M.Sc Semester-III, Paper: CC-11 (Bio-Inorganic Chemistry)

Unit-2 Bioenergetics & ATP Cycle [By Dr. Birendra Kumar, Maharaja College]

⟹ Photosystem or Pigment system (PS I & PS II)

Photosynthetic units occur in the term of two distinct groups called photosystem or pigment system. Green plants possesses two photosystem (PS)-I & II. On the basis of Emerson effect, two conclusions were drawn: (i) There are two groups of pigments (ii) Both groups of pigments act in cooperation with each other. Emerson suggested that one group of pigments is responsible for absorption of longer wavelength of light while other group of pigment is responsible for absorption of shorter wavelength. Even composition of these groups of pigment was suggested by Emerson. Later on Amesz, Duysens & Kamp proposed the concept of two photosystems which were named as PS I and PS II.

PS I absorbs preferentially far red light of wavelength greater than 680 nm while the PS II absorbs red light of wave length ~~greater than~~ of 680 nm. PS I Contains Chlorophyll-a, small amounts of Chlorophyll-b and some β-carotene attached by non-covalent bonds to several proteins. One of Chlorophyll-a molecule is made of some how special by its chemical environment such that it absorbs light near 700 nm and so it is called P700. It is surrounded by other chlorophyll-a molecules, followed by Chlorophyll-b and carotenoids. It has a reducing agent X, FeS centre B or Ferrodoxin, Plastoquinone, cytochrome complex and plastocyanin. It takes part in both cyclic and non-cyclic photophosphorylation. PS I can carry on cyclic photophosphorylation independently. Normally it drives an electron from PS II to $NADP^+$. There are Fe-S proteins which serve as primary electron acceptors for PS I, which means that electrons are first transferred from reaction centre of PS I to Fe-S protein.

PS II is a photosynthetic pigment system along with some electron carrier that is located in the appeared part of the grana thylakoids. PS II contains Chlorophyll-a, β-carotene and a little Chlorophyll-b. Reaction centre chlorophyll is P680 which is a chlorophyll-a molecule in a chemical environment different from that of P700.

Primary electron acceptor of PS II is Pheophytin which is colourless Chlorophyll that lack $Mg^{2+}$. It has two $H^+$ in place of $Mg^{2+}$

A quinone (Q) is closely associated with Pheo, P680 and protein that binds P680.

Finally PS II contains one or more proteins containing manganese protein (mangano-protein). It is believed that four $Mn^{2+}$ ions are bound to one or more proteins in PS II and a chloride ion bridges two $Mn^{2+}$.

PS I produces a very strong reductant capable of reducing $NADP^+$ and a weak oxidant.

PS II produces a very strong oxidant capable of oxidising water and a weaker reductant than the one produced by PS I. This reductant rereduces the oxidant produced by PS I.

PS II is mainly present in grana lamellae. PS I is mainly present in stroma lamellae. Coupling factor enzyme that catalyses formation of ATP are found exclusively in stroma lamellae.

Cytochrome $b_6f$ complex which connects the photosystems is evenly distributed.

In most of cases there is excess of PS II in chloroplasts. However, in cyanobacteria and in bundle sheath chloroplasts of $C_4$ plants there is excess of PS I.

Most pigments of a photosystems serve solely as light gathering antenna pigments, absorbing photons and passing the energy to reaction system/centre. Large number of pigments are associated with each reaction centre and each reaction centre must operate four times to produce one molecule of $O_2$.

Each Photosystem (PS) is generally associated with light harvesting complex (LHC) which like a photosystem collects light energy. The LHC does not contain a reaction centre, instead, it passes the collected energy to a nearby PS by resonance transfer. LHC of plants and green algae have 80-250 chlorophyll-a and b molecules, carotenoids and pigment binding proteins. Red algae and cyanobacteria have different types of LHC, called phycobilisome, which contain phycobilins rather than chlorophyll and carotenoids. Together, a PS associated LHC are referred as PS-complex.

$$PS\,II \xrightarrow[H_2O \;\rightarrow\; 2H^+ + \frac{1}{2}O_2]{Light} PSI \xrightarrow[2H^+]{Light} NADPH + H^+$$

In most cases PSII appears to be dimeric with two reaction centres.
They are located at two different positions in lamellar systems. Despite this they function together. It is due to the fact that cytochrome $b_6f$ complex which connects the photo-systems.

*<u>Mechanism of photosynthesis</u>: In photosynthesis $CO_2$ is reduced with the help of NADPH & ATP. Generation of NADPH & ATP takes place in presence of light, so it is called <u>light reaction</u>. Reduction of $CO_2$ does not require light, so it is called <u>dark reaction</u>.

Light reaction takes place in presence of light. It occurs in lameller system of chloroplasts. It generates NADPH & ATP which represent assimilatory power. Their generation takes place in following manner: (i) Non-cyclic photophosphorylation (ii) Cyclic photophosphorylation.

*<u>Photoreduction (NADPH synthesis) and photophosphorylation in photosynthesis</u>:

Energy captured by antenna pigments of PSII or of associated LHCII [redacted] is funneled to reaction centre. When the energy reaches a pair of P680, a photoexcited electron is then passed to pheophytin, which is pie electron acceptor. To absorb photons repeatedly oxidized P680 must be reduced each time an electron is lost to PQ. To replenish electrons PS II includes an oxygen evolving complex (OEC) that catalyses oxidation of water to molecular oxygen. Two water molecules donate four $H^+$ and one $O_2$ molecule are released within thylakoid lumen. The protons contribute to an electrochemical proton gradient across the membrane and oxygen diffuses out of the chloroplasts.

Each photo excited electron passes from the primary electron acceptor of PSII to PSI via an electron transport chain. The electron transport chain between PS II & PSI is made up of plastoquinone (PQ), a cytochrome complex and a copper containing protein called plastocyanin.

The flow of electron from primary electron acceptor of PS II [redacted] to oxidized reaction centre of PSI is exergonic. The free energy released in this flow is utilized to drive phosphorylation of ADP into ATP.

In the meantime light energy was transferred to reaction centre of PSI, which excites an electron of one of two P700 molecules.

The photo excited electron was captured by PSI's primary electron acceptor. Evidence indicates that one of the early acceptors is a chlorophyll molecule (A) and another is a quinone species, phylloquinone (A). Additional electron acceptor are Fe-S proteins or bound ferredoxin (also known as Fe-S centre). Electrons are transfer through Fe-S centres to Fd which is small water soluble Fe-S protein.

The oxidised P700 gets the electron from PSII through electron transport chain.
The final step in the photoreduction pathway is electron transfer from Fd to $NADP^+$ which is catalysed by enzyme ferredoxin $NADP^+$ reductase (FNR).

Continuous unidirectional flow of electron from water to $NADP^+$ with the help of both photosystems and other component of ETS is called non-cyclic electron flow. The electron flow is often called Z-scheme, because of its overall form. The overall reaction is as follows:

$$4 \text{ photons at PSII} + 4 \text{ photons at PSI} + 2H_2O + 6H^+_{stroma} + 2NADP^+ \longrightarrow 2NADPH + O_2 + H^+_{lumen}$$

Thus, every eight photons absorbed two NADPH molecules are generated and the electron flow is coupled to unidirectional proton pumping across thylakoid membrane. Thus, solar energy is captured and stored in two forms: the reductant NADPH and an electrochemical proton gradient.

ATP synthesis is catalysed by ATP synthase/coupling factor/ATPase of $CF_0-CF_1$. Its hydrophobic membrane bound portion called $CF_0$ and a portion that sticks out into the stroma is called $CF_1$. Passive flow (facilitated diffusion) of $H^+$ through ATP synthase provided energy for synthesis of ATP formation. Light driven phosphorylation of ADP into ATP is called photophosphorylation. It was reported by Arnon et al.

* Cyclic photophosphorylation: When NADPH consumption is low, an optional pathway diverts the reducing power generated at PSI into ATP synthesis instead of reduction of $NADP^+$ into NADPH.

Reduced Fd generated by PSI can pass electrons to Cyt $b_6f$ complex instead of donating them to $NADP^+$. By a mechanism that (involves plastoquinone) the exergonic flow of electron from reduced Fd to PC is coupled to proton pumping across thylakoid membrane. From PC electron returns to an oxidized P700 molecule in PSI, completing a closed circuit and allowing P700 to absorb another proton. This is referred as cyclic electron flow and ATP synthesis that it supports is called cyclic photophosphorylation. No water is oxidised and no $O_2$ is released, since the flow of electron from PS II is bypassed.