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320. Biological Removal of Sulfur from Coal through Use of Microorganism. A Review

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Abstract

During process of combustion harmful gases emitting due to ash and sulfur contain in it had negative effect on environment as well as coal associated plants. Researcher attracted by removal of sulfur and ash from coal regarding environmental problem. Current research paper reviews different microorganism for bio-treatment of coal. Different microorganism was reviewed for process of sulfur removal from coal. For effective removal of inorganic sulfur thiobacillus ferrioxidans had favorable for pyritic sulfur 90% and for organic sulfur speci berilye had candidate condition for organic sulfur removal upto 60%. This reviews conclude further research to reach maximum organic sulfur removal. Study need on further researched of organic sulfur removal from coal.

***Keywords**: Bio-Desulfurization, Microorganism, Coal, Combustion, Sulphur*

1. Introduction

During process of combustion harmful gases emitting due to ash and sulfur contain in it had negative effect on environment as well as coal associated plants. Researcher attracted by removal of sulfur and ash from coal regarding environmental problem. A number of separation techniques were analyzed for sulfur and ash elimination from coal. Bio separation is one of recently tested methods for removal of sulfur from coal[1] two types of sulfur preset in Coal such are inorganic and organic sulfur present variable amount in coal. Inorganic sulfur found in coal as sulfides or sulfate but for as organic sulfur was concerned it occurs in form of organic structure and bound with different forms. [2]. Increasing problem of sulfur containing compound, due to there is need to explore the technology to decrease the emission of sulfur. Bio treatment of fossil fuels can be said to be fitting technology for the desulfurization of oil and coal before combustion, especially for small-scale combustion plants where flue gas cleaning is too expensive [3]. The effect of process parameter were investigated using micro waved/acid washed samples ,the reduction of pyritic, organic and total sulfur were observed from range 26 to 91, 2.6 to 38.4 and 17 to 65% respectively. [4]. Globally more than a quarter of the total primary energy supply is based on coal combustion. The emissions of coal-fired power plants (CFPPs) are regulated in many industrialized countries and therefore power plants use cleaning techniques to minimize emissions such as sulfur dioxide (SO2) and particles [5]. Coal contains inorganic as well as organic materials which are composed of different constituents especially sulfur in coal play an important role in combustion process. Different methods were employed but froth flotation is suitable method for pyritic sulfur removal from coal. [6]. Coal desulfurization prior to usage is a preprocessing in order to get clean fuel and diminish environmental impacts such as acid rain [7]. The main purpose of work is to remove organic sulfur in low rank lignite coal present in Pakistan for cleaner coal production for combustion.

2. Bio-Desulfurization Of Coal

Technique for sulfur removal suggested that by using bacteria for coal is one of the researched methods for sulfur removal from coal. For pyritic and sulfate sulfur *thiobacillus ferrooxiandans* were used. The elimination of organic sulfur from coal depends on the amount of sulfur containing organic compounds present in it. dibenzothiophene were used as sole source for isolation of mixed culture of bacteria from soil for removing thiophene which is present in coal in addition to pyritic and sulfate sulfur mixed bacterial culture proved valuable for removing organic sulfur from coal. Ash content also reduced during removal of sulfur contents from coal treated with coal. But for another hand coking property unaffected during bacterial treatment. [8].Efficiency of sulfur removal by microbial action significantly improved by using air with CO2 [9]. One of the useful methods for coal cleaning and for clean solid fuels making is bio desulphurization Treatments were performed with three types of fungi using Bio desulphurization process are ‘‘Trametes Versicolor” – ATCC No. 200801, ‘‘Phanerochaeta Chrysosporium” – ME446, Pleurotus Sajor-Caju and one Mixed Culture of bacteria – ATCC No. 39327 [10].A microbial inoculums for desulfurization of column packed coal was selected. At pH 1.5 elimination of pyritic sulfur achieved a level of 46% with relatively small changes immediate observation of coal analysis. According these condition 20 to 30 ton pilot plant were developed for desulfurization of coal [11].

2.1. REMOVAL OF INORGANIC SULFUR FROM COAL

Thiobacillus ferrooxidan can be used to remove Pyritic sulphur effectively from different coal samples [12]. Seven days process for removal of sulfur from coal using Thiobacillus ferrooxidans bacteria had optimized process condition at initial concentration of ferrous ions of 15g dm^{-3} and extraction mixture 2.4 wt % [13]. Study were made on the basis of sulfur removal from coal using airlift reactor by treating with sulfur oxidizing bacterium, Thiobacillus ferrooxidan. Different process parameter were studied and evaluate the effect on bio desulfurization process. Using high coal slurry densities (up to 70% w/v). 90 - 95 % sulfur removed from coal within 15-20 days [14]. A number of different microorganisms have been recommended for coal desulfurization. In the present investigation, comparative study of thermophilic and mesophilic bacteria were carried out to see the sulfur removal percentage from coal. The thermophilic archaea Acidianus brierleyi (DSM 1651), Sulfolobus acidocaldarius (DSM 639) and Sulfolobus solfataricus (DSM 1616) were compared with the mesophilic bacterium Thiobacillus ferroxidasez (DSM583). Thiobacillus ferrooxidans and Acidianus brierleyi, were investigated capable of oxidizing pure pyrite as well as oxidizing sulfur in coal [15]. Work were carried out for development of economical process for sulfur removal from coal using microbes by designing a reactor. Removal of sulfur from coal using microorganism established conclusively but as far as petroleum sulfur under active study is aimed to scale up process of bio-desulfurization for removal of sulfur using microorganism [16]. A model developed on the basis of computational fluid dynamic for removal of sulfur from coal using iron oxidizing bacteria (Acidithiobacillus ferrooxidans and Leptospirillum ferrooxidans) through bio leaching [17]. A mixed culture of acidophilic iron- and sulphur-oxidizing mesophilic microorganisms including Acidithiobacillus ferrooxidans, Acidithiobacillus thiooxidans and Leptospirillum ferrooxidans used to remove sulfur from high sulfur containing coal [18-20].

2.2. Removal of Organic Sulfur

Organic sulfur species in coals are mainly thiols, sulfides, disulfides, thiophenes and their derivatives. A number of methods have been explored for removal of organic sulfur prior to combustion. These include:

1. Solvent partitioning
2. Neutralization method
3. Hydrogenation reaction or sulfur reduction
4. Thermal decomposition
5. Oxidation
6. Sodium hydroxide treatment or nucleophilic displacement, and
7. Microbial removal

2.3. Organism for Sulfur Removal from Coal

The organisms can be classified on the basis of whether they can remove inorganic or organic sulfur from coal: (a) obligate autotrophs oxidize only pyritic sulfur, (b) facultative autotrophs oxidize pyritic sulfur and some organic sulfur compounds, (c) heterotrophs oxidize only some organic sulfur compounds.

2.4. Obligate autotrophs

The most widely used obligate autotrophs for coal desulfurization are various strains of *Thiobacillusferrooxidans [29-31]* and almost all strains have been isolated from acid mine waters. These bacteria are Gram-negative rods (0.5 by 1-2 ~tm), flagellated, non-spore-forming [30-32], acidophilic (pH optima: 2-3), mesophilic (temperature optima: 25-30°C) and aerobic. The various strains have not been differentiated taxonomically (e.g. by G/C content). When grown under autotrophic conditions, the organisms fix COz via the Calvin cycle and obtain energy from oxidation of reduced sulfur and iron compounds (Table 2). The organisms have been used for leaching metals(Cu, Zn, U, Ni) from low-grade sulfide ores ~7 and removing pyritic sulfur from coal 2~'2°'21 under autotrophic conditions. Other Thiobacillus species (e.g. T. perometabolis, T. organoparus) canalso oxidize reduced sulfur and iron compounds and can be used in pyritic sulfur removal from coal. While some organic compounds (e.g. agar) are toxic to the obligately autotrophic T. ferroxidase strains, other Thiobacillus species can metabolizesome organic compounds [31]. However, it is believed that Thiobacillusspecies are incapable of removing organic sulfur from coal [21] and even though there are some Thiobacillus-type organisms which metabolize dimethyl sulfide and dimethyl disulfide[29,33], neither these nor the nitrogen fixing Thiobacillus species 23 have been tested in coal desulfurization. Although more than 90% of initial pyritic sulfur can be removed by using Thiobacillus species when coal particle sizes are small enough (diameter ~ < 80 l ~ m), the major problem in using mesophilic species is the low rate of removal (residence times of 4-5 days are required in continuous operations). Some of the autotrophic organisms capable of removing pyritic sulfur from coal are thermophilic (temperature optima: 50-60°C). Thiobacillus-type (TH-bacteria) organisms have been isolated from acidic hot springs or sulfur-rich soil [15, 34, 35]. These organisms require some organic compounds (e.g. yeast extract or cysteine) for growth. Thermophilic, Thiobacillus-type organisms (temperature optima: 55°C) were used for pyritic sulfur removal from coal 26 and it is conceivable that thermophilic strains may increase the rate of removal. Their more important contribution, however, may be to allow operation of reactors at temperatures where the chances of contamination are minimized.

2.5. Thermophilic facultative autotrophs

Several facultative autotr0phic organisms isolated from acidic hot springs of Yellowstone National Park can oxidize reduced iron and sulfur compounds: Sulfolobus brierleyi, for instance, a thermophilic (50-60°C) and facultative autotrophic organism [36], has a potential use for removal of pyritic sulfur and, perhaps, organic sulfur from coal although this has not been tested. The growth of this organism on ferrous iron and elemental sulfur was enhanced by including yeast extract in the nutrient medium. Another thermophilic (60-90°C), acidophilic (pH: 1.5-4) and facultative autotrophic organism capable of oxidizing reduced iron and sulfur, Sulfolobus acidocaldarius [37, 38], can utilize simple organic compounds (e.g. glucose and yeast extract) as its energy source [38]. The organism is typical of the class Archaebacterial in lacking a rigid cell wall (i.e. it has no peptidoglycan layer in its cell wall). It was used extensively for the removal of pyritic and organic sulfur from coal [24-28] and could oxidize dibenzothiophene [27]. Figure 1 shows S. acidocaldarius in suspension culture and Fig. 2 is a scanning electron microscope (SEM) photograph of S. acidocaldarius attached to a coal particle surface.

Cell attachment. Electron probe analysis using SEM indicated the presence of iron and sulfur at the attachment site, which suggests selective attachment of S. acidocaldarius to pyrite surfaces in coal (Kargi, F., unpublished results). For pyrite oxidation, cell attachment to pyrite surfaces in coal is essential - no relevant extracellular enzymes were detected in culture media. However, it is unclear whether removal of organic sulfur requires cell attachment. In general, cell attachment is not only a function of the surface properties of coal/pyrite and the organisms but also of the nutrient medium composition and hydro dynamical conditions in the reactor. Cell density at the surface of the coal should be manipulated to give optimum cell attachment. A fundamental understanding of cell attachment mechanisms in coal desulfurization may contribute to improving the rate of sulfur removal. Several Sulfolobus-like organisms have been isolated from hot sulfatara areas in Italy and Japan [39, 40] and, recently, a new organism, Sulfobacillus thermosulfooxidans was isolated in Russia [41, 42]. This rod-shaped, thermophilic, acidophilic, facultative autotrophic and spore-forming bacterium can oxidize reduced iron and sulfur compounds but there are no reports yet on its use in coal desulfurization or oxidation of model organic sulfur compounds. Thermophilic and facultative autotrophic organisms (e.g. Sulfolobusspp.) have the following advantages over the mesophilic and obligate autotrophic organisms (e.g. Thiobacillusspp.).

- High temperature operations reduce the chance of contamination of growth medium.

- Facultative autotrophs may remove both pyritic and organic sulfur from coal.
- At high temperatures the system can be operated at high cell and coal concentrations without cooling costs.
- Operation at high temperatures (50-80°C) improves the rate of *chemical* oxidation of pyritic sulfur by the ferric iron which is produced by microbial oxidation of pyritic iron in coal

2.6. Heterotrophs

Filamentous fungi. Some organic sulfur compounds can be degraded by certain filamentous fungi. Some fungi produce sulfatases which catalyze oxidation of sulfonated phenol compounds releasing sulfate ions into the medium [43]. This suggests that they might be effective in removing organic sulfur from coal although there are no published reports to this effect. Recently, several fungi (yeasts and molds) have been isolated from coal disposal areas and used to solubilize coal [44]. These organisms oxidize some of the aromatic compounds, converting them into soluble polar compounds and may be potentially useful for coal desulfurization. *Pseudomonads.* Several pseudomonad species have been isolated and used for removal of organosulfur from oil [45-46]. These organisms can oxidize dibenzothiophene and remove substantial amounts of organic sulfur from oil in 6-10 h. Some of these organisms (e.g. *Pseudomonas alcaligenes)* were genetically modified and their capabilities have been improved. Oil desulfurizing organisms might be used for desulfurization of coal, especially liquifledor solubilized coal. Another *Pseudomonas* species (Atlantic Research Company, pets. commun.) Could oxidize dibenzothiophene and remove 20-30% of organic sulfur from coal in 10-12 h. *Mixed cultures.* Mixed cultures of *T. ferrooxidans* and *T. thiooxidans* (an acidophilic and autotrophic organism) performed better in removing pyritic sulfur from coal than pure cultures of *T. ferrooxidans [22, 23]*. The role of *T. thiooxidans* (in the mixed culture) is to oxidize elemental sulfur (produced by oxidation of pyritic sulfur by *T. ferrooxidans)* to sulfate. Similarly, a mixed culture of T. *thiooxidans* and *Leptospirillum ferrooxidans*can also be used for pyritic sulfur removal from c0a114: *L. ferrooxidans*can oxidize ferrous iron to ferric iron; ferric iron oxidizes pyritic sulfide to elemental sulfur, then T. *thiooxidans* oxidizes elemental sulfur to sulfate. Another rather undefined mixed culture of organisms present in acidic coal mine waters was used for pyritic sulfur removal from coal [47].

3. Conclusion

Different microorganism were reviewed for bio-treatment under controlled condition. The maximum organic sulfur removal from coal were observed with the use of () upto the 60-70% and for as inorganic sulfur removal were measured upto 90% by use of thiobacillus ferrioxidans. With removal of sulfur it could advantage over environmental condition and for helping civilization restriction from eco-disturbances.

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