Republic of Iraq
Ministry of Higher Education
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University of Anbar
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Lecture 7

Metabolism

Photosynthesis

Mechanism of photosynthesis:

Light Reactions in Photosynthesis

Noncyclic Photophosphorylation

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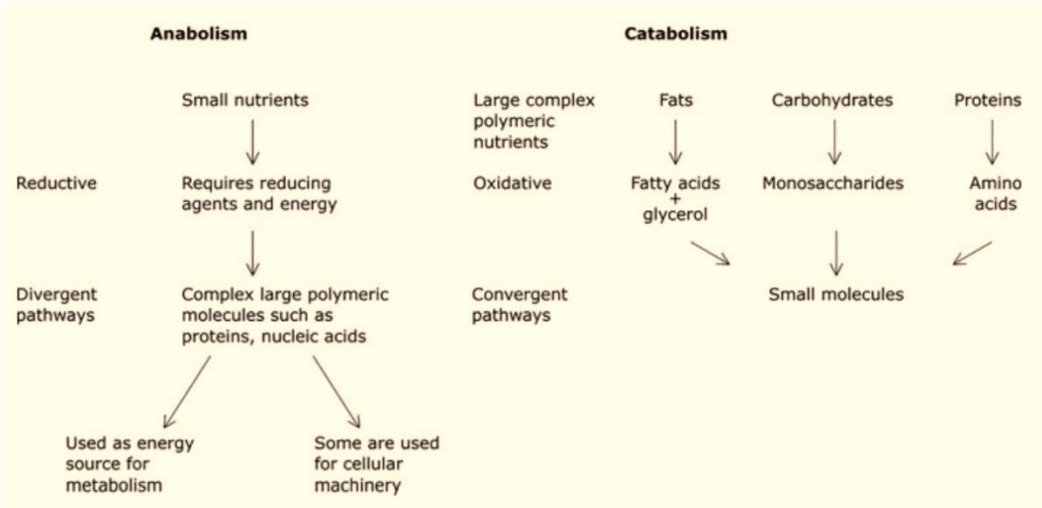
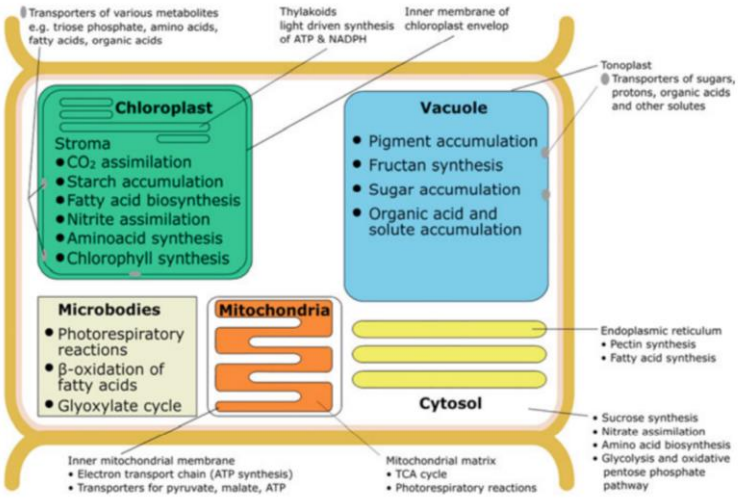
Metabolism:

Sum total of all chemical reactions occurring in a living being are called as metabolism. These occur through enzyme-catalyzed reactions that constitute metabolic pathways. Metabolic pathways include precursors, which are converted to products. Various intermediates are called metabolites. Combined activity of all metabolic pathways involved in interconversion of precursors, metabolites, and products is called intermediary metabolism. Primary metabolites are the intermediates or the products of a pathway, which are used for growth, development, and reproduction of the organism. Secondary metabolites are bioactive specialized compounds produced in a metabolic pathway which are used to protect plants against herbivore and microbial pathogen infection or to attract pollinators or seed dispersal animals. Metabolism includes both anabolic and catabolic reactions. Metabolism include two following processes:

1. **Anabolism:** includes all the reactions involved in conversion of simpler molecules to complex ones. This requires input of energy.
2. **Catabolism**: involves conversion of complex substances into simpler molecules, which is coupled with release of energy.

**The energy transitions in these pathways are mediated through two high-energy molecules which are reduced form of nicotinamide dinucleotide (NADH), and adenosine triphosphate (ATP). ATP is a high-energy phosphate compound, which mediates energy transfer, while NADH is the donor for high-energy electron transfer.





Compartmentalization of metabolic pathways in a plant cell

Photosynthesis:

The term photosynthesis describes the process by which green plants synthesize organic compounds from inorganic raw materials using light. Photosynthesis is the source of all biological energy, Whatever free oxygen is there in the atmosphere is the result of photosynthesis. Since heterotrophic organisms including animals cannot use sunlight as direct source of energy, they consume plants as the source of energy. Photosynthesis is the means for solar energy to enter into the global ecosystem, and it alone is the essential biological process by which solar energy is transformed into metabolic form of energy for all forms of life on earth. So it is:

- **Process in which light energy is used to reduce CO_2 to organic compounds; occurs in chloroplasts in higher plants and algae.**
- **The conversion of light energy to chemical energy by photosynthetic pigments using water and CO_2 and producing carbohydrates.**
- **Process by which green plants manufacture complex carbonaceous substances from CO_2 and water in presence of solar energy and chlorophyll. O_2 being the end product.**

$$6\,CO_2 + 12\,H_2O \xrightarrow[\text{Chlorophyll}]{\text{Light}} C_6H_{12}O_6 + 6H_2O + 6O_2$$

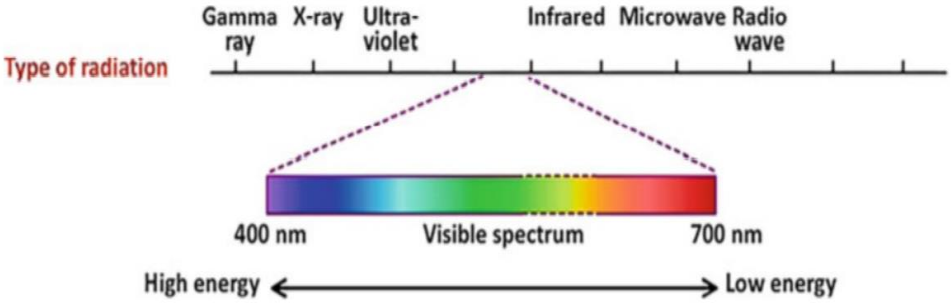
The site of photosynthesis in eukaryotes (algae and higher plants) are the cells that contain few to numerous (about 1–1000) chloroplasts which vary in size and shape. Chloroplasts are unique double-membrane-bound organelles Outer chloroplast membrane is relatively freely permeable, while the inner membrane exhibits more selective permeability. The sites of light reactions in the chloroplast are the saclike structures, known as chloroplast lamellae or thylakoids. The space within the chloroplasts is divided into two compartments, one enclosed within the thylakoids called lumen and the other outside the thylakoids, which is called stroma. Stroma, the matrix around the thylakoid, is the site where CO_2 is assimilated, leading to the synthesis of sugars. Thylakoids exist either as stacks called grana or are unstacked and are interconnected to form stroma lamellae. Each chloroplast contains 10–100 grana.

Light is captured by various pigments which includes chlorophyll molecules as the photoreceptors for photosynthesis. These exist as the chlorophyll-protein complexes which are involved in harvesting light energy and transporting electrons, resulting in generation of reductant and synthesis of ATP.

Photosynthesis is an oxidation-reduction process in which oxidation of water (electrons being removed from water) is coupled with the release of oxygen and reduction of carbon dioxide leads to synthesis of carbohydrates.

Properties of Light:

Human eye is sensitive to a narrow range of light spectrum from 400 to 700 nm, which is called as visible light. The wavelengths shorter than 400 nm (UV light) have very high energy, and they are hazardous for biomolecules, while wavelengths longer than 700 nm (infrared) have much less energy. It is the light with wavelengths ranging from 400 to 700 nm that is significant for most of the photobiological processes.



The solar energy, which is radiating toward earth, out of this 30% is reflected back straight away into outer space, 20% is absorbed by the atmosphere, and the remaining almost 50% is absorbed by earth which is converted to heat. Plants convert, utilize, and store less than 1% of the solar energy which is responsible for all chemical, mechanical, and electrical energy driving all organisms on earth. Oxygenic photosynthetic organisms use visible light with wavelength of 400–700 nm.

Photosynthetic Pigments:

In order for light to be absorbed, plants must possess light-absorbing molecules, which occur as complexes bound with proteins. These complexes are called pigments. The pigments consist of chromophores (Greek, carrier of color), the light-absorbing component, and the associated proteins. Absorption of light by the chromophore-protein complex differs from that of free chromophores. On the basis of structure of the chromophore, photosynthetic pigments are classified as follows:

- **Chlorophylls:** The principal photoreceptor in photosynthesis is chlorophyll which has cyclic tetrapyrrole ring structure termed as porphyrins or chlorin. Chlorophyll molecules have Mg^{+2} which occupies the central position. Chlorophyll molecule consists of a head and tail resembling a tennis racquet. The head is a porphyrin structure made up of four pyrrole rings attached to each other at the centre by an isocyclic ring containing Mg atom at the center. Extending from one of the pyrrole rings is the tail – the alcoholic chain (Phytol). They have different absorption spectra.

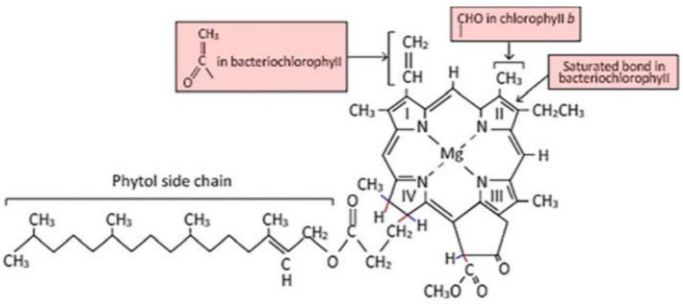
Empirical formula:

Chlo. a: $C_{55} H_{72} O_5 N_4 Mg$

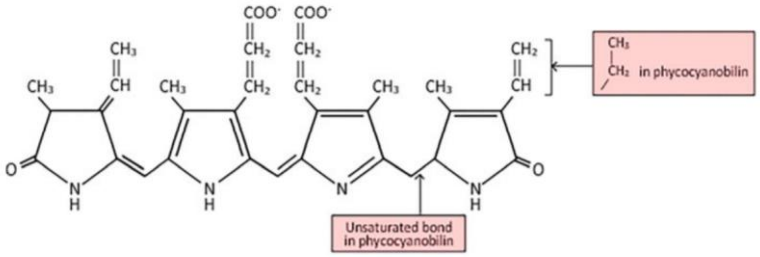
Chlo. b: $C_{55} H_{70} O_6 N_4 Mg$

The phytol chain is estrified on the C atom of one of the pyrrole rings has only one duoble bond . In chlorophyll a C3 atom has a methyl group , while chlorophyll b has an aldehyde group.

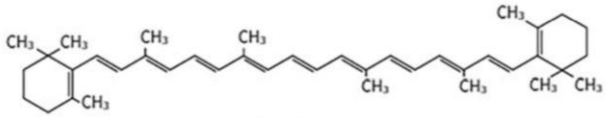
The hydrophobic alcohol, phytol. The presence of phytol tail facilitates its location along with membrane proteins in thylakoids due to hydrophobic interactions, and it makes the chlorophyll molecules soluble in organic solvents. The five-ring heterocyclic structure surrounding Mg^{+2} is responsible for absorption in the visible region of light spectrum. The major forms of chlorophylls in higher plants and green algae are chlorophyll a (Chl a) and chlorophyll b (Chl b) which generally are present in a ratio of 3:1. Chl a is universally present in all organisms which carry out oxygenic photosynthesis.



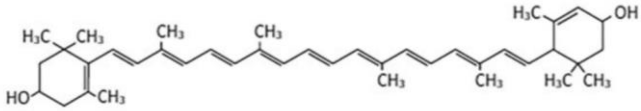
(a) Chlorophyll *a*



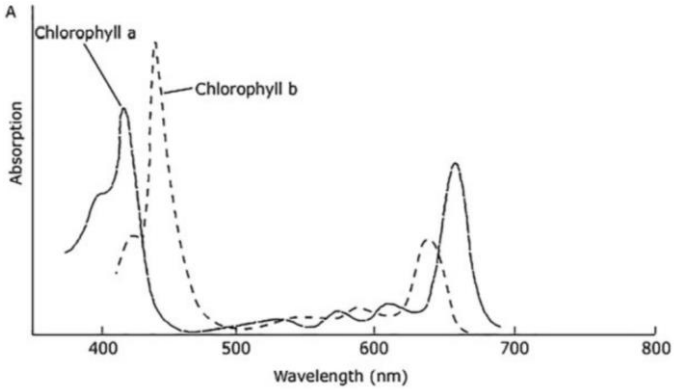
(b) Phycoerythrobilin



(c) β-Carotene



(d) Lutein (xanthophyll)



- **Carotenoids:** These are lipid compounds ranging in colour from yellow to purple, found in animals and plants both. These are also present in microorganisms including red algae, cyanobacteria, photosynthetic bacteria, fungi etc. Main carotenoid is Beta carotene found in plants possess orange yellow colour. Carotenoids and

chlorophylls may be combined with same protein to form a complex known as photosynthein. Carotenoids are associated with transfer of light energy to chlo.a and protection of chlorophyll against photooxiation by forming epoxy ring.

- **Phycobilins:** They are of two types Phycoerythrin (red) and Phycocyanin (blue) found only in algae. They are also involved in transfer of energy to chlorophyll. Phycoerythrin has peaks at 495, 540 and 545 nm and Phycocyanin has peaks at 550 and 615 nm.

Mechanism of photosynthesis:

It is an oxidation and reduction process in which water is oxidized to H^+ and OH^- and CO_2 is reduced to carbohydrate with water and O_2 being by products. During light reaction the energy necessary for reduction of CO_2 is produced, while in dark CO_2 is reduced to carbohydrates utilizing the energy produced in light reaction. Light reaction is also called photochemical decomposition of water and dark reaction is called thermochemical reduction of CO_2.

Phases of Photosynthesis:

In 1905, F.F. Blackman, a British plant physiologist, interpreted the light curve of photosynthesis as an evidence of it being a two-step process. According to Blackman, initial part of the light curve, which shows increase in photosynthesis with increasing light intensity, corresponds to light-limited phase of photosynthesis.

Robert Hill observed that a variety of compounds can act as electron acceptors. This reduction of artificial electron acceptors and release of oxygen by isolated chloroplasts in presence of light and absence of CO2 is called Hill's reaction.

1. Light Reactions in Photosynthesis:

Light reaction takes place in grana within a short period of time there will be synthesis of molecules of ATP and NADPH which are utilized for dark fixation of CO_2. The following steps are covered in light reaction:

Photolysis of water or hill reaction Splitting of water in presence of light to produce H^+ and OH^- ions is called photolysis of water. H^+ ions are used

to reduce CO_2 and OH^- ions recombine to form water along with release O_2 and e- .

$4H_2O = 4\ H^+ + 4\ OH^-$

$4\ OH^- = 2\ H_2O + 4\ e- + O_2$

2NADP + 4H+ = 2NADPH + 2H+

These $4H^+$ are used to reduce CO_2.

$CO_2 + 4H+ = CH_2O + H_2$

Source of O_2

The work of Ruben, Kemen and Randall (1941) using isotope of O_2 (O^{18}) clearly showed that O_2 comes from water not from CO_2. When experimental material was supplied with labelled water (H_2O^{18}), the released O_2 was of O^{18} type and when plant was supplied with labelled CO_2^{18}, the O_2 released was of normal type. Bacteria use H_2S as hydrogen donor in place of water.

$CO_2 + 2H_2S = CH_2O + H_2O + 2S$

Existence of two pigment systems I and II was held responsible for catalyzing two light reactions. Light reaction I refers to reduction of $NADP^+$, while light reaction II refers to photolysis of water. Pigment system I was found to be responsible for light reaction I and pigment system II was for light reaction II. These were later on called as photosystem I and II (PSI and PSII), respectively. Photosystem I and Photosystem II were so called according to the order of their discovery. Photosystem I is rich in chlorophyll a and contains carotenoids and less chlorophyll b then does photosystem II. In both the photosystems most of the pigments operate to harvest light energy and transfer it, possibly by resonance, to chlorophyll a molecules located at photochemically active reactive center termed traps. The active center pigment for photosystem I consists of chlorophyll a, which absorbs at 703 nm and is called P700.

The chlorophyll a collecting pigment at the reactive center of photosystem II to exhibits an absorption peak at 682 nm and is termed P680. The chlorophyll a molecules (donor molecules) reduces specific electron acceptors (A) and become oxidized themselves. The electron carriers that are thus reduced initiate electron flow and the conversion of light energy to chemical energy (transduction).

Light harvesting complexes:

Besides PS I and PS II two other green bands are also present. Each band contains chlo.a + chlo.b + little amount of β carotene. All these pigments are protein bound. One band functions with PS I and another with PS II. Function of these bands is to absorb light energy and transfer it to the appropriate pigment system.

Photophosphorylation:

The addition of phosphate group to ADP under influence of light energy to form ATP.

• The formation of ATP from ADP and inorganic phosphate (Pi) using light energy stored in the proton gradient across the thylakoid membrane. Arnon and others (1954) demonstrated that isolated chloroplasts produce ATP in the presence of light. It was termed as photosynthetic phosphorylation or photophosphorylation. It was shown that the mitochondria are not the alone cytoplasmic organelles involved in the ATP formation. The formation of most ATP in mitochondria takes place by means of process known as oxidative phosphorylation. Also, ATP formation in chloroplasts differs from that it is independent of respiratory oxidants.. ATP is one of the only requirements for carbohydrate production. A reductant must be formed in photosynthesis that will provide the hydrogens or electrons. In the presence of H_2O, ADP and orthophosphate (Pi) substrate amounts of NADP on the side of the thylakoid membrane facing the stroma were reduced accompanied by the evolution of oxygen as follows:

2ADP+ 2Pi + 2NADP + 4 H_2O

light energy chloroplasts

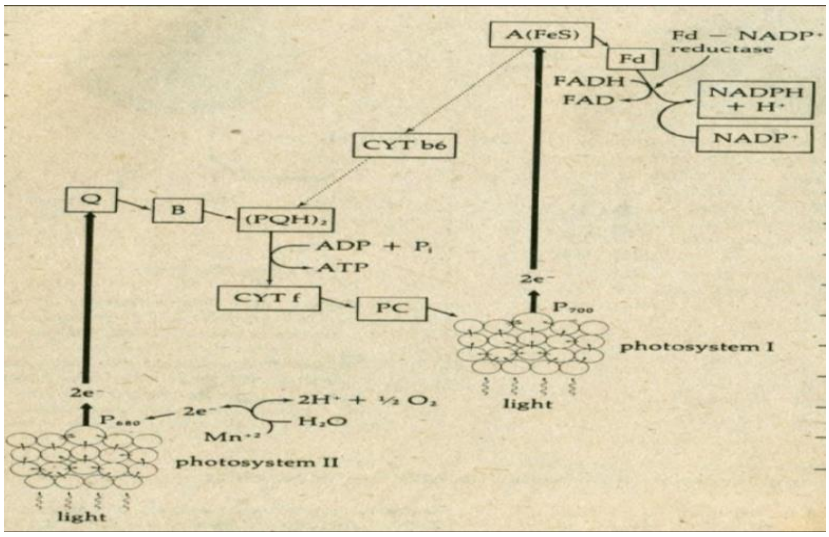
$2ATP + O_2 + 2NADPH + 2H_2O$

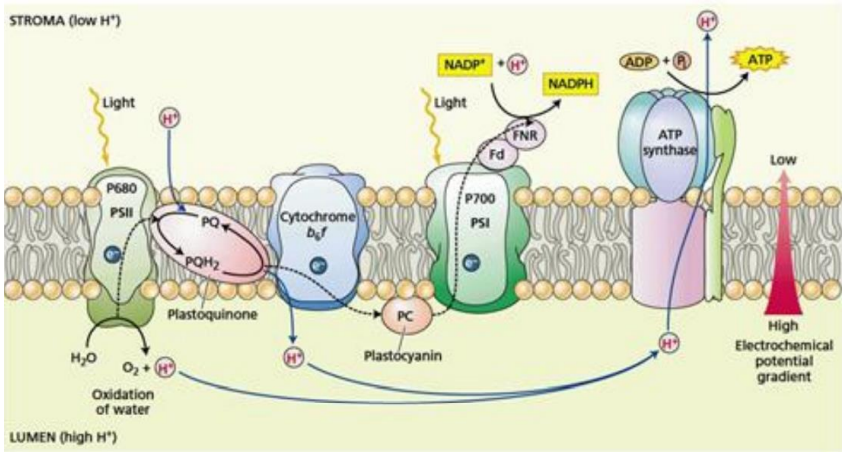
It shows that evolution of one mole of O_2 is accompanied by the reduction of the 2 moles of orthophosphate. Together ATP and NADPH provide the energy and reducing power for CO_2 fixation and reduction. In bacterial photosynthesis NADP is utilized instead of NADPH

Z–Scheme: Electron Transport and Photophosphorylation (Noncyclic Photophosphorylation)

The Z– scheme illustrates electron transport and the production of NADPH and ATP in chloroplasts. It is called Z scheme due to zig zag pattern of electron flow. The primary flow of electrons within a given granum thylakoid may be initiated almost simultaneously for each photosystem through integrated (coupled) reactions and photolysis of water, which provides the necessary electron flow to produce ATP and NADPH. This integration of two photosystems is most commonly referred to as noncyclic photophosphorylation to describe one means of ATP production in chloroplasts. It is also termed noncyclic electron transport to refer to the manner of electron flow during the process. In the process after excitation of P 700 the trap chlorophyll of photosystem I, the electrons are passed on to an unknown primary electron acceptor, believed to be an iron-sulphur protein and designated A (FeS). The electrons are then passed to ferredoxin and ultimately to NADP+ , with the formation of NADPH+ . Normally the reduced form of NADP is written as NADPH. In fact it should be written like NADPH+ H+ . The transfer of electrons to NADP+ creates an electron debit referred to as a hole in photosystem I. However, this deficit is made up by the excitation of P680 of photosystem II, subsequently photo ejection of electrons and their transport through a system of carriers QB, plastoquinone (PQ), cytochrome f (CYT f), and plastocyani (PC). At this point Q and B are unidentified compounds. Figure illustrates that plastoquinone shuttles protons and passes electrons to cytochrome f. At this point ATP is produced. The hole created in photosystem II is filled by electrons that are derived from the splitting (photolysis) of water .Thus the passage of electrons is not in a cyclic manner.

Water is oxidized to oxygen by photosystem II. Four electrons are removed from two water molecules, generating an oxygen molecule and four hydrogen ions. The protons are released into the lumen of the thylakoid. These protons are eventually transferred from the lumen to the stroma by translocation through ATP synthase. In this way, the protons released during water oxidation contribute to the electrochemical potential driving ATP formation. Manganese (Mn^{+2}) is an essential cofactor in the water-oxidizing process.





Electron transport chain

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