Chapter 7

Classification of Dissolved Solids

7.1 CATEGORIES OF DISSOLVED SOLIDS

The number of distinct ionic and molecular species, which constitute the dissolved solids content of natural waters and wastewaters, is quite enormous. In the context of this discussion on separation principles and related technologies, they can be usefully considered under the broad headings: inorganic, organic and dangerous substances.

7.2 INORGANIC DISSOLVED SOLIDS

Inorganic substances in solution may be ionic or molecular. Most inorganics dissociate in solution into their component ions. The predominant ions in natural waters are:

Anions:	HCO_3^-, Cl^-, SO_4^{2-}, NO_3^-, PO_4^-
Cations:	Ca^{2+}, Mg^{2+}, Na^+, K^+, Fe^{2+}, Mn^{2+}

Some industrial wastewaters may have high concentrations of inorganics, e.g. wastewaters from fertilizer manufacture, paint manufacture, electroplating, etc.

Chemical precipitation and ion exchange are the main processes used for the separation of inorganic dissolved solids. For some industrial wastewaters pH neutralization may be the only treatment required before disposal.

The total inorganic dissolved solids in water can be rapidly estimated instrumentally by conductivity measurement. The total dissolved solids (mg l^{-1}) in a sample is approximately obtained by multiplying conductivity (μS cm^{-1}) by an empirical factor. This factor may vary from 0.55 to 0.9, depending on the soluble components of the water and on the temperature of measurement (APHA, 1992). Relatively high factors apply for saline waters, whereas lower factors apply where considerable hydroxide or free acid is present. The ion concentration (meq l^{-1}) may be approximated by multiplying the conductivity (μS cm^{-1}) by 0.01.

7.3 ORGANIC DISSOLVED SOLIDS

The removal and disposal of dissolved organics constitutes a major part of wastewater engineering practice and is a key measure in water pollution control. Dissolved organics occur in domestic sewage and in wastewaters from three main categories of industrial activity: the processing of natural organic materials (meat, vegetables, milk and associated by-products, etc.); the manufacture of synthetic organic compounds (detergents, pharmaceuticals, by-products of the petroleum industry, etc.); and the fermentation industries (alcohol, organic acids, etc.).

All organic compounds contain carbon in combination with one or more elements. The hydrocarbons contain only carbon and hydrogen. Carbon, hydrogen and oxygen are the major elements of a great number of organic compounds. Minor elements in naturally occurring organic substances include nitrogen, phosphorus and sulphur. Synthetic organic compounds may contain, in addition, halogens, certain metals and a wide variety of other elements (Sawyer and McCarty, 1967).

Organic compounds differ from inorganic substances in a number of respects, including:

(1) Organic substances are generally less soluble in water.

(2) The reactions of organic compounds are usually molecular rather than ionic and hence are often quite slow.

(3) The same chemical formula may represent several organic compounds – this is called isomerism.

(4) Many organic compounds have a high molecular weight, often over 1000.

(5) Most organic substances are biodegradable.

Organic compounds can be categorized into three major groupings on the basis of the molecular arrangement of their carbon atoms. These are the *aliphatic, aromatic* and *heterocyclic* compounds. The molecular structure of these groupings is illustrated in Fig 7.1. The aliphatic compounds are characterised by a straight or branched carbon chain. The aromatic compounds have a repeated ring structure, each ring consisting of six carbon atoms an containing three double bonds. The heterocyclic compounds have a ring structure in which one member is an element other than carbon. A listing of organic compounds of sanitary significance is given in table 7.1.

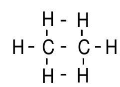
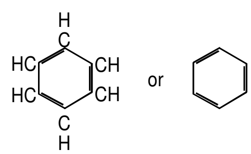
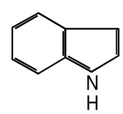
Compound	**Graphic representation**	**Structure**
ethyl alcohol		aliphatic
benzene		aromatic
indole		heterocyclic

Fig 7.1

Table 7.1 Organic compounds of sanitary significance

Aliphatic compounds	Aromatic compounds	Heterocyclic compounds
Hydrocarbons	Hydrocarbons	Furaldehyde
Alcohols	Phenols	Pyrrole
Aldehydes	Alcohols	Pyrrolidine
Ketones	Aldehydes	Indole
Organic acids	Ketones	Skatole
Esters	Organic acids	
Ethers	Amines	
Alkyl halides	Nitrobenzenes	
Polyhalogen compounds		
Amines		
Amides		
Nitriles		
Mercaptans (thioalcohols)		

Naturally occurring organic chemicals fall into three major groupings: *carbohydrates, fats* and *proteins*.

The designation carbohydrate is applied to a large group of organic compounds, having the general atomic composition $(CH_2O)_n$, i.e. the number of hydrogen atoms is twice the number of oxygen atoms, as in water. Carbohydrates are grouped into three general classifications: (1) simple sugars or monosaccharides; (2) complex sugars or disaccharides; (3) polysaccharides (Figs 7.2-7.4).

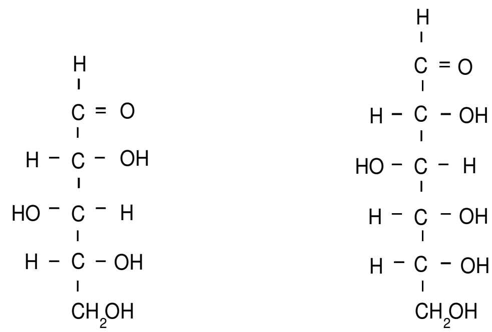


Fig 7.2 **Xylose (pentose)** **Glucose (hexose)**
Simple sugars

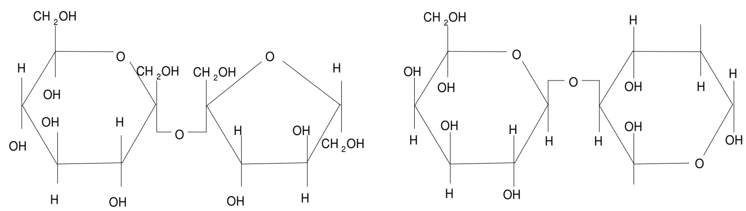


Fig 7.3
Complex sugars **Sucrose (disaccharide)** **Lactose (disaccharide)**

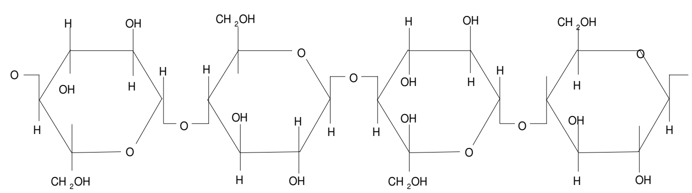


Fig 7.4 **Section of a cellulose molecule (polysaccharide)**

Fats comprise a group of organic substances that have in common the property of being soluble to varying extents in organic solvents, while being only sparingly soluble in water. Because of their limited solubility , biodegradation occurs at a slow rate. Fats and oils are both glycerides of fatty acids. Fig 7.5 shows a typical molecular structure.

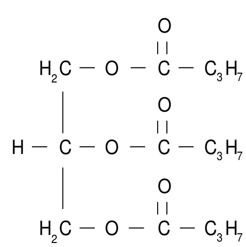


Fig 7.5 **Glyceral tributyrate**

Proteins are complex compounds of carbon, hydrogen, oxygen and nitrogen. Phosphorus and sulphur are present in a few. They are widely distributed in plants and animals. Amino acids constitute the basic building block of proteins. Since there are about 27 known amino acids, the variety of proteins is considerable. Fig 7.6 shows part of a protein molecule containing a string of four amino acids.

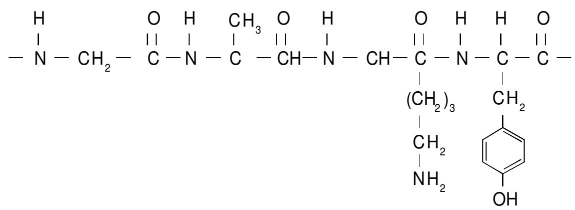


Fig 7.5 **Section of a protein molecule**

7.3.1 Biodegradability of organic substances

The majority of carbohydrates, fats and proteins found in wastewaters are biodegradable. The first step in the biodegradation process is one of hydrolysis in which carbohydrates are converted to simple sugars, fats to short-chain fatty acids, and proteins to amino acids.

Several organic compounds, e.g. cellulose, long-chain saturated hydrocarbons, and other complex compounds such as the various plastics used in industry, are effectively non-biodegradable in the biological wastewater treatment context. Both in the context of their removal in biological wastewater treatment and in their influence on the environment to which they may be discharged, it is useful to classify dissolved organics on a biodegradability scale. Clearly such a scale would range from the easily biodegradable, e.g. food processing wastes, to the biologically inert, e.g. plastics (toxic wastes are considered later in section 7.4), with a whole range of intermediate biodegradability. It would there seem desirable to have a continuous scale of measurement on which biodegradability could be quantified. One such scale is that proposed by Thompson et al. (1969), whose biochemical treatabilty index BTI) is calculated as follows:

$$BTI = t_{05} + t_{Or} + t_{O40} + t_{C50} + t_D$$

where

t_{O5} = time for 5% of the theoretical oxygen demand of the organic chemical to be satisfied;

t_{Or} = time for the theoretical oxygen demand of the organic chemical to be satisfied at the maximum measured rate of oxygen utilisation;

t_{O40} = time measured for 40% of the theoretical oxygen demand of the organic chemical to be satisfied;

t_{C50} = time for 50% carbon removal to be reached;

t_D = time of enzyme activity.

Time measurements are in hours and are related to controlled experimental procedures. Treatability indices for a number of organic substances examined in this way are given in table 7.2.

While a numerical index, such as that presented in Table 7.2, is a useful and convenient guide to relative biodegradability, it should be noted that biochemical metabolism is a complex process. In particular, it is subject to variation within and between species and is influenced by the effects of acclimation and environment. Experience with biological action on specific wastes shows that acclimation and biodegradation are more likely to occur in a full-scale treatment process than in a bench-scale unit, which in turn is likely to show more activity than a BOD test incubation.

Table 7.2 Biochemical treatability index (BTI) for some organic chemicals

Group name	Chemical	Formula	BTI number*
Alcohols	Ethanol	CH_3CH_2OH	14
	Methanol	CH_3OH	240
	n-Propanol	$CH_3CH_2CH_2OH$	12
	Isopropanol	$CH_3CH(OH)CH_3$	117
	Ethylene glycol	$HOCH_2CH_2OH$	43
	tert-Butanol	$(CH_3)_3COH$	321
Acids	Benzoic acid	C_6H_5COOH	21
	Maleic acid	HOOCCH:CHCOOH	219
	Oxalic acid	HOOCOOH	400
Aldehydes	Benzaldehyde	C_6H_5CHO	32
Esters	Ethyl acetate	$CH_3COOCH_2CH_3$	38
Ethers	Diethylenel glycol	$(HOCH_2CH_2)_2O$	180
Ketones	Acetone	CH_3COCH_3	265
	Methyl ethyl ketone	$CH_3COCH_2CH_3$	174
Organic nitrogens	Acrylonitrile	CH_2:CHCN	483
	Aniline	$C_6H_5NH_2$	232
	Monoethylolamine	$H_2NCH_2CH_2OH$	320
	Triethylolamine	$(CH_2CH_2OH)_3N$	123
	Pyradine	C_5H5_N	194
Phenols	o-Cresol	$CH_3C_6H_4OH$	90
	Hydroquinone	$C_6H_4(OH)_2$	184

*increasing index number indicates more resistance to biodegradation
Source: Thompson et al. (1969)

In general, high molecular weight materials and tertiary branched molecular structures are not susceptible to metabolism at a significant rate (Ludzack and Ettinger, 1960). Acclimation may have little effect where structures do not permit enzyme approach of fail to diffuse through cell membranes. Atoms in a chain other than carbon, such as oxygen, sulphur and nitrogen, frequently decrease availability.

The COD:BOD_5 ratio is a useful simple index of biodegradability, subject to the foregoing comments on the potential limitations related to a lack of acclimation. The COD:BOD_5 ratio for untreated municipal sewage is typically in the range 2-3, while that for a biologically treated municipal sewage effluent may be in the range 4-5.

7.3.2 Surfactants

One group of synthetic organics, namely surfactants/detergents or surface-active agents, merit special attention because of their widespread use as aqueous cleaning agents. Although the designation detergent is often interchangeably used with surfactant, it more accurately refers to products that combine surfactants with other substances, organic or inorganic, formulated to enhance cleaning performance. Because of their increasing use in the home and industry, surfactants occurs in significant concentrations in sewage and industrial wastewaters.

Surfactants are distinguished by the following distinctive features (Kirk-Othmer, 1985):

Amphipathic molecular structure - typically containing an oil-soluble hydrocarbon chain and a water-soluble ionic or polar group.

Solubility - a surfactant is soluble in at least one phase of a liquid system.

Adsorption at interfaces - the concentration of a surfactant at a phase interface is greater than its concentration in the bulk solution at equilibrium.

Orientation at interfaces - significant molecules and ions form oriented monolayers at phase interfaces.

Micelle formation - surfactants form aggregates of molecules or ions called micelles when the concentration of the surfactant in the bulk of the solution exceeds a limiting value.

Functional properties - surfactant solutions exhibit combinations of cleaning, foaming, wetting, emulsifying, solubilizing, and dispersing properties.

The presence of two structurally dissimilar groups – a lyophobic (solvent-hating) group and a lyophilic (solvent liking) group – within the same molecule is the most fundamental characteristic of surfactants. The terms polar and non-polar are also used to designate water-soluble and water-insoluble groups, respectively.

Surfactants are classified into anionic, cationic, non-ionic and amphoteric categories. In anionic surfactants the hydrocarbon component carries a negative charge, while in cationic surfactants it carries a positive charge. In non-ionic surfactants there is no charge on the molecule, while in amphoteric surfactants the molecule contains both positive and negative charges. The following are typical examples of molecular composition:

anionic:	$C_{17}H_{35}CO_2^-Na^+$
cationic:	$(C_{18}H_{37})_2$+$N(CH_3)_2Cl^-$
non-ionic:	$C_{15}H_{31}(OC_2H_4)_7OH$
amphoteric:	$C_{12}H_{25}{}^+N(CH_3)_2CH_2CO_2^-$

The hydrophobic part of the molecule typically contains a chain of 10-20 carbon atoms and may include oxygen atoms, amides, esters and other functional groups. The hydrophilic part of anionic surfactants includes carboxylates, sulphonates, sulphates and phosphates. Cationics are solubilized by the amine and ammonium groups. Ethylene oxide chains and hydroxyl groups are the solubilizing agents in non-ionic surfactants. Amphoteric surfactants are solubilized by combinations of anionic and cationic solubilizing groups. The molecular weight of surfactants ranges from a low of ca. 200 to a high in the thousands for polymeric structures.

Environmental concerns relating to surfactants are focussed mainly on two areas: (a) biodegradability and (b) the potential contribution of their phosphorus content to water eutrophication.

The biodegradability of the surfactant molecule is related to the structure of the hydrocarbon radical. Straight chain hydophobes (LAS – linear alkanesulphonate) are readily biodegraded (soft), while highly branched hydrocarbon chains (ABS – alkylbenzenesulphonate) are resistant to biodegradation (hard). The cationic detergents, which are salts of quaternary ammonium hydroxide, are not widely used. They are bactericidal and hence are used for both disinfection and cleansing. Non-ionic detergents are derived from polymers of ethylene oxide and are typically resistant to biodegradation.

7.4 DANGEROUS SUBSTANCES

The designation dangerous, in this context, implies a capacity to damage living organisms by virtue of toxicity, persistence or bioaccumulation. Environmental regulations are generally framed in a manner that prohibits discharge of such substances into the aquatic environment. For example, the European Union Directive (76/464/EEC) on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community lists such substances in two categories. List 1 contains those substances which should not be discharged into the aquatic environment, while List 2 contains substances the discharge of which into the aquatic environment should be strictly controlled.

List 1 substances include:

(1) organohalogen compounds and substances which may form such compounds in the aquatic environment;
(2) organphosphorus compounds;

(3) organotin compounds;
(4) substances in respect of which it has been proved that they possess carcinogenic properties in or via the aquatic environment;
(5) mercury and its compounds;
(6) cadmium and its compounds
(7) persistent mineral oils and hydrocarbons of petroleum origin;
(8) persistent synthetic substances which may float, remain in suspension or sink and which may interfere with any use of the waters.

List 2 substances include:

(1) metalloids and metals and their compounds, including: zinc, copper, nickel, chromium, lead, selenium, arsenic, antimony, molybdenum, titanium, tin, barium, beryllium, boron, uranium, vanadium, cobalt, thalium, tellurium silver;
(2) biocides and their derivatives not appearing in List 1;
(3) substances that have a deleterious effect on the taste and/or smell of the products for human consumption derived from the aquatic environment, and compounds liable to give rise to such substances in water;
(4) toxic or persistent organic compounds of silicon, and substances that may give rise to such compounds in water, excluding those that are biologically harmless or are rapidly converted in water into harmless substances;
(5) inorganic compounds of phosphorus and elemental phosphorus;
(6) non-persistent mineral oils and hydrocarbons of petroleum origin;
(7) cyanides, fluorides;
(8) substances that have an adverse effect on the oxygen balance, particularly ammonia and nitrites.

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