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Magnitude and Mechanism of Siderophore as a Potential Tool in Eco Friendly Agriculture

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ABSTRACT

Siderophores are low molecular weight metal chelating agents which are produced by plants and microorganisms in Fe- limiting conditions. These Siderophores chelate iron and supply to bacterial cell by outer membrane receptors. There is a wide variable seen in siderophore nature and functions from bacterial species to species. Isolation of siderophore agent can only be obtained under Fe restricted media. Siderophore and their derivative have large application in agriculture starting from soil fertility, bio control agent, plant growth promoter and also as a bio remediation against heavy metals. There is still a lot way further to research its mechanism and mode of function so that to explore its potentiality in fields other than agriculture also for plant and human benefits.

Keywords: Siderophores, Fe chelates, Soil health, Eco-friendly agriculture

One of the vital elements, Iron (Fe) is critical for all living organisms to carry out important cellular process viz, electron transport chain and simultaneously as a cofactor for many enzymes (Litwin and Calderwood, 1993) that facilitates various enzymatic process as a catalyst. Fe has also a significant role to play in oxygen metabolism DNA and RNA synthesis (Aguado- Santacruz *et al.* 2012). Soil microorganisms, specially under aerobic environment need Fe for a wide variety of functions that includes reduction of oxygen for the synthesis of ATP, formation of heme protein etc. Fe also helps in bio film formation and controls surface motility and stabilize the polysaccharide matrix (Weinberg, 2004; Chhibber *et al.* 2013). Under aerobic condition free Fe gets oxidize to insoluble oxy hydroxide polymer and reduce the level of free Fe which generates gradually Fe limiting condition. Thus, microorganism adopts an alternate way for Fe acquisition by producing Fe chelating molecule i.e. siderophore. Siderophore are low molecular weight (< 10 KD) Fe chelating compounds synthesized by bacterial population such as *Pseudomonas, Azotobacter, Bacillus, Enterobacter, Serratia, Azospirillum and Rhizobium* (Glick *et al.* 1999; Loper *et al.* 1999). Siderophore combines with free Fe and forms complex which transport into the cell by the help of membrane receptor molecules, these receptor molecules that are encoded by five genes in operon gets off when cells gets sufficient Fe (Lewin, 1984).

With growing concern about soil health and organic agriculture practices, siderophores is getting major attention in the fields of application due to its immense potential in nutrition and plant health and ecofriendly nature. At present nearly 500

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siderophores are reported from microorganisms with great variation in their structure from one species to another. Despite of providing nutrition to plant and microorganism siderophore also contributes in other environmental applications such as soil mineral weathering, biogeochemical cycling of Fe in oceans and biotechnological applications such as enhancing growth and pathogen bio control of plants, bio control of fish pathogens, microbial ecology and taxonomy, bioremediation of environmental pollutants, petroleum hydrocarbons, nuclear fuel reprocessing, optical biosensor, bio-bleaching of pulp (Ahmed and Holmström,2014).

Classification of siderophores

According to the oxygen ligands for Fe^{3+} organization, siderophores can be differentiated to three main categories, namely: hydroxamates, catecholates, and carboxylates. Hydroxymate type of siderophore is mostly produced by the bacteria and fungi. Most hydroxamate groups belong to C (=O) N-(OH) R and R is an amino acid. As for example Ferrioxamine groups of siderophores that produces by *Arthrobacter*, *Chromobacterium* and *Pseudomonas* species of soil bacteria. Catecholate is another important group of siderophore, mainly produced by the soil bacteria. The structure of the backbone can be polyamine, a peptide or a macrocyclic lactone. In 1970, their isolation was done from culture fluids of *E. coli*, *Aerobacter aerogenes*, and *Salmonella typhimurium* which further produced enterobactin (also termed as enterochelin) and was the first tricatechol siderophore. Enterobactin is the most intensively analyzed siderophore because of its exceptional properties pertinent to its physiological reactions as observed. Bacteria like *Staphylococci*, *Rhizobium melilot*, *Mucorals* produce such siderophores namely Staphyloferrin A & B, rhizobactin and rhizoferrin carboxylate siderophore respectively. Phytosiderophores are the Fe^{3+} chelating compounds secreted mostly by the which can form specific strong complexes with Fe^{3+}. When phytosiderophore is released in the rhizosphere region, it chelates the iron from the soil by forming a complex of Fe^{3+} which can be directly transported across the root plasma membrane (Römheld and Marschner 1986; Dell'mour *et al.* 2012). Several studies also suggested that some graminaceous plant like wheat, rye and barley have ability to produce a high concentration of phytosiderophores that makes them more resistant towards Fe deficiency in comparison to other plants like maize, rice and sorghum, which produce comparatively lower concentration of phytosiderophores (Masuda *et al.* 2009; Kobayashi *et al.* 2010).

Mechanism of siderophore

As siderophore is released from the cell, the membrane receptors present in the cell membrane protein binds with free Fe and form Fe-siderophore complex. This complex is transported into the cell via Fec A and Fep A which are an outer membrane (OM) receptor. Later, it is transported to ABC-Transporter systems i.e. Fec C, D, E and Fep C, D, E (from ATP binding cassette) which consists of two proteins, one acts as permease whereas the other protein hydrolyze ATP to give energy for transportation (Boos and Eppler, 2001). Finally, siderophore Fe complex is released under cytosol by membrane protein and finally free iron is separated from the complex by hydrolytic destruction of the siderophore molecule or cell membrane protein or by the reduction of Fe^{3+} by NADPH linked siderophore reductase. The final Fe^{2+} does not show any high affinity towards siderophore and thus get easily separated from the siderophore-iron complex and siderophores either get degraded or recycled by excretion through efflux pump system. Mechanism of Siderophore mediates iron transport in bacteria presented in Fig. 1.

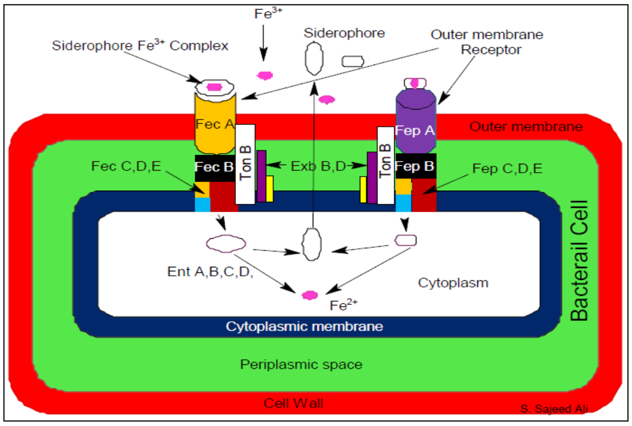

Fig. 1: Mechanism of Siderophore mediates iron transport in bacteria [*Source:* Ali S, 2013]

Potential role of Siderophores in Agriculture

In agriculture, inoculation of *Pseudomonas putida* with the soil, that produces pseudobactin, (siderophore) is found to increase the growth and yield of various plants (Kloepper *et al.* 1980). Plant growth promoting activities of siderophore includes production of HCN protease, antimicrobials, phosphate solubilizing enzymes (Chaiharn *et al*. 2008) etc. Hydroxamate type siderophore present in soil plays an important role to immobilize the metals and prevents in their accumulation in agricultural soils. The effect of siderophore-producing PGPR is also reported recently (Ferreira *et al.* 2019). Siderophore producing bacteria *Pseudomonas putida* was found to increase the tuber yield in potato in a short rotation (Bakker *et al.* 1985). Another study by Gamit, D *et al.* (2014) showed that siderophores from *P. pseudoalcaligen* increased the seed germination and plant growth of pigeon pea crop and also positively affect the yield. In calcareous soils, Fe chelated and Fe siderophore fertilization is also reported to increase the yields, crop growth and Fe uptake of cumin crop (Tortora, M *et al.* 2011).

Siderophore as a Biocontrol agent

Many bacteria suppress the growth of disease causing pathogens by production of siderophore, antibiotics, and cyanide (Edi Husane, 2005). Siderophores acts as a growth inhibitor of various phytopathogenic fungi, such as *Phytophthora parasitica* (Seuk *et al*. 1988), *Phythium ultimum* (Hamdan *et al.* 1991), *Fusarium oxysporum veri dianthi* (Buysens *et al*. 1996) and *Sclerotinia sclerotiorum* (Mc Loughlin *et al*. 1992). Kloepper *et al*. (1980) was first to demonstrate the importance of siderophore production as a biological control against *Erwinia carotovora* by several strains of *Pseudomonas fluorescens*. A direct correlation was also set through *in vitro* experiment between siderophore synthesis in fluorescent pseudomonads and discovered their ability to inhibit germination of chlamydospores which prevent *F. oxysporum* to cause destructive wilt of plants (Elad and Baker, 1985; Sneh *et al*. 1984).

Environmental applications of Siderophore

The most common heavy metal contaminants found in soil and aquatic system are cadmium (Cd), chromium (Cr), copper (Cu), Mercury (Hg), lead (Pb) and Nickel (Ni). Metals are natural components in soil with a number of heavy metals being required by plants as micronutrients. Siderophores and other naturally occurring ligands affects actinide mobility in waste repositories and in the environment and may also used to treat radioactive waste prior to storage or to decontaminate soils and water (Ruggiero *et al*. 2000; Von Gunten and Benes, 1995).

Siderophore as a Plant Growth Promoter

From past few decades, different species of *Pseudomonas*c has been reported to enhance plant growth by producing pyoverdine siderophores (Kloepper *et al.* 1980; Gamalero and Glick 2011). Mahmoud and Abd-Alla (2001) also observed that siderophores (hydroxymate type) producing *Pseudomonas* sp. improves the nodulation and N_2 nitrogen fixation of mung bean plant in comparison to *Bradyrhizobium* strain alone. In addition to pseudomonads, other bacteria under rhizosphere region of plant *Azadirachta indica* had reported to produce ferrioxamines siderophore that transfers the Fe to the plant and helps in growth and development of shoot and root (Verma *et al.* 2011; Crowley 2006). Powell *et al.* (1980) found in his study that hydroxamate siderophores exists in different soils as well as in the aquatic environments also. It has been established that hydroxamate type of siderophore present in soil play an important role to immobilize the heavy metals which is very toxic to most of the plant and soil health status. Other bacterias like *Escherichia coli* from rye grass (*Loliumperenne* sp.) and endo-rhizosphere of sugarcane (*Saccharum* sp.) and an endophytic *Streptomyces* sp. isolated from the roots of a Thai jasmine rice plant enhanced plant growth and significantly elevated root and shoot biomass and lengths (Gangwar and Kaur 2009; Rungin *et al.* 2012).

Siderophore as a Bioremediator

Siderophores also have a significant role to play in chelation of various heavy toxic metals e.g., chromium (Cr^{3+}), aluminium (Al^{3}), copper (Cu^{2+}), europium (Eu^{3+}) and lead (Pb^{2+}) (Nair *et al.* 2007; Rajkumar *et al.* 2010; O'Brien *et al.* 2014). Depending upon the concentration of metals in the growth medium, siderophore production can be regulated (Schalk *et al.* 2011; Braud *et al.* 2010). For example, in presence of Cr^{2+}, Al^{3+}, Cu^{2+}, Ni^{2+} and Mn^{2+} pyoverdine (siderophore) production was found to raise in *P. aeruginosa* (Braud *et al.* 2009), azotochelin biosynthesis was raised by molybdenum (Mo) in

Azotobacter vinelandii (Duhme *et al.* 1998), *N*-dioxyschizokinen production was enhanced by the presence of Al in *B. Megaterium* (Hu and Boyer 1996). Therefore, siderophores is considered as an agriculturally important tool for bio remediation of heavy metals (Rajkumar *et al.* 2010). Siderophores such as azotochelin and azotobactin which are produced by *Azotobacter vinelandii*can found very useful for controlling Mo (molybdenum) and V (vanadium) acquisition (Wichard *et al.* 2009); Studies reported that *P. fluorescens* have observed to mobilize the metals like Ni^{2+} (Nickel) and Co^{2+} (Copper) from mining waste material (Edberg *et al.* 2010). Besides, It is already proved that siderophores produced by *Agrobacterium radiobacter* can eradicate approximately 54% pollutant soil contaminated with heavy metals where pyoverdine siderophore has ability to mobilize uranium (U^{6+}), neptunium (Np^{5+}) & other metals from uranium mine waste (Behrends *et al.* 2012; Wang *et al.* 2011).

CONCLUSION

In a view of focus, sustainable agriculture and resource conserving technologies, organic farming, microbial diversity and soil health has gained considerable attention in recent years. Siderophore thus has a huge potential to be explored in agriculture scenario. In most agricultural land, especially under aerated soil condition and neutral to alkaline pH soil, deficiency of inorganic Fe is widely found as it is insoluble and their concentration is found less than optimal for bacterial growth to acquire Fe bacterial cell produce siderophore. Thus, there can be enormous scope for the application of microbial siderophores in the field of Agriculture to improve growth and productivity of plant. Further research should be carried out to exploit its beneficial role under extremophiles conditions like deep sea, desert and forest for welfare of all living beings as well as for the environment.

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