M.Sc Semester-III, Paper: CC-12, Unit-1 Environmental Chemistry (Contd-2)

⟹ Oxygen Cycle:

Oxygen is the most abundant element of earth, constituting some 47% by weight of all elements. It occurs in the gaseous form in the atmosphere to the extent of 20-21%. water possesses 0·5-0·7% of O_2 dissolved in it. Oxygen also occurs as CO_2, H_2O (water) and a number of salts/minerals. Lithosphere has the maximum oxygen content (89·9%), hydrosphere (10%) and atmosphere only 0·1%.

Oxygen is the major component of all living organism. Its adequate supply is vital for substance or life in the biosphere. It is needed by most plants and animals, and all human beings aerobic respiration. It is absorbed from environment during aerobic respiration but released by plants during photosynthesis here by setting up the oxygen cycle.

Oxygen enters the organic world as CO_2 during photosynthesis. Consequently, most of the organic substances contain oxygen. These substances are passed into consumers through food chains. They are ultimately broken down by decomposers. O_2 is partly released. Atmospheric O_2 seems to be developed originally through Oxygenic photosynthesis, outgassing from interior of earth and photodissociation of water vapours at higher altitudes. Oxygen cycle involves main two processes:

(1) Consumption of Oxygen: (i) Respiration: O_2 is required by living beings (mons animals) for their respiration. The land organisms take it from the atmosphere while the aquatic forms obtain the same from their habitat where atmospheric oxygen enters by diffusion. In respiration, the O_2 combines with hydrogen of the respiratory substrate to produce water $C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O + 680\,kcal$.

(ii) Combustion: Oxygen contributes largely to the processes on the earth's surface. It participates in combustion reactions, e.g. $C + O_2 \longrightarrow CO_2$; $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O + 6$ (Natural gas)

Burning of fuels uses O_2, producing CO_2, H_2O & heat energy. The same is employed in cooling, power generation, running machines & heating.

(iii) Oxidation: Oxygen is consumed by some chemical oxidations, weathering processes of minerals. e.g., $4FeO + O_2 \longrightarrow 2Fe_2O_3$; $2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$.

$S + O_2 \longrightarrow SO_2$, $FeS_2 + 3O_2 \longrightarrow FeSO_4 + SO_2$, $2H_2S + O_2 \longrightarrow H_2O + 2S$

(2) Liberation of Oxygen: (i) Photosynthesis: Green plants return O_2 to atmosphere by photosynthesis.

$6CO_2 + 12H_2O \xrightarrow[\text{Chlorophyll}]{h\nu} C_6H_{12}O_6 + 6O_2\uparrow + 6H_2O$ (Glucose)

This is called photolysis of water since O_2 evolved by splitting of water.

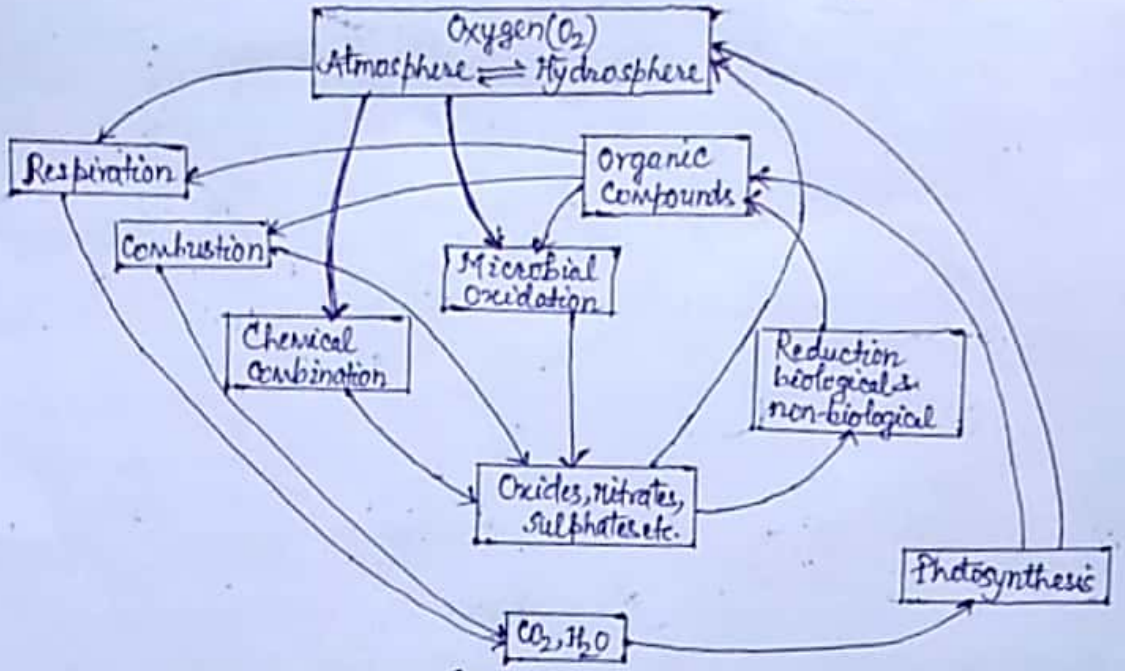
This process is responsible for building and maintaining O_2 stock balance in atmosphere.

(ii) Photodissociation: At higher altitudes water molecules dissociate to form H_2 & O_2.

(iii) Chemical reduction: Chemical reductions occur both biologically and non-biologically to release oxygen (O_2). e.g., $2H_2O + 2F_2 \longrightarrow 4HF + O_2\uparrow$, $2CO_2 \longrightarrow 2CO + O_2\uparrow$

There is also continuous exchange of O_2 between the atmosphere and all water surfaces on the earth. Combustion of fuels and reducing gases (CO) from volcanoes consume large amount

of O_2 still it has little impact on the total O_2 stock in atmosphere due to operation of O_2 cycle. Total amount of O_2 in biosphere is relatively constant so that O_2 cycle is stable.



[Oxygen-cycle]

⟹ Nitrogen Cycle: Nitrogen is a vital element. 78% of atmosphere is gaseous N_2 (3.86×10^{15} tons). It is inert and found in bound state in the rock but only a very small amount of it is useful. Useful nitrogen is nitrate and NH_3. N_2 & its compounds are essential for the maintanance of life process in the biosphere. There is continuous exchange of nitrogen within ecosystem, operating N-cycle. Plants and animals continuously produce proteins, which are organic compounds containing nitrogen. Plants absorb nitrates from the soil. The death and decay of plants and animals as well as excrete of animals comprise the major load of organic residues containing proteins to the soil.

Green plants combine with nitrogen and carbohydrates to make proteins and nucleic acids. Nitrogen is thus, a constituent of various organic compounds which are formed in plants such as proteins nucleic acids, vitamins, enzymes, amino acids, alkaloids etc. It is main constituent of atmosphere but neither animals nor plants are capable of absorbing it directly from the atmosphere.

Due to nitrogen cycle take place in the atmosphere, nitrogen assimilated to the plants and animals is converted into useful products, e.g. NH_3, HNO_3 etc. Nitrogen cycle is a cycle in which atmospheric nitrogen is converted into its compounds, such as nitrates and the combined nitrogen is again constantly passing back to the atmosphere.

Nitrogen in the soil is present in the form of organic nitrogenous substances (due to dead plants and animals) and inorganic nitrogenous substances (NH_3, N_2, NO_3 etc.

Proteins synthesised by green plants are taken by animals/man. It is hydrolysed to simpler organic compounds (amino acids). It is converted to ammonium compounds, such as NH_3 (ammonia), Urea (NH_2CONH_2) & uric acids by certain micro-organism present in the soil by ammonification. The ammonium compounds are excreted

in the urine by animals. It gets decomposed by bacteria and fungi. Some ammonia is also liberated in the atmosphere by volcanic eruptions.

$$\text{Proteins} \xrightarrow{+H_2O} R\text{-}NH_2 \xrightarrow{+H_2O} R\text{-}OH + NH_3\uparrow$$

Ammonia and its salts present in the soil are oxidised to nitrates by nitrosifying bacteria present in the soil. It is further oxidised to nitrates by other kind of bacteria. Thus, the nitrogen assimilated by the plants from the soil is returned back to the soil again through ammonification and nitrification.

$$2NH_3 + 3O_2 \xrightarrow[\text{bacteria}]{\text{Nitrosifying}} 2HNO_2 + 2H_2O \quad (\text{Nitrous acid})$$

$$2HNO_2 + O_2 \xrightarrow[\text{bacteria}]{\text{Nitrosifying}} 2HNO_3 \quad (\text{Nitric acid})$$

Nitrogen which is 78% present in the atmosphere is not useful for most of the plants. Only some plants can absorb nitrogen from atmosphere. This process is called 'Nitrogen fixation'. It is of two types:

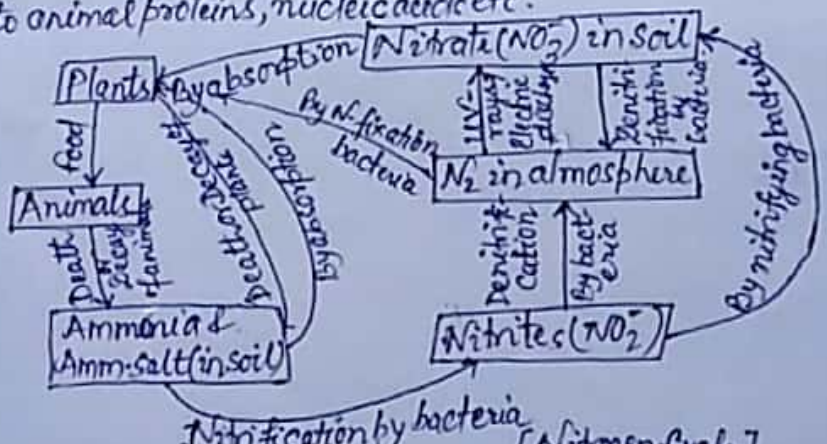
(i) Non-biological nitrogen fixation: Due to thunder in rainy season, nitrogen (N_2) and oxygen (O_2) gases of the atmosphere combine to form nitric oxide (NO), which is finally oxidised to NO_2 (nitrogen dioxide). It combines with rain water to form HNO_3 (Acid rain). It comes to the earth and combine with basic substances present in soil to form nitrates, which are foods for plants.

$$N_2 + O_2 \xrightarrow[\text{Electric storm}]{\text{UV-light}} 2NO \;;\; 2NO + O_2 \longrightarrow 2NO_2 \;,\; 2NO_2 + O \longrightarrow N_2O_5$$

$$N_2O_5 + H_2O \longrightarrow \underset{(\text{Nitric acid})}{2HNO_3}$$

$$2HNO_3 + CaCO_3 \longrightarrow \underset{(\text{Calcium nitrate})}{Ca(NO_3)_2} + CO_2 + H_2O.$$

(ii) Biological nitrogen fixation: It is the major source of N-fixation, brought by prokaryotes, bacteria and cyanobacteria (blue-green algae). They include both free living and symbiotic forms. Nitrogen fixation by cyanobacteria (e.g. Anabaena, Nostoc, Aulosira) is important to water logged soils where denitrifying bacteria are active. N-fixing organisms pick up the N_2 gas from respiratory pathway to form NH_3. NH_3 reacts with organic acids to form amino acids during digestion. Amino acids are then absorbed and converted to animal proteins, nucleic acids etc.



[Nitrogen-Cycle]

In the total cycle, about 4-7 tonnes of N_2 per hectare is added to the soil every year. There is some loss from the soil through the leaching of nitrates into freshwaters. However, by all these processes the N-cycle is balanced and thus the N-conc^n in the atmosphere remains constant.

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