Journal of Pharmacognosy and Phytochemistry
Available online at www.phytojournal.com

E-ISSN: 2278-4136
P-ISSN: 2349-8234
JPP 2019; 8(6): 40-43
Received: 15-09-2019
Accepted: 18-10-2019

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Sulphur oxidizing fungus: A review

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Abstract
Sulphur is an important macronutrient and integral components of organic compounds present in plants, animals, microorganisms and humans. Thus present in nature everywhere, degradation of sulphur compounds become a preliminary unavoidable task. As we know many fungi; either alone or in consortium, takes part in deterioration of minerals thus balancing the environment. Sulphur oxidizing fungus is surprisingly a negligible study area but there are some reports of sulphur oxidizing fungus having applications in many areas. The fungus either use sulphur compounds as substrate for their energy production or dissolve the sulphur compounds by secreting acids thus making them a better alternative for sulphur oxidation purpose. Also they are good bio controlling agent and can be used in agriculture and other environmental applications.

Keywords: Sulphur oxidizing fungus, sulphur compounds

1. Introduction
Degradation of organic compounds by fungi has been studied so far and found in many fungal genera on diverse inorganic materials of natural or man-made like antique marbles, cave rocks, concrete and minerals by means of mycelia penetration and excretion of organic acids [1-4]. It is supposed that in these kind of oligotrophic locations, autotrophic microbes create a chemosynthetic process through sequestration of CO_2 to support energy driving reactions of different life forms of heterotrophic organisms [5]. Heterotrophs, including fungi have the ability to play a significant role in oxidation of sulphur present in soils although the rates of oxidation achieved by *thiobacilli* are high in the in-vitro conditions. In vivo S-oxidation rates by fungi similar to those of heterotrophic bacteria [6], but less than those obtained for *thiobacilli* also recorded. Heterotrophic S-oxidation is also an important process in soils under certain circumstances [7].
Micro-organisms including actinomycetes [8]; bacteria and fungi of the genera *viz*., *Aspergillus, Scolecobasidium*, *Myrothecium* and *Trichoderma* are capable of oxidizing elemental sulphur (S^o) and other reduced forms sulphur in the soil. In the process of oxidation, S^o produces sulphate and H_2SO_4 and both of these products have greatest value to fulfil the S requirement of soil, lowering its pH and also making the other nutrients available to the plants [9]. Armstrong [10] reported a wide range of sulphur oxidizing, while Abbott [11] revealed the ability of *Penicillium* to oxidize S^o to SO_4^{2-} in autoclaved soils.
As we know, approximately 98% of sulphur (S) is present in organic forms and the amount of sulphur, which is available to the plants (inorganic forms), is very less. Therefore the process of S oxidation is of great importance and application of sulphur fertilizer (readily available forms) is essential for obtaining optimum crop yield. One approach to improve its availability is by oxidation of inorganic sulphur compounds by sulphur oxidizing microorganisms, which can make the S available to plants. Presence of S-transforming microbes is of fundamental importance to the global sulphur cycle.

Sulphur oxidizing fungi
The oxidation of sulphur compounds by heterotrophic microbes especially through fungi was discovered by Waksman [12] Armstrong [10] and Abbott [11]. After that there was no much work was done in this particular area. It is only in the past one decade that the environmental and biotechnological importance of sulphur-oxidizing fungi has been realized. Various fungi having capability to oxidize inorganic sulphur compounds and playing an important part in S-oxidation in nature has been reported by Wainwright 1978 and 1989. In their studies for sulphur-oxidizing fungi, organic compounds were added into the nutrient medium. For example, Wainwright and co-workers added 10-100 µg glucose-Cg^{-1} in a synthetic soil medium for fungi *Trichoderma harzianum* oxidizing S^o [13].

They found that *Aspergillus niger* and *T. harzianum* may grow chemolithoheterotrophically in medium having both sucrose and thiosulfate as energy sources [14].

Oxidation of sulphur compounds has been reported over a wide range of fungal genera like *Absidia, Alternaria, Acremonium, Aspergillus, Amanita, Aureobasidium, Epicoccum, Cephalosporium, Fusarium, Hymenoscyphus, Geosmithia, Hypholoma, Mortierela, Monilia, Mucor, Myceliophthora, Paxillus, Paecilomyces, Penicillium, Pisolithus, Phanerochaete, Rhodotorulla, Suillus, Rhizopogon, Trichoderma,* and *Zygorhynchus* etc. [15-7].

Mechanism of sulphur oxidation

Though, the information about sulphur oxidation pathways and enzymes involved in fungi is still unclear, but here some studies are discussed in this section. As it has been reported that some prokaryotes can utilize the generated reductants like NADPH and ATP molecules, in sulphur oxidation process [17, 18], but fungi cannot.

Organic compounds, especially organic carbon, were crucial for sulphur oxidation of fungi in all previous studies except for the one with *Fusarium solani* (THIF01) isolated from deteriorated sandstones of Angkor monuments. It was found able to grow chemolithoautotrophically using S^0 as sole energy source [19]. *F. solani* is a group of about 50 phylogenetic species known as "*Fusarium solani* species complex" [20]. In 2001, F. solani was isoaletd from the floor of Lascaux cave, a nutrient poor environment [21]. *F. solani* harboured an endobacterium *Bradyrhizobium* sp. which was supposed to responsible for sulphur oxidation because *Bradyrhizobium* has sulphur-oxidation capability [22].

In one study, the endobacterium found in *F. solani* was eliminated by curing and S^0 oxidation process was examined [7]. The sandstones at the Angkor site contain 0.01-0.15% (wt.) sulphur, mainly in the form of sulphate salts [23]. It may be a possibility that prokaryotes used by fungus reduce sulphate. One possible reason may be deterioration of inner part of building due to rain washes from exterior wall provide sulphur for microbes. In addition, sulphur compounds in the bats guano inhabit in temples could be a major source of sulphur. But in their study, [7] found the cured *F. solani* still oxidized sulphur and grew in an S^0 containing medium. In presence of organic compounds, S^0 was used as both substrate and energy source.

One other mechanism of sulphur oxidation may by producing acids by fungi, which further reduced the pH and thus help in sulphur dissolution of insoluble elements. [24] recorded related results in cotton and groundnut crops. By observing the soil pH, it was revealed that sulphur oxidizing microbes could reduce pH level of soil.

Applications of sulphur oxidizing fungus

Li and coworkers [19] isolated 19 sulphur-oxidizing fungal strains from the deteriorated sandstones of Angkor temples, which utilize the sulphur as their energy substrate.

In an another study, on sulphur uptake by soybean crop revealed that all the microbial cultures including fungi with or without sulphur treatment increased S-uptake significantly over control. Sulphur oxidizing microorganisms showed synergistic effect on nutrient availability under soybean cropped soil. The multiple culture of microbes *viz*., *Aspergillus terreus, A. niger, Trichoderma harzianum, Myrothecium cinctum and Thiobacillus thiooxidans,* was found to be the most effective in increasing available N, P, potash and sulphur in soil. The available N, P, potash and sulphur were increased from 119.82 to 127.89, 15.47 to 19.31, 140.05 to 145.08 kg/ha and 19.70 to 39.65 mg/kg respectively. The S-uptake of soybean crop increased from 249 to 367 mg/100 g dry weight of plant and soil pH reduced due to inoculation of sulphur oxidizing microorganisms with sulphur use [9].

Elemental sulphur is often applied in alkaline soils to reduce the pH and dissolve insoluble nutrients. S^o oxidation to H_2SO_4 is caused by sulphur- oxidizing microorganisms including chemoautotrophic bacteria [25], fungi [26], actinomycetes [8] and yeasts [27]. Composts behaved differently to the addition of S^o due to differences in the feedstocks and composting process. The addition of S^o to mature composts affected significantly both aspects- from technical and economical points of view [28].

To produce clean solid fuels, one method is bio desulphurization. Use of different types of microorganisms including bacteria and fungus resulted in maximal desulphurization of 26%. Three types of fungi *Trametes Versicolor*, *Phanerochaeta* and Chrysosporium, Pleurotus Sajor-Caju and one mixed culture of bacteria were used. Inorganic sulphur removal of high degree (79%) with bacteria and consecutive reduction of 13% with ‘‘*Phanerochaeta Chrysosporium*” and ‘‘*Trametes Versicolor*” were achieved.

As fossil fuels contain different amounts of S and major S-content in coal is in inorganic form like pyritic and sulphatic-S. Some coals also comprise a large amount of organically bound sulphur. Therefore, during the process of combustion, the S is emitted as SOx, which is a great source for air pollution. So sulphur removal is an important task and the applied technologies of coal utilization are dedicated for removal of S before, during or after combustion processes. It is best, if the amount of sulphur oxide emissions are based on preliminary sulphur decrease [29]. Different applied techniques for removal of S are physical, chemical and biological processes.

The desulphurization process before combustion by means of biotechnological means is an alternative to the costly intensive flue desulphurization [30]. The biotechniques are ofcource based on deterioration of S-compounds by microorganisms. They offer many advantages over the conventional physical and chemical processes. Microbial can easily remove the inorganic sulphur up to 80-90%, while organic sulphur removal is bit more difficult [31]. Extra cellular enzymes produced by white rot fungi have the potential to be an effective biocatalyst, due to their broad specificity and ability to attack high molecular weight substrates [32]. Hence, a possibility was found in this natural fungal strain to remove the organic sulphur from high sulphur coals [33].

A broad range of fungi, including thermophiles have reported to oxidize S^o and heavy metal sulphides to sulphate [34, 35,16, 36]. Spores of S-oxidizing fungi in soil can survive for long periods and after getting carbon source, will germinate into S-oxidizing mycelium.

An additional advantage of these fungi is that technology can be used for large-scale production and also they behave as biocontrol agents such as *Trichoderma harzianum* already exists in soils and readily be adopted to inoculate sulphur-oxidizing fungi. Chemolithotrophic microbes are therefore may called as the most active group of sulphur oxidizers in most soils, though the amount of oxidation achieved might be equalled or even more by this group [16].

The metabolism of S in keratinophilic fungi has been reported as the keratin is a sulphur-rich substrate. Stahl and workers [37] also studied that methionine, cysteine, cystine, and inorganic SO_4^{2-} can serve as sources of sulphur for the growth of *M. gypseum*. Among 10 inorganic sources of sulphur studied, the best sources were found sodium sulphate and sulphite. Kunert [38] investigated S-containing amino acids and their derivatives as sources of sulphur for *M. gypseum*. The best sources were substances known as intermediates of sulphur metabolism or those occurring in natural substrates of dermatophytes like glutathione, cystine, cysteine, cysteic and cysteine sulphinic acids, lanthionine, taurine, sulphocysteine, and also serine-O-SO_4^{2-}.

Metabolism of cysteine is most studied sulphur metabolism of keratinophilic fungi as it is a good source of sulphur, but poor source of nitrogen [39]. Out of 30 non keratinophilic fungi studied, 19 showed ability to utilize cystine not only as a source of S but also as a source of carbon and nitrogen while, six strains consumed all the cystine present [40].

The mycorrhizal fungi *Amanita muscaria, Hymenoscyphus ericae, Paxillus involutus, Pisolithus tinctorius, Suillus booinus* and *Rhizopogon roseolus* oxidized S^o to thiosulphate and SO_4^{2-} in vitro. Even though yeasts is also capable of oxidizing S but could not be isolated from a wide range of soils. Both *Aspergillus niger* and *Trichoderma harzianum* oxidized S^o in mixed culture with *Mucor flaous* [41].

Conclusion

It has been found that the potential role fungi in sulphur oxidation has been neglected from so many years. The sulphur oxidizing fungi may prove better to perform the sulphur oxidation process, since they obtain comparatively large amounts of carbon from their host and also helps in biocontrol naturally. Hence fungi can oxidize sulphur in many ways like by mycorrhizae both in vitro and in peat, by distribution of sulphur-oxidizing yeasts in soils, by mixed cultures fungi and by wood rotting *Basidiomycetes* to oxidize S^o in non-sterilized soils.

Acknowledgement

Financial assistance throughout the degree from DST (INSPIRE) Department of Science and Technology, Technology Bhavan, New Mehrauli Road, New Delhi – 110016, is greatly acknowledged.

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