}$$

$$0.125S_8 + 1.5O_2 + H_2O \rightarrow SO_4{}^{2-} + 2H^+ \tag{2.5}$$

The ferrous iron may be reoxidized by iron-oxidizing organisms to ferric iron.

$$2Fe^{2+} + 0.5O_2 + 2H^+ \rightarrow 2Fe^{3+} + H_2O \tag{2.6}$$

The role of the microorganisms in the solubilization of metal sulfides as described through these mechanisms is to provide sulfuric acid for a proton attack and to keep the iron in the oxidized ferric state for an oxidative attack on the mineral.

These microorganisms are able to grow on pyrite and derive their energy. It is important to note that the natural geomicrobiological processes and bioleaching operations enable conversion of insoluble metal sulfides into water-soluble metal sulfates. At neutral pH and aerobic conditions, ferrous Fe (II) is rapidly oxidized to ferric iron [Fe (III)]. The accessibility of Fe (III) in biological systems becomes low as ferric iron is poorly soluble due to formation of iron hydroxides (as low as 10–18 M at pH 7.0) (Bonnefoy and Holmes 2012). However, it is interesting to note that under acidic conditions in the presence of atmospheric oxygen, Fe (II) is stable. This feature provides an excellent opportunity for the acidophilic microorganisms to use Fe (II) as an electron donor and as an energy source which is not a common feature for microorganisms inhabiting circumneutral environments (Austin and Dopson 2007; Bonnefoy and Holmes 2012).

2.5.2 Interaction Mechanisms for Organic Sulfur Removal

Sulfur is an essential requirement for microbes to sustain their biological activities and growth. It is involved in the formation of disulfide bonds in proteins and is also an integral part of amino acids such as cysteine and methionine. Certain enzyme cofactors such as biotin, thiamine, and coenzyme A incorporate sulfur in order to complete their structure. Since dibenzothiophene (DBT) constitutes a major organic portion of coal, microbes follow one of the different proposed pathways to meet their sulfur requirement from dibenzothiophene. The proposed pathways have been discussed below.

2.5.2.1 Aerobic Bio-desulfurization: The Oxidative C–C Cleavage (Kodama Pathway)

The aerobic bio-desulfurization via the Kodama pathway is followed by microbial species like *Pseudomonas alcaligenes*, *Pseudomonas putida*, *Burkholderia fungorum*, *Brevibacterium* spp., etc. (Kodama et al. 1970; Monticello et al. 1985; Yamada et al. 1968). Several microorganisms that follow the 4S pathway have been discussed in Sect. 2.3.1. These microorganisms use DBT as their carbon source through a series of enzymatic oxidation steps leading to the breakage of carbon–carbon (C–C) bond present in the ring structure. They form water-soluble end products, which inhibit further microbial growth and oxidation of DBT. The pathway is initiated by the attack on one of the phenyl rings and proceeds through three major steps, namely, hydroxylation, ring cleavage, and hydrolysis (Gupta and Roychoudhury 2005; Soleimani et al. 2007). This pathway is reported to be based on microbial plasmids that are associated in certain *Pseudomonas* spp. like *Pseudomonas alcaligenes* and *Pseudomonas putida* (Monticello et al. 1985). These plasmids are believed to mediate biodegradation of some other aromatic compounds such as naphthalene and salicylate in addition to DBT. It has been reported

that a DNA fragment of length 9.8 kb has been responsible in encoding of degrading enzymes in the Kodama pathway (Soleimani et al. 2007). Since sulfur is not specifically attacked in this pathway, it is not considered as an efficient approach for DBT biodegradation. Therefore, this process is often referred to as destructive bio-desulfurization (Soleimani et al. 2007).

2.5.2.2 Aerobic Bio-desulfurization: The Oxidative C–S Cleavage (4S Pathway)

Owing to the nonspecific process of sulfur removal from DBT thiophene ring through the Kodama pathway, several attempts were made to isolate a variety of aerobic and anaerobic microbes that can specifically remove sulfur nondestructively. Several microorganisms that follow the 4S pathway have been discussed in Sect. 2.3.1.

With the isolation and characterization of the strain *Rhodococcus erythropolis* IGTS8 (formerly referred to as *Rhodococcus rhodochrous* IGTS8), a major advancement in DBT biodegradation was achieved, namely, the 4S pathway (Kilbane 1990). The 4S pathway represents a sequential degradation of DBT to DBT-sulfoxide followed by DBT-sulfone, DBT-sulfinate, HBP (hydroxybiphenyl) and finally to sulfite. Through a selective oxidation approach, the bacteria oxidize the sulfur of DBT without affecting the C–C bond. This process is often referred to as the specific oxidative desulfurization (Soleimani et al. 2007). Though bacteria such as *Brevibacterium* sp. DO and *Arthrobacter* sp. K3b partly followed the 4S pathway, they were reported to be carbon destructive because of the degradation of aromatic compounds during bio-desulfurization.

2.5.2.3 Anaerobic Bio-desulfurization: The Reductive C–S Cleavage

Apart from the role of aerobic microbes, several anaerobes have also shown promising results toward biodegradation of DBT. Certain anaerobic bacteria such as *Desulfovibrio desulfuricans*, *Desulfomicrobium scambium*, and *Desulfovibrio longreachii* have shown positive response toward DBT biodegradation. *Desulfovibrio desulfuricans* have been reported to degrade 96 % of BT and 42 % of DBT which can be related to the conversion of DBT to biphenyl and H_2S (Kim et al. 1990). On the other hand, *Desulfomicrobium scambium* and *Desulfovibrio longreachii* have been reported to desulfurize 10 % of DBT dissolved in kerosene. Interesting information through GC analysis was obtained which indicated that these microbes follow a somewhat different pathway from other anaerobes for bio-desulfurization (Yamada et al. 2001). The most fascinating part in anaerobic bio-desulfurization is the minimal formation of undesirable compounds such as colored and gum-forming products upon oxidation of hydrocarbons which calls for an exciting research area on reductive bio-desulfurization (McFarland 1999). However, maintenance of proper anaerobic conditions and precise attack of isolated

microbial strains on DBT are some of the major challenges faced by the investigators for the establishment of a successful anaerobic desulfurization technique (Armstrong et al. 1995).

2.6 Role of Few Microbial Enzymes in Biodegradation of Sulfur Compounds

Various lignolytic enzymes like peroxidases, phenol oxidases, and other supporting enzymes are involved in the depolymerization of coal. Some oxidative enzymes such as monooxygenases are also responsible for distortion of the complex structure of coal.

2.6.1 Oxygenase

Oxygenases are one of the most vital enzymes involved in the degradation of aromatic compounds. They are responsible for the ring cleavage of aromatic ring structure, and based on the number of oxygen atoms they incorporate into, the aromatic ring structure is classified into monooxygenase and dioxygenase (Arora et al. 2009, 2010). Based on their cofactors monooxygenases are classified into two types, namely, flavin-dependent monooxygenase, which contains flavin as prosthetic group and require NADP or NADPH as coenzyme, and P450 monooxygenases, which are heme-containing oxygenases (Pazmiño et al. 2010). Some other bacterial monooxygenases such as pterin-dependent monooxygenases and metal ion-dependent monooxygenases do not have flavin or heme as cofactor (Pazmiño et al. 2010). Monooxygenases, which do not include a cofactor, require only oxygen for their activities and use the substrate as a reducing agent. Similarly, dioxygenases are also grouped into two different classes according to their mode of action, namely, the aromatic ring hydroxylation dioxygenases and aromatic ring cleavage dioxygenases (Arora et al. 2009, 2010).

2.6.2 Lignin Peroxidases

Since coal is composed of dead plant matter, lignin is the major constituent which is present in coal. The coalification process is accompanied by alterations in the physical properties and chemical structures of the basic plant material. But traces of the typical structure of lignin can be found in certain coals. Lignin peroxidase is one of the lignolytic enzymes that was first found in the white rot fungus *Phanerochaete chrysosporium* (Glenn et al. 1983; Tien and Kirk 1983) and later

also isolated from other basidiomycete fungi like *Phlebia radiata* (Hatakka et al. 1987), *Trametes versicolor* (Dodson et al. 1987), *Bjerkandera adusta* (Kimura et al. 1991), and *Nematoloma frowardii* (Hofrichter and Fritsche 1997) and an ascomycete *Chrysonilia sitophila* (Duran et al. 1987). Lignin peroxidase has broad substrate specificity and can act on both phenolic and nonphenolic compounds (Odier et al. 1988; Schoemaker et al. 1985). The catalytic activity of lignin peroxidase is similar to that of horseradish peroxidase.

2.6.3 Manganese Peroxidases

Manganese peroxidase was identified from *P. chrysosporium* for the first time (Kuwahara et al. 1984). Its activity is similar to that of lignin peroxidase but has MnI and MnII as the specific substrate and mediators, respectively. Manganese peroxidase is also found in some other white rot and litter-decaying basidiomycetes like *T. versicolor* (Johansson and Nyman 1987), *P. radiata* (Nikku-Pavola et al. 1990), *Panus tigrinus* (Maltseva et al. 1991), *Lentinula edodes* (Forrester et al. 1990), *Ceriporiopsis subvermispora* (Ruettimann et al. 1992), *Pleurotus ostreatus* (Becker and Sinitsyn 1993, *Agaricus bisporus* (Bonnen et al. 1994), *N. frowardii* (Schneega et al. 1997), *Stropharia rugosoannulata* (Scheibner and Hofrichter 1998), *Clitocybula dusenii* (Ziegenhagen and Hofrichter 1998).

2.6.4 Laccase

It is a copper-containing polyphenol oxidase (Reinhammar and MalstroÈm 1981) produced by most of the lignolytic fungi like *Trametes versicolor* (Fahreus and Reinhammar 1967), *Phlebia radiata* (Kantelinen et al. 1989), *Pycnoporus cinnabarinus* (Eggert et al. 1996), and *Nematoloma frowardii* (Hofrichter and Fritsche 1997). The enzyme oxidizes various compounds simultaneously reducing O_2 to H_2O with a total reduction of four electrons. Laccase activity on phenolic aromatics results in the formation of phenoxy radicals, which can easily participate in radical–radical coupling, disproportionation, deprotonation, and nucleophilic attack by H_2O. Several reactions ultimately result in alkyl–aryl cleavage, C-α-oxidation, or demethoxylation of phenolic reductants (Kirk and Shimada 1985).

2.7 Future Prospects and Potential for a Microbial Technology

Microbial processing of several industrial wastes and/or low-grade ores has been gaining a lot of importance over the past few years (Baba et al. 2011; Panda et al. 2012c, 2013b, 2014). As a result, much focus is being generated for the application of microorganisms towards development of an industrial technology. Coal being a cheap source of renewable energy with numerous industrial applications is a potential material for future development of a microbial biotechnology. Furthermore, research in this field is particularly aimed at removal of sulfur from coal for environmental benefits and enhancement in the calorific value of coal, which would ultimately result in the development of a proficient source of energy with higher output. As already discussed in the above sections, biological application has gained importance to remove sulfur from coal using an eco-friendly approach. Therefore, it is a necessity to improve biological performance to bring about an efficient bio-based technology for coal beneficiation.

Many researchers have proposed numerous methods to improve bio-desulfurization of coal. Improving strain performance is an important aspect in coal biotechnology. Identification of novel strain with higher desulfurization capabilities can be expected to improve overall performance of the biological system employed for coal bio-desulfurization. Very recently, identification of novel microorganisms (iron- and/or sulfur-oxidizing chemolithoautotrophic acidophiles) through a web-based tool has been proposed to identify novel consortiums for bioleaching process (Parida et al. 2014). With the application of such web-based tool, a novel isolated consortium of iron- and/or sulfur-oxidizing chemolithoautotrophic acidophiles can be proposed and tested for bio-desulfurization (inorganic sulfur) efficiency for iron-rich coal. With such knowledge, more and more bioinformatic applications can also be proposed to identify many novel isolates for removal of organic sulfur from coal.

In addition to the microbial aspects of coal bio-desulfurization, nature and mineralogy of coal needs better understanding prior to microbial applications. Since coal varies in rank, composition and occurrence from region to region and its in-depth characterization would immensely help to enable the selection of microbes/microbial consortia, which can be employed to achieve maximum desulfurization for developing an efficient process with the application of novel technologies. For example, very recently, a two-step bio-desulfurization method has been proposed which sequentially removes organic sulfur followed by inorganic sulfur from coal (Mishra et al. 2014). The study presents a two-step sequential method using a microbe *Sinomonas flava* 1C to efficiently remove organic sulfur followed by removal of inorganic sulfur by *A. ferrooxidans*. In the coming years, more and more research in such interesting aspect of coal bio-desulfurization would improve its characteristic features and energy value, arousing the hope to cultivate an industrial-scale bioengineering system for an efficient eco-friendly coal biotechnology.

2.8 Conclusion

Microbe–mineral interactions are the fundamental basis of various geochemical and biogeochemical processes occurring in nature. A detail study into these interactions can open up novel areas of research, which are still waiting to be explored. Since coal is a major source of energy in the present era, understanding the fundamental mechanism behind coal formation, maturation, weathering, and degradation can provide more structural information on coal which would further help to enhance the calorific value, increase the energy output, and decrease negative aspects related to the use of this fossil fuel. In the end, understanding the microbe–mineral interactions in coal would facilitate in achieving the ultimate goal of efficiently engineered microbial processes, which would produce cleaner coal at ambient temperature and pressure in eco-friendly and economic way.

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