Mini review article
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The significance of oxidation states of Mn in oxygen evloving complex and its possible transition states

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Abstract:

Mn, a transition element found in different variable oxidation states, is highly reactive, one of the essential elements among 17 for all living creatures, including humans and plants. It is as essential as Fe and required by plants in the subsequent highest quantity over Fe for sustainable growth of plants. Mn, having critical roles in plant metabolism, is an indispensable cofactor for the oxygen-evolving complex (OEC) in photosystem II (PSII). It catalyzes the water-splitting process to evolve oxygen from leaves, thereby protecting the plant from oxidative stress. When chlorophyll absorbs light, excitation takes place with the release of energy. PSII accomplishes a series of electron transfer reactions by this energy that involves the transition of the OEC in several singlet states viz $S_o – S_1$, $S_1 \rightarrow S_2$, $S_2 \rightarrow S_3$ and $S_o \rightarrow S_4$ during water splitting studied through quantum /molecular mechanisms using chemical sources of Mn in different oxidation states. Although required in low quantity, deficiency causes adverse effects on the growth of the plants. Its bioavailability to the plants is related to the soil pH and high pressure of oxygen as it is rapidly converted into oxides where oxidation states are altered. It significantly contributes to plant growth regulatory systems like photosynthesis, respiration and nitrogen accumulation, pollen tube, root cell germination, and resistance against bacteria. This review article highlights the oxidation and transition states of Mn in OEC linked to photosystem II.

Keywords: Mn, cofactor, OEC, Photosystem II, growth

Highlights:

- Mn, essential nutrients of plant growth
- Mn oxidation state in OEC
- Required to catalyze the water splitting during photosynthesis

1. Introduction

1.1. Manganese in Plants

Manganese (Mn) is a vital plant mineral nutrient major contributor to various biological systems, crucial in numerous physiological processes, predominantly photosynthesis (Millaleo et al., 2010). Mn is important as a growth nutrient like Fe (Ma & Ling,2009; Kobayashi & Nishizawa, 2012). The importance of Mn is related to its variable oxidation states (+2 to +7), where Mn^{+2} is easily converted into Mn^{+4} and plays a role in redox reactions, as electron transport in photosynthesis. Besides this, Mn also acts as an activator of various enzymes, involving oxidation reactions, carboxylation, carbohydrate metabolism, phosphorus reactions and citric acid cycle. The most important role is the oxygen-evolving complex (OEC) (Zhang & Sun, 2018). Manganese has comparatively little phloem flexibility in plants; consequently, specific leaf indications of Mn deficiency primarily grow in younger leaves. Mn plays a significant role in photosynthesis, especially in photosystem II. It is involved in water oxidation, releasing oxygen, hydrogen, and energy to continue the process of photosynthesis, which requires an adequate quantity of Mn as it helps in the photolysis of water molecules and provides energy for photosynthesis (Reiss et al, 2019). Mn is the element of life for this function because, without water splitting, the chain reaction that leads to fixing CO_2 and water to convert it to carbohydrates would be broken. It is a well-known phenomenon that solar radiation in leaves is absorbed by the pigments chlorophyll, which after excitation, releases in the form of chemical energy. This transfers to strike the PSII to initiate the splitting of water molecules into H and O. Each splitting of a water molecule releases a pair of electrons that form the electron transport chain and initiate the pumping of hydrogen molecules into the inner part of the chloroplast called thylakoid.that develops an electrochemical ramp in which ions move through two sets of enzymes called NADP Reductase and ATP synthase that are accountable for creating energy molecules (Adenosine Tri Phosphate aka ATP) and reducing power (NADPH). This leads to the formation of sugars in the outer part of the chloroplast during the Calvin cycle. While deficiency (George et al. 2014) of Mn resulted in a decline in photosynthesis and a decrease in soluble sugar concentrations in diverse parts of plants, consequently declining dry matter production and yield (Hajiboland, 2011). Mn is reported as a cofactor of several enzymes that catalyze the metabolic pathway of lignin synthesis and phytoalexins. The function of the peroxidase enzyme is Mn-dependent which produces hydrogen peroxide, stabilizing the cell wall directly toxic to the pathogens and acts as a fungicide. Approximately all ecological stress factors signify oxidative stress. The vital function of Mn is in improving anxiety tolerance like superoxide dismutase enzymes, accountable for the reclamation of the critical free radicals, need diverse metal cofactors, like Mn, for proper functioning, while Mn increases the activity of Mn-superoxide dismutase contributes significantly to plant tolerance under dissimilar ecological anxiety including winter, drought, hardiness and ozone stress. Losses observed in lignin biosynthesis under Mn deficiency, particularly in the roots, are linked with the augmented infective attack, predominantly soil-born fungi, as lignin acts as a barrier against pathogenic infection.

1.2. Oxidation State and nutrients

The oxidation state is the charge of an atom after the ionic approximation of its bonds, where atoms charge is the number of valence electrons to the free atom, while in the ionic approximation, the atom that contributes more to the molecular orbital becomes negative (Huang et al., 2016). It is a quantitative approach that works on the integer value of calculating electrons. It also plays a significant role when an element is involved in the growth of living beings. Many elements are essential for the growth of plants and refer as micronutrients, having critical roles like i) part of photosynthesis, ii) enzymes activity of the plants, iii) redox reactions) protein synthesis v) N Fixation. A nutrient element like Fe is an active part of chlorophyll synthesis, while Mn is a part of photosystem II and Zn is required for N transformation in plants (Rengel, 2015). Symbiotic fixation of N requires Mo while cell division and seed formation requires B. N is essential for urease enzymes, and Co facilitates rhizobia in soil (Grusak et al,2016; Bertini et al.,2006)

1.3. Mn; essential nutrient of variable Oxidation States

Manganese exists in an oxidation state from +2 to +7 in its compounds. It is commonly found in the oxidation state of 2, +4, and +7, while the compound with oxidation states of +3, +5, and +6 are also reported and prepared. Therefore, Mn is present in the soil in different oxidation states. The compounds (**Table 1**) with different oxidation states are recognized by a different colour (Cecilia et al., 1997)

Table 1 Chemical compounds with different oxidation states of manganese (Schmidt & Max 1968).

Oxidation state	Compounds	Chemical Name
0	$Mn_2(CO)_{10}$	Dimanganese decacarbonyl
+1	$(C_5H_4CH_3)Mn(CO)_3$	Methylcyclopentadienyl manganese tricarbonyl
+2	$MnCl_2$ $MnCO_3$ MnO	Manganese(II) chloride Manganese carbonate Manganese(II) oxide
+3	MnF_3 $Mn(O_2CCH_3)_3$ Mn_3O_4	Manganese(III) fluoride Manganese(III) acetate Manganese(III) oxide
+4	MnO_2	Manganese(IV) oxide
+5	K_3MnO_4	Potassium hypomanganate
+6	K_2MnO_4	Potassium manganite
+7	$KMnO_4$ Mn_2O_7	Potassium permanganate Manganese(VII) oxide

The unusual oxidation-reduction reactions of Mn (i.e. Mn(II) to Mn(VII) are valuable for the structure of the OEC, where gathering four charges is desirable to oxidize water molecules into molecular oxygen and hydrogen. The OEC in photosystem II, which is accountable for water oxidation to oxygen, involves a assemblage of one calcium and four manganese atoms and serves as a model for splitting water by energy through photosystem I. The life on the earth is supported by the oxygen generated by the plants, algae, and cyanobacteria by the photoinduced oxidation of water into dioxygen molecules according to the following equation

$$2H_2O + hv = O_2 + 4e + 4H^+ \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ (1)$$

The OEC or Mn-cluster is widely investigated, located, and bounded by a protein matrix in photosystem II, which accomplishes a series of electron transfer reactions using solar energy. Water splitting under light absorption generates four electrons and four protons from two water molecules. It demands four successive oxidation, catalyzed by the OEC that is completed by diverse redox states, known as singlet transition ($S_{i)}$ states (i = 0–4). The variable oxidation states of Mn (Mn

(II) to Mn(VII) make it a perfect component of the OEC, where four charges are required to oxidize water molecules into molecular oxygen. Oxygenic photosynthesis involves water molecule splitting in the Mn OEC in the chloroplast center and transpiration by cytochrome doxidase in mitochondria. Pal et al. 2013 reported that the S_o – S_1 transition of the OEC during water splitting through quantum /molecular mechanism model linked with X-ray absorption and X-ray diffraction where it established that proton-coupled electron transfer occurs during So – S_1 transition with significant rearrangement in the OEC complex (Fig.1)

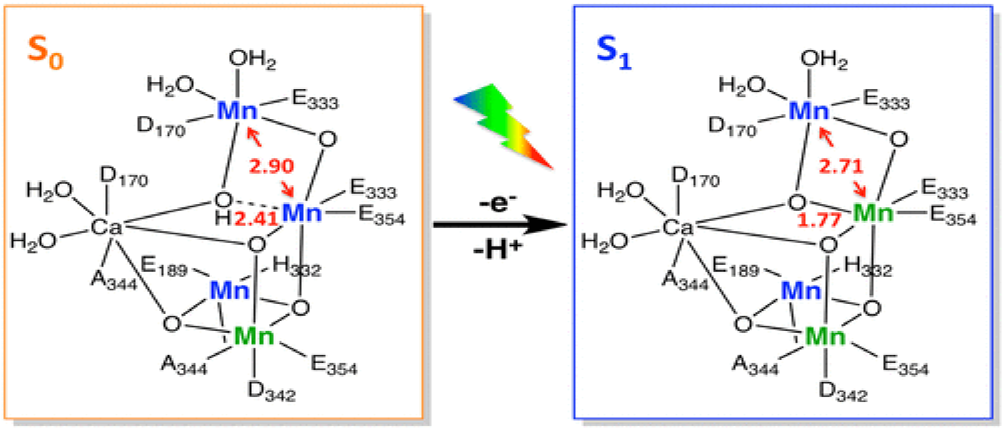

Figure 1 S0-State model of the oxygen-evolving complex of photosystem II. *Biochemistry* (pal,et al 2013)

Hatakeyama et al. (2016) applied DFT calculations compared with the EXAFS data about the S_3 state of the OEC complex in photosystem II by inserting a water molecule into an Mn-based open coordination site on S_2 to S_3 transition. They report that the original S3 state structure consisted of only short 2.7–2.8 Å Mn with the distance of Mn (Fig.2).

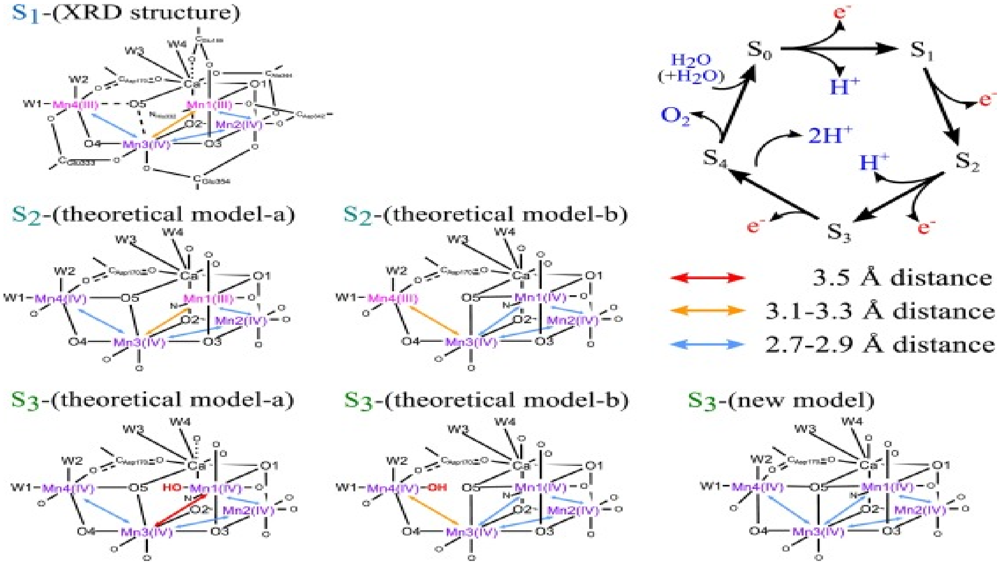

Figure 2 Structural changes in the S_3 state of the oxygen-evolving complex in photosystem II (Hatakeyama et al 2016).

During photosynthesis, plants harvest solar radiation to initiate water oxidation, converting the absorbed radiation or energy into chemical energy, thereby releasing di-molecular oxygen as a byproduct (equation 1). Kok et al (1970) described that biological water oxidation occurs in plants in five steps. Four-electron water oxidation occurs at the oxygen-evolving complex (OEC), followed by the one-electron photochemical reactions at the reaction center. Literature reported that in the photosystem II, Mn_4O_5Ca (OEC) cluster; five intermediate S-states (S0 to S4) work in cycles corresponding to the abstraction of four successive electrons from the OEC followed by several cofactors including non-haem iron, redox-active tyrosine sidechain, quinones, chlorophyll, and pheophytin (Yano, & Yachandra, 2014; Vinyard et al. 2017).

Amin (2022) states that during catalysis in PS II enzymes, the Mn ions are oxidized in the transition between the S-states, and the oxidation state of the Mn ions may be Mn (III, IV, IV, III) in the dark-adapted state of the OEC (S1-state). He built two models of available small molecules from the Cambridge Structure Data to predict the Mn oxidation state in the OEC. It is reported that the DT model exhibited improved results than the GNB model, with a precision of approximately 100% in the prophecy of trivial molecules and ~ 75% in the case of XFEL-S_1 structures (Amin 2022). While Visser 2002 states that according to different spectroscopic studies and techniques, the Mn (III) transition occurs when oxidized to higher S-states till all Mn (III) into Mn (IV) in the S_3 state. Moreover, the model projected transitions $S_1 \rightarrow S_2$ and $S_2 \rightarrow S_3$ states for oxidation of Mn.

Moreover, the estimated model displays that Mn4 is the most vulnerable Mn ion to radiation damage among the four ions (Amin 2022). The variable oxidation states of the Mn play an important part in photosystem II to oxidize water, where the OEC is oxidized and loses one electron. Crabb & Moore (2010) reported five states, S_0, S_1, S_2, S_3, S_4, through spectroscopic studies (Fig. 3) and displayed variations in the state of Mn^{2+} to Mn^{3+} and Mn^{3+} to Mn^{4+} throughout the cycle. The water-splitting process is described by the oxidation of OEC coupled with the excitation of chlorophyll pigment, where a photon of light is absorbed. It is oxidized simultaneously in a series of oxidation steps when the chlorophyll complex is excited. It is established that four photons are required for the excitation of chlorophyll where the $Mn^{IV}{}_2O_x$ group is unchanged while the redox reaction takes place from the S_0 state to the S_1 state where Mn^{2+} is oxidized to Mn^{3+} followed by another oxidation of Mn^{3+} takes place in Mn^{4+} from S_2 state to the S_3 state. A ligand dissociation involved with an unknown base in S_3 to S_4 with the exchange of ligand S_4 to S_o state consequently releases O_2 molecule and hydrogen ion used in ATP (photsystem II)

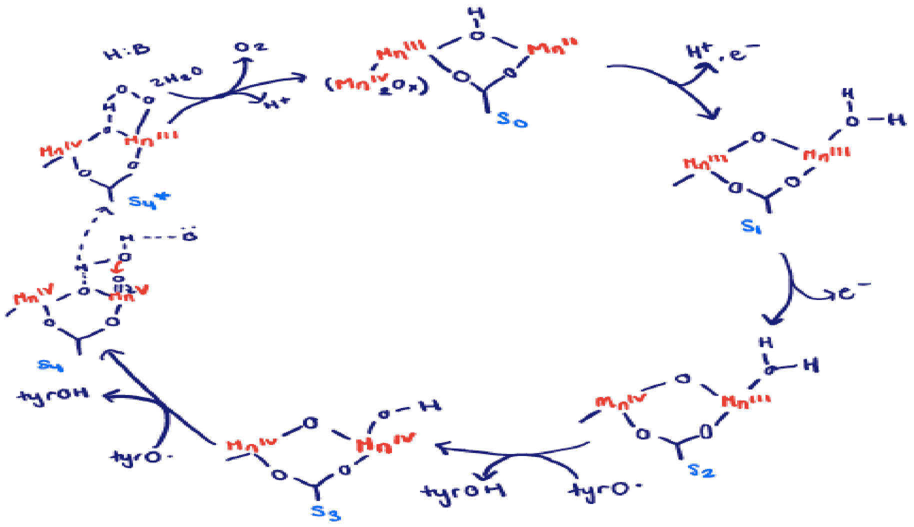

Figure 3. Link of Photon Absorption, Mn and Water Oxidation during the photocatalytic cycle (Crabb, & Moore, 2010).

Petrie et al 2017 established that water oxidation to molecular oxygen and protons in OEC is the most energetically demanding reaction. They proposed two suggestions for oxidation i) 'high' and ii) 'low' oxidation state examples, leading to the firm inference that the low model oxidation state assignment for the function of OEC is favoured. Koumousi et al. (2011) observed that synthetic access had been accomplished into high oxidation state Mn/Ca chemistry with the 4: 1 Mn: Ca stoichiometry of the oxygen-evolving complex (OEC) of plants and cyanobacteria; The anion of (Et3NH) 2 [MnIII4Ca (O2CPh) 4 (shi) 4] has a square pyramidal metal topology and an S= 0 ground state.

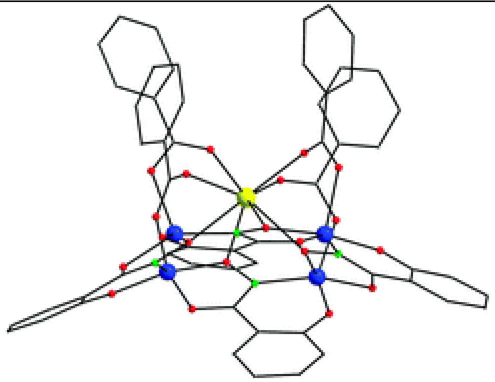

Figure 4. square pyramidal metal topology of (OEC) of plants and cyanobacteria (Koumousi et al. 2011)

2. Conclusions

Mn is reported as an essential nutrient of plant growth. Releasing H and O and the trivial background of the Mn involve a cofactor of several physiological reactions of plants and as an indispensable catalytic metal nutrient in plant growth. It is a significant part of the Photosystem II involved in water splitting, fixes the energy to initiate the release of oxygen and formation of glucose molecules. That leads to the formation of carbohydrates, shows resistance against pathogenic attacks, and cofactor of several vital enzymes, while deficiency leads to a reduction in growth. It was established that Mn oxidation states play a diverse role in said biochemical pathway. In this mini-review, we highlighted the oxidation and transition of the Mn in the OEC involved in water-splitting. A detailed literature survey showed little work on Mn bioavailability in several biochemical pathways. Therefore, it is recommended that plants should be cultivated under various oxidation states of Mn in natural environmental conditions to compare Mn's computational modelling with real growth factors. The catalytic oxidation of the OEC is the utmost energetically challenging reaction in nature. At the same time, diatomic oxygen and H ion are produced during photosynthesis, in which the Mn character is significant. However, much work is required to prove the correct oxidation states of Mn in OEC through computational modelling and cultivation of plants under different oxidation states with different compounds of Mn in different oxidation states. Still, the catalytic mechanism remains unsolved, and the detailed Mn oxidation levels through the cluster cycles during functional turnover are debatable.

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