

## MODULE 1.2

# Environmental Chemistry Of Water

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## MODULE 1.2

### Environmental Chemistry Of Water

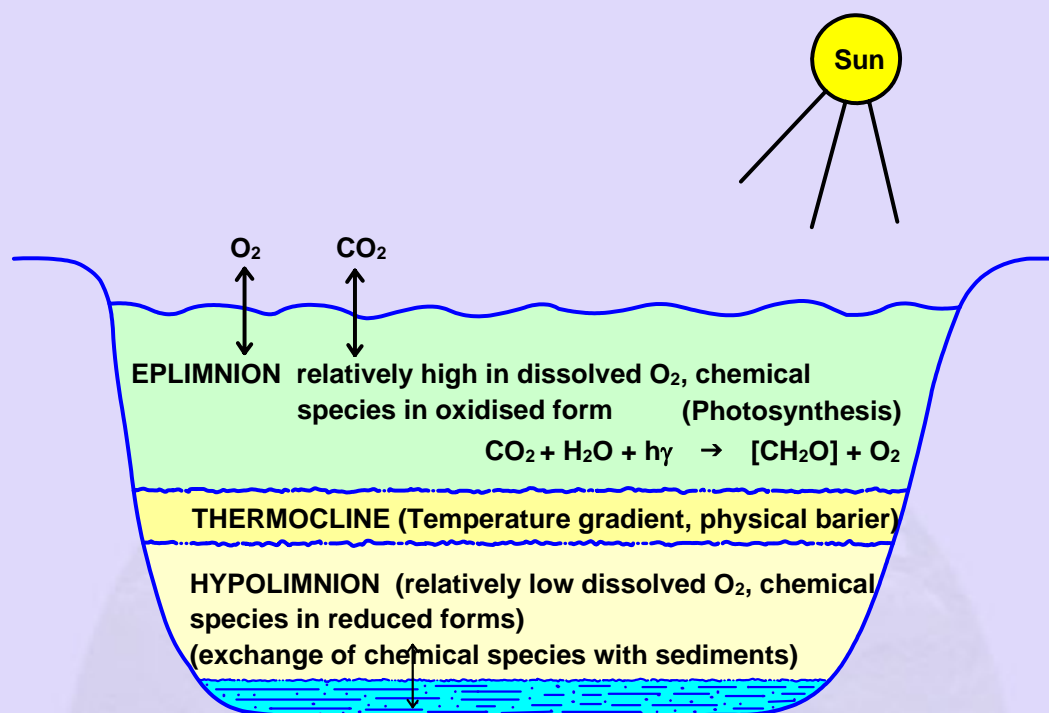
#### Properties Of Water:

Water has a number of unique properties that are essential to life which determine its environmental chemical behaviour. The important properties of water are as follows;

- *It is an excellent solvent which assists in transportation of nutrients and waste products, making biological processes possible in an aqueous medium.*
- *It has the highest dielectric constant among the common liquids, which causes the high solubility of ionic substances and their ionisation in solution.*
- *It is transparent to visible and longer-wavelength fraction of UV light, allowing light required for photosynthesis to reach considerable depths in bodies of water.*
- *It has a maximum density as a liquid at 4°C which restricts vertical circulation in stratified bodies of water.*
- *It has higher heat of evaporation than any other material which determines transfer of heat and water molecules between the atmosphere and bodies of water.*
- *It has higher heat capacity than any other liquid except ammonia which helps in stabilisation of temperature of organism and geographical region.*

## The Characteristics Of Bodies Of Water:

The chemical and biological processes that occur in water are strongly influenced by the physical condition of the body of water. Water's unique temperature-density relationship results in the formation of distinct layers within non flowing bodies of water as shown in fig.1 such as stagnant water in a deep lake. During summer, the surface layer (**epilimnion**) of deep lakes and marine environments is heated by solar radiation. It floats owing to its lower density upon the bottom layer (**hypolimnion**). This phenomenon is called thermal stratification. When a significant temperature difference exists between the two layers, they do not mix, but behave independently and have very different chemical and biological properties. The shear-plane or layer between epilimnion and hypolimnion is called thermocline. The epilimnion which is exposed to light may have a heavy growth of algae. Because the epilimnion is exposed to atmosphere and contains a heavy growth of algae photosynthetic activity in this layer is high. Hence this layer contains higher levels of dissolved oxygen and it contains predominantly oxidised species. On the other hand in hypolimnion, the consumption of  $O_2$  by bio degradable organic material may cause the water to become anaerobic. As a result, chemical species in a relatively reduced form tend to predominate in the hypolimnion. These sequences of events are shown in fig.1.

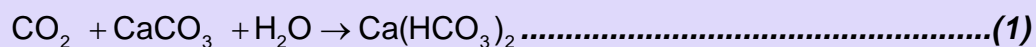


**Fig.1 Stratification of a lake**

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## Alkalinity of water:

The alkalinity of water is a measure of its capacity to neutralise acids. The alkalinity of natural waters is due primarily to the salts of weak acids, although weak or strong bases may contribute. Bicarbonates represent the major form of alkalinity, since they are formed in considerable amounts from the action of carbon dioxide upon basic minerals in the soil as shown in the following equation.



The bicarbonates along with carbonates and hydroxides which are responsible for the alkalinity of water can be explained by the following equations



other contributors to the alkalinity of water in minor amounts are salts of weak acids, such as borates, silicates and phosphates:

A few organic acids that are quite resistant to biological oxidation - for example humic acid-form salts that add to the alkalinity of natural waters. In polluted or anaerobic waters, salts of weak acids such as acetic, propionic, and hydrosulphuric may be produced and would also contribute to alkalinity. In other cases, ammonia or hydroxides may make a contribution to the total alkalinity of water.

The alkalinity of waters is thus due principally to salts of weak acids and strong bases, and these substances act as buffers to resist a drop in pH resulting from the acid addition. Alkalinity is thus a measure of buffer capacity and in this sense is used to a great extent in waste water treatment practice.

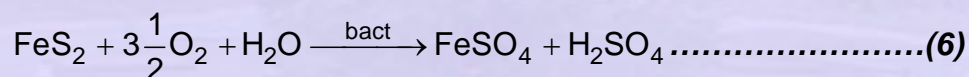
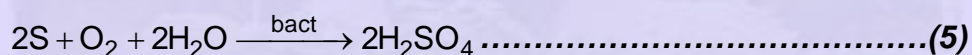
### **Source and nature of Acidity:**

Carbondioxide is a normal component of all natural waters. It may enter the surface waters by absorption from the atmosphere, but only when the partial pressure of carbondioxide in water is less than the partial pressure of the carbondioxide in the atmosphere, in accordance with Henry's law. The surface waters are constantly absorbing or giving up carbon dioxide to maintain an

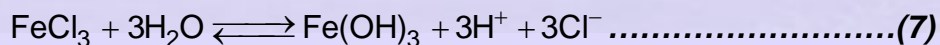
equilibrium . It is not uncommon to encounter ground waters with 30-50 mg l<sup>-1</sup> of carbondioxide. The acidity due to dissolved CO<sub>2</sub> is called CO<sub>2</sub> acidity.

Mineral acidity is present in many industrial wastes, particularly those of metallurgical industry and some production of synthetic organic materials. Certain natural waters also may contain mineral acidity. The drainage from abandoned mines will contain significant amounts of sulphuric acid or salts of sulphuric acid if sulphur, sulphides or iron pyrites are present. Conversion of these materials to sulphuric acid and sulphates is brought about by sulphur-oxidising bacteria under aerobic conditions.

The acidic character of some hydrated metal ion may contribute to acidity as shown by the following example:



Salts of heavy metals, particularly those of trivalent metal ions such as Fe<sup>3+</sup> and Al<sup>3+</sup> hydrolyse in water to release mineral acidity.



Their presence is indicated by the formation of a precipitate as the pH of solutions containing them is increased during neutralisation.

The total acidity in water sample is determined by titration with base to the phenolphthalein end point (pH8.2). The free mineral acidity is determined by

titration with base with methyl orange end point (pH 4.3). The difference between the two gives  $\text{CO}_2$  acidity.

Acid waters are of concern because of their corrosive characteristics and the expense involved in removing or controlling the corrosion-producing substances. The corrosive factor in most cases is  $\text{CO}_2$ , but in many industrial wastes it is mineral acidity.  $\text{CO}_2$  must be reconed with in water softening problems where the lime or lime-soda ash method is employed.

Where the biological processes of treatment are used, the pH must be ordinarily maintained within the range of 6 to 9.5. This criterion often requires adjustment of pH to favourable levels, and calculation of the amount of chemicals needed is based upon acidity values in most cases.

### **Cause and source of hardness:**

Hardness is caused by divalent metallic cations. The principle hardness causing cations are calcium, magnesium, strontium, ferrous ion and manganous ions. Rain water as it falls upon the earth is incapable of dissolving the tremendous amounts of solids found in many natural waters. The ability to dissolve is gained in the soil where  $\text{CO}_2$  is released by bacterial action. The soil water becomes highly charged with  $\text{CO}_2$  which of course, exists in equilibrium with carbonic acid. Under low pH conditions that develop, basic materials particularly limestone formations are dissolved. Since limestone formations are not pure carbonates but includes impurities such as sulphates, chlorides and silicates, these materials become exposed to the solvent action of the water as the carbonates are dissolved, and they pass into solution too.

In general, hard waters originate in areas where the top soil is thick and limestone formations are present. Softwaters originate in areas where the top soil is thin and limestone formations are sparse and absent.

Hard water is as satisfactory for human consumption as softwaters. Because of their adverse action with soap, however, their use for cleansing purposes is quite unsatisfactory, unless soap costs are discarded.

### Methods for the determination of hardness:

Hardness is normally expressed in terms of  $\text{CaCO}_3$ . Many methods of determination have been proposed over the course of the years. The most widely used method is by using EDTA as titrant. The titration is done by adding a small amount of buffer (pH 10) followed by the addition of Eriochrome black T as indicator. Although the EDTA method is subjected to certain interferences, most of them can be overcome by proper modification.

### Types of hardness:

Hardness are classified into temporary hardness and permanent hardness. Temporary hardness (carbonate hardness) is due to the dissolved salts of bicarbonates of calcium and magnesium and can be removed by boiling.



Permanent hardness (non carbonate hardness) mainly is due to the dissolved salts of chlorides and sulphates of calcium and magnesium .

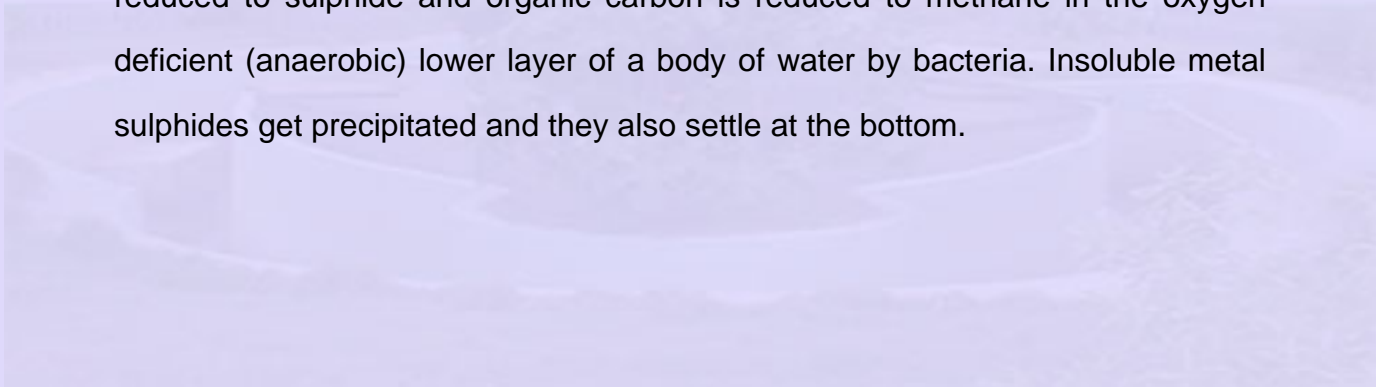
Hardness of water is an important consideration in determining the suitability of water for domestic and industrial uses. The relative amounts of calcium and magnesium hardness and of carbonate and noncarbonate hardness

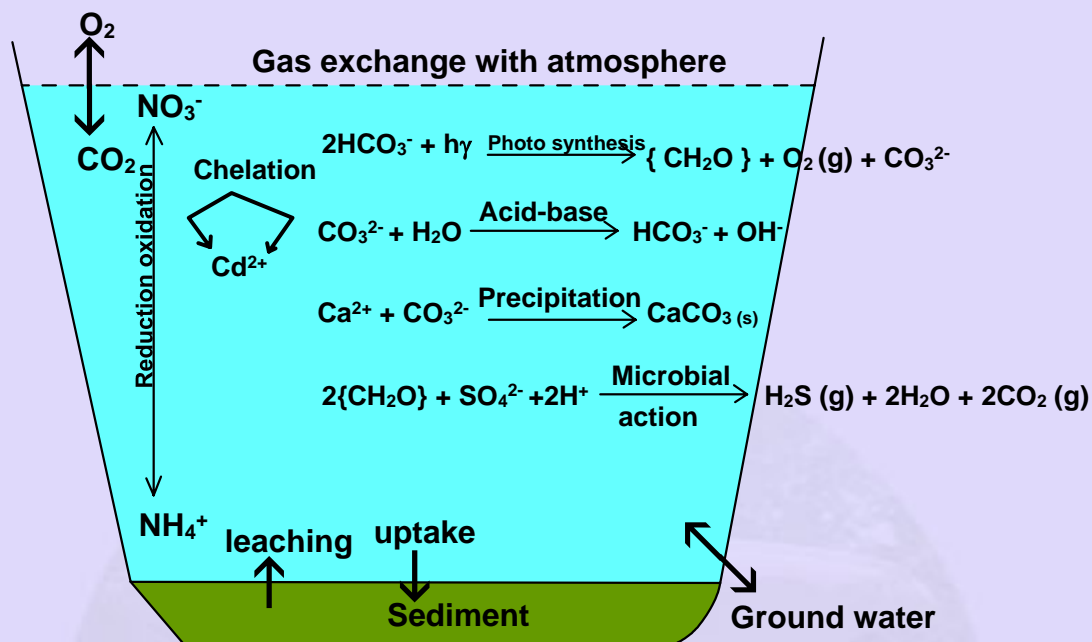


present in water are factors in determining the most economical type of softening process to use, and become important considerations in design. Determination of hardness serve as a basis for routine control of softening process.

### Major aquatic chemical processes:

Water is a medium for many chemical reactions. Algae and bacteria influence many aquatic chemical processes as shown in (fig2). The inorganic carbon from  $\text{HCO}_3^-$  ion is fixed in the form of biomass (represented as  $\text{CH}_2\text{O}$ ) during algae photosynthesis. During this process it also produces carbonate ion  $\text{CO}_3^{2-}$  which hydrolyses to produce  $\text{OH}^-$  ion and raise the pH or it reacts with  $\text{Ca}^{2+}$  ion to precipitate solid  $\text{CaCO}_3$  which settles at the bottom. Many oxidation-reduction reactions that occur in water are catalysed by bacteria. For example, inorganic nitrogen is converted largely to ammonium ion  $\text{NH}_4^+$ , sulphate is reduced to sulphide and organic carbon is reduced to methane in the oxygen deficient (anaerobic) lower layer of a body of water by bacteria. Insoluble metal sulphides get precipitated and they also settle at the bottom.





**Fig. 2 major aquatic chemical processes**

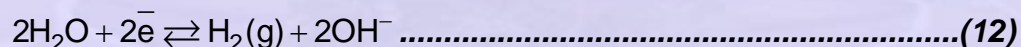
*(Redrawn by permission of Lewis Publishers, Chelsea, Michigan 48118, USA from Fundamentals of Environmental Chemistry, S.E.Manahan, p.378,1993)*

Fungi and bacteria on land convert the dead biomass into inorganic material and degradation resistant organic species like fulvic acids. Some of these products enter the water bodies.

However near the surface of water bodies where  $\text{O}_2$  is available, bacteria convert inorganic nitrogen to nitrate ion  $\text{NO}_3^-$ . Water bodies will be containing naturally occurring complexing agents such as fulvic acids or pollutants such as nitrilo triacetic acid. These will bind some metal ions in water. On the surface of the water bodies gases will be exchanged with atmosphere and there will also be exchange of solutes between water and sediments at the bottom.

## Oxidation – reduction reactions in water:

Many reactions of interest in wastewater treatment such as organic oxidation and methane fermentation, nitrification, and denitrification, are of this type and are mediated by bacteria. Oxidation-reduction reactions are important in the solubilisation and precipitation of iron and manganese. Oxidants such as chlorine and ozone are added to water and waste water to bring about desired inorganic and organic transformations as well to disinfect. As with acid-base, solubility or complex formation, oxidation-reduction reactions tend towards a state of equilibrium. An understanding of oxidation-reduction equilibria can help to indicate whether a particular reaction is possible under given experimental conditions. Bacteria carry out most significant oxidation-reduction reactions in natural water, waste water and soil.. The relative oxidation-reduction tendencies of the system depend upon the activity of the  $\bar{e}$ . When the  $\bar{e}$  activity is relatively high, chemical species tend to accept  $\bar{e}$  s,



and are said to be reduced. When the  $\bar{e}$  density is relatively low, the medium is **oxidising** and the chemical species such as  $\text{H}_2\text{O}$  may be **oxidised** by the loss of  $\bar{e}$  s:



The relative tendency towards oxidation or reduction is based upon the electrode potential, E which is relatively more +ve in an oxidising medium and –ve in a reducing medium. It is defined in terms of the half-reaction



for which E is defined as exactly zero when the activity of  $\text{H}^+$  is exactly 1 (concentration 1 mole per litre) and pressure of  $\text{H}_2$  gas is exactly 1 atmosphere. Since the electron activity in water varies over many orders of magnitude, it will be convenient to discuss oxidising and reducing tendencies in terms of pE, a parameter analogous to pH is defined as negative logarithm of activity of electron in aqueous solution

$$\text{pE} = -\log a_e \text{.....(15)}$$

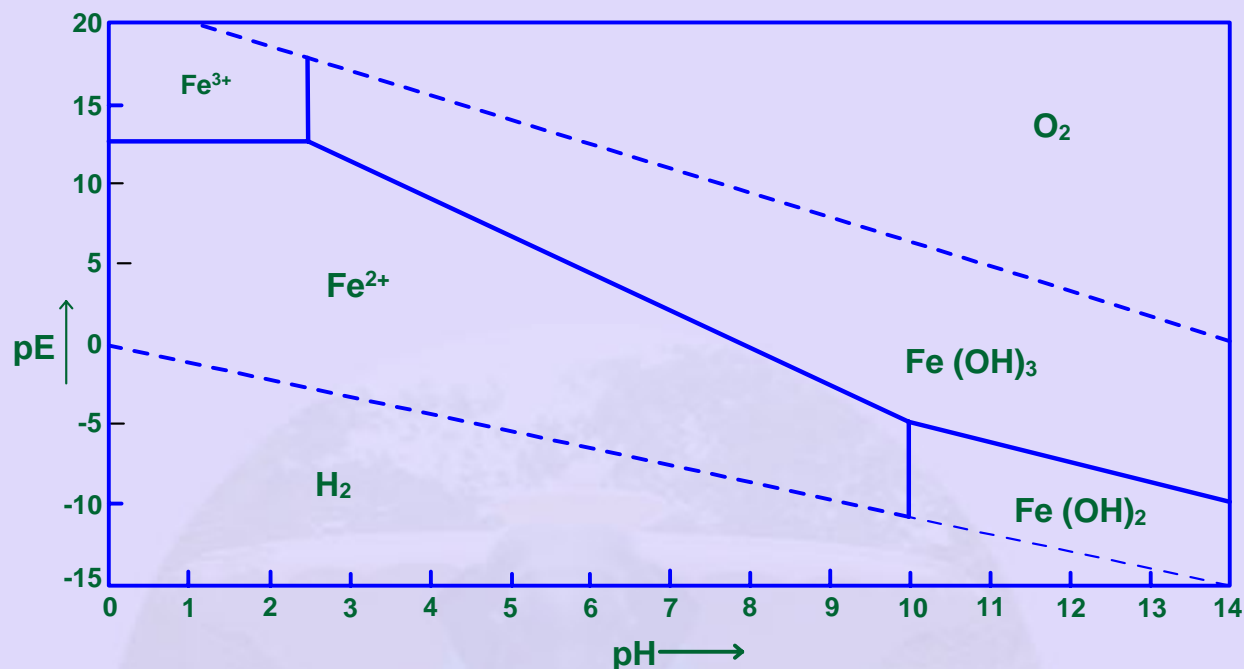
The value of pE calculated from E by the relationship,

$$\text{pE} = \frac{E}{\frac{2.303RT}{F}} \text{.....(16)}$$

At 25°C for E in volts,  $\text{pE} = \frac{E}{0.0591}$  when R is gas constant, T is the absolute temperature and F is the Faraday.

### **pE-pH diagram:**

The nature of the chemical species in water is a function of pE and pH. The oxidation-reduction reactions in aqueous systems can be quite complex. Graphical approaches are used to reduce this complexity and illustrate the significant factors involved for a particular case.



**Fig. 3 A simplified pE-pH diagram for iron in water**

*(Redrawn by permission of Lewis Publishers, Chelsea, Michigan 48118, USA from Fundamentals of Environmental Chemistry, S.E.Manahan, p.385,1993)*

A good example of this is shown by a simplified pE-pH diagram for iron in water, assuming that iron is in one of the four forms of  $\text{Fe}^{2+}$  ion,  $\text{Fe}^{3+}$  ion, solid  $\text{Fe}(\text{OH})_3$  or solid  $\text{Fe}(\text{OH})_2$  as shown in fig 3. Water in which pE is higher than that shown by upper dashed line is thermodynamically unstable towards oxidation (equation 13) and below the lower dashed line water is thermodynamically unstable towards reduction (equation 14). It is seen that  $\text{Fe}^{3+}$  ion stable only in a very oxidising, acidic medium such as that encountered in acid mine water, whereas  $\text{Fe}^{2+}$  ion is stable over a relatively large region as reflected by the common occurrence of soluble iron (II) ion in oxygen-deficient ground waters. Highly insoluble  $\text{Fe}(\text{OH})_3$  is the predominant iron species over a wide pE-pH range.

### Complexation:

Naturally occurring chelating agents like humic acid and amino acids are found in natural water and soils. The abundance of chloride in sea water gives rise to the formation of some chlorocomplexes. There are synthetic chelating agents, like sodium tripoly phosphate, sodium ethylenediamine tetra acetate (EDTA), sodium nitrilo triacetate (NTA) and sodium citrate, which are discharged in small amounts into an aquatic systems from different industrial wastes.

The ligands occurring in natural water and waste water are having a variety of organic groups which are able to coordinate to metal ions, some of which are given below:

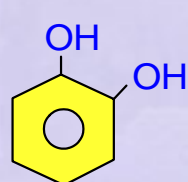


These ligands are known to form complexes with most metal ions ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Ba}^{2+}$ ) which are present in natural water and biological systems.

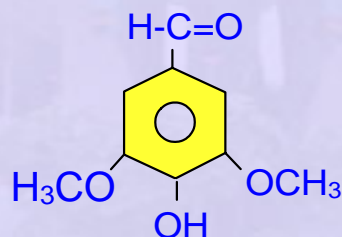
**Humic substances:** These substances are resistant to degradation and they are formed naturally during the decomposition of vegetation. They are found as deposits in soil, marsh sediments and any location where large quantities of vegetation have decayed. They are generally classified on the basis of solubility. If a humic substance could be extracted with a strong base and the resulting solution acidified, the precipitated material is called humic acid. The organic material which is left in the acidified solution is called fulvic acid. The non extractable residue is called humin.

These are complexing agents which are important and found in nature. Although their existence has been known since 1800, yet their structural and chemical properties have been still challenging to chemists. The properties of water have been mainly affected by the humic substances (both soluble and insoluble) because of their acid-base, adsorptive and complexing properties. The soluble fulvic acid is having an effect on properties of water, while the insoluble humin and humic substances are able to alter water quality by involving exchange of cations, organic materials, etc., with water.

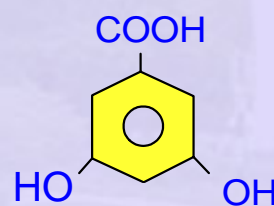
When there occurs the decomposition of humic acid, the following typical decomposition products are obtained.



Catechol

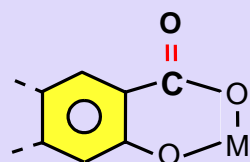


Syring aldehyde

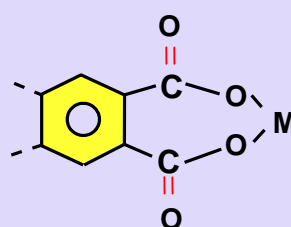


3,5, Dihydroxy benzoic acid

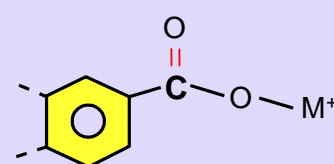
The fulvic acid is having the molecular weight of 666 and chemical formula  $C_{20}H_{15}(COOH)_{16}(OH)_5(CO)_2$ . It contains the following functional groups through which it is able to form complexes with the metal ions in solution.



with Phenolic hydroxyl group



with two carboxyl groups



with a carboxyl group

The fulvic acid is having a carbon skeleton with a high degree of aromatic character and large percentage of functional groups having oxygen. They may also be having protein-like materials and a carbohydrate fraction. These fractions can readily get hydrolysed from aromatic nucleus which is able to withstand chemical and biochemical attack.

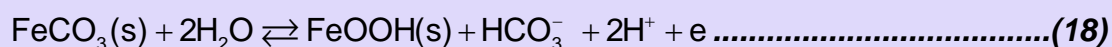
Humin, humic acid and fulvic acid are not applicable to single compounds but to a wide range of compounds. In general, humic substances constitute the high molecular weight polyelectrolytic macromolecules whose molecular weight range from a few hundred (fulvic acids) to tens of thousands (humic acid and humin fractions). Humic substances are able to chelate metal ions through a carboxyl and a phenolic hydroxyl group.

Insoluble humic substances such as the humins and humic acids are able to exchange cations with water and are having capacity to accumulate large amount of metals.

### Redox Reactions Mediated By Bacteria:

The following equation represent some of the many important redox reactions which are mediated by bacteria for their metabolic processes and reproduction.

#### Oxidation:







### Reduction:



In many biogeochemical processes in water and soil and in many important elemental cycles in nature, including those of nitrogen, carbon and sulfur, bacteria are involved. These processes help in the formation of many mineral deposits including some of those of iron and manganese. The formation of iron and manganese deposits in natural water systems and pipes used to transport water are due to the involvement of bacteria.

### Nitrogen Transformation By Bacteria

The nitrogen cycle is one of the most important micro-organism mediated chemical reaction in aquatic and soil environments. It is based on four important chemical transformations:

- *Nitrogen fixation*
- *Nitrification*
- *Nitrate reduction*
- *Denitrification*

All these transformations were already discussed under the nitrogen cycle in chapter 1.1

### Iron and manganese bacteria:

Some of the iron bacteria, e.g. ferrobacillus, gallionella, sphaerotilus utilise iron compound to derive energy for their metabolic processes. The bacteria serve as catalyst for the oxidation of Fe (II) to Fe (III) by O<sub>2</sub>:



The carbon source for some of these bacteria is CO<sub>2</sub>. As they do not depend on organic matter for carbon and because they derive energy from the oxidation of inorganic matter, these bacteria may be able to thrive in environments where organic matter is absent.

